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KONINKLIJKE AKADEMIE
VAN WETENSCHAPPEN
-- TE AMSTERDAM --

PROCEEDINGS OF THE
SECTION OF SCIENCES



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(557)

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday December 30, 1911.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige
Afdeling van Zaterdag 30 December 1911, Dl. XX).

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Physics. — “*Electric double refraction in some artificial clouds and vapours.*” (First Part). By Prof. P. ZEEMAN and C. M. HOOGENBOOM.

(Communicated in the meeting of November 25, 1911).

1. Some time ago one of us¹⁾ suggested a method of attacking the problem to discover an influence of electric fields on radiation frequency, as predicted by VOIGT²⁾ from theoretical considerations. The experiments installed according to the mentioned method have not yet come to a definite close.

We intend to give here a short account of a parallel series of observations relating to a closely connected subject, which were begun already a considerable time ago.

They relate to the KERR electro-optic effect, the double refraction induced by powerful electrostatic fields. Till now the effect has been specially studied in solids and liquids; we intend to investigate the behaviour of some clouds and vapours.

If it is once proved that under the influence of electric forces double refraction is induced in clouds of suspended particles, then the phenomena may be pursued further, when the size of the particles is taken smaller and smaller. By increasing the sensitiveness of the optical method clouds of smaller and smaller values of double refraction and ultimately gases can be investigated.

COTTON and MOUTON³⁾ in the course of their remarkable investigation of magnetic double refraction induced in liquids have formulated the hypothesis, already proposed by Sir JOSEPH LARMOR for the KERR electro-optic effect, that in both cases the double refraction is due to a directive action of the external field on the molecules of the liquid. The only cause interfering with a parallel arrangement of the molecules is their thermal motion. LANGEVIN⁴⁾ has shown in how simple a manner this hypothesis of the molecular orientation explains quantitatively the phenomena mentioned and also others.

It seems still somewhat questionable in how far the hypothesis of molecular orientation may be applied without modification to gases, at least if exhibiting narrow absorption bands.

The study of artificial clouds seems interesting for the reason that the suspended particles play the rôle of the molecules in the

1) ZEEMAN. These Proceedings, January 1911.

2) VOIGT. Magneto- und Electro-optik. 1908. Kapitel 9. u. 10.

3) COTTON et MOUTON. Ann. de Chim. et de Phys. T. 19. 1910, cf. also the interesting paper of CORBINO. Physik. Zeitschr. 11. S. 756. 1910.

4) LANGEVIN. Le Radium T. 7. Sept. 1910.

hypothesis of molecular orientation. It is now possible to examine separately also the constituent particles; they can be shown to possess (or not to possess), before their exposition to the field, magnetically, electrically, and optically the symmetry of a solid of revolution.

Especially interesting are those vapours which exhibit narrow absorption lines. In this case the opinion expressed by VOIGT¹⁾ that in the neighbourhood of absorption lines the amount of the double refraction will assume considerable values, can be tested. Independently of a special form of theory there is much to be said in favour of this opinion.

2. There is only one investigation known to us, which seems to give evidence that electric forces induce double refraction in some clouds. E. BLOCH²⁾ while investigating the influence of dust particles on the electric conductivity of gases, made the following two observations.

In the first place he found that a cloud of sal-ammonia, if present between the plates of a condenser and if seen against a dark background in diffuse light, becomes white and more manifest as soon as the plates are charged.

The other observation made by BLOCH is this. A parallelepipedical box is closed at two opposite sides by glass windows, two other sides consist of metal plates at a distance of a few centimetres and can be connected to an electric machine. If a cloud of sal-ammonia is introduced and the box is placed between crossed Nicols, then the light of a source behind the polariser is seen at once with the making of the field. The rest is perhaps given best in the original: "La modification de la lumière diffusée (ou diffractée) par les particules est donc accompagnée d'une anisotropie du milieu constitué par l'air et les particules. Il reste donc à savoir s'il y a biréfringence ou dichroïsme et à faire l'étude quantitative du phénomène".

It is indeed easily seen that by induced dichroism alone, the light would reappear. Let the electric force be horizontal, and suppose the light issuing from the polariser being polarised under azimuth of 45° . Let the vibrations be resolved into vertical and horizontal components. If we suppose that the horizontal vibrations are absorbed powerfully by the vapour, but the vertical ones not, and that there occur no differences of phase, then on emerging the resulting vibrations will have an azimuth larger than 45° and there will be therefore revival of light.

¹⁾ VOIGT. l.c. p. 381.

²⁾ E. BLOCH. C. R. T. 146. 1908.

3. Our experiments prove that in a cloud of sal-ammonia there is only double refraction but no dichroism. (see § 4).

The light from a NERNST filament is made parallel by means of a lens and polarised in a plane inclined to the horizontal at 45° . The vapour or the cloud is introduced into a horizontal tube, which contains in many experiments interior plates connected with the source of electricity. The tube is closed by plates of thin coverglass; two side tubes served resp. for the introduction and for the egress of the vapours. The analysing Nicol, of course, follows after the tube.

The double refraction to be observed is so small that special means are necessary for observing and measuring it. Between the polariser and the tube we introduce a horizontal bar of glass, perpendicular to the beam of light¹⁾. Near the middle of its length the strip is supported by two small glass cylinders and subjected to a small flexure. It is therefore in a condition of strain and double refraction. Between crossed nicols there is revival of light, especially near the edges of the bar, while near the middle a horizontal band remains dark. It seems superfluous to comment upon the optical theory of the strained glass bar, which is rather simple and moreover given in many text-books. The most refined investigation made with the strained bar, is probably Lord RAYLEIGH's, when discussing the question whether motion through the aether causes double refraction.¹⁾

The position of the band is determined by two horizontal wires inclosing it, and disposed close to the bar. If a double refracting substance, with horizontal and vertical principal directions, is introduced into the beam a motion of the band occurs, upwards or downwards, depending upon the sign of the double refraction.

The sensitiveness of the method can be changed within rather wide limits. It is increased, 1. by diminishing the loads at the ends of the bar, 2. by increasing the distance of the supporting cylinders. We are thus enabled to choose the sensibility according to circumstances.

The absolute value of the amount of double refraction was determined, at least for higher values, by means of a carefully constructed compensator of SOLEIL--BABINET. By its means the displaced band can be moved until it is again in its original position. The compensator is so mounted that it can be easily introduced into or removed out of the beam. For very small values of the double refraction it seems appropriate to use a second strip instead of the compensator, and to restore the original conditions of the field of view by a

¹⁾ RAYLEIGH. Phil. Mag. (6) 4, p. 678, 1902.

flexure of this second bar in a suitable direction. We have not yet had occasion to try this method systematically.

In order to determine the sensitiveness of the method a thin vertical glass plate was introduced in the course of the light and the weight determined necessary to cause a marked shifting of the band. During this operation the compensator of SOLEIL—BABINET is removed. The constant determining the influence of one sided pressure on double refraction is measured in a separate experiment. The glass bar and the compensator are then used simultaneously. The difference of phase just perceptible was in our case $6.10^{-5} \lambda$.

4. The cloud of sal-ammonia was made in an anteroom, preceding the observation tube. The two gases, hydrochloric acid and ammonia, were introduced under slight pressure after being partially dried. After passing the observation tube the cloud escaped in the free atmosphere. The density of the cloud and the magnitude of its constituting particles could be chosen by regulating the ratio of the two gases.

The source of electricity was either an electrostatic machine or a transformer, allowing potentials between 1000 and 10000 Volts being used.

The question whether there is dichroism or double refraction (see § 2) could now be settled immediately. By dichroism a rotation of the plane of polarisation will occur, and therefore a *juding* of the dark band and not a displacement must take place. Double refraction shows itself by a displacement alone. Our first experiments with the sal-ammonia cloud at once made it clear that only double refraction is operative. The effect was nearly proportional to the square of the electric intensity.

If a transformer is used then a displacement of the dark band must take place as well; it can be easily calculated. The direction of the displacement of course depends upon the nature of the substance under consideration.

5. The results of our measurements will be given later on. The sign of the KERR-effect in the sal-ammonia cloud is opposite to that of ordinary glass.

6. We also tried to determine the relation of the specific values of the effects in the sal-ammonia cloud [and in large crystals of salammonia. The latter were never faultless. Perhaps this circumstance accounts for the very small specific action found for a

separate crystal. The result seems too striking to be accepted without further evidence. Or would it be possible that the mobility of the particles in the large crystal is considerably reduced?

7. The experiment of § 4 proves very clearly that in the case of the KERR-effect there is a direct action of the field and not one due to a mechanical pressure from the condenser plates.

8. Besides clouds of sal-ammonia in different degrees of dilution, we have made observations with some other clouds; details will be given later. They were obtained by heating of substances in some cases, in others by chemical processes, among which we count also the process generating TYNDALL'S actinic clouds. In some of our experiments we made use of dust clouds, the substance under review being first reduced to very fine powder and then blown by a current of air between the condenser plates. It is easy to obtain clouds in this manner with glass powder and with different salts of tartaric acid. The effect of a glass cloud is, as is to be expected, in the same sense as that of the original glass.

9. The method, resumed in § 3, and especially the combined use of a glass bar and a compensator of SOLEIL-BABINET (or of a second bar previously gauged), can be used to ascertain sign and magnitude of the KERR-effect of very small quantities of fluids. With condenser plates of only a few square millimeters' area and with voltages of a few hundreds Volts the KERR-effect in nitrobenzene is easily observed.

In order to obtain quantitative results a condenser of some extension in the direction of the beam is necessary. The greatest difficulty in all experiments on electric double refraction give the optical perturbations caused by heating effects from the part of the electric field, which interfere very seriously with observation. The time of observation must therefore be reduced as much as possible. The following mode of operation is advisable. Let the shift of the band be compensated as accurately as possible with the field on. Then put the field off. The band then is shifted again. It is now easily controlled whether the compensation was exact, by putting on the field for one moment. The time necessary to ascertain whether or not the dark band jumps back just, inside the two horizontal wires is very short.

Physics. "On the variability of the quantity b in VAN DER WAALS' equation of state, also in connection with the critical quantities."

III. By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ.)

(Communicated in the meeting of November 25, 1911).

The coefficients found in the preceding paper can be found by another way still. I will call this method the *symmetrical* method, because it is based on *two* logarithmic equations which are symmetrically constructed. We mean the relations

$$\left. \begin{aligned} \frac{8}{3} m \left[\frac{d'}{3(d-d')} \log \left(\frac{d}{d'} \frac{3-d'}{3-d} \right) - \frac{1}{3-d} \right] &= d'-d \\ \frac{8}{3} m \left[\frac{d}{3(d-d')} \log \left(\frac{d}{d'} \frac{3-d'}{3-d} \right) - \frac{1}{3-d'} \right] &= d-d' \end{aligned} \right\}$$

which have been formed by the combination of the two original equations (a). (see II p 432).

If again we put:

$$d = 1 + 2x + 2y = 1 + 2p ; \quad d' = 1 - 2x + 2y = 1 - 2q,$$

in which $x = a\tau + c\tau^3 + \dots$, $y = b\tau^2 + d\tau^4 + \dots$, the two above equations become:

$$\left. \begin{aligned} \frac{2}{3} m \left[\frac{1-2q}{3(p+q)} \log \left(\frac{1+2p}{1-2q} \frac{1+q}{1-p} \right) - \frac{1}{1-p} \right] &= -(p+q) \\ \frac{2}{3} m \left[\frac{1+2p}{3(p+q)} \log \left(\frac{1+2p}{1-2q} \frac{1+q}{1-p} \right) - \frac{1}{1+q} \right] &= p+q \end{aligned} \right\} \quad (b),$$

because $3-d = 2(1-p)$, $3-d' = 2(1+q)$ and $d-d' = 2(p+q)$.

Now the logarithm gives (see II p. 440), after $p+q$ has been placed outside the parentheses:

$$\begin{aligned} 3(p+q) \left[1 - \frac{1}{2} (p-q) + (p^2 - pq + q^2) - \frac{5}{4} (p^3 - \dots - q^3) + \right. \\ \left. + \frac{11}{5} (p^4 - \dots + q^4) - \frac{7}{2} (p^5 - \dots - q^5) + \frac{43}{7} (p^6 - \dots + q^6) \right]. \end{aligned}$$

After division of the *log* by $3(p+q)$, multiplication by $1-2q$, and subtraction of $1 : (1-p) = 1+p+p^2+\dots$ the former of the two above equations passes into

$$\frac{2}{3} m \left[-\frac{1}{2} \cdot 3(p+q) + \frac{1}{6} \cdot 0 - \frac{1}{12} \cdot 9 (3p^3 + p^2q - pq^2 + q^3) + \right.$$

$$\begin{aligned} & + \frac{1}{20}(4p^4 + p^2q - p^2q^2 + pq^2 - q^4) - \frac{1}{30}(27(5p^5 + p^4q + p^2q^2 + p^2q^2 - pq^4 + q^5) + \\ & \left. + \frac{1}{12}(36[6p^6 + p^5q + p^4q^2 + p^3q^3 + p^2q^4 + pq^5 - q^6]) \right) = -(p + q), \end{aligned}$$

in which the coefficients 3, 0, 9, 6, 27, 36, etc. in general are represented by θ , $\theta(\theta-3)$, $\theta(\theta^2-4\theta+6)$, $\theta(\theta^3-5\theta^2+10\theta-10)$, $\theta(\theta^4-6\theta^3+15\theta^2-20\theta+15)$, $\theta(\theta^5-7\theta^4+21\theta^3-35\theta^2+35\theta-21)$, etc., where $\theta=3$.

The corresponding second equation is now evidently obtained by substituting $-q$ for p , and $-p$ for q , as is immediately seen by comparison of the above equations (b). If then the first equation is divided by $-(p+q)$, the second by $p+q$, we get:

$$\begin{aligned} & m \left[1 + \frac{1}{2}(3p^2 - 2pq + q^2) - \frac{1}{5}(4p^3 - 3p^2q + 2pq^2 - q^3) + \right. \\ & \left. + \frac{3}{5}(5p^4 - 4p^3q + 3p^2q^2 - 2pq^3 + q^4) - \frac{1}{7}(6p^5 - 5p^4q + 4p^3q^2 - 3p^2q^3 + 2pq^4 - q^5) \right] = 1 \\ & m \left[1 + \frac{1}{2}(p^2 - 2pq + 3q^2) - \frac{1}{5}(p^3 - 2p^2q + 3pq^2 - 4q^3) + \right. \\ & \left. + \frac{3}{5}(p^4 - 2p^3q + 3p^2q^2 - 4pq^3 + 5q^4) - \frac{1}{7}(p^5 - 2p^4q + 3p^3q^2 - 4p^2q^3 + 5pq^4 - 6q^5) \right] = 1 \end{aligned}$$

Subtraction yields:

$$\begin{aligned} & \frac{1}{2}(2p^2 - 2q^2) - \frac{1}{5}(3p^3 - p^2q - pq^2 + 3q^3) + \\ & + \frac{3}{5}(4p^4 - 2p^3q + 2pq^3 - 4q^4) - \frac{4}{7}(5p^5 - 3p^4q + p^3q^2 + p^2q^3 - 3pq^4 + 5q^5) = 0, \end{aligned}$$

or after division by $p+q$:

$$\begin{aligned} & (p-q) - \frac{1}{5}(3p^2 - 4pq + 3q^2) + \\ & + \frac{3}{5}(4p^3 - 6p^2q + 6pq^2 - 4q^3) - \frac{4}{7}(5p^4 - 8p^3q + 9p^2q^2 - 8pq^3 + 5q^4) = 0 \quad (\alpha) \end{aligned}$$

Addition, and division by $2m$ yields:

$$\begin{aligned} & (p^2 - pq + q^2) - \frac{1}{5}(p^3 - p^2q + pq^2 - q^3) + \\ & \frac{3}{5}(p^4 - p^3q + p^2q^2 - pq^3 + q^4) - 2(p^5 - \dots - q^5) = \tau^2 + \tau^4 + \dots, \quad (\beta), \end{aligned}$$

because $m = 1 - \tau^2$ and so $1 : m = 1 + \tau^2 + \tau^4 + \dots$.

Re-substitution of $x+y$ for p , of $x-y$ for q (see above) transforms (α) and (β) into

$$2y - \frac{1}{5}(2x^2 + 10y^2) + \frac{3}{5} \cdot 2y(6x^2 + 10y^2) - \frac{4}{7}(3x^4 + 42x^2y^2 + 35y^4) = 0$$

$$(x^2 + 3y^2) - \frac{1}{2} \cdot 2y(2x^2 + 2y^2) + \frac{9}{5}(x^4 + 10x^2y^2 + 5y^4) - 2 \cdot 2y(3x^4 + 9x^2y^2 + 3y^4) = \tau^2 + \tau^4$$

which is easily obtained when we consider that $4p^3 - 6p^2q + 6pq^2 - 4q^3 = (p-q)[4(p^2+q^2) - 2pq]$; $5p^4 - 8p^3q + \text{etc.} = 5(p^4+q^4) - 8pq(p^2+q^2) + 9v^2q^2$; etc.

And if finally we substitute the values $ax + cx^3$ and $bx^2 + dx^4$ for x and y , we get:

$$2(b\tau^2 + d\tau^4) - \frac{2}{5}(a^2\tau^2 + (2ac + 5b^2)\tau^4) + \frac{12}{5}b\tau^2(3a^2\tau^2) - \frac{4}{7}(3a^4\tau^4) = 0$$

$$\left(a^2\tau^2 + (2ac + 3b^2)\tau^4 \right) - 2b\tau^2(a^2\tau^2) + \frac{9}{5}(a^4\tau^4) = \tau^2 + \tau^4$$

in which the development need not go any further than τ^4 , whereas in the *asymmetrical* method (see the preceding paper) we had to go as far as τ^8 . In consequence of this amongst others the whole last term of the first member of the second equation in x and y vanishes.

Summarizing this, we get finally:

$$\left(2b - \frac{2}{5}a^2 \right) \tau^2 + \left(2d - \frac{4}{5}ac - 2b^2 + \frac{36}{5}a^2b - \frac{12}{7}a^4 \right) \tau^4 = 0$$

$$a^2\tau^2 + \left(2ac + 3b^2 - 2a^2b + \frac{9}{5}a^4 \right) \tau^4 = \tau^2 + \tau^4$$

from which follows:

$$a^2 = 1; \quad 2ac + 3b^2 - 2a^2b + \frac{9}{5}a^4 = 1$$

$$2b - \frac{2}{5}a^2 = 0; \quad 2d - \frac{4}{5}ac - 2b^2 + \frac{36}{5}a^2b - \frac{12}{7}a^4 = 0$$

and from this by successive substitution and solution:

$$\underline{a = 1} \quad ; \quad \underline{b = \frac{1}{5}} \quad ; \quad \underline{c = -\frac{13}{50}} \quad ; \quad \underline{d = \frac{64}{875}}$$

as in the first method. But here the coefficient e is not required to determine d , because they are not found in pairs together, — always from two equations with two unknown quantities — but *successively*, always from but one equation. It is again self-evident that if we only desire to know a and b , the above calculation is again considerably shortened, and the result is obtained almost immediately. For then only the terms with τ^2 are necessary.

Lastly we will also mention a *third* method, that of the *differential quotient*; the shortest method of all, but yet possibly slightly

longer than the two discussed methods, because first the differential quotient must be derived. Let us start from the two equations (1^a) and (2) [See II, p. 432—433], viz.

$$(3-d)(3-d')(d+d') = 8m \quad ; \quad \log \left(\frac{d}{d'} \frac{3-d'}{3-d} \right) = \frac{3}{8} \frac{d-d'}{m} \left(6 - (d+d') \right).$$

Now we differentiate with respect to τ ($m = 1 - \tau^2$, so $\tau = \sqrt{1-m}$), and obtain in this way from the first equation, putting $\frac{dd'}{d\tau} = x$ and $\frac{dd'}{d\tau} = y$:

$$-\frac{x}{3-d} - \frac{y}{3-d'} + \frac{x+y}{d+d'} = -\frac{2\tau}{1-\tau^2},$$

from which:

$$\frac{3-2d-d'}{3-d} x - \frac{3-d-2d'}{3-d'} y = -\frac{2\tau}{1-\tau^2} (d+d') \quad . \quad . \quad . \quad (a)$$

The second equation yields:

$$\begin{aligned} \frac{x}{d} - \frac{y}{d'} - \frac{y}{3-d'} + \frac{x}{3-d} &= -\frac{3}{8} \frac{d-d'}{m} (x+y) + \frac{3}{8} \frac{6-(d+d')}{m} (x-y) + \\ &+ \frac{3}{8} \frac{2\tau}{m^2} (d-d') (6-(d+d')), \end{aligned}$$

i. e.

$$\begin{aligned} \left[\frac{1}{d} + \frac{1}{3-d} + \frac{3}{8m} (d-d') - \frac{3}{8m} (6-(d+d')) \right] x + \\ + \left[-\frac{1}{d'} - \frac{1}{3-d'} + \frac{3}{8m} (d-d') + \frac{3}{8m} (6-(d+d')) \right] y = \\ = \frac{3}{8} \frac{2\tau}{m^2} (d-d') (6-(d+d')), \end{aligned}$$

or

$$\begin{aligned} \left[\frac{3}{d(3-d)} + \frac{3}{8m} (2d-6) \right] x + \left[-\frac{3}{d'(3-d')} + \frac{3}{8m} (6-2d') \right] y = \\ = \frac{3}{8} \frac{2\tau}{m^2} (d-d') (6-(d+d')). \end{aligned}$$

If in this $(3-d)(3-d')(d+d')$ is substituted for $8m$, we get:

$$\begin{aligned} \left[\frac{1}{d(3-d)} - \frac{2}{(3-d')(d+d')} \right] x - \left[\frac{1}{d'(3-d')} - \frac{2}{(3-d)(d+d')} \right] y = \\ = \frac{2\tau}{8m^2} (d-d') (6-(d+d')), \end{aligned}$$

or also

$$\frac{(d-d')(3-2d-d')}{d(3-d)(3-d')(d+d')}x - \frac{(d-d')(3-d-2d')}{d'(3-d)(3-d')(d+d')}y = \frac{2r}{8m^2}(d-d')(6-(d+d')),$$

hence finally, writing again $8m$ for $(3-d)(3-d')(d+d')$:

$$\frac{3-2d-d'}{d}x + \frac{3-d-2d'}{d'}y = -\frac{2r}{1-r^2}(6-(d+d')) \quad (3)$$

We must now combine (a) and (3) to solve x and y . Elimination of y gives:

$$(3-2d-d')\left(\frac{d'}{d} - \frac{3-d'}{3-d}\right)x = -\frac{2r}{1-r^2}\left[d'(6-(d+d')) - (3-d')(d+d')\right],$$

or

$$\frac{3-2d-d'}{d(3-d)}(-3(d-d'))x = -\frac{2r}{1-r^2}(-3(d-d')),$$

so that we get:

$$\frac{dx}{dr} = x = -\frac{2r}{1-r^2} \frac{d(3-d)}{3-2d-d'}, \dots \dots \dots (4)$$

and a similar expression for $y = \frac{dd'}{dr}$, which differs from the above only in this that d and d' are interchanged. It is this comparatively simple result, which makes us find the coefficients a, b, c , etc. pretty soon. Substitution, namely of $\left\{ \begin{matrix} d \\ d' \end{matrix} \right. = 1 \pm 2ar + 2br^2 \pm 2cr^3 + 2d^2$

immediately gives:

$$2a + 4br + 6cr^2 + 8dr^3 = -\frac{2r}{1-r^2} \frac{(1+2ar+2br^2+..)2(1-ar-br^2-..)}{-2ar-6br^2-2cr^3-6dr^4-...}$$

i. e.

$$(a+2br+3cr^2+4dr^3)(a+3br+cr^2+3dr^3) = \frac{(1+2ar+2br^2+2cr^3)(1-ar-br^2-cr^3)}{1-r^2},$$

or

$$a^2 + 5abr + (4ac + 6b^2)r^2 + (7ad + 11bc)r^3 = \frac{1+ar+(b-2a^2)r^2+(c-4ab)r^3}{1-r^2} = 1 + ar + (1+b-2a^2)r^2 + (a+c-4ab)r^3.$$

And from this follows:

$$a^2 = 1; 5ab = a; 4ac + 6b^2 = 1 + b - 2a^2; 7ad + 11bc = a + c - 4ab,$$

i. e.

$$\underline{a = 1}; \quad \underline{b = \frac{1}{5}}; \quad \underline{c = -\frac{13}{50}}; \quad \underline{d = \frac{64}{875}}.$$

For the knowledge of a and b only we should have to go no further than terms with τ , and so the calculation would then be very simple indeed.

8. After the above digressions, which have made us acquainted to a certain extent with the nature of the problem, and the results of which may later on be used for a comparison, we proceed: in the first place to derive the reduced equations for the case of *association* of the molecules, and in the second place to determine from this the coefficients a and b of the expansion into series:

$$d = 1 + a\tau + b\tau^2$$

in the neighbourhood of the critical point.

From the equation of state

$$p = \frac{1+x\beta}{1+x} RT - \frac{a}{v^2} - \frac{b}{v^3},$$

in which all the quantities are made to refer to single molecular quantities, and in which RT is therefore multiplied by $(1+x\beta) : (1+x)$ instead of by $1+x\beta$, the equation

$$\frac{1}{27} f_2' \frac{a}{b k^2} \varepsilon = \frac{1+x\beta}{1+x} \frac{8}{27} \frac{f_1' a}{b k n} - \frac{a}{(2,1)^2 b k^2 n^2},$$

or

$$\frac{f_2'}{f_1'} \varepsilon = \frac{8}{2,1} \frac{1+x\beta}{1+x} \frac{m}{n} - \frac{27}{(2,1)^2 f_1' n^2}.$$

follows by substitution of

$$p = \varepsilon p_l, \quad T = m T_l, \quad v = n v_l, \quad b = \gamma b_l,$$

in which (see I, p. 296—297)

$$p_k = \frac{1}{27} f_2' \frac{a}{b_l^2}; \quad RT_k = \frac{8}{27} f_1' \frac{a}{b_l}; \quad v_k = 2,1 b_k.$$

Hence, by equalisation of the expressions for $\frac{f_2'}{f_1'} \varepsilon$ for the two co-existing phases:

$$\frac{1-x\beta}{2,1-\gamma d} - \frac{1-x\beta'}{2,1-\gamma' d'} = \frac{6}{8} \frac{d^2-d'}{m}, \quad \dots \quad (10)$$

when we again introduce the densities $d = 1:n$ and $d' = 1:n'$. For

$x=1$ ($v=2$) (association to double molecules) we have viz. (see I p. 297):

$$\frac{27}{(2,1)^2 f_1} = \frac{27}{(2,114)^2 \times 1,004} = \frac{27}{4,469 \times 1,004} = \frac{6,042}{1,0043} = 6,016,$$

for which we have written 6 for brevity's sake. So in later calculations in (10) 2,1 must always be replaced by 2,114 and 6 by 6,016 — at least for $x=1$. At constant b this value 6 becomes $\frac{27}{3^2} = 3$, while $\frac{1+x\beta^2}{1+x}$, γ etc. become all $= 1$, so that then the original relation (1) is found back (see II, p. 432).

The former logarithmic relation, formed from $\int p dv$ must now be obtained in a somewhat different way, because the direct integration would become too intricate in consequence of the variability of β and b . The same result is, however, obtained by equalisation of the thermodynamic potentials of the two coexisting phases¹⁾, and the formula

$$(1+x) \log \left[\frac{p + \frac{a}{v^2} \frac{\beta}{p + \frac{a}{v^2}} \frac{1+x\beta^2}{1+x\beta^2}}{1+x\beta^2} \right] = \frac{a}{RT} \left[2 \left(\frac{1}{v} - \frac{1}{v'} \right) - (1+x)b_2 \left(\frac{1}{v^2} - \frac{1}{v'^2} \right) \right]$$

is then found, as we derived before [see among others Solid State V p. 456 (These Proc. Nov. 1910) and VII p. 89 (June 1911)]. But as here everything refers to double molecular quantities, and in future everything will refer to single quantities, we must substitute $a : (1+x)^2$ for a , b_2 for $(1+x)b_2$, $v : (1+x)v$, and we get:

$$\log \left(\frac{v'-b}{v-b} \frac{\beta}{\beta'} \right) = \frac{a}{RT} \left[2 \left(\frac{1}{v} - \frac{1}{v'} \right) - b_2 \left(\frac{1}{v^2} - \frac{1}{v'^2} \right) \right], \quad (11)$$

when $p + \frac{a}{v^2}$ is replaced by $\frac{1+x\beta^2}{1+x} RT : (v-b)$ and $p + \frac{a}{v'^2}$ by the corresponding expression.

In this connection we will just show that equation (11) is identical with that which would follow from $p = \frac{1}{v-b} \int p dv$. Let us for this

purpose write (11) in the form

$$RT \log \left(\frac{v'-b}{v-b} \frac{\beta}{\beta'} \right) = \left(\frac{a}{v} - \frac{a}{v'} \right) + \left[\left(\frac{a}{v} - \frac{a}{v'} \right) - b_2 \left(\frac{a}{v^2} - \frac{a}{v'^2} \right) \right],$$

in which the expression between [] can be written:

¹⁾ Cf. also Chemisch Weekblad 1909, N^o. 51.

$$\frac{a}{r^2} (c - b_2) - \frac{a}{r'^2} (c' - b_2) = \left(\frac{1 + x\beta}{r - b} RT - p \right) (r - b_2) - \left(\frac{1 + x\beta'}{r' - b'} RT - p \right) (r' - b_2),$$

or

$$RT \left[\frac{1 + x\beta}{1 + x} \frac{r - b_2}{r - b} - \frac{1 + x\beta'}{1 + x} \frac{r' - b_2}{r' - b'} \right] + p (v' - v).$$

Hence after substitution and solution of p :

$$p = \frac{RT}{r' - r} \log \left(\frac{r' - b' \beta'}{r - b \beta} \right) - \frac{a}{r' - r} \left[\frac{RT}{v' - r} \left[\frac{1 + x\beta'}{1 + x} \frac{r' - b_2}{r' - b'} - \frac{1 + x\beta}{1 + x} \frac{r - b_2}{r - b} \right] \right]. \quad (11^a)$$

And now it is immediately seen that in (11^a), for b constant — in which $b = b' = b_2$, while $(1 + \beta) : (1 + x)$ and $(1 + \beta') : (1 + x)$ both become $= 1$ — the last term disappears and the following equation remains:

$$p = \frac{RT}{r' - r} \log \frac{r' - b'}{r - b} - \frac{a}{r' - r},$$

as before. So the second member of equation (11^a) can be considered

as the value of the integral $\frac{1}{r' - r} \int p dv$, but obtained by an indirect course by equalisation of the thermodynamic potentials.

Now, after this short digression, we return to (11). In consequence of the substitutions $v - nr_k$, etc. — to which $b_2 = sb_k$ can be added, this equation reduces to

$$\log \left(\frac{2,1 b_k n' - b_k \gamma' \beta'}{2,1 b_k n - b_k \gamma \beta} \right) = \frac{a}{8 \cdot \frac{a}{27} \cdot \frac{a}{b_k^m}} \left[\frac{2}{2,1 b_k} \left(\frac{1}{n} - \frac{1}{n'} \right) - \frac{s b_k}{(2,1)^2 b_k^2} \left(\frac{1}{n^2} - \frac{1}{n'^2} \right) \right],$$

or to

$$\log \left(\frac{d \cdot 2,1 - \gamma' d' \beta'}{d \cdot 2,1 - \gamma d \beta} \right) = \frac{6}{8} \frac{d - d'}{m} \left[2 \times 2,1 - s (d + d') \right], \quad \dots (12)$$

because $1 : n = d$, etc. and (for $x = 1$) 6 has been substituted for 27 : $(2,1)^2 f_1 = 6,016$. Here too our former relation (2) for b constant (11, p. 433) is found back when we put β and β' , γ and $\gamma' = 1$, replace 6 by 3 (see above), 2,1 too by 3, while also s becomes $= 1$.

Now it is the equations (10) and (12) that quite determine d and d' as functions of m . But the presence of β and γ now makes the problem much more intricate. We shall see that in the expression for the coefficient a of the expansion $d = 1 + ar + br^2$ even the third differential quotient with respect to r of the quantity b of van

DER WAALS'S equation of state occurs, whereas in the expression for the coefficient b even the *fifth* differential quotient $\frac{d^5b}{dv^5}$ plays a part.

9. Of the different ways by which we can arrive at the knowledge of the coefficient a , the following one seems the simplest to me. As (see I p. 283)

$$b = b_2 - (1 - \beta) \Delta b,$$

b_k is also $= b_2 - (1 - \beta_k) \Delta b$, and we find by subtraction:

$$b - b_k = (\beta - \beta_k) \Delta b,$$

i.e. after division by b_k :

$$\beta - \beta_k = \frac{b_k}{\Delta b} (\gamma - 1),$$

because $b = \gamma b_k$. Now we put (see I, p. 283).

$$(1 + x\beta) \frac{\Delta b}{v - b} = q,$$

hence we have also:

$$(1 + x\beta_k) \frac{\Delta b}{v - b_k} = q_k,$$

and so we can substitute $\frac{v_k - b_k}{1 + x\beta_k} q_k$ for Δb , so that we get:

$$\beta - \beta_k = \frac{b_k}{v_k - b_k} \frac{1 + x\beta_k}{q_k} (\gamma - 1),$$

and hence, putting $(1 + x\beta) : (1 + x) = \alpha$:

$$\beta = \beta_k - \frac{(1 - x) \alpha}{1,1 q_k} (\gamma - 1) \dots \dots \dots (13)$$

because $v_k : b_k = 2,1$, so $(v_k - b_k) : b_k = 2,1 - 1 = 1,1$. (This value 1,1 is subjected to a slight modification, just as the other numerical values, when x is taken successively = 1, 2, etc.). Now we have always:

$$b = b_k + b'_k (v - v_k) + \frac{1}{2} b_k'' (v - v_k)^2 + \frac{1}{6} b_k''' (v - v_k)^3 + \text{etc.},$$

in which $b'_k = \left(\frac{db}{dv}\right)_k$, etc. Hence division by b_k gives:

$$\gamma = 1 + 2,1 p' (u-1) + 2,1 p'' (u-1)^2 + 2,1 p''' (u-1)^3 + \text{etc.} \quad (14)$$

$$\begin{aligned} \text{because } \frac{r-r_k}{b_k} &= \frac{(n-1)r_k}{b_k} = 2,1(n-1) \quad ; \quad \frac{(r-r_k)^2}{b_k} = \frac{(n-1)^2 r_k^2}{b_k} \\ &= 2,1(n-1)^2 \cdot r_k \quad ; \quad \frac{(r-r_k)^3}{b_k} = \frac{(n-1)^3 r_k^3}{b_k} = 2,1(n-1)^3 \cdot r_k^2 ; \end{aligned}$$

while

$$b'_k = p' \quad ; \quad \frac{1}{2} b_k'' r_k = p'' \quad ; \quad \frac{1}{6} b_k''' r_k^2 = p'$$

has been put.

In consequence of (14), (13) now reduces to

$$\beta^3 = \beta_k + \frac{2,1(1+x)\alpha_k}{1,1 q_k} p' (n-1) + \frac{2,1(1+x)\alpha_k}{1,1 q_k} p'' (n-1)^2 + \dots \quad (15)$$

and so also, because $\alpha = (1+x\beta) : (1+x)$ (see above):

$$\alpha = \alpha_k \left[1 + \frac{2,1 x}{1,1 q_k} p' (n-1) + \frac{2,1 x}{1,1 q_k} p'' (n-1)^2 + \dots \right] \quad (15a)$$

By the aid of the found expressions for γ and α we shall now calculate the fraction

$$\frac{1+x\beta}{1+x} d = \frac{\alpha d}{2,1 - \gamma d} = \frac{\alpha}{2,1 n - \gamma}$$

in (10). We find for it:

$$\frac{\alpha}{2,1 n - \gamma} = \frac{\alpha_k \left(1 + \frac{2,1 x}{1,1 q_k} p' (n-1) + \frac{2,1 x}{1,1 q_k} p'' (n-1)^2 + \dots \right)}{2,1 n - 1 - 2,1 p' (n-1) - 2,1 p'' (n-1)^2 - \dots}$$

But as evidently $2,1 n - 1 = 1,1 + 2,1(n-1)$, this becomes:

$$\frac{\alpha}{2,1 n - \gamma} = \frac{\alpha_k \left(1 + \frac{2,1 x}{1,1 q_k} p' (n-1) + \frac{2,1 x}{1,1 q_k} p'' (n-1)^2 + \dots \right)}{1,1 + \frac{2,1}{1,1} (1-p') (n-1) - \frac{2,1}{1,1} p'' (n-1)^2 - \dots}$$

If now the second member is represented by

$$\frac{\alpha_k}{1,1} \left[1 - \frac{2,1}{1,1} A (n-1) + \frac{2,1}{1,1} B (n-1)^2 - \dots \right],$$

the coefficients A , B , C , etc. may be determined from

$$\begin{aligned} & 1 + \frac{2,1 x}{1,1 q_k} p' (n-1) + \dots \\ &= \left[1 - \frac{2,1}{1,1} A (n-1) + \dots \right] \left[1 + \frac{2,1}{1,1} (1-p') (n-1) - \dots \right]. \end{aligned}$$

In this we find by equalisation of the coefficients of the different powers of $n-1$:

$$\left. \begin{aligned} A &= 1 - p' \left(1 + \frac{x}{q_k} \right); & B &= \frac{2,1}{1,1} A (1-p') + p'' \left(1 + \frac{x}{q_k} \right) \\ C &= \frac{2,1}{1,1} B (1-p') + \frac{2,1}{1,1} A p'' - p''' \left(1 + \frac{x}{q_k} \right) \\ D &= \frac{2,1}{1,1} C (1-p') + \frac{2,1}{1,1} B p'' - \frac{2,1}{1,1} A p''' + p^{IV} \left(1 + \frac{x}{q_k} \right) \\ E &= \frac{2,1}{1,1} D (1-p') + \frac{2,1}{1,1} C p'' - \frac{2,1}{1,1} B p''' + \frac{2,1}{1,1} A p^{IV} - p^V \left(1 + \frac{x}{q_k} \right) \end{aligned} \right\} \cdot (16)$$

Now equation (10) passes into

$$\begin{aligned} & \frac{2,1 \alpha_k}{(1,1)^2} \left[-A \left\{ (n-1) - (n'-1) \right\} + B \left\{ (n-1)^2 - (n'-1)^2 \right\} - \right. \\ & \left. - C \left\{ (n-1)^3 - (n'-1)^3 \right\} + \dots \right] = \frac{6 (n'-n) (n'+n)}{8 n^2 n'^2 \cdot m} \quad (10a) \end{aligned}$$

In this the coefficient $\frac{6}{8}$ may be replaced by another expression.

We saw, namely (see above), that 6 is properly $= 27 : (2,1)^2 f_1$, in which (see I, p. 297)

$$f_1 = \frac{1+x}{1+x\beta_k} \frac{n_k^2 (3m_k^2 - 2n_k)}{m_k^5}.$$

In this m_k and n_k (given by (5) on p. 288 loc. cit.) have of course another meaning than the above m and n , so that we have marked them with the index k to distinguish them. Now we can also write for f_1 :

$$f_1 = \frac{1}{\alpha_k} \cdot \frac{9}{4} \left(\frac{v_k - b_k}{v_k} \right)^2 \cdot 3 \frac{b_k}{v_k} \cdot m_k,$$

because $\frac{v_k - b_k}{v_k} = \frac{2n_k}{3m_k^2}$, and $\frac{b_k}{v_k} = \frac{3m_k^2 - 2n_k}{3m_k^2}$. (see I, p. 288). In consequence of this we obtain

$$f_1 = \frac{27 (1,1)^2 m_k}{4 (2,1)^3 \alpha_k},$$

because $v_k : b_k = 2,1$ and $(v_k - b_k) : b_k = 1,1$. What we have represented by the figure 6 is therefore, properly speaking:

$$\frac{27}{(2,1)^2} \times \frac{4 (2,1)^3 \alpha_k}{27 (1,1)^2 m_k} = 4 \frac{2,1 \alpha_k}{(1,1)^2 m_k}.$$

So we get, dividing both members of (10a) by $\frac{2,1 \alpha_k}{(1,1)^2} (n'-n)$:

$$A - B \left\{ (n-1) + (n'-1) \right\} + C \left\{ (n-1)^2 + (n-1)(n'-1) + (n'-1)^2 \right\} + \dots = \\ = \frac{1}{m_k} \frac{1}{n^2 n'^2 m} \frac{1}{2} (n+n'), \dots \dots \dots (10b)$$

in which m_k has been given by (see p. 288 loc. cit.):

$$m_k = 1 + \frac{1}{x+1} \beta_k (1-\beta_k) (x+q_k)^2.$$

For $x=1$ m_k is e. g. = 1,107 (see p. 297 loc. cit.). If we now put again, just as in the expansion of $d=1:n$ (the further developments confirm again that $1-n$ and $n'-1$ are really of the order of magnitude $\tau = \sqrt{1-m}$):

$$\begin{aligned} n &= 1 - a'\tau + b'\tau^2 \dots \dots \dots \\ n' &= 1 + a'\tau + b'\tau^2 \dots \dots \dots \end{aligned}$$

we may write for the second member of (10b):

$$\frac{1}{m_k} \frac{1+b'\tau^2}{[(1+b'\tau^2)^2 - a'^2\tau^2]^2} \frac{1}{1-\tau^2} = \frac{1}{m_k} \frac{1+b'\tau^2}{[1-(2a'^2-4b')\tau^2](1-\tau^2)}$$

as $m=1-\tau^2$, and because we shall for the present content ourselves with terms of the degree τ^2 .

Now (10b) passes into

$$A - B(2b'\tau^2) + C(a'^2\tau^2 - a'^2\tau^2 + a'^2\tau^2) = \frac{1}{m_k} \left(1 + (1+2a'^2-3b')\tau^2 \right), (10c)$$

and it is only left to calculate A , B and C . For A we find from (16):

$$A = 1 - p' \left(1 + \frac{x}{q_k} \right).$$

But we can easily show that this $= \frac{1}{m_k}$. For we found in I, p. 292:

$$b' = \frac{db}{dv} = \frac{\frac{1}{x+1} \beta (1-\beta) q (x+q)}{1 + \frac{1}{x+1} \beta (1-\beta) (x+q)^2} = \frac{q}{x+q} \frac{m-1}{m}, \dots \dots (a)$$

because m has been written for the denominator of the expression for $b' = \frac{db}{dv}$ (see above). Hence also, because $b'_k = p'$ has been put:

1) See for the equality of the numerical values of the coefficients a' , b' , etc. for n and n' the observations in II, p. 438-439.

$$A = 1 - \frac{m_k - 1}{m_k} = \frac{1}{m_k},$$

so that the equality of the terms with τ^n identically has been fulfilled. So there remains:

$$-B(2b'\tau^2) + C(a'^2\tau^2) = \frac{1}{m_k}(1+2a'^2-3b')\tau^2. \quad (10d)$$

After substitution of $A = \frac{1}{m_k}$ we find for B from (16):

$$B = \frac{2,1}{1,1} \frac{1-p'}{m_k} + p'' \left(1 + \frac{x}{q_k} \right).$$

In this $p'' \left(1 + \frac{x}{q_k} \right)$ can be expressed in p' by the aid of a relation, holding between p' and p'' at the critical point. We have viz. (see I p. 285):

$$\frac{dp}{dv} = \frac{2a}{v^3} - \frac{RT}{\Delta b(v-b)} \frac{q}{m},$$

and hence:

$$\frac{d^2p}{dv^2} = -\frac{6a}{v^4} + \frac{RT(1-b')q}{\Delta b(v-b)^2 m} - \frac{RT}{\Delta b(v-b)} \frac{d}{dv} \left(\frac{q}{m} \right).$$

At the critical point $\frac{dp}{dv} = 0$ and also $\frac{d^2p}{dv^2} = 0$, hence we have there:

$$\frac{q}{m} = \frac{2a}{v^3} : \frac{RT}{\Delta b(v-b)}; \quad \frac{1-b'q}{v-b} \frac{q}{m} - \frac{d}{dv} \left(\frac{q}{m} \right) = \frac{6a}{v^4} : \frac{RT}{\Delta b(v-b)}.$$

And from this follows:

$$\frac{1-b'q}{v-b} \frac{q}{m} - \frac{d}{dv} \left(\frac{q}{m} \right) = \frac{3}{v} \cdot \frac{q}{m},$$

or

$$\frac{d}{dv} \left(\frac{q}{m} \right)_k = \frac{(1-b'_k - \frac{3}{v_k}) q_k}{(v_k - b_k) m_k}, \quad \dots \dots \dots (\alpha)$$

in which we must bear in mind that this relation only holds for T_k , $\frac{dp}{dv}$ and $\frac{d^2p}{dv^2}$ being = 0 only there.

Now we saw above that $1 - b' \left(1 + \frac{x}{q} \right) = \frac{1}{m}$, so also:

$$q - b'(x+q) = \frac{q}{m},$$

and hence

$$(1-b') \frac{dq}{dv} - b''(x+q) = \frac{d}{dv} \left(\frac{q}{m} \right), \dots \dots \dots (3)$$

which relation holds everywhere, and not only for T_k . But only *there* $\frac{d}{dv} \left(\frac{q}{m} \right)$ may be replaced by its value from (a), and we get:

$$(1-b') \left(\frac{dq}{dv} \right)_k - b''_k(x+q_k) = \left(\frac{1-b'_k}{v_k-b_k} - \frac{3}{v_k} \right) \frac{q_k}{m_k},$$

or after substitution of $\frac{1}{v-b} \frac{q}{m}$ for $\frac{dq}{dv}$ (see loc. cit. p. 285):

$$b''_k(x+q_k) = \left[\frac{3}{v_k} - \frac{2(1-b'_k)}{v_k-b_k} \right] \frac{q_k}{m_k},$$

i. e.

$$\frac{1}{2} b''_k v_k \frac{x+q_k}{q_k} = \frac{1}{m_k} \left[\frac{3}{2} - (1-b'_k) \frac{v_k}{v_k-b_k} \right],$$

or (see above)

$$p'' \left(1 + \frac{x}{q_k} \right) = \frac{1}{m_k} \left[\frac{3}{2} - \frac{2,1}{1,1} (1-p') \right] \dots \dots (17)$$

This is the required relation between p'' and p' at T_k , and in consequence of this the value of B (see above) passes into

$$B = \frac{2,1}{1,1} \frac{1-p'}{m_k} + \frac{1}{m_k} \left[\frac{3}{2} - \frac{2,1}{1,1} (1-p') \right] = \frac{3}{2} \frac{1}{m_j}.$$

Now our last equation (10d) becomes:

$$-\frac{3b'}{m_k} \tau^2 + Ca'^2 \tau^2 = \frac{1}{m_k} (1+2a'^2) \tau^2 - \frac{3b'}{m_k} \tau^2,$$

so that also the terms with the coefficient b' are cancelled, and only

$$Ca'^2 \tau^2 = \frac{1+2a'^2}{m_k} \tau^2 \dots \dots \dots (10e)$$

is left, from which immediately

$$a'^2 = \frac{1}{Cm_k-2} \dots \dots \dots (18)$$

is found.

And now the coefficient a' is found, because C can easily be calculated. Also from the second equation, viz. (12), we might have calculated the value of a' , but then the calculation would have been more lengthy, and the result quite the same, of which we have convinced ourselves for the greater security. For the calculation of the following coefficient b' , however, we shall have to use the equation (12) by the side of (10).

By way of control the following remarks may serve. It follows from (16) for the case b constant, in which p', p'', p''' , etc. are all $= 0$, that $C = \frac{2,1}{1,1} B$, i. e. $Cm_k = \frac{3}{2} \cdot \frac{2,1}{1,1}$. But then $\frac{2,1}{1,1}$ passes into $\frac{3}{2}$ (since $v_k : b_k$ is not $= 2,1$ then, but $= 3$), so that Cm_k becomes $= \frac{9}{4}$. Hence $a'^2 = \frac{1}{2^{1/4} - 2} = 4$, and so $\underline{a' = 2}$ as it should be. (Before we put (see II, p. 438) $d = 1 + 2a\tau$, whereas we now put $n = 1 : d = 1 - a'\tau$, so that $a' = 2a$).

In the general case we find for C from (16):

$$C = \frac{2,1}{1,1} \frac{3}{2} \frac{1-p'}{m_k} + \frac{2}{1,1} \frac{p''}{m_k} - p''' \left(1 + \frac{x}{q_k} \right),$$

so that we get:

$$a'^2 = \frac{1}{\frac{2,1}{1,1} \left[\frac{3}{2} (1-p') + p'' \right] - p''' m_k \left(1 + \frac{x}{q_k} \right) - 2} . . . (18^a)$$

I will just call attention to this, that the value of a' has been derived by me in at least four different ways, and that always identical results were obtained. Moreover I have convinced myself that the coefficients in the development of n and n' have really the same numerical values; only with difference of sign for the odd powers of $\tau = \sqrt{1-m}$ (see also II, p. 438).

It also follows from the expression derived by us just now for the coefficient a' in the expansion into series $n = 1 - a'\tau + b'\tau^2$, that — for the determination of the relations at the critical point — it is *not sufficient* to know the differential quotients $b'_k = \left(\frac{db}{dv} \right)_k$ and $b''_k = \left(\frac{d^2b}{dv^2} \right)$, but that also the knowledge of the *third* differential quotient of b with respect to v , viz. $b'''_k = \left(\frac{d^3b}{dv^3} \right)_k$ at the critical point, is indispensable. And for the coefficient b' in the above expansion into series, which coefficient determines the *direction* of the "straight" diameter in T_k , the knowledge even of the *fourth* and *fifth* differential quotient will appear to be required.

Let us now proceed, therefore, to the calculation of the *third* differential quotient.

10. The third differential quotient. We start from the formula (11) for $b' = \frac{db}{dv}$ (see I, p. 292), viz.

$$b' = \frac{\frac{1}{x+1} \beta(1-\beta)f(x+q)}{1 - \frac{1}{x+1} \beta(1-\beta)(x+q)^2} \text{ of } \frac{1}{b'} = \frac{1}{\frac{1}{x+1} \beta(1-\beta)f(x+q)} + \frac{x+q}{q}. \quad (1)$$

From this follows (representing $\frac{1}{x+1} \beta(1-\beta)q(x+q)$ by N , so that $b' = \frac{N}{m}$):

$$-\frac{b''}{b'^2} = -\frac{1}{N^2} \left[\frac{1}{x+1} \beta(1-\beta)(x+2q) \left(-\frac{1}{v-b} \frac{q}{m} \right) + \frac{1}{x+1} q(x+q)(1-2\beta) \cdot \frac{b'(1+x\beta)}{q(v-b)} \right] - \frac{x}{q^2} \left(-\frac{1}{v-b} \frac{q}{m} \right).$$

taking the values found in I, p. 285 (formulae (d) and (ε)) for $\frac{df}{dv}$ and $\frac{d\beta}{dv}$ into consideration, viz.

$$\frac{df}{dv} = -\frac{1}{v-b} \frac{q}{m}; \quad \frac{d\beta}{dv} = \frac{1+x\beta}{v-b} \frac{b'}{q},$$

bearing in mind that $1 + \frac{1}{x+1} \beta(1-\beta)(x+q)^2 = m$ has been put, and the second member of (d) is evidently $= \frac{b'}{q}$. Hence:

$$\frac{b''}{b'^2} = \frac{1}{N^2(v-b)} \left[-\frac{\frac{1}{x+1} \beta(1-\beta)f(x+2q)}{m} + \frac{1}{x+1} (x+q)(1+x\beta)(1-2\beta) b' \right] - \frac{1}{v-b} \frac{x}{qm}.$$

Now N is evidently $= b'm$ (see above), and $\frac{1}{x+1} \beta(1-\beta)f(x+2q) : m = \frac{x+2q}{x+q} b'$, so that we get:

$$(v-b) b'' = \frac{b'}{m^2} \left[-\frac{x+2q}{x+q} - \frac{x+q}{x+1} (1+x\beta)(2\beta-1) \right] - b'^2 \frac{x}{qm},$$

i. e.

$$(v-b) b'' = -\frac{b'}{m^2} \left[\frac{x+2f}{x+q} + \frac{x+q}{x+1} (1+x\beta)(2\beta-1) + x \frac{mb'}{q} \right].$$

Replacing in this mb' by $\frac{1}{x+1} \beta(1-\beta)q(x+q)$ (see above), we get:

$$(v-b) b'' = -\frac{b'}{m^2} \left[\frac{x+2f}{x+q} + \frac{x+q}{x+1} \left\{ (1+x\beta)(2\beta-1) + x\beta(1-\beta) \right\} \right],$$

i. e.

$$(v-b) b'' = -\frac{b'}{m^2} \left[\frac{x+2f}{x+q} + \frac{x+q}{x+1} (x\beta^2 + 2\beta - 1) \right], \dots (2)$$

identical with (12) in I, p. 293, paying attention to the above expression (1) for b' . This derivation seems somewhat shorter to me than that in I, p. 292—293, and besides confirms the validity of the result, so that we can calculate b''' from it with full assurance.

Clarens, Nov. 13, 1911.

(To be concluded).

Astronomy. — “A photographic method of research into the structure of the galaxy.” By Dr. A. PANNEKOEK. (Communicated by E. F. VAN DE SANDE BAKHUYZEN).

(Communicated in the meeting of November 25, 1911).

In my paper: “Researches into the structure of the galaxy”, published in the Proceedings of the Meeting of June 25, 1910, I have pointed out that the chief difficulty in this kind of researches consists in the lack of completeness and homogeneity in the material of star-countings that is at our disposal. HERSCHEL’s and EPSTEIN’s gauges and the countings on photographic and other stellar charts have relation to small, generally non-coincident parts of the examined galactic region. Owing to this the fluctuations of density, which may be considerable even in smaller regions (comp. MAX WOLF’s and BARNARD’s photographs of the Milky Way), appear with their full amount as errors of the function $N(m)$ (number of stars per square degree as function of the limiting magnitude m). At best we may only hope that in the mean of a great amount of countings these irregularities lose their influence. Still there always remains uncertainty and doubt justifying the question whether these drawbacks may not be avoided by another method.

This may be done by having recourse to photography. In this manner the chief condition may be fulfilled at once : for all magnitudes m exactly the same part of the heavens is taken and counted. Hence the local differences in star-density become altogether harmless ; as the irregularities shown by the function $N(m)$ itself are probably much smaller, this function may now be more easily deduced. If all numbers N for different m can be determined on one and the same exposure then the influence of the transparency of the air, of the different sensitiveness of the plates, of the development etc., disappears at the same time.

Another condition which is of the greatest importance for the practicability of the method, consists in the fact that for the determination of N only countings are wanted without estimates or measurement of the brightness of the stars.

One can e.g. make two photographs on one plate with the same time of exposure, one without and one with a screen interposed, the absorption of which is known to be α magnitudes. This absorption may be determined by photometrical measurements, most precisely by measuring the diminution of surface-brightness by the screen. This is equal to half of the stellar absorption in magnitudes and it is independent of the wave-length of the light. By counting the stars appearing only on the photograph taken without the screen and the stars showing both images we get two numbers $N(m)$ and $N(m-\alpha)$, for which we accurately know the difference α of the limiting magnitudes, which is specially important for determining the value of the gradient $\frac{d \log N}{dm}$. The absolute value of m may be

found by measuring a few individual stars. We might also in order to find a third value, count the number of stars, for which moreover the first diffraction-image is visible. But only when the gauze is so coarse that the first spectrum is contracted practically into a star-shaped image, its visibility depends on the entire quantity of light. Otherwise the limiting visibility depends also on the colour of the stars and the difference in visibility between the diffracted and the principal image is theoretically unknown.

Another method will be more practical. We take a number of photographs on the same plate with *geometrically progressing times of exposure*. Of each star we then obtain a series of images, each time differing in brightness a constant number of magnitudes. Now we simply have to count the number of stars with one visible image, with two images, with three, with four, with five images. These give the numbers N corresponding with the limiting magni-

tudes m , which increase each time with a constant amount. To remove the uncertainty owing to the confusion of the faintest star-images with spots in the plate it is advisable to take the photograph of longest exposure twice. The faintest stars are then all double and undoubtedly recognisable, while there can be no doubt about the visibility of the faintest image of the brighter stars, because the place where we have to look for it is accurately known.

In this method, however, the difference in brightness between the several images is not known beforehand and must therefore be determined by special measurements. We know approximately how many magnitudes are gained by a certain lengthening of the time of exposure,¹⁾ but this increase differs for different plates and must therefore be determined for each plate by itself. Therefore a scale of photographic magnitudes must be fixed on the plate. These magnitudes cannot be derived from a scale of visual brightness since the spectra of the faint stars are unknown. It must be performed independently by photographic methods.

Up till now there does not exist a scale of photographic stellar magnitudes (defined by $m = 2.5 \log L$), which is independent of visual brightness. Generally it is determined in such a manner that they correspond for the stars of a certain spectral class (HARVARD A.) to the visual photometric scale. Also in PICKERING'S "Report on stellar magnitudes in KAPTEYN'S selected areas"²⁾ the necessity for fixing the scale of magnitudes for the fainter stars by means of prismatic companions, of exposures of different length or with wire-gauzes, is only mentioned in general terms. It is plain, however, that the first two methods cannot give an independent scale-value. This can be done only by a wire-gauze the absorption of which has been determined by physical experiments. Another independent method has been proposed recently by HERTZSPRUNG, viz. to use the first diffracted image obtained with a coarse screen in front of the objective, the strips of which are of the same width as the spaces between them.

So a "scale-plate" must be taken of the same part of the heavens of which a "counting-plate" has been made, in order to determine the magnitudes; on the first one two exposures of the same

¹⁾ According to SCHWARZSCHILD (Beiträge zur photographischen Photometrie der Gestirne) is $\log I + p \log t = \text{const.}$; the values found for p were generally lying between 0,7 and 0,9. Accepting 0,8 as mean, then with a tenfold time of exposure $\log I = 0,8$, and the gain is exactly two magnitudes.

²⁾ J. C. KAPTEYN, First and second Report on the progress of the plan of selected areas 1911. p. 31.

duration have to be made, one with a free objective, and one with a wire-gauze, or according to HERTZSPRUNG's method, the second one with the coarse screen. We thus obtain two images of each star on the plate, differing a *known number of magnitudes* and from this there may be deduced a scale of photographic magnitudes on the plate, which is altogether independent of visual magnitudes.

This method, however, has this drawback that the two exposures are taken one after the other, so that, owing to changes in the transparency of the atmosphere the real difference in brightness does not correspond to the difference found on the plate. Hence the basis of the method becomes doubtful. In order to escape this objection another photograph should be taken at the same time with a second apparatus to control the first. Another means is the application of SCHWARZSCHILD's method in which a fine wire gauze is interposed in the cone of rays a little way before the focus. This produces the same kind of images as a gauze before the objective and the diminution of brightness of the principal image is the same. If for the first exposure the gauze is placed before one half of the plate, leaving the rest uncovered, and if for the second the gauze is placed before the other half of the plate, we obtain two images of every star on the plate, one undiminished, the other weakened, except in the central zone which is no use because the rays partially passed through the gauze. If α stands for the absorption-coefficient, d for the difference in brightness owing to the change of the atmospherical transparency, then the difference of the images on the one half of the plate is $\alpha + d$, on the other half $\alpha - d$, and in the mean the influence of d disappears.

As soon as an accurate, independent and reliable scale of photographic magnitudes has been fixed for a definite region of the heavens (e. g. for the zone near the north-pole), then we can determine the stellar magnitudes of any other part simply by taking it together with the polar region on one and the same plate. As long as this ideal has not been attained the scale must be fixed for each region individually, for which purpose SCHWARZSCHILD's method with a half gauze in the cone of rays seems the most practicable.

For a practical determination of the stellar magnitudes we can measure the diameters of both the undiminished and the weakened images of a number of stars forming a series of decreasing brightness. For the faintest images a scale of blackness gives a continuation of the scale of diameters. From this the stellar magnitude as function of the diameter may easily be computed. The same end, however, may be attained just about as accurately by estimates without the

need of measurements. To this end a scale of star-images must be construed, regularly progressing through properly chosen times of exposure with $\frac{1}{5}$ or $\frac{1}{4}$ magnitude. If a group of stars is photographed for instance with exposures of 9, 12, 16, 21, 28, 38, 51, 67, 90, 120, 160, 213, 285, 379, 506, 675 and 900 seconds, we obtain a scale covering 4 magnitudes with intervals of 0,25, between which each stellar image on a plate may be interpolated. It does not matter whether the difference between the extremes deviates more or less from 4 magnitudes. This scale is only a makeshift and fulfils as it were the part of a scale of millimeters in which each star is classed by measuring its diameter. With the help of a few of such overlapping scales, covering together a still greater range of stellar images it is possible to determine by estimate both the images of each star on the scale plate. The known difference between the two images enables us to reduce the brightness expressed on this provisory scale (just as the millimeter-scale of the diameters) into real magnitudes. Thanks to this the photographic brightness of a number of stars, from the brightest to the faintest, is known. The absolute value, the zero-point, may be deduced from a few bright stars of from the 6th to 8th magnitude, and need only be roughly known.

When in this manner the magnitudes of a number of stars have been determined on the scale-plate, which has to be exposed a little longer than the longest exposure of the counting plate, there only rests to be seen which of these stars show 1, 2, 3, 4, 5 images on the counting-plate. In this way the limiting brightness of each of these classes is immediately given.

With this method we therefore only want — besides the scale for estimating the magnitudes — 2 plates for each region of the Milky Way: a counting plate and a scale-plate. Practically without any measurements, hence without any other instrument than a magnifying-glass, only by countings and estimates we can thus obtain all the data which must otherwise be compiled with a great deal of trouble and far more incompletely from the different sources of catalogues, stellar charts and gauges. As Professor SCHWARZSCHILD, Director of the Astrophysical Observatory at Potsdam graciously offered to have a few plates made for this purpose with the exceedingly appropriate Zeiss-triplet of 1500 mm. focal-distance and 150 mm. aperture, and as Mr. HERTZSPRUNG astronomer at the same observatory, kindly made the photographs for me, I take these as a standard of what may be attained in this direction.

On a photograph of the polar region with this instrument on an exceedingly sensitive Lumière Sigma-plate a 10 minutes' exposure

$$\frac{d^2x}{dt_1^2} \cdot q_1(t_1) \cdot c = 0, \dots \dots \dots (C)$$

The form of I as a function of τ , or of q_1 as a function of t_1 , was then governed by the relation existing between x and y :

$$y = q(x), \dots \dots \dots (11)$$

or

$$F(x, y) = 0 \dots \dots \dots (12)$$

or in homogeneous form,

$$F(x, y, z) = 0. \dots \dots \dots (13)$$

If we regard x, y , and z as homogeneous coordinates the triangle of coordinates of which is formed by the two axes and the line at infinity, we can define the line coordinates u, v , and w belonging to this same triangle by the relation

$$Aux + Bvy + Cwz = 0,$$

or passing to the non-homogeneous form by putting $z=1$ and $w=1$

$$Aux + Bvy + C = 0. \dots \dots \dots (34)$$

This equation determines, as is known, either the line (u, v) in point coordinates (x, y) , or the point (x, y) in line coordinates (u, v) .

If now a relation (11) or (12) is given we can determine the tangential equation (in u, v) of the curve represented by them. The line coordinates u and v will then satisfy a certain differential equation. If we note the autodual character of the homogeneous linear transformation, against which the differential equation (A) — resp. (B) and (C) — is proof, we can expect the differential equations for u and v to show a close relationship with those of x and y .

It is our aim here to investigate the differential equations for u and v .

The tangent in point (x,y) of curve (11) or (12) drawn to this curve has as equation

$$Y - y = \frac{dy}{dx} (X - x)$$

or

$$- Xdy + Ydx + (xdy - ydx) = 0.$$

If we call u and v the line coordinates of this tangent, it is determined by

$$AuX + BvY + C = 0.$$

From this ensues (see (14) and (15) 1st communication p. 395).

$$u = -\frac{C}{A} \frac{dy}{xdy - ydx} = -\frac{C}{2A} \frac{dy}{dS} = -\frac{C}{cA} \frac{dy}{dt_1} = -\frac{C}{cA} y',$$

$$r = + \frac{C}{B} \frac{dx}{x dy - y dx} = \pm \frac{C}{2B} \frac{dx}{ds} = \pm \frac{C}{cB} \frac{dx}{dt_1} = \pm \frac{C}{cB} x'$$

so

$$u = - \frac{C}{cA} y' \quad , \quad v = + \frac{C}{cB} x' \quad . \quad . \quad . \quad (35)$$

By differentiation according to t_1 we find with the aid of (C),

$$u' = - \frac{C}{cA} y'' = \pm \frac{C}{cA} q_1 y,$$

$$u'' = + \frac{C}{cA} q_1' y + \frac{C}{cA} q_1 y' = + \frac{q_1'}{q_1} u' - q_1 u,$$

so that u satisfies the differential equation

$$u'' - \frac{q_1'}{q_1} u' + q_1 u = 0. \quad . \quad . \quad . \quad (36)$$

It is easy to see that v satisfies this same equation.

If we wish to put (36) in the canonical form

$$\frac{d^2 u}{dt_2^2} - q_2(t_2) \cdot u = 0 \quad . \quad . \quad . \quad (C')$$

we have to put (see (5) and (6), 1st communication p. 392)

$$dt_2 = \sqrt{\int \frac{q_1'}{q_1} dt_1} \quad dt_1 = q_1 dt_2, \quad . \quad . \quad . \quad (37)$$

$$q_2 = q_1 e^{-2 \int \frac{q_1'}{q_1} dt_1} = \frac{1}{q_1}, \quad . \quad . \quad . \quad (38)$$

where we have discarded an irrelevant constant.

To obtain the standard form (B)

$$\frac{d^2 u}{d\tau_2^2} + \frac{I_2(\tau_2)}{2} \frac{du}{d\tau_2} + u = 0$$

we must put (see (9) and (10) 1st communication p. 394)

$$d\tau_2 = \pm \sqrt{q_2} \cdot dt_2 = \pm \sqrt{q_1} \cdot dt_1 = \pm d\tau, \quad . \quad . \quad . \quad (39)$$

$$I_2 = \pm q_2^{-3/2} \frac{dq_2}{dt_2} = \mp q_1^{-3/2} \frac{dq_1}{dt_1} = \mp I. \quad . \quad . \quad (40)$$

By a proper choice of the algebraical sign and of the constant of integration we can attain that the standard form (B) has for the line coordinates *the same independent variable* as the form (B) for the point coordinates, whilst in this case *the function I(τ) reverses its sign*.

The standard form (B) for u (and v) runs therefore

$$\frac{d^2u}{d\tau^2} - \frac{I(\tau)}{2} \cdot \frac{du}{d\tau} + u = 0. \quad \dots \dots \dots (B')$$

This last result satisfies, with respect to the connection of the differential equations for x and u , in high degree the expectations expressed by us.

Let the tangential equation of the curve (11) or (12) be

$$v = \omega(u), \quad \dots \dots \dots (41)$$

or

$$L(uv) = 0, \quad \dots \dots \dots (42)$$

or, made homogeneous,

$$L(u, v, w) = 0. \quad \dots \dots \dots (43)$$

The equations can also be easily interpreted as equations between the point coordinates $\xi = u, \eta = v$ ($\xi = w$). We obtain them namely by polarising the given curve (11) or (12) and that with respect to the conic

$$Ax^2 + By^2 + C = 0, \quad \dots \dots \dots (44)$$

having its centre in O .

The pole $(\xi \eta)$ has then after all as polar line

$$A\xi x + B\eta y + C = 0,$$

so that ξ and η are really coupled by the same equation to x and y as u and v .

The result obtained by us can therefore also be given as follows:

If we transform the curve (11) or (12) by polarisation with respect to the conic (44) then there is generated a new curve dualistically conjugate to the original one, whose function I is the opposite of the function I belonging to the given curve.

If we had applied for the polarisation instead of the conic (44) the conic

$$Px^2 + 2Qxy + Ry^2 + S = 0, \quad \dots \dots \dots (45)$$

which has its centre likewise in O , we should have attained the same result. The curve $\eta_1 = \omega_1(\xi_1)$ or $L_1(\xi_1, \eta_1) = 0$, obtained by means of polarisation with respect to (45) out of (11) or (12) is then generated, as can easily be shown, out of the curve $\eta = \omega(\xi)$ or $L(\xi, \eta) = 0$, generated by polarisation with respect to (44), by application of the transformation

$$\xi = \alpha \xi_1 + \beta \eta_1, \quad \eta = \gamma \xi_1 + \delta \eta_1,$$

irrelevant for the differential equation.

So we have but to polarise the given curve with respect to a conic having its centre in O .

We shall in future call those curves generated by homogeneous linear substitution out of the given curve, *equivalent* to that given curve. On the other hand we shall call the curves deduced out of the given curve by polarisation with respect to a conic having O as centre, *semi-equivalent* to the given curve. Our result can now be formulated as follows:

Equivalent curves have the same functions I , semi-equivalent curves have opposite functions I .

Whilst the equivalent curves form a *group*, mutually connected as they are by the group of the homogeneous linear substitutions, the semi-equivalent curves form together a so-called *extended group* (Gruppe 2^{ter} Art). The semi-equivalent curves can be deduced from the equivalent curves by extending the group of the homogeneous linear substitutions with one so-called *pseudo-substitution* (Substitution 2^{ter} Art), for which we can choose the polarisation with respect to a definite conic with O as centre, e.g. with respect to $xy = 1$.

We can compare this state of affairs with the group of congruent plane figures (mutually connected by the transformations of the group of the movements in the plane) which is extended by reflections to the extended group of the congruent and symmetric plane figures. The extension to symmetric figures demands but *one* reflection.

From (37) follows still

$$dt_1 \cdot dt - q_1 dt_1^2 = d\tau^2 \dots \dots \dots (46)$$

The increment $d\tau$ of the independent variable of the standard form (B) is therefore mean proportional between the increments of the canonical independent variables conjugate to the given curve and to the curve semi-equivalent to it.

When a curve K is semi-equivalent to itself, it means that there is a homogeneous linear transformation Σ , which transforms the curve K' generated by polarisation out of K into K again.

In this case, although (ξ, η) (apart from Σ) satisfies the same equation as (x, y) , it is not necessary for dt_2 to be equal to dt_1 . For this is moreover necessary that point P' of K' , generated by polarisation out of point P of K , is likewise brought back by transformation Σ to point P . If however this last condition is satisfied, then we have $dt_1 = dt_2$, also $q_1 = 1$ (or equal to a constant). The coordinates of a point of such a curve K satisfy the equation

$$x'' + x = 0.$$

The general relation between two particular integrals of this equation runs as follows

$$Px^2 + 2Qxy + Ry^2 + S = 0.$$

The only curves, satisfying the above mentioned condition, are therefore the conics with centre in O , just those curves with respect to which the polarisation takes place.

We can in the first place regard the canonical variable of the line coordinates as the area described by the radius vector out of O of a point of the curve generated by polarisation. It can however be interpreted in the second place as follows.

Let us call ϱ the perpendicular let down out of O on the tangent of point (x, y) of the given curve K , and θ the angle made by this perpendicular with the X -axis, then ϱ and θ are evidently the polar coordinates of a point of the pedal curve of K .

Let us now compare the normal form of the equation of the tangent

$$X \cos \theta + Y \sin \theta - \varrho = 0$$

with

$$AuX + BvY + C = 0;$$

we then find

$$u = -\frac{C}{A} \cdot \frac{\cos \theta}{\varrho}, \quad v = -\frac{C}{B} \cdot \frac{\sin \theta}{\varrho},$$

from which ensues

$$2dt_1 = u dv - v du = \frac{C^2}{AB} \cdot \frac{d\theta}{\varrho^2}.$$

If we now submit the pedal curve to an inversion with respect to a circle, with centre O and radius R , then

$$\varrho_1 = \frac{R^2}{\varrho}, \quad \theta_1 = \theta$$

holds for the point conjugate to (ϱ, θ) , so that

$$\frac{C^2}{AB} \cdot \frac{d\theta}{\varrho^2} = \frac{C^2}{ABR^4} \cdot \varrho_1^2 d\theta_1.$$

If we now choose

$$R = \sqrt[3]{\frac{C^2}{AB}},$$

we find

$$2dt_2 = \varrho_1^2 d\theta_1 = 2dS_1.$$

So the canonical variable t_2 is the area described by the radius vector out of O of a point of the curve generated by inverting the pedal curve of the given curve K with respect to the circle with

O as centre and radius $R = \sqrt[3]{\frac{C^2}{AB}}$.

We now return to standard form (B).

If we replace here τ by $\tau_1 = -\tau$, we find

$$\frac{d^2x}{d\tau_1^2} - \frac{I(-\tau_1)}{2} \frac{dx}{d\tau_1} + x = 0.$$

With respect to function I we have different cases to distinguish:

1. I is a *univalent even* function of τ .

Then $I(-\tau_1) = I(\tau_1)$, so that the equation (47) belongs to the semi-equivalent curves. As however the change of τ into $-\tau$ has no influence on the connection between x and y , the curve $y = q(x)$ or $F(x, y) = 0$ must be *semi-equivalent to itself*. In other words there must be a homogeneous linear transformation Σ which transforms the curve K' obtained by polarisation again into K . An example is furnished by $I = \text{const}$. We shall look at this example more closely.

Let us put

$$I = 2(k + k^{-1});$$

then the integrals of the equation

$$\ddot{x} + (k + k^{-1})\dot{x} + x = 0$$

are $x = e^{-\frac{\tau}{k}}$ and $y = e^{-k\tau}$, so that the relation existing between x and y runs as follows:

$$y = x^{k^2}.$$

The curve K is therefore a (higher) parabola for $k^2 > 0$ whose singular point lies in O and a (higher) hyperbola for $k^2 < 0$, of which the (multiple) asymptotes meet in O .

The parabola of 2nd order demands $k^2 = 2$ (or $\frac{1}{2}$), so $I = \pm 3\sqrt{2}$.

The hyperbola of 2nd order requires $k^2 = -1$, therefore $I = 0$.

For the cubic parabola holds $k^2 = 3$ (or $\frac{1}{3}$), so $I = \pm \frac{8}{3}\sqrt{3}$.

For the semi-cubic parabola we have $k^2 = \frac{3}{2}$ (or $\frac{2}{3}$) so $I = \pm \frac{5}{3}\sqrt{6}$.

The cubic hyperbola furnishes $k^2 = -2$ (or $-\frac{1}{2}$) so $I = \pm i\sqrt{2}$.

2. I is a *univalent odd* function of τ .

Now $I(-\tau_1) = -I(\tau_1)$ so that the equation (47) is identical to (B).

The given curve is now *not* semi-equivalent to itself.

If we now put

$$\frac{x(\tau) - x(-\tau)}{2} = P_1(\tau) \quad , \quad \frac{x(\tau) + x(-\tau)}{2} = P_2(\tau),$$

then P_1 is an *odd* function of τ , P_2 an *even* one.

We then find

$$\dot{x} + \frac{I(\tau)}{2} \ddot{x} + x = \{\ddot{P}_1(\tau) + \ddot{P}_2(\tau)\} + \frac{I(\tau)}{2} \{\dot{P}_1(\tau) - \dot{P}_2(\tau)\} - \{P_1(\tau) + P_2(\tau)\} = 0 \quad (48)$$

and

$$\begin{aligned} \frac{d^2x}{d(-\tau)^2} + \frac{I(-\tau)}{2} \frac{dx}{d(-\tau)} + x &= \\ &= \left\{ \frac{d^2P_1(-\tau)}{d(-\tau)^2} + \frac{d^2P_2(-\tau)}{d(-\tau)^2} \right\} + \frac{I(-\tau)}{2} \left\{ \frac{dP_1(-\tau)}{d(-\tau)} + \frac{dP_2(-\tau)}{d(-\tau)} \right\} + \\ &- \{P_1(-\tau) + P_2(-\tau)\}; \end{aligned}$$

as \dot{P}_1 and \dot{P}_2 are even functions and \ddot{P}_1 and \ddot{P}_2 odd, we find

$$\begin{aligned} \frac{d^2P_1(-\tau)}{d(-\tau)^2} = \frac{d^2P_1(-\tau)}{d\tau^2} = -\ddot{P}_1(\tau) \quad , \quad \frac{d^2P_2(-\tau)}{d(-\tau)^2} = +\ddot{P}_2(\tau), \\ \frac{dP_1(-\tau)}{d(-\tau)} = +\dot{P}_1(\tau) \quad , \quad \frac{dP_2(-\tau)}{d(-\tau)} = -\dot{P}_2(\tau), \end{aligned}$$

hence:

$$\{-\ddot{P}_1(\tau) + \ddot{P}_2(\tau)\} - \frac{I(\tau)}{2} \{\dot{P}_1(\tau) - \dot{P}_2(\tau)\} + \{-P_1(\tau) + P_2(\tau)\} = 0, \quad (49)$$

so that we find the following equations:

$$P_1 + \frac{I}{2} \dot{P}_1 + P_1 = 0, \quad , \quad \ddot{P}_2 + \frac{I}{2} \dot{P}_2 + P_2 = 0.$$

From this follow three possibilities:

a) all integrals are even functions of τ ,

β) all integrals are odd functions of τ ,

γ) one of the integrals is an even function of τ , a second integral is an odd function of τ .

As an example of case (a) we choose

$$y = e^x.$$

Here is $\varphi = e^x$, $\varphi_x = e^x$, $\varphi_{xx} = e^x$, $x\varphi_x - \varphi = (x-1)e^x$; $\psi = \frac{1}{x-1}$;

$$\tau = \int \sqrt{\psi} dx = 2\sqrt{x-1}, \quad x = 1 + \frac{\tau^2}{4};$$

$$I = \frac{\psi_x - 2x\psi^2}{\psi^{3/2}} = -\frac{2x+1}{\sqrt{x-1}} = -\frac{\tau^2+6}{\tau} = \text{an odd function of } \tau.$$

The integrals $x = 1 + \frac{\tau^2}{4}$ and $y = e^{1 + \frac{\tau^2}{4}}$ are both even functions of τ .

By polarisation with respect to the conic

$$x^2 - y^2 = c$$

the curve $y = e^x$ passes into the curve:

$$\eta = \xi r^{-\frac{\xi+1}{\xi}},$$

which is, as could be expected, not equivalent to $y = e^x$.

Here holds:

$$q = \xi e^{-\frac{\xi+1}{\xi}}, \quad q_{\xi} = \frac{\xi+1}{\xi} e^{-\frac{\xi+1}{\xi}}, \quad q_{\xi\xi} = \frac{1}{\xi^2} e^{-\frac{\xi+1}{\xi}}, \quad \xi q_{\xi} - q = e^{-\frac{\xi+1}{\xi}}.$$

$$\psi = \frac{1}{\xi^3}; \quad \tau = -\frac{2}{\sqrt{\xi}}, \quad \xi = \frac{4}{\tau^2};$$

$$I = \frac{\psi_{\xi} - 2\xi\psi^2}{\psi^{3/2}} = -\frac{3\xi+2}{\sqrt{\xi}} = +\frac{\tau^2+6}{\tau}.$$

Hence too the integrals $\xi = \frac{4}{\tau^2}$ and $\eta = \frac{4}{\tau^2} e^{-\left(2 + \frac{\tau^2}{4}\right)}$ are both even functions of τ .

As an example of case (γ) we give

$$x^6 + y^6 = 1.$$

The calculation shows us

$$x = \sqrt[3]{\sin \frac{3\tau}{\sqrt{5}}}, \quad y = \sqrt[3]{\cos \frac{3\tau}{\sqrt{5}}}, \quad I = \frac{8}{5} \cot g \frac{3\tau}{\sqrt{5}};$$

I is odd, x is odd, y is even.

Physics. -- "*Determinations of refractive indices of gases under high pressures*". First paper. *The dispersion of hydrogen*. By L. H. SIERTSEMA and M. DE HAAS. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of November 25, 1911).

1. The modern theories of light which have been developed from the theory of electrons lead to many relations that can be tested experimentally in various ways. One of us¹⁾, for instance, has endeavoured to obtain from his experiments upon the magnetic

¹⁾ These Proc. V. 1902/03 p. 413. Comm. phys. lab. Leiden N^o. 82.

rotational dispersion of gases values of e/m for the electrons which participate in the light vibration. For this deduction values of $dn/d\lambda$ ($n =$ refractive index, $\lambda =$ wave length) for those gases at high pressure were needed, while only determinations made at atmospheric or, at least, at low pressure were available. It is doubtful whether it is justifiable to apply to high pressure the values thus obtained.

The few measurements which have hitherto been made upon the refractive indices of gases at high pressures have all had the object to obtain the relationship between the index of refraction and the density of the gas. The question as to whether the dispersion varies with the pressure or not has not yet been made the subject of an experimental investigation. We have therefore undertaken a more complete investigation, which includes a determination of refractive indices at high pressures for various wave-lengths.

The high degree of accuracy attainable by the use of an interference method renders it highly advantageous to use such a method for the determination of the refractive indices of gases. Many experimenters have used interference methods for obtaining such measurements. In our experiments we used a JAMIN interferential refractometer. In the path of one of the interfering rays a tube containing the experimental gas is placed, and, by using monochromatic light, the number of bands passing the cross-wire of a telescope can be counted when the quantity of gas contained in the tube is varied. The dispersion is evaluated by counting the bands crossing the field when different wave-lengths are successively employed. For if k_1 and k_2 represent the number of bands crossing the field for light of wave-lengths λ_1 and λ_2 respectively when the density of the gas varies from 0 to a given value, then

$$k_1 \lambda_1 = (n_1 - 1) e \quad , \quad k_2 \lambda_2 = (n_2 - 1) e$$

where n_1 and n_2 are the refractive indices at that particular density for the two colours, and e is the length of the tube. Furthermore in the ratio

$$\frac{n_1 - 1}{n_2 - 1} = \frac{\lambda_1 k_1}{\lambda_2 k_2} = c_{12}$$

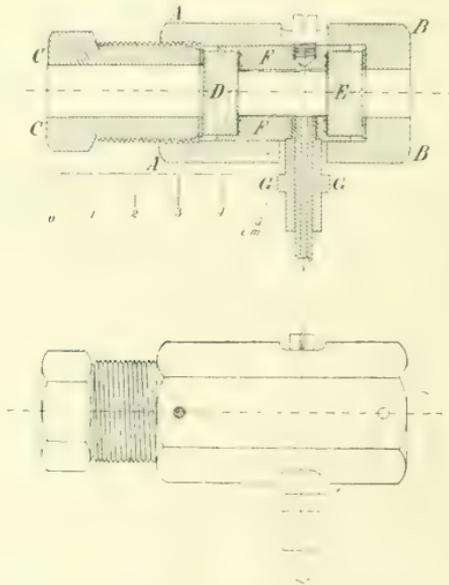
we obtain a quantity which expresses the dispersion of the gas, and which we shall call a dispersion constant.

We may remark that the values of these dispersion constants may be obtained without knowing the length of the tube, e ; this is necessary only for evaluating the refractive indices n_1 and n_2 . A high degree of accuracy can be reached in determining the numbers k_1, k_2, \dots , for the whole numbers involved can be obtained by direct

counting, and fractional portions can be determined from the position of the telescope cross-wire between two successive bands. When the number of bands crossing the field reaches some hundreds, it is obvious that the numbers k can be evaluated to a degree of accuracy far in excess of that possible in the measurement of e . It follows, too, that in measuring refractive indices the temperature and the pressure of the gas must also be known to a corresponding degree of accuracy, while the dispersion constants will vary but little with the density of the gas.

This led us to divide our research into two portions, one involving a determination of dispersion constants, the second a determination of refractive indices. The measurements described in the present paper relate to the first branch of the investigation.

2. A diagram is here given of the tube containing the experimental gas which was placed in the path of one of the interfering light rays.



A B, steel tube, with cylindrical boring, externally hexagonal.

C, nut tightening *D*, *E*, and *F*.

D and *E*, glass plates 8 mm. thick,

F, steel cylinder about 2 cm. long with projecting rims surrounding the glass plates.

Between *F* and the glass plates are washers of klingerit, a packing which is

used for steam joints and which suited the present purpose admirably. Brass rings prevented the squeezing of the packing into the tube. Outside the glass plates and the metal on either side are a brass ring and some paper washers. *P* is coupled to the high pressure system by the screw connection *G*.

This coupling leads to a manometer and to a reservoir filled with the experimental gas under high pressure, while through it connection can also be made with an airpump, GÆDE's rotatory pump ("Kapselpumpe").

The circular scale of the metallic manometer has a diameter of 16 cm., and on it pressures up to about 150 atmospheres can be read to $\frac{1}{10}$ of an atmosphere.

Mr. KOHNSTAMM kindly afforded us an opportunity of comparing this manometer before and after the measurements with the STRÜCKRATH manometer which he has fitted in the Amsterdam Physical Laboratory. We found that the manometer readings remained practically the same, the difference being, at the most, not more than $\frac{1}{10}$ of an atmosphere.

Beside the tube traversed by one of the interfering rays and in the path of the other ray are placed two glass plates identical with those in the experimental tube. By means of three adjusting screws these plates can be moved a little, and the breadth and the direction of the interference bands so regulated that they are in the best position for observation. For this purpose the adjusting screws of one of the glass plates of the interferometer can, of course, also be used. A wide slit in front of the first glass plate of the interferometer was found necessary in order to obtain clearly defined bands. The whole apparatus was enclosed in a sheet-iron case, which in the later experiments was filled with cotton wool leaving free only the paths of the light rays. The openings in this case were closed by glass plates. The high pressure connection and the manometer were also wrapped in cotton wool as far as the first regulating tap. Beside the experimental tube was placed the reservoir of a thermometer whose scale projected outside the case.

3. The measurements discussed in the present paper were made with pure hydrogen which we obtained through the kindness of Prof. KAMERLINGH ONNES from the Leiden laboratory, where it had been prepared from impure hydrogen by freezing out the impurities at a very low temperature¹⁾.

In the first series of measurements the source of light was a

¹⁾ KAMERLINGH ONNES, These Proc. XI. 1908/09, p. 883. Comm. phys. lab. Leiden, No. 109b.

HERAEUS quartz mercury lamp, and the light was concentrated through a lens upon the slit already mentioned in front of the interferometer. By means of light-filters the three wave-lengths (yellow, green and blue) of which the light emitted by this lamp chiefly consists, were isolated¹⁾.

The interference bands were observed through a telescope provided with cross-wires, and the number of bands was determined that passed the point of intersection of the cross fibres as the density of the gas in the experimental tube was altered; to evaluate fractions a JAMIN compensator was used.

The accuracy attained in these measurements was not so great as that of later experiments; we shall not, therefore, describe them in detail but shall content ourselves with communicating the results.

In the accompanying table are given the numbers k_1 , k_2 and k_3 of the bands crossing the field while the density of the gas changed from that determined by the pressures and temperatures given below to zero, for each of the three colours $\lambda_1 = 0,578 \mu$, $\lambda_2 = 0,546 \mu$ and $\lambda_3 = 0,436 \mu$. The table also includes the dispersion constants

$$c_{12} = \frac{n_1 - 1}{n_2 - 1} = \frac{k_1 \lambda_1}{k_2 \lambda_2}, \quad c_{32} = \frac{n_3 - 1}{n_2 - 1} = \frac{k_3 \lambda_3}{k_2 \lambda_2}.$$

k_1	k_2	k_3	c_{12}	c_{32}	Press. atm.	Temp.
190.28	201.98	256.98	0.99713	1.01546	81.7	18.0° C
182.45	193.69	246.31	0.99701	1.01495	76.8	14.0 "
172.48	183.08	232.81	0.99716	1.01492	73.5	16.0 "
164.86	174.99	222.62	0.99716	1.01537	69.6	14.2 "
152.17	161.51	205.38	0.99723	1.01492	64.2	14.1 "
—	114.20	145.20	—	1.01478	44.9	11.0 "
90.07	95.64	121.62	0.99679	1.01493	37.4	11.3 "
		Mean	0.99708 ± 0.00007	1.01505 ± 0.00010		

¹⁾ We used a solution of eosin which transmits only yellow, and a concentrated solution of didymium nitrate, which absorbs the yellow. In the latter case the other two colours were isolated by using green or blue glass. For the blue one of the newer glasses of SCHOTT and GEN. No. 3086, was used with excellent results. These glasses are described in detail by ZSIGMONDY, Z. f. Instrumentenk. 21 p. 97.

In the more recent experiments a HERAEUS quartz amalgam lamp (220 volt, 5 to 6 amp.) was used as a source of light. The spectrum of this light consists of a number of lines among which those of *Hg*, *Zn* and *Cd* are particularly bright. Owing to a copious formation of ozone it was found necessary to put the lamp in a fume cupboard.

A collimator with a rather wide slit was placed close to the lamp, but outside the fume cupboard. The light beam emerging from the collimator passed through the interferometer from which the JAMIN compensator had been removed and then fell upon the prism of a HILGER constant deviation spectroscope. In the field of the telescope we thus obtained a series of images of the slit, each corresponding to one of the wave-lengths emitted by the amalgam lamp. The collimator slit was made so wide that some of its images partially overlapped. Each image of the slit was crossed by a system of interference bands, horizontal in the green, but slightly sloping in the blue and violet. About 3 bands were visible in the red, and about 5 in the violet. It appeared that the bands in any one slit image did not all lie in the same plane, so that they were not all quite in focus at the same time in the telescope. Even their apparent position in the field altered slightly when the density of the gas in the experimental tube varied. The telescope was so adjusted that for all the densities of the gas, occurring during the experiments, one of the bands not far from the central band could be brought into sharp focus.

In these experiments measurements were made upon six different images of the slit; these were:

a. The image of the red cadmium line $\lambda_a = 0.644 \mu$. This image was partially covered by that of the zinc line 0.636μ . The uncovered part, however, was of sufficient width to allow the interference bands in it to be brought under proper observation.

b. The image of the green mercury line $\lambda_b = 0.546 \mu$. This image was very bright. The interference bands were also easily observed, but still they were not so clearly defined as one would expect from their great intensity. Possibly satellites exert here a disturbing influence.

c. The image of the green cadmium line $\lambda_c = 0.509 \mu$. The bands in this case were perfectly dark throughout.

d. The image of the blue zinc line $\lambda_d = 0.472 \mu$. This image was situated amongst a number of others in such a way that only a portion of it was free, in which the bands, which were very well defined, could be examined.

e. The image of the blue mercury line $\lambda_e = 0.436 \mu$. This image was very bright with well defined bands.

f. The image of the violet mercury line $\lambda_f = 0.405 \mu$. The brightness of this band was much less.

These images of the slit, or rather their uncovered portions, were brought in succession into the centre of the field of vision by a rotation of the spectroscope prism. The spectroscope telescope had a micrometer eye piece with a vertical screw. The movable wire could be made to coincide with the bands. In our measurements the difference of phase between the interfering rays was determined in each case for a fixed point in each image of the slit. We tried to do this first by measuring the distances between the fixed point and each of the two bands immediately above and below it. This was done for the six images *a*, *b*, *c*, *d*, *e* and *f* in succession, and then again in the reverse order *f*, *e*, *d*, *c*, *b* and *a*. Some time elapsed before this could be completed and it was found that during that period the bands did not remain sufficiently stationary to obtain accurate results. Another method was therefore adopted in which we were more independent of this disturbance. In this method the distance of only one band from the fixed point was determined, and from that measurement the phase difference at the fixed point was obtained. From separate measurements the variation of the required phase difference with the distance of the bands from the fixed point was determined.¹⁾ By now focussing with the movable wire several times alternately a band in the image *a*, and then a band in the image *b*, the difference (*ab*) between the phase differences at the fixed points in the images *a* and *b* was obtained, and then in the same way, the differences (*cb*), (*db*), (*eb*) and (*fb*). The measurements from which these data were obtained could follow each other in rapid succession, so that sufficient accuracy could be reached even though the bands did not remain absolutely stationary.

Properly speaking only the fractional parts of the differences (*ab*), (*cb*) etc. could be evaluated in this way; the whole numbers were obtained afterwards, by the method indicated below.

These measurements were first made at the highest pressure available; a small quantity of the gas was then allowed to escape while the number of bands was counted which crossed the fixed point in the green image *b*; another series of measurements of differences of phase-difference was then made, and so on until the last series which

¹⁾ From these measurements it was found that the distance between the bands in any one image was not constant, and consequently the desired phase difference could not be represented by a linear function of the distance *z* of the point under examination from the fixed point. For this difference, therefore, we assumed a quadratic law of variation $\varphi = az + bz^2$, the coefficients of which we calculated by the method of least squares from several measurements made upon various bands in the same image.

was made with the tube completely evacuated. The reverse order of operations with rising pressure was not so successful, as during the admission of the gas, the bands became confused and disappeared, which probably resulted from the difference of temperature between the gas in the tube and that in the reservoir.

By a separate investigation we ascertained that the admission of gas at a high pressure occasioned no change of shape in the experimental tube sufficient to influence the values of the dispersion constants.

For the b image, the integral part of the phase differences at the fixed point can be evaluated by the direct counting of the number of bands crossing the field: for this purpose one can give the value zero to the phase-difference at one of the bands in the final state (vacuum). Similarly in the other images the value zero can be assigned to one of the bands in the final state (vacuum), and we then obtain for that state the integral parts of the differences (ab), . . . It is then ascertained from a separate experiment how much these values change if one band is allowed to cross the field in b , and as these changes will be less than one band it is easy to determine them completely. From this follows how many units (ab), (cb) etc. will change when a larger number of bands, e.g. 10, is allowed to cross the field, and in this way we can soon find how great these changes will be for 50 or 100 bands, which were the numbers allowed to cross the field in our series of observations. Finally, if these differences (ab) etc. are completely known for all densities, one can easily find the number of bands that cross the field in each image in passing from any one density to vacuum. We shall represent these numbers by k_a , k_b , k_c , k_d , k_e and k_f . The ratios

$$\frac{k_a}{k_b}, \frac{k_c}{k_b}, \text{ etc.}$$

are then calculated.

As an example we give a series of results for the density determined by a pressure of 71.8 atm. and a temperature of 19,49° C.

$k_b = 367.067$		$k_a = 309.073$		$k_a / k_b = 0.84201$
$k_b = 367.050$		$k_c = 395.687$		$k_c / k_b = 1.07802$
$k_b = 367.023$		$k_d = 428.186$		$k_d / k_b = 1.16665$
$k_b = 366.986$		$k_e = 466.758$		$k_e / k_b = 1.27187$
$k_b = 366.942$		$k_f = 506.037$		$k_f / k_b = 1.37907$

In this way the following results were obtained :

Pressure in atm.	Temperature.	k_b (mean).	$\lambda_b = 0.546$	$\lambda_c = 0.509$	$\lambda_d = 0.472$	$\lambda_e = 0.436$	$\lambda_f = 0.405$
			$\lambda_a = 0.644$	$\frac{k_c}{k_b}$	$\frac{k_d}{k_b}$	$\frac{k_e}{k_b}$	$\frac{k_f}{k_b}$
71.8	19.49	367.014	0.84201	1.07802	1.16665	1.27187	1.37907
62.0	19.77	317.160	0.84199	1.07798	1.16667	1.27179	1.37902
52.1	19.95	267.315	0.84203	1.07799	1.16667	1.27183	1.37897
42.3	19.95	217.264	0.84202	1.07807	1.16666	1.27178	1.37897
32.2	20.01	167.118	0.84206	1.07796	1.16659	1.27170	1.37883
68.5	19.15	345.631	0.84201	1.07803	1.16673	1.27207	1.37925
68.1	19.33	343.616	0.84200	1.07806	1.16680	1.27205	1.37927
58.0	19.49	293.244	0.84202	1.07805	1.16672	1.27208	1.37930
47.8	19.65	243.198	0.84205	1.07807	1.16669	1.27205	1.37923
38.0	19.75	193.451	0.84206	1.07809	1.16668	1.27201	1.37921
27.9	19.85	143.354	0.84212	1.07805	1.16670	1.27192	1.37899
65.4	20.35	336.393	0.84203	1.07799	1.16662	1.27176	1.37882
65.2	20.52	335.013	0.84203	1.07798	1.16669	1.27177	1.37886
63.9	20.67	327.868	0.84203	1.07800	1.16659	1.27181	1.37892
58.8	20.85	302.103	0.84207	1.07798	1.16662	1.27218	1.37891
39.0	20.94	202.607	0.84210	1.07796	1.16667	1.27179	1.37902

The values obtained for the various densities are fairly constant, and the deviations are in no definite direction. As means we obtain

$$\begin{array}{ccccc}
 0.84204 & 1.07802 & 1.16667 & 1.27190 & 1.37904 \\
 \pm 0.9 & \pm 1.1 & \pm 1.3 & \pm 3.7 & \pm 4.0
 \end{array}$$

If these ratios are constant, so also are the dispersion constants

$$c_{ab} = \frac{n_a - 1}{n_b - 1} = \frac{k_a \lambda_a}{k_b \lambda_b}, \quad c_{cb} = \frac{n_c - 1}{n_b - 1} = \frac{k_c \lambda_c}{k_b \lambda_b}, \quad \text{etc.}$$

in which the refractive index for all wave-lengths in the final state is taken as unity.

We thus find as the result of our experiments that the dispersion constant of hydrogen is the same at all densities used, and we obtain for it the following values :

	λ (vac.)	$c = \frac{n-1}{nb-1}$
<i>a</i>	0.64403	0.99280 ± 0.000011
<i>b</i>	0.54623	1
<i>c</i>	0.50873	1.00401 ± 0.000010
<i>d</i>	0.47234	1.00885 ± 0.000011
<i>e</i>	0.43597	1.01516 ± 0.000030
<i>f</i>	0.40478	1.02193 ± 0.000030

We can compare our results with those obtained by other experimenters, especially with those of MASCART ¹⁾, PERREAU ²⁾, SCHEEL ³⁾, HERMANN ⁴⁾, KOCH ⁵⁾ and CUTHBERSON ⁶⁾. To make comparison possible, the values of the dispersion constant for the wave-lengths we used are deduced from their results by graphical interpolation (MASCART, PERREAU, KOCH, CUTHBERSON) or from the dispersion formula given (SCHEEL), while from HERMANN'S observations they were calculated directly. In this way we obtain

λ	MASCART.	PERREAU.	SCHEEL.	HERMANN.	KOCH.	CUTHBERSON.	SIERTSEMA DE HAAS.
0.644	0.9962	0.9927	0.9939	0.9924	0.9934	0.9930	0.9928
0.546	1	1	1	1	1	1	1
0.509	1.0030	1.0041	1.0034		1.0038	1.0037	1.0040
0.472		1.0090	1.0074		1.0085		1.0088
0.436			1.0125	1.0114	1.0152		1.0152
0.405							1.0219

An interpolation formula can be obtained from our values of the dispersion constant. We will take the ordinary form

$$n-1 = a \left(1 + \frac{b_1}{\lambda^2} + \frac{b_2}{\lambda^4} \right)$$

in which λ is the wave length in air; we then get

¹⁾ MASCART, Ann. de l'éc. norm. (2) 6 p. 61 (1877).

²⁾ PERREAU, Ann. de ch. et de phys. (7) 7 p. 335 (1896).

³⁾ SCHEEL, Verh. d. D. phys. Ges. 9 p. 28 (1907).

⁴⁾ HERMANN, " " " " " 10 p. 477 (1908).

⁵⁾ KOCH, Nova acta regiae soc. scient. Upsaliensis (4) 2 No. 5 (1909).

⁶⁾ CUTHBERSON, Proc. R. S. (A) 83 p. 151, 1910.

$$c = \frac{n-1}{n_b-1} = \frac{1 + \frac{b_1}{\lambda^2} + \frac{b_2}{\lambda^4}}{1 + \frac{b_1}{\lambda_b^2} + \frac{b_2}{\lambda_b^4}}$$

The coefficients b_1 and b_2 were calculated by least squares valuing each observation according to the mean error. We thus obtained

$$b_1 = 0.007337, \quad b_2 = 0.000089$$

and hence,

$$c = \frac{n-1}{n_b-1} = 0.97504 \left(1 + \frac{0.007337}{\lambda^2} + \frac{0.000089}{\lambda^4} \right)$$

The following table shows the accuracy with which this formula represents the dispersion constants:

	λ (air)	c (cal.)	c (obs.)	Δ	weight	$\Sigma [p \Delta^2]$
<i>a</i>	0.64385 μ	0.99281	0.99280	$-10^5 \times 1$	8	8
<i>b</i>	0.54608 „	1	1			
<i>c</i>	0.50859 „	1.00399	1.00401	+ 2	9	36
<i>d</i>	0.47221 „	1.00886	1.00885	- 1	8	8
<i>e</i>	0.43585 „	1.01510	1.01516	+ 6	1	36
<i>f</i>	0.40467 „	1.02196	1.02193	- 3	1	9

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Good agreement is also obtained between experimental and calculated values by using the dispersion formula¹⁾

$$\frac{n^2-1}{n^2+2} = \frac{Ne_1^2}{3m_1(r_1^2-r^2)} + \frac{Ne_2^2}{3m_2(r_2^2-r^2)} + \dots$$

of the theory of electrons, in which r , r_1 and r_2 are frequencies and e , N , m_1 , m_2 , ... are the known constants in that theory. Even with *one* term on the right-hand side we obtain a good agreement. We then get the formula

$$c = \frac{n-1}{n_b-1} = \frac{n_b+1}{n+1} \cdot \frac{n^2+2}{n_b^2+2} \times \frac{\frac{1}{\lambda_1^2} - \frac{1}{\lambda_b^2}}{\frac{1}{\lambda_1^2} - \frac{1}{\lambda^2}}$$

in which λ , λ_1 , and λ_b now represent wave-lengths in vacuo. An examination of the factor

$$\frac{n_b+1}{n+1} \cdot \frac{n^2+2}{n_b^2+2}$$

¹⁾ See e.g. LORENTZ, The theory of electrons, p. 144.

shows that its value may be taken as unity without appreciable error. We then get

$$c = \frac{1}{\lambda_1^2} - \frac{1}{\lambda_2^2} \cdot \frac{1}{\lambda_1^3 - \lambda_2^3}$$

An evaluation of λ_1 by the method of least squares valuing the observations on the plan already mentioned gives

$$\lambda_1 (\text{vac.}) = 0.08703 \mu$$

while the following table shows the agreement obtained.

	λ (vac)	c (cal.)	c (obs.)	Δ	weight	$\Sigma [p\Delta^2]$
<i>a</i>	0.64403 μ	0.99274	0.99280	— 6	8	288
<i>b</i>	0.54623 „	1	1			
<i>c</i>	0.50873 „	1.00400	1.00401	— 1	9	9
<i>d</i>	0.47234 „	1.00886	1.00885	1	8	8
<i>e</i>	0.43597 „	1.01506	1.01516	— 10	1	100
<i>f</i>	0.40478 „	1.02185	1.02193	— 8	1	64
						469

We thus find that the natural vibration of hydrogen corresponds to a wave-length of 0,08703 μ , a value that agrees quite well with that determined by KOCH, 0,0880 μ , from dispersion measurements extending to the ultra-red, and still better with the value 0,087 μ deduced by NATANSON¹⁾ from PERREAU's experiments. It differs somewhat from CUTHBERSON's value, 0,08516 μ .

A calculation of the absolute values of the refractive indices is postponed until the completion, in a subsequent part of this research, of the investigation of the refractive index for the wave-length $\lambda = 0,546$ with special reference to its dependence upon the pressure. We also intend if possible to extend these measurements to higher pressures, and to other gases. In the meantime we may remark that, assuming $n-1$ to be proportional to the density of the gas, and that $n = 0,000139$ at 0° C. and 1 atm., the calculation of e/m by the method given by one of us in a previous paper²⁾ leads to the value 1.70×10^6 .

Delft. Physical laboratory of the Technical University.

¹⁾ NATANSON. Bulletin de l'Ac. des sc. de Cracovie 1907, p. 336.

²⁾ SIERTSEMA, These Proc. V. 1902,03 p. 413. Comm. phys. lab. Leiden N°. 82.

Chemistry. — “*On a biochemical method for the determination of small quantities of salicylic acid in the presence of an excess of p-oxybenzoic acid.*” By Prof. J. BÖESEKEN and Mr. H. WATERMAN. (Communicated by Prof. M. W. BEIJERINCK).

(Communicated in the meeting of November 25, 1911).

On the occasion of an investigation as to the proportion in which o. and p. oxybenzoic acid are formed in the KOLBE reaction, the details of which will be described fully in the dissertation of Mr. WATERMAN, we had found that the para-acid (also the meta-) could be used as a carbon nutriment by the penicillium glaucum.

As salicylic acid exerts a retarding influence on the growth of the organism, we have tried to base a quantitative method of determination on the different behaviour of these isomers.

With small quantities of salicylic acid we have been successful, so that the method has been of service to us in the quantitative determination of the acid mixture formed in the KOLBE reaction, when one starts from potassium phenolate.

If an aqueous 0.3 % solution of p-oxybenzoic acid in which are also present 0.05 % of potassium dihydrogen phosphate, 0.05 % of ammonium chloride and 0.02 % of magnesium sulfate (the solution of the inorganic salts must have a faintly acid reaction) is sterilised, cooled to the temperature of the laboratory and inoculated carefully with a culture of penicillium, a perfectly constant development phenomenon is always noticed under the same conditions, the same differences being observed from day to day.

By adding definite quantities of salicylic acid this development phenomenon is changed in a constant manner. Very small quantities cause, at first, a small increase of the growth; with quantities over 1 % a decided retardation sets in.

To carry out the experiment we introduce into small ERLÉNMEYER flasks of the same size, exactly similarly and freshly prepared solutions of p-oxybenzoic acid with inorganic salts to which are added increasing quantities of salicylic acid, the liquids are sterilised by boiling and, when cold, inoculated with a very small quantity of the same penicillium culture. Simultaneously, a 0.3 % solution of the mixture to be analysed, which otherwise is treated in the same manner, is offered to the penicillium and compared with the scale of the standard solutions.

The method is, therefore, somewhat like a colourimetric one. It looks very subjective but this, however, is only apparent, for the

experiment extends over several days, so that onemay at any time repeat and control the observations.

Moreover, the first development phenomena are usually very plainly visible and the period thereof is constantly delayed further by increasing quantities of salicylic acid.

Another drawback to the method might be its too great sensitiveness; small quantities of other substances, which may form in the KolBE reaction, might possibly interfere.

We have been able, however, to demonstrate that of all oxy-compounds which may form, salicylic acid is the only one which exerts a retarding influence.

Care, however, should be taken to start from pure phenol, because the methyl group does act injuriously.

The solution of the inorganic salts must not be kept too long; we have noticed that a solution which had stood in a glass bottle for some months had taken up a retarding constituent the exact nature of which is unknown to us.

We give here in the first place a survey of some standard solutions.

Inoculated on 17 January.

N ^o .	1	2	3	4	5
Quantity of $\left\{ \begin{array}{l} p\text{-} \\ \text{acid} \end{array} \right\}$	0.1507 gr. 0.....	0.1502 0.0004	0.1502 0.0019	0.1499 0.0074	0.1507 0.0178
20 January	+	+	+	-	-
23 >	++	++	++	+	-
25 >	+++	+++	+++	++	-

Inoculated on 24 January.

N ^o .	6	7	8	9	10	11
Quantity of $\left\{ \begin{array}{l} p\text{-} \\ \text{acid} \end{array} \right\}$	0.1501 0.....	0.1494 0.0023	0.1494 0.0046	0.1492 0.0068	0.1493 0.0082	0.1499 0.0132
26 January	+	+	-	-	-	-
27 >	++	++	+	+	?	-
28 >	+++	+++	++	++ < 8	+	-
30 >	+++	+++	+++	++	++ < 9	+

The flasks which had a capacity of about 200 cc all contained 50 cc of solution. The experiments were carried out in the laboratory care being taken however, that the flasks were put in a moderately warm place and in the dark. The observations were made with the naked eye or with the aid of a small lens.

According to this method we can determine, with an accuracy of a trifle over 1 %, quantities of salicylic acid varying from 1 to 10 % in an excess of p-oxybenzoic acid. This accuracy is not great but still not much inferior to that attained in most of the investigations on the simultaneous formation of isomers (HOLLEMAN "Die direkte Einführung").

Afterwards we have subjected the acid mixture, prepared according to KOLBE, to the biological investigation; a preliminary test had shown us that the mould developed on it after some days, so that, in any case, the amount of salicylic acid was but small.

Inoculated on 27.9 1911.

No.	1	2	3	4	Mixture of unknown composition	
Quantity of acid	0.1503	0.1507	0.1505	0.1506	0.1493	0.1500
$\frac{P}{O}$	0	0.0020	0.0043	0.0062		
2 Oct '11	++	+	< 2	< 3	Developed as between 1 and 2	
3 > >	All more firmly developed but becoming less from 1→4				>	
4 > >					>	

From this experiment it follows that in any case the mixture contained less than $1\frac{1}{3}$ % of salicylic acid.

This we have again confirmed by a second series, in which we added increasing quantities of salicylic acid to the flasks containing the mixed "KOLBE" acids; in this manner each succeeding flask controlled its predecessor.

Indeed we notice that *all* flasks with KOLBE's mixture behaved like the artificial mixtures which contained about 2 mg. more; hence we may conclude that this was really the case, so that we can now say with certainty that this quantity is about, but not fully, 2 mg. or $1\frac{1}{3}$ %.

By way of a check, we have confirmed this result by applying one of the methods described by HOLLEMAN ("Die direkte Einführung") namely the extraction process (l. c. p. 17—26) to the KOLBE mixture.

Inoculated on 24/10 '11

No.	1	2	3	4	5	6	
Quantity of acid	p-	0.1505	0.1503	0.1507	0.1505	0.1500	0.1500
	o-	0	0.0021	0.0045	0.0056	0.0082	0.0102
27 Oct. '11	++	+	+ < 2	+ < 3	?	—	
No.		a	b	c	d	e	f
Quantity of Kolbe's mixture of salicylic acid		0.1497	0.1503	0.1504	0.1495	0.1501	0.1495
		0	0.0024	0.0047	0.0060	0.0082	0.0101
Development on 27 Oct.		+	+ < a	+ < b between 4 and 5 but with a distinct growth	? some-what > 5	—	—

For this purpose the mixture was shaken out with dry benzene in which salicylic acid is readily soluble, the acids were determined by titration and from this result was deducted the amount of dissolved p-oxybenzoic acid. As the solubility of *para*-acid is modified by the *ortho*-acid, this influence was determined experimentally and the quantity of dissolved *para*-oxyacid could be corrected graphically. In this way we found 1.1 and 1.2 %.

It is well nigh certain that this method is capable of extension, particularly because we have at our disposal a large variety of organisms and, if necessary, we can also modify the quality of the inorganic nutriment in many directions.

In this case we could restrict ourselves to the macroscopic observation of the growth phenomenon in the solution. It is evident, however, that the "technic" of the method can be refined in many directions.

Delft, 1 Nov.

Org. Chem. Lab. of the Technical
University.

Chemistry. — “On the action of some benzene derivatives on the development of *penicillium glaucum*.” By Prof. J. BÖESEKEN and Mr. H. WATERMAN. (Communicated by Prof. M. W. BELJERINCK).

(Communicated in the meeting of November 25, 1911).

1. The investigation mentioned in the previous communication as to the action of *penicillium glaucum* on the oxybenzoic acids has been extended by us in different directions.

In the first place this was necessary because we wanted more data as to the reliability of the quantitative salicylic acid estimation. In KOLBE's reaction some other compounds can be formed which may have a disturbing influence on the development of the organism.

In the second place we had been struck by the contrast between an orthobenzene derivate on one side and the para- and meta-derivatives on the other side, because in other cases the ortho- and para-derivatives are mostly found opposite the metaderivatives.

As this last contrast is caused by the nature of the benzene ring¹⁾ this natural contrast must, in this case, be surpassed by another one.

It would be obvious to connect this different behaviour with the great dissociation constant of salicylic acid; but this is undoubtedly *not* the cause, as the more strongly dissociated compounds: 2,4-; 2,3-; 2,6-dioxybenzoic acid and even 2,3,4- and 2,4,6-trioxybenzoic acid did not appear to have any particular retarding action, whereas the much weaker benzoic acid and the toluic acids appeared to retard the development of the organism in a still higher degree.

We have, therefore, ascertained whether the theory of H. MEYER²⁾ and E. OVERTON³⁾ could give us a satisfactory explanation of the phenomenon. This theory starts from the idea that the modifications which occur in the fatty or lecithin part of the organism will in the first place exert an influence on the change of the different functions. If, therefore, a substance is more soluble in fat than in water it will for that reason exert a narcotic action, because it will accumulate in the fatty portion.

By determining the division coefficient of a great number of substances between water and olive oil and comparing this with the narcotic action the above investigators were able to test the value

¹⁾ HOLLEMAN and BÖESEKEN, These Proc. 24 Dec. 1909.

²⁾ H. MEYER. Zur Theorie der Alkoholnarkose. Arch. f. exp. Pathol. u. Pharmacol. 42 p. 109 (1899) and 46 p. 338 (1901) s. a. C. ARCHANGELSKY 46 p. 347.

³⁾ E. OVERTON. Studien über die Narkose. Zugl. ein Beitrag zur allgem. Physiologie Fischer. Jena (1901).

of the theory by means of an extensive number of facts, and MEYER could even demonstrate that if the division coefficient was modified by a change in temperature the narcotic action was influenced in the sense expected from the theory.

It appeared to us indeed that, whereas the division coefficient of salicylic acid between olive oil and water at 25° was **11.8**, the same quantity for *p*-oxybenzoic acid amounted to **0.6** and for *m*-oxybenzoic acid to **0.4**.

Further, we have investigated a number of other benzene derivatives as to their action on the development of the penicillium and have also determined, in many cases the division factor between olive oil and water.

In all cases we have noticed a distinct parallelism between the retarding action and the value of the division factor.

The investigation also brought to light some facts as to the maximum of development of the penicillium in solutions of different carbon derivatives, which to us do not seem unimportant. They also support the MEYER-OVERTON theory.

The Method.

2. As the biochemical method employed by us varies somewhat from the usual process and excels by a great simplicity, a short description may be given.

The experiments were always carried out in steamed Erlenmeyer flasks of about 200 cc. capacity in which were placed 50 cc. of water containing $\frac{1}{20}\%$ of potassium phosphate, $\frac{1}{20}\%$ of ammonium chloride and $\frac{1}{30}\%$ of magnesium sulphate and which was, if necessary, acidified with a trace of phosphoric acid. In this was dissolved the substance either alone in varying quantities, or this was added in increasing quantities to a standard of *p*-oxybenzoic acid of generally 150 mg. and otherwise provided with the same inorganic nutriment. The solutions were sterilised in the usual manner and inoculated with a pure culture of penicillium glaucum, which was generally cultivated on *p*-oxybenzoic acid or protocatechuic acid as carbon source. After that they were placed in an incubator at 28°--29° and observed from day to day. The inoculation always took place in the same manner, so that only a very little of the material was introduced.

The solution of the inorganic salts should not have been kept too long, as it has appeared to us that one which had stood for half a year exerted a retarding action on the development of the mould (see previous communication).

The flasks were well aerated and the incubator was closed, so that the experiments took place in the dark.

As stated in our previous communication the progress of the development was always quite normal; in the many series of experiments it very rarely occurred that a single flask exhibited an abnormal phenomenon; in the case of such an exception several abnormalities occurred simultaneously, such as darkening etc.

3. In the experiments on the retarding action a number of these solutions, but now provided with increasing quantities of the substance to be investigated, was presented to the penicillium, besides one (sometimes more) standard solution with pure p-oxybenzoic acid; they were observed during a series of days and compared with each other. The moment at which the development of the organism commenced was noticed very sharply in the clear solution.

In this manner it could be observed whether a same quantity of different substances retarded more or less the development, or what quantity of a substance was required to prevent the development within a definite time 3—10 days, for instance.

When the development set in, the retarding action was still very well perceptible and comparable for a period of several days, so that the observations could, continually, be repeated and controlled.

All this shows that the penicillium is a material eminently fitted for these experiments owing to the quiet growth of the organism and its remarkable power of taking to all kinds of carbon containing material, yet coupled with a satisfactory sensitiveness.

4. Besides these experiments which concern the action of different substances on the growth of the organism in an excess of one very definite carbon source it was ascertained whether the said substances (which were selected in such a manner that their chemical construction exhibited a fairly great similarity to each other and to the carbon source) could act themselves as a source of carbon and, such being the case, in how far the development was dependent on the quantity of these substances.

For this purpose increasing quantities of the said substances, mixed with the above named inorganic nutriment, were offered to the penicillium and the growth of the organism was observed for a series of days. Generally, different series were placed together into the incubator so that the results could be directly compared with each other.

5. We have already pointed out (in 3) some of the advantages of this method; the most important is that all carbon sources, except the one which is to be studied, are carefully avoided so that one may be certain that any development is due to the presence of the substance to be investigated and not to the carbon of the nutrient base.

We had also convinced ourselves that the carbon dioxide from the atmosphere was in itself not sufficient to cause any development and the amount of inoculating material was always so small that this could not in itself be regarded as a source of carbon.

Hence, we could suffice with the very simple observations of the development, and there was no need to trouble about determinations as to the fate of the organic matter.

Owing to this, we were not bound to use considerable quantities of the substance, and often a few mg were found to be sufficient.

It appears to us that the results obtained with those very small quantities of the substance are not the *least* important ones

6. The substances which we have submitted to this biochemical research are as follows:

a. phenol, pyrocatechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol.

b. *o*-, *m*- and *p*-oxybenzoic acid; 2,3-, 2,4-, 2,5-, 2,6-, 3,4-dioxybenzoic acid, anisic acid, guaiacolicarboxylic acid; 2,3,4-, 2,4,6-, 3,4,5-trioxybenzoic acid.

c. benzoic acid and the three toluic acids.

d. A few more distant compounds such as quinic acid.

The phenols were carefully purified, *o*- and *p*-oxybenzoic acid were prepared according to KOLBE from phenol absolutely free from cresol, and used after repeated crystallisation; *m*-oxybenzoic acid by fusing the sulphonation product of benzoic acid with potassium hydroxide.

2,3-dioxybenzoic acid was obtained from guaiacolicarboxylic acid by heating with aluminium chloride; 2,5-dioxybenzoic acid (gentisic acid) by oxidation of salicylic acid with potassium persulphate.

2,6-dioxybenzoic acid has been forwarded to us for this purpose by Prof. BRUNNER to whom we again tender our sincere thanks.

Protocatechuic acid was among the collection and was purified by recrystallisation, the same was the case with anisic acid, guaiacolicarboxylic acid, benzoic acid, and the toluic acids, whilst 2,4,6- and 2,3,4-trioxybenzoic acid were prepared from pyrogallol and phloroglucinol with KHCO_3 .

Experimental.

It is not our intention to give here a detailed account of all the experiments; it will suffice to mention some of the series and to review the results.

TABLE I. Action of larger quantities of different carbon compounds on the development of the penicillium.

Period of inoculation	Name of the compound	Quantity	9 Jan.	19 Jan.	Beginning of March	Remarks
24 Dec.'10	salicylic acid	0.050	—	—	—	
	p-oxybenzoic acid	0.14	} strong development			
	m-oxybenzoic acid	0.20				
	3.4.5-trioxybenz. ac.	0.50				
	3.4-dioxybenz. acid	0.50				
		2.3.4-trioxybenz. ac.	0.15	—	—	
			27 Jan.	30 Jan.	16 Febr.	
25 Jan.'11	quinic acid	0.1015	+			strong development
	2.4.6-trioxybenz. ac.	0.0807	—	?		strong development
			16 Febr.	20 Febr.	1 March	
13 Febr.	2.4-dioxybenz. acid	0.1004	?	+	++	Darkening
			3 Febr.	5 Febr.	8 Febr.	
1 Febr.	p-oxybenzoic acid	0.1500	+	++	+++	Control determination
	p-oxybenz. methyl	0.1500	—	—	—	
	anisic acid	0.1500	—	—	+	Increases regularly
	piperonylic acid	0.1000				
7 Febr.	benzoic acid	0.1500	} after two months no development			
	aspirine	0.1500				
	guaiacolcarbox. ac.	0.0994				
	opianic acid	0.1002				
	anisol	0.0235				

TABLE 1 (continued). Action of larger quantities of different carbon compounds on the development of the *penicillium*.

Period of inoculation	Name of the compound	Quantity	20/6	22/6	24/6	28/6	Remarks	
19 June '11	2,3-dioxybenzoic acid	0.0814	—	—	?	+	Control	
»	2,5-dioxybenzoic acid	0.2376	—	—	—	—		
	p-oxybenzoic acid	0.1	—	+	++	+++		
			3/7	5/7	6/7	7/7	17/7	
1 July	2,4-dioxybenzoic acid	0.1027	—	—	+	+	++	Darkening
			10/7	13/7	17/7			
5 »	resorcinol	0.100	+	++	+++			
8 »	pyrocatechol	0.0992	—	+	> 13/7			Yellowish green solution Reddish brown solution Solution very dark
»	hydroquinone	0.1005	—	—	+ slight			
»	pyrogallol	0.0973	—	—	?			
			3/7	5/7	7/7			
1 July	tannic acid	0.1021	+	++	+++			
»	metaphenolsulfonic acid	0.10	} no development					As mono-potassium salt
»	paraphenol	0.10						
»	»	0.10						
					28/8			As dipotassium salt
20 July	phenol	0.035			++			
»	»	0.070			+			
			8/9	3/10				
1 Sept.	phloroglucinol	0.15	+	+++				
»	»	0.15	+	+++				
			26/9	28/9	2/10			
21 Sept.	2,6 dioxibenzoic acid	0.0476	—	—	+ slight			
			23/10	24/10	26/10	27/10		
20 Oct.	o-phtalic acid	0.124	—	?	+	+		

If we look over the result of these experiments, we notice that the property to serve as a nutriment is not connected with the degree of dissociation of the acids but depends on the nature, the number, and the position of the groups.

A. *The nature.* Favourable in the first place is the OH group:

This is shown from the behaviour of phenol which, in small concentrations promotes the growth. Why, in larger quantities, it begins to exert a retarding action we will state presently.

All polyoxycompounds may be assimilated to a greater or lesser degree.

In the second place the carboxyl group:

That this is much less favourable than the OH group is shown from the comparison of benzoic acid with phenol; o-phthalic acid on the other hand is taken up in fairly large concentrations.

Unfavourable is a methyl or methylene group, and the sulphonic acid group.

This is shown from the comparison of anisic acid and p-oxybenzoic methyl ester with p-oxybenzoic acid; of piperonylic acid with protocatechuic acid; of guaiacolecarboxylic acid with 2,3 dioxybenzoic acid; of p- and m-oxybenzenesulphonic acid with p- and m-oxybenzoic acid.

B. *The number.* A combination of several OH-; COOH-groups, or of both generally increases the liability to attack. Compare the polyoxy-compounds with the mono- etc.

C. *The position.* The *ortho*-position diminishes as a rule the favourable action¹⁾ so that this may even become an unfavourable one; the *meta*-position promotes it most.

The most striking example is the behaviour of salicylic acid towards its isomers; compare also hydroquinone, pyrocatechol, and pyrogallol with resorcinol and phloroglucinol.

In the case of the polyoxycarboxylic acids we must take account of a resolution into CO₂ and polyphenol, which takes place even at the ordinary temperature so that the assimilation does not concern the acid itself but the polyoxy-compound.

This is certainly the case with phloroglucinolcarboxylic acid, so that the favourable action on the growth of the organism must be largely contributed to the phloroglucinol.

That these decompositions may play a role in the other oxy-acids

¹⁾ This seems, however, to depend also on the nature of the groups; thus we have found that o.toluic acid acts in a less retarding manner than p.toluic acid and it was known that o.cresol acts less narcotic than the para. The "positive" methyl group, therefore, behaves differently from the "negative" hydroxyl group or, to be more correct, a combination of two opposed groups behaves differently from one of two analogous ones.

TABLE II. Retarding action of different compounds on the development of penicillium in a nutrient base with 0,15 gram of p-oxybenzoic acid per 50 cc. as a source of carbon.

Salicylic acid. $T=28^{\circ}$ à 29° . Exclusion of light.

Quantity in mg.	1.3	2.2	5.1	8.7
Development 5 days after inoculation.	+++	+++	++	begin

o-Cresotinic acid

Quantity in mg.	1.3	2.1	5.0	8.1
Development 5 days after inoculation	++	+	?	-

Salicylic acid

Quantity in mg.	2.3	4.6	6.8	8.2	10.5	13.2
Development after 3 days	++	++	+	?	-	-
after 4 days	+++	++	+++	+	?	-
after 6 days	+++	+++	++	+	+	?

Gentisic acid (2,5-dioxybenzoic acid).

Quantity in mg.	90.3 to 18.2 mg p oxybenzoic acid	92 mg without p oxybenzoic acid.
Development after 3 days	+	With this experiment it was proved that gentisic acid has no perceptible action on the growth of the organism, although it hardly acts itself as a source of carbon. (See Table I and below).
after 8 days	++	—
after 19 days	+++	—

Resorcinic acid (quantity p-oxybenzoic acid = 0.1014 gr.)

Quantity in mg.	31.1
Development after 5 days	+++
after 17 days	very strong

2,6-dioxybenzoic acid (0.1 gr. p oxybenz.).

Quantity in mg.	20.5
After 4 days	++
Therefore, this acid does not arrest the growth any more than the 2,5 dioxybenzoic acid	

is already evident from the fact that phenol, in smaller concentrations is an excellent carbon nutriment.

Retarding action of different compounds on the growth of penicillium with 0.15 gram of p-oxybenzoic acid as source of carbon.

In order to be able to compare the influence of different substances small but increasing quantities thereof were added to 0,150 gram of p-oxybenzoic acid treated, and observed simultaneously in exactly the same manner.

Table IIIA gives a survey of the quantities with the Nos of the

TABLE III A.

	1 2.5 mg p-oxy- benzoic acid	2 2 mg o- toluic acid	3 2.4 mg m- toluic acid	4 2 mg p- toluic acid	5 2 mg benzoic acid	6 2 mg salicylic acid
Nos of experiments		7	8	9	10	11
Salicylic ac. (in mg)		blank control	1.0	1.8	7.8	13.6
Benzoic acid "			12	13	14	15
			1.0	1.8	6.4	11.9
o-Toluic acid "			16	17	18	19
			1.0	2.0	8.0	13.0
m-Toluic acid "			20	21	22	23
			1.0	2.0	8.0	13.0
p-Toluic acid "			24	25	26	27
			1.0	2.0	8.0	13.0

TABLE III B.

5 days after inoculation

	1	2	3	4	5	6
Salic. acid		7 vigorous growth	8 < 7	9 < 8	10 < 9	11 ?
Benzoic acid			12 < 8	13 < 9 < 12	14 = 10	15 —
o-Toluic acid			16 = 12	17 13	18 14	19 —
m-Toluic acid			20 = 16	21 = 20	22 —	23 —
p-Toluic acid			24 = 20	25 < 21	26 —	27 —

TABLE III C.

7 days after inoculation

	1	2	3	4	5	6
Salic. acid		7 strong	8 = 7	9 < 8	10 < 9	11 +
Benzoic acid			12 < 8	13 < 9	14 < 10	15 beginning
o-Toluic acid			16 = 12	17 13	18 = 14	19 —
m-Toluic acid			20 < 16	21 17	22 —	23 —
p-Toluic acid			24 > 20	25 < 21	26 —	27 —

experiments, III B and III C a survey of the development after 5 and 6 days respectively. Nos. 1—6 relate to very small quantities of p-oxybenzoic acid and the retarding substances investigated, Nos. 7—27 to mixtures of the latter with 0,15 gram of p-oxybenzoic acid:

After nine days the phenomenon had practically remained the same and owing to the vigorous growth, the differences in the low-percentage solutions were no longer plainly perceptible.

An always distinctly perceptible criterium is the commencement of development.

From this investigation it follows with positive certainty that benzoic acid and the toluic acids exert a stronger retarding action than salicylic acid, and that of the four first the m- and p-toluic acids exert a somewhat greater influence than the other two (see note p. 610).

From tables 1 and 2 it is shown that we may divide the substances into three groups although of course no sharp lines can be drawn.

- A. Substances which can serve as a source of carbon, for instance p-oxybenzoic acid.
- B. Substances which do not act as a nutriment and do not exert a retarding influence such as gentisic acid.
- C. Substances which exert a distinct retarding influence such as salicylic acid.

As it appeared to us that after 17 days a distinct growth could be observed in the flasks 2—6 (Table III) in which nothing was present but a retarding substance as a source of carbon, we have also investigated that phenomenon systematically.

It may be observed that we had kept these flasks, because we did expect the growth to take place.

For when we found that quantities of more than 10% salicylic acid in excess of para acid could not prevent a growth in the long run we asked ourselves what happened to this salicylic acid.

Some flasks with increasing quantities of salicylic acid in 150 mg. of p-oxybenzoic acid were treated in the usual manner and after the growth had set in thoroughly the solution was filtered. The filtrate was sterilised and again inoculated; a fresh growth took place which could not be distinguished from that formed in a flask with pure p-oxybenzoic acid; *the salicylic acid is, therefore, consumed*¹⁾.

¹⁾ We were able to demonstrate by means of the very characteristic iron reaction that gentisic acid had been formed; under the influence of the organism an H-atom, which has a para position in regard to the OH-group already present, is substituted and the retarding salicylic acid is simultaneously converted into the harmless gentisic acid.

From this it follows that the retarding substances must possess nutrient powers. This indeed appeared from the behaviour of the flasks 2—6 which all exhibited a slight development after some time.

It seems remarkable that the least development took place in flask 1 albeit a good carbon nutriment was present in the form of p-oxybenzoic acid.

That this was not merely accidental will be shown later.

TABLE IV A. Action of increasing quantities of carbon containing material on the development of penicillium.

p-oxybenzoic acid; $T=28^{\circ}-29^{\circ}$ light excluded, except during the observations.

Nos.	1	2	3	4	5	6	7	8	9	10
Quantity in mg.	2.9	5.2	10.5	38.9	58.0	89.7	119.7	173.5	213.4	283.2
After 2 days	—	—	—	+	+>4	+>5	<6	=7	=8	=9
» 4 »	—	—	+	++	>4	>5	somewhat <6	<7	=8	=9
» 5 »	—	+	+	+++	somewhat >4	>5	<6	much <7	<8	=9
» 6 »	?	+>1	+>2	++	somewhat >4	>5	6	much <7	<8	=9
» 7 »	+	+>1	+>2	+++	somewhat >4	>5	somewhat <6	much <7	<8	=9

In this first series, there is therefore a distinct maximum between 89,7 and 119,7 mg. A second series gave a maximum between 94,4 and 124,7.

TABLE IV B.

m-oxybenzoic acid; as with para.

Nos.	1	2	3	4	5	6	7
Quantity in mg.	4.3	12.8	41.7	93.3	172.8	300	553.6
After 3 days	?	small	+	=3	much <4	=2	?
» 5 »	+	>1	>2	somewhat >3	much <4	very small	<6

Here, the maximum lies also a little beyond 93,3; the harmful action of a large concentration is very evident.

With protocatechuic acid the maximum was only attained at ± 600 mg.; with o-phthalic acid at 71,2—124,0.

TABLE IV C.
 phenol; as with oxybenzoic acid.

Nos.	1	2	3	4	5	6	7
Quantity in mg.	2.6	8.5	10.4	12.9	42.6	60.9	141.7
After 4 days	beginning	= 1	< 2	= 3	—	—	—
6	+	> 1	$\frac{1}{2} < \frac{2}{1}$.1	—	—	—
7	++	> 1	= 2	= 3	—	—	—

The maximum is, therefore, situated between 8,5 and 10,4 mgs., in this concentration it is an excellent source of carbon.

From these experiments it is shown that the substances investigated must be looked upon from a common point of view. They act as a source of carbon as well as in the capacity of a retarder.

If they were exclusively a source of carbon the development would increase continuously with the concentration; if exclusively retarding they could not, of course, allow any development to take place.

Owing to these experiments we have also got acquainted with a method to ascertain the suitability of a definite substance as a carbon nutrient; the higher the maximum lies, the more suitable is the substance. Protocatechuic acid appears to have more favourable properties than m- and p-oxybenzoic acid and these substances are better than phenol.

Finally, it struck us that phenol in small concentrations caused a more *rapid* development than p-oxybenzoic acid, a phenomenon already observed with the other retarding substances such as benzoic acid and the toluic acids. If this were a general phenomenon, the substances which act still more favourably, such as pyrocatechuic acid in small concentrations ought again to cause a less rapid growth than p-oxybenzoic acid.

In fact, 4,5 and 8,2 mgs. of pyrocatechuic acid, respectively, when observed a few days after each other, showed a very much smaller growth than 3,7 and 9,2 mgs. of p-oxybenzoic acid, respectively.

Now it has been decided that there is no essential but a gradual difference between these benzene derivates, the main cause can only lie in a gradual difference of properties, for instance, in a difference of oxidability or even of solubility.

Although it is rather probable that we shall have to search in many directions we have, provisionally, restricted ourselves to the solubility and determined the division factor between olive oil and water of the most important compounds.

*On the division factor of several compounds, between
olive oil and water at 25°.*

For this purpose the solubility of the substances in water as well as in olive oil was determined by shaking them for a long time with the solvents in a thermostat and then estimating the amount taken up. The measurements were always made in duplicate, one of the flasks being shaken for a longer time than the other.

The acids were determined by titration after first ascertaining the accuracy of the process; when dealing with solutions in olive oil this had to be first thoroughly extracted; for this purpose it was shaken repeatedly with fresh portions of water (or boiled) until it yielded practically no more acid; 10 extractions were generally sufficient.

Division factor in connection with retardation and growth.

TABLE V. Factor calculated for 100 grams of solvent.

Name of compound	No.	Division-factor at 25°	Retarding action	Growth at quantities > 50 mg	Maximum development
o-toluic acid	1	40.5	{ +++ < No. 2 and 3	—	
p-toluic acid	2	29.5	+++	—	
m-toluic acid	3	21.0	+++	—	
benzoic acid	4	12.6	++	—	
anisic acid	5	12.5		+	
salicylic acid	6	11.8	++ = No. 4	—	< 2 mg
phenol	7	> 9 < 10.3	+	+	9 à 10 mg
terephthalic acid	8	9.25	+	{ Too difficult to dissolve	
guaiacolcarboxylic acid	9	3.7	+	—	
2,4-dioxybenzoic acid	10	1.0	+ < No. 6	+ > No. 7	
2,6-dioxybenzoic acid	11	} Not yet determined for want of material.	—	{ +	} > No. 10
2,3-dioxybenzoic acid	12		—	{ +	
p-oxybenzoic acid	13	0.6	—	++	± 100 mg
m-oxybenzoic acid	14	0.4	—	++	± 100 mg
2,5-dioxybenzoic acid	15	0.3	—	—	
3,4-dioxybenzoic acid	16	0.05	—	+++	± 600 mg
resorcinol	17	0.04	—	+++	
3,4,5-trioxybenzoic acid	18	0.025	—	+++	
o-phthalic acid	19	0.01	—	++	± 125 mg

The solubility of the non-acids was determined by gradually adding the substance to the solvent until no more was dissolved.

In this way were found the following division numbers, which we at once compare with the growth-phenomena caused by them and the retardation thereof.

The parallelism between the division factor and the retarding action is undeniable.

As regards the promotion of the growth, this is also the case in the reverse sense.

From these experiments we may draw the conclusion that the retarding action increases when the solubility is greater in oil than in water, from which it follows that this action is connected with a fatty constituent of the organism.

There are still two points which are now also elucidated.

1. Small quantities of retarding substances can promote the growth;
2. in very small concentrations they promote the development better than the substances with a small division factor, under the same conditions.

When small quantities are present of substances readily soluble in oil, these will for the greater part accumulate in the fatty part of the organism; from the fact that they are being assimilated it follows at once that the assimilation is also connected with the fatty part of the organism.

The fact that they are assimilated more rapidly than the favourable carbon sources is due to this difference in solubility; the latter which are much less soluble in oil than in water will, at the small absolute concentration of a few mg. per 50 cc., practically not enter the fatty part of the organism and, therefore, be assimilated very much more slowly.

An absolute parallelism does not, of course exist. First of all, olive oil is something else than "a fatty constituent of the *penicillium*" and secondly the division coefficient is only one particular factor (though plainly an important one) among the many factors which may be of importance here.

Among these, the more or less ready oxidability will undoubtedly play a role. In order to eliminate this influence we have used in our research, as much as possible, analogous substances. Yet, we attribute the ready assimilation of phenol as compared with that of guaiacolcarboxylic acid to the ready way it may be attacked.

This perhaps also explains why gentisic acid (N^o. 15 Table 5) although harmless on account of its low division coefficient yet cannot serve as a carbon-containing nutriment, and why ortho-phthalic

acid (No. 19) notwithstanding its very low division factor yet promotes the development not so well as, for instance, 3,4 dioxycarboxylic acid. (Notice the amount required for a maximum development, last column Table 5).

Presumably, this is also the reason why *o*-toluic acid with its large division factor acts somewhat less retarding than *p*-toluic acid; we have shown that *o*-toluic acid is oxidised to a substance which is also formed during the assimilation of *o*-phthalic acid; it is, therefore, very probable that *o*-toluic acid is first oxidised to the favourable *o*-phthalic acid.

The research will be continued by us in various directions.

It is our pleasant duty to thank Prof. Dr. BEYERINCK and Mr. JACOBSEN for their kind support in the biological part of the research.

*Org. Chem. Lab. Techn.
University Delft.*

November 8, 1911.

Chemistry. — “*On the velocity of hydration of some cyclic acid anhydrides.*” By Prof. J. BÖESEKEN, A. SCHWEIZER and G. F. VAN DER WANT. (Communicated by Prof. A. F. HOLLEMAN.)

(Communicated in the meeting of November 25, 1911).

In connection with the research of A. SCHWEIZER and myself, of which a communication is inserted in these Proceedings (November 26, 1910, p. 534), we have measured the velocity of hydration of some saturated cyclic acid anhydrides in order to collect more data as to the value of the figures thus obtained as a measure of the ring tension.

In the said communication we already pointed out that it is not excluded that the velocity of hydration of those anhydrides will be affected by their affinity for water and their ring tension so that in the figure found both these causes will find their expression.

It is, of course, not feasible to ascertain what part is due to the affinity, yet, we may expect that this affinity will be connected with the dissociation constant of the acids obtained from the anhydrides.

The dissociation constant is up to a certain degree a measure for the velocity with which the acid is further divided into its ions; we may expect that the quicker this takes place the more rapidly will the disappeared acid molecules be replenished from the anhydride.

If we compare the figures for the hydration-constant, obtained by ourselves and other investigators, with those of the electrolytic dissociation, a parallelism cannot be denied, particularly when we choose analogous substances for comparison.

The number of substances investigated is, as yet, far too small to enable us to draw general conclusions; still in the succinic acid

Hydration constant of some acid anhydrides calculated for a monomolecular reaction with the minute as time unit; and the dissociation constant K .

Group	Anhydride of	$0.4343 \times K_{55}$	$0.4343 \times K_{60}$	Investigators	Dissociation constant K of the acids
I	succinic acid	0.0736	0.0088	Voerman	0.00652 (V.)
	»	0.0693		Rivett and Sidgwick	
	»			Böeseken and Schweizer	
	methyl succinic acid	0.0965		Riv. and Sidg.	0.0086 (O.)
	s.dimethyl m.p. = 87°	0.110		Bö. and V. d. Want	0.0132 (V.d.W.)
s.dimethyl m.p. = 42°	0.153	0.0194 »			
II	maleïnic acid	0.690	0.125	Riv. and Sidg.	1.17 (Schw.)
	»			Bö. and Schw.	
	itaconic acid	0.0776		Riv. and Sidg.	0.012 (O.)
	citraconic acid	0.459			0.34 »
o.phthalic acid	0.2766		0.121 »		
III	glutaric acid	0.0742	0.0117	Voerman	0.0047 (V.)
	acetyl β oxyglutaric acid	0.096		Bö. and Schw.	0.0157 (Schw.)
	»				

group the increase of the velocity of hydration with that of the dissociation constant is so striking that it cannot be quite accidental.

The same is true for the maleic acid group to which even o-phthalic acid is connected.

The slight increase of the velocity of hydration, noticed by VOERMAN, when one passes from succinic anhydride to glutaric anhydride now finds a very simple explanation in the slight dissociation constant of glutaric acid, as compared with that of the succinic acid.

From this point of view the difference in tension between this 6-ring and the 5-ring of succinic anhydride would be considerably

greater than might be surmised from a comparison of VOERMAN'S figures.

In both the symmetric dimethylsuccinic anhydrides¹⁾, we notice that the two constant-couples are almost proportionate, so that the relation of the dissociation constant with the hydration is particularly striking; the influence of the ring tension (to be expected on account of the difference in configuration) appears to become quite inconspicuous.

In other cases, this affinity is less pronounced, so that we can say, as a rule, that the hydration changes in the same sense as the dissociation constant, but that the changes do not keep equal pace. Whether this bears a relation to the ring tension remains to be seen when a much greater number of experiments have been made.

At present we can, however, state with great probability that in the hydration of acid anhydrides the affinity of water for anhydride plays a very important role.

The description of the experimental part of this research carried out with the assistance of Messrs. A. SCHWEIZER and G. F. VAN DER WANT will shortly appear in the *Recueil des travaux Chimiques*.

Org. Chem. Lab. Techn. University.

Delft, Nov. 20, 1911.

¹⁾ I call attention to the fact that some confusion exists in the denomination of the two symmetric acids. They are indicated by the names *cis* and *trans*, *fumaroid* and *maleinoid*, *para* and *anti*, *racemic* and *meso* (*anti*).

The last is undoubtedly the most rational one, but it cannot be applied, because it is not known, as yet, to which of the stereoisomers the racemic configuration appertains.

One is accustomed to give to the acid with the highest melting point the name of *para*- or *trans*-dimethylsuccinic acid in the idea that this is the racemic acid; but this is only based on some speculative ideas of BISCHOFF (B 24 p. 1086) and v. BAEYER (Ann. 258 p. 180) as to the privileged position of the groups, which in this case have now little value.

So long as not one of these acids has been resolved into its optical components, there is no certainty; it is even more probable that the acid with the lowest melting point (128°) will prove to be the racemic acid because the anhydride of this acid, which melts at 87°, is stable and because we may expect that the methyl-groups on both sides of the ring will render the same more stable than when they are situated at the same side. The *trans*-anhydride belongs to the racemic acid (Compare also MICHAEL Journ. f. pr. Ch. [2] 46 p. 422).

Provisionally, I have indicated the anhydrides with their melting points. (J. B.).

Chemistry. — “On the Iodides of the Elements of the Nitrogen Group”. By H. R. DOORBOSCH. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of November 25, 1911).

§ 1. Frequent investigations have been carried out in regard to the iodides of the elements nitrogen, phosphorus, arsenic, and antimony, but these chiefly concerned the two first elements of this group.

So far as *nitrogen-iodide* is concerned, the question as to the existence of a *free* compound of the formula NJ_3 may now be answered in a negative sense.

As the result of the latest investigations as to this question, such as those of CHATTAWAY¹⁾, RUFF²⁾ and HUGOT³⁾, it is well nigh certain that NJ_3 can exist only in complex molecules with 12, 3, 2 and 1 mols. of NH_3 , respectively, and then only at low temperatures.

Of *phosphorus*, two iodides are known; according to the literature on the subject, the *di-iodide* P_2J_4 m.p. 110° (according to this research 124°), whose vapour under reduced pressure is said to deposit mainly PJ_3 with formation of red phosphorus:



further the *tri-iodide* PJ_3 m.p. 55° — 60° which is said to yield a dissociated vapour, but only at a higher temperature.

With arsenic on the other hand, it is only the compound AsJ_3 , which is accepted with absolute certainty, as the statements⁴⁾ as to As_2J_4 (analogous to the phosphorus compound) must in any case be considered to be of a doubtful nature, particularly so because ARZRUNI'S crystal-measurements of these products do not admit of safe conclusions as to the individuality of the supposed compound. Whilst with the phosphorus, no derivative of the pentavalent element is described, some statement as to AsJ_5 are found in SLOAN'S paper⁵⁾.

Of antimony we find in the first place a compound SbJ_3 described supposed to be isomorphous with BiJ_3 . VAN DER ESPT⁶⁾ and afterwards PENDLETON⁷⁾ have noticed a compound SbJ_5 with a melting point of 78° — 79° ; the existence thereof has, however, been denied

¹⁾ CHATTAWAY, NORTON, and others, Amer. Chem. Journ **23**, 363, 369 (1900); **24**, 138, 159, 318, 331 (1900).

²⁾ RUFF, Ber. d.d. Chem. Ges. **33**, 2025 (1900).

³⁾ HUGOT, Ann. de Chim. et Phys. (7), **21**, 5 (1900).

⁴⁾ BAMBERGER and PHILIPP, Ber. d.d. Chem. Ges. **14**, 2644 (1881).

⁵⁾ SLOAN, Chem. News, **46**, 194 (1882).

⁶⁾ VAN DER ESPT, Arch. Pharm. (2), **117**, 115 (1864).

⁷⁾ PENDLETON, Chem. News. **48**, 97. (1884).

by MAC IVOR¹⁾, in whose opinion only one compound, namely SbJ_3 , can exist.

This incompleteness of the statements in the literature coupled with the experiences gained by EGGINK²⁾ with the chlorine-derivatives of the analogous *bismuth*, and the suspicion that a two-layer formation might occur also here as a confusing complication, caused Prof. JAEGER to suggest to me to investigate some of the disputable questions. We may, therefore, state briefly in this paper the results obtained in the study of the binary systems: $As + J$ and $Sb + J$, also of those of $AsJ_3 + PJ_3$, $SbJ_3 + PJ_3$ and of $AsJ_3 + SbJ_3$. Further details will be communicated later in a dissertation now in hand.

§ 2. *Antimony and Iodine.* The binary molten mixtures investigated, were prepared from SbJ_3 sublimed in a CO_2 -current, with the aid of Sb or J_2 . The fusion, in order to avoid loss of iodine by volatilisation, took place in the case of mixtures rich in Sb , in evacuated and afterwards sealed glass tubes. With the mixtures very rich in Sb the cooling- and heating-curves were also recorded in closed apparatus. In the tables are found, besides the actual temperaturereadings, also the corrected ones; the thermometers were compared with a certificated normal thermometer. By way of comparison, the solidifying- and the melting-points are given side by side, so as to point out the difference between the results of cooling- and heating-experiments. On account of the rapid setting in of the equilibrium, and the want of an appreciable undercooling, these differences are not large in this system.

From these determinations it is shown, that when the binary molten mixtures solidify, Sb and J form only *one* compound, namely SbJ_3 . This compound has a sharp melting-point of $170^{\circ}.8$ C. It does not mix perceptibly with antimony; if more antimony is added than corresponds with the composition SbJ_3 , the melt separates into two liquid layers of which the upper one differs but exceedingly little in composition from SbJ_3 , whilst the lower one has the composition 71.6 at % Sb and 28.4 at % J , as proved by repeated analysis of suddenly cooled mixtures. The transition-temperature is 169° C.; at that temperature the liquid with 28.4 % of J , will, with deposition of Sb , form the layer whose composition practically does not differ from SbJ_3 . As the eutecticum then following between that resulting layer and pure SbJ_3 practically coincides with 75 % of J , the inter-

1) MAC IVOR, Journ. Chem. Soc. 29, 328 (1876); Chem. News. 86, 223.

2) EGGINK, Zeits. f. phys. Chem. 64, 449 (1908).

Binary melting-point-line of *Sb* + *J*.

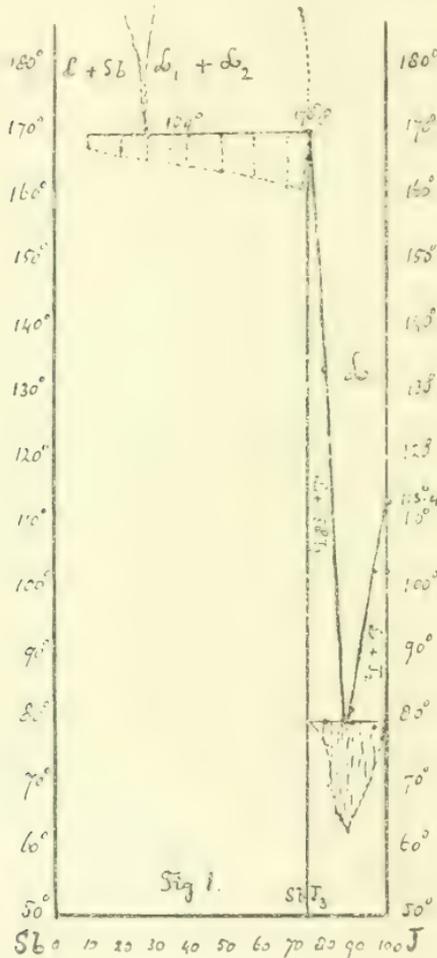
% by weight		% by atoms		Observed temperature.		Corrected temperature.		Duration
<i>Sb</i>	<i>J</i>	<i>Sb</i>	<i>J</i>	Solidi- fying point.	mp.	Solidi- fying point.	mp.	of the effect in seconds.
100.	0.	100.	0.	630. ^o	—	632. ^o	—	—
89.5	10.5	90.	10.	163.4	165.8	166.5	168.9	130
79.1	20.9	80.	20.	164.1 ⁵	—	167.2 ⁵	—	230
75.	25.	76.	24.	165.8	167.2	169.0 ⁵	170.4 ⁵	330
70.9	29.1	72.	28.	165.9	167.2	169.0	170.3	380
58.7	41.3	60.	40.	165.5	167.	168.5	170.1 ⁵	500
48.6	51.4	50.	50.	165.4 ⁵	167.1	168.6	170.2 ⁵	580
38.7	61.3	40.	60.	165.5	166.	168.4 ⁵	168.9 ⁵	630
28.9	71.1	30.	70.	165.2	166.8	168.1	169.7	780
24.0	76.0	25.	75.	167.1	167.6	170.3	170.8	—
					End solidi- fying point.		End solidi- fying point.	
23.4	76.6	24.4	75.6	160.8	77.9	164.4	78.7	300
22.7	77.3	23.6	76.4	154.9 ⁵	79.2	158.3 ⁵	79.7 ⁵	420
20.5	79.5	21.5	78.5	144.8	79.4	147.	79.7	740
18.8	81.2	19.6	80.4	132.8	79.8	134.2 ⁵	80.2	1040
16.5	83.2	17.3	82.7	116.	79.2 ⁵	117.7	80.1 ⁵	1220
14.2	85.8	14.9	85.1	95.3	79.3	96.5 ⁵	80.2	1500
12.4	87.6	13.0	87.0	83.5 ⁵	79.3 ⁵	84.4 ⁵	80.2 ⁵	1520
11.3	88.7	11.8	88.2	79.	79.2 ⁵	79.8 ⁵	80.1	1700
10.7	89.3	11.2	88.8	81.1	79.2 ⁵	82.0	80.1 ⁵	1480
7.9	92.1	8.3	91.7	91.8 ⁵	79.4 ⁵	92.8 ⁵	80.2	1080
4.3	95.7	4.5	95.5	102.4	78.3	103.7 ⁵	79.1 ⁵	720
0.9	99.1	1.0	99.0	110.8	76.8 ⁵	111.8	77	210
0.	100.	0.	100.	112.1	—	113.3 ⁵	—	—

vals superpose each other. Hence, the abnormal course of the time line.

The melting point of iodine ($113^{\circ}.3$ C.) is lowered by addition of SbJ_3 , and the eutectic point appears to lie at 80° C. and a content of 88.2 at. % of iodine. From the fact that the eutectic separation is found quite close to the vicinity of the pure iodine, it follows, that a notable formation of solid solutions does not occur; the same is true for the mixtures in the immediate vicinity of the SbJ_3 . The

composition of the mixtures $SbI_3 + I_2$ was each time determined by direct analysis, after recording the cooling-curve.

The value for the heat of fusion of pure iodine is, according to



an old statement of PERSON (Jahresberichte 1847) 11.7 calories. From this we find for the molecular freezing-point-constant: 253°.2 C. TIMMERMANS (Journ. de Chim. phys. 4 (1906) 171) found a value of 252°.13 C. When this value is accepted we find, for the depression of the melting-point of the iodine by added SbI_3 , amounts which agree well with the temperature on the branch of the melting-point-line at the I -side.

Binary melting-point-line of *As* + *J*.

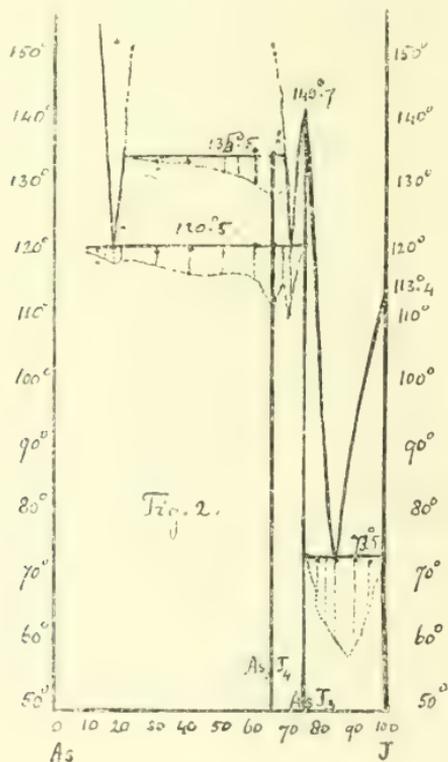
% by weight		% by atoms		Observed Temp.		Corr. Temp.		Duration of the effect in seconds (recalculated for a same number of atoms)	
<i>As</i>	<i>J</i>	<i>As</i>	<i>J</i>	Initial solidifying point	End solidifying point	Initial solidifying point	End solidifying point	Of lowest temp.	Of highest temp.
100	0	100	0		—		—	—	—
84.2	15.8	90	10	—	—	—	117.3	150	—
70.3	29.7	80	20	120.2	—	122.5	120.5	200	90
68.0	32.0	78.2	21.8	125.0	116.7	127.8	118.9	300	60
57.9	42.1	70	30	123.9	116.8	131.5	119.1	290	90
47.0	53.0	60	40	130.8	117.4	133.5	119.7	380	200
37.1	62.9	50	50	132.2	117.4	134.9 ¹	119.7	380	290
28.2	71.8	40	60	132.0	117.7	134.7	120.0	480	370
22.8	77.2	33.33	66.67	130.2	117.8	132.9	120.1	540	310
22.5	77.5	33.0	67.0	131.6	117.3	124.6	119.8	530	400
21.8	78.2	32.0	68.0	134.0	117.3	136.8	119.6	485	490
21.0	79.0	31.0	69.0	133.7	117.0	136.5	119.3	480	—
20.2	79.8	30.0	70.0	128.4	118.4	131.1	120.7	600	—
19.0	81.0	28.5	71.5	119.5	119.2	121.8	121.5	1100	—
18.3	81.7	27.5	72.5	126.4	118.8	128.9	121.2	640	—
17.2	82.8	26.0	74.0	134.8	112.2	137.6	114.3	160	—
16.45	83.55	25	75	138.1	—	140.7 ⁵	—	—	—
16.3	83.7	24.8	75.2	137.2	70.4	139.9	71.1	70	—
15.9	84.1	24.2	75.8	132.5	72.2	134.9	72.9	250	—
13.2	86.8	20.5	79.5	109.7	71.8	111.4	72.4	740	—
9.4	90.6	14.9	85.1	79.5	72.2	80.3	72.9	1380	—
8.9	91.2	14.1	85.9	73	73	73.7 ⁵	73.75	1500	—
7.8	92.2	12.5	87.5	75.8	72	76.6	72.75	1420	—
6.2	93.8	10	90	86.3	71.8	87.2	72.5	1220	—
3.0	97.0	5	95	101.3	71.3	102.6	72.0	850	—
0.3	99.7	0.5	99.5	110.0	68.0	111.7 ⁵	—	110	—
0	100	0	100	112.1	—	113.3	—	—	—

Reversely, as SbJ_3 is not or but little dissociated in the molten mass, and assuming that iodine dissolves therein as molecules of J_2 , we can calculate for the molecular heat of fusion of SbJ_3 : 11 calories; it is, therefore about equal to that of iodine itself and K becomes here $357^\circ C$.

The melting temperature of $79^\circ C$. found by PENDLETON for SbJ_3 answers to the eutectic temperature and a composition of about 88.2 at. % of iodine. In this way nothing is noticed of a compound SbJ_5 or a compound Sb_2J_4 .

I have also carried out experiments to ascertain, whether any of these compounds might perhaps form at a lower temperature, for instance in strong HJ -solutions, or as a double-iodide such as are known of SbJ_8 and $(NH_4)J$, BaJ_2 and RbJ^1). Up till the present we have not succeeded in obtaining such compounds which would confirm the existence of the supposed iodides.

§ 3. Arsenic and Iodine. In a manner analogous to that given



¹⁾ WHEELER. Zeits. f. anorg. Chem. 5. 253. (1894).

for the binary liquids of $Sb + J$, the system $As + J$ has also been investigated. The results are found in the subjoined table.

From these figures which are represented graphically in fig. 2, it follows that there is first of all a compound AsJ_3 stable at its melting point, and that this system exhibits in the main the peculiarities of the system $Sb + J$. The compound AsJ_3 melts at $140^{\circ},7$ and is apparently but little dissociated in the liquid. Secondly, on closer examination of the eventual possibilities, there is no other possible interpretation of the data obtained but this one: from one of the two liquid layers a compound As_2J_4 is deposited which, therefore, has no *real* melting-point, but melts at 135° — 136° to a complex of two non-miscible liquids. The one layer has a composition which corresponds nearly to that of As_2J_4 , but contains a little more iodine. As the mean of various analyses (the J -determinations as AgJ and the As -determinations according to the method of GOOCH and MORRIS¹⁾) the composition of the upper layer was found to be: 79,4% of J and 21,6% of As , or in at. %: 69.5 J and 30.5 As ; the lower layer has a more varying composition so that the arsenic-content (70.8% by weight) is certainly a little too high. The temperature of the eutecticum at the arsenic-side *hardly* differs from that of the first eutecticum, so that it looks as if the eutectic temperature proceeds from 125° further towards the arsenic-side.

Although the whole construction of the diagram already points to the occurrence of a binary compound in compositions which are situated within the sphere of the two liquid layers, there are still more arguments in favour of the existence of As_2J_4 . First of all the plainly perceptible heat-effects which occur in mixtures in the vicinity of 66—68 at. % of J and which appear in the figure as an apparent increase of the two-layer temperature: $135^{\circ},5$. The course of the time-lines also confirms distinctly the above two explanations and makes the impression that we are dealing here again with a superposition of two time-effects.

It admits, moreover, of no doubt that the compound looked upon till now as As_2J_4 has really been nothing else but the upper layer present at $135^{\circ},5$. According to BAMBERGER and PHILIPP a compound AsJ_2 is formed on melting 1 part of arsenic and 2 parts of iodine at 230° in sealed tubes for 7 or 8 hours. They state that "superfluous arsenic" is deposited in the tubes. On repeating their experiments, it appeared to us, that the product of fusion contained 79,73% of J and in a second experiment 79,52%. As AsJ_2 ,

¹⁾ GOOCH and MORRIS, Zeits. f. anorg. Chem. 25, 227 (1900).

requires 77,20% and AsJ_2 83,55% of iodine, the composition of the *product* lies between that of As_2J_4 and AsJ_3 .

Afterwards we have tried, like B. and P. to obtain from the fused mass a compound As_2J_4 by means of carbon-disulphide.

Working in an atmosphere of CO_2 , arsenic seemed to deposit; the solution exhibited definite colour-differences with those of pure AsJ_3 , which compound on boiling with CS_2 always communicates a violet colour to the condensed liquid (owing to iodine split off.) The liquid was filtered, cooled in a CO_2 -atmosphere with ice and salt and the crystals deposited were carefully dried at 50° in a CO_2 -atmosphere. The analysis gave: 80,11 and 80,63% of iodine. These analyses prove that those otherwise homogeneous crystals contain *more As* than AsJ_3 itself. These experiments were now repeated with fusions which contained *more As* to start with, in the hope to obtain perhaps in this way, by extraction with CS_2 , crystals which contain still more *As* than the above named. I succeeded indeed in finding an arsenic-content of 19,23% and 19,58%. The solution was cherry-red, the crystals were dark red, and therefore, of a different colour from those of AsJ_3 .

A mixture of AsJ_3 with much finely powdered *As* was now boiled a long time with xylene (138°) in a current of CO_2 . The filtered liquid was cooled rapidly, the mother-liquor evaporated in vacuo and the residue analysed. Found: 81,86%, therefore again *more As* than corresponds with AsJ_3 . This experiment proves plainly that a solution of AsJ_3 may take up a certain amount of *As* (otherwise insoluble in the solvent) to form a product containing more *As* than AsJ_3 .

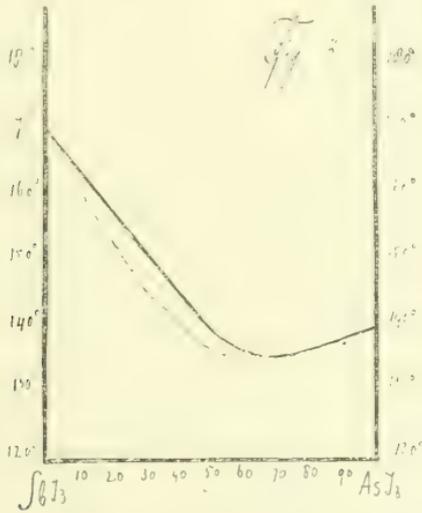
Previously, when recrystallising AsJ_3 from toluene, it had been found that the product obtained always contained more *As* than corresponds with the normal composition.

In diverse experiments were found: 83,16%, 83,33%, 83,05% of *J*; after a single recrystallisation was found: 83,02%, after a double recrystallisation 83,2%, after a third time 82,77% of *J*. Pure AsJ_3 can only be obtained, when the substance is recrystallised from toluene, containing iodine. When subliming AsJ_3 in a current of CO_2 we also noticed an elimination of iodine, so that AsJ_3 belongs to those compounds which very readily dissociate, when in the state of vapour. From the melting diagram it would just appear that, at any rate in the *fused* AsJ_3 , but comparatively little dissociation occurs.

Consequently we may well assume that a dissociation-equilibrium is present, expressed for instance by $2 AsJ_3 \rightleftharpoons As_2J_4 + J_2$; and also that in the liquids, in which AsJ_3 has been brought together with

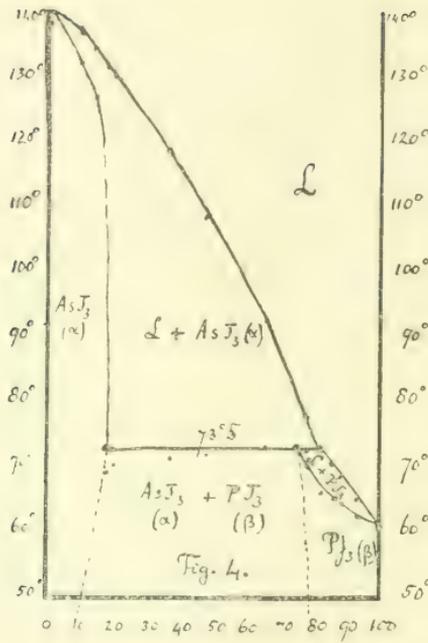
As, according to: $8 \text{AsJ}_3 + \text{As}_4 \rightleftharpoons 6 \text{As}_2\text{J}_4, -6 \text{As}_2\text{J}_4$ may be formed from 8AsJ_3 and As_4 which latter reaction would then dominate the situation in the upper layer of the melt when heat is being abstracted. Up to the present I have not succeeded in obtaining the compound in a *pure* condition; but that it *does* exist can, in my opinion, no longer be doubted.

§ 4. Finally, we have collected data to ascertain the behaviour of AsJ_3 and SbJ_3 , of AsJ_3 and PJ_3 , also that of SbJ_3 and PJ_3 .



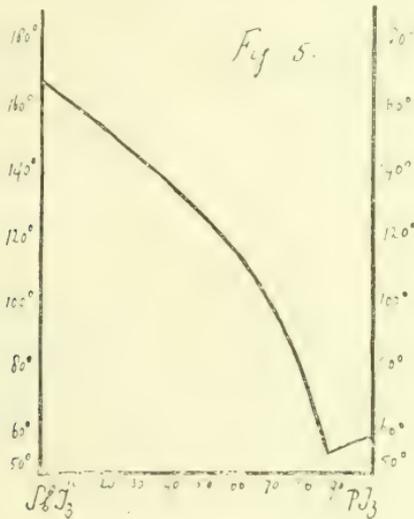
Binary melting-point-line of $\text{AsJ}_3 + \text{SbJ}_3$ (fig. 3).

Composition.		Initial Solidifying point.	End mp.	End Solidifying point.	Initial mp.
$\%$ by weight	mol. $\%$	(corrected).		(corrected).	
AsJ_3	AsJ_3				
0	0	170.3	170.8	—	—
23.3	25	154.75	156.5	149	—
47.6	50	139.6	140.5	136	135
60.3	62.5	135.9	138.6	135.5	135
66.9	69	135.85	138.4	135.5	135
73.2	75	136.35	139.1	135	134
86.4	87.5	182.2	140.1	137	135.5
100.-	100.-	140.75	—	—	—

Binary melting-point-line of $AsJ_3 + PJ_3$ (fig. 4).

Composition in $\frac{0}{100}$ by weight		Composition in mol. $\frac{10}{100}$		Observed Temp.			Observed Temp.			Duration in seconds: calculated on same number of molecules
PJ_3	AsJ_3	PJ_3	AsJ_3	Initial	Effect	End solidifying point	Initial	Effect	End solidifying point	
0	100	0	100	138.4	—	—	141.5	—	—	—
9.0	91.0	9.9	90.1	134.3	—	ca. 130°	137.1	—	ca. 132.5	—
12.8	87.2	14.0	86.0	132.1	—	ca. 125°	134.9	—	ca. 127	—
16.8	83.2	18.3	81.7	129.5	68.5	—	132.2	69.1	—	20
18.5	81.5	20.1	79.9	128.1	69.8	—	130.8	70.5	—	30
34.6	65.4	36.9	63.1	116.7	71.0	—	119.0	71.7	—	110
45.6	54.4	48.1	51.9	108.0	71.6	—	109.9	72.3	—	140
63.5	36.5	65.8	34.2	92.1	73.0	—	93.4	73.7	—	250
76.4	23.6	78.2	21.8	77.4	72.3	ca. 70	78.2	73.0	ca. 70.7	240
80.7	19.3	82.2	17.8	72.7	—	ca. 66	73.4	—	ca. 66.5	—
84.6	15.4	85.8	14.2	70.2	—	ca. 65	70.9	—	ca. 65.5	—
87.0	13.0	88.1	11.9	68.1	—	ca. 64	68.75	—	ca. 64.5	—
92.2	7.8	92.9	7.1	64.9	—	ca. 62	65.5	—	ca. 62.5	—
100.	0.	100.	0	60.4	—	—	61.0	—	—	—

in regard to each other. The results of the determination of the binary melting-point-lines are represented in the subjoined tables and in the fig. 3, 4, and 5.



Binary melting-point-line of $SbJ_3 + PJ_3$ (fig. 5).

Composition in % by weight		Composition in Mol. %		Observed Temperature.		Observed Temperature.		Duration of the second effect in sec. (calculated on a same number of mols).
PJ ₃	SbJ ₃	PJ ₃	SbJ ₃	Initial solidifying point	End solidifying point	Initial solidifying point	End solidifying point	
0	100	0	100	167.1	—	170.3	—	—
2.7	97.3	3.2	96.8	164.3	—	168.0	—	—
8.6	91.4	10.3	89.7	159.1	52.8	162.5 ⁵	53.2 ⁵	100
10.1	89.9	12.1	87.9	157.7	52.5	161.5	52.9 ⁵	—
35.1	64.9	39.7	60.3	135.4	55.8 ⁵	138.0 ⁵	56.3	360
60.4	39.6	65.0	35.0	108.2	55.8 ⁵	110.1 ⁵	56.3	740
83.3	16.7	85.9	14.1	57.9	55.7	58.3 ⁵	56.1 ⁵	900
92.2	7.8	93.5	6.5	—	57.2	—	57.6 ⁵	920
100	0	100	0	60.4	—	61.0	—	—

Fig. 4 needs no further comment: PJ_3 and AsJ_3 form an *isodimorphous mixing series*, with a transition-point at $73^{\circ}.5$ C.

The liquid coexisting with both mixed crystals, contains about 82 mol. % PJ_3 , whereas the two mixed crystals have at that tempe-

perature a composition of about 75 mol. % of PJ_3 and 18 mol. % of PJ_3 , respectively; the solidus-line at the side of the AsJ_3 is so steep, that only a few points could be indicated with some degree of accuracy.

The crystallographic measurements of PJ_3 and AsJ_3 left, up to the present, some doubt as to the isomorphism of the two compounds. According to NORDENSKJÖLD¹⁾ PJ_3 is hexagonal (or trigonal?) with $a:c = 1:1$, 1009 with $\{0001\}$ and $\{10\bar{1}0\}$, when recrystallised from CS_2 , or with $\{10\bar{1}0\}$, $\{0001\}$ and $\{10\bar{1}2\}$ from the melt; twins according to $\{11\bar{2}2\}$.

On the other hand, AsJ_3 , according to FRIEDLÄNDER²⁾, is trigonal with $a:c = 1,2998$ with base $\{211\}$, $\{110\}$, $\{411\}$ and complete cleavage parallel $\{111\}$.

These data indeed do not lead without further confirmation to the assumption of an isomorphism. The melting-experiments now prove, that AsJ_3 and PJ_3 do possess indeed a *different* symmetry; it is not improbable that each of the compounds still exhibits a metastable modification, which corresponds with the more stable form of the other substance.

The case represented in fig. 3 ($AsJ_3 + SbJ_3$) also leaves but little doubt. We have here an isomorphous mixing series with a minimal temperature.

SbJ_3 ³⁾ is trimorphous; the rhombic (yellowish-green) as well as the monoclinic (greenish-yellow) modification, are however metastable, monotropous forms are only obtainable under very particular conditions. On the other hand, the mixed crystals are trigonal and coloured red, just like the more stable, trigonal, red modification of SbJ_3 .

The trigonal SbJ_3 shows $\{111\}$, $\{100\}$ and $\{110\}$; the angles found by COOKE, are, however, not correct as shown by NEGRI (Rivista di Min. Crist. Ital. Padua 9. 43. (1891)). For the angle α he finds $50^\circ 40'$ whilst that for AsJ_3 was determined as $51^\circ 20'$.

All this, in connection with the melting-point-line found, points sufficiently to an actually existing isomorphism between the two compounds.

The case of fig. 5 ($SbJ_3 + PJ_3$) points to an ordinary mixing series with an eutectic temperature at 56° .

Whereas in the case of PJ_3 and AsJ_3 , there was already present an uninterrupted mixing series with a large hiatus, the miscibility in

1) NORDENSKJÖLD, Z. f. Krist. 3, 214 (1897).

2) FRIEDLÄNDER, Bihang K. Svenska Vet. Acad. Stockholm (1874).

3) COOKE, Proc. Amer. Acad. 13. 74. (1877); Abstract Z. f. Krist. 2, 634.

the case of PJ_2 and SbJ_3 , has completely disappeared, or at least been limited to concentrations in immediate proximity to the axes. All this is systematically connected with the steadily increasing distance between the elements phosphorus, arsenic, and antimony, in regard to each other.

November, 1911.

Inorg. Chem. Lab. University.
Groningen.

Physics. — “*The Thermomagnetic Properties of Elements.*” By Mr. MORRIS OWEN. (Communicated by Prof. H. E. J. G. DU BOIS).

A short account was given in a recent communication¹⁾ of experiments upon 43 elements at ordinary and high temperatures. The present investigation was undertaken with the idea of increasing the number of elements to be experimented upon, and also of finding the effects of low temperatures upon the magnetic susceptibility.

I. *Experimental Arrangement.*

This has already been described in detail. It is only necessary here to mention that the method of CURIE and previous investigators was employed with one exception, viz. that the investigated substance was not placed at that point of the magnetic field where $\partial \partial_x / \partial y$ is a maximum.²⁾ This was due to the fact that about this point the field-variation can be quite considerable, especially in the case of a substance of comparatively somewhat large dimensions. In fixing on a point at which to work at more stress was laid upon the attainment of a maximum field, because the iron impurities then exert a proportionally smaller detrimental influence.

Three different adjustments of the apparatus were employed differing only in the length and thickness of the suspending silver wire of the torsion balance, and the inclination of the axes and the distance apart of the two cores of the electromagnet. The latest large type model of the DU BOIS electromagnet, recently described in these Proceedings, was placed at my disposal. The whole arrangement for ordinary temperature work was much more sensitive than any used previously.

The sensitiveness of the torsion balance could be varied: the directive force per unit degree torsion was measured in the ordinary way by means of applied additional moments of inertia.

¹⁾ H. DU BOIS and K. HONDA, These Proc. XII p. 596.

²⁾ K. HONDA, Ann. d. Physik 32, p. 1027, 1910, Fig. 1.

Silvered Dewar-vessel. This had an inner diameter of 15 mm. and was 170 mm. long. It contained a copper tube, closed at its lower end, of 10 mm. diameter, in order to protect the investigated substance from the direct effects of the liquid aid. This was poured into the interspace between the two tubes. It was found advisable to work in nitrogen at low and ordinary temperatures, and in carbon dioxide at high temperatures: this has the further advantage of no correction being necessary for the magnetisation of the surrounding atmosphere. To determine the low temperatures, the thermo-element was standardised by means of a platinum-resistance thermometer.

Electric oven. This consisted of a porcelain tube wound with platinum wire and insulated with kaolin powder. A temperature of 1250° could be attained, measured by the above-mentioned thermo-element connected to a pyrometer: this had previously been standardised by observations on well-known melting-points.

Notation.

a , Atomic weight.	θ , Temperature.
\mathcal{H}_x , Field intensity.	χ , Specific susceptibility.
$\partial \mathcal{H}_x / \partial y$, Field-gradient.	χ_x Limit value of the same.

II. *Test-Samples.*

The same difficulties were encountered as those enumerated by HONDA. Of the 83 (70 + 13 "rare") elements, 58 were tested; many samples of the same element were supplied by different firms, and gave in the majority of cases different results, not always explainable by the influence of iron-impurities. Many of the elements were supplied as pure as possible by KAHLBAUM and MERCK. For particularly pure specimens I am indebted to several chemists. It is important here to mention that the iron-impurity is not homogeneously distributed. This made it necessary for the same piece to be chemically analysed as that magnetically tested. Apparatus containing iron in any shape or form were carefully removed from the chemical room of the laboratory, where the analysis was carried out.

If the susceptibility proves independent of the field, there can be no question of a ferromagnetic impurity. It is interesting here to note that the magnetic method can be made more sensitive than the chemical one in testing for iron. With the majority of the tested samples however the curve showing the relation between the specific susceptibility and the field took the form of a hyperbola; I calculated the most probable value of χ_x , which would hold asymptotically for an infinite field, by the method of least squares; and, in addition,

the influence of the ferromagnetic ingredient, which in the great majority of cases was less than 10% of that which could be imputed to iron in the specimen. As HONDA has already shown, the thermomagnetic properties also afford a test of purity up to a certain point.

As the insertion of my full tables and curves would require too much space, a somewhat short discussion of my principal results is given, no mention being made in most cases of those elements which are independent either of the field or of the temperature.

III. Specific susceptibility¹⁾ at 18°.

Second Series. Contrary to expectations MERCK'S Li ($\chi_x = +3,11$) gave a higher value than KAHLBAUM'S specimen ($\chi_x = +0,25$), which contained the lesser percentage of iron. Be, although containing 4% iron, was still diamagnetic ($-1,03$). It is noteworthy that the three allotropic forms of carbon, viz. diamond, graphite, and amorphous show widely divergent results. The highest diamagnetic value ($-0,71$) for amorphous carbon was obtained with that prepared from ordinary sugar in this laboratory. Gas carbon, taken out of the ordinary iron retorts of a gasworks, gave a still higher numerical value ($-1,31$). Ordinary arc-carbon gave a value of $-1,82$. Ceylon graphite gave very interesting results, for in addition to showing a decided directional effect, incapable of quantitative measurement with the apparatus used, it also gave in one direction the highest diamagnetic value, as yet achieved ($-15,0$). The powdered specimen gave a constant mean value ($-4,0$).

Third Series. Two Mg specimens extracted from the same lump of material, and containing different amounts of iron, gave different values ($+0,31$ and $+0,26$). The iron-impurities in three Al specimens tested were somewhat considerable. The NEUHAUSEN specimen gave ultimately the lowest value ($+0,58$). A difference was shown to exist between Si crystalline ($-0,13$) and amorphous ($-0,15$). This is not the case with regard to S crystalline and amorphous, a fact previously pointed out by CURIE.

Fourth Series. In contradiction to HONDA'S result, K gave a constant value ($+0,58$). Both the KAHLBAUM- and MERCK-specimens of Ca contained much iron: whereas the first was constant ($+1,1$), the second varied considerably with \mathfrak{H} ($+3,7$). It is noteworthy that in the case of Ti the specimen which contained the lesser percentage of iron was more paramagnetic than the other. The best Cr specimen came from KAHLBAUM ($+2,87$); MERCK'S specimen ($+3,90$), on the

¹⁾ Everywhere expressed in millionths.

other hand, proved independent of \mathfrak{H} . The results obtained by various experimenters with Mn show that different specimens of this element behave quite differently. This series is throughout paramagnetic, the susceptibility increasing with the atomic weight.

Fifth Series. Two Ga specimens from the same flask gave different results. One of them proved independent of the field ($-0,12$); the other specimen, however, gave the higher numerical value ($-0,24$). Ge varied only slightly with \mathfrak{H} ($-0,12$). All the other elements of this series are in sufficient agreement with previous experimenters and it is throughout diamagnetic.

Sixth Series. Rb gave a small constant paramagnetic value ($+0,08$). The two Sr specimens tested varied considerably with \mathfrak{H} , and although paramagnetic within the field-range applied, gave ultimately diamagnetic values for χ_x . MERCK'S Zr ($-0,44$), although dependent upon \mathfrak{H} , agrees well with the value found by HONDA for the DE HAËN specimen ($-0,45$). Although POGGENDORFF found his Nb diamagnetic, his result is still questionable on account of the paramagnetic values found by HONDA ($+1,29$) and myself ($+1,65$) for specimens of quite different origins. Different results were obtained with four Mo preparations, all of different origins: the lowest, numerical value was given by MERCK'S specimen ($+0,56$). HONDA'S value for this element is much smaller ($+0,039$). Ru ($+0,43$) decreased rapidly with the field. Rh ($+1,06$) and Pd ($+5,2$) agree sufficiently with previous values.

Seventh Series. With the exception of ordinary tetragonal tin the elements of this series are diamagnetic. Several Ag specimens were investigated, that from HERAËUS giving a value ($-0,20$) identical with that of HONDA'S. I obtained a higher diamagnetic value for Cd than any previously found ($-0,18$). My In specimen, in contradiction to the former value, was throughout diamagnetic ($-0,11$). The results for tin and greytin must form the subject of a special paper. All my Sb preparations showed a magneto-crystalline action. On account of the fact that the values obtained differed by about 50 % with the same specimen, depending on the position of the axis of the crystal in the magnetic field, it is a matter of difficulty to fix upon the value of χ . The powdered material gave a value ($-0,82$) approximately half way between the two extreme values. Te and I agree well with previous values.

Eighth Series. Six elements of this series stood at my disposal. It is noteworthy that Cs ($-0,10$) is the only member of the alkali metals which is diamagnetic, Ba ($+0,93$), containing 15 % Hg, was non-homogeneous. La ($+1,04$) conjecturally contains admixtures of

other cerite earth metals. Two Ce specimens of different origins showed a satisfactory agreement (+ 15,4). Pr (+ 25,2) and Nd (+ 36,2), in spite of the high numerical value, exceeded only by that of oxygen, were independent of ϕ .

Ninth Series. Both the MERCK (+ 22,3) and the DE HAËN (+ 28,3) Er specimens were rich in iron, and varied rapidly with ϕ and are certainly to be considered only as very impure powdered mixtures of several elements.

Tenth Series. This series was completely represented and throughout paramagnetic. Ta (+ 0,81) and W (+ 0,22) gave smaller values than those previously found. Two Os specimens from the same flask gave identical values (+ 0,048). Two small pieces of Pt from the HERÆUS supply were tested, and both varied with ϕ . The calculated χ_{∞} in each case is smaller than the value of χ found by HONDA, who, in addition, found his specimen independent of the field.

Eleventh Series. This series again was completely represented and proved throughout diamagnetic. The calculated χ_{∞} for the HERÆUS Au (- 0,15) agrees well with HONDA's final value. This is not the case with the specimen from the same source of supply. A colloidal specimen gave a constant diamagnetic value (- 0,24). Although only a trace of iron was detected in Hg, this was sufficient to cause the specimen to vary slightly with ϕ . This is one of the cases in which magnetic testing for iron is superior to chemical analysis. The calculated χ_{∞} was - 0,18. The colloidal preparation gave a somewhat higher numerical constant value (- 0,23). Powdered electrolytic Bi gave a susceptibility of - 1,40. Two specimens from the same flask of the colloidal preparation were investigated: one gave a constant value (- 0,45), the other, although containing exactly the same percentage of iron impurity varied with the field ($\chi_{\infty} = - 0,51$).

Twelfth Series. Th (+ 0,081 and + 0,164) contained 15% thorium oxide: this is not of itself sufficient to explain the observed discrepancy in the two above results: in all probability this arises from the non-homogeneity of the iron-impurity. Three different specimens of U were tested: they were all very rich in iron. The smallest calculated value for χ_{∞} was + 2,60.

