COMMUNICATIONS

FROM THE

LABORATORY OF PHYSICS

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 13—24.

September 1894 — April 1896.

EDUARD IJDO — PRINTER — LEIDEN

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CONTENTS.

13. **Dr. J. P. Kuenen.** On the condensation of a mixture of two gases.
(*Versl. Kon. Akad.* **September 1894**).

14. **Dr. H. Kamerlingh Onnes.** On the cryogenic laboratory at Leiden and on the production of very low temperatures.
(*Versl. Kon. Akad.* **December 1894**).

15. **Dr. P. Zeeman.** Measurements concerning Kerr's phenomenon with normal polar reflection from iron and cobalt.
(*Versl. Kon. Akad.* **Januari 1895**).

Dr. P. Zeeman. On the determination of the optical constants of magnetite.
(*Versl. Kon. Akad.* **Januari 1895**).

Dr. L. H. Siertsema. On the dispersion of the magnetic rotation in oxygen.
(*Versl. Kon. Akad.* **Januari 1895**).

A. Lebret. The variation of the Hall-effect with temperature.
(*Versl. Kon. Akad.* **Januari 1895**).

16. **Dr. J. P. Kuenen.** On the condensation and the critical phenomena of mixtures of ethane and nitrous oxide.
(*Phil. Mag.* 40 *p.* 173—194 (1895)).

17. **Dr. J. P. Kuenen.** On the influence of gravitation on the critical phenomena of simple substances and of mixtures (with a plate).
(*Versl. Kon. Akad.* **Mei 1895**).

18. **Dr. J. Verschaffelt.** Measurements concerning the capillary ascension of liquefied gases.
(*Versl. Kon. Akad.* **Juni 1895**).

19. **Dr. A. Lebret.** A new method for measuring the HALL-effect, especially the variation of it with temperature.
(*Versl. Kon. Akad.* **April 1895**).

Dr. A. Lebret. Dissymmetry of the HALL-effect in Bismuth for the opposite directions of the magnetic field.
(*Versl. Kon. Akad.* **April 1895**).

Dr. A. Lebret. Variation of the HALL-effect in Bismuth with temperature (including an investigation on the variation of the electric resistance in Bismuth with temperature).
(*Versl. Kon. Akad.* **September 1895**; *Diss. Leiden* 1895).

20. **Dr. P Zeeman.** Measurement of the refractive index of incandescent platinum.
(*Versl. Kon. Akad.* **September 1895**).

21. **Prof. Dr. Cohn** and **Dr. P. Zeeman.** Observations concerning the propagation of electrical waves in water.
(*Versl. Kon. Akad.* **September 1895**).

22. **Dr. P. Zeeman.** Measurements concerning the Absorption of Electrical Vibrations in Electrolytes.
(*Versl. Kon. Akad.* **October 1895**).

Dr. P. Zeeman. Measurements of the Absorption of Electrical Vibrations in different Electrolytes.
(*Versl. Kon. Akad.* **November 1895**).

23. **Dr. H. Kamerlingh Onnes.** Remarks on the liquefaction of hydrogen, on thermodynamical similarity and on the use of vacuum vessels.
(*Versl. Kon. Akad.* **Januari 1896**).

24. **Dr. L. H. Siertsema.** Measurements on the magnetic rotatory dispersion in gases.
(*Versl. Kon. Akad.* **Maart 1896**)

Dr. L. H. Siertsema. Measurements on the magnetic rotatory dispersion in gases.
(*Versl. Kon. Akad.* **April 1896**)

For insertion in the Volume No. **13—24**.

Erratum Contents of N⁰.13—24.

p. 6 l. 6 from the bottom: after "refractive" read "index".

Errata Communication N⁰. 17.

p. 8 l. 3 from the top: for "almost" read "utmost".
p. 9 l. 7 „ „ „ „ "$\left(\frac{\partial \psi}{\partial x}\right)_v \times (M_2 - M_1)\, gh$"
read "$\left(\frac{\partial \psi}{\partial x}\right)_v + (M_2 - M_1)\, gh.$"

Erratum Communication N⁰. 18.

p. 10 l. 10 from the bottom: before "independent" read "of which B is".

Errata Communication N⁰. 23.

p. 8 l. 1 from the top: for "reserving" read "reversing".
p. 9 l. 8 „ „ „ „ "condition" „ "conduction".
p. 11 l. 16 „ „ „ „ "exhange" „ "exchange".

13

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No. 13.

Dr. J. P. KUENEN. On the condensation of a mixture of two gases.

(*Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Academie te Amsterdam van* **29 September 1894,** *p.* 90—99).

EDUARD IJDO — PRINTER — LEIDEN.

Dr. J. P. KUENEN. *On the condensation of a mixture of two gases.*

In a memoir by DUHEM about mixture of two substances recently published [1] in Chapter III [2] the problem of the condensation of a mixture of two gases is discussed. The results obtained by this investigation are laid down by the author in the 16th [3] and 17th [4] figures of his memoir. It is my intention in this paper by using the theory of VAN DER WAALS [5] as far as is needed to complete DUHEM's representation of the phenomena and to correct some mistakes, which have been made by him. Moreover some experimental data will be communicated, which will confirm the theoretical results of this paper.

DUHEM in his investigation uses the thermodynamical

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[1] Travaux et mémoires des facultés de Lille. III Mémoire 13. P. DUHEM, Dissolutions et mélanges. Troisième mémoire 1894.

[2] l. c. p. 47—75.

[3] l. c. p. 58.

[4] l. c. p. 66.

[5] Archives Néerl. 24. p. 1—56.

potential at constant pressure [1], which he treats as a function of temperature, pressure and composition. He introduces the potentials for the components in the mixture (GIBBS) and arrives at the well-known conditions of equilibrium between two coëxisting phases [2]:

$$\begin{aligned} F_1(\xi\,\pi\,\tau) - f_1(\chi\,\pi\,\tau) &= 0 \\ F_2(\xi\,\pi\,\tau) - f_2(\chi\,\pi\,\tau) &= 0 \end{aligned} \quad \ldots \quad (1)$$

π denotes the pressure, τ the temperature, the F's the potentials in the liquid phase, the f's those in the vapour, ξ and χ the composition of the liquid and the vapour (i. e. the ratio of the mass of the second to the mass of the first substance), whereas 1 refers to the substance of the higher, 2 to that of the lower critical temperature.

If we imagine ξ to have been eliminated from those two equations and regard π, τ and χ as the coördinates of a point, the equation obtained represents a surface, which DUHEM calls: 'surface de rosée' and which exhibits the conditions of equipoise between the two phases, i. e. the pressure and temperature at which in a mixture (χ) the first small quantity of liquid (rosée) will appear. By projecting the sections of this surface by planes perpendicular to the axis of χ on the plane of $\pi\,\tau$ we obtain the so-called 'lignes de rosée', which give a clear image of the corresponding pressure and temperature at which from a mixture of given composition a liquid phase will begin to condensate. By differentiation of the equations (1) with respect to

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[1] DUHEM, Le potentiel thermodynamique 1886.

[2] a. o. l. c. p. 52, formula (9).

ξ, χ, π and τ and elimination of $d\,\xi$ the following equation is obtained [1]:

$$\left[\frac{\delta F_1}{\delta\pi}+\xi\frac{\delta F_2}{\delta\pi}-\frac{\delta f_1}{\delta\pi}-\xi\frac{\delta f_2}{\delta\pi}\right]\delta\pi+\left[\frac{\delta F_1}{\delta\tau}+\xi\frac{\delta F_2}{\delta\tau}-\frac{\delta f_1}{\delta\tau}-\xi\frac{\delta f_2}{\delta\tau}\right]d\tau=$$

$$=-(\chi-\xi)\frac{\delta f_2}{\delta\chi}d\chi \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and from (2) by means of well known thermodynamical relations [2]:

$$\frac{E}{\tau}\left[(1+\xi)\,Q-(1+\chi)q+(\xi-\chi)l_2\right]d\tau+$$

$$+\left\{(1+\xi)\,V-(1+\chi)v+(\chi-\xi)\left[v+(1+\chi)\frac{\delta v}{\delta\chi}\right]\right\}\,d\pi=$$

$$=-(\chi-\xi)\frac{\delta f_2}{\delta\chi}d\chi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which Q, q and l_2 denote definite quantities of heat, V and v specific volumes of the liquid and the vapour.

By aid of this equation and a few hypothesis DUHEM derives the form and relative position of the 'lignes de rosée', as they must be situated between the two curves, which hold good for the pure substances, i. e. between the two vapourpressure-curves; and he adds, what he calls the 'ligne critique', i. e. locus of the points at which the corresponding liquid and vapour-phases become identical. In the way sketched out here the figures 16 and 17 of his memoir have been obtained. His conclusions briefly come to this: for two groups of mixtures, which are contiguous to the pure substances, the process of condensation *must* be

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[1] l. c. p. 53 formula (10).

[2] l. c. p. 54 formula (13).

normal at all temperatures up to the critical temperature: for an intermediate group of mixtures however not contiguous to the pure substances the *possibility* of retrograde condensation exists.

According to DUHEM [1] the principal lines of this theory were drawn by him as early as 1888 [2] in his memoir on the condensation of CAILLETET's mixture of carbonic acid and air. Though not intending to refute this rather vague assertion, I cannot but point out that 1° as DUHEM himself states, in 1888 the 'ligne critique' was not yet taken into consideration by him; 2° the particular form of the 'ligne de rosée' was introduced as an hypothesis, however the phenomenon of retrograde condensation was not predicted from it [3] and 3° entirely in accordance with that,

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[1] l. c. passim, a. o. p. 71: "En 1888 nous avons proposé...." and "en résumé, dès ce moment, nous avons esquissé les principaux traits de la théorie que l'on vient de lire; nous avions seulement omis de considérer la ligne critique du mélange."

[2] P. DUHEM. Journ. de Phys. 2 VII p. 158 1888.

[3] When DUHEM writes (l. c. 1888 p. 166): "à ce moment le liquide disparaît pour ne plus reparaître sous aucune pression" it appears from the accordance with CAILLETET's experiments, which he observes, that he has not in view the disappearing of the liquid phase by a gradual diminishing of the quantity of it, but by the flattening and disappearing of the liquid-surface, though as appears from his recent memoir a logical application of the theory, which he had started, might have led him to draw the conclusion, that CAILLETET's experiments give a false image of the condensation-phenomena. Cf. the abstract of DUHEM's memoir of 1888 in Beibl. 13. p. 156 by M. P.

the results obtained at that time were regarded by him as an explanation of CAILLETET's experiment ("Nous n'avons pas besoin de faire ressortir l'accord, que ces conséquences présentent avec les faits, que M. CAILLETET a observés" [1])), whereas now he writes: "or ces conclusions ne sont pas conformes aux observations de M. CAILLETET etc." [2]). Therefore I think that my priority with respect to the prediction as to the experimental confirmation of retrograde condensation cannot be questioned [3]). Moreover its complete explanation and in general of the critical phenomena of mixtures, which has been derived by me from VAN DER WAALS's theory, is not included in DUHEM's theory, because in it the composition, density and quantities of the coëxisting phases do not come to light properly. Therefore, when DUHEM writes [4]): "la théorie donnée par M. VAN DER WAALS et par M. KUENEN concorde entièrement avec celle, que nous venons de développer" we should read it this, that DUHEM's results regarding the condensation of gaseous mixtures, as far as they are right, are contained in the more complete theory of VAN DER WAALS. It will appear however, that the graphical method, introduced here by DUHEM, with π and τ as the axes of coördination, exhibits the phenomena very clearly and even gives occasion to the pre-

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[1]) P. DUHEM 1888. p. 167.

[2]) P. DUHEM 1894. p. 74.

[3]) Communications etc. n°. 4. Archives Néerland. 26. p. 374 sqq.

[4]) l. c. 1894 p. 73.

diction of new facts, which would not have been directly derived from VAN DER WAALS's surface so easily.

Comparing however DUHEM's conclusions, briefly stated above, with what may be drawn from the thermodynamical surface of VAN DER WAALS, we find a striking difference. The result of VAN DER WAALS's theory, taken generally, regarding the problem now before us comes to the existence of the so-called first plait, the plaitpoint of which appears on the possible part of the surface as soon as the temperature comes between the two critical temperatures of the pure substances. As this plaitpoint can only coïncide with the point, which I have called the critical point of contact, in a special case at one definite temperature and in general must deviate to either of the two sides of the plait, to the liquid-side as a rule, the condensation *must* be retrograde between two definite temperatures for *all* mixtures possible between the two substances and not, as DUHEM has it, for a system of mixtures between certain limits only. The figures 16 and 17 are therefore incorrect. In order to obtain the correct representation of the phenomena we shall follow the way taken by DUHEM and, if needed, make use of the general result of the complete theory as it has been formulated above: in this manner the difference with DUHEM will come to light in due time.

DUHEM, as we saw it, draws the curves, which refer to the beginning of the condensation (lignes de rosée). It seems natural to add the curves giving the relation between π and τ at the end of the condensation of a definite mixture. The pertaining formulas are analogous to the formulas (2) and (3). From the same equations of equilibrium (1) by differentiation and elimination this time of $d\chi$ we get two other formulas, in which only L_2 is a new quantity with a meaning analogous to that of l_2 [1]), whereas for clearness' sake accents have been put to the other letters.

$$\left[\frac{\delta F_1}{\delta\pi}+\chi'\frac{\delta F_2}{\delta\pi}-\frac{\delta f_1}{\delta\pi}-\chi'\frac{\delta f_2}{\delta\pi}\right]d\pi+$$

$$+\left[\frac{\delta F_1}{\delta\pi}+\chi'\frac{\delta F_2}{\delta\tau}-\frac{\delta f_1}{\delta\tau}-\chi'\frac{\delta f_2}{\delta\tau}\right]\delta\tau=-(\chi'-\xi')\frac{\delta F_2}{\delta\xi}d\xi \; . \; . \; (4)$$

from which:

$$\frac{E}{\tau}\left[(1+\xi')\,Q'-(1+\chi')\,q'+(\chi'-\xi')\,L_2\right]d\tau+$$

$$+\left\{(1+\xi')\,V'-(1+\chi')v'+(\chi'-\xi')\left[V'+(1+\xi')\frac{\delta V'}{\delta\xi'}\right]\right\}d\pi=$$

$$=-(\chi'-\xi')\frac{\delta F_2}{\delta\xi}d\xi. \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (5)$$

The direction of the two lines is obtained by putting in (3) and (5) $d\chi=o$ and $d\xi\ o=$ respectively. Of the two formulas obtained in this manner the first occurs in Duhem's memoir [2]):

$$\left(\frac{d\pi}{d\tau}\right)_v=-\frac{E}{\tau}\,\frac{(1+\xi)\,Q-(1+\chi)\,q+(\chi-\xi)l_2}{(1+\xi)\,V-(1+\chi)\,v+(\chi-\xi)\left\{v+(1+\chi)\frac{\delta v}{\delta\chi}\right\}}\;(6)$$

$$\left(\frac{d\pi}{d\tau}\right)_l=-\frac{E}{\tau}\,\frac{(1+\xi')Q'-(1+\chi')q'+(\chi'-\xi')L_2}{(1+\xi')V'-(1+\chi')v'+(\chi'-\xi')\left\{V'+(1+\xi')\frac{\delta V'}{\delta\xi'}\right\}}\;(7)$$

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[1]) Duhem l. c. 1894, p. 6–8.

[2]) Duhem l. c. 1894 p. 56 formula (16).

It should be observed, that (6) and (7) only relate to the same mixture, if we take $\chi=\xi'$, i. e. if the vapour-phase of Duhem's curve has the same composition as te liquid-phase of our curve.

With rise of temperature the two curves will approach each other and at last meet in a point corresponding to the plaitpoint of van der Waals's surface. In the plaitpoint the phases have equal composition and equal density. In order to introduce this condition, we devide the numerator and denominator by $\chi-\xi$ and $\chi'-\xi'$ and by some transformations we find:

$$\left(\frac{d\pi}{d\tau}\right)_v=-\frac{E}{\tau}\,\frac{-q-(1+\xi)\frac{q-Q}{\chi-\xi}+l_2}{-(1+\xi)\frac{v-V}{\chi-\xi}+(1+\chi)\frac{\delta v}{\delta\chi}} \; . \; . \; . \; (8)$$

$$\left(\frac{d\pi}{d\tau}\right)_l=-\frac{E}{\tau}\,\frac{-Q'-(1+\chi')\frac{q'-Q'}{\chi'-\xi'}+L_2}{-(1+\chi')\frac{v'-V'}{\chi'-\xi'}+(1+\xi')\frac{\delta V'}{\delta\xi'}} \; . \; . \; . \; (9)$$

Now, when χ and ξ, and χ' and ξ' approach each other, all quantities in (8) and (9), the four fractions included, will remain finite. Moreover we have;

$$\xi=\chi=\xi'=\chi',\, q=Q=q'=Q',\, v=V=v'=V',$$

$$l_2=L_2,\ \frac{\delta v}{\delta\chi}=\frac{\delta V'}{\delta\xi'},$$

and as the point has the properties of a plaitpoint the differential coëfficients, to which the four fractions:

$$\frac{q-Q}{\chi-\xi},\ \frac{v-V}{\chi-\xi}\quad\text{and}\quad\frac{q'-Q'}{\chi'-\xi'},\ \frac{v'-V'}{\chi'-\xi'}$$

approach. will become identical two by two. The expressions (8) and (9) therefore become equal in the plaitpoint, i. e. the curves meet in such a manner, that the tangents coïncide. A set of two of those curves belonging together we shall call a *border-curve*. The meeting point corresponds with the plaitpoint and is situated on the 'ligne critique' which therefore we prefer to call '*plaitpoint-curve*'. In order to find the direction of the plaitpoint-curve in a given point, we must make use of the conditions fulfilled by a plaitpoint. These are $\chi = \xi$, $V = v$ to begin with. Besides putting $d\tau = 0$ for instance in (3) we find the relation between $d\pi$ and $d\chi$ on the connodal curve of the plait In the plaitpoint we have $\frac{d\pi}{d\chi} = 0$. Introducing this condition we find as the conditions of a plaitpoint: $\frac{df_2}{d\chi} = 0$ and in the same manner from (5) $\frac{dF_2}{d\xi} = 0$ (and consequently $\frac{df_1}{d\chi} = 0$, $\frac{dF_1}{d\xi} = 0$). These conditions added to the other $\chi = \xi$, $V = v$ and $\chi' = \xi'$, $V' = v'$, we can now again introduce into the complete equations (3) and (5): by doing so we get the relation between $d\pi$ and $d\tau$ for the plaitpoint-curve; $\frac{d\pi}{d\tau}$ is found to agree entirely with the same quantity for the border-curve in the plaitpont, and so we arrive at the conclusion, that the border-curves touch the plaitpoint-curve. i. e. that the plaitpoint-curve is the envelop of the border-curves.

We come to the same conclusion by the following reasoning using the properties of the plait. We consider a definite mixture with its plaitpoint-temperature. With rise of temperature towards the plaitpoint-temperature of the mixture the change of pressure of the mixture can be regarded as consisting of two parts: one part is due to the fact that the composition belonging to the plaitpoint approaches the composition of the mixture; the second part is the change of the pressure in the plaitpoint itself. As the temperature approaches the plaitpoint-temperature of the mixture, the first part of the change approaches to zero and becomes zero at last, because $\frac{d\pi}{d\chi} = 0$ along the connodal curve in the plaitpoint. Only the second part, the change of the plaitpoint-pressure itself, remains. Hence $\frac{d\pi}{d\tau}$ for the mixture in the plaitpoint is equal to the same quantity along the plaitpoint-curve *q e. d.* [1]).

Instead of the figures 16 and 17 of Duhem's memoir we obtain a figure like figure 1. The curves are for the greater part experimental. The figure represents the case of mixtures of carbonic acid and methyl chloride. The vapourpressure curve for CH_3Cl is drawn according to my own experimental data [2]), the one for CO_2 according to Amagat's results [3]): they end in the two critical points C_1 and C_2. The border-

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[1]) A meeting of the 'ligne critique' and the 'ligne de rosée' at a definite angle, as is the case in Duhem's figures, is therefore impossible.

[2]) Arch. Néerl. 26, p. 392—395.

[3]) Journ. de Phys. (3) 1. p. 288.

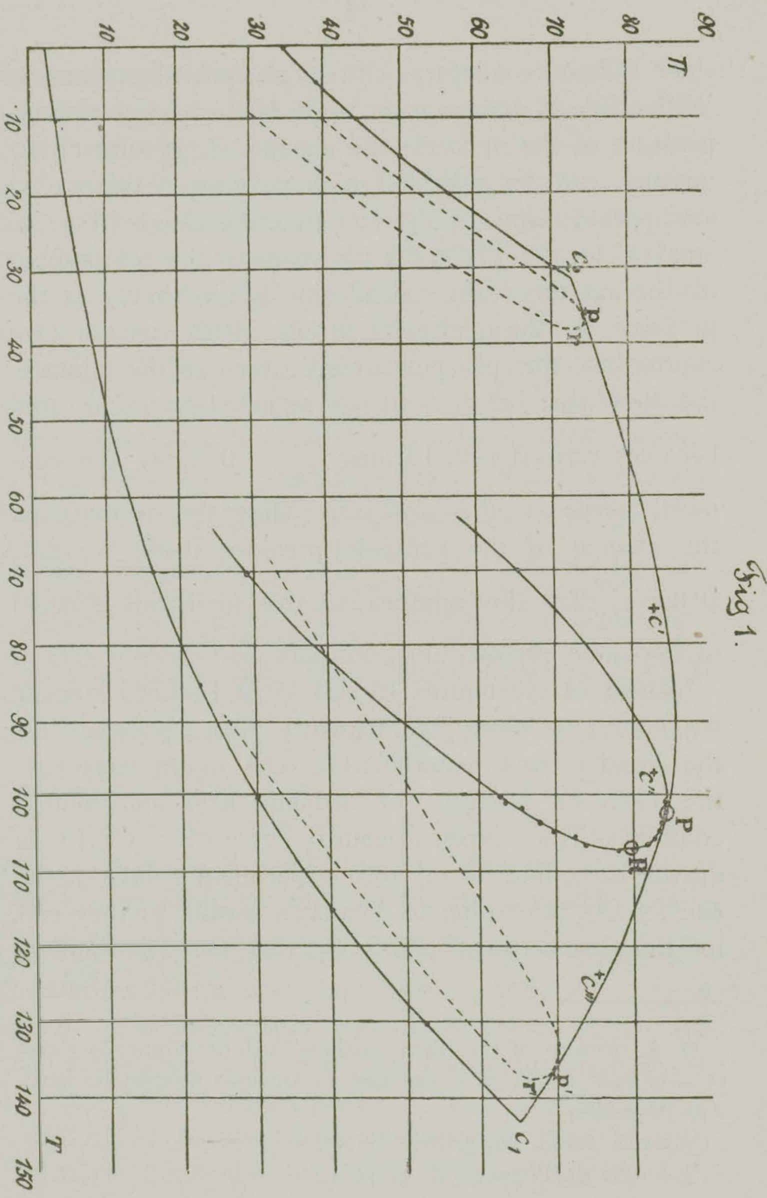

Fig 1.

curve drawn in the figure holds good for a mixture of $^2/_5$ CO_2 and $^3/_5$ CH_3Cl, which I experimented on in 1892. A part of my results was published before on occasion of my first paper regarding retrograde condensation and the critical phenomena of mixtures [1]. Though only few, these observations, now that I have represented them graphically on occasion of the publication of Duhem's memoir, appear to be quite sufficient to show the form of the border-curve with great approximation: it entirely agrees with what was to be expected from the above theory.

Temp.	Press. at the beginning.	Press. at the end.
70	28.8	64.9
100	63.1	—
100.6	63.3	84.4
101.5	65.7	84.7
103.0	67.9	84.0
104.0	69.7	83.8
105.0 [2]	72.2	83.2
106.1	74.0	82.1
106.7	78.6	80.2

From these numbers we derive as probable values for the temperature and pressure of the critical point of contact 106.8 and 79.5 (point R).

The plaitpoint-curve has been drawn in such a

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[1] Communications etc. n⁰. 4. p. 13.

[2] l. c. we gave 73.3 and 83.8: the calculation had been only preliminary then.

manner that it touches the border-curve of the mixture $^2/_5$ CO_2 in its plaitpoint P. We may not expect the critical points of the other mixtures[1] indicated as C′, C″, C‴ to lie on the plaitpoint-curve. For these points were determined before I had made clear the difference between the plaitpoint-temperature and the temperature of the critical point of contact. Hence exactness wass impossible and the only thing, we may say, is that the points as they were fixed must lie somewhere between the two real critical points p and r, rather nearer to r: the plaitpoint-curve is drawn in such a manner that its position with relation to C′, C″ and C‴ is in accordance with that supposition. Two dotted curves have been added to the figure not having an experimental basis; they serve to show the slowly narrowing of the border-curves and the transition into the vapourpressure-curves.

An extensive interpretation of the figure seems hardly necessary. All the border-curves will be seen to have a vertical tangent: consequently all the mixtures must show retrograde condensation between the two critical points p and r. The line drawn through all the points r terminates in the two critical points C_1 and C_2, in contrast to the same line in Duhem's figures, which ends in two points Y_1 Y_2 situated on the plaitpoint-curve. It is evident, how it can be, that without any discontinuity mixtures differing only a little from the pure substances immediately show retrograde condensation and a vertical tangent in contrast to the curves for the pure substances themselves.

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[1] Archives Néerl. p. 398, 401, 403.

It should be observed that only in an exceptional case the plaitpointpressure is a maximums-pressure at the same time: whether the maximum occurs on the liquid branch of the border-curve or on the vapour-branch depends upon the fact whether the curve rises or falls in the point under consideration. Both cases occur in the figure.

The intersection of two border-curves gives the pressure and temperature at which the mixtures, to which the curves belong, may coëxist.

Some time ago[1] the possibility of a second kind of retrograde condensation was pointed out by me, in which compression would occasion the appearance and subsequent disappearance of a vapour-phase, instead of a liquid-phase. In this case the plaitpoint on van der Waals's surface must lie towards the vapour-side of the critical point of contact. Transferring this into the graphical representation used here we get, that the plaitpoint will lie beneath the critical point of contact and this point consequently on the liquid-branch of the border-curve. Taking into account the connection between border-curve and plaintpoint-curve we find that this will be the case, if the vapourpressure-curve belonging to C_1 lies above that for C_2 and also for a part of the mixtures, if the plaitpoint-curve has a vertical tangent, or, which comes to the same, if the

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[1] Archives Néerl. p. 26. p. 388.

critical point of contact of a part of the mixtures lies outside the critical temperatures of the two substances

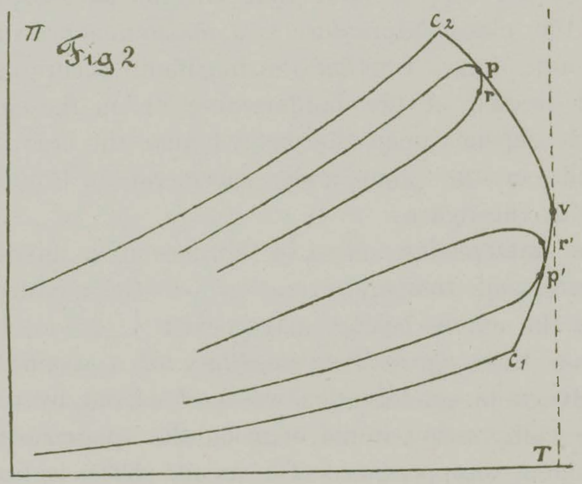

Figure 2 shows, what the situation of the curves might be, if the critical temperatures of a part of the mixtures are higher than those of the pure substances. In one of the border-curves p lies above r; the other has a plaitpoint p', which lies beneath v, at which point the plaitpoint-curve has a vertical tangent: p' therefore falls beneath the critical point of contact r and between the two corresponding temperatures retrograde condensation of the second kind must exist. Experiments will have to decide, whether this case may occur.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 14.

Dr. H. KAMERLINGH ONNES on the cryogenic laboratory at Leiden and on the production of very low temperatures.

Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Akademie van Wetensch. te Amsterdam, **29 December 1894.** p. 164—181.

EDUARD IJDO — PRINTER — LEIDEN.

Dr. H. KAMERLINGH ONNES *on the cryogenic laboratory at Leiden and on the production of very low temperatures.*

§ 1. For more than ten years I have bestowed all my available time upon an investigation of the manipulation of condensed gases in order to make physical experiments in liquid-baths of very low temperature possible. After much labour I have succeeded in my efforts and at present a section of the physical laboratory has been arranged for these operations only.

Only comparatively small means were at my disposal in this investigation. Of the whole of the subsidy, granted to the laboratory by Government, a small portion only could be employed for this purpose, especially of late. I always lacked sufficient assistance. The same instrument-maker who constructed the new apparatuses under my direction was also charged with the care of those already completed and helped me in handling them, when being used. So we were compelled every now and then to put aside the innovations already undertaken. For a short time only, at the beginning of my work, I was helped by a scientific assistant. Consequently the investigation could only progress with intervals of stagnation which sometimes did much harm. It was only recently that I had a couple of instrument-maker's apprentices at my command, to whom I could entrust simple operations.

Even if more money and assistance had been at my disposal for this purpose, it would have been my aim to make experiments at low temperature possible with the simplest means. But in that case not so much time would have been lost by trying work with what was really insufficient.

In mentioning this, however, I must at the same time point out that in our country the State is almost the sole promoter of physical investigations and that in this case too, all the expenses were defrayed by the treasury.

So it is my duty to express my sincere thanks to the Government. Without its collaboration in extending and improving the physical laboratory at Leiden it would have been impossible for me to found a cryogenic laboratory there.

§ 2. I was induced to work with condensed gases by the study[1] of van der Waals's law of corresponding states. It seemed highly desirable to me to scrutinize the isothermal lines of the permanent gases, especially of hydrogen (§ 9), at very low temperatures. And the idea of applying on their determination the new experimental method, introduced by Pictet's ingenious researches attracted me much. It was already in my inau-

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[1] H. Kamerlingh Onnes. General theory of the fluid state. Verh. Kon. Ak. v. Wet. Amsterdam, XXI, 1881. Beibl. z. Wiedem. Ann. 5, p. 718.

gural address in 1882 that, with a view to this, I called the pumps of Cailletet and Pictet indispensable laboratory-instruments. As such they ought to be considered with still more right after the publication of Wroblewski's and Olszewski's [1] paper in 1883.

A first step in the investigation a sketch of which will be given here, was the purchase of a compressor devised by Cailletet [2] in 1883 for condensing any quantity of pure gas.

As Cailletet's experiments on the decantation of liquid gas proved ethylene to be the most important substance for investigations on low temperatures, I began by repeating those experiments. As soon as ethylene was prepared and condensed in rather considerable quantities, I might proceed to a repetition of Pictet's experiments, in which I intended to employ ethylene in the second cycle.

The compression of the ethylene will be attended with great difficulties unless thorough care be taken in the preparation of the gas with regard to its purity. The method of preparing (passing alcohol-vapour through sulphuric acid) was continually improved by availing ourselves of our experience in subsequent preparations. Not until 1890 it was brought to such a degree of perfection that now each time when the gas is wanted we can be sure of a regular distillation of a gas, containing at least 99 pct of ethylene, in quantities exceeding 1,5 M^3. The distillation takes place in three apparatuses, connected

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[1] Wiedemann's ann. XX. 1883.

[2] Ann. de Chimie et de Physique, 5^e série, tome XXIX, 1883.

in the physical laboratory of Leiden by Dr. Kuenen in his academical thesis [1]) (1892) — the described pump is very useful.

By supplying gas under higher pressure from an auxiliary compressor, the capacity is proportionally increased; of this contrivance we also avail ourselves frequently.

§ 4. Let us now, after this digression, return to the state of the investigation in 1885 when it was resolved to purchase the long wished for conjugated pumps, necessary for the repetition of Pictet's experiments. With more right than from Pictet's experiment, the possibility of pouring out oxygen in the manner as Cailletet had poured out ethylene, could be argued from the formerly-mentioned beautiful investigation of Wroblewski and Olszewski. So from that moment the next aim of my investigation became: to make oxygen circulate according to Pictet's method and to use it for experiments in the same way as Wroblewski and Olszewski, in imitation of Cailletet, had taught us to use ethylene.

The possession of the conjugated pumps and of the Cailletet compressor brought this aim within my reach. While I was already negotiating about the conjugated

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Sciences de Cracovie. Jan. 1882, p. XXVII (No abstract in the Beiblätter).

[1]) Diss. Leiden, 1892. Measurements concerning the surface of v. d. Waals for mixtures of carbonic acid and methyl chloride. Versl. en Med. d. Afd. Natk. Kon. Akad. v. Wet. 29 April, 1892. Communic. No. 4.

pumps, Wroblewski's investigation was published in the Wiener Sitzungsberichte of 1885. At that time Wroblewski still worked with no more than a few cubic centimeters of liquid oxygen and also pointed out as the »Methode der Zukunft:" [1]) »Der wesentliche Schritt vorwärts welcher in Hinsicht der Erweiterung der Methode zu thun wäre, ist sie so abzuändern dass man im Stande wäre den Sauerstoff so zu giessen, wie man heutzutage das Aethylen giesst. Die Sache wird aber meiner Ueberzeugung nach nur dann mit Erfolg durchzuführen sein, wenn man zu den Pictet'schen Methoden zurückkommen wird und durch den Kreislauf von mehreren verflüssigten Gasen eine Cascade von den Temperaturen herstellen wird, von denen die letzte Stufe der Strom des flüssigen Sauerstoffs bildet."

In 1886 the above-mentioned pumps one of which was destined for a circulation of sulphurous acid, the other for an ethylene-cycle, could be put into action.

However we were far removed from having obtained with the possession of the pumps a regular circulation of condensed and evaporating gases.

Those pumps were nothing but ordinary technical engines and not calculated to answer to the high requirements of a physical laboratory.

In a laboratory they must be ready for immediate use each time, when it is desired to make an experiment. Even after having been unemployed for a comparatively long time, they may not show the slightest

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[1]) Wiener Sitzungsberichte XCI p. 710.

leakage or other disturbanses. They must be constructed with a view to their being handled and taken care of by people only accustomed to physical laboratory work. Besides, for various operations accessory apparatuses are wanted and had to be constructed.

It took much time to free all pieces from smaller or greater leaks and defects, to lay perfectly tight packings, to make suitable conduits, to make cocks which do not get fixed by the cold, for which purpose such with cork-packings proved the best, to devise gauge-tubes showing the level of the condensed gas and filtering-apparatuses for protecting the cocks. Much that is an article of trade now was not yet known then and had consequently to be made, which was very troublesome. And moreover there had to be acquired practice in all sorts of unusual work.

It is quite another thing to have such an instrument in regular use as an ice-machine or to make experiments with it at very low temperatures. In the latter circumstances their use is attended with much more danger than in the regular manufactory-business and in a college this danger has all the more to be avoided. So there had to be made special arrangements for this purpose. The whole first cycle forms one closed metallic body which is everywhere of amply sufficient strength to bear the maximum-pressure of the liquid gas contained in it at the temperature of the room. Wherever the walls are cooled to low temperatures they are made of copper.

Having all this ready I had as yet made little progress. It is true that as early as 1887 I prepared liquid ethylene in an apparatus similar to that used by PICTET for condensing carbonic acid, viz. in a condenser cooled by evaporating sulphurous acid, but firstly sulphurous acid proved after all to give much trouble when used in a laboratory, and secondly the PICTET refrigerators which I had hoped would have been serviceable at least in the first circulation, proved to be even more impracticable than one might already have expected from the drawing.

Even in the first circulation it was neceseary to put above the refrigerator a regenerator, in which the ethylene to be condensed, in passing through a long coil, was preliminarily cooled by the cold vapours given out by the refrigerator.

This regenerator served at the same time as a precaution against a sudden priming of the condensed gas from the refrigerator to the pump.

As for the sulphurous acid, for this poisonous gas methyl-chloride was substituted. Against using methyl-chloride in the first cycle there is the less objection as in the second cycle large quantities of ethylene are necessarily present.

The precautions dictated by the use of this gas which forms with air an explosive mixture, as: heating of the room by steam, illumination by electric glow-lamps, a powerful ventilator, etc., also take away any danger when using methylchloride.

By choosing methylchloride and ethylene as the first two evaporating liquids, another idea of CAILLETET to whose genius we are so much indebted in this kind of investigation, has been realized; an idea which was suggested f. i. in his communications of 1885 [1]).

Along with what has been mentioned in § § 2 and 3, the next years following on 1887 were devoted to the achievement of the ethylene cycle. Besides difficulties of the same kind as those already summed up for the first circulation, among which should be mentioned that the ethylene had to be freed from the fine cloud of lubricating-oil which it carries along from the pumps, here quite other difficulties of a more scientific character presented themselves.

The ethylene had to be poured down into a metal vessel, which was still considered next to impossible by WROBLEWSKI[2]) and in this vessel it had to boil in a vacuum without causing any danger even in the case of imaginable mistakes or unexpected occurrences. A tube in the form of a coil immersed in that liquid could then serve for continually receiving oxygen, condensing it and letting the liquid oxygen flow away [3].)

To effect this the evaporated ethylene had to be

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[1]) Comptes rendus, tome C. p. 1033.

[2]) Sitz. Ber. Wien XCI. p. 670.

[3]) After the publication of this paper I learned that after PICTET, prof. DEWAR has made as early as 1886 an apparatus wholly of metal, being an arrangement of copper coils in which liquid oxygen was made and decanted. Though the apparatus was constructed on a small scale and was not used for collecting liquid oxygen I wish to point out this anticipation effecting a part of my idea. The description of the apparatus being found in an article on meteorites (Proc. Roy. Instit. 1887) and no abstract having been published in the Beiblätter it escaped my notice.

14

pumped away, condensed and poured again in this vessel. Especially the construction of this ethylene boiling-flask occupied me a very long time. In June 1890 the drawing was finished by me in its final form but the apparatus was not ready before 1891.

The complete ethylene-cycle forms again one metallic body in which the ethylene is moved round by the pump and which, if the circulation is not used, is entirely filled with ethylene under atmospheric pressure with the exception of a welded kettle in which the rest of the ethylene is kept in store under a pressure of 15 atmospheres.

The boiling-flask into which the liquid ethylene is poured when the circulation is in function, forms one whole with a large kettle of a capacity of 600 Litres into which the whole quantity of liquid ethylene might, if necessary, distil without exceeding the pressure which the apparatuses can bear. The pump takes the ethylene from this large safety-reservoir and compresses it into the high-pressure-reservoir, just mentioned, or through a return-valve which prevents the ethylene from flowing back, into an oil-arrester which can bear the maximum-pressure which the ethylene can attain at the temperature of the room. From the oil-arrester it is conveyed in a coil through the methylchloride-regenerator to the methylchloride condenser. Even if the ethylene thrown back into the oil-arrester passed there into the spheroidal state, neither this oil-arrester nor the condensation-coil, connected to it, would burst. By a regulating-cock which may be adjusted with great precision from the outside without conduction of heat, the ethylene can flow into the boiling-flask after having passed through a filtering-apparatus and check-valves which like other details as drying-apparatuses etc. cannot be considered here more closely. Both the pump and the oil-arrester and condensation-coil can discharge themselves through safety-valves into the large safety-reservoir, so that no part of the circulation can become exposed to a higher pressure than for which it has been calculated. Even after the addition of the ethylene which was kept in store this remains the case. In this way the possibility of accidents by confining a large quantity of this dangerous gas in a limited space is completely prevented. The purity of the gas is under continual control while pressure-and exhaust-gauges indicate the momentary state of the system.

The whole apparatus may be left to itself for months and then with the necessary precautions be brought into action within an hour's time. Only if the circulation is going on for a long time without interruption, some ethylene is lost by the quivering motion at those joints which are under high pressure. The ethylene lost is again supplied from the store. By a cock the circulation can be brought into communication with large bags of double india-rubber with intermedial tinfoil into which the ethylene can flow under the ordinary pressure. To the ethylene-condenser and to the large safety-reservoir other (glass) boiling-apparatuses for ethylene can be occasionally connected which are employed in protecting-cases of gauze and plate-glass, but for the rest in much the same way as by WROBLEWSKI and OLSZEWSKI and which

f. i. served for Dr. E. DE VRIES's academical thesis[1]).

§ 5. The aforesaid ethylene-boiling-flask with condensation-coil is made of copper. The walls are very thin. They are strengthened by bars and rings so that they can bear exhaustion or pressure. Among other contrivances the condensation-coil is provided with a safety-cap so that an explosion in the boiling-flask may be considered as an impossibility. In the wider lower part of the boiling-flask, the cylindrical room of 22 cM. diameter in which the boiling takes place, the liquid ethylene surrounds about 10 spiral windings of the condensation-coil. These have a cooling-surface of 0.15 M^2 and a capacity of about 300 cM^3. Above the broad surface of the boiling ethylene we find a tapering conical room of 25 cM. height for bridling the priming of the ethylene. In this room numerous windings with a cooling-surface of 0.15 M^2 utilize particularly the cooling-effect of all splashed drops of liquid ethylene. Farther upward we meet with a regenerating-room in which the cold ethylene-vapours pass between windings of the coil of 0.2 M^2 cooling surface. The passage from the regenerating-room to the strong metal mouthpiece is formed by a brass tube the walls of which are very thin but strengthened by rings. This neck has been soldered to the other metallic parts but

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[1]) E. C. DE VRIES, Diss. Leiden 1893. Mesures relatives à l'influence de la température sur l'ascension capillaire de l'éther sulfurique depuis la température critique de ce liquide jusqu'au point d'ébullition de l'éthylène. Arch. Neerl. XXVIII. Communic. No. 6.

can supply only an insignificant quantity of heat by conduction. The main part of the boiling-flask is not suspended to this weak neck but to a wooden support of light but strong structure firmly fastened to the strong metal mouthpiece to which the neck also has been soldered.

The mentioned mouthpiece is screwed to a beam of a frame and can in the usual way be joined to the large safety-reservoir by copper tubings. Near the mouthpiece we find the handle of the non-conductive regulating-cock for the supply of ethylene (to be adjusted by the ear) and a glass tube, in which a pointer indicates the level of the liquid surface in the flask.

In the construction we have tried to obtain the most favourable ratio between the condensing surface, the quantity of metal to be cooled, the required cooling-liquid, the supplied condensed liquid and the surface which conducts heat from the the outside. Moreover we wished to avail ourselves completely of the cold ethylene-vapour.

Much care has been taken to prevent, as far as possible, condensation of water-vapour and supply of heat by convection, conduction and radiation. In this respect I succeeded sufficiently by enveloping the flask in successive layers of cells coated with felt and filled with wool and by well pasting each layer with cotton and paper and varnishing these.

Within a couple of hours it is possible to pass into the boiling-flask more than a litre of liquid ethylene and make this to boil under a pressure of two or three centimeters. In this case the regenerator works in such a way that the escaping ethylene leaves the boiling-flask at nearly the ordinary temperature.

The solution of the problems, presenting themselves in this circulation, has been very carefully studied. I wished, namely, to obtain a type for working with few kilos of condensed gases and few horsepowers which enables us to use without danger liquid ethylene and liquid oxygen in the laboratory and secondly to arrange several cycles for a temperature-cascade. If we wish to give a still greater cooling-surface to the condensation-coil, the boiling-flask has a downward annular continuation. If more cycles are employed, some of their boiling-flasks can be constructed concentrically. (See § 10).

§ 6. Instead of condensing the ethylene by means of the condenser immersed in methylchloride, I also made use of a coil which is put into a ring-shaped basin kept filled with solid carbonic acid.

When using ordinary commercial carbonic acid the continuous drawing off of large quantities from the bottles offers great difficulties.

Experiments with carefully dried carbonic acid proved me that the obstruction of the cock must nearly always be ascribed to the circumstance that the liquid gas contains water. At my request the Dutch Kaenolite and Carbonic-acid-Company at Rotterdam has undertaken the preparation of dry carbonic acid by distilling the ordinary commercial substance over quick-lime. I strongly recommend this carbonic acid for all laboratory-purposes; it is possible to empty within a few minutes a cylinder filled with ten kilograms of it.

If we wish to dispose of the methylchloride-circulation for another purpose, and if therefore we replace it for cooling the ethylene condenser by solid carbonic acid in the maner just explained, we want considerable quantities of this latter substance every hour, even then if we can prepare the solid carbonic acid beforehand in sufficient quantity, not by letting the gas flow out of the reservoirs at the ordinary temperature but by cooling it in the methylchloride-cycle. Only in the case that a large carbonic-acid ice-machine is at hand or that a friendly manufactory of liquid carbonic acid would procure the solid acid at the cost-price, the cooling by solid carbonic acid could be permanently applied. Hence it will, as a rule, be necessary to cool the ethylene-condenser by a circulation, for which we chose a methylchloridecycle making it further so easy to work at all temperatures between —20° and —70°.

§ 7. But let us return to the ethylene-cycle. Not before 1892 the whole circulation was in so complete function that liquid oxygen could be drawn off from the interior coil of the boiling-flask into the glass apparatuses prepared in the mean time.

Already Wroblewski had convinced himself of the possibility of transferring a few cubic centimeters of liquid oxygen from his condensation-tube into another apparatus. In 1890 Olszewski 1) had made an important step farther in this direction by substituting for the glass tube which he had used with Wroblewski for condensing oxygen a wider steel one. By means of a small tube in the bottom he poured down from it for

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1) Bull. intern. de l'Acad. des Sciences de Cracovie, 1890, p. 176.

the first time liquid oxygen. In the subsequent years he used liquid oxygen baths for most important investigations 1). But for all this the extension of the method such as I tried to find and as it was also wished for bij Wroblewski, was not yet arrived at.

Again, in 1891 Pictet 2) had given a description of the magnificent manufactory for the use of artificial cold, established by this leader in the domain of the liquefaction of the permanent gases at Berlin after 14 years' efforts. »Depuis 1887," he writes, »j'étais hanté par le désir constant d'établir sur une plus large échelle un laboratoire à basses températures . . . . . j'ai été forcé d'attendre et de travailler pour me donner la satisfaction, la grande jouissance de réaliser mon rève."

No less than 50 horse-powers is the power of the steam-engine at his command for his pumps and he believes that »pour opérer normalement et travailler expérimentalement avec de l'air atmosphérique liquide il faut disposer d'une force d'au moins 30 à 40 chevaux vapeur, actionnant 6 à 7 compresseurs 3).

In my experiments 6 or 8 H.P. are required if we wish to reach low temperatures rapidly; in regular

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1) After the publication of this paper a detailed description of prof. Olszewski's work appeared Phil. Mag. Febr. 1895 from which we learn, that in the steel cylinder there was prepared 100 cM. liquid oxygen in 1890 and 200 cM. in 1891. The liquid oxygen baths obtained when this quantity was poured down from the condenser and which prof. Olszewski used in his beautiful researches did not attain 50 cM.

2) Verh. der physik. Gesellsch. Berlin, 24 April 1891.

3) C. R. t. CXIV p. 1245.

action the compressors do not require so much. I was highly astonished to see that Pictet founds his idea about the necessity of great motive power on a new insight into the transport of heat at low temperatures, while my boiling-flask had been very sufficiently protected indeed at —130°.

Moreover it did not appear that Pictet had occupied himself with collecting large quantities of liquid oxygen in glass apparatuses suitable for experiments. In a subsequent communication [1]), Pictet even calls —50° and —165° »températures que nous pouvons considérer comme limite de la zone utile des recherches dans notre laboratoire."

On the 17th of June 1892 condensed oxygen was for the first time drawn from the condensation-spiral of my boiling-flask and collected in a glass vessel suitable for experiments at the ordinary atmospherical pressure.

The quantity collected was but very small indeed — only 20 cM^3 — when the apparatus broke; but that in this way a sufficient quantity could be obtained and kept and that the dimensions of the apparatuses were well chosen was sufficiently proved.

The reparation and improvement of the various contrivances, serving for this purpose in such a way that no oxygen could be lost, lasted till December 1893, when I succeeded for the first time in collecting a quantity of $^1/_4$ Litre of liquid oxygen in a glass without pressure and could show it for hours to several scientific friends. The methylchloride-pump being on that occasion

destined for pumping away the oxygen at low pressure, the carbonic-acid-refrigerator of § 6 did service then.

In the mean time in 1892 Dewar's memorable experiments had been published which first solved the problem in such a splendid manner and enabled him to make with his colleagues Liveing and Fleming a series of extremely difficult measurements in large quantities of liquid oxygen. Yet I have the satisfaction to have independently and in my own way struggled against the same scientific difficulties as this famous scientist and to have founded at Leiden too the means of working with liquid oxygen in a laboratory which for the rest is also well-arranged,

Since December 1893 I have been again engaged in making various slight improvements, so that we can now say that we can obtain with sufficient speed and without considerable expenses a liquid-bath of more than a quarter of a litre of oxygen under the ordinary or under reduced pressure and that this can be kept disposable for any time with a small quantity of circulating oxygen. I had the honour to show a glass of liquid oxygen fit for experiments under these conditions to the President of the Physical Section in May 1894.

Now the work is so far advanced that I shall be happy to show the same thing to every one interested.

§ 8. The manner in which I used liquid oxygen for experiments diverges at one important point from Dewar's, not to speak of the arrangement of his cycles which I don't know. It will be remembered how Dewar, in his lecture at the Royal Institution (on the 10th of June '92) the report of which the newspapers spread over the whole earth, passed the liquid oxygen

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[1]) C. R. 10 Dec. '94.

in vacuum glasses from hand to hand. With my method such a thing is not to be obtained directly. But the construction of the splendid apparatuses, devised by DEWAR, requires much care and after having been used they lose something of their excellence. So it may be of importance to show that also without vacuum glasses liquid oxygen can be used for experiments in rather considerable quantities.

The apparatuses used by me, which I shall for simplicity's sake call boiling-glasses, remind us in many respects of WROBLEWSKI's and OLSZEWSKI's apparatuses and most of all of those which WROBLEWSKI described in 1885 and in which he employed an artifice already used by DEWAR in 1884, viz. to protect the cooled liquid by its own vapour. In fact I had in my mind from the very beginning to unite the beautiful work of CAILLETET, WROBLEWSKI, OLSZEWSKI on one hand and that of PICTET on the other.