The curve $\chi = \text{funct.}(\iota)$ appears to be rather intricate. According to the above remarks, a more or less great uncertainty still exists with regard to many of the solid elements, which at present cannot be overcome. Mn is a good example of this. We can only advance conjectural hypotheses to explain such phenomena. The omissions in the curve are not so great as formerly: if anything, however, the

curve is more intricate than before, although a general relation to the periodic system is still observable. The influence of polymorphy is very pronounced, and the choice of the allotropic modification to be considered offers some difficulties. The general shape of the curve has been described in the previous communication. Beryllium has added a new negative peak to the curve, which divides itself into three analogous parts. Magnetic analogies of secondary importance also exist: elements which belong to the same group and exhibit analogous chemical properties are, in many instances, situated on corresponding parts of the curve.

IV. *Susceptibility at low and high temperatures.*

At low temperatures only readings by increasing temperatures were possible. At high temperatures the path of the curve $\chi = \text{funct.}(\theta)$ was, with the apparent exception of gallium, the same for increasing and decreasing temperatures.

Second Series (Li, Be, B, C). The susceptibility of Be increased numerically with the temperature remaining constant above $+700^\circ$. One may conclude that this is partly due to the iron impurity present. Diamond, arc carbon, and the amorphous modification exhibited a constant diamagnetic value. The mean susceptibility of powdered Ceylon graphite decreased rapidly with the temperature, and particularly so between -170° and $+18^\circ$.

Third Series (Na, Mg, Al, Si, P, S). The susceptibility of Mg decreased somewhat rapidly from -170° upwards. This result, as HONDA has already shown, is due to iron-impurity. The diamagnetism of crystallised Si was only a little greater at -170° than at $+18^\circ$; χ was constant with amorphous Si.

Fourth Series (K, Ca, Ti, V, Cr, Mn). The paramagnetic susceptibility of Ti decreased appreciably between 170° and -80° . In contradiction to HONDA's results for the same element, my specimen of Mn remained constant between -170° and about $+300^\circ$, afterwards suffering a slight decrease; at about $+1015^\circ$ a rather large sudden increase of χ was noticed, which was reversible.

Fifth Series (Cu, Zn, Ga, Ge, As, Se, Br). On increasing the temperature from -170° , Ge showed a small numerical decrease; χ remained constant above $+200^\circ$, increasing suddenly at the melting-point ($+890^\circ$); above $+900^\circ$ χ numerically increased. At the melting-point of Ga ($+30^\circ$) a sudden numerical decrease of χ was observed. The molten element was very weakly diamagnetic, and its susceptibility afterwards increased very slowly with the temperature. On cooling, this weak diamagnetism was still observed until a temperature of

+16° was reached, at which point the element was still liquid; this very characteristic undercooling is known to be possible down to 0°. As and Se scarcely varied with the temperature. No sudden discontinuity in the value of χ was exhibited by Br at its melting-point (—7°).

Sixth Series. (Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd). The value for Y decreased rapidly as the temperature increased: this substance, however, in all probability, contains admixtures with the other highly paramagnetic ytter-earth metals. From —170° to +18°, χ for Zr showed a slight numerical increase. The influence of temperature on paramagnetic Nb was very small. With Mo, χ decreased very slightly as the temperature rose. A decrease was also noticed in the case of Ru. Rh exhibited a practically linear increase of χ with the temperature: χ for Pd suffered a somewhat large decrease from —170° upwards.

Seventh Series. (Ag, Cd, In, Sn, Sb, Te, I). The diamagnetic susceptibility of Ag between —170° and +18° increased slightly numerically, while that of In and Te numerically considerably decreased. I exhibited a numerical increase in the value of χ .

Eighth Series. (Cs, Ba, La, Ce, Pr, Nd). Almost all these elements were investigated at low and high temperatures. Cs showed no deviation from the linear character of the (χ, θ) curve at its melting-point: the same remark applies to all the alkali metals. The value for Ba increased between —170° and +18°.

Only a small decrease was noticed in the case of La on raising the temperature from —100°; the decrease was somewhat larger between —170° and —100°. Ce (MERCK) showed a decrease of susceptibility as the temperature increased: but another specimen exhibited a sudden large increase at about —110°, which is rather difficult to explain. In the case of the latter specimen, χ remained constant between —170° and —140°. Above —80° the value was only slightly greater than that of the MERCK specimen, and the courses of the two curves are nearly similar. Pr and Nd decreased as the temperature rose.

Ninth Series (Er). A decrease of χ with increasing temperature was also observed in the case of this element.

It was found that the four highly paramagnetic elements Ce, Pr, Nd, Er only very approximately obeyed CURIE'S law for paramagnetic bodies.

Tenth Series. (Ta, W, Os, Ir, Pt). The susceptibility of Ta decreased slightly as the temperature increased. χ in the case of Ir increased with θ . The reverse is true in the case of Pt.

Eleventh Series (Au, Hg, Tl, Pb, Bi). χ for Hg between -170° and -150° was approximately constant, and afterwards underwent a gradual numerical increase: at the melting point (-39°) it suffered a sudden change. The susceptibility of Tl numerically decreased between -170° and $+18^\circ$. The same was true for Pb, the change in this case being very slight. For Bi, $\chi = -1,58$ at -175° , a value which agrees well with that found by FLEMING and DEWAR ($-1,61$ at -182°)¹). With regard to some colloidal specimens of this series, χ for Hg was throughout constant: that of Au was constant between -170° and $+50^\circ$, afterwards decreasing slightly numerically. The character of the (χ, θ) curve for colloidal Bi was very peculiar.

Twelfth Series. (Th, U). The susceptibility of Th increased with the temperature. The value for U on the other hand decreased.

On the whole, we may say that the curves $\chi = \text{funct.}(\theta)$ show most varied aspects. Roughly, the elements are more or less distributed over the six possible classes, viz. para- or diamagnetic, each constant, increasing or decreasing as the temperature rises. Only seven diamagnetic elements do not vary within the whole temperature range, amongst them the three that CURIE happened to investigate. The thermomagnetic properties also show a certain correlation with the periodic system.

Physics. — *“Investigations concerning the miscibility of liquids.”*

By Prof. J. P. KUENEN.

Several years ago I began a systematic experimental investigation of the miscibility of liquids, in particular as regards the influence of temperature and pressure, or to express it differently an investigation into the shape and the change of shape of the projected liquid plait of the ψ surface and its position relatively to the vapour-liquid plait²).

A fertile combination and one which turned out interesting in many respects was found in the saturated hydrocarbons with the lower alcohols. The investigation of these and other mixtures which was discontinued from various causes was recently taken up again and I

¹) J. A. FLEMING and J. DEWAR, Proc. Roy. Soc., **63**, p. 311, 1898.

²) I take this opportunity to say that in my communication of October 28 on the geometrical properties of these plaits I did not wish to imply anything but what I thought I had distinctly expressed and that the implications which are attributed to me by Prof. VAN DER WAALS in his paper of November 25 are entirely outside my meaning.

propose to communicate the results to the Society from time to time.

A decided gap in the research was the absence in the series of hydrocarbons of a term with four carbon atoms and in one of my last papers on the subject ¹⁾ I stated, that the preparation of normal butane had been tried and that it had not met with the desired success. The method was by electrolysis of sodium propionate, which yields a very impure gas, the chief products being carbon dioxide and ethylene. The treatment with bromine for the absorption of ethylene showed that bromine acts on butane and a repeated attempt to procure pure butane by this method did not succeed.

Better methods were not then available. In the mean time two new methods of preparing hydrocarbons from bromides or iodides have been published: one by the action of sodium dissolved in liquid ammonia (LEBEAU) and the other (GRIGNARD) with magnesium. Butane has been prepared by the first method by LEBEAU himself ²⁾ and by the second method by OÜÉDIXOFF ³⁾.

The results obtained by them do not agree accurately. I have applied both methods and again obtained results which do not quite agree either with each other or with those of the other investigators. I subjoin a table of the critical constants and boiling points.

Normal Butane.

Observer	Method of preparation	Crit. Temp.	Crit. press.	Boiling point
Lebeau	Lebeau	151–152		0.5
Ouédinoff	Grignard	146.5		0.6
Kuenen	Electrolysis	158.5		
"	"	145.5		— 1.7
(a) "	Lebeau	148.7	± 39	
(b) "	Grignard	150.8	37.5	— 0.1

The experiments communicated below were made with the two samples of butane indicated as (a) and (b) ⁴⁾.

In the mean time some observations have been made by TIMMERMANS

¹⁾ J. P. KUENEN. Phil. Mag. (6) 6 p. 647. 1903.

²⁾ P. LEBEAU. Bull. Ac. R. de Belg. 1908 p. 300–304.

³⁾ OÜÉDIXOFF. Bull. Soc. Chim. de Belg. (23) Juin 1909.

⁴⁾ Later on I hope to communicate a set of physical constants of butane obtained with sample (b), mainly determined by S. H. VISSER, science student at Leiden.

and KOHNSTAMM¹⁾ on mixtures of butane with a few other substances, butane having been given to them by ΟΥΕΔΙΝΟΦ.

I begin by communicating a few critical endpoints²⁾ which I have determined.

Critical endpoints.

methylalcohol	+	isopentane	10.5
,,	+	<i>n.</i> pentane	19.4 ³⁾
,,	+	<i>n.</i> butane (<i>b</i>)	17.0 (<i>T.</i> and <i>K.</i> 16.6 ⁴⁾)
aethylalcohol	+	isopentane	—30
,,	+	<i>n.</i> butane (<i>a</i>)	+ 37.5.

The critical end-point for methylalcohol and normal butane agrees well with the result of the other observers.

Very unexpectedly an entirely different result was obtained when use was made of butane (*a*), although in its constants but little differing from butane (*b*). This difference must be due to some impurity and although I cannot throw any light on the nature or action of this impurity, I will describe the observations, as they have brought to light a new phenomenon, which appears to be of interest.

When a mixture of butane (*a*) and methylalcohol was heated in a compression tube (Cailletet) in the presence of the vapour, the surface between the liquid layers disappeared about 22°, a somewhat higher temperature than for a mixture of butane (*b*) (17°.0). When however the temperature was further raised the meniscus soon reappeared and the definite critical end-point was not reached till 38°. Beyond 38° no separation of two liquids took place. The application of pressure revealed a similar abnormality: at temperatures above 22° a gradual increase of the pressure always had the effect of making the meniscus grow faint and disappear and afterwards permanently reappear.

It is not difficult to see what shape has to be attributed to the liquid plait in the *v-v* diagram in order to represent the above phenomena. The fact that pressure ultimately produces separation

¹⁾ J. TIMMERMANS and PH. KOHNSTAMM. Proc. XII 1909—10, p. 234 table on page 239.

²⁾ By critical end-point is meant the critical point of the liquid layers in the presence of vapour, i.e. the point where the liquid plait touches the vapour-liquid plait. In former papers I have usually called this point the critical mixing-point.

³⁾ Determined by me on a previous occasion (l. c. p. 647) and erroneously attributed by TIMMERMANS and KOHNSTAMM (l. c.) to isopentane instead of normal pentane.

⁴⁾ l. c. p. 239.

of the two liquids shows that the plait is open towards the x -axis. This is in accordance with the result obtained by TIMMERMANS¹⁾, that the critical temperature of the liquids is in this case raised by pressure, which means that beyond the critical end-point the liquid plait lies outside the vapour-liquid plait with its plaitpoint turned towards the latter. But the abnormal phenomenon was not noticed by him, nor have I been able to reproduce it with mixtures of butane (*b*).

If the liquid surface temporarily disappears as described, the plait would have to consist of two parts as shown in fig. 1 where the



Fig 1.

relative position with respect to the liquid branch of the vapour-liquid plait is also indicated. It seems unnecessary to show in detail, that the behaviour of the mixture under changes of pressure or temperature agrees with the assumed diagram. In itself a diagram of this nature is by no means improbable. In this connection it is important to consider the behaviour of a mixture of methylalcohol with isobutane as observed by TIMMERMANS. The critical end-point is in that case very near a point where the liquid plait divides and it would be quite possible for the plait in the case of the nearly allied normal butane to be divided in the manner assumed in fig. 1.

Further investigation of the phenomenon showed however that the assumption was incorrect. It may be remarked that the observations were extremely difficult owing to the great indistinctness of the liquid surface compared to other mixtures (TIMMERMANS notes the same peculiarity for mixtures of methylalcohol and isobutane). When I repeated the observation under the most favourable conditions with regard to illumination I found that the meniscus did not really

¹⁾ J. TIMMERMANS. Thèse Bruxelles 1911, p. 82.

disappear when it seemed to do so temporarily before, but as a rule remained just visible in the form of a dark and sometimes slightly coloured horizontal line near the axis of the tube.

The moment of minimum distinctness could be observed with fair accuracy; in the table are given the observed pressures as also some three-phase pressures. The readings were not more accurate than to about $\frac{1}{2}$ atmosphere.

Temp.	Least distinctness at	Three phase pressure :
14.0	— atm.	$1\frac{1}{2}$ atm.
22.5	2	2
22.8	$3\frac{1}{2}$	—
24.2	$9\frac{1}{2}$	$2\frac{1}{4}$
25.0	$13\frac{1}{2}$	—
25.5	16	—
26.3	$21\frac{1}{2}$	$2\frac{1}{2}$
27.2	$25\frac{1}{2}$	—
28.5	33	—
29.3	$36\frac{1}{2}$	—
31.0	43	—
32.4	$53\frac{1}{2}$	3
33.7	$62\frac{1}{2}$	$3\frac{1}{2}$
36.8	75	—
37.0	78	—
38.1	—	$4\frac{1}{4}$
38.2	—	Cr. end-point
38.6	84	—

The plait cannot therefore be divided as in fig. 1 and our supposition has to be modified in the sense that the plait is only strongly contracted as in fig. 2.

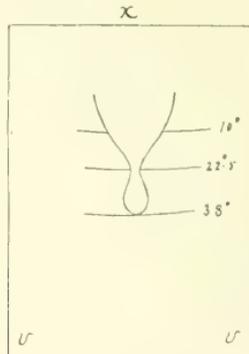


Fig. 2.

But the facts speak against this supposition too; for with fig. 2

one would expect phenomena which also occur near a critical point e.g. a distinct change in the relative volumes of the two phases (at 38° this phenomenon was very marked) and a slow settling down of the liquids after having been stirred up. This was not what happened at the points of indistinctness: in so far as the meniscus was visible at all, it reappeared (after stirring) comparatively quickly as if there was a difference in density between the liquids of the same order as at other points of the plait.

The only explanation which remains is that the refractive indices of the liquids become equal: the plait need not have any abnormal shape, but at some distance from the plaitpoint there is a point where the two coexisting liquids have the same index, which point, if outside the vapour liquid plait i.e. above 22° , may be reached by change of pressure. Though this phenomenon cannot but be very rare, it is not by any means impossible even with two pure substances. When the indices of the components differ little, there is a chance that the phenomenon may occur: there will be a maximum or minimum in the indices in that case for one particular proportion. Probably the index of butane is not much higher than that of methylalcohol (this question is being investigated): the indistinctness of the surface between the liquids even at a distance from the critical region makes this probable.

The question remains what impurity may have occasioned the difference in the behaviour of the two samples of butane in this respect ¹⁾. I am inclined to think, that butane (*b*) was purer than butane (*a*), especially as the experiments were made with the last remaining fraction of the butane (*a*) available, in which an admixture of higher boiling point may have been concentrated and during the operation of introducing the substances into the compression tube some moisture may also have got into the tube. However that may be it is very remarkable that an impurity which cannot have been large, as appears from the constants of the substance, can have had such a strong effect on the mixing phenomena, shifted the critical end-point from 17° to 38° and moreover produced the abnormality in the refractive index.

Finally it may be remarked, that the probable conclusion with respect to the impurity of the butane (*a*), raises some doubt as to the accuracy of the critical end-point for mixtures of ethylalcohol and butane. I hope shortly to be able to throw more light on the questions raised by these observations.

¹⁾ If the mixture contains a third substance it is properly speaking no longer possible to represent the phenomena with the aid of a *p-t* diagram, unless the admixture is so slight that it may be disregarded for the purpose of the graphical representation.

Physics. — “*Note on the insulating power of liquid air for high potentials and on the KERR electro-optic effect of liquid air.*” By PROF. ZEEMAN.

1. In a series of experiments undertaken in order to look for an influence of an electric field on radiation frequency, an account of which I intend to publish rather soon, a small condenser consisting of metal plates immersed in liquid air was made use of. A selectively absorbing crystal the optical behaviour of which was to be studied, when under electric influence, was introduced between the plates of the condenser. A first question to be answered relates to the value of the electric forces which can be sustained by liquid air. The fact that the dielectric constants of various liquid gases could be measured by LINDE¹⁾, DEWAR and FLEMING²⁾, and in the Leyden laboratory by HASENÖHRL³⁾, proves that the gases investigated, among which figure also oxygen and liquid air, are good insulators. The methods of measurement used only involve, however, low voltages. HASENÖHRL gives for the sparklength at the terminals of his secondary wire 0.05 m.m. The small condenser in FLEMING and DEWAR's experiments is charged with 100 volts. The excellent insulating power of liquid air under still much higher potentials, is illustrated in a separate experiment due to the last named physicists, but which only came under my notice while writing the present paper⁴⁾.

The high potentials in my experiments were obtained by means of a motor-driven influence machine. In order to keep the potentials as constant as possible, the arrangement given in the subjoined figure was used; it is the one often employed in analogous investigations. The condenser plates are connected to the inside and outside surfaces of a Leyden jar; between the machine and the jar a very high resis-

1) LINDE. Wiedeman Ann. 56. p. 546. 1895.

2) FLEMING and DEWAR. Proc. R. S. London. p. 358. Vol. 60, 1896.

3) HASENÖHRL. Leiden, Communications n°. 52. These Proc. II, p. 211.

4) “As a further instance of the very high insulating power of liquid air, we may mention that we charged the small condenser when immersed in liquid air with a Wimshurst electrical machine, and, after insulating the condenser and waiting a few moments, closed the terminals of the condenser by a wire. A small spark was seen at the contacts. We have constructed a little Leyden jar, the dielectric of which was liquid air, and the coatings the aluminium plates. This liquid Leyden jar held its charge perfectly.” l. c. p. 361.

It would have been possible in the light of this experiment to shorten somewhat our §§ 1—4.

tance is introduced. Two fine points or two bundles of fine needles shunt the machine. By varying the distance between the points or the needles the potential can be regulated to a given value.

2. The small condenser was placed inside an unsilvered DEWAR

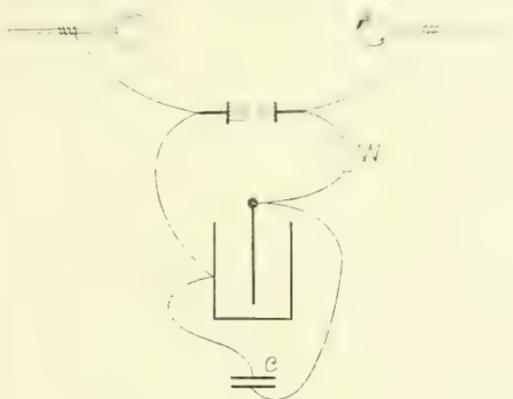


Fig. 1.

vacuum vessel of 5,5 cm. internal diameter. The plates were of 4,5 cm. length, 1 cm. width, their distance being 3 mm. They were soldered to copper wires, covered by glass over their entire length. The wires passed through the ebonite cover of the vacuum vessel, their distance being 2,5 cm. It was immediately clear that liquid air was a very perfect insulator. Loud, brilliant sparks could be taken by means of a discharging rod from the wires in the neighbourhood of the ebonite cover. The potential could be estimated by means of a spark micrometer. Potentials of 30.000 Volts were obtained; this gives, the distance of the condenser plates being $\frac{1}{2}$ cm., an electric force of 90.000 Volt/cm. This value, however, does not indicate the maximum electric intensity in liquid air, nor the one always obtainable.

3. After continuing the observations for a short time the intensity of the sparks in the micrometer rapidly diminished. Even after removing the micrometer none or only poor little sparks could be got from the wires entering the vacuum vessel. It seemed probable that the moisture of the atmosphere after condensing on the ebonite cover produced a conducting layer which prevented any considerable difference of potential between the wires. A small box of glass and ebonite was placed on the ebonite cover and the air of the box dried by means of some chloride of calcium. The result was extremely satisfactory. There was now no difficulty of maintaining very high potentials for hours.

4. Next to the external perturbations resulting from a deposit on the ebonite cover, two other causes of irregularities, originating in the liquid air may be mentioned. One is due to small crystals of ice and solid carbon dioxide present in the liquid air. These small crystals are attracted by the electrically charged plates, the liquid air becoming at the same time very transparent. A discharge between the plates is much favoured by the crystals. As soon as the plates are uncharged the crystals disperse into the liquid. If the air is freed from these crystals by filtration¹⁾, then there is still another cause of disturbance, viz. the generation of gas in the liquid air. The small bubbles take their origin from one or two points of the inner surface of the vessel, and the succeeding bubbles form a file moving irregularly through the liquid. As long as the small bubbles remain outside the space between the condenser plates they do not interfere with the voltage attainable between the plates. If, by some hydrodynamical accident, a gas bubble arrives between the plates their difference of potential immediately goes down, the discharge taking place under intense ebullition of the liquid.

The general conclusion to be drawn from these considerations is, that for attaining high potentials the liquid air must be carefully freed from impurities and that the visible generation of gas must be reduced as far as possible; the DEWAR vacuum vessel must be in excellent condition.

5. After being satisfied that it was possible to maintain high potentials for a considerable time, I tried to prove still more convincingly that large electric forces exist in the interior of the liquid air. For it were possible, though rather improbable, that a surface layer existed at the surface of the condenser plates so that there is a large potential gradient in the neighbourhood of the plates, but only a small one in the liquid air. If we succeed, however, to discover the KERR electro-optic effect in liquid air, we have proved at the same time the existence of large electric forces in the interior of the liquid.

6. It was to be expected that the electric double refraction of liquid air shall be small. Recently R. LEISER²⁾ succeeded in measuring the KERR electro-optic constant of several vapours and gases.

Notwithstanding his method was very sensitive he did not succeed in establishing an effect, even if the gases were under a pressure of 2 atmospheres, for nitrogen, oxygen, carbon monoxide and nitric oxide.

1) The liquid air, which I had the pleasure to receive many times from the Leyden cryogenic laboratory, was remarkably transparent.

2) R. LEISER. *Physikalische Zeitschr.* p. 955. XII. 1911.

The same vacuum vessel with immersed condenser referred to above (§§ 1—4) was also made use of for experiments concerning *electric double refraction of liquid air*. The optical arrangement is partially identical with the one recently described ¹⁾ and figured below.



Fig. 2.

The light of an arc lamp *B*, traverses the nicol N_1 , then the compensator, the vacuum vessel with condenser, the nicol N_2 and is finally analysed by means of a low dispersion spectroscope. An image of the black band exhibited by the compensator between crossed nicols is projected upon the slit of the spectroscope. In the former experiments referred to the spectroscope was absent.

The prismatic analysis had the following meaning. As is well-known the absorption spectrum of oxygen exhibits conspicuous bands. They are strongly developed by the 5.5 cm. of liquid air. As the vacuum vessel is not closed, and as the boiling-point of nitrogen is lower than that of oxygen, the former gas evaporates more quickly and the percentage of oxygen of the residual gas becomes gradually high. The wavelengths of the oxygen bands have been measured ²⁾ by OLSZEWSKI, LIVEING and DEWAR, and BACCEL. The most conspicuous bands, in the most luminous part of the spectrum, are at 581—573 and at 481—478. It seemed possible that the electric double refraction could have a considerable value in the neighbourhood of the absorption lines, being insensible in the other parts of the spectrum. In that case an effect would become apparent only by spectral analysis. In the cases of magnetic double refraction and of magnetic rotation of the plane of polarisation in sodium vapour the absorption lines indeed are lines of exception.

7. Before communicating the results of the investigation for double refraction, a difficulty in the observation must be mentioned. It is due to the strained condition of the imperfectly annealed walls of the vessel, causing irregular double refraction. As the four glass walls to be traversed by the light are all strained, it is not a matter

¹⁾ P. ZEEMAN and C. M. HOOGENBOOM. These Proceedings November 1911.

²⁾ KAYSER. Handbuch. Band III. S. 357.

of surprise that it is only after some trials that a part of the glass wall is found remaining dark between crossed nicols. But even then the dark band, which is so extremely sensitive to small traces of double refraction, may be invisible. It is rather easy to project on the slit the black band of an ordinary BABINET-compensator. These compensators however proved to be not sensitive enough. At last we found a small part of the walls of the vacuum vessel which was in a state of ease, and admitted an observation to be made with a bar only slightly loaded. Probably some compensating device might be used with advantage (see § 9).

In the field of view of the spectroscope now appears the continuous spectrum with the vertical absorption lines due to oxygen and with an approximately horizontal band, which must change its position by eventual double refraction.

8. With this optical arrangement it was observed that by the gradual charging of the Leyden jar the horizontal band was displaced downwards; at a discharge of the liquid air condenser the band jumped back in its original position.

The double refraction is clearly visible along the whole spectrum. In the neighbourhood of the absorption bands no singular behaviour of the refraction was observed. The changes in the neighbourhood of the absorption bands certainly were not very large in comparison with the whole amount of double refraction. It is interesting to compare this result with observations of ELIAS¹⁾ concerning *magnetic* double refraction in a concentrated solution of erbium nitrate. Also in that case only very small anomalies were observed in the neighbourhood of the absorption lines.

Probably the absence of any large anomaly is in both cases due to the want of steepness of the curve representing the index of absorption as a function of the frequency.

9. In order to fix the sense of the electric double refraction in liquid air and to attempt at a rough approximation of its order of magnitude the following experiment was made. After the removal of the vacuum vessel (see fig. 2.) a thin strip of glass was introduced in the beam of light.

By compressing the strip in a vertical direction the dark band in the spectroscope moves downwards. Comparison of this result with § 8 shows that the electro-optic effect of liquid air is positive, like carbon disulfide.

The magnitude of the displacement in the case of the experiment

1) ELIAS, Verhandl. deutsch. physik. Gesellschaft, S. 958, 1919.

with an electric field of 50,000 Volt/cm. is comparable with that caused by the application of 1000 gms. on a strip of 15 mm. width.

According to WERTHEIM (Mascart. *Traité d'Optique* T. 2, p. 232) a load of 7 to 15 kilograms, say 10 kilograms per millimetre of width produces a relative difference of phase of $\frac{1}{2}\lambda$, so that with the strip under consideration a load of 140 kilogrammes would be required.¹⁾ The estimated phase difference is therefore of the order of $\frac{1}{2}\lambda/140$, the electric force being 50,000 Volt/cm. From these data would follow a value for the KERR electro-optic constant of liquid air (oxygen) about 20 times smaller than that of carbon bisulfide.

Hence it need not astonish us that nobody has as yet succeeded in measuring the mentioned constant for oxygen under atmospheric pressure. Our numerical determination for liquid air has to be repeated with a better vacuum vessel. It must not be overlooked that the preceding observations (§§ 6-9), though satisfactory so far as they go, intend nothing more than establishing the existence of an effect and its order of magnitude; we see in its existence a very direct proof that liquid air is a substance, which represents extremely closely an ideal liquid insulator.

Physics. — “*Contribution to the theory of binary mixtures.*” XVII.

By Prof. J. D. VAN DER WAALS.

The concentration of the gas phase between that of two co-existing liquid phases.

In the preceding contributions I discussed some forms of the curve for the course of T, x -figures of the plaitpoints. Leaving the cases in which closed figures occur, or those in which these curves do not extend to $x=0$ and $x=1$, on one side, I have only to deal with the cases beginning in the point $x=0$ and $T=T_{k_1}$, and terminating at $x=1$ and $T=T_{k_2}$. As such a curve must have a gradual and continuous course, and as no double points and cusps can occur in it, the course is always comparatively simple. Thus in the case treated in Contribution XIII, and drawn already in 1905 (These Proc. VIII p. 184) only a highest and a lowest value occur in fig. 3. Some particularities are, however, not perfectly accurate in this figure. So both in the highest and in the lowest point $\frac{dT}{dx}$ must be

¹⁾ c.f. RAYLEIGH. *Phil. Mag.* (6) 4. p. 678 1902.

equal to 0, because these points are *heterogeneous* double plaitpoints, and in such points both $\frac{dT}{dx}$ and $\frac{dp}{dx}$ is zero. In fig. 40 of contribution XIII, however, this has already been paid attention to. Besides in the figures mentioned the course has been indicated for the T, x -curve of the coexisting phases. As there can be *three* coexisting phases for given T , this curve too must possess a maximum and a minimum value of T . At such a value of T the x -values of two of the three coexisting phases coincide, and they indicate the two temperatures between which three-phase pressure can exist. The three-phase pressure exists then between two temperatures, the higher of which is below T_{max} and the lower above T_{min} . This same simple form of the T, x -figure comprises a number of cases which differ from a physical point of view.

Thus T_{max} and T_{min} can both be higher than T_{k_1} . For this case the curve was drawn attention to for the first time in consequence of the observations of KUENEN on mixtures of ethane with higher alcohols. Then T_{k_2} is of course higher than T_{k_1} . But as second case T_{min} can be lower, even much lower than T_{k_1} ; then T_{k_2} need not be greater than T_{k_1} , and T_{k_2} can even lie far below T_{k_1} . Whether retaining the existence of three-phase pressure also the intermediate case (T_{k_1} equal to or almost equal to T_{k_2}) can occur, we have not yet succeeded in deciding. At first sight it seems unlikely, but not impossible. It should be borne in mind that for the possibility or non-possibility of the existence of this three-phase-pressure not only the value of T_{k_1} and T_{k_2} will be decisive, but also that of ρ_{k_1} and ρ_{k_2} , and, these latter values can differ greatly with equality of the critical temperatures if the size of the molecules differs much.

If we keep to the rule to place the components always in such a way that first a maximum, and afterwards a minimum value occurs, there are only two cases viz.: 1. $T_{k_2} > T_{k_1}$ and 2. $T_{k_2} < T_{k_1}$. Of course with reversal of the two components first a minimum, and then a maximum value for T would occur, but this would of course not be a new case.

But it is not my purpose just now to discuss the particularities which refer to this, any further. I will only point out that if we may assume, as has been tacitly supposed up to now, that for given T the saturation pressure of the substance with the greatest value of T_k is smaller than that pressure for the other component, we always find the value of x for the gas-phase in case of three-phase pressure outside the values for the two liquids, at least if no new circumstance is taken into consideration. And this circumstance con-

cerning the concentration of the vapour phase has led me to put the question: "What must be the shape of the T, x -line for the course of the plaitpoints that the concentration of the vapour phase be between that of the two coexisting liquid phases?"

For that this will frequently occur, is certain. And without examining for the moment whether retaining the discussed shape with a maximum and a minimum unchanged, this can be brought about through a deviation from the supposition about the value of the saturation pressures, which was stated above, I will show by a modification in the course of the T, x curve, which I had considered possible for a long time, that the case that the concentration of the gas-phase lies between that of the liquid phases, can be accounted for. At the conclusion of this communication it will however have appeared that strictly speaking the modification which will be applied, is not necessary.

To render plausible the modification which I want to apply to the course of the T, x -curve, and which I have already drawn (Fig. 43 of this Contributions), I consider the case that for a binary mixture for which three-phase pressure occurs, the value of the critical temperature for phases taken as homogeneous, would possess a minimum. If for such a mixture no three-phase pressure occurs, the phenomena are known.

The T, x -curve for the plaitpoints slopes down on both sides to a certain minimum value, which is not very far from the value of x at which the critical temperature of the mixture taken as homogeneous has the minimum value. Also the p, x -curve for the plaitpoints is known, and this has a still simpler shape, for it has neither minimum nor maximum value. If we assume the size of the molecules of the first component to be greater than that of the second, the p, x -line is ascending throughout, just as is the case with the p, x -line for the critical pressures for homogeneous phases. The latter is

namely proportional to $\frac{a}{b^2}$ or $\frac{1}{b} \frac{a}{b}$, and $\frac{dp}{dx} = \frac{1}{b} \frac{d\frac{a}{b}}{dx} - \frac{a}{b^2} \frac{db}{dx}$. If $\frac{a}{b}$

is minimum and $\frac{db}{dx}$ negative, then $\frac{dp}{dx}$ is positive even in the point where T is minimum.

The principal features of the spinodal curve are also known. It consists of a liquid branch and a vapour branch, which intersect at an acute angle at the minimum plaitpoint temperature, and move further apart on the left and on the right of that point of intersection.

I suppose that this point of intersection lies very near the first component, so at very small value of x . As b decreases with x , the point in which at the same value of x a value of p on the liquid branch and on the vapour branch of the binodal line are equal, lies on the righthand side of the point of intersection of the two branches. As we know the value of x , for which this equal value of p occurs, is variable with the temperature, and that in such a way that the distance between the two points mentioned increases with the temperature. At $T=0$ they would coincide. Also the course of the binodal lines is mainly known. These too consist of a liquid branch and a vapour branch, which intersect at $T_{min.}$ in the same point as the spinodal curves, and which have both points in which $\frac{dp}{dx} = 0$

for given T . At T above $T_{min.}$ the spinodal and binodal curves have got detached, and there is question of a lefthand and a righthand curve.

A first question which now presents itself, is this. To what is it owing that there was no question of three-phase pressure in the mixtures discussed up to now, for which $T_{min.}$ occurs? The reason will most likely be found in the circumstance that for these mixtures the critical temperatures of the components differ little, so that the ratio between these temperatures differs little from unity. But also in the circumstance that the size of the molecules of the components differs little, and that accordingly the ratio of the critical pressures of the components was not a high value either. What is most likely also in connection with this is the circumstance that the value of x for which $T_{c,l}$ has a minimum value, was not found very small. In *this* investigation we assume a high ratio between the T_k 's of the components, as for ether and water, which may be put at about 1,4. But most of all a high ratio between the size of the molecules e.g. as 5 to 1, and accordingly a very great value for the ratio of the p_k 's, which would rise to 1 to 7 for the values given, if we viz. disregard the fact that for the critical point the value of b is no longer equal to b_j . And now it is easy to show that the said ratios can be so great that at the given temperature three-phase pressure would occur to all probability. To show this we shall examine the course of the branch of the spinodal curve with small volume, assuming the course of the isobars on the side of the component with small size of the molecules to be known. We need not know this course further than just past the mixture with minimum T_k . To facilitate a survey I shall first suppose that the temperature chosen is exactly this minimum T_k . At this temperature the spinodal line has the double point. Moving from this point to the side of the

component with small value of b , it first cuts isobars with increasing value of p , till it touches a line of constant p in the double point of the isobars, so it reaches a maximum value for p ; hence it further moves to lower p . The decrease of the value of p takes place at an accelerated rate, and if this decrease of p continued to the side which is now supposed far distant, the spinodal curve would at last terminate at an isobar of very low value of p . For ether and water the saturation pressure at T'_k is for ether 35 and about 14 atms. These are pressures in which one is not only a very small fraction of the other. And now it is indeed true that the spinodal curve must not coincide with the volume of the saturation pressure at $x = 0$, but with that of the volume for which $\frac{dp}{dx} = 0$, and then p is smaller.

But at this temperature the influence of this is not great enough to deprive our reasoning quite of its validity. Besides the conclusion I want to draw, can also be derived by means of the binodal curve, and in this the values 35 and 14 would still be of use. From the equation:

$$v_{21} dp = (x_2 - x_1) \left(\frac{d^2 \zeta}{dx_1^2} \right)_{p,T} dx_1$$

if $x_2 - x_1$ had always to keep the same sign, a difference in pressure for water and the minimum pressure would have to be expected, many times smaller than agrees with the values 14 and 35. The difficulty is entirely removed if we assume that the spinodal curve does not proceed continuously in its course to the component with small value of b towards isobars of lower p , but that it will touch an isobar again, and then proceed again to isobars of higher value of p , after which it again touches an isobar, and finally descends to the value of the isobar at $x = 1$. All this may be considered as an attempt to derive the existence of 2 double plaitpoints, and so of three-phase pressure from the course of the isobars and the ratio of the values of b , and to demonstrate that for the existence of three-phase pressure we need not have recourse to the practically meaningless statement that the cause must be found in the abnormality of one of the components. More and more I tend to the opinion that calling a substance *abnormal* only means that some *numerical* data have a somewhat different value from what we should expect. But in the main features of the course of the phenomena no differences occur, nor in the behaviour with regard to other substances — unless there should be real chemical interaction.

The spinodal curve touches an isobar three times, the first time on the side of the great volumes. But the point of contact is no

plaitpoint then. As $\left(\frac{d^2\xi}{dx^2}\right)_{pT}$ is always equal to 0 when we follow the spinodal line, always

$$\left(\frac{d^2\xi}{dx^3}\right)_{pT} + \left(\frac{d^2v}{dx^2}\right)_{pT} \frac{dp}{dx} = 0.$$

In this point $\frac{dp}{dx}$ is $= 0$ for the spinodal curve, and so we have $\left(\frac{d^2\xi}{dx^3}\right)_{pT} = 0$, but not because two phases coincide in this point, but because the spinodal curve has a maximum value for the value of p . Also in the point of intersection of the spinodal curve $\left(\frac{d^2\xi}{dx^3}\right)_{pT} = 0$, because $\left(\frac{d^2v}{dx^2}\right)_{pT} = 0$. There $\frac{dp}{dx}$ is not equal to 0. So not only the plaitpoints are included in the common solution for $\left(\frac{d^2\xi}{dx^2}\right)_{pT} = 0$ and $\left(\frac{d^2\xi}{dx^3}\right)_{pT} = 0$ for given T . Nor does the spinodal curve always touch an isobar in a plaitpoint.

At the second contact the spinodal curve touches a line of equal p on the side of the small volumes. Then we have again a plaitpoint, but a hidden plaitpoint. Or rather a plaitpoint of the second kind. For we saw before (see among others These Proc. VIII p. 184) that both kinds of plaitpoints can be *hidden*. And at the third contact the contact of the spinodal curve with a line of equal p takes place on the side of the great volumes, and we have a plaitpoint of the first kind.

The liquid branch, of whose course we have examined here the particularities which might lead us to expect an intricate shape, has after all a pretty simple form. Starting from the double point $\left(\frac{d^2v}{dx^2}\right)_{spin}$ is positive, and at the end at $x=1$ this quantity must have the same sign. The question which we have had to solve, comes to the same thing as the question whether this quantity has retained the same sign over its whole breadth, or whether it has perhaps been negative between. If the latter is the case, and at this conclusion we have arrived, two points of inflection must occur in the spinodal curve. And when the figure of the p -lines for the case of the small value of b for the second component has been drawn well, we conclude naturally to the existence of these two points of inflection.

But then this is the only complication. The sign of $\left(\frac{dv}{dx}\right)_{spin}$ need not vary. We may, indeed, assert that it is always negative as would be the case when the two points of inflection did not exist.

If for the course of the T, v -curve of the plaitpoints, I refer to fig. 43, some details must be modified. This figure is, indeed, entirely schematic and has not been designed with a view to the special case that we will examine.

Thus in fig. 43 the branch of the plaitpoints of the second kind lies at very low temperatures very near the side of the first component, and the possibility is even to be foreseen that the order of the two first points of contact is reversed, and so that the plaitpoint of the second kind lies at smaller values of x than the first point of contact. I have made a close inquiry into the possibility or non-possibility of such a particularity, and this has taught me that this is not impossible, but on the other hand improbable; whereas the complication that occurs in the shape of the spinodal line, is very great. For the case under consideration it is certainly not necessary, and so it is better to have the descending branch of these plaitpoints run regularly to greater values of x . Also in fig. 43 the course of the three-phase curve has been drawn quite schematically without descending to particulars. There are, namely, different cases possible, in which fig. 43 might be of use. We might ascribe either smaller or greater values of b to the second component. We might make the three-phase pressure terminate on the branch AQ_2 or on the branch Q_2P_{cd} . In fig. 43 I have drawn a middle case, in which the three-phase pressure would just terminate at the minimum plaitpoint temperature, because then I had not yet carried out all the investigations about the meaning of these particular suppositions. But the special investigations about the points mentioned and other not mentioned points I have now quite or partly completed, because I wanted for myself to arrive at a conclusion about what would have to be assumed specially for the case ether-water — and it has become clear to me that we should have to assume for it: 1. possibly the existence of a minimum $T_{p,t}$ on the ether side. 2. the termination of the three-phase pressure on the branch Q_2P_{cd} , so on the again ascending branch of the plaitpoint curve, which runs to the point where it joins the branch of the plaitpoints of the 2nd kind. This ascending branch, however, must rise higher than in fig. 43. Compare the adjoined fig. 52.

I have arrived at this conclusion by drawing the pT -figure for the course of the plaitpoints.

This pT -curve is known for a binary mixture with minimum T_{pl} , if there exists no three-phase pressure. It runs vertically at the minimum temperature, and then turns to higher temperature with a branch with increasing value of p . The upper branch runs to the component with smaller value of p_k , the lower branch to the other component with decreasing value of p . As we suppose the minimum T_{pl} very near the side, the lower branch does not exist, or exists only for a very small part. As is known, on the upper branch is found the remarkable point for which the plaitpoint temperature is the same as the critical temperature of the mixture taken as homogeneous. In it two phases of equal concentration coincide to one.

In the cases examined before with minimum T_{pl} the upper branch soon terminated at a second component, and therefore three-phase pressure did not occur. But for ether and water this branch must be prolonged to much higher temperatures, and this branch must run to exceedingly great pressures. In what precedes I have demonstrated that this branch does not ascend so far beyond the said remarkable point that this would account at T_{k_2} for this very high p_{k_2} . At least this is the interpretation of the former reasoning for the course of the p, T -curve. So three-phase pressure may be expected, and this means for the p, T -curve that there must occur a cusp of the 1st kind past the above mentioned remarkable point on much further prolongation. But already before this cusp, which always lies in the covered region, the point occurs in which the three-phase pressure ends. That part of the ascending branch under discussion which lies between T_{min} and the point in which the three-phase pressure ends, can be observed. And now it happened that just when I had come to this conclusion, Dr. SCHEFFER showed me a drawing in which a part of the p, T -curve according to the observations on the side of ether was represented which had entirely the shape that has always been observed, when the course is normal. The publication of his observations would be very desirable. According to the said drawing it is not perfectly certain that the minimum plaitpoint temperature really occurs for ether and water; but as we shall see presently, this is a point, of minor importance. The observations with such a small quantity of water, or such an exceedingly small value of x are after all not to be carried out with perfect certainty, because it is not certain then whether this insignificant quantity of water really mixes homogeneously with the quantity of ether, or perhaps adheres to the glass wall. But he himself had also drawn

the curve in such a way that there was question of retrogression of the temperature. So this means that the point Q_2 of the fig. 43 (I do not speak here of the point of the three-phase pressure that by accident has been drawn coinciding with Q_2 in the figure) is really present. If this retrogression was not found, the curve would have to begin vertically, or it would immediately have to rise abruptly to higher temperatures. And whether the said remarkable point had already been observed by him also with absolute certainty, I shall leave for him to decide when he communicates his observations. But in the following consideration I shall assume it to be present. At any rate we may consider as perfectly certain the rapid

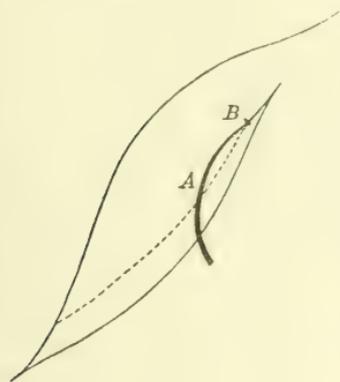


Fig. 48.

rise stretching over an appreciable range of temperature. And this must account for the circumstance that the three-phase pressure for ether and water at given temperature is greater than the saturation pressures of each of the components, and so for the circumstance that the gas phase, as far as its concentration is concerned, lies between that of the two coexisting liquid phases.

We then draw again (fig. 48) the pT -line with two cusps repeatedly drawn before, taking care that the

three-phase curve passes at T_{k_1} through a point that lies higher than p_{k_1} , and this can easily be done without straining the p, T -curve in consequence of the rapid rise in the beginning at T_{k_1} . If we then examine the special points of this line, I mention 1. the point where T has a minimum value, differing little from T_{k_1} , so the point where the tangent is vertical. 2. the remarkable point where $\frac{dp}{dT}$ is equal to $\left(\frac{dp}{dT}\right)_v$. 3. the point where the negative value of $\frac{d^2p}{dT^2}$ passes into a positive value. 4. the 1st cusp, where the retrogressive line has the same tangent, but $\frac{d^2p}{dT^2}$ suddenly changes from positive to negative. 5. probably two points of inflection on this retrogressive line. 6. the second cusp, where the retrogressive line changes again into a progressive one, and thus represents the course of the plaitpoints of the 1st kind. This second cusp need not exist

really, and at such low temperatures as we have to do with here it is of no practical importance, because the circumstances will be quite modified in consequence of the formation of solid states. About the last branch we observe that it must terminate at T_{k_2} , and at a pressure equal to p_{k_2} . This branch need not cut the first rapidly ascending branch, and if it does, there would have to be two points of intersection. If the first and the third branch intersect, there is a temperature at which there lie two plaits above the three-phase line, which lie at the same height. As will appear further the plait on the ether side will be present only for a short time, and it will not be able to reach a height which can be compared with the height of the plait on the side of the other component. If all these particularities have been represented well in the drawing, the course of the three-phase pressure can be traced between a point of the first branch and a point of the second branch. It must, moreover, cut the first branch in order to lie above p_{k_1} at T_{k_1} , and now it also lies above the vapour tension line of the first component at all temperatures below T_{k_1} , and a fortiori at all temperatures above the vapour tension line of the 2nd component.

It might be surmised that in some cases this line does not cut the first branch, and lies somewhat below p_{k_1} at $T = T_{k_1}$ or would lie at a level with p_{k_1} , and I myself did not consider this impossible at first. But in any case there must be intersection, either above or below T_{k_1} , but then with the vapour tension line of the first component. We shall see further on where this intersection is to be found. According to the results obtained in what follows the intersection must take place in the so-called *remarkable* point.

What is the meaning of this situation of the three-phase line below the first branch and of the necessary intersection either with the branch itself or with the vapour tension line? When at given T the three-phase line lies below the plaitpoint line, the p, x -figure has two tops or plaitpoints above the three-phase pressure, that which lies nearest to the first component has a plaitpoint pressure of which we are speaking, and the other top is the plaitpoint of the last branch of the p, T -line, which runs to the critical point of the second component. Then the p, x -curve has the shape drawn already several times before (see among others These Proc. VIII p. 184), which I might almost call the usual one when there is three-phase pressure. At the highest three-phase temperature the width of the first elevation above the three-phase pressure has become equal to 0, and the figure which exists then, is also known; it also being known what must then still happen in the hidden region above this temperature.

In the cases treated before the width of the first elevation above the three-phase pressure continually increases with decrease of temperature, and that of the second elevation continually decreases. This is changed in the case that we are treating now, and of which ether and water is an example.

It is true that the width of the first elevation begins at first to increase with decrease of temperature — but it reaches a maximum. Then it decreases again and becomes again equal to 0 at the temperature of the point of intersection of the three-phase line and plaitpoint line. I shall at least suppose here that the plaitpoint line itself is intersected. And at still further lowering of the temperature the plaitpoint lies on the other hand below the three-phase line. Then there is no longer an elevation above the three-phase line, but there is a plait which hangs at the lower side. The other plait which has remained above the three-phase line, has increased in width at the expense of the first, and extends over the full width, because there is now but one plait *above* the three-phase pressure. At still further lowering of T to T_{k_1} the plaitpoint of the plait hanging on the lower side has got on the side of the first component, and has become the critical point of this component. So the p, x -line for this temperature consists first of two lines ascending from the critical point of the first component, ascending because the three-phase pressure is larger than p_{k_1} . They cut the straight line which contains the three coexisting phases in two points which are not very far distant as yet, and of which the point that lies most to the left is a liquid phase, and the point lying most to the right a vapour phase. Besides these two lines there are also two starting from the righthand component beginning in the pressure of saturation, and they also cut the said straight line in two points. Of course of the two last-mentioned points the lefthand point must coincide with the righthand point of the first pair. We then have a vapour phase with a concentration between that of the two coexisting liquids. Above the straight line on which these three points lie we have then finally the curve for the equilibrium of the two liquids at pressures greater than the three-phase pressure with a highest point, which is then again a plaitpoint. At lower T the two ascending pairs of lines begin of course in the saturation points of the components. At temperatures which lie only little above T_{k_1} the elevation above the pressure of coexistence will only slowly ascend on the side of the component with greater value of b .

If we now direct our attention to the curve of the concentrations of the coexisting phases, fig. 43 may again be of use, of course with

the modifications necessary for the case ether-water¹⁾. First of all, but this I already observed before, the highest point must be chosen on the branch Q_2P_{cd} , and then the point where the conversion occurs in the concentration of the two lefthand phases must lie at much higher temperature, and even when the three-phase pressure at T_{k_1} lies above p_{k_1} , this point must lie above T_{k_1} . In the other case below T_{k_1} . What the shape is of the branch of the vapour concentrations at very low temperatures, is theoretically of importance, but not practically. I have not yet seriously taken the investigation of this point in hand.

If we imagine the pT_x -surface, and the course of the vapour phase plotted on it for coexistence with two liquid phases, it lies according to our results at the highest temperature on the upper sheet, but goes to the lower sheet on decrease of the temperature. So there must be a temperature for which it may be asserted that it lies both on the upper sheet and on the lower sheet. I mentioned the possibility of such a transition already long ago. But I always imagined it in such a way that this had to take place in a point where a section of the p, T_x -surface would have a vertical tangent at constant temperature. For in such a point a curve which first lies on the upper sheet, may go to the lower sheet. If I still held this view, this transition would certainly have to take place above T_{k_1} , and the possibility that this would happen below T_{k_1} was excluded. As the result of the investigation of the preceding pages I must now say that my opinion about the properties of the pT_x -surface in the point where the vapour-phase is transferred from the upper sheet to the lower sheet, has changed. If the section is drawn at the moment of transition, we arrive at the result that this section has not a vertical tangent in the point of transition, but that it has a horizontal tangent there. Or rather two horizontal tangents which have coincided — for there is a cusp. At any rate a configuration where two branches ending in one point, have one and the same tangent. And this follows immediately from our previous considerations. If yet on decrease of temperature this T is reached, in which the lefthand plait on the upper sheet disappears, there is a horizontal tangent and a point of inflection in that point of the upper sheet (see among others fig. 9 These Proc. VIII p. 184). And in the same way there is at least one horizontal tangent on the lower sheet, when with rise of the temperature this same T has been reached, and the plait that hangs down, disappears. But if the point of transition is a

¹⁾ In fig. 52 I have drawn the course of the curve of the concentrations anew, as it is according to these results.

cusps, the possibility that the transition takes place below T_{k_1} seems not to be entirely excluded; but this will be treated presently.

To make it easier for ourselves to form an idea of the p, T, x -surface above T_{k_1} , we imagine the p, x -lines at certain T of a mixture with maximum tension. Then there are two branches which run upwards from the first component and touch each other at a certain distance from the axis. If the line was here broken off, we might speak of a rhamphoid cusp. If the line is prolonged, the two lines descend to the other component, which in our case has the smaller value of b . It has appeared from what precedes that on the side of the first component the existence of three-phase pressure brings about hardly any change; on the other hand a very great change takes place if we draw near the side of the second component. If we think the three-phase pressure entirely confined to beyond the maximum value of p , then contact of vapour- and liquid line has continued to exist; but then the *liquid line* is specially subjected to a very great change and the vapour line is comparatively less changed. Instead of descending the liquid line has been forced to ascend rapidly before it slopes down again. Let us examine after these preliminary considerations what must be the case when we descend from the highest three-phase temperature to lower temperatures, but always remaining above T_{k_1} . The highest three-phase temperature is so high above T_{k_1} , that the entire first part of the p, x -line has disappeared including the point of contact of liquid and vapour line. On decrease of temperature the lefthand top gets slightly above the three-phase pressure, on further decrease it approaches again the three-phase tension and it finally coincides with it. Then the temperature has been reached of the transition of that plaitpoint to the lower sheet. The point in which this takes place, is the point in which two phases of equal concentration have coincided. The disappearance of the first part of the p, x -line is now more restricted, and only that part that must have been present before the contact of liquid and vapour, has disappeared. If this first part was made to disappear for a mixture without three-phase pressure, there would again be question of a rhamphoid cusp. But as in consequence of the three-phase pressure the remaining liquid line ascends steeply, it has become the cusp to which I concluded above. I do not discuss the hidden equilibria here, which would deserve a separate investigation. The point of transition in the order of the two first phases of the three-phase pressure lies 1. of course again on the branch of the plaitpoint curve Q_2T_{cd} of fig. 43; 2. at such a high temperature above T_{k_1} that the ascending part of the p, x -line has just disappeared

at that temperature; 3. closer to the side of the first component than the point in which the three-phase pressure first originated. So the liquid branch of the concentrations has had to change its course to the side of the second component to a rapid retrogression. So at the temperature of transition of the vapour phase from upper sheet to lower sheet, there is properly speaking no three-phase pressure, and the p, x -curve proceeds continuously upwards¹⁾ on the side of the second component, reaches a maximum in the plaitpoint of the remaining plait, runs downwards on the side of the first component, and continues to represent liquid concentrations to the cusp. Descending further from there with negative curvature, it again reaches the second component. We could only still speak in so far of three-phase pressure, if in the case of equilibrium of three phases as special case that is included in which two phases have the same concentration. That then the value of $\frac{dp}{dT}$ for the three-phase equilibrium is equal to $\frac{dp}{dT}$ for the equilibrium of the two phases which have the same concentration, is known. So all this takes place when the three-phase tension and the pT -line of the plaitpoints intersect. At lower T the three-phase tension lies above the line of the plaitpoints. According as the temperature falls and approaches T_k , a larger portion of the p, x -curve, which serves us for illustration of these phenomena, is left, though it is greatly modified by the existence of the three coexisting phases. Now the remaining part has extended to beyond the maximum tension, and so contains also a part of the branch which runs down again towards the first component. For so far as it can be realized the pT, x -surface has now the following shape: Under the line of the three phases there hangs a still closed plait on the side of the first component,

¹⁾ Continuously, just as this is always the case for a two-phase equilibrium above the critical temperature of the first component. Now too there is nowhere three-phase equilibrium throughout the course of the p, x -curve. Nor is this the case in the cusp, for the two phases rich in ether, which are otherwise present, and which differ then, have now united to one single phase. The discussed transition takes place in a plaitpoint. Neither is there anywhere an abrupt change in the character of the phases. That a cusp may be found on the other side is owing to the circumstance that in that point $\left(\frac{d^2\xi}{dx^2}\right)_{p,T}$ is equal to 0. I am, however, not perfectly convinced of the existence of this cusp — and the surest proof of this is certainly that I so often return to this subject. Repeatedly the thought has occurred to me, that after all the p, x -curve might be rounded in this point. I have only reluctantly assumed the existence of this point.

and from the point of intersection lying on the side of the second component another vapour branch goes further to the second component with abrupt change of direction as has already been described. And above the three phase line we have the liquid-liquid plait extended to the side of the first component. The plaitpoint of the hanging plait soon begins to approach rapidly to the side of the first component, and coincides at $T = T_{k_1}$ with the critical point. How the liquid and the vapour line of the hanging plait run then in the hidden equilibria, and whether they proceed there still in unmodified form, and reach the point in which vapour and liquid have the same concentration, cannot be ascertained without a close investigation of the hidden equilibria, but so far as my investigation of these equilibria is advanced at the moment this seems pretty certain.

But if we had only purposed to arrive at a result, we might have obtained this in an easier way. The point of transition for the two first phases is such a point that for points on the side of the component with the lower value of b the line of the pressures is curved in such a way that the top lies above, and that on the other hand it lies lower on the side of the component with greater value of b . If we now have such a temperature that the three-phase tension just passes through the highest point of the p, x -line, the tensions lie really below the three-phase line on the side of the component with the greater value of b . On the other hand the *vapour tension*, indeed, goes down on the other side, but on account of the modification caused by the existence of the two plaitpoints which has been indicated as the cause of the three-phase pressure, this *liquid pressure* runs upward. But though our description will be right in the main, there remain enough questions about further particulars, which render it very desirable that such T, x -lines above the critical temperature of ether should be investigated experimentally.

If this eusp is to occur in the order of the two first phases, the said remarkable point will have to occur on the ascending p, x -line on the ether-side, and that at lower value of T than the highest three-phase temperature. In this remarkable point under consideration the three-phase pressure line cuts the curve of the plaitpoints, and so if there is really minimum $T_{p,l}$ this point of intersection lies appreciably above $(T_{p,l})_{min}$. For this intersection to exist it is not absolutely indispensable that the minimum $T_{p,l}$ really exists. So the minimum Q_2 need not really exist in the T, x -line of the plaitpoints. For T_{k_1} we might also have a point a little past Q_2 , but always in such a way that the rapid rise of the p, T -line continues to exist.

We must, however, not make it rise to that point of the line Q_2P_{cd} where the transition of the two first phases takes place, or above it.

If it coincided with it, the coinciding concentration would be equal to zero — and then a perfectly pure substance could coexist with a mixture at T_{k_1} . In connection with this remark we conclude that the three-phase tension at T_{k_1} will always have to lie above p_{k_1} .

But though I may have to put off the treatment also of the hidden equilibria to a later occasion — yet I will not conclude without pointing out that there are more possibilities than the case I have treated here. For instance in the p, T -figure of the plaitpoints the two points which the line of the three-phase equilibrium has in common with the first branch of the plaitpoints, may coincide, or become one single point (fig. 49). In this case the two concentrations need not reverse their signs any more, because then the gasphase lies between the two others starting from the highest point. Then the highest three-phase pressure begins at a temperature which lies nearer the minimum value of T_{pl} . We might continue in this direction and make the end of the line of

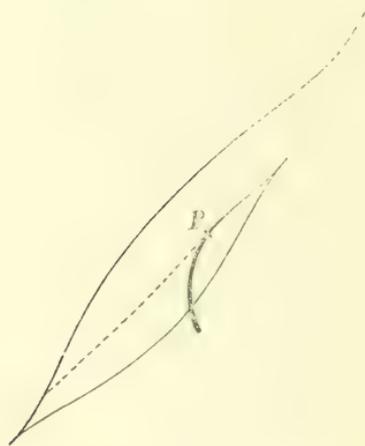


Fig. 49.

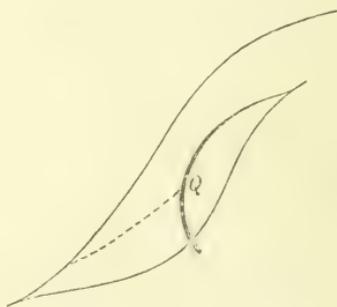


Fig. 50.

coexistence approach to that minimum value (Fig. 50) or if there is room for it through the choice of the substances even below that minimum. (Fig. 51). In this latter case the highest three-phase equilibrium in fig. 43 would have to be drawn on the branch AQ_2 . The elaboration of this latter case has been carried furthest, also as far as the hidden equilibria are concerned; but this requires so many figures that I have not yet decided to publish it. Moreover it is the question whether such mixtures

really occur. I made some reservation with regard to this possibility when treating figure 43, but now I must confess that I have met



Fig. 51.

with no contradictions. I did, however, meet with great complications. For the present it seems to me that in the above example a sufficient number of indications are to be found for the treatment of all these cases. The realisable first branch of the plaitpoint line can at once show which case occurs.

For the case that the minimum T_{pl} is found in the figure of the p, T -line, and we want to find the distance from the plaitpoint of the top hanging under the three-phase line to the three-phase line, there would seem to exist two distances at the same temperature. The greater distance then belongs of course to the plaitpoint which has got detached, and which at last retreats into the first axis at T_{k_1} .

Postscript. I have since examined the course of the line which represents the concentrations of the three coexisting phases also at lower temperatures, or would represent them if the solid state or states did not prevent their formation.

First of all the possibility exists that the point P_{ab} of fig. 43, does not exist at $T = 0$. Then there need not be a heterogeneous double plaitpoint at a certain low temperature. In this case the line of the concentrations, which begins at the highest three-phase pressure with the vapour phase first, and which possesses a point of intersection in the remarkable point of the plaitpoint line $Q_2 P_{cd}$ at the somewhat lower temperature, need not possess a point of intersection again at much lower temperature. Then the three points of this line will have approached a certain limiting position at $T = 0$, the first

liquid phase at $x=0$, the second liquid phase at $x=1$, and the vapour phase at a certain value corresponding to:

$$\lim_{1-x} \frac{x}{1-x} = \lim \frac{p_1}{p_2}$$

when p_1 and p_2 represent the saturation pressures of the two components. Water and mercury, e. g., may be in this position.

But also with retention of the heterogeneous double plaitpoint P_{ab} , which then would again have to be thought at higher value of x than would follow from fig. 43, as I said above, the course of the line mentioned can be accounted for. (See fig. 52). We must premise that the point Q_2 of fig. 52 will have to represent a coinciding of two liquid phases. If this is to be possible, there must exist a second point of intersection in the line of the concentrations at much lower

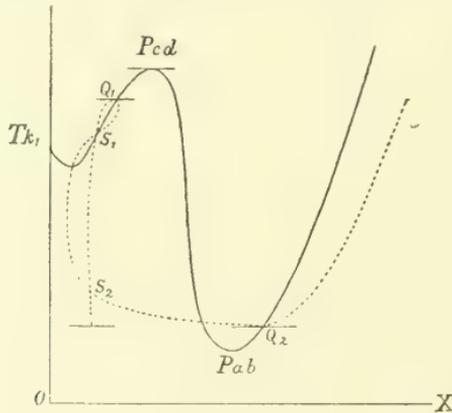


Fig. 52.

temperature. This second point of intersection does *not* lie on a plaitpoint line. And so there is no need to accept the retrogression of the branch of the plaitpoints of the 2nd kind to render the existence of this second point of intersection possible. So it is, indeed, advisable to let this branch keep its usual course.

How is the second point of intersection which lies so much lower, then to be accounted for? Let us again consider the p, x -line of a mixture with minimum T'_{pl} in our case on the other side. Then we have a maximum tension there. First two ascending lines, a liquid and vapour line, which touch each other somewhat higher. Then two descending lines with the vapour line in front. Let us then draw the three-phase line, which must then, of course, have been chosen lower than the maximum tension. The third phase of the three-phase equilibrium lies at much greater x , and is of no

importance for the explanation. If now the three-phase curve has a width such that also the two first-mentioned branches, so the ascending ones, belong to the three-phase equilibrium, the vapour phase lies between the two liquid phases. The intersected descending branches then lie in the hidden region, and the maximum pressure cannot be observed then. If on the other hand the width of the three-phase line is less, so that only the two descending branches are cut by the three-phase line, the vapour phase lies again outside the two coexisting liquids. The transition takes place when the three-phase line just passes through the highest point of the p,x -line. We have then again two phases of equal concentration of the three-phase equilibrium. If only the two descending branches are cut, the maximum of the p,x -line must, accordingly, be able to be realized.

So between the temperatures of the two points of intersection the maximum on the p,x -figure lies in the hidden region. And in the two points of intersection the maximum lies just on the boundary of this region. The value of x for such maxima of pressure approaching to the value of x of the mixture with minimum T_{pl} at fall of temperature, the two points of intersection in fig. 52, will have to lie at greater distance from the first axis than the minimum, but the lower point of intersection nearer the value of x for that point. Only at temperatures below that of the lower point of intersection this maximum is possibly observable; for at temperatures above that of the upper point of intersection the critical state prevents the appearance of the maximum. If my supposition is correct that for this mixture the point P_{ab} exists, a temperature at which ether may possess a minimum of solubility to water lies between the temperatures of the points of intersection; nevertheless the contrary remains possible. If the solid state does not prevent it, it must be possible to realize experimentally both the points of intersection of vapour branch and liquid branch, which have been discussed. The upper point lying above $(T_{pl})_{min}$ by the investigation of the then prevailing system of equilibrium, in our case water in which ether has been dissolved — and particularly by ascertaining the temperature, at which the existing three-phase equilibrium behaves as a two-phase system, or if one likes as a pseudo two-phase system. The lower point by the determination of the temperature at which the maximum pressure in the p,x -line will just present itself. Then, however, there is a real three-phase system, for then the two phases of equal concentration are different, viz. one is a vapour phase, the other a liquid phase.

Physics. — “*Researches on Magnetism. IV. On Paramagnetism at very low temperatures*”. By H. KAMERLINGH ONNES and ALB. PERRIER. Communication N^o. 124a from the Physical Laboratory at Leiden.

(Communicated in the meeting of November 25, 1911).

§ 1. *Solid Oxygen.* In a former Communication (May 1911) we mentioned our suspicion that the susceptibility of oxygen follows a law at liquid hydrogen temperatures quite different from CURIE'S law, which is obeyed at ordinary temperatures. A continuation of our attraction experiments has amply confirmed this suspicion. The susceptibility, indeed, remains practically unchanged as the temperature sinks from the boiling point to the freezing point of hydrogen, and we have even found clear indications that after becoming constant the susceptibility begins to decrease when the temperature is lowered still further.

In our experiments the oxygen was contained in a closed thick-walled glass tube, narrowed at the lower end. The gas enclosed in the tube was at a pressure of about 55 atmospheres at ordinary temperature. The tube was suspended in the apparatus and was kept in an equilibrium position in exactly the same way as the tubes containing powdered substances in our former experiments and, as with those tubes, it was completely surrounded by the vessel which held the bath of liquefied gas. In the present experiments the lower portion of the tube was slowly cooled by pouring liquid hydrogen drop by drop into the vacuum vessel which served to hold the bath of liquid gas. In this way the oxygen was caused to freeze to a solid piece practically cylindrical in shape, filling the lower part of the tube. To make measurements possible, this cylinder was placed in that part of the magnetic field where the attraction was a maximum. The correction to be applied on account of the influence of the glass, which was pretty considerable at very low temperatures, was obtained by control experiments with an evacuated tube. For the specific susceptibility we found the values, given in table I.

The corrections which are still to be applied to these values are insignificant (about 1%). In the Table, A and B refer to two different experiments (different freezings of the oxygen). The difference between the absolute values in Columns A and B can be explained by the fact that the practically cylindrical piece of solid oxygen (11 mm. long and 4 mm. thick) was not of exactly the same length in the two cases. But even so, what we are immediately concerned

with is not so much absolute values as the ratios between the values for the same cylinder at different temperatures.

T A B L E I.

Solid oxygen.

A		B	
T	$\chi \cdot 10^5$	T	$\chi \cdot 10^5$
20.3 K	54.3	20.3 K	52.3
18.5	55.8		
17.0	54.6		
15.5	54.7		
13.9	50.8	13.9	49.1

Our formula from Communication N°. 116 gives for oxygen liquid at -210° C. the much greater value

$$\chi_{63^\circ K} \cdot 10^5 = 288.$$

In the course of our present experiments we have actually been able by direct observation of the magnetic attraction during the melting of the oxygen cylinder to establish as a fact the existence of a considerable sudden change in the susceptibility of oxygen on melting and freezing. In Communication N°. 116 we concluded that such a sudden change must exist, but it now appears that the magnitude of this change is actually much greater (four times) than the value which we then estimated for it.

We cannot yet with certainty say how we are to explain the considerable difference between the values of the susceptibility of solid oxygen which we have now obtained by the attraction method and those which we got before by the method of the couple. We were just on the point of investigating this question more closely when we were obliged for particular reasons to postpone further experiments for a considerable time, so that we shall now content ourselves with giving the explanation which we consider the most probable. This tentative explanation is that solid oxygen possesses magneto-crystalline properties, which was not previously known and which we had no reason to suspect. If the magneto-crystalline anisotropy of oxygen on the track of which our experiments should bring us if our explanation is correct — is somewhat considerable the values of the susceptibility given by the method of the couple can depend to a considerable

extent upon the positions taken up by the crystals on solidification. In this way chance could play a considerable part in the results. We have already obtained an indication that this is the correct direction in which we must look for the proper explanation, for, on repeating our measurements by the method of the couple we obtained great differences in the values of the susceptibility according to the manner in which the freezing of the oxygen took place. While we were at first of the opinion that the manner in which we carried out the freezing for our measurements by the method of the couple was the most suitable for our purpose, and that for correct results we need only attend to the necessity of filling the ellipsoid completely with solid oxygen, we now think, in view of our later knowledge, that it had rather the disadvantage of enforcing a definite distribution of crystals along the walls of the ellipsoid and thus giving rise to a magneto-crystalline couple which was greater than the demagnetizing couple.

It is easily seen that the forces exerted in our recent experiments in a non-homogeneous field (always with small values of the susceptibility) depend to a much smaller extent upon the positions of the crystals than the couples exerted in our former experiments in a homogeneous field. And, on the other hand, both our observations during the process of melting and the correspondence between the values of the susceptibility given by the attraction method for three successive freezings lead us to the conclusion that, as regards the absolute values obtained, our later results should be taken in preference to the others.

The results obtained with the ellipsoid for the change of susceptibility between 20° K. and 14° K. do not conflict with those given by the attraction method if a suitable correction is applied for the glass of the ellipsoid. To get an idea of the influence of the glass we give values for its susceptibility and its specific susceptibility in the following table.

T A B L E II.

Glass.		
T	$\chi \cdot 10^6$	$\chi \cdot 10^3$
290°K	< 0	< 0
78	2.8	1.2
20.3	12.1	4.9
13.9	19.0	7.6

The absolute values are only rough approximations as the shape of the tube was very irregular, but as the correction for the glass was determined independently as a whole in the application of the attraction method to oxygen, uncertainty in the absolute values does not affect the correction in this case.

§ 2. *Anhydrous Ferrous Sulphate.* With ferrous sulphate practically anhydrous we found that the susceptibility at higher temperatures increased, and at lower temperatures decreased as the temperature was diminished. Much to our regret we were compelled for the same reasons as before to postpone for some time a continuation of these experiments. In particular we should have liked to have carried out experiments in a bath of liquid nitrogen to settle definitely at what temperature occurs the maximum susceptibility which is clearly indicated by our other results. This is evident from Table III in which we collect our data. The measurements at 143°·1 K and 170°·6 K were made in a bath of liquid ethylene.

T A B L E III.

Practically anhydrous ferrous sulphate.

T	$\chi \cdot 10^6$
293°K	65.0
170.6	102.6
143.1	117.5
20.3	251
18.0	240
15.9	231
13.9	221

Indeed, these results show without doubt that cases of maximum susceptibility can and do occur. We communicated this result to the Swiss Physical Congress in August, and at the same meeting DEBYE gave an explanation of this maximum which was based on the theory of finite elements of action. This supports the hypothesis communicated last May to which we had been led by our experimental results, that deviations from CURIE'S law are intimately related to the energetic properties of the PLANCK vibrators.

§ 3. *Conclusions.* If we supplement the reasoning developed in § 3 of Communication N°. 122a by the present results for oxygen and

anhydrous ferrous sulphate, we are led to the conclusion that for all paramagnetic substances there exists a region of higher temperatures within which deviations from CURIE'S law are but insignificant, while as the temperature sinks deviations slowly increase so much that a maximum is eventually reached, and then, with further lowering of the temperature, the susceptibility, instead of increasing begins to decrease, disappearing finally at the absolute zero of temperature. This generalisation renders probable the assumption that, with respect to paramagnetism, there exist corresponding (absolute) temperatures (temperatures at which deviations from CURIE'S law are the same) which, for every substance, must be considered proportional to a certain (absolute) temperature characteristic of the particular substance, the *temperature of the maximum specific susceptibility* of the substance. This temperature, then, would be very low for crystallized gadolinium sulphate, for oxygen it would lie not far below the boiling point of hydrogen, and for anhydrous ferrous sulphate it would lie well above the latter temperature. Were this generalisation confirmed for definite classes of substances, it would lead to a general law of which could be taken profit in the evaluation of the number of magnetons in the molecules of solid substances belonging to those classes.

Physics. "*Further Experiments with Liquid Helium. F. Isotherms of Monatomic Gases etc. IX. Thermal Properties of Helium*". By Prof. H. KAMERLINGH ONNES. Communication N°. 124^b from the Physical Laboratory at Leiden.

(Communicated in the meeting of November 25, 1911).

§ 1. *Vapour pressures of helium above the boiling point. Critical pressure and critical temperature for helium.* The helium-cryostat described in Comm. N°. 123 (Proc. June 1911) made it possible for me to undertake an experimental determination of the critical constants for helium. A determination of these constants was particularly desirable with a view to investigating the deviation of helium from the law of corresponding states. With that end in view I had endeavoured as far back as 1909 (see Comm. N°. 112, Proc. June 1909) to measure the critical pressure to at least a first approximation; I then obtained from expansion experiments the value $p_k = 2,75$ atm. while in 1908 I had estimated that p_k should not be much greater than 2,3 atm. and that T'_k should be 5° K.

From the experiments described in the present paper it will be clearly seen that these expansion experiments led to too large a value; but

it must be remembered that in communicating those results (Comm. N°. 112, 1909) it was definitely stated that the measurements made could only be regarded as a preliminary approximation. Those experiments were made under variable temperature, while it is very desirable for determinations of critical constants that one should have available a cryostat giving a range of constant temperatures in the neighbourhood of the critical temperature. Moreover, there was no stirrer inside the tube into which the helium was brought to its critical state. During the experiments the temperature within the experimental tube seems to have been so different at different levels, that the impression of the presence of a meniscus could have been obtained while the pressure was higher than that which we now find to be the critical. Besides, on expansion to 2,5 atm. this would have occasioned the appearance of a local mist such as is seen ordinarily in the critical state. It must be left for further experiment to clear up the exact circumstances obtaining during those expansion experiments, and to explain why they are apparently able to afford only an upper limit to the value of the critical pressure. Under the much more favourable circumstances of temperature constancy and effective stirring under which the present experiments were conducted, vapour pressures could be measured close up to the critical point, and joint with them the critical pressure could be obtained. For this constant, the value 2,26 atm. was obtained, which must, from the nature of the method adopted, be regarded as a lower limit. We must regard it as fortuitous that this value differs so slightly from the estimate of 1908.

In the present experiments the critical temperature was determined directly for the first time. I found $T_k = 5^\circ \text{K}$. In 1908 T_k was estimated as slightly in excess of 5°K . With regard to the value $T_k = 5.08 \text{K}$, which was deduced in Comm. N°. 119 (Proc. March 1911) from the vapour pressures below the boiling point, using the experimental value of p_k of 1909 (Comm. N°. 112), it was even then suspected that the value should prove too high, so that in § 5 of the same communication the value $T_k = 5.05 \text{K}$ was taken. (The reason for its excessive value is now seen to be that the value of p_k used for the deduction was too high).

The present experiments were carried out in the following manner. (See accompanying Plate fig. 1). In the helium glass S_7 of the helium cryostat described in Comm. N°. 123 (These Proc. XIV p. 204), parts of the apparatus are represented on the accompanying Plate by the letters which were used for the same parts in the diagram given with that Communication) is placed another glass reservoir of which the lower

part consists of a double walled vacuum glass a_1 , provided with an outlet spiral a_0 , the upper part a_2 is single-walled, and terminates in two narrow tubes, a_3 and a_4 . One of these tubes, a_4 , is, at its upper extremity, provided with a side tube which is closed by a tap. The ends of both a_3 and a_4 are cemented to the tubes θ_3 and b_4 (b_{40} , b_{41}), whose functions will presently be described, by means of which the reservoir a is completely closed from above. If liquid helium is present in the helium glass S_7 , by opening the valve a_3 it can be forced through a_0 into the inner chamber which is itself protected by the vacuum vessel a_1 . If the tap a_5 is now closed, ordinary communication of heat by conduction and radiation, supplemented, if necessary by development of JOULE heat in the small coil of constantin wire d , will drive the liquid back along a_0 leaving the inner chamber filled with helium vapour. The lower portion of this chamber thus becomes a cryostat chamber, protected by a transparent vacuum glass and immersed in liquid helium, an inner cryostat whose temperature can be brought to *a little above that of the surrounding liquid helium* in the outer cryostat. In this cryostat for temperatures just above the boiling point of helium is now placed the experimental reservoir b_1 , which is used for the determination of the critical constants of helium. This reservoir is concave underneath, b_2 ; it is also provided with two narrow tubes one of which b_{30} contains the thermometer capillary, being fused to it at b_{31} , while the other b_{40} admits the stirrer string, and at the same time allows helium to be admitted or removed through b_{42} or, if necessary, to be blown off through b_{43} .

The temperature is maintained constant and uniform by means of the stirrer b_5 which is operated by the string b_7 by means of an electromagnet acting upon the soft iron cylinder b_8 .

The temperature of the helium inside b was measured by a helium thermometer whose reservoir θ_1 was placed within the experimental reservoir b . In a note at the end of this section we shall return to this thermometer, which is, for the rest, the same in principle as that described in Communication N^o. 119 (see accompanying Plate fig. 3). The thermometer capillary goes by b_3 and then a_4 to the outside.

To fill the experimental reservoir b with liquid helium, pure compressed helium is admitted along b_{42} through the tap h (fig. 2), while the inner cryostat is kept full of liquid helium by drawing off through a_5 the vapour that is formed. Part of the tube which supplies pure helium to the reservoir b consists of a spiral immersed in liquid air, through which the gas must first pass. The necessary connection with the mercury vacuum pump can be obtained through

the tap f' (fig. 2). The pressure of the gas in the supply tube is read on the spring manometer g , and the pressure of the helium in the experimental reservoir is read on the open mercury manometer M . (Fig. 2).

At temperatures a little above the boiling point a constant temperature is obtained within the experimental reservoir by leaving the valve k a little open, so that a small amount of gas flows off uniformly through it. By the resulting vaporization the liquid in b is cooled, and the rate at which the gas escapes is so regulated that while stirring is kept up the temperature remains constant. The pressure difference due to the escape of the gas is neglected. On stirring, the liquid forms an emulsion as if of oily liquid drops. In the neighbourhood of the critical temperature this emulsion of liquid in vapour assumes the appearance of a milky cloud. During the measurements, the stirrer was repeatedly stopped for a moment so as to see at what level in the reservoir the meniscus of the non-emulsified liquid stood.

In this way determinations of vapour pressures were made with perfect regularity up to $5^{\circ}.15$ K., but from that point onwards it was found difficult to complete a temperature measurement in the short time elapsing before the liquid meniscus reached the bottom of the reservoir on account of the rapid escape of vapour. On that account the tap was then closed and the temperature was regulated by passing a current through the warming coil d and at the same time allowing gas to escape through a_6 , so that the experimental reservoir was cooled by the passing over its walls of the colder vapours arising from the helium vaporising within the inner cryostat. In this way measurements were made of vapour pressures to a point very close to the critical temperature. Just a little higher than the highest temperature thus attained, but higher by an amount which could not be measured, there was still a slight trace of milky cloud to be seen following the motion of the stirrer, while at a temperature just a little higher still, but with a temperature difference no more measurable than before, the experimental tube remained quite clear. The indications of the pressure were much more accurate than those of the temperature. I could tell accurately to within a centimetre the pressure of transition of the one state to the other within the reservoir. The temperature change corresponding to this small change of pressure is still a good deal smaller than that which has just been mentioned as too small for measurement. The pressure at which the transition was observed was taken to be the critical pressure. As we have already mentioned, the manner in which this value has been obtained makes us regard

it as a lower limit; but still, the actual value can only be very slightly greater. We may therefore assume $T'_k = 5^{\circ},25$ K, $p_k = 2,26$ atm. (see Table p. 683).

The thermometric measurements with the constant volume¹⁾ helium thermometer, for which, as well as for other assistance, I gladly acknowledge my indebtedness to Dr. C. DORSMAN, were made with a zero pressure of 300 mm. This is about double the zero pressure used in the determinations of Comm. N^o. 119. For other measurements the zero pressure was 667 mm. and for the measurements made in 1908 it was practically 15 atm.

From the agreement between the values of the boiling point of helium obtained under various conditions I think I may safely put the boiling point at $4^{\circ},26$ K, or better in round numbers $4^{\circ},25$ K, with an accuracy greater than $0^{\circ},1$. The same degree of accuracy can be ascribed to the value found for the critical temperature of helium.

The thermometry of these low temperatures, however, must still be made the subject of a special investigation. In particular, an investigation must be made of the correction which is to be applied on account of the influence which, as appears from KNUDSEN'S researches, the mean free path of the gas molecules in the upper part of the thermometer capillary can exert upon the value of the

1) Plate I, fig. 3 shows the helium thermometer modified for very low temperatures. The figure should be compared with fig. 1 of Pl. I Comm. N^o. 119; in the two figures identical parts are indicated by the same letters, while those parts which have undergone modification are indicated in the new figure by accented letters. To avoid development of vapours at cemented joints and to avoid metal capillaries at places where a constant high vacuum is necessary for control experiments, the steel blocks f' and $f'a$ with their reading points have been brought inside the glass tubes and fastened to the walls with a minimum of seating wax. To reduce the dead space, e' has been rounded off above. The connections of the adjusting tubes with the reservoir d'_5 and with the thermometer capillary as far as the tap K'_{0_0} are now made completely of glass d'_2, d'_3 with a ground joint at d'_1 . The connections at g'_0, la'_0, l'_3, la'_3 are also all ground joints (when these joints were being greased, care was taken that the grease did not come in contact with the mercury). K'_{0_0} has been introduced for the filling of the thermometer for which the ground joint K'_{0_2} is also used. l'_2 has been taken of such a size that in filling the thermometer the mercury from g'_1 can be brought over into l'_2 . An internal air-trap is introduced at d'_{51} . The copper thermometer capillary Th'_2 is joined to the capillary d'_{01} by the coupling piece d'_{02} and the capillary d'_{01} is in turn cemented on with the sleeve d'_{0_0} above the tap K'_{0_0} .

A correction of $-0,007$ has to be applied to the figures given in col. II of the Table in § 4 of Comm. No 119 on account of an error ascribed to development of vapour and not introduced into the calculation. The supposed development of vapour has since been ascertained to be due to a small leak.

pressure. It might, for instance, be, that the mean free path could no longer be neglected in comparison with the width of the capillary.

Expressing p in atmospheres, the following results were obtained :

TABLE I.

Vapour pressures of helium.

T	$760 p_{\text{coex}}$.
4.28 K	767
4.97	1329
5.10	1520
5.15	1569
5.22	1668
5.25 critical	1718 critical

§ 2. Values of certain thermal constants of helium.

In Comm. N^o. 119 a value for the constant f_w in the VAN DER WAALS vapour pressure formula (with common logarithms) was found which was strikingly low, viz. 1.2. This value was obtained from the slope at the boiling point of the tangent to the curve giving $\log p$ as a function of $\frac{1}{T}$, and from the value which was then assumed for the critical pressure, viz. 2.75 atm.

If we use the value of p_k now given, we find from the tangent to the curve at the boiling point the value $f_w = 1.3$ for common logarithms, so there is still a large deviation from the ordinary value of f_w . But the figures which we now give have brought to light the important property that *above the boiling point f_w increases very rapidly*. If the tangent is drawn at the critical point the common logarithm constant is found to be $f_{wk} = 1.95$ (round numbers from 1.94). This value of f_{wk} is still smaller than that for any other substance, but still, considering the gradual transformation of the equation of state as one goes from substances of high to substances of low critical temperature, it agrees pretty well with that for other substances (lowest 2,2).

v_k is thus the only one of the critical constants which has not yet been determined from direct observation; it can, however, be assumed in the meantime that it can with sufficient accuracy be deduced by the method adopted in Comm. No. 119 from the obser

ved densities of co-existing liquid and saturated vapour. This method gives $v_{kd} = 0.066$ and $v_{kl} = 0.00271$.

In contradiction to what I have before deduced, our new knowledge of f_{wk} and the improved data for p_k and T_k confirm, at least approximately, VAN DER WAALS' expectation that the relation he deduced between the critical constants should be found to hold for helium also.

The critical virial quotient $\frac{RT_k}{p_k v_k} = K_4$ thus becomes 3.13 (for argon it is 3.283, see Comm No. 120); hence using VAN DER WAALS' relation $K_4^2 = \frac{64}{27} K_c^2 - 1$ we get a value 5.13 for the critical vapour pressure coefficient $\left(\frac{T}{p} \frac{dp_{\text{coex.}}}{dT}\right)_k = K_c$: this leads to the common logarithm constant $f_{wk} = 2.2$, whereas 1.95 is the value actually found. The difference remaining is not great, and, in connection with it, it must be remembered that the value now found for p_k is a lower limit, and that the relation would hold better for a higher value of p_k . We may therefore conclude that the apparent association at the critical temperature is, in the case of helium, still subject to practically the same laws as hold for ordinary normal substances.

The great difference between helium and normal substances makes itself apparent at lower reduced temperatures, as shown by the marked diminution in the value of f_{wk} at lower reduced temperatures at which also the liquid density attains a maximum. This difference can well be the result of an influence of proximity to the absolute zero at very low temperatures quite different from that which obtains ordinarily for the same values of the reduced temperature, due to the fact that the liquid state lies much closer to the absolute zero with helium than with any other substance.

Chemistry. — “*On the chloration of benzoic acid, according to experiments of the late Mr. J. TH. BORNWATER.*” By Prof. A. F. HOLLEMAN.

(This communication will not be published in these Proceedings).

Chemistry. — “*On the magnetism of the benzolsubstitution and on the opposition of the formation of para-, ortho- against meta-substitution products.*” By Dr. T. VAN DER LINDEN. (Communicated by Prof. A. F. HOLLEMAN).

(This communication will not be published in these Proceedings).

Chemistry. — “*On some trinitroanisoles.*” By Dr. H. VERMEULEN. (Communicated by Prof. A. F. HOLLEMAN).

This communication will not be published in these Proceedings).

(January 24, 1912).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday January 27, 1912.

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Astronomy. — “*Investigations into the empirical terms in the mean longitude of the moon and into HANSEN’s constant term in the latitude.*” By Prof. E. F. VAN DE SANDE BAKHUYZEN.

(Communicated in the meeting of December 30, 1911).

It is generally known that the mathematical theory of the motion of the moon has been brought a great deal further these last years by HILL’s, RADAU’s and NEWCOMB’s and especially E. BROWN’s researches. But it is equally well known that the thus acquired accurate knowledge of — we may perhaps say — all appreciable inequalities due to gravitational forces has not yet been able to make theory and observation agree.

For the difference between the theoretical and the observed value of the secular acceleration a plausible explanation may be found in the tidal friction, although the numerical amount of this influence cannot be computed theoretically. The terms of long period in the mean longitude, shown by observation, however, offer absolutely unsolved problems.

The last mentioned deviations were first found by NEWCOMB in his *Investigation* (1876) and were subsequently thoroughly investigated in his *Researches* (1878). After a long time in between he has again taken the problem in hand in the last years of his life and has studied it more closely by means of all occultations observed up to the present time. He succeeded in completing his research before his death and gave a short account of the acquired results in *Monthly Notices* 69, while we may expect a detailed communication about them.

With the help of the observations of the moon made at Greenwich, P. H. COWELL had in the meantime accomplished an “*Analysis of the errors of the moon*” in a series of papers published in the *Monthly Notices* and BATTERMANN had obtained important results by discussing 3 great series of occultations (*Beob. Ergebn. Berlin* 5, 11 and 13). Finally I had also found occasion for a partial investigation into the errors of the tables of the moon (*Proc. Acad. Amst.* 6, 1903, p. 370 and 412) in the observations of lunar altitudes accomplished by Mr. SANDERS on the west coast of Africa.

Lately I returned to some points of this problem owing to occultations observed these last few years by Mr. SANDERS and to the solar eclipse of 1912, the particular circumstances of which will be dependent to a high degree on the errors of the tables of the moon. With a view to its instant importance for the prediction of this eclipse I shall here communicate the results of this — be it fragmentary — investigation.

I shall treat :

1st. the empirical terms of long period in the longitude of the moon.

2nd. the constant term in the latitude introduced by HANSEN and explained by him by the non-coïncidence of the centre of gravity and the centre of figure.

I. The empirical terms of long period in the mean longitude.

In my first paper of 1903 (*Proc. Acad. Amst.* 6, p. 370) I said that for the determination of the mean errors left in the longitude of HANSEN-NEWCOMB (i. e. according to HANSEN with NEWCOMB's *Corrections*) I had computed annual means of the errors in longitude or in R.A. according to the meridian observations of the period 1847—1902. I shall now say something more about the method for deducing these means. Besides the Greenwich observations I had also used the Washington ones according to NEWCOMB's *Investigation*, for 1862—1874; and for 1880—1892 the Oxford ones according to the mean values given by STONE in *Monthl. Not.* 44—54. As it afterwards seemed better to me, however, to confine myself to the Greenwich observations, I shall say a few words of these only.

As far as regards annual means we may consider those of the errors in longitude and those in R. A. as equal; so I have employed indiscriminately the former as well as the latter. In *Monthl. Not.* 50 we find an accurate comparison between the observations of the moon at Greenwich from 1847 up to 1861 and HANSEN's tables. From this STONE has computed annual means of $\Delta \lambda$ which he communicates in *Monthl. Not.* 51. He has also deduced annual means of the errors in λ for the years 1862—1882, the Greenwich observations of which had been directly compared HANSEN (*Monthl. Not.* 51—54). I have simply adopted these means, the only alteration being that I took into account the different fundamental systems in R.A. which have come into use at Greenwich in the course of years. I reduced all to the mean system of the 7 Year Catal., with which the 2nd 10 Y. Cat. agrees almost entirely. From these errors of HANSEN's longitudes those of HANSEN-NEWCOMB had now to be computed and I effected this by adding to the former the differences between Table XLI in the *Corrections* and the original Table XLI in the *Tables de la lune*.

For the years 1883—1894 I derived the mean errors of HANSEN-NEWCOMB from the Greenwich Annual Reports in the *Monthl. Not.*, assuming the means of the $\Delta \alpha$ to be the error of the mean longitude.

Finally, for the period 1895—1902 I used the results of my own investigation of the Greenwich observations. Here too attention was paid to the employed fundamental system. As an instance of the accuracy of these different means we may take that the greatest difference between my means and those derived by NEWCOMB in his *Investigation* from Greenwich and Washington together, amounts to 0".83. Further, the differences between the Greenwich annual means and the Oxford ones increase up to 1".18, while for the years 1895—1902 the greatest difference between my results from the Greenwich observations and those according to the *Reports* amounts to 0".36.

I had not communicated these annual means, as I had not succeeded in finding anything with certainty about the law followed by the deviations. I did remark, however, that the assumption of a term of a period of about 50 years with maxima about 1862 and 1887 and a coefficient of 3" would improve the agreement, but not yet sufficiently.

Not till 1909 did I find occasion to return to the problem and, after having added to my means those of 1904—1908 according to the *Reports to the board of visitors*, I found that the differences Observ.—HANSEN-NEWCOMB for the 62 years from 1847 upwards might be represented tolerably satisfactorily by a formula with 2 terms of a 48-years' and a 24-years' period, viz.

$$+ 1''.29 + 2''.36 \sin 7^\circ.5 (t-1848.0) + 1''.41 \sin 15^\circ (t-1852.8)$$

Of the 62 residuals there were 13 greater than 1".0 and 2 among these exceeded 1".5¹⁾. Especially because in these last years the results according to the observations and those according to the formula had a clearly different gradient, I fully realised that the value of this formula for extrapolation was still doubtful.

Meanwhile about the same time there appeared NEWCOMB's important provisory communication about his last researches. In this paper he gave a new derivation of the secular acceleration and deduced a new empirical "great fluctuation" which again clearly left unaccounted for "minor residuals". For the secular acceleration 7".96 was found, i.e. 0".46 less than the value of 1878 and the period of the great inequality remained practically unaltered: 275 years against the former 273 years, while the coefficient was diminished from 15".5 to 12".95.

The further discussion of the results from the meridian observations had to be preceded by a comparison with NEWCOMB's new

¹⁾ Here, however, the mistake had been made of not taking into consideration that since 1903 the Greenwich R. A. had been reduced to NEWCOMB's system, which is 0s.054 greater than that of the 2nd. 10 Y. C..

empirical theory, which I shall call NEWC. 1909 or NEWC. II. In the very short article in *Monthl. Not.* NEWCOMB, however, does not mention the accepted values for the mean motion and for the longitude of the epoch. I now assumed with BATTERMANN (*Beob. Ergeb. Berlin* 13, p. 44) that the former would be equal to the value of NEWC. 1878 (or NEWC. I) and that the correction $+ 1''.14 + 1''.4 = + 2''.54$ i.e. CORR. HANSEN $\cdot 1.4$ would have been added to the longitude for 1800.0. Therefore the difference between NEWC. II and NEWC. I consists in 1st the constant term, 2^{ndly} the term with the square of the time, 3^{rdly} the difference between the new "great fluctuation" and the old long-period-inequality.

I intended to take the means of the differences between the meridian observ. and NEWC. II and of the corresponding deviations deduced from the occultations (NEWCOMB'S Minor residuals) and then to try and represent these mean deviations by a periodic formula. In the meantime, however, there appeared in *Monthl. Not.* of last November an article by FRANK E. ROSS in which NEWCOMB'S minor residuals are first corrected for a more accurate value of the principal term of the perturbations by the ellipticity of the earth and are then very satisfactorily represented by two periodic terms. I therefore resolved also to compare my mean values with Ross' computation.

Now I first reduced the Greenwich R. A. to NEWCOMB'S system and here follow the corrections added for this purpose:

1847—48	Catal. 1842—45	+ 0.076
1849—55	12 Year Cat. 2 nd . Part	+ 0.076
1856—61	6 Year Cat. 1850.	+ 0.044
1862—69	7 Year Cat.	+ 0.054
1870—77	New 7 Year Cat.	+ 0.064
1878—87	Clock St. 9 Year Cat.	+ 0.049
1888—92	Clock St. 10 Year Cat.	+ 0.049
1893—98	5 Year Cat.	+ 0.054
1899—02	Clock St. 2 nd 10 Year Cat.	+ 0.054
1903—05	Clock St. 2 nd 10 Y. C.	+ 0.054 0.000
1906—10	Stand. R. A. 2 nd 9 Year Cat.	0.000

Leaving my former annual means up to 1902 for the rest unaltered, I tried to deduce more accurate values for the years 1903—09 from the *Greenwich-Observations* using exclusively the results obtained with the transit-circle. Keeping the results from Limb I and Limb II separated to the last, I computed annual means in three ways: 1st directly from all observations of each limb, 2^{ndly} by first forming monthly

means and taking the mean of these with equal weights, 3^{rdly} by taking the mean of the mean values for the different observers, which I could take from the *Greenw. Obs.* up to 1908, computing them myself for 1909. Besides, since 1905 also observations have been made of the crater Mösting A, from which I derived mean values in the first and second way. In the following table all these mean values have been collected; those from the observations of the limbs are the means for the two. Finally mean values have been computed, for the observations of the limbs from those after the three methods, and for the crater-observations from those after the 1st and 2nd. The differences have always been taken in the sense Obs.—Comp.

$\frac{1}{2}$ (Limb I + Limb II)					Mösting A		
1	2	3	Mean	1	2	Mean	
1903	$+0^s 174$	$+0^s 179$	$+0^s 204$	$+0^s 186$			
1904	.238	.246	.244	.243			
1905	.344	.340	.340	.341	$+0^s 339$	$+0^s 337$	$+0^s 338$
1906	.377	.375	.376	.376	.346	.324	.335
1907	.374	.386	.371	.377	.425	.417	.421
1908	.397	.401	.397	.398	.454	.448	.451
1909	.452	.426	.444	.441	.462	.463	.462

For the year 1910 the only result I employed was the one mentioned in that year's report derived from 98 observations of the limbs with the transit-circle, viz. $\Delta\alpha = +0^s.543$. Besides this there is also mentioned in the *Report* as results from 69 observations of the limbs and 36 of the crater with the Altazimuth $\Delta\alpha = +0^s.59$ and $+0^s.55$ respectively.

Now in the following table there are given first of all (col. 2) the mean values representing the differences between Mer. Obs. and Newc. I and from these have been derived (col. 3) the differences between Mer. Obs. and Newc. II. My computation of the great fluctuation according to NEWCOMB'S formula gave values, however, which were in the mean $-0''.18$ greater than those mentioned in the *Monthl. Not.* Whatever may be the cause of this small difference, it seemed advisable to me to keep to the formula and in accordance with this correct also the minor residuals with $+0''.2$ In Ross' formula it is exactly the constant term $-0''.18$ which has to dis-

	<i>M. NI</i>	<i>M. NII</i>	<i>Occ. M.</i>	<i>Ross</i>		<i>M. NI</i>	<i>M. NII</i>	<i>Occ. M.</i>	<i>Ross</i>
1847.5	+0'17	+0'06	+1'64	-0'14	1882.5	+0'81	-1'21	+0'01	+0'08
48.5	+1.38	+1.24	+0.86	+0.66	83.5	+0.26	-1.81	-0.19	-0.52
49.5	+2.09	+1.91	-1.61	+0.19	84.5	+0.45	-1.68	-0.22	-0.30
50.5	+2.16	+1.95	-0.75	+0.56	85.5	+0.36	-1.84	-0.46	-0.28
51.5	+3.32	+3.05	-2.05	+0.91	86.5	+0.28	-1.98	-0.62	-0.40
52.5	+3.18	+2.87	-1.77	+0.67	87.5	-0.16	-2.49	+0.09	-0.26
53.5	+4.01	+3.64	-2.74	+0.66	88.5	-0.63	-3.02	-0.28	-0.78
54.5	+4.40	+3.98	-2.38	+0.78	89.5	+0.57	-1.88	-1.42	0.00
55.5	+3.71	+3.23	-0.93	+0.35	90.5	+0.42	-2.08	-1.12	+0.04
56.5	+3.59	+3.06	-0.96	-0.24	91.5	-0.46	-3.03	+0.13	-0.28
57.5	+4.76	+4.18	-1.88	-0.08	92.5	-0.52	-3.16	+0.76	-0.20
58.5	+5.24	+4.63	-0.93	+0.55	93.5	+0.29	-2.40	-0.10	+0.04
59.5	+5.42	+4.75	-0.65	+0.41	94.5	+1.04	1.70	1.10	+0.14
60.5	+0.85	+6.13	-2.03	+0.90	95.5	+1.53	-1.28	0.72	+0.44
61.5	+6.50	+5.72	2.22	+0.30	96.5	+2.01	-0.86	-0.14	+0.76
62.5	+6.86	+6.04	1.94	+0.86	97.5	+2.75	-0.17	-1.63	+0.30
63.5	+5.98	+5.10	-1.90	-0.14	98.5	+2.85	0.12	1.18	+0.18
64.5	+4.60	+3.66	0.56	-0.24	1899.5	+2.33	-0.70	-0.50	-0.46
65.5	+3.82	+2.82	0.02	-0.40	1900.5	+2.68	-0.41	-0.61	-0.02
66.5	+3.33	+2.27	+0.73	-0.08	01.5	+2.59	-0.56	-0.66	-0.64
67.5	+2.38	+1.27	+0.93	0.73	02.5	+3.26	+0.06	+0.44	-0.54
68.5	-2.14	+0.98	+0.22	-0.32	03.5	+2.79	-0.46	+1.26	-1.04
69.5	+2.40	+1.17	+0.63	+0.67	04.5	+3.64	+0.33	+0.97	-0.70
70.5	+2.43	+1.15	-0.25	+0.81	05.5	-5.12	+1.76	-0.96	
71.5	+0.75	-0.58	-0.52	-0.56		5.07	1.71	-0.01	0.13
72.5	+0.86	-0.54	-1.06	-0.28	06.5	+5.64	+2.23	0.73	
73.5	-0.40	-1.06	0.54	-0.34		5.02	1.61	0.11	-0.37
74.5	0.16	-1.67	-0.33	-0.55	07.5	+5.66	+2.29	0.00	
75.5	0.24	-1.82	0.28	-0.68		6.32	2.86	-0.66	-0.03
76.5	+0.34	-1.31	0.59	0.32	08.5	+5.97	+2.46	-0.16	
77.5	+1.44	-0.27	-1.43	+0.30		6.76	3.25	0.95	+0.12
78.5	-2.75	0.96	-2.16	+1.16	09.5	+6.62	+3.06		
79.5	+1.89	+0.05	0.35	+1.16		6.93	3.37		+0.05
80.5	+1.82	0.08	-1.12	+0.54	1910.5	+8.14	+4.54		+1.18
1881.5	+2.04	+0.08	-1.48	-0.52					

appear and his "outstanding residuals" remain unaltered. For the years 1905—1909 a second line of the table contains the results according to the observations of Mösting A.

Further, column 4. contains the differences between the mean longitude according to the occultations and according to the mer. obs., which have been arrived at by subtracting col. 3 from the min. res. corrected with $+0''.2$. Finally in the last column I have taken down the comparison of Ross' formula with the mean results of occultations and mer. obs. The latter had first been corrected, however, for the mean of their differences with the former, since these may be regarded as more free from constant errors. Although these differences are distinctly fluctuating, the results of all observations of the limbs were corrected with $-0''.63$ ¹⁾, those of the crater observations with $-0''.43$. Equal weights were given to the results from both sources; for 1905—1908 I formed $\frac{1}{3}$ (occult. + obs. limb + obs. crater). For 1909—10 only the results from the merid. observations could be used, and I formed for 1909 $\frac{1}{2}$ (limb + crater).

From the comparison in the last column it appears, just as had been shown by Ross' comparisons themselves, that his formula corresponds fairly well with the observations; and we may say that the errors of the mean longitude are known pretty accurately up to 1909. If we mean, however, to obtain the most reliable value for this error for the epoch of the solar eclipse of 1912.3, we must pay special attention to the last difference for 1910.5 (which is altogether confirmed by the results of the altazimuth-observations) and on the course of the deviations in the last few years and we must take it as probable that also in 1912 there will exist a positive deviation of about $+1''$. Assuming this we find:

	Δ Ross.	Δ Newe. II.	Δ Newe. I.
1911.5	$+1''0$	$+3''9$	$+7''5$
12.5	$+1.0$	$+4.0$	$+7.7$

Although we must not forget that extrapolation by means of an empirical formula is always dangerous, and that also before 1850 the agreement with Ross' formula was less close, I think that we may assume as the most probable correction of the *mean* longitude for 1912.3, a value between $+7''.5$ and $+8''.0$.

2. HANSEN'S *constant term in the latitude of the moon.*

It is generally known that HANSEN believed he had rendered probable that the centre of gravity of the moon does not coincide

¹⁾ The correct mean deviation is $-0''.60$; the difference is immaterial.

with its centre of figure. He showed that two of the three relative co-ordinates, the one in the direction of the radius vector and the one perpendicular to the radius vector and on the ecliptic¹⁾, might be determined by the observations. The first he derived from the values for the great perturbations which he thought were found greater from observation than from theory. The second he derived from a constant difference between the declinations observed at Greenwich and those computed with the assumption that the centre of the moon in the mean describes a great circle.

Now as regards the first point, NEWCOMB has clearly shown in 1868²⁾ that HANSEN's grounds were fallacious and since that time it has been assumed — I believe without closer investigation — that there was no ground either for the assumption of a deviation in the direction of the latitude. HANSEN himself had already pointed out that the last named deviation might be explained by constant errors in the observed declinations, and this is at any rate a point of great importance for the question.

When I commenced my first investigations in 1903, I supposed the constant term in the latitude of $-1''.0$ to have been omitted in the ephemerides already for a long time. I was strengthened in that belief by finding only small amounts for the mean difference $\Delta\delta$ between observation and computation: as mean value for the 5 years 1895—1899 exactly $0''.00$ (*Proceedings Amsterdam* 6 p. 384).

Mr. COWELL's remarks, however, in his first paper on the analysis of the errors of the moon in *The Observatory* (September 1903) made plain to me my mistake. HANSEN's term appeared to be still taken into consideration in the computation of the ephemerides. Yet I could come to no other conclusion than that notwithstanding this the mean differences between observed and computed declinations were small (*Proceedings* 6 p. 413 footnote 3 and p. 421).

As, however, the error in latitude is of special importance for predicting the circumstances of the approaching eclipse, and as the problem of a possible asymmetry of the moon is also worth our attention by itself, I was desirous to elucidate this point if possible. I tried to do this by investigating the mean deviations in δ for the years 1895—1909 according to the Greenwich observations.

To this end there was wanted first the formation of the mean annual deviations $\Delta\delta$ (\equiv Obs. — Comp.), secondly an investigation into the systematic corrections still to be applied to these $\Delta\delta$.

The first work had already been accomplished for the years

¹⁾ *Monthl. Not.* 15 p. 13 et seq. *Memoirs R. Astr. Soc.* 24.

²⁾ *Proceedings of the American Association for the advancement of science* 1868.

1895—1902 (*Proceedings* 6 pp. 384 and 421) and it seems to be better to use the values a of p. 421, which, moreover, differ only slightly for the first 5 years from the $\frac{1}{2}(N+S)$ of p. 384. We must only pay attention to the fact that following NEWCOMB'S *Investigation*, those differences had been taken in the sense Comp.—Obs., so that we have to reverse all the signs.

For the years 1903—09 I formed annual means of the $\Delta\delta$ in the *Greenw. Obs.* ($\Delta N.P.D. C-O = \Delta\delta O-C$) after the same three methods 1, 2 and 3 which I had followed for the Δa (see above). Naturally instead of the observations of Limbs I and II we had now to take apart those of the North and South limbs. Besides, for the last 5 years I could also use the observations of Misting A for which I formed mean values in the same two ways 1 and 2 as I had done for the Δa . Finally I took again the means of the mean values 1, 2, and 3 for the limbs and 1 and 2 for the crater as these seemed to be for the present moment the most reliable results. These different results have been collected in the following table.

	$\frac{1}{2}$ (North Limb + South Limb)				Misting A		
	1	2	3	Mean	1	2	Mean
1903	— 0"26	— 0"16	— 0"26	— 0"23			
1904	— 0.11	— 0.26	— 0.21	— 0.19			
1905	— 0.36	— 0.28	— 0.49	— 0.38	— 0"15	— 0"24	— 0"20
1906	— 0.07	+ 0.28	— 0.28	— 0.21	— 0.05	+ 0.05	0.00
1907	— 0.53	— 0.28	— 0.51	— 0.44	— 0.79	— 0.66	— 0.72
1908	— 0.09	— 0.12	+ 0.25	+ 0.01	— 0.04	— 0.13	— 0.08
1909	— 0.19	— 0.05	— 0.24	— 0.16	— 0.23	— 0.18	— 0.20

We must now consider the systematic corrections which have to be applied to these results. They are of two kinds; 1st those which proceed from the declinationsystem used at Greenwich in the different years, 2ndly those which have special reference to the observations of the moon.

As regards the first mentioned corrections, I thought it best to reduce all $\Delta\delta$ to NEWCOMB'S fundamental system, which offers, at least for low declinations, the best guarantees for freedom from systematic errors. There appears in the introduction to the 2nd 9 Year

Cat. p. 31 a comparison of the declinations of this catalogue with NEWCOMB and taking the mean of the results in this table between 65° and 115° N. P. D. we obtain

$$\sigma_{\text{NEWC.}} - \sigma_{\text{2nd 9 Y. C.}} = + 0''.14.$$

So the only thing left to do is to reduce the results of the different years to the 2nd 9 Y. Cat., paying attention 1st to the employed flexure, 2ndly to the employed colatitude and refraction. The variations in the constant corrections of the zenithpoint are of little importance.

For the flexure used which was always deduced from the difference between direct and reflexion-observations, we can consult p. 18 of the introduction mentioned above. There it also says why it is believed at Greenwich that the *real* flexure has remained unaltered, while the cause of the discordance in the different years must lie in the reflexion-observations. As long as nothing has been proved to the contrary this has to be accepted as probable. So we must add corrections to the declinations of the moon, just as has been done to those of the stars in constructing the 2nd 9 Y. Cat., in order to reduce them to the flexure $+ 0''.60 \sin Z$. From 1906 upwards this value has been used directly for the formation of the annual results. We thus obtain (see for 1895 and 1896 the introductions to the *Obs.*; for 1897—1905 the introduction to the 2nd 9 Y. Cat.), assuming 0.75 as mean value of $\sin Z$ for the moon :

	Δ Flex.-coeff.	$\Delta \sigma$ Moon
1895	+ 0''.19	— 0''.14
1896	+ 0.23	— 0.17
1897	+ 0.50	— 0.38
1898	+ 0.50	— 0.38
1899	+ 0.38	— 0.28
1900	+ 0.28	— 0.21
1901	+ 0.16	— 0.12
1902	+ 0.34	— 0.26
1903	+ 0.34	— 0.26
1904	+ 0.25	— 0.19
1905	+ 0.29	— 0.22

As regards the colatitude and the refraction, up to 1905 $21''90$ and the refractions of the *Tab. Regiom.* have been invariably used, and these values have served also for the construction of the 2nd 9 Y. Cat. Then in 1906 the "Pulkowa-refractions" have begun to be employed and in connection with these the colatitude $21''80$ was adopted. In the intro-

duction to the 2nd 9 Y. Cat. p. 20, a comparison is given between the declinations according to the two systems. There we find as mean difference between N. P. D. 65° and 115° :

$$\sigma \text{ Cat} - \sigma \text{ New syst.} = - 0''.36.$$

Finally a correction has to be applied in particular to the declinations of the moon, which results from the fact that the parallax-values used at Greenwich are not the most accurate. We must distinguish between the correction of the general parallax-constant $d\rho_0$ and that of the local constant for Greenwich $d\rho_0'$. Their difference depends on the ellipticity of the earth and they are connected by the equation $d\rho_0' = d\rho_0 + \rho_0 \frac{d\rho}{\rho}$, in which ρ is the earth's radius for Greenwich. At Greenwich HANSEN'S ρ_0 has been employed and further the ellipticity 1 : 300.

So we must first see what correction is needed for HANSEN'S ρ_0 and for this we must also use the most probable value of the ellipticity. I adopted as its reciprocal value 297.5, the mean of the results of HELMERT and HAYFORD.

The value of ρ_0 is first of all determined by a comparison between the force of gravity on the moon and on the surface of the earth. We find as the most probable correction of HANSEN'S constant assuming ellipt. = 1 : 297.5, according to BATTERMANN 13 p. 12, $d\rho_0 = + 0''.38$, according to *Monthl. Not.* 71 p. 539, $d\rho_0 = + 0''.40$. I adopt

$$d\rho_0 = + 0''.39.$$

In the second place a determination of this value is possible from the corresponding observations of Mösting A made at Greenwich and at the Cape in 1906—1910. Their discussion is to be found in *Monthl. Not.* 71 526—540, from which we obtain with ellipt. = 1 : 297.5 :

$$d\rho_0 = + 0''.26.$$

These results agree very satisfactorily, but as the weight of the first is probably considerably greater I adopt this unaltered.

Further, with ellipt. = 1 : 297.5 we find for Greenwich, taking into account the height of 47 m. above the sea-level, $\log \rho = 9.999114$, while at Greenwich 9.9991136 is employed.

In this way we find

$$\rho_0 \frac{d\rho}{\rho} = - 0''.02$$

and

$$d\rho_0' = + 0''.37.$$

Thus the mean correction of the moon's declination for Greenwich becomes:

$$d\delta = + 0.75 \times 0.37 = + 0''.28.$$

So we finally find as resulting corrections for the declinations of the moon first of all always $+ 0''.14 + 0''.28 = + 0''.42$, and in the second place for 1895—1905 the corrections derived for each year resulting from flexure and for 1906—09 the correction $- 0''.36$ resulting from refraction and colatitude. Our results from the Greenwich observations, the sums total of the corrections and the corrected results are

	$\Delta \delta$	Correction	$\Delta \delta$ corr.	Mean.
1895	$- 0''.16$	$+ 0''.28$	$+ 0''.12$	
96	$+ 0.29$	$+ 0.25$	$+ 0.54$	
97	$+ 0.27$	$+ 0.04$	$+ 0.31$	
98	$- 0.08$	$+ 0.04$	$- 0.04$	
99	$- 0.35$	$+ 0.14$	$- 0.21$	$+ 0''.14$
1900	$- 0''.55$	$+ 0''.21$	$- 0''.34$	
01	$- 0.51$	$+ 0.30$	$- 0.21$	
02	$- 0.43$	$+ 0.16$	$- 0.27$	
03	$- 0.23$	$+ 0.16$	$- 0.07$	
04	$- 0.19$	$+ 0.23$	$+ 0.04$	$- 0''.17$
05	$- 0.38$	$+ 0.20$		
	$- .20$	„	$- 0.09$	
06	$- 0.21$	$+ 0.06$		
	$.00$	„	$- 0.04$	
07	$- 0.44$	$+ 0.06$		
	$- .72$	„	$- 0.52$	
08	$+ 0.01$	$+ 0.06$		
	$.08$	„	$+ 0.02$	
1909	$- 0.16$	$+ 0.06$		
	$- .20$	„	$- 0.12$	$- 0.15$
			Mean	$- 0''.06$

For the years 1905—09 in the second column there are given first the results from the observations of the limbs, then those from Mösting A; in the fourth column they have been taken together. The results from the separate years often show rather considerable fluctuations, but in the mean values from 5 years which are given in the last column, these have already diminished greatly and the final result from the whole of this 15 years' period amounts to $- 0''.06$. The mean result from Mösting A is in good accordance with that from the limbs. In *Proc. Acad. Amst.* 6 p. 422 I observed that from inequalities in longitude with a period of about a month, there proceed terms of

long period in latitude; and that with the greatest inequality of this kind which is neglected in the ephemerides, — the Jovian-evection — corresponds a term of 17 years' period in latitude with a coefficient of about 0.2. The influence of this term, however, must have almost disappeared in the result of the 15 years' work.

Thus the result of our investigation is that HANSEN's constant term in the latitude — 1".0 is necessary to make theory agree with the observations of the limbs and of Mösting A, even when these have been freed as well as possible from systematic errors. We now find $d\beta^{\circ} = -1".06$ while HANSEN found — 1".01¹⁾. Can this result point to the existence of an inequality in the latitude of *very* long period or must we accept HANSEN's hypothesis of asymmetry in the moon? In the latter case the centres of figure and of gravity, according to this computation would be 2.0 kilom. apart, which distance is much less than what HANSEN believed he had found in the direction of the radius vector (59 kilom.) and which perhaps we need not consider too abnormal.

Geology. — "*On the so-called atolls of the East-Indian Archipelago*".

By Prof. A. WICHMANN.

(Communicated in the meeting of December 30, 1911).

The geographer J. F. NIERMEYER pretended a short time ago that hitherto it was generally held that barrier-reefs and atolls "were entirely or almost entirely denied to the coasts of the Archipelago", that "this view was an error" and that the structure of these barrier-reefs "was a new evidence against the theory of DARWIN".²⁾

This "generally" supposed absence of barrier-reefs and atolls had hitherto not been evidenced at all, though a great number of naturalists will have been convinced, that they are wanting, because the reports lacked sufficient conclusive force, and moreover the Archipelago in general bears the character of an extensive upheaval territory in which there is no place for such like coral-formations. In order to remove as much as possible every uncertainty, I intend to investigate in how far these reports are well founded.

When about 80 years ago CHARLES DARWIN first published³⁾ his

1) *Monatl. Not* 15 p. 14.

2) Barrière-riffen en atollen in de Oost-Indiese Archipel. Tijdschr. K. Nederl. Aardr. Genootschap. (2) XXVIII. 1911, p. 877, 893. — Barrière-riffen in den Oost-Indischen Archipel. Handelingen van het 13de Nederl. Natuur- en Geneesk. Congres te Groningen. Haarlem 1911, p. 368.

3) *The Structure and Distribution of Coral Reefs*, London 1842., 2nd ed. 1873, 3rd ed. by T. G. BONNEY, 1889., new. ed. by JOHN W. JUDD, 1900.

work, the evidence he disposed of was still very incomplete and not in every respect to be relied upon, so that he was not always able to decide into which category the mentioned reefs were to be placed. He came to the result that, with sufficient certainty, only fringing-reefs could be pointed out in the East Indian Archipelago, yet he was inclined to think the existence of other forms of reefs possible and even probable. We shall first submit the latter to a further investigation.

According to the then existing charts he thought it possible, as regards the *Aru*, *Tanimbar* and *Timor Laut Islands*, that they were surrounded by barrier-reefs, but on account of the prevailing uncertainty he desisted from colouring them as such on his map¹⁾. From the reports of F. A. A. GREGORY it appears already that there can only be question of fringing reefs²⁾, extending, according to the most recent reports, generally 1—6 sea miles, S. W. from the island of *Trangang* even as far as 13 from the shore.³⁾

Sumba or Sandal-wood Island. On account of a statement of JAMES HORSBURGH regarding a reef, extending at the southern shore of this island as far as 4 miles, and of the great depth of the sea in the neighbourhood⁴⁾ DARWIN thought the existence of a barrier-reef there likewise probable (p. 174). From recent information it appears however that only a fringing-reef exists.

Luang. According to a statement⁵⁾ that the extensive reef of this island is steep outside and there within has a depth of 12 feet, DARWIN supposed that it might be a barrier-reef. The most recent statements however prove it to be a fringing-reef.⁶⁾

Ceram Laut, Goram and Keffing. In his supposition that the reefs extending from these islands into deep water belong to the barrier-reefs, DARWIN refers to G. W. EARL⁷⁾. According to the most recent evidence however the *Ceram Laut Islands* are situated, on a large "very steep coral-reef, extending eastward to the North of *Suruaki*. "In this coral-reef some deep gullies are found among which the

1) *The Structure and Distribution &c.* 1842, p. 172.

2) *Zeemansgids voor de Vaarwaters naar en door den Molukschen Archipel*. Amsterdam. 1853, p. 263, 277, 284.

3) *Zeemansgids voor den Oost-Indischen Archipel* V. 's-Gravenhage 1908, p. 13, 17, 29, 55.

4) *India Directory*. 4th ed. II. London 1836, p. 607.

5) D. H. KOLFF JR. *Reizen door den weinig bekenden zuidelijken Molukschen Archipel*. Amsterdam 1828, p. 130, were it is said 9—12 feet.

6) *Zeemansgids voor den Oost-Indischen Archipel* V. 1908, p. 9.

7) *Sailing Directions for the Arafura Sea*. London 1837, p. 9.

“straits of *Kefjing* and *Kilbaroe* are navigable for large ships.¹⁾

Further DARWIN writes (p. 176): “in the space of the sea, north of the great volcanic chain, from *Timor* to *Java*, we have also other islands, such as the *Postillions*, *Kalatoa*, *Tokan-Bessees*, &c., which are chiefly low, and are surrounded by very irregular and distant reefs. From the imperfect charts I have seen, I have not been able to decide whether they belong to the atoll or barrier-classes, or whether they merely fringe submarine banks, and gently sloping land.

“In the Bay of *Bonin*, between the two southern arms of *Celebes*, there are numerous coral-reefs; but none of them seem to have an atoll-like structure. I have, therefore, not coloured any of the islands in this part of the sea; I think it, however, exceedingly probable that some of them ought to be blue. I may add that there is a harbour on the S. E. coast of *Bouton*, which, according to an old chart, is formed by a reef parallel to the shore, with deep water within, and in the voyage of the *Coquille*, some neighbouring islands are represented with reefs a good way distant, but I do not know whether with deep water within. I have not thought the evidence sufficient to permit me to colour them”. As to the *Sabalana* [*Postillon*] Islands it is known that they form a group of low and overgrown islands, rising above a submarine plateau²⁾. The 528 m. high *Kalao Tua* slopes steeply down towards the sea and is only provided with a fringing-reef³⁾. *Binongka*, the principal island of the *Tukang Besi*-group, consists of terraces of coral-limestone and is surrounded by a narrow fringing reef⁴⁾. What regards the reef on the south-east coast of *Buton*⁵⁾, there reefs of any signification are in reality unknown⁶⁾. DARWIN's expectation that atolls would be discovered in the bay of *Boni* was not realised. Only low coral-

1) Zeemansgids etc. V. 1908, p. 141.

2) F. A. A. GREGORY. Zeemansgids 1853, p. 18. — Zeemansgids voor den Oost-Indischen Archipel V. 1906, p. 380-382. — MAX WEBER. Introduction et description de l'expédition. Siboga-Expeditie I. Leiden 1902, p. 23.

3) G. F. TYDEMAN. Hydrographic Results of the Siboga Expedition. Siboga-Expeditie III. Leiden 1903, p. 18.

4) MAX WEBER. Introduction et description, blz. 95-97. — G. F. TYDEMAN. Hydrographic Results, p. 41-42. — Zeemansgids voor den Oost-Indischen Archipel IV. 1906, p. 208-209.

5) L. I. DUPERREY. Voyage autour du Monde sur la corvette La Coquille. Hydrographie. Atlas. Paris 1827, Pl. 37. Carte du détroit de Wangi-Wangi.

6) Zeemansgids voor den Oost-Indischen Archipel IV. 1906, p. 214. — Aanvullingsblad 2. 1909, p. 28.

islands of the common character ¹⁾ are found there. Two spherical-shaped reefs indicated on the chart, with deep water within, in the Straits of Makassar (4°55' S.), showing a more atoll-like character than any other in the Archipelago, were left uncoloured, because Capt. R. MORESBY doubted this fact.

Karakelang (*Talaut-Islands*) was said by J. HORSBURGH to be lined by a dangerous reef, projecting several miles from the northern shore,²⁾ DARWIN had left the whole group uncoloured, because he could not find any other account. According to recent, more reliable, statements only fringing-reefs are found near *Karakelang* ³⁾.

The *Aju* and *Mapia-Islands* belong indeed to the Dutch possessions, but are situated already in the Pacific Ocean, so that they should not be treated of here. Occasionally we may remark that it was DARWIN, who indicated the atoll-character of the *Mapia-Islands* according to the chart published by PHIL. CARTERET ⁴⁾. DARWIN was less well-informed with regard to the *Aju-Islands* ⁵⁾. These possess no atoll-forms.

Not until the year 1875 new atolls were supposed to have been discovered in the Indian Archipelago. On May 11th, 1875 the corvette "Gazelle" commanded by G. E. G. VON SCHLEINITZ anchored near the island of *Dana* [*Hoki*] situated between Sawu and Sumba 10°49' S., 121°19'27" E.⁶⁾ According to TH. STUDER it consists of a ring-shaped wall of coral-limestone about 120 m. high⁷⁾, and has an opening in the N.E. ⁸⁾. There is a cup-shaped valley within containing a saltwater-lagoon. According to other statements the island is low and only along the north-east coast a ridge of hills reaching a level of 170 feet extends, whilst on the westside a separate hill rises having the shape of a short horn ⁹⁾. There can be no doubt that

¹⁾ *Ibid.*, p. 265 et seq.

²⁾ India Directory. 4th ed. II. London 1836, p. 504.

³⁾ F. A. A. GREGORY. *Zeemansgids* 1853, p. 320. — *Zeemansgids voor den Oost-Indischen Archipel* IV. 1906, p. 68.

⁴⁾ JOHN HAWKESWORTH. *An Account of the Voyages etc.* I. London 1773, p. 608

⁵⁾ THS. FORREST. *A Voyage to New Guinea and the Moluccas*. London 1779, p. 82. — J. DUMONT D'URVILLE. *Voyage de la Corvette l'Astrolabe*. Atlas, Pl. 38.

⁶⁾ Die Forschungsreise S. M. S. "Gazelle" 1874—1876. I. Reisebericht. Berlin 1889, p. 146.

⁷⁾ Elsewhere (*Travaux de l'assoc des Soc. Suisses de Géogr.* II. 1882 Genève. p. 130), STUDER says, that that level amounts to 60 m.

⁸⁾ Die Forschungsreise S. M. S. "Gazelle". III. Zoologie und Geologie. 1889, p. 197—199. According to VON SCHLEINITZ however the opening of that ridge is towards the W.

⁹⁾ A. G. FINDLAY. *A Directory for the Navigation of the Indian Archipelago*. 3d ed. London 1889, p. 747—748. — *Zeemansgids voor den Oost-Indischen Archipel* IV. 1906, p. 457—458. According to the most recent report there are in

though from older descriptions and charts it was obvious that there was no sufficient foundation for this view¹⁾. It was undeniably refuted by the researches of the "Siboga" by which, at the same time, the southern island was determined at 5°30'40" S., 127°33'22" E. (Fig. 1)²⁾. According to the recent investigations of VERBEEK there is no longer any foundation for the supposition that a volcano was hidden under these islands.³⁾

Gisser [Gèsir] (3°52'29" S., 130°52'26" E.). Since the time of F. VALENTIJN we have known about *Gisser*, belonging to the *Ceram Laut Islands* that there was "een fraai bogtje vlak in 't midden"⁴⁾ [a beautiful little bay exactly in the middle]. J. A. C. OUDEMANS too makes mention of a "schoone 4 à 5 voet diepe baai"⁵⁾.

H. VON ROSENBERG called the island a ring-shaped upheaved sandshoal⁶⁾, whereas HENRY O. FORBES was the first to take it for "a mere horseshoe-shaped, cocoonut-fringed atoll"⁷⁾ and most of the later visitors concurred with him in this view⁸⁾. As I remarked before

¹⁾ W. H. ROMBOUT VAN LOON. Mededeeling aangaande de Lucipara- en Schildpadseilanden. Verhandel. en Berigten betrekkelijk het Zeewezen. IV. Amsterdam 1844, p. 752—757 — F. A. A. GREGORY. Zeemans Gids. 1853, p. 153—154. — Gevaren in de Indische wateren. Tijdschr. teegew. aan het Zeewezen. (2) IV. Medemblik 1844, p. 317.

²⁾ Siboga-Expeditie I. MAX WEBER. Introduction et description, p. 97—100. III. G. F. TYDEMAN. Hydrographic Results, p. 42, Pl. XII. — Maatschappij tot Bevordering van het Natuurk. Onderzoek der Nederl. Koloniën, No. 10, p. 14., No. 11, p. 3. — Zeemansgids voor den Oost-Indischen Archipel. V. 1908, p. 88.

³⁾ R. D. M. VERBEEK and R. FENNEMA. Geologische beschrijving van Java en Madoera. I. 1896, p. 3. — R. LANGENBECK l. c. — MAX WEBER l. c.

⁴⁾ Oud en Nieuw Oost Indiën. II. Dordrecht—Amsterdam 1724, p. 60. For the rest VALENTIJN was not thoroughly acquainted with the island, for he called it "high, narrow and mountainous".

⁵⁾ Verslag van de bepaling der geographische ligging van eenige punten in de Molukken. Natuurk. Tijdschr. Ned. Ind. XXX. Batavia 1868, pp. 184—185.

⁶⁾ Beschrijving van eenige gedeelten van Ceram. Tijdschr. voor Ind. T. L. en Volkenk. XVI. Batavia 1867, p. 132. — Der Malayische Archipel. Leipzig 1878, p. 295.

⁷⁾ A Naturalist's Wanderings in the Eastern Archipelago... from 1878 to 1883. London 1885, p. 299. — Wanderungen eines Naturforschers im Malayischen Archipel. II. Jena 1886, p. 21. The cocoonut trees existed only in his imagination. These trees are not found in the island.

⁸⁾ Siboga-Expeditie I. MAX WEBER l. c. p. 79, III. G. F. TYDEMAN l. c. p. 35—36 — Maatschappij tot Bevordering van het Natuurk. Onderz. Bull. No. 31. 1899, p. 12. — [N. M. VAN DEN HAM]. Mededeeling betreffende de reede van Gisser. Meded. op Zeevaartkundig Gebied, No. 17/46. 's-Gravenhage 1900, p. 8 — Zeemansgids voor den Oost-Indischen Archipel V. 1908, pp. 142—143. — H. HIRSCHI. Reisen in Nord-West Neu-Guinea. Jahresbericht der Geogr. Ethnogr. Ges. 1907—8, Zürich 1908, pp. 142—143.



Fig. 2.

W. of *Taglandang* (*Sangi Islands*) was only known as a low, flat little island¹⁾.

A. J. VAN DELDEN added to this that it was lying on the top of a reef rising above the level of the water.²⁾ J. SIDNEY HICKSON, who saw *Pasigi* in 1885 from the top of the volcano in the island of *Ruang* supposed that it might "serve as a diagram of an atoll"³⁾. Afterwards he expressed himself thus: "The part above water covered with trees is only a small arc of the rim of a large almost ringshaped atoll"⁴⁾. He considered this to be a fact not agreeing with the theory of DARWIN. M. KOPERBERG who had seen *Pasigi* from the same standpoint expresses a more reserved opinion. Moreover the commander of the Govern. S.S. "Raaf" J. KAAAN had declared the island to be a coral bank⁵⁾. None of them has ever observed

¹⁾ Maatschappij tot Bevordering van het Natuurk. Onderzoek der Nederl. Koloniën. Bulletin, No. 43, 1903, p. 22, vide likewise R. D. M. VERBEEK. Molukken-Verslag. Jaarboek v. h. Mijnw. XXXVII. Wet. ged. 1903, p. 542.

²⁾ ALFRED VOELTZKOW. Bericht über eine Reise nach Ost-Afrika. Zeitschr. Gesellschaft. f. Erdkunde. Berlin 1904, p. 428.

³⁾ F. VALENTIJN. Oud en Nieuw Oost Indië. I. 1724, p. 61.

⁴⁾ De Sangir-eilanden in 1825. Indisch Magazijn. 1ste Twaalfstal, No. 4, 5 en 6. Batavia 1844, p. 356.

⁵⁾ Omszwervingen in Noord-Celebes. Translated by P. P. C. HOEK. Tijdschr. Aardr. Genootsch. (2) IV. 1887, M. U. A., p. 141.

⁶⁾ A Naturalist in North Celebes. London 1889, p. 44.

⁷⁾ Verslag van een onderzoek naar de uitbarstingen in 1904 op het vulkaan-eiland Roelang. Jaarboek van het Mijnw. N. O.-Indië. XXXVIII. Wet. ged. 1909, Batavia 1910, p. 210.

any thing of a lagoon, and the somewhat bent shape does not authorise us to regard it as an atoll.

According to the most recent statements *Pasigi* has a diameter of about 0,5 mile, is a low coral island surrounded by a reef extended on the south side as far as 0,2, on the north-side as far as 2,5 miles ¹⁾.

The statement of HICKSON that *Tagulandang* was surrounded by a barrier-reef has neither proved to be correct. Besides a reef in the fairway of Ruang and Tagulandang there is only a fringing-reef²⁾.

Agnieten Islands [*Pulu Pangang*], *Hoorn Islands* [*Pulu Ajer*] and *Groot-Kombuis* [*Pulu Lantjang*]. C. PH. SLUITER was of opinion that he had discovered atolls in the Java Sea, namely in the Bay of Batavia. "Auch die grösseren Gruppen, die Agnieten-Inseln und die Hoorn-Inseln, sowie die Inseln "Groote Kombuis" oder "Pulu Lantjang" sind beträchtlich ältere Riffe, welche schon deutliche Atolle bilden. Es ist allerdings bei den Agnieten- und Hoorn-Inseln nicht unmöglich, dass dort ein anderer Zustand besteht, wegen der ziemlich plötzlichen Senkung des Meeresbodens bis zu 50 Faden. Vielleicht kommt hier ein unterseeischer Kraterrand vor, auf welchem die Korallen sich angesiedelt haben"³⁾. SLUITER had previously asserted that in the *Emma Harbour* [*Brandewyns Bay*], near Padang, in the neighbourhood of the islands of *Krakatau* in straits Sunda, and *Buwean* in the Java Sea, barrier-reefs were found. Contrary to this assertion R. LANGENBECK had already remarked that in the above-mentioned regions all those reef-forms are wanting, and that they are to be regarded as coral-formations of the shallow seas (patch reefs), the rims of which are some times higher than the other parts⁴⁾. With regard to the *Agnieten Islands* we are further informed that they consist of 5 low islands, lying on a common reef 4 miles long and 1,3 miles wide⁵⁾. On these reefs one finds basins of which the western one is rather extensive, they can however no more than the others be compared to lagoons of atolls, but are to be regarded as depressions partly formed by sejunction, such as are

¹⁾ Zeemansgids voor den Oost-Indischen Archipel IV. 1906, p. 53-54.

²⁾ Ibid. p. 52.

³⁾ Einiges über die Entstehung der Korallenriffe in der Java-See und Brantweinsbai und über die neue Korallenbildung bei Krakatau. Naturkr. Tijdschr. Nederl. Indië. XLIX. Batavia, 1890, p. 378. — Ueber die Entstehung der Korallenriffe in der Java-See... Biologisches Centralblatt. IX. Erlangen 1889-90, p. 751.

⁴⁾ Die neueren Forschungen über Korallenriffe. Geogr. Zeitschr. III. Leipzig 1897, p. 570.

⁵⁾ Zeemansgids voor den Oost-Indischen Archipel I. 's-Gravenhage 1899, p. 139.

frequently found on coral-reefs¹). In the *Hoorn Islands*, the western ones of which — *Great* and *Little Tidung* — rest on a narrow and low reef, whilst the eastern one — *Pajung* — is surrounded by a separate reef I have not been able to detect any lagoons, no more could I do so in *Groot-Kombuis*, consisting of 2 low islands²).

Muaras [*umaras*-]reef (1°50' N., 112°55' O). This reef situated N. E. of Borneo has become known by the British war-ship "Samarang" which almost stranded on it³). It has in NW.—SE. a length of 30 km. and a breadth of 8.8 km. Whilst some parts fall dry at ebb-tide as shoals, a few rise as little islands above the level of high water. Inside the rim of the reef lies a deep basin which is however not navigable on account of the great quantity of stones⁴). Whilst MAX WEBER writes: "Ce récif rappelle, jusqu'au certain point, un atoll"⁵), J. F. NIEMMEYER considers it an undubitable fact that we have here a real atoll-reef⁶). Though the reef shows indeed some resemblance with an atoll, the north-western part proves already that it is a coral-bank, which on account of the more rapid growth of the rims gave occasion to the formation of a basin.

Maratua (2°15' N., 118°35' E.). Until a short time ago very little was known about the group of the *Maratua-Islands* situated N.E. of Borneo. In the 18th century attention was first fixed on it by ALEXANDER DALRYMPLE⁷), and it was *Maratua* itself that was repeatedly touched at by the Sulu pirates on account of its fresh-water springs. It served likewise as temporal settlements of Badjos. Whilst the general very particular shape of the island had been known for a long time, a more careful survey was only undertaken in the beginning of this century by the Royal Dutch Navy (fig. 3). From this survey and

¹) The above-mentioned Zeemansgids (II. 1900, p. 542) says about the Thousand Islands: With some of these reefs one finds on the outer side dikes of coral stones lying dry, within them more or less deep basins occur. In some of the large reefs there are basins, in which a depth of 3 fathoms and more is sounded, and where proas entering at high-tide can find a safe anchorage.

²) Zeemansgids voor den Oost-Indischen Archipel I. 1899, pp. 132, 138. — Westelijke Vaarwaters naar Reede van Batavia. 's-Gravenhage. 1899. Dep. van Marine, No. 86.

³) SIR EDWARD BELCHER. Narrative of H. M. S. Samarang during the years 1843—46. I. London 1848, p. 247—248, chart at p. 223.

⁴) Zeemansgids voor den Oost-Indischen Archipel III. 1903, p. 843.

⁵) Introduction et description de l'expédition. Siboga-Expeditie I. Leiden 1902, p. 57.

⁶) Barrière-riffen en atollen enz. Tijdschr. K. Nederl. Aandr. Genootsch (2) XXVIII. 1911, p. 890, kaart XIII, No. 13.

⁷) Oriental Repertory. I. London 1793, p. 530.

the additional description it appears that *Maratua* has the shape of a *V*, the opening of which is towards the S. E. It was represented



Fig. 3.

there in such a way, as if the *V*-shaped hill-ridge, the highest point of which is 400 feet high, represents the upheaved northern rim of an atoll, extending NW.—SW. over a length of 16 miles¹⁾. In this form this assertion is decidedly incorrect. The island is a ruin of an older date, the reef on the contrary a real fringing-reef — a recent formation. Whether in earlier times *Maratua* has been an atoll can only be decided by further investigation.

Kakaban. This island situated 4 miles S.W. of Maratua consists of a rock-wall 300 feet high, which in some parts is no more than 150 m. broad and encloses a large salt-water lake. According to the statement of natives this lake must be in connection with the sea, as it is influenced by ebb and tide. If another statement that only small fishes are found in it, should be true, there can be no question of an open connection. In most places the help of ladders is required to land on the island, because the rocks fretted by the sea, beetle. Only by careful investigation it can be decided whether *Kakaban* has in former times been an atoll. In its present state it cannot be regarded — as it is pretended — as an atoll²⁾.

The fact that it is surrounded by a fringing-reef, which however is

¹⁾ Zeemansgids voor den Oost-Indischen Archipel III. 1903, p. 849—851., vide likewise J. F. NIERMEYER. Barrière-riffen en atollen, p. 890.

²⁾ Zeemansgids voor den Oost-Indischen Archipel III. 1903, p. 851—852. — J. F. NIERMEYER. Barrière-riffen en atollen, p. 890.

nowhere broader than 100 m., proves that, for the rest, it is in a normal condition.

The *Bril* [*Taka Rewataya*] ($6^{\circ}4' S.$, $118^{\circ}55' E.$). This very dangerous reef, situated in the middle of the fairway has been known long since ¹⁾. Not before 1792 however a local survey took place, when a boat of the "Pitt" found in some spots 2 feet of water and a sandy nature of the bottom ²⁾. Whereas in former times the *Bril* was always regarded as a bank ³⁾, the latest author calls it a coral-overgrown atoll-shaped bank, which is a *contradictio in terminis*. It runs dry for the greater part at ebb-tide, with the exception of the rather deep basin in the middle, and the southern part where from $3\frac{1}{2}$ to 5 fathoms of water stands ⁴⁾.

Brisbane-reef. On the 15th Januari 1880 the steamship "Brisbane" stranded on a hitherto unknown reef, which was called after this ship ⁵⁾. In 1902 a light-house was erected in the island *Meati Mawany* ($4^{\circ}22\frac{1}{2}' S.$, $128^{\circ}29\frac{1}{4}' E.$) situated near the southern point ⁶⁾. Between this island and the two *Ukenao Islands* (*Meati Rialam* and *Amortau*) situated in the N., extends the very large reef $22\frac{1}{4}$ km. long and $9\frac{1}{4}$ km. broad, enclosing on the East-side a long basin, nearly for the whole length; the southern part only was explored. On the east-side there is an opening ⁷⁾. According to the researches of R. D. M. VERBEEK the three islands mentioned consist of coral-limestone and are consequently older than the reef that is their common fringing reef ⁸⁾. There can be no question of the existence of an atoll, though NIERMEIJER calls it so ⁹⁾.

Angelica-reef [*Pasir Layaran*] ($7^{\circ}46,5' S.$ $122^{\circ}15' E.$) This reef was discovered on 3rd of July 1801 by the ship "Angelica" and described

¹⁾ The *Bril* was apparently called after a ship of that name that was reported in 1694 (F. VALENTIJN. Oud en Nieuw Oost-Indien. I. 2. 1724, p. 29). The reef has been known by its present name since the beginning of the 18th century.

²⁾ The Oriental Navigator. 2d ed. London 1801, p. 516. — J. HORSBURGH India Directory. 4th ed. II. 1836, p. 532.

³⁾ J. SCHRÖDER. Over de Bank de Bril. Verhand. en Berigten betr. het Zeewezen. IV. Amsterdam 1844, p. 651—652.

⁴⁾ Zeemansgids voor den Oostind. Archipel III. 1903, p. 608 2nd edit. 1903, p. 511. — J. F. NIERMEYER. Barrière-riffen en atollen, p. 890, map XIV, fig. 18.

⁵⁾ Rif en eiland ("Brisbane") ontdekt. Bericht aan Zeevarenden. 's-Gravenhage 1880, N^o. 15/397.

⁶⁾ Licht wordt ontstoken. Bericht aan Zeevarenden. 1903, N^o. 229/1713, 248/1870.

⁷⁾ Zeemansgids voor den Oost-Indischen Archipel. V. 1908, p. 8—9.

⁸⁾ Molukken-Verslag. Jaarboek van het Mijneuzen. XXXVII Wet. ged. 1908, p. 445.

⁹⁾ Barrière-riffen en atollen, p. 890, map XIV, fig. 17.

as of a circular shape, 4 miles in diameter and at the north- and south-end nearly dry¹⁾. Repeatedly ships were wrecked on it. When in 1846 the brig "Haai" ran aground on it, it was discovered that the reef was divided into three parts by two small gullies, on the middle-part rocks rose just above the level of the sea²⁾. Not before 1908 an exact survey was made by the exploring vessel "Soembawa", which gave the very remarkable result, that the *Angelica-reef* was to be considered as an atoll, 6.95 km. in WNW.—ESE. long and 4.17 km. broad³⁾. It is the first of all reefs that has a real atoll-shape, though it differs from the normal form, and two basins are found in it.

GosongBoni (8°23' S., 122°14' E.). This reef was discovered in 1851 by P. KONIG⁴⁾ and represented by him as a small island (*Pulu Boni*)⁵⁾ with which a semi-circular reef was united that ran dry. According to the surveyings of the "Soembawa" this reef has likewise the shape of an atoll⁶⁾. It has a diameter of 2½ km., whilst the depth of the basin amounts to 40—50 fathoms⁷⁾.

Lalanga-reef (1°2' S. 120°40' E.). This reef situated in the bay of *Tomim* is described as a large coral reef running for the greater part dry and steeply sloping down everywhere except on the east-side⁸⁾. From the fact that there are on the east-side two diverging off-shoots NIERMEYER supposed he might conclude that the reef had the character of an atoll⁹⁾. This conclusion has no foundation whatever, not even the shape reminds of an atoll.

Somewhat more than 1 km. to the south of the *Lalanga-reef*, a ring-shaped reef is found. A regular fishing is going on in the basin.

¹⁾ JAMES HORSBURGH. *India Directory*. 4th ed. II. London 1836, p. 610.

²⁾ C. F. STAVENISSE DE BRAUW. *Het vastzeilen van Zr. Ms. brik De Haai op de Argelika's Droogte*. *Verhandelingen en Berigten betr. het Zeewezen*. VIII. 1848, p. 704. II. D. A. SMITS. *Zeemansgids voor de Eilanden en Vaarwaters beoosten Java*. 2nd ed. Amsterdam 1859, pp. 39—40.

³⁾ Bericht aan Zeevarenden. 's-Gravenhage 1908, No. 154/232. — *Zeemansgids voor den Oost-Indischen Archipel* IV. *Aanvullingsblad* 2, p. 91. — J. F. NIERMEYER. *Barrière-riffen en atollen*, p. 891, map XIII, fig. 16.

⁴⁾ Chart of part of the North-coast of Flores, Novbr. 1851 (J. G. F. BRUMUND. *Indiana*. I. Amsterdam 1853, at p. 131).

⁵⁾ Boni is the name of the Malay navigators, the inhabitants of the neighbouring north-coast of Flores call it Taping.

⁶⁾ *Zeemansgids voor den Oost-Indischen Archipel*. IV. *Aanvullingsbl.* 2. 1909, p. 90. It is remarkable, that the bottom of the basin consists of white clay.

⁷⁾ NIERMEYER reports l. c. p. 891 l. 5 f. t. a depth of 885 m., l. 9 f. b. of 105 m. and according to map XIV. fig. 19. of 85 m.

⁸⁾ *Zeemansgids voor den Oost-Indischen Archipel* IV. 1906, p. 138.

⁹⁾ *Barrière-riffen en atollen* blz. 891, chart XIV, fig. 21.

This reef is however no atoll. NIERMEYER still supposes that he must regard another reef, likewise in the bay of *Tomini* SW. of the town of *Tomini* about $0^{\circ}24' N.$, $120^{\circ}32'$, as belonging to the atoll-formations. It is impossible for me to recognise an atoll-formation in it¹⁾.

At last two more reefs in the Java-Sea remain, situated NNE. of *Boompjes Island* [*Pulu-Rakit*], which NIERMEYER considers as two remarkable curiosities, beautiful atoll-shaped bars. "One would certainly "call them atolls, if the notion deep-sea upheaval were not inseparably connected with this name"²⁾.

The result of the above considerations is, that among the islands of the East Indian Archipelago, that are supposed to be atolls, *Dana*, the *Luciparas*, *Maratua*, *Kakaban* and *Meati Miarang* are formations of no recent date and provided with fringing-reefs, whilst *Gisser*, *Pasigi*, the *Agnieten Islands* etc. represent coral formations of the shallow sea. Consequently J. F. VAN BEMMELEN's words are still valid: "However rich the Indian Archipelago may be in "such coral reefs, yet the two most known types of coral formations "are wanting: *Barrier-reefs* and *Atolls*"³⁾. As to the reefs, that rise only partly above the level of the sea, among these we meet no more atoll-form with the exception of the *Angelica-reef* and the *Boni-reef*.

Inseparately connected with this question about atolls is that about barrier-reefs. As stated above those reported in former times do in reality not exist. J. F. NIERMEYER supposes he has discovered them now on a much larger scale, and adds the following explanation to his report: "They are always built up along the rims of the "sub-marine plateaus It is easily seen that, as a rule, they "begin as isolated small reefs . . . , which can afterwards arrange "themselves and form longer bars and islands. This structure is a "new proof against DARWIN's theory, according to his theory the "barrier-reefs would have originated in fringing-reefs. For in that "case they would as a rule appear in more serried rows"⁴⁾. It is not very well possible to contest a theory when choosing as point of issue another notion than the author's. DARWIN considered as barrier-reefs "those, which like a wall with a deep moat within" surround the islands, and held that "the lagoon-channels may be compared "in every respect with true lagoons"⁵⁾. The further explanations

1) Ibid. p. 891, map XIV, fig. 20.

2) Ibid. p. 892, map XIV, fig. 22.

3) Encyclopaedie van Nederlandsch-Indië. II. 's-Gravenhage—Leiden, [1899], p. 290.

4) Barrière riffen en atollen, p. 879, 893.

5) The Structure and Distribution of Coral Reefs. 1842, p. 41, 43.

which he gives of these formations do not leave the least doubt that his barrier-reefs are different from those described by NIERMEIJER. These are formations of the shallow seas, patch reefs, or pelagic reefs and no other reefs could be expected in an area of upheaval.

Physics. — “*On the variability of the quantity b in VAN DER WAAALS'S equation of state, also in connection with the critical quantities.*”

IV. (Conclusion). By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of December 30, 1911).

Let us write therefore:

$$q^2 (v-b) b'' = -b' \left(\frac{q}{m}\right)^2 \left[1 + \frac{q}{x+q} + \frac{x+q}{x+1} (x\beta^2 + 2\beta - 1) \right], \quad (a)$$

then we get:

$$\begin{aligned} q^2 (v-b) b''' + q^2 (1-b') b'' - 2qb'' \cdot \frac{q}{m} = \\ = -b' \left(\frac{q}{m}\right)^2 \frac{dA}{dv} - 2Ab' \left(\frac{q}{m}\right)^2 \left[\frac{1-b'}{v-b} - \frac{3}{v} \right] - b'' \left(\frac{q}{m}\right)^2 A, \end{aligned}$$

representing the form between $[\]$ by A , and bearing in mind that

$$\frac{dq}{dv} = -\frac{1}{v-b} \frac{q}{m} \quad ; \quad \frac{d}{dv} \left(\frac{q}{m}\right) = \left(\frac{1-b}{v-b} - \frac{3}{v}\right) \frac{q}{m}.$$

That last relation (see III, p. 575, formula (a)) holds only for the critical point, and is not general; so that we cannot derive b''' etc. from the formula for b'' , which we shall presently obtain. Now in virtue of (a) $\left(\frac{q}{m}\right)^2 A$ may be replaced by $-q^2 (v-b) \frac{b''}{b'}$, and so we get:

$$\begin{aligned} q^2 (v-b) b''' + q^2 (1-b') b'' - 2b'' \frac{q^2}{m} = \\ = -b' \left(\frac{q}{m}\right)^2 \frac{dA}{dv} + 2q^2 (1-b') b'' - 6q^2 \frac{v-b}{v} b'' + q^2 (v-b) \frac{(b'')^2}{b'}, \end{aligned}$$

i. e.

$$q^2 (v-b) b''' = -b' \left(\frac{q}{m}\right)^2 \frac{dA}{dv} + b'' q^2 \left[(1-b') - 6 \frac{v-b}{v} + \frac{2}{m} + (v-b) \frac{b''}{b'} \right],$$

or as $\frac{1}{m} = 1 - b' \frac{x+q}{q}$, which follows immediately from (1) (see III,

p. 578), hence also $\frac{1}{m} = (1-b') - b' \frac{x}{q}$, we obtain:

$$(v-b)b''' = -\frac{b'}{m^2} \frac{dA}{dv} + 3b'' \left[(1-b') - 2\frac{v-b}{v} - \frac{2}{3} b' \frac{x}{q} + \frac{1}{3} (v-b) \frac{b''}{b'} \right].$$

So we still have to determine $\frac{dA}{dv}$. From

$$A = 1 + \frac{q}{x+q} + \frac{x+q}{x+1} (x\beta^2 + 2\beta - 1)$$

follows :

$$\begin{aligned} \frac{dA}{dv} &= \frac{x}{(x+q)^2} \left(-\frac{1}{v-b} \frac{q}{m} \right) + \\ &+ \frac{1}{x+1} \left[\left(-\frac{1}{v-b} \frac{q}{m} \right) (x\beta^2 + 2\beta - 1) + (x+q) (2\beta x + 2) \cdot \frac{b' (1+x\beta)}{q (v-b)} \right], \end{aligned}$$

when we substitute for $\frac{dA}{dv}$ and $\frac{d\beta}{dv}$ their values (see III, p. 578).

Hence we find :

$$\frac{dA}{dv} = \frac{1}{v-b} \left[-\frac{x}{m} \frac{q}{(x+q)^2} + \frac{1}{x+1} \left\{ -\frac{q}{m} (x\beta^2 + 2\beta - 1) + 2 \frac{x+q}{q} (1+x\beta)^2 b' \right\} \right].$$

Now for $\frac{x+q}{q} b'$ we may write $1 - \frac{1}{m}$ (see above), so we have :

$$\frac{dA}{dv} = \frac{1}{v-b} \left[-\frac{q}{m} \left\{ \frac{x}{(x+q)^2} + \frac{x\beta^2 + 2\beta - 1}{x+1} \right\} + \frac{2(1+x\beta)^2 m - 1}{x+1} \frac{1}{m} \right].$$

In consequence of this we get finally :

$$\begin{aligned} (v-b)b''' &= \frac{b'q}{m^2 (v-b)} \left[\frac{x}{(x+q)^2} + \frac{x\beta^2 + 2\beta - 1}{x+1} - \frac{2(1+x\beta)^2 m - 1}{x+1} \frac{1}{q} \right] + \\ &+ 3b'' \left[(1-b') - \frac{2}{3} b' \frac{x}{q} - 2 \frac{v-b}{v} + \frac{1}{3} (v-b) \frac{b''}{b'} \right], \end{aligned}$$

or also

$$\begin{aligned} \frac{b''' v^2}{k^2 v^2} &= \left(\frac{v}{v-b} \right)^2 \frac{b'q}{m^2} \left[\frac{x}{(x+q)^2} + \frac{x\beta^2 + 2\beta - 1}{x+1} - \frac{2(1+x\beta)^2 m - 1}{x+1} \frac{1}{q} \right] + \\ &+ 3b'' v \frac{v}{v-b} \left[(1-b') - \frac{2}{3} b' \frac{x}{q} - 2 \frac{v-b}{v} + \frac{1}{3} \frac{v-b}{v} \frac{b'' v}{b'} \right] \end{aligned} \quad (3)$$

So from this the value of $b''' v^2$ can be calculated at different values of x , however (see above) only at the critical temperature, because for the derivation from b'' we have made use of a relation that only holds at the critical temperature.

The values of $b'' v$ for different values of x will be calculated further from the relation which also only holds at T_k (see III, p. 576 formula (17))

$$p'' \left(1 + \frac{x}{q} \right) = \frac{1}{m} \left[\frac{3}{2} - \frac{v}{v-b} (1-p') \right].$$

In this $p'' = \frac{1}{2}b''v$. With regard to b' (or p') we shall make use of the relation (see above)

$$b' = \frac{m-1}{m} \frac{q}{x+q}.$$

For $x=1$ and $x=2$ we have already the values of β, q, m and $v : b$. (See I, p. 295—296; II, p. 429—430); for $x=3$ and $x=4$ we will first calculate them now.

For $x=3$ we find:

$$\underline{\beta = 0,9600} \quad ; \quad \underline{q = 0,4732}.$$

For then we get (see I, p. 295):

$$n = 0,947 \times \frac{4}{1+3\beta} = 0,947 \times 1,0309 = 0,9763$$

$$m = \frac{8}{7} n = 1,1158,$$

whereas we also have:

$$m = 1 + \frac{1}{4} \beta(1-\beta)(3+q)^2 = 1 + 0,0096 \times 12,063 = \underline{1,1158}$$

$$\begin{aligned} n &= 1 + \frac{9}{8} \beta(1-\beta)(3+q) + \frac{1}{32} \beta(1-\beta)(1+4\beta-9\beta^2)(3+q)^2 \\ &= 1 + 0,0432 \times 3,4732 - 0,0012 \times 3,4544 \times 41,897 \\ &= 1 + 0,1500 - 0,1737 = 0,9763. \end{aligned}$$

For $\frac{v_k}{b_k}$ we find from $\frac{v_k}{b_k} = \frac{3m^2}{3m^2-2n}$ (see I, p. 296):

$$\frac{v_k}{b_k} = \frac{3 \times (1,116)^2}{id. - 1,952} = \frac{3,736}{1,784} = \underline{2,0945}.$$

As $q = (1+x\beta) \frac{\Delta b}{v-b}$, 0,122 is found for the value of $\frac{\Delta b}{v_k-b_k}$ at $x=3$.

At $x=4$ we calculate (again in order that μ may get the value 0,265, and f the value 7 (see I, p. 295)):

$$\underline{\beta = 0,9612} \quad ; \quad \underline{q = 0,4408}.$$

For then we have:

$$n = 0,947 \times \frac{5}{1+4\beta} = 0,947 \times 1,0320 = 0,9773$$

$$m = \frac{8}{7} n = 1,1169,$$

and also:

$$m = 1 + \frac{1}{5} \beta (1 - \beta) (4 + q)^2 = 1 + 0,007458 \times 15,675 = \underline{1,1169}$$

$$\begin{aligned} n &= 1 + \frac{6}{5} \beta (1 - \beta) (4 + q) + \frac{1}{50} \beta (1 - \beta) (1 + 6\beta - 12\beta^2) (4 + q)^2 \\ &= 1 + 0,04475 \times 3,9592 - 0,0007459 \times 4,3197 \times 62,061 \\ &= 1 + 0,1772 - 0,1999 = 0,9773. \end{aligned}$$

So we find further :

$$\frac{v}{b_k} = \frac{3 \times 1,117}{id. - 1,955} = \frac{3,743}{1,788} = \underline{2,093}.$$

For $\frac{\Delta b}{v_k - b_k}$ we find $-0,00842$, so already negative.

Now we are able to calculate the values of b_k' , b_k'' , and b_k''' .

11. With regard to b_k' , we find successively from $b' = \frac{m-1}{m} \frac{\varphi}{x+\varphi}$ (see above):

$$x = 1 \mid b'_k = 0,05335 \quad (\text{see also II, p. 428})$$

$$x = 2 \mid b'_k = 0,03187 \quad (, , , , \text{ 431})$$

$$x = 3 \mid b'_k = 0,01414$$

$$x = 4 \mid b'_k = -0,001079.$$

And for $b_k'' v_k$ we get from (see above)

$$p'' = \frac{1,5 - \frac{2,1}{1,1} (1-p')}{m \left(1 + \frac{x}{\varphi} \right)}$$

successively :

$$x = 1 \mid p'' = -0,1475 \quad b_k'' v_k = -0,2950$$

$$x = 2 \mid p'' = -0,09783 \mid b_k'' v_k = -0,1957$$

(See also II, p. 428 and 431)

$$x = 3 \mid p'' = -0,04720 \mid b_k'' v_k = -0,09441$$

$$x = 4 \mid p'' = 0,003844 \mid b_k'' v_k = 0,007688. \quad \cdot$$

And now we can also calculate the values of $b_k''' v_k^2$, namely from the formula (3) mentioned above.

Writing in (3) for the last part with $b''v$:

$$3b''v \frac{v}{v-b} \left[(1-b') - \frac{2}{3} b' \frac{x}{\varphi} \right] - b''v \left[6 - \frac{b''v}{b'} \right],$$

we find for $x = 1$:

$$b_k''' v_k^2 = 1,9953.$$

This value is very high. We have, however, taken the trouble to

derive a formula for $b'''v^2$ in two more ways; the calculation yielded in both cases 2,00, i.e. an identical result.

For $x=2$, however, this value already becomes lower. We find then:

$$b_k'''v_k^2 = 1,3788.$$

For $x=3$ a still lower value is found. Then we have namely:

$$b_k'''v_k^2 = 0,6830.$$

For $x=4$, just as for b_k' and $b_k''v_k$ reversal of sign takes place. We find:

$$b_k'''v_k^2 = -0,05655.$$

From the available material of numerical values we may draw up the following survey. It gives the values of β and q (and so also of $\frac{\Delta b}{v-b}$, m , n , $\frac{v_k}{b_k}$, b_k' , $b_k''v_k$ and $b_k'''v_k^2$) necessary that we may get $\mu=0,265$ and $f=7$ in the critical point on our condition of partial association to $(x+1)$ -fold molecule-complexes (see I, p. 295). From this follow, indeed, certain values of β and q , and from these the other quantities are calculated.

x	β	q	$\frac{\Delta b}{v_k-b_k}$	m	n	$v_k:b_k$	b_k'	$b_k''v_k$	$b_k'''v_k^2$	N in (18a)
1	0.955	1.227	0.63	1.107	0.969	2.114	0.053	-0.295	2.00	-0.25
2	0.958	0.916	0.31	1.113	0.974	2.102	0.032	-0.196	1.38	-0.23
3	0.960	0.473	0.12	1.116	0.976	2.095	0.014	-0.094	0.68	-0.19
4	0.961	-0.041	-0.0084	1.117	0.977	2.093	-0.0011	+0.0077	-0.057	-0.14

It is certainly striking in this that the values of β and $v_k:b_k$ remain almost constant. When β remains = 0,96, we always find the value 2,1 for $v_k:b_k$. Only q and with it also $\frac{\Delta b}{v-b}$, b_k' , b_k'' , and b_k''' change greatly. We saw in I, p. 296 that the value of $\frac{\Delta b}{v_k-b_k}$ must be about 0,43 to bring the limiting volume at $v=b$ for constant x to about 4-times the critical volume. So according to the above table this would correspond to about $x=1,5$ (association to double or triple molecules). But if we assume x to be variable, it is very well possible that for $T_k \frac{\Delta b}{v-b}$ is e.g. only = 0,12, and increases

when the formation of complexes progresses with decreasing liquid-volume.

This is not inconsistent with the fact that in our above table $\frac{\Delta b}{v_k - b_k}$ becomes smaller and smaller when x increases. For the values given in the table are those which would have to be assigned to the different quantities at the *critical* temperature in order that μ be $= 0,265$ and $f = 7$ — *not* those which can hold below or above it. If we e.g. take $x = 3$ at T_k , then there $\frac{\Delta b}{v_k - b_k} = 0,12$ (in order that f may be $= 7$; etc.), and we may very well suppose that this quantity assumes *greater* values *below* the critical point, when x becomes > 3 , because we may of course assume *arbitrary* values of Δb for the different complexes; e.g. corresponding to the then holding values of the coexisting liquid volumes. Etc. etc.

However, *no greater* complexity may certainly be assumed at T_k than at the utmost on an average quadruple molecules ($x = 3$), because else Δb would become negative, i.e. b would decrease with increasing volume at T_k , which is contrary to reality.

Let us now examine what the value becomes of the coefficient a' in $n = 1$ — $a' \tau = 1 - a' 1 - m$, when we substitute the above values of b' , b'' , and b''' at T_k for different values of x in the formula (18^a) derived by us, viz.:

$$a'^2 = 1 : \left[\frac{2,1}{1,1} \left\{ \frac{3}{2} (1-p') + p'' \right\} - p''' m_k \left(1 + \frac{x}{q_k} \right) - 2 \right] \dots (18^a)$$

For the denominator we get the following values.

For $x = 1$:

$$N = - 0,2537.$$

So we find a *negative* value for a'^2 , viz. $1 : (-0,2537) = - 3,942$.

We shall see presently what the meaning is of this result.

For $x = 2$ we get:

$$N = - 0,2309.$$

For $x = 3$ we find:

$$N = - 0,1924.$$

And finally for $x = 4$:

$$N = - 0,1390.$$

We see from this that the denominator N of the second member of (18^a), indeed, becomes smaller and smaller negative as x becomes greater at T_k , but so slowly that it is the question at what value of x this negative value will pass into a positive one. At any rate

at a value of x for which (see the above table) Δb has long become negative, and so at an impossible value (for T_k).

So we have to deal with the fact that a'^2 is negative, and the question of the meaning of this result.

12. This now is nothing but that the value of q i.e. of Δb , calculated with *constant* x , and hence also the values of b_k' , $b_k''v_k$, $b_k'''v_k^2$ are found too *large*. If we take x as variable — as agrees with reality¹⁾ — also the differential quotients of x (with respect to v) will occur in the expressions which we have derived for b' , b'' , b''' , and it will quite depend on the (as yet unknown) law of the variability of x with v , what value the differential quotients of b will then have.

As we said, nothing is known about the law concerning the increase of the complexity with the diminution of the volume. For it would be required for this that we knew a little more of the *constants of entropy*²⁾. The question: *how many molecules will be associated in a given volume to double, how many to triple, quadruple ones etc.* — this question will have to find its solution in statistical thermodynamics.

At the same time the question will then have to be answered, *what will be the variations of volume Δb — real and apparent ones — accompanying this*; the apparent variation of volume of the associating molecules in connection with the influence on the pressure.

But until these fundamental questions have been solved, we cannot advance in this theory, and we shall have to content ourselves with the obtained results.

If a'^2 became really negative, this would imply that in the immediate neighbourhood of the critical point not $n = 1 - a'\sqrt{1-m}$, but $n = 1 - a'\sqrt{m-1}$ would hold, in other words that when the phases diverge, the temperature did not get below the critical temperature, but *above* it, and that the saturation curve near T_k would present a concave shape turned upwards (viz. in the v, T -diagram).

This now would be impossible, even though it should be proved mathematically that the saturation curve liquid-vapour then formed a closed S-shaped region, which would be entirely enclosed within the more extensive region of the saturation curve solid-vapour. Then

¹⁾ I drew attention to this already in I p. 281 (cf. also Solid State VII p. 98 at the bottom)

²⁾ See among others KOHNSTAMM and ORNSTEIN, These Proc. of Dec. 1910, p. 704 et seq.; ORNSTEIN, Thesis for the Doctorate.

the isotherm in the point K would have the usual shape of the isotherms below T_k , but with a *point of inflection* in the *unstable* part. But this has no physical importance, so that as has been said, we shall have to find the solution in a *diminution* of the values of b'_k , b''_k , and b'''_k in consequence of the increase of x ($r = x + 1$ is the number of molecules united to one complex).

Now it is noteworthy that the *relation* between the said values *changes little with increase of x* .

From the above table (p. 715) we calculate e.g.:

$x = 1$	$- b''_k v_k : b'_k = 5,6$	$b'''_k v_k^2 : - b''_k v_k = 6,8$
2	6,1	7,0
3	6,7	7,2
4	7,1	7,4

If now, *retaining* the values of $v_k : b_k$, m_k , and q_k^1 , we take the values of b'_k etc. found above all e.g. 0,68 times larger, we have:

$$p' = b'_k = 0,68 \times 0,05335 = 0,03628; \quad p'' = \frac{1}{2} b''_k v_k = \\ = 0,68 \times 0,1475 = 0,1003; \quad p''' = \frac{1}{6} b'''_k v_k^2 = 0,68 \times 0,33255 = 0,2261, \\ \text{and further:}$$

$$\frac{2,114}{1,114} \left\{ \frac{3}{2} (1-p') + p'' \right\} - p''' m_k \left(1 + \frac{x}{q_k} \right) - 2 = 0,0985.$$

Hence we find for a'^2 according to (19) $1 : 0,0985 = 10,15$, so that a' becomes = 3,19.

If on the other hand we take the values mentioned 0,70 times larger, the above expression becomes:

$$0,0763$$

with

$$p' = 0,03735 \quad ; \quad p'' = 0,1033 \quad ; \quad p''' = 0,2328.$$

For a'^2 we find $1 : 0,0763 = 13,11$, so for a' the value 3,62²⁾.

We see from this how *sensitive* the value of a' is to even slight changes in the values of b'_k , etc.; so that we need not wonder that a more thorough modification in consequence of neglect of the variability of x with v , can bring about a *reversal* of the *sign* of a'^2 .

1) Really the values $v_k : b_k$ and m_k will only suffer a slight modification when x varies, as appears from the table on p. 715. The value of q_k will probably change much more; but this we leave out of consideration, because the above is only intended for a rough estimation and orientation.

2) We saw in II, p. 437 that for C_6H_5F and SO_2 a' has probably a value between 3,2 and 3,6, so that the values of b'_k , etc. (for $x = 1$) will be about 0,7 of the values calculated in § 11.

So our result about a'^2 becoming negative, found in § II, need by no means be inconsistent with the theory developed by us, but only points to its *incompleteness*.

13. As matters stand now, it is of course useless in connection with what precedes to carry the analysis any further, and to derive an expression for the coefficient b' , for which the knowledge of the fourth and fifth differential quotients of b with respect to v would be required.

But by the determination of the values of n (or d) for some coexisting phases near the critical point we can find out something *by approximation* concerning the direction of the so-called straight diameter. For though the concavity of the saturation curve is turned upwards instead of downwards, the *direction* of the locus ${}_{1,2}(d+d')=f(m)$ determined in this way will not differ much from the *real* direction. And this is so, because we have seen (see the table) that the *place* of the critical point given by the relation $v_k:b_k$ hardly changes at all with change of the value of x , and always remains in the neighbourhood of 2,1, so that also *close* to the critical point, where the values for d and d' in consequence of the varying value of the coefficient a' are augmented, resp. diminished by an *equally large* amount, ${}_{1,2}(d+d')$ continues to keep about the same value.

In order to find the values of d and d' for *coexisting* phases in the case considered, we proceed as follows.

As we have seen, the equations (10) and (12) hold for coexisting phases (see III, p. 568 and 570; α has been put for $\frac{1+x\beta}{1+x}$) viz.

$$\left. \begin{aligned} \frac{\alpha d}{2,1-\gamma d} - \frac{\alpha' d'}{2,1-\gamma' d'} &= \frac{6}{8} \frac{d^2-d'^2}{m} \\ \log \left(\frac{d}{d'} \frac{2,1-\gamma' d' \beta}{2,1-\gamma d \beta} \right) &= \frac{6}{8} \frac{d-d'}{m} \left(2 \times 2,1-s(d+d') \right) \end{aligned} \right\} \text{(10) and (12)}$$

If we now put again, as in II, p. 433, $\frac{\alpha d}{2,1-\gamma d} = A$ and $\frac{\alpha' d'}{2,1-\gamma' d'} = A'$, then we get on division of these two equations:

$$\log \left(\frac{\alpha d}{2,1-\gamma d} \frac{\beta}{1+x\beta} : \frac{\alpha' d'}{2,1-\gamma' d'} \frac{\beta'}{1+x\beta'} \right) = \frac{2 \times 2,1}{d+d'} - s,$$

taking the above value of α into consideration. Hence:

$$\left(\log A + \log \frac{\beta}{1+x\beta} \right) - \left(\log A' + \log \frac{\beta'}{1+x\beta'} \right) = \frac{2,1}{A-A'} - s \dots \quad (4)$$

or also :

$$\log A + \log \beta - \log (1+x\beta) = P \quad ; \quad \log A' + \log \beta' - \log (1+x\beta') = P'$$

putting

$$\frac{P-P'}{A-A'} = \frac{2,1}{\frac{1}{2}(d+d')} \dots \dots \dots \quad (4^a)$$

quite analogous to (3^a) in II, p. 433. With $\beta = 1$, in consequence of which 2,1 becomes 3 and $s = b_2 : b_k$ becomes 1, (4^a) passes namely immediately into

$$\frac{\log A - \log A'}{A - A'} : \frac{6}{d+d'} = 1.$$

We will now sketch the course of the calculation, e. g. in the case $x=1$. From the equation of dissociation (see I, p. 283, equation (1^a))

$$\frac{\beta^x}{1-\beta^2} = \theta \frac{e^{-\gamma}}{q}$$

we calculate first the value of θ from the values of β and q holding for the critical point. This quantity θ is properly speaking a function of the temperature, but we saw in I, p. 291, that as with association under the influence of the molecular forces q_0 and γ may be put equal to 0, θ may be considered as a constant. Now (see the table, and also I, p. 295) for $x=1$ (in order that f' may become = 7 and $\mu = 0,265$ at T_k)

$$\beta_k = 0,9547 \quad ; \quad q_k = 1,227,$$

and from this we find $\theta = 43,079$; $\log^{10} \theta = 1,6343$.

If now for q we take successively values from 1,227 — going to lower values for the vapour phase, to higher values for the liquid phase (as $q = (1 + \beta) \Delta b : (v - b)$) — we find the corresponding values of β from

$$\log^{10} \frac{\beta^2}{1-\beta^2} = 1,6343 - 0,4343q - \log^{10} q \dots \dots \dots (a)$$

From

$$q_k = (1 + \beta_k) \frac{\Delta b}{v_k - b_k} = (1 + \beta_k) \frac{\Delta b : b_k}{1,1}$$

follows :

$$\frac{\Delta b}{b_k} = \frac{1,1 q_k}{1 + \beta_k} = \frac{1,114 \times 1,227}{1,9547} = 0,6922.$$

in consequence of which

$$q = (1 + \beta) \frac{\Delta b}{r-b} = (1 + \beta) \frac{\Delta b : v_k}{2,1n-\gamma}$$

passes into

$$q = \frac{0,6992 (1+\beta)}{2,1n-\gamma}$$

and hence we find for

$$A = \frac{ad}{2,1-\gamma d} = \frac{a}{2,1n-\gamma} = \frac{(1+\beta) : 2}{2,1n-\gamma};$$
$$A = \frac{q}{1,3984} \dots \dots \dots (b)$$

Further from

$$2,1n-\gamma = \frac{0,6992 (1+\beta)}{q}$$

in connection with $b = b_2 - (1 - \beta) \Delta b$, so $\gamma = s - (1 - \beta) \frac{\Delta b}{b_k} = s - 0,6992 (1 - \beta)$, follows :

$$2,1n = s - 0,6992 (1 - \beta) + \frac{0,6992(1+\beta)}{q}$$

and so we find for $d = 1 : n$:

$$d = \frac{2,114}{1,0317 + 0,6992 \left(\frac{1+\beta}{q} - (1-\beta) \right)} \dots \dots (c)$$

because $s = b_2 : b_k = 1,0317$. It follows namely from $b_k = b_2 - (1 - \beta_k) \Delta b$ that $b_2 : b_k = 1 + (1 - \beta_k) (\Delta b : b_k) = 1 + 0,0453 \times 0,6992 = 1,0317$.

Then we calculate P from (see above)

$$P = 2,3026 (\log^{10} A + \log^{10} \beta - \log^{10} (1 + \beta)) \dots \dots (d)$$

In this way we calculate e.g. the following table (p. 722).

For the determination of the coexisting phases we have now only to seek according to (4^a), viz.:

$$\frac{P-A'}{A-A'} = \frac{2,114}{1/2(d+d')} \quad 1,0317 \quad \dots \dots (e)$$

for an arbitrary set of corresponding values of P' , A' and d' the set of values of P , A and d belonging to them in order that (e) be satisfied.

Then m can be determined from (10), namely

$$A-A' = \frac{6}{8} \frac{d^2 - d'^2}{m}$$

	η	$\log^{10} \frac{\beta^2}{1-\beta^2}$	$\frac{\beta^2}{1-\beta^2}$	β^2	$\frac{1+\beta^2}{\gamma} - (1-\beta^2)$	Denominator d	d	A	P
Vapour	0.95	1.2440	17.54	0.973	2.049	2.465	0.8578	0.6794	-1.0936
	1.05	1.1571	14.36	0.9674	1.840	2.318	0.9119	0.7509	-0.9966
	1.15	1.0741	11.86	0.960	1.665	2.196	0.9627	0.8223	-0.9092
	1.20	1.0339	10.81	0.957	1.587	2.142	0.9871	0.8581	-0.8685
Liquid	1.25	0.9955	9.874	0.953	1.515	2.091	1.0110	0.8939	-0.8297
	1.30	0.9559	9.035	0.949	1.448	2.044	1.0341	0.9296	-0.7927
	1.40	0.8801	7.588	0.940	1.326	1.959	1.0793	1.0011	-0.7235
	1.50	0.8067	6.408	0.930	1.217	1.883	1.1230	1.0726	-0.6599
	1.60	0.7353	5.436	0.919	1.118	1.814	1.1656	1.1442	-0.6015

from which follows:

$$m = \frac{6,016}{8} \frac{d^2 - d'^2}{A - A'} \quad , \quad \dots \quad (j)$$

as we saw (see III, p. 569) that for brevity's sake 6 is written for 6,016.

Thus we find e. g. that $d = 1,1230$ about corresponds with $d' = 0,8578$. For then the first member of (e) becomes 1,1030 and the second 1,1028.

But we draw attention to the fact that the determination of the coexisting phases near the critical point is exceedingly difficult on account of this that — in consequence of the almost horizontal course of the saturation curve — also neighbouring values of d give an almost equally good agreement.

Now we find further for m :

$$m = 1,0047.$$

As $\frac{1}{2}(d + d') = 0,9904$, we have:

$$\frac{\frac{1}{2}(d + d') - 1}{1 - m} = 2,0.$$

If however we take an only slightly higher value for d , e. g. $d = 1,1337$, to which $A = 1,0905$ corresponds — in which case (e) is almost as well satisfied as by the above value of d — we find

$$m = 1,0050.$$

But $\frac{1}{2}(d + d')$ is now = 0,9957, so that

$$\frac{1}{2}(d+d')-1 = 0,9.$$

in agreement with what experiment has taught us.

Though it appears in this way that the value of the coefficient b cannot be derived with certainty from the calculated values in the neighbourhood of the critical point: this is certain that it is now *greater* than with the ideal equation of state without association, in which case we found the value $\frac{2}{3} = 0,4$.

The value 0,9 is also in accordance with the well known fact that the limiting density at low temperatures would amount to about 3,8 times the critical density. So for $m = 0$ we have $\frac{1}{2}(d+d') = \frac{1}{2}(3,8+0) = 1,9$, so that the straight line which connects this point with the critical point has as coefficient of direction:

$$\frac{\frac{1}{2}(d+d')-1}{1-m} = 0,9.$$

If for a definite temperature (e. g. the critical) we wish to calculate the isotherm, we have:

$$\frac{f_2'}{f_1'} \varepsilon = \frac{8am}{2,1n-\gamma} - \frac{6,016}{n^2}$$

(see III § 8, p. 568), or as (e. g. for $v = 1$) $f_1' : f_2' = 1,007 : 1,004 = 1,003$, and $\frac{\alpha}{2,1n-\gamma} = A$ is put (see above):

$$1,003\varepsilon = 8,1m - 6,016d^2 \quad . \quad . \quad . \quad . \quad (5)$$

Now we can derive for successive values of q the corresponding values of A and d from the table calculated above (which we can extend to $q = 0$ and $q = \infty$), and in this way easily calculate the successive values of $1,003 \varepsilon$ for a definite value of m .

If in this way we have once calculated an entire isotherm for a definite value of m , e. g. $m = 1$, we find exceedingly easily all the other isotherms by adding $8,1(m'-m)$ to the found values of $1,003 \varepsilon$, when m' is the new reduced temperature.

But we will not enter any further into this subject now, which we think we have now studied from all sides, in the expectation that further theoretical investigations will give us a better insight into this subject.

Clarens, December 12, 1911.

Chemistry. — “*Studies on Tellurium II. On compounds of Tellurium and Iodine*”. By Prof. F. M. JÄGER and J. B. MENKE. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of December 30, 1911).

§ 1. The object of this investigation was to ascertain what compounds of tellurium and iodine can form from the binary fusions of the two elements and such in connection with the experience gained thus far in the study of the mutual behaviour of iodine and one of the other elements of the oxygen-group.

When we provisionally, disregard the oxygen itself, because in any case well defined compounds with iodine such as O_3I_2 are positively known, the chance of forming iodides of these elements is, evidently, not particularly great.

Of iodides of sulphur a great many were supposed to exist, such as S_2I_2 ¹⁾, S_2I_3 ²⁾, SI ³⁾, SI_2 ⁴⁾, SI_3 ⁵⁾.

After a long controversy it now seems well understood that these are merely *mixtures*, and the recent work of SMITH and CARSON⁶⁾ and a little later that of EPHRAÏM⁷⁾ have proved conclusively that from binary fusions of *S* and *I* no compounds are deposited. Iodine can take up 7 to 8% of S in solid solutions; but further there is only a eutecticum at 65°, and 81,3 mol. % of sulphur. The melting-point 66° attributed by GROSOURDY to the so-called S_3I_2 is, therefore, evidently the eutectic temperature. Sulphur in the liquid state has here probably the formula S_8 and the previously accepted double compounds of sulphur-iodides with As_2S_3 and SnI_4 have also proved to be only mixtures.

In an analogous manner we find described iodides of selenium SeI_2 and SeI_4 ⁸⁾. TROMMSDORFF, however, states that these products obtained by melting together the components, allow all their iodine

1) GROSOURDY, Journ. de Chim. Médic. 9 429; LAMERS, Journ. f. prakt. Chem. 84. 349. (1861); EMERSON, MAC IVOR, Chem. News 86. 5. (1902).

2) LINEBARGER, Amer. Chem. Journ. 17. 33. (1895); BOULOUCH, Compt. rend. 136 577. (1903); PRUNIER, Journ. Pharm. Chem. (6). 9. 421. (1899).

3) GAY-LUSSAC, Ann. de Chim. et Phys. 88. 319. (1813); GUTHRIE, Journ. Chem. Soc. 14. 57. (1862); MENKE, Chem. News 39. 19; (1879); MAC LEOD, Chem. News. 66. 111. (1892).

4) Besides the mentioned investigators, also: RATH, Pogg. Ann. 110. (116. 1860); HENRY, Journ. Pharm. Chem. 13. 403. (1848).

5) SMITH and CARSON, Zeits. f. phys. Chem. 61. 200. (1908).

6) EPHRAÏM, Zeits. f. anorg. Chem. 58. 338. (1908).

7) TROMMSDORFF, N. Journ. Pharm. (2). 12. 45. (1826); SCHNEIDER, Pogg. Ann. 129. 627. (1866); GUYOT, Compt. rend. 72. 685. (1871).

to be extracted by alcohol and GUYOT observed that on heating, the iodine volatilises. The SeJ_4 of SCHNEIDER was prepared in different ways; from $C_2H_5J + SeBr_4$; from $SeO_2 + HJ$; by melting Se with J . In all cases the character was doubtful and the little stability of these so-called compounds created suspicion. It is very probable that, as in the case of the sulphur, there is here also only a question of mixtures with a eutecticum, which is situated in the vicinity of 70° . A short time ago this has been finally confirmed by PELLINI and PEDRINA¹⁾, who demonstrated that from binary fusions only mixed crystals are deposited.

§ 2. The analogous problem in the case of the element tellurium is of importance from more than one point of view. On a previous occasion one of us²⁾ was able to conclude, from the behaviour of Te to S , to the complete analogy in this respect, between S, Se and Te . The behaviour of Te and J might therefore be expected to be also analogous to that of the elements S and Se .

Such a behaviour would then be in conflict with the statements as to the tellurium-oxides which are found in literature. On the other hand if we could meet with some compound which is permanent and, therefore, but little dissociated in the melt and which possesses a sharp melting-point, it might be possible to decide whether the atomic weight of tellurium is greater or smaller than that of iodine.

As regards the first fact we find indeed a description of several tellurim-iodides: TeJ_2 , TeJ_4 , TeJ_6 , by BERZELIUS and other investigators³⁾; the latter compound, however, has never been isolated and was only suspected by BERZELIUS to exist in the brown liquid obtained from telluric acid and HJ . TeJ_2 is said to be a substance readily fusible at about 80° and prepared by subliming 1 at. of Te with a little over 1 at. of J ; it readily loses iodine and finally leaves iodine-containing tellurium.

TeJ_4 ¹⁾ can be obtained as a hydrate $TeJ_4 \cdot HJ \cdot 8H_2O$ from TeO_2 and strong HJ -solution; the hydrate melts according to METZNER at 55° , and solidifies on cooling — at least in a closed tube, — again unchanged.

¹⁾ PELLINI and PEDRINA, *Atti dei Lincei* (5). 17. II. 78; *Chem. Centr. Bl.* (1908). II. 1010.

²⁾ F. M. JAEGER, *Proc.* (1910).

³⁾ BERZELIUS, *Ann. de Chim. et Phys.* 58. 113. 150, 225, 282, (1835); METZNER, *ibid.* (7). 15. 203. (1898). WHEELER, *Z. f. anorg. Chem.* 3. 428. (1893); GUTBIER and FLURY, *Z. f. anorg. Chem.* 32. 31, 108. (1902); HAMPE, *J. Chem. Soc.* 54. 887. (1888).