The resemblance is such that the glass into which the liquid oxygen is collected, has partly the same diameter and shape as WROBLEWSKI's glass. But upwards it is widened into an excentric bowl in order to check the vortices occasioned by the issuing and the rapid evaporation of the jet and in order to render priming harmless. In the double copper lid of this bowl are two glass tubes. One is a continuation of the experimental tube, and has about the same width. It serves for plunging apparatuses into the experimental tube with which it forms PICTET's »puits frigorifique.'' In the second double tube beside it is the valve for drawing off oxygen.

14

This cock is moved from the outside by an insulating handle in a glass tube in much the same way as the regulating-cock of the ethylene borling-flask. Together with this cock the well insulated tube which supplies the liquid oxygen is placed in the boiling-glass. The jet of filtered oxygen is directed against the interior wall of a glass tube of a somewhat smaller diameter than the interior side-tube in which it is freely suspended. At the upper part this jet-receiver is almost closed by coils of the oxygen-supply-tube; at the bottom it ends in a nozzle of very thin copper through which the oxygen flows into the bowl-shaped room. Between the jet-receiver and the interior side-tube the oxygen-vapour escapes and then circulates round the whole apparatus between the double side-tube and other double walls. The experimental tube hangs in a small thin glass vessel near the bottom of which the evaporated oxygen is delivered.

The whole boiling-glass is surrounded by a thin copper case which I shall call the boiling-case. The evaporated oxygen issuing into this case is drawn away at the top of the boiling-case which has been so constructed that it can also be evacuated. The oxygen is received into the crompression-pump under normal or reduced pressure; finally, the whole quantity present can escape through a safety-valve into bags of double india-rubber with intermedial tinfoil. The boiling-case is composed of three annular parts, carefully coated at the inside with felt covered at the interior with rings of nickel-paper in order to diminish the radiation. Over the bottom and the lid india-rubber covers are stretched, giving passage to the various tubes. They form herme-

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tical seals and serve at the same time as large safety-caps. For it is true, what DEWAR says as recently as Febr. '94: »The prosecution of researches at temperatures approaching the zero of absolute temperature is attended with difficulties and dangers of no ordinary kind" [1]).

In the case four windows have been made, placed two by two opposite each other, one serving for the illumination, while the other is used for the observation. The upper pair serves for the observation of the jet and for the corresponding regulation of the cock (taking into account the indications of the manometers). The lower couple is oblong and enables us to follow the experiments in the liquid oxygen bath. The spy-windows consist of successive compartments, through the foremost of which, if necessary, hot air, dried by phosphorus pentoxide, can be sent.

Simpler but in some respects of the same construction was the boiling glass with case in which Dr. DE VRIES, when preparing his academical thesis in my laboratory, measured the capillary ascent of ethyloxide at the temperature of boiling ethylene.

One can follow the phenomena in the boiling-glass described now for hours and so sharply that f. i. the height at which liquid oxygen rose in a capillary tube could be observed in this way.

As soon as the apparatus has been sufficiently cooled, the oxygen evaporates from the surface; the troublesome boiling in the liquid, also mentioned by OLSZEWSKI and which DEWAR especially wanted to prevent by

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[1]) Proc. Roy. Instit.

using vacuumglasses, does not occur in this method.

§ 9. Apart from the just-mentioned capillary phenomena which are closely related to the determination of the temperature (See E. C. DE VRIES, thesis p. 43) [1]), I hope I shall shortly be able to give a communication concerning the isothermal linis of hydrogen at extremely low temperatures. To the investigation of these isothermals the last three years of WROBLEWSKI's life were devoted; he did not succeed however in obtaining reliable data of the isothermals at — 180° (in boiling oxygen) from which f. i. the critical temperature of hydrogen might be deduced. I thought it in many respects of high importance (see § 2) to take up this investigation. As early as '93 I made measurements to this end by means of a hydrogen-thermometer with a reservoir of 30 c.M.^{3} while the copper-German-silver thermo-electric couple used by WROBLEWSKI has also been studied again. The determination of the isothermals (or of VAN DER WAALS's ψ-surface)[2]) for mixtures of permanent-gases with hydrogen is so closely related to this investigation that it forms almost a part of it.

If to pour out hydrogen requires more powerful apparatuses than now already in possession of the cryogenic laboratory, for this quantitative investigation of isothermals which can be considered as preliminary to the working whith liquid hydrogen, as well as for numerous other researches, that which was brought about has proved to be amply sufficient.

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[1]) Comp. footnote p. 16 of this Communication.

[2]) Comp. footnote p. 10 of this Communication.

§ 10. Among the problems relating to the liquefaction of hydrogen we must rank the use of liquid methane as an intermediate link between liquid ethylene and liquid oxygen. Methane as a cooling-agent was already mentioned by CAILLETET in a pli cacheté of 1881 [1]; in 1884 DEWAR drew the attention to this very important aid for liquefying the more permanent gases; finally also WROBLEWSKI and OLSZEWSKI occupied themselves with methane (1884). Yet it has not been used in any investigation. One of the main difficulties is that most methods of preparation yield the gas mixed with large quantities of hydrogen so that it is consequently difficult to condense. Now in this respect the aforesaid (§ 3) process of fractional distillation promises good results. When the opportunity presented itself, I had a few cubic meters of methane prepared. The ordinary method of preparation was followed but with special care as to constancy of temperature.

In order to be able to intercalate a new cycle and to compress gases, as in this case the impure methane, in rather considerable quantities, without using the other compressors, I requested from H.E. the Minister of the Navy the loan of a BROTHERHOOD compressor, as are in use for launching torpedos. With great kindness this excellent instrument was put at my disposal by H.E., on condition to return it at the first intimation. It is repeatedly used for supplying in a short time large quantities of air compressed to 100 atmospheres; besides I provided it with the necessary

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[1] C. R. t. 99. p. 213.

contrivances for compressing costly or dangerous gases and so it could also serve in the experiments on pouring oxygen for speedily restoring into reservoirs large quantities of escaped gas. The weight of this admirable instrument is only 90 kilo. It brings about 10 M^3 of gas to a pressure of 100 atm. in one hour. Methane compressed with this compressor was condensed in the condensation coil of the ethylene boiling-flask and poured into the same boiling-glass which serves for the storing of oxygen. The boiling-glass and boiling-case having been constructed to supply the least quantity of heat possible to the liquid, a spiral-wire through which an electric current was conveyed, was immersed in the liquid in order to make it boil. This wire can also serve for determining the latent heat. The liquid having been in ebullition for some time can be drawn away by a small tube reaching to the bottom of the boiling-glass and having been evaporated can be again compressed with the compressor for pure gas (§ 3). The operation taking much time, it was only applied to a small quantity and a judgment of the practicability of the method cannot be formed yet.

For cooling very much oxygen with liquid methane, which for this purpose may boil under the ordinary atmospheric pressure, a similar boiling-flask is destined as was described for the ethylene. In order to contain the numerous coil windings the boiling-room has a downward annular continuation and is surrounded by a vapour-jacket in the same way as the oxygen glass. The liquefaction of the required methane necessitates a condenser with large cooling-surface, consequently a larger ethylene boiling-flask, now containing 6 K. G. of ethylene which commands the necessity of a larger safety-reservoir (to which purpose a welded kettle of 5 M^3 serves) and a greater displacing-capacity in the methylchloride-cycle or otherwise the insertion of a concentric nitrous-oxyde-cycle.

With these apparatuses at which was worked occasionally for a couple of years already, the whole motive power of the steam-engine which otherwise serves principally for the electric plant of the physical laboratory can, if necessary, be gradually used for experiments which require much liquid oxygen. I think it possible to pour out also liquid hydrogen then.

Finally it is an advantage of the present arrangement of the cryogenic laboratory that by the addition of new vacuum-pumps and compressors i. e. refrigerating machinery, such as can be had in the trade, and of the correspondingly required motive power the cascade can be extended to lower temperatures. The now founded installation being of a more scientific character than these additional circulations wil then be completely adapted for working at the very lowest temperatures in the new cascade and so the cryogenic laboratory of the future may be obtained.

15

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 15.

Dr. P. ZEEMAN. Measurements concerning KERR'S phenomenon with normal polar reflection from iron and cobalt.
(*Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Academie van* **26 Januari 1895,** *p.* 221).

Dr. P. ZEEMAN. On the determination of the optical constants of magnetite.
(*Translated from the same: p.* 230).

Dr. L. H. SIERTSEMA. On the dispersion of the magnetic rotation in oxygen.
(*Translated from the same: p.* 230).

A. LEBRET. The variation of the HALL-effect with temperature.
(*Translated from the same: p.* 238).

EDUARD IJDO — PRINTER — LEIDEN.

Dr. P. ZEEMAN. *Measurements concerning* KERR'S *phenomenon with normal polar reflection from iron and cobalt.*

§ 1. The observations till now known on the phase in KERR'S phenomenon were in very good accordance with Prof. LORENTZ'S theory, if to the calcutaled phase was added a nearly constant amount: SISSINGH'S phase.

That SISSINGH'S phase S proved to be nearly constant gave rise to series of measurements which all gave for this quantity, with the same substance, a nearly constant value within wide limits of the angle of incidence. These limits were f. i. with polar reflection: for cobalt 43° and 73°, for nickel 25° and 75°. But it appears from the graphical representation and the adjoined table, communicated in my name to the Academy in April 1894, that in the case of nickel S seems to diminish with the angle of incidence.

It is true the differences between the theoretical (for which $S =$ Const.) and the observed phases were just within the limits of the probable errors, but at 75° the direction of the deviation was contrary to the direction at 25° and on the whole a certain bias in the discrepancies was undeniable. Nothing but a continued investigation could decide whether we had to deal here with a casual error or with a real deviation.

In the meantime, the supposition that SISSINGH's phase would be constant also beyond the limits of the experimental investigation, had been made the foundation of theoretical speculations by GOLDHAMMER [1]) and afterwards by WIND in still close connection with Prof. LORENTZ's theory [2]). Thus it became a matter of the highest importance to investigate whether SISSINGH's phase has really the same value even at an angle of incidence in the immediate vicinity of 0° — which investigation was already prepared at the time of the publication of my academical thesis [3]). If we succeeded in determining the phase at such an angle of incidence, we should be able to form a wide better judgment on the value of the mentioned theories.

The limits between which *S* is known would then still be extended in the case of polar reflection with 50° for iron, with 43° for cobalt and with 25° for nickel. The methods of null- and minimum-rotations which were of so high a value in the KERR-investigation, became wholly impracticable at smaller angles of incidence and still more so at 0°. Consequently it was necessary to try for this kind of investigations a new method which accordingly was found by using a $\frac{\lambda}{4}$ plate of DE SENARMONT.

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[1]) GOLDHAMMER. Wied. Ann. Bd. 46, p. 71. 1892.

[2]) WIND. Verslag Akad. Afd. Natuurkunde, September 1894.

[3]) ZEEMAN. Dissertatie p. 53 en Verslag Akad. Afd. Natuurkunde, April 1894, p. 179. (Communications No. 10.)

§ 2. The use of a plate, for which the difference of phase of vibrations, parallel to two principal directions, is just a quarter of a wave-length, for analyzing elliptically polarized light, is sufficiently known.

From the position which we must give to the plate and to the analyzer in order to extinguish the light, we can easily deduce the ratio of the amplitudes in two arbitrary directions and the difference of their phases.

In this form, however, the method requires for a definite colour plates of strictly determined thickness and if f. i. we wish to make measurements for *D*-light with quartz-plates (for accurate measurements to be preferred to mica!) the grinding of such a plate requires extraordinary skill on the part of the optician; unless we leave it to chance for what colour the thickness of the plate will just [1]) correspond to $\frac{\lambda}{4}$ and then make the observations with light of that special colour. But we can avoid this difficulty by eliminating the thickness of the plate from the measurements themselves. Exactly in the same way as with a $\frac{\lambda}{4}$ plate, we have also with a plate of any thickness and with homogeneous light two (or if you like four) different positions (which are

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[1]) The thickness can be determined with white light and a spectroscope by putting the plate between 2 crossed or parallel nicols, the inclination of the principal direction to the planes of polarization being 45°. From the position of the dark and bright bands we immediately read the colours for which the plate is $\frac{\lambda}{4}$. This position can be determined with greater accuracy than one would suspect from the form of the curve, representing the intensity of the band-spectrum.

not at 90° from each other) in which the plate can be so used that the light can be extinguished by the analyzer; from these the required quantities can be found in the way, explained in § 4.

§ 3. *The apparatus.* The light of an electric lamp is analyzed by a Christie-Hilger [1]) spectroscope and made parallel by a collimator. Then it is polarized, reflected elliptically, polarized at 1° 23′ by the magnetized mirror and finally examined with the plate and analyzer (fig. 1).

The mirrors. In the same way as on former occasions [2]) I used for mirrors disks of polished metal of 5 mM. diameter; they were fixed with shellac to the top of a truncated cone, being the end of a soft-iron cylinder of 23 m.M. thickness and about 6 cM. length. This cylinder is lengthened by a thinner piece on which a screw is cut, by which it could form the continuation of the remaining part of the magnetic cone. By this arrangement the mirror could easily be taken from the apparatus and replaced in the same position. In this way alterations of the surface could be detected without difficulty by examining the optical constants [3]).

The spectrometer was so mounted that in this complementary examination the collimator and polarizer were used in unaltered position.

The electro-magnet. After a few modifications required by my investigation, I could avail myself of an electromagnet, constructed formerly by Dr. SIERTSEMA

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[1]) ZEEMAN. Archives Néerl. I. 27, p. 259. 1893.

[2]) ZEEMAN. l. c. p. 281.

[3]) ZEEMAN. l. c. pp. 270, 283.

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in order to produce a strong field for another purpose.

In fig. 2 and fig. 1 we have a vertical and horizontal sketch of the apparatus. It consists principally of three soft-iron parallelopipeda. The lowest piece measures 50 × 10 × 10 cM., the two erect pieces measure 10 × 10 × 14 and 10 × 10 × 17 cM. The left carries just a little above the middle the cylinder *C* into which the piece with the mirror is screwed. The right one *B*, I had made in such a way that it serves as a sub-magnet [1]) and at the same time does not disturb the passage of the rays. The produced axis of the cylinder is also that of the truncated cone *D* of about 4 cM. length.

The whole piece *P* is pierced by a partly cylindrical and for the rest conical canal, the width of which is 6 mM. near the mirror and 22 mM. at the other end. The coil, as a rule used with 20 Amp., was wound with insolated copper-wire of 4 mM. thickness; during the experiments the elevation of temperature was insignificant. The screw-bolts *T* press the parallelopipeda strongly together by which the magnetic resistance is diminished and displacement of the parts is made impossible.

The distance from the mirror to the front of the sub-magnet was about 3 mM.

In this position of the sub-magnet the mirror was normally magnetized. I could convince myself of this fact by bringing very small pieces of a watch-spring near the mirror; they stood normal to the plane of the mirror even close to the edge.

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[1]) Compare DU BOIS. Phil. Mag. (5) Vol. 29, 1890, p. 293.

As it was of course of great importance to give to the mirror its exact position, the electro-magnet (weighing with its accessories 90 K.G.) was placed upon a large, carefully worked, turning- lathe-support. Rotations round a vertical axis and horizontal displacements in two directions perpendicular to each other, could in this way be effected without difficulty. Also the angle of rotation could be rudely read on a divided circle; small rotations of the mirror round a horizontal axis were effected by putting thin copperplates under the electro-magnet. The whole apparatus was supported by four columns, resting on one of the pillars of the building.

The plate. The quartz-plate used was about 0,31 mM. thick and had a surface of 1×1 cM^2. By choosing quartz, which can be so nicely ground that the image of a wire-cross can be seen in the front, I was enabled to effect the delicate adjustment of the plate. In fig. 3 (scale $^1/_2$ of the original size) the manner is indicated in which the plate is placed before the analyzer, while fig. 4 gives a perspective drawing of the whole measuring-arrangement.

I fixed the plate *P* with collodion on three spots to a perforated piece of cork, placed in a tube, all the required adjustments of which could be effected by means of 3 screws pushing it forward and 3 others drawing it backward. *C* is a copper disk, to which the lever is attached which is used for the delicate adjustments.

The rude adjustment of the plate was made with the circle *D* which I took from a Jamin spectrometer

and also the reductional observations necessary for reducing to minutes the rotations read in scale divisions. Rotations of the whole tube round *A A* were regulated by a fine screw in the tail-piece of the trunnion-plate by which *A A* is supported, rotations round a vertical axis having also been taken into consideration in the construction. The tube *B* was kept down by a counterpoise *G*. By the sketched arrangement I could effect that the plane of the plate *P* was normal to the incident beam of light which at the same time coincided with the axis of the tube *B*. It became clear to me that, if in one position of the plate these conditions were satisfied, only small fluctuations of the image of the cross-wires occurred when it was turned and that consequently the construction of the tube was quite satisfactory.

The analyzer and polarizer were the same that were formerly used with the null- and minimum-rotations [1]).

§ 4. *Calculation of the experiments.* The current was taken strong enough to neglect the disturbing influence of the permanent magnetism residual from former magnetizations on the final magnetic state [2]). From the principle of images it follows that with a reversal of the magnetization the amplitude of the magnetic component of the light changes its sign only [3]), but that the phase remains the same. So there is no

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[1]) Sissingh. Archives Néerl. T. 27. p. 189.

[2]) Du Bois. Phil. Mag. (5) Vol. 29. p. 296.

[3]) Zeeman. l. c. p. 283.

objection against using the difference of the rotations of the analyzer and also of those of the plate at + and — magnetization instead of using rotations from the principal positions. The demagnetization which takes so much time and the difficult determination of the principal position at an angle of incidence of 0° are in this manner avoided. Besides, an occasional residual magnetism can have no influence on the calculation of the phase by the smallness of the magnetic component of the light.

With respect to the signs used I have still to mention the following. It is known that one sees two dark spots near the bright centre of the interference-phenomenon, exhibited by a quartz-plate placed between two crossed nicols in convergent monochromatic light[1]. On the edge of the tube containing the plate, I have marked by two scratches the direction which is perpendicular to these and call it: direction 2; direction 1 coinciding with the scratches. I call rotations positive if they are (for an observer placed before the object-glass of the collimator) in a direction opposite to that of the hands of a watch. It has already been remarked (§ 2) that there are two positions (the difference of which is not 180°) of the plate and the analyzer in which no light is transmitted. The rotations of the plate will for convenience sake be denoted by 2φ, those of the analyzer with respect to the plate by ψ'. The rotation φ_2 be 0 if with crossed nicols direction 2 coincides with the plane of polarization of

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[1] Kohlrausch. Prakt. Physik. p. 193. 1892.

the incident light; φ_1, on the contrary, if direction 1 is perpendicular to it, ψ_2' and ψ_1' are in these cases also 0° and 90°.

According to E. Wiedemann[1] the following equations (derived in accordance with Kichhoff's indications) hold if we use the above-mentioned notation and if B denotes the phase of the magnetic component of the light:

$$\left.\begin{aligned} tg\,\frac{B-C}{2} &= cotg\,\frac{A}{2}\,\frac{Sin\,(\psi'-\varphi)}{Sin\,(\psi'+\varphi)} \\ tg\,\frac{B+C}{2} &= cotg\,\frac{A}{2}\,\frac{Cos\,(\psi'-\varphi)}{Cos\,(\psi'+\varphi)} \end{aligned}\right| \quad \ldots\ldots (1)$$

In these equations A is an auxiliary angle dependent on the thickness of the plate and given by

$$Cos.\ A = \frac{tg\,(\psi_1'-\psi_2')}{tg\,(\varphi_1-\varphi_2)} \quad \ldots\ldots (2)$$

C is an auxiliary angle of no consequence for our purpose.

In (1) both systems for ψ' and φ must be used. Thus 2 results for B are obtained the accordance of which is a measure for the obtained accuracy.

§ 5. *Measurements on iron.* To one position of the polarizer belong eight positions of the quartz-plate, viz. 4 for each position of the analyzer. In each position 4 adjustments are made at + and 4 at — magnetization. Like in all similar observations we may take for granted that the result of those 8 positions will be free from

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[1] E. Wiedemann. Berichte der K. S. Gesellschaft der Wissenschaften. 1872, p. 279.

all systematic errors, resulting from imperfections of the different parts of the apparatus. The observation in the three other positions of the polarizer should then give the same result within the limits of the probable errors. This proved to be the case.

In a more extensive publication the arrangement of the measurements will be described in detail

For one position of the polarizer I give the double values of the rotations, with which those got from the diametrical positions have already been combined.

Iron-mirror *D*-light.

	Position of the plate.	Rotation of the plate.	Rotation of the analyzer.
Position of the polar. 218°.7			
» » anal. 4°	2	35'.8	18'5.
	1	24'.5	43'.2
» » anal. 184°	2	36'.5	16'.5
	1	24'.3	44'5.

From this and 3 other series it now follows:

	φ_1	ψ'_1	$\varPhi_2$	ψ'_2
Pol. 38.7	$-11.2^5 \pm 0.40$	$-9.2^5 \pm 0.55$	$-90^\circ - 18.5 \pm 0.32$	$90^\circ + 9.5^5 \pm 0.60$
128.7	-11.9 ± 0.55	-9.3 ± 0.68	$-90^\circ - 18.3 \pm 0.36$	$90^\circ + 9.7 \pm 0.55$
218.7	-12.2 ± 0.36	$-9.7^5 \pm 0.54$	$-90^\circ - 18.1 \pm 0.35$	$90^\circ + 9.6 \pm 0.47$
308.7	-11.8 ± 0.36	-8.8 ± 0.47	$-90^\circ - 19.7 \pm 0.48$	$90^\circ + 10.5^5 \pm 0.59$

The whole results to:

$$-11.79 \pm 020 \quad -9.23 \pm 0.27 \quad -90^\circ - 18.51 \pm 018 \quad 90^\circ + 9.82 \pm 0.27$$

The adjoined numbers are the probable errors of the adjustments, expressed in minutes, like the rotations.

The optical constants of the mirrors were:

$$\left.\begin{array}{lll} \text{before the experiments} & I = 76^\circ 42' & H = 28^\circ 7' \\ \text{after » »} & \underline{I = 77^\circ 12'} & \underline{H = 27^\circ 18'} \end{array}\right\} D\text{-light.}$$

$$\text{mean value} \quad I = 76^\circ 57' \quad H = 27^\circ 44'$$

The two values for the phase B (taken in the same way as in my former measurements) are:

From position 1.	From position 2.
$B = 30^\circ 26'$	$B = 31^\circ 11'$

mean value $B = 30^\circ 30' \pm 1^\circ 26'$

From this value and from the phase calculated with the measured optical constants, follows for SISSINGH's phase at 0°:

$$S_{Fe} = 69^\circ 19'.$$

With iron-equatorially SISSINGH found $S = 85^\circ$ and with iron-polarly I found $S = 80^\circ$ at an angle of incidence $i = 51^\circ 22'$. So my result is that in this way we find another value for S beyond the formerly given limits.

§ 6. *Measurements on Cobalt.* Here I contented myself (considering what has been said at the beginning of the preceding §) with the 8 series, each of which I put together from 8 observations. The results are the following.

Cobalt-mirror. *D*-light.

$\varPhi_1$	ψ_1'	$\varPhi_2$	ψ_2'
$-15'.33 \pm 0.19$	$-3'.73 \pm 0.32$	$-90^\circ - 18'.26 \pm 0.28$	$-90^\circ + 3'.56 \pm 0.42$

The optical constants were:

$$\begin{array}{lll} \text{before the observations} & I = 77^\circ 0' & H = 31^\circ 24' \\ \text{after » »} & \underline{I = 76^\circ 40'} & \underline{H = 31^\circ 40'} \\ \text{mean value} & I = 76^\circ 50' & H - 31^\circ 34' \end{array}$$

Hence it follows for B

from position 1.	from position 2.
$B = 11^\circ 19'$	$B = 10^\circ 55'$

mean value $B = 11^\circ 10' \pm 3^\circ$.

Calculating the theoretical phase with the given optical constants and comparing B with it, we have:

$$S_{Co} = 42^\circ 4'$$

while formerly I found at angles of incidence greater than 43° on an average $S = 49^\circ 30'$.

Comparing the observations of this § and of § 5 with the former, it would consequently follow, that S diminishes at very small angles of incidence. For the nearer confirmation of this result however, a comparison of the method of the null- and minimum-rotations with the method now followed is necessary. Therefore I intend to make measurements by the two methods at the same angle and with the same mirror.

In order to ascertain myself now already of the reliability of the results of the method now followed (the figures formerly obtained were found accordant by two mutually controlling methods), I have made:

§ 7. *Measurements on a silver-mirror.* At an angle of incidence of 30° I measured the difference of phase of the rays polarized in and perpendicularly to the plane of incidence. For this purpose I gave to the polarizer deflections of 1° from the principal position to the left and to the right. The ellipse now obtained is completely analogous to the one found above, the difference of phase of the components amounting to about 11° if we calculate it by Cauchy's formulae from the measured optical constants.

The measurements with the plate gave results which agreed with the calculated values within the limits of the observational errors.

§ 8. In order to have a complete view of the rate of change of Sissingh's phase it will be desirable to make further measurements between 0° and the limits of the former angles of incidence, even if the measurements mentioned at the end of § 6 confirm (and the probable errors entitle us to this expectation) the values hitherto found at greater angles of incidence. For the present we must doubt whether one of the theories framed is capable of a complete explanation of Kerr's phenomenon. A complete theory will also have to account for the fact that the succession in magnitude of Sissingh's phase for iron, cobalt, nickel (and probably magnetite) is the same as that of their maxima of magnetization.

Dr. P. ZEEMAN. *On the determination of the optical constants of magnetite.*

With a view to further magneto-optic measurements I wanted the optical constants, principal angle of incidence and principal azimuth of magnetite. As these seem never to have been measured until now, I communicate them below. The heads sufficiently explain the table.

Nr.	J.	H.	colour	wave-length	originating from
1.	68°35′	9°0′	D-light	0.589μ	Fort-Henry. N.-York.
2.	68°25′	8°38′	D- »	»	Pfitsch Tirol.
3.	68°33′	7°55′	H-line α	0.656μ	» »
	68°27′	8°48′	D-light	0.589μ	
	68°27′	10°10′	H-line γ	0.434μ	

Dr. L. H. SIERTSEMA. *On the dispersion of the magnetic rotation in oxygen.*

The apparatus described in the former communication 1) with which measurements now have been made with oxygen and with air, has in some important respects been improved and completed.

In the first place it appeared that better precautions were necessary to keep the temperature of the experimental tube constant and so to prevent currents in the gas. Between the tube and the coil concentric brass tubes, connected with the water-conduct have been inserted, so that the water is obliged to flow from one end of the tube to the other and back. From thermometer-readings at the beginning and at the end of this circulation also the temperature of the gas was deduced. Between the experimental tube and the interior water-tube we find still a layer of india-ruber for equalizing the temperature. By this arrangement the just mentioned convection-currents are almost completely avoided in summer, even if by a long continuation of the observations the coils have become sensibly

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1) Zittingsverslag Kon. Ak. Amsterdam Afd. Natuurk. Juni 1893. Comm. Lab. of Physics. Leiden N°. 7.

heated. In wintertime however this proved to be still insufficient owing to the greater difference between the temperature of the room and the water, and the aim was not reached before the bronze endpieces and the ends of the experimental tube had been coated with cotton-wool.

Secondly a better arrangement was devised for turning the small endpiece containing the first nicol. A strong bronze ring provided with a downward handle accurately fits round the nuts of the flange. Two steel-wires are fastened to the handle, one of which is always kept stretched by a heavy weight and the other one goes over a small pulley to the other end of the apparatus where it is fastened to a screw which can be turned by the observer. By this arrangement the observer is enabled to give small rotations to the nicol, while sitting before the telescope.

The screw is attached to the beams on which the coils and the experimental tube are mounted. In the same manner the telescope and scale of the scale and mirror reading-arrangement, with which the rotation of the small endpiece is measured by means of an intermediate mirror, were at first attached to this beam. Now it soon became apparent by the inequality of rotations to right and left that this method of mounting had some drawbacks. By the rotation of the experimental tube and also by the heavy weight with which the steel-wire was loaded at the other end, this beam was no longer absolutely fixed, which could be proved by fixing a small mirror to various parts of the apparatus. For this reason the scale and mirror-reading no longer

answered to its purpose and moreover the measured rotations were inaccurate because the large endpiece with the nicol was also somewhat turned in the same direction. An efficacious improvement in the mounting of the coils could not be effected without much trouble and loss of time, so that it seemed simpler to follow another way. First all parts of the scale and mirror arrangement were mounted, independent of the apparatus, on a fixed pillar which has no contact with the floor of the room, and secondly the rotations of the large endpiece were taken into account by measuring them with a level, attached to this endpiece and previously carefully calibrated. After these improvements the difference between the rotations to left and right existed no longer. For the sake of security however the rotations were limited to values of 3° to 4° by varying the intensity of the current.

The measurement of the intensity of the current was attended with some difficulties. For an accurate measurement of a current of about 60 amp. the ordinary commercial ampèremeters are not suited. Moreover the instrument has, because of the vicinity of the coils, to fulfill the condition that it is not affected by the exterior magnetic field and with a view to the variability of the dynamo-current, it must admit of a quick reading. For this purpose a d'ARSONVAL galvanometer with objective mirror-reading, through which a branch of the main current is sent, proved the most satisfactory. The branch is made by conveying the main current through a copper tube placed in streaming water, the temperature of which is noted every now and then. The calibration of this instrument is effected by measuring a current of 60 amp. from accumulators, simultaneously with this instrument and with a large tangent-galvanometer in another room, consisting of two circles of 1 M. diameter at a distance of nearly 2 M. from each other.

Between these a magnet with mirror is suspended above a revolving divided circle with which a telescope is connected which is always adjusted perpendicularly to the mirror. The deflection for the said current amounts to about 40°. We may suppose that the reductional coefficient of this instrument is constant, which is sufficiently confirmed by a few comparisons with a copper-voltameter.

From these simultaneous measurements it appears that the deflections of the galvanometer may be put proportional to the intensity of the current and besides, that its reductional coefficient is in a simple way related to the temperatures of the shunt and of the galvanometer. It is about 0,023, the deflections being from 150 to 300 scale-divisions.

The temperature of the galvanometer is read on a thermometer placed at its interior. By wrapping up in cotton-wool quick variations of temperature were prevented.

Overheating of the coils was prevented by closing the current in the coils only during the pointings. The difficulties attending the repeated opening and closing of a dynamo-current were obviated by transferring the current each time with a key on an iron-wire resistance-

coil of a resistance nearly equal to that of the coils. Another double key serves for changing the direction of the current in the coils.

The pressure of the gas is read to 0,1 atm. on a large manometer of 25 cM. diameter, the corrections of which have been determined by the Physikalisch-Technische Reichsanstalt at Berlin.

In the measurements I have exclusively employed the method cursorily mentioned in the preceeding communication in which the light of the arc-lamp passes first through a collimator and then through the experimental tube, is then analyzed by a glass prism and is observed with a telescope. The slit of the collimator has been shortened by a couple of little screens to a length of 2 mM. Thus the too obliquely incident light which by reflections in the tube disturbs the pointings, is avoided.

When turning the nicol, one sees, when the current is closed a black band moving through the spectrum, which admits of very good pointings. Only at the ends of the spectrum, especially at the violet end, they are less accurate owing to the small intensity of the light, but it is improved by a diaphragma with broad vertical slit in the eye-glass of the telescope, by which only part of the spectrum is seen. It will be seen that in this method we miss the previously mentioned black line which crosses the field of crossed nicols horizontally and moves vertically over the image of the slit and the accuracy attainable in the pointings is consequently less. For compensating this, however, we have some advantages. First the wave-length can be better determined. If formerly this was done by placing a small spectroscope behind the experimental tube *after* the measurements, now we can find them by pointing the telescope, after having read its position on a divided circle, at a few neighbouring fixed points in the spectrum, for which in the case of oxygen the already formerly mentioned absorption-bands of LIVEING and DEWAR can serve and also some bright lines in the spectrum of the electric light. By comparing these lines and bands with FRAUNHOFER's lines, their wave-lengths have been controlled and the dispersion-curve of the prism has been determined. With the observations on air only the mentioned bright lines can be used as fixed points. The telescope has always been adjusted on the fixed points before and after the adjustment of the black band so that possible small displacements of the spectrum can have no influence. In the adjustments the telescope was always first pointed at a definite point of the spectrum and then, after having closed the current, the band was adjusted by turning the nicol. In this manner it is possible to make a number of successive observations, retaining the same wave-length.

Besides the better and quicker determination of the wave-length, the method followed offers still the advantage that the convection-currents in the gas, occasioned by differences of temperature, which it is very difficult to prevent completely, make the image of the slit very turbulent and the pointing of the horizontal black line very inaccurate, while the band in the spectrum is only influenced by much stronger currents. This influence becomes first apparent in a deviation of the direction of the issuing light, which with stronger

convection-currents can become so considerable that it is no longer possible to pass a ray of light through the tube. If we look in such a case through the tube it seems to be curved. In the method followed, it is possible to continue, with the necessary precautions, the observations for a very long time.

The crossed position of the nicols without current cannot be pointed at so correctly, as here the whole of the spectrum is darkened. This pointing can better be effected by putting a mirror between the experimental tube and the prism and by observing the direct white image of the slit in this mirror. If the nicols in the experimental tube are so placed that the black line in their field is vertical, which is the most favourable position for the band in the spectrum, and if the slit of the collimator is not too narrow, this line can be very well pointed at. Regular observations of this null-position however were made only in the beginning in order to judge of the correctness of the pointings and of the equality of the rotations to the right and to the left. Afterwards the rotations have always been deduced from two pointings with nearly equal currents in opposite directions. The possible loss of accuracy in this method of working is amply compensated by the larger number of observations which can be done in the same time.

The gas which was drawn off after the observations was then also analyzed with HEMPEL's pipetts. It soon became clear that the purity of the gas in the well-known iron cylinders was quite insufficient.

If in the former communications a purity of 94%

was mentioned, the cylinders with which I worked afterwards showed a less favourable percentage, sometimes no more than 60%. The admixture is probably nitrogen. In order to be able to make observations on pure oxygen I was obliged to prepare it myself.

This preparation has been effected by electrolyzing diluted sulphuric acid in ten apparatus with lead electrodes and with a current of 12 to 13 ampères. The gas delivered by the generating apparatus passes through a wash-bottle containing potassium iodide for arresting ozone, which otherwise vigorously attacks the india-rubber connections and is then collected in a reservoir from which, after having been led trough a few wash- and drying-bottles, it is forced into an iron cylinder to upwards of 100 atmospheres by the mercury-compressor described by Prof. Dr. Kamerlingh Onnes [1]). The first gas yielded contained much air and was not collected, but after the production had been continued for some time, this improved, the purity of the gas in the filled cylinder being found, on examination, to be 98,7 perc. Besides with this gas, observations were made with air and with gas from a cylinder of 87.8 percent.

From the observations numbers have been deduced, proportional to the rotation. These have further been reduced to equal intensities of the current and also to a pressure of 100 atmospheres and to a constant temperature, supposing that they are proportional to the current and the density of the gas. The succession of

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[1]) Zittingsversl. Kon. Akad. Amsterdam 1894/95 p. 197. Comm. of the Lab. of Physics. Leiden N°. 14.

the observations has for the rest been so chosen, that each time from readings in immediate succession two rotations are deduced for the same wave-length, which consequently must be equal and the observations were cancelled if their difference was too great. On the whole 184 adjustments were made with oxygen, 68 with air. With the numbers found in this way, to which by means of the observations on air a small correction has been applied for the remaining 1,3% of nitrogen, a curve has been drawn which consequently represents the magnetic rotatory dispersion for oxygen.

These numbers are

wave-lenght in 10^{-3} mM.	ω_o (oxygen)	ω_a (air)	ω_n (nitrogen)
0,423	2897	3544	3715
0,436	2741	3310	3460
0,4455	2674	3173	3305
0,453	2575	3064	3193
0,460	2524	2967	3084
0,477	2384	2754	2852
0,505	2182	2470	2546
0,527	2067	2272	2326
0,5385	2018	2180	2223
0,549	1927	2103	2150
0,578	1831	1900	1918
0,604	1716	1740	1746
0,630	1617	1602	1598
0,664	1545	1464	1442
0,684	1516	1390	1357

The corresponding numbers for air have been added and the numbers deduced from these for nitrogen by extrapolation, for both of which gases also curves have been drawn. (See Fig. 5).

On nitrogen however I hope to be able to give more direct observations afterwards.

In these reductions we have assumed that the rotation ω of a mixture of p vol. of oxygen and q vol. of nitrogen can be represented by

$$\omega = \frac{p}{p+q}\,\omega_o + \frac{q}{p+q}\,\omega_n.$$

The validity of this rule and the accuracy of the observations can be shown by comparing the rotations found for the 87,8 percent gas with the calculated values. As we found only numbers proportional to the rotations these can only be equal, save a constant factor.

wave-length in 10^{-3} mM.	rotation calculated	rotation observed	ratio
0,423	3002	3027	1,008
0,436	2834	2906	1,025
0,4455	2756	2777	1,008
0,453	2655	2700	1,017
0,460	2597	2632	1,013
0,477	2445	2497	1,021
0,505	2229	2290	1,027
0,527	2101	2140	1,019
0,5385	2045	2070	1,012
0,549	1956	2015	1,030
0,578	1842	1863	1,011
0,604	1720	1740	1,012
0,630	1615	1628	1,008
0,664	1532	1531	0,999
0,684	1496	mean	1,015

The accordance may be considered sufficient.

The absolute rotations will be given afterwards.

If we consider the results found for oxygen more closely, we see that the preliminary result mentioned in the former communication, viz. that the rotation in oxygen for violet is about twice that for red, is here confirmed.

Let us now see how far the observed rotations in oxygen can be represented by one of the numerous formulae, given for the magnetic rotatory dispersion. These formulae invariable express the rotation by means of the wave-length, the refractive index and one or two constants. Excepting NEUMANN's formula, which needs not be considered, and taking into account the ordinary slight dispersion in gases, the formulae with one constant give all a rotation very little deviating from $\frac{c}{\lambda^2}$. From what follows it will become clear that such a formula cannot be used here. The formulae with two constants of BECQUEREL [1]), LOMMEL [2]), VOIGT [3]), VAN SCHAIK [4]), all lead, if we take n constant to expressions of the form

$$\omega = \frac{c_1}{\lambda^2} + \frac{c_2}{\lambda^4}$$

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[1]) BECQUEREL. Ann. de Ch. et de Ph. (5) 12. p. 1 (1877).

[2]) LOMMEL. Münch. Sitz-Ber. 1881. p. 454; Wied. Ann. 14.

[3]) VOIGT. Wied. Ann. 23. p. 493 (1884).

[4]) VAN SCHAIK. Dissertatie. Utrecht 1882; Arch. Néerl. 21. p. 1 (1886).

Mascart's formula [1]) on the contrary gives

$$\omega = \frac{c_1}{\lambda} + \frac{c_2}{\lambda^3}.$$

From calculations by the method of least squares in which to each number a weight has been given proportional to the number of adjustments (these weights have been indicated in the curve), it will appear that by a formula of the first-mentioned form the observations cannot but very unsatisfactorily be represented. Only by adding a third term we find with

$$\omega = \frac{937{,}22}{\lambda^2}\left(1 - \frac{0{,}1572}{\lambda^2} + \frac{0{,}01388}{\lambda^4}\right)$$

a sufficient accordance with a mean error of 17,4 or about 1% which agrees with the accuracy to be expected in the final result from the various readings and adjustments.

The second formula on the other hand gives already a sufficient accordance in the given form. We find:

$$\omega = \frac{868{,}028}{\lambda}\left(1 + \frac{0{,}07202}{\lambda^2}\right)$$

with a mean error of 17,5. The preliminary results for nitrogen can also be represented by formula of the same form:

$$\omega = \frac{560{,}41}{\lambda}\left(1 + \frac{0{,}32424}{\lambda^2}\right)$$

with a mean error of 19,1.

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[1]) Mascart et Joubert. Leçons sur l'électricité et le magnétisme I, p. 656. See also: Joubin, Ann. de Ch. et de Ph. (6) 16. p. 78. (1889).

From an investigation of Joubin it appears that Mascart's formula holds in all other known cases. In connection with this we would conclude from the above observations that the formula

$$\omega = \frac{C}{\lambda}\left(n - \gamma\,\lambda\,\frac{\partial n}{\partial \lambda}\right)$$

represents the magnetic rotatory dispersion best of all known formulae.

In this comparison we should however bear in mind that but little is with certainty known about the refractive indices of oxygen under a pressure of 100 atmospheres.

Therefore I intend to make a separate determination of the ordinary dispersion at high pressure, when the investigation will be extended to ultra-violet and ultrared light.

Zeeman. Normal Pol Reflexion

Fig. 3.

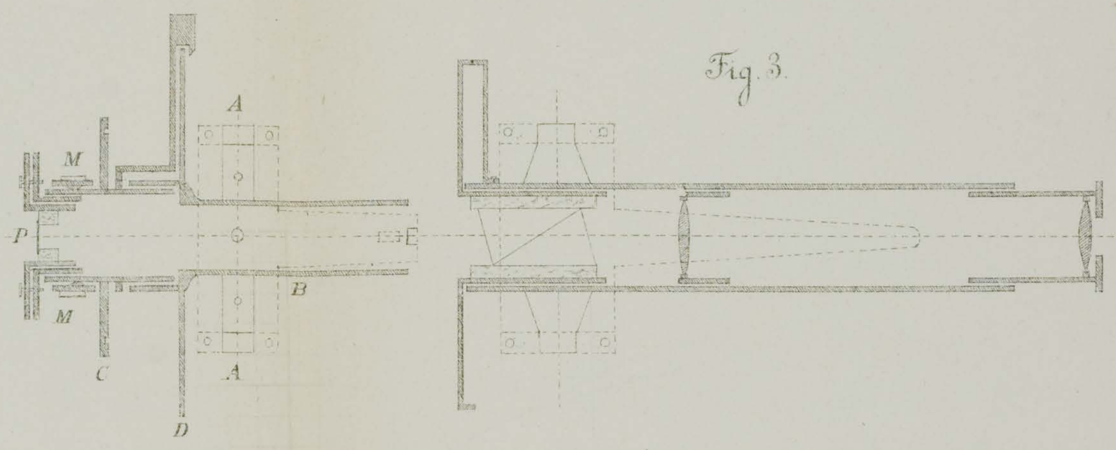


Fig. 2.

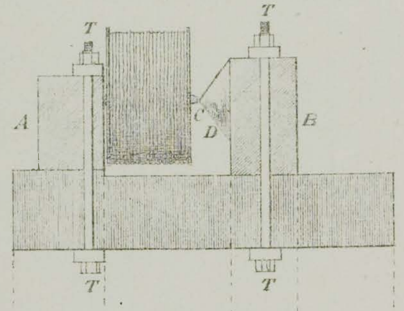


Fig. 4.

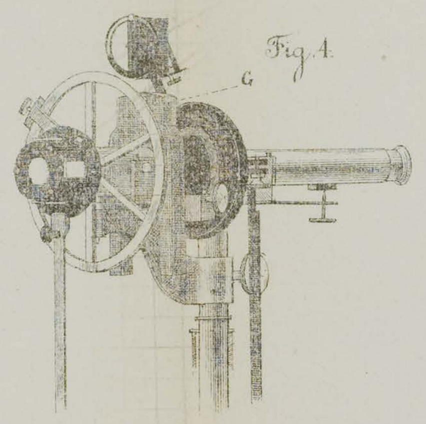


Fig. 1.

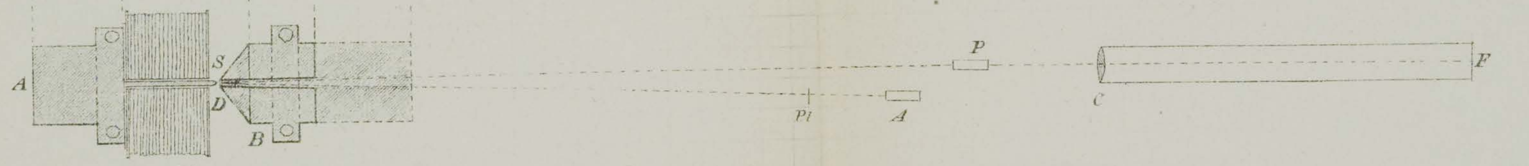
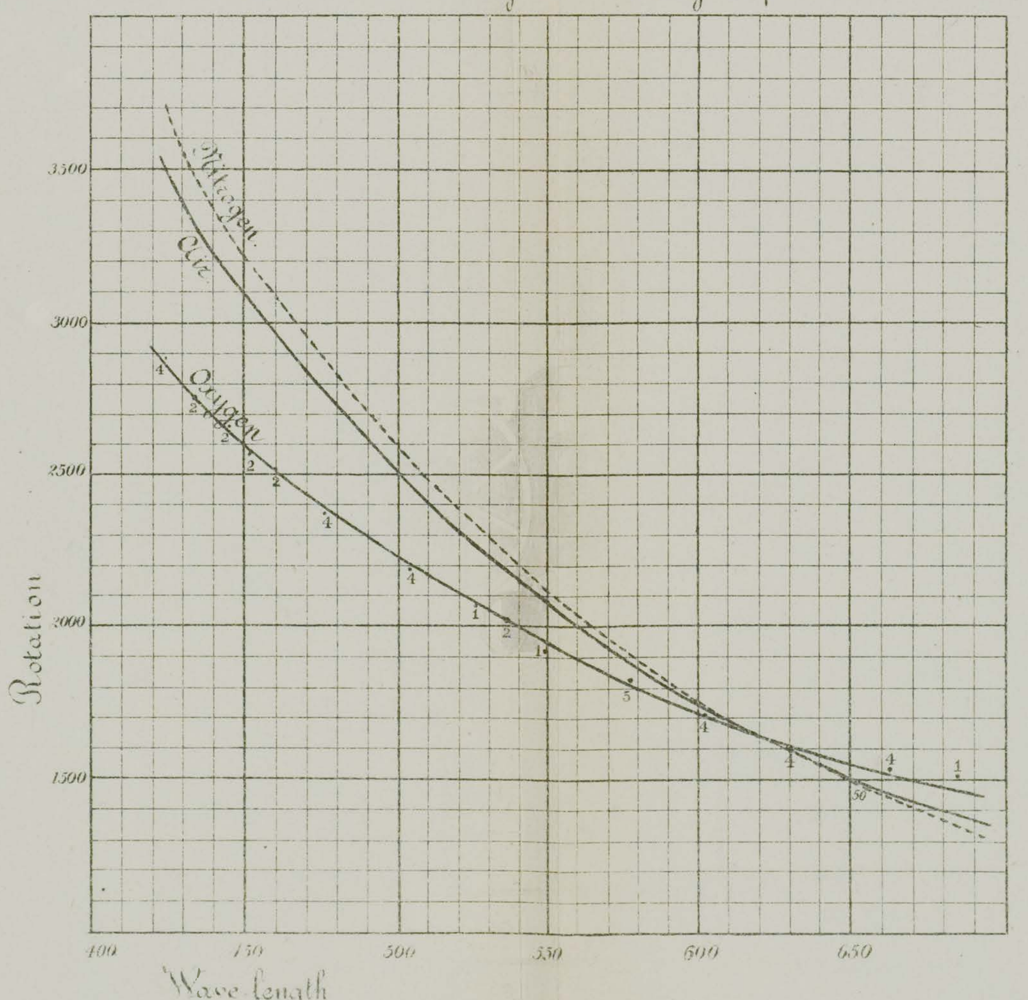


Fig. 5.

Siertsema Magnetic rotatory dispersion



Commun. Labor. of Physics Leiden N°. 15.

Eduard Ydo.- Drukker. Leiden.

A. LEBRET. *The variation of the* HALL-*effect with temperature.*

NERNST and DRUDE found the HALL-effect in bismuth to diminish from 1 to 0.23 by rising the temperature from 14° to 243°. After cooling to 100° they obtained the value 1.23, which is greater than the value at 14° that was taken unity.

From my measurements on the contrary I deduce that the HALL-effect regularly diminishes from 14° to 243°, and rises in the same regular manner by cooling to —38°.

Preliminary observations give:

Temperature	—38°	14°	100°	239°
HALL-effect	1.18	1	0.69	0.29.

The exact relation between temperature and HALL-effect however can only be established when the measurements are finished.

16

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 16.

Dr. J. P. KUENEN. On the Condensation and the Critical phenomena of mixtures of ethane and nitrous oxide.

Revised reprint from
Phil. Mag. 40. *p.* 173—194 (1895).

EDUARD IJDO — PRINTER — LEIDEN.

Dr. J. P. KUENEN. *On the Condensation and the Critical phenomena of mixtures of ethane and nitrous oxide* [1].

Revised reprint from
Phil. Mag. 40 p. 173—194 (1895).

1. Before relating the results arrived at in this investigation I shall have to give a short account of the course of thought which led to the choice of the subject.

My experiments on the conduct of mixtures [2] are based upon the theory of Prof. VAN DER WAALS [3]. VAN DER WAALS "describes" the properties of mixtures by means of an isothermal surface, the coordinates of which are the composition of the mixture x $(0 < x < 1)$, the volume v, and the free energy $\psi (\psi = \varepsilon - t\eta;\ \varepsilon =$ energy, $\eta =$ entropy, $t =$ temperature). On this surface there appear *plaits* [4], which determine the coexistence of two or more phase. Those points of these plaits which have a common tangent plane represent the phases which may coexist at the temperature for which the surface is constructed, and at a pressure indicated by the slope of the tangent plane $\left(p = -\frac{\partial\psi}{\partial v}\right)$. The double curves traced out by rolling the tangent planes over the plaits are the so-called *connodal* curves. It may happen that the plaits terminate on the surface itself (*i. e.* between the planes for which $x = 0$ and $x = 1$). In that case the coexisting phases approach each other and at last coincide in a so-called *plaitpoint*. In studying the plaits on the surface, one may use the projection upon the x—v plane. This projection consists of the x-axis between $x = 0$ and $x = 1$, the two v-axes for $x = 0$ and $x = 1$, the connodal curves with or without the plaitpoints. The points of the connodal curves belonging together may be joined by straight lines. The ratio of the parts into which these lines are divided by a line perpendicular to the x-axis, say for $x = x_1$, represents the ratio of the quantities of the two phases which will be formed when the mixture x_1 is taken at the pressure at which the two phases may coexist. Keeping this in view, it is easy to derive the condensation and critical phenomena of a mixture.