Further, there are double salts of TeJ_4 with NH_4J , KJ etc. described by WHEELER. GUTBIER and FLURY prepared the compound from a very concentrated solution of telluric acid with strong HJ ; it is totally resolved by H_2O with formation of TeO_3 ; alcohol also decomposes the compound. According to their opinion however, the substance TeJ_2 cannot be considered as a compound and no trace of this was observed neither in the case of TeJ_4 . It is, therefore, evidently of importance to obtain a better insight in the matter.

§ 3. For our purpose we have made use of the tellurium obtained and purified ¹⁾ by one of us (J.) in the manner described previously. The investigation on tellurium was quietly continued notwithstanding the alarming statements of BROWNING and FLINT²⁾ on the complicated nature of tellurium, because their method employed — after experiences gained in the hydrolysis of tellurium-chloride — appeared to us very much open to criticism. A short time ago the incorrectness of their conclusions was proved elsewhere³⁾, and after the exact determinations of MARCKWALD and FOIZIK, BAKER and BENNETT, LENHER and HARCOURT and BAKER⁴⁾, the elementary nature of tellurium may be accepted as being undisputable. As atomic weight has been accepted here the most probable value of **127.6** and **126.9** for iodine. The latter was purified and distilled in the usual manner.

In order to prevent any loss of iodine, the binary fusions were prepared in sealed tubes; with mixtures containing 80% of Te or more, this is unavoidable. Weighted quantities of the two elements were thus melted together at 500°. After solidifying, the mass was powdered and the cooling curve repeatedly recorded in another tube made of hard glass which possessed an egg-like form and to which was sealed a hard-glass screening tube for the thermo-element. With mixtures containing 0—10% of Te the heating-curves were determined in an oil-bath; for higher temperatures a small gas-furnace as previously described in the case of the tellurium-sulphur-mixtures was always employed. After the behaviour of the melt was thus sufficiently known, an analysis was made there-of by placing about 0.15 gram in a distilling flask and adding 20 cc. of sulphuric acid

¹⁾ Loco citato.

²⁾ BROWNING and FLINT, Amer. Jour. of Science (4). **28**. 347. (1909); (4). **30**. 209. (1910).

³⁾ HARCOURT and BAKER Trans. Chem. Soc. **99**. (1911); Chem News **104**. 260. (1911).

⁴⁾ MARCKWALD and FOIZIK, Ber. d. chem. Ges. **43**. 1710. (1910); BAKER and BENNETT, Trans. Chem. Soc. **91**. 1849. (1897); LENHER, Jour. Amer. Chem. Soc. **31**. 1. (1899); HARCOURT and BAKER, loco cit.

(1,4). After passing a slow current of CO_2 through the ground-joint apparatus, the liquid was carefully distilled into a receiver filled with Na_2SO_3 -solution, while through the funnel-tube a solution of sodium-nitrite ran continuously into the reaction-mixture. In this manner all the iodine could be carried over. To the distillate was now added an excess of $AgNO_3$ and Na_2SO_3 , then nitric acid (D.1.4) and the liquid boiled for some time. The AgI was then determined by weighing.

For the measurement of the higher temperatures was used a platinum-platinumrhodium thermoelement, which was standardised on the melting points of *ice*, *tin*, *lead* and *zinc*; for the lower temperatures also an element standardised on *ice* and *lead* and made of silver and constantan. Evidently a stirring of the mass was excluded; consequently, undercooling often took place, which rendered the

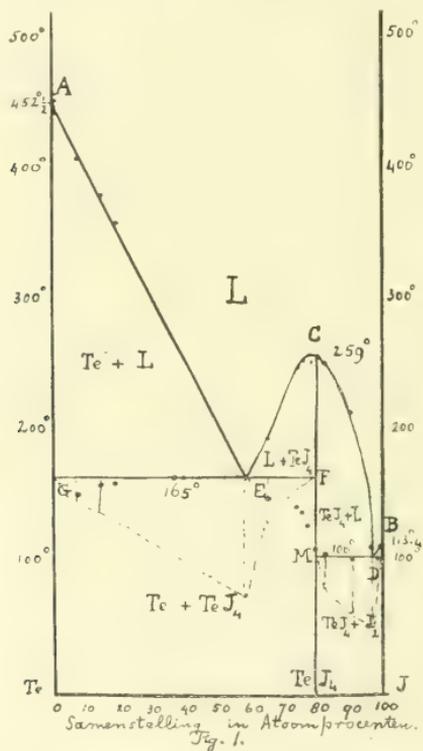
Binary Melting point line from tellurium and iodine.

Composition of the melt				First effect	Under-cooling	* Second effect	Under-cooling	Duration in seconds
in mol. %		in $\frac{0}{100}$ by weight						
<i>Te</i> :	<i>I</i> :	<i>Te</i> :	<i>I</i> :					
100	0	100	0	452°·5	—	—	—	—
92.2	7.8	92.3	7.7	405	29°	152° (155°)	2° (5°)	120"
84.7	15.3	85.3	14.7	385 (386)	5 (10)	159 (161)	6 (5)	180
80.7	19.3	81.3	18.7	362 (360)	10 (10)	161 (161)	3 (3)	—
71.4	28.6	71.6	28.4	306	—	165	—	—
41.66	58.34	41.8	58.2	169	—	165	10 (12)	840
35.0	65.0	35.2	64.8	196 (195)	0 (0)	151 (152)	10 (10)	330
25.6	74.4	25.7	74.3	250 (250)	0 (0)	141 (140)	0 (0)	—
24.8	75.2	24.9	75.1	253 (253)	0 (2)	139 (137)	1 (2)	—
22.4	77.6	22.5	77.5	259 (258)	2 (2)	130 (129)	—	120
20.5	79.5	20.6	79.4	255	—	109 (109)	—	—
20.4	79.6	20.5	79.5	258 (259)	—	110 (110)	—	—
17.5	82.5	17.5	82.5	256 (256)	3 (5)	106 (107)	0 (0)	540
10.0	90.0	10.0	90.0	217	—	106	0	840
3.0	97.0	3.0	97.0	—	—	106	—	900
0	100	0	100.0	113.4	—	—	—	—

measurement of the *time-intervals*, if not quite illusory, still rather uncertain. These must, therefore, be only taken as approximations.

The data obtained are collected below and represented graphically in Fig. 1 in the usual manner.

In previous determinations the eutecticum was always found at 170° up to 60% of *Te*.



§ 4. From these data and from the diagram of Fig. 1, it may be concluded that from binary fusions a single compound is only formed, namely TeJ_4 , which in the melted condition is fairly strongly dissociated. The formerly accepted TeJ_2 is a product which lies in the neighbourhood of the eutecticum, situated between tellurium and this compound; this eutecticum has a content of about 41% of *Te* and corresponds with a temperature of 165° . The eutecticum at the iodine-side lies in the immediate vicinity of the pure iodine and corresponds with a temperature of about 108° . Solid solutions are evidently not formed to any extent. No trace can be found either of a compound TeJ_2 .

§ 5. The compound TcJ_4 was once more recrystallised by us from strong HJ with addition of some NH_3 . Instead of the ammonium-compound, we obtained crystals with a metallic lustre, which on analysis contained 1% more of J than corresponded with TcJ_4 . A little too much iodine was also found in the hydrate obtained from telluric acid.

An investigation by one of us as to the phenomena occurring in solutions of TcJ_4 in strong HJ with excess of iodine, is already in progress.

December 1911.

Inorg. Chem. Laboratory
University, Groningen.

Chemistry. — “*The question as to the miscibility in the solid condition between aromatic Nitro- and Nitroso-compounds*”. III. By Prof. F. M. JAEGER and Dr. J. R. N. VAN KREGTEN. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of December 30, 1911).

§ 1. In consequence of the formation of solid solutions between *o*-Nitroso-benzoic acid and *o*-Nitro-benzaldehyde, also owing to a treatise of BRUNI and CALLEGARI¹⁾ on the formation of solid solutions between aromatic nitroso- and nitro-derivates, as a general phenomenon, investigations have been carried out by one of us (J.) to get a better knowledge of the mutual relation of both classes of nitrogen-derivatives²⁾. This investigation which comprises many nitro-, and nitroso-derivates of analogous structure could only lead to the conclusion, that, certainly, in some cases, there was a question of a morphotropic relation and resulting miscibility, but that in most cases such a relation did not exist and could not, in homologous series, even be called a generally occurring phenomenon.

In the following some more data regarding these questions have been collected, which enable us to supplement the previous statements in some respects.

§ 2. Nitrobenzene and Nitrosobenzene.

The simplest representatives of the compounds to be discussed are nitro- and nitroso-benzene.

¹⁾ BRUNI and CALLEGARI. Gazz. Chim. Ital. **34**. II. 245. (1904).

²⁾ F. M. JAEGER, Proc. 1905. 658, 1908. 436; Zeits. f. Min. und Kryst. **42**. 236. (1906). Comparisons have been made between: *p*-Nitro-, and *p*-Nitroso-diethylamine; Nitro-, and Nitrosobenzene; *p*-Nitro-, and *p*-Nitroso-phenol; *o*-Dinitro-, and *o*-Nitro-nitrosobenzene; *o*-Nitro-, and *o*-Nitroso-aceto-anilide.

The *nitro-benzene* was purified by three times freezing and subsequent distillation. The fraction boiling at $211^{\circ},6$ under 76,7 m.m. pressure was used for the investigation. The thermometer was compared with a normal thermometer; at 0° it appeared to indicate $0^{\circ},2$, and at 100° , $0^{\circ},1$ too low.

The solidifying-point, with different outer-bath-temperatures, appeared to be always $+4^{\circ},9$; the same temperature was also found for the melting-point. In these last experiments the solid substance was heated slowly in an oil-bath. Pure *nitrosobenzene*¹⁾ therefore solidifies and melts at $+4^{\circ},9$.

BINARY MELTING-POINT-LINE OF NITRO-BENZENE
+ NITROSO-BENZENE.

Composition in mol. %		Solidifying point	Eutectic temp.	Time in seconds
% <i>NO₂</i> -Compound	% <i>NO</i> -Compound			
100.0	0.0	$4^{\circ},9$	—	—
97.5	2.5	3.6	—	—
95.7	4.3	3.1	$0^{\circ},8$	—
94.1	5.9	2.1	$-0^{\circ},7$	240
92.3	7.7	1.2	0	480
88.9	11.1	—	0	560
86.0	14.0	—	0	1080
82.8	17.2	1.8	$0^{\circ},1$	990
78.3	21.7	5.2	$0^{\circ},2$	960
67.0	33.0	18.6	$0^{\circ},5$	780
56.5	43.5	27.5	$0^{\circ},2$	630
45.3	54.7	36	$0^{\circ},2$	480
26.4	73.6	46	$-2^{\circ},1$	240
15.0	85.0	54.8	$-4^{\circ},0$	—
7.3	92.7	61	$-10^{\circ},0$	—
4.0	96.0	60	—	—
2.1	97.9	60.2	—	—
0.0	100.0	68	—	—

1) In the literature are given for this temperature-values varying from $+3^{\circ}$ and $+5^{\circ}$; for the boiling-point is found 208° under 760 m.m. pressure. We, however, find both values a little higher.

The *nitroso-benzene* was first repeatedly recrystallised from hot alcohol and then from benzene. The melting-point was always found too low. Afterwards the substance was recrystallised from a mixture of alcohol and ether in an atmosphere of carbon-dioxide to prevent oxidation. After rapid suction it was dried in vacuo over sulphuric acid. The melting-point was then found to be at $+68^{\circ}$. This compound, however, is decomposed a little above its melting-point (at about 7°) suddenly and with great evolution of heat, with formation of a brown liquid.

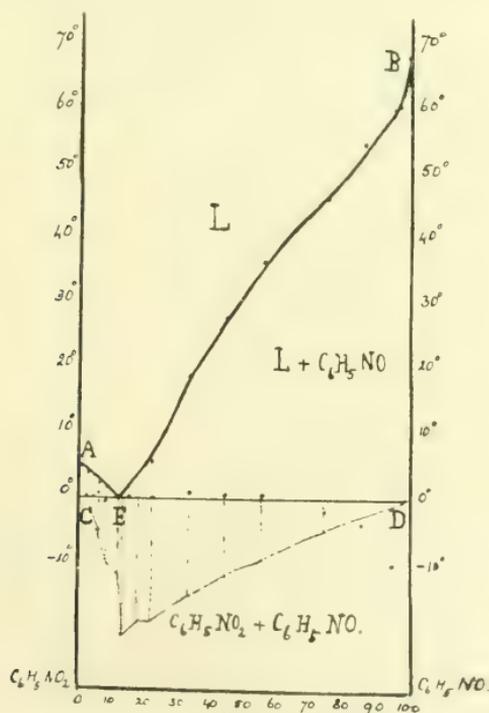
If the decomposition, caused by careless heating, is only partial, the solidifying-point will be found later to be somewhat lower.

Solidifying-points only could be recorded with sufficient sharpness.

The data given in the table on p. 730 have been recorded by us.

These data are represented in fig. 1 in the usual graphical way.

§ 3. From this it appears that *nitro-* and *nitroso-benzene* — perhaps



with exception of concentrations situated in the immediate vicinity of the axes — do not, or hardly at all, form mixed crystals.

A miscibility at exceedingly small concentrations of both components occurs, however, more or less distinctly in all systems formed from carbon-compounds.

Otherwise, the differences in crystal-form are not readily noticed, because the *nitro-benzene* is liquid and can only be obtained from fusions at a low temperature in a crystallisable form. It is, probably, rhombic and analogous to the crystal-form of benzene, at least in one of the two parameter-relations.

Nitroso-benzene is rhombic-bipyramidal ¹⁾ with $a : b : c = 1,4770 : 1 : 0,7006$ and the forms: {100}; {110}; {111}; {310}; {221}; {001}.

Benzene is rhombic, with $a : b : c = 0,891 : 1 : 0,799$; these parameters are in no case analogous to those of the *nitroso-derivative* and probably also not to those of the *nitro-compound*.

All this seems to indicate that there can be no question either of

BINARY MELTING-POINT-LINE OF p-NITRO-ANILINE + p-NITROSOANILINE

Composition in mol. %		Solidifying temperature	2nd Heat effect
% NO_2 -anil.	% NO -anil.		
100.0	0.0	147°	—
91.4	8.6	144	141
82.9	17.1	137.7	—
74.7	25.3	133	—
66.7	33.3	125.3	—
58.6	41.4	120.5	119
50.8	49.2	119	120
43.2	56.8	—	120
35.6	64.4	—	115
21.0	79.0	—	124
13.8	86.2	decomp.	124
6.9	93.1	decomp.	124
3.4	96.6	decomp.	122
0.0	100.0	169°	—

¹⁾ F. M. JÄGER, Zeits. f. Min. u. Kryst. **42**, 246. (1907).

a pronounced form-analogy, or of a perceptible formation of solid solutions between *nitroso-* and *nitro-benzene*.

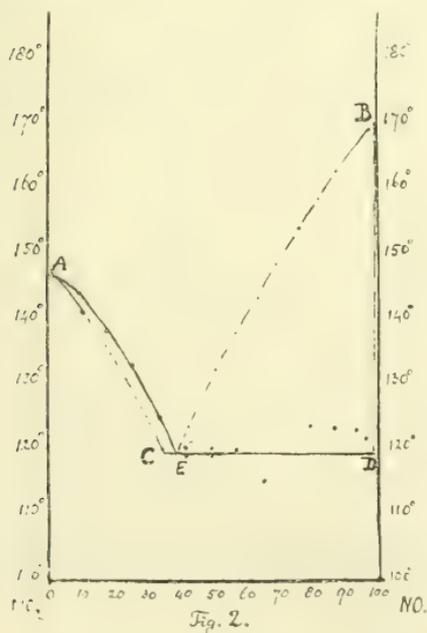
§ 4. *p-Nitro-Aniline* and *p-Nitroso-Aniline*.

Whereas, on account of the presence of *H*-atoms in the amino-group, a tautomeric structure of the *nitroso*-compound is not excluded, this system was sufficiently interesting to deserve further investigation. This investigation, however, was, unfortunately, rather unsatisfactory, owing to the fact that a decomposition of the *p-Nitroso-Aniline* could not be prevented: whereas the melting point is situated at 168° — 169° , the temperature of decomposition is about 170° .

The *p-Nitro-Aniline* used was recrystallised from benzene and also from water; at 100° 2,2 grams of the compound dissolve in 100 cc. of water. The melting temperature proved, on repetition, to be 147° .

The *p-Nitroso-Aniline* was recrystallised from benzene and dried in a current of carbon-dioxide to prevent oxidation. Immediately after melting at 163° — 169° a sudden decomposition took place with evolution of heat and a violent evolution of gas.

By working carefully, the approximate data contained in the table on p. 732 could still be obtained.



In fig. 2 these results are represented graphically; there can be no question of an exact determination of the diverse points, but only of a first orientation. The whole seems to point to a formation of mixed crystals at the side of the *Nitro*-compound to a considerable concentration (35 to 40 %) with the *Nitroso*-compound, but to only a slight mixing at the side of the latter.

As all the fusions were too dark in colour owing to the decomposition, a microscopical investigation did not much avail. In no case, however, is there any question of a continuous mixing-series.

A few remarkable phenomena, which are communicated here, were, however, noticed microscopically.

From the brownish-red melt of 83% NO_2 - and 17% NO -aniline, there are deposited on cooling, at first fairly rapidly, elongated, orange-red needles in thick bundles. After waiting for some time, these apparently become covered with an innumerable number of very small yellow needles; if a primary needle has been placed between two crossed nicols in such a position that it gets dark, it suddenly becomes luminous in the process described. There are now present in the preparation two components: the partly unchanged, original brownish-red needles and the subsequent yellow ones; both are feebly dichroic. In convergent polarised light is seen a remarkable, biaxial interference image can be observed, namely four orange-red, equilateral hyperboles and a green cross; apparently, the axial planes for the diverse colours are crossed, and an enormous dispersion is present.

A mixture with 73% of NO_2 -compound also behaves, optically, like the above. The transformation, however, takes place more slowly than in the first case. With the 51% NO_2 -compound brownish-red needles are obtained; of a transformation little more is visible; with the 21% NO_2 -compound there are present dichroic (red-orange yellow) aggregates, spherulitically built. In these two latter cases it is difficult to decide whether we have one or two structural components; the fused masses are also almost opaque by decomposition.

In each case, the mixed crystals at the NO_2 -side, therefore at a lower temperature, seem to pass into another modification, with considerable changes in their symmetry and volume.

§ 5. *p*-Nitromonoethylaniline and *p*-Nitrosomonoethylaniline.

The *p*-Nitro-Monoethylaniline was recrystallised repeatedly from benzene and afterwards the heating- and also the cooling-curves were several times recorded.

The melting-point was situated at 94°, the solidifying-point at 93°.9. The melting point given in the literature (95°—95°.5) is, evidently, a little too high.

The *p*-Nitroso-Monoethylaniline was also recrystallised repeatedly from benzene; it melted, constant, 75°—76° in a capillary tube; when taking the melting-, and solidifying-points in the more delicate manner, these were, however, always situated at 74°, undercooling was always avoided by inoculation.

The following data were obtained:

BINARY MELTING POINT LINE OF p-NITRO-
 AND p-NITROSOMONOETHYLANILINE

Composition in mol. %		Solidifying temperature	Eutectic temperature
% NO ₂	% NO		
100	0	94°	—
95	5	92	ca. 40°
90	10	89.2	54
80	20	84	53
70	30	77.5	54
60	40	73	51
50	50	64.7	51.4
40	60	58	54.6
30	70	54	—
20	80	59.6	49
10	90	66.9	46
5	95	70.5	53
0	100	74.1	—

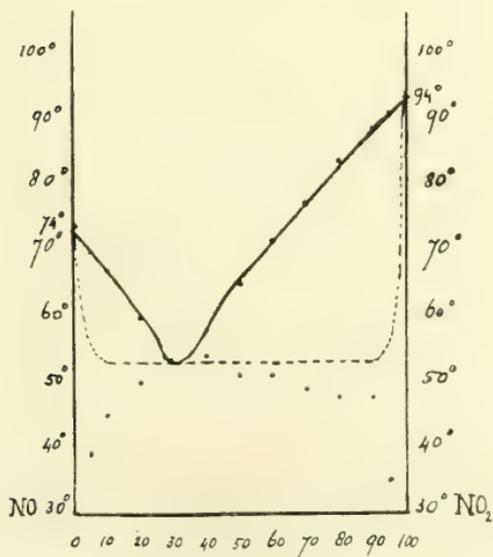


Fig. 3.

As, notwithstanding the inoculation, a great undercooling was sometimes perceptible, the deviations especially from the eutectic temperature are considerable here and there.

§ 6. Although the diagram makes the impression as if no mixing in the solid condition were present here, but that there is only a question of an ordinary binary melting-point-line with a eutecticum, — in each case declining at both sides, — the microscopical investigation still shows that we have no right to look at the matter in this way without further evidence.

The pure *nitroso*-compound presents itself under the microscope in the form of spherulitically-grouped, strongly dichroic platelets; the colours are may-green and grass-green.

The *nitro*-compound forms long, lemon-yellow but faintly dichroic platelets, which between two crossed nicols do not become dark in a single position, but exhibit on turning of the table, a vivid display of colours, green, yellow etc. In convergent light it appears that we have here nearly parallel to the direction of the "normal" of the platelet, the bisectrix of a very remarkable interference image of a biaxial crystal, for we notice a dark horizontal beam which intersects a bright green field in the centre, while in the vertical plane are situated two red fields, which are intersected by dark beams, terminating at some distance from the centre. The green field is limited in four quadrants by a system of bluish-purple equilateral hyperboles.

Evidently we are dealing here with a crystal, whose axial plane for red and green light is the longitudinal direction of the needles, but for blue rays their latitudinal direction: such in connexion with an exceedingly small angle for the diverse colours, while that for the red is larger than that for the green.

If now we investigate the binary, solidified fusions, it is at once visible to the naked eye that they congeal to a homogeneous aggregate of crystals. From solutions in ethyl-acetate are also formed homogeneous green crystals.

With 5% NO_2 -compound were found green fern-like mixed crystals; with an increasing content of the NO_2 -substance their colour turns more and more yellowish-green, but the solidified melt remains existent as a single crystal-form. Only at a 40% NO_2 -compound the remarkable axial image of the pure *nitro*-compound plainly returns; at 70% the crystals are nearly monaxial for red; at 90% and 95% of the NO_2 -compound, the mixed crystals obtained from a solution in ethyl-acetate are beautifully greenish-yellow, very faintly dichroic and exhibit the characteristic axial image in a remarkably plain

manner. These experiments quite confirm the suspicion that a *continuous series of mixed crystals* is formed here. If so, there is no other possibility but to assume that the binary melting-point-line is also a continuous curve with a minimum temperature at 54° and a content of about 30% of the *nitroso*-compound; and that owing to the occurring undercooling, and to the evidently incomplete setting in of the equilibria, the solid line has declined to such an extent that it nearly assumes the form of a eutectic horizontal line. Such has been already observed previously in systems without a minimum in the liquidus-line; compare for instance the case of *Sb + Bi* investigated by HÜTTNER and TAMMANN¹⁾.

True in this particular case the said authors attribute the cause of the deviations to the fact that the mixed crystals which have deposited at first, get coated and that it then becomes impossible for them to get into equilibrium with the melt at any moment; but they still point out that a similar behaviour may be expected each time when the said setting in of the equilibrium takes place with insufficient velocity, and that might be the case here also. The formation of an uninterrupted series of mixed crystals both from solutions and binary fusions, and this without subsequent transformations or dissociations agrees with this view.

§ 7. *p*-Nitro-Monopropyl-Aniline and *p*-Nitroso-Monopropyl-Aniline.

Finally, we have investigated the system of the above compound in the same way.

The *p*-Nitro-derivate was first recrystallised from hot benzene from which splendid, large crystals are deposited. Their melting-point appeared to be 53° — 54° ; moreover they were found to turn soon turbid owing to loss of benzene. The compound was, therefore, powdered, dried and repeatedly recrystallised from absolute alcohol. From this are also sometimes deposited splendid crystals which melt constant, at 64° — 65° . They mostly have curved planes and consequently can only be measured with difficulty.

The *p*-Nitrosomonopropylaniline was also purified by recrystallisation from benzene; it then also contains benzene of crystallisation and melts at 45° — 50° .

After expelling the benzene in vacuo and repeatedly recrystallising from a mixture of absolute alcohol and ligroin, the melting point, in a capillary tube, was found to be 58° , which value is also given in the literature.

¹⁾ HÜTTNER and TAMMANN, Zeits. f. anorg. Chem. **44**, 131. (1905).

BINARY MELTING-POINT-LINE *p*-NITRO- AND
p-NITROSOPROPYLANILINE

Composition in mol. %		Initial solidi- fying point	End solidi- fying point
% NO_2	% NO		
100	0	62.9	—
95	5	61.2	— (weak effect at 58°)
90	10	59.3	— effect at 49°)
80	20	56.5	54.5
70	30	52.9	51
60	40	49.3	47.5
50	50	47.0	44.5
40	60	44.5	43
30	70	42.8	42
20	80	40.5	40.5
10	90	48	—
0	100	56.5	—

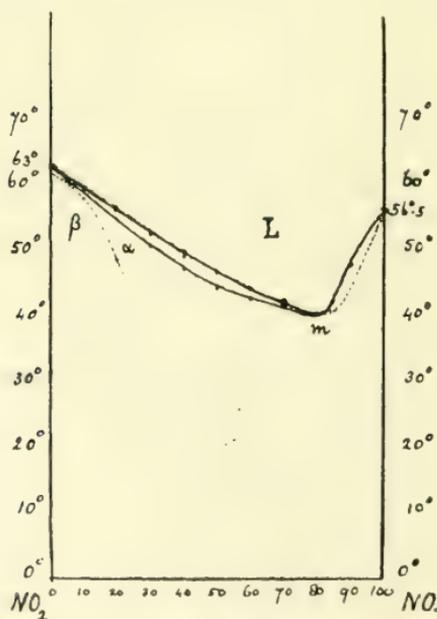


Fig. 4.

First of all, the solidifying points of both derivatives were accurately determined by recording the cooling lines. In this way was found, with slight undercooling, $62,9^{\circ}$ C. for the solidifying point of the *nitro*-compound and $56,3$ — $56,5^{\circ}$ C. for the *nitroso*-derivative.

Successively, the following mixtures were investigated (see table previous page).

§ 8. These data graphically represented in fig. 4, prove that there exists here a continuous series of solid solutions between the two components, with a minimum temperature of $40,5^{\circ}$ C. and a concentration of about 80 % of the *nitro*-compound.

The microscopical investigation also confirms the existence of such a series of mixed crystals.

The *p*-*Nitro*-compound crystallises from its yellow melt with great rapidity in lemon-yellow, hexa- or octangular plates, which are *immediately* followed by a darker coloured modification, generally occurring in parallelogram-like plates, joined in all directions. They are strongly dichroic: yellowish-white and dark yellow. Between crossed nicols they are black and on our turning the table slightly to the right or to the left, the colour changes to brown or green. In convergent polarised light one branch of a hyperbola is visible eccentrically, and coloured red at the inner side and blue at the outer side. Very strong dispersion.

The *nitroso*-derivative has an extraordinarily small crystallisation-velocity; fern-like aggregates exhibit a splendid steel-blue lustre and are strongly pleochroic: green and brownish-yellow.

Mixed crystals with 5, 10, 40, 60, 90% *NO*-compound have been investigated. A yellowish-green melt with 5% *NO*-derivative solidifies to an aggregate of yellow plates of the *NO*₂-form, which after about half a minute suddenly burst and pass into another modification of a more yellowish-green colour and a much stronger double refraction; previously dark crystals become luminous etc. The crystallisation-velocity is still very considerable; whereas the first modification, between two crossed nicols, is dark in two positions, the second is not extinguished in any position. After some time the first crystallisation is succeeded by a feather-shaped aggregate of the second one.

With 90 % of the *Nitro*-compound there is hardly anything more to be observed of the polymorphous conversion, notwithstanding the great velocity of crystallisation. With 60% *NO*₂-derivative we have homogeneous mixed crystals which are strongly dichroic: green and bright-yellow. With 40 % idem; the crystals are: dark-brown and yellow. With 10% *NO*₂-compound the velocity of crystallisation is

already extraordinarily small; mostly spherulitic aggregates which are strongly dichroic: bright yellow and green.

§ 9. The above proves that the *nitro*-compound is here also dimorphous; with the 90% mixed-crystal, the strongly decreased temperature of conversion of the pure NO_2 -substance — which lies just below the melting point, — is still determinable by the corresponding heat-effect.

With a larger content of NO -compound, that determination is, however already impossible owing to the enormous retardation of the polymorphous conversion through the admixture of the slowly crystallising *nitroso*-derivative.

§ 10. From the investigation it has appeared anew, that mixed crystal formation can occur in binary fusions of corresponding aromatic *Nitro*- and *Nitroso*-derivatives, but that this miscibility must *not* be looked upon as a general property of these compounds in regard to each other. Moreover, the mutual behaviour of these two kinds of substances becomes often more complicated by the appearance of polymorphous modifications and by the difference in crystallisation-velocity in the two components. The most simple representatives of this class of substances *nitrobenzene* and *nitrosobenzene* do *not*, or only in an insignificant degree, form solid solutions with each other.

Inorg. Chem. Lab. University Groningen.

Chemistry. — “*Photo-electric phenomena with Antimony sulphide (Antimonite)*”. By Drs. J. OLIE JR. and H. R. KRUYT. (Communicated by Prof. v. ROMBURGH. (Preliminary communication).

(Communicated in the meeting of December 30, 1911).

JAEGER¹⁾ discovered some years ago a very remarkable property of native antimonite which, however, seemed to belong exclusively to the large crystals of this mineral found only in Shikoku (Japan). The mineral exhibited, as regards sensitiveness of the electric conductivity power to irradiation, a very great analogy with selenium. Illumination strongly lessened the resistance of the material. The fatigue so troublesome with selenium for the practical application of this property was here but insignificant. Immediately after stopping the irradiation, the resistance regains about its original value called, briefly, “the darkness resistance”.

¹⁾ Proc. Kon. Acad. v. Wet. Amsterdam 1907, p. 809—814.

JAEGER, however, found that the remarkably strong sensitiveness to light totally disappeared on remelting; the specific resistance then also became several thousand times smaller. On powdering the mineral, the sensitiveness to light also completely disappeared, but the resistance was only little affected. It was therefore obvious to connect the sensitiveness to light with the macrocrystalline structure of the material, to which JAEGER already called attention¹⁾ without, however, attempting to further explain the phenomenon.

As, however, with none of the other substances which exhibit a similar sensitiveness to light in a greater or lesser degree, such as selenium²⁾ tellurium, sulphur, Ag₂S, AgJ etc. (although in most of these substances the causes of the phenomenon are far from being elucidated) anything like a dependence of the photo-electric effect on macrocrystalline structure has up till now been noticed, the antimonite would then constitute a case by itself. This seemed to us somewhat improbable and caused us to investigate whether the explanation of the phenomena observed by JAEGER might not perhaps be found by working in another direction.

Now, according to JAEGER, his Japanese antimonite is very pure and has almost exactly the composition Sb₂S₃; all other specimens (none of which exhibit a light effect) are less pure. We, therefore prepared from pure materials³⁾ an artificial antimonite in order to test this as to its sensitiveness to light. Already at a first experiment we succeeded in obtaining a strongly sensitive preparation⁴⁾ by rapidly heating, in an open tube, antimony powder mixed with a small excess of sulphur. The subsequent orientating experiments gave alternately a positive or negative result, which made us resolve to investigate systematically a series of mixtures of varying quantities of S and Sb in order to ascertain whether small modifications in the composition of the antimony sulphide, which was otherwise quite free from foreign substances, might be the cause of the greater or lesser sensitiveness to light.

As on heating in open tubes in an atmosphere of carbon dioxide a loss of sulphur through volatilisation could not be avoided, we proceeded to operate in sealed evacuated tubes, which could be

¹⁾ Zeitschrift für Krystallographic etc. Vol. XLIV, p. 45—48.

²⁾ By one of us, an explanation of the phenomenon in the case of selenium has been given from a phase-rule point of view H. R. KRUYT, Die dynamische allotropie des Selens Zeitschr. f. Anorg. Chem. 64, p. 305 (1909).

³⁾ Sb from KAHLBAUM. S recrystallised from CS₂.

⁴⁾ The illumination always was done in the same manner with a small Halbertsma arc-lamp at about 30 cm. distance from the preparation.

heated in a specially constructed oven at about 600° and also be regularly shaken to make sure of a complete homogeneous mixing.

As regards the result of this investigation it may be stated provisionally that the pure compound — Sb and S in the exact proportion Sb_2S_3 — appeared to possess the highest photo-electric effect. This sensitiveness to light amounted in some cases to about 400% ¹⁾. This sensitiveness relates to Sb_2S_3 in massive little rods of about 10 mm. in diameter. As the light effect must be a superficial action and as relatively thick massive rods are therefore a less advantageous form to promote this effect, the relative sensitiveness can be very strongly enhanced by choosing a more suitable form of antimonite-cell in which the relation of the surface to be irradiated to the section of the conductor is very much larger. In any case it has appeared that the observed sensitiveness to light in artificial antimonite is of the same order as that found by JAEGER in the native mineral²⁾ and which we have verified ourselves with Japanese Antimonite procured from KAHLBAUM. We hope, shortly, to refer more in detail to the method employed in the investigation of the dependence of the photoelectric effect on the composition of the substance. In the main it amounted to this, that by means of a very sensitive instrument (galvanometer, system SIEMENS HALSKE *Deprez-Arsonval*) we determined the relative conductivity power in darkness of small rods of antimonite of different composition and also the relation of the "conductivity in darkness" to their "conductivity in the light" (namely the conductivity power on illumination).

From the relative conductivity power in darkness and better still from the temperature coefficient thereof we were able to deduce the form of the melting diagram of the system S—Sb in the sphere investigated³⁾ that is in the vicinity of the compound Sb_2S_3 ; starting from the compound towards the antimony side we first found a very small mixed crystal sphere — about 0.3 at % and further a sphere of partial miscibility. All this is greatly in harmony with the investigations published in these proceedings, by JAEGER⁴⁾ on the system S—Sb where the melting diagram was constructed by means of a thermic analysis. JAEGER, however, found no mixed crystals. It is, however, just this mixed crystal series, (notwithstanding its small extent

1) That is to say when the conductivity power in the dark is expressed in an arbitrary measure, say 100, this rose to 500 by illumination.

2) Prof. JAEGER kindly obliged us with one of his antimonite-cells for comparison.

3) From 57—62 at. % of sulphur.

4) *Verslag Kon. Akad.* November 1911 p. 497—510.

and the difficulty to determine thermically such a very small sphere with certainty) which could be determined very sharply by the electric process. And this seems to us all the more of importance because a connection seems to exist between the appearance of solid solutions on the one side, photoelectric or photochemical effects and photoelectro- or triboluminosity on the other side.

We further got the impression that certain very small impurities may be of influence on the sensitiveness to light, and think we have observed at any rate an influence exerted by the kind of glass of which the melting tubes were constructed. In a whole series of experiments which took place, accidentally, with tubes constructed of a different kind of glass, we obtained not a single sensitive preparation, but when again using tubes of the old kind of glass the phenomenon reappeared as expected.

In this may be probably found, in our opinion, a partial explanation of the fact that, contrary to JAEGER's experience, we succeeded in remelting the native (Japanese) antimonite *without* this losing its sensitiveness to light. It is, however, necessary to operate, as we did, in sealed evacuated tubes. The compound at the melting point is already somewhat dissociated so that the operation in an open tube could not take place without loss of sulphur and change in the composition of the melt. According to our observations this loss of sulphur need amount to only 0.5 at % to obtain a totally inert preparation.

The conductivity power in darkness remained, on remelting, also quite of the same order. On the other hand it appeared that on powdering the mineral, which was then again compressed to a very solid pastille, the conductivity power very strongly decreased. The light effect, however, remained unaffected.

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Chemistry. — "*On gas equilibria*". By Dr. F. E. C. SCHEFFER. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of December 30, 1911).

1. It may be accepted as known that the total energy, the free energy, the entropy and the thermodynamic potential are quantities which can only be determined with the exception of an additive constant. In the purely physical processes, i.e. changes of state, in which the molecules of the substances do not change, these constants need not be taken into account, and on the other hand a physical

change can teach us nothing about the values of these constants. In chemical changes, however, this *is* the case, at least partially. If in a mixture of substances a chemical reaction can take place, a determination of the energy of transformation under definite circumstances will make known to us the algebraic sum of the constants of energy of the reacting substances, at least if we know the energy in its dependence on the quantities that determine the state. Each of the constants in itself remains quite indefinite just as for physical changes; experiment only gives us the algebraic sum of the constants of energy, in which the constants of the substances of one member of the equation of reaction are taken positive, those of the other member negative.

We find something similar for the entropy. The constants of entropy for the purely physical processes are without any importance, but a chemical transformation which is conducted isothermic and reversible may make the algebraic sum of the constants of entropy known to us, provided we know how the entropy of each of the substances depends on the independent variables.

Of late the sum of the constants of energy, resp. entropy, and especially the latter have been the subject of many a treatise. As the sum of the constants of entropy occurs in the expression for the chemical equilibrium as a constant, its knowledge is of the greatest importance for the calculation of these equilibria. Hence Prof. HABER in his work on the "Thermodynamik technischer Gasreaktionen" repeatedly calls attention to the so-called "thermodynamisch unbestimmte Konstante", which is the aforementioned algebraic sum of the constants of entropy. And also Prof. NERNST's theorem of heat deals with the determination of these constants, for the so-called "constant of integration" of the chemical equilibrium contains these constants of entropy.

For a calculation of the constants of entropy from the theory a priori an idea of the chemical action i.e. the knowledge of the so-called forces of affinity, will be indispensable — BOLTZMANN carried out a first attempt to do so in his "Gastheorie" — for the present we shall have to content ourselves with a calculation of these constants from the observations.

In the first place, however, the knowledge of the energy and the entropy as function of the quantities which determine the state is required for such calculations. When, to take the simplest case, we confine ourselves to rarefied gases, we know that the molecular energy and the entropy of a simple gas can be represented by:

$$E = E_{T=0} + \int_0^T c_v dT \dots \dots \dots (1)$$

$$H = H_{T=1} + \int_1^T \frac{c_p}{T} dT - R \ln c, \dots \dots \dots (2)$$

in which $E_{T=0}$ and $H_{T=1}$ represent the aforesaid constants of energy and entropy, c_v the real molecular specific heat, T the absolute temperature, c the concentration (number of gramme molecules per Liter), and R the molecular gas constant (1,985 cal.).

If at a definite temperature we now measure the algebraic sum of the energies (ΣnE), i.e. the heat of transformation at constant volume, and the sum of the entropies (ΣnH), i.e. the latent heat for a reversible isothermic transformation divided by the absolute temperature, we can find the values of $\Sigma nE_{T=0}$ and $\Sigma nH_{T=1}$ by calculation, if we know c_v as function of T .

The value of $\Sigma nE_{T=0}$ is generally calculated, indeed, according to equation (1) from the calorimetric data. The sum of the constants of entropy, on the other hand, is generally not determined directly from the latent heat, but indirectly from the value of the constant of equilibrium.

If we suppose a reaction



to be possible, the total change of energy, resp. change of entropy on transformation of n_1 gramme molecules A_1 with n_2 gramme molecules A_2 etc. with formation of n'_1 gramme molecules A'_1 etc. is represented by :

$$\Sigma nE = \Sigma nE_{T=0} + \Sigma n \int_0^T c_v dT \dots \dots \dots (1a)$$

and

$$\Sigma nH = \Sigma nH_{T=1} + \Sigma n \int_1^T \frac{c_p}{T} dT - R \Sigma n \ln c \dots \dots (2a)$$

The algebraic sum of the molecular thermodynamic potentials, which must be equal to zero in case of equilibrium, becomes therefore :

$$\begin{aligned} \Sigma n\mu &= \Sigma nE - T \Sigma nH + \Sigma npV^1) = \\ \Sigma nE_{T=0} + \Sigma n \int_0^T c_v dT - T \Sigma n \int_1^T \frac{c_p}{T} dT - RT \Sigma n \ln c - T \Sigma nH_{T=1} - RT \Sigma n \end{aligned}$$

If now in the state of equilibrium we represent $\Sigma n \ln c$ by $\ln K$, in which K denotes the "constant of equilibrium", then :

1) In this V is the molecular volume, p the partial pressure.

$$\ln K = -\frac{\sum n E_{T=0}}{RT} - \frac{1}{RT} \sum n \int_0^T c_v dT + \frac{1}{R} \sum n \int_1^T \frac{c_v}{T} dT + \frac{1}{R} \sum n H_{T=1} - \sum n \quad (3)$$

So if we have now calculated $\sum n E_{T=0}$ from the calorimetric data (according to equation 1^a), we can calculate the value of $\sum n H_{T=1}$ from an observation of K at a definite temperature.

2. For these calculations c_v is generally represented in a series of terms with ascending powers of T , which is then continued as far as is necessary for agreement with the generally insufficiently known values of the specific heats. For bi-atomic gases the series can already be broken off after the term with T , for tri-atomic gases after that with T^2 .

Hence if we put in general:

$$\sum n c_v = a + bT + cT^2$$

and thus determine the integrals in equation (3), we get:

$$\ln K = -\frac{\sum n E_{T=0}}{RT} + \frac{a}{R} \ln T + \frac{b}{2R} T + \frac{c}{6R} T^2 + C, \quad \dots \quad (4)$$

in which

$$C = \frac{1}{R} \sum n H_{T=1} - \sum n - \frac{2a + 2b + c}{2R} \dots \dots \quad (5)$$

In the above equation (4) the constant of equilibrium is expressed in concentrations; to find the value of the constant in partial pressures from this, which is generally used for gas equilibria, we must bear in mind that

$$p = RTc, \quad \dots \dots \dots \quad (6)$$

in which p is the partial pressure of the gas concerned, and that therefore:

$$\ln K = \sum n \ln c = \sum n \ln p - \sum n \ln R - \sum n \ln T.$$

If we now put $\sum n \ln p = \ln K_p$, in which K_p represents the constant of equilibrium in partial pressures, then after some transformations and transition from Neperian to common logarithms:

$$\log K_p = -\frac{\sum n E_{T=0}}{2.303RT} + \frac{a + \sum n R}{R} \log T + \frac{b}{2 \cdot 2.303R} T + \frac{c}{6 \cdot 2.303R} T^2 + C', \quad (7)$$

in which $C' = 0.4343 C + \sum n \log R$. $\dots \dots \dots$ (8)

In this we must bear in mind that the value of R should be expressed in calories in equation (7), because the energy and the specific heats are measured in calories, whereas in equation (8) the unity in which R is expressed, depends on the unity of pressure and volume in equation (6). If we express the concentrations in

gramme molecules per liter, and so if we choose the liter as volume unity, and the atmosphere as pressure unity, R must be expressed in liter-atmospheres in equation (8). So in this case we must substitute $R=1.985$ in equation (7), on the other hand $R=0.0821$ in equation (8).

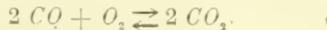
From the equations (7), (8), and (5) we see accordingly that C' , the so-called constant of integration of the chemical equilibrium does not contain only the sum of the constants of entropy, but also Σn and the constants yielded by the integrals occurring in equation (3).

C' owes its name of constant of integration of the chemical equilibrium to this that equation (7) can also be found by integration of the well-known law of VAN 'T HOFF:

$$\frac{d \ln K}{dT} = \frac{Q}{RT^2},$$

in which K represents the constant of equilibrium either in concentrations or in partial pressures, and Q the heat of transformation, in the first case for constant volume, in the second case for constant pressure. If, however, we derive equation (7) in this way, we do not get equations (5) and (8), because in this way the constant of integration does not become known in its dependence on the constants of the reacting substances.

§ 3. We shall now apply the calculation of the constants of entropy to the equilibrium:



The value of ΣnE can be found from the calorimetric determinations of THOMSEN and BERTHELOT, which yielded resp. 67960 and 68200 cal. for the heat of combustion of one gramme molecule CO under constant pressure and at $18^\circ C$. From the mean value $Q_p = 68080$ we calculate $Q_v = 67790$, and so:

$$\Sigma nE = 135580 \quad \text{at} \quad T = 291 \quad . \quad . \quad . \quad . \quad (9)$$

Now we derive from equation 1^a:

$$\Sigma nE_{T=0} = \Sigma nE - aT - \frac{1}{2} bT^2 - \frac{1}{3} cT^3.$$

So for the further calculation we must first know c_v as function of T .

4. For the dependence of c_v on the temperature all kinds of different expressions have been proposed in course of time. From this large number of expressions I will only choose some of the most reliable ones. In the first place I will use the expressions which follow from the experiments of HOLBORN and AUSTIN, which

were carried out in 1905. The real specific heats can be represented pretty accurately up to 800° C by

$$c_p = 4.68 + 0.000536 T \text{ (bi-atomic gas } ^1) \text{ and}$$

$$c_p = 5.112 + 0.00729 T - 22.05 \cdot 10^{-7} T^2 \text{ (carbonic acid } ^2)$$

From these values follows:

$$\sum n c_p = 3.82 - 0.01297 T + 44.1 \cdot 10^{-7} T^2.$$

So in the above equations 7, 8, and 9 must be substituted:

$$a = 3.82 \quad ; \quad b = -0.01297 \quad \text{and} \quad c = 44.1 \cdot 10^{-7} . . . \quad (10)$$

If we substitute these values in equation 9, we get:

$$\sum n E_{T=0} = 134980$$

and the expressions 7 and 8:

$$\log K_p = -\frac{29530}{T} + 2.92 \log T - 0.001419 T + 1.61 \cdot 10^{-7} T^2 + C'. \quad (11)$$

in which:

$$C' = \frac{\sum_{v=1}^{\infty} n H_{T=0}}{4.571} - 2.35. \quad \quad (12)$$

The values of $\log K_p$ in the third column of the following table have been calculated from the most accurate determinations of the carbonic acid equilibrium, which have been inserted in the first two columns³⁾; in the fourth, fifth, sixth and seventh columns the values of the other terms of the second member of equation 11 have been given, and the last column gives the value of C' .

T A B L E I.

T	x	$\log K_p$	$-\frac{29530}{T}$	$2.92 \log T$	$0.001419 T$	$1.61 \cdot 10^{-7} T^2$	C'
1300	$4.14 \cdot 10^{-5}$	-13.45	-22.72	9.09	1.84	0.27	+1.75
1395	$1.42 \cdot 10^{-4}$	-11.84	-21.17	9.18	1.98	0.31	+1.82
1400	$1.5 \cdot 10^{-4}$	-11.77	-21.09	9.19	1.99	0.32	+1.80
1443	$2.5 \cdot 10^{-4}$	-11.11	-20.46	9.23	2.05	0.34	+1.83
1478	$3.2 \cdot 10^{-4}$	-10.79	-19.98	9.26	2.10	0.35	+1.68
1498	$4.71 \cdot 10^{-4}$	-10.28	-19.71	9.27	2.13	0.36	+1.93
1500	$4 \cdot 10^{-4}$	-10.50	-19.69	9.27	2.13	0.36	+1.69
1565	$6.4 \cdot 10^{-4}$	-9.88	-18.87	9.33	2.22	0.39	+1.49

So the value of C' appears to oscillate round a mean + **1.75**. If this value is substituted in equation 12, we get:

¹⁾ See АВЕГГ, Handb. III, 2, 181.

²⁾ Recalculated from the expression of HOLBORN and AUSTIN. Sitz. Ber. preuss Akad. 1905. 175.

³⁾ АВЕГГ, Handb. III, 2, 183.

$$\sum_{v=1}^n H_{T=1} = +18.7.$$

5. The equation derived above deviates only little from the equation given by Prof. NERNST in his "Theoretische Chemie" for the equilibrium of carbonic acid¹⁾, which may be written after recalculation:

$$\log K_p = -\frac{29600}{T} + 2.93 \log T - 0.001286 T + 1.61 \cdot 10^{-7} T^2 + C', \quad (11'')$$

in which $C' = 1.51$ according to Prof. NERNST.

The oscillations of C' appear from the following table:

T A B L E II.

T	$\log K_p$	$-\frac{29600}{T}$	$2.93 \log T$	$0.001286 T$	$1.61 \cdot 10^{-7} T^2$	C'
1300	-13.45	-22.77	9.12	1.67	0.27	+1.60
1395	-11.84	-21.22	9.21	1.79	0.31	+1.65
1400	-11.77	-21.14	9.22	1.80	0.32	+1.63
1443	-11.11	-20.51	9.25	1.86	0.34	+1.66
1478	-10.79	-20.03	9.29	1.90	0.35	+1.50
1498	-10.28	-19.76	9.30	1.93	0.36	+1.75
1500	-10.50	-19.73	9.31	1.93	0.36	+1.49
1565	-9.88	-18.91	9.36	2.01	0.39	+1.29

So C' oscillates round the middle value $+1.57$, which differs but very little from the above mentioned value of 1.51 .

For the value of $\sum_{v=1}^n H_{T=1}$ we find for this case $+17.9$.

The discrepancies between these values and those of § 4 must be partly ascribed to another assumption about $\sum nE$, for the greater part, however, to the changed value of b in the expression of the specific heats.

6. In the second place we can use the more recent determinations of HOLBORN and HENNING²⁾. After recalculation these yield for the real specific heats:

$$c_v = 4.32 + 0.00107 T \text{ (bi-atomic gas)}$$

$$c_v = 4.90 + 0.00783 T - 2.38 \cdot 10^{-6} T^2 \text{ (carbonic acid),}$$

from which follows:

$$\sum n c_v = 3.16 - 0.01245 T + 4.76 \cdot 10^{-6} T^2.$$

So in this case we must substitute in equations 7, 8, and 9:

¹⁾ Theor. Chemie (1909) 681. See also ABEGG Handb. III, 2, 181.

²⁾ Ann. der Physik. (4) 23 809 (1907).

$$a=3,16 ; b=-0,01245 \text{ and } c=4,76 \cdot 10^{-6} \dots (13)$$

This substitution yields :

$$\sum n E_{T=0} = 135150$$

$$\log K_p = -\frac{29570}{T} + 2,59 \log T - 0,001362 T + 1,74 \cdot 10^{-7} T^2 + C', \dots (14)$$

in which :

$$C' = \frac{\sum_{j=1} n H_{T=1}}{4,571} = 2,21 \dots \dots \dots (15)$$

The calculation from the observations will be clear from the sub-joined table without further elucidation :

T A B L E III.

T	$\log K_p$	$-\frac{29570}{T}$	$2,59 \log T$	$0,001362 T$	$1,74 \cdot 10^{-7} T^2$	C'
1300	-13.45	-22.75	8.07	1.77	0.29	+2.71
1395	-11.84	-21.20	8.14	1.90	0.34	+2.78
1400	-11.77	-21.12	8.15	1.91	0.34	+2.77
1443	-11.11	-20.49	8.18	1.97	0.36	+2.81
1478	-10.79	-20.01	8.21	2.01	0.38	+2.64
1498	-10.28	-19.74	8.22	2.04	0.39	+2.89
1500	-10.50	-19.71	8.23	2.04	0.39	+2.63
1565	- 9.88	-18.89	8.27	2.13	0.43	+2.44

So C' oscillates round the mean value + **2.71**.

Now it follows from equation (15) that :

$$\sum_{j=1} n H_{T=1} = + \mathbf{22.5}.$$

7. In the first paper on the theorem of heat⁴⁾ Prof. NERNST proposed the expression :

$$\log K_p = -\frac{29600}{T} + 1,75 \log T - 0,00066 T + C' \dots (16)$$

If we use this expression for the calculation of C' from the observations, we have :

T A B L E IV.

T	$\log K_p$	$-\frac{29600}{T}$	$1,75 \log T$	$0,00066 T$	C'
1300	-13.45	-22.77	5.45	0.86	+4.73
1395	-11.84	-21.22	5.50	0.92	+4.80
1400	-11.77	-21.14	5.51	0.92	+4.78
1443	-11.11	-20.51	5.53	0.95	+4.82
1478	-10.79	-20.03	5.55	0.98	+4.67
1498	-10.28	-19.76	5.56	0.99	+4.91
1500	-10.50	-19.73	5.56	0.99	+4.66
1565	- 9.88	-18.91	5.59	1.03	+4.47

⁴⁾ Gött. Nachr. 1905. 1.

C_v oscillates round the mean value $+ 4.73$ in table IV.

If we calculate the sum of the constants of entropy from this value of C_v we find:

$$\sum_{i=1}^n n_i H_{T=1} = + 30.1$$

8. It will be sufficiently clear from what precedes that the results of the calculations of the constants of entropy depend entirely on the expressions which are assumed for the specific heats as function of the temperature. Up to quite recently we had to content ourselves with the above discussed expansions into series; not long ago, however, appeared a paper by Dr. NIELS BJERRUM, in which two expressions derived from the theory of indivisible units of energy are proposed and tested by the latest observations.¹⁾ It has appeared there that with a suitable choice of the oscillation frequencies of the atoms in the gas-molecules it is possible to account for the observed influence of the temperature on the specific heat. The most remarkable thing is now that with regard to the order of magnitude these frequencies really agree with the vibrations which occur in the absorption spectra of the gases concerned, as was predicted by theory. According to NERNST the specific heat of the gases can be divided into three parts. The translatory energy, which is exclusively determined by the motion of the gas molecules as such, is represented by $\frac{3}{2} RT$ independent of the number of atoms in the molecule.

The rotatory energy is found by multiplying the number of degrees of freedom by $\frac{1}{2} RT$, and amounts to RT for bi-atomic gases, to $\frac{3}{2} RT$ for tri-atomic and multi-atomic gases. So for the specific heats these two parts of the energy yield two expressions independent of the temperature (bi-atomic $\frac{3}{2} R + R$; tri- or multi-atomic $\frac{3}{2} R + \frac{3}{2} R$). The third part, the energy of vibration of the atoms in the molecule will, however, depend on the constitution, of the molecule in a much more intricate way. This energy of vibration, which in its dependence on T furnishes a part of the specific heats which depends on T , is now found by means of the expressions drawn up by EINSTEIN, resp. NERNST and LINDEMANN according to the theory of indivisible units of energy.

The real specific heat of a bi-atomic gas is now found by differentiation of the said three parts of the energy with respect to T :

$$c_v = \frac{3}{2} R + R + \frac{d}{dT}(RTq), \quad (17)$$

in which according to EINSTEIN q is represented by:

¹⁾ Zeitschr. für Elektrochemie. 1911. 731.

$$\frac{\beta r}{T} \cdot \frac{1}{e^T - 1}$$

according to NERNST and LINDEMANN by

$$\frac{1}{2} \frac{\beta r}{T} \frac{1}{e^T - 1} + \frac{1}{2} \frac{\beta r}{2T} \frac{1}{e^{2T} - 1}$$

The universal constant β has here the value $4.86 \cdot 10^{-11}$, r being the frequency of oscillation of the two atoms with respect to each other.

Quite analogously the specific heat of a tri-atomic gas is represented by:

$$c_v = \frac{3}{2} R + \frac{3}{2} R \cdot \frac{d}{dT} \{RT (q_1 + q_2 + q_3)\} \dots \quad (18)$$

in which q_1 , q_2 and q_3 refer to the three vibrations possible in the tri-atomic molecule.

9. If we now also apply these equations for the specific heats to the carbonic acid equilibrium, we find:

$$\sum_n \int_0^T c_v dT = \{1,5 + 2q_A + q_B - 2(q_1 + q_2 + q_3)\} RT \dots \quad (19)$$

and

$$\begin{aligned} \sum_n \int_1^T \frac{c_v}{T} dT &= \frac{3}{2} R \ln T + R \int_1^T \frac{2q_A + q_B - 2(q_1 + q_2 + q_3)}{T} dT + \\ &+ R \int_1^T \{2q_A + q_B - 2(q_1 + q_2 + q_3)\} \dots \quad (20) \end{aligned}$$

in which the indices A , B , 1, 2, and 3 resp. refer to carbonic oxide, oxygen, and carbonic acid.

If now the expressions (19) and (20) are substituted in equation (3), we find:

$$\ln K = - \frac{\sum_n E_{T=0}}{RT} + 1,5 \ln T + \int_1^T \frac{2q_A + q_B - 2(q_1 + q_2 + q_3)}{T} dT + C \dots (21)$$

in which

$$C = -2,5 - \{2q_A + q_B - 2(q_1 + q_2 + q_3)\}_{T=1} + \frac{1}{R} \sum_n H_{T=1},$$

as $\sum_n = +1 \dots \dots \dots (22)$

The integral occurring in equation (21) can, if we use the g -value according to EINSTEIN (see § 8), be found, if we bear in mind that:

$$\int \frac{g}{T} dT = \int \frac{\beta r}{T^2(eT-1)} dT = \int \frac{\beta r e^{-T}}{T^2(1-e^{-T})} dT = -\ln(1-e^{-T}); \quad (23)$$

if we use the value of g of NERNST and LINDEMANN, we get:

$$\begin{aligned} \int \frac{g}{T} dT &= \frac{1}{2} \int \frac{\beta r}{T^2(eT-1)} dT + \\ &+ \frac{1}{2} \int \frac{\beta r}{T^2(e^2T-1)} dT = -\frac{1}{2} \ln(1-e^{-\frac{1}{2}T})(1-e^{-\frac{1}{2}T}) \dots \quad (24) \end{aligned}$$

Finally it appears from equation (1^a) that:

$$\Sigma nE = \Sigma nE_{T=0} + \{1,5 + 2f_A + g_B - 2(g_1 + g_2 + g_3)\} RT. \quad (25)$$

When using the g -expression of EINSTEIN we must, according to BJERRUM, substitute resp. 3.6μ , 3.6μ , 14.7μ , 6.2μ and 6.2μ for λ , or 4050, 4050, 992, 2350, and 2350 for βr in g_A , g_B , g_1 , g_2 and g_3 .

If the g -expression of NERNST and LINDEMANN is used, we must substitute for λ : 2.59μ , 2.59μ , 8.1μ , 5.0μ and 5.0μ and for βr : 5630, 5630, 1800, 2920 and 2920.

If now in equation (25) we substitute these values with the values of ΣnE from equation 9, we get:

$$\begin{aligned} \Sigma nE_{T=0} &= 134850 \text{ (EINSTEIN) resp.} \\ &= 134800 \text{ (NERNST and LINDEMANN).} \end{aligned}$$

Hence the expressions for the carbonic acid equilibrium become:

$$\begin{aligned} \log K_p &= -\frac{29500}{T} + 2,5 \log T - 3 \log \left(1 - e^{-\frac{4050}{T}}\right) + 2 \log \left(1 - e^{-\frac{992}{T}}\right) + \\ &+ 4 \log \left(1 - e^{-\frac{2350}{T}}\right) + C'_E \dots \dots \quad (26) \end{aligned}$$

$$\begin{aligned} \log K_p &= -\frac{29490}{T} + 2,5 \log T - 3/2 \log \left(1 - e^{-\frac{5630}{T}}\right) \left(1 - e^{-\frac{5630}{2T}}\right) \\ &+ \log \left(1 - e^{-\frac{1800}{T}}\right) \left(1 - e^{-\frac{1800}{2T}}\right) + 2 \log \left(1 - e^{-\frac{2920}{T}}\right) \left(1 - e^{-\frac{2920}{2T}}\right) + C'_{NL} \quad (27) \end{aligned}$$

In both expressions the constants C'_E and C'_{NL} have the values:

$$\begin{aligned} C'_E &= 0,4343 C_E + \log 0,0821 \text{ and} \\ C'_{NL} &= 0,4343 C_{NL} + \log 0,0821, \end{aligned}$$

in which the constants without accents are represented by equation (22), because the lower limit of the integral occurring in equation 21 may be neglected.

If we consider that also the values for q in equation (22) for $T=1$ may be put zero, we get finally:

$$C'_E = C'_{NL} = 0.4343 \left(-2.5 + \frac{1}{R} \sum_{\nu=1} n H_{T=1} \right) + \log 0.0821$$

or

$$C'_E = C'_{NL} = \frac{\sum n H_{T=1}}{4.571} - 2.17 \dots \dots \dots (28)$$

T A B L E V.

T	$-\frac{29500}{T}$	$-\frac{29490}{T}$	$2.5 \log T$	$\sum \log E$	$\sum \log NL$	C'_E	C'_{NL}
1300	-22.69	-22.68	7.78	-0.80	-0.78	+2.26	+2.23
1395	-21.15	-21.14	7.86	-0.87	-0.85	+2.32	+2.29
1400	-21.07	-21.06	7.87	-0.87	-0.85	+2.30	+2.27
1443	-20.44	-20.44	7.90	-0.91	-0.88	+2.34	+2.31
1478	-19.96	-19.95	7.92	-0.93	-0.91	+2.18	+2.15
1498	-19.69	-19.69	7.94	-0.95	-0.92	+2.42	+2.39
1500	-19.67	-19.66	7.94	-0.95	-0.93	+2.18	+2.15
1565	-18.85	-18.84	7.99	-0.99	-0.97	+1.97	+1.94

So the mean values of C'_E and C'_{NL} amount to:

$$+ 2.25 \text{ and } + 2.22.$$

From equation 28 follows:

$$\sum_{\nu=1} n H_{T=1} = + 20.2 \text{ and } + 20.1.$$

10. If we now consider the results of the five tables, it appears that all five have been calculated with the aid of the same data concerning the chemical equilibrium, that the same value $\sum n E$ was used for tables I, III, and V, that the values on which tables II and IV are based, differ at the most some tenths of percentages from them, which accordingly can only bring about a deviation of some hundredths in the value of C' , and that therefore the greatly varying values of C' resp. $\sum_{\nu=1} n H_{T=1}$ must be attributed to the different expressions which are introduced for the specific heats.

The term, produced by the constants of energy, differs at the most 0,1 in the five tables; the great influence, to which the difference of the obtained C' values is to be ascribed, lies chiefly in the different factor of $\log T$, which varies between 2,93 (table II) and 1,75 (table IV).

This can bring about a difference of more than 3 in the terms concerned, because $\log T$ is of the order 3.

Though accordingly the different assumptions concerning the specific heats give a maximum deviation in the constants of energy of at the most some tenths of percentages, they give rise to variations from 17,9 to 30,1 for the constants of entropy. So the accuracy of the constants of entropy is far inferior to that of the constants of energy.

It will be clear from the above that the extrapolation of the specific heat from the region of observation to the lower temperatures is the cause of the deviations. For where e.g. for bi-atomic gases the expression $Cv = a + bT$ implies that the specific heat retains its linear dependence with descending temperature, it becomes constant at low temperatures on assumption of the expression of BJERRUM. The line that represents the specific heat as function of the temperature, exhibits the same shape (with a point of inflection) in the latter case as the specific heats for solid substances, which of late have become known specially by the investigations in the laboratory of Prof. NERNST.

We may call here special attention to this that all the five expressions which have been mentioned for the carbonic acid dissociation equilibrium, account equally well for the observations, for the oscillations of C' have the same value in all the tables. And we have here only to take the absolute, not the relative deviations of C' into consideration.

That a change in the expression of the specific heats can have a great influence on the value of C' , is moreover a conclusion which is not new. Everybody who knows the work of Prof. HABER already mentioned in § 1, which appeared already in 1905, and which treats the gas-equilibria with the facts known at the time in a very clear way, will find back this conclusion there. As it appeared to me, however, that this conclusion is not generally known, and the newer data have hardly modified it, I have thought it necessary to elucidate it in what precedes by one of the most fully studied reactions.

If we ask which value of the constants of the entropy must be taken as the most probable, we come to the conclusion that this is certainly the value of Table V. In the first place the expression proposed by BJERRUM has a theoretical foundation in the theory of indivisible units of energy, and besides this formula renders the newest investigations of HOLBORN and HENNING and those of PIER very well, as appears with the greatest clearness from the cited paper by BJERRUM.

A drawback mentioned by BJERRUM, exists, however also when we use this expression. It is namely pretty certain that this formula will not rigorously retain its validity at low temperatures, because the rotatory energy at low temperatures will deviate from the value given in the expression. This, however, does not detract from the fact that in my opinion this theoretical formula is to be preferred to the empirical expansions into series.

11. If we apply BJERRUM's data to the equilibrium of the water-dissociation we find at $T = 273$ for $\sum nE$ the value 115660, resp. 115260 according to BERTHELOT and MATIGNON, resp. to THOMSEN.

If we take a mean from this, we get according to equation 25 :

$$\sum n E_{T=0} = 114650.$$

If the g -values according to EINSTEIN, resp. NERNST and LINDEMANN are used, the expressions for the equilibrium become :

$$\log K_p = -\frac{25080}{T} + 2.5 \log T - 2 \log \left(1 - e^{-\frac{4860}{T}} \right) - \log \left(1 - e^{-\frac{4050}{T}} \right) + 2 \log \left(1 - e^{-\frac{2650}{T}} \right) + 4 \log \left(1 - e^{-\frac{5610}{T}} \right) + C'_E \quad \dots \quad (29)$$

and

$$\log K_p = -\frac{25080}{T} + 2.5 \log T - \log \left(1 - e^{-\frac{7290}{T}} \right) \left(1 - e^{-\frac{7290}{2T}} \right) - \frac{1}{2} \log \left(1 - e^{-\frac{5630}{T}} \right) \left(1 - e^{-\frac{5630}{2T}} \right) + 3 \log \left(1 - e^{-\frac{6075}{T}} \right) \left(1 - e^{-\frac{6075}{2T}} \right) + C'_{NL} \quad (30)$$

The most accurate observations, which were carried out in Prof. NERNST's¹⁾ laboratory, now yield :

T A B L E VI.

T	$\log K_p$	$-\frac{25080}{T}$	$2.5 \log T$	$\sum \log E$	$\sum \log_{NL}$	C'_E	C'_{NL}
1300	-14.01	-19.29	7.78	-0.10	-0.09	-2.40	-2.41
1397	-12.63	-17.95	7.86	-0.12	-0.10	-2.42	-2.44
1480	-11.47	-16.95	7.93	-0.14	-0.12	-2.31	-2.33
1500	-11.42	-16.72	7.94	-0.14	-0.12	-2.50	-2.52
1561	-10.71	-16.07	7.98	-0.15	-0.13	-2.47	-2.49
1705	-9.28	-14.71	8.08	-0.18	-0.16	-2.47	-2.49
2155	-6.08	-11.64	8.33	-0.27	-0.26	-2.50	-2.51
2257	-5.55	-11.11	8.38	-0.29	-0.28	-2.53	-2.54
2300	-5.04	-10.90	8.40	-0.30	-0.29	-2.24	-2.25

¹⁾ Theor. Chem. 1909, 680.

The mean values of C'_E and C'_{NL} amount to **2,43** and **-2,44**. It appears from equation (28), which holds here unmodified that :

$$\sum_{i=1}^n H_{F,i} = -1,19 \text{ and } -1,23.$$

12. The water gas equilibrium can be found by calculation from the water and carbonic acid equilibrium.

From $K_{H_2O} = \frac{c_{H_2}^2 c_{O_2}}{c_{H_2O}^2}$, $K_{CO_2} = \frac{c_{CO}^2 c_{O_2}}{c_{CO_2}^2}$ and $K_w = \frac{c_{H_2} c_{CO_2}}{c_{CO} c_{H_2O}}$ it appears, that

$$\log K_w = 1/2 (\log K_{H_2O} - \log K_{CO_2}).$$

Hence if we subtract equation 26 from 29 resp. 27 from 30, we find after division by 2 :

$$\log K_w = \frac{2210}{T} - \log \left(1 - e^{-\frac{4860}{T}} \right) - \log \left(1 - e^{-\frac{992}{T}} \right) - 2 \log \left(1 - e^{-\frac{2350}{T}} \right) \\ + \log \left(1 - e^{-\frac{4550}{T}} \right) + \log \left(1 - e^{-\frac{2650}{T}} \right) + 2 \log \left(1 - e^{-\frac{5610}{T}} \right) + C'_{w_E} \quad (31)$$

and

$$\log K = \frac{2205}{T} - \log \left(1 - e^{-\frac{7290}{T}} \right) \left(1 - e^{-\frac{7290}{2T}} \right) - \log \left(1 - e^{-\frac{1800}{T}} \right) \left(1 - e^{-\frac{1800}{2T}} \right) \\ - \log \left(1 - e^{-\frac{2920}{T}} \right) \left(1 - e^{-\frac{2920}{2T}} \right) + 1/2 \log \left(1 - e^{-\frac{5631}{T}} \right) \left(1 - e^{-\frac{5630}{2T}} \right) \\ + 3/2 \log \left(1 - e^{-\frac{6075}{T}} \right) \left(1 - e^{-\frac{6075}{2T}} \right) + C'_{w_{NL}} \dots \dots \dots (32)$$

For the calculation of the constants we use the determinations of HAHN¹⁾.

T A B L E VII.

T	K^{-1}	$\log K$	$\frac{2210}{T}$	$\frac{2205}{T}$	$\Sigma \log E$	$\Sigma \log NL$	C'_{w_E}	$C'_{w_{NL}}$
959	0.534	0.27	2.30	2.30	0.23	0.24	-2.26	-2.27
1059	0.840	0.08	2.09	2.08	0.27	0.27	-2.28	-2.27
1159	1.197	-0.08	1.91	1.90	0.30	0.30	-2.29	-2.28
1259	1.571	-0.20	1.76	1.75	0.33	0.33	-2.29	-2.28
1359	1.96	-0.29	1.63	1.62	0.36	0.36	-2.28	-2.27
1478	2.126	-0.33	1.50	1.49	0.40	0.39	-2.23	-2.21
1678	2.49	-0.40	1.32	1.31	0.45	0.44	-2.17	-2.15

So the mean values amount to **-2.26** and **-2.25**.

The constants of entropy can be found from :

¹⁾ АБЕГГ. Handb. III. 2. 198.

$$\sum_{v=1}^{\infty} nH_{T=1} \quad C'',$$

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into which for this case equation (22), in which $\sum n = 0$, passes.

The calculation yields:

$$\sum_{v=1}^{\infty} nH_{T=1} = -10.3 \text{ and } -10.3.$$

If we now compare the values which the direct determinations of the watergas equilibrium have yielded, with the values which are calculated from the constants of the water and carbonic acid equilibrium, we find:

T A B L E VIII.

Carbonic acid		Water		Watergas			
				Calculated		Direct	
C'	$\sum_{v=1}^{\infty} nH_{T=1}$	C'	$\sum_{v=1}^{\infty} nH_{T=1}$	C'	$\sum_{v=1}^{\infty} nH_{T=1}$	C'	$\sum_{v=1}^{\infty} nH_{T=1}$
+2.25	+20.2	-2.43	-1.19	-2.34	-10.7	-2.26	-10.3
+2.22	+20.1	-2.44	-1.23	-2.33	-10.7	-2.25	-10.3

This agreement proves that the observations on which table VII is founded, correspond sufficiently well with those of the tables V and VI. This, however, cannot be advanced as a proof of the accuracy of the used expressions for the specific heats, as such an agreement may also be obtained on other assumptions concerning the specific heats.

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Physiology. — *“The effusion of acoustic energy from the head, according to experiments of Dr. P. NIKIFOROWSKY”.* By Prof. ZWAARDEMAKER.

(Communicated in the meeting of December 30, 1911).

In the months just past, Dr. P. NIKIFOROWSKY from St. Petersburg has carried on in the Physiological Laboratory at Utrecht an investigation as to the effusion of acoustic energy from the head whilst the sound was introduced, either from the head or from the vocal organs or from the crown of the head along the stem of a vibrating tuning-fork which had been placed there. The intensity of the sound produced, was about uniform, which appeared from special measure-

ments (in the case of voice comparatively, by testing the sound at a microphone placed in a camera *silenta* and connected with a small string-galvanometer, in the case of the diapason vertex by measuring the amplitudes of the oscillations).

The problem which the experimenter has set himself, and which he has solved is the following: how does the vocal energy amounting uncorrected to from 1 to 7 megaergs per second according to an investigation made in collaboration with A. DE KLEYN (see my *Leerboek der Physiologie*, Haarlem 1910 Vol I p. 82) distribute itself over the natural egresses (mouth, nose and ears) and the hard and soft parts of skull and face. For obviously not only from the lips but also from all other parts the head will yield sound to its surroundings.

The sound when issuing forth was received in closely fitting leaden funnels or by ear-pieces and was led by sound-proof leaden channels to a microphone, placed in a leaden chamber with very thick walls. The current-fluctuations, produced in the microphone, manifested themselves, after having been transformed in the manner usual in telephony into an induction apparatus, at a string galvanometer with a gold string 5μ thick and about 30 mm. long. The tension of the string was regulated in such a manner that it reverberated distinctly at all vowels and produced a vibration the double amplitude of which could be easily read off on the scale of the instrument. Provided we restrict ourselves to the comparison of sounds of the same pitch, it may be assumed that in spite of the multiple resonance of the system (sound-channels, microphone, transformer, string) the intensity of the sound acting upon the microphone was proportionate with the squares of the amplitudes measured. Sounds of different pitches, however, cannot be compared, as the manifold repeated resonatory strengthening, which the sound undergoes, is very different for different pitches; this became manifest when the micro-telephonic system after it had been constructed was tested, in the manner usual in the Laboratory, by means of a series of uniformly tuned organ-pipes, ranging from a_1 to e_3 . If necessary a comparison of the various vowels might have been attempted with the aid of this supplementary investigation, but on account of the numerous sources of mistakes it gave rise to, the idea was relinquished.

On comparing the values of the same column in the above tables, we become aware of considerable differences in intensity, the more so if we remember that the actual strength of the sounds has been proportionate with the squares of the deviation of the galvanometer. The cause of this great difference will probably have to be sought in the co-operation of two causes:

TABLE I.

Intensity of the sound flowing away, calculated per cm², the chest voice being the sound-source.

Place whence the sounds were transmitted to the micro-telephone-apparatus	Double amplitude whilst the vowels were being pronounced					Remarks
	<i>a</i>	<i>o</i>	<i>oe</i>	<i>e</i>	<i>i</i>	
Nose	84	84	168	84	168	leaden ear-pieces
Mouth	168	168	84	168	84	" "
Ears	4	4	8	4	8	" "
Zygomatic arch (temp. part)	0.4	0.4	0.8	0.4	0.8	leaden funnels
Supra meatum	0.3	0.4	0.4	0.2	0.4	" "
Proc. mastoid.	0.4	0.4	0.4	0.4	0.4	" "
Zygomatic arch (middle)	0.4	0.4	0.8	0.4	0.8	" "
Forehead (side part)	0.4	0.4	0.4	0.2	0.4	" "
Forehead (middle)	0.2	0.4	0.8	0.2	0.8	one funnel
Os parietale	0.4	0.4	0.4	0.2	0.2	leaden funnels
Crown	0.4	0.4	0.8	0.4	0.8	one funnel
Nape	0.1	0.1	0.2	0.1	0.2	one funnel
Cheek	4	4	8	4	8	leaden ear-pieces
Sides of the nose	4	2	2	2	1	" "
Planum submentale	4	4	8	4	8	" "
Chin	4	4	8	4	8	" "

a. the timbre of the various vowels is different, even when pronounced at the same pitch,

b. the width of the mouth-cavity is different in the pronunciation of different vowels, for in the case of the wide vowels of BELL-SWEET the effusion of energy through the mouth will be promoted, in the narrow vowels impeded, in inverse proportion of which the effusion of energy by other channels takes place (*a* and *e* are open vowels, *o* and *i* are closed ones).

From the tables it appears that the greater part of the acoustic energy of the voice leaves the head by the lips, a much smaller part by the nose, and a still smaller part by the auditory canals.

A totally different result is arrived at, if it is not the voice that produces the sound, but if the acoustic energy is derived from a tuning-fork set vibrating by means of electricity, and placed on the

T A B L E II.

Intensity of the sound flowing away calculated per cm², the falsetto voice being the sound-source.

Place whence the sounds were transmitted to the micro-telephone-apparatus	Double amplitude whilst the vowels were being pronounced					Remarks
	<i>a</i>	<i>o</i>	<i>oe</i>	<i>e</i>	<i>i</i>	
Ears	?	0	4	0	4	leaden ear-pieces
Zygomatic arch (temp. part)	0	0	0.3	0	0.3	leaden funnels
Supra meatum	0	0	?	0	?	" "
Proc. mastoideus	0	0	?	0	?	" "
Zygomatic arch (middle)	0.16	0.2	0.4	0.2	0.4	" "
Forehead (side part)	0.1	0.16	0.4	0.16	0.4	" "
Forehead (middle)	0	?	?	?	?	one funnel
Os parietale	0	0	0	0	0	leaden funnel
Crown	0.2	0.4	0.4	0.2	0.2	" "
Nape	0	0	?	0	?	" "
Cheeks	2	4	8	2	8	leaden ear-pieces

crown of the head. In this case mouth and nose orifice get hardly any share at all, the rest of the effusion being thus:

T A B L E III.

Intensity of the sound flowing off calculated per cm², the sound-source being a diapason vertex.

Place whence the sound was transmitted to the micro-telephone-apparatus	Double amplitude	Remark
Ears	32	
Zygomatic arch (middle)	8	The experiments were made with the aid of a tuning-fork of EDELMANN with running-weights at the ends. The double amplitude amounted there uninterruptedly to 1 mm., sustained by electro-magnetic motive force.
Forehead	6	
Supra meatum	4	
Nape	4	
Nasal bone	4	
Soft parts of the nose	1	
Cheeks	2	

We have not succeeded in any other way than the one described above, in introducing an amount of sound-energy into the head, sufficient to import enough intensity to the sound which flowed off, to measure it by means of the microtelephone apparatus and the string-galvanometer. Only very strong sound-sources such as MARAGE'S "sirène à voyelles", when one places oneself before it with open mouth, or a loud speaking telephone, led directly to a nostril, produce enough sound to bring about a measurable deviation of the galvanometer, and that only when the sound is derived from both ears i.e. in the most favourable condition. If we leave out of consideration sounds introduced by actual contact, the sound of one's own voice is evidently the only one which penetrates the skull in great intensity. The sound transmitted by the air to which we listen in ordinary life, acquires only its well-known preponderance by the structure of the middle-ear, eminently calculated to conduct sounds. In itself a tone passing through the air and piercing the skull, is always weak.

It also seemed desirable to make an absolute determination of the sound issuing from the head. For this purpose that which escapes from between the lips when we pronounce the vowel "a" was received into a phonograph (as this was done in the camera *silenta*, the sides of which are covered with thick horse-hair, absorbing sound, better results were obtained than before). Then the impressions made on the wax cylinder were measured according to the method of BOEKE and analyzed according to the method of FOURIER. Finally on the ground of this investigation the vowel was imitated in exactly the same strength by means of organ-pipes¹⁾. The total strength of the imitating sound appeared as follows:

TABLE IV. Vowel "a".

Partial tone	Dominating components	Pitch (v. d.)	Depth of glyptic in $\frac{1}{100}$ mM.	Consumption of air in cm^3 .	Pressure in cm^2 of water	Energy (volume in $\text{cm}^3 \times$ press. in dynes)	Energy in megaergs	Total energy of voice (uncorrected)
6	a sharp ^o	804	1.035	107.5	2	210915	0.04	2.45 Megaergs pro sec.
7	b sharp	938	1.71	308	16	4834368	2.4	
8	c ³	1072	0.825	107.5	2	210915	0.014	

1 Megaerg = 10^6 ergs

Hence it appears that the intensity of Dr. NIKIFOROWSKY'S voice

¹⁾ ZWAARDEMAKER and MINKEMA. Arch. f. Anat u. Physiol., Physiol. Abteilung 1906 p. 433.

issuing from his lips when loudly sounding "a" amounted to 2.35 megaergs per second. According to this standard the effusion of sound from the other parts of the head may be determined. This is set forth in Table V.

T A B L E V.
Acoustic energy emitted by the head per second whilst "a" was pronounced with chest-voice.

Regiones	Energy per cm ² in megaergs	Extent of the sur- face in cm ² .	Total energy in megaergs per sec.	R e m a r k s.
Nose	0.131	1.1	0.144	both nostrils together
Mouth	0.524	4.4	2.306	
Ears	0.000297	0.475	0.00014	both ears together
Bony parts	0.0000297	2233	0.066	
Soft parts	0.000297	559	0.166 2.68	

The total effusion of sound amounted therefore in the above experiment to 2.68 Megaergs per second. Of this the greater part viz. 2.45 Megaergs left the head by the mouth and the ears, an extremely small part by the auditory passages and about $\frac{1}{10}$ by the hard and soft parts together. These data we offer uncorrected i. e. without an estimate of the efficiency of a well-regulated organ-pipe. Not all the energy imparted to the pipe is transformed into sound. Some of it is lost in the vortices of air. Hence our values are greater than the real acoustic values. Though the latter according to a recent publication by ZERNOV ¹⁾ may be esteemed of about the same order, yet it seems to me that the importance of Dr. P. NIKIFOROVSKY'S figures lies in the mutual relation of effusions which differ topographically.

Mathematics. — "*On partial differential equations of the first order*".
By Prof. W. KAPTEYN.

1. When a partial differential equation of the first order

$$F(x, y, z, p, q) = 0 \dots \dots \dots (1)$$

is transformed by a tangential transformation, the new equation will generally show the same form. Sometimes however the transformed equation will be linear. In this case the complete primitive of the

¹⁾ ZERNOV, Ueber absolute Messungen der Schallintensität. Die Rayleighsche Scheibe. Ann. d. Physik. (4). Bd. 26 p. 79. 1908.

non-linear equation and the integralsurface passing through a given curve (the problem of CAUCHY) may be obtained from the transformed linear equation.

The object of this paper is firstly to determine the necessary and sufficient conditions which must be fulfilled by the equation (1) when it may be reduced to the linear form by one of the two known tangential transformations of LEGENDRE and AMPÈRE; secondly to show how in these cases the problem of CAUCHY may be solved.

2. If the tangential transformation of LEGENDRE

$$x = P, \quad y = Q, \quad z = PX + QY - Z, \quad p = X, \quad q = Y \quad (2)$$

reduces (1) to the linear equation

$$A(X, Y, Z) P + B(X, Y, Z) Q = C(X, Y, Z)$$

where A , B and C are arbitrary functions, the former evidently must be equivalent with

$$xA(p, q, px + qy - z) + yB(p, q, px + qy - z) = C(p, q, px + qy - z).$$

Therefore, writing

$$A(X, Y, Z) P + B(X, Y, Z) Q - C(X, Y, Z) = \psi(X, Y, Z, P, Q) = 0$$

we have

$$\frac{\partial \psi}{\partial P} = A(X, Y, Z), \quad \frac{\partial \psi}{\partial Q} = B(X, Y, Z)$$

and

$$\frac{\partial^2 \psi}{\partial P^2} = \frac{\partial^2 \psi}{\partial P \partial Q} = \frac{\partial^2 \psi}{\partial Q^2} = 0.$$

Inversely, these conditions being fulfilled, ψ represents a linear form with regard to the variables P and Q .

These conditions may be transformed in the following way

$$F(x, y, z, p, q) = \psi(X, Y, Z, P, Q)$$

therefore

$$\frac{\partial \psi}{\partial P} = \frac{\partial F}{\partial x} + X \frac{\partial F}{\partial z}, \quad \frac{\partial \psi}{\partial Q} = \frac{\partial F}{\partial y} + Y \frac{\partial F}{\partial z}$$

$$\frac{\partial^2 \psi}{\partial P^2} = \frac{\partial^2 F}{\partial x^2} + 2X \frac{\partial^2 F}{\partial x \partial z} + X^2 \frac{\partial^2 F}{\partial z^2}$$

$$\frac{\partial^2 \psi}{\partial P \partial Q} = \frac{\partial^2 F}{\partial x \partial y} + Y \frac{\partial^2 F}{\partial x \partial z} + X \frac{\partial^2 F}{\partial y \partial z} + XY \frac{\partial^2 F}{\partial z^2}$$

$$\frac{\partial^2 \psi}{\partial Q^2} = \frac{\partial^2 F}{\partial y^2} + 2Y \frac{\partial^2 F}{\partial y \partial z} + Y^2 \frac{\partial^2 F}{\partial z^2}$$

so the necessary and sufficient conditions, in this case, may be written

$$\left. \begin{aligned} \frac{\partial^2 F}{\partial x^2} + 2\rho \frac{\partial^2 F}{\partial x \partial z} + \rho^2 \frac{\partial^2 F}{\partial z^2} &= 0 \\ \frac{\partial^2 F}{\partial x \partial y} + q \frac{\partial^2 F}{\partial x \partial z} + p \frac{\partial^2 F}{\partial y \partial z} + pq \frac{\partial^2 F}{\partial z^2} &= 0 \\ \frac{\partial^2 F}{\partial y^2} + 2q \frac{\partial^2 F}{\partial y \partial z} + q^2 \frac{\partial^2 F}{\partial z^2} &= 0 \end{aligned} \right\} \dots \dots \dots (3)$$

In the same way, considering the tangential transformation of AMPÈRE

$$x = X, \quad y = -Q, \quad z = Z - YQ, \quad p = P, \quad q = Y$$

we obtain the necessary and sufficient conditions

$$\left. \begin{aligned} \frac{\partial^2 F}{\partial p^2} &= 0 \\ \frac{\partial^2 F}{\partial y \partial p} + q \frac{\partial^2 F}{\partial z \partial p} &= 0 \\ \frac{\partial^2 F}{\partial y^2} + 2q \frac{\partial^2 F}{\partial y \partial z} + q^2 \frac{\partial^2 F}{\partial z^2} &= 0 \end{aligned} \right\} \dots \dots \dots (4)$$

3. Assuming now that the equation (1) has been transformed by the transformation of LEGENDRE in the linear form

$$A(X, Y, Z)P + B(X, Y, Z)Q = C(X, Y, Z)$$

we will proceed to examine how the integralsurface of (1) which passes through the curve

$$y = \varphi(x) \quad , \quad z = \psi(x)$$

may be obtained.

Let the integrals of the system of ordinary differential equations

$$\frac{dX}{A(X, Y, Z)} = \frac{dY}{B(X, Y, Z)} = \frac{dZ}{C(X, Y, Z)}$$

be

$$U(X, Y, Z) = a, \quad V(X, Y, Z) = b$$

where a and b are arbitrary constants, the difficulty of the problem consists solely in the determination of the relation or the relations which must exist between the constants a and b .

Designing a point x, y, z and a plane passing through this point with angular coefficients ρ and q by the name of element, the ∞^2 elements which are related by the three conditions

$$y = \varphi(x), \quad z = \psi(x), \quad dz = p dx + q dy$$

are transformed in the ∞^2 elements $(XYZPQ)$ which satisfy the three conditions

$$Q = q(P), \quad PX + QY - Z = q(P), \quad \psi'(P) = X + Yq'(P)$$

or

$$Q = q(P), \quad XP + Yq'(P) - Z = \psi'(P), \quad X + Yq'(P) = \psi'(P).$$

These elements are precisely the elements of the developable surface generated by the plane

$$Xt + Yq(t) - Z - \psi(t) = 0.$$

For this developable is obtained by eliminating t from

$$\left. \begin{aligned} Xt + Yq(t) - \psi(t) &= Z \\ X + Yq'(t) - \psi'(t) &= 0 \end{aligned} \right\} \dots \dots \dots (5)$$

and determining

$$\frac{\partial Z}{\partial X} = t + \{X + Yq'(t) - \psi'(t)\} \frac{\partial t}{\partial X} = t$$

$$\frac{\partial Z}{\partial Y} = q(t) + \{X + Yq'(t) - \psi'(t)\} \frac{\partial t}{\partial Y} = q(t)$$

it is evident that the angular coefficients of the tangent plane through the point X, Y, Z of the developable surface are related by

$$Q = q(P).$$

Hence the constants a and b must be such that the curve

$$U(X, Y, Z) = a, \quad V(X, Y, Z) = b$$

touches the surface (5).

This condition leads to two or one relation between a and b .

In the first case we have

$$U(X, Y, Z) = m, \quad V(X, Y, Z) = n$$

where m and n represent the values found.

If now we transform again X, Y, Z in x, y, z, p, q these relations give

$$U(p, q, xp + yq - z) = m, \quad V(p, q, xp + yq - z) = n$$

and by eliminating p and q from these and

$$F(x, y, z, p, q) = 0$$

we obtain the required integral surface.

In the second case, which is the general one, let

$$b = \theta(a)$$

be the only relation between the constants a and b . From these we deduce

$$V(X, Y, Z) = \theta [U(X, Y, Z)].$$

Differentiating with regard to X and Y , we have

$$\frac{\partial V}{\partial X} + P \frac{\partial V}{\partial Z} = \theta' \cdot \left(\frac{\partial U}{\partial X} + P \frac{\partial U}{\partial Z} \right)$$

$$\frac{\partial V}{\partial Y} + Q \frac{\partial V}{\partial Z} = \theta' \cdot \left(\frac{\partial U}{\partial Y} + Q \frac{\partial U}{\partial Z} \right).$$

Transforming now x, y, z, p, q and eliminating p and q from these, we get the integralsurface passing through the given curve.

4. The first case presents itself in the following problem.

Let

$$z = pq$$

be the given differential equation which satisfies the conditions 3) and let it be the question to determine the integralsurface passing through the curve

$$y = 1, \quad z = x^2.$$

Transforming the differential equation, we get

$$XP + YQ = Z + XY$$

and

$$U(X, Y, Z) = \frac{Y}{X} = a, \quad V(X, Y, Z) = \frac{Z - XY}{X} = b.$$

The developable surface (5) being

$$Z = Y + \frac{X^2}{4}$$

the curve

$$\frac{Y}{X} = a, \quad \frac{Z - XY}{X} = b$$

will touch this surface if

$$4a - 1 = 0 \quad \text{and} \quad b - a = 0.$$

The solution of the linear equation is therefore

$$4Y - X = 0, \quad 4Z - 4XY - X = 0.$$

which transformed to x, y, z, p, q gives

$$4q - p = 0 \quad 4(-z + px + qy) - 4pq - p = 0.$$

Joining to these

$$z = pq$$

and eliminating p and q we obtain the required solution

$$16z = (4x + y - 1)^2$$

which satisfies the differential equation and passes through the curve

$$y = 1, \quad z = x^2.$$

The second case will be met with by taking the same differential equation with the condition that the integral passes through the line

$$y = 2x \quad z = 2x.$$

Here U and V are the same as before, but now the ∞^2 elements ($XYZPQ$) must satisfy the conditions

$$Q = 2P, \quad (X + 2Y - 2)P - Z = 0, \quad X + 2Y - 2 = 0.$$

or

$$Q = 2P, \quad Z = 0, \quad X + 2Y - 2 = 0$$

Here the developable surface reduces to a line and the ∞^2 elements consist of all points of this line with all planes passing through this line. For representing these planes by

$$Z = k(X + 2Y - 2)$$

it is evident that whatever k be, we have the relation

$$Q = 2P.$$

Expressing now that the curve

$$\frac{X}{Y} = a, \quad \frac{Z - XY}{X} = b$$

meets the line

$$Z = 0, \quad X + 2Y - 2 = 0$$

we find but one relation between a and b , viz.

$$2a + b(1 + 2a) = 0.$$

This gives the solution of the linear equation

$$Z - XY = -\frac{2XY}{X + 2Y},$$

and by differentiating with respect to X and Y

$$P - Y = -\frac{4Y^2}{(X + 2Y)^2}$$

$$Q - X = -\frac{2X^2}{(X + 2Y)^2}.$$

Transforming again and taking $p = \frac{z}{q}$ from the differential equation, the first of these equations and the quotient of the second and third give

$$2yq^4 - 4zq^3 + z(2x + y + 2)q^2 - 2z^2q + xz^2 = 0$$

$$2yq^4 - 2zq^3 + z^2q - xz^2 = 0.$$

Adding and subtracting these equations and writing

$$B = 2x + y + 2$$

we obtain

$$4yq^3 - 6zq^2 + Bzq - z^3 = 0$$

$$2q^3 - Bq^2 + 3zq - 2xz = 0$$

so finally

$$\begin{vmatrix} 3z - yB & 6y - B & z - 4xy \\ z(6y - B) & B^2 - 16z - 8xy & z(12x - B) \\ z - 4xy & 12x - B & 3z - 2xB \end{vmatrix} = 0.$$

5. Secondly we suppose that the given equation (1) satisfies the conditions (4). Then the transformation of AMPÈRE reduces it to the linear form

$$A(X, Y, Z)P + B(X, Y, Z)Q = C(X, Y, Z)$$

whose integrals may be written again

$$U(X, Y, Z) = a, \quad V(X, Y, Z) = b.$$

The ∞^2 elements subjected to the conditions

$$y = q(x), \quad z = \psi(x) \quad dz = pdx + qdy$$

will now be transformed in the ∞^2 elements $(X Y Z P Q)$ satisfying the conditions

$$-Q = q(X), \quad Z - YQ = \psi(X), \quad \psi'(X) = P + Yq'(X).$$

These elements consist evidently of every point of the surface

$$Z + Yq(X) = \psi(X) \dots \dots \dots (6)$$

with the corresponding tangent plane. The curve

$$U(X, Y, Z) = a, \quad V(X, Y, Z) = b$$

touching this surface, it is evident that if we eliminate Y and Z , the resulting equation must have equal roots X .

This gives sometimes two, but generally one relation between a and b . Both cases may be treated in the same way as before, the only difference being the transformation, which is now

$$X = x, \quad Y = q, \quad Z = z - qy, \quad P = p, \quad Q = -y.$$

6. As the differential equation

$$z = pq$$

satisfies also the conditions (4), the transformation of AMPÈRE may also be applied if we wish to determine the integrals-surface passing through the curve

$$y = x, \quad z = (x+1)(x+2).$$

This transformation gives

$$YP + YQ = Z$$

whose integrals

$$Y - X = a, \quad \frac{Z}{Y} = b$$

are easily obtained.

Joining to these the equation (6)

$$Z + XY = (X+1)(X+2)$$

and eliminating Y and Z , we get

$$(a+b-3)X + ab - 2 = 0.$$

This equation does not admit equal roots unless

$$a + b - 3 = 0 \quad \text{and} \quad ab - 2 = 0.$$

Hence

$$a = 1, \quad b = 2$$

and

$$Y - X = 1, \quad Z = 2Y.$$

The transformation applied to these equations gives

$$q - x = 1 \quad z - qy = 2q$$

and after elimination of q

$$z = (x+1)(y+2)$$

which is the required solution.

If, in the second place, the integralsurface through

$$y = 2x, \quad z = 2x$$

is required, the constants a and b of the integrals

$$Y - X = a, \quad \frac{Z}{Y} = b$$

must be such that this curve touches the surface (6)

$$Z + 2XY = 2X.$$

This condition gives

$$(b-2a-2)^2 = 16a$$

so the solution of the linear equation may be written

$$Z - 2Y(Y-X+1) = 4Y\sqrt{Y-X}$$

from which by differentiation we obtain

$$P + 2Y = \frac{-2Y}{\sqrt{Y-X}}$$

$$Q - 4Y + 2X - 2 = \frac{6Y - 4X}{\sqrt{Y-X}}.$$

Hence, after transformation

$$z - qy - 2q(q-x+1) = 4q\sqrt{q-x}$$

$$p + 2q = -\frac{2q}{\sqrt{q-x}}$$

$$4q + y - 2x + 2 = \frac{4x-6q}{\sqrt{q-x}}$$

Introducing $z = pq$ and putting $\sqrt{q-x} = t$ the first and the third equation give

$$2t^4 + 4t^3 + Bt^2 + 4xt + xy + 2x - z = 0$$

$$4t^3 + 6t^2 + Bt + 2x = 0$$

therefore the discriminant of the first member of the first equation must be zero.

If we assume

$$24(xy-z) = A$$

this may be written

$$(A + B^2)^2 - \{B(3A - B^2) + 216z\}^2 = 0$$

or, after a slight reduction

$$A(A - 3B^2)^2 - 432zB(3A - B^2) - 46656z^2 = 0.$$

This solution, though different in form from the former result, represents the same surface; that it passes through the line

$$y = z = 2x$$

may be easily verified.

Physics. — “*On some relations holding for the critical point*”. By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

1. In this paper we will derive some important relations which exist between some critical quantities.

If it may be accepted that in the association to multiple molecules no generation of heat (change of energy) takes place, so that $q = 0$ may be put, we saw already in I, p. 291 that the relation

$$j = \left(\frac{T dp}{p dT} \right)_k = 1 + \frac{a}{p_k v_k^2} \dots \dots \dots (1)$$

holds.

If we now put $v_k : b_k = r$, and substitute for p_k its value, viz. (see I, p. 289)

$$p_k = \frac{1}{27} j_2 \frac{a}{b_k^2},$$

we find:

$$(j-1)r^2 = \frac{27}{j_2} \dots \dots \dots (2)$$

If instead of (1) we write:

$$f = \frac{\rho_k + a/v^2}{\rho_k} = \frac{\alpha_k RT_k}{\rho_k (v_k - b_k)},$$

in which $\alpha_k = \frac{1 + a \beta_k}{1 + a}$, and if we substitute the value (see I, p. 288 and 297)

$$RT_k = \frac{8}{27} f_1 \frac{a}{b_k}$$

for RT_k , and further the above values for ρ_k and v_k , we get:

$$f(r-1) = 8\alpha_k \frac{f_1}{f_2} \dots \dots \dots (3)$$

From:

$$\mu = \frac{\rho_k v_k}{RT_k}$$

follows after substitution of the values for ρ_k, v_k and RT_k :

$$\frac{r}{\mu} = 8 \frac{f_1}{f_2} \dots \dots \dots (4)$$

From (3) and (4) follows also the remarkable relation:

$$f \mu \frac{r-1}{r} = \alpha_k \dots \dots \dots (5)$$

Finally by combination of (2) and (4) we find:

$$\mu^2 (f-1) = \frac{27}{64} \frac{f_2}{f_1^2} \dots \dots \dots (6)$$

The relations (2), (4), and (6) have also been derived by VAN DER WAALS (see among others These Proc. June 1910, p. 118, and those of April 1911, p. 1216 et seq.) in the following form:

$$(f-1) r'^2 = 27 ; \quad r's = 8 ; \quad \frac{s^2}{f-1} = \frac{64}{27} \quad (\text{all this by approximation}).$$

In this the quantity s is $= 1 : \mu$, while r' is not $= v_k : b_k$, but $= v_k : b_g$. In consequence of this our relation (5) is VAN DER WAALS's relation (he has not taken into account the factor α by the side of RT)

$$\frac{b_k}{b_g} = r' \left(1 - \frac{s}{f} \right).$$

According to (5) $\frac{r-1}{r}$ would namely be $= \frac{s}{f}$ with $\alpha_k = 1$, or $r \left(1 - \frac{s}{f} \right) = 1$. In this $r = v_k : b_k$. So if we substitute $r' = v_k : b_g$ for r , we get $r' \left(1 - \frac{s}{f} \right) = \frac{b_k}{b_g}$.

It was also already made probable by VAN DER WAALS (loc. cit.), that $(f-1)r^2 < 27$ and $rs < 8$, but $s^2 : (f-1)$ almost exactly = $64 : 27^3$.

The theory developed by us confirms these relations perfectly. We found namely in I (p. 297) and II (p. 430 and 431) for the factors f_1 and f_2 :

$$f_1 = \frac{1+x}{1-x} \frac{n^2(3m^2-2n)}{m^3} = 1,004 \ (x=1) \text{ and } 1,010 \ (x=2)$$

$$f_2 = \frac{(3m^2-2n)^2(4n-3m)}{m^3} = 1,007 \ (x=1) \text{ and } 1,019 \ (x=2)$$

See equation (5) in I, p. 288 for the signification of the quantities m and n .

Really $(f-1)r^2 = 27 : 1,007$ is < 27 , but only little smaller; $rs = 8 \frac{1,004}{1,007}$ also < 8 , but also only little smaller. This holds for $x = 1$ (partial association to double molecules), but the same holds also for $x = 2$ (triple molecules).

But we see also that $\frac{s^2}{f-1} = \frac{64}{27} \cdot \frac{(1,004)^2}{1,007}$ is very near $\frac{64}{27}$; also in the case of $x = 2$, where $\frac{f_1^2}{f_2} = \frac{(1,010)^2}{1,019} = 1,001$, just as $\frac{(1,004)^2}{1,007}$. So the value of $s^2 : (f-1)$ is only a thousandth of the value higher than $\frac{64}{27}$, viz. 2,3727 instead of 2,3703.

As $\mu = p_k v_k : RT_k$ and $f-1 = a : p_k v_k^2$, we have also

$$\mu^2(f-1) = a \cdot \frac{\mu^2}{(RT_k)^2},$$

and so from 6 follows:

$$a = \frac{27}{64} \frac{1}{1,001} \frac{(RT_k)^2}{p_k},$$

which equation together with the equation that follows from (1), viz.

$$a = (f-1) p_k v_k^2,$$

can serve for the determination of a (see also VAN DER WAALS, loc. cit.)

3) I may point out here that the different critical quantities were already expressed by me in experimentally determinable quantities in 1905 in a quite analogous way (see Arch. Teyler 1905 p. 46 and 47). The quantity f was there excluded on account of the possibility that b might be a function of the temperature. For then the fundamental equation (I) no longer holds, as we have proved (I p. 291). And instead of the quantity $r = v_k : b_k$ the quantity $\alpha = a : RT_k v_k$ was then

introduced by me by the side of μ . So α is evidently = $\frac{27}{8f_1} \cdot \frac{1}{r}$.

Our relations (3) and (5) may effectually be used to calculate α_k , i. e. *the state of association* at the critical point. Specially (5) is particularly suitable for this purpose, because f_1 and f_2 no longer occur in it. As α_k has been added by us as a factor to RT_k in the equation of state, it can be also decided whether the associated molecules really behave as one molecule as far as their influence on the *pressure* is concerned, i. e. whether there is *real* association, or — as VAN DER WAALS cautiously expresses it — “quasi-association.”

Now we saw in I, p. 295 that β_k must be = 0,955 for $x = 1$; and in II, p. 429 that β_k becomes 0,958 for $x = 2$ (in order that f may become = 7 and $\mu = 0,265$ for T_k). So we find the value $\frac{1,955}{2} = 0,977$ for α_k if $x = 1$, and if $x = 2$ the value $\frac{2,916}{3} = 0,972$,

so that $f\mu^{\frac{r-1}{r}}$ would have to be = 0,98 à 0,97 and not = 1. Only a very accurate knowledge of the quantities f, μ and $r = v_k : b_k$ could decide this.

It follows from (2) and (3) that

$$f = 1 + \frac{27}{f_2} \frac{1}{r^2} = 8\alpha_k \frac{f_1}{f_2} \cdot \frac{1}{r-1}.$$

If we put f_2 and $\alpha_k f_1 : f_2$ both = 1 (for $x = 1$ $f_2 = 1,007$ and $\alpha_k f_1 : f_2 = 0,977 \times 1,004 : 1,007 = 0,974$), we get by approximation:

$$\frac{8}{r-1} = 1 + \frac{27}{r^2} \dots \dots \dots (7)$$

By approximation this is really fulfilled by values of r in the neighbourhood of 3 (for $r = 3$, where f_1, f_2 and $\alpha_k = 1$, (7) would be quite accurately fulfilled). Thus the two members for $r = 4$ become

resp. $\frac{8}{3} = 2,67$ and $\frac{43}{16} = 2,69$; and for $r = 2$ resp. 8 and 7,75.

If we take the factors f_1, f_2 and α_k into consideration, the first member becomes = $1 + 27 : (1,007 \times 4,469) = 7,00$ for $r = 2,114$, and the second member (= $8 \times 0,9744 : 1,114$) equally = 7,00 (= f).

It is owing to this accidental property of the expression

$$1 + \frac{27}{r^2} - \frac{8}{r-1},$$

namely that it differs only very little from zero for values in the neighbourhood of $r = 3$, that the factors f_1 and f_2 differ so little from 1, and that also in the case $v_k : b_k = 2$ the expressions RT_k

and p_k are again = $\frac{8}{27} \frac{a}{b_k}$, resp. $\frac{1}{27} \frac{a}{b_k^2}$ with close approximation.

With regard to the course of the quantities f , v , and μ for different values of β , we may make the following remarks.

a. With regard to f , given by (see I, p. 294)

$$f = \frac{4n}{4n-3m},$$

in which (for $x=1$)

$$\left. \begin{aligned} m &= 1 + \frac{1}{2}\beta(1-\beta)(1+\varphi)^2 \\ n &= 1 + \frac{3}{4}\beta(1-\beta)(1+\varphi) + \frac{1}{8}\beta(1-\beta)(1-3\beta^2)(1+\varphi)^2 \end{aligned} \right\}$$

(see I, p. 288 and 295), we see immediately that — in view of the fact that m and n assume the value 1 both for $\beta=1$ and for $\beta=0$ — this quantity is $=4$ for $\beta=1$ and also for $\beta=0$. But for intermediate values of β , if φ has only any value (i. e.: if Δb differs from 0), f will be greater than 4 in the neighbourhood of $\beta=1$, and smaller than 4 in the neighbourhood of $\beta=0$. Only if $\varphi=0$, i. e. Δb where $=0$, f would be permanently <4 , which is easy to prove from the above expressions for m and n ¹⁾. So it follows from this — as f is found $=7$ for normal substances — that Δb must necessarily be >0 , if f is to reach so high a value. Accordingly we found in I, p. 295, that β must be $=0,955$ and $\varphi=1,23$ for $x=1$, i. e. $\Delta b : b_g$ about 0,7, if we are to get at the same time $f=7$ and $\mu=0,265$. For $x=2$ we must have for this $\beta=0,958$, $\varphi=0,916$, i. e. $\Delta b : b_g$ about $=0,35$ (see II, p. 429).

¹⁾ So the value found by KAMERLINGH ONNES for Helium, namely $f=2,8$, need not be impossible, as VAN DER WAALS thinks (These Proc. April 1911, p. 1217). When $\Delta b=0$ (hence b remains constant), f is, as we saw, always <4 for values of β between 0 and 1, which is owing to the factor $\alpha=(1+\beta):2$ by the side of RT (which VAN DER WAALS omits; see above). And when Δb has a slight positive value (which may be the case for Helium), and so when b suitably diminishes with v , f will become >4 only near $\beta=1$, but all over the further range between β almost 1 and $\beta=0$ f will be again <4 . So it is very well possible that such an association exists for He at the critical point for not too great value of Δb (it need only be slightly greater than the normal association), that f becomes <4 .

It remains only to consider whether f can be so much smaller than 4. For $\varphi=0$ ($\Delta b=0$), f can decrease to about 3,4 for $\beta=0,5$; but for $\varphi>0$ this value can become considerably lower, if β is only sufficiently lower than 1.

Note added during the correction of the Dutch proof. After the above remarks had been written, K. O. has carried out some new measurements, and found 4,5 for Helium for f at T_k (These Proc. Dec. 1911, p. 684), so $f>4$ also here. But at lower temperatures a considerably lower value is still found, namely $f=3$ at the boiling point, so somewhat higher than the former value 2,8 (see above). Now in normal cases f is always about 4% lower for $m=0,8$ than for $m=1$ (6,7 instead of 7); for Helium, however, this would amount to as much as 33%,

If for $x=1$ and $q=1,23$ we take the value of β only little less than 0,955, e.g. 0,9, we find for f' already the value 17,6 with $m=1,223$, $n=0,973$. (for $\beta=0,955$ these values were resp. 1,107 and 0,969). [For $x=2$ this value, though >7 , would be considerably lower].

But if we take $\beta=0,1$, we find $f'=3,6$ with $m=1,223$, $n=1,271$, so again <4 .

Now for the so-called *anomalous* substances f' is really found >7 ; for water 7,5 is found, for acetic acid 8, for ethylalcohol 9. So it would follow from this that at the critical point these substances have a value of β , which is $<0,955$, resp. $<0,958$. But as the curve $f=f(\beta)$ does not intersect the straight line $f'=4$ until in the neighbourhood of $\beta=1/3$, β could even be considerably smaller than 0,96. But on no account can β be near 0, because then f' would again become <4 .

So for acetic acid, water, alcohol etc. there does exist a *greater* association than for the normal substances at the *critical* point, but most probably not a considerably higher association, and certainly not an almost complete one (β near 0).

b. The value of r . From (see I, p. 288 and 296)

$$r = \frac{r_k}{b_k} = \frac{3m^2}{3m^2 - 2n}$$

we can easily derive that r is always <3 , when $\beta < 1$ and >0 . With the above values of m and n we find e.g. that $r=2,114$ for $\beta=0,955$; assumes the value 1,77 for $\beta=0,90$; the value 2,31 for $\beta=0,1$ (all this with $x=1$).

So for *abnormal* substances a value $<2,1$ must be found for r .

c. The quantity μ . From (see I, p. 289 and 294)

$$\mu = \frac{3}{8} \frac{1 + \beta m^2}{2 n^2} (4n - 3m)$$

follows that $\mu=0,375$ for $\beta=1$, but takes the value 0,1875 for $\beta=0$. Further it can be shown that the curve $\mu=f(\beta)$ always lies above the straight line that joins $\mu=3/16$ with $\mu=3/8$ for $q=0$ ($\Delta b=0$). This is moreover clear from the above formula (5), from which immediately follows that then μ is always $>\frac{3}{8} a_k$.

But if $q > 0$ ($\Delta b > 0$), the curve $\mu=f(\beta)$ lies above the said straight line at $\beta=0$, but falls pretty far below it at $\beta=1$.

So we find already the value 0,265 for $\beta=0,955$; the value 0,124 for $\beta=0,9$; but the value 0,270 for $\beta=0,1$. (again all this at $x=1$, $q=1,23$).

Hence we shall find a value $\leq 0,265$ for μ for abnormal substances. This is actually found. For acetic acid e.g. μ is 0,20, for alcohol we find 0,25.

It is noteworthy that f and μ again approach closely to the ideal values 4 and 0,265 for H_2 ; for f we find namely 4,8, and for μ the value 0,34. So this means that then the state of association at the critical point is less than the normal; i. e. $\beta > 0,96$. From formula (5) the value 2,5 would follow for ν , which also comes nearer to the ideal value 3.

2. The formula for the vapour pressure at the critical point. From the well known formula (see among others my Thermodynamik in der Chemie p. 59 (1893))

$$\frac{dp_{cx}}{dT} = \frac{1}{v' - v} \int_r^{r'} \left(\frac{dp}{dT} \right)_r dv$$

follows, as (see p. 290)

$$\left(\frac{dp}{dT} \right)_r = \frac{1}{T} \left(p + \frac{a}{v^2} \right)$$

for β independent of T ($q=0$):

$$\frac{dp_{cx}}{dT} = \frac{1}{v' - v} \int_r^{r'} \frac{1}{T} \left(p + \frac{a}{v^2} \right) dv.$$

Hence

$$T \frac{dp_{cx}}{dT} = \frac{1}{v' - v} \int_v^{v'} p dv + \frac{1}{v' - v} \int_v^{v'} \frac{a}{v^2} dv,$$

or also

$$T \frac{dp_{cx}}{dT} = p_{cx} + \frac{a}{v'v},$$

in which p_{cx} denotes the pressure of coexistence. If henceforth we omit the index cx , we get:

$$\frac{T dp}{p dT} = 1 + \frac{a}{p v^2} \dots \dots \dots (8)$$

For this we may also write:

$$\frac{m d\varepsilon}{\varepsilon dm} = 1 + \frac{a}{p k v k^2} \frac{dd}{\varepsilon},$$

or as $a : p k v k^2$ is evidently $= f' - 1$, when f' denotes the value of $\frac{T dp}{p dT}$ at the critical point:

$$\frac{d\varepsilon}{dm} - \frac{\varepsilon}{m} = (f-1) \frac{dd'}{m} \dots \dots \dots (9)$$

So this is the most general differential equation, which gives ε as a function of m . But only when d and d' should be perfectly accurately known as functions of m , the integral expression $\varepsilon = f'(m)$ can be found.

Now the solution is possible for two extreme cases: 1 in the neighbourhood of the critical temperature, and 2 at low temperatures when the vapour follows the laws of the ideal gases; and the liquid density does not change much any more.

Near the critical temperature.

Then $d = 1 + a\tau + b\tau^2$, $d' = 1 - a\tau + b\tau^2$, hence

$$dd' = (1 + b\tau^2)^2 - a^2\tau^2 = 1 - (a^2 - 2b)\tau^2,$$

when $\tau = \sqrt{1-m}$. (See II, p. 438). If we now put

$$a^2 - 2b = \gamma,$$

we get accordingly

$$dd' = 1 - \gamma(1-m).$$

If we write further :

$$\varepsilon = 1 - f(1-m) + f''(1-m)^2,$$

then we have :

$$f = \left(\frac{d\varepsilon}{dm}\right)_k; \quad f'' = \left(\frac{d^2\varepsilon}{dm^2}\right)_k,$$

because $m = 1$ at T_k , and $\left(\frac{d\varepsilon}{dm}\right)_k = \left(\frac{m}{\varepsilon} \frac{d\varepsilon}{dm}\right)_k$ was denoted by f .

In consequence of this (9) passes into

$$[f - f''(1-m)] - \frac{1 - f(1-m)}{1 - (1-m)} = (f-1) \frac{1 - \gamma(1-m)}{1 - (1-m)},$$

or in

$$[f - f''(1-m)] - [1 - (f-1)(1-m)] = (f-1) [1 - (\gamma-1)(1-m)],$$

from which immediately follows :

1) From YOUNG'S data in his famous summary in the Proc. R. Dublin S. of June 1910 it appears however, that this relation is not accurately satisfied. We find viz. values for $\theta = \left(\frac{m}{\varepsilon} \frac{d\varepsilon}{dm} - 1\right) : \frac{dd'}{\varepsilon}$, which increase from 6 (at T_k) to about 9 (at $m = 0,5$). In the neighbourhood of T_k even very rapidly. Thus for C_6H_6F the value of θ is already = 6,23 at $m = 0,9935$; for $m = 0,9942$ we find 6,71 etc. etc. VAN DER WAALS already stated that θ is pretty accurately represented by $\theta = 1 + \sqrt{1-m} - \frac{1}{2}(1-m)$. We shall, however, *this* variability, which is also in *that* form with $\sqrt{1-m}$ an impossibility, leave out of consideration in what follows.

$$-f'' + (j-1) = -(j-1)(\gamma-1).$$

i. e.

$$f'' = (j-1)\gamma,$$

or also

$$\frac{f''}{f-1} = \gamma = a^2 - 2b, \dots \dots \dots (10)$$

a very remarkable relation between the quantities $\frac{d\varepsilon}{dm}$ and $\frac{d^2\varepsilon}{dm^2}$ at the critical point, and the coefficients a and b of the densities of the coexisting phases d and d' .

We find for *Argon* according to CROMMELIN'S data (Comm. 118, p. 9):

$$d - d' = \frac{0,4714}{0,509} \text{ at } 1 - m = \frac{3,05}{150,7},$$

and as $a = \frac{1}{2}(d-d') : \sqrt{1-m}$, we get:

$$a = \frac{0,4714}{1,018} \sqrt{49,4} = 0,463 \times 7,03 = 3,26.$$

For b , the coefficient of the direction of the straight diameter, has been found

$$b = 0,9027,$$

so that $\gamma = a^2 - 2b = 10,63 - 1,81 = 8,8$.

The value 5,7 has further been found for f , and by approximation we may calculate:

$$\frac{d\varepsilon}{dm} \text{ at } -123^{\circ},96 = \frac{5,54}{3,05} \cdot \frac{150,7}{48,0} = 1,82 \times 3,14 = 5,70$$

$$\frac{d\varepsilon}{dm} \text{ at } -127^{\circ},66 = \frac{6,61}{4,34} \cdot \frac{150,7}{48,0} = 1,52 \times 3,14 = 4,78$$

from

T	p
- 122°,44 C.	48,00 (crit.)
- 125,49	42,46
- 129,83	35,85

So we find $\frac{0,92}{3,70} 150,7 = 38$ for $\frac{d^2\varepsilon}{dm^2}$.

This value 38 can of course not lay claim to a high degree of accuracy, because the data are too incomplete for this. If we take a round number 40, we get $f' : (f' - 1) = 40 : 4,7 = 8,5$, while we found above about 8,8 for γ . So the agreement is satisfactory.

So for substances where a is about 3,2 (see II p. 437), $b = 0,9$, $f = 7$, we should have to find about $f' = 8,4 \times 6 = 50$.

From the data of Fluorbenzene (see KUENEN, die Zustandsgleichung, p. 99) follows $\frac{d\varepsilon}{dm}$ resp. $\frac{0,322}{0,05} = 6,44$, and $\frac{0,206}{0,05} = 4,12$, so $\frac{d^2\varepsilon}{dm^2}$ approximated $= \frac{2,32}{0,05} = 46$, which really gets very near 50¹⁾.

Formula (10), which is quite accurate and of general application, i.e. in the critical point, can therefore render good services — when the quantities f and f' are known from vapour-tension observations near T'_k — to calculate the quantity $\gamma = a^2 - 2b$, which renders it possible to calculate accurately the quantity a — which in other circumstances is so difficult to determine experimentally, and which indicates the divergence of the two phases just below T'_k — when b is known, i.e. the direction of the straight diameter. Then, however, the direction of this locus should be taken *very near* T'_k , which will probably differ somewhat from the further direction — at least if it is confirmed that very near T'_k the straight diameter undergoes an abrupt inflection to the vapour side [CARDOSO; see II, p. 437 (read p. 430 last line concave instead of convex side)].

I draw here attention to the fact, that the well-known formula of VAN DER WAALS, viz.

$$-\log \varepsilon = f' \frac{1-m}{m},$$

which in this form holds for a large part of the temperature region, is no longer quite accurate in the neighbourhood of T'_k . For though this formula then gives the suitable value for $\left(\frac{d\varepsilon}{dm}\right)_k$, it deviates in the second differential quotient. We have namely:

$$\frac{d\varepsilon}{dm} = \varepsilon \frac{f}{m^2},$$

hence :

1) From YOUNG's tables loc cit. we derive from four successive values of m between 0,9347 and 0,9883 resp. $f'=30$ and 42. For $m=1$ f' will draw near to 59. But for a we find at least 3,4, so that γ becomes = 10, and hence $f' = 60$.

$$\frac{d^2\varepsilon}{dm^2} = f \left[\frac{1}{m^2} \frac{d\varepsilon}{dm} - \frac{2\varepsilon}{m^3} \right],$$

which becomes for T_k :

$$f' = \left(\frac{d^2\varepsilon}{dm^2} \right) = f'(f-2),$$

instead of $f' = (f-1)(a^2-2b)$, as we found above. So according to VAN DER WAALS'S formula f' would be $= 7 \times 5 = 35$, whereas really f' is about $= 6 \times 8,5 \dot{\text{a}} 10 = 50 \dot{\text{a}} 60$.

So according to VAN DER WAALS we should have at T_k :

$$\varepsilon = 1 - f(1-m) + \frac{1}{2}f(f-2)(1-m)^2;$$

and according to our formula:

$$\varepsilon = 1 - f'(1-m) + \frac{1}{2}(f'-1)(a^2-2b)(1-m)^2.$$

Clarens, Dec. 15, 1911.

Anatomy. — “On the relation between the symphysis and the acetabulum in the mammalian pelvis and the signification of the cotyloid bone.” By A. J. P. v. D. BROEK. (Communicated by Prof. L. BOLK).

In the course of investigations on the structure of the pelvis of Primates I met with some phenomena in the acetabulum, namely the development of the cotyloid bone os acetabuli, that induced us to a comparison with the pelvis of other mammals.

In the Primates the cotyloid bone appears as is pointed out by me¹⁾, in the form of two little triangular bones, an anterior and a posterior one. The anterior cotyloid bone lies between pubis and ilium, the posterior between ilium and ischium. The former excludes the pubis from the acetabulum.

An investigation in the cotyloid bone in other mammals brought to light a distinct correlation between the development of the symphysis and the composition of the acetabulum, which I shall explain in this note. This correlation is, as I think, of some value for our knowledge in the morphologic signification of the cotyloid bone.

In the following explanations I shall divide the pelvis of mammalia after the composition of their symphysis.

1. Symphysis composed by the os pubis and os ischii. In the *Monotremes*, as is known, os pubis and os ischii take the same part in the forming of the symphysis, which is very high. The acetabulum is formed by the three components of the os coxae, namely the os

ilei, os ischii and os pubis which take about the same part in it. An os acetabuli has not yet been found in the monotremes.

Marsupialia. In the marsupials the symphysis is high and is for the greater part formed by the os pubis, and for a smaller part by the os ischii.

In the marsupials has been found an os acetabuli as well, but only as a very small calcified piece of cartilage, against the os pubis. It does not extend to the border of the acetabulum, as LECHE ⁴⁾ writes, the pubic bone taking part at that border in the formation of the articular surface. (*Didelphys*, *Phascolumys*).

Rodentia. *Hydrochoerus* and *Sciurus* are two genera by whom the ischium also; but only partially takes share in the symphysis. The os acetabuli is developed in the same manner as in the Marsupials above-mentioned. It is a little bone on the os pubis, excluding this bone partly from the acetabulum. The os acetabuli exists of calcified cartilage.

Carnivora. Only in *Canis familiaris* as is pointed out by LECHE the pubic bone takes part in the formation of the acetabulum, in all the other carnivora it is excluded therefrom by the cotyloid bone.

After ELLENBERGER and BAUM ⁵⁾ the symphysis in the dogs pelvis is a symphysis pubis et ischii.

Ungulata. Except in *Tapirus americanus*, an os acetabuli fails, in *ungulata* so far as we know; the os pubis forming, as is described by GEGENBAUR ³⁾ "einen bedeutenderen Theil der Pfanne" (l.c. p. 234).

It is well known that the symphysis in the *ungulata* is very high and is formed by the pubic and the ischial bones.

It is necessary to remark that WEBER gives a figure of the pelvis of a *Cervus speciosus* (l.c. pg. 107 fig. 85) in which we see a very great cotyloid bone extending over the whole breadth of the acetabulum; yet the os pubis is taking part in the formation of the articular surface.

II. Symphysis formed exclusively by the os pubis.

Tubulidentata. Although the symphysis is very high, it is formed exclusively by the pubic bone.

In *Orycteropus* I found a very great triangular shaped os acetabuli between ilium and pubis. It has quite excluded the pubis from the acetabulum, and reaches for a part the medial surface of the os coxae between the bonepieces above-mentioned.

Rodentia. In the majority of *Rodentia* the symphysis is exclusively a symphysis pubis. In two of them, namely *Cavia* and *Mus*, the os acetabuli which is situated at the ventral side of the acetabulum, has nearly quite excluded the pubic bone and the pubic bone reaches

the acetabulum only at the border; in the others, namely *Lepus-Hesperomys Xerus*, the os pubis is quite excluded from the formation of the articular surface.

As far as I know and could observe (*Hystrix*, *Dasyprocta*) in Rodentia only at the ventral side of the acetabulum between Ilium and Pubis an os acetabuli is found and Ilium and Ischium verge directly upon each other at the back. It consists of calcified cartilage.

Carnivora. In carnivora fissipedia, where the symphysis is limited to the os pubis (*Viverra*, *Mustela*)¹⁾ the os acetabuli is strongly developed, reaches the medial surface of the pelvis and thus separates ilium and pubis, quite excluding the latter from the acetabulum.

For carnivora pinnipedia prevails, according to WEBER²⁾ that the os acetabuli is "besonders ausgedehnt", though, as LECHE describes, the pubic bone reaches the articular surface and takes part in its formation.

As to the symphysis, WEBER²⁾ says that notwithstanding the length of the ossa pubis, "die Kürze der Symphyse auffällt".

Prosimiae and *Primates*. In both these groups and also in homo, by whom the symphysis is exclusively formed by the pubic bone the os acetabuli shows a very important and at the same time remarkable way of development. As has been said already in the beginning, and described some where else more fully we see nearly always two ossa acetabuli, one between the ilium and pubis, the other between ilium and ischium, which I distinguish as a dorsal and a ventral os acetabuli. Both are triangular in shape with their top towards the middle of the acetabulum. They so to say push out the ilium partly from the acetabulum, it is at the cost of this bone that the ossa acetabuli develop themselves further in the articular surface.

They form the transition between the simple os acetabuli and one as I found in *Myrmecophaga* that extends over the whole breadth of the acetabulum and now separates the ilium from the pubis as well as from the ischium.

III. Symphysis formed by a small part of the os pubis and for the greater part by the so called "epiphysenknorpel".

This form of symphysis only appears as far as known in *Galacopithecus*. Here the composition of the acetabulum, which only for the third part is formed by the ilium, for the rest by the ischium and the os acetabuli, is important; while the pubis is quite excluded from the formation of the articular surface.

IV. Symphysis formed exclusively by the so called "epiphysenknorpel." A connection between the two halves of the pelvis exclusively formed by the so called "epiphysenknorpel" is found among the Insecti-

vora, in Myogale-Erinacaeidae-Centetidae-Chrysochloridae. In some (Erinacaeus, Centetes) the os acetabuli shows in its extension conformity with Galaeopithecus, in others — Myogale (in Chrysochloris it has not yet been observed) this bone is developed more strongly, and it excludes the os pubis as well as the os ilei from the formation of the articular surface.

The acetabulum is thus formed only by the ischium and the os acetabuli. When we study the medial surface of the os coxae it appears that the os acetabuli does not quite reach that surface; there ilium and ischium, and also ilium and pubis partly verge directly.

Thus it represents in the main a small piece of bone on the external surface of the ilium. Save in the named Insectivorae a formation of the symphysis by the so called "epiphysenknorpel" is observed in *Manidae*, after the description of LECHE⁵⁾ in "Bronn's Klassen und Ordnungen des Tierreiches". I observed in *Manis* an os acetabuli excluding as well the os pubis as the os ilei from the acetabulum. It did not reach the medial surface of the os coxae. At the ventral border of the acetabulum it is broader than at the dorsal border.

The composition of the symphysis in *Xenarthra* is apparently not yet well known. In the above mentioned study of LECHE⁵⁾ one finds on page 583 "die kurze, stets nur durch das Schambein gebildete Schamfuge", and on the same page further "das Schambein ist ventralwärts ausgezogen in einen langen Process, welcher durch einen Schamfugenknorpel mit den gegenseitigen verbunden ist". A figure of *Tatusia peba* (Plate 92 fig. 10) shows us the presence of an "epiphysenknorpel". The os acetabuli is strongly developed, in Dasypodidae it is still greater than in Bradypodidae. It excludes the os pubis from the acetabulum and reaches the medial surface of the os coxae between these two bones. In *Choloepus* and *Myrmecophaga* the ilium only forms a very little part of the border of the articular surface.

In the Dasypodidae both the pubis and the ilium are, after the description of REINHARDT⁶⁾ excluded from the acetabulum. I found this condition in *Dasypus duodecimocinctus*; in which the os acetabuli reached partially the medial surface of the os coxae. At the dorsal border of the acetabulum it covered only the outer surface of the ilium.

V. Symphysis fails.

At last we have to consider the mammals in which a symphysis is failing in the adult. This condition is, as is well known, only to be observed in some of the *Insectivora*, viz *Soricidae*, *Talpinae* and *Urotrichus*. In these three forms the cotyloid bone is very great and

separates the ilium from the pubis and the ischium. The acetabulum is only composed by the ischium and the os acetabuli. This bone reaches also the medial surface of the os coxae, so that also there the ilium is separated from ischium and pubis.

The above given survey leads to the following conclusions.

1st. The os acetabuli shows among the mammals a very different degree of development. It is greater and forms a more and more important part of the acetabulum as the symphysis is lower.

2nd. The development of the os acetabuli shows no more than the symphysis a regularity, in this sense that it should be otherwise in the so called primitive mammals than in the so called higher mammals.

In more than one order of mammals we meet with very great differences in the degree of development of the os acetabuli and of the symphysis (Edentata-Rodentia-Insectivora-Carnivora).

These two conclusions lead to the question by what reasons would be determined the development of the symphysis and what would be the morphologic value of the os acetabuli.

The answer to the first question must be removed to later; here it can only be said, that, as the result of comparative anatomical and embryological researches one can say, that a high symphysis is a secondary condition (LECHE l. c. p. 23).

Applying this to the mammals above described, it follows that in those mammals which possess, in consequence of their high symphysis a primitive form of pelvis, an os acetabuli seems to fail (Monotremens, Ungulata?). As soon as the symphysis is not so high we can observe an os acetabuli, growing more developed as the symphysis becomes lower.

It is not yet permitted to say that the os acetabuli in mammals is a constant, so called fourth element of the os coxae, for which can be shown a homologon in other vertebrates.

If one wishes to compare the os acetabuli in the mammalian pelvis with the little bone known as the "pars acetabularis" in the pelvis of crocodiles, as is done by LECHE, one has not yet the right to speak of an independent bone, because we know that, after the investigations of WIEDERSHEIM⁸⁾ this pars acetabularis is a secondary part, separated in the course of the development from the processus acetabularis ilei.

If the os acetabuli and the pars acetabularis are homologous bones, the former can only be regarded as a bone of a secondary signification; in his development dependent on development of the pelvis.

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Physics. — “*Electric double refraction in some artificial clouds and vapours*” (second Part). By Prof. P. ZEEMAN and C. M. HOOGENBOOM.

10. The condenser mentioned in the experiment of § 3 was placed in the interior of the horizontal glass tube; the metal plates were of 18 cm. length, their distance being 16 mm. The investigation of gases and vapours, acting chemically upon the metal of the condenser plates is better conducted in an apparatus with external plates and the same apparatus may be serviceable also in other cases as it is more easily cleaned. An apparatus made of glass and of parallelepipedic form was therefore constructed, (length 46,5 cm., distance between the insides of the vertical walls 5 mm., height 10 cm. thickness of glass 3 mm.). At the outside strips of tin foil 40×3 cm. were arranged. The tube is closed by plates of thin coverglass.

11. The experiment with the sal-ammoniac cloud produced in an anteroom (§ 4), was repeated with the new condenser, but with the old optical arrangement (§ 3).

It now appeared that the result obtained in § 4, indicating solely a double refraction induced in the sal-ammoniac cloud, was a rather special case.

The sal-ammoniac cloud now exhibited dichroism also. As it is probably the greater density of the cloud operative in the new apparatus, which made it easier to observe the new property, the anteroom (§ 4) was removed altogether. In our further experiments the gases, hydrochloric acid and ammonia, were introduced directly

into the observation room, the cloud produced being now much denser than before.

Small differences of potential caused a downward motion, accompanied with a slight fading of the black band § 3, a potential difference of 8000 Volts made it disappear completely. It became visible again by a clock-wise rotation of 10° of the analyser, which had been crossed with the polariser before establishing the field. The position of the polariser is defined in § 15.

This experiment proves that in a sal-ammoniac cloud double refraction, accompanied by dichroism is induced by electrostatic fields.

12. No effect was exhibited by the unmixed gases, hydrochloric acid or ammonia.

13. Strong currents of ammonia and of hydrochloric acid were introduced into the apparatus, a dense cloud being produced. Under the action of the electric field or by a slight rotation of the analyser, the transmitted light looks yellow red. If the currents of gases are interrupted after a while there is only a general diminution of the light of the NERNST filament. That there is still absorption by a cloud, is proved by the illumination of the field of view produced when a current of neutral gas displaces the cloud.

The slow change of colour of the sal-ammonia cloud was observed in a separate experiment, using a glass tube of 3 or 4 cm. width and of 50 cm. length. This change of colour apparently varies with the size of the particles in the cloud.

14. It is extremely remarkable that in parallel with this change of colour there occurs a change of the electric double refraction of the sal-ammoniac fog.

Producing a fog as in § 13 above and crossing the nicols with a field zero, the black band became invisible with a potential difference of 9000 Volts. By a clock-wise (§ 11) rotation of the analyser it reappeared; its displacement was *downward*.

The supply of the gases being interrupted the effect remained the same for perhaps a quarter of an hour. Then the effect apparently had diminished and finally the sign of the double refraction appeared to be the reverse of the original one. On throwing on the electric field the black band jumped *upwards*. In order to produce complete blackness of the band, again a clock-wise (§ 11) rotation of the analyser is necessary.

Hence we see that the sal-ammoniac cloud undergoes in the course of time a remarkable change; the induced double refraction is at first positive, afterwards negative; the dichroism does not change its direction.

15. The direction of vibration which is more strongly absorbed is very easily determined.

We know that a clock-wise rotation of the analyser (§ 11) was necessary in order to produce complete blackness of the band. The direction of vibration of the polariser joined the upper left, and the lower right quadrant. Hence it follows, as is easily seen, that *the vibrations parallel to the electric force are the more strongly absorbed ones.*

16. This result may be controlled by the following experiment. If we turn the polariser through an angle of 90° from its former position (§ 15) then we shall expect that in repeating the experiment of § 11, an anti-clock-wise rotation of the analyser will be necessary in order to see most clearly the neutral axis. This consideration is confirmed by experiment.

17. Our observations hitherto given, prove that *at least two* different modifications of sal-ammoniac clouds exist, which exhibit double refractions of opposite sign, at the same time the absorption of vibrations parallel to the field always exceeds that of vibrations at right angles to the field.

One of the special intermediate states of the cloud, when under electric action, exhibits dichroism *alone* and *no* double refraction.

(*To be continued*).

Chemistry. — “*Das Gesetz der Umwandlungsstufen in the light of the theory of allotropy*”. By Prof. A. SMITS. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of December 30, 1911).

Introduction.

Already in 1836 FRANKENHEIM¹⁾ pointed out that it cannot be said that a depositing pure substance will be solid or liquid according as the temperature at which this takes place lies under or above the melting-point of this substance. Thus phosphorus and sulphur, e.g. can deposit from solutions in liquid state, in spite of the temperature lying below the point of solidification. The same phenomenon has sometimes been observed when vapours were cooled.

Concerning this FRANKENHEIM writes as follows:

“Schwerer als aus Auflösungen kann ein Körper aus dem Dampfe flüssig niedergeschlagen werden, wenn die Temperatur unter dem Schmelzpunkte steht. Jod, welches sehr leicht, auch bei gewöhnlicher Temperatur sublimiert, habe ich nur in Krystallen erlangen können.... Bei dem Phosfor war jedoch das Resultat entscheidend. Ich brachte ihm auf ein etwas hohl geschliffenes Glas, legte eine dünne Glas-

¹⁾ Pogg. Ann. 39, 350 (1836).

platte darauf, und hielt diese durch verdampfenden Aether auf einer niedrigen Temperatur.

Der Phosfordampf, mochte er sich schon in der Luft oder erst auf dem Glase niederschlagen, hatte daher nirgends eine höhere Temperatur als die des Zimmers, etwa 20.°5 erlangt, und dennoch bildete er zwar kleine, aber deutliche Tropfen auf der Glasplatte. Der flüssige Aggregatzustand greift daher weit in den festen hinein. Während diese die Temperatur des Schmelzpunktes nie überschreiten kann¹⁾, bleibt der Körper nicht nur in niedriger Temperatur flüssig, sondern er wird es auch, wenn er durch Abkühlung des Dampfes, oder einer Auflösung, oder durch chemisch wirksame Mittel ausgetrennt wird²⁾.

A phenomenon which is in close connection with what precedes, and which has been observed by different investigators, is this that from a super-saturate solution, from which different substances can crystallise, the most soluble often deposits first.

Another peculiar phenomenon, which was brought in connection with what precedes, is the following: If we have a solution of HgJ_2 in methyl alcohol, then on addition of water the yellow modification, which is the metastable and more soluble one, deposits at the usual temperature as BANCROFT describes, whereas the red modification represents under these circumstances the stable and less soluble form. In connection with this BANCROFT³⁾ remarks: "Es scheint, als wenn man die Verallgemeinerung machen könnte, dass bei plötzlicher Fällung die weniger beständige Form die zuerst erscheinende ist".

Starting from FRANKENHEIM's observations OSTWALD⁴⁾ showed that similar phenomena are also to be observed where the change of a state of aggregation is attended with a chemical process.

First of all he cites here the example "phosphorus". Phosphorus vapour does not at once pass into the stable state, red phosphorus, but first into liquid, and then into yellow phosphorus⁴⁾.

He further points out that the vapour of cyanic acid yields the metastable cyanic acid on compression, just as the vapour of paracyanogen yields the metastable liquid cyanogen.

Finally OSTWALD shows that we also meet with such phenomena in chemical conversions, and he pronounces the opinion that all this points to the existence of a law which he calls "das Gesetz der Umwandlungsstufen", and which he formulates as follows: "Beim

¹⁾ Our opinion has changed in this respect.

²⁾ Journ. Phys. Chem. I, 142 (1896).

³⁾ Zeitschr. f. phys. Chemie 22, 306 (1897).

⁴⁾ It was not yet known at the time that there exist three crystallized states of phosphorus.

on the line G''_2G_5 . So the obtained vapour phase is a vapour represented by a point on the line G''_2G_5 , and now it appears experimentally that even on slow cooling to 60° liquid phosphorus is formed. In my opinion this phenomenon is to be explained in the following way. As follows from fig. 1 the different phases in which the phosphorus may occur, are chemically distinguished by the situation of the chemical equilibrium:



Phosphorus vapour and liquid phosphorus contain much αP , whereas red and violet phosphorus are rich in βP .

I think I must assume that in the vapour phase not only *molecule groups* or *quasi associations*¹⁾ occur, which preponderate in the liquid phosphorus, and are to be considered as nuclei for the formation of the liquid phosphorus, but that there will also be molecule groups in it, which preponderate in the solid red resp. violet phosphorus, and from which these phases may arise. This consideration, on which the nucleus theory to be discussed later on, is based, I will pass over in silence. It may only be pointed out here that as the just discussed vapour phase lies nearest the liquid phosphorus so far as its concentration is concerned, it will also be richest in nuclei for the formation of liquid. Moreover the liquid formation has this advantage over the formation of solid phases that for the latter a certain orientation of the movement of the molecules is required.

In consequence of the circumstances mentioned the velocity of condensation of the vapour may be greater than its velocity of crystallisation, in which case liquid will be formed. Whether the liquid remains, will depend on the velocity of crystallisation of the liquid at the condensation temperature. At 60° the number of crystallisation nuclei for *red* and *violet* phosphorus will be very small, first because this temperature lies about 500° under the melting-points of these modifications, secondly because liquid phosphorus differs so greatly in concentration from red and violet phosphorus. So it is owing to these circumstances that in the mentioned experiment the liquid phosphorus may be preserved for an indefinite time in the dark and in the absence of a catalyser.

¹⁾ VAN DER WAALS has first introduced the idea of *quasi association*, but has not brought this into connection with the formation of new phases.

If we now choose another case, and suppose that white phosphorus is kept in a vacuum at the usual temperature, and that part of this vacuum is cooled to a temperature at which the velocity of crystallisation of white phosphorus is still comparatively slight, then liquid is formed in spite of the slight difference in concentration between the vapour and the solid white phosphorus, because the velocity of condensation then still exceeds the velocity of crystallisation. At a temperature at which the velocity of crystallisation is greater, no liquid will be formed or it will disappear again immediately. When in this way liquid phosphorus has once been obtained, experience teaches that this metastable state on further cooling can suddenly turn to the solid white modification, which latter can be transformed to red phosphorus by the influence of light or of a catalyser. The red modification, which is also still metastable can finally still further be transformed to the stable violet phosphorus by means of a catalyser.

In order to explain these conversions I must enter a little more deeply into the process of crystallisation than I did just now, in which at the same time the preceding case will be elucidated further. Let us consider liquid phosphorus at the unary melting-point temperature. The mean concentration will correspond with the point L_1 , but in accordance with what precedes it is now assumed that in this liquid three molecule groups or quasi-associations are found, which are to be considered as nuclei for the three solid phases, the white one, the red one, and the violet one.

In general it may be said that the number of quasi-associations will be smaller as they differ more in concentration from the mean concentration, and therefore the number of nuclei for the white phosphorus will be greater than that for the red, and the number of nuclei for the violet phase will be the smallest.

To all probability the phenomenon of quasi-association is a process that increases with fall of the temperature, and therefore it is to be expected that the number of nuclei will always augment with decrease of temperature. According to these considerations however, nucleus formation is attended with a chemical reaction; when e. g. molecule groups separate to form a nucleus for the white phosphorus, the equilibrium



is disturbed in the immediate neighbourhood, and this will be reestablished by βP being converted to αP . Now it will depend on

the velocity of this reaction, how rapidly the nucleus is formed, and so too how great the number of nuclei is which can form per time unity. In consequence of the rapid decrease of the velocity of reaction with fall of temperature and in consequence of the increase of the viscosity the setting in of the equilibrium will have decreased so much in velocity that we get the phenomenon that the number of nuclei that forms during a certain time in a definite volume of undercooled liquid of constant temperature increases at first with the degree of undercooling, reaches a maximum, and then decreases again. If we now suppose that the liquid phosphorus has got the temperature of 0° , we shall certainly be on the descending branch of the nucleus curve at this temperature, which lies so far under the melting-points of red and violet phosphorus, and that so far from the maximum that the number of red and violet nuclei which has certainly never been very great, will be exceedingly slight.

This is, however, not the case for the white phosphorus. The number of white nuclei must comparatively be great here, so that when we seed the liquid phosphorus with solid white phosphorus, a rapid crystallisation takes place, during which the nuclei pass into the crystallized state after the movement has become "molecular geordnet". The velocity of this crystallisation will increase with the number of nuclei, but fall of temperature will make the velocity of crystallisation decrease also in case of a constant number of nuclei, so that also in the velocity of crystallisation as function of the degree of undercooling a maximum will occur, which need not coincide in temperature with the maximum in the nucleus-curve. That the maximum in the curve for the velocity of crystallisation lies mostly at a higher temperature than the maximum in the curve for the number of nuclei proves that the influence of the temperature on the velocity of crystallisation is very great.

As is known the nuclei may also lead to spontaneous crystallisation, when the number of nuclei is great at not too low temperature.

An analogous reasoning holds for the conversion of one solid modification into another.

For it follows immediately from the foregoing remarks that what holds for liquid phosphorus, must also apply to the white phosphorus, and this remark might suffice. We might, however, also begin at the transition points (metastable or stable) for the conversion of the solid phases, and then starting from these points we might reason in the same way as we did just now.

It is to be attributed to the great difference of temperature between

the point of transition and the temperature of the white phosphorus, and to the great difference in concentration of the phases that there are exceedingly few red nuclei and still fewer violet ones to be found in the solid white phosphorus.

It appears, however, now immediately from the given consideration that if we have recourse to a positive calalyser for the conversion



the number of nuclei will greatly increase, and with it the velocity of conversion. Such a catalyser is now furnished by iodine and now I think that the fact that white phosphorus in contact with a trace of iodine is comparatively quickly converted to the red modification and with rise of temperature also to the violet one, must be attributed to the catalytic acceleration exerted by this substance on the chemical conversion.

In connection with what precedes I will devote a few moments to the transition of the nuclei of crystallisation. Before a nucleus of crystallisation changes into a microcrystalline body the "molecular ungeordnete" motion must pass into "molecular geordnet". For most substances these two processes, the state of motion and the crystallisation getting "ordered", seem to take place at about the same temperature, so that they cannot be observed separately. We know, however, one category of substances, for which this is the case, namely the liquid crystalline substances, which therefore in my opinion distinguish themselves from the ordinary crystallising substances only in this that the two processes mentioned now take place at appreciably different temperatures.

I will further point out here that the given theory of the nuclei is based on the assumption that before the appearance of a new phase processes take place which are to be considered as a preparation for what will happen later on. So when a new phase is formed it may be concluded from this that the molecule complex of which this phase consists, was already present beforehand in the mother phase which *seemed* to be homogeneous, only with this difference that then the movement was "molecular ungeordnet".

If we now proceed to the system HgJ_2 , we shall make use of the T - X -projection, which has been schematically represented in fig. 2 in agreement with the data which we have now at our disposal¹⁾.

In this diagram $G_0 G''_0$, $G'G'_1 G''_1$ and $G''_1 G'_1 G_2$ are the vapour

¹⁾ These Proc. XII, p. 763.

curves, $SS_1S'_1$ and $S''_2S_2S'_2$ the lines of the solid substance and L_0LL' the liquid curve of the unary system.

If we start from the equilibrium at a temperature above the unary point of transition, 127° , it will most probably not be difficult, especially in view of the great difference in concentration between the vapour and the solid substance to obtain first of all liquid HgJ_2 when the vapour is cooled, and not before then the solid phase, just as this was the case for the phosphorus. I cannot go any further into this question here, however, because it has not yet been investigated, and will be further examined later on in the continued investigation.

Therefore we have not referred to the system HgJ_2 because of this possible phenomenon, but in order to account for the repeatedly stated fact that when the vapour of HgJ_2 is cooled below the unary point of transition, not the stable red modification is formed, but first of all the metastable yellow form. This phenomenon follows immediately from fig. 2. From this we see namely that the vapour lines lie very markedly on the side of αHgJ_2 .

As the equilibrium of the system HgJ_2 on the whole sets in slowly it is necessary to point out here two possibilities. It is possible that in the usual sublimation experiments, in which the vapour saturate at higher temperature is cooled down to the ordinary temperature, a fixation of the internal vapour equilibrium takes place, so that solid substance is formed of the concentration of the vapour. In this case it is of course at once clear that this solid substance must then be *light yellow*. If, however, we assume as second possibility that the cooling does not give rise to fixation, the appearance of the yellow phase from the vapour at a temperature under 127° must be attributed to this that the velocity of crystallisation of the

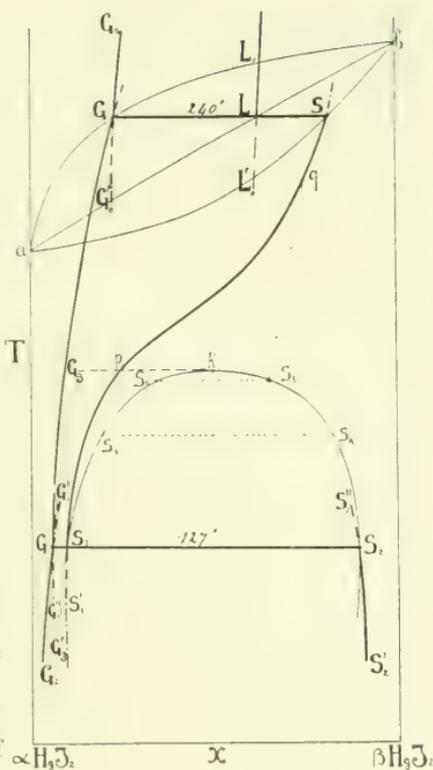


Fig. 2.

yellow modification at the temperature to which the vapour has been cooled is greater than that of the red modification owing to the much greater number of yellow nuclei in consequence of the comparatively small difference in concentration between the vapour and the yellow modification, whereas the difference in concentration between the vapour and the red modification is certainly many times greater ¹⁾).

If we now proceed to the phenomena which have been observed for solutions of HgJ_2 in different solvents, it will appear that it is possible also here to explain the observed facts in a simple way.

One of these facts was already mentioned in the introduction. We namely referred already there to the phenomenon discussed by BANCROFT that on addition of water to the methyl alcoholic HgJ_2 -solutions at the ordinary temperature at first the metastable yellow modification deposits, which is later converted to the stable red form. Another fact which was not yet mentioned here and will be discussed in the second place is this that also on slow cooling of super-saturate solutions of HgJ_2 , e.g. in nitrobenzene the yellow metastable modification can be formed first at temperatures under the point of transition, provided the concentration of the super-saturate solution lie above a certain limit.

Before I can proceed to the explanations of these phenomena, I must mention that I have found from preliminary experiments at higher temperatures that at the same temperature HgJ_2 -solutions assume an intenser red colour according as more HgJ_2 has been dissolved, from which I have provisionally drawn the conclusion that the equilibrium



which lies decidedly on the α -side as long as the concentration is not great, slowly moves to the β -side with increase of the concentration. Most likely we have not to do here with an electrolytic phenomenon ²⁾).

If we now make use of this datum, and if in accordance with the theory of allotropy we suppose the system HgJ_2 -solvent to be pseudo-ternary, the explanation runs as follows:

1) I will avail myself of this opportunity to point out that HgJ_2 is the first system of which we know that it possesses no metastable melting-point, though it presents *heterogeneous allotropy*.

2) The direction of the shifting of equilibrium by change of concentration will be studied more in detail, though it is of minor importance in this case.

The metastable branches of these isotherms will be required to find the degree of super-saturation of a solution with respect to β -, resp. α HgJ_2 .

If we now assume that the equilibrium between α - and β HgJ_2 always sets in, and so that the system does not behave as a ternary system, but as a binary one, it is noteworthy that two of the solid mixed-crystals are in internal equilibrium, a red mixed crystal phase S_R , which is in stable internal equilibrium, and a yellow mixed crystal phase S_G , which is in metastable internal equilibrium. When different solvents are used, it appears that the solution which is in equilibrium with the stable red phase at the ordinary temperature, and in which the two kinds of molecules α and β HgJ_2 will also be in equilibrium, is coloured yellow. From this we derive that the internal equilibrium in this liquid lies very much to the side of α HgJ_2 . It was stated just now that the colour of an HgJ_2 -solution becomes clearly more intensely red with increase of the concentration, which points to the fact that the internal equilibrium is shifted to the β -side with increase of the concentration.

Taking these data into account, we shall have to indicate the internal equilibrium as function of the concentration, as has been schematically indicated by the curve Ug .

So we see from this that f' is the solution which coexists with the red phase S_R , which is in internal equilibrium. This solution must have a light yellow colour, because the ratio $\frac{\text{conc. } \alpha\text{HgJ}_2}{\text{conc. } \beta\text{HgJ}_2}$ is very great in this liquid, and it will now be clear why the point of intersection e of the solubility curve has been assumed to lie so much on one side.

The curve Ug , however, also cuts the metastable branch of the solubility-isotherm of the yellow mixed-crystals and so the point k will be the solution which coexists with the yellow mixed-crystal phase S_G , which is in internal equilibrium.

The difference in solubility between yellow and red HgJ_2 always seems to be very small, and this is the reason why the two solu-

pass into the saturate condition, the nodal lines eu and ev with the isotherms ae and ce indicate the boundaries of the different regions.

The mentioned isotherms cd and ab must not be prolonged to the line AB , because here an equilibrium between red, resp. yellow mixed crystals and a liquid which contains alone α - and β - HgJ_2 cannot occur below the temperature of the melting-point diagram, not even in metastable state, because α - and β - HgJ_2 give a continuous melting-point-line. The isotherms must continuously merge into each other, probably by means of a ridge before the line AB has been reached.

bility isotherms here intersect at an acute angle. Then the difference in concentration in the points f and k will be slight at every temperature.

Before proceeding to the explanation of the mentioned phenomena I will state what are the principal changes to which fig. 3 is subjected with rise of temperature.

All the changes take place here as a rule in the direction of a greater solubility; thus the points a and c will move towards A resp. B. The point C will then be moved further away than a , which makes the point of intersection e move further into the figure.

The equilibrium



shifts a little to the right with increase of temperature, in consequence of which the internal equilibrium curve Cf will move a little upwards.

At the transition temperature 127° the curve Cf passes exactly through the point e , which implies that the solution coexisting with the mixed crystal phases S_R and S_G , is exactly in internal equilibrium, so that the mixed crystal phases which coexist at 127° and which are in internal equilibrium, are the phases S_R and S_G , which, however, have then been somewhat displaced. At higher temperature the line Cf cuts the stable branch of the solubility isotherm ab and the metastable branch of the isotherm cd , from which follows that it is now a yellow phase that is in stable internal equilibrium, whereas the red one is metastable.

In the neighbourhood of 150° $\alpha \text{ HgJ}_2$ and $\beta \text{ HgJ}_2$ mix in all proportions, and instead of two *intersecting* solubility isotherms we then get a continuous isotherm.¹⁾ The curve Cf rises continually and the saturate solution becomes first light and then dark red just as the coexisting solid phase.

If we now return to temperatures lying below the transition point, and for which fig. 3 holds, we see immediately that when the saturate solution f' is poured into cold water, in which HgJ_2 is exceedingly little soluble, the deposited HgJ_2 must be yellow, for then we get a solid phase in which α - and $\beta \text{ HgJ}_2$ occur in exactly the same proportion in which they occurred in the saturate solution.

If we now draw a straight line through C and f' the point where this line meets the side AB will indicate the phase which separates under these circumstances. This phase indicated by S_G' lies markedly

¹⁾ The partly metastable, partly unstable branches of the isotherms have then contracted to a point.

on the yellow side, and so it will have to be *yellow*, as is easy to ascertain in the experiment with solutions in methyl alcohol and nitrobenzene.

If we now consider the case that an unsaturated solution is cooled down so much that a supersaturate solution is formed, we may make the following observations. If the supersaturate solution lies between f and k at the temperature to which we have cooled down, the solution is only super-saturate with respect to red mixed crystals, so that then of course only the red phase can be deposited, and this continues to be so for a permanent deposition of red mixed crystals till the nodal line ev has been reached. If however the supersaturate solution is situated on the righthand side of this nodal line on the curve Cy , different cases may present themselves. If e.g. we have the solution L , we shall have to examine with respect to what this solution is most super-saturate. The point L lies on two nodal lines, on the nodal line nq and on mp , and as $\frac{nL}{qL}$ is greater than $\frac{mL}{pL}$, the solution L is super-saturate more with respect to the yellow than with respect to the red mixed crystal phase.

In consequence of this the number of yellow crystallisation nuclei will be greater than the number of red ones, and the greater this difference is, the more probable it will be that the velocity of crystallisation with respect to the yellow mixed crystal phase is greater than that with respect to the red one, in which case we may expect that the yellow mixed crystal phase will crystallise first.

So we have arrived at the conclusion that the red phase is sure to crystallize when the super-saturate solution lies between f and the nodal line ev . Now it will be clear, however, that the red phase may also appear first when the super-saturate solution lies on the right of this nodal line ev , but as we take solutions which are super-saturate to a greater degree, it becomes more and more probable that the yellow phase appears first, after which then the red one may make its appearance.

Experiment entirely corroborates the theory. Thus from comparatively slightly super-saturate solutions of HgJ_2 in nitrobenzene the red phase deposits, whereas from more super-saturate solutions first of all the yellow phase appears.

When the stable and the metastable substances are of an entirely different concentration, e.g. different compounds of the same elements or when one is an element and the other a compound, we have apparently to do with another class of phenomena, which, however,

do not essentially differ from the discussed ones, and in most cases are still easier to explain than the preceding ones.

To mention an example I will cite the case mentioned in a previous communication, which referred to the deposition of cementite, either from a liquid or from a solid solution which was not only unsaturated with respect to iron-carbide, but also with respect to graphite¹⁾. It is easy to see that on cooling the said solutions we have soon penetrated relatively further into the region for liquid resp. solid solution + cementite than into the region for liquid resp. solid solution + graphite, so that the liquid resp. solid solution has become super-saturated to a greater degree with respect to cementite than with respect to graphite. Hence the velocity of crystallisation with respect to cementite may become greater than that with respect to graphite, and the metastable phase cementite will first separate.

This communication, in which many more examples mentioned in the introduction might have been treated, but which have purposely been left undiscussed for want of space, now enables us to set forth with great clearness the so-called "Gesetz der Umwandlungsstufen" of OSTWALD.

OSTWALD was of opinion that the succession in the appearance of the phases was determined by the free energy, and that this was therefore a purely thermodynamic question. It follows, however, from what has been communicated here that this is decidedly not the case, and that in these phenomena by the side of and in connection with the concentration, an important part is played by the velocity with which one phase is converted into another at a given temperature and pressure, so that it will certainly often happen that the order in which the phases occur is another than would correspond with the free energy of the phases²⁾. It has also appeared clearly from this discussion that the phenomenon is much more intricate than OSTWALD thought, and that the order in which the new phases will make their appearance under definite circumstances of temperature and pressure may be derived in a natural way from the new theory of allotropy, when it is combined with the theory of nuclei given here.

Anorg. Chem. Laboratory of the University.

Amsterdam, December 27, 1911.

¹⁾ These Proc. Nov. 1911 p. 530.

²⁾ BECKER's investigations "Ueber Kondensation von Dämpfen" (Thesis for the doctorate Göttingen (1911)) are in perfect harmony with this view.

Chemistry. --- "NERNST'S theorem of heat and chemical facts". By Prof. PH. KOHNSTAMM and Dr. L. S. ORNSTEIN. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of December 30 1911).

§ 1. We regret that occupied with work of various kinds we have not been able any sooner to answer the objections advanced by Prof. NERNST in These Proc. of June 1911 p. 20 to our paper: "On NERNST'S theorem of heat" in These Proc. of Dec. 1910. We are, however, the more desirous to answer these remarks even now, as it has appeared to us that also others have misunderstood the real intention of our remarks. Though we will readily admit that this misunderstanding may partly be due to a want of clearness on our side, partly we think that it is also owing to a most important modification of ideas about the meaning of the theorem of heat, which has appeared from the publications which have been published after our first paper had already been printed.

Indeed, to attain a *chemical* end (the determination of chemical equilibria) the original theorem of heat of NERNST dealt with the *chemical* question: what is the value of the difference of entropy in a system in which a chemical reaction can take place, before and after the reaction, and it pronounced the thesis that this difference of entropy would be zero, when the reaction should take place at the absolute zero between solid unmixed substances, or in other words it put under these circumstances the entropy of the system before the reaction equal to the entropy after it. Now we first briefly demonstrated in our paper that this thesis cannot be stated in this way because the difference of entropy under consideration is not perfectly determined, unless it is also stated how the reaction takes place, i.e. e.g. under constant or varying pressure. Then proceeding to the theorem proper we have shown that this theorem contains a statement about "the constants of entropy", i.e. that part of the entropy of a definite quantity of a non-dissociating substance, that remains unchanged with change of temperature and volume. Following BOLTZMANN'S example we have further (p. 704—715) inquired into the nature of these constants of entropy, in which we came to the conclusion that they are controlled by some quantities characteristic of the nature of the substance, which, however, bear a specifically *chemical* character: i. e. which only make their influence felt at a chemical conversion or dissociation of the substance, but which are not felt in all variations of volume and temperature in which the

molecules remain unchanged, so variations of volume and temperature as are governed by the equation of state¹).

So far from having adduced VAN DER WAALS'S equation of state against the theorem of heat, as Prof. NERNST says that we should have done, we have, on the contrary, called it absurd if one should try and calculate from this equation of state, or any other equation of state of a substance with invariable molecules, what happens during chemical reactions, because in our opinion in these chemical reactions quite different forces come to the fore as those that are active between the invariable molecules of a simple substance. So we think that Prof. NERNST labours under a misunderstanding with regard to our argumentation; his considerations do not bear on the main point of the question which we discussed (p. 704--715). Prof. NERNST concentrates all his attention to p. 701--703, where for brevity's sake, and as we thought to elucidate the question, we had made use of the hypothesis, emphatically called fictitious by ourselves, that the reagents and reaction products considered separately should follow VAN DER WAALS'S law. This hypothesis, however, did not constitute an essential part of our reasoning; it was only intended to set forth, as we thought in the clearest way: 1. that the original theorem required a more precise definition of its contents, 2. that whatever might be the form of the equation of state of the substances, the theorem of heat always contained also an assertion that is independent of the nature of the equation of state, because it refers to the constants of entropy, which in accordance with their chemical nature are independent of the equation of state.

We were under the impression that we had stated this with perfect clearness on p. 701: "We shall, therefore, begin by putting an imaginary case, chosen as simple as possible, and demonstrate that at least for this case the "theorem of heat" cannot apply. And this, not so much because we consider this case in itself as decisive against the theorem of heat (for we should first have to show that such a case really occurs in nature), but because this case leads us into the very heart of the question, and thus will enable us to get rid of the restricting suppositions from which we started". And on p. 704: "And now it has become clear why we could say above that our result is independent of the special form of the equation of state".

But we will readily admit that this may have been less clear to a reader who is not familiar with our train of thought than it

¹) Of course we mean the ideal equation of state of a chemically invariable substance, not some special approximation of it.

seemed to us, and therefore we give the following, we hope clearer, exposition of our meaning.

§ 2. The theorem of heat is not one simple thesis, but it contains different and dissimilar theses. This is most clearly seen by working out a case of chemical reaction on the assumption of a mathematically perfectly determined equation of state, which can then, however, be at most an approximation, for we do not know the real equation of state of any substance.

It appears then first of all that the validity of the theorem of heat requires that the equation of state fulfils certain conditions which are in contradiction with the law of the corresponding states. This result is of course of secondary importance, because the contradiction may be attributed just as well to the inaccuracy of the theorem of heat as to that of the last mentioned law; and in the light of the considerations borrowed from the theory of indivisible units of energy presently to be discussed it will really be ascribed to the latter; yet it is not devoid of importance, because in the original calculations use has been made of the law of corresponding states to test the theorem of heat, though it be for higher temperatures.

In the second place, however, and *this is what we wanted to set forth*, it appears that besides the just-mentioned purely physical theses about specific heats and coefficients of expansion, the theorem also pronounces a thesis about quantities which do not occur in the equation of state, the already mentioned "constants of entropy" and our objections are directed against the thesis about these constants of entropy.

And though now, let it be once more repeated, we readily admit the possibility that indistinctness in our way of expression has contributed to lead Mr. NERNST to believe that it should have been our intention to derive arguments from the equation of state of VAN DER WAALS against the theorem of heat, as appears already from the title of his reply, we are also of opinion that the shifting of the real meaning of the theorem of heat mentioned in the beginning of this paper must also have had a share in this misunderstanding. Under the influence, namely, of the theory of indivisible units of energy and the theory of EINSTEIN on the specific heats, which is founded on it, and in connection with PLANCK's expositions in the fourth edition of his *Thermodynamik*, which appeared after the publication of our paper, the purely physical side of the question has more and more drawn the attention, and by the aid of the

theory of indivisible units of energy this has been formulated in two purely physical theses, of which there was not yet question in the original theorem of heat. And the confirmation of these physical theses by experience has concentrated attention so much on these theses that the original chemical meaning of the theorem of heat is in danger of being entirely thrown into the background. Now the contents of these physical theses are incompatible with the law of VAN DER WAALS applied to low temperatures, and so when the theorem of heat is identified with these theses, one can be led to expect objections to the theorem of heat on the ground of its contradiction to VAN DER WAALS'S LAW.

We shall first elucidate the meaning of these theses, and then we shall try to show that the original *chemical* contents of the theorem of heat is really in danger of being overlooked, all attention being concentrated on these new *physical* theses.

These theses furnish the more precise definition of the meaning of the theorem of heat required in the beginning of our paper, and as such we accept them of course gladly, though we could not suppose in our previous paper that it was Mr. NERNST'S intention thus to complete the original theorem of heat, because it might still be very well possible, as Mr. PLANCK and Mr. NERNST themselves state that these theses should be wrong after all and the original theorem of heat correct.

Now according to the first of these theses the specific heat at constant pressure approaches to the limit zero for every solid substance with diminishing temperature in such a way, that $c_p \log T = 0$. It follows immediately from this that the difference between the entropy e.g. of a piece of ice at finite temperature and the entropy at $T = 0^\circ$ remains finite, and does not become infinite as would be the case if the specific heat remained finite.

According to the second thesis at the absolute zero the entropy of a solid substance becomes independent of the pressure, so that $\left(\frac{\partial \eta_i}{\partial p}\right)_T = 0$; or in other words on account of the well-known relation:

$$\left(\frac{\partial \eta_i}{\partial p}\right)_T = - \left(\frac{\partial c}{\partial T}\right)_p$$

the coefficients of expansion of all solid substances approach the limit zero. So this thesis supplies, of course, at the same time an answer to the question raised by us how we must imagine the reaction to take place for the application of the original theorem of heat. For if the entropy becomes independent of the pressure it is no longer

of any importance whether the reaction takes place at constant pressure or not.

These two theses are brought in a mutual relation and find a strong support in PLANCK's theory of indivisible units of energy, from which they may be derived. They have proved up to now to be in very good agreement with the observation, particularly as far as the first is concerned.

§ 3. So, to get a clear insight into what the theorem of heat implies in its present form, it should be stated thus. For every chemical reaction at the absolute zero between solid substances, the difference of entropy before and after the reaction is:

1. Not infinitely great, because $\lim (c_p \log T) = 0$ for all solid substances.

2. Independent of eventual modification of the pressure with the reaction, because for these substances $\lim \left(\frac{\partial \eta}{\partial p} \right)_T = 0$.

3. The difference of entropy preserves a finite value if among the reagents or reaction products mixed crystals or amorphous solid solutions occur; it becomes equal to zero for the opposite case.

In the third thesis the original, really chemical contents of the theorem of heat are expressed; in our paper we only referred to this, the two other theses had not even been mentioned in connection with the theorem of heat then. Now, however, as we said before, the remarkable case presents itself that this last thesis has been thrown more and more into the background in recent publications, and it makes the impression as if the first two theses should decide about the theorem of heat. In fact this opinion is repeatedly emphatically expressed by Mr. NERNST himself. Thus we read in the *Sitzungsberichte der Kgl. Pr. Ak. der Wiss.* 1911 IV p. 88 "Sehr einfach gestaltet sich aber nun wiederum die Deutung des neuen Wärmesatzes. Nach der Quantentheorie sind auch bei endlichen, wenn auch bisweilen sehr kleinen Entfernungen vom absoluten Nullpunkt der Temperatur alle festen Stoffe, seien es Kristalle oder unterkühlte Flüssigkeiten, nur ungehener wenig von ihrem Zustande beim absoluten Nullpunkt selber verschieden; hieraus aber ergibt sich sofort als weitere Konsequenz, dass in diesem Gebiete, wie es unser Satz verlangt, die Kurven der gesamten Energie und der freien Energie praktisch zusammenfallen, d.h. sich tangieren müssen. Und es würde sogar wenn, wie es die Formeln von PLANCK und EINSTEIN verlangen, die untere Kurve in Fig. 2 beim absoluten Nullpunkt wirklich die Abszisse mit unendlich hoher Ordnung berührt, das gleiche von der

gegenseitigen Berührung der beiden Kurven in Fig. 1 gelten müssen." And in the same way in These Proc. of June 1911 p. 204: "Indeed the new theorem of heat is intended to account for the entirely different circumstances found here; for the rest it necessarily follows from the theory of indivisible units of energy."¹⁾

The same statement was made in the lecture delivered by Prof. NERNST in May at Amsterdam. Yet it cannot be maintained. The validity of PLANCK and EINSTEIN'S theory on the specific heat says only that the difference of entropy is *not infinite*, the question whether there remains still a finite difference of entropy is not mooted. The logical connection between the original theorem of heat (thesis 3) and the PLANCK-EINSTEIN theory of the specific heat is indeed this that the theorem of heat may be correct, and the PLANCK-EINSTEIN theory incorrect (provided only the law of KOPP is rigorously valid), and that reversely the PLANCK-EINSTEIN theory can be correct, and the theorem of heat incorrect, because there remains a finite difference of entropy also when no mixed crystals are present. Moreover that it does not follow so directly from the PLANCK-EINSTEIN theory that the difference of entropy becomes zero as Mr. NERNST asserts, appears convincingly from this that the difference of entropy remains finite for mixed crystals also according to the theorem of heat, while we have no reason at all to assume that they behave so perfectly differently from unmixed solid bodies with regard to radiation.

§ 4. In opposition to this view as if the theorem of heat would be a consequence of the PLANCK-EINSTEIN theory, and so as if experimental proofs for the latter would be just as well confirmations of the former, it must be most emphatically pointed out that this theorem being of

¹⁾ For this proof Prof. NERNST refers among others to a paper by Mr. SACKUR (Ann. d. Phys. (4) 34 455 (1911)). But Mr. SACKUR has not given a proof of the chemical part of the theorem of heat either. For so far as they concern a simple substance his considerations do not offer anything new, and the question may be raised if the definition of entropy of statistical mechanics may also be applied to the case considered there. With reference to the entropy of a system composed of several substances SACKUR has proved nothing. If all configurations have equal energy and equal probability, the probability of each of them is $-\infty$. If we put that the probability that everything is in bound state is one, and that other states, so e.g. those in which the atoms are free, have a probability zero, we arrive no more at the theorem of heat than in the preceding case. If we assume that at the absolute zero the probabilities of the state, completely bound and of the state that all the atoms are free, are equal, and that the probability of the other states is 0, we arrive at the theorem of heat, but why this should now have to be the case is not explained, and the considerations about mixed crystals make it even improbable.

a chemical nature, can only be confirmed or rejected by means of considerations which rest on *chemical* facts, and the knowledge of chemical forces derived from them. Accordingly we did not adduce VAN DER WAALS'S theory as a proof against the theorem of heat in our paper, but we alleged chemical facts: the fact of valency, the fact of the structure of the chemical molecule, which in our opinion are irreconcilable with the theorem of heat. Now that it appears, however, that the train of thought on which our considerations were based, is not perfectly clear from our paper, we may be allowed on account of the great importance of the question to sketch this train of thought once more here, now deprived of the mathematical garment in which it had to be clothed for a strict reasoning. This train of thought, which is strictly speaking not ours, but BOLZMANN'S, comes to what follows.

Given a complex of chemical substances A, which can be converted to another complex B, e. g. a quantity of oxyhydrogen gas which can be converted to water. Required the increase of the entropy when the reaction takes place, of course under perfectly definite circumstances. When we suppose a complete knowledge of all physical changes which can take place with A and B, so all changes which take place for unchanged molecules, we need only know the difference of entropy for one definite transition from A to B to consider it as known for all transitions.

Where shall we now try to find this one difference of the entropy of the system A and the entropy of the system B. In our opinion the answer should be: Under such circumstances that a reversible conversion $A \rightleftharpoons B$ is possible. We think that it will not be possible to solve the question first of all for the absolute zero, hundreds of degrees below the temperature at which chemical reactions are reversible, or even possible, no more than it would be possible to find the theory of the solid state by paying exclusive attention to the properties which gases exhibit far above their critical point. And of all the reversible reactions those in rarefied gases are no doubt the most suitable, if not exclusively so, for accurate quantitative calculation. So it is by no means "remarkable" as Mr. NERST says that we worked exclusively with rarefied gases for the determination of this difference of entropy, but it is owing to the nature of the problem itself. Nor is it strange that to determine the value of the entropy in case of mixing the substances are thought to be converted into the rarefied gas state, to be mixed there, and finally to be condensed¹⁾.

¹⁾ Cf. e. g. VAN DER WAALS Cont. II p. 94; LORENTZ, Abhandlungen I p. 240
PLANCK Thermodynamik § 254.

In entirely the same way the difference of entropy for a reaction is perfectly determined in all states, if it has been found for the reaction in rarefied gas state.

When we now want to examine on what properties of the reacting substances the difference of entropy that is to be determined, depends, we must of course make such suppositions about the active forces that we do not come in collision with the known chemical facts. Now BOLTZMANN has shown that the fact of the valency of the atoms already excludes certain suppositions about these forces, and renders others probable. Given a substance e. g., iodine, at so large a volume and so high a temperature that it is quite dissociated into the atoms. If we now assume that the forces which the atoms exert on each other spread uniformly all over the surface of these atoms we find on decrease of the volume that the atoms will not exclusively associate to molecules of two atoms, but to complexes of 3, 4 etc. and that even the number of bi-atomic molecules would be very small compared with multi-atomic ones, briefly we arrive at something that is in direct contradiction to the facts. To avoid this we must assume that the chemical attraction does not spread uniformly over the atom, but is localized in certain parts. Also the stereo-chemical facts point to this, in fact properly speaking everything we know of structure formulae. Every somewhat intricate organic formula points to the fact that the atoms are not placed arbitrarily with regard to each other in the molecule, but that a certain organisation prevails, that the atoms are orientated in a definite way with regard to each other.

If we now assume chemical forces of this kind, and if we calculate by the aid of the statistical theory of the entropy the difference of entropy between split and unsplit molecules, or more generally of the system before and after the reaction, it appears that this difference of entropy depends on certain specific quantities, volumes, where these forces are localized and which we have indicated as the "chemical volumes" of the substances concerned. Accordingly the constant of entropy of a certain substance, e.g. hydrogen depends on the "chemical volume" of hydrogen, i. e. that part of the entropy of a certain quantity of hydrogen that remains unmodified, as long as the hydrogen molecules themselves do not change, but varies when e.g. the hydrogen dissociates. What happens further to this hydrogen, whether we liquefy or solidify it, bring it under a high pressure or cool it down very much, in all this the chemical forces are no longer active, the value of the entropy constant is not changed by it, if only the molecules of hydrogen remain intact. But then the

difference of entropy of hydrogen and oxygen before, and water after the reaction, just as it appears to depend on the specific chemical volumes of the three reacting substances at high temperatures will still have to depend on these quantities at the absolute zero, and so may not be put equal to zero in general.

It might be objected to this that here a too pronounced distinction was made between physical and chemical processes, and that it is conceivable after all that in the physical processes of cooling and freezing the same forces are active as in the process of chemical combination, so that, notwithstanding, in consequence of the physical processes at low temperatures, the difference of entropy which is in connection with the specific chemical action would have disappeared finally. But in opposition to this it should be pointed out that it is exactly the theorem of heat itself that insists on the most rigid distinction between physical forces and chemical forces where it states a law which is to hold for all solid substances in pure state, which, however, ceases to hold as soon as mixed crystals or alloys appear.

What we said just now, can be expressed also as follows. According to the theorem of heat the heat of formation of a compound from the composing atoms is the only chemical quantity that is characteristic of it, i.e. when e.g. during a chemical reaction some isomers appear simultaneously, the heat of formation of every compound will perfectly determine the process apart from purely physical quantities as specific heat at constant pressure, heat of evaporation etc. It will depend only on the heat of formation of each of the isomers (and these physical quantities), which substances are formed and how much of each. BOLTZMANN'S view of this point, of which we declared ourselves adherents, is that the wealth of chemical phenomena is not to be explained in this way. By the side of this heat of formation it assumes other factors relating to the place of the atoms in the molecule, the orientation, in short the whole structure of the molecule which cause *this* compound to be formed here, *that* there, and in such quantities. Then as far as the entropy is concerned the sum of the influences issuing from this may be combined in the value of the "chemical volume" on certain suppositions, as calculation teaches us. If we are not mistaken, few chemists, particularly organic chemists, will be disposed to accept the theory that by the side of purely physical quantities only a quantity of energy, the heat of formation, determines the chemical character of a substance.

It is a matter of course that we do not attach importance to the details of the conception of the chemical forces which BOLTZMANN

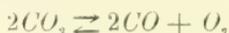
has used for this problem. On the contrary we have pointed out, and so has BOLTZMANN himself, that this conception is only a first rough approximation, and that it must be supplemented to be in agreement with experience, specially as far as the specific heats are concerned. It lies to hand to except this supplement from considerations borrowed from the theory of indivisible units of energy. But so long as attempts to prove the contrary have not been made, and very certainly no proofs have been furnished, we think that we may continue to expect that the fundamental idea from which BOLTZMANN started in his considerations on the nature of chemical action, the localisation of chemical forces, and the organisation of the chemical molecule in connection with this, will prove to be in accordance with the facts, and that accordingly a specifically "chemical" difference of entropy will have to exist between different molecules built up from the same atoms.

§ 4. Of this nature were the objections which we advanced in December 1910 against the theorem of heat; we fail to see that they are less urgent now. But it may be urged that in all questions of science the facts are after all the highest judge, and as the theorem of heat appears to be in such perfect concordance with the facts, it should be accepted.

We should undoubtedly not hesitate for a moment to submit to experimental results which would contain indubious confirmation of the theorem, but one of the few points on which we have modified our opinion since December 1910 is this that we doubt much more strongly now than we did then whether anything can be derived from the experimental data about the difference of entropy in a chemical reaction, which would take place at the absolute zero.

It should first of all be kept in view how great the extrapolations are which we have to make, when we want to test the theorem of heat by the facts. The opinion is frequently expressed that we are already far advanced on the way to the absolute zero in this test, that particularly the work performed by NERNST and his pupils of late years has furnished important contributions to this. But it is then overlooked that this work, however admirable, after all only furnishes material for the *specific heats* at low temperatures for a comparison with the corresponding formulae, which are connected with theses 1 and 2. But when testing thesis 3, the chemical thesis, which is here the only point of interest for us, we remain just as far from the absolute zero for all that, because the nature of the chemical reactions involves that most of them cannot be made rever-

sible any more already at rather high temperatures, while there is hardly one to be found below the freezing-point of water. The most accurate testings of the chemical part of the theorem of heat require extrapolations of hundreds and hundreds of degrees. That the accuracy of the test is greatly impaired in this way, is self-evident. We shall show this by two examples. The well-known constant K for the equilibrium of dissociation:



may be represented by a formula of the form:

$$\log K = -\frac{Q}{T} + A \log T - BT + CT^2 + I$$

Now to test the theorem of heat we shall have to determine the quantity I , the constant of integration of the equation of equilibrium. According to the calculations by Dr. SCHEFFER (Proc. of this meeting p. 743) we find for this quantity from experimental data the values:

$I = 1.75$ or 1.57 when we make use of the specific heats of HOLBORN and AUSTIN for the determination of the coefficients A , B , and C , taking 135580 for the heat of combustion at constant pressure and $T = 291^\circ$, from which Q is to be calculated.

$I = 2.71$ when we make use of the same value for the heat of combustion, and the specific heats of HOLBORN and HENNING.

$I = 4.73$ when the suppositions about the sp. h. are applied which NERNST made in his original calculations on the theorem of heat.

$I = 2.25$ when in the same way as BJERRUM we make use of the formulae of EINSTEIN, resp. of NERNST and LINDEMANN for the sp. h.

If the supposition about the heat of combustion is changed, all these values are again modified, as appears from Dr. SCHEFFER's paper.

The results are not much more favourable in the water reaction. We find for the constant of equilibrium of this reaction:

$I = -0.2$ if we start from NERNST's original suppositions.

$I = -1.2$ if these suppositions are brought into connection with the measurements of HOLBORN.

$I = -2.4$ if we use the formula of EINSTEIN resp. of NERNST and LINDEMANN.

So it appears very clearly how much the value of I , which is derived from the experiments, is controlled by our suppositions on the extrapolation of the sp. h.

But there is more. Let us disregard for a moment the great

variations of the results of the value that is to be determined, and let us assume that this value could be perfectly sharply defined from the experiments. In what way are we to conduct then the testing of the theorem of heat by these values? First of all a vapour-pressure formula for each of the substances participating in the equilibrium, is to be drawn up. NERNST writes it in the form:

$$\log p = -\frac{\lambda_0}{4.571 T} + 1.75 \log T - \frac{\varepsilon}{4.571} T + C.$$

And now the value of the constant C must be determined. According to the theorem of heat the algebraic sum of the constants determined thus will have to be equal to the just-mentioned constant of integration I of the equation of equilibrium. Now it is again clear that the value which we shall obtain for the constant in the vapour-pressure formula will depend to a high degree on the suppositions made about the specific heat and the latent heat of evaporation of the substance, suppositions on which the coefficients of the terms in which T occurs, depend entirely. In his calculation of the chemical constants Mr. NERNST has started from the supposition that the sp.h. of gases may be represented by $c = 3.5 + 1.5n + \alpha T$, and of liquids by $1.5n + \alpha T$, and besides from certain suppositions on the heat of evaporation. But even then the data leave a wide margin as appears from the fact that Prof. NERNST has first found 2.2 for the chemical constant of hydrogen, whereas 1.6 has been substituted for it in the later tables. Yet this value too will have to be modified, because the value for the sp.h. mentioned just now has still been assumed for it, whereas according to the theory of EINSTEIN it ought to be assumed that the sp.h. in condensed state does not become $1.5n$, but 0.

The question might still be raised: Is it possible that the equality which exists according to the theorem of heat between the constants of integration from the vapour pressure curves and from the equation of the equilibrium might possibly be independent of the special suppositions about the sp.h.? If this were so, and if the introduction of other sp.h. should give rise to other values for the equilibria and just as greatly changed values for the vapour pressure curves, this would plead in favour of the theorem. But this is not the case either, as the determination of the constants of the vapour pressure curves, in opposition to those of the equation of the equilibrium, is not only based on the suppositions about the sp.h. in the gaseous state, but also on that in the liquid state. Even a different assumption for the latter, among others that the difference in sp.h. in liquid and gas state is not $1.5n$ at $T=0$, modifies the C -values already appreciably.

§ 5. But let us not dwell on this second objection any longer either. Let us assume for a moment that it would be possible also here to determine the constant of integration with sufficient certainty from the experimental data. What further course have we then to pursue to test the theorem of heat?

The values of the vapour-pressure constants found by means of the above mentioned suppositions appeared about to agree with $1.1f$ for some ten substances, in which f is the well-known constant from the empiric vapour pressure formula of VAN DER WAALS. In how far this factor 1.1 is accurate, appears from the table of the C and f values, which NERNST gives in his original paper¹⁾.

	C	f		C	f
N_2	2.37	2.4	$(C_2H_5)_2O$	3.56	3.0
O_2	2.20	2.6	$CHCl_3$	4.07	2.9
NH_3	3.28	3.0	C_6H_6	3.15	2.85
SO_2	3.42	3.0	H_2O	3.6	3.3
CS_2	3.26	2.75	C_2H_5OH	4.48	3.7

On the assumption that this relation $C = 1.1f$ will probably hold generally, the number of constants was raised from *ten* to about *twenty*. The result of these calculations is then finally summarised in the following list of "chemical constants", which when the chemical side of the theorem of heat is correct, must enable us to calculate the integration constants of the equilibria, in which the substances under consideration take part.

Chemical constants²⁾

H_2	1.6	HCl	3.0	CS_2	3.1
CH_4	2.5	NO	3.5	NH_3	3.3
N_2	2.6	N_2O	3.3	H_2O	3.6
O_2	2.8	H_2S	3.0	CCl_4	3.1
CO	3.5	SO	3.3	$CHCl_3$	3.2
Cl_2	3.1	CO_2	3.2	C_6H_6	3.0

The test of the chemical conclusion must now be carried out in such a way that the algebraic sum of the chemical constants of a certain reaction is derived with the aid of the list, substituted for I in the equation of equilibrium, and the obtained expression is compared with the observations.

¹⁾ Gött. Nachr. 1906, I.