2. We shall only discuss the very simple case here, that there is only one plait on the surface, the vapour-liquid plait, which determines the coexistence of a vapour-phase and a liquid-phase. The plait, roughly speaking, has the direction of the x-axis; its plaitpoint, which will make its appearance if only we raise the tempera-

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[1] Read before the Physical Society on May 24, 1895.

[2] KUENEN, *Archives Néerl.* XXVI. pp. 354—472; *Zeitschr. phys. Chemie*, XI. pp. 38—48; *Verh. Kon. Akad. Amsterdam*, passim; Communications from the Labor. of Physics, Leiden, Nos. 4, 7, 13.

[3] VAN DER WAALS, *Archives Néerl.* XXIV, pp. 1—56; *Zeitschr. phys. Chemie*, V. pp. 133—173.

[4] For the nomenclature used in this treatise, *cf.* KORTEWEG, *Wien. Ber.* XCVIII. pp. 1154—1191; *Archives Néerl.* XXIV. pp. 57—98.

ture to a sufficient height, need not coincide with the end of the plait, *i. e.* with that point of the connodal curve which is nearest to one of the ψv planes (in the projection = v-axis). The latter point was called *critical point of contact* [1]). Now in deriving the critical phenomena two cases have to be distinguished depending on the relative position of these two points, which we shall call P and R. Either P is situated nearer to the ψx plane (x-axis) or this is the case with R.

3. In the first case the condensation of a mixture has the following character. Below a definite temperature (plaitpoint-temperature = T_P), different for every mixture, the quantity of the denser phase increases regularly during compression; the pressure rises, and both the composition and the volume of both phases change continuously. Above another temperature (temperature of the critical point of contact = critical temperature = T_R) there is no condensation possible. At temperatures ranging between T_P and T_R the condensation will have the following character: — With compression the quantity of the appearing liquid first increases, reaches a maximum value, and after that decreases till it disappears. This was called *retrograde condensation of the first kind* (r.c. I.) [2]). The nearer we get to the plaitpoint-temperature the larger becomes the quantity of the liquid

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[1]) KUENEN, *Archives Néerl.* XXVI. p. 379; *Communications from the Lab. of Physics, Leiden,* N°. 4, pp. 7 *sqq.; Zeitschrift phys. Chemie,* XI, p. 44.

[2]) KUENEN, *Archives Néerl.* XXVI. pp. 371—379; *Commun.* N°. 4; *Zeitschr. phys. Chemie,* XI. p. 44.

and the smaller the difference between the phases, apparent from a less distinct liquid surface between the phases. A mixture, therefore, has a critical region instead of one critical point, lying between two critical temperatures.

4. The phenomena predicted in this manner were then observed by me in mixtures of carbonic acid and methyl chloride [1]), and afterwards of carbonic acid and air [2]). The deviation from what had been observed by former experimenters, viz., the flattening and disappearing of the liquid surface throughout the critical region without retrograde condensation, was explained by retardation [3]), which was annihilated in my experiments for the first time by means of a small iron stirring-rod within the tubes, which was moved by an electromagnet outside the tubes.

5. If P lies on the other side of R there are again two definite critical temperatures, T_P and T_R, for every mixture; but the process of condensation beween those two will be different from what it was in the first case. By compression a new phase appears of a larger volume [4]) this time, *i. e.* a vapour-phase, which begins by increasing, then reaches a maximum, and then again diminishes and disappears. This was called *retrograde con-*

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[1]) KUENEN, *Archives Néerl.* XXVI. pp. 382—385; *Commun.* N°. 4; *Zeitschr. phys. Chemie,* XI. p. 47.

[2]) Commun. N°. 7, p. 6.

[3]) KUENEN, *Archives Néerl.* XXVI. pp. 376—377, 380—382; *Commun.* N°. 4; *Zeitschr. phys. Chemie.* XI. p. 47.

[4]) In order to make the volumes in our figures decide about the situation of the phases above each other, we should take the volume of the unit of weight as the unit of volume. In doing so a phase of larger volume is a lighter phase at the same time, and will therefore appear in the upper part of the tube.

densation of the second kind (r.c. H.) [1]). Near the plait-point-temperature T_P the liquid will be very flat and indistinct, and more so at the beginning than near the end of the condensation. Below T_P the condensation is normal.

6. This second case has never been realized till now. I have been considering whether it might be, and the choice of the subject of this paper is the outcome of my reasoning. In explaining this I shall use a different graphical representation, namely the $p—t$ figure. In a recent paper [2]) I have deduced the general features of the $p—t$ curves in the problem before us from VAN DER WAALS's theory. The figure obtained consists of (1) the two *vapour-pressure curves* of the component substances; (2) the *border-curves* [3]) for the mixtures ($x =$ constant) having the form of loops; (3) the *plaitpoint-curve,* being the envelope of the border-curves and connecting the critical points of the two substances. The point of contact between a border-curve and the plaitpoint-curve corresponds to the plaitpoint P of VAN DER WAALS's surface; the critical point of contact R is the point in which the border-curve has a tangent parallel to the p-axis. When going along the border-curve, starting from its lower branch, we may either first reach R or P.

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[1]) KUENEN, *Archives Néerl.* XXVI. pp. 388—389; *Zeitschr. phys. Chemie*, XI. p. 45.

[2]) KUENEN, *Kon. Akad. Amsterdam*, 29 Sept. 1895, pp. 90—91; '*Communications*', &c. N°. 13.

[3]) A border-curve for a mixture represents the conditions (p, t) in which it may coexist with a second phase.

These two cases correspond to the two cases mentioned above. If P is situated beyond R we have r.c. I. (figs. 8, 9); if R lies beyond P we have r.c. II. (fig. 10). Keeping in view the connexion between border-curve and plaitpoint-curve, the question whether the second case can be realised comes to the same as whether the plaitpoint-curve or a part of it may rise, while the border-curves are situated on its left side (fig. 10). Now it appears that there are different cases in which such a situation must occur. If the critical points of some of the mixtures lie outside the critical temperatures of the two substances, a part of the plaitpoint-curve will answer to the above postulate. But this is not a necessary condition. If the substance of the higher critical tempera-

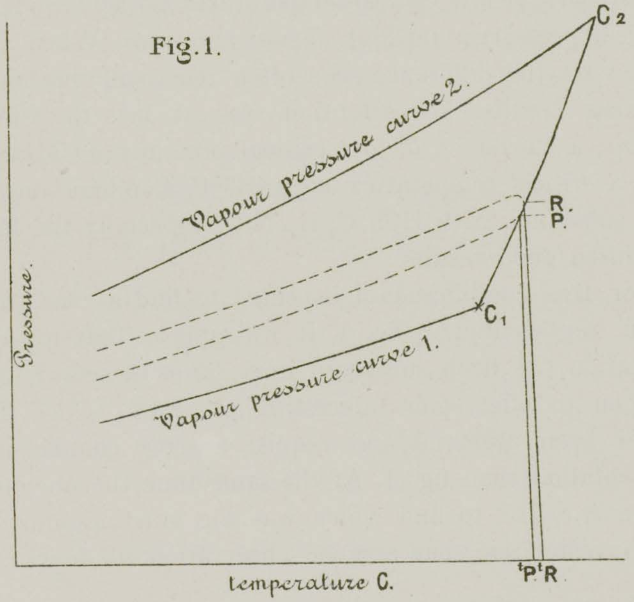

Fig. 1.

ture has at the same time larger vapour-pressures than the substance of the lower critical temperature, the plaitpoint curve will have the same property. This case is represented in fig. 1. R lies beyond P. Between the two temperatures T_P and T_R the mixture, the border-curve of which is drawn in the figure, must show retrograde condensation of the 2nd kind (r.c. II.). Even if the curves are more complicated than is supposed in the figure, the curve $C_1 C_2$ will nevertheless fulfil the condition at least for a part of its course.

7. There is only a small number of combinations of two substances which appear to answer the purpose. Substances of low critical temperatures mostly have high critical pressures and high vapour-pressures. When this is not so, the differences are often too small to promise striking results. My attention was at last drawn to *ethane*, a substance of low critical pressure (± 50 atm.) and a critical temperature of ± 34° C. Combinations of this substance with HCl, C_2H_2, N_2O, especially the last, promised good results.

For this combination I expected to find a case such as is represented in fig. 1. It will appear that my expectation has been surpassed in so far as these mixtures happen to offer some interesting properties which had never been observed and require a more complex representation than fig. 1. At the same time the phenomenom (r.c. II.), to find which was the starting-point of the investigation, has escaped observation till now.

Preparation of Ethane (C_2H_6).

8. The ethane was prepared by electrolysis of a con-

centrated solution of acetate of sodium. By this process a number of other substances are generated, especially CO_2, O_2, C_2H_4, and some esters [1]). The gas was washed in sulphuric acid and a solution of caustic soda, and collected in a big glass bottle (45 litres) again containing a solution of caustic soda. In this manner the CO_2 was absorbed entirely. By aid of a mercury compressing machine of Cailletet, which belongs to the set of apparatus of the Leiden Laboratory for experiments at low temperatures, the ethane was liquefied in a small copper vessel. In this operation it passed again through fuming sulphuric acid, caustic potash, and phosphoric anhydride. In order to expel the permanent gases, the liquid ethane was cooled by solid carbonic acid and made to boil. In filling the tubes the gas was afterwards taken from the liquid.

This method of purification at low temperature has been formerly applied by me to CO_2 and CH_3Cl [2]).

Preparation of Nitrous Oxide (N_2O).

9. This substance was taken from a commercial bottle; it was led through high-pressure tubes containing chloride of calcium and caustic potash and afterwards dried over P_2O_5. The purification was conducted as in the former case. During the boiling of the liquid N_2O the tube could be connected with an air-pump, a sort of

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[1]) Kolbe, *Lieb. Ann.* LXIX, p. 279; Wiedemann, *Electricität*, II. p. 574.

[2]) Kuenen, *Archives Néerl.* XXVI. pp. 356, 359. I discovered lately, that Olszewshi applied this method of purifying gaseous substances before me.

mercury-valve being interposed in order to prevent air from returning to the liquid.

Preparation of the Mixtures.

10. The substances thus purified could be mixed in any proportion by means of my mixing apparatus, for the description of which I refer to previous investigations 1). At present the whole apparatus consists of glass and copper only: the exhaustion was effected by a mercury air-pump.

Method of the Observations.

11. For the observations I made use of Ducretet's apparatus 2). The glass tubes in which the gases were to be compressed were connected with the above apparatus by means of ground joints, and repeatedly exhausted and filled with the gases.

12. The temperatures, all of them ranging between 0° and 40° C., were obtained by means of a continuous current of water through a tube surrounding the experimental tubes.

13. My stirring apparatus 3), which was continually used during the observations, had been slightly modified. The little piece of iron with its knobs of enamel within the high-pressure tubes was the same as before; but the electromagnet, which used to slide over the tube and accordingly within the water-vessel, had been replaced by a larger bobbin sliding over the outside of the water-vessel. In this manner the influence of the

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1) Kuenen. *l. c*, p. 369. 2) *L. c.* pp. 357, 366. 3) *L.c.* pp. 372 *sqq.*

temperature of the bobbin upon the temperature of the water, the constancy of which used to be disturbed during the acting of the apparatus, was removed. The bobbin is worked by four Bunsen cells or two accumulators.

Results obtained with Ethane.

14. In order to test the purity of the substances they were at first investigated separately. The gases appeared still to contain a little impurity: there was a slight increase of pressure during the process of condensation, for the ethane at 20°, 0.56 atmosphere. The amount of impurity of a gas corresponding to a definite increase of pressure at a definite temperature is difficult to decide, and entirely depends upon the substance itself and the admixture. In preparing the gas a second time, the liquid ethane was cooled in liquid ethylene boiling at a low pressure (— 110° C.), itself being connected with an air-pump as in the case of nitrous oxide. The ethane obtained in this manner was found to be a little purer still: the increase of pressure was 0.43 atm. at the same temperature 1).

15. The critical temperature of the gases was determined very carefully: as with the mixtures, a stirring-rod had been put within the tube, and so the determination could be conducted according to the principles explained in the account of my observations with

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1) Andrews, in his experiments on carbonic acid, observed an increase of pressure of more than two atmospheres in a similar case.

CO_2 [1]). The critical temperature for the two samples of ethane amounted to 31°.95 C. and 32°.05 C. respectively. This would point to a critical temperature of ± 32°.3 for pure ethane. By admitting a little air (¼ to ½ per cent) into the last tube the increase of pressure at 20° C. rose to 2.7 atm., *i. e.* more than six times the former value; while the critical temperature had gone down to 31°.25 C. This would point to ± 32°.2 C. as the real critical temperature of ethane. The admixture in my ethane seems to lie far below 0.1 per cent.

16. It is not impossible that, in filling the tubes, a little air remains in the gases, because they have to pass through some long tubes connected with joints before entering the experimental tube, and the air has to be expelled by means of exhaustion. I might probably have got a still purer gas by filling the tube more directly, but I preferred to apply exactly the same method which I used in preparing the mixtures, in order to be warranted against mistakes resulting from differences of purity.

17. The critical temperature of ethane as determined by former observers is somewhat higher. DEWAR [2]) gives 35° C., OLSZEWSKI [3]) 34° C., HAENLEN [4]) from 32° C. to 40° C., probably 34°.5 C. In his experiments retardation has played an important part, and his gas cannot have

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[1]) KUENEN, *Kon. Akad. Amsterdam.* 29 Oct. 1893, pp. 85—90; *Communications, &c.*, N°. 8, pp. 11, 12.

[2]) DEWAR, *Phil. Mag.* [5] XVII. p. 214.

[3]) OLSZEWSKI, *Bulletin Ac. des Sciences de Cracovie*, 1889, p. 27.

[4]) HAENLEN, *Lieb. Ann.* CLXXXII. p. 245.

been very pure; otherwise one finds a definite critical point, not a critical region as he does. He prepared the gas by the method of GLADSTONE, TRIBE, and FRANKLAND [1]) from C_2H_5I. OLSZEWSKI obtained ethane from C_2H_5Zn. Both HAENLEN and OLSZEWSKI purified the gas by cooling and boiling at a low temperature.

I cannot tell what is the reason of this discordance between the values for the critical temperature. Perhaps it has some connexion with the different ways of preparing the gas. I am going to repeat the experiments with ethane prepared from C_2H_5I. But the difference may be due to the method of determining the critical state as well. In my experiments the retardation is entirely annihilated by carefully stirring the gas, which may have lowered the critical temperature.

Results obtained with Nitrous Oxide.

18. Similar results were obtained with this gas. The increase of pressure, however, was still less. At 20° C. it amounted to 0.15 atm. = 11 cm. of mercury. The impurity of the gas may be estimated below 0.0002: for the critical temperature I obtained 35°.95 and 36°.05. The true value will be 36°.1 C. probably.

19. VILLARD, who has prepared pure nitrous oxide by a similar process [2]), fixes the critical temperature of his

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[1]) *J. Chem. Soc.* XLV. p. 154; XLVII. p. 236.

[2]) VILLARD, *C. R.* CXVIII. p. 1096; *Journal de Phys.* [3] III. Oct. 1894. In a letter Dr. VILLARD tells me that his estimation of the critical temperature has been too high. In turning a tube with N_2O at 36°.5 C., the liquid surface disappeared and

gas at 38°.8 C. But this value was obtained by the indirect method of measuring the densities. The liquid surface disappeared below 38° C, but he does not mention an exact value. This gas must have been very pure, judging from the regular phenomena obtained near the critical point, and the purity of the carbonic acid prepared in the same manner. VILLARD states that in a U-tube, in which two quantities of liquid N_2O were separated by a column of mercury, a pressure of a few centimetres sufficed to liquefy one of the portions completely. But this test is not so delicate as the one given above, viz. the entire increase of pressure from the beginning to the end of the liquefaction [1]).

20. The constancy of my results with the pure substances and the smallness of the admixture left, justify me in accepting an influence of the admixture upon the behaviour of the mixtures of a similar small amount.

Results obtained with the Mixtures.

21. The number of mixtures investigated was five. The composition (x parts of ethane in the volume in the gaseous state at one atmosphere) amounted to 0.18, 0.25, 0.43, 0.55, 0.76 respectively. The pressure and volume at the beginning and at the end of the condensation as observed at different temperatures are given in Tables I—VII. The values of the volumes are only approximate. They are expressed in parts of the volume at 1 atm. and 0° C. For N_2O and C_2H_6 only one value for the pressure has been given. Tables VIII—X give the volumes for the temperatures 20°, 25°, and 26° C., as determined by graphical interpolation from the values observed.

TABLES I—VII.

I.—N_2O.

t.	p.	v_v.	v_l.
4.8	35.2	0.0206	0.0022
13.3	43.4	0.0161	
19.9	50.8	0.0125	
25.4	57.4^5	0.0103	0.0027
31.5	65.4	0.0076	0.0031
36.0	71.9	0.0047	

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the tube filled itself with a blue mist. Now as stirring comes to the same as repeated turning, it is quite natural that I obtained a value for the critical temperature below 36°.5 C. I have not noticed the blue mist more than 0°.2 or 0°.3 above 38°.0 C. At any rate the disagreement between VILLARD's result and mine has been reduced to a few tenths of a degree. But it appears from VILLARD's measurements of the densities of N_2O, that the behaviour of this substance near its critical point is less normal, so to speak, than the behaviour of carbonid acid. One feels inclined to ascribe this to the influence of minute impurities.

[1]) In filling a tube with a gas, which is compressed to a liquid afterwards, one works under unfavourable conditions for obtaining a pure substance compared to what can be obtained with liquids. The isopentane prepared by Prof. YOUNG (Phil. Mag. [5] XXXVIII. 1894, pp. 569—572) is remarkable in respect to purity. Here the increase of pressure appears to have disappeared entirely. Experiments by BATTELLI and others prove that even a pure liquid is not easily obtained.

Tables (*continued*).

II.—C_2H_6.

t.	p.	v_v.	v_l.
5.85	27.4	0.0248	0.0033
10.65	30.4^5	0.0215	0.0034
15.4	33.8	0.0184	0.0036
22.4	39.7	0.0140	0.0038
29.35	45.9	0.0103	0.0046
31.0	47.6	0.0089	0.0049^5
32.0	48.8	0.0064	

III.—Mixture 0.18 C_2H_6.

t.	p_1.	p_2.	v_v.	v_l.
2.85	35.34	35.55	0.0205	0.0026^5
11.8	43.57	43.91	0.0143	0.0029
19.05	51.48	51.81		
23.2	56.40	56.57	0.0094	0.0031
29.8	65.32		0.0052 (?)	

IV.—Mixture 0.25 (?) C_2H_6.

t.	p_1.	p_2.	v_v.	v_l.
5.4	37.48	38.07	0.0177	0.0027
13.2	45.08	45.59	0.0131	0.0029
18.3	50.53	51.22	0.0111	0.0031
22.2	55.12	55.63	0.0094	0.0032
26.9	61.38	61.35	0.0066	0.0038
27.6	62.87	62.93	0.0065 (?)	0.0043
28.15	63.36		0.0046	

V.—Mixture 0.43 C_2H_6.

t.	p_1.	p_2.	v_v.	v_l.
9.8	40.59	……	0.0150	0.0030
14.3	44.96	45.57	0.0130	
18.6	……	……	……	0.0034
20.5	51.75	52.29	0.0096	0.0035
24.6	56.67	57.01	0.0073	0.0041
26.05	58.42		0.0055 (?)	

Tables (*continued*).

VI.—Mixture 0.55 C_2H_6.

t.	p_1.	p_2.	v_v.	v_l.
6.4	35.59	36.86	0.0195	0.0036
11.35	40.02	41.05	0.0164	0.0038
18.4	47.02	48.06	0.0126	0.0043
25.4	54.87	55.46	0.0084	0.0050
26.05	56.12		0.0060	

VII.—Mixture 0.76 C_2H_6.

t.	p_1.	p_2.	v_v.	v_l.
5.25	31.31	32.86	0.0217	0.0035^5
12.4	36.99	38.54	0.0173	0.0037^5
18.4	42.22	44.05	0.0140	0.0040^5
21.95	45.81	47.05	0.0118	0.0042^5
26.0	50.25	51.11	0.0092	0.0048
27.15	51.55	52.16	0.0083	0.0053
27.85	52.55		0.0066	

TABLES VIII—X.

VIII.—Volumes at 20° (fig. 3).

$x = 0.0$.	0.18.	0.25.	0.43.	0.55.	0.76.	1.0.
0.0125	106	102	98^5	113	130	155
0.0025^5	30	32	35	42^5	41^5	37^5

IX.—Volumes at 25° (fig. 4).

$x = 0.0$.	0.18.	0.25.	0.43.	0.55.	0.76.	1.0.
0.0104^5	87	78	70^5	84^5	98^5	126
0.0026^5	33	35^5	42	48	45	40

X.—Volumes at 26° (fig. 5).

$x = 0.0$.	0.18.	0.25.	0.43.	0.55.	0.76.	1.0.
0.0101	85^5	73	58^5	69	92	99
0.0027^5	34	37	51	58	48	47

The results are laid down in fig. 2, and, figs. 3, 4, and 5.

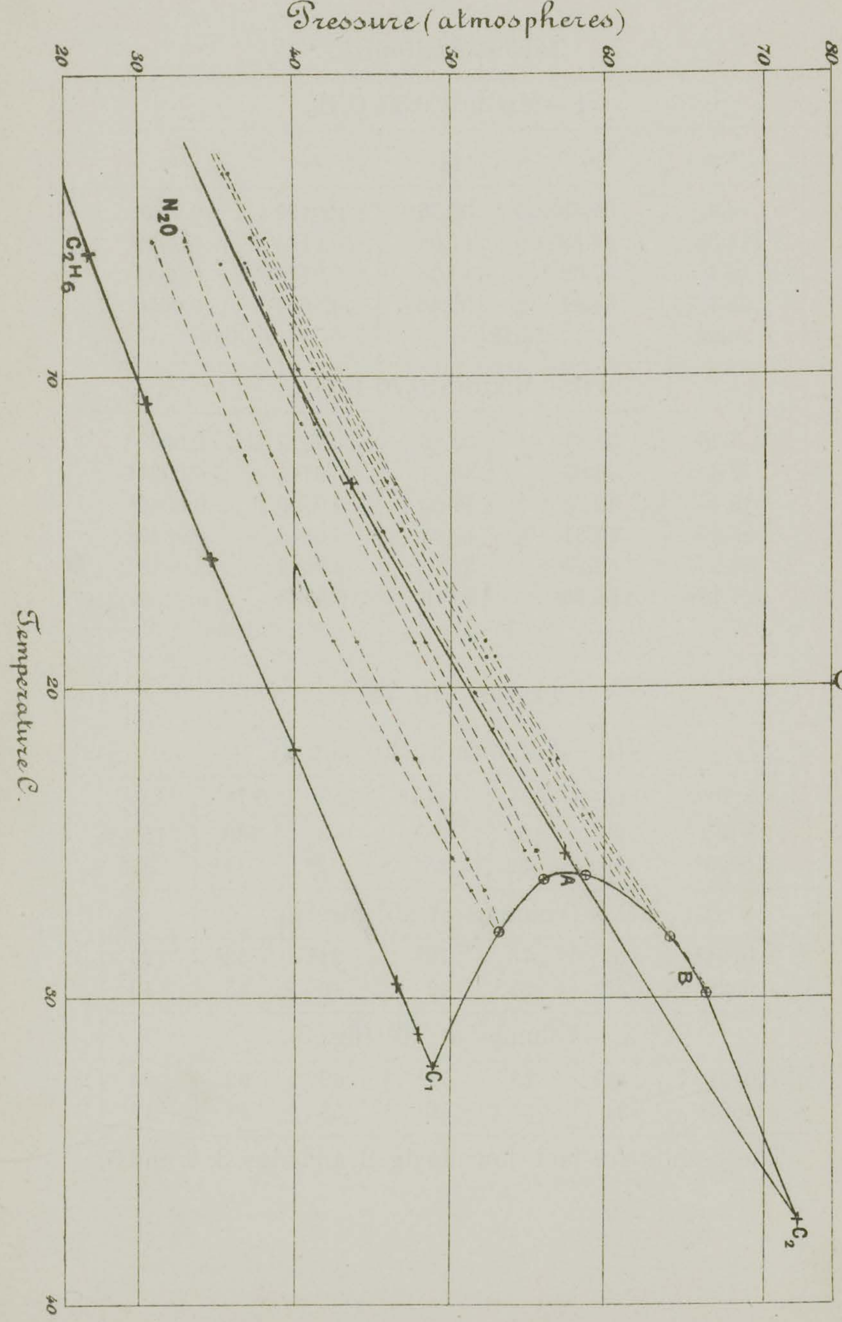


Fig. 2.

Fig. 3.