²⁾ J. de Ch. Ph. 8 253 (1910).

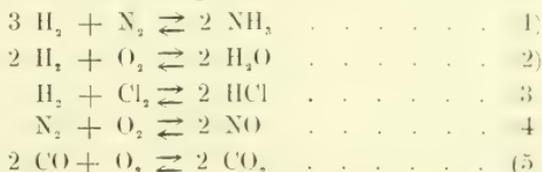
So if we want to prove now that the cited constants are really the true values which are decisive for the equilibrium, we must be able to draw up between the eighteen chemical constants an equal number of relations of the shape:

$$r_1 C_1 + r_2 C_2 + \dots + r_p C_p - r_q C_q - \dots = I.$$

in which I represents the constant of integration calculated from the measurements of equilibrium, C_p the chemical constant for one of the substances that participate in the reaction, and r_p the number of molecules of this substance that takes part in the reaction. Not until then shall we have a proof that the equilibrium is really determined by the adduced values.

When the number of relations is one less than the number of chemical constants, we can choose arbitrarily one of the constants, and then the others are indubiously determined; to satisfy then the experiments we have an arbitrary choice of one of the values. And this arbitrariness becomes of course greater and greater as the number of chemical constants exceeds the number of relations.

If we now examine what reactions between the eighteen substances given in the list have been studied sufficiently carefully, this number proves to be restricted to the following:



So when the equilibria for these five reactions are sufficiently known, we have here *five* relations between the *ten* chemical constants: C_{H_2} , C_{N_2} , C_{O_2} , C_{CO} , C_{Cl} , C_{HCl} , C_{NO} , C_{CO_2} , C_{NH_3} , and $C_{\text{H}_2\text{O}}$. The remaining eight chemical constants do not even seem to admit of testing at all. We will here observe in passing that the water gas reaction, which is obtained by combination of 2 and 5, and the Deacon-process, which is obtained by combination of 2 and 3, yield two equations which are dependent on the mentioned ones, so that these reactions can be left out of account here.

So if we question what requirements a table of chemical constants should meet to account for the observations of the equilibria, we conclude that we can arbitrarily choose five of the ten constants which occur in the five equations of equilibrium, and for the remaining eight substances which besides these occur in NERNST's list we are entirely free, because the equilibria of them are not known, or not sufficiently. So the testing which NERNST can perform for the

chemical side of the theorem of heat with regard to these equilibria comes to this that he has shown that if we choose the constants of integration of the vapour-pressure curves for these ten chemical constants, we get one of the many lists which correspond with the determinations of the equilibrium.

But even under these circumstances there remain still very considerable percentic deviations. To show this we choose the example that NERNST has worked out in his recent paper in the *Journal de Chimie physique*.

From the caloric data about the formation of water from its components, and by the aid of his hypothesis on the specific heats NERNST finds that the equilibrium of dissociation must be represented by

$$\log K = -\frac{113900}{4,571T} + 1,75 \log T + \\ + \frac{2,2}{4,6} 10^{-3} T - \frac{5,5}{4,6} 10^{-7} T^2 - \frac{3}{4,6} 10^{-11} T^4 + C.$$

Now C is determined to be -1.2 from the list of the chemical constants; after substitution we then find the following correspondence:

$$T \text{ observed } 1300^\circ; T \text{ calculated } 1340^\circ.$$

NERNST wishes this correspondence to be considered a proof of the chemical thesis of the theorem of heat.

If, however, we had not taken -1.2 , but -0.6 for C , we had found a perfect agreement with the experiment (1300°), and the constant may even be put 0 without giving a worse correspondence with the experiment ($T=1260^\circ$). By a modification in the supposition about the sp. h. we can reduce the difference between the formula and the observation to 20° , retaining $C=-1.2$ ($T=1320^\circ$) as NERNST has shown in the latest edition of his "Theoretische Chemie". Then too, however, we can arrive at a perfect agreement with a value of $C=-0.9$, and no greater error is made with a value of -0.6 than with a value of $C=-1.2$, which follows from the theorem of heat and the vapour-pressure constants. The same or greater liberties we find for the other reactions, as NERNST himself remarks.

§ 6. The foregoing refers exclusively to gas-equilibria. If we also consider the reactions between solid substances, other no less important questions arise. We will elucidate this by a single example ¹⁾. The

¹⁾ The same circumstance, the occurrence of mixed crystals, which we mention in the text with reference to the system rhombic sulphur \rightleftharpoons monoclinic sulphur, also plays a part in other reactions, e.g. in the cells:

classical example for the chemical side of the theorem of heat, the example that is constantly cited as its strongest confirmation, is the transition of rhombic into monoclinic sulphur. According to the theorem of heat we find for the transition point of these two modifications $369^{\circ}.5$, while the experiment yields $368^{\circ}.4$.

The latest investigations of SMITS¹⁾, however, have shown that this transition point itself is not immutable, but may vary very considerably according to the method of experimenting. Thus a lowering of the transition point of 10° was observed. This is owing to the fact that in the transition of rhombic to monoclinic sulphur we have not to do with chemical individuals, not with the conversion of a unary system, but with a conversion taking place in a binary or ternary system, which behaves in a unary way, provided one waits long enough. Or in other words rhombic and monoclinic sulphur consist both of mixed crystals of two, possibly three kinds of molecules, so that the theorem of heat cannot be applied to them. And even an appeal to the fact that the concentrations which play a rôle here are possibly and even probably very small, cannot enervate this objection, because it is exactly the *variations* in these small concentrations which give rise to the displacement of the transition point by more than 10° .

In virtue of what precedes we think that we may conclude that there is no reason to say that the experimental facts compel us to accept the chemical side of the theorem of heat. Led by these facts one can, in our opinion, only conclude to a non liquet. And there is every appearance that this will continue to be so for a considerable time. For the only really direct experimental test: the examination of chemical reactions close to the absolute zero, is not to be realized.

In these circumstances it seems to us that only the theory can



in which not pure lead, but lead amalgam is used (see e.g. E. COHEN Chem. Weekblad. 1911 N^o. 3). At this place, however, we do not wish to enter any further into the question of these and similar reactions, because Mr. COHEN loc. cit. announces the publication of a paper which will give a full discussion of this point, and we refer for the present only to the cited communication and another of his hand (Z. f. Elektrochemie, 1911, N^o. 4, p. 144), from which in our opinion also only the conclusion can be drawn that the experimental material of facts leads to a non liquet with regard to the chemical side of the theorem of heat.

¹⁾ These Proc. XIV p. 461. DUHEM (Zsch. physik Ch. 23 239 (1897)) and KRUYT (Zsch. phys Ch. 67, 341 and Chem Weekblad N^o. 34 (1911)) had already pointed out the possibility of a variability of the transition point, but before SMITS' experiments, mentioned in the text this shifting was generally thought to be very small.

decide, a theory of course which first of all takes account of the fundamental chemical facts which we mentioned above, but which further succeeds in avoiding the drawbacks — particularly with respect to the specific heats — which adhere to the hypothesis on the chemical forces sketched more at length in our previous paper. And then it cannot be doubtful, in our opinion, by what way we shall have to try to find such a theory. We shall have to extend the theory of indivisible units of energy, which has led to such remarkable results, to the chemical phenomena; it will be necessary to investigate in what way the properties of the reversible chemical reactions are connected with the phenomena of radiation. When this connection has been found, the course is indicated to calculate the difference of entropy of a chemical reaction by the aid of the statistical theory of entropy at temperatures at which this reaction can actually take place, and then it will be very simple to calculate by the aid of the acquired knowledge of the specific heats the difference of entropy also for temperatures, at which there can no longer be question of chemical reactions.

One of us has been occupied with this question, and hopes to be able before very long to publish further communications on this subject.

Physics. — *“Further Experiments with Liquid Helium. G. On the Electrical Resistance of Pure Metals, etc. VI. On the Sudden Change in the Rate at which the Resistance of Mercury Disappears.”* By H. KAMERLINGH ONNES. Communication N^o. 124c from the Physical Laboratory at Leiden.

(Communicated in the meeting of November 25, 1911).

§ 1. *Introduction.* In Comm. N^o. 122b (Proc. May 1911) I mentioned that just before this resistance disappeared practically altogether, its rate of diminution with falling temperature became much greater than that given by the formula of Comm. N^o. 119. In the present paper a closer investigation is made of this phenomenon.

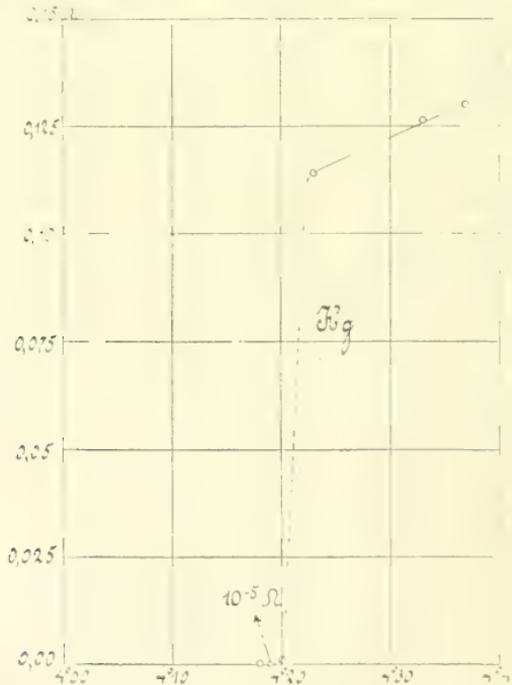
§ 2. *Arrangement of the resistance.* A description was given in Comm. N^o. 123 (Proc. June 1911) of the cryostat which, by allowing the contained liquid to be stirred, enabled me to keep resistances at uniform well-defined temperatures; and in that paper I also mentioned that measurements of the resistance of mercury at the lowest possible temperatures had been repeated using a mercury resistance with mercury leads. The immersion of a resistance with such leads in a bath of liquid helium was rendered possible only by the successful construction of that cryostat.

The accompanying Plate, which should be compared with the Plate of Comm. N^o. 123, shows the mercury resistance with a portion of the leads; it is represented diagrammatically in fig. 1. Seven glass *U*-tubes of about 0.005 sq. mm. cross section are joined together at their upper ends by inverted *Y*-pieces which are sealed off above, and are not quite filled with mercury; this gives the mercury an opportunity to contract or expand on freezing or liquefying without breaking the glass and without breaking the continuity of the mercury thread formed in the seven *U*-tubes. To the *Y*-pieces b_1 and b_2 are attached two leading tubes Hg_1, Hg_2 and Hg_3, Hg_4 (whose lower portions are shown at $Hg_{10}, Hg_{20}, Hg_{30}, Hg_{40}$) filled with mercury which, on solidification, forms four leads of solid mercury. To the connector b_4 is attached a single tube Hg_5 , whose lower part is shown at Hg_{50} . At b_1 and b_2 current enters and leaves through the tubes Hg_1 and Hg_4 ; the tubes Hg_2 and Hg_3 can be used for the same purpose or also for determining the potential difference between the ends of the mercury thread. The mercury filled tube Hg_5 can be used for measuring the potential at the point b_4 . To take up less space in the cryostat and to find room alongside the stirring pump *Sb*, the tubes which are shown in one plane in fig. 1 were closed together in the manner shown in fig. 2. The position in the cryostat is to be seen from fig. 4 where the other parts are indicated by the same letters as were used in the Plate of Comm. N^o. 123. The leads project above the cover *Sb*, in a manner shown in perspective in fig. 3. They too are provided with expansion spaces, while in the bent side pieces are fused platinum wires $Hg'_1, Hg'_2, Hg'_3, Hg'_4, Hg'_5$ which are connected to the measuring apparatus. The apparatus was filled with mercury distilled over in vacuo at a temperature of 60° to 70° C. while the cold portion of the distilling apparatus was immersed in liquid air.

§ 3. *Results of the Measurements.* The junctions of the platinum wires with the copper leads of the measuring apparatus were protected as effectively as possible from temperature variation. The mercury resistance itself with the mercury leads, which served for the measurement of the fall of potential seemed, however, on immersion in liquid helium to be the seat of a considerable thermo-electric force in spite of the care taken to fill it with perfectly pure mercury. The magnitude of this thermo-electric effect did not change much when the resistance was immersed in liquid hydrogen or in liquid air instead of in liquid helium, and we may therefore conclude that it is intimately connected with phenomena which occur in the neigh-

bourhood of the transition of solid to liquid mercury. A closer investigation of the true state of affairs was postponed for the meantime, and the thermoelectric force was directly annulled during the measurements by an opposed electromotive force taken from an auxiliary circuit. The magnitude of this thermoelectric force, which for one pair of the leads came to about half a millivolt, made it impracticable to reverse the auxiliary current as is usually done in the compensation method. The resistance of the mercury thread was then obtained from the differences between the deflections of the galvanometer placed in circuit with Hj_2 and Hj_3 and the compensating electromotive force, when the main current passing through the resistance was reversed. The galvanometer was calibrated for this purpose.

In the accompanying figure is given a graphical representation of the resistances observed ¹⁾.



¹⁾ For the resistance of the solid mercury at 0° C. extrapolated from the melting point nearly 60 Ohm can be accepted. In the solidifying process differences occur which make necessary special measurements to be able to give the exact proportion of the resistance of the wire at helium temperatures to that at 0° C. (solid extrapolated from the melting point). Therefore the resistances themselves are given here. [Note added in the translation].

As a former experiment showed that there was a pretty rapid diminution of the resistance just below the boiling point of helium, there arose in the first place a question as to whether there exists between the melting point of hydrogen and the boiling point of helium a point of inflection in the curve which represents the resistance as a function of the temperature. The temperature of the bath was therefore raised above the boiling point by allowing the pressure under which the liquid evaporated to increase, an operation possible with this cryostat by closing the tap *Eak*₂ leading to the liquefier. The excess pressure was read on an oil manometer connected to *S*₃. These measurements showed that from the melting point of hydrogen to the neighbourhood of the boiling point of helium the curve exhibited the ordinary gradual lessening of the rate of diminution of resistance, practically the same as given by the formula of Comm. N^o. 119. A little above and a little below the boiling point, from 4^o,29 K. to 4^o,21 K. the same gradual change was clearly evident (cf. the fig.), but between 4^o,21 K. and 4^o,19 K. the resistance diminished very rapidly and disappeared at 4^o,19 K. (Temperature measurements are here given with 4^o,25 K. as the boiling point of helium).

During the discussion initiated by the communication of these results to the Brussels "Conseil Solvay" (2 Nov. 1911) M. LANGEVIN asked if other properties of the substance displayed similar sudden changes, as would be the case if mercury underwent a structural modification at 4^o,20 K. Experiments with the object of settling this point were, of course, immediately planned when this phenomenon was observed, but they have not yet been concluded. It can well be, however, that, should there exist such a new modification, it would differ from ordinary mercury at higher temperatures chiefly by the property that the frequency of the vibrators in the new state has become greater, and therefore the conductivity rises to the extremely large value exhibited below 4^o,19 K.

§ 4. *The motion of electricity through mercury at temperatures below 4^o,19 K.*

The next step was as in the earlier experiments to try by sending a comparatively strong current through the resistance, to obtain an upper limit to the value which must be ascribed to the resistance when this has practically vanished, as is the case at 3^o,5 K. The peculiarities of the phenomena which then occur make it desirable to experiment first with a modified apparatus before proceeding further.

Physics. “*Energy and mass.*” II¹⁾. By J. D. VAN DER WAALS JR.
(Communicated by Prof. J. D. VAN DER WAALS.)

HERGLOTZ²⁾ has assumed that we can deduce the equations of motion of a system after the method of PLANCK with the aid of the principle of least action from a kinetic potential, and he has investigated what conditions are necessary and sufficient in order that that potential has the property to depend only on the “rest-deformations” after a “LORENTZ-transformation to rest”. With rest-deformation of a moving element of volume we mean the deformation which it shows after being transformed to rest, compared with the shape which it shows when it rests and is not subjected to any stress. For this he finds the following conditions: 1st. the tensor of the “absolute stress” must be symmetrical, i. e. $p_{xy} = p_{yx}$, etc., 2nd. the current of energy must be equal to $c^2 \times$ the momentum, 3rd. a set of equations ((77) p. 508 of his treatise), which in the notation used by me may be represented as follows:

$$\left. \begin{aligned} \mathfrak{E}_x &= v_x F' + v_x p_{xx} + v_y p_{xy} + v_z p_{xz} \\ \mathfrak{E}_y &= v_y F' + v_x p_{xy} + v_y p_{yy} + v_z p_{yz} \\ \mathfrak{E}_z &= v_z F' + v_x p_{xz} + v_y p_{yz} + v_z p_{zz} \end{aligned} \right\} \dots (1)$$

$$W = F + \frac{1}{c^2} v_x \mathfrak{E}_x + \frac{1}{c^2} v_y \mathfrak{E}_y + \frac{1}{c^2} v_z \mathfrak{E}_z$$

The fourth equation may be considered as the definition of the quantity F' .

When these equations are satisfied, the hypothesis of relativity is satisfied. For when we use different coordinate systems moving with different velocities, the equations of motion are always derived in the same way from the kinetic potential, and this potential depends in the same way on the rest-deformations and on the velocities of the elements of mass relative to the coordinate systems. From this it follows that as well the equations of motion as the conditions found by HERGLOTZ are covariant for a LORENTZ-transformation, and that

¹⁾ In Sept. 1911, when I wrote “Energy and Mass” I, it was not known to me, that investigations of the same kind and with partly the same results had already been published by

D. F. COMSTOCK Phil. Mag. 15, p. 1. Anno 1908.

G. N. LEWIS. Phil. Mag. 16, p. 705. Anno 1908.

G. N. LEWIS and R. C. TOLMAN. Proc. Amer. Akad. of Arts and Sc. 44, p. 711, Anno 1909.

²⁾ G. HERGLOTZ. Ann. d. Phys. 36, p. 493. Anno 1911.

they are therefore satisfied in the same way for the different coordinate systems, i.e. that for moving systems x', y', z' depend on t' according to the same laws, as for a stationary system x, y, z depend on t .

So we cannot deduce from the way in which different processes take place, whether the coordinate system which we are using moves or is stationary. In particular, — and this consequence, which is not separately mentioned by HERGLOTZ seems to me to be of enough importance to draw attention to it, — it is possible to conclude that if these conditions are satisfied the LORENTZ-contraction must take place. For we saw, that if these conditions are satisfied the rest-tensions (i. e. the quantities p , which we find in a volume-element after we have transformed it to rest) depend only on the rest-deformations. If therefore for a moving system the relative (elastic) tensions are zero, then the rest-tensions are zero and also the rest deformations; and the volume element shows in a coordinate system in which it rests, its normal shape. In a coordinate system relative to which it moves, it shows then a shape which is shortened in the direction of motion in the well known way.

The equations (1), however, deduced by HERGLOTZ from the postulate of relativity in the way indicated above, are identical with the equations

$$\begin{aligned} \mathfrak{E}_x(1 + \beta^2) &= (W + p_{xx})v \\ \mathfrak{E}_y &= p_{xx}v^1) \end{aligned}$$

as we see by choosing in (1) the direction of motion as direction of X , i.e. by putting $v_y = v_z = 0$.

Now these equations had been derived by me i.e. without making use of the hypothesis of relativity, but only basing my deductions on the supposition $m = \frac{1}{c^2} W$. I therefore conclude that we may derive the whole theory of relativity from classical mechanics, when we change the principles of mechanics only in this one point, that we assume the mass of the bodies to vary with their energy according to this formula; and that therefore by working out the idea advanced by POINCARÉ in 1900, that the energy possesses mass, we could have arrived at a theory from which the negative result of the experiments of MICHELSON, etc. might have been predicted.

SOMMERFELD ²⁾ declares the theory of relativity not to be any more

1) *Energy and mass' I p. 252. The symbol \mathfrak{E}_{xy} occurring there is evidently a printer's error for \mathfrak{E}_y .

²⁾ A. SOMMERFELD. Phys. Zeitschr. 12, p. 1057. Anno 1911.

actual. If he means to say that in this theory only details should have been left for further investigation because the principal ideas have been sufficiently established, this assertion seems to me to be inaccurate. In my opinion the present state of the problem could be more aptly compared with the state of planetar mechanics at the time, when some laws of the planetar motion were known, — namely the laws of KEPLER — but when the causal explanation of these laws with the aid of the principia of mechanics of NEWTON had not yet been furnished. Thus in the theory of relativity we have known up till now some laws, — namely the laws of LORENTZ for the contraction in the direction of motion and for the variation of the mass with the velocity — but an explanation of this variation of mass and shape was not known. I think I have shown here that the principia of NEWTON together with the supposition $m = \frac{1}{c^2} W$ are sufficient to give this explanation.

Yet, and I will state this most emphatically, this is no more than a first step. Many questions are still waiting for a solution. In what way for instance must the kinetic energy be explained, or in other words why does the mass of a body vary when its motion is accelerated; why is an acceleration accompanied with a flow of mass towards the body?

A second question is the following one: how must the equation

$$\frac{1}{c^2} \frac{\partial \mathfrak{E}_x}{\partial t} = \frac{\partial p_{xx}}{\partial x} + \frac{\partial p_{xy}}{\partial y} + \frac{\partial p_{xz}}{\partial z}$$

be interpreted? It has exactly the form of an equation of continuity. A great (perhaps a too great) importance has of late been attached to such like analogies in the ways in which some quantities occur in some equations. But this equation suggests the question whether it is really an equation of continuity and whether it perhaps signifies that the momentum moves continuously through space.

Finally, the question has often been raised whether the theory of electricity must be deduced from mechanics or vice versa. Are we not to consider also a third possibility, namely that they are both to be derived from a still more fundamental law which determines the motion of the energy through space? So we should get a theory which might rightly be called energetics. Moreover the hidden masses which formerly played a part in mechanics, would have to be introduced again, but we should have advanced so much that we now know, that these hidden masses are nothing but the energy residing in the medium.

current follows from the transformation formula for the density of the energy W and for its velocity w . He assumes there, if I understand him rightly, that the addition theorem of EINSTEIN applies to w as well as to the velocity of a material point.

This, however, is not the case. For if we start from the transformation for \mathfrak{E} and W , we find quite a different law for the transformation formula for w . It is the question if an objection to that transformation can be derived from this fact.

To me this seems not to be the case. The claim that the addition theorem should apply presupposes that for energy as for matter we can distinguish individually the particles of which it consists. Only on this supposition can the paths of a particle relative to two differently moving coordinate systems be possibly compared with one another, which then leads to the addition theorem of EINSTEIN. This assumption, however, does certainly not hold, for the transformation formula for W , i. e. the equation

$$W = \frac{W' + \beta^2 p'_{xx} + 2 \frac{v}{c^2} \mathfrak{E}'_x}{1 - \beta^2}$$

shows, that energy can also then be present in the accentuated system, when in the unaccentuated system no energy of the same kind is to be found.

It is true that in the electromagnetic field in vacuo this case cannot occur. But it can occur for the elastic energy of a body subjected to a tension which is equal in all directions.

If the body rests relatively to the accentuated system, then we have

$$\mathfrak{E}' = 0, \quad p'_{xx} < 0, \quad W' > 0$$

and if the body is only little compressible:

$$p'_{xx} \gg W'$$

We shall then have $W = 0$ if the relative velocity of translation of the two systems reaches the not very large value

$$v = c \sqrt{1 - \frac{p'_{xx}}{W'}}$$

If v increases to a still higher value, W will even become negative. In such a case it is certainly impossible to compare the motion of a particle of energy when evaluated with the aid of the two systems.

Perhaps the objection may be raised against this consideration that in the last equation the tensor transformation has been used, whereas its applicability is just to be proved. Therefore I will adduce an instance which shows independently of every special theory, that the

velocity of the energy cannot be transformed in the same way as the velocity of a material point. We consider three coordinate systems, K^0 , K^+ , K^- moving uniformly relative to one another; the latter two will have the velocity $\pm v$ relative to K^0 . A body subjected to a tension (negative pressure) equal in all directions is in rest relative to K^0 . In the system K^+ it has the velocity $-v$, in K^- the velocity $+v$. In the same way the elastic energy which is imparted to the body by the tension is in rest relative to K^0 , but flows in the other systems.

This flow of energy is compounded of the convection current of the energy carried along by the matter and the conduction current occasioned by the tensions. Only the first component agrees in direction with the velocity of the body, the second has on the contrary the opposite direction. If now, as above, we imagine the body to be only little compressible, then the density of the energy W^0 in the system K^0 is small compared with p . In this case the conduction current will far exceed the convection current, the velocity of the energy in the system K^+ will therefore have the direction $+v$, in the system K^- the direction $-v$; this direction is therefore exactly opposite to that of the velocity of a point resting relatively to K^0 . Now it is true that VAN DER WAALS JR. tries to evade these difficulties, which he himself, no doubt, has also noticed, by splitting up the energy current for one and the same kind of energy into some components differing in direction and value. It seems to me still doubtful for the present whether this is the way to reach the desired end.

Is the conception of a velocity of the energy, which of course can always be defined and calculated by means of equation (1), after all efficient? In some cases it is doubtless so. O. REYNOLDS¹⁾ e. g. has calculated the group-velocity for water waves, and the present writer²⁾ and in a still more general manner M. ABRAHAM³⁾ have done so for light waves according to the electron theory. In both cases we can imagine a closed surface moving with the velocity w through which passes no energy. As we can disregard the absorption, this surface always includes the same quantum of mechanical or electromagnetical energy. It has, however, always only its signification for *one* coordi-

Put in the equation 102 of my book "das Relativitätsprinzip" (Braunschweig 1911) $\mathfrak{E} = wW$.

¹⁾ O. REYNOLDS: Nature 6 p. 343, 1877; H. LAMB: Hydrodynamik, p. 446. Leipzig u. Berlin 1907.

²⁾ M. LAUE: Ann. d. Phys. 18, 523, 1905.

³⁾ M. ABRAHAM. Rendiconti R. Inst. Lomb. d. x. e. lett. (3) 44, 68, 1911.

nate system. For another system the energy flows in general through the surface. (We find an instance for this fact in the outer surface of the body, mentioned in the last paragraph but one, which is in rest relatively to K° . For K° no energy current passes through the surface, it does, however, in K^{+} and K^{-}). But this representation fails altogether when absorption takes place, because then inside such a surface the energy would gradually diminish indefinitely. Therefore it seems to me that no great importance can be attributed to the conception of the velocity of the energy.

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Physics. — “*On the conception of the current of energy*”. By J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS).

In the preceding paper Mr. LAUE advances some objections against the way in which I make use of the conception “current of energy” in my considerations¹⁾. He was so kind as to send me his remarks in manuscript, in consequence of which I can answer them in this same number. LAUE is of opinion, that we cannot conceive the current of energy as a product of two factors: the density and the velocity of the energy; and more emphatically that in case of a LORENTZ transformation such a velocity must not be transformed according to the ordinary formula for the transformation of velocities.

As a proof for this assertion he points out, that the elastic energy of a moving body can become zero or negative²⁾, but that the corresponding current of energy does not become zero or change its sign at the same time. This difficulty, however, is not decisive, if we accept the decomposition of the energy current in components moving with different velocities, as I have indicated, l. c. § 5. And the circumstance, that energy is transferred from one point of the body to

¹⁾ These proceedings p. 239.

²⁾ At first sight it seems to be paradoxal that the elastic energy should become negative. Still it is really possible, as can be explained in the following way. We imagine a stationary body. Now we apply equal and opposite forces at the ends of it. These forces in stretching out the body, do positive work. Then we set the body in motion, in consequence of which it contracts. During this contraction the external forces do a negative amount of work. If this negative amount is in absolute value equal to, or larger than the positive work for the extension, the elastic energy of the body can become zero or negative.

another, makes the conception of energy moving with another velocity than the body very plausible.

The main point, however, on which the opinion of LAUE is based seems to me to be the fact, that we have no experimental data for ascribing a definite velocity to the energy and for decomposing the energy current in a definite way in components with different velocities. And it is his conviction, if I understand him rightly, that we are not justified in introducing such like suppositions, which are founded only on logical and not on experimental considerations. So he is of opinion that we are not justified in ascribing a definite velocity to the energy, because we cannot individualise an amount of energy, and therefore cannot determine experimentally the velocity with which the energy moves.

In connection with this I will remark, that in the case of an electrical current in a wire we are no more able to individualise the separate amounts of electricity and we have not the least experimental datum concerning the velocity of the current. Yet several physicists have tried to find values for the density and for the velocity of the electrical charge. And though the values they give are not very reliable in consequence of our scanty knowledge of the motion of electrons in metals, yet it seems to me that in principle no objection against such endeavours can be raised. We choose, of course, such a value for the velocity as enables us to represent the conceptions and the laws of the theory of electricity in the simplest manner possible, and to ascribe to them the most general applicability. In the same way the close connection between energy and mass induces me to apply the considerations which hold for the current of mass, as far as possible also to the energy current.

If however a person who is so intimately acquainted with the theory of relativity as LAUE, and who has contributed himself so much to its development, can think that we are not justified in introducing suppositions which are not capable of being directly experimentally tested, and which only serve for the simplification and the more general application of the theory, then it seems to me not be superfluous to investigate, which part of the theory of relativity as it is at present pretty generally adopted, has after all an experimental basis, and which suppositions have been introduced in consequence of more "logical" considerations. In the first place we see that the conception of an energy current lacks an experimental basis, at least the current which is assumed to exist in a moving body, when it is subjected to elastic stress and of which LAUE makes a so frequent use. The observations only teach us that in one

point of the body a force is applied which does work, in another point a force which absorbs work. We might assume that in one point energy is annihilated and that at the other point an equal amount of energy is created. An energy current existing between those two points is not shown to us by any experiment. Only in consequence of our more "logical" tendencies, we want the conception of a continuous motion of the energy, and this leads us to assume that the current exists. The analogy with the motion of material mass in space has here undoubtedly been of influence. This current of energy once admitted, it seems to me only a small step to carry this analogy somewhat further and speak of a definite density and a definite velocity of the energy in that current.

But, and this is a more important question, the whole fundamental assumption, that the laws of nature will be covariant for a LORENTZ-transformation, has no experimental basis. The most obvious explanation of the experiments of MICHELSON, etc. is certainly to assume that light propagates with a velocity c relative to its source, but that the velocity relative to an observer who is in motion relative to the source would have another value. Then the propagation of light would take place in the way of emitted particles. There would then no longer be any question of the ether, nor therefore of the equations of the field. Not the equations of MAXWELL, but the expressions for the electromagnetic potentials would have to be considered as the basis of the theory of electricity. W. RITZ¹⁾ has drawn these conclusions with the greatest consistency in two papers, to which too little attention has been paid²⁾.

What can be a sufficient reason to reject this natural and obvious explanation of the experiments? It appears to me that for this only one reason can exist, namely that we believe the ether to exist, and therefore assume that light, being a vibration in this medium, propagates in vacuo with a constant velocity c relative to this medium. Then one coordinate system must exist, relative to which light propagates always with the same velocity (according to the theory of RITZ this is not the case). But then the experiments of MICHELSON, etc. postulate that for moving coordinate systems we should use

1) W. RITZ. Ann. de Chim. et de Phys. 8th series 13. p. 145. Anno 1908. W. RITZ. Arch. des Sc. Phys. et Nat. (Genève) 26 p. 209, Anno 1908.

2) I do not mean to pretend that I consider everything that RITZ asserts in his papers to be accurate. The assertion e.g. that the theory of LORENTZ should be in contradiction to the principle action = reaction, is decidedly erroneous, I even think I have demonstrated that a consistent application of that principle leads to LORENTZ's theory of relativity, and that this might perhaps be adduced as an argument to prefer LORENTZ's theory to that of RITZ.

such variables as measure of length and time, that we find for the velocity of light also c when measured with them.

So the only argument to justify a choice between the theory of relativity of LORENTZ (covariance of the laws of nature for the LORENTZ-transformation) and that of RITZ¹⁾ (covariance for the GALLILEI-transformation) can for the present in my opinion only be the logical consideration whether we think the explanation of the electrical phenomena more plausible with or without the use of the conception of an ether.

Fortunately this need not always be the case. Though both theories may be equally adopted to explain the hitherto observed phenomena, other experiments are possible which may enable us to get a decisive test which of them is the correct one. A direct measurement of the velocity of light emitted by sources showing the Doppler effect, can evidently give such a decision. The two theories give here a difference of the first order. It is not known to me whether other experiments which can more easily be executed, would according to the two theories yield different results.

1) It appears to me that only these two theories need be taken into consideration. In my opinion no reason can be found for assuming that the ether does not exist, and on the other hand yet to assume that one or more coordinate systems should exist relative to which the velocity of light is always c . Certainly no experimental reason can be found. Yet this assumption is probably the most widely prevailing. WIECHERT (Phys. Zeitschrift 12, p. 689. Anno 1911) has called it "unbedingtes Relativitätsprincip". This name, however, seems to me to give rise to misunderstanding. For one might think that the "bedingte" theory claims that the postulate of relativity is only partially fulfilled. The danger for such an interpretation is the greater, because according to the original formulae of LORENTZ in his paper of 1904 the postulate of relativity was in fact not fulfilled with perfect accuracy. This, however, was only due to an error in the determination of the transformation formula for the velocity. This error has been corrected by POINCARÉ and by EINSTEIN. It has no connection whatever with the difference of the theories called "bedingte" and "unbedingte" theory by WIECHERT, who both claim the same absolute accuracy, and which are in fact identical in all equations they make use of. The only difference consists in the assumption or denial of the existence of the ether and in the answer they give to the question whether t' is really the time or an auxiliary quantity. As the "unbedingte" theory assumes that a difference between a moving and a stationary system is not to be observed and *therefore* does not exist, and that it therefore is based on the thesis "esse est percipi" I should rather call it the sensualistic theory of relativity.

Mathematics. — “Homogeneous linear differential equations of order two with given relation between two particular integrals.” (3rd communication). By Mr. M. J. VAN UVEN. (Communicated by Prof. W. KAPTEYN).

(Communicated in the meeting of December 30, 1911).

Before giving an example of case (3) (I is an *odd* function of τ , all integrals are odd functions of τ) we wish to make a few observations holding in general when I is a univalent odd function. Here we continually suppose that no roots of even power appear in the integrals (as, indeed, we have up to now always tacitly done).

As in the case mentioned here we may always suppose the integral to be either even or odd, a change in the algebraic sign of the integral is exclusively due to the substitution of $-\tau$ for τ .

If an integral $x(\tau)$ of (B) is known, a second integral $y(\tau)$ can be found in the usual way by putting

$$y = zx.$$

From this ensues then

$$\begin{aligned} \dot{y} &= \dot{z}x + z\dot{x}, & \ddot{y} &= \ddot{z}x + 2z\dot{x} + z\ddot{x}, \\ \ddot{y} + \frac{I}{2}\dot{y} + y &= zx - z\left(2\dot{x} + \frac{I}{2}x\right) + z\left(\ddot{x} + \frac{I}{2}\dot{x} + x\right) = \\ &= \ddot{z}x + z\left(2\dot{x} + \frac{I}{2}x\right) = 0, \end{aligned}$$

so that

$$\frac{\ddot{z}}{z} = -\frac{2\dot{x}}{x} - \frac{I}{2},$$

or

$$\dot{z} = x^{-2} e^{-\frac{1}{2}\int I d\tau}.$$

As x is either even or odd, x^{-2} is certainly an *even* function of τ . To judge whether \dot{z} will be even or odd, we have nothing else to do but to investigate $e^{-\frac{1}{2}\int I d\tau}$.

We suppose the odd factor I developed according to positive and negative powers of τ . Let the highest positive power be $2n+1$, the lowest negative $-(2m+1)$. If necessary n or m or both can later on be regarded as infinite. So we write

$$\frac{I}{2} = \sum_0^m a_k \tau^{-2k-1} + \sum_0^n b_k \tau^{2k+1}.$$

By integration we find

$$\int \frac{I}{2} d\tau = - \sum_1^m \frac{a_k}{2k} \tau^{-2k} + a_0 \log \tau + \sum_0^n \frac{b_k}{2k+2} \tau^{2k+2} + c = Q_2(\tau) + a_0 \log \tau,$$

where $Q_2(\tau)$ denotes an *even* function of τ .

The expression

$$e^{-\frac{1}{2} \int I d\tau} = e^{-Q_2(\tau)} \cdot \tau^{-a_0} = \tau^{-a_0} \cdot R_2(\tau)$$

is therefore the product of an *even* function $R_2(\tau)$ of τ and τ^{-a_0} .

It will be an even or odd function of τ according as a_0 is even or odd. If a_0 is an (irreducible) fraction, we then claim in connection with the above, that a_0 has not an even denominator. We then call a_0 even or odd according as the numerator is even or odd.

If a_0 is *odd*, then \dot{z} is also odd, hence z is even. The second integral has then the same parity as the first; we are then in the case of (α) or (β).

If a_0 is *even*, then \dot{z} is even, hence z odd. The second integral is of an other parity than the first; we are in the case (γ).

The equal or unequal parity of the integrals is then governed by the nature of the coefficient of τ^{-1} in $\frac{I}{2}$.

If $\frac{I}{2}$ is an odd function which does not become infinite in $\tau = 0$ and which can therefore be developed according to positive powers of τ , then $a_0 = 0$, therefore even. We are then in case (γ).

For instance (a) $x = \sinh \tau$

Here holds $\frac{I}{2} = -\frac{\ddot{x} + x}{x} = -2 \tanh \tau$, so $e^{-\int \frac{I}{2} d\tau} = \cosh^2 \tau$, $z = \coth^2 \tau$,

$z = \tau - \coth \tau$, $y = \tau \sinh \tau - \cosh \tau$.

Here too x and y are of different parity.

(b) $x = \cosh \tau$

Now $\frac{I}{2} = -\frac{\ddot{x} + x}{x} = -2 \coth \tau$, so $a_0 = -2$; $e^{-\int \frac{I}{2} d\tau} = \sinh^2 \tau$,

$z = \tanh^2 \tau$, $z = \tau - \tanh \tau$, $y = \tau \cosh \tau - \sinh \tau$.

Here too x and y are of different parity.

We shall now regard the case in which a_0 is *odd*.

It may be possible to develop the integral $x(\tau)$ according to positive and negative powers of τ ; let the highest positive exponent be μ , the lowest negative $-\mu$. We can then write

$$x = \sum_1^{\mu} \alpha_k \tau^{-k} + \sum_0^{\nu} \beta_k \tau^k,$$

from which ensues

$$\dot{x} = - \sum_1^{\mu} k \alpha_k \tau^{-k-1} + \sum_1^{\nu} k \beta_k \tau^{k-1},$$

$$\ddot{x} = + \sum_1^{\mu} k(k+1) \alpha_k \tau^{-k-2} + \sum_2^{\nu} k(k-1) \beta_k \tau^{k-2},$$

so that

$$\begin{aligned} \frac{I}{2} &= - \frac{\ddot{x} + x}{\dot{x}} = - \frac{\mu(\mu+1) \alpha_{\mu} \tau^{-\mu-2} + \sum_{-\mu-1}^{\nu} \gamma_k \tau^k}{\sum_{-\mu-1}^{\nu-1} \delta_k \tau^k} = \\ &= - \frac{\mu(\mu+1) \alpha_{\mu} + \sum_{-\mu-1}^{\nu} \gamma_k \tau^{\mu+2+k}}{\tau \sum_{-\mu-1}^{\nu-1} \delta_k \tau^{\mu+1+k}} = - \frac{\mu(\mu+1) \alpha_{\mu} + \sum_{-\mu-1}^{\nu} \gamma_k \tau^{\mu+2+k}}{\tau \left\{ \delta_{-\mu-1} + \sum_{-\mu}^{\nu-1} \delta_k \tau^{\mu+1+k} \right\}} = \\ &= - \frac{\mu(\mu+1) \alpha_{\mu} + \sum_{-\mu-1}^{\nu} \gamma_k \tau^{\mu+2+k}}{\tau \delta_{-\mu-1}} \left\{ 1 + \frac{1}{\delta_{-\mu-1}} \sum_{-\mu}^{\nu-1} \delta_k \tau^{\mu+1+k} \right\}^{-1} = \\ &= - \frac{\mu(\mu+1) \alpha_{\mu} + \sum_{-\nu}^{\infty} \varepsilon_k \tau^{\mu+1+k}}{\tau \delta_{-\mu-1}}, \end{aligned}$$

or, as we have $\delta_{-\mu-1} = -\mu \alpha_{\mu}$,

$$\frac{I}{2} = \frac{\mu+1}{\tau} + \sum_0^{\infty} p_k \tau^k$$

so that

$$\alpha_0 = \mu + 1.$$

If is desired as in case (β) that x be an odd function of τ , and if the latter has a pole of finite order in $\tau = 0$, then μ is odd, so $\alpha_0 = \mu + 1$ is even. The integral y is in this way of a different parity than x , therefore even. Hence we have not case (β) but case (γ) under consideration.

If x is an integer odd function of τ then holds

$$x = \sum_{\rho}^{\nu} \beta_k \tau^{2k+1}, \quad \dot{x} = \sum_{\rho}^{\nu} (2k+1) \beta_k \tau^{2k}, \quad \ddot{x} = \sum_{\rho}^{\nu} 2k(2k+1) \beta_k \tau^{2k-1},$$

so

$$\frac{I}{2} = - \frac{\ddot{x} + x}{\dot{x}} =$$

$$\frac{2\rho(2\rho+1)\beta_{\rho} \tau^{2\rho-1} + \{(2\rho+1)(2\rho+2)\beta_{\rho+1} + \beta_{\rho}\} \tau^{2\rho+1} + \sum_{\rho+1}^{\nu} \varepsilon_k \tau^{2k+1}}{(2\rho+1)\beta_{\rho} \tau^{2\rho} + \sum_{\rho+1}^{\nu} (2k+1)\beta_k \tau^{2k}}$$

$$= \frac{2\rho(2\rho+1)\beta_\rho + \{(2\rho+1)(2\rho+2)\beta_{\rho+1} + \beta_\rho\}\tau^2 + \sum_{k=\rho+1}^{\infty} \epsilon_k \tau^{2k-2\rho+2}}{\tau\{(2\rho+1)\beta_\rho + \sum_{k=\rho+1}^{\infty} (2k+1)\beta_k \tau^{2k-2\rho}\}}$$

As β_ρ is supposed ≥ 0 we can transfer the form between $\{\}$ in the denominator (treated as binomial) to the numerator. In this way we get in the numerator a series of positive powers of τ and we finally find for $\frac{I}{2}$ an expression in which the lowest power of τ is τ^{-1} and that with the coefficient

$$a_0 = -\frac{2\rho(2\rho+1)\beta_\rho}{(2\rho+1)\beta_\rho} = -2\rho.$$

Here too a_0 is even, so that we have again hit upon case (γ).

The only manner to obtain with odd x an odd value for a_0 is reached by assuming that the negative powers of τ in the series for x continue to infinity, hence by putting $\mu = \infty$. We then evidently start from the supposition that x in $\tau = 0$ has a *really-singular* point.

We remark, that we are allowed in as far as it regards parity, to assume that the series for x and y are built up out of powers of τ with broken exponents if but the denominator of that exponent is *not* even. We then find accordingly for a_0 broken values.

Example :

$$x = \sin\left(\frac{1}{\tau}\right).$$

Here holds $\dot{x} = -\frac{1}{\tau^2} \cos\left(\frac{1}{\tau}\right)$, $\ddot{x} = +\frac{2}{\tau^3} \cos\left(\frac{1}{\tau}\right) - \frac{1}{\tau^4} \sin\left(\frac{1}{\tau}\right)$, so that

$$\begin{aligned} \frac{I}{2} &= -\frac{\ddot{x} + x}{x} = \\ &= -\frac{-\frac{1}{\tau^4} \sin\left(\frac{1}{\tau}\right) + \frac{2}{\tau^3} \cos\left(\frac{1}{\tau}\right) + \sin\left(\frac{1}{\tau}\right)}{-\frac{1}{\tau^2} \cos\left(\frac{1}{\tau}\right)} = \left(\tau^2 - \frac{1}{\tau^2}\right) \operatorname{tg}\left(\frac{1}{\tau}\right) + \frac{2}{\tau}. \end{aligned}$$

For a_0 we find restricting ourselves to the domain of convergence,

$$a_0 = \frac{7}{3}.$$

So here we are really in case (β).

In the first case I was an *even* function of τ . As instance we have discussed the case where I is constant. We shall imagine that I is

not constant and we give as example :

$$x = e^{e^{\tau}} .$$

Now $\dot{x} = e^{\tau} e^{e^{\tau}}$, $x = e^{\tau} e^{e^{\tau}} + e^{2\tau} e^{e^{\tau}}$, so that

$$-\frac{I}{2} = \frac{\ddot{x} + \dot{x}}{x} = \frac{e^{2\tau} + e^{\tau} + 1}{e^{\tau}} = 1 + 2 \cosh \tau .$$

So here I is really an even function of τ . The substitution $-\tau$ instead of τ now leaves $I(\tau)$ unchanged whilst the differential equation passes into

$$x - \frac{I}{2} \dot{x} + x = 0 .$$

so into the one belonging to the semi-equivalent curve.

In order to find the second integral $y(\tau)$ we again put $y = xz$. Then the function z is defined by

$$\dot{z} = x^{-2} e^{-\frac{1}{2} \int I d\tau} = e^{-2e^{\tau}} \cdot e^{\tau + 2 \sinh \tau} = e^{\tau - e^{\tau} - e^{-\tau}} .$$

Furthermore holds

$$\dot{x} = e^{\tau} + e^{\tau} .$$

We thus find

$$x \frac{dy}{dx} - y = x^2 \frac{dz}{dx} = x^2 \frac{z}{x} = e^{2e^{\tau}} \cdot e^{\tau - e^{\tau} - e^{-\tau}} \cdot e^{-\tau - e^{\tau}} = e^{-e^{-\tau}} .$$

The coordinate (§) of the points of the curve obtained by polarisation is now (but for a constant factor):

$$\xi = \frac{dx}{x dy - y dx} = e^{e^{-\tau}}$$

So the coordinate ξ proves to be really obtained by replacing τ in x by $-\tau$.

Out of

$$x \frac{dy}{dx} - y = e^{-e^{-\tau}} \quad \text{and} \quad x = e^{e^{\tau}}$$

follows:

$$\log \left(x \frac{dy}{dx} - y \right) = -e^{-\tau} \quad \text{and} \quad \log x = e^{\tau} ,$$

so

$$\log \left(x \frac{dy}{dx} - y \right) \cdot \log x = -1 ,$$

or

$$\left(x \frac{dy}{dx} - y \right)^{\log x} = e^{-1},$$

or

$$x \frac{dy}{dx} - y = e^{-\frac{1}{\log x}},$$

so

$$\frac{dy}{dx} - \frac{y}{x} = \frac{1}{x} e^{-\frac{1}{\log x}}.$$

so that

$$y = x \int \frac{1}{x^2} e^{-\frac{1}{\log x}} dx, \dots \dots \dots (50)$$

where the constant of integration is put equal to zero, as this does not harm the generality of the integral.

The curve represented by (50) is evidently semi-equivalent to itself.

Chemistry. — “*The nitration of benzene*”. By Prof. A. F. HOLLEMAN and J. VERMEULEN.

(This communication will not be published in these Proceedings)

Chemistry. — “*On the addition and the addition products of chlorine to the chlorbenzenes*”. By Dr. T. VAN DER LINDEN. (Communicated by Prof. A. F. HOLLEMAN).

(This communication will not be published in these Proceedings).

E R R A T A.

In the Proceedings of the meeting of December 30, 1911:

p. 674 l. 17 from the top: for “narrowed at the lower end” read “having an upper wider and a narrower lower end connected to the first by a capillary”.

l. 13 from the bottom: for “lower” read “lowest”.

p. 676 Table II in the heading of the third column read $\chi \cdot 10^6$

p. 678 l. 2 from the top: for “all” read “a class of”.

(February 22, 1912).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday February 24, 1912.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige
Afdeling van Zaterdag 24 Februari 1912, Dl. XX).

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Physics. — “*Entropy and Probability.*” By Dr. L. S. ORNSTEIN.
(Communicated by Prof. LORENTZ).

(Communicated in the meeting of September 30 1911).

EINSTEIN¹⁾ has defined the probability of state in a way by which he emancipates himself from special hypotheses concerning the structure of the systems to which he applies his reasonings. He puts the logarithm of the probability thus defined proportional to the entropy. If therefore $d\varepsilon$ is the difference of energy between two states of the system, and if dA represents the work done by the system if it passes in a reversible way from one state into the other we have

$$d\eta = \frac{R}{N} d \log W = \frac{d\varepsilon + dA}{T},$$

R is the gas constant and N the number of molecules of the gramme-molecule. The reasoning, used to deduce the proportionality of η and $\frac{R}{N} \log W$, is perhaps not quite convincing, for on the one side it is presumed that a system runs through all states possible with the given energy, and on the other that $\log W$ like the entropy tends to a maximum value. It is possible by means of statistical mechanics (as well with the help of the canonical as with that of the micro-canonical ensembles) to find the relation of entropy and probability, however using many less general hypotheses as those employed by EINSTEIN. I will try to show this in the following communication.

1. We consider a system of a great number (s) of degrees of liberty. We suppose that the changes of the state in this system are governed by the equations of HAMILTON. Observation does not teach us anything on the s general coordinates (q) and the s moments of momentum (p) but we obtain knowledge of certain (e. g. geometrical) quantities A . Suppose that there are k quantities A_k which are discernable for observation. The number k is small in comparison to $2s$. We shall indicate these quantities by $A_1, \dots, A_k, \dots, A_k^{(2)}$.

To the $2s$ values of the coordinates and the moments in a given

¹⁾ Ann. der Phys. Vol. 33, 1910, p. 1276.

²⁾ The quantities A may be geometrical quantities but also densities in given spaces. The quantities determining deformation must be used in several cases, also the optical qualities of the system, in other cases we have to do with thermal quantities relating to parts of the system accessible to observation, and which may be said to characterise the system for it.

state of the system corresponds a perfectly determined set of values \mathcal{A} , on the contrary it must be kept in mind that a great number of systems with greatly differing values for the p 's and the q 's corresponds to a given set of values of the \mathcal{A} 's.

Moreover we must presume that the quantities \mathcal{A}_x are observable with moderate accuracy, so that systems for which \mathcal{A}_x has a value between \mathcal{A}_x and $\mathcal{A}_x + d\mathcal{A}_x$ are undiscernible for observation. The quantities $\Delta\mathcal{A}$ are once for all fixed (in relation to the given accuracy of observation); $\Delta\mathcal{A}_x$ will be small compared with \mathcal{A}_x .

A system having its \mathcal{A} 's between the limits mentioned will be called the system $(\mathcal{A}_1 \dots \mathcal{A}_x \dots \mathcal{A}_k)$. For the sake of simplicity we shall suppose that the quantities \mathcal{A}_x depend only on the general coordinates¹⁾.

The $2s$ -dimensional space in which the system can be represented in the ordinary way can be dissolved into the extension in configuration, (the coordinates being the variables) and into the extension in moments or velocity. The part of the extension in configuration where the systems lie for which the value of the \mathcal{A}_x is between \mathcal{A}_x and $\mathcal{A}_x + d\mathcal{A}_x$ will be represented by

$$\chi(\mathcal{A}_1 \dots \mathcal{A}_x \dots \mathcal{A}_k) d\mathcal{A}_1 \dots d\mathcal{A}_x \dots d\mathcal{A}_k$$

or shortly by

$$\chi d\mathcal{A}_1 \dots d\mathcal{A}_x \dots d\mathcal{A}_k .$$

We shall further suppose that the potential energy ε_q of the system of given \mathcal{A} 's is totally determined by the values of the quantities \mathcal{A}_x . This is only approximately true, for ε_q depends on the coordinates, which can still be greatly different for systems of which the \mathcal{A} 's are the same. We shall represent the potential energy by

$$\varepsilon_q(\mathcal{A}_1 \dots \mathcal{A}_x \dots \mathcal{A}_k, a_1 \dots a_n),$$

the quantities a denoting parameters on which the potential energy may also depend; the same parameters shall appear generally also in the function χ .

Finally we could suppose that there exist relations between the quantities \mathcal{A}_x , suppose for example b ($b < k$) of the form

$$f_\beta = 0.$$

For such a case we can always introduce $k-b$ new quantities \mathcal{A} which are mutually independent, we therefore shall suppose that this is yet the case for the \mathcal{A} 's mentioned above²⁾.

¹⁾ It is however not difficult to extend the considerations to those cases where this is not so and where the \mathcal{A}_x can be thermal quantities.

²⁾ This need not be the case if we take as variables such quantities which are suggested by the nature of the problem, e. g. there exists a relation between the

2. We shall now consider a microcanonical ensemble between the energies ε and $\varepsilon + d\varepsilon$, consisting of the systems described above. I shall represent the part of the extension in configuration for which the quantities A_i are situated between the limits A_i and $A_i + dA_i$ by $\Omega(A_1 \dots A_k)$. The value of Ω may be expressed by the equation.

$$\Omega(A_1 \dots A_k) = C \{(\varepsilon - \varepsilon_q(A_1 \dots A_k))\}^{\frac{s}{2} - 1} \chi \cdot dA_1 \dots dA_k / d\varepsilon;$$

C being a determined numerical constant which is of no importance to us. The quantities A_i must have such values that $\varepsilon_q \leq \varepsilon$.

We shall first consider the question for which values of A_i , Ω is a maximum, i.e. which values of the A_i occur in a maximal region.

We find for the maximum condition, proceeding in the usual way,

$$-\left(\frac{s}{2} - 1\right) \frac{1}{\varepsilon - \varepsilon_q(A_1 \dots A_k)} \frac{\partial \varepsilon_q}{\partial A_i} + \frac{1}{\chi} \frac{\partial \chi}{\partial A_i} = 0.$$

The quantity $\varepsilon - \varepsilon_q(A_i)$ being the kinetic energy of the system occurring maximally, this quantity is, as is proved by GIBBS, proportional to the absolute temperature T and it can be expressed by the formula

$$\frac{s}{2} \frac{R}{N} T.$$

Neglecting 1 with respect to $\frac{s}{2}$, s being very large, we find as a condition for the maximum of Ω

$$-\frac{N}{RT} \frac{\partial \varepsilon_q}{\partial A_i} + \frac{1}{\chi} \frac{\partial \chi}{\partial A_i} = 0.$$

The further conditions that $d^2 \log \Omega < 0$ lead to a number of relations of the form:

$$\begin{aligned} & -\frac{s-2}{2} \frac{1}{\varepsilon_p^2} \left(\frac{\partial \varepsilon_q}{\partial A_i}\right)^2 - \frac{s-2}{2\varepsilon_p} \frac{\partial^2 \varepsilon_q}{\partial A_i^2} \\ & - \frac{1}{\chi^2} \left(\frac{\partial \chi}{\partial A_i}\right)^2 + \frac{1}{\chi} \frac{\partial^2 \chi}{\partial A_i^2} < 0, \end{aligned}$$

and to a number of relations in which the quantities $\frac{d^2}{\partial A_i \partial A_j}$

densities in fixed elements of volume in a gas. In practice one will not use the relations to eliminate the A_i but will use the Laplacian method of undetermined coefficients. It is also possible that inequalities appear as relations in every case; it follows from our first hypothesis that we may assume that the relations are fulfilled without any approximation.

play a part. The complication offered by the appearance of these quantities may always be avoided by a linear substitution which removes those differential coefficients. I shall suppose that such-like A_x 's are introduced (further representing them by the same symbol A_x); A_{x_0} represents the value of A_x in the maximum system.

3. The region Ω where those systems are represented for which A_x is situated between $A_{x_0} + \xi_x$ and $A_{x_0} + \xi_x + d\xi_x$ can be easily calculated; we find for it:

$$\Omega_{\Delta} = \Omega_{0'} \frac{1}{2} \sum_{x=1}^k p_x \xi_x^2 / d\xi_1 \dots d\xi_k d\varepsilon$$

where

$$\Omega_0 = C \chi(A_{1_0} \dots A_{x_0} \dots A_{k_0}) (\varepsilon - \varepsilon_q)^{\frac{s}{2} - 1}$$

and

$$p_x = -\frac{N}{RT \varepsilon_{p_0}} \left(\frac{\partial \varepsilon_q}{\partial A_x} \right)^2 - \frac{N}{RT} \frac{\partial^2 \varepsilon_q}{\partial A_x^2} - \frac{1}{\chi^2} \left(\frac{\partial \chi}{\partial A_x} \right)^2 + \frac{1}{\chi} \frac{\partial^2 \chi}{\partial A_x^2}.$$

The expression found above can be used to calculate the total volume of the extension in phase of the space where the energy is contained between the given limits. For this purpose we have to take the sum of Ω_{Δ} for all the values of A_x 's which are compatible with the given energy. However, we can integrate with respect to the ξ_x from $-\infty$ to $+\infty$, the values of ξ_x which deviate considerably from 0, attributing only very small amounts. Proceeding in this way we find for the extension in question, which we shall represent by the notation of GIBBS $e^{\varepsilon} d\varepsilon$ or $\frac{\partial V}{\partial \varepsilon} d\varepsilon$

$$\frac{\partial V}{\partial \varepsilon} d\varepsilon = e^{\varepsilon} d\varepsilon = \frac{C \Omega_0}{(p_1 \dots p_x \dots p_k)^{1/2}} d\varepsilon,$$

C being again a determined constant, the value of which is without importance for our conclusions.

With the help of the found expression we can express the value of the function $V(\varepsilon)$ which determines the magnitude of the part of the extension in phase for which the energy of the represented systems is smaller than ε .

We obtain for $V(\varepsilon)$ the expression

$$V = C' \int_{\varepsilon(V=0)}^{\varepsilon} \frac{\chi(A_{1_0} \dots A_{x_0} \dots A_{k_0})}{\sqrt{(p_1 \dots p_x \dots p_k)}} (\varepsilon - \varepsilon_q(A_{1_0} \dots A_{x_0} \dots A_{k_0}))^{\frac{s}{2} - 1} d\varepsilon.$$

The value of the integral can easily be obtained in case that the

value of the A_s , for which Ω is a maximum, is independent of ε . Then we may assume $\varepsilon(V=0) = \varepsilon_q(A_{1_0}, A_{s_0}, \dots, A_{k_0})$. Substituting this value we find

$$V = C' \frac{\chi(A_{1_0}, A_{s_0}, \dots, A_{k_0})}{V(p_1, \dots, p_r, \dots, p_k)} \frac{2}{s} (\varepsilon - \varepsilon_q(A_{1_0}, A_{s_0}, \dots, A_{k_0}))^{\frac{s}{2}}$$

But the same relation holds for other cases. The quantity A_{s_0} depending on ε , we have

$$\begin{aligned} V &= \int_{\varepsilon(V=0)}^{\varepsilon} (\varepsilon - \varepsilon_q(A_{1_0}, \dots, A_{s_0}, \dots, A_{k_0}))^{\frac{s}{2}-1} \chi(A_{1_0}, \dots, A_{s_0}, \dots, A_{k_0}) d\varepsilon \\ &= \frac{2}{s} (\varepsilon - \varepsilon_q(\dots, A_{s_0}, \dots))^{\frac{s}{2}} \chi(A_{s_0}) \Big\{ + \int_{\varepsilon(V=0)}^{\varepsilon} (\varepsilon - \varepsilon_q(\dots, A_{s_0}, \dots))^{\frac{s}{2}-1} \chi(\dots, A_{s_0}, \dots) \\ &\quad \sum_1^k \left\{ \frac{\partial \varepsilon_q}{\partial A_{s_0}} \frac{\partial A_{s_0}}{\partial \varepsilon} \right\} d\varepsilon \\ &\quad - \frac{2}{s} \int_{\varepsilon(V=0)}^{\varepsilon} (\varepsilon - \varepsilon_q(A_{s_0}))^{\frac{s}{2}-1} \sum_1^k \frac{\partial \chi}{\partial A_{s_0}} \frac{\partial A_{s_0}}{\partial \varepsilon} d\varepsilon. \end{aligned}$$

Combining the integrals we find

$$\frac{2}{s} \int_{\varepsilon(V=0)}^{\varepsilon} (\varepsilon - \varepsilon_q(A_{s_0}))^{\frac{s}{2}} \chi(A_{s_0}) \left\{ \sum_1^k \left(\frac{s}{2(\varepsilon - \varepsilon_q)} \frac{\partial \varepsilon_q}{\partial A_{s_0}} - \frac{1}{\chi} \frac{\partial \chi}{\partial A_{s_0}} \right) \frac{\partial A_{s_0}}{\partial \varepsilon} \right\} d\varepsilon.$$

Every term of the integrals is zero. The kinetic energy being essentially positive we have at the limit $\varepsilon(V=0) \cdot \varepsilon = \varepsilon_q$, so that we obtain

$$V = \frac{2}{s} C (\varepsilon - \varepsilon_q(A_{s_0}))^{\frac{s}{2}} \chi(A_{s_0})$$

A_{s_0} having the value relating to the energy ε .

In this demonstration V/p_s has been neglected, the influence however of these factors is small, they deviate only very slightly from 1, if compared with the quantities taken into consideration.

4. GIBBS has proved that $\log V$ is equivalent with the thermodynamic entropy. If two microcanonical ensembles whose energy differs $\Delta\varepsilon$ and whose parameters differ by Δa there exists an equation of the form

$$e^{-\varphi} V \Delta \log V = \Delta \varepsilon + \overline{A} \Delta a^3) \dots \dots \dots (I)$$

in this equation \overline{A} is the average force in the ensemble exercised with

1) For the case under consideration we can prove without applying the general discussions of GIBBS that $\frac{\varepsilon p}{2s}$ shows a perfect analogy with the temperature, and the relation (I) can be proved somewhat more simply than it has been done by GIBBS.

Let us imagine two systems of the kind described above, which can interchange energy but which considered as a whole are isolated. Let us suppose that the first has s_1 , the second s_2 degrees of freedom, the energy of the first being ε_1 , that of the second ε_2 . The total energy being constant we have

$$\varepsilon_1 + \varepsilon_2 = \varepsilon.$$

The quantity φ_{12} of the combined system can be expressed (GIBBS l.c. p. 98 form. 316) by

$$e^{\varphi_{12}} = \int e^{\varphi_1 + \varphi_2} d\varepsilon_2.$$

If we represent the value of (Λ_{ν}) when the Λ_{ν} have their maximum value by $\chi(\Lambda_{\nu_0})$, and if we distinguish for the first system k parameters Λ_{ν} , and for the second n parameters λ_{ν} , we obtain

$$e^{\varphi_{12}} = \int (\varepsilon_1 - \varepsilon_{q_1})^{\frac{s_1}{2} - 1} \chi_1(\Lambda_{\nu_0})(\varepsilon_1 - \varepsilon_{j_2})^{\frac{s_2}{2} - 1} \chi_2(\lambda_{\nu_0}, \varepsilon_2) d\varepsilon_2.$$

The maximum system will contribute a maximal amount to the integral. We can find this system asking for what values of ε_1 and ε_2 the function under the integral is a maximum $\varepsilon_1 + \varepsilon_2$ being a constant. We then find

$$\begin{aligned} & \left(\frac{s_1}{2} - 1 \right) \frac{1}{\varepsilon_1 - \varepsilon_{q_1}} d\varepsilon_1 + \left(\frac{s_2}{2} - 1 \right) \frac{1}{\varepsilon_2 - \varepsilon_{q_2}} d\varepsilon_2 + \\ & \sum_1^k \left(- \left(\begin{matrix} s_1 & & \\ & 2 & \\ & & 1 \end{matrix} \right) \frac{\partial \varepsilon_{q_1}}{\partial \Lambda_{k_0}} + \frac{1}{\chi_1} \frac{\partial \chi_1}{\partial \Lambda_{k_0}} \right) \frac{d\Lambda_{k_0}}{d\varepsilon_1} d\varepsilon_1 + \\ & \sum_1^n \left(- \left(\begin{matrix} s_2 & & \\ & 2 & \\ & & 1 \end{matrix} \right) \frac{\partial \varepsilon_{q_0}}{\partial \lambda_{\nu_0}} + \frac{1}{\chi_2} \frac{\partial \chi_2}{\partial \lambda_{\nu_0}} \right) \frac{\partial \lambda_{\nu_0}}{\partial \varepsilon_2} d\varepsilon_2. \end{aligned}$$

From the above considerations it follows that the summations in this equation are zero, the Λ_{ν} being the values for the most frequent forms of the separate systems. We therefore find for the systems occurring maximally

$$\frac{s_1 - 2}{2(\varepsilon_1 - \varepsilon_{j_1})} = \frac{s_2 - 2}{2(\varepsilon_2 - \varepsilon_{j_2})} = \mu$$

or

$$\frac{\varepsilon_{j_1}}{s_1} = \frac{\varepsilon_{j_2}}{s_2}$$

i. e. that system is most frequent for which the kinetic energies of the composing systems are proportionate to the number of degrees of freedom.

If we separate the systems, their contents of kinetic energy will fulfill with

respect to the parameter α . GIBBS has shown that $e^{-\epsilon/\alpha}$ corresponds with temperature. With the help of the given relations we can cal-

culate the probability the theorem of equipartition. Also two systems the energies of which are proportionate to their number of degrees of freedom will be, after that communication of energy has been made possible, in a probable state and it is therefore almost certain that one system will not give or obtain energy from the other. If two systems are brought into contact whose energies are in another proportion, their state is improbable and the total system will probably change in such a way that the system for which $\frac{\epsilon p}{s}$ is too great, loses energy. What has

been said is sufficient to show that $\frac{\epsilon p}{s}$ can be used as a measure for the temperature.

We have next to consider the mean force in a micro-canonical ensemble. I will give a somewhat simpler deduction than that of GIBBS. (HERTZ has also given another treatment).

Consider an ensemble for which the density ρ in phase is a function of ϵ , the function $\rho(\epsilon)$ being zero everywhere except between narrow limits in the proximity of ϵ_0 ; between the limits $\rho(\epsilon)$ shall be supposed everywhere positive. Suppose that ϵ_1 and ϵ_2 are values of ϵ lying outside this region but so, that $\epsilon_1 < \epsilon_0 < \epsilon_2$; we have identically

$$\int_{\epsilon_1}^{\epsilon_2} Q dp_1 \dots dq_s = \int_{\epsilon_1}^{\epsilon_2} Q e^{\epsilon/\alpha} d\epsilon.$$

Differentiating with respect to the parameters α we obtain

$$\begin{aligned} \int_{\epsilon_1}^{\epsilon_2} \frac{\partial Q}{\partial \epsilon} \frac{\partial \epsilon}{\partial \alpha} dp_1 \dots dq_s &= + \int_{\epsilon_1}^{\epsilon_2} Q \frac{\partial \rho}{\partial \alpha} e^{\epsilon/\alpha} d\epsilon = - \int_{\epsilon_1}^{\epsilon_2} \frac{\partial Q}{\partial \epsilon} A dp_1 \dots dq_s = \\ &= - \int_{\epsilon_1}^{\epsilon_2} \frac{\partial Q}{\partial \epsilon} \overline{A} e^{\epsilon/\alpha} d\epsilon = \int_{\epsilon_1}^{\epsilon_2} Q \left(\frac{\partial \overline{A}}{\partial \epsilon} e^{\epsilon/\alpha} + \overline{A} \frac{\partial e^{\epsilon/\alpha}}{\partial \epsilon} \right) d\epsilon. \end{aligned}$$

The transformation on the second line follows directly from the signification of \overline{A} ,

The last expression is obtained by integration in parts. The density ρ being zero for the limits, we may neglect the fact that ϵ_1 and ϵ_2 can depend on α . We therefore obtain

$$\int_{\epsilon_1}^{\epsilon_2} Q \left(\frac{\partial \overline{A}}{\partial \epsilon} + \overline{A} \frac{\partial e^{\epsilon/\alpha}}{\partial \epsilon} - \overline{A} \frac{\partial e^{\epsilon/\alpha}}{\partial \alpha} \right) e^{\epsilon/\alpha} d\epsilon = 0.$$

Now ρ being positive and $e^{\epsilon/\alpha}$ differing from 0, we have

$$\frac{\partial \overline{A}}{\partial \epsilon} + \overline{A} \frac{\partial e^{\epsilon/\alpha}}{\partial \epsilon} - \overline{A} \frac{\partial e^{\epsilon/\alpha}}{\partial \alpha} = 0.$$

The values ϵ_1 and ϵ_2 can be taken as near to each other as we like, therefore

culate $e^{-\gamma} V$ and find for it

$$\frac{2}{s} \varepsilon_{p_0}.$$

It is worth noticing that (comp. GIBBS form. (377) p. 119)

$$e^{-\gamma} V = \frac{2}{s} \overline{\varepsilon_p},$$

where $\overline{\varepsilon_p}$ represents the average kinetic energy in the ensemble.

We therefore have

$$\overline{\varepsilon_p} = \varepsilon_{p_0}.$$

The same relation can be obtained with the help of the given formulae. Using the definition of an average value, we have

$$\begin{aligned} \overline{\varepsilon_{p_2}} &= \frac{\int \varepsilon_p \Omega_\Delta}{\int \Omega_\Delta} = e^{-\gamma} \int \varepsilon_p \Omega_0 = e^{-\gamma} \int \chi(A_1 \dots A_x \dots A_k) \\ &\quad (\varepsilon - \varepsilon_q(A_1 \dots A_x \dots A_k))^{\frac{s}{2}} dA_1 \dots dA_k \dots dA_k. \end{aligned}$$

The last integral can be transformed into

$$C (\varepsilon - \varepsilon_q(A_{1_0} \dots A_{k_0})) \Omega_0 \int e^{\frac{1}{2} \sum_1^k} \left(p_k - \frac{1}{\varepsilon_p^2} \left(\frac{\partial \varepsilon_q}{\partial A_x} \right)^2 - \right.$$

we can always take care that the sign of e^{γ} does not change in the interval.

Now e^{γ} being $\frac{\partial V}{\partial \varepsilon}$ we can transform the last equation to

$$\overline{A} e^{\gamma} = \frac{\partial V}{\partial a} + C;$$

C depending only on a . Taking for ε the least value consistent with the energy, we have to take e^{γ} and $\frac{\partial V}{\partial a}$ equal to zero and we find the same value for C .

To prove (I) we have only to keep in mind that

$$\Delta \log V = \frac{1}{V} \left(\frac{\partial V}{\partial a} \Delta a + \frac{\partial V}{\partial \varepsilon} \Delta \varepsilon \right);$$

remembering that $e^{\gamma} = \frac{dV}{d\varepsilon}$ we find

$$e^{-\gamma} V \Delta \log V = \overline{A} \Delta a + \Delta \varepsilon.$$

Further $e^{-\gamma} V = \frac{2}{s} \overline{\varepsilon_p}$ is equivalent to the temperature; this note shows therefore that (I) is indeed an expression which is comparable with that of thermodynamics.

$$-\frac{1}{\varepsilon_{p_\nu} \partial A_\nu^2} \xi_\nu^2 - \frac{1}{\varepsilon_{p_0} \left(\frac{\partial \varepsilon_\eta}{\partial A_\nu} \right)} \left\{ d\xi_1 \dots d\xi_\nu \dots d\xi_k = C \frac{\varepsilon_{p_0} \Omega_0}{(p_1 \dots p_\nu \dots p_k)^{1/2}}, \right.$$

which can easily be seen if one remembers that the terms which enter besides p_ν in the exponent are very small in comparison to the p_ν terms. Using the given value for e^ε we obtain

$$\overline{\varepsilon}_\varepsilon = (\varepsilon - \varepsilon_\eta (A_{10} \dots A_{\nu 0} \dots A_{k0})) = \varepsilon_{p_0}$$

The mean energy in the ensemble and that of the most frequently occurring systems are equal. The same is true for the force in the maximum system A_0 and the mean force \overline{A} .

The force exercised with respect to a parameter in a system of the energy ε , amounts to $-\frac{\partial \varepsilon}{\partial a}$. We therefore have

$$\overline{A}_\varepsilon = -e^{-\varepsilon} \int \frac{\partial \varepsilon}{\partial a} \Omega_\Delta dA_1 \dots dA_\nu \dots dA_k.$$

The value of $\frac{\partial \varepsilon}{\partial a}$ can be expressed for a system for which $A_\nu = A_{\nu 0} + \xi_\nu$ and for which ξ_ν is not too great by

$$\frac{\partial \varepsilon}{\partial a} = \left(\frac{\partial \varepsilon}{\partial a} \right)_0 + \sum_1^k \left(\frac{\partial^2 \varepsilon}{\partial A_\nu \partial a} \xi_\nu + \frac{1}{2} \frac{\partial^3 \varepsilon}{\partial A_\nu^2 \partial a} \xi_\nu^2 \right) + \sum_{\nu \neq \mu} \frac{\partial^2 \varepsilon}{\partial A_\nu \partial A_\mu} \xi_\nu \xi_\mu.$$

In the integration those systems for which ξ_ν are great have very small influence, we can therefore adopt the given expansion for all values of ξ_ν . Introducing the value of Ω_Δ we easily see that the terms with $\xi_\nu \xi_\mu$ disappear in the integration. We also find:

$$\overline{A}_\varepsilon = - \left(\frac{\partial \varepsilon}{\partial a} \right)_0 - \sum_1^k \frac{2}{p_\nu} \frac{\partial^2 \varepsilon}{\partial A_\nu^2 \partial a} = A_0 - \sum_1^k \frac{2}{p_\nu} \frac{\partial^2 \varepsilon}{\partial A_\nu^2 \partial a}.$$

In general p_ν is large compared with $\frac{\partial^2 \varepsilon}{\partial A_\nu^2 \partial a}$, we therefore have

$$\overline{A}_\varepsilon = A_0.$$

Comparing the values of $\log V$ and $\log \Omega_0$, we see that we have if s is very great

$$\log V = \log \Omega_0 - \frac{1}{2} \sum_1^k \log p_\nu + \text{Const.}$$

The sum $\sum_1^k \log p_\nu$ may be neglected with respect to $\log \Omega_0$ if k is small in comparison with s ; this being the case we have

$$\log V = \log \Omega_0 + \text{Const.}$$

Comparing therefore $\log \Omega_0$ for two ensembles for which the energy differs by $\Delta \varepsilon$ we find:

$$\frac{RT}{N} \Delta \log \Omega_0 = \Delta \varepsilon + A_0 \Delta a. \quad \dots \quad (II)$$

The quantity $\frac{R}{N} \log \Omega_0$ fulfills therefore the same relation as the thermodynamic entropy in the corresponding case. The correspondence however ought no longer to be considered as to be formal, all quantities relating now to real systems, i. e. to the most frequently occurring system of an ensemble, that may be identified with the system in stationary state. The function $\log V$ showing the properties of entropy, the same will be the case for $\log \Omega_0$.

5. I shall define the probability $W(A_1 \dots A_k)$ of a system $(A_1 \dots A_k)$ as the integral of Ω taken for a region whose magnitude is given by observation and which is characterised by the quantities ΔA_r (comp. (1)). We therefore have

$$W(A_1 \dots A_k) = \int_{\frac{\Lambda_1 - \Delta \Lambda_1}{2}}^{\frac{\Lambda_1 + \Delta \Lambda_1}{2}} \dots \int_{\frac{\Lambda_k - \Delta \Lambda_k}{2}}^{\frac{\Lambda_k + \Delta \Lambda_k}{2}} \Omega(A_1 \dots A_k).$$

Substituting in this formula the obtained value of Ω we find

$$W(A_1 \dots A_k) = \Omega_0 \int_{\frac{-\Delta \Lambda_1}{2}}^{\frac{\Delta \Lambda_1}{2}} \dots \int_{\frac{-\Delta \Lambda_k}{2}}^{\frac{\Delta \Lambda_k}{2}} e^{\frac{1}{2} \sum_1^k p_r \tilde{\xi}_r^2} d\tilde{\xi}_1 \dots d\tilde{\xi}_k.$$

The ΔA_r being relatively small quantities compared with the $\tilde{\xi}_r$, we can put this into the form

$$W(A_1 \dots A_k) = \Omega_0 e^{\frac{1}{2} \sum_1^k p_r \tilde{\xi}_r^2} \Delta A_1 \dots \Delta A_k.$$

We shall now prove that $\frac{R}{N} \log W = \eta_\Delta$ shows the properties of the entropy, i. e. that

$$\eta_\Delta = \frac{R}{N} \log W = \frac{R}{N} \log \Omega_0 + \frac{R}{2N} \sum_1^k p_r \tilde{\xi}_r^2 + \text{Const.} \quad \dots \quad (III)$$

answers to the relation.

$$\eta_{\Delta} - \eta_0 = \frac{d\varepsilon + dA}{T} \dots \dots \dots (IV)$$

Putting η_0 in stead of $\frac{R}{N} \log \Omega_0 + \text{Const.}$ we can transform (III) to

$$\eta_{\Delta} = \eta_0 + \frac{R}{2N} \sum_1^k p_x \xi_x^2 \dots \dots \dots (III^a)$$

The energy being the same for the systems under discussion the relation (IV) reduces to

$$\frac{R}{N} d \log W = \frac{dA}{T}$$

or

$$\eta_{\Delta} = \eta_0 + \frac{dA}{T}.$$

In order to prove the correspondence of the entropy η and $\frac{R}{N} \log W$, we have to show that

$$\frac{RT}{2N} \sum p_x \xi_x^2$$

represents the work done if the system is brought in a reversible way from the stationary state to that indicated by Δ .

We can make this transformation reversible in two ways:

In the first place we can imagine an external field of force, applied in such a manner that the deviating state in the old ensemble is the most frequently occurring in the new and change this field of force in such a way that the most frequently occurring state passes continually from the states A through the state $A + \xi$. In the second place we can imagine fictitious forces influencing the parameters A_x in such a way that they allow the non-stationary state to exist. These forces can be changed in such a way, that the said states follow each other as a series of states of equilibrium ¹⁾.

I will follow the second way. In order to find the forces wanted, we can take the quantities ξ_x as parameters and determine the forces Ξ_x working on the stationary system by the relation

$$\dots \dots V \frac{\partial \log V}{\partial \xi_x} = \Xi_x.$$

The region V to be used here is found substituting $A_{x_0} + \xi_x$ for A_x in the value found for $V(\varepsilon_1, \dots, A_{x_0}, \dots)$, $A_{x_0} + \xi_x$ being now the equilibrium value for A_x .

¹⁾ If we have for example a gas the density of which deviates from the normal we can as well by introducing a field of force as by fictitious walls change the non-stationary state into a state of equilibrium.

In this way we find for the force working on ξ_z ,

$$\Xi_z = \frac{RT}{N} \left\{ \left(\frac{\partial \log V}{\partial \mathcal{A}_z} \right) + \left(\frac{\partial^2 \log V}{\partial \mathcal{A}_z^2} \right) \xi_z \right\}.$$

Introducing these forces in the expression for the work we obtain

$$\begin{aligned} dA &= \frac{RT}{N} \sum_1^k \left\{ \int_0^{\xi_z} \left(\frac{\partial \log V}{\partial \mathcal{A}_z} \right) + \left(\frac{\partial^2 \log V}{\partial \mathcal{A}_z^2} \right)_0 \xi_z \right\} d\xi_z \\ &= \frac{RT}{2N} \sum_1^k \xi_z^2 \left(\frac{\partial^2 \log V}{\partial \mathcal{A}_z^2} \right)_0 \end{aligned}$$

the first term being zero as follows from the condition of equilibrium.

It has been shown also that $\frac{R}{N} \log W$ corresponds with entropy for a non-stationary state. For two deviating states from different ensembles the same is true, because it is always possible to pass from one to the other, passing through the stationary states of the ensembles, for which states the formula (II) is true.

6. I will shortly indicate what is obtained if we apply the above formulas to a gas (or liquid), the molecules of which answer to the hypothesis of VAN DER WAALS. Suppose that we have n perfectly rigid and elastic spherical (diameter σ) molecules in a volume V .

Let us divide the volume in k equal elements V_z , which contain n_z molecules. The volume of the extension in configuration can be represented, as I have shown, by

$$\frac{n!}{n_1! n_2! \dots n_k!} \left(\omega \left(\frac{n_z}{V_z} \right) V_z \right)^{n_z},$$

$\omega(n) = \omega \left(\frac{n_z}{V_z} \right)$ being a function of density. For the potential energy we shall use the expression

$$- \frac{\alpha}{2} \sum_1^k \frac{n_z^2}{V_z}.$$

The quantities n_z are joined by the relation

$$\sum_1^k n_z = n.$$

The function χ of (1) has the form

$$n_1^{-n_1} n_2^{-n_2} \dots n_k^{-n_k} (\omega(n_z) V_z)^{n_z}$$

the members n_z being chosen for \mathcal{A}_z .

The condition for the most frequently occurring system is

$$-\log \frac{n_x}{V_x} + \frac{\alpha N}{RT} \frac{n_x}{V_x} + \log \omega(n_x) + n_x \frac{d \log \omega(n_x)}{dn_x} = -t_1.$$

The quantities n_x are normal coordinates, the value of p_x is

$$p_x = -\frac{1}{n_{x_0}} + \frac{2}{V_x} \frac{d \log \omega(n_x)}{dn_x} + \frac{n_x}{V_x} \frac{d^2 \log \omega(n_x)}{dn_x^2} + \frac{\alpha N}{RT} \frac{1}{V_x} - \frac{N}{RT} \frac{1}{\varepsilon_p} \alpha n_x^2.$$

The last term is again small in respect to the others, we therefore find

$$p_x = -\frac{1}{n_x} \frac{d}{dn_x} \left(n_x - n_x^2 \frac{d \log \omega(n_x)}{dn_x} - \frac{2n_x^2 N}{2RT} \right).$$

ε_p being $\frac{3n}{2} RT$.

If we take into consideration that the pressure π of a gas (comp. my dissertation p. 125) is expressed by

$$\pi = \frac{RT}{N} \left(n - n^2 \frac{d \log \omega(n)}{dn} - \frac{\alpha n^2}{RT} \right),$$

we can put p_x in the form

$$p_x = -\frac{1}{n_x} \frac{N}{RT} \frac{d\pi(n_x)}{dn_x}.$$

The expression $\log V$ can easily be used to calculate the pressure.

7. The mean value of $(A_x - A_{x_0})^2$ i. e. of ξ_x^2 , can easily be calculated. One finds for it

$$\overline{\xi_x^2} = \frac{1}{p_x},$$

or $p_x \xi_x^2 = 1$. We can apply this formula to calculate the mean work necessary to bring the system from the normal into the deviating state, we obtain for it

$$\overline{dA} = k \frac{RT}{2N}.$$

For each quantity A_x this mean work amounts to $\frac{RT}{2N}$ i. e. the mean work is equal to the energy pro degree of freedom.

The result has also been obtained by EINSTEIN. Indeed it can be shown that for our case the definition which EINSTEIN has given and the definition used are identical, if only it may be supposed that the path of the representing point of the system fills the space $\varepsilon = \text{const.}$ everywhere dense. EINSTEIN defines the probability of a state $A_1 \dots A_x \dots A_k$ as the fraction of a very long time T for which the

system is in the said state. I have shown¹⁾ that the probability in a time ensemble can be expressed by

$$C \frac{ds}{V},$$

ds being an element of the path of the system and V being the velocity of the representing point on its path. The quantity C is given by $\int \frac{ds}{V}$ integrated along the whole path.

The probability defined by EINSTEIN now can be expressed by

$$C \int \frac{ds}{V},$$

where the integration covers all those elements for which the values of \mathcal{A}_k have the given magnitude. If the hypothesis of EINSTEIN may be used the value of this integral can be expressed by the part of the space $\varepsilon = C$ which is the limit of $d\varepsilon \Omega(\mathcal{A}_1 \dots \mathcal{A}_k \dots \mathcal{A}_l) \Delta \mathcal{A}_k$ if $d\varepsilon$ approaches zero, and the space has been filled in such a way with systems, that $\varrho d\varepsilon$ has a finite value if $d\varepsilon$ approaches zero.

For by EINSTEIN'S hypothesis all the points for which \mathcal{A}_k is between \mathcal{A}_k and $\mathcal{A}_k + \Delta \mathcal{A}_k$ are on the path of the representing point, and the given expression represents the part of the space for which the \mathcal{A}_k 's have the given values. The integral $\int \frac{ds}{V}$ taken over the elements indicated above and $\Omega(\mathcal{A}_k)$ are identical.

Using these conditions limiting, however, the generality, we have proved that the probability as defined by EINSTEIN is proportional to the entropy.

Groningen, Sept. 1911.

Physics. — *Remarks on the relation of the method of GIBBS for the determination of the equation of state with that of the virial and the mean free path.* By DR. L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of December 30, 1911).

In determining the equation of state by means of statistical mechanics it is useful to introduce a function ω , which for a system of n molecules of diameter σ is given by an integral

$$\int dx_1 \dots dz_n = \omega^n V^n. \dots \dots \dots (1)$$

¹⁾ Comp these Proc. of Jan. 28 1910, p. 804.

The coordinates of the centres $x_1 \dots z_n$ can be situated in all the parts of a space V^n where

$$(x_x - x_i)^2 + (y_x - y_i)^2 + (z_x - z_i)^2 > \sigma^2. \dots (1a)$$

In my dissertation I have shown that with the help of this function the pressure of the gas can be expressed by the form

$$p = rT \left(n - n^2 \frac{d \log \omega}{dn} \right) - \alpha n^2. \dots (2)$$

In this formula n represents the number of molecules pro unity of volume. The function ω depends on n and σ . From a simple dimensional consideration can be shown that ω must be a function of $n\sigma^3$. In my dissertation I have calculated the three first terms of a serial expansion of this function.

It is worth mentioning that the same function plays a role when p is calculated by the method of virial and that it appears too in the theory of mean free path. For the total surface of the part of the spheres free for a collision, the quantity which CLAUDIUS represents by S can be expressed as a function of ω . Prof. LORENTZ fixed my attention on the fact that such a relation exists. The equation of state calculated by the method of virial takes the form

$$\frac{3}{2}pv - \frac{1}{4}nr T \sigma \frac{1}{v\omega} e^{-n \frac{d \log \omega}{dn}} S = \frac{3}{2}nr T; \dots (3)^1$$

the virial of attracting forces being neglected. In order that (2), where α must be put 0, and (3) be identical it is necessary that

$$S = -6 \frac{V}{\sigma} n \frac{d\omega}{dn} e^{n \frac{d \log \omega}{dn}}.$$

It is easy to prove this relation.

I shall represent the integral (1) by $\chi(n, \sigma)$. In differentiating with respect to σ we find

$$\frac{\partial \chi(n, \sigma)}{\partial \sigma} = n V^n \omega^{n-1} \frac{\partial \omega}{\partial \sigma}$$

and taking into account that ω is a function of $n\sigma^3$, we obtain

$$\frac{\partial \chi(n, \sigma)}{\partial \sigma} = n \chi(n, \sigma) \frac{3}{\sigma} n \frac{d \log \omega}{dn} \dots (4)$$

The differential coefficient can also be expressed with the help of the free surface S . We shall determine the change of $\chi(n, \sigma)$ if σ increases with $d\sigma$. In order to determine the variation of $\chi(n, \sigma)$,

¹⁾ For the deduction of this formula compare the translation of my dissertation which will shortly appear in the Arch. Néerl.

which is caused by an infinitesimal change $\delta\sigma$ we can presume that either only the diameter of the first molecule or that of the second, or the third etc. increases with $\delta\sigma$.

The variation of $\chi(n, \sigma)$ then is given by the sum of the variations of this quantity in those several cases, we therefore find $\delta\chi(n, \sigma)$ by multiplying the variation in one of those cases by n . Supposing that only the n^{th} molecule undergoes the variation, then the radii of the spheres described round the centres of the $n-1$ others must be increased by $\frac{1}{2} \delta\sigma$, and the variation — of χ amounts to

$$-\frac{1}{2} S\delta\sigma$$

and $\chi(n-1, \sigma)$ remaining the same, the variation in question comes to

$$-\frac{1}{2} \chi(n-1, \sigma) S\delta\sigma.$$

Hence

$$\delta\chi(n, \sigma) = -\frac{1}{2} n \chi(n-1, \sigma) S\delta\sigma$$

and

$$\frac{\delta\chi(n, \sigma)}{\delta\sigma} = -\frac{n}{2} \chi(n-1, \sigma) S \dots \dots \dots (5)$$

The combination of (4) and (5) gives

$$S = -\frac{\chi(n, \sigma)}{\chi(n-1, \sigma)} \frac{6}{\sigma} n \frac{d \log \omega}{dn}.$$

Taking into account that, as I have shown in my dissertation,

$$\frac{\chi(n, \sigma)}{\chi(n-1, \sigma)} = g(n) = V\omega e^{n \frac{d \log \omega}{dn}}$$

we find

$$S = -\frac{6}{\sigma} n \frac{d \log \omega}{dn} g(n) = -\frac{6}{\sigma} V n \frac{d\omega}{d n} e^{n \frac{d \log \omega}{dn}} \dots \dots (6)$$

which agrees with the formula mentioned above.

CLAUSIUS¹⁾ has shown that the mean free path is given by

$$l = \frac{4W}{S\sqrt{2}} = \frac{4g(n)}{S\sqrt{2}} \dots \dots \dots (7)$$

The quantity W is the space free for the situation of the centre

¹⁾ R. CLAUSIUS. Die kinetische Theorie der Gase p. 46—83. This formula can also be obtained by means of statistical mechanics.

of a molecule in a system of n molecules, i. e. the quantity which we have represented by $g(n)$.

The mean free path l_0 for the case that the intersection of the spheres (of repulsion) is neglected and where $g(n)$ is made equal to V , amounts to

$$l_0 = \frac{V}{n\pi\sigma^2} \cdot 2 = \frac{1}{n\pi\sigma^2} \cdot 2.$$

Introducing in (7) the value of $g(n)$ which follows from (6), and using the abbreviation l_0 , one finds

$$l = \left(-\frac{2}{3} \pi\sigma^3 \right) l_0 \frac{1}{\frac{d \log \omega}{dn}} \dots \dots \dots (8)$$

These expressions can be used to put the equation of state in a new form. Substituting for l the value following from (8) we find

$$p = rTn \left(1 + \frac{2}{3} \pi\sigma^3 n \frac{l_0}{l} \right) - an^2.$$

If we have to do with a gramme-molecule of the gas we have

$$p + an^2 = \frac{RT}{V} \left(1 + \frac{b}{V} \frac{l_0}{l} \right).$$

The quantity b is the known constant of VAN DER WAALS, aN^2 is equal to his a , N being the number of molecules for the gramme-molecule. Prof. KOHNSTAMM¹⁾ has deduced a similar relation, however without indicating rigorously the relation, existing between the free volume and the free surface. The fact that there exists such an intimate relation between these quantities shows that each further approximation of one of them allows to find the following approximation for the other. At the same time it is shown that the method of statistical mechanics gives the most simple calculation, as all is reduced to the determination of one function ω and to the differentiation of this function.

Groningen, Dec. 1911.

Meteorology. — “*The relation between changes of the weather and local phenomena*”. By Dr. J. P. VAN DER STOK and P. H. GALLÉ.

(Communicated in the meeting of Januari 27, 1912).

1. Every one whose daily task it is to formulate expectations concerning the coming weather, knows that the theory of cyclones, based upon the conditions for *steady motion*, is of little use.

What he wants to know is what happens, or at least what may happen, when the situation alters with the time: whether the centre

¹⁾ KOHNSTAMM. These Proc. VI, p. 787 and p. 794.

of the cyclone is filling up or receding, deepening or approaching or, also, whether the centre moves along the arc of a circle, distance and intensity remaining the same.

Obviously if, in the latter case, the velocity of rotation is of the same order as that of the earth's rotation, the effect of the latter may be lessened so that the angle between gradient of pressure and winddirection becomes smaller or is reduced to zero, or, also, that this effect is increased thus causing an angle of deviation greater than the normal value.

On the other hand a disturbance of the equilibrium between the three concurring forces: viz. pressure gradient, influence of the earth's rotation and friction caused by a decrease of the gradient force must become perceptible as an apparent increase of the effect of the earth's rotation and friction, from which results an angle of deviation and a proportion between windvelocity and gradient force greater than in the case of normal adjustment.

When these influences are such that their effect becomes clearly visible in the comparatively rough observations (estimation of windforce according to the BEAUFORT scale and of direction in 16 points) as inscribed in a weather chart, for rates of variation corresponding to actually occurring velocities of variation, then these effects would afford a means of drawing conclusions concerning the coming weather based on deviations from normal values, i. e. on purely local phenomena: the normal condition being defined as what occurs when the motion is steady.

2. In order to investigate in how far these deviations satisfy the conditions for practical use, let us consider the simple case of currents moving in horizontal planes, i. e. when the isobars are straight lines or, also, curvilinear but then at a considerable distance from the centre of curvature where the vertical motion is nil.

Choosing the place of observation as origin of polar coordinates, and assuming that, at that distance from the centre, the terms:

$$v \frac{\partial v}{\partial r} \text{ and } v \frac{\partial u}{\partial r}$$

may be neglected, the equations of motion become:

$$\begin{aligned} \frac{\partial v}{\partial t} - \frac{u^2}{r} + nau + lv &= -\frac{1}{\rho} \frac{\partial p}{\partial r} \\ \frac{\partial u}{\partial t} + \frac{uv}{r} - nav + lu &= -\frac{1}{\rho} \frac{\partial p}{r \partial \theta} \end{aligned}$$

If now the problem is restricted to the question what happens at

the point of observation ($r = 0$), all terms containing the angular velocity :

$$u = r \frac{\partial \theta}{\partial t}$$

vanish, except :

$$\frac{uv}{r} = v \frac{\partial \theta}{\partial t}$$

and the equations assume the simple form :

$$\begin{aligned} \frac{\partial v}{\partial t} + knv &= -\frac{1}{\rho} \frac{\partial p}{\partial r} \dots \dots \dots (1) \\ r \left(\frac{\partial \theta}{\partial t} - n u \right) &= -\frac{\partial p}{r \rho \partial \theta} \end{aligned}$$

where v indicates the windvelocity,

θ the direction in which the air moves, counting from North to East,

$a = 2 \sin q$, $q =$ geogr. lat. of the place.

n the angular velocity of the earth $= 7.29 \times 10^{-5}$,

$kn = l$ the frictioncoefficient,

p the atmospheric pressure,

ρ the density of the air.

If we wish to know the coming variation for a short time only, we may choose an arbitrary function for the gradient such that the integration is easily effected.

We assume that the variation in intensity of the gradient can be represented by the function

$$e^{\eta t}$$

and that the variation in direction can be represented by a uniform rotation with an angular velocity sn counting clockwise.

Then, if β denotes the angle between the gradient and the North direction at the time $t = 0$, the equations (1) become :

$$\begin{aligned} \frac{\partial v}{\partial t} + knv &= He^{\eta t} \cos(\theta - \beta - snt) \\ v \left(an - \frac{\partial \theta}{\partial t} \right) &= He^{\eta t} \sin(\theta - \beta - snt) \dots \dots (2) \end{aligned}$$

They are satisfied by the values :

$$v = \frac{He^{\eta t}}{n \sqrt{(k + \eta)^2 + (a - s)^2}}, \quad \theta = \theta_0 + snt$$

from which follows for the angle of deviation :

$$\text{tang } (\theta_0 - \beta) = \text{tang } \alpha = \frac{a - \varepsilon}{k + q} \dots \dots \dots (3)$$

so that we may also write :

$$v = \frac{H}{n} \frac{e^{mt}}{(k + q)} \cos \alpha = \frac{H}{n} \frac{e^{mt}}{(a - s)} \sin \alpha \dots \dots \dots (4)$$

The other part of the complete solution, derived from (2) by equalizing to zero the terms on the right hand side of (Δ), can be

TABLE I. Angle of deviation, Departures from normal values.

$q =$	Wind backing				$s =$ 0	Wind veering			
	$-a$	$-0.75a$	$-0.5a$	$-0.25a$		$+0.25a$	$+0.5a$	$+0.75a$	$+a$
-2	50°	52°	55°	59°	64°	72°	84°	101°	122°
-1.5	40	42	44	46	50	55	64	84	122
-1	32	32	32	32	32	32	32	32	—
-0.5	24	22	20	18	14	9	0	20	58
0	14	12	9	5	0	8	20	37	58
+0.5	7	3	0	5	12	20	30	43	58
+1	0	4	8	13	20	27	36	47	58
+1.5	6	10	15	20	26	33	40	49	58
+2	12	15	20	25	30	36	43	51	58

TABLE II. Proportion of windvelocity to normal value.

$q =$	Wind backing				$s =$ 0	Wind veering			
	$-a$	$-0.75a$	$-0.5a$	$-0.25a$		$+0.25a$	$+0.5a$	$+0.75a$	$+a$
-2	0.6	0.6	0.7	0.8	1	1.2	1.5	1.7	1.9
-1.5	0.6	0.7	0.8	0.9	1.1	1.5	2.0	2.9	3.8
-1	0.6	0.7	0.8	0.9	1.2	1.6	2.4	4.7	—
-0.5	0.6	0.7	0.8	0.9	1.1	1.5	2.0	2.9	3.8
0	0.6	0.6	0.7	0.8	1.0	1.2	1.5	1.7	1.9
+0.5	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3
+1	0.5	0.6	0.6	0.7	0.7	0.8	0.9	0.9	1.0
+1.5	0.5	0.5	0.5	0.6	0.6	0.7	0.7	0.7	0.8
+2	0.4	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.6

left out of consideration. Its meaning would be a superposed wind of arbitrary velocity :

$$C_r = k v,$$

gradually waning under the influence of friction and rotating with an angular velocity an .

If we define as normal values :

$$\tan \alpha_0 = \frac{a}{k} \text{ and } V_0 = \frac{H \cos \alpha_0}{n} = \frac{H \sin \alpha_0}{n} = \frac{H}{n} \frac{1}{\sqrt{k^2 + a^2}}$$

then

$$\frac{v}{v_0} = \frac{k \cos \alpha}{(k+q) \cos \alpha_0} = \frac{a \sin \alpha}{(a-s) \sin \alpha_0} = \frac{\sqrt{k^2 + a^2}}{\sqrt{(k+q)^2 + (a-s)^2}}$$

Tables I and II exhibit the quantities $\alpha - \alpha_0$ and v/v_0 calculated for different values assigned to q and s , for a latitude of 52° N and the value $k = 1$, corresponding with a normal angle of variation :

$$\alpha_0 = 58^\circ.$$

Positive differences and proportions greater than unity are printed in heavy type, negative differences and proportions smaller than unity in italic type.

The values given to q and s in the tables correspond with the following rates of variation :

	Time necessary for in- or decrease with 50% in hours.			Rate of rotation per hour.
$q = -2$	1.32	$s = -a$		— 23.7
— 1.5	1.76	— 0.75a		— 17.8
— 1	2.64	0.5a		— 11.9
— 0.5	5.28	— 0.25a		— 5.9
0	—	0		
0.5	3.09	0.25a		5.9
1	1.55	0.50a		11.9
1.5	1.03	0.75a		17.8
2	0.77	a		23.7

The results given in the tables lead to the following conclusions :

1. An angle of deviation greater than the normal value mostly indicates a decrease of the gradient force; too small a deviation an increase of this force; when the direction of the gradient is veering the differences are considerably larger than when it is backing.

2. A wind velocity greater than the normal value generally indicates a decreasing gradient and veering wind, and is often associated with abnormally large angles of deviation.

A deficient windvelocity, together with too great an angle of deviation is an indication of an abating and backing gradient.

A windvelocity smaller than the normal value combined with too small an angle of deviation always indicates an increase of the gradient; when the wind is backing, the negative deviations are smaller than with a veering wind; the latter case only obtains when the rate of variation is very great.

In applying these rules two cases can be taken into consideration; firstly when the isobars are straight lines; then an increase or weakening of the gradient is not necessarily associated with a rising or falling barometer at the place of observation and its variation may merely indicate a crowding or dispersing of the isobars in the pressure field.

When, secondly, wind and angle of deviation are evidently under the influence of a distant atmospheric depression, then an increase of the gradient may denote a deepening of the depression, the distance remaining the same, as well as an approach of the centre, for according to the theory of cyclones, the pressure gradient in the outer part of the cyclonic area varies inversely with the distance from the centre.

The relation of windvelocity and angle of deviation to their normal values at places situated around the centre will then enable us to discriminate which of the two cases obtains.

A decrease of the gradient, i.e. a negative value of q , therefore, in a cyclonic field, is an indication of a rising, an increasing gradient of a falling barometer.

Too strong a wind, mostly associated with too large an angle of deviation is an indication of an increasing distance of the centre of depression accompanied by a change in azimuth in the clockwise direction, and a rising barometer from right to left when standing with the back to the wind.

These rules for weather forecasting (or rules otherwise formulated and based on the data of the tables) correspond for the greater part with the rules advocated in several publications by Mr. GUILBERT.¹

In some respects they are more complete in so far that the case of rectilinear isobars has been taken into consideration, when a rise or fall of the barometer need not occur, and also because here the influence of a rotation has been pointed out. In West-Europe where the weather depends upon the motion of centra of depression, often

¹) G. GUILBERT. Nouvelle méthode de prévision du temps, avec une préface par B. BRUNHES, Paris, Gauthiers-Villars, 1909.

moving with great velocity in the Norwegian sea or in the Channel, this factor is certainly of some importance.

The weather rules, as found by GUILBERT in an empirical manner, may therefore be explained on rational mechanical principles and can supply valuable insights and indications, provided it is kept in mind that they are applicable only to places situated at a considerable distance from the centre of depression and when the rate of variation is rapid.

Only then the deviations from normal values will be sufficiently evident, but in such cases they are of considerable value as they enable us to ascertain and timely signalize rapidly evolving variations which otherwise would perhaps have remained unnoticed.

In the neighbourhood of the centre the rules fail as well as the formulæ given above because there ascending currents play an important part, and a slackening of wind and gradient may mean, not an increasing, but a decreasing distance from the centre, as in this area the gradient varies directly with the distance.

In practice the use of the simple rules is hampered by many difficulties; the conditions are rarely so simple as implied in the premises on which the computations in the tables are based and even the simple case of two gradients, one of which of constant magnitude and direction and the second variable (e. g. a constant centre of high pressure and a centre of depression moving with respect to the first, which often occurs) would lead to formulæ too complicated for practical use. Moreover it is difficult to estimate at first sight the direction and magnitude of the gradient, the estimation of wind force and direction is a source of uncertainty and it is difficult to ascertain what values are to be considered as normal.

3. Although the fact that GUILBERT has found these indications in a purely empirical manner is a proof of their usefulness in practice, only a systematical application extended over a considerable time can lead to a reliable estimate of their merits, and such experiments will be valuable only when the prognostics are subjected to a severe and systematic criticism.

Even then it will be difficult to point out what gain the application of GUILBERT'S rules has afforded because, in formulating the expectation, now as before, various factors must be taken into account which bear no relation to these rules.

In our experiment, some results of which are communicated in this paper, the prognostics were criticized by dividing the area of the weather chart into nine compartments by means of two sets of

parallel lines perpendicular to each other and by noticing in each compartment what change in pressure was expected according to the observed local symptoms.

This was done by the signs + and —, with sometimes the addition of the words “much” or “little”; also the symbols ± and ∓ were used in order to indicate that the expected variations were small (less than 2 or 3 mm.) in positive or negative direction. By drawing

TABLE III. Frequencies of percentages of success.

" 0	May 1910		June		October	November	December	January 1911		February	March	April	November	Total
	24 ^u	12 ^u	24 ^u	12 ^u				January	February					
0/4	—	—	—	—	—	—	—	—	—	—	—	—	—	—
5/9	—	—	—	—	—	—	—	—	—	—	—	—	—	—
10/14	—	—	—	—	1	—	—	—	—	—	—	—	—	1
15/19	—	—	—	—	—	—	—	—	—	—	—	—	—	—
20/24	—	—	—	—	—	—	—	1	—	—	—	—	—	1
25/29	—	—	—	—	—	—	—	—	—	—	—	—	—	—
30/34	—	—	1	—	—	—	—	—	1	—	—	—	—	2
35/39	—	—	—	—	—	—	—	—	1	—	—	—	1	2
40/44	—	—	1	—	1	1	—	1	—	—	—	—	—	4
45/49	—	1	—	1	—	—	—	—	1	1	—	—	—	2
50/54	5	—	—	—	1	2	3	1	1	—	—	—	—	13
55/59	3	3	3	2	5	2	—	2	—	1	—	—	—	16
60/64	6	4	1	1	1	2	2	4	1	3	1	3	—	24
65/69	3	9	3	1	3	2	3	2	1	3	1	3	—	24
70/74	4	7	5	5	1	7	3	2	2	3	1	1	—	30
75/79	3	3	7	8	6	4	3	4	4	5	2	4	—	42
80/84	2	1	7	2	4	4	3	5	5	6	1	4	—	41
85/89	1	1	—	5	3	4	2	2	3	—	3	5	—	23
90/94	2	1	2	3	4	1	—	2	2	—	—	5	—	18
95/100	1	—	—	2	1	—	—	—	1	1	—	2	—	6
Total	30	30	30	30	31	29	19	27	23	23	9	28	—	249
Mean	68.4	69.1	71.9	77.6	72.8	71.5	71.2	71.3	74.3	73.5	78.4	79.1	—	72.4

imaginary diagonals it was often possible to form a clearer image of the future situation.

The experiments were made during the months of May to June, October to December 1910, January to April and November 1911. Besides these weatherforecasts also the desirability of hoisting storm-signals was noted.

With a view of obtaining numerical values for the fulfilment of the expectation the chart was compared with that of the next day and the following numbers were given separately for each compartment:

- 4 for complete success
- 3 „ nearly complete success
- 2 „ half success
- 1 „ variation in the right direction, but too small
- 0 „ no success.

During the months of May and June a critique was made up as well for a period of 12 as of 24 hours afterwards. The percentage of success for the total area has been calculated from the frequencies given in the following table, from which appears also on how many days in each month a forecast was made up.

It appears from this table that in May and June after 12 hours the percentage of success was somewhat higher than after 24 hours, as might have been expected. As the greater part of disturbances come from the West and no stations are situated on the left side of the westerly compartments (I *a, b, c*), it is evident that there and in the south-eastern compartment (III*c*) the percentage of success must be smallest; this conclusion is confirmed by the following summary :

TABLE IV.

	I	II	III
a	65%	75%	77%
b	70%	79%	76%
c	70%	76%	69%

The results of this experiment, separately for the forecasting of wind, temperature and rainfall and concerning the relation between gradient and windforce will be communicated in extenso in the publications of the R. Meteor. Institute.

In making up these prognostics, founded on the observations inscribed in a weather chart, it is, of course, impossible to apply the GULBERT rules without taking into account also the manifold other indications suggested by the synoptical image.

A better idea of the profit to be gained by the application of these symptomatic indications might be gathered by determining the percentage of success if a forecast were made exclusively on the base of local wind observations and the knowledge of the gradient for *one* given station, *without* consultation of a weather chart.

This has been done for the station Swinemunde and the years 1909 and 1910.

Magnitude and direction of the gradient were computed from the barometric heights at the stations Hamburg, Whisby and Breslau, forming a triangle in the centre of which Swinemunde is nearly situated.

The method of criticizing the degree of success was about the same as applied to the area of a weatherchart; the result was an average success of 65.4%, which may be considered as a pretty fair result of the method without the application of other means.

As to the signalling of storms, the result was favourable as might have been expected especially for rapidly advancing disturbances, a number of which could be foreseen considerably earlier than if the relative windforce and angles of deviation were not taken into account.

Meteorology. — “*On the angle of deviation between gradient of atmospheric pressure and air motion.*” By J. P. VAN DER STOK.

(Communicated in the meeting of January 27, 1912).

In a previous communication¹⁾ I have shown how the average friction coefficient, and therefore also the average angle of deviation between gradient of pressure and windvelocity, can be derived from the semidiurnal variation of barometric pressure and wind.

As a result of this inquiry for two sets of observations made at de Biit and on board the lightvessel Terschellingerbank, it was thus found that the angle of deviation computed according to the well known expression for steady motion

$$\tan \alpha = \frac{2 n \sin \varphi}{l} = \frac{a}{k}$$

$$a = 2 \sin \varphi, \quad l = \lambda n$$

$$\varphi = \text{geogr. latitude}$$

$$n = \text{angular velocity of the earth's rotation}$$

$$l = \text{frictioncoefficient}$$

in winter and autumn was considerably smaller than in spring and summer.

¹⁾ These proceedings: Meeting of May 27, 1911.

If we assume that this result is not due to disturbances in the expressions for the semidiurnal variation or to shortcomings of the theoretical reasoning, if further we take into account that (at least in our country) the angle of deviation strongly depends on the direction of wind and gradient, then two explanations may be examined.

Firstly it is possible that the specific deviation (i. e. the deviation as considered separately for each direction) actually remains the same during the whole year, but that the variability of the mean deviation must be ascribed to the distribution of the wind directions in the different seasons.

The fact e. g. that in our country during spring northerly winds prevail and that for this direction the deviation is unusually large, must cause a greater angle of deviation in spring than for the whole year.

Secondly it is possible that the friction coefficient varies with the temperature and possibly also with the turbulence of the air; in this case the specific deviation would be a variable quantity in different seasons.

With a view of putting these results of a theoretical treatment to the test of direct observation, we can make use of the values of the pressure gradient as computed for the hours 7^h and 9^h30^m a.m. of each day from the barometric height at the five Dutch stations which, since March 1904, are printed in the daily weathercharts.

Its mean direction, holding good for de Bilt situated in the centre, is expressed in 16 points and therefore has an uncertainty of $\pm 11^{\circ}.25$: in the original computations these directions are, of course, calculated to a much higher degree of precision, but a simple consideration of the weather charts shows clearly that angles of deviation of the most different values are associated with gradients equal as regards magnitude and direction; the use of more accurate values would, therefore, be of little use and it is only from a great number of observations that reliable average values can be derived.

After some trials it likewise did not appear desirable to consider those cases only in which the gradient exceeds a given minimum, as frequently the value of a small gradient is evidently accurate and, conversely, for large gradients the complicated general situation and irregular curvatures of the isobars give rise to unreliable results.

Therefore, in the following investigation, all observations of the angle of deviation computed during the period March 1904 to December 1910 for the five stations are used, without considering the magnitude of the gradient, with the exception only of those rare

cases in which the values were greater than 135° or smaller than 0° .

Further it is assumed that the same direction of gradient, holding good for de Bilt, may also be used for the other stations because the radius of curvature of the isobars generally is large in comparison with the distance between the different stations.

In table I the frequencies of the angular values corresponding with different directions of the gradient are given for the central station de Bilt.

TABLE I. Frequencies of angle of deviation, de Bilt, 1904—1910.

Direction gradient	0°	$22^\circ.5$	45°	$67^\circ.5$	90°	$112^\circ.5$	135°	Total
N	20	98	202	165	67	17	9	578
NNE	19	60	105	158	101	17	9	469
NE	10	14	47	123	111	46	9	360
ENE	2	4	24	73	73	38	4	218
E	—	6	16	46	60	23	9	160
ESE	2	3	21	34	25	13	3	101
SE	1	7	14	55	44	9	1	131
SSE	—	6	28	84	27	13	3	161
S	2	13	70	70	39	7	6	207
SSW	3	17	58	73	39	16	7	213
SW	4	13	39	62	51	14	3	186
WSW	2	10	29	68	30	14	1	154
W	1	5	75	85	34	4	2	206
WNW	4	22	74	147	23	4	—	274
NW	8	28	179	125	31	5	1	377
NNW	9	80	246	195	41	7	1	579
Total	87	386	1227	1563	796	247	68	4374

It appears from this table that the spreading out of the values is considerable so that the simple relation between angle of deviation, earth's rotation and friction, as expressed in the foregoing formula, is but rarely realized. In table II the values of the angle of deviation are given as computed from frequency tables of the same kind as table I for the five stations and 16 gradient directions.

TABLE II. Average angle of deviation for different directions of gradient.

Direction Gradient	Groningen	Helder	de Bilt	Flushing	Maestricht
N	62° .9	68° .6	54° .7	63° .0	50° .8
NNE	69 .4	81 .1	61 .7	64 .9	49 .9*
NE	82 .4	93 .1	75 .3	81 .0	54 .8
ENE	81 .4	94 .5	80 .2	94 .0	70 .3
E	82 .7	93 .7	82 .3	92 .3	70 .9
ESE	81 .9	88 .4	73 .5	86 .4	71 .2
SE	74 .0	84 .0	73 .3	85 .0	67 .9
SSE	76 .8	78 .1	70 .6	71 .0	59 .0
S	79 .0	77 .1	64 .1*	69 .4	57 .1
SSW	75 .4	70 .5	66 .5	62 .2	52 .8*
SW	72 .8	70 .4	68 .8	61 .0*	55 .3
WSW	64 .1	65 .3*	68 .4	65 .7	69 .1
W	64 .0*	68 .5	63 .1	65 .4	72 .8
WNW	68 .1	70 .9	59 .4	70 .2	68 .8
NW	64 .2	66 .6	54 .7	70 .5	62 .5
NNW	60 .7*	65 .9*	52 .9*	61 .8	52 .6
Mean	67° .9	77° .3	66° .9	72° .7	61° .6

For the first four stations the principal maximum is situated between the directions NE and E of the gradient; the principal minimum is spread out over a larger area but mostly associated with N and NNW directions; secondary maxima and minima occur more or less distinctly at all stations. Maestricht shows a considerable divergence from the other stations as there two equivalent well defined maxima occur for the directions ESE and W, and two minima for the NNE and SSW directions.

The differences between the extreme values amount to: for Groningen 22°, Maestricht 23°, Helder and de Bilt 29°, for Flushing 33°.

As has been pointed out in another communication, these large differences can be ascribed to the fact that in our climate steady motions are of comparatively rare occurrence and that then the simple formula is not generally applicable

A westerly gradient often indicates an approaching depression

associated with an increase of gradient; an easterly gradient intimates an increase of distance from the centre with a filling up and extinction of the depression.

In the first case the tangent of the angle of deviation will be larger, in the second case smaller than the normal value owing to an apparent increase or decrease of the friction coefficient.

When northerly or southerly gradients obtain, the eastward movement of the centre of depression is associated with a rotation of the gradient with constant magnitude and the effect of this rotation must be equivalent to an apparent decrease or increase of the earth's deviating force; this explains the occurrence of two maxima and minima. The distribution of the different values for Maestricht finds a ready explanation in the fact that this station is situated in the river basin of the Maes where the friction experienced by N and S winds must be considerably less than for E and W winds.

In table III, showing the values of the angle of deviation cor-

TABLE III. Average angle of deviation for different wind directions.

Direction Wind	Groningen	Helder	de Bilt	Flushing	Maestricht	Magnetic 14° West	
						Helder	Flushing
N	82°.4	93°.8	77°.4	92°.5	71°.2	94°.4	93°.6
NNE	77.5	88.0	73.0	86.2	68.0	92.2	90.1
NE	75.7	81.9	71.0	76.8	58.2	85.9	85.6
ENE	75.6	77.5	64.4*	69.6	54.6	79.8	70.6
E	76.9	71.7	66.6	61.9	54.3*	77.2	66.3
ESE	73.5	70.4	68.7	62.1	59.7	70.5	61.4
SE	64.1*	65.6*	68.4	65.7	63.4	68.8	63.6
SSE	64.5	68.4	62.2	65.7	72.0	66.6	65.6
S	68.0	70.6	57.3	69.7	69.1	69.2	67.3
SSW	63.6	66.6	53.6*	70.5	58.6	70.6	70.3
SW	61.1*	66.1*	54.0	62.1*	51.9	66.3	67.0
WSW	62.6	68.5	57.7	63.3	50.1*	67.0	62.5
W	68.6	76.2	63.9	66.0	53.1	71.2	63.1
WNW	76.9	84.2	72.4	75.4	60.0	79.3	73.3
NW	82.0	92.0	77.9	84.3	69.2	87.2	77.5
NNW	81.9	94.2	81.0	92.5	70.8	93.4	87.4

responding to different wind-directions, this effect is more clearly visible than in table II; it is derived from the latter by linear interpolation.

This proves that the variability of the gradient in direction and magnitude may be regarded as the principal cause of the spreading out of the angles of deviation, but that local circumstances also play an important part and the friction coefficient kn is certainly not the same for different directions.

When N and NNW winds obtain the path of the air particles mostly traverses a sea surface where friction is small; but this is, to some extent, contradicted by the fact that, if the wind is SW, when it also blows over the sea (although to a smaller degree), a minimum rather than a maximum value of the angle of deviation is observed.

TABLE IV. Values of the angle of deviation, de Bilt.

Frequencies					Angle of deviation				
Direction Gradient	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	
N	486	323	439	378	55°.4	61°.7	57°.8*	50°.2	
NNE	413	298	388	308	61.9	71.2	62.5	56.5	
NE	282	242	305	218	65.3	77.5	70.6	63.5	
ENE	154	199	234	151	75.5	80.1	80.1	75.8	
E	50	147	175	107	82.4	80.8	78.0	78.6	
ESE	35	128	131	98	83.5	76.1	74.4	79.4	
SE	40	145	119	89	74.2	72.9	69.4	74.1	
SSE	77	178	133	111	68.7	70.3	66.3	68.7	
S	121	191	122	147	63.2	70.4	67.1	64.6	
SSW	133	189	96	188	63.3	70.6	66.8	64.1	
SW	121	158	67	207	59.1	73.1	70.8	67.8	
WSW	108	146	69	223	57.9	70.7	70.4	66.8	
W	149	148	99	238	56.0	66.4	67.5	62.8	
WNW	225	205	163	264	59.9	61.2	64.0	54.3	
NW	360	268	274	328	55.3	58.3	60.9	53.0	
NNW	450	323	396	365	54.2*	58.0*	58.6	48.6*	
Total	3204	3288	3210	3420	Mean	64°.7	70°.0	67°.8	64°.3

As might have been expected, the difference between land- and seastations is clearly visible in the general mean values of table II; the most inland station, Maestricht, showing the smallest value viz. 68°, Helder, the most maritime station, the greatest value viz. 77°.

When we calculate the angle of deviation for different gradient directions and different seasons (Table IV), the frequency of occurrence becomes often too small, principally for E—S directions and in winter. Therefore, as has been indicated in Table IV, all frequencies have been taken together for each set of three subsequent directions, so that the computed average values bear relation to an angular area of 67,5 and not of 22,5 as those of the foregoing tables.

Even then the number of observations in the SE quadrant is hardly sufficient, but still the average values run in a continuous manner.

TABLE V. Values of the angle of deviation.

Direction Gradient	Groningen				Helder			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
N	62°.3	68°.2	70°.7	61° .7	69° .6	68° .9	69° .1	78° .2
NNE	68 .4	74 .7	69 .3	69 .5	79 .1	76 .0	73 .4	90 .2
NE	75 .2	83 .0	72 .9	75 .6	87 .8	86 .1	82 .2	100 .0
ENE	84 .3	88 .0	77 .2	80 .0	94 .7	93 .7	89 .3	98 .9
E	91 .6	88 .4	75 .6	77 .8	98 .6	93 .4	89 .4	96 .4
ESE	92 .9	84 .4	70 .7	80 .3	101 .9	89 .6	84 .1	90 .8
SE	91 .1	80 .1	69 .1	77 .4	98 .0	83 .6	77 .1	80 .3
SSE	88 .8	78 .1	67 .3	78 .5	90 .0	79 .1	72 .8	79 .6
S	80 .1	75 .8	70 .4	81 .9	77 .4	75 .5	68 .8	76 .8
SSW	78 .6	74 .3	69 .5	78 .9	77 .6	71 .4	65 .6	74 .5
SW	69 .9	72 .2	66 .8	73 .0	71 .4	69 .3	59 .0*	70 .8
WSW	64 .8	69 .3	68 .2	66 .1	71 .5	66 .9*	66 .2	68 .1
W	59 .8	69 .1*	74 .5	64 .3	64 .8	69 .4	72 .8	69 .2
WNW	59 .3*	69 .5	74 .7	61 .8	62 .1	72 .1	78 .3	65 .1
NW	59 .5	68 .6	69 .5	59 .1	61 .5*	72 .3	73 .3	64 .4*
NNW	60 .0	66 .6	66 .6*	57 .9*	63 .3	69 .0	69 .8	67 .3
Mean	74° .2	75° .6	70° .8	71° .5	79° .3	77° .3	74° .5	79° .4

In the same manner the angles of deviation for the other four stations have been calculated and are given in tables V and VI, for the sake of brevity without the corresponding frequencies.

TABLE VI. Values of the angle of deviation.

Direction Gradient	Flushing				Maestricht			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
N	58°·7	66°·7	65°·0	62°·9	47°·4	52°·3*	57°·4	45°·2
NNE	66·4	69·9	67·2	69·3	48·7	55·8	54·8*	46·7
NE	74·8	79·4	75·5	75·2	54·9	60·8	58·4	49·1
ENE	86·5	87·6	86·5	88·5	56·9	67·7	65·0	58·2
E	96·3	93·2	88·6	94·2	66·5	73·0	67·2	75·4
ESE	92·9	87·8	82·2	96·6	62·7	70·4	65·4	77·9
SE	82·8	78·1	75·2	86·6	58·3	63·8	61·3	76·1
SSE	77·0	71·2	72·5	78·7	56·1	61·6	59·0	64·8
S	65·2	64·6	69·2	70·7	51·9*	58·2	57·9	55·4
SSW	63·0	62·1	66·0	66·5	54·0	57·6*	57·4*	52·2*
SW	58·3	60·1*	64·2*	66·4	57·0	60·8	58·3	55·8
WSW	64·2	64·4	64·6	63·4	67·2	69·1	69·2	61·3
W	68·0	65·4	73·4	66·3	67·7	75·6	74·6	66·3
WNW	64·7	68·4	74·4	63·3	62·0	71·3	74·5	62·2
NW	58·7	68·4	71·4	62·9	53·7	64·4	68·1	52·4
NNW	56·5*	68·2	68·1	61·5*	48·3	60·2	62·0	47·9
Mean	70°·9	72°·2	72°·8	73°·3	57°·1	64°·1	63°·8	59°·2

It appears from the average values for all directions taken together that the specific angle of deviation is greater in spring and summer for the landstations de Bilt and Maestricht but that, at the maritime stations Helder and Flushing, as also at Groningen, this difference is slight or nihil, while for Helder they are of opposite sign. This result cannot be considered as final owing to the small frequencies of some directions, and although for some directions the rule holds good (e.g. for NW and NNW directions, Table VII), it fails for others (e.g. the E. direction).

TABLE VII. Mean specific angle of deviation for
NW and NNW directions of the gradient.

	Winter	Spring	Summer	Autumn
Groningen	59° .8	67° .6	68° .1	58° .5
Helder	62 .4	70 .7	71 .6	65 .9
de Bilt	54 .8	58 .2	59 .8	50 .8
Flushing	57 .6	68 .3	69 .8	62 .2
Maestricht	51 .0	62 .3	65 .1	50 .2

The question in how far the distribution of winddirections in different seasons may cause a difference between the average angles of deviation can be answered by calculating not the specific means, in which every direction is regarded as equivalent, but by giving to each direction the weight of its frequency.

The values thus computed and shown in table VIII apply to the period March 1904—December 1910 and the winddistribution during these years.

TABLE VIII. Mean angle of deviation according to the frequencies
of direction, 1904—1910.

	Winter	Spring	Summer	Autumn	Year
Groningen	67° .8	74° .5	70° .1	68° .1	70° .2
Helder	73 .5	76 .6	75 .3	77 .0	75 .6
de Bilt	60 .8	69 .0	65 .8	60 .3	63 .6
Flushing	65 .3	71 .6	72 .3	68 .8	69 .5
Maestricht	53 .5	62 .9	61 .9	55 .4	58 .4

It appears then that, with the only exception of autumn for Helder, the average angles of deviation in spring and summer are actually larger than in winter and autumn and that this phenomenon must be principally ascribed to the distribution of winddirections.

As the meteorological conditions are extremely variable, a period of seven years (1904—1910) is decidedly too short to furnish wind frequencies for different seasons which may be considered as normal values, it is interesting to apply the results of tables V and VI for Helder and Flushing to two series of wind observations extending over 25 years and made on board the lightvessels Terschellingerbank

and Schouwenbank situated in the vicinity of the two landstations. Table IX shows the windfrequencies for magnetic directions, the average deviation being 14° (Westerly).

For application to the data of this table, the angles of deviation corresponding with magnetic winddirections are given in Table III for Helder and Flushing.

TABLE IX. Frequencies of winddirection at two lightvessels, pro 1000, magnetic.

Direction Wind	Terschellingerbank 1884—1908				Schouwenbank 1882—1906			
	W	Spr.	Sum- mer	A	W	Spr.	Sum- mer	A
C	24	51	56	27	15	28	36	18
N	37	81	95	63	32	65	78	45
NNE	16	41	46	23	20	62	62	32
NE	36	92	61	36	31	138	101	48
ENE	23	52	40	20	47	73	51	43
E	52	95	61	59	77	64	42	79
ESE	47	32	20	45	57	30	23	56
SE	80	45	29	85	62	36	30	55
SSE	35	22	18	43	36	24	18	34
S	80	42	28	81	71	39	28	61
SSW	64	34	26	53	93	39	28	72
SW	133	122	115	100	139	86	68	111
WSW	64	58	86	62	73	102	132	70
W	138	84	111	125	82	77	130	90
WNW	59	35	55	52	56	37	59	72
NW	77	73	91	84	77	56	67	79
NNW	35	41	62	42	32	44	47	35

The computation leads to the following results:

	Winter	Spring	Summer	Autumn	Year
Terschellingerbank	$74^{\circ}.5$	$77^{\circ}.8$	$78^{\circ}.5$	$75^{\circ}.6$	$76^{\circ}.59$
Schouwenbank	$70^{\circ}.0$	$73^{\circ}.9$	$73^{\circ}.6$	$71^{\circ}.0$	$72^{\circ}.11$

It appears then that, although at Helder the specific angles of deviation are greater in winter and autumn than in summer and

spring, still the total means follow the general rule, owing to the distribution of the wind in the different seasons.

The angles of deviation as computed in this manner for Terschellingbank are much larger and probably more accurate than those derived from the semidiurnal variation of wind and barometric height; from which we may conclude that these variations are influenced by various disturbing elements so that a direct application of theoretical reasonings is premature.

Physics. — “*Contribution to the theory of binary mixtures.*” XVIII.
By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of January 27, 1912).

In the preceding contribution some points have been mentioned which deserve a fuller elucidation, and the discussion of others was omitted, which I will now take in hand. In the first place it seems desirable to me to discuss more fully in how far the course of the isobars in connection with well-known properties of the spinodal curve is sufficient to enable us to decide beforehand whether three-phase pressure will occur for a mixture with minimum T_{pl} , so that we need not attribute its existence to other unknown causes, and that accordingly the existence of three-phase pressure must not be considered as an anomalous phenomenon.

In the preceding contribution the question was put as follows: has the spinodal line on the liquid side for mixtures with minimum T_{pl} one value for x where $\frac{dp}{dx}$ is equal to 0 for this line, or are there three values for x where this is the case, always for given T . Thinking that the calculation would not be feasible, I had intended to try and answer this question for myself by a graphical way. And I had come to the conclusion that the existence of 3 values had to be expected 1 if the place where T_{pl} is minimum is close to the side, 2 if the range of temperature for T_k is not too small for the components, and 3 especially if the value of the ratio of the critical pressures of the components is *large*. And strictly speaking, calculation is not feasible yet, and this will continue to be so until the equation of state is known with perfect accuracy. Probably the intricacy of the calculations will then prevent us from obtaining a result. But if we content ourselves with an approximate calculation, and if the quantity b is kept constant in the equation of state, and if quasi-

association is left out of account, an answer may be found to the raised question in a simple way, which will enable us to see which of the three causes mentioned which would promote the existence of three-phase pressure, would have to be called the real one after all. And already in contribution II I indicated the real cause.

For a mixture with minimum T_{pl} there is always at least one value of x , for which for constant T the pressure possesses a maximum value in a point of the liquid branch of the spinodal line. This point lies in the double point of the isobars. So it is required for this that this double point exists. And as this point lies on that side of the x -value for minimum T_{pl} which lies nearer to the component with small value of b , and not far from this value, we are sure of the existence of this double point for the mixture ether-water, at least at temperatures which do not greatly exceed the minimum critical temperature of the mixtures, or which remain below it. In this double point the two lines $\left(\frac{dp}{dv}\right)_x = 0$ and $\left(\frac{dp}{dv}\right)_v = 0$ intersect, and it follows immediately from the course of the isobars that if we follow the line $\frac{dp}{dv} = 0$, the value of the pressure is a maximum, both for the liquid branch and for the vapour branch, in the two points in which the said two branches intersect.

If for the different values of x we draw this pressure for the liquid branch, we should obtain a line with a greatest value, touching the p of the loop-isobar. Whether this contact may be taken in the mathematical sense of the word, is after all of no importance for our purpose. There would probably occur a discontinuity in this p, x -figure for the course of the line $\frac{dp}{dv} = 0$. Also the spinodal line passes through that point, and so this has certainly one point in common with the line $\frac{dp}{dv} = 0$. As for the rest the spinodal line lies everywhere outside the line $\frac{dp}{dv} = 0$, the question might again be put if it touches this line in the mathematical sense of the word. This, however, is not of importance for our purpose either. But it seems probable to me that the line $\frac{dp}{dv} = 0$ in the v, x -figure is continuous in the considered point, but the spinodal line discontinuous, because it has only a single point in common with $\frac{dp}{dv} = 0$. On the

other hand the line $\frac{dp}{dv} = 0$ is discontinuous in the p, x -figure, and the spinodal line continuous. Then $\frac{dp}{dx}$ would really be $= 0$ for the spinodal line in the mentioned point, as I have always put in my former communication. But as I observed already above these problems are not of practical importance for the investigation which I wanted to carry out¹⁾.

1) A discussion carried on during the correction of the proof, but which has not led to agreement, has even led me to doubt the continuity of the v, x -figure for the line $\frac{dp}{dv} = 0$ in the double point of the isobars. In this double point both dv and dp are zero, and $\frac{dp}{dv}$ assumes the form $\frac{0}{0}$.

It is true that for the determination of the loop-isobar we have started from the value $\frac{dp}{dv} = 0$; but this does not alter the fact that in the result repeatedly new values appear for some quantities, which at first we had not assigned to them.

As an example I mention $\left(\frac{dv}{dx}\right)_p$. On the line $\frac{dp}{dv} = 0$ this quantity is infinite, and on the line $\frac{dp}{dx} = 0$ it is 0. The result is that in the point of intersection 2 more new values appear besides. In the same way the quantity $\left(\frac{d^2v}{dx^2}\right)_p$. On the first line it is infinite. Moreover it is equal to 0 in the double point, and has besides two more new values.

There are other difficulties attached to the existence of this point. The quantity $\left(\frac{d^2S}{dx^2}\right)_{pT}$ is infinitely great on the line $\left(\frac{dp}{dv}\right) = 0$, and it is equal to zero on the spinodal line. What is its value in the point that these two lines have in common?

As $\left(\frac{dv}{dx}\right)_p = -\frac{\left(\frac{dp}{dx}\right)_v}{\left(\frac{dp}{dv}\right)_x}$, we find the ratio of the quantities to which we had intended

to assign but one value equal to 0, infinite, or zero, or equal to two different values.

I have finally, however, convinced myself that also the spinodal line in the v, x -figure is continuous and touches the line $\frac{dp}{dv} = 0$ in the double point of the isobars. A proof of this has been furnished to me in the discussion mentioned in this note, but this proof seemed to me only valid when a priori we assume the continuity of the spinodal line in the v, x -figure. I have now convinced myself of the contact in the mathematical sense of the word by the following consideration.

It follows from the equation of the spinodal line that:

Only, now that I do call attention to these questions, I think that

$$-\frac{\frac{d^2\psi}{dx^2}}{\frac{dp}{dv}} = \frac{\left(\frac{dp}{dx}\right)^2}{\left(\frac{dp}{dv}\right)_p} = \left(\frac{dv}{dx}\right)_p$$

or if $\frac{dp}{dv} = 0$, $\left(\frac{dv}{dx}\right)_p = \infty$. Then the two branches of the p -line, which lie both on the left of the double point, are considered as belonging together, as should be done. Now:

$$-\frac{dv}{dx_p T} = \frac{\left(\frac{dp}{dx}\right)_v}{\left(\frac{dp}{dv}\right)_x}$$

And numerator and denominator being equal to zero:

$$-\left(\frac{dv}{dx}\right)_p = \frac{\frac{d^2p}{dx dv} \left(\frac{dv}{dx}\right)_{spin} + \frac{d^2p}{dx^2}}{\frac{d^2p}{dv^2} \left(\frac{dv}{dx}\right)_{spin} + \frac{d^2p}{dx dv}}$$

But because $\left(\frac{dv}{dx}\right)_p = \infty$, the denominator is equal to 0.

And then:

$$\left(\frac{dv}{dx}\right)_{spin} = \left(\frac{dv}{dx}\right)_{\frac{dp}{dx}=0}$$

And so there is nothing left but to assume for both lines, viz. spinodal and $\left(\frac{dp}{dv}\right) = 0$ discontinuity in the p, x -figure, or to investigate this.

This proof would not be valid if $\frac{dp}{dv} = \frac{0}{0}$ was really indefinite in the double point. But as appears in the differentiation of p with respect to v, x being kept constant, this quantity does not admit of any indefiniteness.

Now we can easily derive:

$$\left(\frac{dv}{dx}\right)_{spin} = \left(\frac{dv}{dx}\right)_{\frac{dp}{dv}=0} = \frac{1}{2} \left\{ \left(\frac{dv}{dx_p}\right)_1 + \left(\frac{dv}{dx_p}\right)_2 \right\},$$

when $\left(\frac{dv}{dx_p}\right)_1$ and $\left(\frac{dv}{dx_p}\right)_2$ represent the directions of the two branches of the p -line in the double point.

And finally it has appeared to me that for every line that passes through the double point, the value $\frac{dp}{dx}$ is 0, and that for the line $\frac{dp}{dv} = 0$ the value of $\frac{d^2p}{dx^2}$ is not infinitely great, so that also in the p, x -figure the spinodal line is continuous. So we must consider the double point, also for the direction of the X -axis, as two coinciding points.

I ought to point out that the differential equation of the spinodal line :

$$\left(\frac{d^2\xi}{dx^2}\right)_{pT} + \left(\frac{dp}{dx}\right)_{spin} \cdot \left(\frac{d^2v}{dx^2}\right)_{pT} = 0$$

does not justify us, as I put in my previous communication, in putting

$\left(\frac{d^2\xi}{dx^2}\right)_{pT}$ equal to 0 in the considered point. Then $\frac{dp}{dx}$ is, indeed, = 0,

but then it is perhaps also logical to put $\frac{d^2v}{dx^2}_{pT} = \text{infinite}$.

If we put T above $(T_{pl})_{min}$, then both the line $\frac{dp}{dv} = 0$, and the spinodal line have split up into a lefthand and a righthand part. Then there may be indicated two values for x , on either side of the x of $(T_{pl})_{min}$, between which there lie neither binodal nor spinodal lines, and also two values of x , wider apart, inside which the line $\frac{dp}{dv} = 0$ no longer exists. And also the double point of the isobars, which lies on the side of the component with the smallest value of b , has been shifted further to the side of that component. But at the value of T , which is equal to the critical temperature of the remarkable point, the limits of x between which there are no binodal lines, no spinodal lines, no points of the line $\frac{dp}{dv} = 0$, have overtaken each other. On the side of the component with the greatest value of b that component has perhaps long been reached, but on the other side the said limit has extended to the double point of the isobars. In the x of that point we find then: 1 an extreme point of the line $\frac{dp}{dv} = 0$, and that one for which the liquid branch and the vapour branch have merged into each other; 2 an extreme point of the spinodal line, and that one, at which the liquid branch and the vapour branch have united; 3 a similar point for the binodal line; 4 a double point of the isobars.

In the v, x -diagram the 3 first-mentioned lines have a vertical tangent, and also one of the branches of the loop isobar. So it is, indeed, a point with remarkable properties from a mathematical point of view, and no less from a physical point of view. It is a point in which a binary mixture behaves exactly as if it were a simple substance. It is that point that I have always called the *remarkable* point in the previous communication. The plaitpoint temperature of this point satisfies the same relations as the critical temperature of

a simple substance. So we can put $\frac{8}{27} \frac{a_x}{b_x}$ for RT_k and the value $\frac{8}{27} \frac{a_x}{b_x^2}$ for p_k . At that temperature and in that point $\frac{dp}{dx}$ is then with perfect certainty equal to 0 for the spinodal line, and $\left(\frac{d^2\psi}{dx^2}\right)_{pT} = 0$, though $\left(\frac{d^2v}{dx^2}\right)_{pT}$ is infinite.

Now it was the question in the preceding communication whether $\frac{dp}{dx}$ for the liquid branch of the spinodal line could, moreover, be equal to 0 in two points of the said spinodal line that lie further, and then in two heterogeneous plaitpoints. By a graphical way I concluded to the existence of a point for the case ether-water where the spinodal line would possess a minimum value of p and so where a plaitpoint of the 2nd kind would be present. But as the existence of this plaitpoint required that another plaitpoint of the 1st kind was to follow later, I have assumed this existence as a certainty, though I must confess, that I could not have concluded to it from the course of the isobars alone. This is what I meant when I said above that besides the course of the isobars also the knowledge of properties of the spinodal line is wanted. I have since tried if the existence of that plaitpoint of the 1st kind, where p again possesses a highest value, could be derived from the course of the isobars, without our having to take into account a property as the one mentioned. But this attempt has failed. And I have been confirmed in the conclusion that as I had already put in Contribution II, the circumstance from which the necessity of the existence of the two heterogeneous plaitpoints ensues, is to be found in the existence of the curve $\left(\frac{d^2\psi}{dx^2}\right)_{pT} = 0$, which intersects the line $\frac{dp}{dx} = 0$. As may be seen from fig. 8 of Contribution II, the spinodal line is suddenly pushed far back to smaller volumes or greater pressures over a certain width in consequence of the existence of the curve $\left(\frac{d^2\psi}{dx^2}\right)_{pT} = 0$. But from the plaitpoint of the 2nd kind to the component with the greatest value of b the spinodal line continues to pursue its usual course, and remains at a small distance from the line $\frac{dp}{dx} = 0$. And this it was exactly what I had succeeded in concluding from the isobars. That the said curve still exists at temperatures above T_k for

ether and still cuts $\frac{dp}{dv} = 0$ is to be ascribed to the difference in the size of the molecules of water and ether. I have discussed this curve and its influence in Contribution III.

There it can appear how difficult it is to account for its influence in the different cases. The temperature of the disappearance of this curve, at which it has contracted to a single point, is in the notation of Contribution III

$$MRT_j = \frac{d^2\alpha}{b} x(1-x) \frac{1-y}{(1+y)^2}.$$

If according to the little table occurring in this contribution we take with the ratio of the size of the molecules \bar{v} , for x a value somewhat smaller than $0,4$ and y somewhat greater than $0,358$, we find for $\frac{T_j}{(T_k)_{ether}}$ a value of about $\frac{1}{2} \frac{b_{ether}}{b_c} \frac{\alpha_1 + \alpha_2 - 2\alpha_{12}}{\alpha_{ether}}$. This may yield a value for $\frac{T_j}{(T_k)_{ether}}$ which is greater than 1 ; but this formula is entirely based on the approximate equation of state, and can only be considered to give more or less an idea of the value of T_j . Yet the great ratio of the values of b seems to be the main cause of the existence of the three-phase tension, by the side of the value of $\frac{d^2\alpha}{dx^2}$. Whether there may be more causes for the appearance of two heterogeneous plaitpoints, I do not know. I can only state that up to now I have not yet been able to find another cause for it; at least for plaitpoint lines which join the two critical points. And the situation of the two plaitpoints is quite as it follows from fig. 8 of contribution II. The plaitpoint of the 1st kind lies on the side where the pressure of saturation at given T is smallest, and the plaitpoint of the 2nd kind on the other side of $\frac{d^2\psi}{dx^2} = 0$. So for ether and water the 1st plaitpoint on the side of the water.

Also the coincidence of these plaitpoints is to be expected according to this figure. So the point P_{ab} at the temperature at which $\frac{d^2\psi}{dx^2} = 0$, which lay entirely inside $\frac{dp}{dv} = 0$ at still lower T , gets outside it for the first time. So this takes also place in the covered region. Then the points recede further from each other with rise of T . The point P_{cd} above the critical temperature of ether and above the temperature of the transformation when the transition from main

plait to branch plait has taken place, occurs when the plaitpoint of the 2nd kind coincides with one of the 1st kind belonging to the plait which makes its appearance for the first time in the critical point of ether. I thought in contribution II that I had to find a particularity in the behaviour of $\frac{d^2\psi}{dx^2} = 0$ also for this coincidence; but erroneously, as I have seen now. This coincidence must take place with increase of the temperature, just when $\frac{d^2\psi}{dx^2} = 0$ continues to get further and further outside $\frac{dp}{dv} = 0$, of course contracting more and more then, and approaching to a single point. If $\frac{d^2\psi}{dx^2} = 0$ continues to get outside $\frac{dp}{dv} = 0$, the two plaitpoints which lie on the right and on the left of this curve according to contribution II fig. 8 move further and further away from each other. The lefthand plaitpoint of the first kind approaches more and more the lefthand component, in our case water. The righthand plaitpoint, viz. that of the second kind, approaches the second component more and more, in our case ether. In this plaitpoint $\left(\frac{dv}{dx}\right)_p = \left(\frac{dv}{dx}\right)_q$ and $\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q$ according to the description in contribution II. But there is, moreover, intersection of the p - and the q -line, so that the q -line on the left side, before the point of contact, has greater volume than the p -line, and afterwards smaller. I point out, what is perhaps superfluous, that according to fig. 8 the first component would have to be compared with water. But with further rise of the temperature and the ensuing further course of this plaitpoint of the 2nd kind to the side of ether caused by this, a new plaitpoint, one of the 1st kind, makes its appearance, when $T = (T_k)_{ether}$ is reached. Starting from this moment there are 3 plaitpoints present. For this new plaitpoint too $\left(\frac{dv}{dx}\right)_p = \left(\frac{dv}{dx}\right)_q$ and $\left(\frac{d^2v}{dx^2}\right)_p = \left(\frac{d^2v}{dx^2}\right)_q$ and moreover there is intersection. But this intersection is opposite to the preceding. The course of this new plaitpoint is of course so that it moves further and further away from the ether side, and approaches the plaitpoint of the 2nd kind.

Before the appearance of this third plaitpoint there existed only 2 plaitpoints at all temperatures above that of P_{ab} , a pair of heterogeneous ones. I purposely say a *pair*, to express in this way that

they belong together, and together give rise to the binodal curve in the v, x -figure which I shall call the binodal of Korteweg. And this figure is then the representation of a branch plait, indicating partly equilibria which are to be realized, and partly hidden equilibria. Then the top must be found in the neighbourhood of the top of $\frac{d^2\psi}{dx^2} = 0$, and is then lefthand plaitpoint of fig. 8. This figure assumes larger and larger dimensions with rise of T — I should almost say, it strives to become the only figure of equilibrium and it will succeed. But before this has come about, a great deal must happen. It is required for this in the first place that a new plaitpoint of the 1st kind makes its appearance, and that is the critical point of ether. To bring this about it is necessary that such a new plaitpoint appears; for to be the only figure of equilibrium the plaitpoint of the 1st kind must get rid of the plaitpoint of the 2nd kind — and this can only take place when the latter can unite to a pair with a plaitpoint heterogeneous with it. Not immediately when this third plaitpoint appears, is this new pair formed. It is required for it that the temperature has been reached at which the transformation of branch plait to main plait has taken place. At this temperature the intermediate plaitpoint, that of the 2nd kind has got detached from the first plaitpoint, and it has gone to the 3rd. Now the first plaitpoint has got rid of the heterogeneous plaitpoint, and has become the top of a main plait. But now too this is not the only equilibrium. There is still three-phase pressure and the main plait must still get rid of the branch plait¹⁾. And also the way in which it gets rid of it, has still a history. Properly speaking it has already got rid of it, at least for the stable region, when the third plaitpoint has got on its visible circumference. Then it is to all appearances entirely master of the field, and the three-phase pressure has disappeared. But internally, so in the region that is covered by what has now become main plait, the two plaitpoints still exist which must be considered as a pair from $T_{transf.}$ Before this pair can be annihilated by their being united to a double plaitpoint, they had both to get into the hidden region, because a plaitpoint of the 2nd

1) That this transformation temperature is necessary, and has a rather great significance, is clear. But up to now I have looked in vain for the considerations in consequence of which the way to determinè them mathematically, would be clearly indicated. It appears, indeed, from fig. 5 or fig. 2 (These Proc. VII p. 626) that at this temperature the point where the binodal line produced in the covered region e. g. AB , meets the line BC , will have to lie on the spinodal line, but it does not seem feasible to me to express this in mathematical form.

kind can never be found outside such a region. And at last at the temperature of P_{cd} , the plaitpoint that lies close to the top of $\frac{d^2\psi}{dx^2} = 0$, is entirely master of the ground. Perhaps already at this moment or soon after the whole line $\frac{d^2\psi}{dx^2} = 0$ has already contracted to a single point, and then disappeared, and everything behaves then as if there had never been three-phase pressure.

This description holds exactly for the system ether-water, but it must be modified for other cases. Thus in cases in which both P_{ab} and P_{cd} lie above T_{k_1} , the temperature at which $\frac{d^2\psi}{dx^2} = 0$, gets outside $\frac{dp}{dv} = 0$ will lie above T_{k_1} , and so also nearer the temperature at which it disappears. But for the rest no modifications need be applied to the above given description than those that naturally follow from this.

Before I drop this subject, I will make one more remark. In this description we have always started from the thought that a plaitpoint of the 2nd kind belongs to one of 1st kind to form a pair with it. Such a plaitpoint can only leave the plaitpoint that is heterogeneous with it if there is another of the 1st kind present in the field, with which it can unite to a pair, and the temperature at which this can take place, we have called the transformation temperature. And I have also wanted to make clear the necessity of this transformation. Of course a plaitpoint of the first kind can be present by itself, but never one of the 2nd kind. The observation of this rule will often show us at a glance what T, x or p, T -figures are possible or impossible for the course of the plaitpoints. Thus I have mentioned as a mathematical possibility for a T, x -figure with a maximum in front and a minimum at the end, the case that T_{k_2} would be smaller than T_{k_1} . If we consider this case in the light of the just-mentioned rule, we see that this must be considered impossible from a physical point of view. If we design such a figure, it appears that then only one plaitpoint would be found between the two critical temperatures, namely one of the second kind. To consider this possible would lead to an absurdity. Then there would be three-phase pressure, but there would be no top for the elevation above it or for the plait that hangs on it. In the same way a p, T -line must be rejected, for which the value of $\frac{dp}{dT}$ would be negative for the middle branch, viz. that of the plaitpoints of the 2nd kind.

When $\frac{dp}{dT}$ is negative, $\frac{dp}{dx}$ and $\frac{dT}{dp}$ have the reversed sign. Though then the T,x -figure need not be rejected, this would, indeed, be the case for the p,x figure and vice versa. From this ensues that where the T,x -figure has a maximum value for T , the p,x -figure will also have to show a maximum for p . In the same way for the value of x for the minimum.

I will avail myself of this opportunity to discuss another question about the shape of the plaitpoint line, the solution of which is not only of importance for the discussed case of ether and water, but for all the cases, in which three-phase pressure is found. This question was first suggested to me by the p,T -figure for the system ether-water of the preceding communications, and that in the following form: Should not a break be drawn in the p,T -curve for the plaitpoints, which begins in the critical point of ether, in the point where the p,T -curve for the three-phase equilibrium cuts the former curve?

As an argument in favour of the existence of such a break in the course of the plaitpoint curve the consideration might be alleged that the part of the plaitpoint curve that begins at the critical point of ether, is still unaffected by the influence of the three-phase pressure, while that part that lies above the line of the three-phase pressure is to be considered as the locus of the tops of the plaits which rise above the three-phase line. But I point out that this would not only hold when the three-phase line cuts the plaitpoint line, but also when it has a point in common with the plaitpoint line, and ends or begins in it, and so the question would not only have significance for our case, but everywhere where a three-phase pressure must be drawn which connects the two realisable branches of the plaitpoint line. That the plaitpoint line is greatly, and sometimes exceedingly greatly modified by the causes, from which also the existence of three-phase pressure ensues, appears when we direct our attention to the realisable branch, which in the case under consideration, ether-water, is the third branch that ends in the critical point of water. This branch begins, namely, for pressures which can be exceedingly small. But from this the existence of sudden changes follows by no means in the direction of the plaitpoint line, which would then also have to appear in the T,x , and p,x -representations of this line. Of course now that there are causes for the three-phase pressure, this plaitpoint line is different from what it would be without the existence of these causes, but

then throughout its course. But the main features remain — and the modifications are of great importance only when a realisable plaitpoint comes under the influence of a plaitpoint heterogeneous with it. Thus the character of the plaitpoint line on the ether side has been preserved till a plaitpoint of this branch, before or beyond the remarkable point, has begun to form a pair with a plaitpoint of the second kind — and on the other hand a plaitpoint of the branch on the side of the water, when it had got detached from the heterogeneous plaitpoint with which it had formed a pair till then, has begun to exhibit the usual characteristic of a plaitpoint on the side of the component with the highest value of T_k .

It may be of use on this occasion to examine the course of the critical pressure equal to $\frac{8}{27} \frac{a}{b^2}$ for the mixture, if we assumed it to have the character of a simple substance. For a mixture with minimum plaitpoint pressure this locus for the points of the curve formed by these points, begins in the critical point of ether and then remains (see fig. 48) on the lefthand side of the first branch of the plaitpoints to the remarkable point. There it coincides with this point, and cuts the first branch¹⁾. All this time it remains hidden by the liquid-vapour line, except in the remarkable point. When it has passed this point, it continues to ascend to the critical point of the second component, and a point of this locus is hidden at given temperature in the two-phase equilibrium that exists above the temperature of the remarkable point on the water side, and has been discussed above. So it also possesses a point in the cusp which was repeatedly mentioned in the preceding paper. It is certainly remarkable that the only point of the locus $p_k = \frac{1}{27} \frac{a}{b^2}$ that can ever show itself, continues to show itself with the existence of three-phase pressure. At higher temperatures it remains hidden in the then still existing figure of equilibrium, which differs in form according as fig. 48 or fig. 49 is followed. In fig. 49 it is an ordinary two-phase figure, but in the case of fig. 48 it is at first still a figure of three-phase equilibrium during a greater or smaller range of temperature. In the case of fig. 49 the temperature of transformation lies of course lower than that of the remarkable point, but in the case of fig. 48 this is not certain. So this temperature of transformation, indeed, always lies above $(T_{pl})_{min}$, but not always below

¹⁾ Perhaps I overlooked this intersection formerly too, and then I erroneously supposed it to be further to the left.

the mentioned temperature; always, however, on the branch that runs from $(T_{pl})_{min}$ to the point P_{cd} (see fig. 52), either below the point s_1 or somewhat above it.

The following remark may perhaps serve to show the correct use of the T, x and the p, T -figure of the plaitpoints and the situation of the plaitpoints with respect to the three-phase tension. If we take a point of the three-phase curve in the p, T -figure, then the value of T and the corresponding p of the three-phase tension is determined by this point, so that we can draw a straight line at the height of the three-phase pressure, at this value of T above a line on which the value of x will be measured. The three values of x , which exist at this T and at this pressure, are then read in the T, x -curve. If the gas phase comes first, as is the case in fig. 48, when the chosen point of the three-phase tension lies between A and B , there are two elevations above the three-phase pressure, which, of course, lie side by side. The height of these elevations is then indicated by the p, T -curve, by reading from it, how high the first and the third branch indicate the plaitpoint pressure at the chosen value of T . In this case there does not exist a plait which hangs on the three-phase line. The basis of the first elevation has a breadth equal to the distance of x_1 from x_2 , and that of the second elevation equal to the distance of x_2 from x_3 , which distances are indicated in the T, x -figure at T . If the gas phase lies in the middle, which is the case in fig. 48 for points on the left side of A , and in fig. 52 for points below s_p , there is one elevation above the line of the three-phase tension, the basis of which has a breadth equal to $x_3 - x_2$, which is then the whole width, over which the three-phase tension extends. But moreover, there is a plait which hangs down over a width $x_1 - x_2$. The tops of these plaits are again determined by the p, T -curve. If we had chosen the point A itself, then $x_3 - x_1 = 0$, and we have the discussed cusp. If we had chosen a point in the three-phase tension line of the p, T -curve, which belongs to a temperature smaller than $(T_{pl})_{min}$, there is only one elevation, and instead of the plaitpoint of the plait which hangs down, we then have a point of the vapour tension line of ether, which we must think added in fig. 48.

Of course we can also proceed in the same way in the cases represented by figs. 49, 50, and 51, to which might be added a figure representing the termination of the three-phase pressure above the remarkable point. Whether all these cases will occur, is not to be decided beforehand. But the case represented by fig. 48 is the least simple one, and that to such a degree, that it seems more and more improbable to me that it will occur.

For the determination of the temperature of the point P_{ab} of fig. 52, we have 3 equations:

$$\left(\frac{dp}{dv}\right)_{vT} = 0, \quad \left(\frac{d^2\psi}{dv^2}\right)_{vT} = 0 \quad \text{and} \quad \left(\frac{d^3\psi}{dv^3}\right)_{vT} \times \left(\frac{d^2p}{dv^2}\right)_{xT} = - \left(\frac{d^2p}{dx^2}\right)_{vT} \left(\frac{d^2p}{dvdx}\right)_T$$

The last of these three equations supposes that the three-phase pressure begins as soon as the curve $\frac{d^2\psi}{dv^2} = 0$ gets outside $\left(\frac{dp}{dv}\right)_{vT} = 0$, and expresses that these two curves touch. Compare fig. 8 of Contribution II, in which, however, water has been chosen as first component. Then the contact of the two curves takes place in a point in which $\frac{d^2p}{dv^2}$ is positive, and $\frac{d^2p}{dvdx}$ is negative, $\frac{d^2\psi}{dx^2}$ being positive and $\frac{d^3\psi}{dvdx^2}$ negative. The latter quantity being equal to $-\frac{d^2p}{dx^2} \frac{d^2p}{dv^2}$ itself is positive. If we introduce the value of $\frac{MRT}{(v-b)}$ in these functions, as it follows from $\left(\frac{dp}{dv}\right)_{vT} = 0$, we find the following four conditions for the point P_{ab} :

$$\begin{aligned} \frac{2}{v-b} &> \frac{3}{v} \\ \frac{db}{dx} &> \frac{1}{2} \frac{da}{a} \\ \left(\frac{db}{dx}\right)^2 &> \frac{1-2x}{(v-b)^3} \\ &> \frac{1-2x}{x^2(1-x)^2} \end{aligned}$$

and

$$\left(\frac{db}{dx}\right)^2 > \frac{1}{4a} \frac{d^2a}{dx^2}$$

But though it is not difficult to derive two equations for the determination of the value of v and x of the point P_{ab} , the intricacy of one of these equations hampers the determination of these two quantities themselves. We see, however, that as $\frac{db}{dx} = b_2 - b_1$ is greater, the more easily these 4 conditions will be satisfied¹⁾. The

¹⁾ This latter part has already partly been treated in Contribution II, but the conclusions drawn there, rest on insufficient grounds. That long before T_k for water the non-miscibility has ceased to exist, has not been sufficiently kept separate from the existence of non-miscibility at T_k for ether.

two equations for the determination of v and x are :

$$\frac{(v-b)^2}{x(1-x)} + \left(\frac{db}{dx}\right)^2 = \frac{1}{2a} \frac{d^2a}{dx^2} v^2$$

and

$$\begin{aligned} \frac{1-2x}{x^2(1-x)^2} \frac{(v-b)^2}{v^2} - \frac{3b-v}{v} + 6 \frac{\left(\frac{db}{dx}\right)^2}{v^3} &= 2 \frac{\left(\frac{db}{dx}\right)^2}{v^2} \frac{1}{a} \frac{da}{dx} + \\ &+ 2 \frac{\left(\frac{db}{dx}\right)}{v} \frac{1}{a} \frac{d^2a}{dx^2} - \frac{1}{a} \frac{da}{dx} \frac{1}{a} \frac{d^2a}{dx^2}. \end{aligned}$$

It is of course not our intention to accurately determine the systems of values for v and x , which satisfy these equations, as our whole solution must only be considered as an approximation. But the following course might be taken to indicate in the first place the value of $\frac{v-b}{v}$ as function of x at least approximately.

If we put $\left(\frac{v-b}{v}\right)^2 = Z$, then according to the first of the above equations :

$$\frac{Z}{x(1-x)} + \frac{\left(\frac{db}{dx}\right)^2}{v^2} = \frac{1}{2a} \frac{d^2a}{dx^2}$$

and according to the second equation :

$$\frac{db}{dx} \left\{ 6 \frac{\left(\frac{db}{dx}\right)^2}{v} - \frac{2}{a} \frac{d^2a}{dx^2} \right\} = \frac{\left(\frac{db}{dx}\right)^2}{v^2} \frac{2}{a} \frac{da}{dx} - \frac{1}{a} \frac{da}{dx} \frac{1}{a} \frac{d^2a}{dx^2} - \frac{1-2x}{x^2(1-x)^2} \frac{(v-b)^2}{v} - \frac{3b-v}{v}$$

If we substitute the value for $\frac{\left(\frac{db}{dx}\right)^2}{v^2}$ as it follows from the first equation, for this quantity, we get :

$$\frac{db}{dx} \left\{ \frac{1}{a} \frac{d^2a}{dx^2} - \frac{(v-b)}{v} \frac{6}{x(1-x)} \right\} = -2 \frac{da}{a} \frac{(v-b)^2}{v} \frac{1}{x(1-x)} - \frac{1-2x}{x^2(1-x)^2} \frac{(v-b)^2}{v} - \frac{3b-v}{v}$$

Taking into consideration that x will not differ much from $\frac{1}{2}$, it appears from this last form that :

$$\frac{1}{a} \frac{d^2a}{dx^2} < \left(\frac{v-b}{v}\right)^2 \frac{6}{x(1-x)}$$

and by equating $\frac{\left(\frac{db}{dx}\right)}{v}$ from the two equations, we find :

$$Z^2 \left\{ \frac{2}{a} \frac{da}{dx} \frac{1}{x(1-x)} + \frac{1-2x}{x^2(1-x)^2} \frac{3b-v}{v} \right\}^2 = \frac{1}{2a} \frac{d^2x}{dx^2} - \frac{Z}{x(1-x)}.$$

$$\left\{ \frac{6Z}{x(1-x)} - \frac{1}{a} \frac{d^2x}{dx^2} \right\}^2 = \frac{1}{2a} \frac{d^2x}{dx^2} - \frac{Z}{x(1-x)}.$$

If we transfer the numerator of the 1st member as denominator to the 2nd member, the 1st member may be represented as a curve, which we need only follow for values of Z greater than $\frac{x(1-x)}{6} \frac{1}{a} \frac{d^2x}{dx^2}$.

This curve begins infinitely high at this value and runs asymptotically to $Z = \infty$. The second member may also be represented as a curve, which begins infinitely high at $Z = 0$, and cuts the Z -axis at $\frac{Z}{x(1-x)} = \frac{1}{2a} \frac{d^2x}{dx^2}$; so at a value that is 3 times as great as the abscissa

of the value at which the 1st curve lies infinitely high. So it appears that two values for $\left(\frac{v-b}{v}\right)$ or Z satisfy. The first, which we want to know, is somewhat larger than $\frac{x(1-x)}{6} \frac{1}{a} \frac{d^2x}{dx^2}$, and the second,

which belongs to the position in which $\frac{d^2\Psi}{dx^2} = 0$ touches the line $\frac{d\rho}{dx} = 0$ externally, is somewhat smaller than 3 times this value. As

a rule $\frac{d^2\Psi}{dx^2} = 0$ will undoubtedly differ little from a point there. Of course, if we can express v and x in this way, one more equation would have to be used to determine x .

On the supposition that x differs little from $\frac{1}{2}$ we find about :

$$Z = \left(\frac{v-b}{v}\right)^2 = \frac{8}{24} \frac{a_1 + a_2 - 2a_{12}}{a_1 + a_2 + 2a_{12}}.$$

So the value of $\frac{v-b}{v}$ depends in a high degree on the value of $2a_{12}$. With $2a_{12} = a_1 + a_2$ we should even find $v-b = 0$, and so also $T = 0$. With $a_{12} = 0$ we should find $\frac{v-b}{v} = \sqrt{\frac{1}{3}}$. With

$a_{12} = \frac{a_1 + a_2}{4}$ we should find $\frac{v-b}{v} = \frac{1}{3}$ and $T = \frac{1}{2} T_k$.

The second point of intersection of the curves for the determination of $\left(\frac{v-b}{v}\right)^2$ has no meaning for the determination of the point P_{ab} , nor for the determination of the point P_{cd} , but might serve to get to know the temperature at least by approximation, above which the branch of the plaitpoint line, which belongs to the second component, will assume a normal course.

The two curves which serve to determine the value of Z , need not necessarily intersect. The two points of intersection may e. g. coincide, or the two curves may not even come in contact with each other. When the two curves touch or are not at all in contact, this means that the plaitpoint line has a normal character throughout its course, and that there can be no question of three-phase pressure. As the two points of intersection lie further apart, the temperature range for the three-phase pressure is more considerable. Inversely also a very *limited* range of temperature is possible for such a pressure, or this can disappear entirely.

The condition whether or no three-phase pressure occurs, might also be expressed more directly in the following way. If the point, in which the curve $\frac{d^2\psi}{dx^2} = 0$ has contracted to a single point, lies outside $\frac{dp}{dv} = 0$, there is three-phase pressure; if it lies inside $\frac{dp}{dv} = 0$, there is no three-phase pressure. The transition case requires that the point lies exactly on $\frac{dp}{dv} = 0$.

In contribution III the value of x , v , and T has been calculated for the point in which $\frac{d^2\psi}{dx^2} = 0$ has contracted for given value of

$\frac{b_1}{b_2 - b_1}$. If $\frac{MRT}{(v-b)^2} - \frac{2a}{v^2} = 0$, we should have the condition for the transition case. But the values of T , x , and v occur in such an intricate shape, that the substitution in $\frac{dp}{dv} = 0$ does not lead to clear results.

Then the course to find the relation which must exist between the quantities b_1 , b_2 , a_1 , a_2 , and a_{12} would be this that after elimination of T , which is easy to perform, also the quantity v were eliminated from a third power equation in v and two second power equations in v . Then we have two relations in x , and the constants that determine the properties of the substance. Eliminating finally

we have the relation between the constants of the substance, which contains the criterion for complete miscibility.

In the notation of contribution III we can write the condition for non-miscibility, at least in the discussed cases as follows :

$$\frac{a_1 + a_2 - 2a_{12}}{a_1 \frac{1-x}{x} + a_2 \frac{x}{1-x} + 2a_{12}} \begin{matrix} > 4y^2 \\ < 1+y \end{matrix}$$

If we take the sign $>$, this equation expresses that $\frac{d^2\psi}{dx^2} = 0$ disappears outside $\frac{dp}{dv} = 0$. That this does not always mean *three-phase pressure* at the temperature at which $\frac{d^2\psi}{dx^2} = 0$ vanishes, has appeared again here, and this had already been pointed out in contribution II. The three-phase pressure can, namely, already have ceased to exist, in consequence of the $\frac{d^2\psi}{dx^2} = 0$ disappearing above T_{k_1} .

If the sign $<$ holds, there is no three-phase pressure. The quantities y and x depend on $\frac{b_2 - b_1}{b_1}$ in this equation of condition. So by the side of the ratio of the size of the molecules, also the value of $a_1 + a_2 - 2a_{12}$ is decisive for miscibility or non-miscibility.

According to the representation at which we have now arrived, the temperature P_{cd} is that at which $\frac{d^2\psi}{dx^2} = 0$ touches $\frac{dp}{dv} = 0$ inside the latter line. At higher T there is intersection and three-phase pressure. If $\frac{d^2\psi}{dx^2} = 0$ disappears, three-phase pressure has ceased to exist; and this may happen before one of the components is in the critical state. This case was treated before in these contributions. But if this disappearance does not take place until above the critical temperature of the component with the lowest value of T_{k_2} , the three-phase pressure also continues to above this temperature. So if three-phase pressure occurs, the intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{dp}{dv} = 0$ appears always to be the cause.

Physiology. — “*On the comparative nocuousness of concentrated and diluted arsenobenzene solutions. The dilution to be applied in intravenous injections.*” By Dr. CHARLES FLEIG (Montpellier), Lauréat de l’Institut et de l’Académie de médecine de Paris. (Communicated by Prof. H. J. HAMBURGER).

(Communicated in the meeting of December 30, 1911).

I pointed out last year that though some authors, particularly K. ALT, K. TAEGE, R. DUHOT, C. FRAENKEL, and C. GROUVEN had applied the acid solutions of 606 in intra-muscular or even intravenous injections (discontinuing them immediately in the latter case) none had used then for the intra-venous injection the *diluted* acid solution and, as an outcome of clinical results which authorized me in doing so, I have been the first to recommend strongly the application of *strongly diluted acid intra-venous injections*. The preparation of the solution is very simple; it is sufficient to dissolve 0.50 or 0.60 gr. of 606 in from 350 to 500 gr. of artificial serum at 7 per 1000 for which it may be found useful to substitute, especially in cases in which chlorine may be kept back in the system, by an equal volume of isotonic or paraisotonic serum where glucose has been substituted for chlorine (glucose at 40—47 per 1000). The injection itself is as simple as an ordinary injection with artificial serum.

From a therapeutic point of view the method is extremely active (FLEIG, DUHOT); according to DUHOT and others its therapeutic activity is even far superior to that of the alkaline method.

I have expressly stated that the innocuousness of the injection was due to its great dilution, and I have attributed the unfavourable symptoms observed by the authors after the intra-venous acid injection, to the solutions being too concentrated. These symptoms, characterized in the first place by congestion of the blood in the head, difficult breathing, an intense feeling of anxiety, vomiting, diarrhoea, etc. are entirely different from the weak reactionary symptoms (hyperthermic symptoms, shivering) which attend properly diluted acid injections. The latter grow much slighter or disappear even entirely if, as has been advised by WECHSELMANN, only *newly* distilled ¹⁾ water

¹⁾ These reactionary phenomena which are especially due to water which has been sterilized a long time after it was distilled, must, as has been very well understood by WECHSELMANN, be attributed to decomposition products of animal and vegetable origin in water, which has been distilled long before, which products are set free by sterilization. I have ascertained that they are by no means due, as one might be led to believe, to the action of the CO₂, which such water may contain.

is used in preparing the artificial serum. On the other hand the troubles caused by the injection into the veins of too concentrated solutions of 606 are of a far more serious nature. FRAENKEL and GROUVEN have even published a case in which death followed in about three hours and a half, after the injection, and yet in this case a certain amount of soda (entirely insufficient, however, to neutralize the acidity) had been added to the solution, used for the intra-venous injection.

These very marked differences between the clinical results of concentrated and diluted acid solutions made it interesting to study experimentally the toxicity of solutions of different concentrations and to trace the cause of the fact why the concentrated solutions are hypertoxic. This research was even very important, as it might serve to combat the error of certain authors who, having applied concentrated acid solutions in intra-venous injections with injurious and even mortal results, have believed themselves entitled to do away entirely with the intra-venous acid method, a method which, when applied under the conditions pointed out by me, presents only advantages and seems to be superior to the others. After the publication of my first results (November 1910) the method has been employed with great success and in a great number of cases by DUHOT (from the end of May 1911) who after having given up the *concentrated* intra-venous acid injection, to replace it successively by the intra-muscular acid injection, and the intra-venous alkaline injection, has been induced on his part (at the advice of EHRLICH, and probably without knowing my first researches) to try and afterwards to apply systematically, the intra-venous acid injection in strong dilutions. Since then other authors have followed the same method and their results only show its value.

Of the experimental researches which I have made on the comparative nocuousness of concentrated and diluted acid solutions I shall summarize here only the chief results as regards the toxicity of acid solutions of 0.60 gr. on 400 cc., injected into the veins of rabbits and dogs, and of acid solutions, at the rates of concentration in which they were *at first* used by DUHOT, and by FRAENKEL and GROUVEN.

The doses injected into the veins by DUHOT went from 0.50 gr. to 1 gr. of 606, dissolved into 1 c.c. of methyl-alcohol, the whole diluted to a volume of 30 c.c. by means of artificial serum. I have thus studied the toxicity of the most concentrated solution, that is to say 1 to 30 (with or without methyl-alcohol).

The dose injected by FRAENKEL and GROUVEN, more especially in their mortal case, was 0.40 gr. of 606 dissolved into 1 c.c. of methyl-alcohol to which were added 1 or 1.5 c.c. of $\text{NaOH} \frac{\text{N}}{10}$ (on an average 1.2 c.c.) the whole being brought with distilled water to a volume of 15 c.c. I also have studied experimentally the toxicity of this solution (with or without methyl-alcohol).

In order to be exact and to facilitate comparisons I shall add the following data.

The acidity in HCl of the solution 1 to 30 of DUHOT amounts to 5.10 gr. per 1000 and that of the solution of FRAENKEL and GROUVEN (with 1 cc, 2 $\text{NaOH} \frac{\text{N}}{10}$) is 3.91 per 1000; that of the solution diluted to 0.60 gr. of 606 to 400 c.c., which represents a type of a *diluted* solution is only 0.23 gr. per 1000¹⁾.

As the toxicity of the acid solution is due above all as we shall see, to the phenolic functions of OH of 606 much more than to the acidity in HCl, and more exactly, to their degree of concentration in the solution, it may be interesting to give the concentrations in —OH per 1000 for the three types. These concentrations are for the first solution 2,233 —OH per 1000 c.c.; for the second 1.733 gr.; for the third 0.100 gr.

It follows that in the solutions of DUHOT and of FRAENKEL and GROUVEN the concentrations in acidity or in phenolic function are from 17 to 22 times as strong as in solutions of the diluted type.

We may finally point out that the doses injected into man *per kilogramme* (taking an average weight of 65 kilogrammes) were in the mortal case of FRAENKEL and GROUVEN 0.006 gr., and 0.0153 gr (the highest limit) in the case of DUHOT, where the injection was attended by a "tableau assez impressionant".

From the numerous experiments on their toxicity which I have made, it follows that the solutions of DUHOT and of FRAENKEL and GROUVEN are much more poisonous than the solutions diluted to 0.60 gr. per 400 c.c., the latter being already much less poisonous than the solution of 0.60 gr. per 200 c.c.

On an average the *immediate toxicity* of the first two may be fixed at from 0.006 gr. to 0.010 gr. per kilogramme of rabbit²⁾; that of the latter at 0.130 gr. that of the most diluted solution at 0.180 gr., the immediate toxicity of the latter is therefore from about 20 to 30 times lower than that of the concentrated solutions used by above-mentioned authors!

¹⁾ These acidities are calculated whilst taking for the formula of dichlorhydrate of dioxidiaminoarsenobenzene the formula $(\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2\text{As}_2 \cdot 2\text{HCl} + 2\text{H}_2\text{O})$, given by EHRLICH.

²⁾ The toxicity of 606 being very great when applied in these concentrations, only trifling differences can be established in the toxicity of solutions with and without methyl-alcohol.

When studying these values and comparing them with those mentioned before we are immediately struck by the fact that the toxicity of these last solutions — and not the toxicity after a long time, but the *immediate toxicity* is represented :

1 — in the case of FRAENKEL and GROUVEN's solution by a *figure equal or very nearly equal to that representing the dose injected per kilogramme into man* ;

2 — in the case of DUHOT's solution by a *figure evidently lower than the maximum dose which he says he has injected into man per kilogramme*.

On the other hand when studying no longer the immediate toxicity of the two types of concentrated solutions, but their secondary toxicity, that means to say that, relating to the dose which kills the animal after a somewhat longer time (from 12 to 24 hours for example) I have ascertained that the dose grows still much smaller.

Finally when studying the effect on dogs and rabbits of the same solution, injected *in equal or somewhat smaller doses than those injected by the authors into man* (holding in view the difference in weight) I have ascertained that these doses were invariably and often immediately mortal, in the case of the solution 1:30, and nearly always mortal in the case of the other solution.

From these facts I think I may draw the following conclusions :

1 — It is not at all surprising that the case of FRAENKEL and GROUVEN proved mortal after a very short time ; there is no reason to assume, as the authors have done, an excessive sensibility of the patient to the action of arsenic, as death was not due to acute arsenic poisoning (contrary to what they believe, and as I shall prove lower down) but simply to the solution being too concentrated ; it is very surprising that the two other cases, treated by the authors, have not had the same fatal ending.

2 — It is in the highest degree surprising that the patients injected with the DUHOT-solution have shown only the symptoms mentioned, and that "le tableau assez impressionnant", described by the author, has not ended in death, as the dose injected per kilogramme was 0.153 gr. whilst the dose, *immediately* toxical for the animal, is upon an average 0,010 gr., that means to say 15 times as weak. And our astonishment increases if we remember, as I observed before, that the secondary toxicity is represented by a still smaller figure ! According to several experiments, too numerous to be classed as exceptions, the figure in question, calculated for a man weighing 65 kilogrammes, would come to a toxical dose somewhat less than

0.50 gr., that means to say less than half the maximum dose which DUNOT says, he could inject man with.

As, however, the immediate toxicity of the two types of solutions studied, was for the dog sometimes lower than for the rabbit, one might be inclined to infer from this that man, nearer to the dog in the zoological scale than to the rabbit, is less sensible to 606 than the animals. But this supposition, not very likely at first sight, is decidedly wrong, for when experimenting with diluted solutions (either alkaline or acid) it is discovered that animals, in proportion to their weight, can bear without any trouble, doses of 606 much greater than those which would cause the first symptoms of poisoning in man.

Scientifically it is therefore incomprehensible, I should almost say inadmissible that into the veins of man may have been injected several times and without fatal results such a considerable amount of 606 (1 gramme) in such a concentrated solution as the one described (1 to 30). It is in every respect to be regretted that no detailed clinical observations have been published for the cases in question.

We shall realize still better how well founded these conclusions are if we consider *the nature of the disorders* attending concentrated acid intravenous injections.

In the experiments relating to *immediate toxicity* death is caused by *acute asphyxy* with more or less general convulsions. At the autopsy the heart may beat still, but the lungs are marked by hemorrhagic points and in some places by large violet coloured zones of infarcts in connection with emboli throughout the vascular part of the organ. The right cavities of the heart and the large bloodvessels entering it, contain blood which, if not coagulated, can be made to coagulate very easily *in vitro*. If this blood is spread in a thin layer over the sides of a glass, we can discover without difficulty, even with the naked eye, little clots, in the centre of which we see a yellowish precipitate, originating as we shall see in the action of 606 on the albumenoids of the plasma. The nervous centres may also be subject to emboli or infarcts. The same facts may be observed in those cases where, though the doses injected were, in proportion to the weight of the animal, not so great as those with which man was injected, death has nevertheless been the consequence.

In the experiments relating to toxicity after a longer period, the animals die after having shown an increasing difficulty in breathing, in connection with either acute congestion and oedema of the lungs

or pneumonia or broncho-pneumonia. At the autopsy pulmonary lesions are discovered analogous to those which have just been described when discussing immediate toxicity, but with a permeability of the lung to air, the smaller as the survival has been shorter; large zones of red hepatization are met with, and often the bronchia and the trachea are filled with a fine spume and a considerable amount of fluid oedematous transude, and sometimes in the pleura itself a sero-fibrinous very slightly hematic fluid is met with. In those cases in which death followed after a few days it was found that to the preceding lesions others were added of a more distinctly infectious nature (grey hepatization for instance).

One or two weeks after the injection we also observe diffuse pulmonary lesions even in those animals (more especially in dogs) which were injected with doses too slight to cause death, and which, though losing flesh temporarily, only showed passing symptoms of dyspnoea.

In the 3 kinds of cases quoted we *have to do with troubles and lesions of a mechanical¹⁾ origin* owing to the considerable precipitation in the blood of 606, injected in too strong a concentration. This fact can very well be explained at the hand of researches made on the arsenic compound, found in the blood, after the acid intravenous injection.

In a former treatise I pointed out, in the first place that the precipitate caused in the blood by the acid solution of 606, was by no means due to the acidity in HCl of the solutions; I believed moreover I had to admit, as a result of reactions I had studied between the salts of the form CO_2NaH of the blood and 606, that the latter precipitated in the blood in the form of an insoluble base $\left(\begin{array}{c} \text{NH}^2 \\ \text{OH} \end{array} \right) > \dots \dots < \begin{array}{c} \text{NH}^2 \\ \text{OH} \end{array}$; but further researches have shown me that the precipitates, produced in an albuminous medium, are in reality more complex than my initial scheme indicated, and that moreover, probably to a great extent, *reactions took place between the phenol group —OH of 606 and the albuminoid substances of the blood*, so that the precipitate formed, far from being exclusively

¹⁾ It must be noted that in the case of sub-cutaneous acid or alkaline injections in toxic doses, frequent congestive lesions in all the principal interior organs have been pointed out by different authors. Especially in experiments on the Guinea-pig DESMOULIÈRE and PARIS have found little hemorrhagic centres in all the inner organs. Probably the nature of these lesions is akin to that of lesions of the same kind, caused by intra-venous injections of toxic doses.

due to the base $\frac{\text{NH}^{\oplus}}{\text{OH}}$ > represents perhaps almost exclusively a phenolic combination of albumenoid.¹⁾

This precipitate, at any rate when it is formed in a concentrated solution of 606, takes the form of *compact clots not easily divisible into smaller particles*: hence its physical state does not fulfil the conditions I specified in 1907 in connexion with my method of insoluble intra-venous injections, which conditions would be necessary in order that its being set free in the current of the blood should not give rise to the formation of emboli.

When on the other hand the same precipitate is formed under the influence of a sufficiently diluted solution of 606 (0.60 gr. to 400 cc. for instance) it presents itself in a much finer state of division, and is from a physical point of view much better suited than the former, owing to its mechanical fitness for the blood and the possibility of its passing the smaller blood vessels and the capillaries.

This explains why the toxicity of the diluted acid solution is much weaker than that of the concentrated solution: the reason being that the noxiousness of a mechanical kind is much less in the diluted solution.

A noxiousness of this kind, however, also manifests itself in these solutions, as was shown by the condition of the lungs of those rabbits on which their immediate toxicity was tried and the intense dyspnoea, observed at the time of the injection, but this noxiousness makes itself felt only for much more considerable doses of 606 than the doses therapeutically used on man; *the limit of mechanical noxiousness is far distant from the limit of the maximum therapeutic doses*; so that for man these doses possess practically no toxicity. The serious dangers of the concentrated acid solutions form in no way an objection to the method by which strongly diluted acid solutions are employed, which method, owing to its great therapeutic activity should be applied more and more.

It is interesting to observe that the most poisonous factor, from a pharmacodynamic point of view, of the dichlorhydrate of dioxy-diaminoarsenobenzene in acid solutions is not due to the acid, for the catastrophes observed are especially of a mechanical kind, as a

¹⁾ The reactions are also complicated as regards the much weaker precipitation of weakly alkaline solutions. A more detailed account of the precipitates caused in the blood by alkaline and acid injections will be found in my treatise: "*La méthode des injections intraveineuses acides d'arsénobenzol à forte dilution, au sérum artificiel ordinaire et au sérum achloruré glucosé.*" (Maloine, éditeur. Paris. 1911).

result of the precipitate which was formed, and we have seen, that hydrochloric acid plays no part in the precipitation. I may expressly state that this is also the case in a concentrated solution, such as the solution 1 to 30, corresponding to an acidity in HCl of 5.10 gr. per 1000, as an HCl-solution of 5 per 1000 does not precipitate blood-serum; moreover the amount of HCl, fixed in even strong doses of 606, is not great enough to be poisonous.

Hence the most directly toxic function of arsenobenzene in concentrated acid solutions is the phenolic function OH, the coagulating effect of which on the albuminoid substances of the blood results in evils of a mechanical kind, evils manifesting themselves immediately, that is to say before the chemical toxicity of the arsenic complex has set in.

The preceding remarks on the nature and the great danger of the disorders and injuries which follow rapidly upon intra-venous injections of acid solutions of concentrated 606 show that I was fully warranted in emphasizing how difficult it is to understand that the injection of large doses of these solutions should not have been attended with graver troubles, ending more frequently in death, than those which have been published. Viewed in the light of the above investigations, I have a right to be surprised at the *scientifically inexplicable* discrepancies between the experimental and the published clinical results.

The former are at any rate highly instructive. They mark in the first place *the highly important part played by dilution in the diminution — practically it might even be said in the removal of the toxicity.* This fact should be known to all therapeutists, for it is far from new, but though, as far as I am concerned, I have always acted upon it, whenever I have applied clinically the results of my experimental researches¹⁾, yet I have often seen it misappreciated — or at least forgotten — by eminent clinical lecturers. Therefore I purposely recommend it again and should wish to see it applied in all cases in which the intra-venous injection implies the use of a substance (of an artificial or biological origin) which, when applied in concentrated solutions, perhaps might be given in doses, which

¹⁾ Cf., especially for intra-venous injections of bloodserum, the following treatise: CHARLES FLEIG. "Sur les injections de solutions isotoniques de chlorure de calcium ou de sérums fortement calciques, de solutions isotoniques ou hypertoniques de sucres et sur l'ingestion ou les lavements d'eau abondants, avant et après l'anesthésie chirurgicale." *Académie des Sciences et Lettres de Montpellier*, 7 Juin 1909, et *Presse médicale*, 29 Janvier 1910, 69—72.

would not exclude the possibility of toxial symptoms. Another advantage of diluted solutions may be found in the necessarily much greater slowness with which the solution enters into the blood; this slowness may be attended in some cases by phenomena denoting rapid adaptation, which phenomena, according to their internal mechanism may be reduced to ROGER's *tachysynethy* or to CHAMPY and GLEY's *tachyphylaxis* or to ANCEL, BOUIN, and LAMBERT's *skeptophylaxis*. Moreover I have advised, when applying solutions of 606 to carry out the diluted injection itself always *very slowly*.