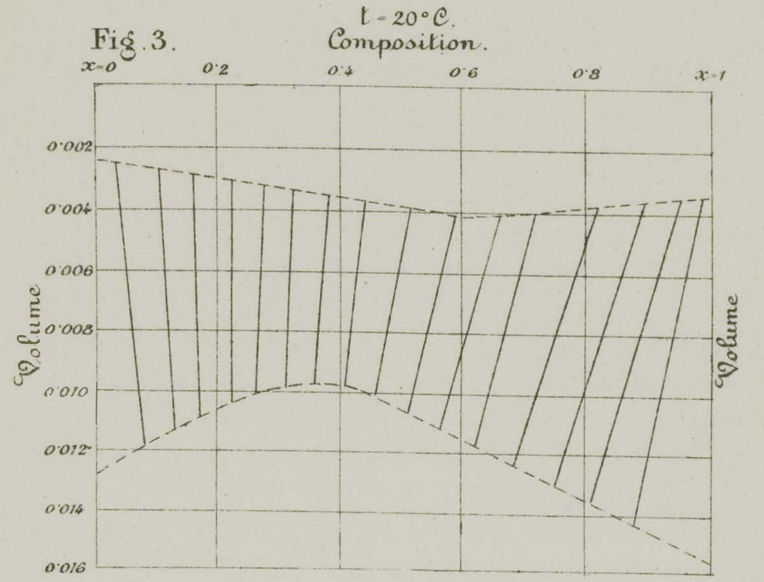


Fig. 4.

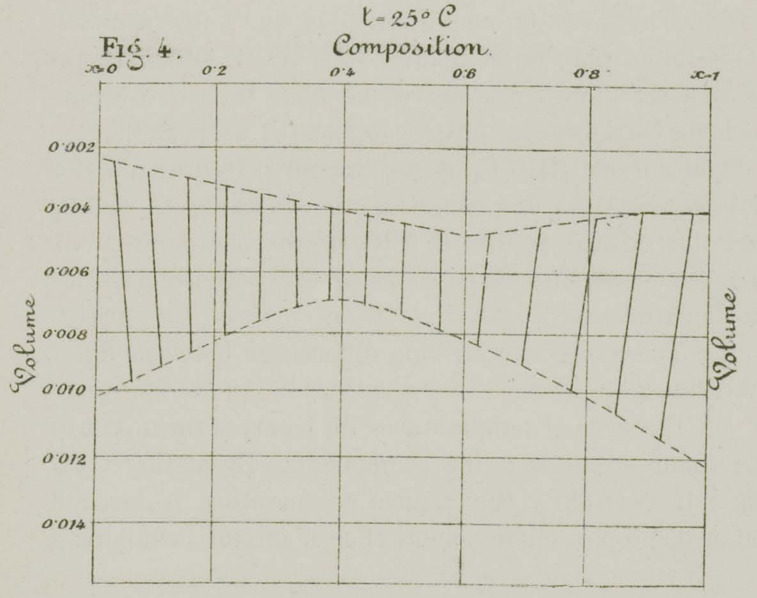
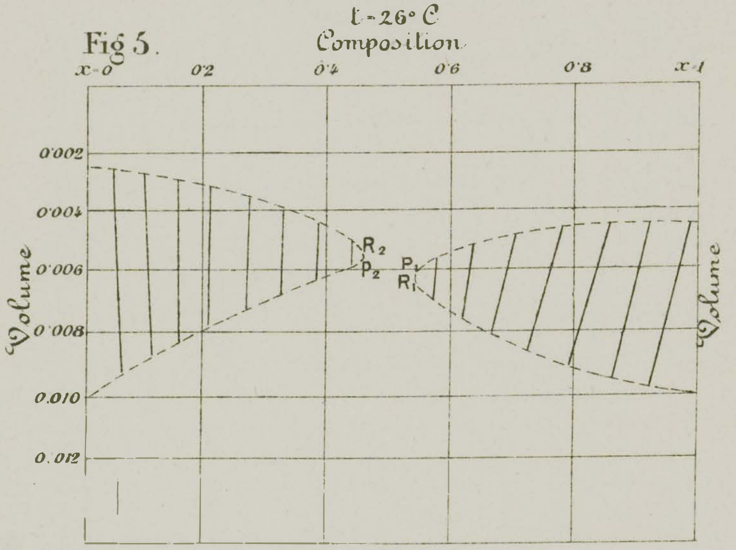


Fig 5.



22. The axes of coordination in fig. 2 are *p* and *t*. This figure may be compared with fig. 1, which represented the curves as they would have been if the phenomena had been as little complicated as possible.

The curve C_2H_6—C_1 is the vapour-pressure curve for ethane, N_2O—C_2 the same for nitrous oxide. C_1 and C_2 are the critical points. C_1ABC_2 is the plaitpoint-curve. The curves of the shape of loops are border-curves for the mixtures.

23. There are two striking differences between fig. 1 and fig. 2.

(1) The critical temperatures for a part of the mixtures lie below those for the components. By adding C_2H_6 (32°) to N_2O (36°), the critical temperature is lowered to a disproportionate extent. For a mixture containing ±0.1 of C_2H_6 the critical temperature has gone down as far as to 32°, the c. t. for pure ethane. All mixtures containing more ethane than 0.1 have critical temperatures below 32°. Addition of N_2O to C_2H_6 therefore makes the critical temperature decrease instead of increase. The lowest critical temperature (± 25.8) belongs to a mixture containing ± 0.5 of ethane.

A case like this has never been observed till now; VAN DER WAALS's theory shows the possibility of the critical temperature lying outside those for the components [1]).

24. (2.) There is another difference between fig. 1 and fig. 2. The border-curves of the mixtures do not all of them lie between the vapour-pressure curves of C_2H_6 and N_2O. Some of them lie above the N_2O curve. It follows that at every temperature there is a maximum of pressure for one of the mixtures. From the figure it appears that this maximum lies somewhere between the mixtures the composition of which is 0.18 and 0.25, say ± 0.2. The border-curves of the mixtures 0.18 and 0.25 differ only very slightly and in the figure almost coincide. The meaning of this is that the maximum belongs to almost the same mixture at all temperatures represented in the figure. If the mixture for which the pressure is a maximum varied quickly with change of temperature, the border-curves of the mixtures in that neighbourhood would intersect at perceptible angles. If we tried to draw the curve giving the maximum pressure

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[1]) There is one instance of a mixture, the critical temperature of which lies *above* those for the components, opserved by DEWAR, namely, of CO_2 and C_2H_2 (*Proc. Roy. Soc. of Lond.* XXX. p. 543).

at any temperature, it would lie a very little above the border-curves for $x = 0.18$ and $x = 0.25$, and be about parallel to those. This curve we shall call the *maximum-curve.*

25. There is another remarkable quality of the border-curves in this region near the maximum, viz. the narrowness of the border-curves, *i. e.* the very small increase of pressure during the condensation. The value of this increase amounts to 0.2—0.3 atm. for the first mixture, which is only a very little more than what still remained in the pure nitrous oxide itself [1]. We may therefore almost take it equal to zero. This agrees with what follows from the theory of mixtures. In a maximum-point (and also in a minimum-point) the two coexisting phases have the same composition (x) though different volumes (v), and there is no increase of pressure during the condensation. In order to determine the exact value of the maximum, a large number of mixtures lying about $x = 0.2$ should be investigated: only the small

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[1] The increases for the second mixture (0.25) are somewhat higher, viz. ± 0.6 atm., which must be due to a somewhat larger impurity of that mixture. Probably the pressures of this mixture are therefore a little too high at the same time. The maximum will therefore be nearer to the first mixture (0.18). That is why I have put it equal to ± 0.20. On the whole the values for the increase of pressure are a little irregular, which is quite natural considering the difficulty of these observations with mixtures. From the observations one might, perhaps, conclude that the maximum with rise of temperature shifts a little towards the N_2O; but as this seems rather uncertain, I prefer taking it constantly equal to 0.20.

admixture in the components themselves would of course impede the fixing of the maximum-curve.

26. In itself the existence of a maximum (or minimum) pressure is not a new phenomenon. GUTHRIE [1], KONOWALOW [2], and others have found the same with different mixtures. Only, so far as I know, a maximum (or minimum) has never been traced up to the critical temperature. In KONOWALOW's mixtures the maximum appears sometimes to shift with change of temperature, and accordingly probably to disappear below the critical temperature. The above results prove that this need not be the case at all. This fact may be expressed in this manner: the maximum-curve need not reach the vapour-pressure curve of one of the substances. In my experiments it reaches the plaitpoint-curve, near B.

27. These results will be much better understood by inspecting figs. 3, 4, 5. The curves in these figures give the relation between the composition of the mixtures and the volumes at which the condensation begins and at which it ends (vid. § 1 *sqq.*), and may at the same time be considered as the projection of the connodal curves of the plait in VAN DER WAALS's surface upon the v—x plane. The figures belong to the temperatures 20°, 25°, and 26° C. respectively.

28. If the phenomena were such as would correspond to fig. 1, the plait with rise of temperature would get narrower near the C_2H_6 plane ($x = 1$). At 32° C. the curve would loose itself from the v-axis for $x = 1$, whilst

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[1] *Phil. Mag.* [5] XVIII. p. 510 *et sqq.*

[2] *Wied. Ann.* XIV. p. 34.

forming a plaitpont there; above 32° C. it would withdraw towards the N_2O axis ($x = 0$), where it would disappear at 36° C. (critical temperature of N_2O).

29. However, this is not what really happens. With rise of temperature the plait becomes narrower somewhere near the middle. Consequently, at a temperature far below 32° C., near 25°.8 C. the plait divides into two parts. At that moment two plaitpoints appear (P_1 and P_2)[1]. The two parts into which the plait is divided henceforth withdraw towards $x = 0$ and $x = 1$ separately. At 32° C. the right-hand plait disappears at $x = 1$. At 36° C. the left-hand plait disappears in $x = 0$. Above 36° C. there is no plait left: the surface is convexo-convex henceforth, and all its points represent stable phases.

30. A maximum pressure (or minimum) manifests itself in the v—x figure in the position of one of the lines connecting the pairs of coexisting phases being parallel to the v-axis. The lines on both sides of the maximum line will be turned in opposite directions (with a minimum the direction in which the lines turn is the opposite of what it is here). But the angles of the lines are very small in the case of C_2H_6 and N_2O. On the right-hand plait the lines differ more: the increase of pressure is accordingly larger on that side of

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[1] In two interesting papers (*Wien. Ber.* XCVIII. pp. 1154—91; *Archives Néerl.* XXIV. pp. 57—98, 295—368) Prof. KORTEWEG has derived the geometrical properties of the plaits and plaitpoints. The case occurring here, viz. the formation of two plaitpoints of the same kind at the same time, is discussed on pp. 303—305.

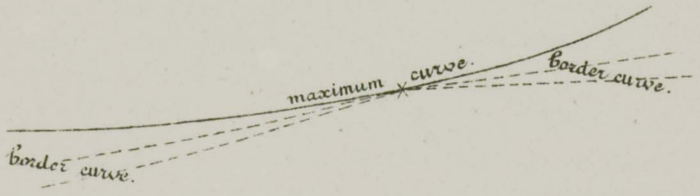
the surface. In the figure the turning to the lines had to be exaggerated in order to show their direction.

31. The critical phenomena of the mixtures were much simpler than I expected to find them. All the mixtures showed normal condensation up to the critical point, and a difference between plaitpoint temperature and critical temperature could not be determined with any certainty. The probable cause of this disagreement I shall refer to after having deduced more completely the theoretical consequences of the experimental results laid down in fig. 2, and figs. 3, 4, 5 (*vid.* § § 40—43).

Theoretical Conclusions to be drawn from the Experimental Curves.

32. A. *Maximum-Curve.* — It may be proved that the border-curve of a mixture for which the pressure becomes a maximum touches the maximum-curve with both its branches. This is represented in fig. 6. In every

Fig. 6.



point of the maximum-curve a similar meeting of three curves takes place. If the maximum-mixture does not change much with the temperature (as we found was the case with C_2H_6 and N_2O), the border-curve of the maximum mixture must have nearly shrunk to *one* curve coinciding with the maximum-curve.

33. Apparently the p—t figure is not at all convenient for showing the situation of the border-curves near the maximum-curve. The border-curves for the mixtures situated on both sides near the maximum-mixture cover each other in the figure. In a case like this it is much better to add as a third axis of coordination the x-axis, and to draw the p—t-curves for the mixtures each in its own plane. The curves together in this manner form the p-t-x-surface. Sections of the p-t-x-surface perpendicular to the t-axis again give curves having the shape of loops (p—x-curves), which may be considered as an extension of KONOWALOW's curves [1]): he only gives the upper branches of the p—x-curves. A complete p—x-curve is given by Prof. VAN DER WAALS in his treatise [2]).

34. The maximum-curve meets the plaitpoint-curve in B. Fig. 7 shows on a larger scale, how the maximum-

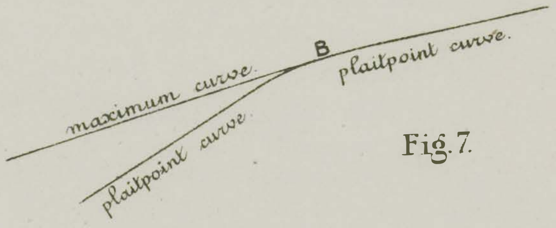


Fig. 7.

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[1]) *Wied. Ann.* XIV. p. 34.

[2]) *Arch. Néerl.* XXIV. p. 21.

curve comes to an end in B, in which point it touches the plaitpoint-curve [1]).

35. B. *Critical phenomena.* The plaitpoint-curve (fig. 2) consists of three parts, being situated between the critical point C_1 and C_2 and separated by the two points B (§ 34) and A.A is the point, where the plaitpoint-curve has a vertical tangent and the critical temperature reaches a minimum [2]).

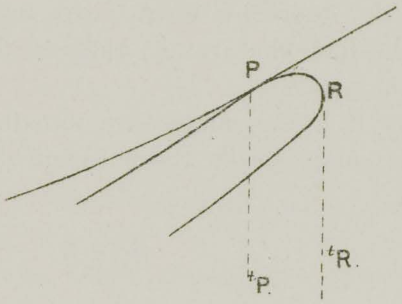

Fig. 8.

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[1]) In my paper in its original form (*Phil. Mag.* 40, August 1895 p. 189) it was left undecided whether the maximum-curve would touch the plaitpoint-curve in B or not. In the meantime Prof. VAN DER WAALS has proved (Verslagen Kon. Akad. van Wet. Amsterdam 1895/96 p. 20—30, . . .) that the plaitpoint-curve is continuous in B and that therefore also B is the point of contact of both curves.

[2]) In my paper in the Phil. Magazine I accepted the existence of a singular point of the plaitpoint-curve in A, as suggested by the experimental curves. Prof. VAN DER WAALS in his paper quoted above (note § 34) proves that the plaitpoint-curve is continuous on its whole course. My supposition as regards A lead to some erroneous conclusions and figures, which have been omitted in this paper.

36. In the part C_2B the relative position of plaitpoint-curve and border-curves is like fig. 8. P lies in the direction we called beyond R, and the border-curves touch the plaitpoint-curve on its right side. The mixtures having their plaitpoint between C_2 and B, *i. e.* containing less than 0.2 C_2H_6, therefore must have retrograde condensation of the first kind (r.c. I.) between the temperatures t_P and t_R.

37. In the part C_1A the curves are situated as in fig. 9. The border-curves lie on the left-hand side, but the plaitpoint-curve falls. P lies beyond R. The mixtures having their plaitpoint here, *i. e.* containing more than 0.5 C_2H_6, must also have r.c. I. between t_P and t_R.

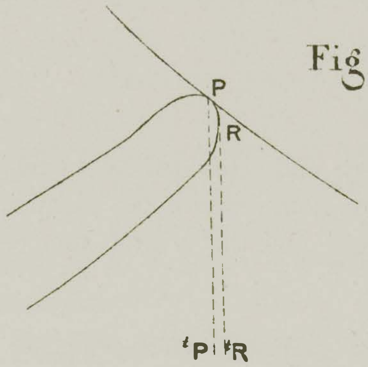
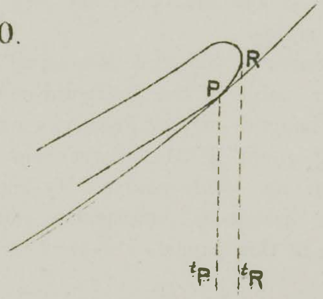


Fig 9.

Fig 10.



38. The part BA, however, fulfils the condition for the existence of r. c. II., as is shown in fig. 10 (*vid.* § 6). The plaitpoint-curve rises, and the border-curves lie on its left side. R lies beyond P. In this region lie the mixtures the composition of which is between 0.2 and 0.5 C_2H_6.

In consequence of the complexity of the curves as compared to fig. 1, the region of r. c. II. is a great deal smaller than it would have been according to fig. 1 (BA instead of C_1C_2). It is easy to see that this was the only thing which could happen: r. c. II. could not disappear entirely.

39. These rather strange conclusions are entirely made clear by figs. 3, 4, 5. These represent exactly the same phenomena, only in a different manner. If P lies above R we have r. c. I.; if it lies below R, we have r. c. II. At first, after the dividing of the plait, the plaitpoints P_1 and P_2 lie on opposite sides of R_1 and R_2 in the two plaits. This corresponds to the existence of r. c. I. below A, and r. c. II. above A in fig. 2. While with rise of temperature the plait P_2 R_2 shrinks together, R_2 approaches the maximum-line. P_2 approaches R_2 at the same time, and at the moment that the maximum reaches the end of the plait, P_2 and R_2 coincide. At that moment there is no retrograde condensation. The mixture $x = 0.2$ behaves at its crittical point like a pure substance. P_2, however, now continues to move upwards, and henceforth lies a little above R_2. That explains the existence of r. c. I. between B and C_2. If there had not been a maximum, r. c. II. would have existed all the way from A to C_2.

40. How is it that in my experiments the mixtures

did not show any of those critical phenomena, and almost behaved like pure substances near their critical points? (§ 31). The reason lies at hand: I have pointed out the smallness of the increase of pressure, *i. e.* the approximate parallelism of the straight lines in fig 3 (§ 30), and the exceeding narrowness of the loops (border-curves) in fig. 2 (§ 25). Accordingly, as will be noticed in both figs. 2 and 5, the two critical points P and R lie close together, and the distance between the temperatures of the plaitpoint and the critical point of contact (t_P and t_R), for the same mixture, can be very small only. An estimation from the original figure 2 gives ±0°.1 C. at the utmost for the distance between t_P and t_R, and in some parts of the plaitpoint-curve—for instance near B— much less still. Now in order to fix so small a difference the temperature ought to be perfectly constant for a long while, which was not the case in my water-vessel. There were slow changes, which of course did not prevent the determination of the critical point taken as a whole. I think this circumstance may be taken as a sufficient explanation of the disagreement between theory and experiments.

41. However, there is another cause which must have cooperated in confusing the pure phenomena, viz. the influence of gravitation. It was Gouy 1) who, in the case of pure substances, first pointed out the importance of this factor near the critical point, where the substances become so highly compressible. In the case of mixtures

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1) *Compt. Rend.* CXV. p. 720, CXVI. p. 1289; *cf.* Kuenen, *'Communications, etc.'* N°. 8, p. 10.

the influence of gravitation is not of a quite simple nature. The result is this: near the plaitpoint there is a small region in which the complete process of the condensation is confused; namely in this manner, that with compression at a certain moment the liquid surface between the phases disappears at some distance from the ends of the tube. In this manner the process of retrograde condensation is cut off halfway; and if the distance between the two critical temperatures is very small, the phenomenon may perhaps disappear entirely 1). This suggests the use of horizontal, or at least nearly horizontal, tubes for experiments on the critical phenomena.

42. Now in this region, where gravitation plays an important part, the stirring of the substance cannot be of any avail; on the contrary, the equilibrium, which is very much influenced by gravitation, is spoilt rather by mixing together the different layers. So in this region the only thing we can do is, to wait a long time, and Gouy's experiments with an almost pure substance show that "long" means "days" here; and of course that would be of no use unless the temperature and the volume could be kept absolutely constant, which is practically impossible.

43. Though the special critical phenomena predicted by means of van der Waals's theory have escaped observation so far, there is no reason to doubt their reality or to see any contradiction between them and my experimental result, I believe.

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1) Kuenen, *Verslagen Kon. Akad. Amsterdam*, 25 Mei 1895; *Communications etc.* N°. 17.

44. Some of the results arrived at in this investigation may be enumerated here once more:—

1. The mixtures of C_2H_6 and N_2O containing more than 0.1 of C_2H_6 have critical temperatures lying beneath those of the substances (§ 23).

2. The pressures of the mixtures lie partly above those of N_2O, and accordingly show a maximum situated near 0.2 C_2H_6 (§ 24).

3. The maximum does not disappear with increase of temperature, but remains up to the critical region: the maximum-curve reaches the plaitpoint-curve (§ 26).

4. The mixtures ranging between 0.2 and 0.5 C_2H_6 have r.c. II., the rest r.c. I.

I intend now to investigate mixtures of acetylene and carbonic acid, a group of which according to DEWAR [1]) has critical temperatures lying above those of the components. If I should be able to confirm this result, I shall treat that combination in the same manner experimentally and theoretically as I have done the combination of C_2H_6 and N_2O in this paper.

The experiments described in this paper have been carried out in the Physical Laboratory Leiden, to the Director of which, Professor KAMERLINGH ONNES, I am indebted for continuous and invaluable advice and help.

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[1]) *Proc. Roy. Soc. of Lond. XXX.* p. 543.

17

COMMUNICATIONS

FROM THE

LABORATORY OF PHYSICS

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 17.

J. P. KUENEN. On the influence of gravitation on the critical phenomena of simple substances and of mixtures. (With a plate).

(*Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam, van* **25 Mei 1895,** *p.* 41—53.)

EDUARD IJDO — PRINTER — LEIDEN.

J. P. KUENEN. *On the influence of gravitation on the critical phenomena of simple substances and of mixtures.*

I. The fact, that in the neigbourhood of the critical point in consequence of the large compressibility, gravitation must exercice an important influence, has been remarked by GOUY [1]). The influence results in making the density of the substance enclosed in a tube perceptibly different at different levels. As usual the corresponding changes of the pressure and the height are determined by the relation $dp = -\frac{1}{v} g \, dh$, where v denotes the volume and g the acceleration of gravitation; but to a small value of dp near the critical point corresponds a large value of dv. For numerical determination the shape of the isothermals in that neigbourhood should be accurately known. GOUY calculated some values for carbonic acid by aid of SARRAU's formula for that substance; his results are laid down in a table to be found in his paper quoted above.

In the graphic representation with p and v for coördinates, the greater compressibility is expressed by the

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[1]) Compt. Rend. 115, p. 720—722.

small slope of the isothermals. The different conditions of a substance present in a vertical column are represented by some subsequent points of an isothermal, which form together a small section of an isothermal. While at some distance from the critical point this section is very short and may be treated as one point for differences of level as may occur in experiments on the critical state, say from 10 to 20 cm., the length of the curve becomes perceptible near the critical point. From GOUY's table one finds that at the critical temperature of carbonic acid near the critical point to a difference of height of 10 cm. corresponds a difference of density of 6 percent: at 20 cm. distance the change of density would amount to about 10 per cent. At a definite temperature and a definite mean volume of the substance, the lenght of the little curve, or what comes to the same the number of the phases, which are in equilibrium above each other in the tube, is only dependent on the height of the column, and this in its turn is connected in a simple manner with the quantity of the substance and the bore of the experimental tube.

Let us suppose the temperature to be lowered towards the critical temperature, the total volume of the substance being kept constant. The mean volume (or density) will remain the same during this process. The lenght of the curve however will increase because the slope of the isothermals decreases and the curve as a whole will shift more or less along the direction of the v-axis, because the distribution of the densities above and below the middle is unsymmetrical. Now three cases may occur: when the temperature reaches the critical temperature the little curve may either be on the left of the critical point ¹) or it may be on the right ²), or finally the critical point may fall on the section of the curve itself ³). In the cases A and B the substance will still be homegeneous. Not till after lowering the temperature a little further the curve will reach the so called border-curve also given in the figure with one of its ends. At that moment a very small quantity of a second phase will appear (retardation being excluded): in case A a bubble of vapour will appear in the top of the tube, corresponding to q', in case B a drop of liquid at the lower end of the tube, corresponding to p''. When the temperature goes on being lowered, these small quantities will increase from zero upwards. The conditions of the substance then present in the tube are represented by two sections of the isothermal the one coming on to the border-curve from the vapour-side, the other from the liquid side. From the point in the tube, where the vapour and liquid are in contact, i. e the liquid surface, the phases increase in density downwards and decrease upwards. Gravitation cannot bring any change in the condition of equilibrium and the phases which are in equilibrium with each other at any temperature remain the same. When the temperature reaches some distance below the critical temperature, the lengths of the curves diminish and very soon they may practically be treated as two points, belonging to the border-curve. With a given quantity of substance

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¹) (case A, p' q' in fig. 1)

²) (case B, p'' q'')

³) (case C, $p\ r\ q$)

enclosed in a tube above mercury the different cases may of course be realised by taking the volume first a little smaller than the critical volume, afterwards somewhat larger. What will happen however, if the volume is taken very near the critical volume (case *C*)? At the critical temperature one of the phases, at a certain distance from the ends of the tubes, will have exactly the critical density and pressure. This phase is represented by point *r*, in which the critical isothermal touches the border-curve. Immediately below the critical temperature in that point of the tube a cloud and then a flat meniscus will appear. The place in the tube, where that will happen, depends on the volume chosen. Consequently: between two limits of volume situated on both sides of the critical volume the distance of which might be calculated from the shape of the critical isothermal and the height of the column, a flat liquid surface will appear at different levels in the tube, the higher the smaller the volume, and, as follows from the consideration of the figure, always exactly at the same temperature, the critical temperature of the substance. In the case of carbonic acid enclosed in a tube of about 10 cm. length, the distance of these limits, between which the liquid surface will appear in the body of the tube, will amount to about 6 percent of the entire volume, as calculated from GOUY's table. The value for this distance resulting from GOUY's experiments ¹) and given by my own ²) is of the same order of magnitude.

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¹) GOUY, Compt. Rend. 116, p. 1289.

²) KUENEN, Communic. etc. n⁰. 8, p. 11—12.

From the above follows immediately what will be observed by reversing the process, i. e. by heating the substance at different constant volumes. If the volume is smaller than a definite volume v_1, the liquid will increase regularly and at a temperature mose or less below the critical temperature fill up the whole tube. If the volume is greater than a larger volume v_2, the liquid will decrease during the heating and evaporate entirely. Between v_1 and v_2 however the liquid surface will rise or fall, but at last become flat and disappear, at a definite temperature independent of which volume between the limits v_1 and v_2 has been chosen. That temperature is the critical temperature and no other.

This result was mentioned by me on a former occasion ¹) without further explanation. It justifies completely 'the method of the meniscus' for determining critical temperatures. The same may be said about the method as it was originally described by ANDREWS in which, instead of change of temperature at constant volume, was used change of volume at constant temperature, although the first for reasons of practice seems to me to be preferable; with pure substances the method is bound to give correct values for the critical temperature and differences from the results of other methods find their explanation in impurities or in many cases in the uncertainty of the rival methods. The method of the densities (MATHIAS) ²) which serves very well for determining the critical volume, when the critical tem-

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¹) KUENEN, Communic, etc. n⁰, 8 p. 10.

²) CAILLETET et MATHIAS, Compt. Rend. 102 p. 1202, 104 p. 1563.

perature is already known, is not to be recommended for the critical temperature itself as some extrapolation ⌐ut is always wanted, even when it is applied with the almost care[1]). Whichever method is used, it will always be very desirable to stir the substance, because impurities, which are never entirely absent, produce retardation and also differences of density[2]).

It may also be observed, that the method in question makes it possible to measure the critical pressure and also, with a near approximation, the critical volume of the substance. In taking the volume equal to the volume at which the meniscus appears and disappears in the middle of the column the mistake is only very small. Sometimes the critical volume has been taken equal to the volume at which the liquid at the moment of the disappearing of the meniscus filled the tube entirely: this erroneous procedure leads to great mistakes.

II. In deriving the influence of gravitation on the critical phenomena of mixtures of two substances, I shall make use of the ψ-surface of VAN DER WAALS[3]). I shall only consider the case of one plait, the vapour-liquid plait, existing on the surface. On page 35 of his treatise he treats of the action of exterior forces on the mixture. The results obtained by him have therefore simply to be applied here. The ψ-surface may be described either for a constant weight of the mixture

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[1]) AMAGAT. Compt. Rend. 114 p. 1093—98.

[2]) KUENEN. Commun. etc. n⁰. 11.

[3]) VAN DER WAALS. Archives Néerl. 24, p. 1—56, Zeitschrift für Phys. Chemie 5, p. 133—173.

or for a constant number of molecules. In the case before us the first method is preferable as regards simplicity. In fact VAN DER WAALS proves that in that case for phases being in equilibrium under the influence of gravitation $\left(\frac{\delta\psi}{\delta x}\right)_v$ [1]) has a constant value, while in the other case that quantity still depends on the height h and only: $\left(\frac{\delta\psi}{\delta x}\right)_v \cancel{-} (M_2-M_1)\,gh$ (M = molecular weight) ⌐+ is a constant. We shall therefore use the first method. In order to show by means of the surface, what phases will be present in a vertical column, we imagine curves to be drawn on the surface, for which $\left(\frac{\delta\psi}{\delta x}\right)_v$ has a constant value. I shall call these curves 'gravitation-curves'. The phases in question form together a section of a gravitation-curve. (For simple substances the gravitation-curve coincides with the isothermal). A second condition makes it possible to determine which points of a gravitation-curve correspond to definite heights of the column. This condition is simply $dp = -\frac{g}{v}\,dh$, and is in itself clear apart from its thermodynamical derivation. If not only the gravitation-curves but also the isopiestics $\left\{p = -\left(\frac{\delta\psi}{\delta v}\right)_x = \text{constant}\right\}$, the determination of which is entirely analogous to that of the gr.-curves, are drawn on the surface these two sets of curves make it possible to derive the phases present in the tube

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[1]) x = composition. The v added to the differential coëfficient expresses that v is kept constant during the differentation.

completely. For our purpose it is sufficient to consider the course of the curves in the critical region. We obtain this soonest, if we use the relation between *dp* on the one and *dx* (or *dv*) on the other side along the gravitation-curve. This relation is given by a formula on page 37 of van der Waals's treatise, viz:

$$\left\{ \frac{\partial^2 \psi}{\partial x^2} - \frac{\left(\frac{\partial^2 \psi}{\partial x\, \partial v}\right)^2}{\frac{\partial^2 \psi}{\partial v^2}} \right\} d\,x = -\left(\frac{\partial v}{\partial x}\right)_p d\,p \quad . \quad . \quad (1)$$

or also by aid of well known relations:

$$\left\{ \frac{\partial^2 \psi}{\partial^2 x} \frac{\partial^2 \psi}{\partial v^2} - \left(\frac{\partial^2 \psi}{\partial x\, \partial v}\right)^2 \right\} d\,x = -\left(\frac{\partial p}{\partial x}\right)_v d\,p \quad . \quad (2)$$

Let:

$$\frac{\partial^2 \psi}{\partial x^2} \frac{\partial^2 \psi}{\partial v^2} - \left(\frac{\partial^2 \psi}{\partial x\, \partial v}\right)^2 = A \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

this A is the expression that with $\frac{\partial^2 \psi}{\partial v^2}$ and $\frac{\partial^2 \psi}{\partial x^2}$ determines the stability. In all the points of the connodal curve $A > o$ except in the plaitpoint, that being a point of the spinodal curve at the same time: there $A = o$. If we substitute that in (1) or (2), as in the plaitpoint we have in general $\left(\frac{\partial v}{\partial x}\right)_p$ or $\left(\frac{\partial p}{\partial x}\right)_v \gtrless o$, we find

$$\frac{d\,p}{d\,x} = o \qquad \text{or} \qquad \frac{d\,x}{d\,p} = \infty \,.$$

This result has no other meaning than that in the plaitpoint an element of the isopiëstic coïncides with an element of the gravitation-curve. As the isopiëstic

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touches the connodal-curve in the plaitpoint the gravitation-curve will do the same. In fig. 2 is represented the case of the plaitpoint lying to the side of the small volumes. The pressure in the plaitpoint in that case is a maximum-pressure and

$$\left(\frac{\partial v}{\partial x}\right)_p > o \qquad \text{or} \qquad \left(\frac{\partial p}{\partial x}\right)_v > o$$

not only in the plaitpoint but also close by it. As at the same time $A > o$, $d\,x$ and $d\,p$ according to (1) and (2) have the opposite sign and the two curves isopiëstic and gravitation-curve will intersect in the manner shown in fig. 2. Two curves which intersect and touch each other in the same point have a mutual contact of the 2nd order. Hence it follows that in the v, x projection not only $\frac{d\,v}{d\,x}$ is equal for both curves in P but also $\frac{d^2\,v}{d\,x^2}$. The curves have the same radius of curvature.

The proof of this proposition may also be given thus. In corresponding points of the connodal curve not only $\left(\frac{\partial \psi}{\partial v}\right)_x$ but also $\left(\frac{\partial \psi}{\partial x}\right)_v$ have the same value. The first can be expressed by saying that the pressure is the same in the two points. In approachting the plaitpoint the two corresponding points approach each other and at last coïncide, in the plaitpoint. From this we conclude at once that the isopiëstic in P has an element in common with the connodal curve, i. e. touches the connodal curve. Exactly the same reasoning holds good for the curve along which $\left(\frac{\delta \psi}{\delta x}\right)_v$ is a constant; i. e. the gravitation-curve also touches the connodal curve in P. Therefore the two curves touch each other and as they have to intersect at the same time the mutual contact will be of the second order: accordingly $\frac{d^2 v}{d x^2}$ equal for both.

We need therefore only determine $\frac{d^2 v}{d x^2}$ for one of the two curves in order to know the same quantity for the other. We shall calculate here $\left(\frac{d^2 v}{d x^2}\right)_p$, i. e. for the pressure-curve [1].

From $d p = \left(\frac{\delta p}{\delta x}\right)_v d x + \left(\frac{\delta p}{\delta v}\right)_x d v$ follows:

$$\left(\frac{\delta v}{\delta x p}\right) = - \frac{\frac{\delta^2 \psi}{\delta x \delta v}}{\frac{\delta \psi^2}{\delta v^2}}$$

As moreover for any function ϕ

$$\left(\frac{\delta \phi}{\delta x}\right)_p = \left(\frac{\delta \phi}{\delta x}\right)_v + \left(\frac{\delta \phi}{\delta v}\right)_x \left(\frac{\delta v}{\delta x}\right)_p$$

one finds:

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[1] The idea of considering the sign of $\left(\frac{d^2 v}{dx^2}\right)_p$ in the plaitpoint I took from a letter from Prof. VAN DER WAALS, written on occasion of my paper communicated to the Physical Society of London. May 24th.

$$\left(\frac{\delta^2 v}{\delta x^2}\right)_p =$$

$$= \frac{-\left(\frac{\delta^2 \psi}{\delta v^2}\right)^2 \frac{\delta^3 \psi}{\delta x^2 \delta v} + 2 \frac{\delta^2 \psi}{\delta x \delta v} \frac{\delta^3 \psi}{\delta x \delta v^2} \frac{\delta^2 \psi}{\delta v^2} - \left(\frac{\delta^2 \psi}{\delta x \delta v}\right)^2 \frac{\delta^3 \psi}{\delta v^3}}{\left(\frac{\delta^2 \psi}{\delta v^2}\right)^3}$$

Into this expression we now introduce the quantity A as defined by (3). This leads to:

$$\left(\frac{\delta^2 v}{\delta x_2}\right)_p = - \frac{\left(\frac{\delta A}{\delta v}\right)_x}{\left(\frac{\delta^2 \psi}{\delta v^2}\right)^2} + \frac{\frac{\delta^3 \psi}{\delta v^3}}{\left(\frac{\delta^2 \psi}{\delta v^2}\right)} A.$$

This expression is generally true. It may be used to determine the course of the p-curves in the v, x projection. In P, where we want to know the value at present, $A = o$, while $\frac{\delta A}{\delta v} > o$ because a point shifting from P in the direction of the positive v-axis enters the unstable region. Hence in the plaitpoint:

$$\left(\frac{\delta^2 v}{\delta x^2}\right)_p = - \frac{\left(\frac{\delta A}{\delta v}\right)_x}{\left(\frac{\delta^2 \psi}{\delta v^2}\right)^2} > o.$$

i. e. the curvature of both isopiëstic and gravitation-curve is turned to the same side as that of connodal curve.

A similar reasoning may be used to determine the relative situation of the curves in case the plaitpoint should lie towards the side of the large volumes of the plait. In that case $\left(\frac{\delta_2 v}{\delta x^2}\right)_p < o$ because $\frac{\delta A}{\delta v} > o$ and it appears that again the curvature has the same sign as that of the connodal curve in the plaitpoint.

As regards the second surface described for a constant number of molecules mentioned before, the conditions belonging to it may be decuded from those for the first surface by means of the substitutions.

$$\psi = \frac{\psi'}{M_1\ (1-x') + M_2\, x'} \qquad v = \frac{v'}{M_1\ (1-x') + M_2\, x'}$$

$$x = \frac{M_2\, x'}{M_1\ (1-x') + M_2\, x'}$$

where the dashes denote the quantities belonging to the 2^{nd} surface. They can also be derived independently. It has already been stated that the formulas become less simple. Instead of (1) one obtains ¹):

$$\left\{ \frac{\delta^2 \psi'}{\delta x^2} - \frac{\left(\frac{\delta^2 \psi'}{\delta x'\ \delta v'}\right)^2}{\frac{\delta^2 \psi'}{\delta v^2}} \right\} d\, x' = - \left\{ \left(\frac{\delta v'}{\delta x'}\right)_p + \right.$$

$$\left. + \frac{(M_1 - M_2)\ v'}{M_1\ (1-x') + M_2\, x'} \right\} d\, p$$

The sign of the second side in this case cannot be fixed in general. Excluding the special case in which the coëfficients become zero the conclusion with respect

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¹) Van der Waals l. c. p. 42 by putting $P_1 = P_2 = gh$.

to the plaitpoint remains the same. If $M_1 > M_2$ as in the case of CO_2 and CH_3 Cl ¹) the coëfficient is still positive: but this need not be so. With very large volumes, where $\left(\frac{\delta v'}{\delta x'}\right)_p$ is about zero, the sign depends entirely upon $M_1 - M_2$, but near the plaitpoint such is not the case. In every special case one will have to determine the sign of the second side. However all that cannot affect the general conclusion about the plaitpoint, which forms the basis of the whole argument.

The conclusion in question is sufficient to derive the critical phenomena of a mixture under the influence of gravitation. The most natural way to describe the phenomena is to consider what will happen during continuous change of volume at the temperatures that come into account. In the case represented in fig. 2 if we do not take into account the influence of gravitation we obtain the following result ²): between two definite temperatures, different for every mixture, the temperature of the critical point of contact T_R and the plaitpoint temperature T_P ($T_R > T_P$), with increase of volume, the point representing the condition of the mixture will pass through the connodal curve between the points P and R. In those cases so called retrogade condensation of the first kind (r. c. I.) takes place, i. e. a liquid appears the quantity of which increases regularly from zero up to a certain point and then decreases and at last disappears. Below T_P the condensation is

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¹) Communications etc. n⁰. 4.

²) Communications etc. n⁰. 4, p. 8.

normal, i. e. the liquid surface appears right at the top of the tube and the quantity decreases down to zero, all this with slow increase of volume. Exactly at the plaitpoin-ttemperature the point on the surface passes through the plaitpoint and in that case only a flat liquid surface will appear somewhere in the body of the tube, which falls on further increase of volume and in the meantime becomes more and more distinct, until the liquid is evaporated.

We shall now take into account gravitation. The condition of the mixture is now no longer represented by one point but by a small section of a gravitation-curve, the length of which as with a simple substance is connected with the height of the column. The values of v and x in the different points of the tube are situated on both sides of the mean value of these quantities for the whole mixture. The mean value of x of course does not change with change of volume. If the course of the gravitation-curves, some of which have been drawn in fig. 2 [1]), is considered, three cases will be seen to be possible. If the temperature is somewhat below T_P the little curve will with its left end, corresponding to the top of the tube, reach the connodal curve on the right of P. At the top of the tube therefore a liquid surface will appear and the liquid will decrease continually (case A). It may also happen that the temperature is so much above T_P, that the curve-

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[1]) These curves may be continued within the plait and the parts contained between the connodal-curve are those which will play a part in the theory of capillarity of a mixture.

section reaches the connodal-curve with its right end between P and R. In that case liquid appears down at the lower end of the tube: the liquid increases, reaches a maximum value, then decreases and disappears (case B). Within a region of definite extent, situated on both sides of T_P, a different thing happens. The gravitation-curve comes into contact with the connodal-curve, the two curves touching each other always exactly in P (case C) [1]). At the point in the tube corresponding to the point of contact (the height of which depends on the temperature at which the change of volume takes place) occur the plaitpoint-pressure, volume and composition. At that point therefore with gradual increase of volume a cloud and afterwards a flat liquid surface will appear. At a certain distance above T_P (the plaitpoint temperature of the homogeneous mixture) the motion of the meniscus will still preserve the character of retrograde condensation I, but at temperatures very near T_P the appearing meniscus will not rise perceptibly, but move downwards from the beginning after its appearance. Hence the region in which retrograde condensation exist will be somewhat smaller than without gravitation. It must not be overlooked that the temperature T_R will also appear a little

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[1]) An accurate contemplation of the figure will make clear that these three cases are the only ones possible. In that lies the point of the whole reasoning. It will never happen that the curvesection reaches the connodal-curve between P and R with its left end, which corresponds to the top of the tube. This would lead into extraordinary difficulties.

higher, because the curve-section will reach the connodal curve even if its mean point lies a little beyond the plait. But this rise of $T_{\mathfrak{R}}$ is probable less than the rise of the lower limit of r. c. I, because the influence of gravitation is bound to be greatest near P.

On reversing the process, i. e. in compressing the mixture at constant temperature, the following phenomena appear. Below a definite temperature: normal condensation; next above that a range of temperatures at which the liquid surface disappears during compression before the whole of the mixture is liquid; next a region, in which the meniscus before disappearing begins to fall more or less and at last a region in which the liquid evaporates entirely [1]. This last one is really the only one in which the typical critical phenomenon of mixtures, viz. retrograde condensation, is manifested completely.

This result may explain the difficulty which the determination of the plaitpoint temperature gave me in my experiments on CO_2 and CH_3 Cl [2].

Entirely analogous phenomena will be the consequence of gravitation in the other case, when the plaitpoint lies on the other side of the critical point of contact. I shall not go into this at length. In this case also gravitation will reduce the region in which retrograde condensation (here r. c. II [3]) comes clearly to light. In an experimental investigation which I have carried out lately, originally undertaken with a view to realise the case of r. c. II, the results of which have been communicated by me to the Physical Society of London in its meeting of May 24th, gravitation must have largely contributed in concealing the phenomenon, the possibility of which however could be proved. A circumstance which in the case of mixtures encumbers the observation of the phenomena is, that stirring, though desirable for eliminating retardation, on the other hand disturbs the gravitation-equilibrium and therofore is of little use. With simple substances this drawback of course does not exist.

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[1] This result was briefly mentioned by me some time ago. Communications etc. No. 4, p. 9 note.

[2] Kuenen, Communications etc. No. 4, p. 12.

[3] „ „ „ „ 13, p. 15.

For insertion in Volume II, N⁰. **13—24.**

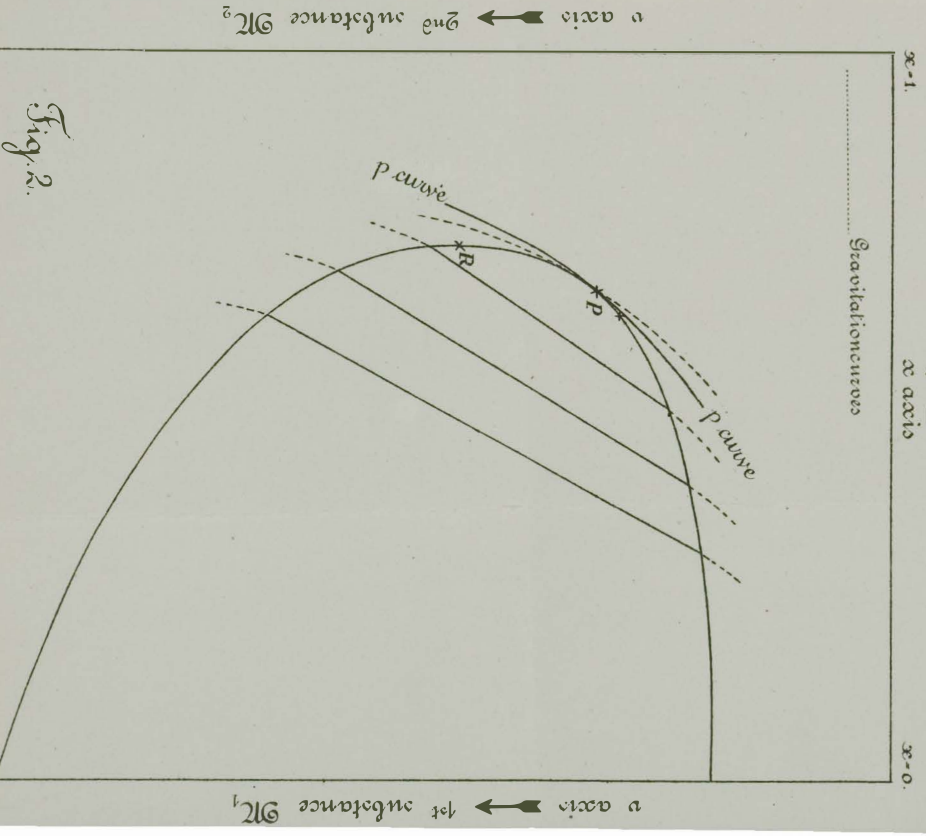
Erratum Communication N⁰. 18.

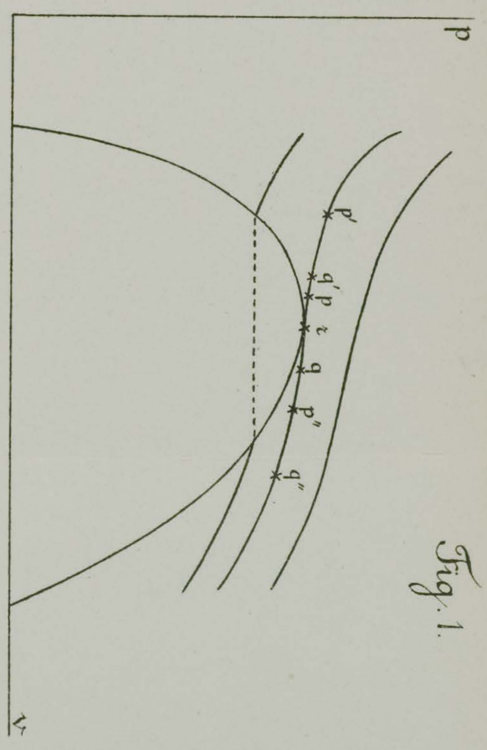
In part of the copies of this Communication the formula on p. 9 line 9 from the top has been printed incorrectly. Read:

$$h^1 = (h + 0{,}029)\frac{\dfrac{2d}{(r_3-r_2)^2}}{\dfrac{1}{r_1}-\dfrac{2d}{(r_3-r_2)^2}}$$

Erratum Communication N⁰. 20.

In part of the copies of this Communication on the title-page in the title: for plantinum read platinum.





Commun. Labor. of Physics Leiden N°. 17.

18

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 18.

Dr. J. VERSCHAFFELT. Measurements concerning the capillary ascension of liquefied gases.

(*Translated from: Verslagen en Mededeelingen der Kon. Akad van Wetenschappen*, 29 Juni 1895.)

Dr. J. VERSCHAFFELT. *Measurements concerning the capillary ascension of liquefied gases.*

1. *Method.* The experiments were made with carbonic acid and nitrous oxide. Investigations made by Dr. KUENEN have shown that we may get these two gases quite pure out of the iron cylinders in which they are sold. I therefore purified these gases bij following the method already described by Dr. KUENEN in his paper. [1]) The purification-apparatus is shown by fig. 1. A is the iron cylinder which contains the still impure, liquid gas, B a thick iron tube filled with pentoxide of phosphorus, and C a thick copper-walled cylinder, into which the pure liquid gas is to be collected. The whole apparatus can be emptied of air by means of the mercury air-pump L; the brass cock 6 separates the purifying apparatus from that used for observation.

The arrangement for measuring the capillary ascension is chiefly the same as used by DE VRIES. [2]) The thick glass tube *b* (fig. 2) in which the capillary tube is shut up, supports at its upper end a piece of narrow manometer tube, which itself bears a wider reservoir *g* filled with glasswool; this glasswool is useful for stopping the dust carried away, by the streaming gas, from the junction tubes and cocks Two cork-pieces *k* keep the observation tube well centered in the liquid bath, and support a thermometer *t*.

The upper end of the observation-tube is cemented by means of sulphur in a brasspiece *d*, which is connected through a long steel capillary tube and a cock *m* to a long copper capillary tube *x*, and communicates through the cocks 4 and 5 (fig. 1) with the cylinder C and the air-pump L.

The filling of the observation tube takes place in the following way; cocks 5 and 6 are opened and the tube emptied of air; 5 is afterwards shut and 4 opened. If the temperature in the tube *b* be lower than in the cylinder C, distillation of the liquid takes place from C into *b*; as soon as a sufficient quantity of liquid has been collected in the observation tube, the cocks 4 and 6 are shut again. After this operation the liquid thread in the capillary tube is generally broken, either by residues of air, or by vapour bubbles. The continuity of the thread of liquid could always be obtained by causing the liquid to boil slowly; for this purpose the cocks 5 and 6 were opened a little way; the gas escaped through the safety-manometer *v*.