Although the dilution is a factor which diminishes the toxicity, it should not be carried too far: *the therapeutic activity of the 606 injected being, as I have shown, to a certain extent connected with its temporary insolubility*, and the latter bears a direct proportion to the length of the period during which the substance is in the organism and an inverse proportion to the rapidity with which it is eliminated¹⁾, too strong a dilution, which would cause too rapid a solubilisation of the precipitate and leave the arsenic compound for too short a time in the tissues, would diminish its therapeutic activity too much. It will also be found advisable, in the case of 606 not to go beyond a dilution of 0.60 gr. per 500 cc. so as not to make the organism lose the benefit of the *most favourable condition* brought about by the *first precipitation*.

Finally the facts which I have discussed enable us to explain various cases in which death followed sooner or later after the injection (from a few days to more than two weeks) and which have injudiciously been ascribed to some other cause than to an action of 606.

When examining the symptoms of these cases, we read that the patients have died of disorders of an intermittent nature, sometimes affecting the lungs, sometimes the nerves, whilst the autopsy shows lesions of the same nature as those which I described as following upon too concentrated injections. As some precipitate may be caused by the contact of blood even with alkaline²⁾ solutions, the mechanical nocuousness may be taken as a factor having caused lesions which are fatal in the long run, and a connection may easily be established with the experiments quoted above, in which death followed only after a few days; this factor has certainly intervened in some cases

1) These facts explain why alkaline solutions have a weaker therapeutic activity than acid solutions: in the case of the former the insolubility in blood exists only to a small extent, and the arsenic is, as I have observed, much more rapidly eliminated.

2) This precipitation increases as the alkalinity of the solution decreases.

in which the solutions used were not sufficiently diluted. Thus it may easily be understood that only moderately strong concentrations may cause insignificant pulmonary lesions, attended by no fatal consequences whatever, in the case of sufficiently strong persons, and be attended on the other hand with the gravest results for other individuals in a state of local or general debility.

For the details relating to the experiments on toxicity mentioned here, and a general study of the acid intra-venous method, I beg to refer to the general survey already mentioned in this paper.

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Geology. — "*On an essential condition for the formation of over-thrust-covers.*" By Dr. B. G. ESCHER. (Communicated by Prof. Dr. G. A. F. MOLENGRAAFF).

(Communicated in the meeting of January 27, 1912).

E. HAUG¹⁾ has called the attention to the fact that only such territories as were formerly occupied by geosynclinals give occasion to the formation of over-thrust-covers. I suppose I can point out a second condition that evidently must be satisfied, that tangential propelling-forces form a mountain-system, built of over-thrust-covers.

Comparative studies in the Western Alps prompted me to point out²⁾, that the hercynic folding of the sub-structure of the present Northern border of the Alps was the *indirect* cause of the formation of the alpine covering-system of the Western Alps in the tertiary period.

Whilst formerly a resistance of the Central Plateau of France of Vosges and Schwarzwald was spoken of I think I have proved, that not these parts of the hercynic mountains in Europe, stiffened by a previous folding, offered resistance to the alpine propelling forces, but other parts of the pretriassic folding-mountain system of Central-Europe, situated more E., S.E. and S. The Eastern South-Eastern and Southern border of the hercynic mountains of Central-Europe was evidently formed by the autochthonic "Zentral-Massive" of the West-Alps: Mercantour, Pelvoux, Belledonne, Grandes-Rousses, Mont Blanc, Aiguilles Rouges, + Dents de Moreles, Aarcentre.

¹⁾ E. HAUG. *Traité de Géologie*.

²⁾ B. G. ESCHER. *Ueber die praetriassische Faltung in den Westalpen etc.* Diss. Zürich 1911.

That a part of the Alps was already folded in the hercynic orogenetic period, and that this folding did not take place at one time, but was performed in two phases²⁾ that can clearly be distinguished, has lately been proved by M. LUGEON³⁾ for Mont-Blanc, Aiguilles-Rouges and Aar-centre. LUGEON speaks even of a regional division into zones, of which one was folded by the "phase ségalaunienne" (= prae-Stéphanien) the other only by the "phase allobrogiennne" (= prae-triadic). This regional "dualisme" may be correct for Mont Blanc, Aiguilles-Rouges and Aar-centre, LUGEON has still to afford sufficient proof for the existence of these two folding-mountain-systems for the Franco-Italian Alps.

Most authors agree about the resistance of a mountain system that has already been folded, to a second folding.

The fact that a plate that has already been folded offers resistance to a second folding in another direction⁴⁾ may be a mechanical explanation for the case that the direction of the strikes of the two foldings form an angle. In nature however it often occurs that these two directions run almost parallel, and then of course this explanation cannot be applied. It seems however quite natural, that a folding stiffens a certain part of the earth-crust, and that such a territory afterwards offers a greater resistance to a second folding in the same direction, than another part lying behind it that has not yet been folded. The absolute resistances are here of course not of as much interest as the relative ones, and as, at a subsequent tangential propelling force, the part that has not yet been folded, offers less resistance in the beginning, a folding will here of course likewise take place. That folding can last here at least as long as the now folded beds offer the same resistance as, in their time, the previously folded beds, lying before them, could offer.

After PAULCKE⁵⁾ has proved by his splendid successful experiments, that if, at the experimental tectonics, really forces are applied and suppositions made that are somewhat in conformity with those occurring in nature, good results may be expected, it is, in my

^{3a)} M. LUGEON. Sur l'existence de deux phases de plissements paléozoïques dans les Alpes occidentales. Comptes Rendus de l'Acad. d. Scienc. Paris 30 Oct. 1911.

^{3b)} M. LUGEON. Sur quelques conséquences de l'hypothèse d'un dualisme des plissements paléozoïques dans les Alpes occidentales. Comptes Rendus de l'acad. d. Scienc Paris 13 Nov. 1911.

⁴⁾ CH. TH. GROOTHOFF. Verslag v. d. geol. excursie naar de Zwitsersche Jura en het Alpenged. Bijlage bij het Jaarboekje 1909 v. d. mijnbouwkundige Vereeniging 1909.

⁵⁾ W. PAULCKE. Kurze Mitteilungen ueber tektonische Experimente. Jahresber. d. Oberrhein. Geol. Vereins. Neue Folge. Bd. 1. Heft 22. p. 58—66. 1911.

opinion, not impossible to study with the help of such apparatuses as PAULCKE used, experimentally the influence of an old folding on a new one.

From the most recent researches in the Western Alps follows that the *Helvetian covers* are but small slides compared with the *Penninian covers*. According to E. ARGAND⁶⁾ these are stowed *against* Mont-Blanc and the Aar centre, whilst the Helvetian covers were slid *over* these autochthonic centres.

LUGEON⁷⁾ and ARBENZ⁷⁾ suppose that the Mont-Blanc-centre and the Southern (Protogin)-territory of the Aar-centre have partly been slid over the Aiguilles-Rouges and over the Northern border of the Aar-centre lying to the N.W. and N.

This overthrust took place during the Alp-folding in the tertiary period, but according to LUGEON⁸⁾ it was only restricted to the South-western hercynic chain (chaîne allobrogiennne) whilst the autochthonic territory lying more northward is separated from it by the alpine synclinal of Chamonix and its continuation: Oberer Jungfrau-keil-Fernigen-Windgällenmulde⁷⁾, and was not slid by the alpine folding.

Whereas HEIM⁸⁾ and SUESS⁹⁾ suppose that at the tertiary folding the autochthonic centres were forced upward, a supposition supported by K. TOLWINSKI¹⁰⁾, on the authority of local tectonic researches, I am of opinion²⁾ that the vaults in the autochthonic centres were already extant before the tertiary Alp-folding, and ARBENZ⁷⁾ is likewise of the same opinion: "Die Massivwölbungen sind dagegen in ihrer Anlage älteren Datums"⁷⁾.

Though there may be perhaps some objection to the view that the vaults in the hercynic southern border were extant before the alpine folding, a view that is a. o. supported by the fact that between Belledonne and Mercantour local slide-covers occur (Devoluy, Embrunais), yet it may be admitted as certain, that the covering mountain of the tertiary Alps has been slid *against* and *over* a territory, that had already experienced an older orogenetic movement and was already folded at the end of the Carbon-period.

BERTRAND, who compared the Glarneralps with the great over-thrusts in the Carbonbasin of North-France, gave the first stimulus to the

6) E. ARGAND, Les nappes de recouvrement des Alpes pennines etc. Beiträge z. geol. Karte der Schweiz. Neue Folge. 31 Lief. 1911.

7) P. ARBENZ, Der Gebirgsbau der Zentralschweiz. Protokoll d. Sitzung vom 4 Dec. 1911 der Naturforschende Gesellschaft, Zürich.

8) ALB. HEIM, Eclogae geol. helv. Vol. IX. p. 43. 1906.

9) E. SUESS, Das Antlitz der Erde. III Band. 2e Hälfte. p. 124. 1909.

10) K. TOLWINSKI, Die grauen Hörner. Vierteljahrsschrift der Zürcher Naturf. Gesellschaft 1910.

development of the theory of over-thrusts in the Alps. Since this theory gained ground in the territory of the Alps and the hercynic folded beds in North-France and Belgium were in their turn compared with the mountain-system of the Alps.

FOURMARIER¹¹⁾ points to some tectonically corresponding features of Ardennes and Alps and discusses in this connection a. o. the fan-shaped folds. GROOTHOFF⁴⁾ compares the three territories: Alps, Chain Jura, Table Jura with North-France (over-thrusts) the folded Carbon of South-Limburg and the flat Carbon of North-Brabant.

It seems to me that there is another important conformity in the fact that *likewise in the Ardennes an older folded chain of mountains is lying under the over-thrusts*¹¹⁾. Most likely the Southern border of the Caledonic mountains is extant here, *against and over which* the hercynic mountains formed over-thrusts. In this territory we find likewise evidently, *a resistance caused by already folded beds* (here caledonic folded Cambrium-Silurian beds against a later folding, by which a cover-structure (here a hercynic one) was formed. Whereas consequently in the Alps a previous hercynic folding was the indirect cause of the formation of a later alpine structure of slides, the Ardennes are to be regarded as a territory in which likewise two orogenetic movements took place, here however the younger of the two movements, by which the over-thrust-structure was formed, coincides with the old folding of the Alps.

Great over-thrusts have long since been known in Scotland. E. B. BAILEY¹²⁾ gave lately a description of a very complicated over-thrust-structure SE of Loch Linnhe, showing great conformity with the profiles through the Western Alps. This territory belongs to the *caledonic mountains* of Western-Europe, i.e. to the Northern part. The general direction of the strike is here SW—NE. According to BERTRAND¹³⁾ lie to the North-West of this territory the *huronian mountains*, which were folded in the algonkium. Evidently there is here likewise a relation between the appearance of an over-thrust-structure and a previously folded mountain-system lying before it. Here the first folding however took place during the huronic period, and the territory, stiffened by it, formed a buffer with regard to a subsequent folding which threw up, here in the *caledonic* period, a *slide structure*.

¹¹⁾ P. FOURMARIER. La tectonique de l'Ardenne. Annales d. l. Soc. géol. d. Belg. t. 34. mémoires 1907.

¹²⁾ E. B. BAILEY. Recumbent folds in the schists of the Scottish Highlands. Quart. Journ. Geol. Soc. pp. 586—620 1910.

¹³⁾ M. BERTRAND. La chaîne des Alpes et la formation du continent européen. Bull. de la Soc. géol. de France. 3e Serie. T. 15. 1887.

As early as 1887 BERTRAND¹²⁾ published two maps with the Northern frontiers of the caledonic and hercynic foldings in Europe and partly those of North-America. As an important acquisition since that time may be regarded the description of the over-thrust in

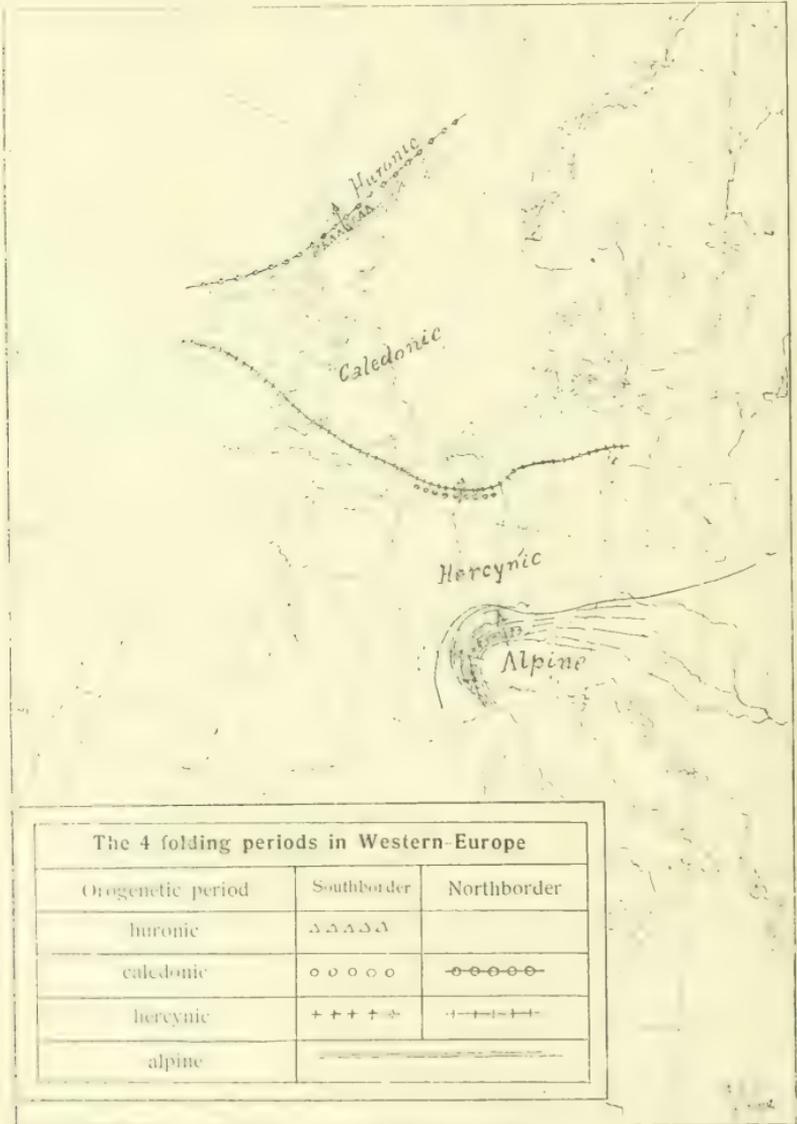


Fig. 1.

Scandinavia, where caledonic masses have been slid over huronic territories to the SE. To my knowledge the latest map concerning this subject is to be found with E. HAUG¹⁾ (1st Vol. p. 209). Only the Northern frontiers of the caledonic and herecynic foldings in Western- and Central-Europe however are indicated here, whilst *for the formation of over-thrust-structures* in Western and Central Europe evidently the Southern frontiers of these foldings are *of importance*. For this reason I indicate on the annexed map (Fig. 1) very schematically, besides the Northern frontiers, likewise the Southern frontier of the herecynic folding of the Alps, and the *presumptive Southern frontier* of the caledonic folding in the Ardennes, and of the huronic folding in Scotland.

I represent myself a profile of North-Scotland over the Ardennes to the inner-border of the Alps, in the main as fig. 2 in which those parts that are not occupied by over-thrusts, are represented much fore-shortened.

An essential condition for the formation of overthrust-structures is in my opinion, the existence of a mountain-system folded in a previous orogenetic period and afterwards abraded, that served as a buffer against the ensuing folding.

In Fig. 1. I have indicated the southern frontiers of the huronic and caledonic mountains for part of Western-Europe, these frontiers being for the present entirely hypothetical. The older foldings have only been observed before i.e. in the cases discussed here to the North of, the overthrust-structures, whilst I have admitted in analogy with the Alpine-mountains, that the older foldings extend to some distance southward under the slide-covers. The map and profile are meant to elucidate the principle I pronounced here. I am very well aware that in reality the circumstances are much more intricate. So I am convinced that likewise at the inner-border of the Alps a remainder of a herecynic mountain-system is extant (Manno²⁾), and that the mesozoic sediments of the Alps are inclosed between two already herecynic folded territories. A similar old folded territory may perhaps likewise be found to the South of the over-thrusts of the Ardennes (there caledonic) and to the South of the Scottish slide-covers (there huronic); but for the present we are still fully uninformed in this respect.

That part of the earth-crust which we contemplated in profile Fig. 2 shows, in my opinion accidentally, a regular repetition of over-thrusts that have been slid in a Northern direction. Somewhat more to the South in the territory of the Mediterranean, the directions

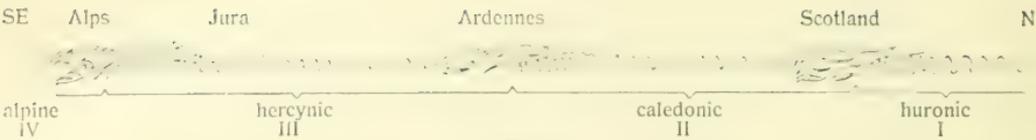
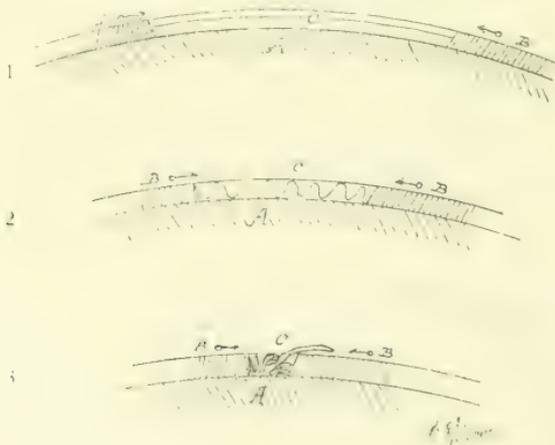


Fig. 2.

of the Alpine foldings show great variety; in Scandinavia the caledonic territories have been slid in a S. E. direction.

With the notion that in the tertiary period the Alps come, as it were, between the two clamps of a set-screw is necessarily united the hypothesis that the Alps were passive during the alpine movement, and the seat of the active force originating e. g. in the contractive strains, was more in the depth. I suppose that these forces, working in the depth, were transferred to the surface by the old already folded and abraded remains of the mountains, and that the young level sediments were squeezed between two such stiffened territories which had been pushed towards each other. When the force in the depth continued for a considerable time, and consequently the two stiffened territories were pushed closely together then an over-thrust-structure was formed (vide Fig. 3).



- | | |
|-------------------------------------|--------------------------|
| A. Territory of the active forces | 1. before the folding. |
| B. Territories previously folded | 2. after slight folding. |
| C. Territory of the young sediments | 3. after strong folding. |

Fig. 3.

The movement towards each other of the old, already folded remains of the mountains may, in my opinion, be explained by tangential, but also by centripetal movements. In the former case we

can imagine, that the remains of the mountains are firmly united with the actively working zone, in the second case we need not make this supposition.

Only if we admit, that the active forces do not lie in the folded beds themselves, the use of compressive machines is allowed in the experimental tectonics, for there the folded beds are likewise passive during the folding.

Amsterdam, January 16, 1912.

B. G. ESCHER.

Astronomy. — “*Star systems and the Milky Way*”. By Prof. J. C. KAPTEYN.

(Communicated in the meeting of January 27, 1912).

In the November-meeting of last year, I tried to show that there is an evident relation between the Milky Way and the star-streams. The relation consists in the fact, that the motion in the great star-streams *relatively to the centre of gravity of the whole system* is perfectly, or very nearly, parallel to the plane of the Milky Way. This is true separately for the stars of the *B*, *A*, and *G* types. Consequently it is true also for the relative motion of these several streams and it was this relative motion which was then particularly considered.

I have found since that this approximate parallelism with the plane of the Milky Way subsists for the motion of *all* the somewhat rich systems for which sufficient data are available.

Relatively to the centre of gravity of the whole system let:

h = yearly linear motion of the solar system;

β = galactic latitude of the Apex of this motion;

V = yearly linear motion of a determined stargroup;

B = galactic latitude of the true vertex (convergent);

and furthermore, *relatively to the solar system*:

r = yearly linear motion of this same group:

b = galactic latitude of the apparent vertex (convergent).

Then r is the resultant of V and $-h$.

Therefore, if we project on the normal to the Milky Way,

$$r \sin b = V \sin B - h \sin \beta \quad (1)$$

For the coordinates of the Apex let us adopt:

$$\alpha = 269^{\circ} \quad \sigma = + 32^{\circ}, \text{ consequently } \beta = + 23^{\circ}.$$

For h the best available value must be that which CAMPBELL has

produced from his rich — unfortunately to other astronomers still inaccessible — storehouse of radial velocities:

$$h = 19.5 \text{ kil. p. sec.}$$

The equation (1) thus becomes:

$$r \sin b = -7.6 + V \sin B. \quad . \quad . \quad . \quad (2)$$

For those groups for which our present data are more or less reliable we find the following values of r , resp. $r \sin b$. I add the values of $V \sin B$, furnished by (2), i. e. the component of the true velocity at right angles to the Milky Way.

Group	r	$r \sin b$	$V \sin B$
Hyades	45.6	— 3.4 kil.	+ 4.2
Ursa Major	18.4	— 11.1	— 3.5
Scorp-Centaur	18.8	— 6.7	+ 0.9
Perseus	18.0	— 4.1	+ 3.5
G I	32.6	— 8.4	— 0.8
A I	27.7	— 6.0 ^s	+ 1.5 ^s
He I	22.0	— 6.7 ^s	+ 0.8 ^s
G II	18.4	— 8.5	— 0.9
A II	24.5	— 10.2 ^s	— 2.6 ^s
		— 7.25	+ 0.35

The uncertainty

a in the position of the vertices;

b in the group velocities r ;

c in the direction and amount of the sun's velocity;

d in the position of the Milky Way,

is still considerable. Presumably the values found for $V \sin B$ are *not* or *hardly* greater than their uncertainty. They are smallest for the best determined groups.

This result, if confirmed by further observation, must be of great importance for the investigation *in detail* of the cosmic motions. For it would enable us to find out all the elements of the stream-motion of any small local group of stars showing common proper motion. We might thus hope to find out any differences in the motion of parts of the stellar system situated in different quarters of the sky or at different distances.

As an example take the *Pleiades*.

I find *six* stars for which the radial velocity has been measured. In the mean of all we get:

α 1900	δ 1900	μ	p	q corrected
$8^h 40^m$	$+ 23^\circ 53'$	$0''053$	158°	$+ 5.5$ kil p.s.

in which μ represents the total proper motion, p its angle of position, q the corrected radial velocity. Direct observation gave $+9.8$ for this velocity, but the Pleiades are Helium stars and it has been found that these require a correction of -4.3 kil. p. sec. which not improbably may be due to pressure shift. By the use of the just mentioned working hypothesis that the true motion is parallel to the Milky Way, I derive from these data:

Direction of the motion (relatively to the sun) towards the point of the sphere $5^h 28^m - 38^\circ 7'$; stream-velocity 15.0 kil. p. sec.; parallax $0''018$, consequently distance 181 light-years.

In addition to my communication at the November meeting, I wish to draw attention to two more facts which seem hardly reconcilable with EDDINGTON'S theory.

1st. The fact that according to EDDINGTON'S and our own determinations, neither do the elements of stream II for the *A* stars coincide with those of the *G* stars, nor are they intermediate between these and the elements of the *B* stream.

2nd. The fact that, according to a provisional investigation, the average value of the radial velocities of the *A*, *F*, *G*, *K*-stars with insensible astronomical proper motion, corrected for the sun's motion through space and taken all positively, does not coincide with and is much in excess of that for the helium-stars. This result, if it is further confirmed, would at least prove that, even in the regions of space more remote than the bulk of our helium-stars, the motion of the stars is still dependent on their spectral class.

It seems desirable to wait for some additional materials which will very soon be available, before discussing these points further.

Finally, in order to prevent misconception, it may be well to remark that, where I concluded to *expansion* of matter, I meant expansion in a determined direction.

Such an expansion does not in the least exclude contraction in other directions. On the contrary. In my opinion there is good reason to assume that the kinetic energy of the system is increasing. If this is the case and if there is no action from without, we cannot but admit contraction of some sort.

Botany. — “*On the cell-wall of Closterium together with a consideration of the growth of the cell-wall in general.*” By Prof. C. VAN WISSELINGH. (Communicated by Prof. J. W. MOLL).

(Communicated in the meeting of January 27, 1911).

Investigations of FISCHER, HAUPTFLEISCH, and LÜTKEMÜLLER.

Although the interesting Closteria, which occur commonly in ditches and pools, have frequently been investigated, yet only a small number of investigators have studied in detail the structure of the cell-wall in Closterium, the cell-division and growth in their mutual relationship. There are only three prominent investigators, namely, FISCHER¹⁾, HAUPTFLEISCH²⁾, and LÜTKEMÜLLER³⁾. Their publications give evidence of serious investigation.

Some time ago when I studied karyokinesis in Closterium Ehrenbergii Menegh. and Closterium acerosum (Schrank) Ehrenb., the cell-walls with their peculiar appearance also attracted my attention, and consequently I studied the work of the investigators mentioned above. But their explanations did not satisfy me, and hence I also made a special study of the structure of the cell-wall, the cell-division and the growth in both these species.

I will briefly mention the most important results of the three investigators referred to. LÜTKEMÜLLER succeeded in distinguishing two layers in the thin wall of Closterium, an inner one, which showed a distinct cellulose-reaction with iodine and sulphuric acid, and an outer one which only gave a weak cellulose-reaction or none at all. LÜTKEMÜLLER also showed that whenever the cell-wall is coloured yellow or brown in consequence of an iron content, the outer layer must be considered to be that which contains the iron.

As is well known, Closteria mostly show a peculiar marking of the cell-wall, namely longitudinal lines, dots, and transverse lines. According to HAUPTFLEISCH and LÜTKEMÜLLER the longitudinal lines are caused by the presence of delicate alternating ribs and furrows. In HAUPTFLEISCH's opinion what presents the appearance of a dot, is in reality a depression or pit in the cell-wall, and he holds that, in addition, real pores occur in the cell-wall, namely, at the ends

1) A. FISCHER, Ueber die Zellteilung der Closterien, Bot. Zeitung, 1883, No. 14, p. 225.

2) P. HAUPTFLEISCH, Zellmembran und Hüllgallerte der Desmidiaceen, Inaug. Dissert. 1888.

3) J. LÜTKEMÜLLER, Die Zellmembran der Desmidiaceen, Beiträge zur Biologie der Pflanzen, 8. Bd. 1902, p. 347.

of the cells where, according to KLEBS¹⁾, they are of great importance to the mucilage secretion and movement of *Closterium*. LÜTKEMÜLLER does not mention any depressions or pits in the wall; in his opinion the wall possesses real pores.

The transverse lines are limited in number. They mostly occur only in the middle of the cell: sometimes there is only one: sometimes several are present. According to the investigators mentioned, there is found in the so-called belted *Closteria*, in addition to the lines in the middle, a transverse line at a relatively great distance from the middle, about half way between the middle and the end of the cell, in one, or, as more often happens, in both halves of the cell. LÜTKEMÜLLER states that pores are absent from the parts where the transverse lines occur. According to HAUPTFLEISCH the arrangement of the transverse lines in the different species is so constant that they can very well serve for the systematic classification of the genus *Closterium*.

In the opinion of the three investigators the transverse lines show where the different parts constituting the cell-wall come into contact. For all three hold that the wall of *Closterium* consists of pieces of membrane of differing length. According to HAUPTFLEISCH and LÜTKEMÜLLER the pieces of membrane fit into each other with oblique, bevelled edges. These pieces of membrane have been given different names. The small circular pieces in the middle of the cell are called by HAUPTFLEISCH and LÜTKEMÜLLER "Querbinden" (transverse bands), the large end pieces "Schalen" shells and the large cylindrical pieces between the "Querbinden" and "Schalen" which occur in the belted *Closteria*, are called "Gürtelbänder" (belts).

The same three writers hold that the transverse lines arise through two different processes, namely, by cell-division and by a process to which FISCHER has given the name "periodisches Ergänzungswachstum" and which depends on the intercalation of a new cylindrical piece of membrane. In the cell-division "Querbinden" and transverse lines arise in the middle of the cells; in the "periodisches Ergänzungswachstum" "Gürtelbänder" and also the transverse lines between the middle and the ends of the cells are formed. In some respects the conclusions of the three investigators differ from one another. FISCHER assumes that before the beginning of the formation of the transverse wall begins, the cell of *Closterium* constricts itself somewhat in the middle and that soon after that on the right and left of the constriction a circular tear appears in the wall and that the

¹⁾ G. KLEBS, Ueber Bewegung und Schleimbildung der Desmidiaceen, Biologisches Centralblatt, V. Bd. Nr. 12, 1885, p. 353.

wall opens. Thus two circular openings would arise. On the short circular piece of membrane which has been cut out, the formation of the transverse wall begins which grows further inwards until the protoplast is divided into two. Whenever the cell of *Closterium* divides into two daughter-cells, the transverse wall splits and the short, dissected piece of membrane to which the transverse wall is attached. The process begins at the periphery and continues inwards. The walls of the new cell-halves, arisen by fission of the transverse wall, grow out rapidly during and after the fission.

In HAUPTFLEISCH'S opinion the cell-division in *Closterium* does not always take place in the same way. He distinguishes between species of *Closterium* with and without "Querbinden". In the latter in cell-division the two shells separate somewhat and a new, very short cylindrical piece of membrane becomes intercalated. On this new piece of membrane the transverse wall appears which grows forward in the manner described above. In the *Closteria* with "Querbinden" the two shells do not separate but a circular tear appears in the younger shell close to the older one. Where the tear has appeared, the wall opens and a very short cylindrical piece of membrane becomes intercalated. On this new piece of membrane the transverse wall appears. The further process of cell-division takes place in both species in a corresponding manner. In fission the short, cylindrical piece of membrane is first divided into two, and after that fission of the transverse wall begins, which process continues inwards. When the cell-division is completed, the new cell-halves develop to their normal growth.

LÜTKEMÜLLER calls attention to the fact that the place where the cell-division is to take place, is already indicated in advance. This place is in the younger half-cell close to the older one, and there is a feebly marked fold at this place in the cell-wall, called "Ringfurehe" by LÜTKEMÜLLER. The only transverse line, which the younger cell-half shows, is caused by this fold. It is only absent in very young cell-halves, in which the wall is not yet completely developed. At the point of the "Ringfurehe" the cell-wall broadens out somewhat and the transverse wall appears, which grows inwards until the protoplast is divided into two. Then the transverse wall splits, whilst the cylindrical membrane tears, at the point at which the transverse wall is attached. From each half of the transverse wall a new membrane-half arises. LÜTKEMÜLLER does not believe that in cell-division the cell-wall opens, through the formation of one or two circular tears. Nevertheless he agrees with HAUPTFLEISCH that cell-division leads to a union of younger and older parts of the cell-wall, that these

parts fit into each other with bevelled edges and that the older part of the cell-wall overlaps the younger.

The three investigators have arrived at the following results with regard to the origin of "Gürtelbänder" (belts). According to FISCHER after the cell-division of belted Closteria the new cell-half is not yet similar to the old one; it consists only of a shell piece and as yet possesses no belt; in the new half-cell at a little distance from its base intercalation of a cylindrical piece of membrane takes place, which develops into the belt of the new half-cell. In this process a circular tear also appears and the wall itself opens at the place where the new piece is intercalated. The description, which HAUPTFLEISCH gives, of the formation of the belts, agrees in the main with that of FISCHER. In LÜTKEMÜLLER'S opinion no tear appears near the base of the wall of the new half-cell, but a fold of the cell-wall (Ringfurche) develops, which grows into a cylindrical piece of membrane, namely the belt.

The present investigation.

Attention may be directed to the following points which concern the methods of investigation I have followed. I employed living as well as fixed material. As fixing solutions FLEMMING'S mixture (osmic acid 0.5, chromic acid 0.9, glacial acetic acid 6, water 120 and absolute alcohol were used. The fixed and the fresh material were treated with different reagents, such as a solution of chromic acid (from 20 to 50 %), SCHULTZE'S macerating fluid (warming with potassium chlorate and nitric acid), iodine in potassium iodide solution and slightly diluted sulphuric acid (of 76 % and of 85 $\frac{1}{2}$ %, 4 parts by weight of 95 % to 1 part by weight of water and 9 parts by weight of 95 % to 1 part by weight of water); the Algae were also warmed in glycerine to 300°, and stains were also employed, especially ruthenium red in a weak solution of ammonia. Generally different methods of investigation were combined.

The Closteria were grown in ditch-water, not only in wide-mouthed bottles and in dishes but also separately on microscope slides. In the latter case they were examined daily, and in that way various measurements were obtained; finally they were treated with reagents in order to determine exactly what changes the cell-wall had undergone.

The following pages will principally be devoted to an account of the results obtained in this inquiry, whilst I intend to explain the foundations on which they rest more completely elsewhere.

In the first place it must be pointed out that I cannot agree with the view of FISCHER, HAUPTFLEISCH, and LÜTKEMÜLLER according to which in *Closterium* the cell-wall is composed of various pieces of membrane joined together (Schalstücke, Querbinden, Gürtelbänder) which fit into each other with sharp edges and have been formed separately at various times by the protoplasm. On the contrary, I have come to the conclusion that the wall of *Closterium* must be regarded as one whole. It is composed of various superposed layers. The innermost enclose the whole protoplast, whilst the outermost only partly cover the underlying ones. In agreement with this the cell-wall is not everywhere equally thick. It does not arise piecemeal, but develops as a whole from the protoplast, out of which layers of cell-wall successively originate. The transverse lines show the parts where the older layers, which only partly cover the younger ones, cease. By using reagents it is easy to show that the innermost part of the cell-wall, which is rich in cellulose, uninterruptedly encloses the whole protoplast. It already follows from this fact, which escaped the attention of earlier investigators, that the cell-wall does not consist of separate parts.

The innermost layers of the cell-wall are the youngest and the richest in cellulose, the outermost are older and in them the cellulose-content is greatly diminished. Using iodine in potassium iodide solution and slightly diluted sulphuric acid the stratified structure of the cell-wall and the differing cellulose-content of the innermost and outermost layers are clearly seen. The cell-wall swells considerably on being treated with sulphuric acid, especially the outermost part, whilst the cells as a whole contract. In the presence of iodine the wall is at the same time coloured blue. The innermost part that extends uninterruptedly along the whole protoplast, becomes dark-blue. The outermost layer gives no cellulose reaction; it is stained yellow by iodine and extends continuously over all the layers of the cell-wall. Between the innermost part of the cell-wall which is rich in cellulose and the yellow-stained peripheral layer, lies a portion poor in cellulose which takes only a light blue stain. In *Closterium acerosum* there is sometimes no cellulose-reaction at all to be observed directly under the peripheral layer.

With some preparations, it can be seen that the innermost part of the cell-wall, rich in cellulose, as well as the outermost part which is poor in cellulose, consist of different layers. Evidently the layers, in proportion to their age, undergo a chemical modification; the cellulose-content becomes smaller; the cellulose gives place to a material which gives no cellulose-reaction and the tendency to swell

up considerably in sulphuric acid increases. Also to some extent a coalescence of the layers takes place. In the outer portion they are not so easy to distinguish as sometimes in the inner portion.

In the outermost layer, which is stained yellow by iodine, another modification has moreover evidently taken place, in which more external factors have come into play. Transverse lines are clearly seen on the cell-wall after treatment with iodine and sulphuric acid. The older layers which lie over the younger ones project somewhat and at the base of the older layers the underlying younger ones are poorer in cellulose; the wall there is more subject to modification; in consequence of this the blue-coloured wall shows light lines along the older layers, which project somewhat.

With respect to the dots and the longitudinal stripes, I observe that I could see them best with different focussing. The dots were then most clearly seen on the outermost part of the cell-wall and the longitudinal stripes in the innermost part of it. This observation is not in agreement with the view of LÜTKEMÜLLER, in whose opinion the dots were produced by pores, but it is more in accordance with that of HAUPTFLEISCH, who speaks of depressions or pits. The fact that the lines are most clearly visible in the innermost part of the wall is hard to reconcile with the view of the investigators who maintain that the wall is provided with peripheral ribs and furrows. I may remark with respect to *Closterium acerosum* that the dots are absent from the parts where the transverse lines occur.

Like LÜTKEMÜLLER I am of opinion that the part where cell-division is to take place is already indicated beforehand on the cell-wall. The cell-wall there shows a pronounced modification. In my opinion, LÜTKEMÜLLER's explanation of the phenomenon is, however, not tenable. According to this author, the cell-wall forms, at the place of division, a small fold directed inwards, so that there appears to be a slight thickening on the inner side and on the outer side a furrow (Ring-furche). LÜTKEMÜLLER obtained his results with dead material. With fixed and other dead material I also have observed at the place of division a little fold in the cell-wall, but never with living material, and hence I do not think that in living specimens any fold of the cell-wall occurs at the place of division. My own conviction is that the cell-wall in the part under discussion has undergone an important change. It shows there a transverse line which can be distinguished from the other transverse lines. The cell-wall at the altered place is poorer in cellulose and less strong. After treatment with iodine and somewhat diluted sulphuric acid a light line can be noticed. During treatment with reagents (chromic acid) it often happens that

the cell-wall tears at the place of division. The little fold seen in dead material is also probably connected with the fact that the cell-wall at the place of division is less strong.

It is easy to answer the question why no fold is to be observed in living material. During life the wall is stretched by turgor, so that no fold is to be expected. To this I must add that in fixed material I have sometimes seen much larger folds of the cell-wall, namely, in the younger, still thin walled half of the membrane. The cell-wall then showed a triple circular fold. In living material such folds do not occur either. This strengthened my belief that the little fold also first appears after death.

In connection with the fact that in *Closterium* the part at which cell-division is to take place is determined beforehand and that at this place the cell-wall shows a marked modification, I will here describe results which I obtained formerly with *Spirogyra*. As in *Closterium*, so in *Spirogyra* the formation of the primary transverse wall begins on the membrane cylinder opposite the nucleus and then continues inwards, until the protoplast is divided into two. In *Spirogyra*, the part where the formation of the transverse wall is to begin, does not show special characters in the cell-wall, yet by a series of centrifugal experiments I¹⁾ have proved that the place is already determined before the beginning of the nuclear-division, by the influence which the nucleus exerts. I am inclined to attribute the like kind of influence to the nucleus of *Closterium*. The important modification of the cell-wall at the place of division in *Closterium* is connected with the subsequent separation of the daughter-cells.

In *Closterium* I could demonstrate no cellulose in the primary transverse wall. It is characterised by a greater solubility in chromic acid solution. When the primary wall has been formed, a layer of cell-wall; rich in cellulose is produced in each daughter-cell; it surrounds the whole protoplast and covers the old cell-wall and the primary transverse wall. This new layer of the cell-wall is produced by apposition. Results in agreement with this were earlier obtained by me with *Spirogyra*.²⁾

In *Closterium* a fission of the cell-wall follows the thickening of the primary transverse wall. At the modified part the old cell-wall is stretched until it tears asunder and then the transverse wall splits. It is the primary transverse wall which splits. The process begins

¹⁾ Zur Physiologie der Spirogyrazelle, Beihefte zum Bot. Centralbl. Bd. XXIV (1908), Abt. I. p. 165.

²⁾ Over wandvorming bij kernlooze cellen, Reprint, Bot. Jaarboek, Vol. 13, 1904, p. 11 and 12. Zur Physiologie der Spirogyrazelle, l. c. p. 174.

on the old cell-wall and continues inwards. At the place of division a slight constriction occurs which slowly becomes more marked. It is peculiar that the new part of the cell-wall which is thus exposed, i.e. the split transverse wall, shows a sharp contour in contradistinction to the old cell-wall, and this is probably to be ascribed to the fact that the old wall is more modified chemically. The two halves of the transverse wall assume during fission a convex position with regard to each other; finally they separate. In the fission of the cell-wall which is induced by a chemical modification, turgor also plays an important part. Without the action of turgor it is difficult to imagine that the thin halves of the transverse wall could take up a convex position with regard to one another. Through the same force which brings this about, the old wall tears at the modified weak part and the transverse wall splits.

Nothing can be traced of the occurrence of circular openings (FISCHER, HAUPTFLEISCH) in the old cell-wall and of intercalation of a new, narrow annular piece of membrane which projects (FISCHER). When the old wall tears each daughter-cell has already a new wall, so that when cell-division proceeds normally, no openings can arise in the cell-wall. The occurrence of openings in the wall is moreover hardly tenable. As a consequence of turgor the protoplasm would pass out and a speedy death of the protoplasm might be expected. PRINGSHEIM¹⁾ has also previously assumed that in the cell-division of *Oedogonium* the wall opens by means of a circular tear, but later investigations have shown that this does not take place in *Oedogonium*.²⁾

When the cell-division is finished, the halves of the transverse wall grow out quickly to the new halves of the cell-wall. These soon approximate in shape and size to the old halves of the cell-wall. The wall of the young halves is at first very thin. Later the difference in thickness between the new and the old half becomes smaller, sometimes indeed it is no longer of any significance. Chemical modification seems to take place quickly in the new halves of the cell-wall. Quite soon with iodine and slightly diluted sulphuric acid the thin peripheral layer which is stained yellow, can be distinguished, as well as the subjacent layer poor in cellulose and the innermost layer which is rich in cellulose. When the daughter-cells are still connected, the peripheral layer can already be demonstrated. When the wall becomes older and thicker, the peculiar markings on it become visible, namely

1) N. PRINGSHEIM, *Morphologie der Oedogonien*, 1858, Pringsheims Jahrb. f. wiss. Botanik Bd. I. p. 13.

2) C. VAN WISSELIINGH, *Über den Ring und die Zellwand bei Oedogonium*, Beihefte zum Bot. Centralbl. 21. XXIII (1908), Abt. I. p. 182.

the longitudinal lines and in *Closterium acerosum* also the dots. It has already been stated above that the chemical modification also causes the disappearance of the dots at the place of the future cell-division. Consequently the old cell-wall has no dots round its edge. While the new membrane-half acquires dots, no new ones develop at the part where they have disappeared. In consequence there occurs on the border of the old and new membrane-half, a small strip free from dots.

With regard to the question how the growth of the cell-wall in *Closterium* must be interpreted, the following remarks may be made. Apposition, addition of new layers of cell-wall substance must certainly be assumed. This is in agreement with the stratified structure of the cell-wall and also with some observations concerning its development. How, for example, can the existence of the layer of the cell-wall rich in cellulose in the daughter-cells after the formation of the primary transverse wall be explained without accepting apposition? For one cannot believe that one and the same layer at one place develops by intussusception from the primary transverse wall which contains no cellulose and in another part develops from the old cell-wall. Less easy to answer is the question whether in *Closterium* intussusception, intercalation of new material in the already formed cell-wall, takes place. Superficial observation might cause the impression that intussusception is very probable on account of the rapid surface growth of the thin wall of the new cell-half. I do not think, however, that it is necessary to postulate intussusception in the case of *Closterium*. Nevertheless the growth of the cell-wall cannot be completely explained by apposition. There is no doubt that in the development of the cell-wall an important modification takes place in the layers already formed by apposition. The new layers rich in cellulose are produced by apposition on the inner side of the cell-wall. Slowly they become poorer in cellulose and richer in a substance which does not give a cellulose reaction. In agreement with this layers rich in cellulose are found on the inner side of the cell-wall and others poor in cellulose and free from it are found on the periphery. The chemical modification makes the wall more extensible, consequently turgor can contribute to the increased size of the cell. In order that the wall may retain its required strength, it must be strengthened on the inner side by new layers. From this it follows, that by rapid surface growth as in the case of the new membrane halves, chemical modification and apposition must also be intensive. I believe that apposition is considerably stronger in the new membrane halves than in the old ones, for

when the surface growth of the new halves ceases, probably in consequence of the increase in volume of the cell and resultant decrease in turgor, then especially a growth in thickness occurs and the difference in thickness between the two halves of the wall becomes much less.

A study of cell division in *Closterium* makes it specially clear that in the development of the cell-wall, chemical modification is of great significance. At the place of the cell-division chemical modification of the cell-wall is very extensive; it here produces not only stretching of the cell-wall, but even the tearing asunder of the old cell-wall.

Apposition of new cell-substance, chemical modification of that already formed and finally turgor are the three important factors in the development of the cell-wall in *Closterium*. With respect to intussusception, its occurrence can neither be proved nor disproved. It is not necessary to accept it in order to explain the development of the wall in *Closterium*.

The conflict between the adherents of the intussusception theory and those favouring the apposition theory of growth of the cell-wall has in my opinion formerly often been so unproductive because the chemical nature of the cell-wall and especially the chemical modification which it undergoes has received little or no attention. Neither apposition nor intussusception can alone completely explain the development of the cell-wall.

When the "Urmeristem" of a vegetation-point is compared with the "Dauergewebe" of the adult organ which arises from it, it is impossible with the help of the intussusception- or apposition-theory to form a conception of the growth of the cell-walls and even, when one accepts both processes, no satisfactory explanation of the development of the cell-walls and tissues results. If, however, continuous chemical modification, as well as apposition, is assumed, then the explanation of the phenomena observed does not any longer present insurmountable difficulties. It may now be accepted with certainty that the stratified composition of the cell-wall has its origin in the fact that on the inner side layers are successively formed by the protoplasm, which layers cover one another. If these layers underwent no chemical modification, it could not be explained why, for example, the outermost layers of the cell-wall of many parenchymatous bark-cells show a much weaker cellulose-reaction than the innermost-layers and sometimes seem to be quite devoid of cellulose content. Where the cells are in contact with intercellular spaces, one can sometimes observe that the outermost of the layers containing cellulose have been modified to a varying extent, so that the self-

same layers in one place still show cellulose reaction and in another place do not. In some tissues it appears as if the cells in agreement with the old conception are imbedded in intercellular substance. Frequently it is no longer possible in adult tissue to recognise sister-cells, although this would present no great difficulty if no modification of the cell-wall had taken place. It can easily be imagined that by chemical modification of the cell-walls the relationship of cells is effaced.

Although I am inclined to believe that generally apposition, modification and turgor play a great part in the growth of cell-walls, yet I also think that intussusception is not always excluded; thus for example, in the cuticularisation of cell-walls containing cellulose it is necessary to assume intussusception.¹⁾

In *Closterium*, no growth in length of any importance can be observed in either the old or the new full grown halves of the wall; nevertheless a considerable increase in length can frequently be noted in some individuals. The phenomenon is caused by a process which investigators have called "periodisches Ergänzungswachstum". It amounts to an addition to the cell-wall of new pieces of membrane. Opposite the nucleus, the cell-wall undergoes a modification, which is similar to that which happens to the cell-wall before cell-division. At the modified part the cell-wall becomes stretched, whilst on the inner side it becomes strengthened by new layers through apposition. The old layers of the cell-wall finally tear asunder and the underlying new cell-wall is exposed. It shows a sharp outline just as the cell-wall which was laid bare in cell-division. Whilst the thin, new, weaker piece of the wall is stretched by the influence of turgor, the cell-wall becomes strengthened on its inner side by apposition. In this manner a whole new piece of wall is intercalated. An opening of the cell-wall, as FISCHER and HAUPTFLEISCH maintain, takes place no more than in cell-division, for, when the old layers are torn asunder, a new wall is already present. After intercalation of a new piece, the cell-wall shows two new transverse lines. The walls of the older cell-halves are thicker and project somewhat.

Between cell-division and intercalation of a new, cylindrical piece of membrane there are some important points of agreement. The process in both cases is induced by a modification of the old cell-wall, which finally tears asunder, after a new cell-wall has been formed. In both cases, rapid surface growth of the newly exposed parts of

¹⁾ C. VAN WISSELINGH, Over Cuticularisatie en Cutine. Reprint from the Proc. Koninkl. Akad. v. Wetensch. Amsterdam, 2nd Sect. D. III, N^o. 8, p. 26. Sur la cuticularisation et la cutine, Extrait des Arch. Néerl. T. XXVIII, p. 32.

the cell-wall takes place. The processes take place at the same places in both cases, namely opposite the nucleus in the younger half of the cell near the older half or in the middle of a new intercalated cylindrical piece of membrane also opposite the nucleus, always therefore in parts where the cell-wall is younger and thinner. Cell-division is distinguished from intercalation in that it is accompanied by division of the nucleus and the formation of a transverse wall.

It has been stated above that the intercalation of a new, cylindrical piece of membrane can also take place in a similar piece of membrane which has already been intercalated. This process can therefore be repeated in one and the same cell. Cell-divisions and intercalation of pieces of cell-wall are not processes which regularly alternate in a certain group of Closteria (belted Closteria), as the three investigators already mentioned have imagined. In the species I have studied both processes occur; sometimes there are 10 or more successive cell-divisions without any intercalation. It may also happen that after repeated cell-divisions intercalation of a new piece of membrane takes place a few times in succession. The name "periodisches Ergänzungswachstum" is not correct.

As already described, the transverse lines which the cell-wall shows; arise by cell-division and by intercalation of new pieces of cell wall. As LÜTKEMÜLLER has observed the young individuals which arise from spores originally possess not a single transverse line and later one transverse line only at the place of future cell-division. At this stage one cannot therefore distinguish an older and a younger cell-half, but this is possible in the daughter-cells, where the cellwall at the border between them shows a transverse line, whilst later the young cell-half at the place of division also shows a transverse line which can be distinguished from the first-mentioned one. At each cell-division there is cut off from the wall of the younger cell-half a short piece, which remains connected with the older one. The daughter-cell with the oldest half of the cell wall possesses after each cell-division a strip more than its mother-cell. In this way cells with 10 or more median transverse lines can be formed.

By intercalation of pieces of membrane cells arise which show transverse lines at a considerable distance from the middle. It must be borne in mind that the two processes can alternate with each other in various ways, that the pieces of membrane which in cell-division are cut off from the younger half may be of different sizes, that the mother-cell in cell-division is frequently divided into two unequal parts, that intercalated pieces of membrane can grow to different lengths and that in general, in proportion as the parts of cell-wall

are older, they are also thicker and the marking on the cell-wall is more distinct. Moreover the growth in thickness of some parts of the cell-wall sometimes shows abnormalities, so that it may happen that younger parts have thicker walls than older ones and give a stronger cellulose-reaction (sometimes in *Closterium Ehrenbergii*). When all this is taken into account, it is clear that the cell-wall in *Closterium* even in one and the same species shows an enormous diversity, especially with respect to the number and position of the transverse lines or the length of the parts of the cell-wall and the thickness of the cell-wall in different parts. For this reason I cannot agree with HAUPTFLEISCH that the arrangement of the transverse lines in different species is so constant that they can serve for the systematic classification of the genus *Closterium*.

Chemistry. — “On the system: Water — Alcohol — Manganous sulphate.” By Prof. F. A. H. SCHREINEMAKERS and Dr. J. J. B. DEUSS.

(Communicated in the meeting of January 27, 1912).

The equilibria occurring in this system are represented in fig. 1; the points *W* and *A* indicate the components water and alcohol, the third apex of the components-triangle which is not drawn here therefore represents the $MnSO_4$. The temperature axis is taken perpendicular to the plane of the components-triangle.

The curve *hl* situated in the side plane $MnSO_4 - A - T$ of the prism is the solubility line of the anhydrous $MnSO_4$ in absolute alcohol; as this salt is practically insoluble in absolute alcohol the curve *hl* must lie in very close proximity to the axis *AT* of the prism.

The equilibria occurring in the binary system: water — $MnSO_4$

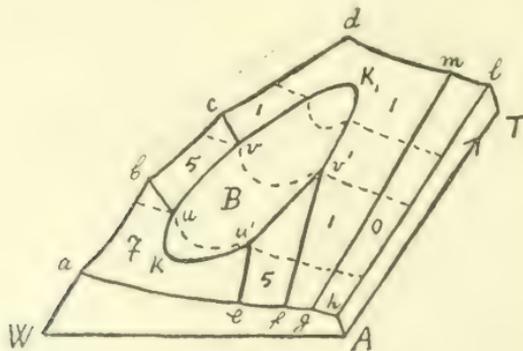


FIG. 1.

have been investigated by F. G. COTTRELL¹); these equilibria, so far as they are required in the ternary system are represented in fig. 1 by the curves *ab*, *bc*, and *cd* situated in the side plane $MnSO_4$ — W — T .

The curve *ab* indicates the solutions saturated with $MnSO_4 \cdot 7 H_2O$, the curve *bc* those saturated with $MnSO_4 \cdot 5 H_2O$ and the curve *cd* the solutions saturated with $MnSO_4 \cdot H_2O$.

The equilibria occurring in the ternary system are represented by the surfaces situated within the prism, their intersecting lines and intersecting points:

<i>abuku'e</i>	is the saturation surface of the	$MnSO_4 \cdot 7 H_2O$
<i>efv'u'</i> and <i>bcvu</i>	„ „ „ „ „ „	$MnSO_4 \cdot 5 H_2O$
<i>fgmdcvk_1v'</i>	„ „ „ „ „ „	$MnSO_4 \cdot H_2O$
<i>ghln</i>	„ „ „ „ „ „	$MnSO_4$.
<i>kwk_1v'u'</i>	„ „ binodal surface.	

In order to facilitate the survey, the figures 7, 5, 1 and 0 are drawn on the saturation surfaces, and the letter *B* on the binodal surface. For the sake of brevity we will call the salts in future Mn_7 , Mn_5 , Mn_1 and Mn_0 .

The saturation surface of the Mn_5 consists of two parts separated from each other; the one to the left indicates the saturated solutions of Mn_5 rich in water, the one to the right those rich in alcohol.

The binodal surface *B* should be imagined to be divided into two parts by the critical line KK_1 ; with each solution L_1 of the one part, a definite solution L_2 of the other part can be in equilibrium. The binodal surface therefore represents the two-layer systems $L_1 + L_2$.

The intersecting lines of the saturation surfaces of a solid substance form the saturation lines representing the solutions saturated with two salts.

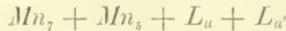
<i>eu'</i> and <i>ub</i>	is the saturation line of	$Mn_7 + Mn_5$
<i>fv'</i> and <i>vc</i>	„ „ „ „ „ „	$Mn_5 + Mn_1$
<i>gm</i>	„ „ „ „ „ „	$Mn_1 + Mn_0$.

The intersecting lines of the binodal surface with the saturation surfaces of the solid substance represent the conjugated liquid-pairs which are saturated with a solid salt. Because as seen in fig. 1 the binodal surface intersects each of the saturation surfaces of Mn_7 , Mn_5 and Mn_1 in two curves, it follows that one series of liquid-pairs is saturated with Mn_7 , another series with Mn_5 and a third series with Mn_1 . In fig. 1 are represented:

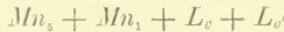
¹) F. G. COTTRELL, Journ. Phys. Chem. 4 637 (1900).

the liquid-pairs saturated with Mn_7 by Ku and Ku'
 " " " " " Mn_5 " wv " $u'v'$
 " " " " " Mn_1 " vK_1 " $v'K_1$

Each of the points u and u' is the intersecting point of the binodal surface with the saturation surfaces of Mn_7 and Mn_5 . These points, therefore represent a liquid pair $L_u + L_{u'}$ saturated at the temperature $T_u = T_{u'}$ with $Mn_7 + Mn_5$ or, in other words, the system:

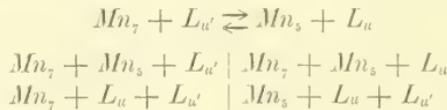


The same is true for the points v and v' which at $T_v = T_{v'}$ represent the two liquids of the equilibrium:



The saturation line of $Mn_7 + Mn_5$ consists (experimentally) of the two parts cu' and ub ; as, however $T_u = T_{u'}$, the complex $Mn_5 + Mn_1 + L$, traverses an uninterrupted temperature series; the solution however, changes its composition abruptly, at $T_u = T_{u'}$, from L_u into $L_{u'}$, or reversedly so. The same is true for the complex $Mn_5 + Mn_1 + L$ in the points v and v' .

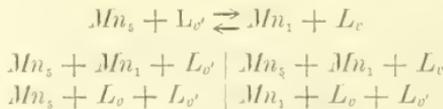
From the composition of the solutions L_u and $L_{u'}$ it follows that at $T_u = T_{u'}$ the reaction:



occurs.

From this reaction it follows that from $T_u = T_{u'}$ one saturation line of $Mn_7 + Mn_5$ must proceed to a lower, and another one to a higher temperature. Further, it follows that the liquid-pairs saturated with Mn_7 occur below and those saturated with Mn_5 above $T_u = T_{u'}$.

From the composition of the solutions L_v and $L_{v'}$ it follows that at $T_v = T_{v'}$ the reaction:



occurs. The situation of the curves proceeding in fig. 1 from the points v and v' is in accordance with this reaction.

From the figure it follows that the dissociation region, if we only consider stable conditions, extends from $T_k = 5,^c3$ to $T_{k_1} = 43.5^\circ$. Between T_k and T_{k_1} a separation into two liquids in the stable condition is possible, below T_k and above T_{k_1} , this is, however, no

longer the case and, as has been confirmed experimentally, only a separation in the metastable condition can take place.

In general the mixtures: water + alcohol + salt, in which the separation only takes place in ternary solutions, exhibit a minimum critical mixing temperature. That is to say that below this critical temperature no dissociation into two liquids can take place; above this temperature, however, decomposition may occur.

For instance, in water-alcohol mixtures KNO_3 can cause dissociation only above 79.5° , NH_4NO_3 only above 67.6° , $(NH_4)_2SO_4$ only above 8° , and Na_2CO_3 only above 27.7° .

Similar systems with a maximum critical temperature, namely with a temperature above which no separation can any longer occur have to our knowledge not yet been found. In the system water-alcohol- $MnSO_4$, however, now investigated by us, not only a minimum critical temperature T_k , but also a maximal critical temperature T_{k_1} seems to exist.

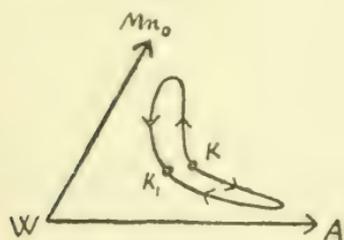


Fig. 2.

If we project the special curve $kuvk_1v'u'$ on the plane of the components-triangle $W-A-MnO$, we obtain something as in fig. 2. The triangle, however, has only been drawn partially in this figure. The projection of the special curve consists of two conjugated branches which form a closed curve of a peculiar form; the arrows indicate the direction in which the temperature increases.

Each of the branches kk_1 must, of course, exhibit a discontinuity in two points corresponding with the temperatures T_u and T_v .

If we intersect the spacial representation by planes perpendicular to the temperature axis, we obtain the isotherms; these have been determined at 50° , 35° , 30° and 25° . A few points of the isotherm of 0° have also been determined.

The isotherm at 50° can be represented schematically by the curves dm and ml and the isotherm of 0° by the curves ae , ef , fg and gh . A few other isotherms are represented in fig. 1 by the dotted curves.

Bio-Chemistry. — “*On the action of some carbon derivatives on the development of penicillium glaucum and their retarding action in connection with solubility in water and in oil.*” By Prof. J. BÖESEKEN and Mr. H. WATERMAN. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of January 27, 1912).

I.

In our previous communication ¹⁾ we have shown that there exists no essential difference between the benzene derivatives investigated by us, as regards their action as retarding, as well as nutrient substances for the penicillium glaucum.

The compounds readily soluble in oil exert a retarding action even in small concentrations, whereas with substances sparingly soluble in oil, this retardation only occurred with higher concentrations, but all these substances *which dissolve fairly readily in water* give, finally, a development although with compounds like salicylic acid, benzoic acid and the toluylic acids, this takes place only with very low concentrations at which a vigorous vegetation is excluded owing to the small total quantity of organic nutriment.

In each case we may take it for granted that all these substances are capable of providing the penicillium with carbon-containing material, if we only take care (by the choice of a fitting concentration) that the organism cannot overload itself with the same.

Our continued investigation has shown that the penicillium is not very particular as to its food, but that it is capable of development in solutions of nearly all the carbon derivatives.

Even chloroform, formic acid, methyl alcohol and carbon tetrachloride, given as exclusive carbon-containing nutriment, cause growth and, therefore, can yield the material from which the penicillium constructs its undoubtedly very complicated system of organic compounds.

Only a few derivatives of the highest oxidation stage of carbon, such as carbon dioxide and urea are unsuitable.

The results are shown in Table I. For the description of the experimental process we refer to the first communication.

If we survey these experiments which have been collected in this table at random from a much greater number, we notice in the first place that by far the greater number, chosen from the most varying groups of organic compounds, can promote the growth.

¹⁾ These Proc. of December 30, 1911, p. 608.

Besides carbon dioxide itself, formaldehyde, pyrene, urea and also the two naphthols cause no development.

As regards formaldehyde we are going to extend the investigation to still lower concentrations; urea is very closely allied to carbon dioxide, and the two naphthols have a particularly favourable division factor oil: water, *while they are still very perceptibly soluble in water.*

In the second place it strikes us that there are some compounds such as palmitic acid, stearic acid, benzene, naphthalene, cetyl alcohol, and olive oil, whose division factor olive oil: water is undoubtedly much larger than that of salicylic acid and benzoic acid and which, evidently, can yet promote the development of the mould.

These substances, however, are distinguished from the above strongly retarding substances (to which belong also the naphthols) by their *extremely sparing solubility in water.*

In order to demonstrate the significance of the rapid dissolving of the substances in water in connection with their nutrient or retarding action, we are obliged to consider the quality of the protoplasmic wall which those substances must traverse in order to be absorbed in the organism. Let it be presupposed that a too large concentration of any substance whatever will cause a retardation of the growth. Without further arguments as to the possible structure of the protoplasmic wall we may well take it for granted that it must not be put on a line with a layer of oil, without further evidence.

So long as it forms a part of the living organism it must be regarded as a wall limited by an aqueous liquid, and therefore as a membrane which, in a certain sense, is protected by a layer of water.

If we were dealing with an oily layer immediately accessible, all substances readily soluble in oil, and particularly those insoluble in water, would penetrate and exert their retarding action.

[On the other hand, substances insoluble in oil would be unable to penetrate and thus serve as a nutriment. This point, which may be connected with the differences existing between lecithin-cholesterol mixtures and true oils, will be disregarded for the present].

This, however, is evidently incorrect, for the higher fatty acids (which are very sparingly soluble in water) naphthalene, cetyl alcohol and olive oil itself, which dissolve in oil freely or very readily, do not act at all retardative on the growth of the *penicillium* and, on the whole, form in the long run a fairly good organic nutriment.

This behaviour may be explained very readily when, as stated above, we suppose that all the substances before they arrive at the protoplasmic wall must traverse a layer of water; the substances very sparingly soluble in water can perform this only in an extremely tardy manner and the concentration of these substances in the protoplasm can, therefore, increase but very slowly. If, when the concentration in the protoplasm is but small the organism can use up these substances — and the penicillium seems capable of this in a very high degree — they may act as an organic nutriment.

The substances which are readily soluble in water but very sparingly soluble in lecithine etc. such as (presumably) succinic acid, glutaric acid etc. will, of course, be prevented by this last property from rapidly overloading the organism. If these can be readily assimilated they will form a good carbon-containing nutriment.

Not merely the great division factor lipid: water marks a substance as a narcotic, but it must be capable of entering rapidly into the organism and, besides a rapid and ready absorption in the protoplasmic wall proper, a decided solubility in water is therefore required ¹⁾.

From this and the previous investigation it follows that from any organic substance devoid of any particularly pronounced basic or acid properties we may predict ²⁾ whether it will exert a strongly retarding action on the growth of lower organisms. If so, it must be (*a*) somewhat soluble in water and (*b*) dissolve considerably more in oil than in water ²⁾.

II.

In order to confirm the results obtained and the conclusions drawn therefrom, by a larger number of experimental data we have extended our investigations over a large number of saturated fatty acids with normal carbon chain.

These offer the great advantage that, in this series of substances we have at disposal a material of which, while retaining analogous chemical properties, the physical characters, so far as the solubility

¹⁾ Whether colloidal solutions must be regarded here as distinct from true solutions must be decided later.

²⁾ This prediction, of course, only relates to aqueous solutions; as soon as much fat is present, for instance in butter, the retarding substance, on account of the large division factor will accumulate in the fat and can only act in a retarding manner for so far it is still present in the water-phase. We will refer to this question later on account of its practical importance.

in water and oil is concerned, undergo from term to term a continuous modification.

The preparations, which we have used, were mostly obtained

TABLE II. Development of the *penicillium* in solutions of $\frac{1}{20}$, $\frac{0}{10}$ potassium phosphate, $\frac{1}{20}$, $\frac{0}{10}$ ammonium chloride and $\frac{1}{30}$, $\frac{0}{10}$ magnesiumsulphate which contain the saturated fatty acids as exclusive organic nutriment.

$T=20^{\circ}-21^{\circ}$; quantity of liquid = 50 c.c.

Compound	N ^o	quant. in mg.		Development after a given number of days			Maxim. development	Remarks
formic acid	1	9	2-	4+	6+	10+	?	small development
	2	45	2-	4-	6?	10?		
	3	91	2-	4-	6-	10-		
acetic acid	4	10	2+	4++	6+++	fairly strong	50-99	acetic acid does not dissolve in olive oil in all proportions
	5	50	2?	4++	6 strong	s'rong		
	6	99	2-	4++ < N ^o 5	6+++	fairly strong		
prop. acid	7	9.5	2+	4+	6++	10++	±48	dissolves in olive oil in all proportions
	8	48	2-	4+	6++ > 7	10++++		
	9	96	2-	4-	6+	10+		
n butyr. acid	10	11	2-	4+	6+	10++	some- what <55	,
	11	55	2-	4-	6+ < 11	10++		
	12	110	2-	4-	6-	10-		
valeric acid (Hexoic) caproic acid	13	8.3	3+	5++	7++	10+++	far below 90.3	,
	14	90.3	3?	5+	7+ slight	10+		
	15	95.4	3-	5+ < 14	7+	10+		
	16	208.4	3-	5?	7?	10-		
	17	221.1	3-	5-	7-	10-		
heptonic acid	18	1 drop	2?	4++	6+++	9 strong	,	
	19	2 drops	2-	4?	6+	9+		
(Octoic) caprylic acid	20	1 drop	2-	4-	6+	9++		2 drops no longer dissolved entirely in water
	21	2 drops	2-	4-	6-	9-		
(Decoic) caprylic acid	22	1 drop	2+	4++	6+++	9 strong		
	23	2 drops	2-	4-	6-	9-		
nonoic acid	24	1 drop	2-	4?	6+	9+		,
	25	2 drops	2-	4-	6-	9-		
(Decoic) capric acid lauric acid myristic acid palmitic acid stearic acid arach. acid cerotic acid	26	very small quantity	+	++	+++	strong	Of the other fatty acids a small quantity no longer dissolves in water. The solubility of palmitic acid and stearic acid in olive oil is still very considerable > 0.4 $\frac{0}{10}$ (of palm. acid > 1)	
	27		+	++	+++	strong		
	28		+	++	+++	+		
	29		2	4	6	9		
	30		+	+	+	+		
	31		+	+	+	not observed		
	32		+	+	+	+		

from KAHLBAUM; of the lower fatty acids the concentration was determined by titration, whereas the higher ones, if perceptibly soluble in water, were weighed out.

In the case of the practically insoluble acids a little of the substance was added; on sterilising they did not perceptibly dissolve. Of the acids soluble in water different concentrations were investigated in order to determine, if possible, the maximum of development.

For the rest, we refer to our first communication.

When, for a moment, we exclude formic acid, we notice that the fatty acids behave exactly as was to be expected from their solubility in water and in oil.

Acetic acid, favoured by its solubility in water, can serve as an exclusive carbon-containing nutriment up to fairly high concentration.

The concentration of maximum growth is situated about as high as with *p*- and *m*-oxybenzoic acid (see previous communication).

With propionic acid, *n*-butyric acid and *n*-valeric acid which are miscible with oil in all proportions, this maximum is situated much lower.

As they dissolve sufficiently in water, they can act either as a nutriment or as a retarding agent according to the concentration.

This is still very plainly perceptible with the acids C_4 to C_9 included; in very low concentration they give an excellent development but very soon, however, the maximum is attained, so that in a very dilute but still saturated solution (<2 drops to 50 cc.) no, or but little, growth takes place.

From capric (Decoic) acid upwards nothing more is noticed of a retarding action. Notwithstanding the undoubtedly very high division factor oil: water they all cause development.

Here, the solubility in water has become so trifling that the organism can no longer absorb the fatty acid rapidly (see previous communication).

As the penicillium can use up this carbon-containing material also, it becomes assimilated before the unfavourable concentration in the organism is arrived at.

As is to be expected, the growth becomes less marked with the increase in the number of carbon atoms (see palmitic compared with lauric acid) *not* owing to a strong decrease of the solubility in the fatty portion of the organism but, in the first place, to the gradual diminution of the solubility in water, which so impedes the entering into the organism that the assimilation can only take place with slight rapidity.

As regards the formic acid, the less favourable development might be due to the hydrogen ions. This, however, is not the case with the smaller concentrations as shown from an investigation as to the retarding action of the H -ions (see later).

It is much more likely that the slow growth is due to the simple construction and the high state of oxidation of this acid. An assimilation in the organism is here attended with grave difficulties.

We, rather, ought to be surprised to find that the *penicillium* is capable of development in a solution of formic acid as sole organic nutrient, of forming spores, etc.

In the higher concentrations this slow assimilation must also play a rôle, because in such a case the organism, not being able to use up the formic acid quickly enough, will be overloaded and the development will cease.

We notice, indeed, that the maximum development is situated much lower than in the case of acetic acid, although the division factor oil: water will, presumably, be smaller.

Summary.

An investigation was instituted as to the influence which certain carbon derivatives, when given as exclusive organic nutriment exert on the growth, and the retardation thereof, of the *penicillium glaucum*.

Here it was shown :

1. That the development may be induced by the majority of the carbon derivatives investigated, which belong to widely different groups of compounds.
2. That the growth takes place readily on compounds fairly soluble in water but not, or but slightly, soluble in oil.
3. That the growth only takes place at very low concentrations in the case of compounds which are more readily soluble in oil than in water, whereas at somewhat more considerable concentrations it is retarded or does not take place at all.
4. That this growth is not considerably interfered with when the solubility in water is exceedingly small even though the solubility in oil be very considerable.
5. That this growth is very weak or imperceptible :
 - a. on compounds nearly insoluble in water,
 - b. on simple highly oxidised compounds such as carbon dioxide, urea and formic acid.
 - c. on some compounds which readily dissolve in oil and are also soluble in water to a not inconsiderable extent, such as the naphthols, carbon tetrachloride, formaldehyde (3).

We have endeavoured to explain these facts by assuming that the organism is protected by a layer of water through which it has to be reached by the nutrient as well as by the retarding substances. In the case of substances soluble in water it will depend mainly on their solubility in fat whether they will penetrate the organism rapidly and eventually overload the same.

a. If they are absolutely insoluble in water they will have neither a nutrient, nor a toxical action.

b. If they are *very* little soluble in water but fairly so in oil (cetyl alcohol, palmitic acid, naphthalene) they will have a nutrient but no toxical action.

c. If they are considerably soluble in water, but still much more so in oil, they can act as a nutrient in small concentrations only; at higher concentrations they cause retardation.

d. If they are readily soluble in water but very little so in oil, they cannot act as a toxical substance, but only as a nutrient.

Finally, we have drawn from this the conclusion that an anti-septic ¹⁾ must have a large division factor oil: water, also a sufficient solubility in the last solvent.

Delft, January 1912.

Org. Chem. Lab. Techn. University.

Astronomy. — "*Calculations concerning the central line of the solar eclipse of April the 17th. 1912 in the Netherlands*".

By Mr. J. WEEDER. (Communicated by Prof. E. F. VAN DE SANDE BAKHUYZEN).

(Communicated in the meeting of January 27, 1912).

Although the central line of a solar eclipse is given in the astronomical ephemerides through many points on the surface of the earth, it may be useful for the observation of the approaching eclipse to communicate a few results which have been calculated for Holland in particular. Owing to the small width of the zone of annularity in Dutch Limburg the data given in the almanacs for this eclipse are not sufficient to predict whether or no a particular place will be situated within this zone; this is obvious as the differences between the different calculations surpass the width of the zone.

This disagreement arises principally from the differences between the geocentric places of the moon which have been adopted for the calculations; the employed values of the ellipticity of the earth have had some influence too.

¹⁾ No strong acid or strong base is meant here, but a chemically-indifferent substance.

For the basis of my computation I have employed the HANSEN-NEWCOMB values, for the longitude, latitude, and parallax of the moon taken from the Berliner Jahrbuch, but with some corrections added to them. The longitudes have been increased with the sum of 1. an empirical correction deduced by Prof. E. F. v. D. S. BAKHUYZEN from NEWCOMB's results of the occultations and from the Greenwich observations up to 1910¹⁾, 2. a few theoretical terms of short period, according to NEWCOMB²⁾ RADAU³⁾ and HILL⁴⁾, partially modified according to E. F. v. D. S. BAKHUYZEN's results from the observations⁴⁾ and 3. the corrections deduced by the latter, dependent on perigee and eccentricity⁵⁾. The corrections to the latitudes proceed partly from those to the longitudes, partly from those to the node and the inclination of the moon's orbit. The deviation in latitude between the centre of gravity of the moon and its centre of figure to the amount of $-1''.00$, incorporated by HANSEN in his tables, I have kept unaltered according to E. F. v. D. S. BAKHUYZEN's investigation⁷⁾. The parallax constant has been increased with $+0''.37$ according to NEWCOMB and BATTERMANN⁸⁾.

The formulae for the moon's places adopted by me are:

$$l = l(B.J.) + (1 + 0.110 \cos g + 0.008 \cos 2g) \cdot \{ + 7''72 + 1''.69 \sin D - 0''.33 \sin 2D - 0''.24 \sin (D + g') + 0''.09 \sin g' + 0''.16 \sin (D - g) - 0''.21 \sin (2D - g) \} - 0''.43 \sin g - 0''.17 \cos g + 1''.28 \sin \{g + 217^\circ + 19.36 (t - 1876.0)\} + 0''.32 \sin \{g + 198^\circ - 9''.67 (t - 1876.0)\} + 0''.45 \sin \Omega \cos g = l(B.J.) + 9''.55$$

$$b = b(B.J.) + \Delta i \times \sin u + (9''.55 - \Delta \Omega) \times 0.09 \cos u = b(B.J.) - 0''.10.$$

$$\pi = \pi(B.J.) + 0''.37.$$

The angles in these formulae, have for the mean time of my computations, 1912 April the 17th 1^h 11^m mean time Berlin, the following values:

mean anomaly of the moon	$g = 278.1^\circ$
" " " " sun	$g' = 103.8$
longitude of the ascending node	$\Omega = 21.4$
angle from node to perigee	$\omega = 93.1$
angle from node to the sun's perigee	$\omega' = 260.0$

1) Proc. Acad. Amsterdam **14** 1912 p. 686 et seq.

2) Investigations of Corrections to HANSEN's Tables of the Moon p. 37 (1876).

3) Annales Paris. Mémoires **21**.

4) Papers Americ. Ephemeris **3** Part 2.

5) Proc. Acad. Amst. **6** 1903 p. 370 et seq. and p. 412 et seq.

6) Ibid.

7) Proc. Acad. Amsterdam **14** 1912 p. 692 et seq.

8) Beobachtungs-Ergebnisse der Königlichen Sternwarte zu Berlin N^o **13** p. 12.

mean elongation of the moon from the sun

$$g + \omega - g' - \omega' = D = 7.4$$

mean longitude of the moon $\text{C} = 32.6$

mean argument of latitude $\text{C} - \Omega = u = 11.2$

In the formula for l , t is expressed in years, here 1912.29; in that for b I have adopted as corrections to the inclination and the longitude of the node

$$\Delta i = - 0''.10$$

$$\Delta \Omega = + 10''.50$$

according to E. F. v. D. S. BAKHUYZEN *Proc. Acad. Amst.* 6 p. 426.

For the ellipticity of the earth I adopted the mean of the values according to HELMERT¹⁾ and to HAYFORD²⁾. My computations have been accomplished with $\log(1 - c) = 9.9985\ 385$ corresponding with the ellipticity 1 : 297,65.

For the calculation of the width of the zone of annularity there is also needed the ratio of the radius of the moon to the equatorial radius of the earth. For this ratio I have employed $\log s = 9.435\ 3888$, which, adopting as mean parallax of the moon $57' 2''.65$, corresponds with a radius of the moon of $15' 32''.68$. The last value, which I take from Prof. E. F. v. D. S. BAKHUYZEN, is founded on the results of heliometric observations (by BESSEL, WICHMANN, and HARTWIG) and of occultations, (some occultations of the Pleiades and those calculated by L. STRUVE and BATTERMANN), the former of which gave $32''.75$, the latter $32''.65$.

The geocentric longitude l , latitude b' and distance of the sun R' and the obliquity of the ecliptic ϵ have been taken from the *Berliner Jahrbuch*; further I adopted AUWERS' value $\Delta' = 15' 59''.63$ for the mean radius of the sun and $8''.80$ for the solar parallax.

Calculation of the central line.

According to HANSEN³⁾ we have the following relations between the co-ordinates of a given place on the surface of the earth and those of the sun and the moon, if these bodies seen from that particular place seem to be in contact with each other.

1) Sitzungsber. Berlin. 1901 p. 328.

2) J. F. HAYFORD, The figure of the earth and isostasy (1909).
Supplementary investigation (1910).

3) P. A. HANSEN, Theorie der Sonnenfinsternisse und verwandten Erscheinungen. Abhandl. d. K. SÄCHS. Ges. d. Wissensch. IV (1858) p. 305—334.

$$\begin{aligned}\Phi_1 &= P \cos h - Q \sin h - \cos \varphi_I \sin (t + \Delta\alpha') = u \sin \theta \\ \Phi_2 &= P \sin h + Q \cos h - \{(1-c) \sin \varphi_I \cos \delta' - \cos \varphi_I \sin \delta' \cos (t + \Delta\alpha')\} = u \cos \theta \\ u &= s \sec f + \{Z - (1-c) \sin \varphi_I \sin \delta' - \cos \varphi_I \cos \delta' \cos (t + \Delta\alpha')\} \operatorname{tg} f.\end{aligned}$$

The factor $1 + x$ which still appears in these formulae of HANSEN and through which the influence of the atmospheric refraction is brought into account, could here be neglected.

In these equations the quantities P , Q , and Z depend in the following way on the co-ordinates of the sun and moon.

$$P = \frac{\cos b \sin (l - \lambda')}{\sin \pi} \quad Q = \frac{\sin (b - \beta')}{\sin \pi} \quad Z = \frac{\cos (b - \beta') \cos (l - \lambda')}{\sin \pi}$$

$$l - \lambda' = (l - l') \left(1 + \frac{\sin 8''.80}{R' \sin \pi} \right) \quad b - \beta' = (b - b') \left(1 + \frac{\sin 8''.80}{R' \sin \pi} \right).$$

The quantities δ' , $\Delta\alpha'$, and h refer to the direction of the straight line between the centres of the sun and moon. The declination of this direction is δ' and if to its right ascension α' we add $\Delta\alpha'$, we obtain the right ascension of the sun. For the point on the celestial sphere whose co-ordinates are α' and δ' , h is the angle between the hour-circle and the circle of latitude. The quantities δ' , $\Delta\alpha'$, and h are calculated from the co-ordinates of the sun and moon and the obliquity of the ecliptic by means of the auxiliary angles da' , d' , and h_0 , in the following way :

$$\begin{aligned}\operatorname{tg} \alpha' &= \cos \varepsilon \operatorname{tg} l' & \delta' &= d' - \frac{P \sin h_0 + Q \cos h_0}{R'} \cdot 8''.80 + b' \cos h_0 \\ \operatorname{tg} d' &= \operatorname{tg} \varepsilon \sin \alpha' & \Delta\alpha' &= \frac{P \cos h_0 - Q \sin h_0}{R' \cos d'} \cdot 8''.80 + b' \frac{\sin h_0}{\cos d'} \\ \sin h_0 &= \sin \varepsilon \cos \alpha' & h &= h_0 + \sin d' (\Delta\alpha').\end{aligned}$$

The quantities φ_I and t depend on the time and the place of observation, since we have

$$\operatorname{tg} \varphi_I = (1-c) \operatorname{tg} \varphi \quad \text{and} \quad t = \tau + \lambda$$

where φ and λ denote the geographical latitude and longitude of the place of observation and τ is the true solar time for that meridian from which λ is reckoned as eastern longitude.

The angle f , which appears in the 3rd of HANSEN'S equations only, is the semi-angle of the cone which is in contact with the sun and the moon; for an apparent external contact the value of f , which we shall denote by f_e , is determined by :

$$\sin f_e = \frac{\sin \Delta' + s \sin 8''.80}{R' \sin \pi - \sin 8''.80} \sin \pi$$

while for an apparent internal contact, the corresponding value f_i is determined by :

$$\sin f_i = -\frac{\sin \Delta' - s \sin 8''.80}{R' \sin \pi - \sin 8''.80} \sin \pi.$$

For other phases of the eclipse the angle f may be determined, when time and place of observation are known, as a third unknown quantity, together with the angles u and θ , from HANSEN'S three fundamental equations¹⁾. By means of this angle the phase of the eclipse is obtained by calculating the quantity m from:

$$\sin m \Delta' = \frac{\sin f}{\sin \pi} (R' \sin \pi - \sin 8''.80) - s \sin 8''.80,$$

and the fraction of the apparent diameter of the sun which is eclipsed by the moon²⁾ will be

$$\frac{1}{2}(1 - m)$$

If we define the angle f as a continuous variable, the three fundamental equations hold good for all phases of the eclipse. The quantities u and θ determine the position of the place of observation relatively to the straight line through the centres of the sun and moon, i. e. to the axis of the shadow-cone; u is the perpendicular distance of the place of observation from this axis and θ is the position-angle of the great circle, parallel to the plane going through the hadow-axis and this place, in the point of the celestial sphere, the co-ordinates of which are α' and δ' .

The central line of an eclipse is the curve on the surface of the earth along which that surface is intersected by the axis of the shadow. Therefore for the points of this line we have $u = 0$, so that the line is determined by the equations $\phi_1 = 0$ and $\phi_2 = 0$, i. e. by:

$$\cos \varphi_f \sin (t + \Delta \alpha') = P \cos h - Q \sin h$$

and

$$(1 - c) \sin \varphi_f \cos \delta' - \cos \varphi_f \sin \delta' \cos (t + \Delta \alpha') = P \sin h + Q \cos h.$$

Suppose the perpendicular distances from all points on the surface of the earth to the plane of the equator to be enlarged in the ratio $1 : \frac{1}{1-c}$, then this surface becomes spherical. By giving corresponding displacements to the centres of the sun and moon we somewhat simplify the problems exclusively regarding the central line.

If the declination of the direction of the axis of the shadow,

¹⁾ In this way we always find two values for the angle f , the sum of which is equal to the apparent diameter of the moon with negative sign. We have always to take the greater of the two.

²⁾ For annular as well as for total phases the physical interpretation of the expression $\frac{1}{2}(1-m)$ is no longer the same.

now also altered, is denoted by θ'_I , then we have $\text{tang } \theta'_I = \frac{\text{tang } \theta'}{1-c}$.

The right ascensions are not altered by our transformation, neither are the geographical longitudes. The co-ordinate φ_I takes the place of the geocentric latitude.

If we replace $\sqrt{(1-c)^2 \cos^2 \theta' + \sin^2 \theta'}$, by w' , then

$$\sin \theta' = w' \sin \theta'_I \quad \text{and} \quad (1-c) \cos \theta' = w' \cos \theta'_I .$$

After the introduction of the auxiliary quantities U and M , which are computed by the formulae:

$$\text{tg } H = \frac{Q}{P} \quad \text{and} \quad M = P \sec H \quad (I)$$

we obtain as equations of the central line:

$$\begin{aligned} \cos \varphi_I \sin (t + \Delta\alpha') &= M \cos (H + h) \\ \cos \theta'_I \sin \varphi_I - \sin \theta'_I \cos \varphi_I \cos (t + \Delta\alpha') &= \frac{M}{w'} \sin (H + h) . \end{aligned}$$

By subtracting the sum of the squares of the two members of these equations from unity, we find:

$$\sin \theta'_I \sin \varphi_I + \cos \theta'_I \cos \varphi_I \cos (t + \Delta\alpha') = z_I ,$$

an equation, the 2nd member of which is the positive root of an expression which may be computed by means of the formulae (II).

$$F' = \frac{c(2-c)}{(1-c)^2} \cos^2 \theta'_I ; \quad z_I^2 = 1 - M^2 \{1 + F' \sin^2 (H + h)\} . \quad (II)$$

If further we calculate the auxiliary quantities w' , U , and N fulfilling the conditions

$$w' = \frac{1}{\sqrt{1+F'}} ; \quad \text{tg } U = \frac{M \sin (H+h)}{w' z_I} \quad \text{and} \quad N = z_I \sec U . \quad (III)$$

then the geographical longitude is given by the equations

$$\text{tg} (t + \Delta\alpha') = \frac{M \cos (H+h)}{z_I \cos (U + \theta'_I)} \quad \text{and} \quad \lambda = (t + \Delta\alpha') - \tau - \Delta\alpha' . \quad (IV)$$

and the geographical latitude by:

$$\text{tg } \varphi = \frac{1}{1-c} \text{tg} (U + \theta'_I) \cos (t + \Delta\alpha') (V)$$

With this set of formulae I calculated the longitude and latitude of two points in the central line for two moments, one 5 min. mean solar time after the other. In the results following below we have $T_0 = 0^h 32^m 26^s . 20$ Amsterdam mean time = $0^h 12^m 54^s . 06$

Greenwich mean time, and the geographical longitudes are given relatively to the signal of the Dutch Survey at Ubagsberg¹⁾.

Times	Geogr. long. E. of Ub.	Geogr. lat.
$T_0 + 0^n$	$- 2^\circ 28' 11''.9$	$49^\circ 41' 5''.2$. (C_0)
$T_0 + 5^m$	$+ 0 13 56.5$	$51^\circ 7' 37''.8$. (C_1)

The first point C_0 is still far in Belgium and the second lies already in Germany. In order to determine better the central line for Limburg I have calculated a third point C_4 , which comes into the axis of the shadow one minute earlier than C_5 , and I obtained

Time	Geogr. long E. of Ub.	Geogr. lat.
$T_0 + 4^m$	$- 0^\circ 19' 53''.3$	$50^\circ 50' 22''.7$. . (C_4)

This point C_4 is still situated in Belgium, but near the Limburg frontier. By interpolation between these three points the following values were found for the longitudes and latitudes which hold good for the topographical and military map of Holland²⁾.

Geogr. long. E. of Amst.	Geogr. lat.
$0^\circ 45'$	$50^\circ 50' 38''.3$
50	53 12.8
55	55 46.7
1 0	58 20.1
5	51 0 53.0
10	3 25.2
15	5 56.9

*Computation of the place where the vertex
of the moon's shadow leaves the earth.*

The solar eclipse of April 17 will probably be distinguished by the peculiarity that in the central line at first it is annular, later on it becomes total, then to grow annular again. One of these points of transition, viz. where the total eclipse becomes annular, will be situated in Belgium, if the above mentioned values of the apparent radii of the sun and moon are accurate. First I shall derive the

¹⁾ The difference in longitude between Berlin and Ubagsberg ($7^\circ 26' 34''.9$) I took from the determination of the differences of long. between Ubagsberg and the observatories at Bonn, Göttingen and Leyden: Veröff. K. Preuss. Geod. Inst. Topographische Längenbestimmungen in 1890, 1891 und 1893; and Publication de la Commission Géodésique Néerlandaise: Déterminations de la différence de longitude Leyde-Ubagsberg, etc.en 1893.

²⁾ From the last mentioned publication I also derived the latitude of Ubagsberg, in order to reduce the computed latitudes to those of the topographical map which are in accordance with the "Meetkunstige beschrijving v. h. Koninkrijk d. Nederlanden."

time of this transition ; subsequently the point where it takes place.

If $\frac{1}{\sin \pi}$, α and δ are the geocentric spherical coordinates of the moon and $\frac{s}{\sin f_i}$, α' and δ' the selenocentric ones of the vertex of the shadow, both referred to the equator and the equinox, then the rectangular geocentric co-ordinates of this vertex are :

$$\xi = \frac{1}{\sin \pi} \cos \delta \cos \alpha + \frac{s}{\sin f_i} \cos \delta' \cos \alpha'$$

$$\eta = \frac{1}{\sin \pi} \cos \delta \sin \alpha + \frac{s}{\sin f_i} \cos \delta' \sin \alpha'$$

$$\zeta = \frac{1}{\sin \pi} \sin \delta + \frac{s}{\sin f_i} \sin \delta'$$

In these expressions I substitute for the declinations the quantities δ_I and δ'_I , just as I have done before, so that here the auxiliary quantity $w = \sqrt{(1-c)^2 \cos^2 \delta + \sin^2 \delta}$ has to be introduced.

At the times of transition the vertex of the shadow falls on the transformed surface of the earth, the sphere with radius 1, hence

$$\xi^2 + \eta^2 + \frac{\zeta^2}{(1-c)^2} = 1$$

From this equation we derive:

$$(1-c)^2 = \frac{w^2}{\sin^2 \pi} + \frac{s^2 w'^2}{\sin^2 f_i} + 2 \frac{sw w'}{\sin \pi \sin f_i} \left\{ \cos \delta_I \cos \delta'_I \cos (\alpha' - \alpha) + \sin \delta_I \sin \delta'_I \right\}.$$

by which the time of transition is determined.

For the angle ψ between the directions ($\alpha \delta_I$) and ($\alpha' \delta'_I$) the relation

$$\cos \psi = \cos \delta_I \cos \delta'_I \cos (\alpha' - \alpha) + \sin \delta_I \sin \delta'_I,$$

holds good and from this we find

$$\sin^2 \frac{1}{2} \psi = \frac{\left(w + sw' \frac{\sin \pi}{\sin f_i} \right)^2 - \{ (1-c) \sin \pi \}^2}{4 sw w' \frac{\sin \pi}{\sin f_i}} \dots (VI)$$

Another form for the angle ψ is found by using the expressions $P \cos h - Q \sin h = \Psi$ and $P \sin h + Q \cos h = \Omega$, which occur in HANSEN'S fundamental equations.

Ψ , Ω , and Z are the rectangular co-ordinates of the centre of the moon referred to axes through the centre of the earth as origin.

The axis of Z has been taken in the direction ($a'd'$) and the axis of Ψ perpendicular to the plane of the declination-circle a' .

After having applied the transformation described above, which reduces the surface of the earth into a sphere, we can adopt a system of rectangular co-ordinates analogous to the former. The co-ordinates of the displaced centre of the moon with reference to these axes are distinguished from the corresponding co-ordinates of the real centre of the moon by the index I .

So the axis of Z_I is parallel to the direction ($a' d'_I$) and the axis of Ψ_I is perpendicular to the plane of the declination circle a' . The radius vector of the centre of the moon after the transformation is denoted by R_I .

The following relations hold between these quantities with and without the index I .

$$\Psi_I = \Psi \quad ; \quad \Omega_I = \frac{\Omega}{w'} \quad ; \quad R_I = R \frac{w}{1-c} = \frac{w}{(1-c) \sin \pi}.$$

Since $\sin^2 \psi = \frac{\Psi_I^2 + \Omega_I^2}{R_I^2}$, we thus derive:

$$\sin^2 \psi = \left(\Psi^2 + \frac{\Omega^2}{w'^2} \right) \frac{(1-c)^2}{w^2} \sin^2 \pi$$

As $\Psi = M \cos(H+h)$ and $\Omega = M \sin(H+h)$ we find:

$$\Psi^2 + \frac{\Omega^2}{w'^2} = \left\{ 1 + \left(\frac{1}{w'^2} - 1 \right) \sin^2(H+h) \right\} M^2 = 1 - z_I^2,$$

so that for the calculation of ψ we can also employ the equation

$$\sin \psi = \frac{(1-c) \sin \pi}{w} \cdot \sqrt{1 - z_I^2}. \quad \dots \quad (VII)$$

The instant at which the transition from totality into annularity takes place is that for which the formulae (VI) and (VII) give the same value for ψ . I calculated $\frac{1}{2}\psi$ for the time T_0 , $T_0 + 4$ min. and $T_0 + 5$ min. from both these formulae and found, interpolating for the minutes between T_0 and $T_0 + 4$.

Time	$\frac{\psi}{2}$ from (VI)	$\frac{\psi}{2}$ from (VII)
$T_0 + 0$ min.	0°18'41".69	0°18'21".05
„ + 1 „	42.59	29.88
„ + 2 „	43.49	38.85
„ + 3 „	44.40	47.98
„ + 4 „	45.30	57.25
„ + 5 „	46.20	19 6.67

These values are equal at $T_0 + 2^m 33^s.9$.

For this instant I have now calculated from the formulæ (I) to (V) the place of C_0 on the central line where the totality passes into annularity, and obtained for the geographical length east of Ubagsberg and for the geographical latitude of this point:

$$\lambda_0 = -1^\circ 7' 7''.6$$

$$\varphi_0 = 50^\circ 25' 34''.0.$$

Calculation of the angle at which the limiting-lines of the area of internal contact on the surface of the earth intersect each other in C_0 .

The equations which are satisfied at the limiting-lines, are:

$$\phi_1^2 + \phi_2^2 = u^2 \quad \text{and} \quad \phi_1 \frac{\partial \phi_1}{\partial T} + \phi_2 \frac{\partial \phi_2}{\partial T} = u \frac{\partial u}{\partial T}$$

if in the expression for u we replace the angle f by f_i .

The first equation follows from HANSEN'S fundamental equations. When in that equation the expressions for ϕ_1 , ϕ_2 , and u have been substituted, it gives the relation between λ , q_I and the moment at which the internal contact occurs at the place of observation (λq_I). In the limiting-lines this equation will hold for two consecutive moments. From this condition follows the second equation which is derived from the first by differentiation with respect to the time.

At the point C_0 the three functions ϕ_1 , ϕ_2 , and u are equal to zero for the time $T_0 + 2^m 33^s.9$. In the vicinity of this point at a small distance L and at a time differing from the first by the small quantity T , it is sufficiently accurate to use linear relations for the computation of the 3 functions. Hence we may put $\phi_1 = \left(\frac{\partial \phi_1}{\partial L}\right)_0 L + \left(\frac{\partial \phi_1}{\partial T}\right)_0 T$ and the same will do for ϕ_2 and u .

As all partial derivatives appearing in these equations relate to the point O , I shall henceforth simply write $\frac{\partial \phi_1}{\partial L}$, etc. instead of $\left(\frac{\partial \phi_1}{\partial L}\right)_0$, etc.

After the substitution of the linear expressions for ϕ_1 , ϕ_2 , and u , the equations of the limiting-lines become:

$$\left\{ \left(\frac{\partial \phi_1}{\partial L}\right)^2 + \left(\frac{\partial \phi_2}{\partial L}\right)^2 - \left(\frac{\partial u}{\partial L}\right)^2 \right\} L^2 + 2 \left(\frac{\partial \phi_1}{\partial L} \frac{\partial \phi_1}{\partial T} + \frac{\partial \phi_2}{\partial L} \frac{\partial \phi_2}{\partial T} - \frac{\partial u}{\partial L} \frac{\partial u}{\partial T} \right) L T + \left\{ \left(\frac{\partial \phi_1}{\partial T}\right)^2 + \left(\frac{\partial \phi_2}{\partial T}\right)^2 - \left(\frac{\partial u}{\partial T}\right)^2 \right\} T^2 = 0$$

and

$$\left(\frac{\partial \Phi_1}{\partial L} \frac{\partial \Phi_1}{\partial T} + \frac{\partial \varphi_2}{\partial L} \frac{\partial \varphi_2}{\partial T} - \frac{\partial u}{\partial L} \frac{\partial u}{\partial T} \right) L + \left\{ \left(\frac{\partial \varphi_1}{\partial T} \right)^2 + \left(\frac{\partial \varphi_2}{\partial T} \right)^2 - \left(\frac{\partial \dot{u}}{\partial T} \right)^2 \right\} T = 0$$

We now eliminate from the two equations the relation of L to T and thus we obtain an equation between the differential co-efficients which after reduction becomes :

$$\left(\frac{\partial \Phi_1}{\partial L} \frac{\partial \Phi_2}{\partial T} - \frac{\partial \Phi_2}{\partial L} \frac{\partial \Phi_1}{\partial T} \right)^2 = \left(\frac{\partial \varphi_1}{\partial L} \frac{\partial u}{\partial T} - \frac{\partial u}{\partial L} \frac{\partial \varphi_1}{\partial T} \right)^2 + \left(\frac{\partial \varphi_2}{\partial L} \frac{\partial u}{\partial T} - \frac{\partial u}{\partial L} \frac{\partial \varphi_2}{\partial T} \right)^2 \quad (VIII)$$

In developing the terms of this equation, I assume the linear element L to lie in an arbitrary azimuth A on the surface of the earth transformed into a sphere.

Then we find :

$$\frac{\partial \varphi_I}{\partial L} = \cos A \quad \text{and} \quad \frac{\partial \lambda}{\partial L} = \sec \varphi_I \sin A$$

Further we have $\frac{\partial(t + \Delta\alpha')}{\partial \lambda} = 1$ and for $\frac{\partial(t + \Delta\alpha')}{\partial T} = \frac{d(t + \Delta\alpha')}{dT}$ I put \varkappa .

By differentiation we find for the derivatives with respect to L :

$$\frac{\partial \Phi_1}{\partial L} = \sin \varphi_I \sin(t + \Delta\alpha') \cos A - \cos(t + \Delta\alpha') \sin A$$

$$\frac{\partial \Phi_2}{\partial L} = -\{(1-c) \cos \theta' \cos \varphi_I + \sin \theta' \sin \varphi_I \cos(t + \Delta\alpha')\} \cos A - \sin \theta' \sin(t + \Delta\alpha') \sin A$$

$$\frac{\partial u}{\partial L} = \text{tg } f_i \{(1-c) \sin \theta' \cos \varphi_I - \cos \theta' \sin \varphi_I \cos(t + \Delta\alpha')\} \cos A + \text{tg } f_i \cos \theta' \sin(t + \Delta\alpha') \sin A$$

and for those with respect to T :

$$\frac{\partial \Phi_1}{\partial T} = \frac{d\mathfrak{P}}{dT} - \varkappa \cos \varphi_I \cos(t + \Delta\alpha')$$

$$\frac{\partial \Phi_2}{\partial T} = \frac{d\mathfrak{Q}}{dT} - \varkappa \mathfrak{P} \sin \theta' + (Z + s \text{cosec } f_i) \frac{d\theta'}{dT}$$

$$\frac{\partial u}{\partial T} = \text{tg } f_i \left(\frac{dZ}{dT} + \varkappa \mathfrak{P} \cos \theta' - \mathfrak{Q} \frac{d\theta'}{dT} \right) - s \text{cosec } f_i \frac{df_i}{dT}$$

The last two derivatives have been simplified by means of the relations $\Phi_1 = 0$, $\Phi_2 = 0$ and $u = 0$, which hold good for the point C_0 .

Attributing to the linear element L the azimuthal direction of the central line on the sphere A_c , and denoting the derivatives with respect to L in this case by $\frac{\partial \Phi_1}{\partial L_c}$ et seq., we find the following equation for the determination of A_c :

$$\frac{\partial \Phi_2}{\partial L_c} \frac{\partial \Phi_2}{\partial T} - \frac{\partial \varphi_2}{\partial L_c} \frac{\partial \varphi_1}{\partial T} = 0 \dots \dots \dots (IX)$$

Substituting the following relations :

$$\frac{\partial \phi_1}{\partial T} = -\frac{\partial \phi_1 L_c}{\partial L_c T} \quad \text{and} \quad \frac{\partial \phi_2}{\partial T} = -\frac{\partial \phi_2 L_c}{\partial L_c T},$$

from which the equation (IX) can be derived, in the expression in brackets in the first member of (VIII), we get

$$\left(\frac{\partial \phi_1}{\partial L_c} \frac{\partial \phi_2}{\partial L} - \frac{\partial \phi_2}{\partial L_c} \frac{\partial \phi_1}{\partial L} \right) \frac{L_c}{T}$$

Here $\frac{\partial \phi_1}{\partial L_c}$ and $\frac{\partial \phi_2}{\partial L_c}$ are the same functions of A_c as $\frac{\partial \phi_1}{\partial L}$ and $\frac{\partial \phi_2}{\partial L}$ are of A . We further find by developing :

$$\frac{\partial \phi_1}{\partial L_c} \frac{\partial \phi_2}{\partial L} - \frac{\partial \phi_2}{\partial L_c} \frac{\partial \phi_1}{\partial L} = \{ -\sin \theta' \sin q_I - (1-c) \cos \theta' \cos q_I \cos (t + \Delta \alpha') \} \sin (A - A_c)$$

The expression between {} is equal to $-w' z_I$ according to former notations, hence :

$$\frac{\partial \phi_1}{\partial L_c} \frac{\partial \phi_2}{\partial L} - \frac{\partial \phi_2}{\partial L_c} \frac{\partial \phi_1}{\partial L} = -w' z_I \sin (A - A_c) \cdot \frac{L_c}{T} \quad . \quad . \quad . \quad (X)$$

Employing the numerical values which I needed for calculating the position of the point of transition, I first solved the equation (IX), from which I found :

$$A_c = 50^\circ 5' 46'' 03.$$

Subsequently I replaced in the equation, which followed from (VIII), the angle A by $\Delta = A - A_c$, and obtained for the calculation of Δ an equation of the following form :

$$c_0^2 \sin^2 \Delta = (c_1 \sin \Delta + d_1 \cos \Delta)^2 + (c_2 \sin \Delta + d_2 \cos \Delta)^2$$

with the following numerical values of the co-efficients :

$$\begin{array}{lll} c_0 = 6138''.9 & c_1 = -7''.24 & c_2 = -10''.24 \\ & d_1 = +9''.80 & d_2 = -13''.09. \end{array}$$

For the solution of this equation I first computed the auxiliary quantities $C = c_0^2 - c_1^2 - c_2^2$, $D = d_1^2 + d_2^2$ and $E = 2(c_1 d_1 + c_2 d_2)$; afterwards the angles B and I from the formulae :

$$\sin B = + \sqrt{\frac{4CD + E^2}{(C+D)^2 + E^2}} \quad \text{and} \quad \text{tg } I = \frac{E}{C+D}$$

and finally found these two solutions :

$$\Delta_1 = + \frac{1}{2} (B + I) \quad \text{and} \quad \Delta_2 = - \frac{1}{2} (B - I)$$

The numerical calculation led to :

$$\Delta_1 = + 0^\circ 9' 8''.1 \quad \text{and} \quad \Delta_2 = - 0^\circ 9' 10''.3$$

So the central line almost bisects the angle between the limiting-lines in C_0 . East of this point the north limit deviates a little more from the central line than the south limit. The angle between the

two limiting-lines in point C_0 is $\Delta_1 - \Delta_2 = B$; so that for this angle the result of the calculation is: $B = 0^\circ 18' 18'' .4$.

Measured on the surface of the sphere the distances of C_4 and C_5 from C_0 amount to 2338" and 3985", so that according to the adopted data the width of the annular zone at these points comes respectively to 12".4 and 21".2 or 380 and 650 meter.

From relation (X) we find co-efficient $c_0 = w' z_I \frac{Lc}{T}$; accordingly $\frac{Lc}{T} = \frac{c_0}{w' z_I}$ = the velocity V_0 , with which in C_0 the shadow-axis moves along the central line over the surface of the earth. For points in the central line near C_0 the duration of the totality or annularity is given by :

$$2 \left(V_0 \frac{\partial u}{\partial L} + \frac{\partial u}{\partial T} \right) \sqrt{\left(\frac{\partial f_1}{\partial T} \right)^2 + \left(\frac{\partial f_2}{\partial T} \right)^2} \\ - \frac{\left(\frac{\partial f_1}{\partial T} \right)^2 + \left(\frac{\partial f_2}{\partial T} \right)^2 - V_0^2 \left(\frac{\partial u}{\partial L} \right)^2}{T}.$$

The value of this expression is in casu: 0.00542 T and from this it follows that the annularity lasts 0".47 in C_4 and 0".80 in C_5 .

Calculation of the differential coefficients of the geographical longitude and latitude of the points in the central line with respect to the longitude, latitude, and parallax of the moon.

In these calculations we may neglect the very slight variations of the quantities Δ' , δ' (or δ'_I) and h in consequence of small variations in the places of the moon. In the differentiation I have therefore treated them as constant quantities.

From formula (IV) for $tg(t + \Delta')$ we deduce

$$\frac{2d\lambda}{\sin 2(t + \Delta')} = \frac{d\psi}{\psi} - \frac{dY}{Y}, \text{ where } \psi = M \cos(H + h) \text{ (see form. IV)}$$

and $Y = N \cos(U + \delta'_I) = z_I \cos \delta'_I - \frac{\Omega}{w'} \sin \delta'_I$, hence

$$dY = \cos \delta'_I dz_I - \frac{\sin \delta'_I}{w'} d\Omega$$

From the relation $z_I^2 = 1 - \psi^2 - \frac{\Omega^2}{w'^2}$ we obtain

$$dz_I = - \frac{\psi}{z_I} d\psi - \frac{\Omega}{w'^2 z_I} d\Omega, \text{ and, substituting in the formula for } d\lambda,$$

the values of the differentials dY and dz_I , we find $d\lambda$ expressed in $d\psi$ and $d\Omega$ as follows :

$$\frac{2d\lambda}{\sin 2(t + \Delta')} = \left(\frac{1}{\psi} + \frac{\psi \cos \delta'_I}{Y z_I} \right) d\psi + \frac{X}{Y z_I w'} d\Omega$$

where $z_I \sin \theta'_I + \frac{\Delta}{w'} \cos \theta'_I = X = N \sin (U + \theta'_I) = \sin \varphi_I$

In order to profit as much as possible by the quantities already calculated I substitute $tg(U + \theta'_I)$ for $\frac{X}{Y}$ and $tg(t + \Delta\alpha)$ for $\frac{\Psi}{Y}$.

By employing the differential relations

$$d\Psi = \cos h dP - \sin h dQ \text{ en } d\Delta = \sin h dP + \cos h dQ$$

and by introducing the auxiliary angle μ , variable between -90° and $+90^\circ$, which is determined by

$$tg \mu = w' \cotg (U + \theta'_I) \left\{ \frac{z_I}{\Psi} + \cos \theta'_I tg (t + \Delta\alpha) \right\} \quad (XIa)$$

we may reduce the differential expression for $d\lambda$ to:

$$d\lambda = \frac{Sec \mu}{2w'z_I} \sin 2(t + \Delta\alpha) tg (U + \theta'_I) \{ \sin (\mu + h) dP + \cos (\mu + h) dQ \} \quad (XIb)$$

For the deduction of the corresponding differential expression for the geographical latitude, it is necessary to eliminate $d\varphi_I$, $d\Delta$, and $d\Psi$ between the equations

$$\frac{d\varphi}{\sin 2\varphi} = \frac{d\varphi_I}{\sin 2\varphi_I}$$

and

$$\cos \varphi_I d\varphi_I = dX = \left(\frac{\cos \theta'_I}{w'} - \frac{\Delta \sin \theta'_I}{w'^2 z_I} \right) d\Delta - \frac{\Psi \sin \theta'_I}{z_I} d\Psi$$

and the expressions formerly found for $d\Delta$ and $d\Psi$. To simplify the second equation I employed the relation

$$\frac{\cos \theta'_I}{w'} - \frac{\Delta \sin \theta'_I}{w'^2 z_I} = \frac{Y}{w' z_I}$$

The introduction of the auxiliary angle v variable between -90° and $+90^\circ$, according to the formula

$$tg v = \frac{w' \Psi \sin \theta'_I}{Y} \dots \dots \dots (XIIa)$$

also simplifies the calculations. We then find:

$$d\varphi = \frac{\sin 2\varphi \cos (t + \Delta\alpha)}{\sin 2\varphi_I w' z_I \cos v} \{ - \sin (v - h) dP + \cos (v - h) dQ \} \quad (XIIb)$$

For the calculation of the differentials dP and dQ I have employed the following approximate formulae

$$dP = Z dl - P tg b db - P \cotg \alpha d\alpha \dots \dots \dots (XIII)$$

$$dQ = \dots \dots \dots Z db - Q \cotg \alpha d\alpha \dots \dots \dots (XIV)$$

The numerical values of the partial derivatives of λ and φ with respect to l , b , and α have been calculated for the two instants $T_0 + 4$ min. and $T_0 + 5$ min. This calculation gave the following result :

for $T_0 + 4$ min.	for $T_0 + 5$ min.
$\frac{\partial \lambda}{\partial l} = + 94.7$	$\frac{\partial \lambda}{\partial l} = + 96.0$
$\frac{\partial \rho}{\partial l} = + 25.8$	$\frac{\partial \rho}{\partial l} = + 25.7$
$\frac{\partial \lambda}{\partial b} = - 18.6$	$\frac{\partial \lambda}{\partial b} = - 17.3$
$\frac{\partial \rho}{\partial b} = + 73.7$	$\frac{\partial \rho}{\partial b} = + 74.1$
$\frac{\partial \lambda}{\partial \pi} = - 21.2$	$\frac{\partial \lambda}{\partial \pi} = - 23.2$
$\frac{\partial \rho}{\partial \pi} = - 50.2$	$\frac{\partial \rho}{\partial \pi} = - 50.6$

For a given longitude we find for the differential variation of the latitude of the central line $(d\varphi) = d\rho - d\lambda \cos \varphi \cot g A \frac{\sin^2 \varphi}{\sin^2 \varphi_1}$, where A denotes the azimuth of that line in the point (λ, φ) . In the present case we find for the two instants

$$(d\varphi) = d\rho - 0.516 d\lambda \quad \text{and} \quad (d\varphi) = d\rho - 0.504 d\lambda$$

From the above mentioned values of the partial derivatives of φ and λ with respect to l , b , and π we finally derive for the time $T_0 + 4$ min.:

$$(d\varphi) = - 23.1 dl + 83.3 db - 39.3 d\pi,$$

and for the time $T_0 + 5$ min.:

$$(d\varphi) = - 22.7 dl + 82.8 db - 33.9 d\pi.$$

As may be seen from these differential formulae, it is in particular the latitude of the moon that influences the situation of the central line. The empirical correction of $-1''.0$, applied by HANSEN to the latitude of the moon diminishes with $1'23''$ the geographical latitudes of the central line of this eclipse in our country; this corresponds to a transposition of 2,5 K.M. towards the south.

If it appears that corrections are necessary for the places of the moon accepted by me for these calculations, there will be no difficulty in computing their influence on the position of the central line. I myself am not able to give any corrections with any certainty. The only thing would be to take into account the influence of the height above sea-level, owing to which the geographical latitudes for given longitudes are about $2''.1$ per 100 M. smaller.

Postscript.

When I commenced these calculations Prof. E. F. v. D. SANDE BAKHUYZEN'S investigations into some points, regarding the longitude and latitude of the moon¹⁾, were not yet completed. In the meantime the results he arrived at appeared to agree well with the values I employed. The sum of all the terms of short period in the

¹⁾ Proc. Acad. Amst. 14, 1912, p. 686 et seq.

longitude according to BROWN, which were also calculated, amounts, however, when we add to it the influence of the adopted corrections of perigee and eccentricity, to $+0''.67$, i. e. $1''.10$ less than the value I derived from the originally adopted formula. The previous investigation of Prof. BAKHUYZEN into the observations of the moon up to 1902 led him to believe that the co-efficient of $\sin g$, which is of special importance here (as we have $g = 278^\circ$) would be in 1912 at least $-0''.6$ greater than its theoretical value, using also the adopted values for the corrections of perigee and eccentricity. From this remark a value of the longitude results, which is $+0''.6$ greater, so that the most probable correction of the longitude I employed would be $-0''.5$. Thus we should have $dl = -0''.5$ and $db = -0''.05$, hence $(dl) = +7''$. In more than one respect, however, some uncertainty remains.

Anatomy. — “*On the structure of the Dental system of Reptiles.*”

By Prof. Dr. L. BOLK.

(Communicated in the meeting of January 27, 1912).

If we compare the dental system of mammals with that of reptiles two points of difference come especially to the front. One of them bears a more physiological character and regards the fact that with mammals, as a rule, the dental shelf gives off only two series of buds, one for the milk-set and another for the permanent set. With the majority of reptiles on the contrary a shedding of teeth takes place several times during their life-time, though among this group of vertebrates species are known to us, where the shedding of teeth does not take place at all, or is restricted to a special part of the dental system, as may likewise be the case with mammals. These however are exceptions and in general the dental system of mammals as diphyodont (in some cases monophyodont) is placed over against that of reptiles as polyphyodont. It is pretty well the current view that the diphyodontism of mammals must be derived from the polyphyodontism of the lower vertebrates, and it is supposed that the number of renewals of the dental system was gradually reduced from many to a few, whilst the duration of the existence of the teeth was lengthened. Only a few authors take a different stand-point, and are of opinion that the shedding of teeth of mammals should be a property obtained by that group of animals themselves, and the primitive mammals should consequently have been monophyodont (LECHE).

The second point of difference is of a more morphological nature. The dental system of mammals namely is, save a few exceptions,

built of more complicated teeth. The crown shows two or more cusps. In the first case both cusps, the lingual and the buccal, can be well developed, and at first view the tooth is to be recognized as a bicuspidal one, or the lingual cusp is so much reduced that the tooth becomes apparently monocuspidal as with caninus and incisivi. By the variation in the number of the cusps the teeth of the dental system of mammals present a great diversity in the shape of the crowns, the set is anisodont, contrary to the more isodont set of reptiles, whose teeth are in general of a more equal and simple conical form.

There are different views of the way in which the anisodont dental system of mammals has developed out of an isodont primitive form.

Two theories on this subject have their supporters and their opponents. The so-called conerescence-theory teaches that the complicated mammal tooth developed itself by fusion of a number of cone-teeth of reptiles, each cusp of such a tooth should represent a primitive cone tooth. The differentiation-theory on the contrary teaches that every mammal-tooth, however complicated it may be, should be homologous with one single cone-shaped reptile-tooth, the crown of which lost its simple form and developed a more complicated relief.

Herewith the two chief points of difference between the dental system of reptiles and the dental system of mammals are indicated as briefly as possible. With the formation of the dental system of mammals from that of reptiles, a polyphyodont isodont dental system was transformed into a diphyodont anisodont one. Is there any relation between these two points of difference? In my opinion too little attention is paid in literature to this question. When animadverting on the formation of the complicated form of the tooth, the question whether there may be some relation between the fact that the tooth becomes complicated, and the diminution of the number of tooth-generations from several to two, is not referred to at all by the differentiation-theory, and hardly ever by the conerescence-theory. It is true that every now and then the supporters of the conerescence-theory express the view that the fusion of several cones to one whole must have diminished the number of tooth-generations. RÖSE has tried to give a scheme of this phenomenon. I suppose that this essay is to be regarded as incorrect, but I refrain from further criticism. I entirely chime in however with the principle of which this essay is the expression. For I hold that for the derivation of the mammal dental system from the reptilian dental system, one must try, as much as

possible, to find a process of transformation, by which the two chief characteristics of the mammal dental system are derived from a single cause. I think I have succeeded in this attempt. I could however only come to the solution I have found of this problem, after I had come to the conviction, especially on account of researches about the development of the dental system of reptiles, that our conception of the structure of this system must be rather importantly modified. It is my intention to restrict myself in this communication to this fundamental point of my theory, in order to explain in a subsequent communication the relation existing, in my opinion, between diphyodontism and polyphyodontism, and how the relation between the diminution of the number of tooth-generations, and the complication of mammal-teeth must be understood.

The dental system of most of the now living reptiles consists of a sometimes great number of little teeth, placed in a single straight line in the upper- and underjaw. Besides these teeth we find with several species, especially with those having lived in former periods, other teeth in different skeleton parts of the roof of the mouth (Palatinum and Vomer), but as these have not been inherited by mammals, we can leave them out of discussion, and restrict ourselves to the rows of teeth united with the jaws.

I should like to indicate a dental-system, the teeth of which are placed in a single row as a monostichical one. And if we regard the grouping of the teeth in the skull of a reptile, this term might justly be applied to such a system. But if we carefully examine the development of the dental system of reptiles, we discover symptoms that seem to place that system in a somewhat different light, and that awake the supposition that the simplicity of the rows of teeth of reptiles is only a semblance, or to express it more correctly forms a secondary situation which renders the real character of this dental system irrecognizable. As it is, my researches with regard to the teeth of the vertebrates convinced me that this dental system is not a monostichical system, but what I wish to call a "distichical" one. Though the teeth stand in a single row, they must after all be regarded as belonging to two rows, the elements of which have secondarily been placed in one single row, because they have interposed themselves between each other. This fact has as yet not been recognized because teeth that in reality were not replacing-teeth, have been considered as such. If once the attention has been fixed on this primary distichism, the development of the dental system of reptiles teaches still more: namely that originally the dental system of reptiles was not a distichical one, but even a "tristichical" i. e.

that this dental system is to be deducted from a form in which the teeth stood in three parallel rows, an outer, a middle, and an inner one, consequently a circumstance as is known to us with anamniotes. Of these rows the outer one however has become rudimentary and is still found with several of the now living reptiles in the form of abortive teeth, which offer a much more primitive mode of development, never function, and are very soon removed or resorbed. Consequently only two rows remain, an outer one and an inner one, which I shall distinguish as the "*exostichos*" and the "*endostichos*" whilst I shall distinguish the just mentioned row that has become rudimentary as the "*parastichos*". I shall now briefly demonstrate my views.

There exist about the development of the dental system of reptiles already several researches. For instance of RÖSE (Crocodile, Chamaelaeon) LECHE (Iguana) HARRISON (Hatteria) LEVY (Anguis, Lacerta). In how far my views deviate from those of these authors will soon be apparent.

In my elucidation I shall proceed from the dental system of a *Crocodyllus porosus* having sixteen teeth in the upper-jaw. I can directly corroborate for this form an observation of RÖSE that with this group of reptiles directly from the mouth-epithelium, consequently not from the dental shelf a number of rudimentary teeth is formed on the spot where the dental shelf is connected with the mouth-epithelium. LECHE found these teeth likewise with Iguana, and HARRISON with Hatteria, and myself observed them with *Lygosoma*. I differ in my view of the value of these teeth in so far, that they form for me a rudimentary row — the above-mentioned "*parastichos*", whilst RÖSE and LECHE conceive them as a rudimentary first generation of teeth. It must be well understood that to both authors the notion of rows of teeth is unknown. I shall not expiate further upon this difference of view.

When comparing the sixteen enamel buds in the teeth-shelf I was struck by the fact that they behaved differently with regard to that lamina. Some were placed at the buccal side of the peripheric half, whilst the tooth-papilla formed by the mesenchym grows from aside in the enamel-organ. A second group of lamina buds was formed at the free border of the lamina and the tooth-papilla grows in the thickened rim of the shelf. Fig. 1 shows the diagram of a section of the dental lamina with the two types of dental-organs. Further I give in Fig. 2, as

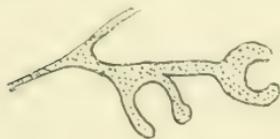


Fig. 1.

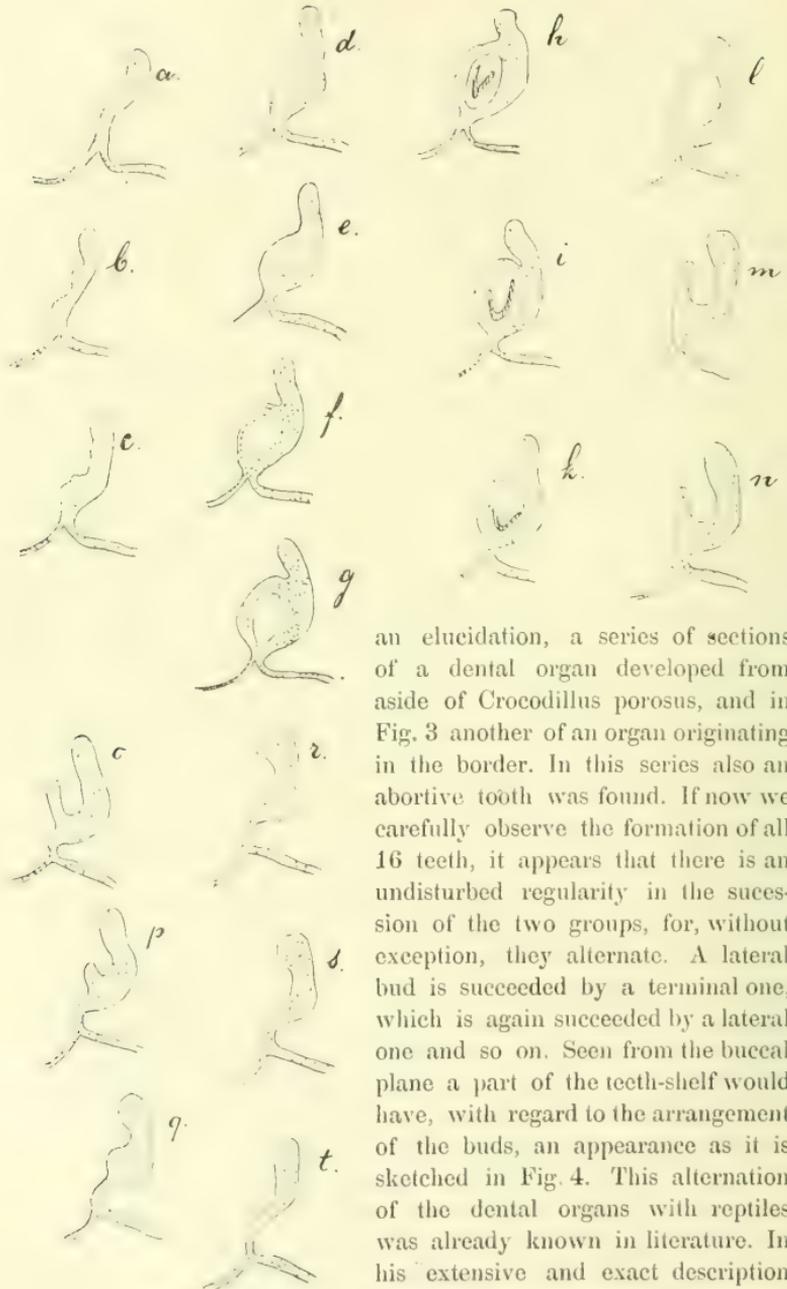


Fig. 2.

an elucidation, a series of sections of a dental organ developed from aside of *Crocodillus porosus*, and in Fig. 3 another of an organ originating in the border. In this series also an abortive tooth was found. If now we carefully observe the formation of all 16 teeth, it appears that there is an undisturbed regularity in the succession of the two groups, for, without exception, they alternate. A lateral bud is succeeded by a terminal one, which is again succeeded by a lateral one and so on. Seen from the buccal plane a part of the teeth-shelf would have, with regard to the arrangement of the buds, an appearance as it is sketched in Fig. 4. This alternation of the dental organs with reptiles was already known in literature. In his extensive and exact description of the dental system of *Hatteria*

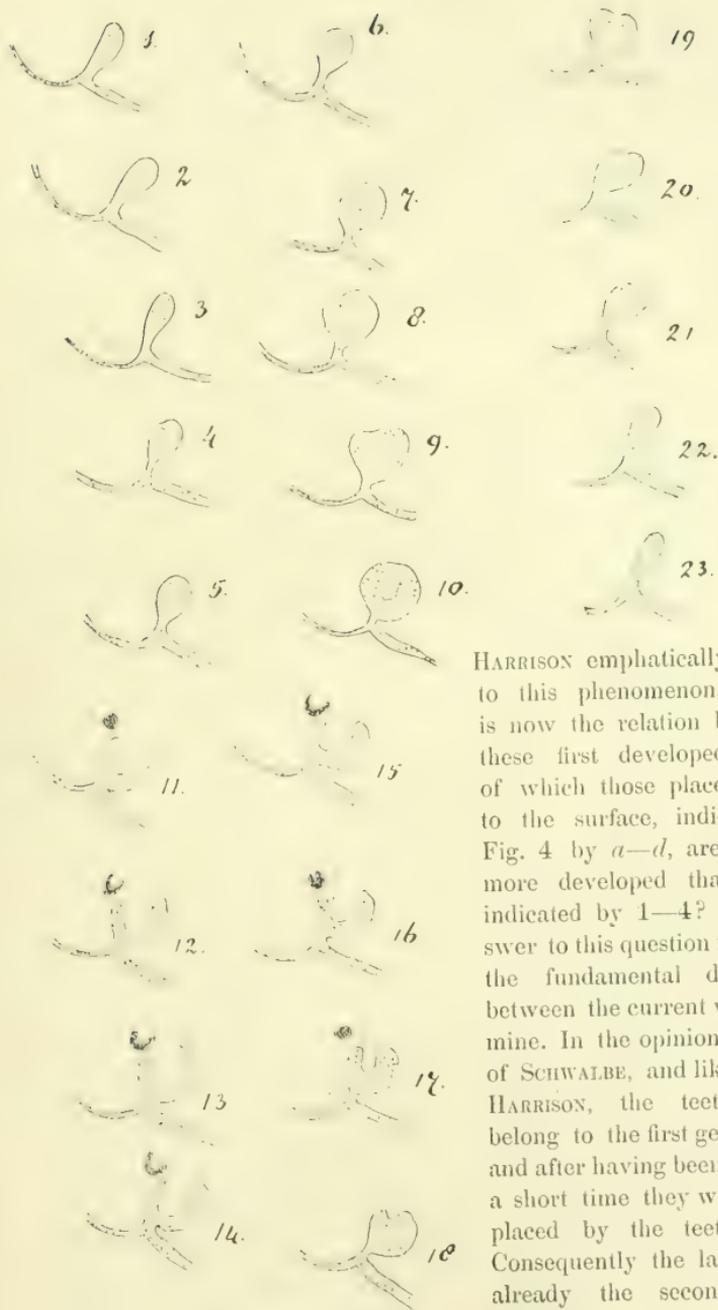


Fig. 3.

HARRISON emphatically points to this phenomenon. What is now the relation between these first developed teeth, of which those placed more to the surface, indicated in Fig. 4 by *a-d*, are a little more developed than those indicated by 1—4? The answer to this question indicates the fundamental difference between the current view and mine. In the opinion of RÖSE, of SCHWALBE, and likewise of HARRISON, the teeth *a-d* belong to the first generation, and after having been used for a short time they will be displaced by the teeth 1—4. Consequently the latter form already the second teeth-generation.

In this process tooth *a* would be replaced by tooth 1, tooth *b* by tooth 2 and so successively. I shall immediately prove that this conception cannot be correct. The mutual relation between the eight teeth sketched in Fig. 4 is of a wholly different nature. We have to do here with two rows of four teeth, which are not to be regarded

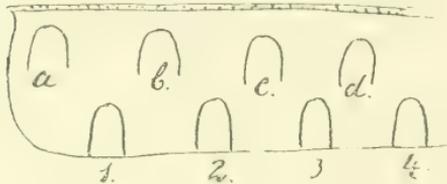


Fig. 4.

as first and second generations, for the teeth 1 to 4 will not displace the teeth *a—d*. In their further development every time a tooth of the row 1—4 penetrates between two teeth of the row *a—d*. Consequently instead of there being question of a first and a second generation, we have here two primary rows, the teeth *a—d* and the teeth 1—4 are entirely equivalent. In its first development the dental system of the *Crocodyllus* is consequently distichic, the teeth *a—d* represent the first generation of the exostichos, the teeth 1—4 the first generation of the endostichos.

This structure-principle of the dental system of the *Crocodyllus* can however not be observed in a more advanced stage of development, because the teeth of the two rows unite in a single line with the border of the jaws.

In order to confirm my view that in the first stage of development the dental system of reptiles consists of two rows of teeth running parallel and not of two generations, I refer in the first place to Fig. 5 in which a horizontal section through the upper jaws and the teeth in a young stage of development of *Lacerta* is represented. In the section both the premaxillary and the maxillary ones have been struck. We shall restrict ourselves to the origin of the maxillary teeth. Touching the maxillary bone we find three teeth, *a*, *b* and *c*. As the direction of the section is somewhat slanting, the teeth have been struck in a different level. These three teeth belong to the exostichos. Alternating with these there are three teeth, indicated by 1, 2, 3. According to the views of Röse and other authors these teeth, belonging to the inner row or endostichos, should form the second generation of the teeth *a*, *b*, and *c*, they should displace the latter. But from the figure it is, without more, clear that this view cannot be correct, that 1, 2, and 3 cannot become the substituting teeth of *a*, *b*, and *c*, but will, between the latter, grow together with the maxilla.

It is true, that here likewise the teeth *a*, *b*, and *c* are a little more developed than 1, 2, and 3, but the difference is so slight,

that on this ground already it might be doubted if in reality there exist here two generations. Consequently *Lacerta* appears to have likewise a distichical dental system, and both the teeth *a*, *b*, and *c* and the group 1, 2, and 3 represent a first generation, the former of the exostichos, the latter of the endostichos. In Fig. 5 the origin of a second generation is perceptible indeed, though in a young stage of development. In the section of the dental lamina we see namely the origin of three teeth.

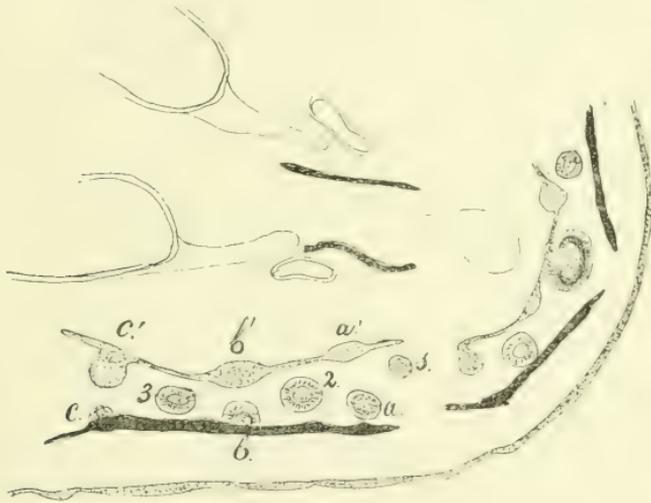


Fig. 5.

It is these teeth that at their further development, whilst moving towards the maxilla, will displace and substitute the teeth *a*, *b*, and *c*. These three teeth indicated as *a'*, *b'*, and *c'* form the second generation of the exostichos. In this preparation a second generation for the endostichos had not yet originated. In several reptile-embryos I found similar phenomena as in *Lacerta*. It is self-evident that for such like observations horizontal sections through the origin of the dental system are preferable. In Fig. 6 we find such a section through the premaxillar dental system of *Lygosoma olivaceum*.

The section is in a transversal direction somewhat slanting, so that on the right half of the figure the origin of more teeth is struck than on the left side. In the median line lies the unpaired tooth. The exostichos consists on both sides of two teeth *a b* and *c d*, and the endostichos of an equal number 1 2 and 3 4. It is likewise clear in this section that 1 2 3 and 4 are not the substituting teeth

of *a b c* and *d*, not a second generation, but a first generation of an independent row. They will soon have shoved between the elements of



Fig. 6.

the exostichos. In this preparation the second generation both of the exostichos and of the endostichos had originated already. The teeth *a' b' c'* and *d'* form the second generation of the exostichos. Exactly as with *Lacerta* also with *Lygosoma* a tooth is not displaced by another lying askance before or behind it, consequently not by an alternating tooth, but by a tooth originating directly behind the tooth that must be substituted. In our subsequent communication we shall revert to this point, as, with regard to the shedding of the teeth of mammals, it is not devoid of interest. Of the endostichos the second generation has likewise originated; on account of the slanting direction of the section its elements are only visible in the right half of the figure. It is the two teeth which, still connected with the dental lamina, are situated to the right behind the teeth 3 and 4.

Consequently it is very evident that *Lygosoma* possesses a distichical

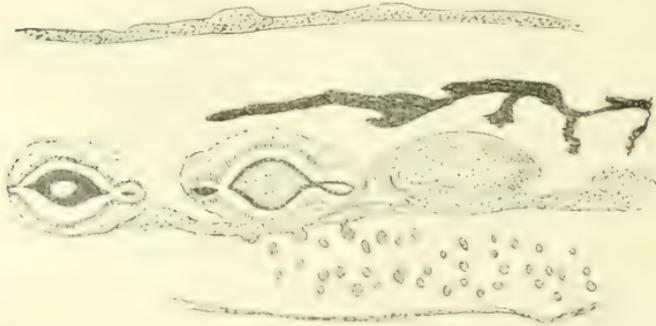


Fig. 7.

dental system. Whether this property of structure is still peculiar to the dental system of all reptiles, must be proved by subsequent investigations. Perhaps these will show that it is not the case. In my opinion e. g. it is doubtful whether the dental system of *Calotes*, of which I give a horizontal section in Fig. 7, is of a distichical nature.

I do not find an indication of it in the stage represented here. Neither was there any vestige of substituting teeth. It may certainly be imagined that, with some groups of reptiles, one of the two rows is checked in its origin and development, which would render the dental system monostichical. That this circumstance does not occasion a suppression of the shedding of the teeth requires no further argument.

We fixed already the attention to the fact that in its origin and development the exostichos is somewhat in advance of the endostichos. If this relation is not disturbed by later influences, the renewal of the teeth in the exostichos will also every time take place a little earlier than in the endostichos. A beautiful example of this fact is



Fig. 8.

sketched in Fig. 8. It regards the premaxillary dental system, as I found it in a skull of *Tupinambus nigropunctatus*. The teeth of this part of the dental system are regularly provided at their rims with two notches. Besides the unpaired tooth standing in the median line, one finds on either side five premaxillary teeth. And now it is very interesting to see, that, regularly alternating, a still intact tooth and an already partly resorbed tooth with an underlying substituting tooth succeed each other. Here has evidently the chronological difference in origin and substitution of the elements of the two rows been preserved in such a degree that in this part of the full-grown dental system the composition from two rows can still be demonstrated.

This latter fact seems finally to be especially distinctly the case with *Hatteria*, as here according to HARRISON's¹⁾ representations and description the teeth differ in size, so that regularly a large and a little tooth alternately succeed each other. HARRISON's very accurate description of the development of the dental system removes every doubt that the two sorts of teeth belong to a different row. Yet this naturalist has neither been able to free himself from the notion of two generations, and consequently describes as a peculiarity of the dental system of *Hatteria* that, what he calls the teeth of the second generation do not seem to displace those of the first generation, but the latter give way and receive the elements of the second generation among them. The dental system consists consequently, as the author expresses himself, of two dentitions: "The teeth which are developed on the dental lamina during the incubation period and which function during the early life of the living animal, are almost certainly the members of two distinct dentitions, the later teeth instead of displacing the earlier coming to alternate with them". (l.c. p. 202). The distichous character of the dental system of *Hatteria* appears likewise from the further details in the development which HARRISON informs us of, but into which I do not enter here.

As I hope the given examples are indeed sufficient to show that our conception of the dental system of reptiles needs modification. It will be necessary to distinguish in it a functionary and a genetic structure. According to the former the dental system consists of a single row of teeth, but the history of the development teaches that this condition is not a primitive one, and that this simple row is in reality a compound one built of two primary series to which, with different species (*Crocodyllus*, *Iguana*, *Lygosoma*, *Hatteria*) at the lateral side another rudimentary row is joined, the elements of which develop themselves in the same way as with amphibia. This new aspect on the one hand connects the dental system of reptiles more closely with that of the Anamnia, and forms, on the other hand, a point of issue for a modified conception of the relation between the dental system of reptiles and that of mammals.

With regard to the first part I remind of the fact that especially with the tailed amphibia "Polystichism" of the dental system is by no means rare. Now we can imagine that, with regard to the maxillar dental system, this Polystichism, through diminution of the rows, has become a Tristichism, respectively a Distichism. The way in which this diminution was accomplished is closely connected with

¹⁾ Quarterly. Journal of micr. sc. Vol. XLIV.

the way in which, with reptiles, a dental lamina has been developed. As a rule it is represented, as if a fold of the epithelium had penetrated into the jawmesenchym. I do not think that this view is entirely correct, but I suppose that the dental lamina has been developed because both in the upper-jaw and in the lower-jaw in medio-lateral direction, a fold of the mucous membrane has overgrown the area in which the teeth were developing. This area was, as it were, operculated. In order to prove this view I could add several observations, but I restrict myself to simply mentioning it in order to revert to this point at length elsewhere. We only call the attention to the fact, that by this conception of the origin of the dental-lamina it is clear, why teeth never originate from the medial surface of this lamina. By this operculation the formation of enamel-organs became possible. Now I imagine that with reptiles two primary rows of teeth came to development in this operculated area whilst a third outside row was not overgrown and remained at the surface. The elements of this series — indicated above as “parastichos” — preserved the primitive character of their origin and developed themselves like the teeth of amphibia. These simple teeth however gradually lost their function on account of the greater strength of the elements of the two operculated rows. This short indication of the relation between the dental system of reptiles and that of lower vertebrates, may suffice here. I intend to develop my views about the relation between that of mammals in a next communication. Only for completeness' sake be communicated here as the essential part of my views that, in my opinion, mammals have inherited the distichism of the dental system of reptiles, and that this distichism comes to the front here in a much more distinct form namely as the laetal teeth and the permanent teeth. In my opinion the laetal dentition represents the exostichos of reptiles, the permanent dentition the endostichos whilst the so-called prelaetal dentition must be derived from the parastychos. Consequently there would not exist the least relation between the diphyodontism of mammals and the polyphyodontism of reptiles.

Mathematics. — “On some relations between Bessel's functions”.

By Prof. W. KAPTEYN.

1. When r and s are real numbers and

$$\alpha = x \sin \omega \quad \beta = x \cos \omega$$

the following expressions

$$S = \cos r\alpha \cos s\beta + \cos r\beta \cos s\alpha$$

$$T = \sin r\alpha \sin s\beta + \sin r\beta \sin s\alpha$$

may be developed in trigonometrical series.

For, writing

$$r\alpha + s\beta = rx \sin \omega + sx \cos \omega = \varrho \cos (\omega - \varphi)$$

from which

$$\varrho = x \sqrt{r^2 + s^2} \quad \operatorname{tg} \varphi = \frac{r}{s}$$

the equations

$$2S = \cos (r\alpha + s\beta) + \cos (r\alpha - s\beta) + \cos (r\beta + s\alpha) + \cos (r\beta - s\alpha)$$

$$2T = \cos (r\alpha - s\beta) - \cos (r\alpha + s\beta) + \cos (r\beta - s\alpha) - \cos (r\beta + s\alpha)$$

may be reduced by means of the known series

$$\cos (r\alpha + s\beta) = \cos [\varrho \cos (\omega - \varphi)] = I_0(\varrho) - 2I_2(\varrho) \cos 2(\omega - \varphi) + \\ + 2I_4 \cos 4(\omega - \varphi) - \dots$$

$$\cos (r\alpha - s\beta) = \cos [\varrho \cos (\omega + \varphi)] = I_0(\varrho) - 2I_2(\varrho) \cos 2(\omega + \varphi) + \\ + 2I_4 \cos 4(\omega + \varphi) - \dots$$

$$\cos (r\beta + s\alpha) = \cos [\varrho \sin (\omega + \varphi)] = I_0(\varrho) + 2I_2(\varrho) \cos 2(\omega + \varphi) + \\ + 2I_4 \cos 4(\omega + \varphi) + \dots$$

$$\cos (r\beta - s\alpha) = \cos [\varrho \sin (\omega - \varphi)] = I_0(\varrho) + 2I_2(\varrho) \cos 2(\omega - \varphi) + \\ + 2I_4 \cos 4(\omega - \varphi) + \dots$$

Thus we obtain

$$2S = 4I_0(\varrho) + 8I_4(\varrho) \cos 4\varphi \cos 4\omega + 8I_8 \cos 8\varphi \cos 8\omega + \dots$$

and in the same way

$$2T = 8I_2(\varrho) \sin 2\varphi \sin 2\omega + 8I_6(\varrho) \sin 6\varphi \sin 6\omega + 8I_{10}(\varrho) \sin 10\varphi \sin 10\omega + \dots$$

2. We may also express the quantities S and T by multiplication of trigonometrical series.

For if

$$f(x) = \frac{1}{2} a_0 + a_1 \cos x + a_2 \cos 2x + \dots$$

$$= b_1 \sin x + b_2 \sin 2x + \dots$$

$$\varphi(x) = \frac{1}{2} a'_0 + a'_1 \cos x + a'_2 \cos 2x + \dots$$

their product may be represented in one of the following forms

$$f(x) \varphi(x) = \frac{1}{2} A_0 + A_1 \cos x + A_2 \cos 2x + \dots$$

$$f(x) \varphi(x) = B_1 \sin x + B_2 \sin 2x + \dots$$

where ¹⁾

$$A_n = \frac{1}{2} \sum_0^n a'_m a_{n-m} + \frac{1}{2} \sum_1^\infty (a'_m a_{m+n} + a_m a'_{m+n})$$

$$B_n = \frac{1}{2} \sum_0^n a'_m b_{n-m} + \frac{1}{2} \sum_1^\infty (a'_m b_{m+n} - b_m a'_{m+n}).$$

These coefficients may be written more compactly by observing that $a_{-p} = a_p$, $a'_{-p} = a'_p$, $b_{-p} = -b_p$ and $b_0 = 0$.

Hence

$$\sum_{-n}^0 (a'_m a_{m+n} + a_m a'_{m+n}) = 2 \sum_0^n a'_m a_{n-m}$$

$$\sum_{-n}^0 (a'_m b_{m+n} - b_m a'_{m+n}) = 2 \sum_0^n a'_m b_{n-m}$$

and

$$4A_n = \sum_{-n}^\infty \varepsilon_m (a'_m a_{m+n} + a_m a'_{m+n})$$

$$4B_n = \sum_{-n}^\infty \varepsilon_m (a'_m b_{m+n} - b_m a'_{m+n})$$

where ε_m represents the value 1 if $m = -n, -n+1, \dots, -2, -1, 0$ and the value 2 if $m = 1, 2, 3 \dots$

3. Now let us apply these formulae in the first place to expand S in a trigonometrical series.

Multiplying

$$\frac{1}{2} \cos r\alpha = \frac{1}{2} I_0(rx) + I_2(rx) \cos 2\omega + I_4(rx) \cos 4\omega + \dots$$

$$\frac{1}{2} \cos s\beta = \frac{1}{2} I_0(sx) - I_2(sx) \cos 2\omega + I_4(sx) \cos 4\omega - \dots$$

we have, m being an even integer

$$a_m = I_m(rx) \quad a'_m = (-1)^{\frac{m}{2}} I_m(sx)$$

therefore, writing the product

$$\frac{1}{4} \cos r\alpha \cos s\beta = \frac{1}{2} A_0 + A_2 \cos 2\omega + A_4 \cos 4\omega + \dots$$

the coefficients A are determined by

$$4A_n = \sum_{-n}^\infty (-1)^{\frac{m}{2}} \varepsilon_m [I_m(sx) I_{m+n}(rx) + (-1)^{\frac{n}{2}} I_m(rx) I_{m+n}(sx)].$$

In the same way supposing

$$\frac{1}{4} \cos r\beta \cos s\alpha = \frac{1}{2} A'_0 + A'_2 \cos 2\omega + A'_4 \cos 4\omega + \dots$$

¹⁾ Proceedings of the meeting of Febr. 29, 1908.

we have

$$4 A'_n = \sum_{-n}^{\infty} (-1)^{\frac{m}{2}} \varepsilon_m [I_m(rx) I_{m+n}(sx) + (-1)^{\frac{n}{2}} I_m(sx) I_{m+n}(rx)],$$

and adding the two results

$$4 (A_n + A'_n) = \left\{ 1 + (-1)^{\frac{n}{2}} \right\} \sum_{-n}^{\infty} (-1)^{\frac{m}{2}} \varepsilon_m [I_m(sx) I_{m+n}(rx) + I_m(rx) I_{m+n}(sx)].$$

Therefore, if n has the values $2, 6, 10, \dots$ this coefficient vanishes, and if $n = 0, 4, 8, \dots$ we obtain

$$2 (A_n + A'_n) = \sum_{-n}^{\infty} (-1)^{\frac{m}{2}} \varepsilon_m [I_m(sx) I_{m+n}(rx) + I_m(rx) I_{m+n}(sx)].$$

Hence, writing

$$\frac{1}{2} S = C_0 + 2 C_4 \cos 4\omega + 2 C_8 \cos 8\omega + \dots$$

the coefficients are determined by

$$2 C_{4q} = \sum_{-2q}^{\infty} (-1)^p \varepsilon_{2p} [I_{2p}(sx) I_{2p+4q}(rx) + I_{2p}(rx) I_{2p+4q}(sx)].$$

Comparing this with the first expansion

$$\frac{1}{2} S = I_0(\varrho) + 2 I_4(\varrho) \cos 4\varphi \cos 4\omega + 2 I_8(\varrho) \cos 8\varphi \cos 8\omega + \dots$$

we obtain the remarkable relation

$$I_{4q}(x \sqrt{r^2 + s^2}) \cos 4q \varphi = \frac{1}{2} \sum_{-2q}^{\infty} (-1)^p \varepsilon_{2p} [I_{2p}(sx) I_{2p+4q}(rx) + I_{2p}(rx) I_{2p+4q}(sx)] \quad (1)$$

where $tq \varphi = \frac{r}{s}$.

In the special case that $r = s$, we have $\varphi = \frac{\pi}{4}$ and $\cos 4q \varphi = (-1)^q$,

so

$$(-1)^q I_{4q}(xr \sqrt{2}) = \sum_{-2q}^{\infty} (-1)^p \varepsilon_{2p} I_{2p}(rx) I_{2p+4q}(rx),$$

which gives for $q = 0$

$$I_0(xr \sqrt{2}) = \sum_{\psi}^{\infty} (-1)^p \varepsilon_{2p} I_{2p}^2(rx).$$

a result which may be verified by expanding $I_0(xr \sqrt{2})$ by NEUMANN'S method in a series of the form

$$I_0(z \sqrt{2}) = \alpha_0 I_0^2(z) + \alpha_1 I_1^2(z) + \alpha_2 I_2^2(z) + \dots$$

4. To determine in the second place T we multiply the series

$$\begin{aligned} \frac{1}{2} \sin r\alpha &= I_1(rx) \sin \omega + I_3(rx) \sin 3\omega + I_5(rx) \sin 5\omega + \dots \\ \frac{1}{2} \sin s\beta &= I_1(sx) \cos \omega - I_3(sx) \cos 3\omega + I_5(sx) \cos 5\omega - \dots \end{aligned}$$

which, compared with the notations of Art. 2, give

$$a'_0 = 0 \quad a'_m = (-1)^{\frac{m-1}{2}} I_m(sx) \quad b_m = I_m(rx)$$

m being odd in this case.

Therefore writing

$$\frac{1}{4} \sin r\alpha \sin s\beta = B_2 \sin 2\omega + B_4 \sin 4\omega + \dots$$

the coefficients are determined by

$$4B_n = \sum_{-n}^{\infty} (-1)^{\frac{m-1}{2}} \epsilon_m [I_m(sx) I_{m+n}(rx) - (-1)^{\frac{n}{2}} I_m(rx) I_{m+n}(sx)]$$

and in the same way

$$\frac{1}{4} \sin s\alpha \sin r\beta = B'_2 \sin 2\omega + B'_4 \sin 4\omega + \dots$$

where

$$4B'_n = \sum_{-n}^{\infty} (-1)^{\frac{m-1}{2}} \epsilon_m [I_m(rx) I_{m+n}(sx) - (-1)^{\frac{n}{2}} I_m(sx) I_{m+n}(rx)]$$

Hence

$$4(B_n + B'_n) = \{1 - (-1)^{\frac{n}{2}}\} \sum_{-n}^{\infty} (-1)^{\frac{m-1}{2}} \epsilon_m [I_m(sx) I_{m+n}(rx) + I_m(rx) I_{m+n}(sx)]$$

vanishes for $n = 0, 4, 8, \dots$ and reduces to

$$2(B_n + B'_n) = \sum_{-n}^{\infty} (-1)^{\frac{m-1}{2}} \epsilon_m [I_m(sx) I_{m+n}(rx) + I_m(rx) I_{m+n}(sx)]$$

for the values $n = 2, 6, 10, \dots$

From this we may infer that

$$\frac{1}{2} T = D_2 \sin 2\omega + D_6 \sin 6\omega + D_{10} \sin 10\omega + \dots$$

where

$$D_{4q+2} = \sum_{-2q-1}^{\infty} (-1)^j \epsilon_{2j+1} [I_{2j+1}(sx) I_{2j+4q+3}(rx) + I_{2j+1}(rx) I_{2j+4q+3}(sx)]$$

Comparing this result with the first expansion

$$\frac{1}{2} T = 2I_2(\varrho) \sin 2\rho \sin 2\omega + 2I_6(\varrho) \sin 6\rho \sin 6\omega + \dots$$

we find the identity

$$I_{4q+2}(x\sqrt{r^2+s^2}) \sin(4q+2)\varphi =$$

$$= \frac{1}{2} \sum_{-2q-1}^{\infty} (-1)^j \epsilon_{2j+1} [I_{2j+1}(sx) I_{2j+4q+3}(rx) + I_{2j+1}(rx) I_{2j+4q+3}(sx)] \quad (2)$$

which gives for $r = s$

$$I_{4q+2}(xr\sqrt{2}) = \sum_{-2q-1}^{\infty} (-1)^p \varepsilon_{2p+1} I_{2p+1}(sx) I_{2p+4q+3}(rx)$$

and reduces to

$$I_2(xr\sqrt{2}) = \sum_{-1}^{\infty} (-1)^p \varepsilon_{2p+1} I_{2p+1}(sx) I_{2p+3}(rx).$$

if $q = 0$.

5. It seems desirable to verify the two formulae (1) and (2). This may be done in the following way.

The first member of (1), considered as a function of x , satisfies the differential equation

$$\frac{d^2 y}{dx^2} + \frac{1}{x} \frac{dy}{dx} + \left(r^2 + s^2 + \frac{16q^2}{x^2} \right) y = 0$$

therefore the second member must also satisfy the same equation. To prove this we put

$$I_{2p}(rx) = u_{2p} \quad , \quad I_{2p}(sx) = v_{2p}$$

then it is evident that

$$\begin{aligned} \frac{d^2 u_{2p}}{dx^2} + \frac{1}{x} \frac{du_{2p}}{dx} + \left(r^2 - \frac{4p^2}{x^2} \right) u_{2p} &= 0 \\ \frac{d^2 v_{2p}}{dx^2} + \frac{1}{x} \frac{dv_{2p}}{dx} + \left(s^2 - \frac{4p^2}{x^2} \right) v_{2p} &= 0. \end{aligned}$$

Now, if $\frac{d}{dx}$ be represented by D , we will apply the operation

$$D^2 + \frac{1}{x} D + \left(r^2 + s^2 - \frac{16q^2}{x^2} \right)$$

on the general term

$$u_{2p} v_{2p+4q} + v_{2p} u_{2p+4q}$$

of the series in the second member of (1).

Determining in the first place

$$\left\{ D^2 + \frac{1}{x} D + \left(r^2 + s^2 - \frac{16q^2}{x^2} \right) \right\} (u_{2p} v_{2p+4q}) = M_1$$

we have

$$\begin{aligned} D^2(u_{2p} v_{2p+4q}) &= u_{2p} D^2 v_{2p+4q} + 2D u_{2p} D v_{2p+4q} + v_{2p+4q} D^2 u_{2p} \\ \frac{1}{x} D(u_{2p} v_{2p+4q}) &= \frac{1}{x} (u_{2p} D v_{2p+4q} + v_{2p+4q} D u_{2p}) \end{aligned}$$

so by addition

$$u_{2p} \left(D^2 v_{2p+4q} + \frac{1}{x} D v_{2p+4q} \right) = \left(\frac{(2p+4q)^2}{x^2} - s^2 \right) u_{2p} v_{2p+4q}$$

Observing that

$$u_{-n} = (-1)^n u_n \quad \text{and} \quad v_{-n} = (-1)^n v_n$$

it is easily seen, that the preceding series vanishes, which gives

$$\frac{d^2 P}{dx^2} + \frac{1}{x} \frac{dP}{dx} + \left(r^2 + s^2 - \frac{16q^2}{x^2} \right) P = 0$$

and thus

$$P = C I_{4q} (x \sqrt{r^2 + s^2})$$

for the second integral is out of the question.

To determine the constant C , we must compare the coefficient of $\left(\frac{x}{2}\right)^{4q}$ in P with the coefficient of $\left(\frac{x}{2}\right)^{4q}$ in $C I_{4q} (x \sqrt{r^2 + s^2})$, the latter being $\frac{(r^2 + s^2)^{2q}}{(4q)!} C$.

To obtain the former we may observe that $\left(\frac{x}{2}\right)^{4q}$ only will be found in these terms of P

$$\frac{1}{2} \sum_{-2q}^{\infty} (-1)^p \varepsilon_{2p} [I_{2p}(sx) I_{2p+4q}(rx) + I_{2p}(rx) I_{2p+4q}(sx)]$$

where ε_{2p} has the value 1 for all the terms existing.

By changing p in $-p$, this expression may be written

$$\frac{1}{2} \sum_0^{2q} (-1)^p [I_{-2p}(sx) I_{4q-2p}(rx) + I_{2p}(rx) I_{4q-2p}(sx)]$$

or

$$\frac{1}{2} \sum_0^{2q} (-1)^p [I_{2p}(sx) I_{4q-2p}(rx) + I_{2p}(rx) I_{4q-2p}(sx)].$$

Expanding the functions in this expression the coefficient of $\left(\frac{x}{2}\right)^{4q}$ is found to be

$$\frac{1}{2} \sum_0^{2q} (-1)^p \frac{s^{2p} r^{4q-2p+r^{2p}} s^{4q-2p}}{(2p)! (4q-2p)!}$$

or

$$\frac{s^{4q}}{(4q)!} \left[1 - \frac{4q(4q-1)}{2!} \lambda^2 + \frac{4q(4q-1)(4q-2)(4q-3)}{4!} \lambda^4 - \dots + \lambda^{4q} \right]$$

where $\lambda = \frac{r}{s}$.

Now

$$(1 + i\lambda)^{4q} + (1 - i\lambda)^{4q} = 2 \left[1 - \frac{4q(4q-1)}{2!} \lambda^2 + \frac{4q(4q-1)(4q-2)(4q-3)}{4!} \lambda^4 - \dots + \lambda^{4q} \right]$$

or, supposing

$$1 + i\lambda = \sqrt{1 + \lambda^2} (\cos \varphi + i \sin \varphi)$$

$$1 - i\lambda = \sqrt{1 + \lambda^2} (\cos \varphi - i \sin \varphi)$$

$$(1 + \lambda^2)^{2q} \cos 4q\varphi = 1 - \frac{4q(4q-1)}{2!} \lambda^2 + \frac{4q(4q-1)(4q-2)(4q-3)}{4!} \lambda^4 - \dots + \lambda^{4q}$$

thus the required coefficient may be written

$$\frac{s^{4q}}{(4q)!} (1 + \lambda^2)^{2q} \cos 4q\varphi = \frac{(r^2 + s^2)^{2q}}{(4q)!} \cos 4q\varphi$$

where

$$\tan \varphi = \lambda = \frac{r}{s}.$$

Comparing both coefficients we have

$$\frac{(r^2 + s^2)^{2q}}{(4q)!} C = \frac{(r^2 + s^2)^{2q}}{(4q)!} \cos 4q\varphi$$

or

$$C = \cos 4q\varphi$$

and finally

$$P = I_{4q} (x \sqrt{r^2 + s^2}) \cos 4q\varphi$$

which proves the identity (1). In the same way the formula (2) may be verified.

6. From the formulae of Art. 1 we may at once deduce definite integrals for Bessel's functions of order $4q$ and $4q + 2$.

For these give immediately by integration between the limits 0

and $\frac{\pi}{4}$

$$\frac{1}{2} \int_0^{\frac{\pi}{4}} S \cos 4q\omega d\omega = \frac{\pi}{4} I_{4q} (x \sqrt{r^2 + s^2}) \cos 4q\varphi$$

$$\frac{1}{2} \int_0^{\frac{\pi}{4}} T \sin (4q+2)\omega d\omega = \frac{\pi}{4} I_{4q+2} (x \sqrt{r^2 + s^2}) \sin (4q+2)\varphi$$

so when $r = s$

$$\int_0^{\frac{\pi}{4}} \cos (rx \sin \omega) \cos (rx \cos \omega) \cos 4q\omega = \frac{\pi}{4} \cos (q\pi) I_{4q} (rx\sqrt{2})$$

$$\int_0^{\frac{\pi}{4}} \sin (rx \sin \omega) \sin (rx \cos \omega) \sin (4q+2)\omega = \frac{\pi}{4} I_{4q+2} (rx\sqrt{2}).$$

Physics. — “*The magneto-optic KERR-effect in ferromagnetic compounds and alloys.*” II. By DR. STANISLAW LORIA. (Communication from the BOSSCHA-Laboratory). (Communicated by Prof. H. DU BOIS).

In a previous paper ¹⁾ I communicated to the Academy the results of an experimental investigation of the polar KERR phenomenon in ferromagnetic compounds and alloys and promised an extension of the investigations. Among the results presented at that time the following are to be considered.

1. The dispersion curve of the polar KERR-effect in the cases of cupri-ferrite ($\text{CuO} \cdot \text{Fe}_2\text{O}_3$) and of naturally occurring magnetite (Fe_3O_4) in the region of the visible part of the spectrum ($436 \mu\mu$ to $668 \mu\mu$) exhibited points of inversion similar to those previously established by INGERSOLL ²⁾ for magnetite and nickel in the infra-red region (1μ to 3μ).

2. The rotation, produced in the magnetic field, of linearly polarised monochromatic light perpendicularly reflected initially increases proportionally to the field and then, notwithstanding a further increase of the field, attains a maximum constant value.

The purpose of the further investigation was the elucidation of the physical meaning of the points of inversion in the dispersion curve of the KERR-effect obtained from the experimental results. In other words to search in the first place for any regular relation between this peculiarity of the dispersion of the magnetic KERR phenomenon and the other optical and magnetic properties of the substances concerned.

To solve this question it becomes necessary to know the refractive and extinction indices of those substances for which these characteristic points of inversion in the KERR phenomenon have been observed. It was justifiable to expect that perhaps the position of the points of inversion stood in close relation to the form of the usual dispersion curves. In conjunction with C. ZAKRZEWSKI I have carried out the optical investigations in the cases of cupri-ferrite, of magnetite and of invar. The measurements yield the elements of the ellipticity of parallel light reflected from the mirror. The procedure was the same as that previously used by C. ZAKRZEWSKI ³⁾.

¹⁾ ST. LORIA, These Proc. XII, p. 835 (1910).

²⁾ L. R. INGERSOLL, Phil. Mag, (6) **11** p. 41 1906 and **18** p. 74 1909.

³⁾ C. ZAKRZEWSKI; Bull. Acad. Cracov. (A) **22** p. 77, 1910; ST. LORIA and C. ZAKRZEWSKI: l. c. p. 278.

As a conclusion from these measurements for the questions we are now concerned with there can be no suggestion of a direct *simple* connection between, on the one hand, the points of inversion of the magnetic KERR-effect and, on the other hand, the dispersion of the optical constants. Neither the dispersion curve of the refractive index nor that of the index of extinction show any characteristic indication in those parts of the spectrum where the above mentioned inversion points occur. Taking into consideration the quite sufficient accuracy of these measurements it becomes necessary to search for the explanation of the inversion of the KERR effect in another direction. In the following some new results will be brought to bear upon the matter.

By means of the apparatus described in my first publication and using the same method and procedure, the KERR polar rotation was examined in its dependence on the wave-length of the light and on the intensity of the magnetic field. The measurements extend over the region of the spectrum between $436 \mu\mu$ and $688 \mu\mu$; the field employed was varied between 0,9 and 21 kilogauss.

The choice of suitable materials for observation was determined by the above mentioned and still undecided question. The following are the substances examined :

1. Pure artificially prepared *magnetite* (Fe_3O_4) for which I am indebted to the friendliness of Prof. P. WEISS. The specimen was that which WEISS had employed in his magnetic observations. According to his results the saturation value of its magnetisation is 476, 5 c. g. s. ¹⁾.

2. Pure *nickel* (by MERCK), also one of the pieces magnetically investigated by WEISS and for which he gives the maximum value 479.0 c. g. s. for its magnetisation.

3. A *nickel* mirror from the collection of the Bosscha-Laboratory which nominally contained 99% Ni.

4. *Iron-nickel alloys* of the compositions 73 Fe + 27 Ni and 74.6 Fe + 25.4 Ni respectively, which were placed at my disposal by Dr. S. HILPERT.

5. Ferromagnetic *manganese* which was also placed at my disposal by Prof. WEISS and had been magnetically examined by him.

6. *Haematite* (Fe_2O_3) (Kakuk Berg, Hargitta Gebirge in Siebenbürgen) obtained from the Comptoir Minéralogique Suisse, in Geneva.

To the above named gentlemen, who have by their friendly loan of the materials made these experiments possible, I beg to express my warmest thanks.

¹⁾ P. WEISS, Journ. de Physique (4) 9, p. 373, 1910.

In order to facilitate a clear analysis of the results obtained I will divide them into two sections. In the first the question of dispersion will be considered and in the second that of saturation.

DISPERSION CURVES.

1. *Magnetite*. The optical constants were first determined by ZEEMAN¹⁾ for a natural crystalline surface (Pfitsch, Tyrol of unknown orientation; they are given in table 1, being the principal incidence J and azimuth H , from which the refractive index n and the extinction index κ are now calculated from DRUDE's equations²⁾ to a second approximation, Mr. DE HAAS being so good as to carry out the calculations.

TABLE 1

λ	J	H	n	κ
434	68°27'	10°10'	2.36	0.32
589	68°27'	8°48'	2.41	0.27
656	68°33'	7°55'	2.45	0.25

Measurements with two other crystals gave appreciably the same values.

In conjunction with ZAKRZEWSKI, according to the method already referred to, I found the following values.

TABLE 2.

λ	n	κ
439	2.46	0.28
589.6	2.42	0.23
665.5	2.45	0.21

The numbers hold for an octahedral plane of the same crystal as that used by me in the magneto-optical experiments; the polish was incomplete and even with the naked eye irregular fissures and pores were to be seen; the mirror was cleaned with toluol vapour; the azimuth of the plane of incidence was without influence.

¹⁾ P. ZEEMAN, Versl. Afd. Nat 3 p. 230, 1895.

²⁾ P. DRUDE, in Handbuch der Physik 2. Aufl. 6 p. 1298 seq., 1906.

There is obviously rather a good agreement of the values and although differences of about 15% in the indices of extinction exist they can be attributed to the lack of cleanliness of the surface. Corresponding to the smaller conductivity, the index of absorption is appreciably smaller than in the case of metals.

Although the regular magnetite, as is known, exhibits itself as aeolotropic in its ferromagnetic and probably also in its elastic properties yet it is difficult to assume the same in purely optical processes. In any case, up to the present, only two optical constants have been postulated for regular crystals and for isotropic bodies. To examine the magneto-optical effect in this relation the above mentioned artificial magnetite — obtained by calcination of ferric oxide Fe_2O_3 — was ground to a small plate and attained a somewhat dull polish. In this case there could be no uniform orientation of the mirror, at most only a minute crystalline structure.

Nevertheless the dispersion curve obtained showed quite the same characters as in the case of perpendicular reflection from a natural octahedral surface of the crystalline magnetite. The results of the measurements are collected together in table 3.

TABLE 3.

$\varepsilon = \text{Funct}(\lambda)$		Magnetite		$H = 18.8 \text{ Kgs.}$
N	$\lambda(\mu\mu)$	$\Delta(\text{mm})$	$\varepsilon(\text{Minutes})$	$\delta\varepsilon$
14	436	- 28.4	- 4.40'	$\pm 0.15 = \text{ca } 3\%$
15	453	- 23.7	- 3.67'	
15	477	- 10.1	- 1.56	
12	497	+ 3.4	+ 0.53'	
15	510	+ 9.9	+ 1.53	
16	539	+ 20.1	+ 3.11'	
12	565	+ 28.6	+ 4.43'	
12	589	+ 31.0	+ 4.80'	
12	610	+ 33.2	+ 5.14'	
17	637	+ 31.5	+ 4.88'	
16	688	+ 29.3	+ 4.54'	$\pm 0.04 = \text{ca } 0.9\%$

The vertical column denoted by N gives the number of the readings belonging to one series; λ gives the wave-length of the light used

in $\mu\mu$; Δ gives the double rotation, as read off directly from the scale in mms., produced by a commutation of the current in the electromagnet. The fourth column gives the mean value of the simple rotation ϵ .

To characterize the exactitude of the measurements I have calculated the mean error for the points lying on the borders of the spectrum used, and this is given in minutes and percents respectively in the fifth column.

As is to be seen from fig. 1 the rotation, which is *negative* for

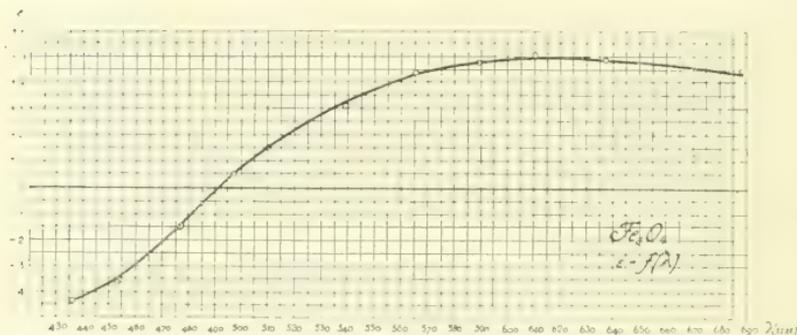


Fig. 1

436 $\mu\mu$, decreases rather rapidly with increase of wave-length, becomes zero in the neighbourhood of 492 $\mu\mu$, then becomes *positive* until for 615 $\mu\mu$ it attains a rather flat maximum and finally slowly decreases. If one compares the shape of this dispersion curve with that of the natural magnetite crystal it is seen that the general characters of the two curves are the same, the only differences being that the zero and maximum points are displaced towards greater wave-lengths by 30 to 40 $\mu\mu$.

2. *Nickel-steels.* Until the present I had only investigated "invar" containing 36% Ni. The interesting magnetic properties of this alloy demanded an investigation of the KERR-effect in nickel-steels of another composition. In particular those alloys of the two metals, which at ordinary temperatures appear feebly or not at all ferromagnetic, deserved a closer observation.

Nickel-steel with 25.4% Ni, whose magnetical properties have been tested by HILPERT and COLVER—GLAUERT¹⁾ is at ordinary temperatures as good as non-magnetic. None the less it shows a distinct

¹⁾ S. HILPERT and E. COLVER—GLAUERT, Zeitschr. f. Elektrochemie 17 p. 750, 1911.

KERR-effect. The sign of the rotation through the whole of the visible spectrum is negative. The dispersion curve has a similar form to that of invar. Steel with 27% Ni, which also at ordinary temperatures shows hardly any magnetic effect, behaved similarly magneto-optically. The sign of the rotation here again is negative for the whole range of the visible spectrum. Its absolute value is even greater than in the case of the rather strongly magnetic invar. The shape of the dispersion curve is very similar to that of the 25,4% nickel-steel, the difference being that the rotation changes somewhat less with the wave-length. The results of the measurements of the rotation as a function of the wave-length for the two nickel-steel alloys are collected together in Tables 4 and 5 and also shown in fig. 2.

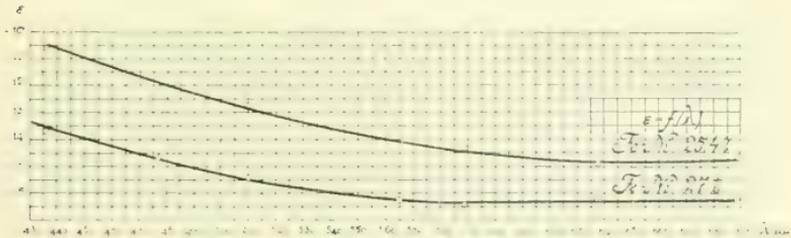


Fig. 2.

TABLE 4.

$\varepsilon = \text{Funct } (\lambda)$		Fe—Ni 27%		$\xi = 14.4 \text{ Kgs.}$
N	$\lambda (\mu\mu)$	$\Delta (\text{mm})$	$\varepsilon (\text{Minutes})$	$\partial\varepsilon$
15	436	— 88.2	— 13.67'	$\pm 0.13 = \text{ca } 0.90\%$
10	453	— 89.6	— 13.88'	
10	477	— 94.6	— 14.66'	
10	510	— 99.5	— 15.42'	
10	565	— 105.0	— 16.27'	
10	589	— 106.1	— 16.45'	$\pm 0.04 = \text{ca } 0.30\%$
10	537	— 104.5	— 16.19'	
10	688	— 104.9	— 16.25'	

The existence of the KERR-effect in nickel-steel, whose magnetisation according to HILPERT's results has an extremely low value is most surprising. Moreover DU Bois ¹⁾ had previously found a quite

¹⁾H. du Bois, Phil. Mag. (5) 29 p. 304, 1890.

TABLE 5.

$\varepsilon = \text{Funct}(\lambda)$		Fe-Ni 25.4 ⁰ / ₀		$\mathfrak{H} = 14.9$ Kgs.
N	λ (μ)	Δ (mm)	ε (Minutes)	$\delta\varepsilon$
10	436	- 68.6	- 10.63'	$\pm 0.08 = \text{ca } 0.7\%$
10	510	- 82.4	- 12.75	
10	589	- 92.0	- 14.32'	$\pm 0.07 = \text{ca } 0.5\%$
10	637	- 96.1	- 14.89'	
10	688	- 95.1	- 14.74'	

analogous result for twelve per cent manganese-steel whose permeability amounts only to about 1,01. The value of the negative rotation varied from point to point on a highly polished mirror relatively to different surface elements of the same piece, the rotation amounting to one third of the maximum rotation for iron. These effects were then attributed to inhomogeneity of structure as was borne out by a metallographical examination by simple methods. Such results — as also the opposite behaviour of HEUSLER'S alloy — may offer a certain interest when applied to the theory of alloys and to metallography although the method is hardly sufficiently simple for frequent application. The physical interpretation however involves great difficulties owing to the assumption of the continuity and homogeneity of the substance, which is in general tacitly assumed.

SATURATION CURVES.

1. *Nickel-steel* with 25,4 % *Ni*. The mirror had the form of a circular disk of about 25 mm. diameter and 2 mm. thickness. The conically bored pole end-piece had a vertex semi-angle of 55°—57°. The boring at the end remote from the mirror had a diameter of 6,3 mm., and at the end nearer to the mirror a diameter of only 3,6 mm. The distance of the pole end-piece from the mirror was about 1 mm.

The form of the function $\varepsilon(\mathfrak{H})$ is determined by the numbers contained in table 6.

As is to be seen the negative rotation increases proportionally with the field. Up to about 17 Kgs. there is scarcely a distinct trace of saturation to be noticed¹⁾.

¹⁾ I am compelled to take this opportunity of correcting an assertion appearing in a paper by S. HILPERT and E. COLVER—GLAUERT. They state there "The optical

TABLE 6.

$\varepsilon = \text{funct. } (\dot{\nu})$		Fe — Ni 25.4%		$\lambda = 589 \mu\mu$
N	$\dot{\nu}$ (Kgs.)	Δ (mm.)	(Minutes)	$\delta\varepsilon$
10	3.0	— 18.0	— 2.80'	$\pm 0.03 = \text{ca } 1.0\%$
10	4.5	— 27.7	— 4.29'	0.03 = „ 0.7 „
10	5.9	— 36.1	— 5.60'	0.05 = „ 0.8 „
10	10.5	— 64.9	— 10.06'	0.06 = „ 0.6 „
10	13.0	— 80.9	— 12.50'	0.06 = „ 0.5 „
10	14.9	— 92.0	— 14.32'	0.07 = „ 0.5 „
10	16.0	— 97.8	— 15.25'	0.06 = „ 0.4 „
10	16.8	— 102.7	— 15.92'	0.09 = „ 0.5 „

2. *Nickel-steel with 27% Ni.* The mirror was a circular disk of 6 mm. diameter. All the other experimental conditions were as above. The results are contained in table 7.

TABLE 7.

$\varepsilon = \text{funct. } (\dot{\nu})$		Fe — Ni 27%		$\lambda = 589 \mu\mu$
N	$\dot{\nu}$ (Kgs.)	Δ (mm.)	ε (Minutes)	$\delta\varepsilon$
15	0.5	— 4.3	— 0.66'	$\pm 0.05 = \text{ca } 8\%$
12	1.1	— 9.1	— 1.41'	0.04 = „ 4 „
12	1.8	— 13.1	— 2.03'	0.04 = „ 2 „
12	2.9	— 23.2	— 3.59'	0.04 = „ 1 „
10	4.4	— 34.5	— 5.35'	0.08 = „ 1.5 „
15	5.9	— 45.5	— 7.05'	0.07 = „ 1 „
10	10.4	— 80.1	— 12.41'	0.06 = „ 1 „
10	12.7	— 95.4	— 14.78'	0.19 = „ 1 „
10	14.4	— 106.1	— 16.45'	0.04 = „ 0.3 „
10	15.4	— 109.7	— 16.99'	0.09 = „ 0.5 „
10	16.3	— 111.6	— 17.29'	0.09 = „ 0.5 „

investigations of the KERN-effect which Dr. LORIA carried out gave a saturation intensity of only a few units". The statement of HULBERT is, as he himself agrees, due to a misunderstanding and does not correspond to the above facts.

Up to about 10,5 Kgs. the rotation increases proportionally with the field. In the region of the stronger fields the tendency to a saturated condition becomes evident. Up to 17 Kgs. this state was however not attained.

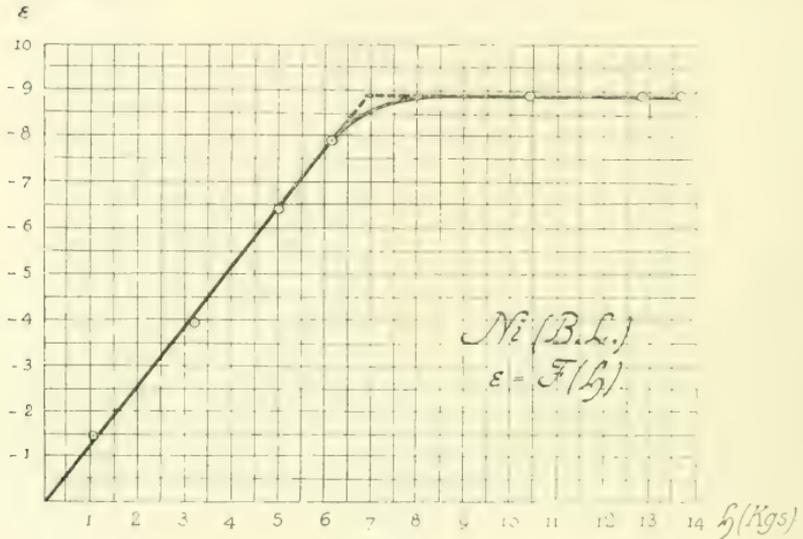


Fig. 3.

3. *Nickel*. Measurements carried out with a nickel mirror (a circular disk of about 18 m.m. diameter) belonging to the collection of the Bosscha-Laboratory, gave the following results (Tab. 8, Fig. 3 :

TABLE 8.

$\epsilon = \text{funct} ()$		Ni (B. L.)		$\lambda = 477 \mu\mu$
N	\hat{h} (Kgs)	L (mm)	ϵ (Minutes)	$\partial\epsilon$
15	1.07	- 9.7	- 1.53'	$\pm 0.03 = \text{ca } 2 \%$
15	3.16	- 25.1	- 3.97'	0.07 = $\gg 1.7 \gg$
15	4.99	- 40.7	- 6.44'	0.07 = $\gg 1 \gg$
15	6.20	- 49.6	- 7.85'	0.07 = $\gg 0.9 \gg$
15	10.4	- 56.3	- 8.91'	0.09 = $\gg 1 \gg$
15	12.8	- 56.2	- 8.90'	0.09 = $\gg 1 \gg$
20	13.6	- 56.1	- 8.88'	0.08 = $\gg 0.9 \gg$

The maximum rotation, for $\lambda = 477 \mu\mu$, amounted to $\epsilon_m = 8,9'$.

If the abscissa of the point of intersection of the two straight lines (Fig. 3) be denoted by x , then $x/4\pi = 550$ C. G. S.

As a result of direct magnetic measurements, as stated above, WEISS gives for his nickel tested at 18°

$$\mathfrak{N}_m = 479,0 \text{ C. G. S.}$$

I have therefore repeated my measurements for the nickel specimen placed at my disposal by Prof. WEISS. The mirror had the figure of a rectangle, about 6 mm. long and 3 mm. wide, but was not quite regular in form. It was still small enough to allow some doubt to subsist as to how far the results are interpretable. The configuration of the field right on the surface of the mirror is influenced by the form of the bored pole end-piece as well as by its distance from the mirror; the choice of the two conditions is more or less at the disposal of the experimenter.

First measurement: The end-area of the pole end-piece (V) was circular and of a diameter of approximately 5 mm.; the boring was rectangular, about 2,5 mm. broad and 4 mm. high, the distance of the mirror amounted to about 1,5 mm. The results are collected together in Table 9, and Fig. 4.

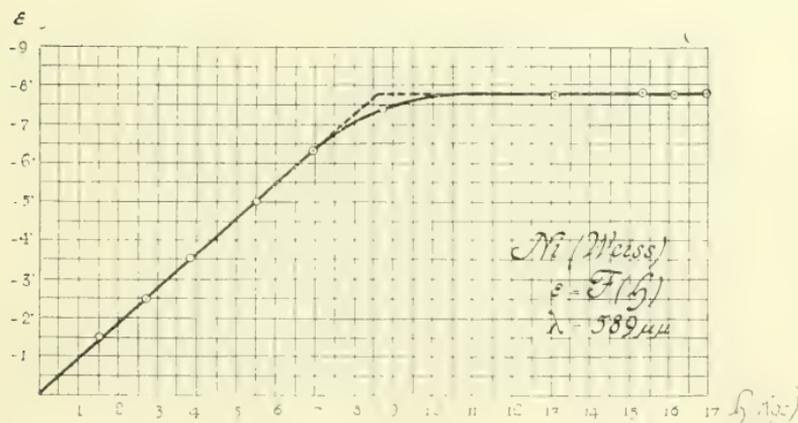


Fig. 4.

For $\lambda = 589 \mu\mu$: $\epsilon_m = 7,8'$, and $x/4\pi = 640$ C. G. S.

Second measurement: Here the same conical bored pole end-piece was employed as in the case of the investigation of nickel-steel.

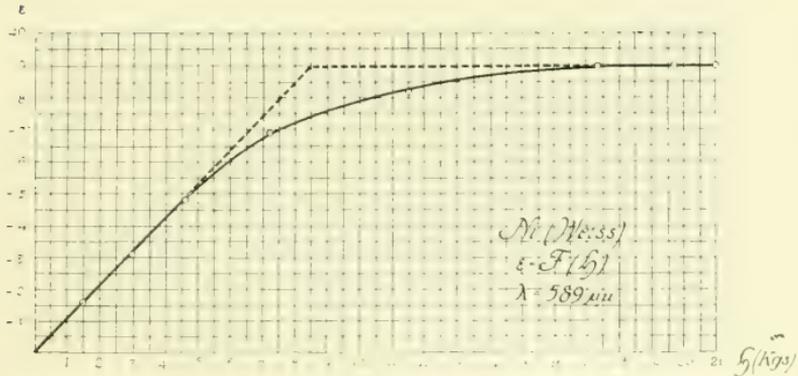
The results are given in Table 10 and Fig. 5.

TABLE 9.

$\varepsilon = \text{funct. } (\bar{\gamma})$		Ni (WEISS) I		$\lambda = 589 \mu\mu$
N	$\bar{\gamma}$ (Kgs)	Δ (mm)	ε (Minutes)	δz
5	1.5	- 9.4	- 1.46'	$\pm 0.09 = \text{ca } 6 \frac{0}{10}$
10	2.7	- 16.4	- 2.54'	0.08 = $\gg 3 \gg$
7	3.8	- 22.6	- 3.50'	0.1 = $\gg 3 \gg$
10	5.5	- 32.3	- 5.02'	0.1 = $\gg 2.5 \gg$
10	6.9	- 40.6	- 6.30'	0.1 = $\gg 1.5 \gg$
11	8.7	- 47.7	- 7.39'	0.1 = $\gg 1.3 \gg$
10	13.1	- 50.5	- 7.82'	0.08 = $\gg 1 \gg$
10	15.3	- 50.7	- 7.85'	0.15 = $\gg 2 \gg$
10	16.1	- 50.1	- 7.75'	0.15 = $\gg 2 \gg$
10	16.9	- 50.3	- 7.79'	0.1 = $\gg 1.3 \gg$

TABLE 10.

$\varepsilon = \text{funct. } (\bar{\gamma})$		Ni (WEISS) II		$\lambda = 589 \mu\mu$
N	$\bar{\gamma}$ (Kgs.)	Δ (mm.)	(Minutes)	δz
12	1.49	- 10.5	- 1.62'	$\pm 0.03 = \text{ca } 2 \frac{0}{10}$
13	2.97	- 20.3	- 3.14'	0.06 = $\gg 2 \gg$
12	4.6	- 31.1	- 4.82'	0.04 = $\gg 0.8 \gg$
15	7.2	- 44.3	- 6.86'	0.06 = $\gg 0.8 \gg$
13	11.5	- 52.9	- 8.20'	0.07 = $\gg 0.4 \gg$
14	17.3	- 58.3	- 9.02'	0.05 = $\gg 0.6 \gg$
11	19.7	- 58.2	- 9.02'	0.04 = $\gg 0.5 \gg$
10	21.0	- 58.4	- 9.05'	0.07 = $\gg 0.8 \gg$



In this case for $\lambda = 589 \mu\mu$: $\varepsilon_m = 9,0'$; and $x/4\pi = 640$ C.G.S.

4. *Magnetite.* The measurements were performed on the same mirror as that for which the dispersion of the KERR-effect has been given above; it shewed many fissures and pores. According to WEISS the saturation value of the magnetisation of this magnetite is

$$\zeta_m = 476,5 \text{ C.G.S.}$$

The first series of measurements was carried out with $\lambda = 589 \mu\mu$. As is known the rotation in this region of the spectrum is *positive*. From the numbers given in Table 11 it is found that

$$\varepsilon_m = + 4,7' \text{ and } x/4\pi = 370 \text{ C.G.S.}$$

TABLE 11.

$\varepsilon = \text{funct. } (\zeta)$		Magnetite (WEISS)		$\lambda = 589 \mu\mu$
N	ζ (Kgs.)	Δ (mm.)	ε (Minutes)	$\delta\varepsilon$
12	0.9	+ 4.64	+ 0.72'	$\pm 0.04 = \text{ca } 6 \%$
12	2.2	+ 14.0	+ 2.17'	0.06 = „ 2.7 „
15	3.2	+ 20.8	+ 3.22'	0.04 = „ 1.3 „
15	5.0	+ 27.0	+ 4.18'	0.09 = „ 2 „
10	7.3	+ 30.7	+ 4.75'	0.05 = „ 1 „
15	9.0	+ 30.4	+ 4.71'	0.04 = „ 1 „
12	11.4	+ 30.5	+ 4.72'	0.05 = „ 1 „
14	17.0	+ 30.5	+ 4.72'	0.05 = „ 1 „

This value does not agree with the results of the measurements I have previously carried out under the same conditions but in the region of *negative* rotation. If one measures the dependence of the KERR rotation on the field for $\lambda = 436 \mu\mu$ i.e. in the region of *negative* rotations, the following numbers contained, in Table 12, are obtained.

TABLE 12.

$\epsilon = \text{funct. } (\dot{v})$		Magnetite (WEISS)		$\lambda = 436 \mu\mu$
N	\oint (Kgs.)	Δ (mm.)	ϵ (Minutes)	$\partial\epsilon$
19	1.15	— 6.7	— 1.03'	$\pm 0.05 = \text{ca } 5 \%$
14	2.1	— 11.9	— 1.81'	0.05 = „ 3 „
17	3.1	— 15.9	— 2.46'	0.14 = „ 5 „
18	5.3	— 24.4	— 3.79'	0.18 = „ 5 „
15	7.4	— 28.3	— 4.38'	0.13 = „ 3 „
12	10.7	— 29.3	— 4.54'	0.14 = „ 3 „
11	15.2	— 30.9	— 4.79'	0.09 = „ 2 „
15	18.7	— 29.8	— 4.61	0.07 = „ 1.5 „

These give $\epsilon_n = -4.7'$ and $x/4 \tau = 450$ C.G.S.

5. *Manganese*. For a ferromagnetic specimen of this element WEISS and KAMERLINGH ONNES found a specific magnetisation up to about 2,5 C. G. S. In relation to the KERR-effect it gave a negative result in so far that the rotation cannot in any case be greater than 0,35'.¹⁾

6. *Haematite* (specular iron Fe_2O_3). DU BOIS²⁾ had already in vain searched for an effect in the case of a mirror normal to the optical axis. The mirror investigated by me was also parallel to the base surface and reflected perfectly without however being magneto-optically active. According to the investigations of KUNZ³⁾ this is also rather

¹⁾ P. WEISS and H. KAMERLINGH ONNES, These Proc. XII, p. 657, (1910).

H. BEHRENS arrived at the same negative results in the case of the KUNDT-Effect. Dissert., Münster 1908.

²⁾ loc. cit. § 18.

³⁾ J. KUNZ, Neues Jahrb. f. Mineral. etc. 1 p. 62, 1907.

improbable. With regard to my earlier negative result for ilmenite no pains were taken to obtain mirrors of different orientation.

The last described measurements in the region of saturation are only to be regarded as preliminary experiments which I had regretfully to discontinue owing to external circumstances.

The conclusion arrived at previously by DU BOIS viz.: that $\alpha/4\pi = \mathfrak{I}_m$ must hold in the first place for an indefinitely extended plane mirror of physically as well as chemically homogeneous material, which is uniformly magnetized normally; also the thin glass test-plate used must in the whole beam of light measure a normal field equal to the induction inside the metal of the mirror, on account of normal continuity. Neither the nickel-steel as an alloy of complicated structure nor the magnetite on account of its many fissures and pores satisfy the first condition. So there remains only the metallic nickel. How far the departures from the assumed configuration influence the saturation curves in this case cannot be estimated without further investigation; an opinion on this question can only be based on rather tedious preliminary experiments.

Physics. — “*On the solid state. I. — Mon-atomic substances.*” By
Dr. L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENTZ).

Already a considerable time ago G. MIE developed a theory of mon-atomic solid substances by the aid of the statistical considerations of BOLTZMANN¹⁾. He derived the condition for the coexistence of solid and gaseous phases, and determined the equation of state (equation of compressibility) by the aid of the method of the virial. By the aid of the theory of canonical ensembles the same results may be reached in a somewhat simpler manner. Shortly ago GRÜNEISEN²⁾ derived the equation of state for a mon-atomic solid substance in an analogous way as MIE, introducing, however, the hypothesis of PLANCK'S energy-quanta. It is, however, not devoid of interest to examine how these matters may be treated by the aid of the canonical ensembles modified in so far that PLANCK'S hypothesis is taken into account, because then also the coexistence of phases is easy to examine.

It is true that if the ensembles are modified in this way, we are no longer allowed to suppose without further proof that Ψ (the statistical free energy) is identical with the thermodynamic free energy,

¹⁾ Ann. der Phys. 11 1903 p. 675.

²⁾ Phys. Zeitschr. XII p. 1023. Zur Theorie einatomiger Körper.

because for the proof of the identity of these quantities we make use of the supposition that the systems of nature are mechanical in this sense that their movements are controlled by HAMILTON'S equations, which cannot be the case for the systems for which the hypothesis of PLANCK holds. I shall, however, suppose in this communication that we are allowed to apply to the modified ensembles all the arguments which are of force for the ensembles of GIBBS. On a later occasion I shall try to show on what premises this is allowed.

1. Consider a system built up of mon-atomic molecules. We suppose that these molecules exert attractive powers on each other up to distances that are large with respect to their mutual distances. We shall further suppose that they repel each other with very great force when their distances are small. We may leave undecided whether only adjacent molecules exert this repulsive force on each other or also those lying further apart.

We consider a gramme molecule containing N molecules. The volume be v .

Now we suppose with ME that the nature of the solid state consists in this that in this state the only movement is such that the molecules can execute vibrations round stable states of equilibrium. In the state of equilibrium the molecules form some net of a regular distribution through space, e.g. a cubical net.

So the energy of the considered system can be brought into the form: minimum potential energy plus energy of the vibratory motion. The energy at the boundaries is disregarded. It is natural to represent the minimum potential energy by:

$$-\frac{N^2\alpha}{v} + \frac{N^2\beta}{v^m}.$$

ME has demonstrated that the energy can be brought to this form if we suppose the repulsive forces to be proportionate to a negative power of the distance.

The condition that this energy is minimum for the given volume leads to the equation:

$$\alpha v^{m-1} = \beta m$$

If we apply this for the absolute zero ($v = v_0$), we find:

$$\alpha v_0^{m-1} = \beta m.$$

a relation which GRÜNEISEN derives as the condition that the pressure is zero at the absolute zero of temperature.

I now consider a canonic ensemble of the modulus Θ ($\Theta = \frac{R}{N} T$).

if T is the absolute temperature and R the gas constant for a gramme-molecule).

When E represents the energy and $d\lambda$ an element of the $6N$ dimensional extension in phase for the displacements from the positions of equilibrium and the corresponding moments, Ψ is given by:

$$e^{-\frac{\Psi}{\Theta}} = \int e^{-\frac{E}{\Theta}} d\lambda,$$

for which in our case may be written:

$$e^{-\frac{\Psi}{\Theta}} = e^{\frac{N^2\alpha}{v\Theta} - \frac{N^2\beta}{v\Theta}} \int e^{-\frac{Etr}{\Theta}} d\lambda = C \int e^{-\frac{Etr}{\Theta}} d\lambda.$$

Now the supposition may be introduced that the energy of the vibrations can only be whole multiples of the indivisible unity of energy ε . I shall follow EINSTEIN'S method of representation¹⁾. In the first place it may then be assumed that the integrations with respect to the coordinates and moments need be extended over only very narrow regions in the neighbourhood of $0, \varepsilon, 2\varepsilon$ etc. In the second place we suppose that the system can be taken as consisting of $3N$ independent resonators. If in a definite case n_k of these resonators possess an energy $k\varepsilon$, we may represent the contribution to the integral for this case:

$$A^{3N} \prod_{k=1}^{\infty} e^{-\frac{n_k \varepsilon k}{\Theta}},$$

$$\sum n_k = 3N.$$

If we take into consideration all the states in which n_k arbitrary molecules have the energy $k\varepsilon$ they yield a contribution:

$$(3N)! A^{3N} \prod \frac{e^{-\frac{n_k \varepsilon k}{\Theta}}}{n_k!}$$

If we examine for what combination of the n_k this is a maximum we find:

$$n_k = a e^{-\frac{k \varepsilon}{\Theta}}$$

a , determined by means of $\sum n_k = 3N$, becoming:

$$a = 3N \left(1 - e^{-\varepsilon/\Theta} \right).$$

¹⁾ Ann. der Phys. 22 1907. See Postscript.

The contribution of the most frequently occurring system becomes :

$$\frac{\sqrt{6\pi N}}{\sqrt{2\pi n_k \dots}} \frac{C}{(1 - e^{-\epsilon/\Theta})^{3N}},$$

from which follows by summation with respect to all possible values of r_R :

$$\frac{\Psi}{e} - \frac{\Psi}{\Theta} = \frac{\alpha N^2}{e} \frac{\beta N^2}{v^m \Theta} \frac{1}{(1 - e^{-\epsilon/\Theta})^{3N}}$$

or

$$\Psi = \frac{\alpha N^2}{v} - \frac{\beta N^2}{v^m} - 3N\Theta \log(1 - e^{-\epsilon/\Theta}) + 3N\Theta \log A.$$

If we apply $\bar{E} = \Psi - \Theta \frac{\partial \Psi}{\partial \Theta}$, we find for the mean energy \bar{E}

$$\bar{E} = \frac{3N\epsilon}{e^{-\epsilon/\Theta} - 1}.$$

If r is the frequency of the vibrations, so that $\epsilon = \frac{R}{N} \beta r$, then:

$$\bar{E} = \frac{3R\beta r}{e^{\frac{\beta r}{T}} - 1} = \int_0^T c_v dT,$$

from which follows the value for the specific heat given by EINSTEIN.

To find the pressure we have to determine $\frac{\partial \Psi}{\partial v}$. In this we should bear in mind that r is dependent on v .

On the supposition that the repulsive force varies as $\frac{1}{r^{3m}}$, MIE has determined the frequency of the vibrations; he finds for it:

$$(2\pi r)^2 = \frac{N^2 \beta^2 3m \cdot 3m + 1}{M v^{m+2/3}},$$

in which M is the weight of a molecule. If we apply this, we get:

$$\frac{2}{r} \frac{\partial r}{\partial v} = \left(m + \frac{2}{3}\right) \frac{1}{v}.$$

Making use of this result we find for the pressure:

$$p = - \frac{\alpha N^2}{v^2} + \frac{m\beta N^2}{v^{m+1}} + \frac{1}{e^{\frac{\beta r}{T}} - 1} \frac{3R\beta r}{2} \left(m + \frac{2}{3}\right)$$

$$= -\frac{\alpha N^2}{v^2} + \frac{m\beta N^2}{v^{m+1}} + \frac{3m+2}{6} \int_0^T c_v dT,$$

a formula which perfectly agrees with that given by GRÜNEISEN. For $T=0$ we find $p=0$, when between α , β , m , and v_0 the given relation exists.

If we do not make any supposition on the dependence of v on v , we find:

$$p = -\frac{\alpha N^2}{v^2} + \frac{m\beta N^2}{v^{m+1}} + \frac{1}{v} \frac{\partial v}{\partial v} \int_0^T c_v dT.$$

Just as in the derivation of the specific heat A drops out of the formula. A is supposed independent of v .

2. Coexistence of vapour and solid substance on the supposition that the vapour is an ideal gas.

Suppose n molecules to be in a volume v . Consider the system in which n_1 molecules are found as solid substance in the volume v_1 , n_2 molecules as gas in the volume v_2 . We have $v_1 + v_2 = v$, $n_1 + n_2 = n$. The number of such systems in a canonical ensemble amounts to:

$$e^{-\frac{\mathbf{Y}}{\Theta}} \frac{n!}{n_1! n_2!} v_2^{n_2} (2\pi\Theta M)^{\frac{3}{2}n_2} \frac{3}{2} n_2 e^{\left(\frac{\alpha}{v_1} - \frac{\beta}{v_1^m}\right) \frac{n_1^2}{\Theta}} A^{3n_1} \frac{1}{(1 - e^{-\varepsilon/\Theta})^{3n_1}}.$$

To find the most frequently occurring system, and so the real one, we must examine when this number will be maximum, varying the v 's and the n 's. This yields the conditions:

$$p_1 = p_2,$$

$$-\log n_1 + 3 \log A - 3 \log (1 - e^{-\varepsilon/\Theta}) + \frac{2n_1}{\Theta} \left(\frac{\alpha}{v_1} - \frac{\beta}{v_1^{m+1}} \right) =$$

$$-\log n_2 + \log v_2 + \frac{3}{2} \log 2\pi\Theta M.$$

In these relations which are sufficient to determine everything, A occurs. In this we find a way to indicate the value of A . For high temperatures the second condition may be replaced by that found by ME, as everything referring to the theory of energy-quanta must disappear then; for this it is necessary and sufficient that

$$A = \frac{R\beta}{N} = h$$

a result which was to be expected¹⁾.

As a condition that the system is really maximum we find among others:

$$\frac{dp_1}{dv} < 0$$

3. Coexistence of two solid phases. Let us suppose that two solid phases are possible, so that there exist two different nets of minimum potential energy.

These may differ as to the values of α , β , and ν , and also with regard to m a difference is possible, though improbable. I shall distinguish the phases by the indices 1 and 2. Let us again suppose that there are n molecules in the volume v , which are distributed over the volumes v_1 and v_2 , so that they contain n_1 and n_2 molecules.

For the number of such systems in a canonical ensemble, we find:

$$\frac{n!}{n_1! n_2!} e^{\frac{\Psi}{\Theta}} + \frac{\alpha_1 n_1^2}{v_1^{m_1} \Theta} - \frac{\beta_1 n_1^2}{v_1^{m_1} \Theta} + \frac{\alpha_2 n_2^2}{v_2^{m_2} \Theta} - \frac{\beta_2 n_2^2}{v_2^{m_2} \Theta}$$

$$\frac{1}{(1 - e^{-\epsilon_1/\Theta})^{3n_1}} \frac{1}{(1 - e^{-\epsilon_2/\Theta})^{3n_2}}$$

The search for the maximum system again yields the conditions of coexistence; they are, as is easily seen,

$$p_1 = p_2 \cdot$$

$$-\log n_x - 3 \log (1 - e^{-\epsilon_x/\Theta}) + \frac{2n_x}{\Theta} \left(\frac{\alpha_x}{v_x} - \frac{\beta_x}{v_x m_x} \right) \Big|_x = 0.$$

If we apply this at the absolute zero, we find:

$$\frac{n_1}{v_{10}} \left(\alpha_1 - \frac{\beta_1}{v_{10}^{m_1-1}} \right) = \frac{n_2}{v_{20}} \left(\alpha_2 - \frac{\beta_2}{v_{20}^{m_2-1}} \right),$$

Making use of GRÜNEISEN'S condition we can write for this, putting the densities ϱ_1 and ϱ_2 :

$$\varrho_1 \alpha_1 \left(1 - \frac{1}{m_1} \right) = \varrho_2 \alpha_2 \left(1 - \frac{1}{m_2} \right)$$

or if $m_1 = m_2$,

$$\varrho_1 \alpha_1 = \varrho_2 \alpha_2.$$

The entropy of a gramme molecule is for the two phases:

1) See Postscript.

$$\eta = - \frac{\partial \Psi}{\partial \Theta}$$

$$\eta_1 = - 3 N \log (1 - e^{-\epsilon_1/\Theta}) + \frac{3 N}{e^{\epsilon_1/\Theta} - 1} \frac{\epsilon_1}{\Theta} + 3 N \log A,$$

$$\eta_2 = - 3 N \log (1 - e^{-\epsilon_2/\Theta}) + \frac{3 N}{e^{\epsilon_2/\Theta} - 1} \frac{\epsilon_2}{\Theta} + 3 N \log A.$$

Which yields at the absolute zero:

$$\eta_1 - \eta_2 = 0.$$

So the theorem of heat of NERNST holds for the systems described above.

Postscript. We can derive Ψ in a similar way if we make use of the suppositions made by SOMMERFFLD¹⁾.

Then we have to take as non discernible regions in the two two-dimensional spaces that correspond to every degree of freedom of a resonator such regions that the energy lies between $k \epsilon$ and $(k + 1) \epsilon$. If we introduce this in the formula for Ψ , we get:

$$e^{-\frac{\Psi}{\Theta}} = \sum e^{-\frac{N^2 \alpha}{\Theta v} - \frac{N^2 \beta}{\Theta v^m}} \prod \frac{\int_{k\epsilon}^{(k+1)\epsilon} e^{-\frac{E}{\Theta}} dh}{n_k!} (3N)!$$

$$\sum n_k = 3N.$$

If we substitute $(k + \frac{1}{2}) \epsilon$ for E , in the integrals which are to be extended over a region h , and if we determine the maximum in the usual way, we get:

$$n_k = a h e^{-\frac{k + 1/2}{\Theta} \epsilon}$$

a being given by

$$a = \frac{3N \left(1 - e^{-\frac{\epsilon}{\Theta}}\right)}{h e^{-\frac{3\epsilon}{2\Theta}}}$$

This yields for Ψ

$$e^{-\frac{\Psi}{\Theta}} = \frac{N^2 \alpha}{v \Theta} \frac{N^2 \beta}{v \Theta^m} \frac{3N}{h} \frac{3N \epsilon}{e^{-\frac{3N \epsilon}{2\Theta}}} \frac{1}{\left(1 - e^{-\epsilon/\Theta}\right)^{3N}}$$

¹⁾ Phys. Zeitschr. XII 1911, p. 1057.

So there is agreement with what precedes, while A becomes $= h$.
We find for the mean energy:

$$E = \frac{3 N \epsilon}{e^{\epsilon/h} - 1} + \frac{3 N \epsilon}{2}$$

the result also given by SOMMERFELD and PLANCK in his later considerations.

NOW Prof. LORENTZ fixed my attention on the fact that POINCARÉ, has made the remark that we are not justified in identifying the N resonators of 3 degrees of freedom with 3 N resonators of one degree of freedom. I will show in what way we can meet this difficulty.

The energy of every resonator may be represented in the form:

$$\frac{1}{2m}(p_1^2 + p_2^2 + p_3^2) + \frac{f}{2}(\xi_1^2 + \xi_2^2 + \xi_3^2) = E$$

(p are the moments, ξ the coordinates with respect to the positions of equilibrium). Now this energy can amount to $0 \dots \epsilon \dots 2\epsilon$ etc. According to the hypothesis of the energy-quanta there is no difference between the systems for which the energy of the resonator lies between 0 and ϵ , ϵ and 2ϵ , $k\epsilon$ and $(k+1)\epsilon$.

The extent of the region in the 6 dimensional space where the energy is smaller than E , amounts to:

$$\frac{1}{6} U^3$$

The content of the shell for which the energy lies between $k\epsilon$ and $(k+1)\epsilon$ amounts to:

$$\frac{1}{2} k^2 \epsilon^3$$

If we consider that $\epsilon = hr$, we find for the extent of regions of equal probability

$$\frac{1}{2} k^2 h^2$$

In such a region we may put the energy $(k + 1/2)\epsilon$. Thus we find for the contribution to Ψ of the system where the energy for n_k resonators amounts to $(k + 1/2)\epsilon$

$$\frac{\Psi}{\Theta} = \frac{1}{2^N} h^{2N} (N!) \prod \frac{\left(\frac{(k + 1/2)\epsilon}{\Theta} \right)^{n_k}}{n_k!}$$

$\sum n_k = n$.

This yields for the most frequently occurring system

$$n_k = a k^2 e^{-\frac{(k+1/2)\epsilon}{\Theta}},$$

while

$$N = \frac{a e^{-\frac{3\epsilon}{2\Theta}} (1 + e^{-\epsilon/\Theta})}{(1 - e^{-\epsilon/\Theta})^2}$$

which is easily found if we bear in mind that:

$$\sum k^2 e^{-\frac{k\epsilon}{\Theta}} = \Theta^2 \frac{\partial^2}{\partial \epsilon^2} \left(1 + e^{-\frac{\epsilon}{\Theta}} + e^{-\frac{2\epsilon}{\Theta}} \dots \right).$$

For small values of Θ the formula deviates from the one given before because then we may put:

$$N = a e^{-\frac{3\epsilon}{2\Theta}} \left(1 - e^{-\frac{\epsilon}{\Theta}} \right)^{-4}.$$

For the mean energy we find for small value of Θ

$$E = \frac{3}{2} \epsilon N + \frac{4\epsilon N e^{-\epsilon/\Theta}}{(1 - e^{-\epsilon/\Theta})}.$$

This value differs from EINSTEIN'S by a numerical factor. Fundamental modifications, however, need not be applied, in consequence of this, to the above considerations.

Groningen, Febr, 1912.

Astronomy. — "*Further researches into the constant term in the latitude of the moon according to the meridian observations at Greenwich*". By Prof. E. F. VAN DE SANDE BAKHUYZEN.

Since my previous communication about this subject in the Proceedings of last December, I have continued my investigations. I was brought to it principally by the entirely different results found by BATTERMANN from his 3 great series of occultations of 1884—85, 1894—97, and 1902—03. I therefore resolved also to discuss the Greenwich observations for the years 1883 (the first year in which *Newcomb's* corrections have been introduced into the Nautical Almanac) up to 1894 and further to subject the systematic corrections of the declinations to a close revision.

In doing this I found to my regret that a mistake had slipped

into my reduction to Newcomb's fundamental system¹). I had taken the differences Greenw. 1900 — NEWC. Fundam. on page 31 of the introduction to the 2nd 9 Y. Cat. for the differences holding good for this catalogue, and had not noticed that on p. 27 is said that for *this* comparison the catalogue had first been reduced to "Pulkowa refractions" and colatitude 21".80. The correction of this mistake has altered the results of the previously discussed years with about 0".3.

First of all I will now revise my discussion of the systematic errors of the Greenwich-declinations. Of course I was quite conscious that for the present I could not think of a treatment of this important subject, even aspiring to thoroughness. For my present purpose, however, the determination of the mean declination-error of the moon over many years, I believed that a very summary treatment would be sufficient, also because it was not my intention to obtain absolute places, but only places reduced as well as possible to NEWCOMB'S system.

1. *Systematic corrections of the declinations determined at Greenwich.*

The different elements of these corrections I shall discuss successively.

Division-errors. In 1898 a new determination was accomplished of the division-errors for every 1°, and account was taken of corrected values for these errors for the observations of 1897 and following years. The *Greenw. Obs.* of 1897 and the introduction to the 2nd 10 Y. Cat. contain tables of the corrections consequently to be applied to the observations of 1880—96. The mean value of these

¹ I take this opportunity to observe that another slight inaccuracy has been committed in deriving the differences between the computed R. A.-of the moon and the results of the meridian observations at Greenwich, communicated in my previous paper. It is due to the fact that I took the results for the years 1895—1909 from the first of the two tables contained in the volumes of the *Greenwich Observations*, in which the observations are compared with the calculated places, not for the real but for the calculated moment of transit through the Greenwich-meridian. All my Δz must therefore be diminished with about the 28th part of their amount. Hence the real mean values of Δz , i. e. the values of the corrections to the mean longitude, become for the last two years:

	Δ NAUT. ALM.	Δ ROSS
1909.5	+ 5".96	— 0".17
1910.5	+ 7".27	+ 0".91

Assuming also for 1912 Δ ROSS = +0".9, then we find for this year Δ NAUT. ALM. = + 7".6 as far as regards the correction to the mean longitude.

The influence of this mistake on the yearly means for $\Delta \delta$ is practically zero.

corrections between N. P. D. 65° and 115° amounts, however, only to $-0''.02$ (to $-0''.04$ between 65° and 90° ; to $+0''.01$ between 90° and 115°) and might therefore be neglected.

Zenithpoint. At Greenwich the values for the zenithpoint are deduced partly from nadir determinations, but chiefly from direct and reflexion-observations of stars. Between the zenithpoints determined in these two ways Z_N and Z_S there exist, however, systematic differences which are found different for different periods. These differences seem partly to be dependent on the errors of the micrometer-screws in the microscopes and in the telescope. According to a very recent investigation by W. G. THACKERAY ¹⁾, however, they seem also partly to be due to personal bisection-errors of the observers.

In the 3 following periods the following mean values for $Z_S - Z_N$ were found :

1882—1885	$Z_S - Z_N = -0''.40$
1886—1891	0.00
1892—1909	-0.30

In each of these 3 periods the results of the separate years agree very well inter se. Between the first and second periods, in Dec. 1885, new steel micrometer-screws were applied to the microscopes, while in Oct. 1891, the micrometer-screw in the telescope was replaced by a new one and the objective was repolished. Moreover, in 1892 great changes took place in the staff of observers (comp. THACKERAY p. 182), which have certainly influenced the value of the $Z_S - Z_N$ too. No influence, however, can be traced of later changes in 1902 and following years, owing to which none of the observers of 1892—1901 has observed at the transit-circle after 1905. In the table given by THACKERAY I namely find :

1892—1901	Mean $Z_S - Z_N$	$-0''.32$
1902—1905		-0.26
1906—1910		-0.27

It is therefore not quite clear in how far personal influences have played a part in these differences and further the question remains whether these have chiefly influenced the nadir-determinations or the observations of the stars. Meanwhile, at Greenwich, the zenithpoints have always been principally based on the Z_S derived from the direct and reflexion observations of north and south stars. Before 1886 the mean difference between the Z_S and the Z_N was applied to the Z_N . Later on in forming the zenith-points a weight $\frac{1}{2}$ was assigned to the Z_S , and only a weight 1 to the Z_N . From 1897

¹⁾ Monthl. Not. 72 p. 178, Jan. 1912.

again a correction of $-0''.25$ was applied to the nadir determinations when only these were available.

As far, however, as by this method of reduction we have not yet obtained a declination-system that is homogeneous for the different years, we can only take into account the remaining discrepancies by applying for the periods of the 3 catalogues 1883—86, 1887—96, 1897—1905 and for the years 1906—09 the mean corrections to a fundamental system.

Flexure-corrections deduced from the differences R—D. As regards the two periods 1897—1905 and 1906—09, I have kept to the method explained in my previous paper; i. e. for the first period I applied corrections in order to reduce the results to the flexure $+0''.60 \sin z$ and for the second, for which this value had already been used at Greenwich, no further correction was applied.

For the period 1883—86 the employed co-efficients of $\sin z$ for the direct observations were resp. $+0''.69$, $+0''.66$, $+0''.69$ and $+0''.69$, while also for the 10 Y. Cat. $+0''.69$ is used. A further correction seemed unnecessary.

Finally, for the period of the 2nd 10 Y. Cat. 1887—96 the following flexure-formulae were originally employed:

1887	$+0''.68 \sin z$	1892	$+0''.58 \sin z$
88	$+0.75 \text{ ,,}$	93	$+0.70 \text{ ,,}$
89	$+0.68 \text{ ,,}$	94	$+0.55 \text{ ,,}$
90	$+0.56 \text{ ,,}$	95	$+0.41 \text{ ,,}$
91	$+0.54 \text{ ,,}$	96	$+0.37 \text{ ,,}$

In forming the star-places of the 2nd 10 Y. Cat. the separate annual results have been used without further correction. While the mean of the 10 co-efficients amounts to $+0''.58$, I have also reduced the declinations of the moon of each year to the flexure $+0''.58 \sin z$.

The flexure-formulae derived from the R—D always contain also a constant term which has to be regarded as a correction to the adopted zenithpoint. This is always small, however, and amounts till 1891 to about $-0''.01$, afterwards to about $+0''.05$. For our purpose we need not consider it.

According to THACKERAY'S investigation the personal errors of the observers would seem to depend also on the zenith-distance and thus to give rise to apparently different flexure-values. We can only attempt here to obtain final reductions to a fundamental system, which hold as well as possible for the average observer.

Colatitude and Refraction. From 1883 to 1905 the colatitude $21''.90$ has been used without alteration and also the refraction of

the Tab. Reg. These values have also been employed for the formation of the three catalogues.

In 1906, however, the "Pulkowa refraction" has come into use and as a consequence of this 21".80 has been adopted as colatitude. For the difference between the two systems we find from the Table in the Introduction to the 2nd 9 Y. C. p. 20.

N. P. D.	Mean difference New Syst. — Old Syst.
66° to 114°	+ 0".34
62 „ 118	+ 0. 35
72 „ 108	+ 0. 32

For the annual means of the declinations of the moon I have adopted + 0".34.

Since 1902 corrections have been applied to the annual results for the variation of the latitude according to ALBRECHT. For the formation of the 2nd 9 Y. C. also the results of the years 1897—1901 have been corrected for it. For my annual means, however, these corrections have but little importance as appears from the following annual means of the reductions holding for Greenwich, i.e. of the values of ALBRECHT'S $x + z$.

	$x + z$
1900	— 0".03
1901	+ 0. 04
1902	+ 0. 03
1903	+ 0. 05
1904	+ 0. 02
1905	— 0. 01
1906	— 0. 05

I have paid no further attention to these reductions. Their influence on longer periods and therefore also on the catalogue-comparisons may be entirely neglected.

Reduction to Newcomb's Fundamentalsystem. The last two Greenwich-catalogues have been compared there with NEWCOMB'S Fundamental catalogue for 1900 and the results of these comparisons have been given in the introductions to these catalogues.

From these I find the following mean differences in which Gr. 1900 red. means the declinations of the 2nd 9 Y. C. reduced to the new system with Pulkowa refraction, and Gr. 1890 the declinations of the 2nd 10 Y. C.

N. P. D.	Newc.	Gr. 1890	Newc.
	Gr. 1900 red.	Gr. 1900	Gr. 1890
65°—115°	+ 0".14	+ 0".07	+ 0".31
60 —120	+ 0. 10	+ 0. 06	+ 0. 31
70 —110	+ 0. 16	+ 0. 10	+ 0. 30

I adopt for my purpose the mean values between 65° and 115° and now find first of all from the 2nd column and the differences New Syst. -- Old Syst. given above :

$$\text{Newc.} - \text{Gr. 1900} + 0".48.$$

Adjusting this value with the other two we finally obtain :

$$\text{Newc.} - \text{Gr. 1900} + 0".45$$

$$\text{Newc.} - \text{Gr. 1890} + 0.34$$

Further I adopt as reduction on NEWCOMB for the years 1906—1909 + 0".45—0".34, and according to the introduction to the 2nd 10 Y. C. we find as mean differences between Gr. 1890 and the 10 Y. C. = Gr. 1880 :

N. P. D.	65°—115°	Gr. 1880—Gr. 1890	— 0".08
	60 —120		— 0. 08
	70 —110		— 0. 11

I thus finally adopt :

$$\text{Newc.} - \text{Gr. Obs. 1906—09} + 0".11$$

$$\text{Newc.} - \text{Gr. 1880} + 0.42$$

Resuming what we have found in this paragraph, we have to apply to the Greenwich-declinations of the moon : 1. the above given reductions to NEWCOMB, 2. for 1887—1905 reductions owing to flexure, and 3. for all observations corrections to reduce the results to the corrected value of the parallax-constant given in my previous paper.

2. *Investigation into the declinations of the moon.*

Besides extending my previous investigation to the years 1883—1894, I have also repeated the discussion for the years 1895—1902, in order to accomplish it in the same way as for the other years. The former method of investigation had this advantage that, besides the constant error in latitude, also the periodic errors, dependent on the argument of the latitude were introduced as unknown quantities. On the other hand no attention was paid to possible personal

errors of the observers. The comparison of the former results with the present ones thus gives us some information about the influence of the method of investigation on the obtained results.

I compared the new results, i.e. the mean of the three mean values formed in the previously indicated way, with those derived in my paper of 1903, and I found differences oscillating between $-0''.10$ and $+0''.12$, while the mean difference for the 8 years amounts to $+0''.01$ only. The outcome is therefore very satisfactory and also for 1895—1902 I have exclusively employed the new results.

In the following Table I the results have been collected of the observations of the limbs for the 27 years from 1883 to 1909. The 2nd to the 4th columns contain the annual means formed in the 3 ways, the 5th gives the mean of these three. Further the systematic corrections have been put down in the 6th column and the 7th contains the corrected $\Delta\delta = \text{Obs.} - \text{Naut. Alm.}$

Table II contains the results of the observations of Mösting A, which have been derived in entirely the same way as those for the limbs, as I now calculated also for the crater mean values after the 3rd method, i.e. from the means for the different observers separately. The columns of tables I and II wholly agree.

Besides deriving the mean results as they are collected in Tables I and II, I have also combined my results in another way, viz. by keeping those of the different observers separate but combining their results for the different years. For those observers who only occasionally made observations, I combined these in one group under the heading "Others", just as had already been done for the formation of the annual means in the 3rd way, and as is generally done at Greenwich. Otherwise some few observations, which moreover are likely to be less accurate, would become too preponderant.

The mean results derived in the last way follow in Table III for the obs. of the limbs, in Table IV for those of Mösting A. The former contains, besides the results for the mean of both the limbs, which had first been corrected for the systematic errors for each year, also those for half the difference between the two, hence for the radius of the moon according to each observer. Also the $\Delta\delta$ of Table IV had first been corrected for the systematic errors for each year. The weights given in Table III are the quantities $nn' : (n + n')$ where n and n' are the numbers of observations for each limb. In order to make the weights in Table IV comparable to the former, the 4th part of the number of observations has been taken for these.

TABLE I. Observations of the limbs.

	$\Delta \delta_{\frac{1}{2}}$ (North-limb + South-limb)				Corr.	$\Delta \delta$ corr.
	1	2	3	Mean		
1883	-0"73	-0"89	-0"68	-0"77	+0"70	-0"07
1884	-0.60	-0.60	-0.59	-0.60	+0.70	+0.10
1885	-0.64	-0.54	-0.72	-0.63	+0.70	+0.07
1886	-0.67	-0.69	-0.75	-0.70	+0.70	0.00
1887	-0.69	-0.88	-0.58	-0.72	+0.70	-0.02
1888	-1.36	-1.31	-1.31	-1.33	+0.75	-0.58
1889	-0.81	-0.67	-0.82	-0.77	+0.70	-0.07
1890	-0.93	-0.89	-0.86	-0.89	+0.60	-0.29
1891	-0.45	-0.60	-0.48	-0.51	+0.59	+0.08
1892	-0.24	-0.08	-0.32	-0.21	+0.62	+0.41
1893	-0.44	-0.51	-0.49	-0.48	+0.71	+0.23
1894	-0.52	-0.46	-0.55	-0.51	+0.60	+0.09
1895	-0.16	-0.49	-0.08	-0.24	+0.49	+0.25
1896	+0.44	+0.23	+0.31	+0.33	+0.46	+0.79
1897	+0.34	+0.34	+0.22	+0.30	+0.35	+0.65
1898	+0.08	-0.10	+0.10	+0.03	+0.35	+0.38
1899	-0.34	-0.18	-0.27	-0.26	+0.45	+0.19
1900	-0.74	-0.54	-0.66	-0.65	+0.52	-0.13
1901	-0.53	-0.66	-0.63	-0.61	+0.61	0.00
1902	-0.30	-0.25	-0.38	-0.31	+0.47	+0.16
1903	0.26	-0.16	-0.26	-0.23	+0.47	+0.24
1904	-0.11	-0.26	-0.21	-0.19	+0.54	+0.35
1905	-0.36	-0.28	-0.49	-0.38	+0.51	+0.13
1906	-0.07	-0.28	-0.28	-0.21	+0.39	+0.18
1907	-0.53	-0.28	-0.51	-0.44	+0.39	-0.05
1908	-0.09	-0.12	+0.25	+0.01	+0.39	+0.40
1909	-0.19	-0.05	-0.24	-0.16	+0.39	+0.23

TABLE II. Observations of Mösting A

	$\Delta \delta$				Corr.	$\Delta \delta$ corr.
	1	2	3	Mean		
1905	0.15	-0.24	0.29	0"23	+0.51	+0.28
1906	0.05	+0.05	0.23	-0.08	+0.39	+0.31
1907	-0.79	-0.66	0.75	-0.73	+0.39	-0.34
1908	0.04	-0.13	+0.23	+0.02	+0.39	+0.41
1909	-0.23	-0.18	+0.21	-0.07	+0.39	+0.32

TABLE III. Observations of the limbs.

Observ.	Period	Weight	$\Delta \frac{N-S}{2}$	$\Delta \frac{N+S}{2}$
H	83-01	79	- 0.19	+ 0.12
L	83-92	35	- 0.62	+ 0.14
A D	83-90	27	- 0.29	0.33
T	83-91	28	- 0.79	+ 0.03
A C	91-03	67	- 0.48	+ 0.46
T H	92	4	- 0.45	+ 0.02
B	92-05	72	- 0.40	+ 0.40
C D	96-02	17	- 0.80	+ 0.14
R	96-02	17	0.08	+ 0.29
W B	96-02	15	- 0.61	+ 0.42
W	02-09	41	- 0.93	- 0.57
J S	03-08	24	- 1.86	- 0.09
R C	03-09	26	- 1.15	- 0.51
S D	03-05	5	- 0.99	+ 0.55
E	04-09	29	- 0.98	+ 0.22
S E	06	1	- 2.46	+ 0.59
B E	09	5	- 1.21	+ 1.36
Others	83-09	118	- 0.46	- 0.29

TABLE IV. Observations of Mösting A.

Observ.	Period	Weight	$\Delta \delta$
R C	05-09	15	- 0.65
W	05-09	16	+ 0.76
E	05-09	11	+ 0.17
J S	05-08	8	- 0.57
B E	06 and 09	4	+ 0.36
Others	05-09	5	+ 1.12

The results as arrived at in the tables I-IV now must be examined more closely. Looking first at the annual results of tab. I, we notice some fluctuations in it. These may be partly real, because they may contain inequalities of long period of the form $\delta\sigma = -0.20 s \sin(\pi - \chi)$, — in which π is the longitude of the perigee and χ a slowly varying angle, which are due to inequalities in longitude of the form $\delta l = s \sin(\eta + \chi)$ caused by the action of the planets and not included in HANSEN'S theory. So from the Jovian evection a term of 18 years' period with a co-efficient of more than $0''.2$ must proceed, from a perturbation by the Earth and Venus a term of 95 years' period with a co-efficient of $0''.13$ and from another perturbation by Jupiter a term of 7 years' period with a co-efficient of $0''.09^1$.

Probably, however, the greater part of the fluctuations alluded to is due to personal bisection-errors. This appears from table III, and especially if we consider the results of each observer for the separate years, which are not given here. From these it is evident that often considerable personal differences exist between the different observers, and not only for the $\frac{1}{2}(N-S)$, but just as well for the $\frac{1}{2}(N+S)$. E. g., for observer W the 8 results for $\Delta \frac{1}{2}(N+S)$ from 1902—09 lie between $+0''.22$ and $+1''.82$ and for R. C. the 7 results from 1903—09 between $-0''.02$ and $-1''.27$, while the 6 results of J.S. from 1903—08 are situated between $-0''.64$ and $+0''.95$. For the 13 chief observers with weights of at least 15, i.e. with at least 60 observations, I further found as mean deviation of their results for $\Delta \frac{1}{2}(N+S)$ by comparing these with the mean of the 13, $\pm 0''.31$, while their mean error, according to the agreement of the different years inter se would amount to $\pm 0''.14$ only and the mean error of the annual means, (generally from fewer observations than the "personal means") is found to be, by comparison with the general mean, $\pm 0''.27$.

Also for the observations of Misting A it appears that the personal errors may reach amounts that cannot be neglected. The two observers W. and R. C. found e. g. from the crater-observations the same deviating results as from those of the limbs.

I have now derived final results from those of the 4 tables as follows. From those of table I I first formed mean results I, II and III for the 3 nine yearly periods and from these the general mean

¹⁾ In my investigation of 1903 it seemed to me that for these inequalities theory and observation did not completely agree. Lately a new investigation into this subject has been started at Leyden using the Greenwich observations of the last years.

IV, but also a mean value $\frac{1}{4}I + \frac{1}{2}II + \frac{1}{4}III = V$ in order to eliminate a periodic term of an 18 years' period. From table III I combined the results of the 13 chief observers with equal weights (VI) and added to those of the "Other observers" the results of the 4 observers with weights 1—5, which until now had been kept apart (VII). Finally I combined the results VI and VII with weights 13 and 4 to a general mean VIII. For the crater observations I simply formed mean values from the resp. 5 and 6 results of the tables II and IV.

In this way I found :

Observations of the limbs :

I 1883—1891	$\Delta \sigma = - 0''.09$
II 1892—1900	+ 0 .32
III 1901—1909	+ 0 .18
IV = $\frac{1}{3}(I + II + III)$	+ 0 .14
V = $\frac{1}{4}I + \frac{1}{2}II + \frac{1}{4}III$	+ 0 .18
VI 13 chief observers	+ 0 .14
VII other observers	+ 0 .34
VIII = $\frac{1}{17}(13 \times VI + 4 \times VII)$	+ 0 .19

Crater observations :

IX All the years 1905—09	$\Delta \sigma = + 0''.20$
X All the observers	+ 0 .20

I would consider the mean of the results V and VIII as the final result of the observations of the limbs and the mean of IX and X as that of the crater-observations. Since these 4 results practically agree, I find at last:

$$\Delta \sigma_{\text{HANSEN}} = + 0''.19$$

And as the mean correction of the declinations is = $0.96 \times$ the mean correction of the latitude, my result is

$$\Delta \beta_{\text{HANSEN}} = + 0''.20$$

In the course of my investigation I was checked several times by circumstances which would make its results less accurate. Especially the personal errors in observing the limbs of the moon and also those in bisecting Misting A brought a very uncertain factor in the problem. Still the agreement found finally between the results of the different computations and in particular between those from the observations of the limbs and of the crater would make me believe that, owing to the long period and the many observers, the

uncertainty was lessened to such a degree that my final result would still to some extent be reliable. There is one circumstance, however, preventing this. My result cannot be made to agree with that which BATTERMANN derived from the accurate treatment of his 3 large series of occultations.

According to a personal communication which Prof. BATTERMANN was kind enough to send me, he found, after a revision of his calculations and a homogeneous reduction to NEWCOMB'S fundamental system, as results from his 3 series of observations :

1884—85	$\Delta \beta = + 1''.04$
1894—97	+ 0 .63
1902—03	+ 0 .99
	Mean $\Delta \beta = + 0''.89$

He thinks that the 2nd result might still need a positive correction.

Thus the results obtained by the two of us differ $0''.7$ and this difference cannot be explained by casual uncertainties alone.

Prof. BATTERMANN drew my attention to the different nature of the two limbs of the moon and observed the possibility that the very mountainous south limb might be always observed too far south by meridian observers. Occultations and meridian observations would then not only yield a different diameter of the moon but also a different centre. The difficulty remains, however, that the observations of Mösting A lead to the same centre as those of the limbs. This would mean that also in making the micrometric determinations of the crater the south limb would have been taken too far south. A study of the selenographic determinations and of HAYN'S investigations will be necessary to settle this point. That a large personal error would have remained in the mean result of the crater-observations by all Greenwich observers seems to me not very probable in itself. It becomes very improbable, by the fact that the corresponding observations at Greenwich and at the Cape both reduced to BOSS' system, have led to a value of the parallax constant which cannot be far from the truth.

Postscript.

Thanks to Prof. DYSON'S great kindness I have received from him the mean results yielded by the just completed reduction of the R. A. of the moon, observed at Greenwich during 1911. I take this opportunity to communicate this important item for the knowledge of the place of the moon on April 17.

From 124 observations of the limbs there was found $\Delta\alpha = +0^{\circ}.603$ and from 80 observations of Mösting A $\Delta\alpha = +0^{\circ}.640$, so that since 1910 the error in longitude has again increased considerably.

Probably these results have to be regarded as "apparent errors" and must therefore be lessened with a 28th part of their amount. Since I had not paid attention to this circumstance in discussing the results of former years (comp. note in the beginning of this paper), the then derived differences between the results of occultations and meridian observations, are not quite accurate. Moreover I did not feel justified now in employing the difference, derived from the whole period 1847—1908, also for the reduction of the last years, since it obviously did not hold for these. I now adopt, according to the last years only, as reduction for the observations of limbs and crater resp. $0^{\circ}.00$ and $-0^{\circ}.20$. Thus I obtain as correction to the mean longitude according to the Naut. Alm. or NEWC. I:

1908.5	$\Delta N. I = + 6^{\circ}.04$
09.5	$+ 6 .43$
10.5	$+ 7 .75$
11.5	$+ 8 .89$

Extrapolating with the mean difference per annum between 1908 and 1911 $= +0^{\circ}.95$, I find as correction to the mean longitude for 1912.3 $+9^{\circ}.65$. In order to obtain the correction to the true longitude on the day of the eclipse, I add to it $+1^{\circ}.33$, as equation of the centre, corrections of the elements and perturbations, thus obtaining finally $+10^{\circ}.98$.

As correction to the latitude I now find: 1 as a consequence of the corrections to the longitude and to the longitude of the node $+0^{\circ}.03$, 2 for a perturbation-term $-0^{\circ}.08$, and 3 as correction to HANSEN'S constant term according to the occultations after BATTERMANN'S calculations $+0^{\circ}.9$, according to the Greenwich observations after my calculation $+0^{\circ}.2$.

We thus obtain :

$$1912 \text{ April } 17.0 \quad \Delta \lambda = + 11^{\circ}.0$$

$$\Delta \beta = + 0^{\circ}.85 \text{ or } + 0^{\circ}.15.$$

Physics. — “*Magnetic Researches. V. The initial susceptibility of nickel at very low temperatures.*” By ALB. PERRIER and H. KAMFLINGH ONNES. Communication N^o. 126*a* from the Physical Laboratory at Leiden.

§ 1. *Introduction.* To establish the general law for the effect of temperature upon magnetic phenomena is a much more complicated problem in the case of ferromagnetic substances than for substances whose susceptibility is independent of the field; for, with ferromagnetic substances — even when an investigation is being made of the influence of change of field upon susceptibility at constant temperature — a distinction has at once to be drawn between three entirely different cases. The region of *weak* fields is identified by a practically total absence of hysteresis: in the region of *moderate* fields the susceptibility changes very rapidly and hysteresis plays an all-important part; while in the region of *strong* fields or of *saturation* magnetisation changes but very little further with change of field. The intricacy of the general problem embodying these successive cases as well as various further peculiarities i.e. the irreversibilities depending on temperature and on time arises from the very nature of ferromagnetism itself. In these circumstances, therefore, an experimental investigation as well as a theoretical treatment of the whole problem of the change of ferromagnetism with temperature can hardly be treated otherwise than by a systematic subdivision of the investigation into various sections each of which can be treated separately. The natural method of treating the problem seems to be to ascertain the temperature functions which hold good throughout each of the regions, and in that case the two extreme regions are obviously the easiest to investigate, for then at least one of the phenomena, hysteresis, is no longer of any account.

The investigation of one of these extreme regions, that of saturation, has already been pretty well completed, not only at high but also at very low¹⁾ temperatures. The results then obtained were used by WEISS in the research which led him to the important discovery of the magneton. In his recent dissertation RADONAVOVITCH has worked in the other extreme region, that of initial susceptibility (i.e. susceptibility in weak fields) but only at temperatures above 0° C. His results, which were obtained exclusively with nickel, led principally to the following result.

¹⁾ P. WEISS and H. KAMERLINGH ONNES, Comm. N^o. 114 from the Physical Laboratory at Leiden. (These Proceedings' XII p. 649).

If I is the magnetisation induced by a field of strength H , then, for fields below 0,5 gauss about, and at constant temperature,

$$I = aH + bH^2$$

or

$$k = a + bH$$

RADOVANOVITCH has now found that between 17° C, and the CURIE point a and b are determined for nickel as functions of the temperature by

$$a = .1 \sqrt[4]{\left(\frac{I_0}{I} - 1\right)}$$

$$b = B \left(\frac{I_0}{I} - 1\right).$$

I and I_0 are the saturation magnetisations at the experimental temperature and at the absolute zero respectively, A and B are constants. At the CURIE point therefore a and b become infinite, while they both vanish at the absolute zero; b is much smaller than a , as long as we come not near the CURIE point (at 18° C, $b = 0,04 a$).

The present paper relates to the susceptibility at temperatures below 0° C. down to very low temperatures — the boiling point of hydrogen — of the same nickel ring which was used by RADOVANOVITCH in his research; for the use of this ring we are indebted to the kindness of Prof. WEISS to whom we now wish to record our thanks.

We wished to ascertain in the first place if the important deductions concerning magnetisation in the neighbourhood of the absolute zero to which the above formulae lead, are confirmed by experiment. From the more general point of view indicated above, it is also of importance to ascertain if all ferromagnetic magnitudes could be expressed *as functions of the saturation magnetisation*. And lastly the result can be of fundamental importance in the *physics of crystals*, for there are weighty reasons for ascribing ferromagnetic initial susceptibility to a *reversible twisting of the direction of magnetisation* in the elementary crystals as saturation is reached. A knowledge of the susceptibility can therefore lead to a better grasp of the magnetic structure of the crystal itself.

§ 2. *Experimental method and results.* We confine ourselves to a very short description of the research the details of which we shall publish in full later.

The ballistic method was used with a toroid built up of circular plates of nickel. Absolute values were obtained by calibrating the

galvanometer with a standard solenoid. The toroid, wrapped with its primary and secondary winding, was placed in a large silvered vacuum glass, into which a sufficient quantity of liquid gas was poured to ensure that the liquid surface of the bath was well above the toroid. The cryogenic part of the experiments gave rise to many serious difficulties on account of the large mass of metal which had to be cooled. For the measurements at liquid hydrogen temperatures the toroid was first immersed in liquid air in the cryostat; the air was then syphoned off, the cryostat evacuated and then filled with liquid hydrogen.

The numerical results are collected in the following table.

INITIAL SUSCEPTIBILITY OF NICKEL.		
Bath	T	$k_{H=0}$
Ordinary temperat.	291°K	3,045
Liquid oxygen	90	0,955
	76,5	0,881
Liquid hydrogen	20,5	0,782

Each of the values given above is the result obtained from measurements made with five fields between 0,017 and 0,090 gauss. The quantity b , which is extremely small even at ordinary temperature, vanishes altogether at very low temperatures within the limits of accuracy of the observations.

It is quite evident that with falling temperature a (or k) continues to decrease regularly. Just as with regard to the value of b , the results with regard to a leave no doubt of good *qualitative* correspondence with those obtained by extrapolation from the figures given by RADOVANOVITCH. As for the *quantitative* correspondence¹⁾ it must be remarked that it cannot, from the nature of the case, be well defined; for it is a question of a difference between 1 and a figure which at very low temperatures differs from unity by a very small quantity. I and I_0 would have to be known with very great accuracy before we could be at all sure of the value of $\frac{I_0}{I} - 1$. Taking the formula given by RADOVA-

¹⁾ The difference of the absolute values at ordinary temperature obtained by RADOVANOVITCH from those given by us are caused by the change with time of the magnetic properties of the nickel toroid ("Alterung", "vieillissement"). This change has been taken into account throughout our experiments.

NOVITCH, for a as a function of I to be correct, however, and using it to determine I from our results, we find that between $90^{\circ} K$ and $20^{\circ} K$ the saturation magnetisation does not increase much more than 0,0003, a result which is not inconsistent with what is accepted on behalf of experiment concerning saturation magnetisation at low temperatures.

Chemistry. — “*On the activity of the halogene-dinitro-pseudo-cumoles and their addition productivity with nitric acid.*”

By A. HUENDER. (Communicated by Prof. A. F. HOLLEMAN).

(Will not be published in these Proceedings).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday March 30, 1912.

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Afdeling van Zaterdag 30 Maart 1912, Dl. XX).

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- M. STUYVAERT: "On the lineo-linear congruences of right lines and the cubic surface". (Communicated by Prof. JAN DE VRIES), p. 1018.
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Mathematics. — “Homogeneous linear differential equations of order two with given relation between two particular integrals”. (4th communication). By Dr. M. J. VAN UVEN. (Communicated by Prof. W. KAPTEYN).

(Communicated in the meeting of February 24, 1912).

In the preceding communications we have discussed the parity of function $I(\tau)$, in connection with the parity of the functions $x(\tau)$ and $y(\tau)$. It then became evident that the same function $I(\tau)$ determines two mutually semi-equivalent curves $F(x, y) = 0$ when it is a univalent even function of τ .

Let us now suppose that $I(\tau)$ is determined as root of even power out of a certain function of τ ; then to the same curve $F(x, y) = 0$ belong two opposite functions I , from which ensues that $F(x, y) = 0$ is then semi-equivalent to itself.

We shall occupy ourselves in the following, in connection with the remark made here, in particular with algebraical curves $F(x, y) = 0$.

Just as in equation (31) and (32) (1st communication page 398) we have expressed I in the integrals x and y , we shall now also give $\dot{I} = \frac{dI}{d\tau}$ such a form.

We shall make use of the following abridgments:

$$\overline{\Phi} = \Phi_x F_y - \Phi_y F_x,$$

$$\overline{\overline{\Phi}} = (\overline{\Phi})_x F_y - (\overline{\Phi})_y F_x$$

etc.

With the aid of this we can write equation (31) in the form

$$G = F_z \overline{H} - 3H \overline{F}_z.$$

We then find

$$\dot{I} = \frac{dI}{d\tau} = I_x \frac{dx}{d\tau} + I_y \frac{dy}{d\tau} = \frac{(n-1) F_z^{\frac{1}{2}}}{z^{\frac{1}{2}} H^{\frac{1}{2}}} (I_x F_y - I_y F_x) = \frac{(n-1) F_z^{\frac{1}{2}} \overline{I}}{z^{\frac{1}{2}} H^{\frac{1}{2}}}.$$

If we calculate I_x and I_y out of (32), we shall finally find:

$$I = \frac{dI}{d\tau} = \frac{(n-2)^2}{2z F_z H^2} (4F_z H \overline{F}_z \overline{H} + 2F_z H \overline{H} \overline{F}_z + 6F_z H^2 \overline{F}_z - 3F_z^2 \overline{H} + 3H^2 \overline{F}_z^2). \quad (51)$$

For I^2 we can write

$$I^2 = \frac{(n-1)^2}{z F_z H^2} (F_z \overline{H} - 3H \overline{F}_z)^2. \quad (52)$$

In the supposition that $F(x, y, z) = 0$ is an algebraical equation we shall arrive by eliminating the homogeneous variables x, y , and z out of (51), (52), and $F(x, y, z) = 0$ at a rational equation between I and I^2 .

$$\dot{I} = \mathcal{Y}(I^2),$$

If the solution is

$$\Phi(I^2, I) = 0, \dots \dots \dots (53)$$

we then find τ out of

$$\tau - \tau_0 = \int \frac{dI}{\Psi(I^2)} = \Omega(I) \dots \dots \dots (54)$$

and $I(\tau)$ by reversing the function $\Omega(I)$.

As $\Psi(I^2)$ is an algebraical function τ is an algebraical integral-function of I , and $I(\tau)$ is the reverse of it.

If we take $I^2 = X$ and $I = Y$ as rectangular coordinates then

$$\Phi(X, Y) = 0$$

will represent some algebraical curve.

We can conjugate the curve $\Phi(X, Y) = 0$ to the system of all curves $F(x, y) = 0$ which are mutually equivalent. A curve $F_1(x, y) = 0$, which is semi-equivalent to $F = 0$, determines an opposite I , hence an equal X and an opposite Y . The curve $F_1 = 0$ conjugate to $\Phi_1 = 0$ is thus the *image* of $\Phi = 0$ with respect to the X -axis.

The curve $\Phi = 0$, which is conjugate to a curve $F = 0$ *semi-equivalent to itself*, is therefore symmetrical with respect to the X -axis.

We shall now give a somewhat extensive treatment of the case in which $F = 0$ represents a conic.

By means of a homogeneous linear substitution (if necessary with complex coefficients) we can always make one of the points at infinity to be in the direction of the Y -axis. In this case the equation $F(x, y) = 0$ is linear in y and the equation $y = g(x)$ is rational, so that operation with the equations (20), (21), and (22) (1st communication page 366) gives rise to few algebraic complications.

However as we have our formulae ready for I and \dot{I} expressed by means of the implicit equation $F(x, y, z) = 0$ we shall, likewise with a view to greater symmetry, make use of the unsolved equation $F(x, y, z) = 0$.

Beforehand we remark that not all conics can be transformed into each other by means of homogeneous linear substitutions. For, only those conics can be transformed into each other by means of these substitutions where the anharmonic ratio σ between the points S_1 and S_2 at infinity and the points of contact R_1 and R_2 of the tangents out of the origin have the same value; in other words: equivalent conics have equal σ .

We shall now first express the value of σ in the coefficients of the Σ equation $F = 0$.

The anharmonic ratio $\sigma = (S_1, S_2, R_1, R_2)$ is the anharmonic ratio of the four rays which join these points with a fifth point of the

conic or of the four points which their tangents describe on a fifth tangent of the conic. Let us take as fifth tangent one of the tangents OR_1 out of O , then the point of contact R_1 must be considered as point of intersection of OR_1 with itself. The second tangent OR_2 out of O intersects OR_1 in O . Let us moreover call S_1', S_2' the points of intersection of OR_1 with the asymptotes of S_1^∞ and S_2^∞ then we can write

$$d = (S_1 S_2, R_1 R_2) = (S_1' S_2', R_1 O) = \frac{S_1' R_1}{S_2' R_1} : \frac{S_1' O}{S_2' O}$$

or, because $S_1' R_1 = -S_2' R_1$,

$$d = -\frac{S_2' O}{S_1' O}$$

The ratio $\frac{S_2' O}{S_1' O}$ can now be replaced by the ratio of the abscissae x_2 and x_1 of S_2' and S_1' , so that we find as simplest expression

$$d = -\frac{x_2}{x_1} \dots \dots \dots (55)$$

The conic may be represented by the equation

$$F(x, y, z) \equiv a_{11}x^2 + 2a_{12}xy + a_{22}y^2 + 2a_{13}xz + 2a_{23}yz + a_{33}z^2 = 0. \quad (56)$$

We now put

$$\begin{matrix} a_{11}, & a_{12}, & a_{13} \\ a_{12}, & a_{22}, & a_{23} \\ a_{13}, & a_{23}, & a_{33} \end{matrix} \equiv \Delta$$

and we indicate the subdeterminants of $a_{11} \dots a_{33}$ respectively by $A_{11} \dots A_{33}$. The pair of asymptotes is then represented by the equation

$$a_{11}x^2 + 2a_{12}xy + a_{22}y^2 + 2a_{13}xz + 2a_{23}yz + \left(a_{33} - \frac{\Delta}{A_{33}} \right) z^2 = 0.$$

The points of intersection of this pair of lines with the line

$$y = mx$$

through O are now determined by

$$(a_{22}m^2 + 2a_{12}m + a_{11})x^2 + 2(a_{23}m + a_{13})xz + \left(a_{33} - \frac{\Delta}{A_{33}} \right) z^2 = 0. \quad (57)$$

If the indicated line through O is to touch the conic, then m must satisfy

$$A_{12}m^2 - 2A_{12}m + A_{22} = 0,$$

or

$$(a_{22}a_{33} - a_{23}^2)m^2 - 2(a_{13}a_{23} - a_{12}a_{33})m + (a_{11}a_{33} - a_{13}^2) = 0,$$

or

$$(a_{23}m + a_{13})^2 = a_{33}(a_{22}m^2 + 2a_{12}m + a_{11}) \dots \dots (58)$$

Out of (57) and (58) follows for both roots $x_1 : z_1$ and $x_2 : z_2$ or x_1 and x_2 :

$$\frac{(x_1 + x_2)^2}{4x_1x_2} = \frac{(a_{23}m + a_{13})^2}{(a_{22}m^2 + 2a_{12}m + a_{11}) \left(a_{33} - \frac{\Delta}{A_{33}} \right)} = \frac{a_{23}}{a_{12}} = \frac{a_{33}A_{33}}{a_{33}A_{33} - \Delta}$$

hence

$$\frac{(x_1 + x_2)^2}{(x_1 - x_2)^2} = \frac{a_{33}A_{33}}{\Delta},$$

and, on account of (55),

$$\left(\frac{1-d}{1+d} \right)^2 = \frac{a_{33}A_{33}}{\Delta} = \lambda^2 \dots \dots \dots (59)$$

From this ensues

$$\frac{1-d_1}{1+d_1} = +\lambda \quad , \quad \frac{1-d_2}{1+d_2} = -\lambda.$$

so

$$d_1 = \frac{1-\lambda}{1+\lambda} \quad , \quad d_2 = \frac{1+\lambda}{1-\lambda} \dots \dots \dots (60)$$

So we find as was to be expected two reciprocal values for d . Equivalent conics have equal d , therefore also equal λ . So for equivalent conics holds

$$\frac{a_{33}A_{33}}{\Delta} = \text{constant}.$$

To investigate how the value of d depends on the form of the conic and on its situation with respect to the origin and of the line at infinity we can invert the relative situation of conic and origin. So we base our considerations on a fixed conic and we have then to investigate how the value of d depends on the situation of the point O thought as variable with respect to the fixed conic.

We take for the conic of reference the hyperbola

$$\frac{x^2}{a^2} - \frac{y^2}{b^2} = 1.$$

If later on we wish to transfer our results to the ellipse, we have but to suppose b imaginary.

If x_0, y_0 are the coordinates of point O , and x_1, y_1 and x_2, y_2 those of the points S_1' and S_2' , then holds

$$d = - \frac{OS_2'}{OS_1'} = - \frac{x_2 - x_0}{x_1 - x_0} = - \frac{y_2 - y_0}{y_1 - y_0},$$

so

$$(1 + \delta)x_0 = \delta x_1 + x_2 \quad , \quad (1 + \delta)y_0 = \delta y_1 + y_2.$$

Because (x_1, y_1) and (x_2, y_2) lie on the asymptotes and their midpoint $\left(\frac{x_1+x_2}{2}, \frac{y_1+y_2}{2}\right)$ on the conic, we find

$$\frac{x_1}{a} = \frac{y_1}{b} \quad , \quad \frac{x_2}{a} = -\frac{y_2}{b} \quad , \quad \frac{(x_1+x_2)^2}{a^2} - \frac{(y_1+y_2)^2}{b^2} = 4,$$

from which ensues

$$\frac{x_1 x_2}{a^2} - \frac{y_1 y_2}{b^2} = 2,$$

so that

$$1 + \delta)^2 \left(\frac{x_0^2}{a^2} - \frac{y_0^2}{b^2} \right) = a^2 \left(\frac{x_1^2}{a^2} - \frac{y_1^2}{b^2} \right) + 2\delta \left(\frac{x_1 x_2}{a^2} - \frac{y_1 y_2}{b^2} \right) + \left(\frac{x_2^2}{a^2} - \frac{y_2^2}{b^2} \right) = 4\delta,$$

or

$$\frac{x_0^2}{a^2} - \frac{y_0^2}{b^2} = \frac{4\delta}{(1 + \delta)^2} = 1 - 2^2 = k \quad . \quad . \quad . \quad (61)$$

So points O of equal δ lie on a conic similar and homothetic to the conic of reference.

In this way we can represent the values of δ in connection with those of k and λ in the following plan :

	I	II	III	VI	V	VI	VII=I
k	$(+)$ $-\infty$	$> -\infty, < 0$	0	$> 0, < +1$	+1	$> +1, < +\infty$	$(-)$ $+\infty$
λ	$+x$	$< +x, > +1$	+1	$< +1, > 0$	0	$0 < \lambda < \infty$	$i\infty, +\infty$
δ_1	-1	$> -1, < 0$	0	$> 0, < +1$	+1	$e^{-i\psi}, 0 < \psi < \pi$	-1
δ_2	-1	$< -1, > -\infty$	$-\infty$	$< +x, > +1$	+1	$e^{+i\psi}, 0 < \psi < \pi$	-1

For the parabola $\lambda_{33} = 0$, hence $\lambda = 0$, so always $\delta_1 = \delta_2 = +1$.

For the hyperbola we find the following state of affairs :

- I. At infinity $\delta_1 = -1$, $\delta_2 = -1$;
- II. in the domain of the conjugate hyperbola $-1 < \delta_1 < 0$, $-1 > \delta_2 > -\infty$;
- III. on the asymptotes $\delta_1 = 0$, $\delta_2 = \mp \infty$;
- IV. between the asymptotes and the curve $0 < \delta_1 < +1$, $+\infty > \delta_2 > +1$;
- V. on the curve $\delta_1 = +1$, $\delta_2 = +1$;
- VI. at the concave side of the curve $\delta_1 = e^{-i\psi}, 0 < \psi < \pi, \delta_2 = e^{+i\psi}, 0 < \psi < \pi$.

For the ellipse holds:

VII. At infinity	$d_1 = -1$, $d_2 = -1$;
VI. outside the curve	$d_1 = e^{-i\tau}, \tau > \psi > 0$,	$d_2 = e^{+i\tau}, \tau > \psi > 0$;
V. on the curve	$d_1 = +1$, $d_2 = +1$;
IV. inside the curve	$+1 > d_1 > 0$, $+1 < d_2 < +\infty$;
III. in the centre	$d_1 = 0$, $d_2 = +\infty$.

We shall now determine the form of the function $I(\tau)$.

From (53) follows:

$$F_x = 2(a_{11}x + a_{12}y + a_{13}z) \quad , \quad F_y = 2(a_{12}x + a_{22}y + a_{23}z).$$

$$F_z = 2(a_{13}x + a_{23}y + a_{33}z) = 2g.$$

$$2a_{11} \quad , \quad 2a_{12} \quad , \quad 2a_{13}$$

$$H = : 2a_{12} \quad , \quad 2a_{22} \quad , \quad 2a_{23} \quad = 8\Delta \quad , \quad H=0 \quad , \quad \bar{H}=0.$$

$$2a_{13} \quad , \quad 2a_{23} \quad , \quad 2a_{33}.$$

$$\begin{aligned} \bar{F}_z = F_x F_y - F_y F_x &= 4 \{ a_{13} (a_{12}x + a_{22}y + a_{23}z) - a_{23} (a_{11}x + a_{12}y + a_{13}z) \} = \\ &= 4(A_{13}g - A_{13}g). \end{aligned}$$

$$\begin{aligned} F_z &= (F_x, F_y) - (F_y, F_x) = 8 \{ A_{13}(a_{12}x + a_{22}y + a_{23}z) - A_{23}(a_{11}x + a_{12}y + a_{13}z) \} = \\ &= 8 \{ (a_{11}A_{13} + a_{12}A_{23})x + (a_{12}A_{13} + a_{22}A_{23})y + (a_{13}A_{13} + a_{23}A_{23})z \} = \\ &= 8 \{ -a_{13}A_{33}x - a_{23}A_{33}y + (\Delta - a_{33}A_{33})z \} = 8(\Delta z - A_{33}g). \end{aligned}$$

$$I^2 = \frac{3^2 \cdot 2^{10} \cdot \Delta^2 (A_{23}x - A_{13}y)^2}{2^{10} z g \Delta^2} = 9 \frac{(A_{23}x - A_{13}y)^2}{z g \Delta^2}.$$

$$i = \frac{-3 \cdot 2^{11} \cdot \Delta^2 g (\Delta z - A_{33}g) + 3 \cdot 2^{10} \cdot \Delta^2 (A_{23}x - A_{13}y)^2}{2^{11} z g \Delta^3}$$

$$= \frac{3}{2 z g \Delta} \{ (A_{23}x - A_{13}y)^2 - 2g(\Delta z - A_{33}g) \}.$$

We now find :

$$\begin{aligned} &(A_{23}x - A_{13}y)^2 + A_{33}g^2 - 2\Delta gz = \\ &= (A_{23}^2 + a_{13}^2 A_{33})x^2 + 2(-A_{13}A_{23} + a_{13}a_{23}A_{33})xy + (A_{13}^2 + a_{23}^2 A_{33})y^2 + \\ &+ 2(a_{12}a_{33}A_{33} - \Delta a_{13})xz + 2(a_{22}a_{33}A_{33} - \Delta a_{23})yz + (A_{33}a_{33}^2 - 2\Delta a_{33})z^2 = \\ &= (a_{33}A_{33} - \Delta)(a_{11}x^2 + 2a_{12}xy + a_{22}y^2 + 2a_{13}xz + 2a_{23}yz + a_{33}z^2) - \Delta a_{33}z^2 \\ &= (a_{33}A_{33} - \Delta)F - \Delta a_{33}z^2, \end{aligned}$$

or, because (x, y, z) satisfy $F = 0$,

$$(A_{23}x - A_{13}y)^2 + A_{33}g^2 - 2\Delta gz = -\Delta a_{33}z^2.$$

Hence we find

$$I^2 = \frac{9}{z g \Delta} (-A_{33}g^2 + 2\Delta gz - \Delta a_{33}z^2), \quad . \quad . \quad . \quad (62)$$

$$i = \frac{3}{2 z g \Delta} (A_{33}g^2 - \Delta a_{33}z^2) . \quad (63)$$

By elimination of g we find

$$36 \dot{I}^2 = I^4 - 36I^2 + 324 \left(1 - \frac{a_{33} A_{33}}{\Delta} \right), \dots \quad (64)$$

or, on account of (59),

$$36 \dot{I}^2 = (I^2 - 18)^2 - 18^2 \lambda^2, \dots \quad (65)$$

so

$$6 \dot{I} = \pm \sqrt{\{I^2 - 18(1 + \lambda)\} \{I^2 - 18(1 - \lambda)\}},$$

or

$$\tau - \tau_0 = \pm \int \frac{6dI}{\sqrt{\{I^2 - 18(1 + \lambda)\} \{I^2 - 18(1 - \lambda)\}}}, \dots \quad (66)$$

So I proves to be an *elliptic* function of τ .

If we introduce $I^2 = u$ as variable we find :

$$36 I^2 \dot{I}^2 = I^6 - 36 I^4 + 324 (1 - \lambda^2) I^2,$$

or

$$\begin{aligned} 9 \left(\frac{du}{d\tau} \right)^2 &= u^3 - 36u^2 + 324 (1 - \lambda^2) u \\ &= u \{u - 18(1 + \lambda)\} \{u - 18(1 - \lambda)\}, \end{aligned}$$

thus

$$\tau - \tau_0 = \pm \int \frac{3du}{\sqrt{u \{u - 18(1 + \lambda)\} \{u - 18(1 - \lambda)\}}}, \dots \quad (67)$$

The singular points are now $u_1 = \infty$, $u_2 = 0$, $u_3 = 18(1 + \lambda)$, $u_4 = 18(1 - \lambda)$.

One of their six anharmonic ratios is therefore

$$\frac{u_4}{u_3} = \frac{1 - \lambda}{1 + \lambda} \sigma_1.$$

The anharmonic ratio of the elliptic function $u = I^2 = Q(\tau)$ is therefore equal to the anharmonic ratio of the four characteristic points $S_1^\infty, S_2^\infty, R_1, R_2$ of the conics $F = 0$.

Evidently the invariant of this elliptic function is :

$$i = \frac{4(\sigma^2 - \sigma + 1)^2}{27\sigma^2(1 - \sigma)^2} = \frac{(1 + 3\lambda^2)^3}{27(1 - \lambda^2)^2 \lambda^2} = \frac{(\Delta + 3a_{33}A_{33})^3}{27a_{33}A_{33}(\Delta - a_{33}A_{33})^2} \quad (68)$$

Before transforming the elliptic integral we shall first investigate in what case it degenerates. Degeneration takes place, when the

equation $\frac{du}{d\tau} = 0$ has two coinciding roots. This occurs :

1. When $\lambda = 0$, thus $\sigma_1 = \sigma_2 = +1$; in this case either $a_{33} = 0$, holds or $A_{33} = 0$, i.e. either the conic passes through O , or it touches the line at infinity, in other words it is a parabola. These two types of curves are *not* equivalent, but they are semi-equivalent: so they have opposite functions I . This now coincides with the fact, that for

$\lambda = 0$ the form under the sign of the root in (66) is a perfect square, so that two separated functions I appear. To distinguish the types $a_{33} = 0$ and $A_{33} = 0$ properly we shall return to the equations (62) and (63). For $a_{33} = 0$ these take the following forms :

$$z \Delta I^2 = 9 (-A_{33}g + 2\Delta z),$$

$$2z \Delta \dot{I} = 3A_{33}g.$$

By elimination of g we find

$$6\dot{I} = 18 - I^2, \dots \dots \dots (69a)$$

so

$$\tau - \tau_0 = \int \frac{6dI}{18 - I^2} = +\sqrt{2} \cdot \tan h^{-1} \frac{I}{3\sqrt{2}},$$

or

$$I = + 3\sqrt{2} \cdot \tan h \frac{\tau - \tau_0}{\sqrt{2}} \dots \dots \dots (70a)$$

If on the other hand we put $A_{33} = 0$, then (62) and (63) pass into

$$gI^2 = 18g - 9a_{33}z,$$

$$2g\dot{I} = -3a_{33}z.$$

Elimination of g now leads to

$$6\dot{I} = I^2 - 18, \dots \dots \dots (69b)$$

from which ensues

$$\tau - \tau_0 = - \int \frac{6dI}{18 - I^2} = -\sqrt{2} \cdot \tan h^{-1} \frac{I}{3\sqrt{2}},$$

or

$$I = - 3\sqrt{2} \cdot \tan h \frac{\tau - \tau_0}{\sqrt{2}} \dots \dots \dots (70b)$$

2. A second case of degeneration appears when $\lambda = +1$ (or $\lambda = -1$), so for $\sigma_1 = 0, \sigma_2 = \infty$ or $\sigma_1 = \infty, \sigma_2 = 0$; in this case we have $a_{33}A_{33} = \Delta$ or $a_{13}A_{13} + a_{33}A_{23} = 0$; the geometric meaning of this is that O lies on one of the asymptotes (for the ellipse in the centre). The equation (66) now runs :

$$\tau - \tau_0 = - \int \frac{dI}{I\sqrt{I^2 - 36}} = \pm \sin^{-1} \frac{6}{I},$$

so that

$$I = \pm \frac{6}{\sin(\tau - \tau_0)} \dots \dots \dots (71)$$

3. When at the same time $a_{33} = 0$ and $A_{33} = 0$ holds, i.e. when the conic is a parabola passing through O , then the equation (62) furnishes

$$I = \pm 3\sqrt{2}.$$

This result has formerly been found (see 2nd communication page 590); we can regard it as the combination of (70a) and (70b) for $\tau_0 = \infty$.

Mathematics. — “On the lineo-linear congruences of right lines and the cubic surface”. By Mr. M. STUYVAERT at Ghent (Belgium). (Communicated by Prof. JAN DE VRIES).

(Communicated in the meeting of February 24, 1912).

1. In pursuing our studies on the geometrical interpretations of matrices whose elements are algebraical forms¹⁾, we have been led to deduce certain consequences of a wellknown theorem of Geometry of n dimensions.

The theorem runs²⁾:

“If in space of n dimensions S_n two simplexes with $n+1$ vertices “are reciprocal polars with respect to a quadratic variety, the spaces “ S_{n-2} common to the homologous limiting spaces S_{n-1} of the two “simplexes are such that every right line resting on n of these “spaces rests also on the $(n+1)$ th”.

Let us apply this to the space S_5 and to the quadratic variety Q of this space giving the properties of the ordinary ruled space; the limiting spaces S_4 of two simplexes with six vertices, reciprocal polars with respect to the quadratic variety Q , furnish, by their intersections with this Q , varieties being the images of six pairs of linear complexes

$$\begin{array}{cccccc} c_1 & c_2 & c_3 & c_4 & c_5 & c_6 \\ c'_1 & c'_2 & c'_3 & c'_4 & c'_5 & c'_6 \end{array}$$

in such a way that two complexes taken in the two rows and with different indices are always in *involution*; it is known that this notion has been introduced into science by Mr. F. KLEIN.

The theory of SCHLÄFLI mentioned above indicates that every line of S_5 which rests on five of the spaces common to the homologous limiting spaces S_4 also rests on the sixth.

Now, there exist such lines, at least in infinite number on the variety Q itself, for the lines of a quadratic variety of S_5 form a system ∞^5 ; hence there is at least a finite number which verifies five conditions³⁾.

On the other hand the right lines of the variety Q furnish plane pencils of lines in ordinary space⁴⁾. Hence the plane pencils at least in finite number which contain a ray of five out of six lineo-linear congruences $c_i = c'_i = 0$ contain a ray of the sixth.

In particular if the complexes c_i, c'_i are all special, their axes form

¹⁾ M. STUYVAERT, Cinq Etudes de Géométrie analytique, applications diverses de la théorie des matrices et de l'élimination, Gand, Van Goethem, 1908.

²⁾ Cf. SCHLÄFLI, *Journ. f. Math.* t. 65; L. BERZOLARI, *Rend. circ. mat. Palermo* t. 20; M. STUYVAERT, *Rend. R. Ist. Lomb.* 1911.

³⁾ Cf. E. BERTINI, *Introduzione alla geometria proiettiva degli iperspazi*,... Pisa, Spoerri, 1907, page 131.

⁴⁾ Cf. E. BERTINI, *loc. cit.* page 136.

a double six of a cubic surface and we see that the plane pencils which contain a ray of five out of the six congruences $c_i \equiv c'_i \equiv 0$ also contain a ray of the sixth.

2. The investigation of the plane pencils containing a ray of n congruences with distinct directrices has been made for $n = 3$ by Mr. J. NEUBERG ¹⁾ and for $n = 3, 4, 5$ by Mr. JAN DE VRIES ²⁾.

For the case of three congruences the problem consists of the study of the planes which cut the three pairs of directrices according to two homologous triangles. Mr. J. NEUBERG has found that these planes envelope a surface of the 4th Class, whilst the centres of homology describe a surface of order four reciprocal to the preceding. This surface of order four contains as simple lines the three pair of directrices of congruences and the three pair of rays common to two of these congruences.

It is perhaps suitable to make known a method with the double advantage of solving the problem at the same time for three, four, or five congruences and of giving an analytical representation serving for a later eventual study. Let us designate by

$$y + lz, \quad y' + mz', \quad y'' + nz''$$

a variable point on a directrix of each of the three given congruences; the other directrices shall be determined by the intersections of planes:

$$\begin{cases} aX = 0, & a'X = 0, & a''X = 0, \\ bX = 0, & b'X = 0, & b''X = 0. \end{cases}$$

Let x be the centre of a pencil to be found; the plane of this point and of the line ab has as equation

$$a_X b_x - a_x b_X = 0$$

and it cuts the line yz in a point L whose parameter l is determined by

$$a_y b_x - a_x b_y + l(a_z b_x - a_x b_z) = 0;$$

so the coordinates of this point L are:

$$L_i = y_i(a_z b_x - a_x b_z) - z_i(a_y b_x - a_x b_y) = 0 \quad (i = 0, 1, 2, 3).$$

This point, as well as the analogous points M, N , and the point x are in the same plane, hence

$$F_i = \begin{vmatrix} y_i(a_z b_x - a_x b_z) - z_i(a_y b_x - a_x b_y) \\ y'_i(a'_z b'_x - a'_x b'_z) - z'_i(a'_y b'_x - a'_x b'_y) \\ y''_i(a''_z b''_x - a''_x b''_z) - z''_i(a''_y b''_x - a''_x b''_y) \end{vmatrix} = 0.$$

¹⁾ *Mathesis*, 1903, page 105.

²⁾ Proceedings *Kon. Ak. v. Wet. Amsterdam*, 1911 page 259.

This is the equation of the locus to be found. This surface of order four forms a particular case of that which was investigated by Mr. F. SCHUR in his *Habilitationschrift*¹⁾ and which is the locus of a point whose homologous ones in four collineations are in a same plane. The fact that the fourth of these collineations is the identical transformation does not harm the generality and supposes only a convenient choice of points of reference; but the first three collineations are three very special ones, for they make always a point of a line yz , or $y'z'$ or $y''z''$ to correspond to each point x of the space.

The following are some consequences :

I. If we give four or five lineo-linear congruences with distinct directrices, the same reasoning substitutes for the determinant F_4 , a matrix with four columns and five or six rows of linear forms, a matrix which in general annuls itself respectively for a curve of order²⁾ ten or for twenty isolated points.³⁾

So, "the locus of the centres of the plane pencils which contain a ray of four lineo-linear congruences is a twisted curve of order ten; and there are twenty plane pencils each containing a ray of five lineo-linear congruences."

These properties have been geometrically demonstrated bij Prof. JAN DE VRIES.

II. The determinant F_4 annuls itself visibly for the points of the six lines ab , $a'b'$, $a''b''$, yz , $y'z'$, $y''z''$. By hypothesis two of these lines do not meet; if, for instance ab and yz had a common point, it would be a node on F_4 .

III. If in the determinant F_4 we omit one of the first three rows e.g. the third, we have the locus of the point x collinear to the corresponding points L and M ; this matrix with twelve linear elements represents therefore four right lines ab , $a'b'$, yz , $y'z'$ and their two transversals. In general a matrix of twelve linear forms annuls itself for a twisted sextic of genus three; so, in this representation the curve can break up into four straight lines and their two transversals.

From this results also that the couples of rays common to the given congruences taken two by two are simple right lines of F_4 .

If in the determinant F_4 we omit the last row we find the locus of a point x for which the corresponding points L , M , N are col-

¹⁾ *Math. Ann.* t. 18.

²⁾ Cf. M. STUYVAERT, *Cinq Etudes*... p. 37 where various properties have been indicated of the curve resulting from the representation by matrix and finding their application here; for shortness, sake we omit these developments.

³⁾ M. STUYVAERT, *Cinq Etudes*... p. 15.

linear; this locus breaks up into a twisted cubic accompanied by its three bisecants $ab, a'b', a''b''$.

If we add to the determinant F_4 a row of constants $\alpha_1, \alpha_2, \alpha_3, \alpha_4$, forming the homogeneous coordinates of a point α , we find a matrix annulling itself for a curve of order six, locus of the point x the corresponding points L, M, N of which lie with point x in the same plane passing through α .

IV. In the reasoning which has revealed the locus of the vertices of the plane pencils containing a ray of three, four, or five linear congruences it suffices to call u_i the coordinates of the plane of such a pencil, to express that this plane contains x and the corresponding points L, M, N, \dots , then to eliminate the x to have the system of the planes of the pencils; we find a determinant or matrices with linear elements in u analogous to the formulae mentioned above; their duality is complete.

3. The preceding calculation may be done in different other ways and notably in such a manner that it is unnecessary to use the directrices of the congruences and therefore neither to suppose them distinct.

We silently pass by these other processes and we restrict ourselves to the investigation of a special case, the one where — the congruences (1), (2), (3) having distinct directrices which we shall designate by $a^{(1)}, b^{(1)}; a^{(2)}, b^{(2)}; a^{(3)}, b^{(3)}$ — the line $a^{(1)}$ meets $b^{(2)}$ and $b^{(3)}$, just as $a^{(2)}$ meets $b^{(1)}$ and $b^{(3)}$, and $a^{(3)}$ meets $b^{(1)}$ and $b^{(2)}$ (but $a^{(1)}$ meets neither $b^{(1)}$, nor $a^{(2)}$, nor $a^{(3)}$, etc.).

The right lines $a^{(1)} b^{(2)} a^{(3)} b^{(1)} a^{(2)} b^{(3)}$ taken in this order form a skew hexagon. Let us project it out of a point J of the corresponding surface F_4 ; the rays issuing from J and resting respectively on $a^{(1)}$ and $b^{(1)}$, on $a^{(2)}$ and $b^{(2)}$, on $a^{(3)}$ and $b^{(3)}$ are in the same plane; hence, in the projected hexagon the intersections of the opposite sides are three points in a straight line; the projected hexagon is a hexagon of PASCAL; its vertices are on a conic; hence J is the vertex of a cone of order two passing through the six points $(a^{(i)} b^{(i)})$ and reversely. The surface F_4 is the locus of the vertex of a quadratic cone passing through six points and we know that it is of order four and has the six given points as double points, that it contains the 15 lines joining these points two by two and the 10 intersections of two planes determined by the six points distributed in two triplets.

Let us now take a double six on a cubic surface

$$\begin{array}{cccccc} a^{(1)} & a^{(2)} & a^{(3)} & a^{(4)} & a^{(5)} & a^{(6)} \\ b^{(1)} & b^{(2)} & b^{(3)} & b^{(4)} & b^{(5)} & b^{(6)} \end{array}$$

In retaking the analysis of the preceding number or in imitating the reasoning of Prof. JAN DE VRIES, we recognize that the pairs 1, 2, 3 or 1, 2, 4 or 1, 3, 4 or 2, 3, 4 furnish every time a surface F_4 analogous to the one defined above and that these surfaces have in common a curve of order ten, c_{10} ; that if we set apart three by three the pairs 1, 2, 3, 4, 5 we have ten surfaces F_4 having in common twenty points, vertices of plane pencils having a ray resting on $a^{(i)}$ and $b^{(i)}$ ($i = 1, 2, 3, 4, 5$).

But by virtue of the property given at the commencement of this paper each of these twenty pencils contains also a ray resting on $a^{(6)}$ and $b^{(6)}$.

4. To wind up with let us consider once more the skew hexagon $a^{(1)}b^{(2)}a^{(3)}b^{(4)}a^{(2)}b^{(3)}$ of the preceding number, whose edges we suppose to lie on a general cubic surface F_3 and let us find the intersection of this surface F_3 with the surface F_4 locus of the vertices of the quadratic cones passing through the vertices of the hexagon (by supposition no four of the six vertices of which lie in the same plane).

Of the 25 right lines of F_4 only nine are on F_3 , namely

$$a^{(1)}, b^{(1)}, a^{(2)}, b^{(2)}, a^{(3)}, b^{(3)}$$

$$a^{(1)}b^{(2)} = a^{(2)}b^{(1)} = 0, \quad a^{(2)}b^{(3)} = a^{(3)}b^{(2)} = 0, \quad a^{(3)}b^{(1)} = a^{(1)}b^{(3)} = 0,$$

where we indicate by $a^{(i)}b^{(k)} = 0$ the equation of the plane passing through $a^{(i)}$ and $b^{(k)}$.

In reality 1 the nine lines differing from $a^{(1)}, b^{(1)}, a^{(2)}, b^{(2)}, a^{(3)}, b^{(3)}$, joining two nodes of F_4 , are not on F_3 , for a cubic surface without a singular point cannot bear three concurring right lines; 2 if the plane determined for instance by the line $a^{(1)}$ and the point $(b^{(1)}a^{(2)})$ intersected still F_3 according to two right lines, one of these would pass through $(b^{(1)}a^{(2)})$ and through this point there would be three right lines on F_3 ; 3 remains the 25th right line g of F_4 , intersection of the planes through the alternating vertices of the hexagon. We state without difficulty that it cannot meet any of the right lines common to F_4 or F_3 , otherwise the hexagon would have four coplanary vertices, it cannot be moreover on F_3 , otherwise it would intersect the plane $a^{(1)}b^{(2)}$ or one of the lines common to F_4 and F_3 .

The intersection of F_4 and F_3 completes itself by a cubic c_3 . The right line g of F_4 intersects F_3 three times in points which are not on the lines common to the two surfaces; these points are thus on c_3 ; from this ensues that *this cubic is plane and non-degenerated*.

The line connecting the point $(a^{(1)}b^{(2)})$ with the point $(a^{(2)}b^{(1)})$ is

entirely on F_4 and intersects F_5 on the cubic c_3 ; the same remark holds for the right lines $(a^{(1)} b^{(3)}) (a^{(3)} b^{(1)})$ and $(a^{(2)} b^{(3)}) (a^{(3)} b^{(2)})$; the three points obtained in this way determine the plane of c_3 and consequently this curve itself, as it is a plane section of F_5 .

In any case we must show that the three points under consideration are not in general collinear.

Indeed through the six edges of the hexagon we can lay a pencil of cubic surfaces. The three diagonals connecting the opposite vertices intersect still one of these surfaces in three points situated according to what precedes in a plane passing through the intersection of the planes laid through the alternating vertices of the hexagon; we have there a pencil of planes cutting the three diagonals in triplets of points which are not always collinear, for then it would be the same with the alternating vertices of the hexagon which has been excluded by hypothesis. And yet two planes of the pencils touch the hyperboloid determined by the three diagonals and they furnish three collinear intersections.

We can consider if we like these remarks as properties of the skew hexagon.

Ghent, January 1912.

Anatomy. — “*On the splitting of the nucleus trochlearis.*” By Dr. C. T. VAN VALKENBURG. (Communicated by Prof. Dr. L. BOLK).

(Communicated in the meeting of February 24, 1912).

In a previous communication ¹⁾ I called the attention to the fact that in man (fetus, new-born, grown up) the nucleus of the trochlear nerve need not consist of a continuous column of cells. In many cases its continuity is interrupted: a smaller distal part is separated from the more frontal nucleus principalis by a zone in which no rootcells are found. The human material I dispose of, is by no means sufficient to venture a valuation of the percentage of the cases in which such a splitting is extant. It seems however that we had better call it the rule than an exception. ²⁾ Besides from the nature and situation of the cells of the caudal nucleuspart the connection

¹⁾ C. T. v. VALKENBURG; Nucleus facialis dorsalis, nucleus trigemini posterior, nucleus trochlearis posterior. These Proceedings June 25, 1910.

²⁾ U. TSUCHIDA; Ueb. die Ursprungskerne der Augenbewegungsnerven etc. Arb. a. d. Hirnanatom. Institut in Zürich. Heft II 1906. On page 35 this author values the number of cases in which the nucl. IV is split at 20 to 30%. In my opinion this number is too low. I find also the “hiatus” always in the distal part of the nucleus, T. finds it frontal, medial or distal.

of the latter with nucleus principalis trochlearis is directly proved by the possibility of following a separate nervestem which in its sagittal course through the central substantia grisea of the aquaeductus Sylvii situated ventrally from the other trochlearfibres, unites with the latter at its emersion, after having likewise been crossed in the velum medullare anticium.

The situation of nucleus and root of the fourth pair of nerves to the right and to the left is never identical. The above-mentioned discontinuity is found either exclusively or much more distinctly at one of the two sides than at the opposite one. As long as their number is not much greater, the fact that, in the cases known to me, this was always the left side, does not give me a right of generalising.

For a comparison I have investigated the structure of the nucleus trochlearis in representatives of various classes of mammals, especially with a view to the presence or the absence of a nucleus trochlearis posterior.

I examined: a marsupial (*Didelphys marsupialis*) an anodont (*Myrmecophaga jubata*) three rodents (*Lepus cuniculus*, *Cavia cobaya*, *Mus musculus*), three carnivores (*Phoca vitulina*, *Felis domestica*, *Canis familiaris*) a monkey (*Oedipomidas oedipus*).

Of all these animals only the rabbit showed a nucleus trochlearis posterior: I found it in two of the six series of the brains of this animal that the "Centraal Instituut voor Hersenonderzoek" possesses. In the other rodents that I examined I did not find it (the Institute possesses several series of the mouse).

The list on p. 1025 represents the relation — in sagittal dimension — existing between the nucleus posterior and the nucleus principalis of both before-mentioned rabbits. As preparation 1 is indicated the most distal section, in which the nucleus trochlearis posterior is found. The sections have been stained according to the VAN GIESON method. They alternate with sections treated according to PAL's method, which of course have not been used in counting. Their thickness is 30 μ . It is obvious that the numbers of the rootcells found in a section have no absolute value.

The counting was done with a magnification Zeiss Oc. 2 Obj. A. No difference was made between distinctly polygonal and apparently more oval rootcells.

The unequal number of preparations in which a nucleus trochlearis is found may be explained by the difference in size of the two animals, perhaps likewise by individual difference. The distal boundary both of the nucleus posterior and of the nucleus principalis — is perfectly sharp. The frontal boundary is exceedingly indistinct on

account of the gradual transition into the nucleus oculomotorii. The latter begins — from behind — to show cells which are situated dorsal from the nucleus trochlearis in the central grey substance

Preparation	Rabbit 1		Rabbit 8	
	left	right	left	right
1	3	0	0	5
2	6	0	0	7
3	6	0	0	13
4	4	0	0	8
5	2	0	0	10
6	0	0	0	2
7	0	0	0	0
8	0	0	0	0
9	0	0	0	0
10	0	0	0	0
11	0	6	0	0
12	0	6	1	3
13	0	4	11	15
14	0	0	36	32
15	0	0	39	36
16	0	0	52	54
17	2	12	60	56
18	3	22	63	66
19	16	29	55	69
20	27	45	50	49
21	?	?	28	26
12	37	54		
23	47	52		
24	56	54		
25	45	39		
26	35	37		
27	32	38		
28	21	28		
29	14	16		
30	7	10		

ventral from the aquaeductus Sylvii, these are very well to be distinguished (separated) from the nucleus trochlearis. The number of cells that are situated on the place of the nucleus trochlearis increases already after a few preparations, so that it cannot be decided how great the oculomotoriusingredient of the nucleus is now, no more can the exact place be assigned where oculomotoriuscells begin to mix with trochlearic elements.

Remarkable is the very lateral situation of the nucleus trochlearis, not on the most lateral part of the fasciculus longitudinalis posterior but very distinctly laterodorsally from it, a little imbedded in the

marrow fibres that are found there and border the central grey substance. This strongly lateral situation is less pronounced in man though extant in principle, as appears from the figures subjoined to my previous communication (i.e.).

As to the nucleus trochlearis principalis, its situation corresponds to a high degree in all examined animals. In its entire length however it is imbedded in a more lateral part of the fasciculus longitudinalis than with rabbits. Slight local differences — apparently depending upon a stronger dorsal curvature of the posterior longitudinal bundle — occur however. Only in the cat the gradual transition into the nucleus oculomotorii is missing. The most distal cells of this nucleus are not situated strictly dorsal from the place where the nucleus trochlearis was found, but almost in the prolongation of the latter. Only a few preparations further frontal these cells pass into elements situated dorsomedially that have been developed in the mean time. In the dog the medial nucleus part however is found already in the same level where the nucleus trochlearis is still present. The transition of the latter into the lateral cells of the oculomotorian nucleus is gradual, as in all other examined animals (with the exception of the cat).

At last I still fix the attention to the great asymmetry of the split nuclei trochleares of the two rabbits which is distinctly expressed in the above lists. In rabbit 1 to the left a nucleus posterior “lagging far behind”, to the right another lying only 180 μ farther caudal. In rabbit 8 to the left no splitting at all, to the right a very distinct one, which caused the formation of a nucleus posterior comparatively very rich in cells.

No certain information can be given about the significance of the phenomenon which I could only ascertain in man and rabbit. It seems only clear that by the distolateral direction of the trochlearic-root the situation of the nucleus trochlearis is at least partially determined.

Mathematics. — “*Calculus rationum*”. By Dr. G. DE VRIES. (Communicated by Prof. JAN DE VRIES).

(Communicated in the meeting of February 24, 1912).

So far mathematicians have adhered to the opinion that an operation of the fourth rank would teach nothing new; this opinion was in part founded on the conviction that base number and exponent of a power cannot be submitted to the commutative, associative, and distributive properties. I have done away with this objection by introducing the notion “*mutual power of two numbers*”.

Doing so I have at the same time indicated the means of intro-

ducing operations of an arbitrary rank for which the above mentioned properties hold.

I hope I have opened a new field of investigation. The future must show whether it is of importance. At all events the considerations have led me to investigate groups of transcendent curves, to a logical classification and to a new analysis of them.

I have the outcome of my investigations in manuscript, the contents of which I wish to sketch in some lines. Starting from the algebraical part I arrive in connection with the above mentioned analysis to the geometrical applications. Only the operation of the fourth rank will be under discussion and for the rest only considerations relating to two variables will be allowed.

§ 1. If a power is submitted to a new involution the exponents may be mutually interchanged. In this truth lies practically the validity of the commutative property. Only a symbol is wanting for the continual involution together with the settling of a base number to determine univalently the mutual power of numbers. If we choose for this e then the forms in their simplest shape appear. This supposition is made in the following, whilst the Nap. logarithm shall be indicated by L .

“The mutual power of two numbers is the power of e having the product of the logarithms of those numbers as exponents.”

If we put

$$x = e^a ; \quad y = e^b,$$

we shall write:

$$x, y = e^{pq} = x^{Ly} = y^{Lx} = y, x.$$

That for the mutual power of more numbers also the associative and the distributive property holds, will need no reasoning.

In a form as

$$u = x, y, z$$

we shall call $x, y,$ and z *efficients*.

§ 2. A continued involution or evolution with equal exponent is called “*gradation*” and the upper exponent appearing here *gradation index*. The symbol used for it follows out of:

$$e^{n^p} = {}^n(e^p) ; \quad (V^p)^n e = e^{p^{-n}} = {}^{-n}(e^p).$$

These can be summarized in the form

$${}^n(x) = e^{L^n x}.$$

"A continued mutual power with equal efficient is called gradation".
The inverse operation is called "descension".

"The n^{th} descension of a number is the number which put to the n^{th} gradation furnishes the original number".

The descension will be indicated by an inverse rootsign; a distinction of power and root descension is superfluous. The forms

$${}_n\sqrt[n]{e^p} = \sqrt[n]{e^p} ; e^{\sqrt[n]{\frac{1}{p}}} = \sqrt[n]{\sqrt[p]{e}} = \sqrt[n]{\sqrt[p]{e}}$$

can therefore be written as

$${}_n\sqrt[n]{x} = e^{\sqrt[n]{Lx}}$$

When introducing negative and broken indices of gradations everything can be summarized in ${}_n(x)$.

The gradation has the precedency of the involution, the evolution of the descension.

§ 3. For a first consideration it is desirable to allow only positive base numbers. By means of the operation, however, complex powers may appear. Thus the number

$${}_2\sqrt[e]{1} = e^i$$

will prove to act here the part of $\sqrt{-1}$ in common mathematics.

The elementary operation is multiplication; when comparing two quantities we must therefore pay attention to their ratio. For the construction of figures the axes of coordinates are divided in such a manner, that the successive abscissae (and ordinates) form a geometrical series. The lines drawn through the dividing points parallel to the axes form a net of coordinates which shall be called "field of ratio" (in contrast to the wellknown "field of difference").

For constructions it is advisable to take as base a number differing but little from unity.

Just as the difference of two numbers is bivalent this proves likewise the case with their ratio. Referring to what HOÛEL.¹⁾ says about operation-modulae we shall assign the same absolute value (in a rational sense) to

$$\frac{x}{y} \text{ and } \frac{y}{x}$$

(Numbers smaller than unity have for the field of ratio the same

¹⁾ Cours de calcul infinitésimal I; § IV etc.

meaning as negative numbers for the field of difference). The following can serve as a confirmation of the assumed:

$$1 \times \frac{x}{y} = 1 : \frac{y}{x} \text{ and } \sqrt[1]{\left(\frac{x}{y}\right)} = \sqrt[2]{\left(\frac{y}{x}\right)}.$$

§ 4. Out of the definition of mutual power follows that only one indirect operation can be deduced from this, viz.:

$$x = 1^{\frac{Lx}{Ly}} ; \quad y = 1^{\frac{Ly}{Lx}}.$$

If we use the word "mutual root" there is still ambiguity. The absolute value of the two mutual roots (represented as follows):

$$x|y = \sqrt[Ly]{x}; \quad y|x = \sqrt[Lx]{y}$$

must, however, be regarded as an equal one for the field succeeding the field of ratio. We might call the former the root of x to y .

It is useful to give forms as

$$e|x = 1^{\frac{Lx}{Lx}} = -1(x)$$

the name of "reciprocal power".

For gradations and descensions we might mention a series of properties corresponding entirely to those for powers and roots. The further development of rational algebra is analogous to ordinary algebra. So we can speak here of a gradation binomium, of remarkable roots, continuous roots, etc. In the geometrical part of course the logarithmic proportion

$$a^b = c^d$$

comes to the foreground. And for different base numbers the form

$${}^a L_u : {}^a L_r = {}^b L_u : {}^b L_r$$

is of importance. Likewise is of importance for geometry: "the middle descent of two numbers". This is the number whose 2nd gradation is equal to the mutual power of the two numbers.

As was to be expected this is independent of the chosen base number. So if instead of e we take the base number a then, if we introduce this as index,

$$\sqrt[2]{\mathcal{A}(u, v)_a} = \sqrt[2]{\mathcal{A}(u, v)_e}.$$

This property corresponds thus to the property that the geometrical mean is independent of the chosen unity. Further on holds

$$\sqrt[2]{uv} > \sqrt[2]{\mathcal{A}(u, v)}.$$

§ 5. The question arises whether in the equation

$$y = {}^x(x) = e^{x^2},$$

when y and p have an assumed value, there is always a value to be found for n . To show the possibility of this we have but to follow the reasoning of the algebra handbooks for the existence of logarithms. The immensurability of this number is, however, in general of a different order from that of the logarithms.

If n is called the second logarithm of y then this number is not definite until a definite value is indicated for p . The simplest assumption is $p = e$. There the e^{th} power of e shall be taken as "base power."

If now immensurable numbers are allowed as index of gradation the result is regarded as limit to which a descension (changing in a definite manner) of a gradation tends, and as definition of the 2nd logarithm follows:

"The 2nd logarithm of a number is the number indicating to which gradation the base power must be brought to furnish the given number."

The four principal properties are:

$$LL(u, v) = LLu + LLv; \quad LL^n(u) = n \cdot LLu;$$

$$LL(u|v) = LLu - LLv; \quad LL \sphericalangle_n u = \frac{1}{n} \cdot LLu.$$

By the introduction of the notion "mutual gradation" of two numbers the difference between the two indirect operations which are deduced out of a gradation disappears. If we put

$$x = e^{d^2}; \quad y = e^{e^d}.$$

then x and y can be interchanged in the following equation (their mutual gradation)

$$z = [x; y] = LLx(y) = LLy(x) = [y; x].$$

This form is equivalent to

$$LLz = LLx \cdot LLy.$$

The mutual gradation as starting point leads to the investigation of the "rootfield". For this the evolution is the elementary operation. The operation of the fifth rank following out of this shares the fundamental properties of the operations of lower rank.

Just as operations of an arbitrary higher rank may be introduced and may give rise to the investigation of definite groups of curves, operations of a rank lower than the first may also be introduced geometrical considerations may also be connected with these.

§ 6. The equation of the curves of the first gradation is found

by elimination of n out of the following two

$$x = a_0 a^n \quad \text{and} \quad y = y_0 b^n.$$

For the construction of the points we must make use of different base numbers for abscissa and ordinate, unless the logarithms of the base numbers (a and b) used have a measurable ratio.

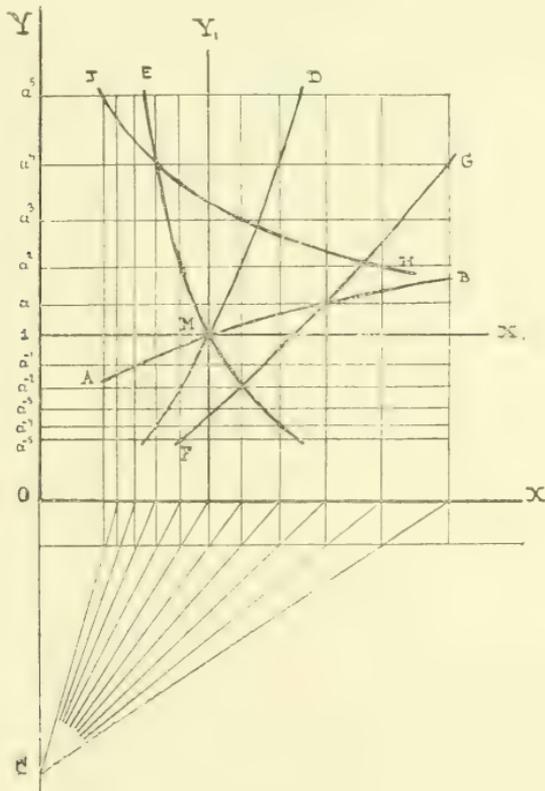


Fig. 1.

The lines of fig. 1 are drawn on this supposition; the above mentioned ratio is 3 for AB ; $\frac{1}{2}$ for MD ; $\frac{1}{2}$ for ME ; $\frac{2}{3}$ for FG and -3 for HI . In the field of ratio the lines whose equation is:

$$\frac{y}{y_0} = b = \frac{x}{x_0} | a$$

are the simplest; they shall be called "*rationals*". They have the form of parabolae or hyperbolae according to their "director exponent" $\lambda = Lb : La$, being positive or negative. So

$$m = y_0 x_0 \begin{matrix} Lb \\ La \end{matrix}$$

represents the part cut off the line $x=1$, counted to $M(1, 1)$. The lines $x=1$ and $y=1$ must be regarded as axes. They divide the positive field of ratio into four quadrants which are unequal, but which must be considered as equal in a rational sense (as will be evident later on); $x=0$ and $y=0$ correspond to $-\infty$ in the field of difference. Lines with equal director exponent are "*rational equidistant*". A pencil of straight lines through O (rationals for which $\lambda=1$) intersects two equidistant rationals in corresponding points. If the points of intersection of a selfsame rational are joined, then the corresponding figures are similar. So we might say that equidistant rationals are parallel in the smallest parts.

For $x_0=1$, $y_0=1$ the lines shall be called central rationals; they correspond to the right lines in the field of ratio drawn through the origin of coordinates. Rationals with measurable director exponent find a continuation in one of the three other fields of ratio.

§ 7. The director exponent of the rationals has a simple geometrical meaning. Out of the equation

$$y = mx^2 \quad \text{or} \quad Ly = \lambda Lx + Lm$$

we find for it

$$\lambda = \frac{dLy}{dLx} = x : y \cdot \frac{dy}{dx},$$

that is "*the ratio of abscissa to subtangent*." For points of equidistant rationals with equal abscissa the tangents pass through one and the same point of OX (fig. 2); for given value of ordinates they intersect each other in one point of OY . Furthermore all rationals divide the rectangles of coordinates proportionally, so that the director exponent can be regarded as ratio of two integrals. Calling the parts J_x and J_y in which the line divides a rectangle (J) we find

$$\lambda = \int_0^y x dy : \int_0^x y dx = J_y : J_x.$$

As now the differences of the terms of a geometric series form again a geometric series that ratio also holds for area differences and differentials:

$$\lambda = \frac{\Delta J_y}{\Delta J_x} = \frac{dJ_y}{dJ_x}$$

For $\lambda > 0$ the strips lie outside each other; for $\lambda < 0$ overlapping takes place (fig. 2). Here

$$\lambda = tg \ AOB$$

represents the director exponent of the 3 equidistant rationals OP_1 , OP_2 , and OP_3 .

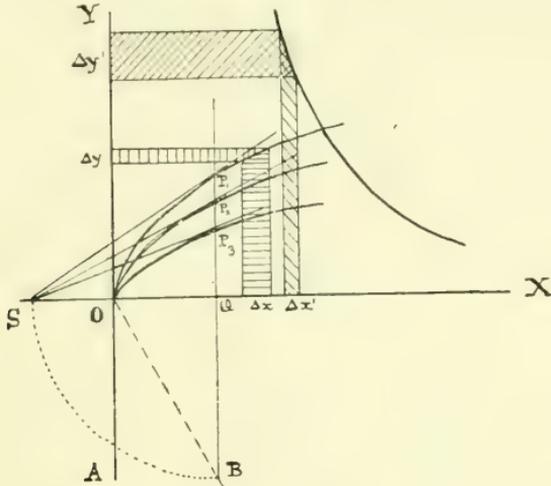


Fig. 2.

As we can also write

$$\frac{y_2}{y_1} \left| \frac{x_2}{x_1} = e^i \right.$$

a rational is a line for which the mutual root of the ratio of coordinates of two points is constant.

§ 8. In the field of proportion coordinates and areas are quantities of the same exponential order. The area of the rectangle of coordinates determined by the point:

$$P_n(a^n, b^n) \text{ is } J_n = (ab)^n.$$

The rational laid through this point and through P_m contains likewise P_{m+n} . The area of the rectangle of coordinates determined by this point is:

$$J_{m+n} = (ab)^{m+n} = J_m \times J_n,$$

so it is deduced out of a multiplication. Furthermore the coordinates can be regarded as areas namely of rectangles having the coordinates as base, the distance between OX_1 and OX (resp. OY_1 and OY) as height. A point is not yet determined by the area of a rectangle of coordinates only (equilateral hyperbola), an element for the direction must also be known. To a sum in the field of difference always

here the rational direction is identical to the direction of the line. Following GRASSMANN'S notation for the field of ratio we might write:

$$P_0 : M = M : P_8 \quad \text{and} \quad P_3 : M = M : P_9.$$

To arrive now from the value

$$r = r^{-1} = \begin{pmatrix} 1 \\ r \end{pmatrix}$$

at the value:

$$r^{-1} = r^{-1} = \begin{pmatrix} 1 \\ r \end{pmatrix},$$

we must allow the index of gradation to vary continuously from 0 to 1. If by this change the index has reached the value $\frac{1}{2}$ (resp. $-\frac{1}{2}$), then the direction as well as the rational direction seen out of M is halved. Considered in this way the points P_3 and P_8 are therefore determined by

$$e^i \quad \text{and} \quad e^{-i}.$$

In all intermediate positions the exponent is complex. For all points of a logarithmic circle the modulus is constant with variable argument. Here we have the widest definition of the notion "ratio". For two diametral points is

$$\begin{pmatrix} 1 \\ r \end{pmatrix} : 1 = 1 : \begin{pmatrix} 1 \\ e \end{pmatrix}.$$

Also to the areas of the rectangle of coordinates (or the partial one separated by the rational) is applicable:

$$xy : 1 = 1 : x^{-1}y^{-1}.$$

If the radius of the log. circle is *one*, then by

$${}^2(x) {}^2(y) = 1$$

is represented the point M , so that for all values of q holds:

$$\bar{r} = 1(-1)^{\bar{r}} = 1.$$

The directed area represented by $P_0 q_0 OI$ is therefore

$$J_n = e \times 1^i,$$

the one belonging to P_3 is

$$J_n = e^i \cdot 1$$

§ 10. Although the curves of the field of ratio ought to be compared to the rationals, a good idea can be formed of their course by the comparison to straight lines. When tracing the inflectional points we must frequently strike into a particular path. As example the log.

circle will be investigated in its simplest position. Out of the equation :

$${}^2(x) \cdot {}^2(y) = {}^2(r)$$

follows by differentiation

$$y' = -\frac{L\sqrt{x}}{L\sqrt{y}}; \quad y'' = \frac{y}{x^2(Ly)^3} \{Lx \cdot Ly \cdot Lxy - (Lr)^2\}.$$

As y cannot become zero, x and Ly not ∞ , the inflectional point condition is :

$$Lx \cdot Ly \cdot Lxy = L^2r.$$

If we now introduce the area of the rectangle of coordinates, then

$$xy = J,$$

furnishes, connected with the identity, where for convenience, sake we write L^2r for $(Lx)^2$, the condition :

$$L^2J - L^2r \cdot LJ - 2L^2r = 0.$$

There are six inflectional points when

$$r \geq e^3\sqrt{3},$$

is satisfied.

The value of r , for which two more inflectional points exist, is deduced from the necessary condition for real values

$$L^2(xy) \geq 4Lx \cdot Ly.$$

In connection with the inflectional point condition this becomes :

$$\frac{L^4r}{L^2x \cdot L^2y} \geq 4Lx \cdot Ly,$$

from which ensues

$$Lx \cdot Ly \leq \sqrt[3]{\frac{1}{4}L^4r} \quad \text{and} \quad Lxy \geq \sqrt[3]{4L^2r}.$$

For decreasing value of r the two inflectional points therefore coincide into a stationary point, if

$$L^2r = L^2xy - 2Lx \cdot Ly = \sqrt[3]{2L^4r};$$

so that the radius of the *log.* circle is then :

$$r = e^{\sqrt{2}}.$$

§ 11. For the study of the general equation of the 2nd gradation comprising all logarithmic conics we should first have to treat the rational displacement and rational revolution round the axis. As this would lead us too far, I restrict myself to the logarithmic parabola and *log.* equilateral hyperbola.

The rational translation offers no great difficulties in this way ; the logarithmic circle given by

$$\begin{pmatrix} x \\ a \end{pmatrix} \cdot \begin{pmatrix} y \\ b \end{pmatrix} = {}^2(x)$$

will pass by means of the translation of the axes from $x = a, y = b$ into the above mentioned form. The figure changes then according to the assumed notions, but as figure of the field of ratio it remains congruent to itself. The congruence in the field of ratio is equal to the similarity in the field of difference, when the translation takes place along straight lines through O ; in general it takes place along arbitrary rationals, so that the notion of similarity must be extended, where the skew ratios come into consideration.

Whilst now in general the points of the logarithmic curves are constructed by means of a logarithmic line, they can be found in simple position by means of rectilinear constructions.

§ 12. If we draw in the field of ratio a series of lines whose equation is:

$$x_n = a_n a^n.$$

and then, with the aid of a pencil of rays through O the points $P_0, P_1, P_{-1}, P_2, P_{-2}, P_3, P_{-3} \dots$ and likewise $Q_0, Q_1, Q_{-1}, Q_2, Q_{-2} \dots$ on the above mentioned lines, we then find ordinates given by means of:

$$y_n = y_0 a^{n^2}$$

By elimination of n out of these equations (regarding x_n and y_n as variable coordinates) we find the equation:

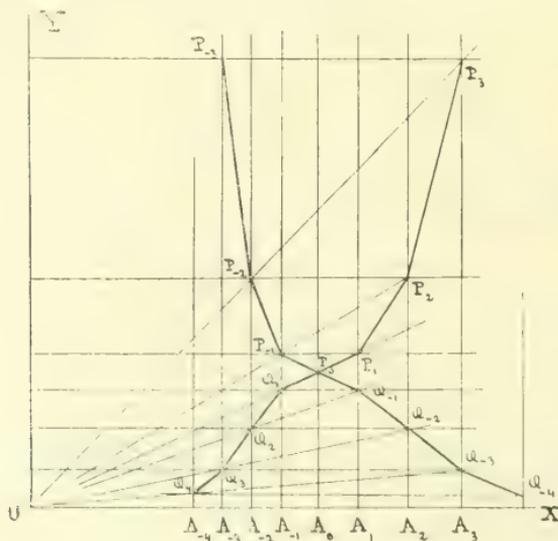


Fig. 5.

$$y \cdot a = \left(\frac{x}{x_0} \right)^2$$

The points P form part of the logarithmic parabola: the points Q of the anti-parabola, having as parameter the reciprocal value of a .

For $x_0 = y_0 = 1$ we find the abscissa of the point of inflection out of

$$L \cdot x = \frac{1}{4} L \cdot a \cdot \left(1 \pm \sqrt{1 - \frac{8}{L \cdot a}} \right).$$

From this we can see that the anti-parabola has always two inflectional points; for the rest the condition for the existence of the inflectional points is for the former $r > e^8$. As locus of the inflectional points we find $y^2 = x : e$. At the interpolation the centre O displaces itself along the X -axis.

§ 13. Likewise the points of the logarithmic equilateral hyperbola

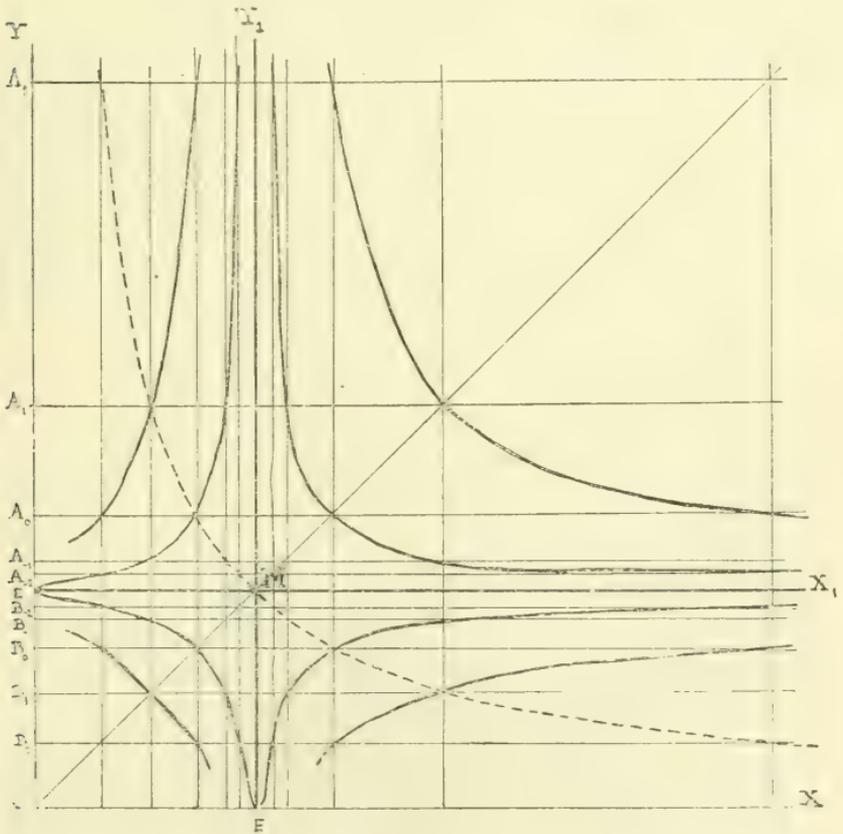


Fig. 6

and of the conjugate hyperbola can be immediately constructed, when OX_1 and OY_1 are the asymptotes; the equation is then

$$x, y = {}^2(a)^{\pm 1} \text{ or } Lx \cdot Ly = \pm L^2 a.$$

In this form it belongs to the curves of gradation; those are the simplest lines in the rootfield. In case the exponent be 2, the net of coordinates of the rootfield can be found by means of compasses and ruler. (The construction is not mentioned here). By OX_1 and OY_1 the positive field of ratio is divided into four rootfields; in these lie the branches of the logarithmic hyperbola and the conjugate one. In fig. 8 the above mentioned line is drawn, likewise the one with the base number a^2 (resp. a^{-2}). For the points A and B holds:

$$OA_n = a^{2^n} ; \quad OB_n = a^{-2^n}.$$

The log. hyperbola is satisfied by: $x = a^{\pm 2^n}$; $y = a^{\pm 2^{-n}}$:

The conjugate one is satisfied by: $x = a^{\pm 2^n}$; $y = a^{\mp 2^{-n}}$.

Inflectional points appear in all root quadrants except the first. In the points E the line passes continually into the conjugate one. The locus of the inflectional points is $xy = e^{-2}$. Out of the fact that inflectional points are present follows already, that the curves touch the x - and y -axis in E ; this is also to be seen algebraically in a round-about way. So

$$y' = - (Ly^y : Lx^x)$$

seems to be indefinite in E . By the substitution :

$$x = p^z, \quad y = \sqrt[p]{p},$$

in which p is a constant, the differential quotient becomes :

$$y' = - p^z : z^2.$$

For $z = -0$ that form is not any more decisive but taking

$$u = \frac{1}{z} - z$$

we find for $u = -\infty$

$$\lim y' = \lim [p^u : (\frac{1}{2} u^2 + 1 - \frac{1}{2} u \sqrt{u^2 + 4})] = 0.$$

§ 14. The investigation of the log. ellipse is again simplified by connecting p with two log. circles, whose radii are equal to the half axes. The simplest position is indicated by

$${}^2(x|a) \cdot {}^2(y|b) = e \text{ or } ({}^a Lx)^2 + ({}^b Ly)^2 = 1.$$

The points of the line are points of intersection of the above mentioned circles with central rationals; the construction is based on the substitution :

$$x = a, crn, \quad y = b, sru.$$

cr and sr representing the rational sinus and cosinus. Of importance is still the log. equilateral hyperbola in the position answering to:

$$x(x): (y) = x(a):$$

it can be found by elimination of n out of:

$$x : y = 1 : a^n, \quad xy = a^n$$

and is in this way constructed by points. This one as well as the conjugate one contains *one* inflectional point on each branch. Out of the condition for inflectional points it is evident that there is also one in O . If the line and its conjugate form one line, this is a cusp. As however the line in the 3rd field of ratio (3rd quadrant of difference) can be brought to the same form, viz :

$$(xy), (x:y) = x(a)$$

by means of power decomposition, O can just as well be regarded as inflectional point.

§ 15. When reducing the general equation of the 2nd gradation we must have besides a translation also a rotation round the axis. The coordinates lose the rectilinear form, are measured as rational distance along rationals. The connection between old coordinates and new ones is then established by means of rational projection. The new axes are central rationals in perpendicular position, whose director exponents therefore satisfy : $1 + \lambda \lambda' = 0$.

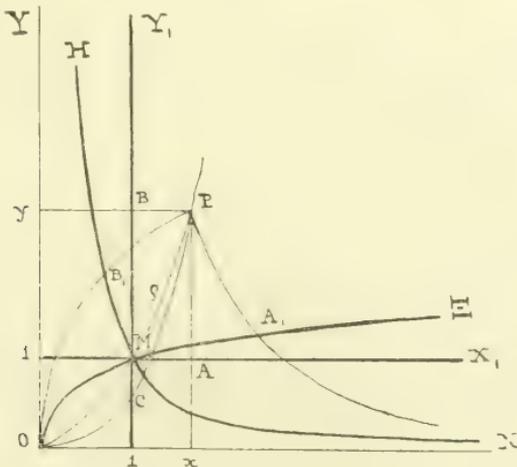


Fig. 7

Naming the new coordinates (ξ, η) we find :

$$\xi = x^{\cos \varphi}, y^{\sin \varphi} ; \quad \eta = y^{\cos \varphi} : x^{\sin \varphi}$$

whilst for the rational distance to M holds :

$$Q = (\xi)^2 + (\eta)^2 = (x)^2 + (y)^2$$

We must continually keep in view that rational distances are ratios; in the lack of a denominator we must assume 1 for it. If CP is an arbitrary rational through P , then — just as for rectilinear axes — the ratio of the parts into which OB_1PA_{1*} is divided by this, is constant.

Let us call λ the director exponent of $M\xi$, thus $-\frac{1}{\lambda}$ of $M\eta$; then PB_1 and PA_1 are given by :

$$y = px^\lambda, \quad y = qx^{-\frac{1}{\lambda}}$$

Let furthermore that exponent be μ for PC , then

$$J_x = xy(\mu - \lambda) : (1 + \mu)(1 + \lambda) ; \quad J_\xi = xy(1 + \lambda\mu) : (1 + \mu)(1 - \lambda)$$

holds, when we put: $OB_1PCO = J_x$ and $OCPA_{1*}O = J_\xi$.

If λ and μ are moreover replaced by tq and $tq\psi$, then follows from this :

$$J_x : J_\xi = tq(\psi - q) : tq \left(\frac{1}{4} \pi - q \right)$$

which relation passes into the known one for $q = 0$.

Finally we mention still that the connection between old coordinates and new ones can be given by *one* formula :

$$xy^i = \xi^{(-1)^i} \cdot \eta^{(-1)^i + \frac{1}{2}}$$

With respect to the new axes the rational equation takes the form :

$$\eta = n \xi^{2g(\frac{\psi}{2} - \varphi)} \quad (\text{out of } y = mx^n)$$

in which we put for n :

$$m^{\cos \frac{\psi}{2}} \mid e^{\cos(\frac{\psi}{2} - \varphi)}$$

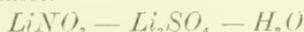
Chemistry. — “*Some compounds of nitrates and sulphates*”. By Prof. F. A. H. SCHREINEMAKERS and A. MASSINK.

(Communicated in the meeting of February 24, 1912).

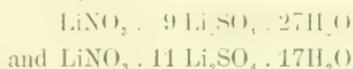
As has been known for a long time, several hydrated double salts can be obtained from solutions containing NaNO_3 and Na_2SO_4 . It, therefore, was deemed important to investigate how the nitrates and sulphates of other metals, in the first place those of the alkali group would behave in this respect. The behaviour of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$

has already been investigated previously¹⁾; Mr. MASSINK has now also investigated the double salt formation between the nitrates and sulphates of Lithium, Sodium and Potassium. In order to investigate this double salt formation the isotherms were determined in the respective ternary systems and the compositions of the solid phases were deduced therefrom with the aid of the "residue-method".

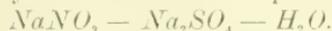
We will not now discuss these isotherms, which sometimes present very peculiar forms, but will restrict ourselves solely to the solid phases.



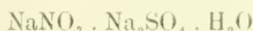
It appears from the investigation that at 35°, besides the components $LiNO_3$ and Li_2SO_4 and their hydrates $LiNO_3 \cdot \frac{1}{2}H_2O$ and $Li_2SO_4 \cdot H_2O$, two double salts, namely



may also occur as solid phases in equilibrium with saturated solution.

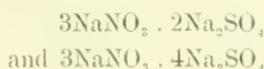


At 20°, besides $NaNO_3$ and $Na_2SO_4 \cdot 10H_2O$, the double salt



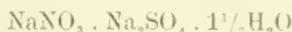
also occurs as a solid phase.

At 35° is found, besides the two anhydrous salts $NaNO_3$ and Na_2SO_4 also the anhydrous double salts:



The double salt found at 20° and no longer existing at 35° was already known and agrees in its composition with the mineral Darapskit²⁾. Contrary to the statement that this compound is readily soluble in water, it follows from the isotherm at 20° that, at this temperature, it is decomposed by water with separation of $Na_2SO_4 \cdot 10H_2O$.

The existence of a double salt:



is also recorded³⁾. In a continued investigation of this system at other temperatures this double salt may perhaps also be found.

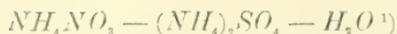


As solid phases at 35°, only the anhydrous components KNO_3 and K_2SO_4 have been found.

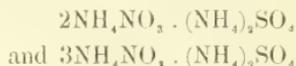
¹⁾ F. A. H. SCHREINEMAKERS and P. H. J. HOENEN. Chem. Weekbl. 6 p. 51. (1909).

²⁾ NAUMANN-ZIRKEL. Mineralogie p. 574 (1901).

³⁾ DAMMER. Handbuch der Anorg. Chemie (1894) II. 2. p. 171. MARIIGNAC. Ann. des Mines [5] 12 44.



Besides the two anhydrous salts NH_4NO_3 and $(NH_4)_2SO_4$ there occur also at 0° , 30° and 70° the two anhydrous double salts



as solid phases.

So far as they have been investigated up to the present, the ammonium salts behave quite differently from the potassium salts and in their behaviour show more resemblance with the lithium and sodium salts.

These investigations are being continued at other temperatures and also with nitrates and sulphates of other metals.

Chemistry. — “*On Dipterocarpol*”. (Preliminary communication)

By Prof. L. VAN ITALLIE. (Communicated by Prof. A. P. N. FRANCHIMONT).

(Communicated in the meeting of February 24, 1912).

In the investigation of the balsam of *Dipterocarpus Haseltii* and *D. trinervis* (Minjak Lagam) a substance was obtained in well-defined crystals.

When the balsam is mixed with petroleum ether, the solution decanted and the remainder extracted with petroleum ether until nothing more dissolves therein 34% of the balsam is left behind in the form of small white crummy pieces, mixed with small particles of wood. On boiling with alcohol and filtering, a liquid is obtained from which on cooling, colourless crystals are deposited to the extent of 19% of the original balsam.

The crystals have a melting point of 128° which by repeated crystallisation from alcohol, may be raised to 134° — 135° , but then remains constant. On warming with alcoholic potash and subsequent crystallisation from alcohol the melting point also remains constant.

The substance obtained gives the colour reactions characteristic for phytosterols, with acetic anhydride and sulphuric acid, with chloroform and sulphuric acid etc. As it differs, however, in more than one respect, from the known phytosterols, it will be designated provisionally by the name of *Dipterocarpol*.

¹⁾ F. A. H. SCHREINEMAKERS and P. H. J. HOENEN. l.c. Determination of the isotherm at 30° . A. J. C. DE WAAL. Dissertation, Leiden 1910; determination of the isotherms at 0° and 70° .

Dipterocarpol forms colourless biaxial crystals showing double refraction and straight extinction. They are readily soluble in chloroform, ether, and acetic ether, but with difficulty in cold alcohol.

At 130° they lose no water of crystallisation.

In the elementary analysis the following results were obtained :

combustion with copper oxide : combustion with lead chromate :

C = 80.78 80.68 80.69 80.53

H = 11.43 11.41 11.45 11.35

Average : C 80.67 H 11.41.

In the determination of the molecular weight, according to the method of the lowering of the freezing point, was found $M = 433$.

The formula $C_{27}H_{46}O_2$ requires C. 80.59, H. 11.44 and a molecular weight of 402. The values found are, therefore, sufficiently in agreement therewith.

Dipterocarpol is dextrorotatory ; α_D (determined in chloroform) $+ 64.6^\circ$.

In the ordinary way of acetylation by boiling with acetic anhydride and sodium acetate, in which the time of boiling was much varied, no crystallisable acetyl derivative could be obtained ; also none with acetic anhydride and sulphuric acid or zinc chloride. As phytosterols are generally so readily acetylated, dipterocarpol therefore forms an exception.

When dipterocarpol is heated with sodium acetate and acetic anhydride for 3 hours at 160°, the contents of the tube when cold solidify to a crystalline mass from which, after washing with water may be obtained by recrystallisation from alcohol, colourless crystals showing double refraction and straight extinction and melting at 69°—70°.

These crystals form the anhydride of dipterocarpol.

In the elementary analysis was found :

I	II	The formula $C_{27}H_{44}O$ requires :
C 84.74	84.20	84.37
H 11.82	11.36	11.47

Dipterocarpol anhydride is also formed together with diphenylurea by heating dipterocarpol for a short time with phenylisocyanate.

When dipterocarpol is dissolved in benzene and shaken for 6 or 7 hours with Kiliani's chromic acid mixture, it is converted into a ketone (dipterocarpone) which can be obtained from alcohol in well-developed crystals.

Dipterocarpone forms pillar-shaped, pointed rhombic crystals melting at 183°—184°. They contain no water of crystallisation and

give, on application of the well-known phytosterol reactions, less intense colorations than dipteroicarpol and its anhydride. The latter, in particular is characterised by very strong colour reactions.

In the elementary analysis was found :

	I	II	The formula $C_{27}H_{44}O_3$ requires :
C	77.85	77.45	77.88
H	10.43	10.58	10.66

The molecular weight was found to be: 409; the calculated molecular weight 416.

When dipteroicarpone was dissolved in benzene and again shaken for 6 hours with the chromic acid mixture it could be recovered unchanged from the benzene solution. The melting point was found to be 182° — 183° and the C-content and H-content 77.69 and 10.30, respectively.

Dipteroicarpone is dextrorotatory; α^D (in chloroform) = $+71.03^{\circ}$.

From the dipteroicarpone was made an oxime by means of hydroxylamine hydrochloride and potassium hydroxide. This oxide is only very little soluble in alcohol and is best recrystallised from glacial acetic acid. It then separates in microscopic small crystals which melt at 249° — 250° with decomposition.

The nitrogen content was found to be 3.5%. The formula: $C_{27}H_{44}(NOH)$ requires 3.48%.

When dipteroicarpone is dissolved in glacial acetic acid and oxidised with chromic acid we again obtain dipteroicarpone m.p. 183° — 184° . A solution of dipteroicarpol in acetone is not acted upon by potassium permanganate.

The action of bromine did not lead to the formation of a crystallised product. Only amorphous, resinous substances were obtained, with evolution of hydrogen bromide.

On treating a solution of dipteroicarpol in carbon tetrachloride with Wils's iodine monochloride solution a little more than 3 atoms of halogen was absorbed. The halogen not only acted additive, but also caused substitution. On adding water to the iodised liquid, fumes of halogen-hydrogen were noticed.

In the reduction of dipteroicarpol with sodium in boiling amyl alcohol, no crystallised dihydro-product was obtained, but only an amorphous resinous mass.

As the result of this preliminary investigation it may be stated that dipteroicarpol is a phytosterol of the formula $C_{27}H_{46}O_2$ from which one molecule of H_2O can be readily eliminated.

Leiden, February 1912.

Chemistry. — “*On Minjak Lagam.*” By Prof. L. VAN ITALLIE and M. KERBOSCH. (Preliminary communication). Communicated by Prof. A. P. N. FRANCHIMONT).

(Communicated in the meeting of February 24, 1912).

1. In the literature of the last 60 years mention is made repeatedly of a balsam called by the name of Minjak Lagam, which is obtained from Sumatra. The balsam is occasionally described as a liquid, oily product, in appearance much resembling oil of copaiba, sometimes as a mass of a dirty white colour and tallowy consistency.

From the oily balsam HAUSSNER (Archiv. der Pharm. **21**, 241, 1883) isolated a hydrocarbon from which he prepared a hydrochloride of the formula $C_{20}H_{32} \cdot 4HCl$, m.p. 114° .

2. It is generally stated that the Minjak Lagam is derived from *Canarium eupteron* Miq. Provisionally this origin must be accepted for the liquid variety of the balsam. There is, however, some reason to believe that the balsam is not derived from the said Burseraceae, but from a Dipterocarpus.

Both kinds of balsam have been investigated by us.

The liquid variety happened to be in a collection got together by DE VRIESE during a journey in the Dutch East Indies (about 1857). As to the botanical origin, the bottle was labelled *Canarium eupteron* Miq.

The more solid variety was procured through the mediation of the department of Agriculture in the Dutch Indies and was obtained from Central Sumatra. At first, the botanical origin was unknown, but the investigation by Dr. JANSSEN of Groningen of the woody particles which occurred in the balsam shows that this must have been derived from a kind of Dipterocarpus; this was confirmed by the determination of herbarium material obtained with great trouble. The determination executed by Dr. VALETON and Dr. SMITH at Buitenzorg showed *Dipterocarpus Hasseltii* Bl. and *Dipterocarpus trinervis* Bl. to be the parent plants.

3. The balsam of *Canarium eupteron* Miq. is thin-fluid; odour, taste and faint greenish fluorescence remind of oil of copaiba. The behaviour towards solvents is about the same as that of copaiba. Mixed with an equal volume of carbon disulphide the balsam gelatinises so that the tube can be inverted without the contents running out.

When the balsam is heated in a waterbath it turns viscid at 80° ; when cold the contents are found to have gelatinised. Probably, this phenomenon is due to polymerisation. In connection with the fact that a similar behaviour on warming is stated of some Dipterocarpus balsams, and also with the similarity with oil of Copaiba quoted

above, a new investigation as to the origin of the liquid Minjak Lagam appears to us to be desirable.

This Minjak Lagam consists largely of compounds indifferent to alkalis. The acid-number is 10.45; the saponification number 14.8. The amount of volatile oil which can be passed over with water vapour amounts to about 49%. This oil is colourless, has a density of 0.9051 (15°/15°) and a refraction of 1.4972 (24°); in a 10 c.m. tube the rotation amounts to -7.5°.

On fractional distillation, fully 93% of the oil pass over between 258° and 261°. Of this fraction the following constants were obtained:

Boiling point (corr.) 261°—263°.

Rotation in 10 c.m. tube -7.46°.

Refraction 1.49935 (16.5°).

Density 0.905 (15°/15°).

This fraction appeared to consist entirely of caryophyllin.

On combustion, 206.7 mG. yielded 668.1 mG. of CO₂ and 220. mG. of H₂O.

	Found.	Calculated.
C	88.10 %	88.15 %
H	11.96	11.85

The molecular weight determined by the lowering of the freezing point in benzene was found to be 205 (calculated for C₁₅H₂₄—204).

The identity of the hydrocarbon with caryophyllin was further established by the formation of the caryophyllin alcohol (m.p. 92°—94°) and of the splendidly blue nitrosite (m.p. 111°—112°).

The occurrence of such a large quantity of caryophyllin in the liquid Lagam balsam justifies the supposition that this is not derived from a Burseraceae, but from a Dipterocarpus.

Up to the present caryophyllin, in large quantity, has only been met with in oil of cloves and in oil of Copaiba.

As to the botanical origin of the balsam and the composition of the resin contained therein we hope to be able to communicate later.

4. The balsam of *Dipterocarpus Hasseltii* Bl. and *D. trinervis* Bl. These two trees mutually differ so little that they are regarded by some botanists as belonging to the same species.

The balsam forms a dirty white mass, which it is almost impossible to pour out; small woody particles are present, also a little water. The odour is disagreeable, reminding somewhat that of oil of Copaiba.

On distillation with water, 2 samples of the balsam yielded 10.5% and 22% of volatile oil respectively.

This oil was colourless and viscid and had somewhat the odour of oil of Copaiba.

Density 0.9132 ($^{15^{\circ}}_{15^{\circ}}$); refraction 1.50137 (16.5°); rotation in 10 c.m. tube — 9.75° (15°).

When rectifying the oil water was split off. The oil was, therefore heated for some time with metallic sodium and then distilled. The following data were obtained:

Boiling point (corr.) 261° — 264° .

Rotation in 10 c.m. tube — 8.9° (15°).

Refraction 1.50029 (16.5°).

Density 0.9065 ($^{15^{\circ}}_{15^{\circ}}$).

By the formation of the blue nitrosite (m.p. 112° — 113°) the identity of the oil with caryophyllin could be demonstrated, so that this hydrocarbon also occurs in large quantity in the balsam of *Dipterocarpus trinervis* Bl. and *D. Hasseltii* Bl.

About that balsam it may yet be stated that, besides a resinous body, not yet investigated, 19% of a crystallisable phytosterol occur therein.

Leiden, February 1912.

Physics. — “Contribution to the theory of binary mixtures.” XIX.

By Prof. J. D. VAN DER WAALS.

In Contribution X (These Proc. XI p. 317) I occupied myself with the conditions for the existence or non-existence of a locus for the points of intersection of the two curves $\left(\frac{d^2\psi}{dx^2}\right)_v = 0$ and $\left(\frac{d^2\psi}{dx^2}\right)_x = 0$. I had been induced to do so by a remark in Contribution II, where it had appeared to me that when $\frac{d^2\psi}{dx^2} = 0$ gets outside $\frac{d^2\psi}{dx^2} = 0$ at a certain value of T , this gives rise, at least as a rule, to the existence of a heterogeneous double plaitpoint, and so to the existence of three-phase pressure. So long as the former curve remains at all temperatures inside the region in which $\frac{d^2\psi}{dx^2}$ remains negative, this double plaitpoint does not occur, and there is no question of a complication in the ordinary transverse plait, and three-phase pressure will not be found.

But I did not bring this problem to an end then. Occupied with

other questions, I put off the further discussion again and again to a future opportunity, and never gave the simple representation which may be given of the existence or non-existence of three-phase pressure, and never discussed on what circumstances about the properties of the components the existence of three-phase pressure depends.

The case that I treated at length, is this for which the auxiliary quantities ε_1 and ε_2 are positive, and the points of intersection of the above-mentioned curves have a closed figure as locus. In this case there are two temperatures at which $\frac{d^2\psi}{dt^2} = 0$ touches $\frac{d^2\psi}{dx^2} = 0$.

At the lower of these two temperatures begins the existence of the two plaitpoints, which originally still lie in the covered region (e.g. the point P_{ab} of fig. 52. Contribution XVII). And not before somewhat higher temperature does three-phase pressure begin to appear (e.g. at the temperature of the point Q_2 of fig. 52). For the meaning of the higher of these temperatures I must refer to preceding Contributions.

I have not treated the case that the quantities ε_1 and ε_2 are negative. It does not offer, however, any great difficulty. That then there certainly exists a locus for the equations of the two mentioned curves, is clear from the equations of Contribution X, e.g. (β), (β'), and (γ). The value of x , at which this locus begins or ends, is given by :

$$b^2 + x(1-x) \left(\frac{db}{dx} \right)^2 = 1 - x(1-x) \frac{c}{a}$$

or

$$x(1-x) \frac{c}{a} = \frac{x(1-x) \left(\frac{db}{dx} \right)^2}{b^2 + x(1-x) \left(\frac{db}{dx} \right)^2}.$$

If we leave the factor $x(1-x)$, which has no practical importance, out of consideration, this condition becomes :

$$\frac{c}{a} > 1 - \frac{(n-1)^2}{(n^2-1)x}.$$

And the locus is found on that side of this value of x , for which

$$\frac{c}{a} > 1 - \frac{(n-1)^2}{(n^2-1)x}.$$

or for which

$$\frac{a}{c} < \frac{1 + (n^2-1)x}{(n-1)^2}.$$

As I already observed in Contribution X, the case $1 < n(1-x) c$ is left out of consideration in all these derivations. This is of little importance and can be treated separately. Now $\frac{a}{v}$ may be represented by a curve which begins at $x=0$ with the value $\frac{a_1}{c}$, and terminates at $x=1$ with the value $\frac{a_2}{c}$. As $\frac{d^2a}{dx^2} = 2c$ is positive, this curve has its convex side turned downward. The second member of this latter inequality may be represented by a straight line. So there is certainly intersection of these two lines, when $\frac{a_2}{c} > \frac{n^2}{(n-1)^2}$ and $\frac{a_1}{c} < \frac{1}{(n-1)^2}$ or reversely. But as we put $\frac{a_2}{c} = \frac{n^2(1+\varepsilon_2)}{(n-1)^2}$ and $\frac{a_1}{c} = \frac{1+\varepsilon_1}{(n-1)^2}$ the former supposition implies ε_2 positive and ε_1 negative.

The reverse supposition, which will have a far greater chance to occur with great value of n , implies ε_2 negative and ε_1 positive. On both suppositions the equation β' or γ of Contribution X has a positive root for $N = \frac{v}{1-x}$, when the sign $>$ in it is replaced by $=$.

The locus for the intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ begins at this value of N , and lies for the latter case, viz. ε_2 negative, between this value of N and $N = \infty$. If the case ε_1 negative and ε_2 positive should be possible, this locus occurs between $N = 0$ and the value of N at which the two lines intersect, so on the side of the component with the smaller size of the molecules. But both for $N = 0$ and for $N = \infty$, or what is the same, for $x = 0$ and $x = 1$, the equation a' of Contribution X shows that $v = b$, and that the intersection of the two mentioned curves begins already at $T = 0$. This means that the point P_{ab} of fig. 52 does not begin only at a certain value of T , as we thought probable for the mixture water-ether, but that it has descended to the absolute zero of the temperature, which we thought probable for the case water-mercury.

If the two quantities ε_1 and ε_2 are negative, the straight line extends over the full width from $x = 0$ to $x = 1$ above the curve $\frac{a}{v}$, and the locus of the points of intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ takes up the full width. A case which will probably not occur, but that we shall yet include in our further considerations as not impossible.

Summarizing we may put that if the components of a binary mixture possess such properties that the values of ϵ_1 and ϵ_2 considered as ordinates of points, lie in the quadrant in which ϵ_1 and ϵ_2 are positive, the mixture cannot present three-phase pressure until above a certain value of T . If the points, of which ϵ_1 and ϵ_2 are the ordinates do lie in that quadrant, but in that part that is situated below the part QRP of the parabola of fig. 36, there is still three-phase pressure, but it begins above a certain value of T . For the other points of this quadrant three-phase pressure is entirely wanting. According as the points indicated by ϵ_1 and ϵ_2 still lie below the part of the parabola, but approach it, the temperatures between which three-phase pressure exists, lie closer together. For the points of the branch QRP the two temperatures of the points P_{ab} and P_{cd} of fig. 52 coincide, and so properly speaking there exists no longer three-phase pressure.

If we consider it only as a mathematical problem, the space in which ϵ_1 and ϵ_2 are negative is 3 times as large as the space in which ϵ_1 and ϵ_2 are positive and which represent cases of complete miscibility; and the space in which ϵ_1 and ϵ_2 are positive, and yet three-phase pressure is possible between two given temperatures, is only an insignificant part of the whole region. To conclude to the chance for the occurrence of these three cases merely from this is, however, entirely unjustifiable. It follows from the restriction ensuing from the condition that a_1 and a_2 be positive, that neither ϵ_1 nor ϵ_2 can descend below -1 . This in itself already restricts the number of cases in which three-phase pressure can already occur at $T=0$, to a high degree. But moreover in consequence of the non-occurrence in nature of different mathematical possibilities for the value of the quantities on which ϵ_1 and ϵ_2 depend, whole series of points represented by ϵ_1 and ϵ_2 are excluded. Thus the whole number of the points which lie below a line drawn in fig. 37 from O' at an angle of 45° with the axes will be excluded, if a value of $\frac{T_{k_2}}{T_{k_1}} > n$ does not occur for a substance with a size of the molecules n times greater, as is probable at least for the substances which we generally know as liquids. Further we must exclude very high values for ϵ_1 and ϵ_2 , unless for very high values of n , and also very small values for $1 + \epsilon_1$ and $1 + \epsilon_2$ unless for very small values of $n - 1$.

The quantities which serve to determine ϵ_1 and ϵ_2 are according to the definition the value of a_1 , a_2 , n , and, because also l occurs in $c = a_1 + a_2 - 2a_{12} = a_1 + a_2 - 2\frac{h}{a_1 a_2}$, also this latter quantity.

In Contribution X fig. 37 I have given a construction which enables us with given value of n and l to see at a glance which of the 3 mentioned cases, either complete miscibility or the two cases of incomplete miscibility, will occur at given value of $\frac{a_2}{a_1}$ or $n \frac{T_{k_2}}{T_{k_1}}$.

Besides the parabola of fig. 36 we have then still to construct the curve of the second degree :

$$4n^2 l^2 (1 + \varepsilon_1) (1 + \varepsilon_2) = (2n + \varepsilon_1 + n^2 \varepsilon_2)^2, \dots \dots (1)$$

the equation of the parabola being rendered by :

$$4n^2 \varepsilon_1 \varepsilon_2 = \{(n-1)^2 - (\varepsilon_1 + n^2 \varepsilon_2)\}^2. \dots \dots (2)$$

The curve of the second degree, represented by (1), is a parabola when $l=1$, an ellipse when $l < 1$, and a hyperbola when $l > 1$.

As it is possible to give an answer to all questions without difficult calculations when $l=1$, I shall start with this supposition.

The parabola represented by (1) is then exactly the same as that represented by (2) with only this exception that the points of the former parabola are found by displacing those of the latter in a negative direction both in vertical and in horizontal sense, by an amount of $+1$. In fig. 37 an ellipse has been drawn, so $l < 1$ was supposed. It cannot be difficult to think this too transformed to a parabola, in which case the branch which has now been drawn a little to the left of O, must pass through that point, as has been indicated by the dotted line of fig. 36.

If in fig. 37 we trace a line from point O' to an arbitrary point of the curve drawn in this figure, $n^2 \frac{1 + \varepsilon_2}{1 + \varepsilon_1} = n^2 \cot q$ represents the

value of $\frac{a_2}{a_1} = n \frac{T_{k_2}}{T_{k_1}}$. If this line is made to rotate round the point O'

as centre, successively all the values of $\frac{T_{k_2}}{T_{k_1}}$ are represented from ∞

to 0. Now we have only to determine where the point lies in which such a line intersects the curve of fig. 37 to know whether

at the given value of n and l , and the value of $\frac{T_{k_2}}{T_{k_1}}$ determined by the direction of the line, the binary system will possess perfect miscibility or only incomplete miscibility.

So long as for $l=1$ the value of q is smaller than 45° , the points of intersection of the line with the curve lie in the region

in which ε_2 and ε_1 are negative, and so with $\frac{T_{k_2}}{T_{k_1}} > n$ there is incom-

plete miscibility already at the absolute zero. If the line is made to rotate further upwards, and so $\frac{T_{k_2}}{T_{k_1}}$ is made to descend below n , the extremity of this line gets into the region where ϵ_1 and ϵ_2 are positive, and there is still incomplete miscibility, but it does not begin until above $T=0$. This continues to the point where the curve of fig. 37 intersects the parabola of fig. 36. At the value of $\frac{T_{k_2}}{T_{k_1}}$ that belongs to this point, the points P_{ab} and P_{cd} of fig. 52 coincide, and on still further rotation of the line and so on decrease of $\frac{T_{k_2}}{T_{k_1}}$ no plaitpoint of the 2nd kind exists any longer, and there is complete miscibility. On still further rotation of the line, when $ty\varphi = n$, we get equality of T_{k_2} and T_{k_1} . If $ty\varphi = n^2$, $T_{k_2} = \frac{T_{k_1}}{n}$; this direction coincides with the direction of the axis of the parabola of fig. 36, and in the case of $l=1$, also with that of fig. 37. Then the values of ϵ_1 and ϵ_2 would be infinitely large, and the physical possibility of the occurrence of such a case exists only if n should be $=\infty$. On still further rotation the line would intersect the ϵ_1 -axis, and so $\epsilon_2 = 0$. Now the parabola of fig. 37 cuts the ϵ_1 -axis in a point where $\epsilon_1 = 4n(n-1)$, and so $\frac{n^2(1+\epsilon)}{1+\epsilon_1} = \frac{n^2}{1+4n^2-4n} = \frac{n^2}{(2n-1)^2}$ and we find for $\frac{T_{k_2}}{T_{k_1}}$ a value equal to $\frac{n}{(2n-1)^2}$. On still further rotation the complete miscibility stops again, and so at $\frac{T_{k_2}}{T_{k_1}} < \frac{n}{(2n-1)^2}$ there is again three-phase pressure already at $T=0$ for the case $l=1$. But it is not very likely that the case that a substance with a molecule n times as large would possess a critical temperature n times smaller, should exist.

Now that we have to do with an intersection of two equal parabolae with parallel axes, the place of the point of intersection can be easily calculated, and so also the value of $\frac{T_{k_2}}{T_{k_1}}$, at which the complete miscibility sets in, can be indicated.

Assuming an arbitrary value of l for the determination of the points of intersection of (1) and (2) for the sake of further investigation, the following equation may be derived:

$$4n^2(1-l^2)(1+\epsilon_1)(1+\epsilon_2) = (n-1)^4 + 2(n^2-1)(\epsilon_1 - n^2\epsilon_2) \quad (3)$$

This equation is obtained when the difference of (1) and (2) is

subtracted from the identity :

$$4n^2(1+\varepsilon_1)(1+\varepsilon_2) - 4n^2\varepsilon_1\varepsilon_2 = 4n^2 + 4n^2\varepsilon_1 + 4n^2\varepsilon_2.$$

If now $l=1$, we find $\varepsilon_1 - n^2\varepsilon_2 = -\frac{(n-1)^2}{2(n+1)}$. And as :

$$n-1 = \sqrt{\varepsilon_1} + n\sqrt{\varepsilon_2}$$

for the branch of the parabola of fig. 36 which lies below the line

PQ , $\sqrt{\varepsilon_1} - n\sqrt{\varepsilon_2}$ will be equal to $-\frac{(n-1)^2}{2(n+1)}$, or

$$2\sqrt{\varepsilon_1} = (n-1) \left\{ 1 - \frac{n-1}{2(n+1)} \right\}$$

and

$$2n\sqrt{\varepsilon_2} = (n-1) \left\{ 1 + \frac{(n-1)}{2(n+1)} \right\}$$

or

$$\sqrt{\varepsilon_1} = (n-1) \frac{(n+3)}{4(n+1)}$$

and

$$n\sqrt{\varepsilon_2} = (n-1) \frac{(3n+1)}{4(n+1)}$$

From this ε_1 and $n^2\varepsilon_2$, and so also $\frac{T_{k_2}}{T_{k_1}}$ can be determined.

The thus determined value of $\frac{T_{k_2}}{T_{k_1}}$ is of a complex form, and depends on n in this way :

$$\frac{T_{k_2}}{T_{k_1}} = n + \frac{(n-1)^2}{16(n+1)^2} \cdot \frac{(3n+1)^2}{n}.$$

This value is smaller than n . With increasing value of n it becomes a smaller and smaller part of n ; for n somewhat greater than 20 it becomes equal to 1, and for still greater value of n it descends even below 1.

When l deviates from the value 1, the calculation of $\frac{a_2}{a_1}$ or $\frac{T_{k_2}}{T_{k_1}}$ for the limit at which complete miscibility sets in, is not very well feasible. It is then prevented by the difficulty to determine the place of the points of intersection for two curves of the second degree, which is then only possible by solution of a 4th power equation. I need, however, hardly point out that at any rate the possibility remains for an approximate determination by means of graphical construction.

It remains, however, also then easy to determine the said value for

the limits of incomplete miscibility from $T=0$. For then only the points of intersection with the axes need be determined.

Let us begin with the case $l < 1$, in which case the curve of fig. 37 is an ellipse. Then there can only be intersection with the ϵ_1 -axis, and only between the values of ϵ_1 lying between 0 and $4n(n-1)$. The way in which these values of ϵ_1 depend on l and n will then be found by solution of (1), if we put $\epsilon_2 = 0$. And so by the aid of the equation :

$$4l^2 n^2 (1 + \epsilon_1) = (2n + \epsilon_1)^2.$$

Then we find :

$$\epsilon_1 = 2n(l^2 n - 1) \pm 2nl\sqrt{l^2 n^2 - (2n-1)} \quad \dots \quad (4)$$

If $l^2 < \frac{2n-1}{n^2}$ or $1 < l^2 < \frac{(n-1)^2}{n^2}$, the ellipse no longer cuts the region where ϵ_1 is positive. So for a value of $l^2 < \frac{2n-1}{n^2}$ no complete miscibility is possible, whatever the value of $\frac{a_2}{a_1}$ or $n \frac{T'_{k_2}}{T'_{k_1}}$ should be. But for a value of l^2 between 1 and $\frac{2n-1}{n^2}$ part of the ellipse gets into the region where ϵ_2 is positive. If this whole part of the ellipse should lie above the branch QP of the parabola of fig. 36, two values of $\frac{a_2}{a_1}$ would be indicated between which complete miscibility would occur. But if this part of the ellipse should remain entirely below the branch QP , no complete miscibility is possible, but there are two values for $\frac{a_2}{a_1}$ to be given between which incomplete miscibility exists, which, however, begins and ends only above $T=0$, as is represented in fig. 52. There is, however, still a third and a fourth case possible, in which the said part of the ellipse intersects the branch PQ of the parabola of fig. 36, either once or twice. Which of these four cases will occur depends on l and n . Always the part of the ellipse that lies above the branch PQ will indicate complete miscibility, and reversely.

We shall proceed to investigate in what way the 4 cases mentioned depend on l and n , knowing from the above that l^2 must be $> \frac{2n-1}{n^2}$.

If l^2 is exactly equal to $\frac{2n-1}{n^2}$, the two points of intersection of the ellipse and the ϵ_1 -axis are equal according to (4), they are namely

equal to $2(n-1)$ as can also be derived from (4). So if the first of the 4 cases mentioned can occur, this value must be larger than that of OQ in fig. 36. And so:

$$2(n-1) > (n-1)^2$$

or

$$3 > n.$$

Not until l^2 has become somewhat greater than $\frac{2n-1}{n^2}$ does part of the ellipse appear in the positive quadrant and when l^2 has become equal to the value of l^2 which follows from (1) when we put $\varepsilon_2 = 0$ and $\varepsilon_1 = (n-1)^2$ viz.:

$$l^2 = \frac{(n^2+1)^2}{4n^2 [1 + (n-1)^2]} \dots \dots \dots (5)$$

the third case occurs, and the branch QP is cut once. For $n=2$ there is no great difference between these two values of l^2 .

The former amounts to $\frac{24}{32}$, and the latter to $\frac{25}{32}$.

If on the other hand $n > 3$, for which again the quantity $\frac{2n-1}{n^2}$ corresponds as minimum value of l^2 , the second case occurs for somewhat greater value of l^2 . It is again possible to increase l^2 so greatly that the value of (5) is reached, and so the third case can occur again. But moreover the value of l can be chosen such that QP is not only intersected once, but even twice; then l^2 must be, indeed, chosen above $\frac{2n-1}{n^2}$, but remain below (5). It is not easy to determine within what limits for the value of l^2 this double intersection will take place. For this it would again be necessary to indicate the place of the points of intersection of an ellipse and a parabola. That this presents difficulties is to be regretted, because the possibility or impossibility of this double intersection must decide whether or no complete miscibility is still possible for the chosen value of n and l . As transition case we have then to examine, what the value of l^2 must be for chosen value of n if the ellipse is to touch the parabola.

We might also put the problem that is to be solved thus: where for given value of n does the point lie in which the value of l^2 is minimum on the branch of the parabola of fig. 36, between Q and R , and what is this minimum value? Between this minimum value and the value of (5) the parabola is twice intersected by the ellipse. It is self-evident that we cannot introduce the restriction (between Q and R) at once into our solution, and that we should really propose

a more general problem, viz. to seek the points in which the value of l^2 becomes minimum or maximum, when the whole parabola of fig. 36 is followed. For the points that lie in infinity this value $\equiv 1$, as appears from (1), when in this equation we neglect the value of n and 1 by the side of the infinitely great value of ε , and $n^2\varepsilon_2$, and then put $\varepsilon_1 = n^2\varepsilon_2$. If we follow the lefthand branch of the parabola beginning infinitely high, l^2 begins with 1, and reaches again the same value in the point R . Between lies a minimum value which still lies above Q for $n < 3$, but lies between Q and R for $n > 3$. On the righthand branch there lies a maximum value for l^2 , beyond the point P . Yet we shall give an answer to the proposed question in which it seems as if it only holds for the portion of the parabola between Q and P , because the minimum of l^2 that lies on this portion of the parabola, is only of direct importance. So for this purpose equation (3), which only holds for points which are common to the ellipse and to the parabola, will serve. By making use of the relation which holds for the portion PRQ of the parabola, viz.

$$\sqrt{\varepsilon_1} + n\sqrt{\varepsilon_2} = n - 1$$

we write (3) as follows:

$$4(1-l^2)(1+\varepsilon_1)(n^2+n^2\varepsilon_2) = (n-1)^4 + 2(n-1)^2(n+1)(\sqrt{\varepsilon_1} - n\sqrt{\varepsilon_2})$$

or

$$4(1-l^2)(1+\varepsilon_1)(n^2+n^2\varepsilon_2) = (n-1)^4 + 2(n-1)^2(n+1)(n-1-2n\sqrt{\varepsilon_2})$$

or

$$4(1-l^2)(1+\varepsilon_1)(n^2+n^2\varepsilon_2) = (n-1)^3(3n+1) - 4(n-1)^2(n+1)n\sqrt{\varepsilon_2}.$$

If we now also substitute $\varepsilon_1 = [(n-1) - n\sqrt{\varepsilon_2}]^2$, we have a 4th power equation for the determination of $n\sqrt{\varepsilon_2}$. If we put $n\sqrt{\varepsilon_2} = x$, this equation has the following form:

$$\left\{ [n^2 + n^2(n-1)^2] - \frac{(n-1)^3(3n+1)}{4(1-l^2)} \right\} - 2x \left\{ n^2(n-1) - \frac{2(n-1)^2(n+1)}{4(1-l^2)} \right\} + x^2 \{ n^2 + 1 + (n-1)^2 \} - 2(n-1)x^3 + x^4 = 0 \quad (6)$$

If this equation is represented by a curve, the second differential quotient is always positive, and so it can possess at most two real roots. If the known term is negative, there is only one positive root possible for $n\sqrt{\varepsilon_2}$, and then we have the case that we had mentioned as the third case. If on the contrary the known term is positive, and moreover the factor of x negative, the 4th case is possible. The transition of the known term from positive negative takes place when $1 - l^2$ has the value corresponding to the Q of fig. 36. Equation (6) becomes then:

$$2x \cdot \frac{n^2(n^2+1)(n-3)}{(n-1)(3n+1)} + x^2 \{ n^2 + 1 + (n-1)^2 \} - 2(n-1)x^3 + x^4 = 0 \quad (7)$$

Then there is a root $x=0$, and so long as $n > 3$, another root which is positive. If $n=3$, there is a second root $=0$, and then the ellipse touches the parabola of fig. 36 in the point Q . For $n < 3$, there would still be a negative root for x , and this root would refer to the point of intersection of the ellipse with the branch of the parabola above the point Q , but this intersection is immaterial for our problem. If, however, $n > 3$, there is besides the root $x=0$ another positive root, which then indicates the intersection of the ellipse with the branch PR of the parabola.

If we put $x=4$, (7) becomes in numerical values :

$$-14 + 26x - 6x^2 + x^3 = 0$$

there is then a root between 0 and 1, viz. about 0.6. For $n=5$ (7) becomes :

$$-40^5/n + 42x - 8x^2 + x^3 = 0$$

then there is a root that does not differ much from 1.

At any rate x must be smaller than that of the point R .

For a value of $n\sqrt{\epsilon_2}$ between 0 and the positive root of (7), and the value of $\sqrt{\epsilon_1}$ and $\frac{a_2}{a_1}$, answering to such a value, there will still be complete miscibility for the chosen value $1-l^2$.

If we now take l^2 smaller or $1-l^2$ greater, the known term of (7) becomes positive, and the possibility exists that (7) possesses two positive roots for x , the first somewhat greater than 0, and the second somewhat smaller than the above calculated value. And we may decrease l^2 so much that these roots become equal. Then the complete miscibility has quite disappeared. The ellipse no longer cuts the branch QP of the parabola, but touches it. The point in which this contact takes place, is then the point of the branch QP of the parabola in which l^2 is minimum.

If we write (3) in x , and differentiate logarithmically with respect to l and x , keeping n constant, and if we then put $dl^2 = 0$, $1-l^2$ is eliminated, and we obtain the equation for the determination of the value of x , at the place where for given value of n the value of l^2 is minimum or maximum. We then get after some reduction :

$$2 \{ (n-1) - x \} (n^2 + x^2) - x \{ 1 + (n-1-x)^2 \} \left\{ (n-1) \frac{(3n+1)}{4(n+1)} - x \right\} - (n^2 + x^2) \{ 1 + (n-1-x)^2 \} = 0$$

or

$$\frac{n^2 (n-3) (n^2 + 1)}{2(n+1)} - x \frac{(n-1)(3n+1)}{(2n+1)} \{ n^2 + 1 + (n-1)^2 \} +$$

$$+ x^2 \left\{ 3(n-1)^2 \frac{(3n+1)}{2(n+1)} + n^2 + 1 + (x-1)^2 \right\} \dots$$

$$x^3 \left\{ 2(n-1) \frac{(3n+1)}{2(n+1)} + 4(n-1) \right\} + 3x^4 = 0.$$

This equation too can have two real roots at the most, as the second differential quotient is always positive. There is always a root for x greater than that which belongs to the point R , for the value is negative with $x = (n-1) \frac{3n+1}{4(n+1)}$, while x can always be taken so large that the value is positive. This value belongs to the maximum of l^2 , and is of no importance for our investigation. But then there must be a second positive root, at least when the known term is positive. And it is this second root that we seek. This root is $= 0$, if $n=3$, and to this we already concluded above. If $n < 3$, this root is negative — and then this means that the minimum of l^2 lies on the parabola of fig. 36 above the point Q . I have determined the numerical value of x for $n=4$ and $n=5$. For $n=4$ the equation becomes:

$$27,2 - 101,4 x + 61,1 x^2 - 19,8 x^3 + 3x^4 = 0.$$

The root is then about equal to $\frac{1}{3}$, and lies then almost halfway the above determined value of the point of intersection, viz. 0,6, which, however, was then determined only approximately for the corresponding value of $1-l^2$.

If we wanted to determine not $x = n\sqrt{\varepsilon_2}$, but $\sqrt{\varepsilon_2}$ itself, we should have to divide the successive coefficients successively by n^4, n^3 etc. And for increasing value of n the equation converges then to:

$$\frac{1}{2} - 3(x') + \frac{13}{2}(x')^2 - 7(x')^3 + 3(x')^4 = 0.$$

This equation can be written:

$$3(1-x') \left(\frac{1}{3} - x' \right) \left\{ \left(x' - \frac{1}{2} \right)^2 + \frac{1}{4} \right\} = 0.$$

So the value of $\sqrt{\varepsilon_2}$ for the minimum of l^2 will approach to $\frac{1}{3}$ for increasing value of n , while that for the maximum approaches to $\frac{1}{2}$, so to that of the point P of the parabola of fig. 36. The value of $\sqrt{\varepsilon_2}$ for the point R approaching to $\frac{3}{4}$, the point R will always continue to lie between the maximum and the minimum

value of l^2 . The values of l^2 corresponding to $x' = \frac{1}{3}$ and $x' = 1$ are 0 and ∞ .

Before concluding the description of these ellipses I will first discuss as an example the case already repeatedly treated by us of ether and water. We shall begin with determining ϵ_1 and ϵ_2 , putting $n=5$.

For the determination of ϵ_1 we must know $\frac{a_1}{a_2} = \frac{1}{1 - \frac{a_1}{a_2} - 2l \sqrt{\frac{a_1}{a_2}}}$.

The quantity $\frac{a_2}{a_1} = n \frac{T_{k_1}}{T_{k_2}}$ is known, and the choice of l is not doubtful.

For $l^2 = \frac{2n-1}{n^2}$ the mixture would lie on the border of the region,

in which complete miscibility begins already at $T=0$. We have arrived at the conclusion that this is not probable for this mixture and so we have to put $l > 0,6$. But l cannot be much greater, for

already for $l = \frac{2}{3}$ the point ϵ_1, ϵ_2 lies in the region of complete miscibility.

If we put $l = 0,61$, we calculate $\epsilon_1 = 6$ and $\epsilon_2 = 0,008$ or $n^2 \epsilon_2 = 0,2$. With these values we can calculate the limits of x

between which the locus of the points of intersection of $\frac{d^2 \Psi}{dx^2} = 0$

and $\frac{d^3 \Psi}{dx^3} = 0$ is contained, and then we find $x_2 = 0,98$ and $x_1 = 0,383$.

So the locus of the points of intersection lies almost entirely on the

ether-side. To this conclusion the consideration that $x_1 x_2 = \frac{\epsilon_1}{(n-1)^2}$ might

already have led us, from which we at once derive $\frac{n^2 \epsilon_2}{(n-1)^2} = (1-x_1)(1-x_2)$.

We obtain the second relation from the first by changing n into

$\frac{1}{n}$, ϵ_1 into ϵ_2 , and x into $1-x$.

With these relations we write:

$$\frac{\epsilon_2}{\epsilon_1} = \frac{n^2}{(n-1)^2} \frac{(1-x_1)(1-x_2)}{1 + x_1 x_2}$$

And so $x_1 x_2$ very great with respect to $(1-x_1)(1-x_2)$.

But though the given values are correct on the whole, yet there is a circumstance which shows that they should be somewhat revised

If we examine for the locus contained between $x = 0.98$ and $x = 0.383$, how the intersection is of the two curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dn^2} = 0$, it appears that at the highest temperature, when these curves touch, $\frac{d^2\psi}{dn^2} = 0$ must still exist, because for $n = 5$ or more accurately $n = 5.5$, this curve disappears for a value of x that is smaller than $x = 0.383$. If we then draw $\frac{d^2\psi}{dx^2} = 0$ at the contact, it must necessarily lie in the region where $\frac{d^2\psi}{dn^2} = 0$ is negative. And then it would also disappear in that region, which must not be the case for that high value of n . This compels us to consider $x = 0.383$ too great. But in the calculation of $x = 0.383$, we had put $n = 5$, and for $n = 5.5$ we obtain for water and ether a higher value of α_1 and a smaller one of x .

Thus I have once more returned to a thesis which I have expressed more than once viz. that the disappearance of $\frac{d^2\psi}{dx^2} = 0$ in the region where $\frac{d^2\psi}{dn^2}$ is positive, would be the criterion of three-phase pressure. I have, however, not yet quite succeeded in proving this thesis. I am of course convinced of the validity of the application of this thesis in our case. But I am not yet perfectly convinced of the validity in all possible cases. At all events we can here use this thesis to calculate the value of l from:

$$cx_g \frac{(1-x_g)}{a} > \frac{4y_g^2}{1+y_g}$$

Using the symbol k for $\frac{4y_g^2}{1+y_g}$, we derive:

$$2l < \sqrt{\frac{a_1}{a^2} \left\{ 1 - \frac{k^2}{1+k^2} \frac{1}{x_g} \right\}} + \sqrt{\frac{a_2}{a_1} \left\{ 1 - \frac{k^2}{1+k^2} \frac{1}{1-x_g} \right\}}$$

and from this we calculate $l < 0.64$.

Moreover it should be borne in mind that by a thesis as: "the existence of three-phase pressure depends on the circumstance whether $\frac{d^2\psi}{dx^2} = 0$ disappears in the region where $\frac{d^2\psi}{dn^2}$ is positive or negative",

not what I shall again call the mathematical possibility of three-phase pressure can be meant. This exists of course for all values of n and l . But I hope to return to this question later on. The possibility will have to be considered whether if n is small not naturally only great value of l will occur, and if then all arbitrary values of a_1 and a_2 may be chosen. (To be continued.)

Chemistry. — "*Investigations on the radium content of rocks.*" III.
By Dr. E. H. BÜCHNER. (Communicated by Prof. A. F. HOLLEMAN).
(Communicated in the meeting of February 24, 1912).

According to the method described in my first communication¹⁾ on this subject I have now investigated a number of rocks which are partly originating from the isle of Borneo and the Moluccas and partly from the Dutch province of Limburg.

a. Borneo and Moluccas. Prof. WICHMANN of Utrecht was kind enough to present me for this purpose with a number of rockspecimens from the museum of his laboratory, which were for the greater part collected by Prof. MOLENGRAAFF during his scientific exploration of Central Borneo. I take this opportunity to openly thank Prof. WICHMANN for his kindness.

The results of the investigation, expressed in 10^{-12} gr. of radium per gram of rock, are given in the following table.

Amphibole biotite granite, Karangan near Toemb. Temangooi	10,0
Amphibole granitite, Soengei Menjoekoei	1,3
Biotite amphibole andesite, S ⁱ Tebaceng	0,8
Amphibole andesite, S ⁱ Embakoe	doubtful
Garnet andesite, Boekit Oejan	1,4
Amphibole andesite, Boekit Ampan	0,8
Amphibole andesite, S ⁱ Tepoewai	1,6
Biotite amphibole dacite, Riam Toentoen	2,8
Olivine diabase, Riam Pandjang	1,4
Rhyolitic pitchstone, S ^{ei} Kawan	0,7
Vitrous amphibole dacite, S ⁱ Embakoe	0,9
Diorite porphyry, S ^{ei} Sebilit	1,5
Diorite porphyry, N ^a Gaäng	0,6
Andesitic amphibole porphyry, Boekit Sedaroeng	1,4
Norite, S ^{ei} Menjoekoei	0,7
Andesite, Isle of Sangi	4,3
Augite andesite, Isle of Ternate	1,3
Pitchstone, Tandjong Hatoelawe, Amboina	0,5

¹⁾ Proc. XIII, 359 (1910), second commun. XIII, 818 (1911).

The table gives rise to some remarks. The general average amounts to $1,73.10^{-12}$ gr. and thus agrees closely with that found previously for the rocks from Sumatra, namely $1,65.10^{-12}$ gr. It also tallies fairly well with the mean of all the igneous rocks investigated which amounts to $1,4.10^{-12}$ in a number of 104 specimens; in this calculation, however, are not included the figures obtained by JOLY. As I remarked previously ¹⁾, JOLY always finds higher numbers than other investigators; these without exception give average values varying from about 1 to 2, but as the result of the measurements of 126 rock specimens, JOLY arrives at a final figure of 7. LABY, in a very recent publication ²⁾ rightly concludes that it would be desirable to have JOLY's measurements repeated by another investigator, so that this great difference may be explained. The only specimen that far exceeds the average is the first-named granite; here again we find to some extent a confirmation of the fact that granites often show a higher radium content. On the other hand we find the andesite (N^o. 4) where the presence of radium remained doubtful, by which I mean that the figure is smaller than 0.3 (in the usual measure). If I am not mistaken, the only other example of an igneous rock where radium cannot be detected in this manner, is a basalt from Ross SOUND ³⁾.

The differences shown by specimens of a same rock but derived from different localities are not smaller than those which occur between rocks of a different character, so that a connexion with the nature of the rock does not seem to exist.

I will also correct a mistake which has slipped into the first communication. There the basalt of the volcano Asar is stated to contain $13,0.10^{-12}$ gr. of Ra. This figure was much larger than was ever found in other specimens of basalt (the average amount is only 0.6) and seemed suspicious. A fresh quantity of this basalt has, therefore, been dissolved and investigated in the usual manner with the result that now only 0.5 was found, quite in agreement with the other results. Presumably, the original solution had become contaminated in some way or other with a trace of a radium salt and, of course, the merest trace of this is sufficient to vitiate the result. The risk of such an error is hardly avoidable, when one is occasionally concerned with radium preparations. I have, therefore, now taken the

¹⁾ Handelingen 13e Ned Natuur- en Geneeskundig Congres 1911, p. 374; also compare my second communication in these Proc.

²⁾ Le Radium, IX, 21 (1912).

³⁾ FLETCHER, Phil. Mag. 21, 770 (1911).

precaution, to make a determination in duplicate, when the figures are exceptionally high, and have only trusted the figures when concordant.

b. Limburg. In the discussion following the reading of a paper on this same subject at the "Natuur- en Geneeskundig Congres" at Groningen, Mr. WATERSCHOOT VAN DER GRACHT inquired, whether there was likely to be a connection between the radium content and the depth, at which the specimen was taken. In order to test this idea experimentally, this gentleman placed at my disposal an excellent material, namely a series of carboniferous rocks obtained from a deep bore near Baarlo in Northern Limburg.

They consist of very sandy shales and quartziferous sandstones, which are met with at different depths from 685 to 1398 M.

The results are given in the subjoined table.

Bore near Baarlo, depth 685 M.	. . .	1,0
.. .. .	850 M.	. . . 0,8
.. .. .	1023 M.	. . . 1,4
.. .. .	1124 M.	. . . 1,2
.. .. .	1223 M.	. . . 7,5
.. .. .	1262 M.	. . . 0,3
.. .. .	1295 M.	. . . 0,8
.. .. .	1397 M.	. . . 0,3

These rocks may, therefore, be classed in general amongst those poor in radium, with the exception of n^o. 5. It will be interesting to ascertain whether from a geological point of view also this rock occupies a special place.

But in regard to the particular question asked I do not think a sharp conclusion can be made. Rocks found at depths below 1223 M. appear, as a rule, to contain less radium than those met with at smaller depths; but there, as well as at 850 M., we find a specimen with a content of 0,8. A plain connection, in the sense of a regular increase, or decrease of the radium content is not noticed. In order to resolve this question it will be necessary to investigate similar material from a great many other borings. JOLY has in fact, started this already; in his work Radioactivity and Geology (p. 60) we find the radium content of shales, from the BALFOUR-Bore in Fifeshire, found at depths between \pm 700 and 1000 M.; the quantity of radium met with varies from 3,5 to 4,1 and is fairly evenly distributed over the whole series. Only one exception occurs; at a depth of \pm 800 M. a carboniferous limestone is

found with the figure 10.9; so at a comparatively small depth we find a very high radium content. But at 40 M. lower and at 100 M. higher the figure 3.5 is observed. Another example is also mentioned by JOLY; recent coral-rock from the Funafuti Bore at depths of 225 M. to 300 M. also shows but small differences without a definite relation. I now call attention also to the fact, that in my investigation of limestones and marbles, I have found already that the figures for the radium content in the succeeding ancient deposits were absolutely irregular; consequently we may arrive at the provisional conclusion that there exists no relation between depth and radium content. In this direction the investigation of plutonic rocks is also a desideratum.

It will be noticed that the average figure in this series also comes to 1.6 or, if excepting no. 5, to 0.8. The order of magnitude, therefore, remains the same; if, however, we compare these figures with the average figure 4.3, given by JOLY as the mean of 46 sedimentary rocks, we are again struck by the remarkably high figure, always obtained by this investigator.

In conclusion I wish to express my hearty thanks to Mr. WATER-SHOOT VAN DER GRACHT for his friendly cooperation.

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Chemistry. — *“The configuration of benzene, the mechanism of the benzene substitution and on the contrast between the formation of para-ortho- and of metasubstitution products.”* By Prof. J. BÖESEKEN. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of February 24, 1912).

I. In consequence of the almost synonymous title of the communication of Dr. T. VAN DER LINDEN (Dec. 30, 1911) I wish to make a few observations in order to explain my stand-point in this matter.

1st. For this purpose it is desirable to explain the reasons which make me prefer the original ring of KÉKULÉ as symbol for benzene and all its derivatives to any other configuration, so long as one starts from the hypothesis of the four valencies of carbon of constant direction.

To begin with, all the representations in space, where the six carbon atoms are not supposed to be in one single plane, may be rejected because the optically active substitution products, then to be expected, have never, as yet, been noticed.

Of all symbols, only those call for discussion in which the hydrogen atoms are distributed quite symmetrically.

Of these, there are only two that take due account of all the properties of benzene; they are the well-known rings of KÉKULÉ and of ARMSTRONG-V. BAEYER.

The first is based entirely on the tetravalency of carbon; it is a consistent continuation of the symbols of all compounds which consist exclusively of carbon and hydrogen; it accounts for most of the properties of benzene and may be applied directly to all condensed systems.

It gives us, however, no satisfactory elucidation of the relative saturation of benzene and of the uncertainty as to the existence of possible isomers (such as two *ortho*-derivatives). ARMSTRONG has endeavoured to overcome these difficulties by proposing the centric formula. This has been accepted by VON BAEYER on account of the sharp difference between benzene and the true unsaturated *di*- and *tetra*-hydroderivatives.

It needs, however, no comment that with the introduction of the common bond of all carbon atoms towards the centre — in fact a new kind of bond — no explanation is given of the deviations met with in benzene; they are symbolised and there the matter rests.

An explanation can only be expected when apart from the ring-systems, one arrives at a casual relation between the stability of the benzene and of a definite grouping of six carbon and six hydrogen atoms.

A step in the right direction has been made by THIELE. If we divest THIELE'S work from hypothetical arguments, it remains firmly established that, in a conjugated system, the unsaturation is accumulated in the termini.

In the benzene ring, which is an endless conjugated system, such an accumulation is not to be expected; each carbon atom will therefore, possess quite as much, or as little, unsaturation and a strong decrease of the additive power might be caused thereby. Although we can well understand that the regularity of the distribution can make the same less pronounced, this view yet gives us no satisfaction because cyclobutadiene and cyclooctatetraene then ought to possess an unsaturated character quite as slight as that of benzene, which certainly is not the case with the first as it has never been obtained as yet, and as regards the latter, it has been proved quite recently by WILLSTÄTTER and WASER (B. 44 pg. 3423) that it behaves as a very unsaturated substance.

This renders it probable that the ring with alternate double and single bonds cannot explain satisfactorily the relative saturation of

benzene. In so far, I agree with WILLSTÄTTER and WASER (i.e.), not however, with their idea that the ring of KÉKULÉ ought to be replaced by that of v. BAEYER.

For as little as it is to be understood why, among the endless conjugated systems, the 6-ring only should occupy such a prominent place is it to be understood why only *this ring* and not all the other ring systems should possess centric bonds.

There is, however, another circumstance owing to which the ring of KÉKULÉ, as regards its stability in space, is distinguished favourably from all other unsaturated ring systems; it has the smallest ring tension.

For if we adhere consistently to the conception of the valencies of constant direction, the angle between the sides of the benzene hexangle amounts to $(360^\circ - 109^\circ 28') : 2 = 125^\circ 16'$. The ring tension according to von BAEYER is therefore $2^\circ 38'$, i. e. much smaller than that of the saturated 6-ring¹⁾.

Every other condition of the bond between the atoms situated in one plane, therefore also and in a very strong degree, the central one (for so far as it signifies an attraction between atoms, and it surely can mean nothing else) is more unfavourable.

In KÉKULÉ'S benzene ring there is, therefore, in each of the apexes but a slight ring tension while also in none of the apexes an excess of unsaturation is present. So long as the conception of the four valencies of constant direction is adhered to, this symbol is more capable than any other of accounting for the slightly pronounced unsaturation of benzene.

The second difficulty, that more derivatives are possible than have actually been found, is of less significance. In other cyclic and non cyclic substances one has so often been obliged to assume a very readily mutual shifting of double and single bonds with a simultaneous displacement of H-atoms that, in my opinion such shiftings in the benzene ring (where a displacement of atoms is not even necessary) may be accepted without any hesitation.

Of course, it speaks for itself that in accepting KÉKULÉ'S ring, it is not taken for granted that this represents the true condition of the molecule.

Our representation remains defective, but the cause of this is situated deeper; it roots in the unsatisfactory conception of the valencies of constant direction.

¹⁾ The tension caused eventually by the double bonds acts perpendicularly to the ring-plane and so does not influence the real ring tension.

II. **THEILE**, in order to arrive at an explanation of the unequal distribution of the unsaturation noticed by him in a conjugated system, has started the hypothesis that each doubly-linked atom possesses a certain residual-valency which remains free at the terminal carbon atoms, whereas these residues would neutralise each other in the middlemost atoms.

With this, **THEILE** abandoned the valency theory; this is shown strongly in the benzene ring proposed by him where each carbon atom obtains five valencies.

ARMSTRONG and **v. BAEYER** also abandoned the valency theory to some extent by introducing an entirely new kind of bond between all carbon atoms simultaneously.

Both efforts, from their very nature are undecisive, but they must be looked upon as an awakening as to the imperfection of the conception of the valencies of constant direction which threatens to strand on the properties of benzene.

I have come to the conclusion that indeed the ordinary theory of valency should be shelved, but this should be done in a consistent manner.

A. WERNER in his well-known treatise on the theory of affinity and valency (*Vierteljahrsschrift d. Zürich. naturf. Gesell.* 1891) was the first to conceive the fundamental idea of an affinity working in all directions (Universal). In his "Neuere Anschauungen" 2nd Ed. p. 81 he gives the following definition: "affinity is an attracting force working regularly from the centre of the atom towards the surface" and further "valency is an empirically obtained numerical relation, independent of valency units, in which the atoms combine with each other." It is a pity that these fairly sharp definitions lose somewhat of their significance by the introduction of the idea of the attracting surfaces (*Bindefläche*) in order to illustrate the amount of the affinity fixed.

The distinction into chief and auxiliary valencies, which must play an important rôle, particularly in the inorganic symbols, is also, in my opinion, a less fortunate one; it must cause arbitrariness and confusion.

But these are, comparatively, trifles; it must be admitted that the acceptance of the idea of the universal affinity has facilitated in a high degree the survey of the inorganic compounds, while it has given to the organic compounds a rational foundation.

The carbon atom can group four atoms around itself thus forming a tetrahedron.

When only three atoms are fixed by the carbon atom they will

place themselves with the carbon in one plane in such a manner that the carbon arrives in the centre and that the other atoms group themselves around it in as regularly a manner as possible.

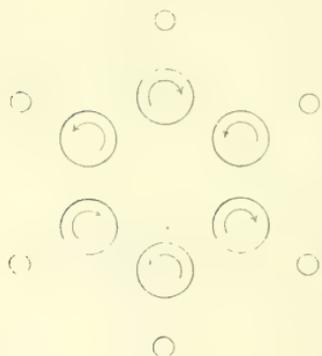
But in such a complex there remains a tendency to completion. (This has already been felt by WOLLASTON in 1808 for the case of all the combinations of a central atom with three others grouped around it).

If, for whatever reason, the total completion cannot be attained, a 6-ring, in which all lines between the centres of the cyclic atoms and the atoms directly combined thereto make the equilibrium angle of 120° , will amongst all conceivable constellations, be the most equilibrated condition in which six carbon and six hydrogen atoms can place themselves. With this representation all carbon atoms as regards their insaturation become quite equal as this is distributed evenly over the whole of the molecule.

I pointed out some time ago (Rec. 29, 86) that for the retention of two homonymous atoms such as, for instance, of two nitrogen atoms in the molecule N_2 , we must assume a certain inequality or contrast, as otherwise they would not attract each other so energetically.

As these atoms, however, must possess in regard to third ones a same difference of energy, this inequality must be of the same nature as that between two optic isomers.

We can imagine this inequality to be caused, for instance, by an adverse movement of the corpusculae.



If this idea is applied to the benzene ring this inequality might be symbolised with the annexed figure.

By means of this — and this is an important advantage over the ring of KÉKULÉ — not only the contrast between *ortho-para* and *meta* would be shown, but also the equality of the two *ortho*-placed carbon atoms. Each substituent will accentuate the contrast.

Hence, by a combination of the Werner fundamental principle of the universal affinity and my idea as to the contrasts — also between homonymous atoms — we arrive at a symbol which keeps account with all the properties of benzene and also with its relative saturation. For owing to the completely equilibrated position of the C and H atoms all tension is removed and owing

to the even number of carbon atoms the said contrasts may be in a condition of almost complete equilibrium¹⁾.

III. Let us now consider how we must conceive the benzene substitution. For the moment it does not matter much whether we choose the symbol of KÉKULÉ or the one proposed by me.

In any case we know for certain that it is a molecule in a condition of a relatively low chemical potential so that each change in the configuration or condition of bond must cause a rise in the potential. Now, the mixture of $C_6H_5Br + HBr$ will certainly lie again on a lower potential plane in regard to the mixture of $C_6H_6 + Br_2$ because the reaction in presence of a little powdered iron takes place with a considerable evolution of heat, but in order to arrive in that new condition, a resistance has, evidently, to be overcome, as this reaction takes place with extreme slowness without the presence of a third substance.

This resistance may be due to the bromine as well as to the benzene; here it is only rational to look for it in the benzene more in particular because all other unsaturated hydrocarbons of a similar simple construction are brominated very rapidly. If now we were dealing with an immediate exchange this resistance could not be expected to that extent (and this applies very generally to substitution reactions, see below). If, however, we accept an "addition", this behaviour then follows directly from the consideration that the stable equilibrium will then have been disturbed altogether. The regularity of the affinity distribution as well as that of the spacial distribution is destroyed.

It is, therefore, no matter of surprise that this condition of a much higher potential will be attained only by an extraordinarily small number of molecules and will not be permanent because this additive product may make room immediately for the mixtures of $C_6H_5Br + HBr$. Only the simultaneous attack on all unsaturated carbon atoms — formation of a hexabromide — leads to a condition whose potential can be smaller than that of the mixture of bromine and benzene.

In benzene hexabromide the molecule has reached an equilibrium comparable to that of benzene, owing to its condition of saturation and also to the largely (though not completely) equilibrated spacial distribution of its atoms.

Now this is what T. VAN DER LINDEN (l.c.) has noticed. On adding to benzene an insufficiency of halogen he obtained a product consist-

¹⁾ The predilection in nature for a compound with an even number of carbon atoms may perhaps be attributed to this same more complete saturation.

ing of hexahalogen benzene, anyhow it did not contain appreciable quantities of the above mentioned intermediate products.

It is also evident why, with the aid of a catalyst, the hexa-additive product did not show in the least a particular inclination to eliminate hydrogen as this *splitting off* reaction will be accompanied, particularly at the commencement, by a rise in the potential.

VAN DER LINDEN argues that the rôle of the catalyst will consist chiefly in this, that from eventually formed additive products such as $C_6H_6Br_2$, it will accelerate the elimination of the halogen hydrogen molecule, but to me this appears to be incorrect.

In my opinion its action will really consist in this that it promotes the entry of the bromine into the benzene in such a manner that, the simplest additive product is formed first; the elimination of the halogen hydrogen molecule from this first additive product in connected with so large a potential fall that the aid of a catalyst is not required here.

It speaks for itself that in the method employed by VAN DER LINDEN none of the additive products were met with.

From my above explanation it follows — and this has also been proved experimentally by VAN DER LINDEN — that *without a benzene catalyst* benzene itself will undergo substitution with extreme slowness. The chance of forming the first additive products is too small and the chance of retaining them will undoubtedly be less still as they may pass into a more stable condition in two directions ¹⁾. On the other hand there will be more chance of obtaining the said additive products of less completely equilibrated condensed systems in which the conversion of hydrocarbon into a dihydro-product means a less great disturbance in the said equilibrium.

Naphthalene, phenantrene, and anthracene give us at once the desired examples thereof and also the proof that catalysts are by no means necessary for the elimination of the halogen hydrogen molecule because this *splitting off* readily takes place without a catalyst.

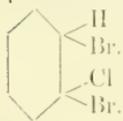
I, therefore, consider it probable in a high degree that in the formation of a monosubstitution product of benzene a temporary additive substance is formed.

The question, however, now arises: What will be the configuration of this ephemerie product?

If we accept the symbol of KÉKULÉ (or the one proposed by me)

¹⁾ When this exit is closed by the choice of the acting molecule the first additive product can be isolated. Indeed *o*- and *terephthalic acid* give, on reduction with sodium amalgam first of all the dihydro-products.

the product obtained by the bromination of chlorobenzene ought to possess the adjoined configuration ¹⁾.



VAN DER LINDEⁿ thinks that a configuration like this is excluded because in his opinion, in the bromination of chlorobenzene, the formation of *o*-dibromo- in presence of *o*-chlorobromobenzene has never been noticed, which

might yet have been expected because the elimination of hydrogen chloride from the above molecule is at least quite as probable as that of hydrogen bromide.

To this one might reply that there has never been made a serious search for the presence of these products. The otherwise so carefully conducted experiments described, for another purpose, by T. VAN DER LINDEⁿ in his dissertation (p. 71—90) admit the possibility of the presence of *traces* and cannot very well be accepted here because catalysts have been employed and these, as I will explain presently, are sure to modify the course of the reaction ²⁾.

So long as it has not been proved with positive certainty that with benzene as well as with the other condensed systems not a trace of dichloroderivative is formed when the monobromo-substitution product is chlorinated, the possibility of the above configuration may not be rejected ³⁾.

But even if this did not succeed I still believe I must adhere to an analogous configuration of the additive products even though the additive molecular parts therein must not be assumed to be wholly equivalent to the atoms or atomic groups already present in the benzene. I remind here of the conversion of maleic acid into fumaric acid with the assistance of HBr, in which case must also be assumed an influence of HBr on maleic acid without this leading to the formation of bromosuccinic acid.

In case only such influences or shifting products are present, we should almost be inclined to think that we may assume with equal right a direct substitution and to this conclusion VAN DER LINDEⁿ arrives at the end of his argument (l. c. p. 745).

Yet, as we explained above, this is not the same. The for-

¹⁾ HOLLEMAN and BÖESEKEN, Proc. 1909, p. 535.

²⁾ I found some time ago that ethyl bromide when heated with aluminium chloride causes the formation of ethyl chloride, whereas Mr. SIEGER has found in my laboratory that FeCl₃ reacts with ethyl bromide with formation of ethyl chloride, ferrous bromide and free bromine.

³⁾ An investigation in that direction has already given the result that *p*-dibromobenzene gives with chlorine without a catalyst, an elimination of very large quantities of bromine. The existence of a primary addition product, if not proved, has been, therefore, rendered very probable.

mation of shifting as well as of true additive products must be accompanied by a considerable rise in energy and will, therefore take place very slowly, if it takes place at all. The assumption of similar products fully explains the extreme slowness of the substitution reactions of benzene (and of all substitution reactions) if we take great care that no benzene catalyst is present.

IV. This naturally leads me to the question: In what does the action of catalysts consist? A catalyst can cause a modification in the condition of benzene as well as in that of the acting molecule.

When it exclusively renders active the last molecule, when we may think of a dislocation of this molecule, it becomes evident that the benzene still wholly equilibrated, will be attacked in its entirety and yield a hexa-additive product. From benzene and chlorine or bromine, under the influence of light or of hypohalogenic acid, will therefore be formed exclusively benzene hexachloride (bromide). The number of these cases will, however, be limited because some of the stronger catalysts also act on benzene.

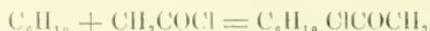
Substances such as AlCl_3 , FeCl_3 , SO_3 which so eminently promote the polymerisation and monomerisation of unsaturated compounds will undoubtedly exert on benzene a shifting action.

Let us imagine the catalyst entering somewhere into the benzene ring; the second molecule which can also have been made active will then be able to act there. No longer the entire ring but a single point thereof will be attacked owing to this change of equilibrium. As the catalyst can facilitate afterwards the elimination of molecules such as HCl , HBr , and H_2O , the formation of a monosubstitution product is to be expected.

The following will show that the action of the catalyst is based in the first place on a "shifting" in the benzene.

With Mr. SIEGER, I have studied the ethylation of chlorobenzene and noticed that under the influence of the mercuric-aluminium chloride couple¹⁾ ethylene is rapidly absorbed by chlorobenzene. The latter may also be obtained but not so rapidly by the action of ethyl chloride on chlorobenzene when hydrogen chloride is eliminated.

DARZENS (C. R. **150**, 707, **151**, 758) has found that with tetrahydrobenzene and acetyl chloride under the influence of AlCl_3 the reaction did not proceed further than to the hydrochloride of tetrahydroacetophenone



1) The intensifying action of this is based on the formation of mercurous-aluminium chloride which being soluble in chlorobenzene, increases the concentration of the catalyst. GULEWITZ B. **37**, 1560 (1904).

and that the unsaturated ketone could only be obtained by heating this hydrochloride with chinoline at 180° .

PRINS and I (Rec. **30**, 158) have found that although C_2Cl_4 can unite with chloroform to heptachloropropane, yet no perceptible elimination of hydrogen chloride takes place at the boiling point of chloroform. This starts very slowly at 80° and only becomes more considerable at 250° , a temperature at which the elimination is very perceptible even without the presence of $AlCl_3$. It will be noticed that all depends on the relative energies which take part in the reaction. If the elimination of the halogen hydrogen molecule is accompanied by a potential fall it will take place. Catalysts such as $AlCl_3$, etc. evidently do not promote this part of the reaction to any extent and this is easily comprehensible because in most cases a previous potential rise is not required here.

But with $C_6H_6Cl_6 \rightarrow C_6H_3Cl_2 + 3 HCl$ it may be assumed that this is the case¹⁾ because at the parting of the *first* molecule of HCl , the molecule passes into a condition of much less stability both as regards the unsaturation and the spacial distribution of the atoms.

From all this it follows that the catalyst starts with the rendering active of the benzene and that in consequence of the disturbance of the equilibrium caused by the catalyst, a monosubstitution product is to be expected.

The entering molecule is also rendered active. By a series of investigations I have endeavoured to prove that substances as $AlCl_3$, $FeCl_3$, etc. render the molecules active by a dislocation (which may lead to dissociation); for instance, I have been able to demonstrate that a substance like SO_2Cl_2 reacts as entire molecule and also as a mixture of its products of resolution.

In the case of heptachloropropane, I have noticed that the elimination of HCl etc. is, finally, also accelerated, as this, in presence of much $AlCl_3$, commences at 80° at which temperature the decomposition, without catalyst, is hardly perceptible. Under the influence of cuprous chloride this decomposition takes place, at 300° , undoubtedly somewhat more rapidly than without a catalyst.

Hence, the separation of the eventually formed first additive product of the benzene is sure to be more difficult in the presence of a catalyst than without one.

On the other hand there remains the possibility of isolating the products of conversion which are to be expected such as dichloro-

¹⁾ The observations of T. VAN DER LINDEN l. c. make it however more probable that $C_6H_3Cl_3 + 3HCl$ possesses more free energy than $C_6H_6Cl_6$. (Note in the English Ed. of these Proc. only.)

benzene, from bromobenzene and chlorine. They, however, cannot be of service to prove the existence of primary additive products, because the catalyst itself has taken part in the reaction.

The reactions which we have considered up to the present proceed, without a catalyst, either not at all or extremely slowly; some, however, are known that can take place very rapidly even without intentional addition of a third substance (or foreign energy); to these belong the "nitration" and to a certain degree the "sulphonation".

It must, however, be observed that the velocity is largely dependent on the concentration of the acid so that it increases in a much stronger degree than corresponds with the strength of the acid.

This can be explained in a very simple manner by assuming that in nitric acid and in sulphuric acid a catalyst is present; this will then be the anhydride N_2O_5 and the anhydride SO_3 of which we know for certain that they are present in small quantities and in the free state in the 100% acid. Here the catalyst and the substituting molecule are to a certain extent identical.

It is known indeed that fuming sulphuric acid is a considerably more active sulphonating agent than the ordinary 98% acid and, in the acetylation, I have been able to demonstrate that sulphuric acid may be put on one line with $AlCl_3$ and $FeCl_3$.

The dilution previous to, or during the reaction decreases first of all the concentration of these powerful catalysts. During the reaction this decrease will be extremely strong because the catalyst itself is, in the first place, fixed by the benzene and afterwards also by the water generated. This, of course, causes that the course of the nitration is very complicated and proceeds in the end much slower than at the beginning.

But in the nitration in presence of a large excess of sulphuric acid and nitric acid we can expect a more regular course of the reaction because the condition of the nitration mixture, and consequently the concentration of the catalyst, then remains practically unchanged.

Catalysts such as SO_3 , $AlCl_3$, N_2O_5 , $FeCl_3$ etc. may, therefore, be considered as substances which attack the benzene molecule in a definite place, thereby causing a disturbance of the equilibrium which renders possible the formation of labile addition compounds which may afterwards be converted into the much more stable monobenzene derivatives.

Naturally this does not explain the action of the catalyst. We do not understand why the condition of benzene should be modified by $AlCl_3$ and not by bromine alone. In order to solve this we cannot

restrict ourself to the study of the system benzene + catalyst, on one side, and of the mixture of catalyst + substituting molecule on the other side, but by an efficient combination of the phenomena observed in these two systems we must arrive at a satisfactory elucidation of the progressive change of the reaction.

Let us now consider the case where one of the H-atoms of benzene has been replaced. In the benzene there is now a disturbance of the equilibrium so that the unsaturation cannot any longer be equally distributed.

In the ring of KÉKULÉ (as explained previously by HOLLEMAN and myself) as well as in the ring proposed by me the carbon atoms in the ortho- and para-position must be distinguishable from those in the meta-position.

By HOLLEMAN and me (l. c.) it has been assumed that when the group entered renders the benzene more liable to attack we may then expect an addition to the double bond and the conjugated system, so that in the main para-ortho-substitution will take place.

In the reverse case, however, this addition will be retarded; an addition to the third double bond takes place which will cause the formation of meta (in presence of ortho)-derivative. VAN DER LINDEN thinks he must conclude from his experiments that chlorobenzene is attacked less rapidly while it is yet substituted ortho-para. Although I quite agree with HOLLEMAN (Verslag 30 Dec. 1911) that these experiments are not comparable because in the bromination of benzene a powerful catalyst, NaOBr, was present, but none in the case of chlorobenzene, I still feel convinced that the sulphonation, acetylation and benzylation of chlorobenzene proceed slower than those of benzene in otherwise comparable conditions. Yet, I do not agree with VAN DER LINDEN that the whole hypothesis as to the cause of the contrast between ortho-para and meta should now be rejected.

It wants a not principiant modification and a considerable extension by keeping account also with the nature of the entering molecule in regard to the substituents already present.

Two points have to be kept in view.

1st. Each group X in the nucleus causes, just like a catalyst a shifting of the equilibrium owing to which the benzene will as a rule be more readily attacked, and at the same time the contrast between ortho-para and meta is formed or accentuated.

2nd. In consequence of the nature of the acting molecule in regard to the substituent X already present the privilege accorded to the

ortho-para-positions (I) can be opposed, to finally make room for meta-substitution.

Explanation. According to this view there are at work two influences independently of each other; the first is the disturbance of the equilibrium caused by X which will be different from group to group but will always give preference to the carbon atoms in the ortho-para-position, just as a catalyst renders active the place where it has attacked the benzene molecule.

The second influence which can act in the same or in the opposite direction is determined by the affinity of the already present group X towards the entering molecule B.

Of this, we can discern three cases.

A. The affinity of the acting molecule B for X is very great. B will then act in the first place, on X, and be retained therein after which the action ceases.

For instance. The reduction of the nitro-group, oxidation of the SII-group, bromination, under definite conditions, of the alkyl group etc.

B. The affinity of the acting molecule B for X is less considerable so that, at most, labile additive products can be retained.

The group B will then further accentuate the disturbance of the equilibrium caused by X alone, and the molecule enters into the nucleus ortho-para.

For instance. Chlorination of sulphides, amides, bromides, iodides; hydrogenation of ortho- and terephthalic acid, oxidation, under the influence of potassium hydroxide, of nitro-compounds, mercuration of acids etc.

C. The affinity of the acting molecule B for X is not present.

X will then oppose the addition and substitution ortho-para so that the influence of the disturbance of the equilibrium can be lessened or destroyed by this adverse action so that the meta-substitution can become predominant.

For instance: Nitration, sulphonation, and chlorination of nitro-compounds, sulphonic acids and carboxylic acids, but also hydrogenation of amide and oxy-compounds.

Up to the present one has almost entirely overlooked the influence of the entering molecule and this is chiefly caused by the fact that among the acting molecules mainly those have been studied which are mutually of the same nature (H_2SO_4 , HNO_3 , Cl_2 , CH_3COCl etc.).

If, however, one considers the effect of other molecules such as mercuric compounds, hydrogen, potassium hydroxide, hydroxylamine etc. the substitution representation becomes quite different.

In the above survey, I have included all cases in a general scheme

from which it is seen that the reactivity of the substituted benzene is dependent on the substituent as well as on the acting molecule and that the type of the substitution will depend on this mutual and common influence.

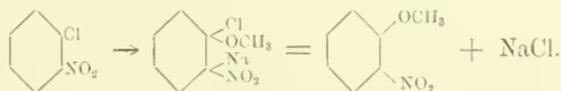
I will illustrate this with a few very striking examples.

I. The nitro-group in nitrobenzene renders the molecule much less accessible for nitric acid, sulphuric acid, chlorine, bromine etc. and in agreement therewith we obtain with the last mentioned molecules a meta-substitution.

Nitrobenzene, however, is very strongly attacked by potassium hydroxide and, as was to be expected, we obtain orthonitrophenol. *s*-Trinitrophenol is very readily oxidised in alkaline solution.

The nitro-group does not render the benzene molecule absolutely unattackable. As soon as it is acted upon by molecules that possess some affinity to the nitro-group, the ortho-positions become accessible. Quite in harmony herewith is the behaviour of substances such as *o*-chloronitrobenzene and particularly of picrylchloride. The chlorine atoms present therein are not *as a rule* readily substituted but are replaced by molecules such as H_2 , $NaOCH_3$, KOH , $NH_2C_6H_5$ etc. etc. which are driven by the nitro-group in the ortho-para-direction.

The objection raised by VAN DER LINDEN (i.e. p. 741) to this substitution in connection with our theory is therewith quite neutralized and at the same time these substitutions are the cases which he has searched for and which we can formulate as follows:



II. The COOH -group directs nitric acid, sulphuric acid, the halogen molecule towards the meta-position; the nitration, sulphonation, and halogenation proceed again much slower than of benzene and toluene.

But we may not characterise the influence of the carboxyl group as a generally retarding one. Benzoic acid and, in a still higher degree, the phthalic acids are more readily reduced than benzene and aniline; in regard to hydrogen, aniline is therefore more firm than benzoic acid.

In agreement with my explanation, VON BAEYER (Ann. **251**, 264 and **269**, 192) found that the carbon atoms at which the carboxyl groups are situated, i. e. 1.2 or 1.4 gave the expected additive product. Orthophthalic acid gives primary Δ 3.5 dihydro 1.2 dicarboxylic acid.

This again is a case which VAN DER LINDEN has searched for, namely of the isolation of the primary additive products.

The separation could of course, be expected sooner than in the case of a dibromo or dichloro additive product because there exists here no other exit towards the stable benzene derivative, except either by the loss of the hydrogen absorbed or of the entire carboxyl group.

I call attention to the fact that from BAEYER's research (l.c.) it follows that there exists indeed a certain affinity of the hydrogen for the carboxyl groups, as beside the hydro-acids other products are also formed, such as phthalide at which the side chain has been attacked.

III. A very illustrative case is the hydrogenation of α -naphthylamine. The amido group is considered to be the one that renders the benzene molecule extremely accessible; this also is caused by the affinity of this group for the great majority of the entering molecules.

In harmony therewith, it directs almost exclusively towards ortho-para.

This, however, may not be generalised. In regard to the hydrogen molecule it behaves differently. Aniline is not at all readily reduced and the resistance is evidently of such a nature that in a binucleated system such as naphthalene, the unsubstituted nucleus is more readily reduced than the substituted one. As α -nitronaphthalene directs the second nitro-group towards the other nucleus, α -naphthylamine directs the hydrogen to the same.

Just by overlooking the influence of the acting molecule, these cases were considered as exceptions and it was endeavoured to find an explanation in the indirect substitution described by BLANKSMA (Rec. **21**, 281 and **23**, 202).

This means to say that the acting molecule first enters the side chain then to pass into the nucleus. On studying more carefully the cases wherein a similar course of the reaction has been noticed, such as in the chlorination of acetanilide, one was able to prove (J. C. S. **95**, 1456) that the chlorine atom only then enters the nucleus quite as rapidly as in the direct chlorination, when a substance like HCl is present which again liberates the chlorine atom. The formation of chloroacetanilide can, therefore, by itself, never explain the ortho-para substitution. We must, however, attribute that formation, like the ortho-para substitution, to a same cause, namely to the influence of the group NHCOCH_3 on the chlorine molecule.

When this side chain substitution gives rise to the formation of a relatively very stable compound such as $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, this will at once be noticed and HOLLEMAN has quite rightly pointed out that the formation of these products cannot explain the ortho-para substitution in the nucleus.

As has been observed, this explanation lies in what happens before that substitution, viz. in the influence of the acting molecule on the group X.

The cases of true, indirect substitution, in which this linking or decomposition product is changed into the nucleus substitution product, such as, for instance, in the halogenation of acetanilide or of diphenyl sulphide (Rec. **29**, 315), the chlorination of iodobenzene etc. ought hence to be classed under heading A as well as B. In a certain sense they are placed between the two.

The acting molecule has so much affinity to the group X that it can either unite (or react) with it, or else enter the nucleus.

Benzene catalysts will, in such cases, lead the acting molecule undoubtedly to the nucleus, whereas the substances or energies which render the entering molecule active will facilitate the chain substitution.

The bromination of toluene gives us a very good instance thereof; under the influence of catalysts as FeCl_2 , AlCl_3 etc. the action of the group X on the nucleus is strengthened and ortho-para substitution occurs; on the other hand, light and heat promote the chain substitution.

The nitration of toluene also comes under the same point of view. When we dilute the acid to such an extent that not a trace of N_2O_5 can be present, then, and particularly at a high temperature, the chain substitution will gain over the nucleus substitution and phenylnitromethane or benzoic acid will form.

The indirect substitution as suggested by BLANKSMA is therefore not directly related to the nucleus substitution. But still we may say, that the same cause which originates this indirect substitution, namely the affinity of the group X for the acting molecule, promotes the para-ortho substitution.

It appears to me that this contemplation, which is nearly entirely based on a single assumption, namely of the shifting of the equilibrium caused by a molecule or part of a molecule which finds itself in a more or less solid combination with the nucleus of the benzene, and which keeps account with the influence of this group on the acting molecule, has placed the question of the substitution on a rational foundation.

Delft, 18 February 1912.

Anatomy. — “*The red nucleus in Reptiles*”. By Dr. S. J. DE LANGE.
(Communicated by Prof. C. WINKLER).

When studying the midbrain of Reptiles I was struck, first in *Lacerta agilis*, by big multipolar cells, which I found in the region of the most frontal oculomotor roots and which had much resemblance with the multipolar cells of the red nucleus such as are known in mammals.

With this aim in view, it was not difficult to state the same group of cells in other reptiles.

The group of cells, determined in this way, was localized almost in the same region, which VON MONAKOW¹⁾ and HATSCHKEK²⁾ have given for the magnocellular part of the nucleus ruber, only with this difference, that the fibres of the oculomotor roots do not run through the nucleus as we see it in mammals. Consequently there is a little dislocation of the whole nucleus in a lateral direction, which can find an interpretation by the fact, that in mammals the second part is situated laterally from the magnocellular part and therefore the former part is displaced in higher vertebrates to a medial position.

In the *Varanus Salvator* it seemed as if there were also a parvocellular part of the red nucleus, situated lateroventrally from the magnocellular part and extending towards the front. On more exact examination the above mentioned interpretation appeared not to be the correct one, for it was very improbable, that in the lower vertebrates we should find some parvocellular group of the red nucleus, this group being one of the connexions of the neocortex with the lower parts of the central nervous system and reptiles having no neocortex. It is rather to be granted, that the conclusion of HATSCHKEK is true when he says, that both parts of the red nucleus in mammals show us variations relative to the higher or lower place in the system, occupied by the animal we have to examine. He has stated, that the magnocellular part is diminishing in higher mammals and that in man we can find back but a rudiment of this magnocellular part. This rudiment is situated near the oculomotor nucleus and among the rootfibres. In man the magnocellular part, in which the tractus rubro-spinalis originates, is localised in a more caudal region than the part we are accustomed to call in man the nucleus ruber and which is composed exclusively of small cells. Therefore the highest mammal

¹⁾ C. VON MONAKOW. Der rote Kern, die Haube und die Regio subthalamica bei einigen Säugetieren und beim Menschen. Arb. a. d. Hirnanat. Inst. in Zürich 1910.

²⁾ R. HATSCHKEK. Zur vergleichenden Anatomie der Nucleus ruber tegmenti. Festschrift z. Feier. d. 25 j. Best. d. Neurol. Institut an der Wiener Universität 1907.

has a great development of the parvocellular part of the red nucleus and only a rudiment of the magnocellular part. This is the reason of the fact that the tractus rubro-spinalis in man is also rudimental. Moreover we find in the localisation of both parts the reason, that tumors in the nucleus ruber in man but seldom cause degeneration of the rubro-spinal tract, unless the tumor has a caudal extension by which the rest of the magnocellular part is destroyed.

Descending in the series of mammals we see the parvocellular part diminishing, the magnocellular part growing on the contrary. With good reason v. MOXAKOW calls the parvocellular part "the cortical part" of the red nucleus. He means that this part by its connexion with the neocortex is changing in size relatively to the extension of the neocortex, hence it is diminishing in the lower vertebrates with smaller evolution of the neocortex.



Fig. 1.
Section of the midbrain of *Lacerta agilis*.

In reptiles the cortex cerebri having hardly any but genuine olfactory qualities (it may be that we can suppose in some of the highest reptiles an indication of a neocortex in the thalamo-striato-cortical tract) we might expect only the pars magnocellularis of the red nucleus to be developed.

Subjoined I have collected some sketches of the principal representatives of reptiles. In all of them the bigness of the cells and their



Fig. 2.

Section of the midbrain of *Varanus Salvator*.

characteristic multipolar form are clear. It makes an impression as if scattered reticular cells as they are found everywhere in the reticulum (See VAN HOEVELL's article)¹⁾ have concentrated in one place by a biological stimulus and in this way have formed a nucleus.

By the wealth distinctly of fibres in this region it was impossible forme to see which fibres descend from the nucleus caudally; therefore I have no right to speak of a tractus rubro-spinalis. Perhaps (and I am sure it will be as I think) it will be possible

¹⁾ J. J. L. A. BARON VAN HOEVELL. Remarks on the reticular cells of the oblongata in different vertebrates. Kon. Acad. v. Wetenschappen 1911.

to show us this tract also in reptiles by experimental degenerations.

In fig. 1 I have sketched the nucleus ruber of *Lacerta agilis*, such as we find it in rather a great series of sections coloured after the method of Nissl. The section is taken from the middle part of the midbrain, there, where the tectum opticum shows its greatest development. It shows the frontal beginning of the oculomotor nucleus. So we have here the frontal pole of the red nucleus.

I give also the nucleus at its greatest development, somewhat more caudally (fig. 2). Here the oculomotor nucleus is distinctly divided in its three parts and laterally from the place, where the root fibres are going out of the central trunk we find a great deal of big multipolar cells, being of the same type as those we have seen in



Fig. 3.
Nucleus ruber in *Boa constrictor*.

Lacerta. It is clear, that here the nucleus is situated more ventrally than in *Lacerta*, but partly we have to seek the reason of this localisation in the fact, that this section is a more caudal one. This

very distinct preparation is coloured with an infusion of elderberries according to a method, which soon will be described by C. U. ARIENS KAPPERS.

Figure 3 shows the nucleus in *Boa constrictor*. The section is coloured after the method of VAN GIESON. There are much fewer cells than in the former species of animals, but the form of the cells and their localisation just near the oculomotor root fibres make the identification with the former groups of cells undoubtful.

Much clearer is the situation in the Alligator sklerops (fig. 4). The Central Institute of Brain research has a very beautiful series in



Fig. 4.

Nucleus ruber in Alligator sklerops.

two colours (VAN GIESON and WEIGERT-PAL). The localisation of the distinctly circumscribed group of cells near the roots of the nervus oculomotorius makes the diagnosis very easy.

Also in the lower reptiles we can find back without difficulty the group of cells. In fig. 5 I sketched the situation in *Testudo graeca*. Here also we find the oculimotor nucleus in the section and we see



Fig. 5.

Nucleus ruber in *Testudo graeca*.

several big multipolar cells, united to a distinct nucleus. The preparation is coloured with cresylviolet.

To my knowledge the red nucleus has never been described in reptiles yet. By the annexed figures I think I have demonstrated with sufficient certitude the existence of the magnocellular part of the nucleus ruber in reptiles.

But it is not only in reptiles that I found the red nucleus, also in amphibians it is possible to see a distinctly circumscribed nucleus, localized absolutely in the same way, so in the region of the root-fibres of the oculimotor nerve. It is again the same reticular elements which have concentrated to a nucleus. In fig. 6 I give a section of the brain of *Rana*, showing very clearly the group of cells. Two sections more caudally we find the frontal pole of the oculimotor nucleus, whilst the oculimotor roots are going out of the central trunk, as we can see in the control-section, which is coloured after

the method of WEIGERT-PAL. In this section, only the cells are coloured and therefore the rootfibres are invisible.

When for the identification we use the scheme of TRETJAKOFF ¹⁾ such as he made it for *Ammocoetes*, we see, that he mentioned a

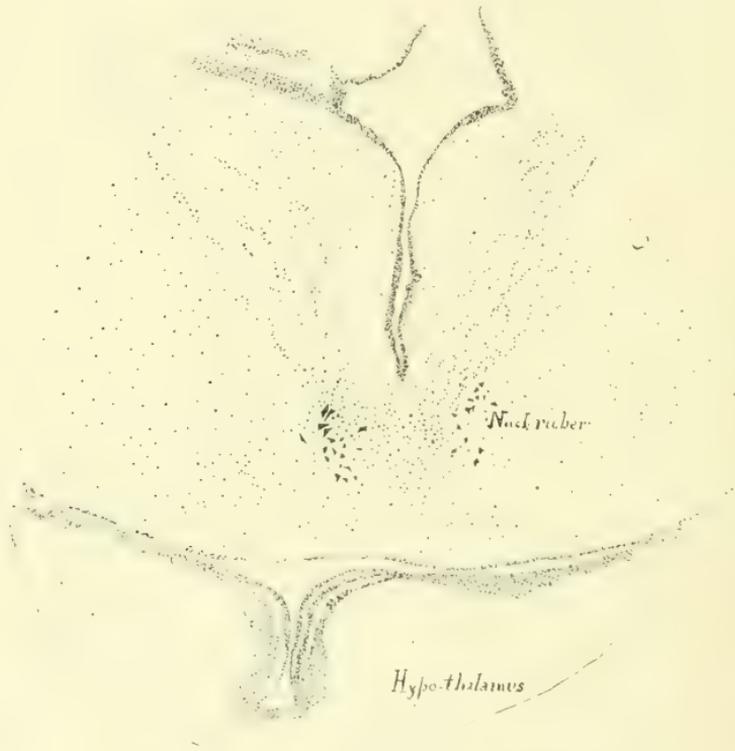


Fig. 6.
Nucleus ruber of *Rana*.

mesencephalic group of reticular cells, except the more caudal groups of reticular elements which all have been reformed by VAN HOEVELL²⁾.

In this lowest vertebrate the group consists of few very big multipolar cells, which we may consider as the prototypes of the magnocellular part of the nucleus ruber and which we can find back in all fishes. The cells are always localized in the region of the oculi-

¹⁾ D. TRETJAKOFF. Das Nervensystem von *Ammocoetes*. II. Gehirn. Arch. f. micr. Anat. und. Entwicklungsges.

²⁾ Loc. cit.

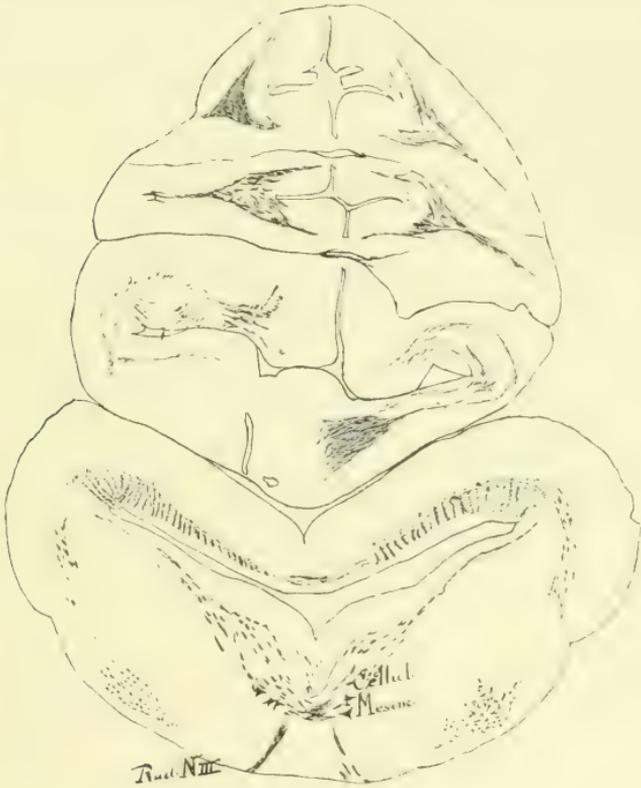


Fig. 7.
Section of the mesencephalon of Selachie.



Fig. 8.
Nucleus ruber in Ciconia alba.

motor rootfibres. As a specimen I give here a sketch of Selache (fig. 7) where on both sides we find two big multipolar cells.

To show the situation in birds and the transition to the lower mammals I add two figures.

1st a bird, 2nd one of the lower mammals.

I chose the *Ciconia alba*, having a very fine series of this bird (fig. 8), but it is very easy to find back the red nucleus in all other birds. I saw it in *Columbus*, in *Casuaris*, in *Spheniscus*.

At last the form as it is to be seen in the opossum (*Didelphys marsupialis*) (fig. 9).

I am of opinion that in all these cases the identification is so easy and so simple, that all confusion on this point is excluded.



Fig. 9.

Nucleus ruber in *Didelphys marsupialis*.

Physics. — “On the value of some differential quotients in the critical point, in connection with the coexisting phases in the neighbourhood of that point and with the form of the equation of state.” By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

1. In some previous papers we showed that the densities d_1 and d_2 resp. of the liquid and vapour phase in the immediate neighbourhood of the critical point are represented by the expressions ¹⁾:

$$\begin{aligned} d_1 &= 1 + \alpha \sqrt{1-m} + \beta(1-m) + \gamma(1-m)^{3/2} + \delta(1-m)^2 + \dots \\ d_2 &= 1 - \alpha \sqrt{1-m} + \beta(1-m) - \gamma(1-m)^{3/2} + \delta(1-m)^2 - \dots \end{aligned} \quad (1)$$

so that for values of $m = T : T_k$ near 1 the quantities $d_1 - 1$ and $1 - d_2$ are of the order of magnitude $\sqrt{1-m}$, and *not* of the order $\sqrt[3]{1-m}$ (VAN DER WAALS, These Proc. XIII, p. 116 and 1259) or of $\sqrt[4]{1-m}$ (GOLDHAMMER, Z. f. phys. Chem. 71, 577 (1910)).

In his “Thermodynamische Theorie der Capillariteit” (1893) VAN DER WAALS also gives the correct expressions (see p. 44), and finds the value 2 for α with the ideal equation of state, and the value 3,5 for real (normal) substances — quite in accordance with what we found for them (loc.cit., cf. These Proc. XIV, p. 437) where the value 3,6 is given. For Fluorbenzene α may even be put 3,9 see further. Also MATHIAS (Ann. de Toulouse V) gave as *empirical* formulae the theoretically correct ones.

For substances for which the ideal equation of state would hold, we find loc. cit.

$$\alpha = 2; \quad \beta = \frac{2}{5}; \quad \gamma = \frac{13}{25}; \quad \delta = \frac{128}{875}; \quad \epsilon = \frac{1359}{17500}.$$

The coefficient α indicates the *divergence* of the phases in the critical point; the coefficient β is nothing but the coefficient of direction of the so-called straight diameter $\frac{1}{2}(d_1 + d_2) = f(m)$ in that same point.

When we pass from the ideal equation of state to the real one, β increases from 0,4 to about 0,9, whereas α increases from 2 to about 3,9.

2. We shall now demonstrate that the expressions (1) will hold for any form of the possible equation of state, and that $d_1 - 1$ and $1 - d_2$ would only be of the order $\sqrt{1-m}$, when in the critical point not

1) See among others These Proc. XIV, p. 438 et seq., 563 et seq. and 574.

only $\frac{dp}{dv}$ and $\frac{d^2p}{dv^2}$ are equal to 0, but also $\frac{d^3p}{dv^3}$ and $\frac{d^4p}{dv^4}$. And as the latter is evidently an impossibility (for then there would be *relations* between the coefficients of the equation of state), $d_1 - 1$ can never be of the order of magnitude $\sqrt[3]{1-m}$ either. Other exponents, like $\sqrt[3]{1-m}$, are of course quite excluded.

For if we put quite generally

$$p = f(v, T),$$

we have, when ε , n , and m represent resp. "reduced" pressure, volume and temperature, in the neighbourhood of the critical point:

$$\begin{aligned} \varepsilon = 1 + & \left[\varepsilon'_{v'}(n-1) + \varepsilon'_{t'}(m-1) \right] + \left[\frac{1}{2} \varepsilon''_{v^2}(n-1)^2 + \varepsilon''_{v,t}(n-1)(m-1) + \right. \\ & \left. + \frac{1}{2} \varepsilon''_{t^2}(m-1)^2 \right] + \left[\frac{1}{6} \varepsilon'''_{v^3}(n-1)^3 + \text{etc.} \right] + \text{etc.} \end{aligned}$$

In this $\varepsilon'_{v'}$ represents $\left(\frac{\partial \varepsilon}{\partial n} \right)_{kr}$; $\varepsilon'_{t'}$ represents $\left(\frac{\partial \varepsilon}{\partial m} \right)_{kr}$; ε''_{v^2} represents $\left(\frac{\partial^2 \varepsilon}{\partial n^2} \right)_{kr}$; etc.

The determination of the coefficient a will require no other differential quotients than the above mentioned ones. In this $\varepsilon'_{v'}$ and ε''_{v^2} are both = 0 at the critical point, so that by equation of the values of ε in the two coexisting phases

$$\varepsilon'_{v,t}(m-1) \left[(n_2 - 1) - (n_1 - 1) \right] + \frac{1}{6} \varepsilon'''_{v^3} \left[(n_2 - 1)^3 - (n_1 - 1)^3 \right] + \dots = 0$$

remains, because also the terms with only $m-1$ and $(m-1)^2$ vanish in consequence of the equality of the temperature.

If we now put:

$$n_2 = 1 + \alpha\tau + \beta^3\tau^3 + \dots; \quad n_1 = 1 - \alpha\tau + \beta^3\tau^3 + \dots$$

in which τ represents a power of $1-m$ as yet unknown, we get

$n_2 - 1 = \alpha\tau + \beta^3\tau^3 \dots = \theta_2$; $n_1 - 1 = -(\alpha\tau - \beta^3\tau^3 \dots) = -\theta_1$, and hence:

$$\varepsilon''_{v,t}(m-1)(\theta_2 + \theta_1) + \frac{1}{6} \varepsilon'''_{v^3}(\theta_2^3 + \theta_1^3) + \dots = 0,$$

or

$$\varepsilon''_{v,t}(1-m) \frac{\theta_2^3 + \theta_1^3}{\theta_2 + \theta_1} + \dots$$

Now evidently (the higher powers we shall want presently):

$$\begin{aligned} \theta_2 + \theta_1 &= 2\alpha\tau \dots; & \theta_2^3 - \theta_1^3 &= 4\alpha^3\beta^3\tau^3 \dots; & \theta_2^3 + \theta_1^3 &= 2\alpha^3\tau^3 \dots \\ \theta_2^3 - \theta_1^3 &= 6\alpha^2\beta^3\tau^4 \dots; & \theta_2^5 - \theta_1^5 &= 8\alpha^3\beta^3\tau^5 \dots; & \theta_2^5 + \theta_1^5 &= 2\alpha^5\tau^5 \dots \end{aligned}$$

so that

$$\frac{\theta^3_2 + \theta^3_1}{\theta_2 + \theta_1} = a^2 \tau^2 \dots$$

Hence we get:

$$\varepsilon''_{v,t}(1-m) = \frac{1}{6} \varepsilon'''_{v^3} (a^2 \tau^2 \dots) + \dots \dots \dots (\alpha)$$

so that it now appears with the utmost clearness that τ^2 must be of the order $1-m$, and so τ of the order $\sqrt[4]{1-m}$.

Even if n_2 were $= 1 + a \tau \dots$, $n_1 = 1 - a' \tau \dots$, in which a' is *not* $= a$ (which, however, is impossible: see also These Proc. XIV, p. 439 and 440), even then τ would appear to be of the order $\sqrt[4]{1-m}$ according to the above. For then $\theta_2 + \theta_1$ would be $= (a + a') \tau \dots$, $\theta^3_2 + \theta^3_1 = (a^3 + a'^3) \tau^3 \dots$, and hence $\frac{\theta^3_2 + \theta^3_1}{\theta_2 + \theta_1} = (a^2 - aa' + a'^2) \tau^2$, so that the conclusion would remain the same.

Only when also ε'''_{v^3} , i. e. $\left(\frac{\partial^3 \varepsilon}{\partial n^3}\right)_{t,v}$ were $= 0$ — but then ε'''_{v^4} would also have to be $= 0$ on account of the form of the critical isotherm (which of course runs from $p = \infty$ to $p = 0$) — only then we should have:

$$\begin{aligned} & \varepsilon''_{v,t}(m-1)(\theta_2 + \theta_1) + \frac{1}{6} \left[3\varepsilon'''_{v^2,t}(m-1)(\theta^2_2 - \theta^2_1) + \dots \right] + \\ & + \frac{1}{24} \left[4\varepsilon'''_{v^3,t}(m-1)(\theta^3_2 + \theta^3_1) + \dots \right] + \frac{1}{120} \varepsilon^V_{v^5}(\theta^5_2 + \theta^5_1) + \text{etc.} = 0. \end{aligned}$$

But from this would follow:

$$(m-1) \left[\varepsilon''_{v,t} \cdot 2a\tau \dots \right] + \dots + \frac{1}{120} \varepsilon^V_{v^5}(2a^5 \tau^5 \dots) + \dots = 0,$$

and so $1-m$ would be of the order τ^4 , i. e. τ of the order $\sqrt[4]{1-m}$. So for this the (impossible) supposition ε'''_{v^3} and $\varepsilon'''_{v^4} = 0$ would be required¹⁾.

3. Let us proceed after these considerations to the expressions for the coefficients α and β' .

As now henceforth τ^2 can be replaced by $1-m$, (α) passes into

$$\varepsilon''_{v,t} = \frac{1}{6} \varepsilon'''_{v^3} \alpha^2,$$

after equation of the coefficients of the different powers of $1-m$:

¹⁾ If only $\varepsilon'''_{v^3} = 0$, we should have got $\frac{1}{24} \varepsilon'''_{v^4}(\xi^4_2 - \xi^4_1)$ instead of $\frac{1}{120} \varepsilon^V_{v^5}(2\xi^5_2 \tau^5 \dots)$, hence as $\xi^4_2 - \xi^4_1 = 8\alpha^3 \beta'^5$, $1-m$ is again of the order τ^4 .

from which follows:

$$\alpha^2 = \frac{6\varepsilon' \varepsilon_{v,t}}{\varepsilon'''_{v^3}} \dots \dots \dots (1)$$

being the quite general formula for the coefficient α , whatever may be the form of the equation of state $\varepsilon = f(m, n)$ ¹⁾.

What follows may serve as a control. The ideal equation of state

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \quad \text{or} \quad \varepsilon = \frac{8m}{3n-1} - \frac{3}{n^2}$$

gives for the different differentialquotients:

$$\begin{aligned} \frac{\partial \varepsilon}{\partial n} &= -\frac{24m}{(3n-1)^2} + \frac{6}{n^3} \quad \left| \quad \frac{\partial^2 \varepsilon}{\partial n^2} = \frac{144m}{(3n-1)^3} - \frac{18}{n^4} \quad \right| \quad \frac{\partial^3 \varepsilon}{\partial n^3} = -\frac{9 \times 144m}{(3n-1)^4} + \frac{72}{n^5} \\ \frac{\partial^4 \varepsilon}{\partial n^4} &= \frac{9 \times 12 \times 144m}{(3n-1)^4} - \frac{360}{n^5} \quad \left| \quad \frac{\partial^2 \varepsilon}{\partial n^2 \partial m} = -\frac{24}{(3n-1)^2} \quad \right| \quad \frac{\partial^3 \varepsilon}{\partial n^2 \partial m} = \frac{144}{(3n-1)^3} \end{aligned}$$

So this becomes for T_k :

$$\begin{aligned} \varepsilon'_{\varepsilon} &= -6 + 6 = 0, \quad \varepsilon''_{\varepsilon^2} = 18 - 18 = 0, \quad \varepsilon'''_{\varepsilon^3} = -81 + 72 = -9 \\ \varepsilon'''_{\varepsilon^3} &= 486 - 360 = 126 \quad \left| \quad \varepsilon''_{\varepsilon^2, t} = -6 \quad \right| \quad \varepsilon'''_{\varepsilon^2, t} = 18. \end{aligned}$$

Thus we find for α^2 according to (1):

$$\alpha^2 = \frac{6 \times -6}{-9} = 4.$$

hence $\alpha = 2$, as it should be.

If in (α) we also take the terms with τ^4 into account, we get an equation between the coefficients α , β' , and γ' . So we cannot determine β' from this. For this we shall have to find the relation of coexistence between the two phases. This is found from (ε_c denotes the pressure of coexistence)

$$\varepsilon_c = \frac{1}{n_2 - n_1} \int_{n_1}^{n_2} \varepsilon \cdot d(n-1).$$

With

$$\begin{aligned} \varepsilon = 1 + \varepsilon'_t(m-1) + \left[\varepsilon''_{\varepsilon^2, t}(n-1)(m-1) + \frac{1}{2} \varepsilon''_{\varepsilon^2}(m-1)^2 \right] + \\ + \left[\frac{1}{6} \varepsilon'''_{\varepsilon^3}(n-1)^3 + \frac{1}{2} \varepsilon'''_{\varepsilon^2, t}(n-1)^2(m-1) + \frac{1}{2} \varepsilon'''_{\varepsilon^2, t^2}(n-1)(m-1)^2 + \right. \\ \left. + \frac{1}{6} \varepsilon'''_{\varepsilon^3}(m-1)^3 \right] + \frac{1}{24} \varepsilon'''_{\varepsilon^4}(n-1)^4 + \dots \end{aligned} \quad (a)$$

this becomes:

¹⁾ Cf. v. D. WAALS, Capillariteit, p. 44.

$$\begin{aligned} \varepsilon_c = 1 + \varepsilon'_t(m-1) + \left[\frac{1}{2} \varepsilon''_{v,t} \frac{\theta_2^2 - \theta_1^2}{\theta_2 + \theta_1} (m-1) + \frac{1}{2} \varepsilon''_{t^2} (m-1)^2 \right] + \\ + \left[\frac{1}{24} \varepsilon'''_{v,t} \frac{\theta_2^3 - \theta_1^3}{\theta_2 + \theta_1} - \frac{1}{6} \varepsilon'''_{v,t} \frac{\theta_2^2 + \theta_1^2}{\theta_2 + \theta_1} (m-1) - \frac{1}{4} \varepsilon'''_{v,t^2} \frac{\theta_2 - \theta_1}{\theta_2 + \theta_1} (m-1)^2 + \dots \right. \\ \left. + \frac{1}{6} \varepsilon'''_{t^3} (m-1)^3 \right] + \frac{1}{120} \varepsilon''''_{v^4} \frac{\theta_2^5 + \theta_1^5}{\theta_2 + \theta_1} + \dots \end{aligned}$$

as $(n_2-1) - (n_1-1) = \theta_2 + \theta_1$, $(n_2-1)^2 - (n_1-1)^2 = \theta_2^2 - \theta_1^2$, etc. (see above).

If in (a) we substitute successively n_2 and n_1 for n , and then take half the sum, we get:

$$\begin{aligned} \varepsilon = 1 + \varepsilon'_t(m-1) + \left[\varepsilon''_{v,t} \frac{\theta_2 - \theta_1}{2} (m-1) + \frac{1}{2} \varepsilon''_{t^2} (m-1)^2 \right] + \\ + \left[\frac{1}{6} \varepsilon'''_{v^3} \frac{\theta_2^3 - \theta_1^3}{2} + \frac{1}{2} \varepsilon'''_{v^2,t} \frac{\theta_2^2 + \theta_1^2}{2} (m-1) + \frac{1}{2} \varepsilon'''_{v,t^2} \frac{\theta_2 - \theta_1}{2} (m-1)^2 + \dots \right. \\ \left. + \frac{1}{6} \varepsilon'''_{v^3} (m-1)^3 \right] + \frac{1}{24} \varepsilon''''_{v^4} \frac{\theta_2^4 + \theta_1^4}{2} + \dots \end{aligned} \quad (a')$$

Equation of (b) and (a') now yields with $1 - m = -(m-1) =: \tau^2$:

$$\begin{aligned} - \varepsilon''_{v,t} \left[\frac{1}{2} \frac{\theta_2^2 - \theta_1^2}{\theta_2 + \theta_1} - \frac{\theta_2 - \theta_1}{2} \right] + \frac{1}{6} \varepsilon'''_{v^3} \left[\frac{1}{4} \frac{\theta_2^3 - \theta_1^3}{\theta_2 + \theta_1} - \frac{\theta_2^2 + \theta_1^2}{2} \right] - \\ - \frac{1}{2} \varepsilon'''_{v,t^2} \tau^2 \left[\frac{1}{3} \frac{\theta_2^3 + \theta_1^3}{\theta_2 + \theta_1} - \frac{\theta_2^2 + \theta_1^2}{2} \right] + \frac{1}{2} \varepsilon'''_{v,t^2} \tau^4 \left[\frac{1}{2} \frac{\theta_2^2 - \theta_1^2}{\theta_2 + \theta_1} - \frac{\theta_2 - \theta_1}{2} \right] + \\ + \frac{1}{24} \varepsilon''''_{v^4} \left[\frac{1}{5} \frac{\theta_2^5 + \theta_1^5}{\theta_2 + \theta_1} - \frac{\theta_2^4 + \theta_1^4}{2} \right] + \dots = 0. \end{aligned}$$

With the values of $\theta_2 + \theta_1$, $\theta_2^2 - \theta_1^2$, etc. given above in § 2 this becomes (the coefficients of $\varepsilon''_{v,t}$ and ε'''_{v,t^2} are evidently = 0):

$$\begin{aligned} \frac{1}{6} \varepsilon'''_{v^3} \left[\alpha^2 \beta^3 \tau^4 - 3 \alpha^2 \beta \tau^4 \dots \right] - \frac{1}{2} \varepsilon'''_{v,t^2} \tau^2 \left[\frac{1}{3} \alpha^2 \tau^2 - \alpha^2 \tau^2 \right] ; \\ + \frac{1}{24} \varepsilon''''_{v^4} \left[\frac{1}{5} \alpha^4 \tau^4 - \alpha^4 \tau^4 \right] = 0, \end{aligned}$$

because evidently $(\theta_2^4 + \theta_1^4) : 2 = \alpha^4 \tau^4$. In this way we only get the terms with τ^4 , and find:

$$-\frac{1}{3} \varepsilon'''_{v^3} \alpha^2 \beta^3 + \frac{1}{3} \varepsilon'''_{v^2,t} \alpha^3 - \frac{1}{30} \varepsilon''''_{v^4} \alpha^4 = 0,$$

hence finally:

$$\beta' = \frac{\epsilon' \epsilon'' - \frac{1}{10} \alpha^2 \epsilon' \epsilon''}{\epsilon''' \epsilon^3}, \dots \dots \dots (2)$$

in which α^2 is given by (1).

So the expression derived by VAN DER WAALS (Capillariteit, p. 44), viz. $\beta' = \epsilon''' \epsilon^3 : \epsilon''' \epsilon^3$, is inaccurate on account of the neglect of the term with $\epsilon''' \epsilon^3$. Besides, the control by means of the ideal equation of state confirms this. As we put $n_2 = 1 + \alpha\tau + \beta\tau^2 \dots$, $d_2 = 1 - \alpha\tau + \beta\tau^2 \dots$, evidently

$$\beta = \alpha^2 - \beta',$$

because $d_2 = 1 : n_2$.

Now by means of the above given values of the differential-quotients ($\alpha^2 = 4$) we find from (2):

$$\beta' = \frac{18 - \frac{2}{5} \cdot 126}{-9} = -2 + \frac{28}{5} - 3 \frac{3}{5},$$

giving $\beta = 4 - 3 \frac{3}{5} = \frac{2}{5}$, in accordance with what we found before (see § 1).

VAN DER WAALS'S expression would have given an entirely erroneous value for β .

4. The value of the characteristic function.

If we put

$$\frac{m d\epsilon_c}{\epsilon dm} = j,$$

we shall understand by the "characteristic function" q the value of:

$$q = \frac{j-1}{j_k-1} \cdot \frac{\epsilon}{d_1 d_2},$$

of which we know that it is equal to 1, when the quantities a and b of the equation of state do *not* depend on the temperature T (or a only linearly on T). But in any other case q will no longer be $= 1$, but it will be represented in the neighbourhood of the critical point by

$$q = 1 + \lambda (1 - m),$$

in which we shall determine the coefficient λ .

In our previous paper (These Proc. XIV, p. 777) we have viz. already shown, that when the said suppositions are fulfilled, formula (8) given there holds, viz.

$$\frac{T}{p} \frac{dp_c}{dT} = 1 + \frac{a}{pv_1 v_2},$$

i. e.

$$f = \frac{m}{\varepsilon} \frac{d\varepsilon_c}{dm} = 1 + \frac{a}{pv_1 v_2} \frac{d_1 d_2}{\varepsilon},$$

when ε_c denotes the pressure of coexistence, through which we distinguish $\frac{d\varepsilon_c}{dm}$ from $\left(\frac{\partial m}{\partial \varepsilon}\right)_n$. So we have also:

$$fk = 1 + \frac{a}{p k v k^2},$$

hence

$$\frac{f-1}{fk-1} = \frac{d_1 d_2}{\varepsilon},$$

in other words $g = 1$.

If, however, a and b are also functions of the temperature, we have generally according to (b) of § 3, taking the values of $\theta_2 + \theta_1$, etc. into account, and disregarding all the powers of $m-1$ higher than the second:

$$\begin{aligned} \varepsilon_c = 1 + \varepsilon'_t(m-1) &+ \left[\frac{1}{2} \varepsilon''_{v,t} \cdot 2\beta^2 \tau^2(m-1) + \frac{1}{2} \varepsilon''_{t^2} (m-1)^2 \right] + \\ &+ \left[\frac{1}{24} \varepsilon'''_{v^3} \cdot 4\alpha^2 \beta^2 \tau^4 + \frac{1}{6} \varepsilon'''_{v^2,t} \cdot \alpha^2 \tau^2(m-1) \right] + \frac{1}{120} \varepsilon''''_{v^4} \cdot \alpha^4 \tau^4, \end{aligned}$$

or as $\tau^2 = 1-m = -(m-1)$:

$$\begin{aligned} \varepsilon_c = 1 + \varepsilon'_t(m-1) &+ \left[-\varepsilon''_{v,t} \beta^2 (m-1)^2 + \frac{1}{2} \varepsilon''_{t^2} (m-1)^2 \right] + \\ &+ \left[\frac{1}{6} \varepsilon'''_{v^3} \alpha^2 \beta^2 (m-1)^2 - \frac{1}{6} \varepsilon'''_{v^2,t} \alpha^2 (m-1)^2 \right] + \frac{1}{120} \varepsilon''''_{v^4} \alpha^4 (m-1)^2. \end{aligned}$$

From this follows:

$$\begin{aligned} \frac{d\varepsilon_c}{dm} = \varepsilon'_t &+ \left[2\varepsilon''_{v,t} \beta^2 (1-m) - \varepsilon''_{t^2} (1-m) \right] + \\ &+ \left[-\frac{1}{3} \varepsilon'''_{v^3} \alpha^2 \beta^2 (1-m) + \frac{1}{3} \varepsilon'''_{v^2,t} \alpha^2 (1-m) \right] - \frac{1}{60} \varepsilon''''_{v^4} \alpha^4 (1-m), \end{aligned}$$

i. e.

$$\frac{d\varepsilon_c}{dm} = \varepsilon'_t - (1-m) \left[\varepsilon''_{t^2} - 2\varepsilon''_{v,t} \beta^2 + \frac{1}{3} \varepsilon'''_{v^3} \alpha^2 \beta^2 - \frac{1}{3} \varepsilon'''_{v^2,t} \alpha^2 + \frac{1}{60} \varepsilon''''_{v^4} \alpha^4 \right].$$

In this $-2\varepsilon''_{v,t} \beta^2 + \frac{1}{3} \varepsilon'''_{v^3} \alpha^2 \beta^2 = 0$ according to the formula (1) for α^2 derived above, so that we keep:

$$\frac{d\varepsilon_c}{dm} = \varepsilon'_t - (1-m) \left[\varepsilon''_{t^2} - \frac{1}{3} \alpha^2 \left(\varepsilon'''_{v^2,t} - \frac{1}{2} \alpha^2 \varepsilon''''_{v^4} \right) \right].$$

Further according to formula (2) we have:

$$-\frac{1}{20} \alpha^2 \varepsilon''''_{v^4} = \frac{1}{2} \varepsilon'''_{v^3} \beta' - \frac{1}{2} \varepsilon''_{v^2,t},$$

so that we get:

$$\frac{d\varepsilon_c}{dm} = \varepsilon'_t - (1-m) \left[\varepsilon''_{t^2} - \frac{1}{6} \alpha^2 \left(\varepsilon'''_{v^3} \beta' + \varepsilon''_{v^2,t} \right) \right],$$

or as $\alpha^2 \varepsilon'''_{v^3} = 6 \varepsilon''_{v,t}$ according to (1), also

$$\frac{d\varepsilon_c}{dm} = \varepsilon'_t - (1-m) \left[\varepsilon''_{t^2} - \beta' \varepsilon''_{v,t} - \frac{1}{6} \alpha^2 \varepsilon''_{v^2,t} \right] = \varepsilon'_t - \omega (1-m), \quad (3)$$

in which $\varepsilon'_t = \left(\frac{\partial \varepsilon}{\partial m} \right)_{kr}$. [With the ideal equation of state, where (see above) $\varepsilon''_{t^2} = 0$, $\varepsilon''_{v,t} = -6$, $\varepsilon''_{v^2,t} = 18$, ω becomes = $0 - \frac{18}{5} (-6) - \frac{1}{6} \cdot 18 = \frac{108}{5} - 12 = 9 \frac{3}{5}$].

So for $f_k = \left(\frac{m d\varepsilon_c}{\varepsilon dm} \right)_{kr} = \left(\frac{d\varepsilon_c}{dm} \right)_{kr} = \varepsilon'$ we find properly:

$$f_k = \varepsilon' = \varepsilon'_t.$$

The value of this is $= \frac{8}{3n_k - 1} = 4$ for the ideal equation of state, and becomes $= 7$ for all ordinary normal substances.

As $m = 1 - (1-m)$ and $\varepsilon = 1 - \varepsilon' (1-m)$, we now get for q :

$$q = \frac{1 - (1-m) \left[\varepsilon'_t - \omega (1-m) \right] - 1}{\varepsilon'_t - 1} \times \frac{1 - \varepsilon'_t (1-m)}{1 - (\alpha^2 - 2\beta) (1-m)},$$

seeing that $d_1 d_2 = [1 + \alpha \sqrt{1-m} + \beta(1-m)] [1 - \alpha \sqrt{1-m} + \beta(1-m)] = 1 - (\alpha^2 - 2\beta) (1-m)$.

After some reduction this becomes:

$$q = \frac{\varepsilon'_t - \omega (1-m) - 1}{\varepsilon'_t - 1} \times \frac{1}{1 - (\alpha^2 - 2\beta) (1-m)},$$

or

$$q = \frac{1 - \frac{\omega}{\varepsilon'_t - 1} (1-m)}{1 - (\alpha^2 - 2\beta) (1-m)} = 1 + \lambda (1-m). \quad (4)$$

As now $\lambda = 0$ with the ideal equation of state, i.e. with that in which a and b are no functions of T (or a only depends linearly on T), in this limiting case must hold:

$$\frac{\omega}{\varepsilon^{1-m}-1} = \alpha^2 - 2\beta.$$

But as ω is evidently $= \left(\frac{d^2 \varepsilon_c}{dm^2} \right)_{kr} = f'_{k'}$, we may also write for this:

$$\frac{f'_{k'}}{f_{k'-1}} = \alpha^2 - 2\beta,$$

which relation was derived in my preceding communication (These Proc. XIV, p. 779). But in all other cases λ is not equal to 0, and we have:

$$\lambda = \frac{\alpha^2 - 2\beta}{f_{k'-1}} - \frac{f''_{k'}}{f_{k'-1}} \dots \dots \dots (5)$$

From (4) we see also that q cannot be $1 + \sqrt{1-m} - 1/2(1-m)$, i.e. of the order $\sqrt{1-m}$ near T'_k , but must be of the order $1-m$. I pointed this already out in my preceding communication (loc. cit. p. 778, footnote). So though the empirical formula for q drawn up by v. D. WAALS very well renders the values following from YOUNG's tables — theoretically it cannot be upheld.

5. After the above derivations we may proceed to determine the values of some differential quotients for a normal substance as e.g. Fluorbenzene. From YOUNG's tables (Dublin Soc. June 1910), the following values of m , ε , d_1 , d_2 , $1/2(d_1 + d_2)$, $1/2(d_1 - d_2)$ and q have been calculated. (See p. 1100).

For T'_k has been found $286^\circ,55$; for p_k YOUNG gives 33912 mm. of mercury; for d_k the value 0,3541 has been assumed. The values of F' are those which can be calculated from the vapour pressure formula

$$-\log \varepsilon_c = F' \frac{1-m}{m}.$$

The values of $f' = \frac{\varepsilon}{m} \frac{d\varepsilon_c}{dm}$ have been calculated as follows. From the above formula follows:

$$-\frac{1}{\varepsilon} \frac{d\varepsilon_c}{dm} = -\frac{F'}{m^2} - \frac{1-m}{m} \frac{dF'}{dm},$$

so that we get:

$$f' = \frac{m}{\varepsilon} \frac{d\varepsilon_c}{dm} = \frac{F'}{m} - (1-m) \frac{dF'}{dm}.$$

A minimum ($F' = 6,67$) is observed in the values of F' at $m = 0,77$. If we had continued the table up to $m = 0,45$, F' would already have increased again to 7,11. The value of q at first rapidly in-

m	ϵ	d_1	d_2	$\sqrt{\frac{1}{2}(d_1+d_2)}$	$\sqrt{\frac{1}{2}(d_1-d_2)}$	F	$f = \frac{m \frac{d^2 \epsilon}{dm^2}}{\epsilon \frac{d\epsilon}{dm}}$	τ
0.6309	0.01902	2.682	0.008144	1.345	1.337	6.773	10.80	1.41
0.6488	0.02604	2.645	0.01086	1.328	1.317	6.740	10.44	1.41
0.6667	0.03471	2.607	0.01422	1.311	1.296	6.723	10.11	1.41
0.6845	0.04547	2.569	0.01844	1.294	1.275	6.706	9.822	1.40
0.7024	0.05865	2.529	0.02357	1.276	1.253	6.694	9.547	1.39
0.7203	0.07460	2.488	0.02974	1.259	1.229	6.685	9.293	1.38
0.7381	0.09354	2.447	0.03716	1.242	1.205	6.678	9.053	1.37
0.7560	0.1159	2.406	0.04600	1.226	1.180	6.678	8.837	1.35
0.7739	0.1424	2.362	0.05625	1.209	1.153	6.672*	8.617	1.35
0.7917	0.1722	2.317	0.06814	1.193	1.124	6.685	8.425	1.34
0.8096	0.2066	2.270	0.08221	1.176	1.094	6.705	8.270	1.33
0.8275	0.2470	2.219	0.09873	1.159	1.060	6.708	8.095	1.32
0.8453	0.2919	2.166	0.1182	1.142	1.024	6.728	7.937	1.30
0.8632	0.3426	2.112	0.1403	1.126	0.986	6.759	7.804	1.30
0.8811	0.3996	2.052	0.1668	1.109	0.943	6.797	7.690	1.29
0.8989	0.4637	1.987	0.1987	1.093	0.894	6.833	7.579	1.28
0.9168	0.5355	1.917	0.2373	1.077	0.840	6.882	7.487	1.26
0.9347	0.6165	1.837	0.2847	1.061	0.776	6.921	7.388	1.24
0.9525	0.7065	1.740	0.3463	1.043	0.697	6.972	7.305	1.22
0.9704	0.8069	1.621	0.4335	1.027	0.594	7.036	7.250	1.18
0.9883	0.9205	1.450	0.5744	1.012	0.438	6.984	7.071	1.11
1.0000	1.0000	1.000	1.0000	1.000	0.000	—	—	1.00

creases from $m=1$, but then more slowly, and it seems to approach asymptotically to about 1.5. Its course is very well represented by VAN DER WAALS'S formula, but as we already stated, near T_c $q-1$ is not of the order $\sqrt{1-m}$, but of the order $1-m$.

How closely the empirical formula $q = 1 + \frac{1}{1-m} - \frac{1}{1+m}$ renders the course, may appear from the following table, p. 1101.

Whereas the agreement between the calculated and the found values of $q-1$ at $m=0.70$ and 0.86 is perfect, the discrepancies at $m=0.97$ and 0.99 amount to about 10%.

From the values of m and ϵ occurring in the table, we can now

m	ε_c	Found
0	$1 + 1 - 0.50 = 1.50$	--
0.7024	$1 + 0.543 - 0.149 = 1.394$	1.39
0.8632	$1 + 0.370 - 0.068 = 1.302$	1.30
0.9704	$1 + 0.172 - 0.015 = 1.157$	1.18
0.9883	$1 + 0.108 - 0.006 = 1.102$	1.11

easily calculate, making use of the six values of m from 0,8632 to 0,9525 (the last included):

$$\varepsilon_c = 1 - 7,065 (1 - m) + 19,8 (1 - m)^2 - 24,0 (1 - m)^3,$$

so that we have:

$$f_k = \varepsilon' = \varepsilon'_t = 7,065 \quad f''_k = \varepsilon'' \left(= \left(\frac{d^2 \varepsilon_c}{dm^2} \right)_{kr} = \omega \right) = 39,6.$$

So 6,6 is found for $\frac{f''_k}{f_k - 1}$. [With the ideal equation of state this value is $= \frac{9,6}{4-1} = 3,2$].

Let us now determine the values of the coefficients α and β in the expansions into series for d_1 and d_2 .

With $\frac{1}{2}(d_1 + d_2) = \beta(1-m) + \delta(1-m)^2$ we calculate from the table for $m = 0,8632$ etc. the following values:

$$\beta = 0,913 \quad \delta = 0,055.$$

And from $\frac{1}{2}(d_1 - d_2) = \gamma(1-m) + \varepsilon(1-m)^2$ we can calculate:

$$\alpha = 3,9 \quad \gamma = -15,3 \quad \varepsilon = 48.$$

Now the value of $\beta' = \alpha^2 - \beta$ (β' is the coefficient of $1 - m$ in $n_2 = 1 + \alpha \sqrt{1-m} + \beta'(1-m) + \dots$, see above) becomes:

$$\beta' = 15,2 - 0,9 = 14,3,$$

which for the ideal equation of state $= 4 - 0,4 = 3,6$, so exactly the fourth part.

And for $\alpha^2 - 2\beta$ we find $15,2 - 1,8 = 13,4$. [With the ideal equation of state $4 - 2 \times 0,4 = 3,2$ is found for the value of $\alpha^2 - 2\beta$].

For λ we find now according to (5):

$$\lambda = 13,4 - 6,6 = 6,8,$$

so that according to (4) close to T_c :

$$\underline{q = 1 + 6,8(1-m)}.$$

So for $m = 0,9883$ q would be $= 1 + 6,8 \times 0,0117 = 1,08$, and for $m = 0,9704$ q would be $= 1 + 6,8 \times 0,0296 = 1,20$ (found 1,11 1,18). So $\lambda = 6,8$ is possibly still somewhat too low, but it is also possible — and this I think more likely — that the values of d_1 and d_2 , found experimentally near the critical point, are not quite accurate, in consequence of which q is found too high. So most likely the value of the product $d_1 d_2$ is too low, on account of the density of the liquid phase being measured too small in consequence of imperfect homogeneity (presence of vapour bubbles), or because the thickness of the capillary layer, which is of measurable dimensions at the critical point, has not been taken into account, in which layer the density is of course smaller than in the *homogeneous* liquid phase.

In consequence of this the locus $\frac{1}{3}(d_1 + d_2) = f(m)$ deviates seemingly too much to the liquid side quite near the critical point, and accordingly the abrupt deflection of this locus close to T_c , found by YOUNG, CARDOSO and others, would disappear, when the density of the liquid phase could be measured more accurately.

6. The value of the differentialquotients $\varepsilon''_{v,t} = \left(\frac{\partial^2 \varepsilon}{\partial n \partial m} \right)_{kr}$ and $\varepsilon'''_{v^2,t} = \left(\frac{\partial^3 \varepsilon}{\partial n^2 \partial m} \right)_{kr}$ may be calculated from data of isotherms quite near the critical temperature. Those for C_6H_6F not being at my disposal, I could only make use of DORSMAN'S data (Thesis for the Doctorate) for CO_2 . For $33^\circ,1$ he finds e. g. $\rho = 75,30, 76,10, 77,75$ resp. for $v = 551, 449$ and 343 . From this we can calculate that $\frac{dp}{dv}$ for $v = 438$ (the volume on the isotherm of $33^\circ,1$ that agrees with the critical volume) has the value $-0,01245$. From this the value $\frac{438}{73} \times -0,01245 = -0,0747$ follows for $\left(\frac{\partial \rho}{\partial n} \right)_{33,1}$ (the critical pressure is viz. $= 73$).

So we have ($31^\circ,1$ is the critical temperature):

$$\left(\frac{\partial \varepsilon}{\partial n} \right)_{31,1} = 0 \quad ; \quad \left(\frac{\partial \rho}{\partial n} \right)_{33,1} = -0,0747 \quad (\text{both for } v = v_k).$$

Hence (the absolute temperature at $t = 32^\circ,1$ is $305,2$)

$$\varepsilon''_{v,t} = \left(\frac{\partial^2 \varepsilon}{\partial n \partial m} \right)_{kr} = -\frac{0,0747}{2} \times 305,2 = -11,4.$$

We saw above that the ideal equation of state gives for this —6. From the same data the value $0,00007432$ can be derived for

$\frac{d^2\rho}{dv^2}$ at $v = 438$ and $33^{\circ}.1$ [The data can viz. be rendered by the formula $\rho = 76,10 - 0,01163(v - 449) + 0,00003716(v - 449)^2$, from which easily $\frac{d\rho}{dv}$ and $\frac{d^2\rho}{dv^2}$ for $v = 438$ can be derived].

So for $\frac{\partial^2\varepsilon}{\partial n^2}$ we find $\frac{(438)^2}{73} \times 0,00007432 = 0,1953$. Hence we have:

$$\left(\frac{\partial^2\varepsilon}{\partial n^2}\right)_{31.1} = 0 \quad ; \quad \left(\frac{\partial^2\varepsilon}{\partial n^2}\right)_{33.1} = 0,1953 \quad (\text{both for } v = v_k),$$

and from this follows:

$$\varepsilon'''_{v^2,t} = \left(\frac{\partial^2\varepsilon}{\partial n^2 \partial m}\right)_{kr} = \frac{0,1953}{2} \times 305,2 = 29,8.$$

For the ideal equation of state we find 18 for this.

Now in virtue of considerations which will presently be explained, we shall raise the values $-11,4$ and $29,8$ to -12 and 36 , as these values cannot differ much from *double* the values in case the ideal equation of state is used. It follows also from the nature of the above indicated calculation, that the found values $-11,4$ and $29,8$ cannot lay claim to very great accuracy.

Now we can also find the values of ε'''_{v^3} and ε'''_{v^1} . From (1) follows viz.:

$$\varepsilon'''_{v^3} = \frac{6\varepsilon''_{v,t}}{a^2} = \frac{6 \times (-12)}{15,2} = -4,7.$$

The ideal equation of state gives about double the value, viz. -9 .

We find further from (2):

$$\frac{1}{10} a^2 \varepsilon'''_{v^1} = \varepsilon'''_{v^2,t} - \beta' \varepsilon'''_{v^3} = 36 - 14,3 \times (-4,7) = 103,2,$$

hence

$$\varepsilon'''_{v^1} = 103,2 : 1,52 = 67,9,$$

for which with the ideal equation of state also about double the value is found, viz. 126.

Finally we can calculate $\varepsilon''_{v^2} = \left(\frac{\partial^2\varepsilon}{\partial m^2}\right)_{kr}$ from $\varepsilon'' = \omega = 39,6$, in which ω is represented according to (3) by

$$\omega = \varepsilon''_{v^2} - \beta' \varepsilon''_{v,t} - \frac{1}{6} a^2 \varepsilon'''_{v^2,t}.$$

So we find:

$$\varepsilon''_{v^2} = 39,6 + 14,3 \times (-12) + \frac{1}{6} \times 15,2 \times 36,$$

or

$$\varepsilon''_{v^2} = 39,6 - 171,6 + 91,2 = -40,8.$$

The value of this differentialquotient is = 0 with the ideal equation of state. The great negative value of ϵ''_{t^2} for real substances points as we shall presently see — to a great positive value of $\frac{d^2a}{dt^2}$.

We have now the following survey (all this at T_k).

α	β	$\beta' = \alpha^2 - \beta$	$\epsilon'_t = \epsilon' = f_k$	ϵ''_{t^2}	$\epsilon'' = f'_k (= \omega)$	$\epsilon'''_{v,t}$	$\epsilon'''_{v^2,t}$	ϵ''''_{v^3}	ϵ''''_{v^4}	$\alpha^2 - 2\beta$	$\frac{f'_k}{f_k - 1}$	λ
3.9	0.9	14.3	7	-41	39.6	-12	36	-4.7	68	13.4	6.6	6.8
[2	[0.4	[3.6	[4	[0	[9.6	[-6	[18	[-9	[126	[3.2	[3.2	[0]

The lower series of values refers to the ideal equation of state.

We may add the following remarks to what precedes. According to (5) we may write for λ :

$$\lambda = \frac{(\alpha^2 - 2\beta)(f_k - 1) - f'_k}{f_k - 1}.$$

The numerator of this is = $(\alpha^2 - 2\beta)(f_k - 1) - (\epsilon''_{t^2} - \beta' \epsilon''_{v,t} - \frac{1}{6} \alpha^2 \epsilon'''_{v^2,t})$, as $f'_k (= \epsilon'') = \omega$. But as $f_k = \epsilon'_t$, and $\beta' = \alpha^2 - \beta$, we may also write for this:

$$-\epsilon''_{t^2} + \alpha^2 \left[(\epsilon'_t - 1) + \epsilon''_{v,t} + \frac{1}{6} \epsilon'''_{v^2,t} \right] - \beta \left[2(\epsilon'_t - 1) + \epsilon''_{v,t} \right].$$

Now with the ideal equation of state $\lambda = 0$ (see above); and this is what we expected, for then the above form becomes:

$$0 + \alpha^2 (3 - 6 + 3) - \beta (6 - 6).$$

Both ϵ''_{t^2} and the coefficients of α^2 and β are then, namely, = 0.

But with the real equation of state the value of this form is:

$$41 + \alpha^2 (6 - 12 + 6) - \beta (12 - 12),$$

so that the coefficients of α^2 and β would be again = 0. It is not difficult to find a cause for this.

7. If viz. $\frac{\partial b}{\partial T} = b'_t$ is very small (just as $\frac{\partial b}{\partial r} = b'_v$ is slight), we may write for $\frac{\partial p}{\partial T}$, following from $p = \frac{RT}{r-b} - \frac{a}{r^2}$, i. e.

$$\frac{\partial p}{\partial T} = \frac{R}{r-b} + \left[\frac{RT}{(r-b)^2} b'_t - \frac{a'}{r^2} \right];$$

$$\frac{\partial p}{\partial T} = \frac{R}{r-b} - \frac{a'}{r^2} = \frac{1}{T} \left[\frac{a - Ta'}{r^2} \right] = \frac{1}{T} \left(\nu + \frac{1}{r^2} \right),$$

so that

$$\frac{\partial^2 p}{\partial r \partial T} = -\frac{2A}{T v^3}, \quad \frac{\partial^2 p}{\partial r^2 \partial T} = \frac{6A}{T v^4},$$

in which $A = a - T a'$, and a' represents $\frac{da}{dT}$. Hence we have at T_k :

$$\epsilon'_t = \left(\frac{\partial \epsilon}{\partial m} \right)_{kr} = \left(\frac{T \partial p}{p \partial T} \right)_{kr} = 1 + \frac{A_k}{p_k v_k^2},$$

and so the well known relation (only now we have A_k instead of a_k)

$$\epsilon'_t - 1 = \frac{A_k}{p_k v_k^2}.$$

But at T_k we have also, according to what we found just now.

$$\epsilon''_{v,t} = \left(\frac{\partial^2 \epsilon}{\partial n \partial m} \right)_{kr} = -\frac{2A_k}{T_k v_k^3} \cdot \frac{T_k v_k}{p_k} = -\frac{2A_k}{p_k v_k^2} = -2(\epsilon'_t - 1);$$

$$\epsilon'''_{v^2,t} = \left(\frac{\partial^3 \epsilon}{\partial n^2 \partial m} \right)_{kr} = \frac{6A_k}{T_k v_k^4} \cdot \frac{T_k v_k^2}{p_k} = \frac{6A_k}{p_k v_k^2} = 6(\epsilon'_t - 1).$$

So the coefficient of a^2 in the numerator of the above expression for λ passes (with small value of b'_t) really into

$$(\epsilon'_t - 1) - 2(\epsilon'_t - 1) + (\epsilon'_t - 1) = 0,$$

the coefficient of a^3 then also passing into

$$2(\epsilon'_t - 1) - 2(\epsilon'_t - 1) = 0$$

That the quantities $\epsilon'_t - 1$, $\epsilon''_{v,t}$ and $\epsilon'''_{v^2,t}$ have *double* the value of those for the ideal equation of state, is owing to this that where the critical pressure is always about $\frac{1}{27} a_k : b_k^2$, $\epsilon'_t - 1$ with $v_k = r b_k$ passes into

$$\epsilon'_t - 1 = \frac{A_k}{a_k} \cdot \frac{27}{r^2}.$$

In this $A_k : a_k = 1 - T_k a'_k : a_k$. If now also $T_k a'_k$ is small compared with a_k , unity may be written for $A_k : a_k$ by approximation; so that then $\epsilon'_t - 1$ would become $= 27 : r^2$ for the real equation of state with $r = 2,114 = 27 : 4,5 = 6$, and $= 27 : 9 = 3$ for the ideal equation of state. And as really the value 6 is found for $\epsilon'_t - 1 = f'_k - 1$, a'_k (and also b'_t) *must* really be exceedingly small.

In any case (for small b'_t) $\epsilon''_{v,t} = -2(\epsilon'_t - 1)$ by high approximation, and hence $= -12$, which is the reason that above we raised the value $-11,4$ found for $\epsilon''_{v,t}$ from experimental data to -12 . Reversely the slight difference between the two values justifies the supposition that b'_t is really very small. But as then too $\epsilon'''_{v^2,t} = 6(\epsilon'_t - 1) = 36$, we have found a sufficient ground in this to raise the value 29,8, i.e. 30, which was calculated from only few experimental data, to 36.

The numerator of the expression λ now passing into $-\varepsilon''_v$, we get simply :

$$\lambda = \frac{\varepsilon''_v}{f_k - 1} \dots \dots \dots (5'')$$

from which then $\lambda = 40,8 : 6 = 6,8$ follows, as above.

8. As for small b'_t we may write $\frac{R}{v-b} = \frac{a'}{v^2}$ for $\frac{\partial p}{\partial T}$ (see above), $\frac{\partial^2 p}{\partial T^2}$ becomes $= -\frac{a''}{v^3}$ (if namely b''_t is also small), hence

$$\varepsilon''_v = \left(\frac{\partial^2 \varepsilon}{\partial m^2} \right)_{kr} = -\frac{a''_k T_k^2}{v^2_k p_k}$$

So we get for λ with $f_k - 1 = \varepsilon_t - 1 = A_k : p_k v^2_k$ (see above) :

$$\lambda = \frac{T_k^2 a''_k}{a_k - T_k a'_k}$$

when we substitute its value for A_k . If we put

$$T_k^2 a''_k : a_k = a''_k, T_k a'_k : a_k = a'_k,$$

we get :

$$\lambda = \frac{a''_k}{1 - a'_k}$$

because a'_k must be exceedingly small (see above). As now the value 6,8 was found for λ , this comes to this that a''_k is almost 7, so *great positive* (i. e. $T_k^2 \times (a''_k : a_k)$).

Summarizing everything that we investigated in the above and in previous papers, we come to *this* conclusion that the deviations from the ideal equation of state chiefly find their explanation, besides in the association of the molecules, in the following circumstances :

1. That with small value of $\frac{\partial b}{\partial v}$ the value of $\frac{\partial^2 b}{\partial v^2}$ is *great*. In consequence of this v_k becomes $= 2,1b_k$ instead of $v_k = 3b_k$ for the critical volume.

2. That with small value of $\frac{\partial b}{\partial t}$, $\frac{\partial^2 b}{\partial t^2}$, and $\frac{da}{dt}$ the value of $\frac{d^2 a}{dt^2}$ is *great*. This accounts for the great increase of the characteristic function q (which has the value 1 at T_k) in the neighbourhood of T_k .

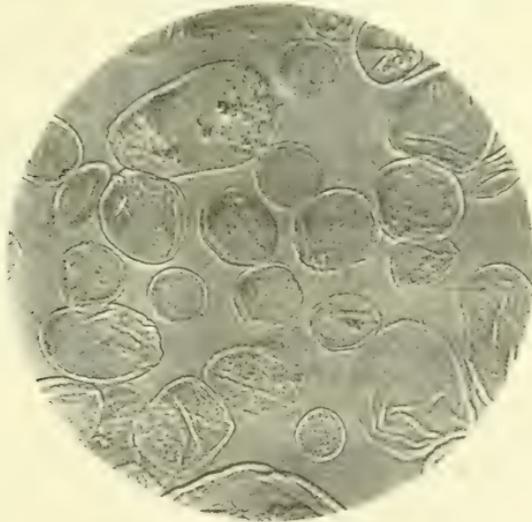
In conclusion we point out that for the determination of the values of ε'''_{v^2} and ε'''_{v^3} the knowledge of the values of b'''_v and b''''_v is required, and so without the complete knowledge of the quantity b as function of v we cannot possibly predict anything regarding the values of ε'''_v and ε''''_v . That these values are about half the ideal values — from this would follow among others that $v_k^2 b''''_v$ would be not far from 1.

Clarens, March 1912.

Botany. — “*Structure of the starch-grain*”. By Prof. Dr. M. W. BELJERINCK.

If one gram of potato-starch is boiled with 100 cM³ of distilled water this is just sufficient to bring the grains to their maximum of swelling and make the starch take up about 70 % of the water so that it remains suspended and cannot precipitate, as the swollen grains touch one another. Each grain swells thereby to a somewhat irregular globule whose diameter is about 3.5 times that before the ebullition. Whether the boiling lasts shorter or longer is of no consequence. If more water is used for the boiling no further swelling takes place; when left to sedimentation the liquid above the starch colours but feebly blue with iodine.

When a microscopic preparation is made, containing but few starch-grains, and a strong tannin solution flows sideways under the cover-glass, the following is seen (compare the figure).



EXPLANATION OF THE FIGURE.

Magnified 200 times.

Potato-starch after prolonged boiling and treatment with a tannin solution. The grains are by the boiling changed into little vesicles with dissolved contents. The wall of the vesicles consists of amylocellulose (amylopectose), the contents of granulose (amylose), the latter being precipitated by the tannin.

At the moment the tannin comes into contact with them, the grains, which at first sight seem homogeneous, show a very distinct membrane through which the tannin easily diffuses to the inside where it directly forms a characteristic precipitate. When using a more

dilute solution¹⁾ this precipitate consists of little droplets in very lively Brownian movement and with a more concentrated tannin solution, of solid particles, adhering together and filling up the whole inner space of the vesicle. This experiment is so simple and convincing that it cannot be doubted for a moment but the boiled starch-grain consists of a solid, sac-shaped, quite closed wall, containing a liquid.

How it is possible that this fact seems unknown I cannot understand, but I have nowhere found it mentioned in the extensive literature about this subject.

The liquid in the vesicle is a granulose solution, or as is said at the present day, an amylose solution, containing 0.6 gram of the 1 gr. originally used, which diffuses but with difficulty through the walls into the surrounding water. If, however, the boiled starch is rubbed fine with sand the delicate sacs burst and the granulose solution diffuses in the water, which then becomes intensely blue with iodine.

That the wall consists of a very soft substance may be observed as well by its great variability of shape at pressure, as by the ease with which it is distended to short threads by moving the cover-glass, to which it adheres, when touched by it. When the boiled starch-grains are washed out during some days with water constantly renewed, it is possible finally to obtain the vesicles without their contents and filled with water only; after drying they weigh 0.4 gr. if one gr. of starch has been used. With iodine they colour lighter than the granulose and somewhat violet. When preserved they become partly soluble in water containing chloroform. By leukodiastase they are easily converted into maltose and dextrine, quite like granulose; by erythrodiastase a little less easily, but a marked difference does not exist.²⁾

If the boiling is effected not in distilled but in canal water, the starch shows a strong disposition to precipitate whereby after 24 hours a layer results of $\frac{1}{3}$ to $\frac{1}{4}$ of the whole volume if again 1% starch is used. If 4% starch or more is boiled in canal water

¹⁾ Very much diluted tannin solutions give no precipitate at all with starch- or granulose solutions.

²⁾ By leukodiastase I understand the slowly diffusing diastase secreted by the germs of germinated corn-grains, which on starch-gelatin plates, when treated with iodine, produces diffusion fields which remain uncoloured. By erythrodiastase the more quickly diffusing diastase of the endosperm of the grain, which on the said plates after treating with iodine, is recognisable by the erythro-dextrine reaction. WIJSMAN (De diastase beschouwd als mengsel van maltase en dextrinase, Amsterdam, 1889) called leukodiastase "dextrinase" and erythrodiastase "maltase", but these terms are not well chosen.

no sedimentation at all occurs, the swollen grains again touching one another. The precipitation may be caused in the starch boiled with distilled water by addition of dilute solutions of salts, acids, or alkalis. At 0,001 % a slight contraction of the vesicles is already visible and it reaches its maximum at about 0,1 % .¹⁾ With still stronger concentrations an increase in thickness of the precipitated layer is observed, probably because the vesicles then lose somewhat of their weight in the heavier liquid.²⁾ As non-electrolytes such as cane sugar, urea, aethylalcohol, and methylalcohol, even in 1 % solutions, cause no sedimentation at all, it is evident that we have to deal here with an ionreaction, which perhaps will prove to be very well apt for exact measure. Aethylalcohol of 5 % and methylalcohol of 6 %, however, distinctly bring the vesicles to precipitation, but then the superstanding liquid becomes rather turbid, the dissolved granuloose precipitating also. Above 10 % methylalcohol the precipitation is complete.

If the starch is boiled in dilute salt solutions, the volume of the sediment after standing is as large as if the salt had been added later to the starch boiled in distilled water.

When the sedimentation is caused by ammonium sulphate it is easy to show that as well the ammonium as the sulphuric ion are present in stronger concentration in the precipitate than in the liquid above it.

The foregoing is quite in accordance with the results of an investigation of M^{me} Z. GATIN-GRUZEWSKA.³⁾ By extraction of starch with dilute caustic soda she obtained a soluble substance, amylose, and an insoluble rest of amylopectose in about the same proportion as the above (0.6 and 0.4). Her view, however, of the localisation of the two constituents is another than that which follows from my observations.

She says that amylopectose forms little scales or sacs, evidently corresponding with the layers of the starch-grain, so that this constituent would occur as well within as outside the grain, whilst, according to my experience, the whole inner portion dissolves in boiling water and is homogeneous, the outerwall only being insoluble and thus materially different.

¹⁾ No great difference in the thickness of the precipitated layer (ca. 4 cm. from a liquid layer of 17 cM.) was perceptible after 24 hours at room temperature when using 0,1 % K_2HPO_4 , KCl, NaCl, $(NH_4)_2SO_4$, $CaCl_2$, Al_2Cl_3 , KNO_3 , HCl, or Na_2CO_3 .

²⁾ More dilute solutions of sugar and urea do cause some sedimentation for a not yet explained reason. Stronger solutions do the same perhaps because of contamination by electrolytes.

³⁾ Comptes Rendus T. 146 p. 540, 1908.

The words "amylose" and "amylopectose" have first been used by L. MAQUENNE and E. ROUX,¹⁾ but they consider both these substances as perfectly mixed and say: "L'empoix d'amidon est constitué par une solution parfaite d'amylose, épaissie par l'amylopectose" (l. c. pag. 219).

That MAQUENNE, even after the communication of M^{me} GATIN-GRUZEWSKA, had by no means the view here given follows from the observations which he adds to the said communication.²⁾

The change of the terms "amylocellulose" and "granulose", so long existing in the literature, into "amylopectose" and "amylose" by MAQUENNE, seems not necessary.

The difference between the walls and the contents of the starch-grain probably reposes on incrustation. We have namely to think the surface of the grain as consisting of the albuminous matter of the amyloplast mixed with the secreted granulose by which the thus formed mixture has become insoluble in boiling water. This would be in accordance with the general observation, that incrusting substances highly alter the solubility of bodies susceptible of imbibition, of which the lignified and suberified cell-walls of plant cells and tanned leather are good examples. This conception would lead to the conclusion that the amyloplast does originally incrust the membrane of the starch-grain, but later draws back from it, wherewith the change of amylocellulose (amylopectose) into granulose (amylose) would correspond.

If this view is right the quantity of albuminous matter, which occurs in the membrane, must be very small, for in the rate of nitrogen no distinct difference between amylocellulose (amylopectose) and starch could be found, in both cases it being about 5 milligrams per 100 grams of dry matter.

MAQUENNE says that his amylopectose is not coloured by iodine; the amylocellulose (amylopectose) obtained from starch after extraction of the granulose (amylose) in the manner here described, proves to colour violet blue with it. It is not impossible that in this case, too, a kind of incrustation should occur, namely of an adsorption of granulose in the amylocellulose wall, which then itself would in pure condition remain uncoloured by iodine.

All other species of starch examined by me behave in the same way as potato-starch.

¹⁾ Recherches sur l'amidon et la saccharification diastasique. Ann. d. Chimie et de Physique, 8e Série, T. 9, pag. 179, 1906.

²⁾ Observation sur la Note de M^{me} GATIN-GRUZEWSKA. Comptes Rendus T. 106 p. 542, 1908.

Physics. — “On the law of molecular attraction for electrical double points”. By Prof. D. J. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS).

Prof. REINGANUM was so kind as to point out to me two errors which occur in my communication under the above title¹⁾.

In the first place the formula for \mathcal{E} on page 134 l. c. must be:

$$\mathcal{E} = \frac{m}{r^3} \sqrt{4 \cos^2 \vartheta + \sin^2 \vartheta}$$

The factor $\frac{1}{3}$, occurring l. c. in this formula and in all formulae derived from it, has been inserted erroneously.

But moreover — and this is a more serious error — the chance that the angles q and ϑ lie between definite limits, must be represented by:

$$C \times \frac{1}{4} \sin q dq \sin \vartheta d\vartheta e^{-\frac{m^2 \cos^2 \vartheta \sqrt{3 \cos^2 \vartheta + 1}}{r^2}}$$

It is not allowed to omit the constant C as I did l. c. This constant can of course be determined by means of the consideration, that the sum of all chances is equal to unity. So we find:

$$C = \frac{1}{\int_0^{\pi/4} \int_0^{\pi/2} \sin q dq \sin \vartheta d\vartheta e^{-\frac{m^2 \cos^2 \vartheta \sqrt{3 \cos^2 \vartheta + 1}}{r^2}}}$$

After a deduction analogous to that which was performed l. c. we easily find:

$$C = \frac{1}{2\pi \sqrt{3} \int_1^{\sqrt{2}} \frac{dx}{(x^2 - 1) \sqrt{x^2 - 1}}$$

where $c = \frac{m^2}{r^2}$.

So we get for E :

$$E = \frac{1}{2\pi} \left(\int_1^{\sqrt{2}} \frac{dx}{(x^2 - 1) \sqrt{x^2 - 1}} - \int_1^{\sqrt{2}} \frac{dx}{(x^2 - 1) \sqrt{x^2 - 1}} \right)$$

¹⁾ These proceedings, XI p. 132 and 315.

For $t = 0$ i. e. $c = \infty$ this becomes $E = -\frac{2m^2}{r^3}$.

For $t = \infty$ i. e. $c = 0$ it becomes $E = -\frac{2}{3} \frac{m^4}{r^6 t}$.

If we want to find the mean force in the direction r , we must differentiate the value of the potential energy with respect to $-r$ before performing the integrations. This comes to multiplying it by $\frac{3}{r}$. This factor remains unaltered by the integrations; so we find

for the mean force in the two cases respectively $-\frac{6m^2}{r^4}$ and $-\frac{2}{3} \frac{m^4}{r^7 t}$.

My conclusion i. e., that the mean force would vary more rapidly with the distance than $1/r^2$, proves not to be correct: for $t = \infty$ it varies as $1/r^7$, at lower temperatures it varies less rapidly. These conclusions however only hold for densities, which are so small, that interaction of more than two molecules at the same time need not be taken into consideration. If we take this circumstance into consideration we shall undoubtedly again find a more rapid decrease of the force with the distance.

Biochemistry. — “Action of substances readily soluble in water, but not soluble in oil, on the growth of the *penicillium glaucum*”. By Prof. J. BÖESEKEN and Mr. H. WATERMAN. (Communicated by Prof. BELERINCK).

I.

The influence of the hydrogen-ions.

In our previous communications¹⁾ we have made mention of two kinds of retarding substances. The first kind to which belong salicylic acid and butyric acid, penetrates on account of its great solubility in oil, coupled with a sufficient solubility in water, too rapidly into the organism and causes it to be overloaded.

The second kind to which belongs formic acid is much more readily soluble in water than in oil, but can only be used up very slowly so that an overloading is still possible.

As, both with salicylic acid and formic acid an injurious action of the hydrogen-ions was not excluded, owing to their great dissociation constants, it had to be determined by a special research at what concentration the hydrogen-ions became a hindrance.

¹⁾ Proc. of Dec. 30 1911 p. 608 and Febr. 24, 1912 p. 628.

It may be observed here that with oxalic acid, malonic acid, tartaric acid and lactic acid we had met with retardation phenomena which, in our opinion, ought to be attributed to the action of hydrogen-ions.

These substances, readily soluble in water, but not at all soluble in oil, exhibited, at definite concentrations, retardations which, from their nature, were quite different from those observed with substances soluble in oil.

These phenomena could be prevented by neutralisation; on adding an acid harmless in itself (gentisic acid) to a solution of tartaric acid below the harmful concentration they could be revived.

By calculation from the dissociation constants of the acids investigated and comparison with the action of a sulphuric acid solution of definite concentration it could be demonstrated that these phenomena were indeed connected with a definite quantity of hydrogen-ions, and that this corresponded for the *penicillium glaucum* with a concentration of about 1×10^{-5} ; in the case of the *aspergillus niger* this concentration was higher, namely about 4.5×10^{-5} in grm. equiv. All this will be seen from a survey of the experiments. (Table p. 1114.)

From this survey it is quite evident that the retarding action observed with oxalic acid and tartaric acid must be attributed to a definite concentration of the hydrogen-ions. To begin with, ammonium oxalate is assimilated even at higher concentrations; the same is the case with acid and with normal potassium tartrate (II, IV, V).

Further, a solution of ammonium oxalate does not affect the growth of the *penicillium* in *p*-oxybenzoic acid. (IX).

On the other hand, oxalic acid does retard the development of the organism in *p*-oxybenzoic acid and even in concentrations lower than usual (Compare VIII with I), for the hydrogen-ions of the *p*-oxybenzoic acid, although themselves harmless, join those of the oxalic acid so that the harmful concentration is attained sooner.

The same happens on adding together tartaric acid and gentisic acid, both being below the injurious concentration; a harmful concentration is then reached (VI).

If, by making use of OSTWALD'S dissociation-constants of the acids (for oxalic acid we have used the data of ENKLAAR (Chem. Weekbl. 8, 381 (1911)), we calculate from our observations the harmful concentration of the hydrogen-ions we obtain:

d-Tartaric acid; $K = 0.097$; harmful concentration = 500 mg. per 50 c.c.

From this about 0.8×10^{-5} m. gram equivalent.

Malonic acid; $K = 0.158$; harmful concentration observed = 300

t = temperature of the room; 50 ccm. of a solution with usual inorganic nutriment.

N ^o .	Name of the compound.	Conc. in mg.	after inoculation observed after						Remarks.
			2 days	3 days	4 days	5 days	6 days	9 days	
I	Oxalic acid.	5.5			+		+		Generally the development is slight. After some time a decided yellow colour is noticed in the concentrations where a development is still noticed.
		7	?	+		+			
		17.5	?	?		+			
		27			+		+		
		29	-	+		+			
		60	-	?		+			
		81	-	-		+			
		97.5			-		+	?	
		101	-	-		+			
497			-		-		After 25 days, no development.		
1498			-		-				
II	Ammonium oxalate.	7	+?	+?		+		Slight development the strongest at the largest concentration.	
		30	+?	+?		+			
		102	+	+		+			
		300	+	+		+			
III	<i>d.</i> Tartaric acid	10	+	++		++		The retarding action, therefore, commences above 300 mg.; with 500 mg. it is very pronounced in the first 5 days.	
		51	+	+++		+++			
		101	+	+++		+++			
		301	+?	+		+	strong		
		501	?	?		+	+++		
		1001	?	?		+?	?		
IV	Potassium tartrate.	10	+	++		++		Not the slightest retardation noticed.	
		100	?	+++		+++			
		500	+	+++		+++			
V	Potassium hydrogen tartrate	10	+	++		++		Not the slightest retardation noticed.	
		100	+	+++		+++			
		500	+	+++		+++			
VI	<i>d.</i> Tartaric acid to which has been added each time 100 mg. of gentisic acid.	300	-	-		-		100 mg. of gentisic acid added to little <i>p</i> -oxybenzoic acid cause no disturbance.	
		500	-	-		-			
		1001	-	-		-			
VII	Malonic acid	5	?			+	 Maximum	
		25	+?			+			
		50	+			++			
		70	+			+++			
		100	+			+++			
		200	+			+++			
		300	-			+			
400	-			+					
VIII	Oxalic acid to which has been added each time 150 mg. of <i>p</i> -oxybenzoic acid.	0	+			++			
		10	+?			++			
		25	-			+			
		40	-			?			
		60	-			-			
		80	-			-			
		150	-			-			
IX	Ammonium oxalate to which has been added each time 150 mg. of <i>p</i> -oxybenz. acid	40	+			++			
		80	+			++			
		150	+			++			
		300	+			++			

mg. per 50 c.c. from which is calculated 1×10^{-5} m. gram equivalent.

Oxalic acid; the harmful concentration lies at 50 mg. per 50 c.c.; this agrees with a concentration of $1,2 \times 10^{-5}$ hydrogen-ions.

From this we may conclude that the retarding action becomes very pronounced when the concentration of the hydrogen-ions amounts to about 1×10^{-5} ; it is independent of the compound used.

Naturally, the observations only admit of an approximate estimation, so in the calculation we could assume that the dibasic acids employed had only resolved one hydrogen-ion.

Yet we have been able to use it for demonstrating that on adding gentisic acid to tartaric acid the retarding action must start at a concentration previously determined.

300 mg. of tartaric acid per 50 c.c. represent a concentration of $0,6 \times 10^{-5}$ gram equivalent of hydrogen-ions.

100 mg. of gentisic acid ($K = 0.108$) represent fully 0.3×10^{-5} hydrogen-ions.

Separately, both these substances are quite harmless (Proc. Dec. 1911, p. 615); when mixed they totally prevent the development of the *penicillium* (VI).

Finally, we give a survey of the action of increasing quantities of sulphuric acid added to 150 mg. of *p*-oxybenzoic acid, from which it appears again that the harmful concentration lies between 5×10^{-6} and $1,3 \cdot 10^{-5}$.

Quantity of H ₂ SO ₄ in mg. per 50 cc.	H in gram eq.	Observed after <i>n</i> days.					Remarks.
		2	4	6	8	11	
0	1×10^{-6}	+	++	+++			
2	1.8×10^{-6}	+	++	+++			strong growth Yellow coloration
5	3×10^{-6}	+	++	+++			
8	5×10^{-6}	+	++	+++			
29	1.3×10^{-5}	—	—	?	++	+	
47	1.9×10^{-5}	—	—	—	—	—	
95	3.9×10^{-5}	—	—	—	—	—	
Added 131 mg. (NH ₄) ₂ SO ₄ to 150 mg. <i>p</i> -oxybenzoic acid in 50 cc.	1×10^{-6}	+	++	++			strong growth

For *p*-oxybenzoic acid $K = 0.0029$ from which is calculated, for 150 mg. per 50 c.c., a hydrogen-ion concentration of about 9×10^{-7} (in round numbers 1×10^{-6}).

If we compare the action of the hydrogen-ions with that of substances like salicylic acid, the great difference is at once evident.

The retardation sets in fairly suddenly above a certain concentration and the development still taking place in unfavourable conditions is readily distinguished macroscopically from the normal growth. It looks as if the mycelium has been shrivelled and after some time it turns orange-yellow. As this coloring matter diffuses in the liquid this becomes in the long run bright yellow.

If we ask wherein consists the harmful action of the hydrogen ions we cannot answer this without referring to the protoplasmic wall.

In our previous communication (Proc. Febr. 24, 1912, p. 930) we have stated that this could not be merely an oily layer:

If, however, we look upon this wall as a very concentrated colloidal solution of a lecithine-like substance in which albuminous matters are also present the *rapid* entering of the substances readily soluble in fat or lecithine becomes, on the one hand, intelligible while on the other hand, we can understand why the substances readily soluble in water can also penetrate.¹⁾

All substances that exert a decided action on the condition of the wall will disturb its regular functions and thus cause a retardation. Now it has been shown from a number of experiments that hydrogen-ions are capable of coagulating colloidal solutions; for instance, this is the case with lecithine solutions.

(J. FEINSCHMIDT, Biochemische Zeitsch. **38**, p. 344 (1912). Also compare the researches of MICHAELIS and his pupils, Bioch. Zeits. **19**, **24**, **27**, **28**, **29** and **30**, particularly MICHAELIS and TAKAHASHI **29**, 439 and **30**, 143).

Here, it was found that the maximum concentration for the coagulation of colloidal lecithine solutions was situated between 1×10^{-2} and 1×10^{-4} and that it, on addition of solution of albumen, was shifted towards the weaker acid concentrations.

It is now obvious to assume that the retarding action of the hydrogen-ions exerted on the development of the *penicillium glaucum*,

¹⁾ The velocity with which the substances soluble in water can penetrate a similar wall will depend on all kinds of circumstances not yet foreseen; in any case it must be assumed to be much smaller than the velocity with which the substances soluble in fat are absorbed, as in the opposite case the wall could not be semi-permeable for substances like sugars, salt solutions etc.

will be connected with a coagulation phenomenon of the colloidal plasmic wall.

The fact that the organism is here more sensitive than a commercial preparation of lecithine will not be an obstacle to this assumption. That this sensitiveness is also much dependent on the special organism is evident from the fact, that the harmful concentration of the H-ions with the *Aspergillus niger* lies at 4.5×10^{-5} therefore considerably higher than with the *penicillium* (the temperature being 32°).

The last concentration 1×10^{-5} agrees with that stated by MICHAELIS and TAKAHASHI for the haemolysis of fresh blood corpuscles in an isotonic medium and which is also attributed to the coagulation of a stromatic substance.

The coagulation of these albumens is, however, again dependent on their electric charge; if this is neutralised by taking up hydrogen ions, then as M. and T. assume, they can no longer retain the haemoglobin and haemolysis sets in.

With the organisms investigated by us it can be very well possible that the negative charge of the plasmic colloids (and here we need not think of the wall only) protects them against the hydrogen ions so long as the concentration remains below a certain limit. If this limit is exceeded, in other words if the isoelectric point is reached a coagulation will take place and consequently a disturbance of the function and retardation of the growth.

In this respect, the diffusion of the yellow colouring matter from the organism in the surrounding liquid made us think somewhat of haemolysis.

S U M M A R Y.

It has been shown that the retarding action of some acids soluble in oil must be attributed to the hydrogen-ions.

The harmful concentration of the H-ions for the *penicillium glaucum* was determined at 1×10^{-5} gm. equiv. (for the *aspergillus* at 4.5×10^{-5}).

It has been assumed that this injurious action was caused by a coagulation of the colloidal constituents of the plasm.

In connection with researches of other investigators, it was surmised that the coagulation was attended by a neutralisation of the colloids having a negative charge by the hydrogen-ions with a positive charge.

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Delft, March 1912.

Anatomy. — "*Caudal connections of the corpus mammillare*". By
Dr. C. T. VAN VALKENBURG. (Communicated by Prof. WINKLER).

Four connections of the corpus mammillare with other parts of the brain are known: part of the fornixfibres unites it with the ammon's horn; the tractus VICQ D'AZYR with the nucleus anterior thalami; the tractus GUDDEN with the nucleus of the same name; the pedunculus corp. mammillaris has a hitherto unknown destination.

This communication regards the two last-mentioned fibre-systems.

With regard to the origin and the extremity of either of these there is no unanimity: whether the tractus GUDDEN originates or ends in the nucl. tegmenti profundus; whether pedunculus corp. mam. commences or finishes in the lateral nucleus of this ganglion, the communications on this point disagree. A rabbit of a series of operated animals had got an exceptional lesion. The pedunculus and tractus GUDDEN were injured, whilst tractus VICQ D'AZYR and the fornix remained unhurt. The animal was killed after half a year; the examination of the brain that had been cut in a continuous series (coloured after PAL's method, alternating with v. GIESON's) brought to light, with regard to the mentioned tractus and nuclei, the following facts. The knife that had entered from the dorsal side, had partly cleft a.o. the diencephalon to the left of the middle line as far as the basis. In this way the pedunculus corp. mammillaris was nearly sectioned, a little distal from the lateral nucleus mammillaris; the distoventral direction of the section made it possible that the tractus GUDDEN was struck on the spot where it separates from the tractus VICQ D'AZYR; only its most medial fibres had remained unhurt. The fasciculus retroflexus (MEYNERT) was entirely destroyed. Further the section had gone through the most lateral part of the fasciculus longitudinalis posterior, the commissura posterior and the splenium corporis callosi. By hemorrhage the most medial ventral nucleus of the thalamus opticus had been severely injured. More distally the wound gradually retracted in a dorsal direction, going along the left edge of the central substantia grisea of the aquaeductus Sylvii through the lamina commissuralis. The right half of thalamus and stem was completely uninjured, so that the secondary degenerations could distinctly be followed.

1. The examination showed that the *pedunculus corporis mammillaris*, after its originally entirely ventral position — medially from the pes pedunculi (pyramid tractus) — turns gradually partly medi-dorsal. This part is placed dorsal from the lemniscus medialis arranged in some thick loosely cohesive fascicles. Towards the end of the

dienecephalon it becomes constantly more difficult to separate it from the medial lemniscus, and apparently it ends near the cross-plane immediately caudal from the nucleus trochlearis. It was however impossible for me to get from my preparations a strong conviction of this fact. On its way hither, already during its entirely basal position healthy fibres add themselves to the degenerated bundle; these are not met with among the above-mentioned fascicles dorsal from the medial lemniscus. Presumptively they are partly originary from the lemniscus sensu strictiori, joining the pedunc. c. mammillaris (WALLENBERG) in the proximal protuberantial regions, and extending partly towards the ganglion laterale? partly over it towards groups of cells between fornix and tractus VICQ D'AZYR.

In my case I could only follow fibres of the latter sort. The absolute absence of large ganglion-cells, well preserved on the right, proves that in reality the pedunculus c. mam. originates in the lateral nucleus. It is an irrefutable fact that fibres situated laterally extend, during the praepontine course of the ped. c. mam. from the latter in the direction of the substantia nigra ventral from the lemniscus. I intend to give further information about this connection in a subsequent communication.

2. The *tractus Gudden* (mammillo-tegmentalis), consisting of much finer poorly medullated fibres had been primarily destroyed, as was already noted, with the exception of the most medial part. The secondary degeneration could be followed as far as the nucleus Gudden (tegmenti profundus). The cells of this nucleus had moved more closely together than in the healthy right side. At all events it was not possible to discover a loss of cells of any signification. Only a smaller group of cells, more dorsal, situated nearly between the parts of the fasciculus longitudinalis posterior had very considerably diminished in number on the left side. As to the medial nucleus of the mammillare, the left dorsal nucleus of it, with the exception of a small part lying near the median line, had lost its ganglioncells.

It is obvious that we may conclude from this that the tractus Gudden originates in the dorsal nucleus of the medial mammillar ganglion; that this tractus ends in the nucleus tegmenti profundus with the exception of its dorsal smaller part; that the fibres of that tractus are arranged in the same way as they originate from the mentioned dorsal mammillar nucleus, because only the medial cells of those giving origin to the tractus Gudden, were preserved according to the fact that only the medial part of the tractus mammillo-tegmentalis had not been destroyed by the operation.

In my opinion it is probable that the cells lying dorsal from the

nucl. tegm. prof. s.s. give origin to fibres, situated laterally in the fascic. longit. posterior, having a frontal direction, as they had primarily been destroyed near the nucleus oculomotorius.

About 30 years ago VAN GUDDEN had already indicated the dorso-medial nucleus mammillaris as the origin of the tractus called after him, without finding however general agreement (vide e.g. KÖLLIKER: Gewebelehre).

The present standpoint is that of CAJAL according to whom the tractus of VICQ D'AZYR and GUDDEN originate from the same cells, (fascic. mammillaris princeps); one part of the fibres goes in a fronto-dorsal direction to the nucl. anterior thalami (VICQ D'AZYR) another runs caudally to the nucl. GUDDEN (vide above). From the uninjured state of the medial-ventral nuclei of the corp. mamillare — in agreement with the conservation of the tractus VICQ D'AZYR — it appears that the question is not so schematic as CAJAL represented it in his drawing¹⁾ in which are represented fibres, originating in the mamillare, dividing each dichotomically, producing in this way ingredient parts for the two mentioned tractus.

In order to control my results obtained in the degenerative way I examined embryos of rabbits of different ages.

I communicate here only what a specimen of 11 cm. length and another of 2 $\frac{1}{2}$ cm. show. The brains of both embryos were, after enclosure in paraffine coloured with cresylviolet by Dr. DROOGLEEVER FORTUYN (frontal series).

Embryo 11 cm. Here principally all the relations so as they exist in the fullgrown animal can distinctly be found. With greater distinctness however the separate connections of the tractus GUDDEN and VICQ D'AZYR with the mamillare can be observed. Dorso-proximal from the latter the two systems are united. The most median part of the apparently common stem radiates first downward as soon as the dorsal nucleus of the medial mamillare-ganglion appears. An examination of the series in a caudal direction shows that these fibres are the continuation of the tractus GUDDEN, which, where the lateral (VICQ D'AZYR-) fibres run ventrally, appears as a distinct tractus, passing the fascic. retroflexus at its medial side.

The dorsal nucleus of the medial mamillare has here the same somewhat dish-shaped form as in the full-grown animal and lies on the proximal half. The tractus VICQ D'AZYR first sends its lateral, more distally the other fibres into the ventral part of the medial

¹⁾ Text. del. sist. nervioso Tomo II, segunda parte, Fig. 636, pag. 746.

ganglion, in which they run for a short distance sagittally backward, (just as the fascic. retroflexus does in the gangl. interpedunculare).

By the way I mention the very distinct radiation of fornix fibres, in this stage of development, dorsal from the corp. mammillare to the opposite side of the hypothalamus.

Embryo $2\frac{1}{2}$ cm. A fasciculus VICQ D'AZYR is still missing. The corpus mammillare has only a very slight ventral curvature, in which the ventral nucleus of the medial ganglion will be formed, its dorsal nucleus however is very well recognisable. The tractus GUDDEN is likewise perfectly distinct, passing on the typical point the fasc. retroflexus. As in the other embryo the lateral nucleus and the ped. c. mammill. are extant. Judging from such young stages one should however not easily reckon this nucleus among the mammillary elements, as it is situated too lateral. The peduncle originates in it strongly sagittally (in the same way as in the full-grown animal) and is therefore rather difficult to recognize.

The fact that only the tractus GUDDEN is extant whereas the tractus VICQ D'AZYR is missing, is a striking proof of the comparative independence of these two bundles. The existence of the dorsal nucleus is in agreement with this fact. Evidently GUDDEN's tractus is *older* and its alliance with VICQ D'AZYR is especially of a secondary, topographical nature. It is possible that the lateral nucleus with pedunculus corporis mammillaris, the dorsal nucleus of the medial ganglion with tractus GUDDEN, are of an older date than the ventral nucleus of the medial ganglion with which part of fornix and the tractus VICQ D'AZYR are connected. A system of fibres perhaps homologous with the pedunculus c. mam, with a very similar originary nucleus is already known to comparative anatomists, in many fishes (teleostei) [according to a communication of Dr. ARIENS KAPPERS]; this is not the case (hitherto) with the tractus mammillotegmentalis.

According to the majority of authors it is an undeniable fact, that in submammalia nothing is found either of a corpus mammillare sensu strictiori or of a tractus VICQ D'AZYR. This excludes likewise the possibility of the existence of fornixfibres that might unite the ammon's formation with the medial ganglion of the mammillare. They radiate all towards the hypothalamus, in correspondence with the majority of the fornix-ingredients in rabbits, which run towards the crossed hypothalamus (and tegmentum. ?)

Mathematics. — “On two linear congruences of quartic twisted curves of the first species”. By Prof. JAN DE VRIES.

In a communication in the *Proceedings* of this Academy (Vol. XIV, p. 255) I have considered the congruence generated by the curve of intersection of two quadrics each of which belongs to a given pencil. This congruence is of the *first order* and of the *first class*.

In the following pages will be treated properties of two other congruences of quartic twisted curves also of the *first order* but of the *second* and *third* class.

1. We consider a pencil (q^2) of quadrics q^2 passing through the conics α^2 , β^2 , and a pencil (q^3) of cubic surfaces q^3 the base curve of which breaks up into α^2 and a twisted curve γ^2 . By the intersection of each surface q^2 and each surface q^3 a congruence I' of quartic twisted curves q^4 of the first species is generated. Through an arbitrarily chosen point passes *one* surface of both pencils and therefore *one* q^4 ; so I' is linear or of the *first order*.

Through any point C of γ^2 passes *one* surface γ^2 of (q^2) containing ∞^1 curves q^4 passing through C ; therefore γ^2 may be called a *singular curve*, C a *singular point of the second order*.

Also β^2 is *singular*; through any of its points B passes *one* surface β^2 containing all the curves q^4 cutting B^2 in B ; so B is a *singular point of the third order*.

Finally α^2 is *singular* too. For a q^2 and a q^3 touching each other in a point A of α^2 have a q^4 passing through A in common. By making to correspond to each surface q^2 the surface q^3 touching it in A , the pencils, brought thereby in projective correspondence, generate a surface α^3 with α^2 as nodal curve and A as triple point, containing ∞^1 curves q^4 cutting α^2 in A ; so A and α^2 are *singular of order five*.

2. On an arbitrary straight line l the two pencils determine two involutions I^2 , I^3 ; as these involutions admit two common couples, l is bisecant of two q^4 and therefore I' a congruence of the *second class*.

Any generator s of one of the q^2 is cut by (q^3) in an involution I^2 and therefore a *singular bisecant*. All these lines s form the congruence (2, 4) of the lines cutting α^2 and β^2 in two different points.

The planes α , β bearing α^2 , β^2 form together a surface φ^2 intersected by any q^3 in the combination of a line α with a cubic curve

of β having with that line one point in common. Every line of β is a *singular trisecant*; for it has three points in common with each of the α^1 degenerated curves q^4 determined by (φ^3) and (α, β) .

A straight line t of any q^3 not meeting α^2 is cut by (q^2) in an l^2 and therefore a *singular bisecant*. It has three points in common with γ^7 and intersects α on the line of intersection a of q^3 and α . This line a is met by ten lines of q^3 ; all these lines are trisecants of γ^7 . Moreover a is cut in its point of intersection with γ^7 in five other trisecants. So the singular bisecants t form a *ruled surface* of *order fifteen* with γ^7 as *fivefold curve*.

3. Let x be the order of the surface \mathcal{A} formed by the curves q^4 meeting the line l . Then the surfaces \mathcal{A} and \mathcal{A}' corresponding to l and l' have in the first place the x curves q^4 in common, meeting l and l' . Through any other point of their intersection passes a q^4 meeting l and an other q^4 meeting l' ; therefore the residual intersection can only be composed of singular curves. As l cuts the surfaces α^5 , β^3 , and γ^2 , corresponding according art. 1 to points A , B , C of α^2 , β^2 , γ^7 , into 5, 3, and 2 points respectively, α^2 , β^2 , γ^7 are respectively fivefold, threefold and double curves on \mathcal{A} . So for the determination of x we find the relation $^1) x^2 = 4x + 5^2 \times 2 + 3^2 \times 2 + 2^2 \times 7$ giving $x = 12$.

We can verify this result as follows. If we make to correspond to each other any two surfaces q^2 and q^3 meeting one another on l we generate a correspondence (3,2) between them; thereby the points of an other line m are arranged in a (6,6)-correspondence, any coincidence of which is a point of intersection of two surfaces q^2 and q^3 having a point of l in common, and therefore a point of an q^4 resting on l . Therefore \mathcal{A} is of *order twelve*.

Besides the three multiple curves above mentioned \mathcal{A} admits still as double curves the two q^4 with l as bisecant.

4. On a plane q the congruence Γ determines a quadruple involution. If the point L describes the line l of q the three points joined to L by a quadruple will generate a curve λ^{11} determined by the surface \mathcal{A}^{12} corresponding to l (art. 3).

Among the points of intersection of l and λ^{11} the two couples of points of the q^4 for which l is a bisecant present themselves; the remaining seven are points of coincidence, i. e. points of contact of q with curves q^4 .

¹⁾ The surfaces \mathcal{A} have been used in a similar way by E. VENERONI, *Sopra alcuni sistemi di cubiche gobbe* (Rend. Palermo, XVI, 210).

The *curve of coincidences* q^7 , locus of these points, is obviously also the locus of the points of contact of the curves q^2 and q^3 of the pencils determined by the pencils (q^2) and (q^3) . These pencils have two base points A_1, A_2 in common, whilst (q^2) admits still the base points B_1, B_2 and (q^3) the base points $C_k (k = 1, 2, \dots, 7)$. Through B_k passes one curve q_k^3 containing ∞^1 quadruples with the common point B_k : one of these groups has a double point in B_k , from which ensues that B_k lies on q^7 . In an analogous way C_k belongs to ∞^1 quadruples lying on a q_k^2 and is therefore likewise a point of q^7 . Finally A_k is a triple point of q^7 and belongs to ∞^1 quadruples situated on the curve q_k^5 in which α_k^5 (art. 1) meets q . So the points of contact of the plane q with curves q^4 lie on a curve of order seven with two threefold points.

5. We will now consider the *branch curve*, i. e. the locus of the couples of points completing the coincidences to groups of the quadruple involution.

Any curve q^2 is touched in the double points of the I^4 determined by (q^3) on q^2 by six curves q^2 . By a quadratic transformation with A_1, A_2, B_1 as fundamental points we find that q^2 is touched by eight conics q^2 . So by considering as conjugate to each other two curves q^2, q^3 touching one another a correspondence (8, 6), is generated determining on any line m a correspondence (16, 18). The curve of order 34 generated by the two pencils breaks up into the curve of coincidences q^7 counted twice and the branch curve q^{20} .

By drawing m successively through A_k, B_k, C_k we find respectively an (8, 12), an (8, 18), a (16, 12). Taking into account the known multiplicity of these points on q^7 we come to the result that q^{20} passes eight times through A_k , six times through B_k , four times through C_k .

6 By using once more a quadratic transformation with the fundamental points A_1, A_2, B_1 the curve of coincidences q^7 is transformed into a curve π^7 having likewise triple points in A_1, A_2 and passing through B_1 and through the points B'_2, C'_k corresponding to B_2, C_k . The pencil (q^2) passes into the pencil of lines with vertex B'_2 , whilst the pencil (q^3) is transformed into a pencil of quartic curves φ^4 , the base of which consists of double points in A_1, A_2 and the points B_1, C'_k . Obviously π^7 is the polar curve of B'_2 with respect to (φ^4) , i. e. the locus of the points of contact of the curves φ^4 with tangents passing through B'_2 . The class of π^7 is 30; to the 28 tangents concurring in B'_2 belong the lines through A_k, B_1, C'_k (in each of these points a curve φ^4 is touched by the corresponding

line through B'_2). According to the definition of the polar curve the 18 other tangents are inflectional tangents of as many curves ψ^4 and therefore curves ψ^4 corresponding to conics q^2 osculated by a q^3 . So the quadruple involution contains 18 groups with three coinciding points. In other words, *each plane is osculated by eighteen curves q^4 .*

The curves q^7 and q^{30} will touch each other in 18 points. In the base points A, B, C they have $2 \times 3 \times 8 + 2 \times 6 + 7 \times 4 = 88$ points in common. The remaining 16 points of intersection form 8 couples of coincidence and belong to eight quadruples. Otherwise, *each plane is bitangent plane for eight curves q^4 .*

7. Let us now consider the bisecants of the curves q^4 through a point P and the surface Σ , locus of the couples of points S in which they meet these curves¹⁾. The curve q^4_P through P is projected from P by a cubic cone σ^3 , the edges of which touch Σ in P ; so P is a threefold point of Σ . Each line through P contains moreover two couples S ; so Σ is a surface of order seven.

On each edge of σ^2 still lies a second couple of points S ; so these couples generate a curve σ^6 of order six. As σ^3 and Σ^7 with the common curves q^4_P and σ^6 can have furthermore only straight lines in common, we find that *eleven singular bisecants* pass through P . To these belong the two common transversals s of α^2 and β^2 (art. 2); on the other ones (q^3) and (r^3) must determine the same l^2 , therefore they must meet γ^7 . So there is still a congruence of *order nine of singular bisecants* with γ^7 as *director line*.

An analogous consideration furnishes with respect to a congruence of twisted curves q^o of *order o* and *class c* the result that a point P bears in general $o(n-1)^2 + (n-2)$ singular bisecants²⁾. So this number is independent of the class.

However we must remark that this consideration does not hold for $o=1$, $c > 1$ and $n=2$; for then the cone projecting the conic through P out of P becomes a plane and the curve of intersection lying in this plane will also pass through P . But then the singular bisecants are lines of the surface enveloped by the planes of the conics and in general they form no congruence.

The surface Σ^7_P contains the singular curve γ^7 , for through each point C passes *one* q^4 cutting CP a second time. However the singular

¹⁾ For bilinear congruences the surfaces Σ have already been used by VENERONI (l.c. p. 212).

²⁾ For $o=1$, $c=1$ this number is n^2-n-1 . It was found in an analogous way by VENERONI (l.c. p. 212).

curves α^2 and β^2 are nodal curves of Σ_P^7 , each of their points A (B) bearing two curves φ^4 with AP (BP) as bisecant.

Any φ^4 has in common with Σ_P^7 the two couples of points on its two bisecants through P . Every other point of intersection is evidently singular. As the 8 points of intersection with α^2 and β^2 have to be counted for 16, these conics being nodal curves of Σ_P^7 , φ^4 must have eight points in common with γ^7 . *So the curves φ^4 of Γ have eight points in common with γ^7 , four points with α^2 and with β^2 .*

8. The points of contact of the tangents through P to the surfaces φ^2 and φ^3 lie on the polar surfaces Π^3 and Π^5 of P with respect to these pencils. In a point A of α^2 a φ^3 is touched in such a manner by a φ^2 that the tangent plane passes through P ; but in general the tangent in A to the common φ^4 does not pass through P . The surfaces Π^3 and Π^5 , touching each other along α^2 have still a curve π^{11} in common, which passes through P and through the points of contact of tangents through P to curves φ^4 . From this ensues that *the tangents to the curves φ^4 of Γ form a complex of order ten.*

Any plane through P cuts Σ_P^7 in a curve σ^7 with a triple point in P and four double points on α^2 and β^2 , and therefore of class 28. Of the 22 tangents through P ten belong to the complex of the tangents of Γ . The remaining 12 coincide in pairs to double tangents of σ^7 , i.e. in lines on which the involutions determined by (q^3) and (q^2) have two coincided pairs in common, so they are cut by only *one* φ^4 in two points. Evidently the lines possessing this property form a *complex of order six.*

9. The surface A^{12} corresponding to a line l (§ 3) is cut by a plane according to a curve λ^{12} passing respectively 5 times, 3 times, 2 times through the base points A_k, B_k, C_k (art. 4). So it has in common with the curve of coincidences q^7 in the base $2 \times 5 \times 3 + 2 \times 3 + 7 \times 2 = 50$ points; so there are 34 points of contact of q with a curve φ^4 cutting l ; in other words, the curves φ^4 touching a plane form a *surface of order 34 .*¹⁾

The surface α^5 corresponding to a point A of α^2 intersects q in a curve, passing twice through A_k , and once through B_k, C_k , and having therefore besides these points still $5 \times 7 - 2 \times 2 \times 3 - 2 - 7 = 14$ points in common with q^7 . So the surface φ^{34} mentioned just now meets 14 times the conic α^2 ; this agrees with the fact

1) This shows once more that the branch curve is a φ^{20} , for the surface under consideration has with φ in common the curve of coincidences counted twice.

that the curves q^7 and q^{20} , common to q and q^{24} pass together 14 times through $A_k^{(1)}$.

In the same manner can be shown that β^2 is an eightfold curve and γ^7 a sixfold curve of q^{24} .

The curve of coincidences ψ^7 of a plane ψ has in its points of intersection with $\alpha^2, \beta^2, \gamma^7$ evidently $2 \times 14 \times 3 + 2 \times 8 + 7 \times 6 = 142$ points in common with q^{24} ; in each of the remaining 96 points a q^4 touches ψ . So two arbitrary planes are touched by 96 curves q^4 .

10. Let us now consider the projective nets of quadrics represented by

$$\lambda a^2_x + \mu b^2_x + \nu c^2_x = 0 \text{ and } \lambda f^2_x + \mu g^2_x + \nu h^2_x = 0.$$

The congruence Γ of the quartic twisted curves q^4 , forming intersections of corresponding surfaces, is *linear*. For through any point Y passes the curve determined by the relations

$$\lambda a^2_y + \mu b^2_y + \nu c^2_y = 0 \text{ and } \lambda f^2_y + \mu g^2_y + \nu h^2_y = 0.$$

But under the condition

$$M = \begin{vmatrix} a^2_y & b^2_y & c^2_y \\ f^2_y & g^2_y & h^2_y \end{vmatrix} = 0$$

Y is a singular point bearing ∞^1 curves q^4 .

As $\begin{vmatrix} a & b \\ f & g \end{vmatrix} = 0$ and $\begin{vmatrix} a & c \\ f & h \end{vmatrix} = 0$ determine two quartic surfaces

having in common the curve $a = 0, f = 0$ not lying on $\begin{vmatrix} b & c \\ g & h \end{vmatrix} = 0$, the locus of the singular points is a twisted curve σ^{12} passing through the 16 base points of the two nets.

Evidently σ^{12} is the partial intersection of the quartic surfaces determined by

$$\begin{vmatrix} a & \beta & \gamma \\ a^2_y & b^2_y & c^2_y \\ f^2_y & g^2_y & h^2_y \end{vmatrix} = 0, \quad \begin{vmatrix} \alpha' & \beta' & \gamma' \\ a^2_y & b^2_y & c^2_y \\ f^2_y & g^2_y & h^2_y \end{vmatrix} = 0.$$

For these surfaces have in common the curve of the congruence Γ determined by

$$\Delta \equiv \begin{vmatrix} \alpha & \beta & \gamma \\ \alpha' & \beta' & \gamma' \\ a^2_y & b^2_y & c^2_y \end{vmatrix} = 0 \text{ and } \Delta \equiv \begin{vmatrix} \alpha & \beta & \gamma \\ \alpha' & \beta' & \gamma' \\ f^2_y & g^2_y & h^2_y \end{vmatrix} = 0.$$

and the curve σ^{12} denoted by $M = 0$.

¹⁾ In connection with this it must be remarked that in art. 8 of my communication quoted above an error has slipped in. The surface A^{24} mentioned there passes six times through the curves β^4 and β'^4 . So only 72 curves q^4 touch two planes.

Out of $\Delta = 0$ and $M = 0$ follows $\Delta' = 0$ or $a = b = c = 0$; out of $\Delta' = 0$ and $M = 0$ follows $\Delta = 0$ or $f = g = h = 0$. So $\Delta = 0$ and σ^{12} have, besides the 8 base points of the first net, 16 points in common lying at the same time on $\Delta' = 0$. Consequently each curve ϱ^4 of F cuts the *singular curve* σ^{12} in *sixteen* points.

11. On the line UV represented by $x_k = u_k + qv_k$ the nets $\sum_3 \lambda a^2 x = 0$ and $\sum_3 \lambda f^2 x = 0$ determine the pairs of points

$$\sum_3 \lambda (a^2_u + 2qa_u a_v + q^2 a^2_v) = 0, \quad \sum_3 \lambda (f^2_u + 2qf_u f_v + q^2 f^2_v) = 0.$$

These two equations will determine the same pair, if the relations

$$\sum_3 \lambda a^2_u = \sigma \sum_3 \lambda f^2_u, \quad \sum_3 \lambda a_u a_v = \sigma \sum_3 \lambda f_u f_v, \quad \sum_3 \lambda a^2_v = \sigma \sum_3 \lambda f^2_v$$

hold. Eliminating λ, μ, r we find the relation

$$\left. \begin{array}{ccc} a^2_u - \sigma f^2_u & b^2_u - \sigma g^2_u & c^2_u - \sigma h^2_u \\ a_u a_v - \sigma f_u f_v & b_u b_v - \sigma g_u g_v & c_u c_v - \sigma h_u h_v \\ a^2_v - \sigma f^2_v & b^2_v - \sigma g^2_v & c^2_v - \sigma h^2_v \end{array} \right| = 0,$$

which proves that UV is bisecant of three curves ϱ^4 ; so *the congruence is of the third class*.

12. Through a singular point S pass ∞^1 curves ϱ^4 lying on a surface Σ^4 , generated by two projective pencils of quadrics and having therefore a node in S .

The surface \mathcal{A} formed by the ϱ^4 having a point in common with a line l passes four times through σ^{12} , for l cuts Σ^4 in four points. So the order x of \mathcal{A} can therefore (§ 3) be deduced from the equation $x^2 = 4x + 192$ giving $x = 16$. So *two lines are met by sixteen* ϱ^4 .

The ϱ^4 cutting l meet any plane q through l in three points more lying on a curve λ^{15} ; among the points common to l and λ^{15} occur the three couples of points which l has in common with the curves ϱ^4 of which it is a bisecant; in each of the remaining 9 points q is touched by a curve ϱ^4 . So *a plane is tangential plane for nine curves* ϱ^4 .

The quadruple involution which the curves ϱ^4 determine in q has therefore a curve of coincidences q^9 of order nine. This curve is at the same time the locus of the double points of the net of quartic curves determined by

$$\left. \begin{array}{ccc} \alpha & \beta & \gamma \\ \alpha_x^2 & \beta_x^2 & \gamma_x^2 \\ f_x^2 & g_x^2 & h_x^2 \end{array} \right| = 0.$$

As this net admits 12 base points (points of intersection of q and σ^{12}) q^9 has *twelve double points*.

Geology. — *“Further considerations about the geology of Java.”*

By Prof. K. MARTIN.

(This communication will not be published in these Proceedings).

ERRATUM.

In the Proceedings of the meeting of Dec. 30, 1911, p. 678,
line 18 from the bottom: for IX read XII.

(April 25, 1912).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Friday April 26, 1912.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige
Afdeling van Vrijdag 26 April 1912, Dl. XX).

C O N T E N T S.

- V. E. NIERSTRASZ: "Some calorimetrical investigations relating to the manifestation and amount of imbibition heat in tissues". (Communicated by Prof. H. ZWAARDEMAKER), p. 1130.
- F. J. J. BUTTENDIJK: "On the ciliary movement in the gills of the mussel". (Communicated by Prof. H. J. HAMBERGER), p. 1138.
- D. F. TOLLENAAR: "On the influence of the earth's rotation on pure drift-currents". (Communicated by Dr. J. P. VAN DER STOK), p. 1149.
- C. P. COHEN STUART: "A study of temperature-coefficients and VAN 'T HOFF's rule". (Communicated by Prof. F. A. F. C. WENT), p. 1159. (With one plate).
- JAN DE VRIES: "On a congruence of the second order and the first class formed by conics", p. 1173.
- C. U. ARIENS KAPPERS: "The arrangement of the motor nuclei in *Chimaera monstrosa* compared with other fishes". (Communicated by Prof. L. BOLK), p. 1176.
- J. E. DE VOS VAN STEENWIJK: "Provisional results from calculations about the terms in the longitude of the moon with a period of nearly an anomalistic month, according to the meridian observations made at Greenwich". (Communicated by Prof. E. F. VAN DE SANDE BAKHUYZEN), p. 1180.
- W. KAPTEYN: "New researches upon the centra of the integrals which satisfy differential equations of the first order and the first degree", p. 1185.
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- J. D. VAN DER WAALS: "Contribution to the theory of binary mixtures". XX, p. 1217.
- A. F. HOLLEMAN and J. P. WIBAUT: "The nitration of ortho-chlorotoluene", p. 1230.

Physiology. — “*Some calorimetrical investigations relating to the manifestation and amount of imbibition heat in tissues*”. By Dr. V. E. NIERSTRASZ. (Communicated by Prof. ZWAARDEMAKER).

(Communicated in the meeting of February 27, 1912).

Amongst the numerous physico-chemical processes which throw more light upon the nature of function, an important place has been occupied of late years by imbibition¹⁾.

We mean of course the real molecular swelling, mostly viewed as a diffusion phenomenon²⁾, not the capillary or endosmotic imbibition. As a point of departure for some investigations in this direction we took imbibition-heat, other characteristics of the swelling viz. volume-contraction of the entire mass of substance + water³⁾, and swelling pressure, being more remotely connected with the nature of imbibition.

Keeping in view the fact that most calorimetrical determinations take up much time, we did not take the ice-calorimeter, generally⁴⁾ adopted for this purpose, but followed a method which, to a great extent, obviated this difficulty, and moreover, allowed of the determinations being made at the temperature of the room.

Our method was in principle a bolometrical one; the heat developed was measured by resistance-modifications in a thin copper-wire isolated with silk and wound bifilarly (thickness 0.1 millimètres, resistance 25 Ohms). We used two bolometers as much like each other as possible (b_1 and b_2 in the figure, length of tube 14 c.m., inner diameter 1,9 c.m., outer diameter 3 c.in.); the side was formed by a DEWAR's glass, which made the isolation as perfect as possible. These were taken up as branches in a system, based on the principle of WHEATSTONE's bridge, and had each as a counter-resistance

¹⁾ W. OSTWALD, Koll. Zustand der Stoffe, Oppenheimer's Hdb. d. Biochemie. Bd. I. p. 839.

L. MICHAELIS, Physik. Chemie der Kolloide in Handbuch Physik. Chemie und Medizin, Korányi und Richter. Bd. II. Leipzig 1908.

M. H. FISCHER, Das Oedem. Dresden 1910.

H. FREUNDLICH, Kapillarchemie. Leipzig 1909.

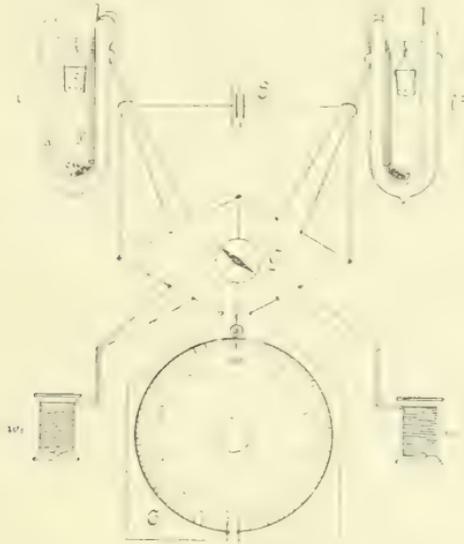
²⁾ J. Reinke, Untersuchungen über die Quellung einiger vegetabilischer Substanzen. Botanische Abhandlungen. Bd. IV. Heft 1.

³⁾ The substance itself of course increases in volume.

⁴⁾ O. KRUMMACHER, Ueber die Quellungswärme des Muskelfleisches. Zeitschrift für Biologie. Bd. 52 Heft 4 und 5.

V. D. HOEVE, Opzwelwarte der lenszelfstandigheid. Ned. Tijdschrift v. Geneeskunde. 28 Oct. '11.

a thin copper wire wound on a bobbin (w_1 and w_2) and a thin niccoline wire, any part of which could be added to the resistance



by means of a movable post, enabling us to fix the resistance at the length required. These two counter-resistances could undergo with respect to each other some modification in size by the insertion of a round compensator c of DU BOIS REYMOND, which on being turned effected another division of the lengths of the two parts to be passed by the current ($S =$ key, $G =$ galvanometer).

The DEWAR'S glasses were placed in a cube shaped calorimeter (length of the ribs 42 cm.) consisting of two layers, an inner layer of cork (thickness 3.5 cm.) and an outer layer of wood. A cover of the same materials closed the whole. The DEWAR'S glasses, fixed in a wooden stand, had been placed in the middle of the calorimeter on a narrow horizontal plank, the round extremity of which pierced the calorimeter on one side, and was connected with a wooden handle, which rendered it possible to make the whole revolve round a horizontal axis. An advantage of this was, that whilst the calorimeter and the DEWAR'S glass were closed, it was possible to effect the contact between tissue and fluid in the manner to be described below.

On either side the counter-resistances had been fastened to the inside on a little plank. The round compensator stood apart, likewise in a secluded space. It was covered by a glass plate, provided with a little opening from which a magnifying glass projected, which

allowed the divided scale to be read off accurately. The turning was effected by means of two cords, wound in different directions round the axis; these on being drawn rotated the divided scale in opposite directions. As these cords (like the current-wire) passed out through openings in the side, it was possible to effect the rotation with the box closed. In the same way the wire-connections of the calorimeter passed out.

All these were united, according to the above-mentioned plan, on a system of posts fastened on the outside (see fig.). It goes without saying that thorough isolation was necessary against the changes in the temperature (wadding, felt) for the counter-resistances inside, as well as for the connections outside.

The bolometer itself was composed as follows (see fig.). On the bottom of the DEWAR'S glass (*d*) were the clew-shaped¹⁾ copper wires, which were wound bifilarly. The two ends were led upward through a thin glass tube (*γ*) (fastened to the side with sealing-wax) and were connected by means of a thicker copper-wire with the posts.

The DEWAR'S glasses were closed by means of an india-rubber stopper, to the bottom of which a hook was attached on which the little pail (*e*) was hung, destined to contain the tissue to be experimented upon. Before the experiment began this had to remain of course above the level of the fluid in the tube (dimensions of the pail were: height 2.5 cm. outer diameter 1 cm.).

Thus it was possible, the bolometer being closed, to wait till the needle of the galvanometer was at rest, a state of perfect equilibrium having set in; then the handle was turned, which caused the pail to drop from the hook bringing it into contact with the fluid. Pail and bolometer-wire always came down immediately in the same position, side by side.

In order to determine the amounts of heat we did not make use of the deviations of the galvanometer needle, but of the extent to which the compensator had to be turned in order to keep the needle at zero. The divided scale of the compensator rendered it possible to read off this change. For shortness, sake we shall henceforward call the round compensator of DE BOIS REYMOND measuring-wire. It goes without saying that the relations between the volumes of heat developed, were different from those indicated by the measuring-wire (the measuring-wire forming only a small part of the counter-

¹⁾ At first we used a copper-wire, wound spirally on a pin 5 cm. high, in the middle of which the tissue came down. Its sensibility was, however, 5 times smaller than if the clew form was adopted, so that the latter was always used.

resistances), and that every point had to be separately determined. More will be said about this later on.

Now we intended to collect by means of the imbibition heat some data relating to the imbibition of different tissues of different animals. For this purpose we chose the fresh-water mussel, the rabbit, the pigeon, the neat.

Anodonta fluviatilis has two adductors, the central yellow part of which has the function of a fast muscle, whilst the peripheric white part may be for a long time in a state of tonus¹⁾. The parts of these muscles also differ histologically.

Since according to ENGELMANN the contraction is attended by a water displacement in the muscular fibrils, it is conceivable that the colloid substances of the hypothetical inotagmas absorb this water. It might be supposed then that in such muscles more substances liable to swelling are found than in the peripheric parts of the muscle, which are in a state of autotonus.

We experimented upon chopped up tissue, which was then exposed for half an hour to a hot current of air (40° C.) and was further dried during two days in a vacuum-exsiccator at 40°.

We then obtained a fine powder of which we established the amount of water lost, by weighing it before and after it was dried. When it was left longer in the exsiccator, this loss increased at most with 1—2%.

It is generally held that an arithmetrical decrease of water-percentage causes a geometrical increase of imbibition-heat. Here, however, the differences in water-percentage, during the various determinations of one tissue, were so small that they could not be recognized as influencing the results any more than the small temperature changes during the experiment (the extremes were 10 and 14° C.).

We subjoin the relative results of 10 series of experiments on anodonta-organs, both for the tissue-powder and calculated for the fresh tissue from these values, and the loss of water caused by exsiccation, which was known. To facilitate comparisons we fixed the value of the fast muscle at 100 whilst the other results were reduced in the same proportion. Our determinations were always made with doses of 50 milligrammes and we took the average scale-movement of the measuring-wire. In this way a slight mistake is made as these deviations are not quite proportional to the heat developed, but in the case of small differences this is not of much importance.

¹⁾ J. PARNAS, Energetik glatter Muskeln. Pflüger's Archiv., Bd. 13¹.

The time taken up by the experiment was 3, at most 5 minutes, after that no more heat was taken up. We always worked with equal volumes of fluid, the other conditions being likewise always the same, so that, to compare the results, the capacity for heat of the apparatus need not be taken into account. We may safely assume that with heat-quantities such as these the distribution of heat over copper-wire, fluid and glass is always effected in the same way, when the experiments are carried out in this manner.

Fresh water mussel.

Relative and average values of the imbibition-heat of:

	yellow (fast) muscule	white (autonomous) muscule	lever	organ of Bojanus	mantle	corpus
a. tissue-powder	100	80.9	71.7	65.1	36.5	38.3
b. calculated for fresh tissue .	100	80.3	40.2	51.1	41.9	47.8
c. loss of water by exsiccation	84.2%	83.5%	90.6%	88%	80.6%	78.9%

We observe indeed distinct differences and that most between the muscle-tissue on the one hand and the other tissues on the other.

These differences are still more manifest in the fresh tissue.

The difference between the two kinds of muscules exists so far that the fast muscle swells most, but it is too slight to admit of general conclusions being drawn from it as to the nature of the functions.

From the results obtained with dry powder it might further be inferred that the secretion or excretion organs such as liver and organ of Bojanus contain these substances in a higher degree than the other, more indifferent, organs. Possibly this may be connected with the secretory function of these organs; it may be conceived that the process of imbibition is of importance as a preparation to further stages.

Under exactly the same conditions the following series of experiments was carried out with the organs of the rabbit.

The loss of water caused by the exsiccatory process varied in different organs from 77 to 83%. We subjoin again some average relative results. On every organ at least 10 determinations were made (10—18).

Rabbit.

Relative and average values of the imbibition-heat of:

	white muscle	red muscle	kidney	brain	liver
<i>a.</i> tissue powder .	100	104.7	126.1	91.2	94.1
<i>b.</i> calculated for . fresh tissue . . .	100	114.4	114.4	78.3	93
<i>c.</i> average loss of water by exsiccation	78.6%	76.6%	80.6%	81.7%	78.9%

Here we find the differences between the tissues not so great as with anodonta; moreover we find, besides the muscles, especially the red one, the swelling of the kidneys at the head of the list; for the dry tissue it is even greatest. The swelling of the liver too, is above that of the central nerve-system. As in the case of anodonta we see here too that the secretion (excretion) organs have a relatively great imbibition-heat.

In order to be able to put absolute values by the side of these relative ones, various methods of measurement were adopted. The most satisfactory was that effected by JOULE'S heat.

For the current-circuit to be constructed the various wire-connections were chosen in such a manner that their resistance could be neglected; besides, however, a thin isolated niccoline-wire of a given resistance was also inserted into the circuit; this wire, wound in a spiral of no great height was put on the bottom of the pail.

Thus the spiral had exactly the same position as the tissue-powder in the experiment.

This resistance had been taken up into the circuit by being soldered to two thicker varnished wires, which issued from between stopper and glass side, and which were connected with the current-circuit by means of posts.

We had to experiment of course with such currents that their heat-development caused deviations on the measuring wire of about the same magnitude as those effected by the tissue-imbibition.

From the preceding determinations with glass-powder we knew approximately how much heat was set free at a given deviation; and could therefore establish, starting from the physical formula: heat =

$\frac{1}{4.2} i^2 \Omega t$, the quantities we had to deal with. The duration of the

current was fixed at 3 minutes, that is the time during which heat is still absorbed. The resistance of the niccoline-wire was 21 Ohms

at a thickness of 0.15 millimetres and a length of 40 centimetres.

At a temperature of 14° C. ¹⁾ we now got at a current-strength (\hat{i}) of 30, 40 and 50 milliampères (m.a.) deviations on the measuring-wire of 46, 66 and 105 division-marks respectively. These deviations, therefore, increased proportionately more than the strength of the current and less than its square, which might indeed be expected.

Of the deviations between two determined points which were pretty close to each other, we found the absolute value by linear interpolation. The trifling mistake thus made, could not be of much importance.

We saw that for the white muscle tissue of the rabbit the average deviation was 68.5, that is about as great as the one obtained at a current of 40 m.a. at the absolute determination (66). As, however dissolved and jelly-like substances gather on the clew of the bolometer, causing the deviations on this side to be 2 or 3 times smaller than on the other ²⁾ the determination of the absolute value ³⁾ must always take place immediately before or immediately after a series of experiments.

In the following series of experiments made with the muscle-tissue of the pigeon and neat, we made, therefore, an absolute determination in connection with every series and under the same conditions. Of the pigeon we used three kinds of muscles viz. the smooth tonic stomach muscle, the heart muscle, and a striated thoracal muscle and compared these values, both as regards their relative and their absolute imbibition-heat. In these experiments we used doses of 100

¹⁾ The current being the same the deviations increased somewhat at the ganging when the temperature fell.

²⁾ When it is thoroughly rinsed and left in water for one day, the old sensibility of the wire is restored, as compared with the other side. In the long run, however, some decrease seems to take place on both sides possibly by defects of the isolation manifesting themselves.

³⁾ This method we also applied in determining the effect of the volume of the fluid in the DEWAR'S glass. It was found to be very small.

We mostly put on both sides 10 cm³. into the tube but double this volume and a current of 40 ampères had no effect on the deviations. Also when we took 4 times this volume (5 and 20 cm³.) and a current of 100 m.a. the effect remained doubtful, at any rate but slight (a difference of only 4 division-marks). Hence the capacity for heat of that part of the fluid which was heated is at any rate but small, and moreover always the same; as we may further assume that the relative distribution of the heat over copper-wire, water and glass is always the same for the quantities of heat under consideration, it is unnecessary to pay any further attention to the capacity for heat of glass and water.

milligrammes; in the case of -pigeon I we made for every muscle 10 determinations, for pigeon II 5.

Pigeon I

	stomach muscle	heart muscle	thoracal muscle
a. average relative values.	100	90.2	89.9
b. absolute values per 1 gramme of tissue-powder	8.1	7.1	7.0 gramme-calories

It follows from the above figures that the tonic smooth stomach muscle has a somewhat greater imbibition-heat than the others, whilst there is no marked difference between the imbibition heat of heart-muscle and thoracal muscle.

Pigeon II.

	stomach muscle	heart muscle	thoracal muscle
a. average relative values.	100	86.9	97.8
b. absolute values.	10.2	8.5	9.9 gramme-calories

Here too the stomach muscle has the greatest imbibition-heat though the difference with the other values is smaller. The thoracal muscle has a somewhat greater imbibition-heat than the heart-muscle.

The average absolute values of the two series are therefore 9.15, 7.8 and 8.5 gramme calories.

Finally we shall compare these absolute values with those which were obtained by KRUMMACHER¹⁾ by means of BUNSEN'S ice-calorimeter as modified by SCHULTEN and WARTHA, so that an opinion can be formed about the two methods. KRUMMACHER determined the imbibition-heat of the musculus gluteus max. of a newly killed neat (killed one hour before); we did the same and proceeded as before.

As an average of 10 determinations with 100 milligrammes of tissue-powder we found per gramme of muscle-tissue an imbibition-heat of 11.6 gramme-calories.

KRUMMACHER found for dried muscle tissue, which, for the rest had been left unchanged, 8.3 gramme-calories, for flesh which had been extracted first 13.1 gramme-calories.

¹⁾ O. KRUMMACHER. Ueber die Quellungswärme des Muskelfleisches, Zeitschrift für Biologie, Bd. 52, Heft 4 und 5.

Our values are between these; somewhat greater, however, than his for flesh which had only been dried. Our method is superior to his in the following respects:

1. the imbibition takes place at a more physiological temperature.
2. the determination takes much less time; 4 determinations can be made in one hour.

Only further researches can bring to light the best method of investigation; for the present it seems to me that the advantages mentioned are of some importance.

The great amount of imbibition-heat developed even by inconsiderable volumes of tissue, is at all events remarkable.

Conclusions.

1. In a dried state the organs of anodonta as well as those of warmblooded animals are found to be liable to imbibition, which imbibition is attended by a considerable development of heat.

2. Generally speaking the muscle-tissue develops the greatest heat; then follow kidney and liver.

3. Between muscles contracting rapidly and those contracting more tonically (white and yellow adductors of anodonta, heart- and stomach-muscle of pigeon) the differences in imbibition-heat are too slight to be of much value for contraction theories. At any rate it is not found that muscles with rapid contraction always develop the greatest heat.

4. The amount of imbibition-heat is for muscle-tissue of the pigeon on an average 8.5 for that of the neat 11.6 gramme-calories.

5. Advantages of the bolometrical method are a more rapid determination, and imbibition at a more physiological temperature.

6. The sensibility of the method is very great, one division-mark on the measuring wire denoting on an average 1 or 2 hundredths of a gramme-calorie.

Physiology. — *“On the ciliary movement in the gills of the mussel”.*

By Dr. F. J. J. BUYTENDIJK. (Communicated by Prof. HAMBURGER).

(Communicated in the meeting of February 24, 1912).

Since the time when VALENTIN¹⁾ enumerated four chief forms of ciliary movement viz. the motus uncinatus, vacillans, undulatus and infundibuliformis, deviating forms of motion have been described by other investigators. Although even the untrained observer can, upon the whole, recognize these forms of ciliary movement in various

¹⁾ VALENTIN. Flimmerbewegung in WAGNERS Handbuch der Physiol. Bd. I p. 484—516.

objects, the further description of them, as given by VALENTIN and others, is subject to the greatest difficulties. An estimate as to the frequency of the ciliary movement can be formed with only a moderate degree of certainty, even by the best observers. MARTIUS¹⁾, however, applied the stroboscopic method in such a manner that the rapid rhythmical movements can be studied more easily. If we light up the cilia for a short time, every time when they are in the same position, then it seems as if the cilia are perfectly motionless. Now if the number of illuminations is greater than the number of periods of the ciliary movement, then it seems as if the cilia make a very slow periodical movement. According to MARTIUS' description a slow wave-like motion runs over the series of cilia. Already at the investigation of this author, however, the drawbacks of the stroboscopic method made themselves felt. The rapidity of the ciliary motion is either such that even at a very short exposure only a hazy picture is formed, or the vibration is so irregular that the moment of the exposure corresponds every time with another position of the cilium. Hence neither MARTIUS nor any other investigator gave an accurate description of the ciliary movements, based upon observations with the stroboscopic disc²⁾.

Therefore I gladly availed myself of an opportunity to study in the "Institut MAREY" the ciliary motion of the mussel, by means of the mikro-kinematographic method. I chose for the object of my experiments the gills of the mussel as it appeared to me that in other objects, for instance the epithelium at the bottom of the mouth of frogs, the cilia were much smaller, and that especially one row of them could not be obtained so easily in a preparation. For the purpose I held in view, a thin preparation, with cilia which were placed not too close together, was highly desirable.

The apparatus at my disposal was a kinematograph moved by a motor. To intercept the light a revolving disc was used, placed immediately before the film; this disc had a slit which could be regulated, so that the exposure could be reduced to 0,001 second. This short exposure could only be applied when the object was slightly magnified, apochromatic objective 16 millimetres, as the light which was concentrated on the preparation by means of an arc

¹⁾ MARTIUS. Verhandl. der physiol. Ges. zu Berlin Archiv. f. (Anat.) und Physiol. Physiol. Abt. 1884 p. 456—460.

²⁾ L. BULL writes for instance (Travaux de l'assoc. de l'Institut MAREY 1910 Tome II p. 51), "Son emploi (de la méthode stroboscopique), toutefois, est assez restreint, puisqu'elle ne fournit des résultats précis que lorsqu'il s'agit de mouvements absolument périodiques".

lamp with an objective-condenser of ZEISS, was found to be too weak when the preparation was strongly magnified. A second disc placed with its slit between lamp and microscope was likewise moved by the motor, so that the object was exposed as short as possible to the intense light and heat of the arc-lamp. Yet it was found in my experiments that a heating of the object could not be avoided. Especially whilst a suitable part of the preparation was looked for and during the adjustment, the heating was such as to render a further investigation of the motion impossible. On the other hand the ciliary motion remained unimpaired if the heating was compensated by a thin chamber, placed between condenser and object, in which ice-water was circulated. This chamber consisted of a brass ring, into which two thin brass tubes had been soldered, which was closed at the bottom by a slide, and at the top by a cover glass. The preparation was placed immediately on the cover glass, and covered with another glass.

In spite of all these imperfections I succeeded in obtaining good pictures, which could be of use in the analysis of ciliary vibrations.

ENGELMANN observed already that, besides the *motus uncinatus*, the *motus undulatus* is very often met with in the mussel. In explanation he writes on this subject¹⁾: “Obsehon nun eine derartige Form (*motus undulatus*) wenigstens bei sehr biegsamen längeren Cilien in derselben Weise, wie die erstbeschriebene (*motus uncinatus*) durch aktive Bewegungen ausschliesslich an der Basis hervorgerufen sein könnte, so lehrt doch das Vorkommen hakenförmiger Krümmungen und das mitunter zu beobachtende Schwingen ausschliesslich der Haarspitzen bei ruhendem Basalstück, dass die Haare auf allen Punkten ihrer Länge aktiv kontraktile sein können”.

Whilst the *motus uncinatus* can be sufficiently accounted for by a movement at the base, this “whip-like” movement seemed to be more complicated.

If we examine a preparation of the gill of a mussel, then we shall mostly see the cilia move backward and forward, perpendicularly on the plane in which the cilia are placed. Only in some places they move in the plane of the cilia. Although as a rule a *motus uncinatus* is to be observed then, yet it appeared to me as if a kind of wave-like motion was also observable. I have repeatedly kinematographed such rows of cilia, but the rows in the immediate neighbourhood disturbed the analysis of the movement. Yet I could very well recognize the *motus uncinatus* from these pictures. I cannot, however, describe it better than in the words of

¹⁾ ENGELMANN, Handbuch der Physiol. van Herman. Bd. I 1879. p. 387.

ENGELMANN: "das Haar krümmt sich während der Vorwärtsbewegung stark concav, etwa wie ein Finger by starker Biegung".

Sometimes, however, I succeeded, after long seeking, in finding in a preparation a cilium standing alone, which was mostly much longer than the other cilia. Such a cilium made then sometimes very regular whip-like movements. The entire period of such a



Fig. 1.

movement is represented in Fig. 1. The length of the whole period is $\frac{7}{28}$ sec., the characteristic difference between forward and backward movement is already visible. This was still more manifest in another film, made of another preparation. It shows the nature of the movement very distinctly. The number of pictures taken, amounted to 28 per sec.; the magnified pictures had been obtained with apochromatic objective 8 m.m. and projection-eye-piece No. 2, the film being about $\frac{3}{4}$ metres away from the eye-piece. The movements of the cilium had been made much slower by the refrigeration, and the periods took somewhat less than one second. By projecting a series of photos of this film at one place on paper, the drawings in Fig. II, III, IV, and V were obtained.

Let us now view Fig. II and IV. Although not alike they are of exactly the same type. The outstretched cilium, a small part of the basal part of which is visible, begins to bend, traversing whilst it is stretched out a circle segment, the basal part being approxi-

mately the centre; evidently the place where the cilium enters the cell-tissue is not the centre of the movement. When part of the



movement has been performed, the cilium looks like a stick, stuck into the ground in a slanting position. The point round which the circular motion takes place lies deeper in the tissue.

The simplest explanation is to assume that the tissue before the rootlets, by being contracted, causes the rootlets, and with it the whole cilium, to undergo this circular motion. The part of the cell-tissue which in the case in question is the probable cause of it, has been shaded in Fig. II to V.

The rapidity of the forward flexion of the hair is slight at first, increases fast, reaching its maximum between positions 4 and 5, 31 and 32 respectively; then the rapidity decreases fast again. It is difficult to ascertain at what point in the movement the greatest amount of labour is performed, as for a strictly mechanical (hydrodynamic) analysis too many data are still wanting. Presumably the greatest amount of labour is done at the point where the rapidity is greatest, at least if the curvature backward, coinciding with it, is supposed to be due to the resistant force. As at this time, moreover, the amount of fluid displaced is greatest, the labour performed will

have been all the greater at this stage. The positions 9 to 16, and 33 to 38 respectively, correspond in my opinion more or less with a period of rest, during which the slight and especially irregular movements downward would have to be explained from a passive motion of the cilium, caused by the fluid.

How the bent down cilium is raised again the figs. III and IV demonstrate. Examination of the positions 17, 18, 19 and 39, 40, 41, 42 respectively, reveals a curve setting in at the rootlet. From the shape of this curve, but more especially from the backward movement of the point where the cilium enters the tissue, it may be inferred that the starting-point of the upward movement is found *in that part of the cilium which is enclosed within the cell*. From the positions 19 and 42 a contraction wave runs to the top of the cilium. This contraction wave, however, is of a peculiar kind. That half of the cilium which is turned away from the direction of the movement, is found to contract in its successive parts. This contraction can only result in the erection of the cilium, as it cannot bring about a shortening of the whole. The velocity of the propagation is not a perfectly uniform one, but it seems to increase towards the top. Whether this is due to mechanical causes or is to be looked upon as being peculiar to the contractionwave in these cilia, is difficult to decide. When the cilium is erect, the downward movement, described above, sets in again.

To give a clearer insight into the mechanism I have added a schematic drawing in Fig. VI. *a* represents the point of entrance of

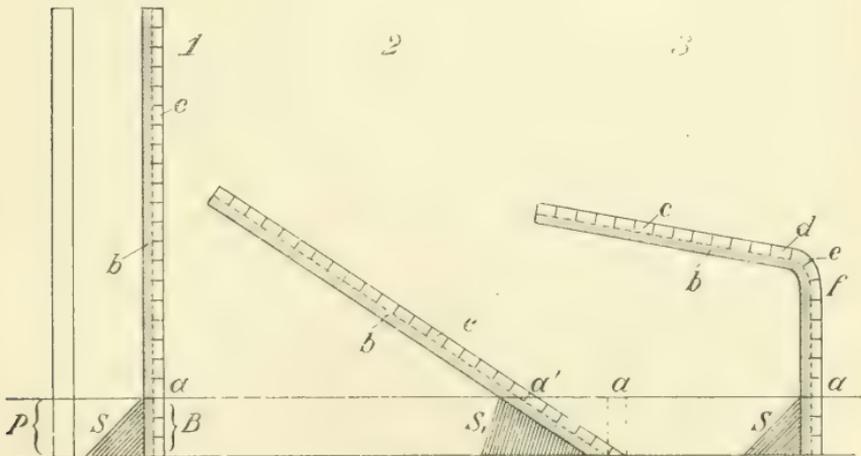


Fig. VI

a cilium, drawn in a bent down position, whilst it is in course of erection, *b* is the non-contractile part, which, besides this one, also has the following properties. It is flexible to the left, in the figure, inflexible on the other side, incompressible length-wise. We can, therefore, aptly compare this half of the cilium by a long bag, filled with fluid, being non-elastic on that side which is always exposed to the pressure of the fluid. That side, however, which joins the second contractile part of the cilium is elastic. *c*. Represents the contractile part of the cilium, in which a number of contractile elements (inotagmas) have been drawn. *f*, in position 3, represents an inotagma which has just shortened itself and is now in tonus. *e* is the succeeding element, which is stretched and about to shorten itself; *d* an inotagma which is still in a state of rest and will be stretched by the contraction of *e*. The shaded parts *S, S, S*, represent the protoplasm of the basal-border which contracts rhythmically. If we assume that the motus uncinatus is caused by such a mechanism as the one described here, then it need only be supposed that part *b* of the cilium is less flexible, and that hence part *c*, (which is stretched out in its full length in position 2) contracts entirely when the contraction in *S* relaxes. We arrive then at the simple conception *that the co-ordinated movement of the cilia is effected exclusively by the contraction-wave in the hyaline border*. The contraction of the successive parts causes the bending down of the backward cilia; the cause or stimulus of their erection must be sought in the relaxation of these contractile parts. Besides those mentioned here, many observations lend support to this supposition. KRAFT¹⁾ for instance found that stimuli are also transmitted through places where the cilia moved no longer. Hence he concludes: "Die Coordination beruht nicht bloss auf einer äusseren sondern wesentlich auch auf einer inneren, von Oberzelle zu Unterzelle stattfindenden Reizübertragung beziehungsweise Leitung". VERWORN²⁾ demonstrated that the ciliary organs of etenophora never moved unless a slight quantity of protoplasm was fixed to them.

On the other hand it seems that flagelli, tails of spermatozoa etc. can make movements independent of the body³⁾. Moreover it should be observed that the movements of only the tops of the cilia seem to prove that exceptions to this movement-scheme may occur, *although under abnormal conditions*.

To effect a forward movement of the fluid, whilst the cilia only move to and fro, the forward movement must be more rapid than

1) KRAFT. Pflüger's Archiv. Vol. 47. pp. 196—235.

2) VERWORN. Pfl. Archiv. Vol. 48 pp. 149—181.

3) See Pütte's Ergebnisse Physiologie. Vol. 1, 2. pp. 40 and foll.

the return one (ENGELMANN)¹⁾. KRAFT estimated at a retarded ciliary motion in the mucous membrane of the mouth of the frog the "Vorschwung viel schneller (vielleicht fünfmal so schnell) als der Rückschwung". Besides by a difference in velocity, the mechanical effect on the surrounding fluid may be brought about by a difference in the manner of movement of downward and upward stroke, of which our case forms an example.

I have also tried to trace in my film this difference in velocity when forward and backward stroke were symmetrical.

It appears that the cilia could be measured most easily on those films on which cilia had been photographed which move in a direction, perpendicular to the row of cilia. Although at these measurements it was found that the frequency of the ciliary movement was not great as a rule (2—5 per second) yet at this small frequency the velocity of the forward movement was so great that it was difficult to draw from my films (28 photos per second) accurate conclusions as regards this matter.

I, therefore, gladly availed myself of the photos of the ciliary motion in the gills of mussels which M. NOGÛÈS, technical assistant at the Institut Marey, kindly put at my disposal²⁾. These photos had been made at a velocity of 120 per sec., and were perfectly clear. I take this opportunity of offering again my hearty thanks to M. NOGÛÈS for his kindness.

The very difficult measurement of the cilia was made on the copies of the film on bromide paper. By strongly magnifying them they

T A B L E I.

Numb. of the photo	length of cilium	N ^o .	length										
1	1.7	9	2.2	17	4.5	55	4.5	63	1.4	71	3	79	4.6
2	1.7	10	2.3	18	4.5	56	4.4	64	1.4	72	3.4	80	4.6
3	1.7	11	2.6	19	4.5	57	3.6	65	1.4	73	3.9	81	4.6
4	1.7	12	3.4	20	4.5	58	2.2	66	1.5	74	4.2	82	4.6
5	1.7	13	4	21	4.5	59	1.4	67	1.5	75	4.2	83	4.6
6	1.7	14	4.5	22	4.5	60	1.4	68	1.9	76	4.4		
7	2	15	4.5	23	4.5	61	1.4	69	2.2	77	4.6		
8	2.1	16	4.5	—	—	62	1.4	70	2.4	78	4.6		

¹⁾ ENGELMANN. *Jenaische Zeitschr.* l.c.

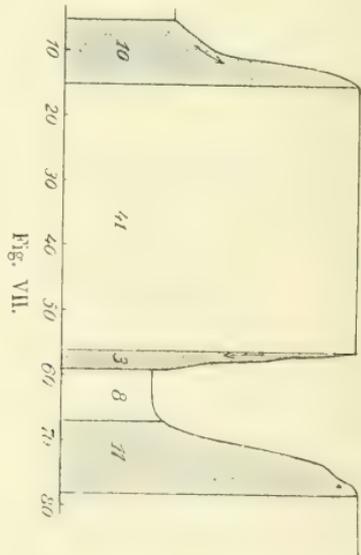
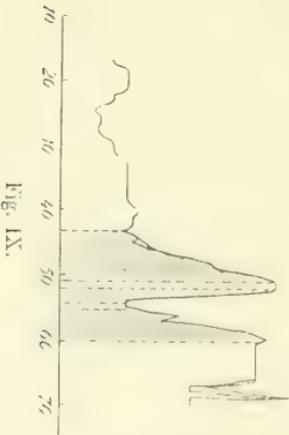
²⁾ For technicalities see the article of Mr. CARVALLO in the *Travaux de l'Institut Marey*, I. 1909, containing also the picture of part of a film.

could accurately be measured to $\frac{1}{10}$ of a m.m. It is often difficult, however, to identify the same cilia on the successive photos. The values found, were united in a table and then drawn on millimetre paper. An example of the figures follows in Table I belonging to Fig. VII.

It was now found that the resulting curves could be reduced to some types of which I shall give a few examples here.

If we look upon the movement of the cilium as that of a bar, describing with one of its ends as a centre a certain angle to and fro, then the values measured by me are only proportional to the sines of the angles, which values when represented graphically might give a correct picture of the movement. As, however, both from the examination of the films and from all observations of ciliary motion it must be presumed that the stroke of the cilia does not entirely correspond with this simple form of motion, it seemed useless to me to base any further calculations on the values arrived at. Likewise speculations on the mechanical and hydrodynamical action of the ciliary stroke ¹⁾ must, owing to the great number of unknown factors, be so inaccurate as to be absolutely unreliable.

In the first place the figures VII, VIII, IX and X show that the



¹⁾ See a.o. O. WEISS, Handbuch von NAGEL Vol. 4 p. 679.

downward movement is indeed much more rapid than the upward one. It is true the proportion is not 1 : 5 (as stated by KRAFT l.c

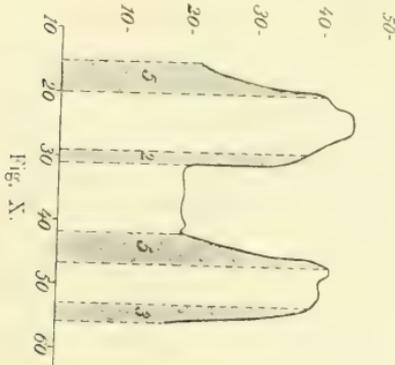


Fig. X.

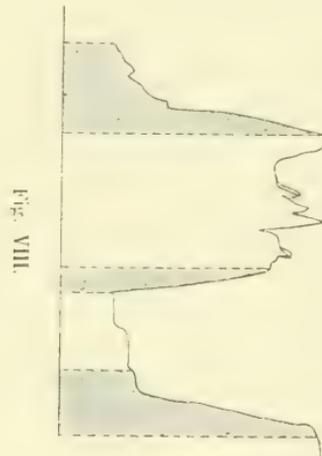


Fig. VIII.

but 3 : 10 (11); 4 : 10 (14); 2 : 8 (6) in Fig. X on the other hand 2 (3) : 5 and in Fig. XII : 4 to 1 : 1 $\frac{1}{2}$. To what extent this irregularity has been caused by

abnormal physiological or mechanical conditions is difficult to trace. In the preparation of the mussel-gill hardly ever the almost perfect regularity is to be observed, which characterizes the mucous membrane in the mouth of the frog.

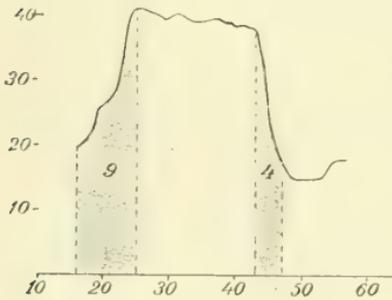


Fig. XI.

This inequality is also met with when viewing the periods of rest. The period of rest occurs in Fig. VII almost entirely in the outstretched position of the cilium ; in Fig. IX on the contrary, whilst bent. In Fig. VIII and X the period of rest is divided and lasts about as long in the outstretched as in the bent position.

This seems to be the rule according to my measurements.

The relation of the time of rest to that of motion may be seen from the curves. As an average value I should fix it at 5 : 1. The only conclusion which may safely be drawn is, that relatively the period of rest as opposed to that of motion is much greater than for instance with the heart. Yet in the normal condition stated here,

modifications may manifest themselves. The three deviations which



Fig. XII.



Fig. XIII.

must be defined sharply were probably caused by excessive heating. They were :

1. Too great an acceleration of the frequency. If it increased considerably (to 20 strokes per second) then it was at the expense of the period of rest ; moreover the movement grew more irregular. The drawing in Fig. XII illustrates this phenomenon. In this abnormal motion the difference in time of forward and return-movement disappeared ; this occurred also in the second case.

2. Movement of the tops of the cilia only. Fig. XIII gives an instance of this. We see the regular vacillating motion, with motions up and down which take up the same time, alternated with an equal period of rest.



Fig. XIV.

3. The combination of the 2 abnormal conditions. In Fig. XIV a rapid, irregular motion of the top of a cilium has been drawn. Only the extreme fifth part of the cilium is still in motion (whether active or passive cannot be ascertained).

Finally I beg to tender my thanks to Dr. L. BULL for his great kindness in putting time and materials at my disposal, thus enabling me to carry out this investigation.

Groningen, February 20th 1912.

Metereology. — “*On the Influence of the Earth's Rotation on pure Drift-Currents*”. By Dr. D. F. TOLLENAAR. (Communicated by Dr. J. P. VAN DER STOK).

(Communicated in the meeting of March 30, 1912).

The water of a laterally unbounded sea, initially at rest, is supposed to be suddenly subjected to the influence of a wind of constant magnitude and direction. Assuming a left-handed axial system of which the Z -axis points vertically downwards, the current-components u and v will have to satisfy the differential equations:

$$\begin{aligned}\frac{\partial u}{\partial t} &= av + b \frac{\partial^2 u}{\partial z^2} \\ \frac{\partial v}{\partial t} &= -au + b \frac{\partial^2 v}{\partial z^2}\end{aligned}$$

in which

$$a = 2n \sin \varphi.$$

$$n = \text{angular velocity of the earth} = 7.3 \times 10^{-5}.$$

φ = geographical latitude.

$$b = \frac{\mu}{\rho}.$$

μ = viscosity coefficient of water

ρ = density.

Starting with the assumption of a sea of infinite depth, we have the conditional equations: $u = v = 0$ for $t = 0$ and $z = \infty$. The assumption of a constant wind, whose direction we take along the Y -axis, may be expressed by the equations:

$$\begin{aligned}\left(\frac{\partial u}{\partial z}\right)_{z=0} &= + \frac{k}{\mu} V_0 \\ \left(\frac{\partial v}{\partial z}\right)_{z=0} &= - \frac{k}{\mu} (V - v_0),\end{aligned}$$

if V represents the magnitude of the wind and k the external viscosity coefficient.

The differential equations are solved in the simplest way by introducing a new variable $u + iv = w$, by which substitution they are transformed into:

$$\frac{\partial w}{\partial t} = - iaw + b \frac{\partial^2 w}{\partial z^2} \dots \dots \dots (1)$$

Putting likewise $iV = W$ the conditional equations become: $w = 0$ for $t = 0$ and for $z = \infty$;

$$\left(\frac{\partial w}{\partial z}\right)_{z=0} = -\frac{k}{\mu} (W - w_0).$$

Putting $w' = we^{iat}$, the equations change to

$$\frac{\partial w'}{\partial t} = b \frac{\partial^2 w'}{\partial z^2}, \dots \dots \dots (2)$$

$w' = 0$ for $t = 0$ and $z = \infty$,

$$\left(\frac{\partial w'}{\partial z}\right)_{z=0} = -c (W e^{iat} - w'_0),$$

$\frac{k}{\mu}$ being $= c$.

If we now introduce a function q , connected with w' by

$$q = -w' + \frac{1}{c} \frac{\partial w'}{\partial z} \dots \dots \dots (3)$$

q will also have to satisfy the differential equation (2) and secondly we must have

$$q_0 = -w'_0 - (W e^{iat} - w'_0) = -W e^{iat}.$$

Hence q satisfies the differential equation $\frac{\partial q}{\partial t} = b \frac{\partial^2 q}{\partial z^2}$ and q_0 is a function of t .

The solution of this equation is known from the theory of heat-conduction and is

$$q = -\frac{2}{\sqrt{\pi}} \int_{\frac{z}{2\sqrt{bt}}}^{\infty} W e^{-\beta^2 + ia} \left(t - \frac{z^2}{4b\beta^2}\right) d\beta, \dots \dots \dots (4^1)$$

Here W is constant by assumption; if W , the magnitude of the wind, were itself a function $W(t)$ of t , we should have under the sign of integration instead of W : $W\left(t - \frac{z^2}{4b\beta^2}\right)$. This remark will be useful later on.

(3) gives

$$w' = -ce^{cz} \int_{\frac{z}{2\sqrt{bt}}}^{\infty} e^{-c\lambda} q(\lambda) d\lambda$$

and finally

$$w = \frac{2ce^{cz}}{\sqrt{\pi}} W \int_{\frac{z}{2\sqrt{bt}}}^{\infty} e^{-c\lambda} d\lambda \int_{\lambda}^{\infty} e^{-\beta^2 - \frac{ia\lambda^2}{4b\beta^2}} d\beta \dots \dots \dots (5)$$

1) RIEMANN—WEBER. Partielle Different gleich. II p. 106.

The form of solution (5) gives rise to the following remarks: One would feel inclined, since (5) holds for a sea of infinite depth, to suppose that the solution for a sea of finite depth h could be given in the same form, the upper limit of integration for λ being h instead of ∞ , since the differential equations and other conditional equations remain the same in this case. This conclusion would be wrong, however; the modified integral would be found no longer to satisfy the differential equation. The reason of this is found in the circumstance that although the function φ , of eq. (3) must satisfy the same diff. eq. as w' , this by no means involves that w' will satisfy this diff. eq. together with φ . On closer investigation this appears to be the case only when the upper limit is infinite.

By introducing the new variable ξ and putting $\beta^2 = \frac{\lambda}{2V/b\xi}$ the solution (5) may be transformed into

$$w = \frac{ce^{cz}}{2\sqrt{b\pi}} W \int_z^\infty e^{-c\lambda} d\lambda \int_0^t e^{-\frac{\lambda^2}{4b\xi} - i\alpha\xi} \frac{d\xi}{\xi^{3/2}}$$

Now putting $\lambda = 2b\xi \left(\frac{\lambda}{2b\xi} + c \right) - 2cb\xi$, we obtain:

$$w = cW \sqrt{\frac{b}{\pi}} \int_0^t e^{-\frac{z^2}{4b\xi} - i\alpha\xi} \frac{d\xi}{\xi^{3/2}} - c^2 W \sqrt{\frac{b}{\pi}} \int_0^{\xi=t} \int_0^\infty e^{-\frac{(\lambda+c\xi)^2}{4b\xi} - c\xi - i\alpha\xi} d\lambda d\xi \quad (6)$$

The solution for w was reduced to the form (6) in order to render comparison easier with the solution, given for the same problem by FREDHOLM¹⁾ and which for various reasons seemed to me to be theoretically inaccurate. For the assumption of a constant wind along the Y -axis is expressed by FREDHOLM in the conditional equations $\left(\frac{\partial u}{\partial z} \right)_{z=0} = 0$, $\left(\frac{\partial v}{\partial z} \right)_{z=0} = -\frac{T}{\mu}$, T being taken constant. To this form of the conditional equation he was probably led, because EKMAN had already found the solution of the stationary problem (in which the first members of the diff. eq. are put zero), and had used the same conditional equations as expressing a constant wind. Now these are right indeed in the stationary problem. For it is always possible to choose the axial system such that the X -axis has a direction along which the constant wind-velocity and the in this case constant surface-current velocity have equal components. The Y -axis then lies in the

¹⁾ EKMAN. On the influence of the earth's rotation on ocean currents. Archiv für Matematik, etc. p. 16. 1905.

direction of the relative motion of the wind with respect to the water of the surface. It will presently be shown that in this case also a similar choice of axes is not to be recommended. Still it is theoretically the correct expression for the existence of a wind of constant direction and magnitude. But in the non-stationary problem matters are different. Here also it is possible to choose at a certain moment the axes such that the components of wind and surface current along the X -axis are equal and hence the conditional equation $\left(\frac{\partial u}{\partial z}\right)_{z=0} = 0$ holds, but this direction would have to rotate with the time, since now the current velocity is variable. Hence the conditional equations only express the condition of a constant wind with a variable system of axes. Since, however, the diff. equations only hold for a set of axes fixed in the earth, FREDHOLM's solution cannot be theoretically correct. FREDHOLM indeed finds a solution for which the u and v at the surface are, as we might expect, functions of t . Now if we bear in mind that his conditional equations have no other meaning than that the wind component in the X -direction is always equal to that of the surface current and that the difference of these components along the Y -axis remains constant, it follows at once that his conditional equations really presuppose a wind which is the same function of the time as the surface current.

Consequently, if FREDHOLM finds

$$w = \frac{iT}{\mu} \sqrt{\frac{b}{\pi_0}} \int_0^t \int_0^{2\pi} \frac{e^{-\zeta^2} \sin \alpha \zeta}{\zeta^{3/2}} d\zeta \dots \dots (7)$$

this solution can only be correct for the assumption of a wind, the components of which must be given by

$$U = \frac{T}{\mu} \sqrt{\frac{b}{\pi_0}} \int_0^t \int_0^{2\pi} \frac{\sin \alpha \zeta}{\zeta^{3/2}} d\zeta$$

$$V = \frac{T}{k} + \frac{T}{\mu} \sqrt{\frac{b}{\pi_0}} \int_0^t \int_0^{2\pi} \frac{\cos \alpha \zeta}{\zeta^{3/2}} d\zeta.$$

Comparing FREDHOLM's solution (7) with the solution (6) found by us, and remembering that $W = iV$ and $c = \frac{k}{\mu}$, it will be seen that the first part of (6) corresponds with FREDHOLM's solution and the second part ought to contain the theoretically required correction.

Now the following reasoning suggests itself: If in formula (6) we

suppose W not to be constant, but some function of t (which would modify this formula as explained under (4)) and if for this special function of t we take the above given expressions for U and V , which according to me contain FREDHOLM's equations of condition implicitly, we must obtain the solution of FREDHOLM. After some reductions of the integrals this appears to be indeed the case.

In order to judge of the practical value of the correction, we write (6) in this way:

$$w = cW \sqrt{\frac{b}{\pi}} \int_0^t \frac{e^{-\frac{z^2}{4b\zeta^2} - ia\zeta}}{\zeta^{1/2}} \left(1 - c \int_0^\infty \frac{e^{-\lambda^2 + 2\lambda x - c\lambda}}{4b\zeta^2} d\lambda \right) d\zeta.$$

Introducing the variable $\lambda' = \frac{\lambda}{2\sqrt{b\zeta}} + c\sqrt{b\zeta}$ we have for the surface current

$$w_0 = cW \sqrt{\frac{b}{\pi}} \int_0^t \frac{e^{-ia\zeta}}{\zeta^{1/2}} \left(1 - 2c\sqrt{b\zeta} \int_{c\sqrt{b\zeta}}^\infty e^{-\lambda'^2} d\lambda' \right) d\zeta.$$

Now $2xe^{x^2} \int_x^\infty e^{-\lambda'^2} d\lambda'$ is a function, the value of which is zero at $x = 0$, then rapidly rises and amounts already to 0.91 at $x = 2$ and then slowly approaches the value 1 for $x = \infty$. At $x = 0.06$, however, its value is only $1/10$. Now if t is such that the $c\sqrt{b\zeta}$ belonging to this limit does not exceed 0.06, the correction may practically be neglected. The data for a determination of $c\sqrt{b\zeta}$ are very scarce, but still it is possible to state something about the order of magnitude. This turns out, as will be explained presently, to be of the order 10^{-7} . Hence the correction may be neglected in practice if $c\sqrt{bt} < 0.06$ or $t < 4.10^4$ i.e. about eleven hours. Thus FREDHOLM's formula, although theoretically inaccurate, is practically serviceable for studying the development of the current. If in formula (6) without a correcting member we put W not constant but a function of t , the solution is, as we saw,

$$w = c \sqrt{\frac{b}{\pi}} \int_0^t W(t-\zeta) \frac{e^{-\frac{z^2}{4b\zeta^2} - ia\zeta}}{\zeta^{1/2}} d\zeta,$$

which formula would enable us to follow the development of the current if we assumed a time-function for the wind, which would then e.g. gradually increase or decrease.

Putting $t = \infty$ in formula (5) we must find the formulae for the

stationary case. Introducing the quantity $a' = \sqrt{\frac{a}{2b}}$ we find:

$$w = \frac{cV}{c + (1+i)a'} e^{-(1+i)a'z},$$

from which follows for the current components

$$u = \frac{cV}{\sqrt{a'^2 + (a'+c)^2}} \sin(a'z + \xi) e^{-a'z},$$

where $tg \xi = \frac{a'}{a'+c}$

$$v = \frac{cV}{\sqrt{a'^2 + (a'+c)^2}} \cos(a'z + \xi) e^{-a'z}$$

Hence for the surface current

$$\begin{aligned} u_0 &= \frac{cV}{\sqrt{a'^2 + (a'+c)^2}} \sin \xi = \frac{a'cV}{a'^2 + (a'+c)^2} & \frac{u_0}{v_0} &= tg \xi \\ v_0 &= \frac{(a'+c)cV}{a'^2 + (a'+c)^2} \\ s_0 &= \frac{cV}{\sqrt{a'^2 + (a'+c)^2}} \end{aligned}$$

If in the accompanying figure OV represents the magnitude of the wind, OS_0 the surface current, $\angle VOS_0 = \xi$. It is easily found that

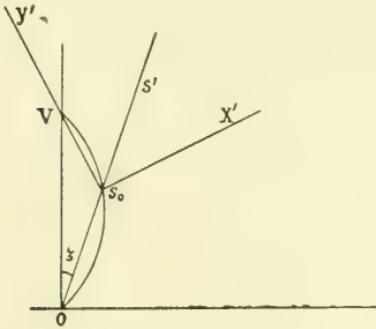
$$S_0V = \frac{a'\sqrt{2}}{\sqrt{a'^2 + (a'+c)^2}} V \quad \text{and} \quad \sin S_0VO = \frac{c}{\sqrt{a'^2 + (a'+c)^2}} \frac{1}{2} \sqrt{2}$$

This shows that the terminal point S_0 lies on a circular arc with chord OV and apical angle 135° . S_0V now represents the relative velocity of the wind which EKMAN took for V -axis in his solution of the stationary case. Referring the result to these axes and putting $S_0V = V'$ we have:

$$\begin{aligned} u' &= \frac{cV'}{a'\sqrt{2}} e^{-a'z} \cos(45-a'z) & u'_0 &= \frac{cV'}{2a'} & \angle VS_0S' &= 45^\circ. \\ v' &= \frac{cV'}{a'\sqrt{2}} e^{-a'z} \sin(45-a'z) & v'_0 &= \frac{cV'}{2a'} \\ s'_0 &= \frac{cV'}{a'\sqrt{2}} \end{aligned}$$

These are indeed the formulae obtained by EKMAN, if $cV' = \frac{kV'}{\mu} = \frac{T}{\mu}$.
EKMAN'S choice of axes and his formulae in the shape $u'_0 = v'_0 = \frac{T}{2\mu a'}$,

the angle between surface current and relative wind velocity = 45° , reckoned to the right for northern, to the left for southern latitude, led him to the wrong conclusion that, since a' becomes zero at the equator, the current there would become infinite and also that a sudden change in the direction of the current would take place there. It is not difficult to see now where the error in his conclusion lies. It is only as long as one remains on the same spot that the quantity T' , used by him, is constant; as soon as the results for different



latitudes are compared $T' = kV' = \frac{ka'\sqrt{2}}{V'a'^2 + (a'+c)^2}$ changes its value together with a' . And since T' becomes zero at the equator together with a' , the result is by no means that the current velocity becomes infinite, but simply that it becomes equal to V , as is obvious. At the same time we see from the value of ξ , that at the equator ξ approaches zero and that consequently the current, although rapidly, yet gradually approaches the absolute wind velocity and begins to deviate to the left for southern latitude.

If we put in the result for the stationary current velocity $s_0 = \frac{T}{\mu a' \sqrt{2}} = \frac{kV' \sqrt{b}}{\mu \sqrt{a}} s_0 a = n$ ($f=30^\circ$), it follows that $\frac{s_0^2}{V'^2 n} = \frac{k^2 b}{\mu} = c^2 b$. This now enables us to make an estimate of the value $c^2 b$, which we wanted for the correction of FREDHOLM's formula. According to MONN's observations $\frac{s_0}{V'}$ is of the order 4×10^{-2} , so that $c^2 b$ is $16 \times 10^{-4} \times 0.73 \times 10^{-4}$ i. e. of the order 10^{-7} , as we assumed.

The solution for a sea of finite depth was given by EKMAN only for the stationary case, neither does FREDHOLM deal with the non-stationary problem for this case. Since, as we saw, the theoretical correction of FREDHOLM's formula may be practically neglected for infinite depth, I felt justified in treating this case with FREDHOLM's equations of condition $\left(\frac{\partial u}{\partial z}\right)_{z=0} = 0$, $\left(\frac{\partial v}{\partial z}\right)_{z=0} = -\frac{T}{\mu}$; the formulae with the theoretically correct conditional equation become in this case unnecessarily complicated for practical application.

The differential equations for the case of finite depth remain the same. The conditional equations now become

$$u = v = 0 \quad \text{at} \quad t = 0 \quad \text{and} \quad z = h, \quad \left(\frac{\partial u}{\partial z} \right)_{z=0} = 0, \quad \left(\frac{\partial v}{\partial z} \right)_{z=0} = -\frac{T}{\mu}.$$

The solution is here found, as in the analogous problem in heat conduction, when the length of the bar is assumed finite, in the form of a FOURIER series. It runs:

$$w = j(z) = \frac{2}{h} \sum_{m=0}^{\infty} e^{-\frac{(2m+1)^2 \pi^2}{4h^2} t - i\alpha t} \cos \frac{(2m+1)\pi z}{2h} \int_0^h f(\lambda) \cos \frac{(2m+1)\pi \lambda}{2h} d\lambda \quad (8)$$

where

$$f(z) = \frac{T(1+i) \sinh.(1+i)a'(h-z)}{2\mu a' \cosh.(1+i)a'h}$$

a' being $= \sqrt{\frac{a}{2b}}$. This $f(x)$ is the solution for $t = \infty$, i.e. for the stationary problem. It is easy to show that this solution satisfies the differential as well as the conditional equations.

Since

$$\int_0^h f(\lambda) \cos \frac{(2m+1)\pi \lambda}{2h} d\lambda = \frac{h}{2} \frac{T(1+i)}{2\mu a'} \frac{8(1+i)a'h}{(2m+1)^2 \pi^2 + 4(1+i)^2 a'^2 h^2}$$

(8) may be written

$$w = j(z) = \frac{2iTb}{\mu h} \int_0^{\infty} e^{-i\alpha t} d\lambda \sum_0^{\infty} e^{-\frac{(2m+1)^2 \pi^2 b}{4h^2} t} \cos \frac{(2m+1)\pi z}{2h} \quad (9)$$

Now the summation in (9) may be reduced to another form. We have namely:

$$\sqrt{\frac{p}{\pi}} \sum_{n=-\infty}^{\infty} e^{-\rho(2n+y)^2} = 1/2 + \sum_{q=1}^{\infty} e^{-\frac{q^2 \pi^2}{4\rho}} \cos q\pi y \quad (1)$$

Putting likewise

$$\sqrt{\frac{p}{\pi}} \sum_{n=-\infty}^{\infty} e^{-\rho(2n+1-y)^2} = 1/2 + \sum_{q=1}^{\infty} e^{-\frac{q^2 \pi^2}{4\rho}} \cos q\pi (1-y)$$

and subtracting, we find

$$\begin{aligned} \sqrt{\frac{p}{\pi}} \left\{ \sum_{n=-\infty}^{\infty} (e^{-\rho(2n+y)^2} - e^{-\rho(2n+1-y)^2}) \right\} &= \\ &= \sum_{q=1}^{\infty} (1 - \cos q\pi) e^{-\frac{q^2 \pi^2}{4\rho}} \cos q\pi y = 2 \sum_{m=0}^{\infty} e^{-\frac{(2m+1)^2 \pi^2}{4\rho}} \cos (2m+1)\pi y. \end{aligned}$$

1) RIEMANN-WEBER, l. c. II, p. 117.

Putting $y = \frac{z}{2h}$, $p = \frac{h^2}{b\lambda}$ we have

$$\sum_{n=0}^{\infty} e^{-\frac{(2m+1)^2 \pi^2 b \lambda}{4h^2}} \cos \frac{(2m+1) \pi z}{2h} = \frac{1}{2} \frac{h}{\sqrt{b \pi}} \sum_{-\infty}^{\infty} \left(e^{-\frac{(4nh+z)^2}{4b\lambda}} \frac{1}{\lambda^{1/2}} - e^{-\frac{(4nh+2h-z)^2}{4b\lambda}} \frac{1}{\lambda^{1/2}} \right).$$

This transforms (9) to

$$w = f(z) - \frac{iT}{\mu} \sqrt{\frac{b}{\pi}} \int_0^t \sum_{-\infty}^{\infty} \left\{ e^{-\frac{(4nh+z)^2}{4b\lambda}} \frac{1}{\lambda^{1/2}} - e^{-\frac{(4nh+2h-z)^2}{4b\lambda}} \frac{1}{\lambda^{1/2}} \right\} e^{-ia\lambda} d\lambda$$

Since at $t=0$ $w=0$, the final result is

$$w = \frac{iT}{\mu} \sqrt{\frac{b}{\pi}} \int_0^t (F' - F'') e^{-ia\lambda} d\lambda, \dots \dots (10)$$

where

$$F = \sum_{n=-\infty}^{+\infty} \frac{e^{-\frac{(4nh+z)^2}{4b\lambda}}}{\lambda^{1/2}}$$

$$F' = \sum_{n=-\infty}^{+\infty} \frac{e^{-(4nh+2h-z)^2}}{\lambda^{1/2}}$$

As the way, followed in deriving (10) is rather long, it may not be superfluous to show that (10) satisfies the conditions of the problem. That the expression satisfies the diff. equat. needs no

further proof, as this is the case with any form $\int_0^t \frac{e^{-\frac{(4nh+z)^2}{4b\lambda} - ia\lambda}}{\lambda^{1/2}} d\lambda$.

Besides at $t=0$, $w=0$ and similarly $w=0$ for $z=h$, because the solution has the form $q(z) - q(2h-z)$. It remains to be shown that $\frac{\partial w}{\partial z} = -\frac{iT}{\mu}$. Now

$$\frac{\partial w}{\partial z} = \frac{iT}{\mu} \sqrt{\frac{b}{\pi}} (P - Q)$$

where

$$P = \int_0^t \sum_{-\infty}^{\infty} \left(-\frac{4nh+z}{2b\lambda} e^{-\frac{(4nh+z)^2}{4b\lambda}} \right) d\lambda$$

$$Q = \int_0^t \sum_{-\infty}^{\infty} \left(-\frac{(4nh+2h-z)}{2b\lambda} e^{-\frac{(4nh+2h-z)^2}{4b\lambda}} \right) d\lambda.$$

Now it appears that for $z=0$ all the terms of P and Q annul each other excepting the term P for $n=0$, so that there finally remains :

$$\frac{\partial w}{\partial z} = \frac{iT}{\mu} \sqrt{\frac{b}{\pi}} \int_0^t -\frac{4nh}{2b\lambda} e^{-\frac{(4nh)^2}{4b\lambda} - ia\lambda} d\lambda_{n=0} \dots (11)$$

The value of this integral is found by introducing the variable $x^2 = \frac{(4nh)^2}{4b\lambda}$ equal to $-\sqrt{\frac{\pi}{b}}$, so that $\frac{\partial w}{\partial z_{z=0}} = -\frac{iT}{\mu}$.

The solution (10) admits of a remarkable interpretation. The analogon of the problem here dealt with in the theory of heat conduction is to find the temperature in a bar of small cross-section of length h , while at the end $z=0$ a definite temperature interval $\frac{\partial u}{\partial z} = -\frac{iT}{\mu}$ is maintained. Our result says that the temperature to be found can be conceived as due to a distribution of an infinitely large number of heat sources and sinks of equal strength.¹⁾ The heat-sources lie at $z=0$ and $z = \pm [4nh]_{n=1}^{\infty}$, the sinks at $z = 2h(1 \pm 2n)_{n=0}^{\infty}$. This shows that with respect to the point $z=h$ the sources lie symmetrically with the sinks, so that to every source at distance p corresponds a sink at distance $-\rho$ and that consequently the temperature (and by analogy in our problem the current velocity) will remain zero here, if it is zero at $t=0$. With respect to the point $z=0$, however, the heat-sources lie symmetrically to each other and likewise the heat-sinks, while in addition there is one more heat-source at the point $z=0$. The symmetrical distribution of the sources makes at this point $\frac{\partial u}{\partial z} = 0$, and also the sinks do not contribute to this quantity, so that for $\frac{\partial u}{\partial z}$ at the point $z=0$ there results only the influence of the source there situated. Now this was calculated above and amounted exactly to $-\frac{iT}{\mu}$.

For the surface current we find thus:

$$w = \frac{iT\sqrt{b}}{\mu\sqrt{\pi}} \int_0^t \frac{e^{-ia\lambda}}{\lambda^{1/2}} \left[1 - 2e^{-\frac{4h^2}{4b\lambda}} + 2e^{-\frac{16h^2}{4b\lambda}} - 2e^{-\frac{36h^2}{4b\lambda}} + \text{etc.} \right] d\lambda.$$

Comparing this expression with that of Fredholm for infinite depth, we see that it is equal to the surface current for infinite depth, diminished by twice the current which in that case would exist at depth $z=2h$, increased by twice the current at depth $z=4h$, etc. As soon as z increases beyond a certain value, the current there is quite negligible against the surface current. With increasing h fewer terms will suffice and for $h = \infty$ only the first term remains, being Fredholm's formula for infinite depth.

1) W. THOMSON. Math. and Phys. Papers 2, p. 41.

Botany. — “*A study of temperature-coefficients and VAN 'T HOFF's rule.*” By C. P. COHEN STUART. (Communicated by Prof. F. A. F. C. WENT).

(Communicated in the meeting of March 30, 1912).

§ 1. *Introduction.*

In connexion with a number of investigations into the influence of temperature on physiological processes, I have made a study of the available data. At the meeting of the Dutch Botanical Society in October 1911, I already communicated some of the results to which the study of the literature had led me, and although the further deductions are of a somewhat hypothetical character (for which reason I have started an investigation to clear up some doubtful points) I nevertheless feel it may be as well to publish already the main results, because in the discussions which took place they suggest some new points of view.

I may not omit to acknowledge here my indebtedness to Professors WENT and COHEN for their advice and interest.¹⁾

§ 2. *What is VAN 'T HOFF's rule?*

In the literature of physical and physiological chemistry there is found again and again the phrase “*According to VAN 'T HOFF for every 10° rise of temperature the reaction velocity becomes twice to thrice as great*” (“R. G. T. rule”). It is the physiologists especially who like to make use of the determination of the temperature-coefficient in order to decide from its magnitude whether a given process is “chemical” or “physical”, and who to that end invoke the above *erroneously* quoted rule. I shall endeavour to show that the *formula* of VAN 'T HOFF itself makes clear that the usual interpretation of the “R. G. T. rule” with regard to the constancy of the coefficient rests on a misunderstanding.

By temperature-coefficients I mean the quotient (Q) of two reaction-velocities which are separated from each other by a constant interval of temperature, usually 10°. Proceeding on the hypothesis that this temperature-coefficient for every 10° increase equals 2—3 then it is evident that this function may be graphically represented by a curve ascending exponentially. “Bilden die Temperaturen eine arithmetische Reihe, so bilden die Geschwindigkeiten eine geometrische”²⁾. It is clear, that, when the temperature-coefficients of this function are

¹⁾ The dissertation of Miss VAN AMSTEL, “On the influence of temperature on physiological processes in yeast”, just now appeared, in which she makes a detailed communication. To my regret too late for me to make use of it in this paper

²⁾ VAN 'T HOFF-COHEN, Studien z. chem. Dynamik 1896, p. 128.

again plotted against the temperatures as abscissae, the new function is represented by a line parallel to the abscissa, for the coefficient is assumed to be *constant*.

It has long been known and moreover VAN 'T HOFF already stated ¹⁾, that this coefficient is not constant, but that it decreases when the temperature is raised and vice versa. But if the coefficient decreases, then this signifies, that the reaction-velocity is diminished and this again indicates, that the curve of the reaction-velocity *is no longer exponential*.

TRAUTZ and VOLKMANN ²⁾ were the first to pay full attention to the lowering of the temperature-coefficients. In the saponification of a large number of esters with Ba(OH)₂ and NaOH ³⁾ they obtained acceleration-curves (Pl. II, fig. 1) which agreed very well, and which all possessed the peculiarity of showing a maximum at about $\frac{20^\circ}{10^\circ}$ and assuming a flat course at a high temperature of $\frac{50^\circ}{40^\circ}$. The investigators then chiefly occupied themselves with the search for a reason for this maximum at 20° and succeeded in finding one, namely, an irregularity in the function $\frac{d\eta}{dT}$ (in which η = viscosity) and a maximum in $\frac{d^2\eta}{dT^2}$, both at 20°. I will not here discuss the formula they put forward; and only say that by the introduction of $\sqrt{\frac{d\eta}{dT}}$ a maximum in the curve calculated was indeed obtained ⁴⁾.

Here again appears the long suspected connection between reaction-velocity and internal friction, that has been regarded by many as a postulate for formulating in absolute measure the reaction-velocity of chemical processes ⁵⁾. This however is not the point to which I wish to call attention here.

Our ultimate aim is to establish the shape of the complete curve of the coefficients in connection with the course of the complete curve of reaction-velocity and temperature. Although this aim cannot at present be attained, we may still begin by making some deductions from the formula which already presents some properties of the

¹⁾ Studien, p. 128. Vorlesungen 1898, I. p. 224.

²⁾ Zschr. f. physik. Chem. LXIV (1908).

³⁾ Executed by VOLKMANN, Inaug. Diss., Freiburg i. B., 1908.

⁴⁾ See however v. HALBAN, Zschr. f. physik. Chem. LXVII (1909), p. 179.

⁵⁾ The well-known analogy to OHM's law. E.g. NERNST, Theor. Chemie, 6. Aufl. (1909), p. 672. VAN 'T HOFF, Vorles. I, p. 171.

desired function, namely, the formula suggested by VAN 'T HOFF¹⁾ and simplified by ARRHENIUS²⁾

$$\frac{d \ln k}{dT} = \frac{A}{T^2} \dots \dots \dots (1)$$

in which k = the reaction-velocity at a constant (abs.) temperature T ; on integration from T_1 to T_2 this becomes

$$\ln \frac{k_1}{k_2} = A \cdot \frac{T_1 - T_2}{T_1 T_2} \dots \dots \dots (2)$$

or, if $T_1 - T_2 = 10^\circ$ and $\frac{k_1}{k_2} = Q$ (coefficient)

$$\ln Q = \frac{10 \cdot A}{T_1 T_2} \dots \dots \dots (3)$$

In the formula A is equal to $\frac{q}{2}$ of VAN 'T HOFF³⁾ or $\frac{H}{2}$ of ARRHENIUS⁴⁾ and represents half the heat change (e.g. heat of dissociation). This quantity is a function of temperature, but since i is so to a much smaller extent than the coefficient Q and since I only aim at a first approximation, it will be supposed constant and 5500 cal. will be substituted, which number is about the average of the values obtained by VOLKMANN.

The Q -curve of course begins with $T_1 = 10^\circ$ absolute temperature. Thus

$\log Q_{10} = \frac{10 \cdot A}{2.3 \times 10 \times 10} = \dots$	$Q_{10} = \dots$
$\log Q_{20} = 1.19$	
$\log Q_{30} = .40$	
$\log Q_{50} = .12$	
$\log Q_{100} = 1.67$	
$\log Q_{200} = 0.628$	$Q_{200} = 4.25$
$\log Q_{333} = 0.309$	$Q_{333} = 2.04$
$\log Q_{333} = 0.222$	$Q_{333} = \frac{1.67}{\dots}$
$\log Q_{700} = 0.047$	$Q_{700} = 1.11$
$\log Q_{\infty} = \frac{10 \cdot A}{\infty} = 0.$	$Q_{\infty} = 1.00$

The coefficient Q_{200} for $\frac{-73^\circ}{-83^\circ}$ approaches very closely the value

1) Études de dynam. chim. 1884, p. 115. Studien, p. 127, 152.

2) Zschr. f. physik. Chem. IV (1889), p. 234.

3) Studien, p. 154. Ostw. Klass. 110, p. 29.

4) Immunochemie 1907.

6.2 found by PLOTNIKOW¹⁾, but this is quite intelligible when it is remembered that for this reaction and this temperature A equals about 6000. In the same way at 640° — 719° abs. temp. Kooz's²⁾ coefficient which is 1.17 at 700° , is connected with the value of $A = 7790$ at that temperature. Further it is clear that the Q -curve must take an asymptotic course with respect to the ordinate as well as to the abscissa.

The above figures seem to me to render obvious the meaning of the critical passage³⁾: "Bei der grössten Zahl der bis jetzt in dieser Richtung untersuchten Fälle, welche sich auf das Temperaturintervall 0° — 184° beziehen, ist nun sehr auffallend das Geschwindigkeitsverhältniss für 10 Grad Temperaturerhöhung etwa 2 bis 3 bei gewöhnlicher Temperatur, m. a. W.: eine Temperaturerhöhung um 10 Grad verdoppelt, resp. verdreifacht die Reaktionsgeschwindigkeit". Emphasis must be placed, not on "10 Grad Temperaturerhöhung" but on "etwa 2 bis 3 bei gewöhnlicher Temperatur". It is indeed very curious that in curves of the most varied processes in which A can have widely different values, and therefore in the most diverse curves by far the larger portion of lines pass through the rectangle which is formed by the abscissae 0° and 50° C. and the ordinates (coefficients) 2 and 3. Whether the lines within the rectangle descend quickly or slowly, whether they run through the whole of its length or only touch one point of it, *does not matter!* It is but a general principle, a *rule*, not a *law*.⁴⁾

Now it would be of great importance to obtain an exact mathematical definition of the Q curve.

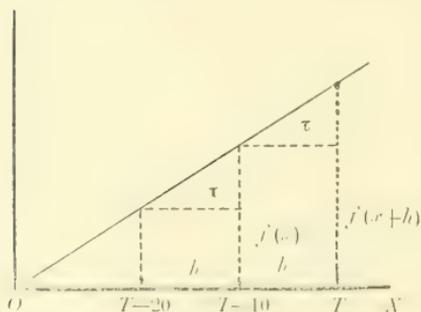


FIG. 1.

mathematical definition of the Q curve.

If we for the moment imagine the simplest case, namely, that the k line (reaction-velocity) is a straight line — which supposition, it must be here stated emphatically, is purely mathematical and completely independent of any physical or physiological-chemical hypothesis — then the Q curve is also a simple function of temperature.

¹⁾ Diss. Leipzig 1905. — Zschr. f. physik. Chem. LIII (1905), p. 630. — If the formula of ARRHENIUS is used instead of that of BERTHELOT, then $Q = 5.77$ is obtained.

²⁾ Diss. Amsterdam 1893. — Zschr. f. physik. Chem. IV (1889), p. 226.

³⁾ VAN 'T HOFF—COHEN, Studien, p. 128.

For, in general, if

$$Q = \frac{k_1}{k_2} = \frac{f'(x' + h)}{f'(x)} \quad (\text{see fig. 1 in the text})$$

then

$$\begin{aligned} Q &= \frac{f'(x+h)}{f'(x)} = 1 + \frac{f'(x+h) - f'(x)}{f'(x)} \\ &= 1 + \frac{h}{f'(x)} \cdot \frac{f'(x+h) - f'(x)}{h} \\ &= 1 + \frac{h}{f'(x)} \cdot f''(x) \quad \dots \quad \dots \quad (4)^2 \end{aligned}$$

If one bears in mind that h is always supposed $= 10^\circ$ and that $f'(x)$ is the smallest of the ordinates under consideration and may be represented by k_{T-10} , the latter general equation changes to

$$Q = 1 + \frac{10}{k_{T-10}} \cdot f''(x) \quad \dots \quad \dots \quad (5)$$

It is now clear what formula (5) tells us with respect to the shape of the Q curve, when k is a linear function. For since $f'(x) = t\gamma \tau = m$ constant, hence

$$Q = 1 + \frac{10m}{k_{T-10}}$$

therefore $(Q-1) \cdot k_{T-10} = 10m = \text{constant}$.

Now since the function is according to hypothesis linear and since, as is actually the case, it passes through the origin (i.e. at 0° abs. temp. $k=0$), k_{T-10} is proportionate to the absolute temperature, and we may also write:

$$(Q-1) \cdot T = \text{constant} \quad \dots \quad \dots \quad 6$$

and from this again it at once follows that the Q curve is a *rectangular hyperbola*, of which the one limb asymptotically approaches the y -axis (coefficient) and the other at distance 1 runs parallel to the abscissa (abs. temp.). If both sides of equation (5) are multiplied by k_{T-10} , it is at once seen that this hyperbolic shape is nothing peculiar and only signifies that in a straight line the *difference* between two successive k -values is constant.

The application of the result will appear from the following section.

1) Cf. v. HALBAN, l.c. p. 168 a. f. "Die R. G. T.-Regel kann also höchstens in der Form bestehen bleiben, dass sich die Temperaturkoeffizienten in dem Gebiete der messbaren Geschwindigkeiten zwischen zwei und drei häufen" (p. 171). Also TRAUTZ, Zschr. f. physik. Chem. LXVI (1909), p. 506.

2) Instead of the elementary deduction given above, use can be made of the TAYLOR'S theorem (Dr. M. J. VAN UVEN very kindly pointed it out to me) or of the method in CHWOLSON Lehrb. d. Physik III (1905), p. 12.

I have already stated that the Q function for an exponential k curve is a horizontal straight line.

If we attempt to establish the Q function for an arbitrary reaction, the formula of VAN 'T HOFF-ARRHENIUS does not take us further.

What is the reason for this? The sole and only reason is our ignorance concerning the quantity A . For not until this quantity becomes known as $f(T)$, is a conclusive opinion possible with respect to the geometrical meaning of the formula in question. Therefore it is above all necessary that the formula of VAN 'T HOFF-ARRHENIUS should not be used to interpolate velocity-constants or coefficients (for these should be obtained experimentally) *but in order to discover the dependence of A or μ on the temperature*. The determinations directed to this end must be made at *regular* intervals (preferably from 1° to 5°) because at the present time determinations at arbitrary temperatures and interpolations with the formula of ARRHENIUS or BERTHELOT are of no value.

Now there are two standpoints from which this problem can be viewed. In the first place the formula can be considered as purely theoretical (founded on thermodynamics) and then A can be identified with half the heat of dissociation; if it turns out that the reaction-velocity is governed by still more factors, then these must be *introduced* into the formula. I have here in mind, for example, the viscosity. Since the second law of thermodynamics only pronounces on the *possibility* of energy transformations and not on the way in which energy transformation comes about, and therefore not on the loss of energy through friction, it is therefore intelligible that there should be this omission in a thermodynamical formula. If, on the other hand, we consider VAN 'T HOFF's formula as an interpolation formula, viz. as an expression which agrees as closely as possible with the observations, in which A represents a so-called interpolation constant, that is to say, rather a note of interrogation than a "non-variable", then it must be our aim to break up this quantity into several others, among which for instance the dissociation and the friction might occur.

It seems to me that there is much to be said in practice for the latter view. In that case, however, there is absolutely no sense in giving a single μ -value for a reaction (at an entirely arbitrary temperature) as has been frequently done of late on the example of ARRHENIUS; indeed, it is a very rash generalization. This is at once obvious if we construct for the experiments of VOLKMANN for instance, the corresponding A -curves. It will be also clear from the next section.

As a matter of fact one may therefore say that *any reaction* (and

not even necessarily a chemical process!) *may be represented by VAN 'T HOFF's formula*: it is only necessary to give suitable values to the interpolation constant A. But in that case there is little value in pointing out this "applicability", as for instance in serum reactions (experiments of MADSEN and others, and of ARRHENIUS¹⁾).

The results of our considerations may be summarized thus:

I. The curve representing for chemical reactions the relationship between reaction-velocity and temperature is not an exponential one; the relationship between temperature-coefficients and temperature is hence not a horizontal line.

II. If the function of reaction-velocity is represented by a straight line the curve of coefficients is a rectangular hyperbola.

III. Nothing definite can be said with regard to the true form of the desired functions before the quantity A has been completely defined.

§ 3. *The temperature-coefficients of vital processes.*

After all that has been said above with regard to the fact that temperature-coefficients of chemical processes generally diminish with rise of temperature, it can hardly create surprise when it is found that the processes in the living organism are equally subject to this rule. KANITZ²⁾ was the first to notice this and evidently regarded it as an essential relationship, but it is obvious from discussions occurring in the literature after 1905, that his remarks have remained quite unnoticed, as (just to quote two recent instances) in the papers of Miss VAN AMSTEL and Professor VAN ITERSON³⁾, and the research of Mlle FILON⁴⁾. The reasoning is as follows: "the rule of VAN 'T HOFF is not applicable to living processes, because the coefficient diminishes and is *too* high at low temperatures and *too* low at high ones". It is hardly necessary to say that this conception *should* have been already entirely abandoned. But, e. g., against RUTGERS's⁵⁾ argument (namely, that TRÄUTZ and VOLKMANN had also found diminishing coefficients — with which he did indeed hit the nail on the head) VAN AMSTEL and VAN ITERSON defend themselves as follows⁶⁾: "Admitting that for physiological processes, also at harmless temper-

¹⁾ Immunochemie 1907.

²⁾ Zschr. f. Elektrochem. XI (1905), p. 689. See also Jost, Biol. Cbl. XXVI (1906), p. 229. Afterwards KANITZ, Biol. Cbl. XXVII (1907), p. 15. GONEX, Vorträge f. Aerzte üb. physik. Chem. 1907, p. 50.

³⁾ These Proceedings. 1910, p. 227 and 598.

⁴⁾ Journ. d. physiol. et d. pathol. génér. XIII (1911), p. 19.

⁵⁾ Diss. Utrecht 1910, p. 152. These Proceedings 1910, p. 484.

⁶⁾ L. c. p. 605.

atures, the rule of VAN 'T HOFF is of no consequence, what then remains of BLACKMAN's theory?" Here all depends on *what is understood by VAN 'T HOFF's rule*, which these processes are obliged to obey!

Recently a paper by SNYDER¹⁾ appeared "On the meaning of variation in the magnitude of temperature coefficients of physiological processes". In this the principle of diminution is plainly stated and supported by many numerical data. It does, however, seem to one that all these figures, taken from the most complicated processes of animal physiology, do not form any trustworthy foundation on which to erect even a small structure of theoretical deductions. What, however, deserves great credit is that, in collaboration with TODD²⁾, he at once made an attempt (in connection with VOLKMANN's hypothesis) to measure the change of viscosity of the body-fluids (dog's peptone plasma) under the influence of temperature. He finds a diminution of η with rise of temperature parallel to $\frac{d\eta}{dT}$ for water.

As usual, the observations are here also restricted "within physiological limits" while it is exactly the study of the phenomena of death that can furnish most important data with respect to the condition in which the *unharmed* protoplasm finds itself³⁾. The extension of the experiments to higher and lower temperatures, which is a comparatively small difficulty in the course of an investigation, should make these experiments much more productive.

In view of the slight results which the above research has yielded (BLACKMAN's theory with all its appurtenances is clearly still unknown in animal physiology⁴⁾) I may leave this and proceed to a survey of the botanical publications from which data can be gathered for our object. I add below a list of the literature I have used.

In my calculations and constructions I have proceeded from the hypothesis that the figures given for the reaction velocities are free from error. I am aware that I am thus guilty of a heresy. My excuse is in the first place that a critical selection is impossible because in almost all cases the sources of error are not given, both as regards number and magnitude. Moreover I wished to see what an exact calculation would yield from data, which in general could indeed

¹⁾ Amer. Journ. of Physiol. XXVIII (1911), p. 167.

²⁾ Ibid. p. 161.

³⁾ See H. W. FISCHER's interesting paper, Beitr. z. Biol. d. Pfl. IX (1910), p. 133. Koll. Zschr. VIII (1911), p. 291.

⁴⁾ HÖBER in his comprehensive work (Physik. Chem. d. Zelle u. d. Gewebe, 3. Aufl. 1911) still devotes only a single chapter to physiological-chemical kinetics, and in this only a few words to the question of optima.

vary in *all* directions. I believe I may say that the result which is represented in the sub-joined *Q*-curves, justifies to some extent my procedure.

And this for three reasons especially: firstly because the course of the curves is very regular — secondly because in those investigations, especially those of KUYPER, in which account is taken of the duration of warming (for which in animal experiments *all* data are wanting) the curves for one and the same duration of warming take an accurately parallel course, — and finally there is the more remarkable quality, that the course of the coefficient curves are of *one general type*. This type can perhaps be best characterized by comparing it to the well-known inflected gas-isothermals.

Although the following considerations apply to a greater or less extent to all constructed curves, I shall always pay special attention to KUYPER's curves (Plate I) since his figures (especially those for *Pisum*) are presumably the most accurate which we possess with respect to temperature-coefficients in physiology.

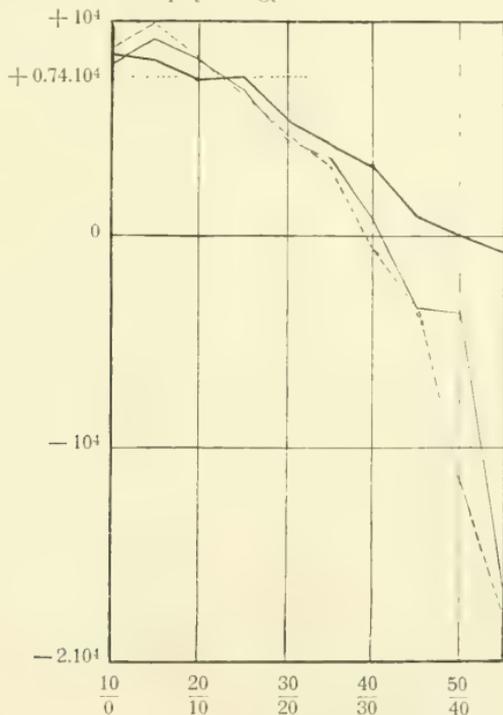


Fig. 2. *A*-curves for the respiration of *Pisum sativum* (KUYPER).

— 1 hours' — 2 hours' --- 3 hours' warming.

The following peculiarities may now be noticed :

1. Many curves have a maximum at $\frac{15^\circ}{5^\circ}$.
2. In successive hours the curves of the coefficients show a tendency to pass from a gradual to a steep descent.
3. All curves show a tendency up to 35 or 40° to approach the coefficient 1 asymptotically. Afterwards the direction changes to one of rapid descent.
4. The curves of NÄGELI, VELTEN, VAN RIJSSELBERGHE and RUTGERS descend much more steeply than the others.
5. All curves descend much more rapidly than those of VOLKMANN¹⁾.

Further I have constructed from the five Q -curves for *Pisum* the corresponding A -curves with the aid of ARRHENIUS' formula, for from every value of Q a value of A can be calculated; from the latter curves it is obvious that A is by no means constant and therefore here also a previous remark on the rash generalization of A -values applies. In fig. 2 of the text I have indicated the place where according to ARRHENIUS²⁾ "the" A -value lies, namely at $\mu = 2A = 14800$ (calculated according to CLAUSSEN³⁾). It will be seen that there is no question of a real "mean", not even if we limit ourselves to "innocuous" temperatures. It is also seen that for supra-optimal temperatures A soon acquires very large negative values. This results from the formula $\ln Q = \frac{10A}{T_1 T_2}$, since, when $Q = 1$, $A = 0$, and when $Q = 0$, $A = -\infty$.

The latter result of course means that the respiration has stopped and that death has occurred. The coefficient Q itself never becomes negative.

We now proceed to a discussion of the property mentioned above sub 1. Is the maximum which appears in many Q -curves a real maximum? It occurs so frequently that we must consider it appears according to a rule and we are at once reminded of the maximum which TRAUTZ and VOLKMANN always found at $\frac{20^\circ}{10^\circ}$. It should further be noted that these authors leave open the possibility of the maximum being somewhat lower, since they made determinations at intervals

1) The rate of descent could of course be again expressed by $\frac{Q_1}{Q_2}$. In practice this, however, introduces large errors (compare v. HALBAN, l.c.).

2) *Immunochemie* 1907, p. 88.

3) *Landw. Jahrb.* XIX (1890), p. 893.

Fig. 1.

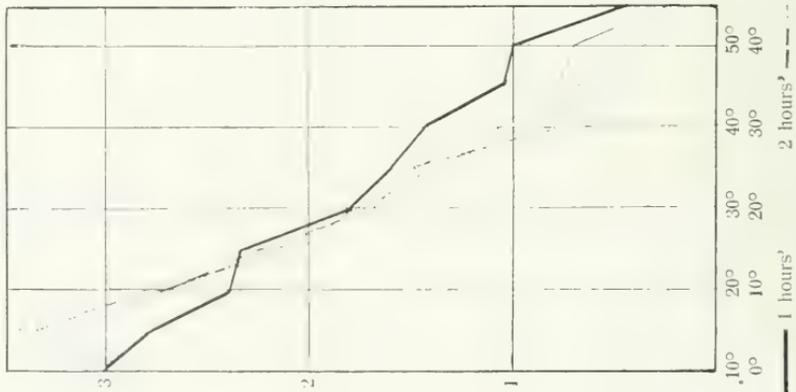


Fig. 2.

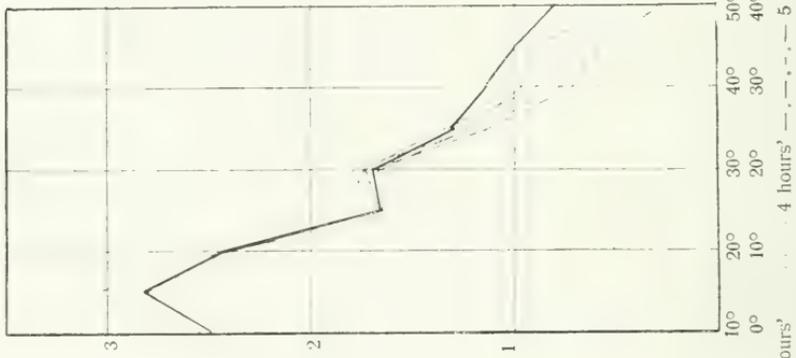
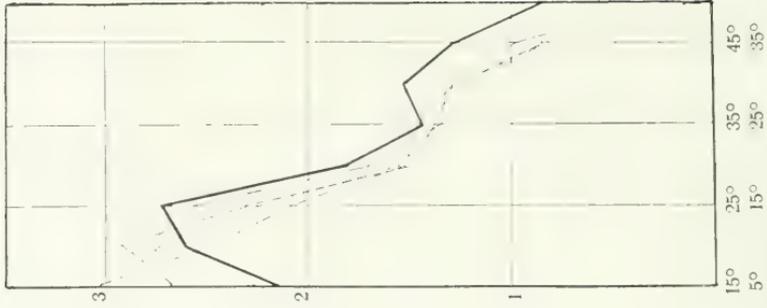


Fig. 3.



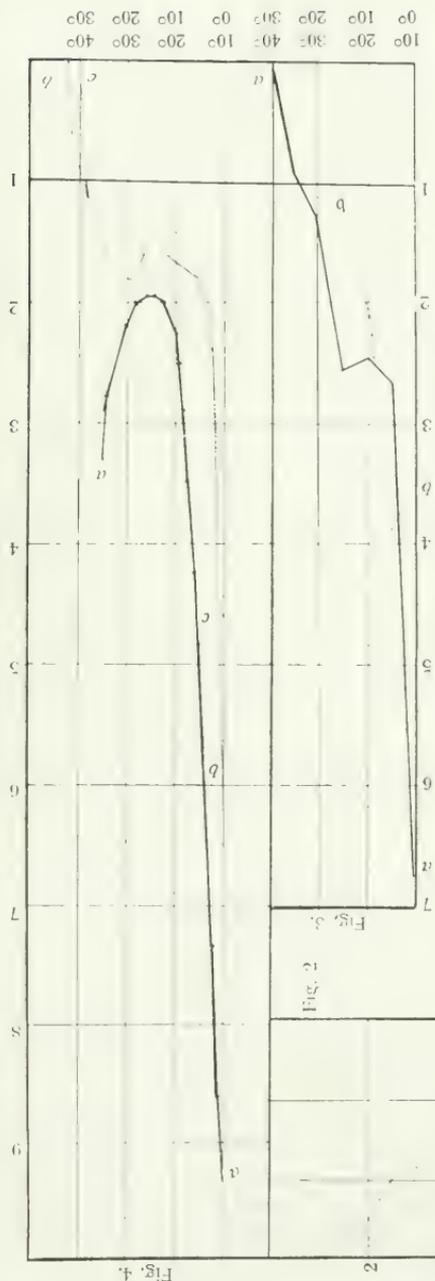


Fig. 4.

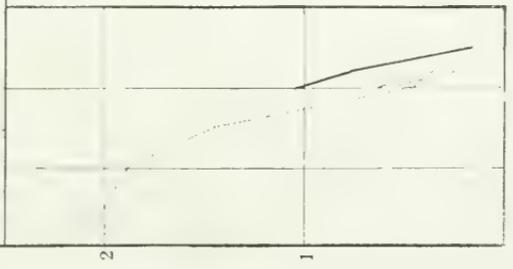


Fig. 2

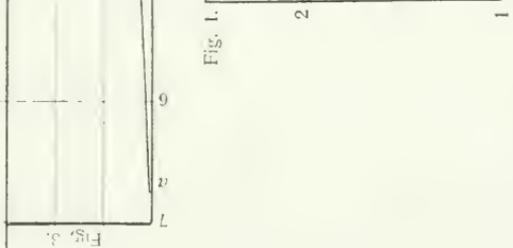


Fig. 3

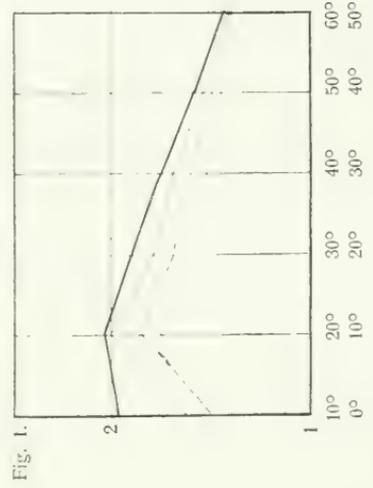


Fig. 1.

— 5' — 10' — 15' — 20' warming.

of 10°). It would be worth while to investigate this maximum also for physiological processes, in order to demonstrate a possible connexion with $\frac{dn}{dT}$. Too much importance may, however, not yet be attached to this maximum, since at 0° the experimental errors may be considerable, and these errors influence the quotient $\frac{10^{\circ}}{0^{\circ}}$.

As regards the second point, i.e. the decrease of the coefficients in successive hours, we may note that the line of 1 hour's warming often shows (irregular?) oscillations, whereas the other lines generally succeed one another more or less regularly. If we now bear in mind, that VOLKMANN's lines were very slightly inclined, we obtain the impression *that the line for 1 hour's warming approximates to those for reactions in vitro*¹⁾ and that the subsequent lines deviate more and more from this. This is exactly what BLACKMAN has asserted for reaction velocities and with him we may assume that the correspondence would be complete if observations could be made after an infinitely short time of preliminary warming.

It should be noted in passing that the construction of the Q -curves affords a means of demonstrating almost imperceptible irregularities of the k -curve. *Since the various Q -curves are moreover directly comparable* (assuming that the units are in constant equal proportions), in contradistinction to the k -curves, which change their slope in accordance with a change in the choice of the values of the units, *the construction of the Q -curves is much more correct and important than that of the k -curves.*

The third point deals with the asymptotic course when $Q=1$. In the preceding section we said that in reactions which are linear functions of temperature the coefficient at 1 runs asymptotically, and in agreement with this is the behaviour of the physiological coefficients at "harmless temperatures". The upper limit of these temperatures varies between 25° and 40° according to the process and the object. Starting from this temperature one could draw further a "theoretical" asymptotic line. (The same is seen in the A -curves.) The explanation of this phenomenon is of course simply that at infra-optimal temperatures the k -curves frequently differ very little

1) Dissert. p. 25 Zschr. f. physik. Chem. LXIV (1908). "Wir sehen nur, dass ein Maximum der Beschleunigung in der Nähe, *wahrscheinlich unterhalb von 20 Grad* liegt."

2) Later physico-chemical investigations will be required to show whether my generalisation from VOLKMANN's experiments is justified.

from *straight* lines. In that case the Q -curve must necessarily resemble a hyperbola.

There are finally the fourth and fifth points, concerning the more or less rapid diminution. The curve of NÄGEL shows that the "abnormally" high coefficient of RUTGERS for $\frac{10^{\circ}}{0^{\circ}}$, namely 6.75, no longer stands by itself but is even surpassed by the enormously high figure 9.33 for *Nitella* (which figure, it should be noted, was obtained by extrapolation from $\frac{10^{\circ}}{1^{\circ}}$ and is therefore probably too low). RUTGERS¹⁾ attributed the high value of his coefficient to the cessation of growth at 0° . We are here at once reminded of the cessation of protoplasmic streaming and the very slight diosmosis at 0° . What is the cause of this "Kältestarre", which one is inclined to neglect as "freezing"? What is more characteristic in the cooling of an emulsion-colloid than the enormous *increase* in the increment $f'(x)$, therefore also in Q , of the *viscosity*?²⁾

I am indeed convinced that by the investigation of the influence of temperature on the viscosity of emulsoids, the mystery which still surrounds heat and cold-rigor, will be solved, at least in part. It is impossible to discuss this further, but I only desire to record my scepticism as to the "chemicity" of a process possessing a high temperature coefficient.* The real distinction between a Q -curve under purely physical influence and a purely chemico-physiological one would perhaps become perfectly clear at once if one could compare the two kinds of curves. It is, however, very remarkable, that *hitherto not a single case has come to light in which the coefficients throughout have "physical" values*³⁾ not even there, where a purely physical influence *might have been expected* (e.g. protoplasmic streaming, diosmosis). Now is it legitimate to refer this result without further to a (chemical) metabolic influence? That is indeed somewhat too simple. I entirely concur with SUTHERLAND⁴⁾ in his severe judgment: "*In order that the chemical theory of nerve-impulse may prove helpful it must show in some reasonable way how the velocity of propagation of a chemical reaction along a nerve can be proportional*

1) Dissertation p. 133. These Proc. 1910, p. 479.

2) W. OSTWALD. Kolloidchemie 1911, p. 204, 221.

3) See the numerous instances cited by SYDÉN. Univ. of Chicago Publ., Physiol. II. (1905), p. 125. Arch. f. Anat. u. Physiol., Physiol. Abt. 1907, p. 113. Amer. Journ. of Physiol. XXII (1908), p. 309.

4) Amer. Journ. of Physiol. XXIII (1908) p. 128.

to the metaphorically so-called velocity of reaction at any point in the nerve."

In my opinion it is legitimate to "deduce" the chemical nature of a process from the coefficient 2 to 3 only in such cases . . . of which one can be certain in advance (respiration, assimilation). —

Finally I wish to indicate very briefly the conclusions to be drawn from the above with regard to BLACKMAN's theory¹⁾, which interprets the temperature optimum in physiological processes as the resultant of a favourable and a harmful influence. This theory is entirely based on the *assumption* (found to be erroneous) that the reaction velocity (k -)curve according to VAN 'T HOFF is an exponential function; to this curve ("the line of zero time") all the observed reaction velocities are extrapolated, and if these extrapolated curves end in the points "required by theory" the matter is sound, according to BLACKMAN, and VAN 'T HOFF's rule also applies to harmful temperatures.

BLACKMAN's theory has been controverted by VAN AMSTEL and VAN ITERSON (loc. cit.). These authors start with a totally different extrapolation method and with its aid obtain results entirely opposed to BLACKMAN's. This question cannot here be discussed further, and the correctness of VAN AMSTEL and ITERSON's extrapolation method is therefore also left out of consideration.

A different question, however, is, whether BLACKMAN's method has any use. *Of course* it has not. Since BLACKMAN extrapolates his heating curves to a line which is not "chemical", but quite imaginary and *arbitrary*²⁾, the end-points of these curves are as inaccurate as the conclusions, which are drawn from the supposed agreement between fact and theory, and the proof of his theory, based on these conclusions, is worthless. Is therefore his theory also worthless?

No, at least I do not think so; *only the validity of* BLACKMAN's *theory cannot at present be proved*. If the true curve were known (but this awaits a chemical definition of A) then, and then only, something might be attained by extrapolating. Meanwhile one can only adduce grounds of probability. Some of these have already been mentioned. A further argument results from the following consideration. If the last portion of the k -curve, before the concave bend, is *produced rectilinearly* and if we extrapolate to this, much smoother curves are obtained than with BLACKMAN's exponential line. This is for instance well shown by KUYPER's curves for *Triticum*; with *Pisum* a line is required intermediate between a rectilinear

¹⁾ Ann. of Bot. XIX (1905), p. 281.

²⁾ KANITZ, Biol. Cbl. XXVII (1907), p. 20.

and an exponential lengthening. Hence it follows that the sharp antagonism between the lines of zero time of BLACKMAN and of VAN AMSTEL and VAN IJERSON is considerably lessened. It is clear, however, that this gives scope for a most arbitrary procedure. There is no positive proof.

It should be expressly pointed out that the above results in no way diminish BLACKMAN's merit — a merit based on his opposition to the general misuse of the terms "Reiz" and "Auslösung" as meaningless principles¹⁾, thought to explain everything, and more especially on the manner in which he traced a clear and logical connection between the theory of reaction velocity in chemical and in physiological systems, the theory of limiting factors and the theory of the origin of the optimum. —

The above considerations may be summarized as follows:

I. The falling of temperature-coefficients with rise of temperature is also the rule in physiological processes.

II. BLACKMAN's theory, which is thus deprived of its "chemical curve" and its extrapolation method, is at present not susceptible of proof.

III. Probably the study of temperature-coefficients will furnish a better insight into the mode of action of temperature than that of reaction velocity.

IV. Both the velocity curves and the coefficients point to a close correspondence between physiological and chemical processes.

V. This correspondence is, however, rendered less evident by the influence of viscosity, which plays presumably a very important part in the heterogeneous, colloidal protoplasm.

VI. The study of the influence of temperature on the viscosity of colloidal systems will probably explain a large proportion of the apparent deviations of vital processes from the course of chemical reactions in homogeneous systems.

Utrecht, University Botanical Laboratory.

EXPLANATION OF THE FIGURES.

PLATE I. *Fig. 1.* Q-curves for the respiration of *Pisum sativum* (1—5 hours' warming). According to KUYPER, These Proceedings Vol. XII p. 219.

Rec. trav. bot. Néerl. VII (1910), p. 164.

Fig. 2. The same for *Triticum vulgare*. According to KUYPER, Proc. 1909, p. 225 Rec. trav. bot. Néerl. VII (1910), p. 194.

Fig. 3. The same for *Lupinus luteus*. According to KUYPER, Proc. p. 225 Rec. p. 190.

¹⁾ Nature LXXVIII (1908), p. 556.

PLAAT II. *Fig. 1.* Q-curves for the saponification of some acetic esters. According to VOLKMANN, Diss. Freiburg i. B. 1908.

Fig. 2. The same for the evolution of CO_2 in alcoholic fermentation. According to v. AMSTEL and v. IERSON, Proc. XIII p. 233

Fig. 3a. The same for the geotropic sensibility of Avena seedlings. According to RUTGERS, Proc. XII p. 476 Dissertation, Utrecht 1910, p. 92.

Fig. 3b. The same for the permeability of the medullar protoplasm of Sambucus. According to v. RIJSEELBERGHE. Rec. Institut. Léo Erréra, Bruxelles, V (1901), p. 223 (by graphical interpolation in fig. 1).

Fig. 4a. The same for the velocity of streaming of the protoplasm of Nitella syncarpa. According to NÄGELI, Beitr. z. wiss. Bot. H. 2 (1860), p. 77.

Fig. 4b and 4c. The same for Chara foetida and Elodea canadensis, respectively. According to VELTEX, Flora LIX (1876), p. 210 and 198 respectively.

Mathematics. — “On a congruence of the second order and the first class formed by conics.” By Prof. JAN DE VRIES.

The theory of the linear congruences of conics (congruences of the first order) has been completely developed by MONTESANO¹⁾ (1892--'95). For the determination of the relations between the characteristic numbers this author among others made use of two auxiliary surfaces: the locus *A* of the conics meeting a given line and the locus *B* of the conics the planes of which pass through a given point. An extension of this method to congruences of higher order remains infertile by the fact that in these cases a point common to two conics is not necessarily a singular point. Until now general considerations on congruences of higher order have not been published.

In these pages we consider a special congruence of order two and class one, showing a family-likeness with the congruence (2,1) described in 1908 by L. GODEAUX²⁾.

1. The congruence *F* under consideration consists of the conics γ^2 passing through a given point *O*, having three points in common with a given twisted cubic q^3 and meeting a given line *r*.

The locus of the conics passing through *O* and through any point *P* and meeting q^3 thrice is a quadratic surface Σ^2 . By the points common to *r* and Σ^2 two conics γ^2 of *F* are individualized; so *P* lies on two γ^2 and *F* is of the *second order*.

¹⁾ Atti Torino, XXVII (1892), Rend. Ist. Lombardo XXVI (1893), Rend. Napoli (1895) p. 93, p. 155.

²⁾ Sur une congruence (2,1) de coniques. (Mém. Soc. des Sciences du Hainaut, 6me série, t. X).

In 1904 we dealt with a special congruence (2,2). (These Proceedings Vol. VII, p. 311).

Moreover Γ is of the *first class*, for an arbitrary line l determines with O one plane, containing only one conic γ^2 .

If l passes through O it is a *singular bisecant*; the conics γ^2 with l as bisecant lie on a surface Σ^4 of which l is a nodal line and O a triple point¹⁾. The straight lines of the plane (Or) are also singular bisecants, this plane containing a pencil (γ^2).

The surfaces Σ^2 form a pencil, the base curve of which consists of ϱ^3 and its bisecant b through O . Each Σ^2 contains two systems of γ^2 ; if R_1 and R_2 are the points common to that Σ^2 and r , these two systems have OR_1 (resp. OR_2) for bisecant. So Σ^2 is at the same time the locus of the γ^2 meeting twice a determined γ^2 lying on it.

The line r is touched by two Σ^2 , any point P of one of these surfaces is characterized by the property that the two γ^2 through it coincide.

The conics γ^2 passing through any point S of ϱ^3 form a surface Φ^4 with OS as nodal line and O and S as triple points; for the bisecants t of ϱ^2 meeting r lie on a ruled surface of order four and the two bisecants t cutting OS in points different from S form with SO two degenerated γ^2 .

2. Each line t determines *one* degenerated γ^2 ; the second line g of that pair of lines joins O to the third point S of ϱ^3 in the plane (Ot) . The lines g generate a cubic cone with nodal edge b , projecting ϱ^3 out of O . Each line g belongs to two pairs (g, t) ; the locus of the point (g, t) is a twisted sextic.

The plane (Or) contains three lines $d_k := OS_k$. The bisecants f of ϱ^3 meeting d_k generate a regulus; each (d, f) is a γ^2 .

Each plane through b contains a line c meeting ϱ^3 and r . A plane through r contains three lines c . So the locus of the line c is a ruled surface of order four with b as triple line and r as single director line. Each c forms a γ^2 with b .

3. We now consider the surface A , locus of the γ^2 meeting l .

The γ^2 lying in plane (Ol) meets l twice and is therefore nodal curve on A ; moreover this plane contains three lines g each of which is cut by two lines t and therefore likewise nodal line. Finally l is double line too. From this ensues that A is of *order twelve* and admits in O an eightfold point.

On this A^{12} the line r is double line and the curve ϱ^3 fourfold curve, as l has two points in common with any Σ^2 and four points with any Φ^4 .

As the locus of the line t is a ruled surface of order four, A^{12}

¹⁾ Evidently Σ^4 is at the same time surface Π for any point l , and it passes once through r .

contains, besides the six lines l indicated above, four lines t and four lines g . Moreover \mathcal{A}^{12} contains six lines f and three lines d as nodal lines. Finally \mathcal{A}^{12} contains four lines c and the fourfold line b .

4. Let d be a ray of the pencil with vertex D lying in the plane σ . Each line d is bisecant of *one* γ^3 ; the locus of the points of intersection of d and γ^2 is a curve of order four with D as node. Through D pass six rays d each of which touches a γ^2 . So the tangents of the γ^2 form a *complex of order six*.

From this ensues that the planes γ of the γ^2 touching σ envelop a cone of class six, with (Or) as bitangent plane, the trace of this plane with σ being touched by two γ^2 .

Any surface Σ^4 (art. 1) is cut by any line l in four points; the planes γ of the γ^2 meeting l in these points pass through a ray of the sheaf O . So the planes γ of the γ^2 meeting l envelope a cone of class four, admit also (Or) as bitangent plane, any γ^2 lying in that plane having r for bisecant¹).

Both cones admit twenty common tangent planes, besides (Or) . So there are *twenty* γ^2 meeting a given line and touching a given plane.

5. In any plane λ the conics of the congruence determine a correspondence (2,2). The two Σ^2 touching r intersect λ according to two conics, each of which bears an involution of pairs P, P' ; the points corresponding to $P(P')$ coincide in $P(P')$.

Let l be an arbitrary line of λ . The corresponding surface \mathcal{A}^{12} is cut by λ according to a curve λ^{10} containing the points P' conjugate to the points P of l in the correspondence (2,2).

To the points common to l and λ^{10} the points of intersection of l and the γ^2 of which l is bisecant belong; the remaining eight are points of coincidence $P \equiv P'$.

So the *curve of coincidences* is of *order eight*; the four points of intersection of λ with q^3 and b are threefold points of it.

These four points are at the same time fundamental points of the (2,2) and threefold points of the corresponding fundamental curves of order four. Likewise the four points of intersection of λ with r and the three lines d are fundamental points with conics as fundamental curves.

¹) The cones corresponding to l and l' admit 12 common tangent planes, besides (Or) . From this the order of Λ can be deduced once more.

Anatomy. — “*The arrangement of the motor nuclei in Chimaera monstrosa compared with other fishes*” By C. U. ARIËNS KAPPERS.
(Communicated by Prof. L. BOLK).

(Communicated in the meeting of February 24, 1912).

Examining the oblongata in different orders of fishes great differences are found in the topographic relations of the motor nuclei.

On the other hand there is a striking resemblance in the arrangement of those nuclei within the limits of an order. Cyclostomi show principal differences in this respect if compared with the Selachii, and the oblongata of the latter is again very different from that in Teleosts. Recently DROOGLEEVER FORTUYN¹⁾ found that Ganoids (*Amia Calva*) are again different from both.

These observations add to establish more differences between classes and orders drawing the lines of limitation sharper.

In the end of last and the beginning of this year I had a chance to examine a specimen of the order of Holocephali. This seemed important to me because the animal (*Chimaera monstrosa*) represents a separate order and because in several respects its brain stands in between that of the Selachii and Teleostei.

I wanted to know: 1. If the arrangement of the motor nuclei in the oblongata of *Chimaera* revealed such characteristics as should be expected in a separate order; 2. if these characteristics stand in between those of the Selachii and Teleostei.

Although I did not expect a great difference in the internal structure of the oblongata with the Selachian type, on account of the striking macroscopical resemblance between this oblongata and the Selachian, my studies gave very interesting results, which proved on one hand that also on account of the arrangement of the motor nuclei in the oblongata *Chimaera* deserves a special place in the classification of vertebrates and that on the other hand it stands in between the Selachian and Teleostean type.

The facts are these:

The selachii have only a dorsal oculomotor nucleus; IIUET²⁾. A real ventral nucleus as in Cyclostomes or in Teleosts and Ganoids (*Amia Calva*, DROOGLEEVER FORTUYN) is not present. In this respect *Chimaera* resembles the selachii. The IVth nucleus has the same features in Selachii, Holocephali and Teleostii.

¹⁾ Notiz über den Eintritt der motorischen Nervenwurzeln in die Medulla Oblongata und die Lage der motorischen Kerne bei *Amia calva*. *Folia Neurobiologica* Bnd. VI, 1912, Heft I.

²⁾ Notes on the trochlear and oculomotor nuclei and roots in the lower vertebrates. Proceedings of the Koninkl. Akademie v. Wetenschappen te Amsterdam, March 23, 1911 p. 897.

Also the Vth nucleus of Chimaera has a great resemblance with the dorsal Vth nucleus of Teleostei, as it is found in *Lophius* e.g.

The position of the VI cells in Chimaera stands in between the location found in most Selachii and the one found in the Teleosts in so far as they have a less dorsal position than in the former and a less ventral position than in the latter. Division into two groups as is frequently found in the latter does however not occur. The nucleus is very diffuse, its cells are rather scattered.

The position resembles very much the one found in *Amia Calva* by DROOGLEEVER FORTUYN (l.c.)

As I have already pointed out formerly¹⁾ the roots of the VIth nucleus in Chimaera come much nearer the VIIth root as is generally found in sharks. Also in this respect Chimaera approaches the Teleosts. Not however in the number of rootlets which is *even more* than in many sharks (6 or 7).

The most interesting topography is however exhibited by the VII nucleus.

Whereas in all Sharks the VIIth nucleus forms a continuous row of cells with the IXth and Xth root entrance, and keeping a dorsal place, we found very regularly two facialis nuclei in Teleosts, one, more frontal between the level of the VIIth and IXth roots, containing also the IX cells (as has been equally found by TELLO²⁾ and another one caudally from the IXth root entrance, remaining continuous with the X cells³⁾ and keeping a more dorsal position than the VII—IX cellgroup.

Chimaera exhibits a structure of the VII system, which has its own special features, but in some respects resembles the Teleostean character.

As in Teleosts there are two VIIth nuclei in Chimaera, of which one is located between the level of the VII and IX root, without being connected however with IX cells and not exhibiting any ventro-lateral shifting as the VII—IX nucleus in Teleosts generally does.

1) The migration of the bulbar Vth, VIth, and VIIth nucleus in the series of vertebrates and the differences in the course of their root fibers.

Verhandeling v. d. Kon. Akad. v. Wetensch. te Amsterdam (Tweede sectie) No 16, 1910.

2) Contribucion al Conocimiento del encefalo de los Teleosteos: Losnucleos bulbares.

1o, 2o fascicolo, tomo VII 1909. Trabajos del laboratorio de investigaciones biologicas de la Universidad de Madrid, p. 8 and 9.

3) Only in *Gadus* also this VII nucleus was isolated from the X cells. Concerning *Lophius* I refer to my paper in these Proc. 1910.

The posterior VII nucleus lies behind the IX rootlevel and in about the middle of the bulb, being entirely separated from the vagus nucleus. It is several times larger than the anterior nucleus. The real vagus nucleus contains no VII elements. In so far a certain resemblance with *Gadus* and *Lophius* is present as in those animals the vagus nucleus is also free from VII elements. Specially *Lophius* offers a point of resemblance as the posterior VII nucleus has a more ventral position than the anterior VII nucleus in this animal. It seemed probable to me that the posterior VII nucleus of *Chimaera* contains at the same time the IX root to its origin with certainty. The caudal part of the posterior VII nucleus is however a pure VII nucleus again, the facialroot entering this nucleus in its frontal and in its caudal part.

In so far the resemblance with the Teleosts is greater than one would say at the first glance, because the sequence of cells in the whole visceral system of this region in *Chimaera* is VII—IX—VII—X, just as in Teleosts, whereas in Selachii the primitive arrangement is kept: VII—IX—X, being in harmony with the arrangement and sequence of roots. The difference with the Teleostean topography would consequently be only this that in Teleosts the IX nucleus is combined with the anterior VII nucleus, whereas in *Chimaera*, it is combined with the posterior VII nucleus.

Concerning the reason of the difference between Selachii and Holocephali no definite opinion can be given at present. It may be that it has to do with the innervation of the operculum, but we may not forget that *Amia* has also an operculum and that the Selachian arrangement is kept there. Few words suffice for the arrangement of the vagus column. Besides its freedom from facial cells its structure and length is the same as in the Teleosts. The vagal cell column in Fishes offers generally very few differences.

The spino-occipital system remains. Its cells have a more dorsal place in Selachii than in Teleosts and so they have in *Chimaera*. The cellcolumn is poorly developed in that animal reminding of the scattered spino-occipital cells of *Amia*.

In *Chimaera* a more considerable overlapping of the vagus-column and the spino-occipital column is found than in sharks or Teleosts.

At last I may mention that the topography of the large reticular cells in *Chimaera* is about the same as has been described by VAN HOËVELL in the Selachii.¹⁾ In the caudal part of the oblongata

¹⁾ Remarks on the reticular cells of the oblongata in different vertebrates. Proceedings of the Kon. Akad. v. Wetensch. te Amsterdam. April 20, 1911, p. 1048—1049.

a large nucleus magnocellularis inferior is found, in the raphe extending laterad underneath the fasciculus, longitudinalis dorsalis in form of "guirlande". More frontally in the region of the octavus, V and in front of the Vth, hardly any reticular cells are found in the raphe, the greater part being scattered in the lateral parts of the oblongata, forming the nucleus reticularis medius (octavus-region) and nucleus reticularis superius (praetrigeminal region). The last contain hardly central elements in contrary to the Reptilian, and specially avian and mammalian nucl. retic. superius, which is clearly divided into a dorso-central (nucl. centralis) and a ventrolateral (n. ventro-lat.) group.

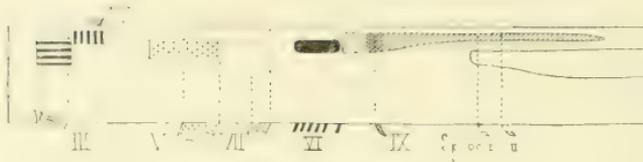
Summarizing my results I may conclude: 1. that Chimaera also on account of the topography of the motor root cells in the oblongata and midbrain has a special place amongst the orders of fishes;

2. that it resembles in some points the Selachian in other the Teleostean type, as has also been found in the forebrain of this animal by CARPENTER and myself²⁾.

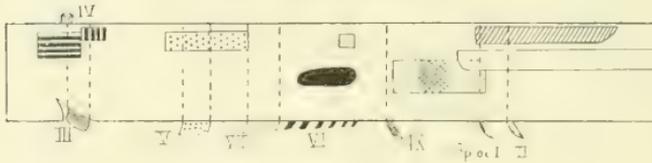
The number of data which show that the nervous system of Chimaera in many respects stands in between that of Selachii and Teleostei, and sometimes reminds more of the Teleostean than the Selachian type is enlarged by an interesting remark made by Prof. G. RETZIUS (Das Gehörorgan der Wirbeltiere Teil I, 1881: Das Gehörorgan von Chimaera monstrosa) who says "in sehr interessanter Weise bildet das Gehörorgan der Holocephalen d. h. der Chimaera ein Uebergangsstadium zu dem der Plagiostomen, ein Verbindungsglied zwischen ihm und den anderen Fischen". In a letter which I received from Prof. RETZIUS in December 1908 he writes "In letzten Sommer bekam ich ein ganz grosses Exemplar von Chimaera und machte mir neue Präparate vom Gehörorgan, welche sehr gut gelangen. Es ist wirklich merkwürdig zu sehen, wie näher das Organ steht an dem der Teleostier als an dem der Selachier".

It results from all this that my researches on the nervous system of this animal give a further illustration of the interesting results of the Swedish anatomist as also several somatic features of the Holocephali prove their transitory character between the Plagiostomi and Teleosts.

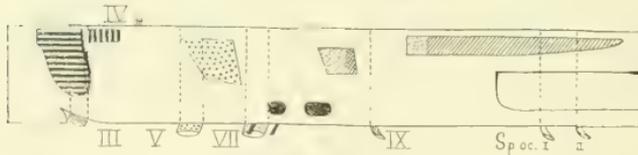
2) Das Gehirn von Chimaera monstrosa, Folia Neurobiologica Band V, Heft 2.



HEXANCHUS

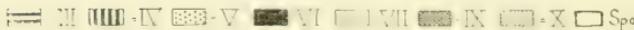


CHIMAERA



COTTUS

EXPLANATION:



Topographic relation of the motor nuclei of midbrain and bulb in regard to the roots of the III, IV, V, VI, VII, IX and Spino-occipital nerves in a shark (*Hexanchus*) Holocephal (*Chimaera*) and a Teleost (*Cottus*).

Astronomy. — *Provisional results from calculations about the terms in the longitude of the moon with a period of nearly an anomalistic month, according to the meridian observations made at Greenwich*”. By J. E. DE VOS VAN STEENWIJK. (Communicated by Dr. E. F. VAN DE SANDE BAKHUYZEN).

(Communicated in the meeting of March 30, 1912).

In 1903 Prof. E. F. VAN DE SANDE BAKHUYZEN had come to the conclusion that theory and observation did not perfectly agree about the so called Jovian evection in the longitude of the moon; nor had he been able to find in the observed places indications of another inequality of the same kind caused by Venus and the Earth¹⁾.

¹⁾ Proc. Acad. Amsterdam 6, 1903 pp. 370 et seq. and 412 et seq.

The agreement as regards the Jovian evection was improved by the introduction of a corrected value found by HILL for the perturbations dependent on the ellipticity of the earth, and afterwards new theoretical calculations of the amplitude by NEWCOMB, HILL, and BROWN yielded a value agreeing very satisfactorily with the results of the observations¹⁾, but in the phase and hence in the length of the period a deviation seemed to remain.

Recently Prof. VAN DE SANDE BAKHUYZEN proposed that I should undertake a new investigation into this question founded on a longer series of Greenwich-observations than those used by him, and I gladly assented.

Since E. F. v. D. S. BAKHUYZEN had discussed the years 1895 - 1902, the first thing was now to take the years after 1902 in hand and further it was desirable to go back a little further than 1895, in order to have at our disposal the results of an uninterrupted series of eighteen years' observations. This work has been only just begun and if, notwithstanding this, I make bold to communicate already a few provisional results, this is owing to the desirability of deriving just now corrected places of the moon for the moment of the approaching solar eclipse.

I shall therefore communicate here the results of a provisional discussion of the 3 last years of the Greenwich-observations, which were at my disposal: 1907 up to 1909. I derived from it the co-efficients of the terms with $\sin g$ and $\cos g$, which still had to be added to HANSEN's longitude of the moon and compared these with the sums of the corrections resulting from corrected values of the eccentricity and longitude of the perigee according to BAKHUYZEN and from the perturbations by the planets according to BROWN.

In my discussion of the observations I mainly followed the method indicated by NEWCOMB in his *Investigation* just as BAKHUYZEN had done; i. e. I employed as basis for my calculations directly the deviations in R. A. For the present, however, I had to be satisfied with a less rigorous course. The corrections of the co-efficients of the great perturbations I adopted from NEWCOMB's *Investigation* and as co-efficient of the parallactic inequality I employed the value which according to HANSEN's calculation would correspond to the solar parallax $8''.80$ (or $8''.796$), although this is no longer the case according to the more accurate calculation by BROWN. I did this because I could now use extant auxiliary tables, while the influence of this inaccuracy

¹⁾ NEWCOMB found $1''.15$, BROWN $1''.14$, while E. F. v. D. S. BAKHUYZEN had derived $1''.28$ from the observations

on my results could not be but slight, since the periods of these terms are not commensurable with that of g .

An investigation into personal errors dependent on the age of the moon offered little chance of success, as I had only the observations of 3 years at my disposal. I therefore, after having corrected the observations as indicated above, only applied a mean correction to each category of observations in order to reduce the yearly mean of the differences comp.—obs. to zero. I employed all the observations made in the meridian including those obtained with the altazimuth and thus had for each of the two instruments three categories of observations, those of Limb I, of Limb II and of crater Mösting A, i. e. six in all. I formed for each of these the annual mean and subtracted this from the individual $\Delta\alpha$. I should certainly have done better by leaving out of account the observations made at an age of the moon less than $4^d.5$ and more than $25^d.5$ (comp. the former investigation by E. F. v. D. SANDE BAKHUYZEN), but of the 835 observations used, only 12 were in this case.

g	1907	1908	1909
0° — 20°	+ 0 ^h 87	+ 2 ^h 29	+ 2 ^h 23
20 — 40	+ 2.55	+ 2.12	+ 2.83
40 — 60	+ 2.29	+ 1.87	+ 2.33
60 — 80	+ 2.70	+ 1.02	+ 3.22
80 — 100	+ 3.18	+ 1.21	+ 0.67
100 — 120	+ 2.21	+ 2.28	+ 0.69
120 — 140	+ 0.93	— 0.36	— 0.57
140 — 160	+ 1.03	+ 1.20	— 0.60
160 — 180	— 0.63	+ 0.28	— 1.78
180 — 200	— 2.17	— 1.24	— 1.63
200 — 220	— 1.38	— 2.87	— 2.93
220 — 240	— 1.61	— 1.00	— 2.48
240 — 260	— 2.35	— 2.66	— 2.39
260 — 280	— 2.52	— 1.80	— 2.56
280 — 300	— 1.20	2.32	— 1.81
300 — 320	— 2.19	— 0.68	+ 0.92
320 — 340	— 0.54	— 1.07	+ 1.46
340 — 360	— 1.20	+ 1.88	+ 2.47

The thus corrected and reduced $\Delta\alpha$ (obs. — comp.) were now arranged for each year into 18 groups formed according to the value of the mean anomaly: from $g = 0^\circ$ to 20° , 20° — 40° etc. The means found for those groups are found in the table on p. 1182.

The 18 results r obtained for each year have now been represented by equations of the following form

$$c + h \sin g + k \cos g = r$$

in which c stands for a constant deviation still extant in the results of the year under discussion, while

$$dl = -h \sin g - k \cos g$$

represents the correction to be applied to HANSEN'S true longitude.

The weights of the values of r in one and the same year often differ considerably, and these weights have to be taken into account, if we wish to obtain a solution yielding the most accurate values of h and k . This has been done for 1909 but for the two other years the weights were momentarily neglected. Another solution was also made for 1909 without taking the weights into account and by comparing the results obtained in these two ways it appeared that the influence of the omission probably is not great. I obtained with and without weights for h resp. $+1''.81$ and $+1''.69$ and for k $+2''.17$ and $+2''.20$.

Adopting for 1909 too the solution obtained without weights the following values are to be regarded as the results of this first investigation:

	h	k
1907.5	$+2''.49$	$+0''.62$
1908.5	$+1''.67$	$+1''.06$
1909.5	$+1''.69$	$+2''.20$

It stands to reason that from the results of only 3 years no immediate conclusions can be drawn about the individual inequalities influencing the h and k . The only thing I could do was to compare my results with the co-efficients of $\sin g$ and $\cos g$ according to the complex of the element-corrections as derived by E. F. VAN DE SANDE BAKHUYZEN in 1903 and the perturbations as calculated by BROWN. I have extended this comparison of the empirical with the theoretical values of $-h$ and $-k$ to the years 1895—1902 discussed by VAN DE SANDE BAKHUYZEN¹⁾.

For the constant parts of $-h$ and $-k$ I adopted $-h_0 = -0''.43$ and $-k_0 = -0''.17$; and I borrowed the variable parts arising from the differences between the perturbations BROWN—HANSEN, from BATTERMANN *Beob. Ergebn. Berlin*. **13** p. 16—18. Of the perturbations by the planets we have to consider those numbered 23—29; the

¹⁾ Proc. Acad. Amsterdam **6**, 1903, p. 377.

terms 1—7 cannot contribute noticeably to the h and k , for reducing these to the form $a \sin(g + \chi)$, the annual variation of χ for N. 1 becomes 225° , for N. 5 $330'$ and for the rest of the terms $> 360^\circ$. Further, of the perturbations by the sun N. 39 has to be taken into account and of those owing to the ellipticity of the earth N. 44.

These 9 terms calculated for the middle of each year were reduced to the form $a \cos \chi \sin g + a \sin \chi \cos g$, so that we obtain as computed values

$$(-h)_{comp.} = -h_0 + \Sigma a \cos \chi \text{ and } (-k)_{comp.} = -k_0 + \Sigma a \sin \chi.$$

The following table contains the values deduced from the observations $(-h)_{obs.}$ and $(-k)_{obs.}$ and the differences $(-h)_{obs.} - (-h)_{comp.}$ and $(-k)_{obs.} - (-k)_{comp.}$.

	$(-h)_{obs.}$	$(-h)_{obs.} - (-h)_{comp.}$	$(-k)_{obs.}$	$(-k)_{obs.} - (-k)_{comp.}$
1895.5	- 0'29	+ 0"23	- 0"44	+ 0'43
1896.5	- 0.66	- 0.58	- 1.16	+ 0.57
1897.5	- 0.57	- 1.09	- 1.77	- 0.16
1898.5	- 0.51	- 1.01	- 2.10	- 0.49
1899.5	+ 0.93	- 0.28	- 2.83	- 1.13
1900.5	+ 1.66	- 0.01	- 1.12	- 0.50
1901.5	+ 1.46	+ 0.38	- 0.52	- 0.73
1902.5	+ 1.18	+ 0.33	- 0.01	- 0.59
1907.5	- 2.49	- 0.04	- 0.62	- 0.61
1908.5	- 1.67	+ 0.28	- 1.06	+ 0.07
1909.5	- 1.69	- 0.48	- 2.20	- 1.05

We now see that the differences between observation and computation have still a systematic character. Yet we cannot deduce from this comparison with any certainty an empirical correction to the computed longitude of the moon for the moment of the solar eclipse of April 17. For that moment we have $g = 278^\circ$, so that especially the value of h is of importance and it does not seem feasible to extrapolate a value of $(-h)_{obs.} - (-h)_{comp.}$ for 1912.3.

Prof. E. F. V. D. SANDE BAKHUYZEN'S opinion, (comp. J. WEEDER, Calculations etc., Proc. Acad. Amst. 14 p. 950), based on his former calculations, that the real value of $-h$ would probably be at least

0".6 greater than the computed one, is therefore not corroborated by the results I have obtained thus far.

Mathematics. — *New researches upon the centra of the integrals which satisfy differential equations of the first order and the first degree*. (First Part) by Prof. W. KAPTEYN.

1. In a very interesting memoir¹⁾ “Détermination et intégration d’une certaine classe d’équations différentielles ayant pour point singulier un centre” H. DULAC has investigated the conditions which must be fulfilled when the origin of coordinates is a centrum for the differential equation

$$\frac{dy}{dx} = - \frac{y + ax^2 + bxy + cy^2}{x + a'x^2 + b'xy + c'y^2}$$

that is, when the general integral may be written in this form

$$xy + F_3(xy) + F_4(xy) + \dots = Const,$$

where $F_k(xy)$ represents a homogeneous polynomial of degree k . Supposing that the coefficients are real or complex he shows that the differential equation must be reducible to one of the following eleven forms, where μ and ν are arbitrary constants

$$(x + x^2 + \mu xy + \nu y^2) dy + (y + y^2 + \mu xy + \nu x^2) dx = 0. \quad (1)$$

$$(x + x^2 + 2xy + \mu y^2) dy + (y + y^2 + 2xy + \nu x^2) dx = 0. \quad (2)$$

$$(x + x^2 + \mu y^2) dy + (y + y^2 + \nu x^2) dx = 0 \quad (3)$$

$$(x + 2x^2 - xy + \mu y^2) dy + \left(y + 2y^2 - xy + \frac{1}{\mu} x^2 \right) dx = 0. \quad (4)$$

$$(x + x^2) dy + (y + \mu x^2 + \nu xy) dx = 0 \quad (5)$$

$$(x + x^2 + y^2) dy + (y + \mu x^2 + 2xy) dx = 0. \quad (6)$$

$$(x + x^2 + y^2) dy + (y + \mu x^2) dx = 0 \quad (7)$$

$$(x + 2x^2 + y^2) dy + (y - xy) dx = 0 \quad (8)$$

$$(x + xy + \mu y^2) dy + (y + xy + \mu x^2) dx = 0 \quad (9)$$

$$x dy + (y + xy + \mu x^2) dx = 0 \quad (10)$$

$$(x + \mu y^2) dy + (y + \nu x^2) dx = 0. \quad (11)$$

The object of this memoir is the same as that which we have treated in our paper “On the centra of the integral curves which satisfy differential equations of the first order and the first degree”. Our point of view however was narrower than that of DULAC, because we only considered real coefficients and real integrals. The object of the present paper now is to extend our former results by adopting also the wider supposition that the coefficients as well as the integrals may be either, real or complex. Our way of solving the

¹⁾ Bull. Sci. math. Paris (Sér. 2) 32, 1908.

²⁾ These Proceedings 10 May 1911.

problem, being very different from that of DULAC, leads to a new classification of the results. Having obtained this we wish finally to compare the two solutions.

2. Let the differential equation be written in POINCARÉ'S form

$$\frac{dy}{dx} = \frac{-x + a'x^2 + 2b'xy + c'y^2}{y + ax^2 + 2bxy + cx^2} = \frac{-x + Y}{y + X} \dots \dots (1)$$

which is different from the form adopted by DULAC, and let the coefficients be real or complex.

By substituting

$$\xi = hx + ky \quad \eta = -kx + hy$$

the form of the equation is not changed, for we get

$$\frac{d\eta}{d\xi} = \frac{-\xi + \alpha\xi^2 + 2\beta'\xi\eta + \gamma'\eta^2}{\eta + \alpha\xi^2 + 2\beta\xi\eta + \gamma\eta^2}$$

where

$$\begin{aligned} (h^2 + k^2)^2 \alpha &= ah^3 + (a' + 2b)h^2k + (2b' + c)hk^2 + c'k^3 \\ (h^2 + k^2)^2 \beta &= bh^3 - (a - b' - c)h^2k - (a' + b - c')hk^2 - b'k^3 \\ (h^2 + k^2)^2 \gamma &= ch^3 - (2b - c')h^2k + (a - 2b')hk^2 + a'k^3 \\ (h^2 + k^2)^2 \alpha' &= a'h^3 - (a - 2b')h^2k - (2b - c')hk^2 - ck^3 \\ (h^2 + k^2)^2 \beta' &= b'h^3 - (a' + b - c')h^2k + (a - b' - c)hk^2 + bk^3 \\ (h^2 + k^2)^2 \gamma' &= c'h^3 - (2b' + c)h^2k + (a' + 2b)hk^2 - ak^3. \end{aligned}$$

Hence

$$\begin{aligned} (h^2 + k^2)(\alpha + \gamma) &= (a + c)h + (a' + c')k \\ (h^2 + k^2)(\alpha' + \gamma') &= (a' + c')h - (a + c)k \end{aligned}$$

and

$$\begin{aligned} \frac{h}{h^2 + k^2} &= \frac{(a + c)(\alpha + \gamma) + (a' + c')(\alpha' + \gamma')}{(a + c)^2 + (a' + c')^2} \\ \frac{k}{h^2 + k^2} &= \frac{(a' + c')(\alpha + \gamma) - (a + c)(\alpha' + \gamma')}{(a + c)^2 + (a' + c')^2}. \end{aligned}$$

Now generally h and k may be so chosen as to satisfy two conditions, for instance

$$\alpha + \gamma = 0, \quad \alpha' + \gamma' = \lambda$$

and thus the differential equation may be written in the simpler form

$$\frac{dy}{dx} = \frac{-x + a'x^2 + 2b'xy - a'y^2}{y + ax^2 + 2bxy + cy^2}.$$

This general case we examined in our former paper. If however

$$(a + c)^2 + (a' + c')^2 = 0$$

this reduction is impossible. In addition to our former paper we therefore now must investigate the consequences of this supposition.

3. If $a + c = a' + c' = 0$

the corresponding differential equation

$$\frac{dy}{dx} = \frac{-x + a'x^2 + 2b'xy - a'y^2}{y + ax^2 + 2bxy - ay^2}$$

admits three particular integrals of the form

$$y = Ax + B$$

for, substituting this value and equalizing the coefficients of the different powers of x in the two members, we have

$$-aA^3 + (2b + a')A^2 + (a - 2b')A - a' = 0$$

$$A^2 + 1 - \{2aA^2 - 2(b + a')A + 2b'\}B = 0$$

$$B\{(aA - a')B - A\} = 0$$

which are satisfied by the roots of the cubic

$$aA^3 - (2b + a')A^2 - (a - 2b')A + a' = 0$$

and by

$$B = \frac{aA}{aA - a'}$$

In this case, the general integral may be written

$$(y - y_1)^{\lambda_1} (y - y_2)^{\lambda_2} (y - y_3)^{\lambda_3} = \text{const.}$$

where y_1, y_2, y_3 stand for the three particular integrals and $\lambda_1, \lambda_2, \lambda_3$ are certain constants. To prove this, we may follow the way indicated by G. DARBOUX¹⁾ in his fundamental memoir "Mémoire sur les équations différentielles algébriques du premier ordre et du premier degré".

Writing the differential equation in homogeneous coordinates we have

$$L(ydz - zdy) + M(zdx - xdz) + N(xdx - ydy) = 0$$

where

$$L = -2b'x^2 + a'xy - ay^2 + yz$$

$$M = a'x^2 - axy - xz - 2by^2$$

$$N = -(a + 2b')xz + (a' - 2b)yz.$$

Supposing

$$L \frac{\partial f}{\partial x} + M \frac{\partial f}{\partial y} + N \frac{\partial f}{\partial z} = Kf.$$

and replacing f by $A_i x - y - B_i z$, the function corresponding with this value of f is easily found, for

$$A_i L - M - B_i N = K_i (A_i x - y - B_i z)$$

gives immediately

$$K_i = - \left(2b' + \frac{a'}{A_i} \right) x - (2b - aA_i) y. \quad (i = 1, 2, 3)$$

¹⁾ Bull. Sci. math., Paris (Sér. 2) 2. 1878.

Remarking that $z=0$ is a fourth particular integral, and putting $f=z$, we obtain a fourth value for K

$$K_4 = \frac{N}{z} = -(a+2b')x + (a'-2b)y.$$

If now four numbers $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ may be found such that

$$\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 = 0$$

and

$$\alpha_1 K_1 + \alpha_2 K_2 + \alpha_3 K_3 + \alpha_4 K_4 = 0$$

the general integral may be written

$$(A_1 x - y - B_1 z)^{\alpha_1} (A_2 x - y - B_2 z)^{\alpha_2} (A_3 x - y - B_3 z)^{\alpha_3} z^{\alpha_4} = \text{const.}$$

or in inhomogeneous form

$$(y-y_1)^{\lambda_1} (y-y_2)^{\lambda_2} (y-y_3)^{\lambda_3} = \text{const.}$$

where $\lambda_1 : \lambda_2 : \lambda_3 = \frac{\alpha_1}{\alpha_4} : \frac{\alpha_2}{\alpha_4} : \frac{\alpha_3}{\alpha_4}$.

The numbers $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ must satisfy the equations

$$\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 = 0$$

$$a' \left(\frac{\alpha_1}{A_1} + \frac{\alpha_2}{A_2} + \frac{\alpha_3}{A_3} \right) + a \alpha_4 = 0$$

$$a (\alpha_1 A_1 + \alpha_2 A_2 + \alpha_3 A_3) + a' \alpha_4 = 0$$

hence

$$\frac{\alpha_1}{\alpha_4} = \frac{A_2 - A_3}{A_2 A_3} \left[-\frac{a'}{a} + A_2 + A_3 - \frac{a}{a'} A_2 A_3 \right] : D$$

$$\frac{\alpha_2}{\alpha_4} = \frac{A_3 - A_1}{A_1 A_3} \left[-\frac{a'}{a} + A_1 + A_3 - \frac{a}{a'} A_1 A_3 \right] : D$$

$$\frac{\alpha_3}{\alpha_4} = \frac{A_1 - A_2}{A_1 A_2} \left[-\frac{a'}{a} + A_1 + A_2 - \frac{a}{a'} A_1 A_2 \right] : D$$

D representing the determinant formed by the coefficients of the first members of the three preceding equations.

After a slight reduction we find

$$\lambda_1 = (A_2 - A_3) (aA_1^2 - 2bA_1 - a)$$

$$\lambda_2 = (A_3 - A_1) (aA_2^2 - 2bA_2 - a)$$

$$\lambda_3 = (A_1 - A_2) (aA_3^2 - 2bA_3 - a).$$

For small values of x and y the general integral may be expanded in the form

$$x^2 + y^2 + F_3 + F_4 + \dots = \text{const.}$$

which proves that in this case the origin is a centrum.

4. Assuming in the second place $a' + c' = i(a + c)$, and referring to our former paper, the origin will be a centrum if it is possible to determine an infinite series of homogeneous polynomials P_k of degree

k such that the following conditions are satisfied:

$$x \frac{\partial P_1}{\partial y} - y \frac{\partial P_1}{\partial x} = \left(\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y} \right) P_0$$

$$x \frac{\partial P_2}{\partial y} - y \frac{\partial P_2}{\partial x} = X \frac{\partial P_1}{\partial x} + Y \frac{\partial P_1}{\partial y} + \left(\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y} \right) P_1$$

$$x \frac{\partial P_3}{\partial y} - y \frac{\partial P_3}{\partial x} = X \frac{\partial P_2}{\partial x} + Y \frac{\partial P_2}{\partial y} + \left(\frac{\partial X}{\partial x} + \frac{\partial Y}{\partial y} \right) P_2$$

etc.

where $P_0 = 2$.

To expand the integral in the common form

$$x^2 + y^2 + F_3 + F_4 + \dots = \text{Const.}$$

we must observe that between the functions F and P the following relations exist

$$(xY - yX) P_{n-3} - (x^2 + y^2) P_{n-2} + n F_n = 0.$$

Considering now the infinite series of conditions we easily see that it is always possible to determine P_1 by the first condition. Proceeding to the second it is evident that every constant factor of P_1 may be omitted.

Writing therefore

$$P_1 = p_0 x + p_1 y$$

$$p_0 = -(b + c) \quad p_1 = a + b$$

and putting

$$P_2 = q_0 x^2 + q_1 xy + q_2 y^2$$

the second condition gives

$$q_1 = (3a + 2b)p_0 + a'p_1$$

$$2q_2 - 2q_0 = (4b + 2c)p_0 + (2a + 4b)p_1$$

$$-q_1 = cp_0 + (2b + 3c)p_1.$$

These equations can only be satisfied when

$$(3a + 2b + c)p_0 + (a' + 2b + 3c)p_1 = 0$$

or introducing the values p_0 and p_1 , when

$$aa' - cc' = b(a + c) - b'(a' + c').$$

From this condition and the given relation

$$a' + c' = i(a + c)$$

we deduce

$$a = b - i(b' - c) \quad , \quad c' = -b + i(a + b')$$

so

$$p_0 = -i(a + b')$$

$$p_1 = a + b'.$$

If therefore

$$a + b' = 0$$

P_1 and all the following functions P_2, P_3, \dots vanish, which proves that the origin is a centrum in this case.

To determine the integral we have

$$2(xY - yX) + 3F_2 = 0$$

which gives

$$x^2 + y^2 - \frac{2}{3} [a'x^3 + (2b' - a)x^2y + (c' - 2b)xy^2 - cy^3] = \text{const.}$$

with

$$a' = b + i(a+c) \quad , \quad b' = -a \quad , \quad c' = -b$$

5. When

$$\begin{aligned} a' + c' &= i(a+c) \\ aa' - cc' &= (b - ib')(a+c) \end{aligned}$$

and

$$a + b' \neq 0$$

the factor $a' + b$ may be omitted; thus

$$P_1 = -ix + y.$$

Determining now P_2 , the coefficient q_0 may be chosen arbitrarily. Putting $q_0 = 0$, we get

$$P_2 = q_1 xy + q_2 y^2$$

where

$$q_1 = a' - i(3a + 2b') \quad q_2 = 2a + 3b' - ib.$$

Assuming

$$P_3 = r_0 x^3 + r_1 x^2 y + r_2 x y^2 + r_3 y^3$$

$$P_4 = s_0 x^4 + s_1 x^3 y + s_2 x^2 y^2 + s_3 x y^3 + s_4 y^4$$

the following conditions give

$$\begin{aligned} r_1 &= a' q_1 \\ 2r_2 - 3r_0 &= (3a + 4b') q_1 + 2a' q_2 \\ 3r_3 - 2r_1 &= (4b + 3c') q_1 + (2a + 6b') q_2 \\ -r_2 &= c q_1 + (2b + 4c') q_2 \end{aligned}$$

which always can be satisfied, and

$$\begin{aligned} s_1 &= (5a + 2b') r_0 + a' r_1 \\ 2s_2 - 4s_0 &= (8b + 2c') r_0 + (4a + 4b') r_1 + 2a' r_2 \\ 3s_3 - 3s_1 &= 3c r_0 + (6b + 3c') r_1 + (3a + 6b') r_2 + 3a' r_3 \\ 4s_4 - 2s_2 &= 2c r_1 + (4b + 4c') r_2 + (2a + 8b') r_3 \\ -s_3 &= c r_2 + (2b + 5c') r_3. \end{aligned}$$

which are impossible unless

$$(5a + 2b' + c) r_0 + (a' + 2b + c') r_1 + (a + 2b' + c) r_2 + (a' + 2b + 5c') r_3 = 0.$$

This condition may be written

$$Ar_1 + B(2r_2 - 3r_0) + C(3r_3 - 2r_1) + D(-r_2) = 0$$

where

$$\begin{aligned} A &= 5a' + 10b + 13c' \\ B &= -(5a + 2b' + c) \\ C &= a' + 2b + 5c' \\ D &= -(13a + 10b' + 5c). \end{aligned}$$

Introducing q_1 and q_2 this takes the form

$$\begin{aligned} q_1 [a' A + (3a + 4b') B + (4b + 3c') C + cD] \\ + q_2 [2a' B + (2a + 6b') C + (2b + 4c') D] = 0 \end{aligned}$$

or, eliminating a' and c'

$$\begin{aligned} q_1 [- (30a^2 + 40ab' + 32ac + 12b'^2 + 20b'c + 10c^2) + i(12ab + 8bc + 4bb')] \\ + q_2 [(12ab + 8bc + 4bb') - i(42a^2 + 44ab' + 28ac + 12b'^2 + 16b'c + 2c^2)] = 0. \end{aligned}$$

To simplify this condition we write

$$\begin{aligned} q_1 [-(3a + b' + 2c)(10a + 10b' + 4c) - 2(b' - c)^2 + 4ib(3a + b' + 2c)] \\ + q_2 [4b(3a + b' + 2c) - i(3a + b' + 2c)(14a + 10b') - 2i(b' - c)^2] = 0, \end{aligned}$$

or

$$\begin{aligned} -2(b' - c)^2 (q_1 + iq_2) + \\ + (3a + b' + 2c)[4b(iq_1 + q_2) - 10b'(q_1 + iq_2) - 10a(q_1 + iq_2) - 4cq_1 - 4iaq_2] = 0. \end{aligned}$$

Now

$$4b(iq_1 + q_2) - 4cq_1 - 4iaq_2 = 4(2a + 3b' - c)(q_1 + iq_2)$$

so

$$-2(q_1 + iq_2)(a + c)(3a - 2b' + 5c) = 0$$

or

$$(a + c)[2b - i(a - c)](2b' - 3a - 5c) = 0.$$

This breaks up into three conditions which will be considered separately.

6. When, in the first place

$$\begin{aligned} a' + c' &= i(a + c) \\ aa' - cc' &= (b - ib')(a + c) \\ a + c &= 0 \end{aligned}$$

the second relation depends upon the first and the third.

This case has already been considered in Art. 2.

7. Supposing secondly

$$\begin{aligned} a + c' &= i(a + c) \\ aa' - cc' &= (b - ib')(a + c) \\ 2b &= i(a - c) \end{aligned}$$

which may be written

$$2a' = i(a - 2b' + c)$$

$$2c' = i(a + 2b' + c)$$

$$2b = i(a - c)$$

then again the general integral of the corresponding differential equation may be constructed from a system of particular integrals.

Substituting

$$y = Ax + B$$

in the differential equation we find that it is satisfied when

$$B = \frac{A}{c' - cA}$$

and A is the common root of the two cubics

$$cA^3 + (2b - c')A^2 + (2b' - c)A + c' = 0$$

$$cA^3 + (2b - c')A^2 + (2b' + a)A - a' = 0.$$

Therefore

$$-(a + c)A + a' + c' = 0$$

which combined with the relation

$$a' + c' = i(a + c)$$

gives $A = i$ whence the corresponding particular integral may be written

$$y = ix + \frac{i}{c' - ic}$$

or

$$p \equiv x + iy - \frac{2i}{a + 2b' - c} = 0.$$

This being the only possible integral of the first degree, now we will try to satisfy the differential equation by an equation of the second degree

$$Ax^2 + 2Hxy + By^2 + 2Gx + 2Fy + C = 0.$$

Therefore

$$\frac{Ax + Hy + G}{Hx + By + F} = \frac{-x + a'x^2 + 2b'xy + c'y^2}{y + ax^2 + 2bxy + cy^2}$$

must be equivalent with

$$(Ax^2 + 2Hxy + By^2 + 2Gx + 2Fy + C)(mx + ny) = 0$$

Thus the following relations must be satisfied

$$aA + dH = mA$$

$$2bA + aH + 2b'H + a'B = 2mH + nA$$

$$cA + 2bH + c'H + 2b'B = mB + 2nH$$

$$cH + c'B = nB$$

$$\begin{aligned}
 aG - H + a'F &= 2mG \\
 A + 2bG - B + 2b'F &= 2mF + 2nG \\
 H + cG + c'F &= 2nF \\
 -F &= mC \\
 G &= uC'.
 \end{aligned}$$

The last two equations give $mG + nF = 0$, therefore adding the 5th and 7th equations we get

$$(a+c)G + (a'+c')F = 0$$

which compared with the given relation

$$a' + c' = i(a+c)$$

shows that we may take

$$G = 1, \quad F = i, \quad C = -\frac{i}{m}, \quad n = im.$$

Considering now the 1th, 4th, and 5th equation we get

$$A = \frac{a'}{m-a}H, \quad B = \frac{c}{im-c'}H, \quad H = a + ia' - 2m$$

and substituting these values in the 2th, 3th and 6th, we see that m must be such as to satisfy the following three relations

$$\begin{aligned}
 \frac{a'(2b-im)}{m-a} + \frac{a'c}{im-c'} + a + 2b' - 2m &= 0 \\
 \frac{a'c}{m-a} + \frac{c(2b'-m)}{im-c'} + 2b + c' - 2im &= 0 \\
 \left(\frac{a'}{m-a} - \frac{c}{im-c'} \right) (a + ia' - 2m) + 2(b + ib' - 2im) &= 0
 \end{aligned}$$

The roots of the last equation are easily found, for

$$H = a + ia' - 2m = \frac{1}{2}(a - c + 2b' - 4m) = -i(b + ib' - 2im)$$

so a first root is

$$m_0 = \frac{a + ia'}{2} = \frac{a + 2b' - c}{4}$$

and consequently the others

$$m_1 = \frac{3a + 2b' + c}{4}, \quad m_2 = \frac{a + 2b' - c}{2} = 2m_0$$

Now m_0 does not satisfy the first and second equations, but m_1 and m_2 do. Corresponding with m_1 and m_2 we have therefore two solutions

$$u \equiv H_1 \left(\frac{a'}{m_1 - a} x^2 + 2xy + \frac{c}{im_1 - c'} y^2 \right) + 2x + 2iy - \frac{i}{m_1} = 0$$

and

$$H_2 \left(\frac{a'}{m_1} x^2 + 2xy + \frac{c}{im_2 - c'} y^2 \right) + 2x + 2iy - \frac{i}{m_2} = 0.$$

the last solution however may be easily reduced to

$$\left(x + iy - \frac{i}{2m_0} \right)^2 = 0$$

which is the square of the first particular integral, so that only one integral of the second degree is left.

To construct the general integral from the two solutions found, we write homogeneously

$$L(\eta dz - z dy) + M(z dx - x dz) + N(x dy - y dx) = 0$$

where

$$L = -2b' x^2 - c' xy + cy^2 + yz$$

$$M = a' x^2 - axy - xz - 2b y^2$$

$$N = -(a + 2b') xz - (2b + c') yz.$$

Remarking that $z = 0$ is also a particular integral and replacing f in

$$L \frac{\partial f}{\partial x} + M \frac{\partial f}{\partial y} + N \frac{\partial f}{\partial z} = Kf$$

by p , u , and z , we find the corresponding values of K to be

$$K_1 = -\frac{1}{2} (a + 2b' + c) x - iay$$

$$K_2 = -\frac{1}{2} (a + 6b' - c) x - \frac{i}{2} (3a + 2b' - 3c) y$$

$$K_3 = \frac{N}{z} = -(a + 2b') x - \frac{i}{2} (3a + 2b' - c) y.$$

Now three numbers α_1 α_2 α_3 may be found which satisfy the equations

$$\alpha_1 K_1 + \alpha_2 K_2 + \alpha_3 K_3 = 0$$

or

$$(a + 2b' + c) \alpha_1 + (a + 6b' - c) \alpha_2 + 2(a + 2b') \alpha_3 = 0$$

$$2a \alpha_1 + (3a + 2b' - 3c) \alpha_2 + (3a + 2b' - c) \alpha_3 = 0$$

and

$$\alpha_1 + 2\alpha_2 + \alpha_3 = 0.$$

With these values

$$\frac{\alpha_1}{\alpha_3} = -\frac{3a + 2b' + c}{a - 2b' + 3c} \quad \frac{\alpha_2}{\alpha_3} = \frac{a + 2b' - c}{a - 2b' + 3c}.$$

the general integral may be written

$$p^{\alpha_1} u^{\alpha_2} z^{\alpha_3} = \text{const.}$$

or returning to the inhomogeneous coordinates

$$\left[\frac{a+c}{a-2b'-c} \{i(a-2b'+c)x^2 - (a-2b'-c)xy + 2icy^2\} + x + iy - \frac{2i}{3(a-2b'-c)} \right]^{a+2b'-c} \\ \frac{\left(x + iy - \frac{2i}{a+2b'-c} \right)^{3a+2b'+c}}{3} = const.$$

For small values of x and y the first member of this equation may be expanded in the form

$$x^2 + y^2 + F_3 + F_4 + \dots = const.$$

which proves that in this case the origin is a centrum.

A remarkable case presents itself when

$$3a + 6b' - c = 0$$

for then

$$\alpha_1 = -\frac{4}{3}(a+c) \quad \alpha_2 = -\frac{2}{3}(a+c) \quad \alpha_3 = \frac{8}{3}(a+c)$$

$$p = x + iy + \frac{3i}{a+c}$$

$$u = (a+c) \left[i \frac{4a+c}{2a-c} x^2 - 2xy + i \frac{3c}{2a-c} y^2 \right] + 2(x+iy) - \frac{3i}{a+c}$$

and the general integral

$$p^2 u = const.$$

Physics. — *“Preliminary account of some results obtained by the Netherlands Eclipse Expedition in observing the annular solar eclipse of April 17th, 1912.”* By Prof. W. H. JULIUS.

The observation of the annular solar eclipse of April 17th, 1912 near Maastricht was favoured by an exceptionally clear sky.

The general plan included:

1. Visual observations on contacts and on positions of crescents.
2. Exposures with the photoheliograph.
3. Exposures with the objective prism spectrograph.
4. Determination of the minimum value of the total radiation at the instant of centrality.
5. Measurement of the entire process of radiation from the first until the fourth contact.
6. Photometric determination of the varying intensity of the sunlight from the first until the fourth contact for five spectral regions of 30 Å each.
7. Observation of various secondary phenomena.

The full treatment of the observational data obtained by the numerous (nearly 40) members of the expedition will of course require a long time. Certain results, however, came out at once with sufficient evidence to justify a preliminary communication.

To begin with we may safely conclude from the observations sub 1, 2, and 3, that at our station the eclipse really was very nearly central, corresponding to the prediction of the Leiden astronomers — although the small corrections, necessary to determine *a posteriori* the exact position of the line of centrality, are yet to be calculated from these very observations.

With the objective prism spectograph (prismatic camera) Prof. NILAND obtained results even surpassing the expectation. Out of five exposures two were made so near the time of centrality, that both photographs show the hydrogen lines H_α , H_β , H_γ , H_δ , and the calcium lines H and K as complete chromospheric rings; besides, thanks to the valleys and mountains of the moon's edge, far over a hundred lines are in evidence partly as FRAUNHOFER lines, partly as flash lines. A careful study of this plate looks promising.

Special attention was given to the measurements of *integral radiation*, because an annular eclipse was expected to separate the radiation due to the entire solar atmosphere from the radiation due to the photosphere in a more convincing manner, than a total eclipse could do.

The measurements sub 4 and 5 were made in duplo with two independent equipments: *a*) a *thermopile* (the same that was used in observing the total eclipses of 1901 on Sumatra and of 1905 near Burgos¹⁾) in combination with a moving coil galvanometer of SIEMENS & HALSKE; *b*) a *bolometer* with a quick, sensitive and dead-beat galvanometer constructed by Dr. W. J. H. MOLL.

As in arrangement *a*, after a sudden access or interception of radiation, an interval of 10 seconds was required for the dead-beat galvanometer to attain its final position, and because the annular phase of the eclipse would probably last not much longer than one second, the set of apparatus *b* was designed so as to become stationary in less than one second. Dr. MOLL had succeeded in making his bolometer and sensitive galvanometer answer this condition.

Both thermopile and bolometer were directly exposed to the sun's rays, without intervention of any lenses or mirrors. The sensitiveness of the arrangements was under easy control during the observations

¹⁾ Total Eclipse of the Sun. Reports on the Dutch Expedition to Karang Sago, Sumatra, No 4. Heat Radiation of the Sun during the Eclipse, by W. H. JULIUS, (1905). — Cf. also: These Proc. VIII, p. 503 and 668 (1905—1906).

by regulating resistances; if necessary it could be made such, that $\frac{1}{100000}$ of the total radiation of the uneclipsed sun would have been perceptible; but referring to the results obtained with the total eclipse in 1905 at Burgos¹⁾, I expected the minimum not to fall below $\frac{1}{10000}$ on the occasion of this annular eclipse.

The constancy of the zero readings of the galvanometers was all that could be desired. During the whole lapse of time from the first until the fourth contact visual readings on both instruments were made at known epochs; moreover, the equipment *b* allowed of a continual photographic record of the motion of the galvanometer coil to be made during an interval of 10 minutes including the annular phase.

The principal result derived from the radiation measurements at this eclipse is, that an *upper limit* has been found, which the total emitting and diffusing power of the entire solar atmosphere (the so-called reversing layer, the chromosphere, and the corona together) cannot exceed.

Indeed, at the instant of centrality, the sky being perfectly clear, the photographically recorded radiation curve passed through a sharp minimum, proving that the remaining intensity was less than $\frac{1}{5000}$ of the intensity of the radiation emitted by the uneclipsed sun.

After the readings furnished by equipment *a* had been plotted down on coordinate paper, the intensity curve came out so regular and perfectly symmetrical in the same interval of 10 minutes covered by the photographic curve, that the results claim great trustworthiness. In the visual curve the minimum ordinate did not correspond to $\frac{1}{5000}$ of the maximum radiation, but to $\frac{1}{2000}$, and the curve was somewhat rounded off as compared with the photographic record — a natural consequence of the relative slowness of the apparatus *a*.

As the minimum value indicated by the quickest instrument must come nearest to truth, we may conclude that this eclipse made the integral solar radiation fall below $\frac{1}{5000}$ of its ordinary value.

Part of that remnant must still be due to the small uncovered ring of the solar disk. Estimating the apparent surface of that ring at $\frac{1}{1000}$ of the surface of the disk, its apparent radiating power per square unit at $\frac{1}{10}$ of the average intrinsic radiating power of the disk (thus allowing for the decrease of brilliancy toward the edge), we may admit, that at the epoch of centrality the photosphere was still able to furnish us with $\frac{1}{10000}$ of the ordinary amount of radiation. Thus no more than $\frac{1}{10000}$ of the sun's total radiation toward the

¹⁾ W. H. JULIUS, These Proc. VIII, p. 672.

earth is left, as originating from the part of the so-called solar *atmosphere* projecting outside the moon's edge. Let us suppose that atmospheric emission to proceed chiefly from the lower, thin absorbing layer.

The next question is: what is the proportion between the volume of the part of that lower atmospheric layer, visible during the annular phase, and the volume of the half-spherical shell from which, without an eclipse, the radiation emitted and diffused by the same layer reaches the earth. By simple considerations we feel that it would scarcely be possible to put the value of that fraction lower than $\frac{1}{10}$; so half the solar atmosphere radiates, at most, ten times as much as the part visible during the annular eclipse.

Consequently: *Less than $\frac{1}{1000}$ of the total (ultraviolet, visible, and infrared) solar radiation proceeds from those parts of the celestial body which lie outside the photospheric level.*

This result proves that it is impossible to maintain the theory, which considers the photosphere to be a layer of incandescent clouds, whose decrease of luminosity from the centre toward the limb of the solar disk would be caused by absorption and diffusion of light in an enveloping atmosphere ("the dusky veil"). For if this theory were right, then, according to the calculations made by PICKERING, WILSON, SCHUSTER, VOGEL, SEELIGER, and other astrophysicists such an atmosphere should absorb an important fraction ($\frac{2}{4}$ to $\frac{1}{3}$) of the sun's radiation. Now, as the fraction emitted appears to be smaller than $\frac{1}{1000}$, and yet the atmosphere must be in a stationary condition, one would be forced to conclude, that the main part of the absorbed energy is continually being dissipated through space in some absolutely unobserved form. This necessary inference not being acceptable, we must look for another interpretation of the photosphere.

As to the measurements of radiation mentioned sub 5 we can only state, for the present, that they ran well (although occasionally slightly affected by some haze); we therefore may hope to deduce from them, with greater accuracy than was hitherto attained, the law of decrease of the integral radiation when passing from the centre toward the limb of the disk.

The photometric observations (sub 6) made by Mr. B. J. VAN DER PLAATS included 480 settings, from which the distribution of luminosity on the disk for five different regions of the spectrum (closely corresponding to the regions selected by H. C. VOGEL) has to be computed.

Chemistry. — “*Confirmations of the theory of the phenomenon allotropy.*” II. By Prof. A. SMITS and Dr. H. L. DE LEEUW. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of March 30, 1912).

The investigation set on foot more than a year ago to test the above-mentioned theory by different substances, the results of which have already been communicated as far as the substances *mercury iodide*, *phosphorus*, and *sulphur* are concerned, has now already advanced so far also with regard to some other substances, that some results may be published.

As the investigation chiefly concerns the curves of heating and cooling, we will first give some preliminary general considerations about these curves. If we think the temperature (T)-axis to be the vertical one, and the time (S) axis the horizontal one, we find as temperature-time-curve a continuous line, which in the most favourable case has a horizontal middle part.

If we consider the curve of heating $abcd$, and begin at a , we commence with the curve of heating of the solid substance, and $\frac{dT}{ds}$ will depend first of all on the quantity of heat that is supplied per sec., and secondly on the specific heat of the solid substance.

Before the point b is reached, $\frac{dT}{ds}$ decreases continuously to the value 0, and the cause of this is that the conductivity of heat of the solid substance is not infinitely great, in consequence of which melting sets already in in the outer layers,

before the mass in the immediate neighbourhood of the thermometer, which is thought quite surrounded by the solid substance, has reached the temperature of melting, by which at the same time the supply of heat to the inner layers is greatly diminished.

This rounding, which takes place before the point b , where the horizontal part begins, has been reached, will therefore become the greater as the conductivity of heat of the solid substance is smaller, the specific heat smaller, and the supply of heat greater.

If once a liquid layer has been formed, we must allow for the phenomenon of *super-heating*. Without any doubt the liquid which



Fig. 1.

surrounds the solid substance in the experiment discussed here, will always assume a higher temperature than corresponds with the melting-point of the solid substance and now with a certain supply of heat it will depend on the rapidity with which the heterogeneous equilibrium sets in in the border layer, and also on the value of the melting heat, whether the solid substance which surrounds the thermometer will possess a constant temperature for some time.

If the heterogeneous equilibrium in the border layer was established with infinite rapidity, a horizontal part of the curve of heating would have to occur even for the *smallest* melting-heat, and the *greatest* supply of heat, if namely, as has been supposed from the outset, the system behaved in a perfectly unary way.

It follows from this at the same time, that when as is most likely the case, the heterogeneous equilibrium in the border layer is *not* established with infinite rapidity, a substance with small melting-heat will be much sooner super-heated than a substance with a great melting-heat, and if this phenomenon occurs a line will be found for which $\frac{dT}{ds}$ has a positive value in all points instead of the horizontal portion.

Now, however, it has been supposed here that the substance behaves in a perfectly unary way, and *for this case* we have arrived at the conclusion that when a horizontal part is wanting in the curve of heating, this must point to super-heating of the solid substance in consequence of the retarded heterogeneous equilibrium. In most cases, however, we are still entirely ignorant about whether a substance behaves as a unary one or not under definite circumstances, and as the horizontal part will also be wanting for the case that the substance *does not* behave in a unary way in the heating-experiment, but the heterogeneous equilibrium *does* set in rapidly enough, because then superheating occurs in consequence of the retarded homogeneous equilibrium, the curves of heating can teach us anything about the behaviour of the substance only when the circumstances are made as much as possible the same for different heating experiments, while the previous history of the substance is greatly varied.

Before passing on to another subject it is still necessary to point out about the curve of heating that though a horizontal part has appeared, there yet occurs a curvature at *c* where $\frac{dT}{ds}$ increases continuously till all the solid substance has disappeared.

This rounding is owing to this that the liquid, which is certainly superheated and will be the more superheated as the surface of the solid substance decreases, comes more and more into contact with

the sensible part of the thermometer (mercury vessel or windings of the resistance thermometer).

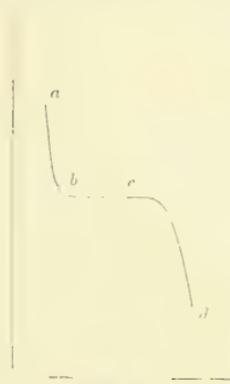


Fig. 2.

Both roundings *b* and *c* will be diminished by slow heating, and augmented by greater supply of heat. Moreover the rounding *c* may be greatly reduced by stirring, which circumstance is, however, expressly excluded here.

Let us now consider the curve of cooling *abcd*. This curve indicates the temperature-time curve which we get when a substance behaves entirely as a unary substance, and the heterogeneous equilibrium between the solid substance and the border layer sets in rapidly enough for the loss of heat to be compensated by the heat of crystallisation.

Starting from *a* we first get the curve of cooling of the liquid.

Before the horizontal part is reached, the value of $\frac{dT}{ds}$ becomes here continuously smaller negative over a certain range of temperature, because of the appearance of solidification in the outer layers already before the liquid in the immediate neighbourhood of the thermometer has assumed the temperature of solidification. So this phenomenon is due to the insufficient conductivity of heat of the liquid.

If when the liquid round the thermometer has reached the temperature of solidification, the said compensation takes place, the curve of cooling will present a horizontal part. Before the mass has, however, become entirely solid, a change sets in, because the thermometer comes more and more in contact with the solid substance, which for so far as it is not in direct contact with the liquid will possess a lower temperature than the liquid, which will render $\frac{dT}{ds}$ again continuously stronger negative, till the last trace of liquid has vanished.

If the heterogeneous equilibrium is not established with infinite rapidity, the loss of heat can no longer be compensated by the heat of crystallisation, in consequence of which the liquid in contact with the solid substance is undercooled. In this case a more or less descending line will be found instead of the horizontal part.

To simplify the case it has been supposed here that the substance behaves as a unary one, which in reality is very doubtful, and therefore we may not conclude when we find a curve of cooling

without a horizontal middle part, that the *heterogeneous* equilibrium has not set in rapidly enough, for it is also possible that the *undercooling* is partly or wholly to be attributed to the fact that the *homogeneous* equilibrium does not set in, or in other words that the substance does not behave as a unary one.

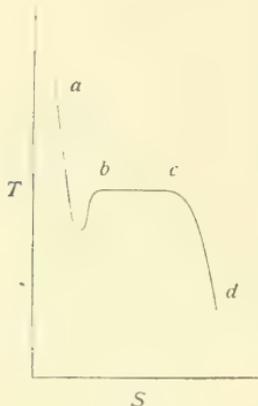


Fig. 3.

The practically ideal curve has then a form as is indicated in fig. 3.

MERCURY.

In the first place we will communicate what results the investigation of the element *mercury* has yielded, because this substance is distinguished from other substances examined up to now by the great chance it offers for an ideal behaviour when heated.

For mercury we meet namely with the case that even on a considerable supply of heat a temperature-time curve is found with a horizontal middle part, from which follows that the substance behaves in a *unary* way under these, in general disturbing, circumstances, and the heterogeneous equilibrium sets in with great rapidity in case of *heating*.

So in a case like this we need not apply the method mentioned just now, for if a substance continues to behave in a unary way when not only the previous history, but also the circumstances during the melting are chosen different, this will certainly be the case when a modification is applied only to the previous history.

Fig. 4 refers to an experiment, in which a wide test-tube, partially filled with mercury, is heated from -80° by being exposed to the air. In the mercury a resistance thermometer had been placed which

was inserted in one of the branches of a WHEATSTONE bridge. The observation of the image of a NERNST-lamp cast by the mirror of

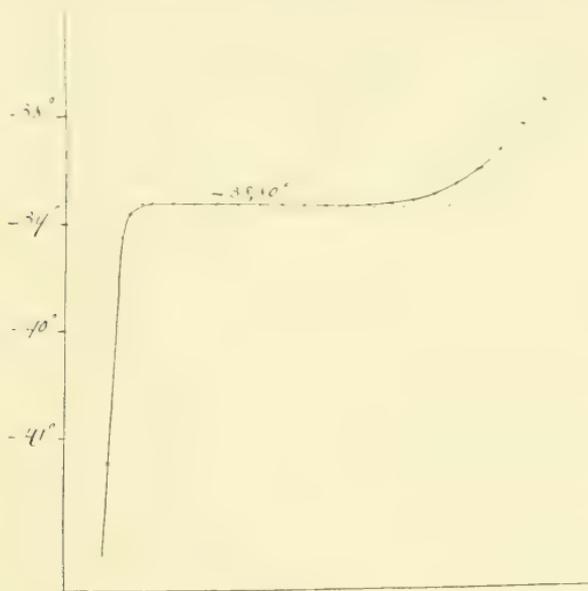


Fig. 4.

the galvanometer on a scale, enabled us to follow the change of the temperature. From the readings, which were made every 10 seconds it appeared that the resistance thermometer, and so also the mercury in the immediate neighbourhood, maintained the same temperature for 95 seconds, which temperature is exactly the same as that which is found, when solid mercury is melted in a bath of low temperature, and for which $-38^{\circ}.80$ was found with the gas-thermometer. So in spite of the great difference in temperature between the mercury and the surroundings no superheating of the solid mercury took place.

The following fig. 5 shows the result that we obtained when we rapidly heated mercury from -80° in an air-jacket placed in boiling water. It appears from the observations, which were recorded here every 5 seconds, that the temperature now remained perfectly constant for 45 seconds. The melting proceeded, indeed, more rapidly now, in consequence of the great supply of heat, but in spite of this the ideal course was observed, which points to a unary behaviour and perfectly heterogeneous equilibrium.

Now it was to be expected, however, that the equilibrium of the

substance mercury, which continued to behave in an ideal way under greatly disturbing circumstances, might nevertheless be upset, when

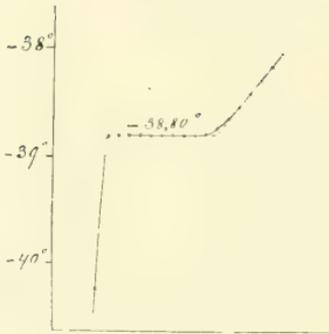


Fig. 5.

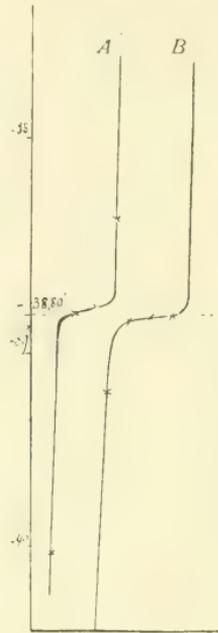


Fig. 5a.

the disturbing influences are only made strong enough. To ascertain this the experiment was repeated under much intenser circumstances: a quartz tube with solid mercury of -80° was suddenly placed in water of 80° resp. in water of 100° *without* an air-jacket. We then found the lines *B* and *A* fig. 6, the crosses indicating the readings every 5 seconds. It follows from these lines that this experiment was too much even for mercury, which was in no way astonishing. As it now appeared that the previous history had absolutely no influence on the shape and the situation of the curve, we thought we were justified in concluding from this that the mercury had been superheated here in consequence of a retardation of the heterogeneous equilibrium.

In connection with what precedes it is exceedingly interesting to see what was found in the determination of the curve of cooling. Whereas it is exceedingly difficult to make the mercury behave in a non-ideal way when it is heated, this is much easier to reach in case of cooling, and this is very remarkable, for the foregoing has

perfectly convinced us of the unary behaviour of mercury, unless in cases of very excessive treatment, so that the fact that a horizontal middle part in the curve of cooling fails to appear under *not* extraordinarily disturbing circumstances, must undoubtedly be attributed to the too slow setting in of the heterogeneous equilibrium.

If mercury is cooled down in an air-jacket which is placed in a bath of -80° , we may succeed when the jacket is wide enough, and the cooling in consequence of this takes place very slowly, to obtain a curve of cooling with horizontal middle part, as Fig. 6 (readings every 40 seconds) shows, but as soon as the cooling takes

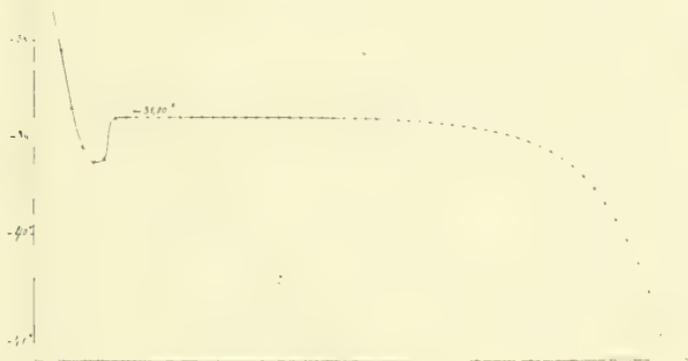


Fig. 6.

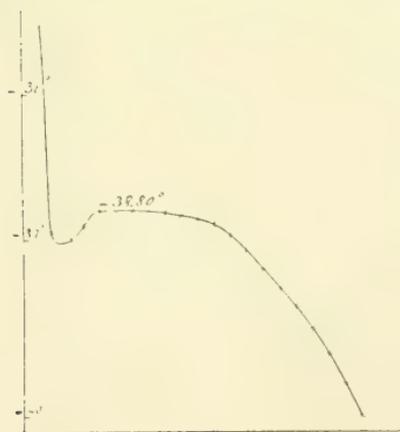


Fig. 7.

in exceedingly rapidly in case of heating, but slowly in case of cooling. It follows from this that superheating of the solid substance

place somewhat more rapidly, e.g. by the use of a somewhat less wide air-jacket, the mercury does *not* behave ideally, as fig. 7 shows. The top, indeed lies at $-38^{\circ},80$ here, but a purely horizontal part is wanting, in spite of the comparatively slow process of the solidification. With a still narrower air-jacket, the curve was much steeper. So we arrive at the surprising result that the *heterogeneous equilibrium between solid mercury and the border layer sets*

is not ascertained or only under very particular circumstances, whereas undercooling of the liquid in contact with solid substance seems to appear very easily.

T I N.

In the second place tin was investigated, because the existence of points of transition led us to expect here that the experiment might be able to reveal the complexity of the system.

We expected this the more confidently, as phenomena have been observed in the technique that point to this that the temperature of the liquid tin at the moment of casting has an influence on the properties of the solidified mass.

In DAMMER'S "Handbuch der chemischen Technologie" this has been expressed as follows. "Glanz und Festigkeit des Zinns hängen von der Temperatur beim Giessen ab. Es darf weder so sehr erhitzt sein, dass seine Oberfläche in Regenbogenfarben spielt, noch so kalt, dass sie matt ist. In beiden Fällen, zu heiss oder zu kalt gegossen, büsst das Zinn an seinem Glanze und an seiner Festigkeit ein: im ersteren Fall wird es roth, im letzteren kaltbrüchig".

The apparatus used by us in the investigation of tin, has been represented in fig. 8. The resistance thermometer has been ground at *c* into the melting-vessel *A*, which consisted of not very readily fusible glass. This ground joint is surrounded by a jacket, which

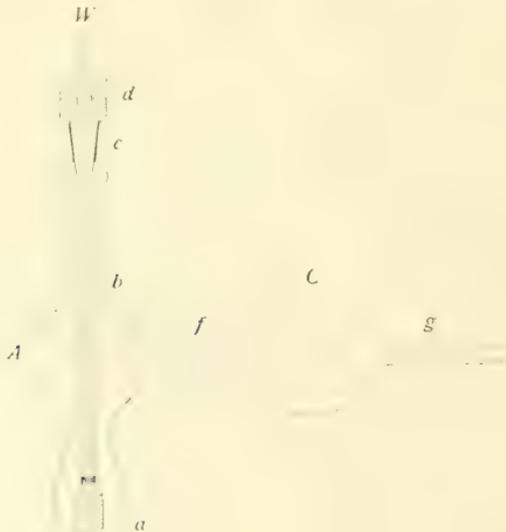


Fig. 8.

was filled with mercury, and was then closed by a layer of paraffin.

The melting-vessel had been blown out to a diameter of 5 c.m. at the bottom, there where the windings of the resistance thermometer are found, so that this part could contain 250 gr. of tin. Above this the vessel had been blown out to a still wider bulb b^1), which could be fused to a second bulb C by means of a capillary, which was supplied on the opposite side with a second capillary.

Before it was fused to bulb b , bulb C had been filled with pieces of very pure tin, excellently prepared by KAILBAUM. The only impurity it contained was lead, and only 0,04 %.

Then first of all the capillary g was connected with the Gaedepomp by means of an air-pump rubber tube, and so far exhausted that a Geissler tube, which was permanently in connection with the P_2O_5 -vessel of the Gaedepump, no longer showed phenomena of discharge.

Then the capillary g was melted off, and the bulb C was heated to melt the tin that is in it. At the same time also the bulb b of the melting-vessel A was heated, and the whole apparatus was held horizontal. The melted tin was now covered with a coat of oxide, and the capillary f served to remove this before the tin arrived in the melting-vessel A . If, viz., now the apparatus was made to rotate a little round the resistance thermometer as horizontal axis, the tin flowed from the bulb C through the capillary f into the bulb b , the coat of oxide remaining behind in C . The melting-vessel remained in a horizontal position, till all the tin had solidified in the bulb b , after which the capillary f was melted off.

The tin filtered in this way was so perfectly free from the coat of tin-oxide, that in its melted condition it looked quite like mercury, and in solid condition it consisted of fine glittering crystals.

Of course we cannot guarantee that our tin was *perfectly* pure, for though the solid tin-oxide had been removed, the tin will have contained some tin-oxide in a dissolved condition. As this quantity was, however, very small, and as it was at all events the same in the different experiments, this circumstance did not afford an insuperable difficulty for our purpose.

Now the apparatus was ready for the experiment, and was carefully immersed in a bath of melted potassium-sodium nitrate in order to melt the tin, and make it flow into the widened part a . The quantity of tin had been chosen so that the melting-vessel was

¹⁾ After the experiment the liquid tin was conducted to this bulb to solidify here. This was done in order to prevent damage of the resistance thermometer in the solid mass.

filled up to the constriction between *a* and *b* in a vertical position.

Now in order to find the point of solidification of tin for an it possible unary behaviour, the melting vessel, which had only been heated a few degrees above the melting-point of tin, was suddenly conveyed to an air-jacket, which was found in another larger potassium-sodium nitrate bath of a constant temperature $\pm 220^\circ$.

The connection of the thermometer with the WHEATSTONE bridge had already been effected before, and the image of a NERNST lamp, cast on the graduated scale by the mirror of the galvanometer showed, that the liquid undercooled on cooling. If the liquid was lightly shaken, crystallisation set in, and the image rose to a maximum, where it remained immovable for more than 2,5 minutes;

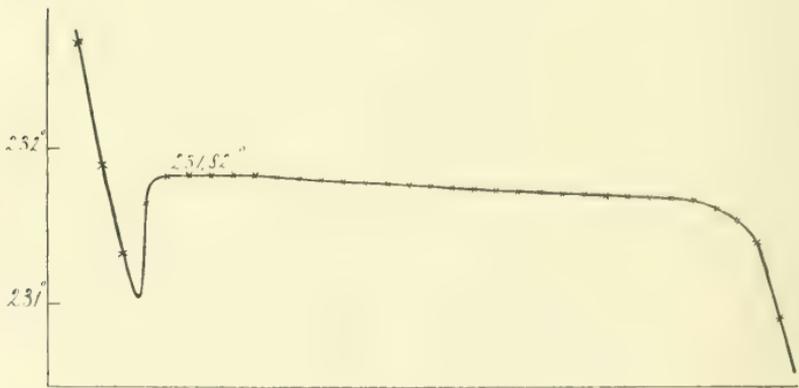


Fig. 9.

then it descended very slowly for a long time, after which it pretty suddenly began to descend rapidly. The temperature-time curve that follows from these experiments, which were repeated every 10 seconds, has been drawn in figure 9, in which only the observations every 40 seconds are indicated to restrict the number of crosses.

It appears from this line that the solidifying mass round the thermometer maintained the same temperature of 231.82° for more than 2.5 minutes, and that it then slowly decreased to about 231.63° , after which the temperature pretty suddenly decreased rapidly. As it always appeared that the mass had already solidified for the greater part at the moment that the slow decrease first commenced, we thought that we had to conclude from the above very peculiar line that the system really behaved in a unary way here on solidification, and that the slow decrease, which preceded the rapid

decrease was not owing to the trace of tin-oxide, but had to be ascribed to an exothermic process, which took place in the solid mass after the solidification, which supposition was corroborated by the subsequent experiments.

HOLBORN and HENNIG¹⁾, who determined the point of solidification of tin in an open vessel found 231.83° , when they used 1.5 K.G., a value which only differs 0.01° from ours.

If we use an open vessel, tin gets covered with a layer of oxide, and strictly speaking, we do not determine the point of solidification of pure tin, but the temperature of the eutectic point of tin oxide — tin. Accordingly we might conclude from the exceedingly small difference between HOLBORN and HENNIG's result and ours that tin-oxide dissolves exceedingly little in tin, and that it is not necessary for the determination of the point of solidification to work in vacuum.

Yet for our purpose the determination of the influence of the previous history of tin on its point of solidification, the vacuum, and the absence of solid tin-oxide appeared an indispensable requirement, as with rapid cooling of liquid tin which had been heated to a high degree exposed to the air, perfectly unreliable and widely divergent results were obtained, whereas they were always the same in vacuum and in absence of solid tin-oxide.

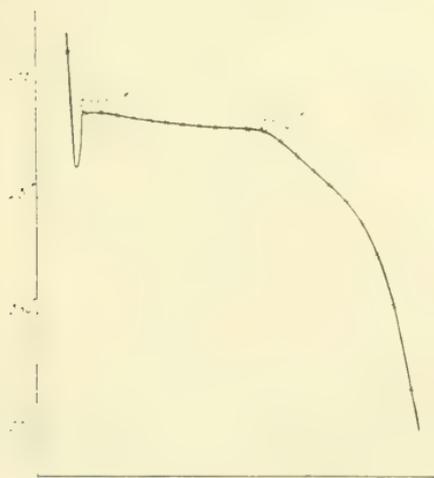


Fig. 10.

As in order to ascertain the influence of the previous history it is necessary to work rapidly, and so also to make the solidification take place rapidly, first the curve of cooling was determined of tin that was heated only just above the melting-point, and was cooled simply by exposure of the apparatus to the air without jacket.

This experiment yielded the curve as seen in fig. 10. Of the observations, which were made every 10 seconds, only those of every 40 seconds

have been indicated. So the temperature remained constant for about 40 seconds, but the unary point of solidification could not be reached

¹⁾ Ann. der Phys. **35**, 761 (1911).

in consequence of the more rapid cooling, though there was without doubt a tendency to the setting in of internal equilibrium. The maximum temperature here amounted to 231.74° , and so was 0.08° under the unary point of solidification. Then the temperature first decreased slowly to 231.6° , after which it decreased pretty suddenly with continually accelerated rapidity, just as was observed in the preceding experiment ¹⁾.

After having obtained this result, we could proceed to the investigation about the influence of the previous history. The melting-vessel was then heated to a temperature of $\pm 300^{\circ}$ and then cooled as rapidly as possible to about 3° above the point of solidification by a current of air produced by means of a foot-bellows. The further cooling then took place without this means.

Fig. 11, which gives the result of this experiment, shows that

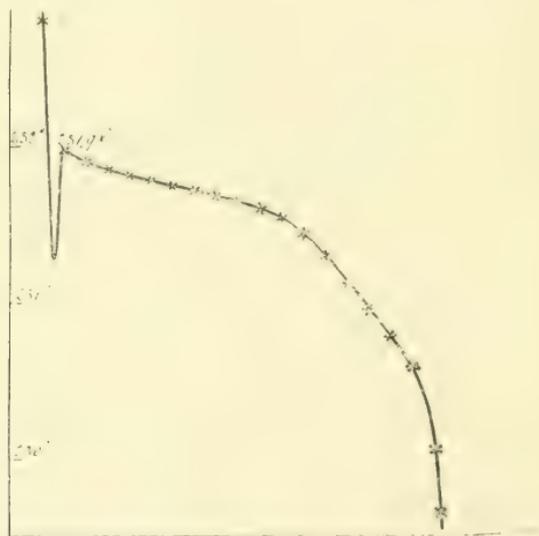


Fig. 11.

after the solidification of the undercooled liquid had set in by means of shaking, the temperature quickly rose to 231.98° , so 0.24° above the temperature maximum of the preceding experiment, and even 0.16° above the unary point of solidification, but the fall of the temperature was now very much quicker than in the former expe-

¹⁾ Thermo-currents were seldom noticeable with our resistance thermometers, and when this was the case, the connection was made so that the effect to be expected was diminished by the thermo-current.

riment, and so the curve deviates very much more from the ideal curve of cooling than any of the other lines (the crosses mark the observations every 40 seconds)¹). Now it had been proved that the system tin, as had been expected, presents the same peculiarities as phosphorus, though in a much less degree, which is not surprising, because the point of solidification of tin lies so much higher, and the transformations at that higher temperature will probably take place pretty rapidly.

Finally we proceeded to the determination of the curve of heating of tin which had solidified slowly beforehand, and had not been cooled further than a few degrees below the point of solidification.

With slow heating in a wide air-jacket, which had been placed in a nitrate-bath of $\pm 300^\circ$, the curve represented in fig. 12 was obtained.

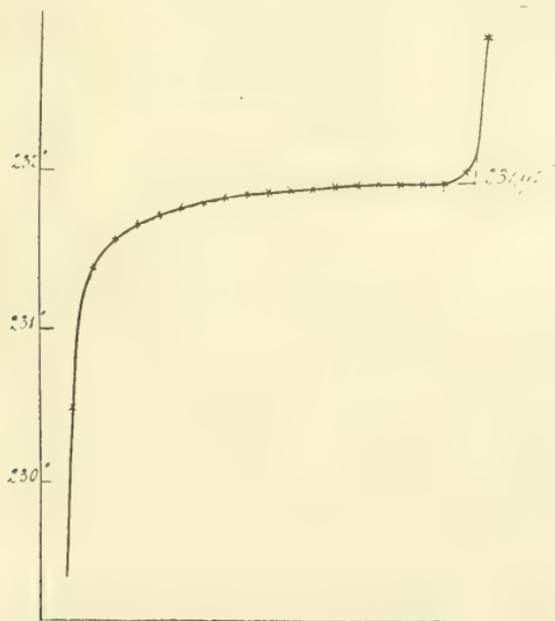


Fig. 12.

Characteristic is the long bend on the left, which for a pure substance with such a great conductivity of heat as the metal tin, points to a conversion in the solid mass, which is accompanied by an absorption of heat.

¹ Here it deserves notice that the damping of the galvanometer was so perfect that the image never passed through the zero-position, even though the mirror moved very rapidly at first.

An almost horizontal part was found at $231,92^\circ$, but this point lies $\pm 0,1^\circ$ above the unary point of solidification.

As we have observed, tin can also melt in a unary way at $231,82^\circ$ in case of very slow heating, but we must heat more rapidly if we wish to get good regular lines, because else the temperature depends too much on accidental disturbances; this is the reason that the nitrate-bath had to be regulated at $\pm 300^\circ$.

The more rapid the heating is the more gradually do the two parts of the curve of heating, the righthand one and the lefthand one, merge into each other, and with heating without an air-jacket, so directly in the nitrate-bath of 300° , we obtained the curve as it is drawn in fig. 13. The final melting-point here lies only $0,04^\circ$ higher than in the preceding experiment. So it has appeared from what precedes that when we work rapidly the system tin betrays its complex nature, as the theory of allotropy led us to expect in virtue of the three different solid modification of tin.

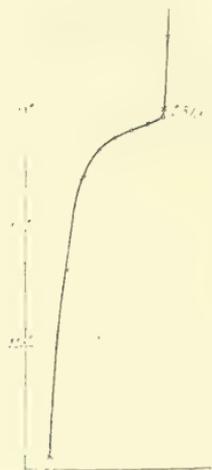


Fig. 13.

In connection with the said supposition that the internal equilibrium in the solid state under the point of solidification is subjected to a pretty considerable displacement, some more experiments were made according to the capillary-method of Soehn. Powdery pure tin was put in very thin-walled capillaries of about 0,5 mm. diameter. These capillaries were heated in a bath of $\text{KNO}_3 - \text{NaNO}_2$ for some time at a certain temperature, and then suddenly conveyed to another bath, the temperature of which was varied till the tin was just going to melt after 10 seconds. The result was the following :

Temperature at which the equilibrium of the tin had set in.	Temperature at which the melting began after 10 seconds.
165°	238°
200°	237.5°
228°	235°
230°	234°

So the lower the temperature at which the tin has assumed its equilibrium, the higher the initial melting point lies with very rapid heating.

That the observed differences cannot be owing to the fact that more heat is to be supplied to tin of 165° than to tin of 230° before it melts, in consequence of the difference of temperature of 65° , is at once seen, as the initial melting-point appeared to have changed only 0.5° , when the initial temperature was brought from 165° to 200° . This result, to which of course, only qualitatively value can be ascribed, shows that really in the solid state, chiefly a little below the point of solidification, a considerable displacement of the internal equilibrium seems to take place¹⁾.

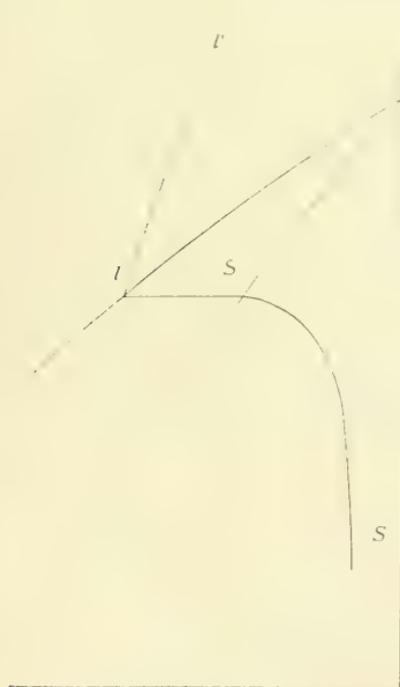


Fig. 14.

supported by the investigation communicated here to such an extent that without any doubt the most obvious explanation of the so-called *recrystallisation* is the transformation of a solid state out of equilibrium to one of internal equilibrium, as the theory of allotropy led us to expect. It follows from this theory that the phenomenon of

Though the system tin seems to be so complicated that we scarcely venture to assume anything about the pseudo $T-x$ -figure, we might now say this, that when there were only two kinds of molecules, the lines for the internal equilibria in the liquid phases and in the solid phases might run as indicated in fig. 14. So the quantity $\frac{\partial T}{\partial x}$ would differ in sign for the two said lines, which, however, is very well possible.

Before leaving the system tin we refer once more to what one of us communicated in these Proc. March 26, 1910 p. 774 about the metastability of the metals, to which we can now add that the supposition made there with regard to tin is

¹⁾ This phenomenon is also studied dilatometrically.

recrystallisation will be of frequent occurrence, just as those which, not very appropriately, have been compared to diseases by COHEN. These phenomena occur in more or less degree for every polymorphous substance, and so it is absolutely senseless to assign a special place to tin on this account¹⁾.

W A T E R.

The third substance subjected by us to an investigation was the substance water. The experiments were made in open vessels, so that the water contained some air, of which, however, not the slightest disturbing influence was observed.

In the first experiment distilled water was put in a test-tube of 2.5 cm. diameter, in which the resistance-thermometer had been placed. The water was carefully made to solidify. For this purpose the melting-vessel was first placed in a second empty wider tube, and then the whole was immersed in a bath of common salt and ice. On purpose we did not allow the temperature of the ice to descend below -0.3° , and then we conveyed the melting-vessel with air-jacket to a water-bath of 30° .

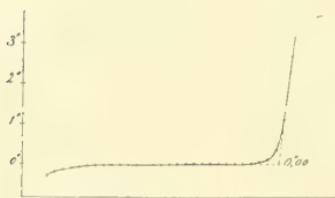


Fig. 15.

In this way we succeeded in making the water melt ideally, which clearly appears from the curve of heating of Fig. 15 (observations every 10 seconds).

This curve has namely a pretty long horizontal piece, which lies exactly at 0° .

That it is absolutely required to cool down the ice only very little below 0° in order to make the ice melt ideally, follows from the figures 16 and 17. The line of Fig. 16 was obtained by keeping the ice at -7° for some time beforehand, and then to convey the melting-vessel with air-jacket into a bath of 30° , just as in the preceding experiment. The result was now that the ice did not melt ideally, but showed a clear melting range from -0.22 to -0.04° and when the ice had been kept for some time beforehand at the temperature of -80° , the deviation from the ideal behaviour was still somewhat greater, as fig. 17 shows, from which a range of

¹⁾ Cf. what WYROUBOW says about this [Bull. Soc. franç. Minéral 33 296-300 Nov. (1910)].

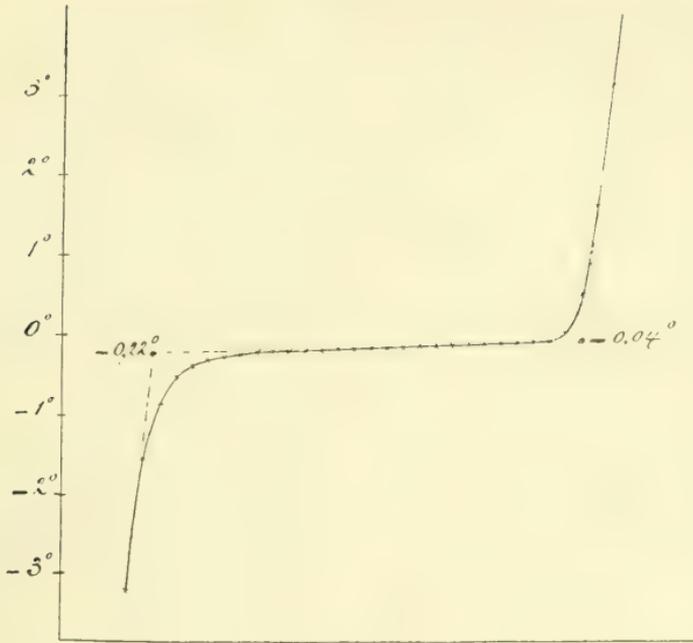


Fig. 16.

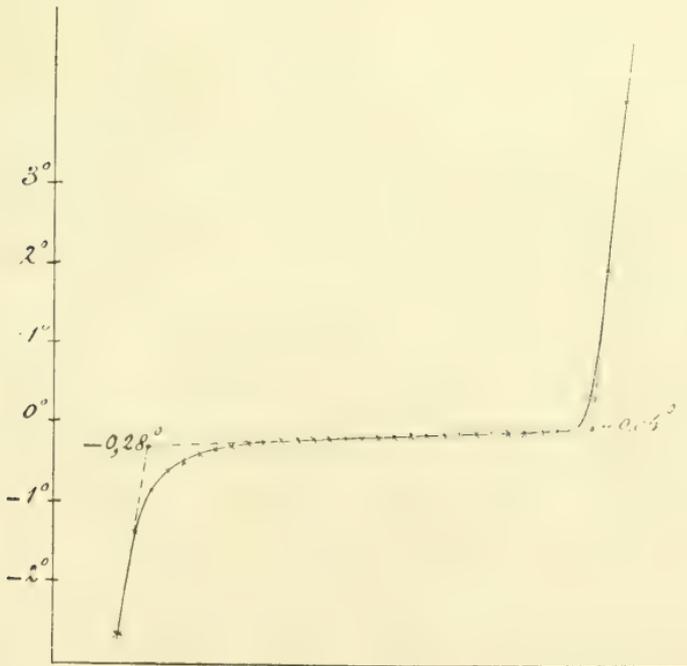


Fig. 17.

melting-temperature follows from -0.28° to -0.06° . So these experiments afforded the proof that the substance water did *not* behave as a unary one under these circumstances.

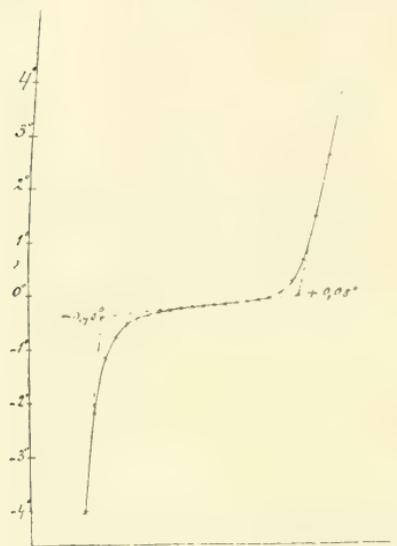


Fig. 18.

because in this way of procedure the ice often possesses hollows, which render the result less reliable.

The investigation of ice communicated here, however; shows with the greatest clearness that the substance water is a complicated state, and can easily be treated in such a way that it reveals its complexity ¹⁾.

The investigation of the testing of the theory of allotropy will be continued with different elements, and with both anorganic and organic substances, the results of which will be communicated here in due course.

*Anorganic Chemical Laboratory
of the University.*

Amsterdam, March 29 1912.

¹⁾ The application of the theory of allotropy to the four modifications of ice will be given later on.

Physics. — “*Contribution to the theory of binary mixtures*” XX.

By Prof. J. D. VAN DER WAALS.

In the preceding Contribution I repeatedly pointed out that not all mathematical possibilities for partial miscibility really occur. Among others the case of only partial miscibility seems to be mathematically possible for all values of n and l , whereas for small value of n this partial miscibility has only been seldom observed. So if we want to find decisive rules for the occurrence of incomplete miscibility, this seems not possible to me without first having found a rule for the determination of the quantity l in the formula $a_{12}^2 = la_1a_2$. And this will no doubt require that we have first succeeded in forming a clear idea of what the cause is of the attraction of the molecules, so also of the cause which determines its value for a simple substance. But though the knowledge of the properties of the different mathematical possibilities, also in connection with the temperature, is not sufficient — and not even the principal factor that should be studied, still this knowledge is indispensable. And therefore I will start with giving some results about this.

In the formula:

$$\frac{(v-b)^2}{x(1-x)} + \left(\frac{db}{dx}\right)^2 = \frac{c}{a} v^2$$

the projection on the v, x -plane has been given of the section of the two curves $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$ at the different temperatures, though on simplified suppositions. Of course there might also be given two such projections of this section on the v, T -plane and on the x, T -plane, which would also be closed curves. But the formulae for them would not be simple, and so we shall not try to give them. In both there would occur a minimum and a maximum of T , the minimum and the maximum value of v or of x being the same which also occur in the v, x -projection. If we imagine the three axes, an x -axis, a v -axis, and a T -axis, there is a closed curve in the space — and then the differential equation of this curve is given by a relation between dv , dx , and dT , which is derived from the simultaneously existing relation between these three differentials for the two functions $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$. These two relations are:

$$\frac{d^3\psi}{dT dv^2} dT + \frac{d^3\psi}{dv^3} dv + \frac{d^3\psi}{dx dv^2} dx = 0$$

and

$$\frac{d^3\psi}{dTdv^2} dT + \frac{d^2\psi}{dv dx^2} dv + \frac{d^2\psi}{dx^3} dx = 0$$

If we take into account that $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$ for the points of this section, we may also write:

$$\begin{aligned} -\frac{2a}{v^3} \frac{dT}{T} + \frac{d^2\rho}{dv^2} dv + \frac{d^2\rho}{dx dv} dx &= 0 \\ +\frac{2c}{v} \frac{dT}{T} - \frac{d^2\rho}{dx^2} dv + \frac{d^3\psi}{dx^3} dx &= 0. \end{aligned}$$

We find for the relation between dT , dv , and dx then:

$$\frac{dT}{T} = \frac{dv}{\left| \begin{array}{cc} \frac{d^2\rho}{dv^2} & \frac{d^2\rho}{dx dv} \\ \frac{d^2\rho}{dx^2} & \frac{d^3\psi}{dx^3} \end{array} \right|} = \frac{dx}{\left| \begin{array}{cc} \frac{d^2\rho}{dx dv} & -\frac{2a}{v^3} \\ \frac{d^3\psi}{dx^3} & \frac{2c}{v} \end{array} \right|} = \frac{dx}{\left| \begin{array}{cc} -\frac{2a}{v^3} & \frac{d^2\rho}{dv^2} \\ \frac{2c}{v} & -\frac{d^2\rho}{dx^2} \end{array} \right|}$$

or

$$\frac{dT}{T} = \frac{dv}{\frac{d^2\rho}{dv^2} \frac{d^3\psi}{dx^3} + \frac{d^2\rho}{dx dv} \frac{d^2\rho}{dx^2}} = \frac{dx}{\frac{2a}{v^3} \frac{d^3\psi}{dx^3} + \frac{2a}{v} \frac{d^2\rho}{dx dv} - \frac{2a}{v^3} \frac{d^2\rho}{dx^2} - 2 \frac{c}{v} \frac{d^2\rho}{dv^2}} \quad (1)$$

If the denominator of $\frac{dT}{T}$ is equal to 0, then T is either minimum or maximum; if the denominator dv is equal to 0, then v is either maximum or minimum, and if the denominator of dx is equal to 0, this holds for the limiting values of x .

We may also write the denominator of $\frac{dT}{T}$ thus:

$$\frac{d^2\rho}{dv^2} \frac{d^2\rho}{dx^2} \left[\left(\frac{dv}{dx} \right)'_T - \left(\frac{dv}{dx} \right)_T \right];$$

indicating by $\left(\frac{dv}{dx} \right)'_T$ the tangent of the angle which the tangent to the curve $\frac{d^2\psi}{dx^2} = 0$ makes with the x -axis, and by $\left(\frac{dv}{dx} \right)_T$ the same quantity for the curve $-\frac{d\rho}{dv} = 0$. For T minimum or maximum these curves touch, and also the locus of the points of intersection touches in that point. If at the minimum value of T we draw the

three said curves in the v, x -projections, $\frac{d^2\psi}{dv^2} = 0$ lies in the neighbourhood of the point of contact little above $v=b$, and with a curvature $\frac{d^2p}{dv^2}$ positive. The second curve $\frac{d^2\psi}{dx^2} = 0$, also with a slight positive curvature, but yet somewhat more pronounced than the former curve, and finally the locus of the points of intersection, again with a somewhat intenser positive curvature. But at the maximum value of T the relative position of the three said curves is another, and there are even different possibilities.

First of all the relative position of $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$ may have remained the same, just as the sign of the curvature, and there may only be a difference in the position of the locus of the points of intersection, which has then the same point of contact as the two said curves, but lies on the other side of the tangent. Secondly the curvature of $\frac{d^2\psi}{dx^2} = 0$ can be of inverse sign in the point of contact compared with that of $\frac{d^2\psi}{dv^2} = 0$, and have the same sign as that of the locus of the points of intersection. Then $\frac{d^2\psi}{dx^2} = 0$ must be quite contained within this locus at the moment of contact, and for higher T the curve $\frac{d^2\psi}{dx^2} = 0$ must disappear in the region in which $\frac{d^2\psi}{dv^2}$ is positive, while in the former case this happens in the region where $\frac{d^2\psi}{dv^2}$ is negative.

This latter remark holds both if the second component, viz. that with molecules of greater size, has a higher T_k , and when T_{k_2} should be smaller than T_{k_1} , as for the system water-ether. But in all cases the value of the denominator of $\frac{dT}{T}$ in (1) begins with 0 at T_{min} , and it ends with the same value at T_{max} . If $\frac{d^2p}{dx^2}$ and $\frac{d^2p}{dv^2}$ could not become equal to 0, the difference of the value of $\left(\frac{dv}{dx}\right)_T$ for the two curves $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$ must begin with 0 for T_{min} , and end

with 0 for T_{max} . So on that side of the locus of the intersections where this difference is positive, there must be a maximum value for this difference, and on the side where this difference is negative, there must be a maximum value for this difference, and on the side where this difference is positive, a minimum value. Now this difference is positive on the side of the component with the greater size of the molecules and reversely. But also if it should be possible that $\frac{d^2p}{dr^2}$ and $\frac{d^2p}{dx^2}$ should be able to become equal to 0, the same remark

holds for the denominator of $\frac{dT}{T}$, viz. that this denominator is always positive on the righthand side between $T_{min.}$ and $T_{max.}$ and reversely. But we shall yet have to return to the value of the denominator of $\frac{dT}{T}$, because the fact whether $\frac{d^2p}{dx^2}$ and $\frac{d^2p}{dr^2}$ can become equal to 0, is not entirely devoid of importance.

After this remark about the course of the value of the denominator of $\frac{dT}{T}$, we may also make a remark about the course of the value of

the two other denominators in equation (1). First about the denominator of dx . If this denominator is equal to 0, x is either minimum or maximum. So if we examine the value of this denominator at the locus of the points of intersection, this value will begin with 0 and end again with 0 both on the lower and on the upper branch. On the upper branch it is negative, and on the lower branch it is positive.

We can verify this by examining the sign of $T \frac{dx}{dT}$.

The denominator of dv is 0, when v has minimum or maximum value. Both on the righthand branch of the locus of the points of intersection of $\frac{d^2\psi}{dr^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$ and on the lefthand branch the value of this denominator begins with 0 and ends with 0 at the minimum volume.

On the righthand side this value is always positive and reversely. We can verify this either by examining the sign of $T \frac{dv}{dT}$, or by examining the sign of $\frac{dv}{dx}$ for the locus of the points of intersection.

We shall now have to show that really from the value of the discussed denominators the above given sign of the value is to be

derived. For this it is necessary to know the values of $\frac{d^2p}{dv^2}$, $\frac{d^2p}{dx dv}$, $\frac{d^2p}{dx^2}$ and $\frac{d^3\psi}{dx^3}$, bearing in mind that we have to do with points for which $\frac{d^2\psi}{dv^2} = 0$.

For these values ¹⁾ we find the following equations :

$$\left. \begin{aligned} \frac{d^2p}{dv^2} &= \frac{2a}{r^4} \frac{3b-v}{r-b} \\ \frac{d^2p}{dx dv} &= -\frac{4a}{v^3} \left\{ \frac{db}{ax} \frac{1}{r-b} - \frac{1}{2} \frac{da}{dx} \frac{1}{a} \right\} \\ \frac{d^2p}{dx^2} &= \frac{4a}{v^2} \left\{ \frac{\left(\frac{db}{dx}\right)^2}{v(v-b)} - \frac{c}{2a} \right\} \\ \frac{d^3\psi}{dx^3} &= \frac{2a}{v^3} (v-b)^2 \left\{ 2 \frac{\left(\frac{db}{dx}\right)^3}{(v-b)^3} - \frac{1-2x}{x^2(1-x)^2} \right\}^1 \end{aligned} \right\} \dots \dots (2)$$

With introduction of these values the denominator of $\frac{dT}{T}$ has the complicated form :

$$\frac{4a^2}{v^4(v-b)} \left\{ -6 \frac{\left(\frac{db}{dx}\right)^3}{v} + 2 \frac{da}{dx} \frac{\left(\frac{db}{dx}\right)^2}{v} + 2 \frac{c}{a} \frac{\left(\frac{db}{dx}\right)}{v} - \frac{c \frac{da}{dx} v - b}{a^2 v} - \frac{3b-v}{v} \left(\frac{v-b}{v}\right)^2 \frac{1-2x}{x^2(1-x)^2} \right\}$$

And the condition that the denominator of $\frac{dT}{T}$ be equal to 0, may be written as a third power equation in v , which in connection with the second power equation in v which holds for the intersection of $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$, can yield a relation in x for the determina-

¹⁾ These values were already used in Contribution XVIII, p. 888, where however

the factor 2 has been omitted, which must be put for $\frac{\left(\frac{db}{dx}\right)^3}{(v-b)^3}$. On account of this here is an error in the equation following there.

tion of the points where this denominator is 0. This relation in x , however, has such an intricate form as to render it useless. We shall, however, return to this denominator later on.

The denominator of dx is equal to 0, when $\frac{a}{v^2} \frac{d^2p}{dx^2} = c \frac{d^2p}{dv^2}$. Now $\frac{d^2p}{dv^2}$ is positive, so long as $v < 3b$. And though it is not impossible that for limiting values for x the circumstance $v = 3b$, or even $v > 3b$ can occur, this is among the very exceptional cases. As for the limiting values of x the value of $\frac{v}{b}$ is $= \frac{1}{1-x(1-x)} \frac{c}{a}$, the value of $x(1-x) \frac{c}{a}$ must be $> \frac{2}{3}$ for $v > 3b$. For the present we shall not assume this case, but suppose $\frac{d^2p}{dv^2}$ positive for the limiting values of x .

Then it follows immediately from this that also $\frac{d^2p}{dx^2}$ is positive for the limiting values of x . From the given values for $\frac{d^2p}{dv^2}$ and $\frac{d^2p}{dx^2}$ follows:

$$4a^2 \left\{ \left(\frac{db}{dx} \right)^2 - \frac{c}{2a} \right\} = c \frac{2a}{v^4} \frac{3b-r}{v-b}$$

or

$$\frac{\left(\frac{db}{dx} \right)^2}{v(v-b)} - \frac{c}{2a} = \frac{c}{2a} \frac{3b-r}{v-b}$$

or

$$\frac{\left(\frac{db}{dx} \right)^2}{v(v-b)} = \frac{c}{2a} \frac{2b}{v-b}$$

or

$$\left(\frac{db}{dx} \right)^2 = \frac{c}{a} bv.$$

And if we substitute this value of $\left(\frac{db}{dx} \right)^2$ in the equation of the curve for the intersecctions, we find back:

$$r = \frac{b}{1 - x(1-x) \frac{c}{a}}$$

That we were justified in calling the case that $\frac{d^2p}{dv^2} \lessgtr 0$ for the limiting values very exceptional, may appear in the following way.

Let us write :

$$\frac{a}{cx(1-x)} = \frac{a_1}{c} \frac{1-x}{x} + \frac{a_2}{c} \frac{x}{1-x} + \left(\frac{a_1}{c} + \frac{a_2}{c} - 1 \right)$$

or

$$\frac{a}{cx(1-x)} = \frac{a_1}{c} \frac{1}{x} + \frac{a_2}{c} \frac{1}{1-x} - 1$$

or

$$\frac{a}{cx(1-x)} = \frac{1+\varepsilon_1}{(n-1)^2} \frac{1}{x} + \frac{n^2(1+\varepsilon_2)}{(n-1)^2} \frac{1}{1-x} - 1$$

For the limiting values of x :

$$\frac{\varepsilon_1}{(n-1)^2} \frac{1}{x} + \frac{n^2\varepsilon_2}{(n-1)^2} \frac{1}{1-x} - 1 = 0.$$

And so we have for these values of x :

$$\frac{a}{cx(1-x)} = \frac{1}{(n-1)^2} \frac{1}{x} + \frac{n^2}{(n-1)^2} \frac{1}{1-x}.$$

For limiting values of x near 0 or 1 this value would be very large. For the system water-ether we find with $n = 5\frac{1}{2}$ and x about 0.36 a value about equal to 2.3 and for $x = 0.98$ a very large value — so that the inverse value is by no means greater than $\frac{2}{3}$. If one of the limiting values of x happened to be equal to

the value of x , for which $\frac{1}{x} + \frac{n^2}{1-x}$ has the minimum value, then

$\frac{a}{cx(1-x)}$ would be equal to $\left(\frac{n+1}{n-1}\right)^2$, and if this value is to be smaller than

$\frac{2}{3}$, n would have to be greater than 10 for the accidental case of the coincidence of the two said values of x .

The denominator of dv is positive so long as $\left(\frac{db}{dx}\right)^2$ is greater than $\frac{c}{a} bv$.

If we put this condition in the equation of the curve of intersection, we find :

$$\frac{v}{b} < \frac{1}{1-x(1-x) \frac{c}{a}}$$

So the denominator of dx is positive throughout the lower branch of the curve of intersection, and inversely, as we had predicted above from the value of $T \frac{dx}{dT}$. But on the other hand this also shows that we have rightly made the denominator of $\frac{dT}{T}$ reverse its sign in the point where $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ touch.

The denominator of dv is equal to 0 when $\frac{a}{v^2} \frac{d^2\psi}{dx^2} = -c \frac{d^2\rho}{dx dv}$. After some reduction of this relation if we introduce the above given value of $\frac{d^2\psi}{dx^2}$ and $-\frac{d^2\rho}{dx dv}$, we get of course the same equation as is yielded by differentiating $\frac{(c-b)^2}{x(1-x)} + \left(\frac{db}{dx}\right)^2 = \frac{c}{a} v^2$ with respect to x , and putting the form obtained in this way equal to 0. I fully discussed the equation, which we then get, in Contribution XI (1908) and accordingly refer to this Contribution with an addition, however, which is not devoid of importance. It refers to the discussion about the obtained equation :

$$n = \frac{1 + \left\{ \frac{1}{x} \right\} \cdot 1 \cdot (1-x) \frac{d \cdot 1}{dx}}{1 - \left\{ \frac{1}{x} \right\} \cdot 1 \cdot x \frac{d \cdot 1}{dx}}$$

In this equation (These Proc. Vol. XI p. 429) the sign $+$ must be used in the numerator, when the value of $v < b_2$, and reversely. I have now come to see that this may also mean that the sign $+$ holds in the numerator for the determination of the minimum value of v , whereas the sign $-$ must be taken in the numerator for the determination of the maximum value of v .

For the determination of the value of x for the minimum volume the preceding equation may also be reduced to the form :

$$n = \frac{1 + \frac{x(1-x)c}{a} \sqrt{\frac{a_1}{cx^2} - 1}}{1 - \frac{x(1-x)c}{a} \sqrt{\frac{a_2}{c(1-x)^2} - 1}}$$

or $(n-1) \frac{a}{cx(1-x)} = n \sqrt{\frac{a_2}{c(1-x)^2} - 1} + \sqrt{\frac{a_1}{cx^2} - 1}$, while the

sign between the two radical signs has to be replaced by — for the maximum volume.

By way of control I have calculated the different quantities in this formula for a system that cannot differ much from the system water-ether, and in this way computed the two values of $\frac{r}{b_1}$ corresponding to every value of x . For the limiting values of $x = 0,3$ and $0,97$ we compute from $x_1 x_2 = \frac{\epsilon_1}{(n-1)^2}$ and from $(1-x_1)(1-x_2) = \frac{n^2 \epsilon_2}{(n-1)^2}$, for $n = \frac{11}{2}$ the value of $\epsilon_1 = 5,893$ and $\epsilon_2 = 0,0141$ and $n^2 \epsilon_2 = 0,426$.

Then the value of $\frac{a}{cx(1-x)} = \frac{1+\epsilon_1}{(n-1)^2} \frac{1}{x} + \frac{n^2(1+\epsilon_2)}{(n-1)^2} \frac{1}{1-x} - 1$ is:

x	$\frac{a}{cx(1-x)}$
0,3	2,294
0,4	2,374
0,5	2,709
0,6	3,352
0,7	4,533
0,8	7,021
0,9	14,517

From the equation:

$$\left(\frac{v}{b_1}\right)^2 \left[1-x \frac{c}{1-x} \frac{1}{a}\right] - 2\left(\frac{v}{b_1}\right) \left[1 + \frac{1}{n-1}x\right] + [1 + (n^2 - 1)x] = 0$$

we find then for the following values of x the subjoined values of $\frac{v}{b_1}$ and $\frac{b}{b_1}$:

x	$\frac{v}{b_1}$	$\frac{b}{b_1}$
0,3	4,46	2,35
0,4	7 and 3	2,8
0,5	7,6 and 3,4	3,25
0,6	6,4 and 4,2	3,7

We see from this table that the minimum volume will occur for x about equal to 0,4, while the maximum volume occurs at x about 0,5. If we now also calculate $\sqrt{\frac{a_2}{c(1-x)^2} - 1}$ and $\sqrt{\frac{a_1}{cx^2} - 1}$, we find:

x	$\sqrt{\frac{a_2}{c(1-x)^2} - 1}$	$\sqrt{\frac{a_1}{cx^2} - 1}$
0,3	1,465	1,67
0,4	1,8006	1,0625
0,5	2,238	0,5981
0,6	2,923	<i>imaginary</i>

If to the n -fold of a value of the second column we add a corresponding value from the third column, and if we divide the sum by $n - 1$, we find beginning with $x = 0,3$, successively the values 2,162, 2,437, and 2,87. From this we should conclude that the minimum value of v lies just before $x = 0,4$. With the sign $-$ we find successively 1,42, 1,9645, and 2,602; and so the maximum volume at x somewhat above 0,5.

But to conclude from this example that the maximum volume is always greater than b_2 , and the minimum volume always smaller, would be just as rash as my conclusion in Contribution XI that both maximum volume and minimum volume would always be smaller than b_2 . Probably the case may occur that they are both smaller than b_2 , and possibly also that they are both even greater than b_2 .

If they are both smaller than b_2 , the equation :

$$(n-1) \frac{a}{cx(1-x)} = n \sqrt{\frac{a_2}{c(1-x)^2} - 1} + \sqrt{\frac{a_1}{cx^2} - 1}$$

must be satisfied for two values of x , for both with the sign $+$; and if they could both be greater than b_2 , then also if the sign between the two terms of the second member has been replaced by $-$. To examine what conditions the binary systems must satisfy for one of these three cases to take place, we should examine the properties of the 3 functions which occur in this equation.

The first function $\frac{a}{cx(1-x)}$ is infinitely great for $x = 0$ and $x = 1$, and has a smallest value for certain value of x . From the form :

$$\frac{1 + \epsilon_1}{(n-1)^2} \frac{1}{x} + \frac{n^2(1 + \epsilon_2)}{(n-1)^2} \frac{1}{1-x} - 1$$

follows for the value of x at which the minimum occurs :

$$x = \frac{\sqrt{1 + \epsilon_1}}{1 + \sqrt{1 + \epsilon_2}}$$

or $x = 0,325$. The minimum value itself is equal to :

$$\frac{[1 + \frac{1 + \epsilon_1}{n^2} + \frac{n^2(1 + \epsilon_2)}{n^2}]^2}{(n-1)^2} - 1$$

and is calculated from it equal to 2,265. Those numerical values, of course, only hold for the system water-ether. So in the little table on p. 1225 the first value still refers to the descending branch.

The first term of the second member, viz. $\sqrt{\frac{a_2}{c(1-x)^2} - 1}$, begins at $x = 0$ with the value $\sqrt{\frac{n^2(1+\varepsilon_2)}{(n-1)^2} - 1}$, and ends at $x = 1$ with an infinite value. It is ascending throughout, and nowhere imaginary; the third quantity, viz. $\sqrt{\frac{a_1}{cx^2} - 1} = \sqrt{\frac{1+\varepsilon_1}{(n-1)^2 x^2} - 1}$, becomes equal to 0 for $x = \sqrt{\frac{1+\varepsilon_1}{(n-1)^2}}$, if $\frac{1+\varepsilon_1}{(n-1)^2} < 1$. It begins infinitely great, is descending throughout, and becomes, as we shall suppose, equal to 0; in that point its differential quotient is infinite.

If we write the equation which is to be satisfied, in the following form:

$$\begin{aligned} & \frac{a_1}{c} \frac{1}{x^2} + \frac{a_2}{c} \frac{1}{1-x} - (1-x) - x = \\ & = \frac{n}{(x-1)} \frac{1}{\sqrt{(1-x)}} \sqrt{\frac{a_2}{c(1-x)} - (1-x)} \pm \frac{1}{(n-1)} \frac{1}{\sqrt{x}} \sqrt{\frac{a_1}{cx} - x} \end{aligned}$$

we can to decide which of the three cases about the value of maximum or minimum volume is to be expected, in the first place propose the question whether the first member is greater or smaller than the second member for the value of x , which makes the third term equal to 0.

For this value of x the first member is equal to $\frac{a_2}{c} \frac{1}{1-x} - (1-x)$

and the second member $\frac{n}{n-1} \sqrt{\frac{a_2}{c(1-x)} - (1-x)}$, and so we have to put the question whether

$$\sqrt{\frac{a_1}{c(1-x)} - (1-x)} \begin{cases} \geq \\ \leq \end{cases} \frac{n}{n-1} \frac{1}{v} (1-x)$$

or

$$\frac{c_2}{c} \frac{1}{1-x} - (1-x) \begin{cases} \geq \\ \leq \end{cases} \frac{n^2}{(n-1)^2} \frac{1}{1-x}$$

or

$$\frac{n^2}{(n-1)^2} (1+\varepsilon_2) - (1-x)^2 \begin{cases} \geq \\ \leq \end{cases} \frac{n^2}{(n-1)^2}$$

or

$$\frac{n^2 \epsilon_2}{(n-1)^2} \begin{matrix} > \\ < \end{matrix} (1-x)^2$$

or

$$\frac{n \sqrt{\epsilon_2}}{n-1} \begin{matrix} > \\ < \end{matrix} 1 - \frac{1}{n-1} (1 + \epsilon_1)$$

or

$$n \sqrt{\epsilon_2} \begin{matrix} > \\ < \end{matrix} (n-1) - \sqrt{1 + \epsilon_1}.$$

Now for the system water-ether the sign $<$ holds as ϵ_2 is so small, and this implies that for the mentioned value of x

$$\frac{a}{c x (1-x)} < \frac{n}{n-1} \sqrt{\frac{a_2}{c (1-x)^2}} - 1.$$

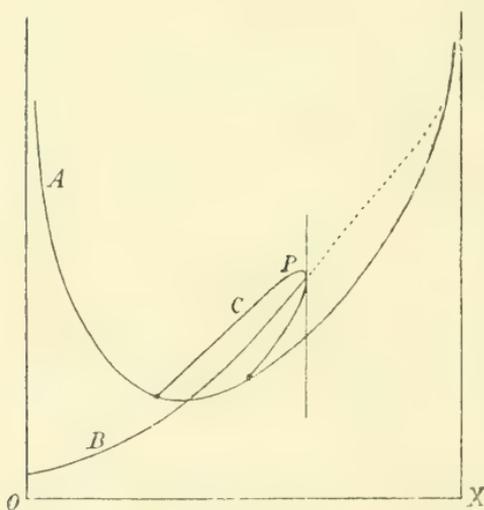


Fig. 53.

If this result is represented graphically, as has been done in fig. 53, the point P of the curve B lies within the curve A , and the ordinates of B must be both augmented and diminished by an amount indicated by the third curve C , to intersect the curve A . Then the point where the curve B itself intersects A must lie at a value of x between that for which the volume is minimum or maximum; and this is quite

in accordance with our former results for the system under consideration. And always when the point P lies within A , or when $n \sqrt{\epsilon_2} < (n-1) - \sqrt{1 + \epsilon_1}$, the maximum volume will be greater than b_2 , and the minimum volume smaller than b_2 .

But there are other cases possible for which:

$$n \sqrt{\epsilon_2} > (n-1) - \sqrt{1 + \epsilon_1}$$

and then the result is different. Then the point P lies outside the curve A . First of all we might think, that B had not yet intersected the curve A before the point P , and then intersection with A can only be brought about by increase of the ordinates of B by a certain amount in which case two points of intersection appear. Then both

maximum and minimum volume are smaller than b_2 , and this case I had considered as the only possible one in Contribution XI. We might possibly also think that the point P lies below A , but that B had first intersected this curve twice, and then we might even ask whether intersection with A might not be brought about both by increase of the ordinates of B and by diminution with those of C . Then we should get 4 points of intersection. But then the extreme values of x would have to be rejected as lying outside the locus of the sections of $\frac{d^2\phi}{dv^2} = 0$ and $\frac{d^2\phi}{dx^2} = 0$. That I think a closer investigation necessary for this apparently unimportant matter is owing to my desire to get more certainty about the mixtures of hydrocarbons and alcohols. Are systems conceivable for them which account for the phenomena without it being necessary for us to attribute them to an unknown abnormality of the alcohols? Would perhaps the case $v > b_2$ occur for them for both volumes?

So

$$n\sqrt{\varepsilon_2} > (n-1) - \sqrt{1+\varepsilon_1}$$

for the systems for which the two terms in the second member of the equation are connected by the same sign for maximum and minimum volume, and also $n\sqrt{\varepsilon_2} < (n-1) - \sqrt{\varepsilon_2}$ must hold. And so there must be a perceptible difference between ε_1 and $1 + \varepsilon_1$ or ε_1 not much greater than 1, as for water-ether. It must be rather smaller than 1; and ε_2 must not be small, as for water-ether. If we lower the parabola of fig. 36 in the direction of the ε_1 -axis with unity, the point $\varepsilon_1, \varepsilon_2$ must lie within the new parabola, but it must remain below the original one. Only for values of n which are greater than 2 does this new condition diminish the place for the choice of the points $\varepsilon_1, \varepsilon_2$. But if we put $n < 2$, the equation which we have used to determine the value of x for the point P , could no longer be satisfied. This value, equal to $\frac{\sqrt{1+\varepsilon_2}}{n-1}$, would then be greater than 1, and then no such point could be indicated between $x=0$ and $x=1$. But this is a drawback only in appearance. Nothing compels us to restrict the discussion about the equation:

$$cx \frac{a}{1-x} = \frac{n}{n-1} \sqrt{\frac{a_2}{c(1-x)^2} - 1} \pm \frac{1}{n-1} \sqrt{\frac{a_1}{cx^2} - 1}$$

to values of x lying between 0 and 1. Only if we should find $x > 1$ we should have to reject a point for which $x > 1$ as irrelevant to our question. But if the use of $x > 1$ should be objected to, we might confine our consideration to values of $x < 1$, but so near 1,

that the value of $\frac{1}{1-x}$ far exceeds all other terms. It then appears that the value of the first member, in any case in which ϵ_2 is positive, far exceeds the value of the first term of the second member. Then the two values under consideration are:

$$c \frac{a_2}{(1-x)} \text{ and } \frac{n}{n-1} \sqrt{\frac{a_2}{c(1-x)^2}}$$

If the two quantities are divided by the same factors, it appears that so long as $1 + \epsilon_2$ is > 1 , the curve A lies above the curve B .

Also in a simpler way we might arrive at the result that if:

$$n\sqrt{\epsilon_2} > n - 1 - \sqrt{1 + \epsilon_2}$$

both maximum volume and minimum volume lie on the same side of a straight line $v = b_2$.

If we write in

$$\frac{(v-b)^2}{x(1-x)} + (b_2 - b_1)^2 = \frac{c}{a} v^2$$

the value b_2 for v , and seek the values of x , for which this then holds, we get the equation:

$$x^2 - x \left\{ 1 + \frac{1 + \epsilon_1}{(n-1)^2} - \frac{n^2 \epsilon_2}{(n-1)^2} \right\} + \frac{1 + \epsilon_1}{(n-1)^2} = 0.$$

So the value of $v = b_2$ is not possible if:

$$1 - \sqrt{\frac{1 + \epsilon_1}{(n-1)^2}} < \frac{n\sqrt{\epsilon_2}}{n-1}.$$

According to our above remark this condition is satisfied for $n < 2$. Most probably this means then that all the values of v are smaller than b_2 . Then the case that all the values are greater than b_2 , could not occur for n small; then the abnormality of alcohol would consist in this that it behaves as if it consisted of very great molecules.

Accordingly I have not yet succeeded in finding a system for which the curve B intersects the curve A twice in such a way that also the phenomena of unmixing if n is not great, are accounted for. For the present, however, I shall go on with the subject treated in this and in the preceding contribution.

Chemistry. — "*The nitration of ortho-chlortoluene*". By Prof. A. F. HOLLEMAN and Dr. J. P. WIBAUT.

(This communication will not be published in these Proceedings).

(May 23, 1912).

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