For observations made at about the temperature of the room, the observation tube was placed in a glass-cylinder having nearly the same length (nearly 1 M.) and a diameter of about 5 cM.; through this cylinder

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[1]) Arch. Néerl., 26, 35; 1893.

[2]) Measurements on the influence of temperature on the capillary elevation of ether between the critical state and the boiling point of ethylene. Dissertation, Leiden 23 Jan. 1893. Arch. Néerl., 28, 212; 1894. Short abstract in Communic. n°. 6.

water from the main was conducted, so that it entered at the inferior part, and streamed out at the upper end through a lateral tube. In order to avoid a deposit of moisture on the bath, this was enclosed in a second glasscylinder, and the space left between the two dried by means of pentoxide of phosphorus.

Fig. 2 shows the arrangement when experiments were taken in boiling methylchloride. The glass apparatus is the same as the one used by DE VRIES during his observations made in boiling ethylene; the temperature however being not so low allowed me to leave out some complications.

The observation tube was put in another tube which had nearly the same length, about 1 M., and a diameter of nearly 3 cM.; and which was in connection with a lateral tube down through which the liquid methylchloride was to be poured; both tubes were shut by stopples and rendered quite air-tight by means of collodium elasticum. The main tube *h* has a brass **T**-piece T of nearly the same width, that communicates, through a wide and stiff caoutchouc tube *u*, with bags for keeping the gaseous methylchloride. Through the stopple which shuts the lateral tube *z*, comes a copper capillary tube *r* through which the liquid flows, and a small glass tube that communicates with an air-pump through a thick caoutchouc tube *w*; *f* is a small glasswool filter for purifying the methylchloride. Before any methylchloride is introduced, the apparatus and bags are emptied. Because the space in which the liquid boils communicates with the bags, which support the atmospheric pressure, the methylchloride itself boils under the same pressure; the small difference however which might arise from the stiffnes of the bags may be read on a differential-manometer; a notable difference I never observed.

All around the inferior part of the main tube are placed several glass cylinders as in the experiments of WROBLEWSKI and OLSZEWSKI. By these glass cylinders the observations are also rendered more safe; after the following experiments were finished, the observation tube burst; the effect was that in the immediate neighbourhood all was broken, the outermost cylinder however remained intact.

2. *Experiments.* The liquid gas being introduced into the observation tube, and after it had boiled for the purpose of eliminating the last bubbles from the capillary tube, its temperature differed always a little from that of the surrounding bath. The thick walls of the observation tube, caused the equilibrium to be reached but very slowly, so that the capillary ascension became constant only after half an hour.

In order that we might be sure that the carefully chosen capillary tube had everywhere the same diameter, capillary ascension was observed at several spots; the diameter had really everywhere the same value. This trial being made once, capillary ascension might in the following experiments be measured at every part of the capillary tube. The following ascensions *h* were observed: the observed ascension is the vertical distance between the lower point of the meniscus in the capillary tube, and the lower point of the meniscus in the annular space, left between the capillary and the observation tube. To estimate the correction, which the ascensions must undergo, the height d of the annular meniscus has also been observed.

I. Carbonic acid.

1^0. Temperature of the room; the water bath remained at rest during a long time, till its temperature had become constant:

$t = 20°,9 \quad h = 4,20$ mM. $\quad d = 0,61$ mM.

2^0. Temperature of the water distribution:

$t = 15°,2 \quad h = 6,55$ mM. $\quad d = 0,75$ mM.

3^0. Cooled water bath; obtained by conducting the water from the distribution through a copper spiral placed in melting ice:

$t = 8°,9 \quad h = 9,20$ mM. $\quad d = 0,88$ mM.

4^0. Boiling methylchloride:

$t = -24°,3 \quad h = 21,75$ mM. $\quad d = 1,18$ mM.

II. Nitrous oxide.

1^0. Temperature of the room:

$t = 19°,8 \quad h = 6,60$ mM. $\quad d = 0,72$ mM.

2^0. Temperature of the water distribution:

$t = 14°,4 \quad h = 8,71$ mM. $\quad d = 0,85$ mM.

3^0. Boiling methylchloride:

$t = -24°,0 \quad h = 23,20$ mM. $\quad d = 1,24$ mM.

If we make a graphical representation of the heights of ascension, we see that the observations made at the highest temperatures lie upon a straight line which cuts the axis of temperatures at the critical point: 31°,1 for carbonic acid, and 36°,1 for nitrous oxide. The observations made in boiling methylchloride give points that lie a little below these lines; the ascension curve turns its concavity towards the axis of temperatures.

It is remarkable that, when we transfer the two curves so, that their origins begin at the same point, they coincide almost over their whole length; at the same distance of the critical temperature carbonic acid and nitrous oxide have nearly the same capillary ascension.

We usually consider the meridian section of an annular meniscus as circular; if this supposition is right, the height of this meniscus must have the value $\frac{r_3 - r_2}{2}$ r_3 being the inner radius of the observation tube, and r_2 the outer radius of the capillary tube. I observed $r_3 = 3,30$ mM., and $r_2 = 0,52$ mM.; consequently $\frac{r_3 - r_2}{2} = 1,39$ mM. By representing graphically the d-values, we see that points thus obtained are situated upon a curve, which ascends rapidly from the critical point, and approaches slowly to the limit-value 1,39 mM. at lower temperatures.

3. *Corrections.* The surface energy σ, in ergs, is to be calculated by means of the formula

$$\sigma = \tfrac{1}{2}\, g\, H\, (\rho v - \rho d)\, r_1$$

in which are

r_1 the inner radius of the capillary tube in cM.

ρv and ρd the densities of liquid and vapour.

H the real ascension in cM.

$g = 981,1$.

The real ascension may be obtained from the observed one by means of two corrections; the first, due to the meniscus in the capillary tube, has the value $\frac{r_1}{3}$. I observed $r_1 = 0{,}0873$ mM., consequently $\frac{r_1}{3} = 0{,}029$ mM.

As for the second correction, its signification is this: we observed the distance between the lowest points of both menisci, while we must know the height above an infinite horizontal plane. We therefore must try to determine the distance between that plane and the lowest point of the annular meniscus; if h^1 is that distance, we have

$$H = h + h^1 + \overset{\frac{r_1}{r_3}}{\cancel{0.029}}.$$

Assuming as generally admitted the meridian section of the meniscus to be a circular one, we would have $d = 1{,}39$ mM.; observations have shown that this is not correct.

De Vries [1]) did not succeed in finding out a good basis for making this correction; I believe I have found one in the value of d itself; we feel indeed that this correction is intimately connected with this value. For correcting the ascensions in wide circular tubes we sometimes consider the surface of the meniscus as obtained by the revolution of an ellipse. Let us assume the same hypothesis for our annular meniscus; if the meridian section be really an ellipse, half of the greater axis is then $= \frac{r_3 - r_2}{2} = 1{,}39$ mM., while half the smaller axis is $= d$.

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[1]) Dissertation, p. 40.

18

If our hypothesis be right, the radial radius of curvature must be

$$\frac{\left(\frac{r_3 - r_2}{2}\right)^2}{d}$$

and the other one is infinitely great. Consequently

$$\tfrac{1}{2} g\, (\rho_v - \rho_d)\, h^1 = \frac{\sigma}{2}\left[\frac{d}{\left(\frac{r_3 - r_2}{2}\right)^2} \pm \frac{1}{\infty}\right] = \sigma\, \frac{2d}{(r_3 - r_2)^2};$$

and since

$$\sigma = \tfrac{1}{2} g\, r_1\, (\rho_v - \rho_d)\, (h + h^1 + \overset{\frac{r_1}{3}}{\cancel{0{,}029}})$$

is

$$h^1 = (h + \overset{\frac{r_1}{3}}{\cancel{0{,}029}})\, \frac{\frac{2d}{(r_3 - r_2)^2}}{\cancel{\frac{1}{r_1} \quad \frac{2d}{(r_3 - r_2)^2}}}.$$

Redactie [illegible]:

$$(h + 0{,}029)\,\frac{\frac{2d}{(r_3 - r_2)^2}}{\frac{1}{r_1} - \frac{2d}{(r_3 - r_2)^2}}$$

$$\frac{1}{r_1} - \frac{2d}{(r_3 - r_2)^2}$$

HK.

By means of these formulae the following table has been drawn:

I. Carbonic acid.

$t = 20°,9$	$h^1 = 0{,}058$ mM.	H = 4,29 mM.
15°,2	0,112	6,69
8°,9	0,186	9,41
—24°,3	0,594	22,37.

II. Nitrous oxide.

$t = 19°,8$	$h^1 = 0{,}109$ mM.	H = 6,74 mM.
14°,4	0,170	8,91
—24°,0	0,668	23,90.

4. *Surface-energy.* The real ascension thus being determined, we can now proceed to calculate the surface-energy σ. The densities of carbonic acid and nitrous oxide have been taken from CAILLETET and MATHIAS [1]) m represents the reduced temperature.

I. Carbonic acid.

$m = 0{,}9665$	$\rho_v - \rho_d = 0{,}5430$	$\sigma = 1{,}00$	σ (calculated)$=1{,}00$
0,9477	0,6341	1,82	1,79
0,9270	0,7203	2,90	2,78
0,8178	0,9631	9,21	9,21

II. Nitrous oxide.

$m = 0{,}9473$	$\rho_v - \rho_d = 0{,}6092$	$\sigma = 1{,}74$	σ (calculated)$=1{,}77$
0,9298	0,6712	2,50	2,55
0,8056	0,9983	9,92	9,92

These numbers can be represented by means of a formula

$$\sigma = A\,(1 - m)^B,$$

A and B being constants, independent of the liquid; [2]) we find

of which
B is

CO_2	$log\ A = 1{,}934$	$B = 1{,}311$
N_2O	$log\ A = 1{,}945$	$B = 1{,}333$

by means of these constants, the column σ (calculated) of the last table has been found.

Let us make a comparison of the constants with those found for some other liquids:

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[1]) Journal de Physique, 2e série, t. 5; 1886.

[2]) See v. D. WAALS, Zeitschr. f. physik. Chem., 13, 716, 1894.

Ethyloxide	$log.\ A = 1{,}761$	$B = 1{,}270$
Benzol	1,839	1,230
Ethylacetate	1,810	1,230
Chlorbenzol	1,827	1,214
Carbontetrachloride	1,811	1,228

we see that the agreement is satisfactory. It is remarkable that for carbonic acid and nitrous oxide, the value of B comes nearer to the theorical value $^3/_2$, found by v. D. WAALS, for temperatures very near the critical one.

The molecular surface-energy is

$$\sigma_M = \sigma\,(M\,v)^{2/3} = \sigma\,\frac{M^{2/3}}{(\rho_v)^{2/3}}.$$

M being the molecular weight $= 44$ for carbonic acid and nitrous oxide.

Carbonic acid.

$t = 20°,9$	$\sigma = 1{,}00$	$\rho_v = 0{,}7550$	$\sigma_M = 15{,}0$
15°,2	1,82	0,8023	26,2
8°,9	2,90	0,8540	40,2
− 24°,3	9,21	1,0097	114,1

Nitrous oxide.

19°,8	1,74	0,7580	26,1
14°,4	2,50	0,8006	36,1
− 24°,0	9,92	1,0392	120,5

The theory shows [1]) that for all substances $\frac{d\sigma_M}{dt}$ is

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[1]) J. D. v. D. WAALS; Versl. Kon. Akad. 21, 1881.
H. KAMERLINGH ONNES, „ „ „
R. EÖTVÖS, Wied. Ann. 27, 448; 1886.
v. D. WAALS. Zeitschr. f. physik. Chem., 13, 713; 1894.

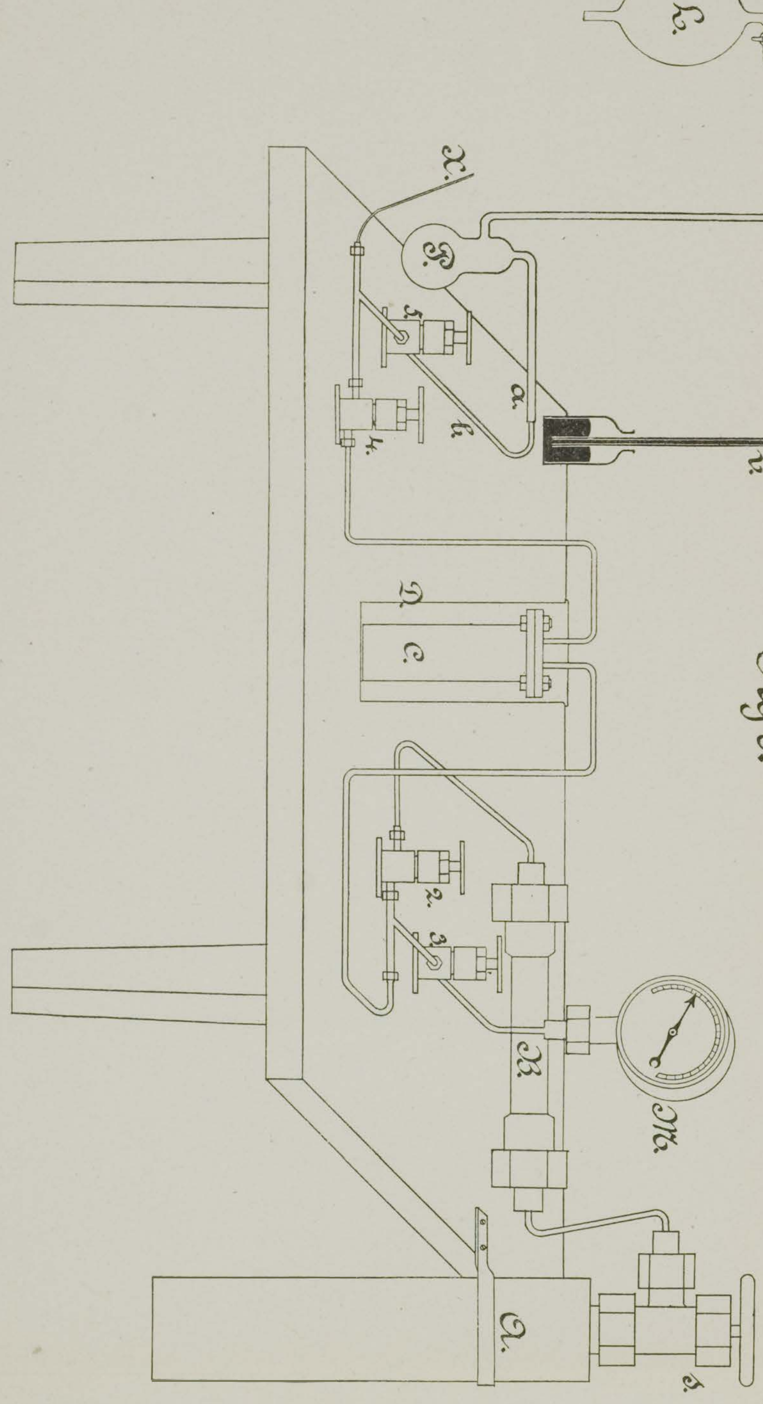

Fig. 1.

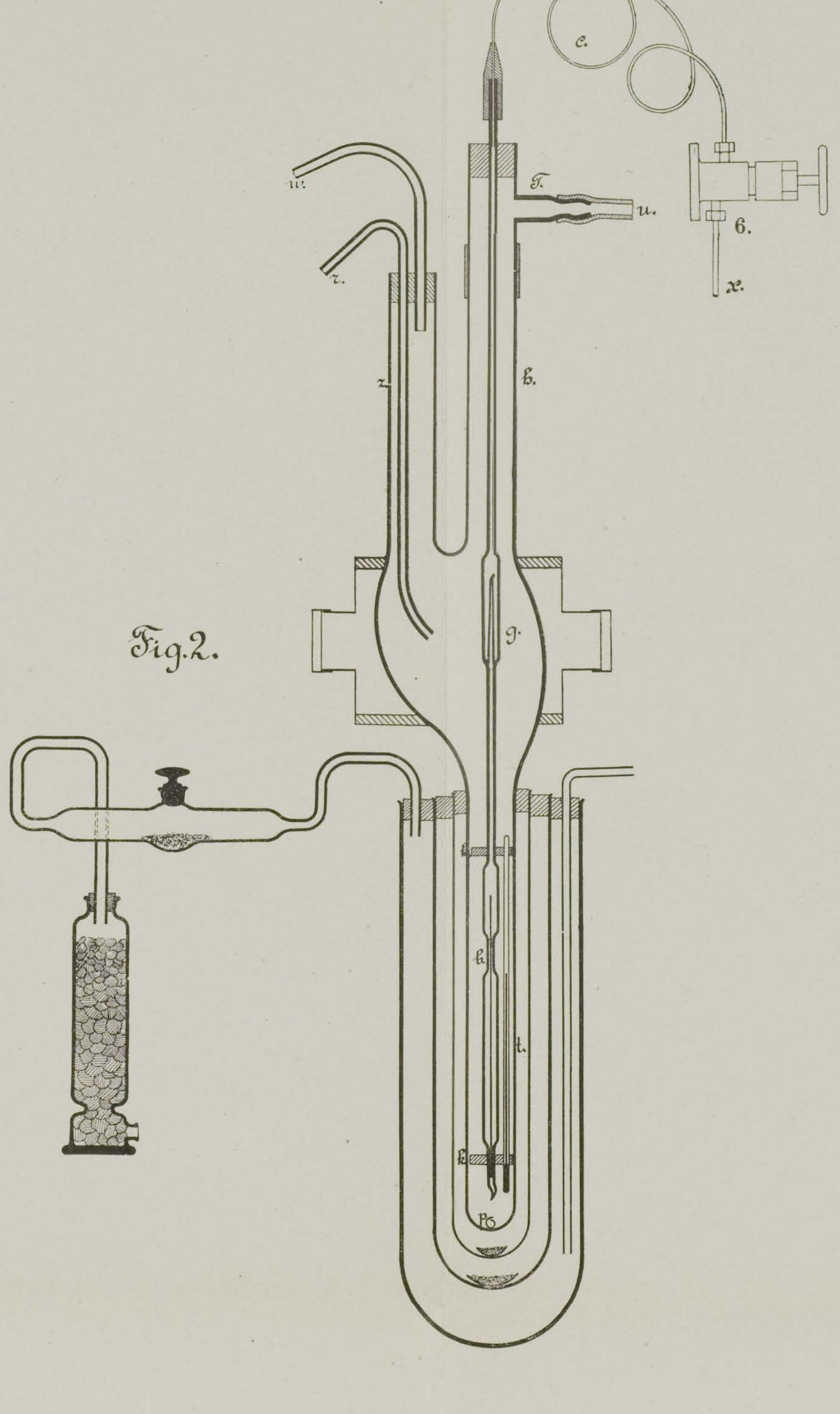

Fig. 2.

Verschaffelt. Capillary Ascension.
Comm. Physical Lab. Leiden. N°. 18.

the same function of the temperature; the experiments have indeed shown that for all substances, at some distance from the critical temperature $\frac{d\sigma_M}{dt}$ is a constant, [1]) the value of which is for all liquids nearly the same: mean-value 2,27.

The numbers found above give for carbonic acid

$$\frac{d\sigma_M}{dt} = 2{,}222 \qquad \text{between } 15°{,}2 \text{ and } 8°{,}9$$
$$2{.}223 \qquad \text{»} \qquad 8°{,}9 \text{ » } -24°{,}3;$$

and for nitrous oxide

$$\frac{d\sigma_M}{dt} = 2{,}198 \qquad \text{between } 14°{,}4 \text{ and } -24°{,}0.$$

Here also the agreement with the law of the corresponding states is very satisfactory.

According to the criterium, given by RAMSAY and SHIELDS, for discerning associated from not-associated liquids, carbonic acid and nitrous oxide are to be classed among the not associated ones; that agrees quite with the calculations made by CAILLETET and MATHIAS, [2]) concerning the accuracy of the law of the corresponding states for these gases, and the law of the straight diameter.

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[1]) R. EÖTVÖS, loc. cit.

[2]) W. RAMSAY and J. SHIELDS, Zeitschr. f. physik. Chem., 12, 433; 1893.

[3]) Loc. cit.

19

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

Director of the Laboratory.

No. 19.

Dr. A. LEBRET A new method for measuring the Hall-effect, especially the variation of it with temperature.

(*Translated from:* "*Verslagen en Mededeelingen van de Kon. Akademie van Wetenschappen*", van **18 April 1895,** p. 284.)

Dr. A. LEBRET. Dissymmetry of the Hall-effect in Bismuth for the opposite directions of the magnetic field.

(*Translated from the same:* p. 292).

Dr. A. LEBRET. Variation of the Hall-effect in Bismuth with temperature. (*Including an investigation on the variation of the electric Resistance of Bismuth with temperature*).

(*Translated from:* "*Verslagen en Mededeelingen van de Kon. Akademie van Wetenschappen*" van **28 September 1895,** p. 103, extracted from the inaugural dissertation of **12 July 1895.**)

EDUARD IJDO — PRINTER — LEIDEN.

Dr. A. LEBRET. *A new method for measuring the Hall-effect, especially the variation of it with temperature.*

The preliminary numbers for the variation of the Hall-effect in bismuth with temperature, communicated in n⁰. 15 of this series, have been acquired by a method, wholly independent of any variation of the primary current. This method, which I will call the method of compensation is a null-method. It requires but a momentary observation, and therefore all disturbances fall away, which need some time before entering. Of these the principal is the "galvano-magnetic difference of temperature" [1] discovered by von Ettingshausen. The error occasioned by this disturbance is not eliminated by any method employed as yet.

By means of this method, I also have studied the dissymmetry of the Hall-phenomenon in bismuth. To judge about the experiments, which explain the dissymmetry and are treated of in this Communication, it will be necessary to know the method and therefore it is described as follows.

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[1] Wied. Ann. 31, p. 737.

Through one of the two windings of a galvanometer a branch of the primary current is sent, the Hall-current passing through the other. The branch, shunted by the small resistance L M, contains besides the winding of the galvanometer a rheostat, from which we introduce as much resistance as is necessary for the effects of the two windings of the galvanometer on the needle to neutralize each other. The magnetic field being constant, the relation of the difference of potential due to the Hall-effect to the strength of the primary current must be proportionate to $\frac{1}{W}$, W being the resistance of the resistance-box.

We give two schemes of the circuit [1]). The wires of the primary current are fastened to the plate [2]) in *A* and *B*. To *C* and *D* are joined the ends of that winding of the galvanometer, which is destined for the secondary current. In the more elaborate scheme II we also have delineated the "by-current", joining the primary circuit to the secondary current and containing the rheostat 2.

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[1]) See engraving II.

[2]) The plate of bismuth, length and breadth 2.9 cM., thickness 3.5 mM. has been obtained by founding in a case of mica, especially manufactured for the purpose. The fastening of the plate to the wires has been accomplished by screwing in.

It was placed in a vessel of hard-soldered copper, filled with some liquid. This vessel consists of three parts (see the engraving I) the middle (B) of which is flat and placed between the poles of the magnet. The uppermost (A) and the undermost (C) parts are cylindrical, the latter jutting out in an angle of 45° so that we may put a burner of Bunsen under it.

On the wholer we have placed the cooler D.

Besides one may see in this scheme the mercury cups, serving to reverse the primary and the "compensative current" [1]).

The secondary electrode, which is fastened in *D*, divides itself into two parts, mounted up symmetrically with respect to the wire fastened in *D*. These parts come together in *E*.

Method of measurement.

1. *Preparations.*

Take order that the needle of the galvanometer is unaffected when closing the magnetizing current, the primary and the secondary circuit being opened.

No deviation either may occur if we close the primary current, the compensative, secondary and magnetizing circuits being opened.

Now close the secondary circuit, the primary circuit remaining opened. Closing also the magnetizing current we do not observe a shock of induction, the plate of bismuth having been placed in the middle between the poles, and the two parts, into which the secondary electrode is divided being mounted up wholly symmetrically with respect to the wire fastenend in *C*. By bending the wires this may be obtained.

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[1]) In making preliminary or auxiliary experiments, but not for the principal measurement we want a commutator in the secondary circuit yet. In the scheme we have not marked the electromagnet, between the poles of which the plate of bismuth has been placed. For reversing the current, which excites the magnetic field, a commutator is yet required.

Now close the primary current, the secondary circuit remaining closed, the compensative and the magnetizing currents opened. We will see a deviation if the secondary electrodes do not lie in one equipotential line.

In this case, search which of the two corners of the mercury cup I, which are to be taken into consideration must be connected with the previously chosen secondary electrode in order to reduce that deviation. Then choose the resistance in such a manner that the deviation be annulled [1]).

2. *Principal measurement.*

First close the secondary circuit. A small deviation may occur in consequence of a thermo-electric current. Close the magnetizing current. After the preparations taken, but a small deviation will occur [2]).

Now close the compensative current. This does not produce any deviation, the primary current being opened.

Now close the primary circuit, the secondary and compensative currents then being produced at once. A very great deviation will not take place, the actions of both currents on the galvanometer-needle being of op-

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[1]) The annulling of the deviation has not been acquired yet for a zero magnetic field, in consequence of the remanent magnetism. Therefore we will research how much resistance musbe introduced into the by-current in order to annul the deviation for the remanent magnetism of opposite direction and we use the mean of these values for the principal measurement.

[2]) See the Chapter „Sources of Errors" A 2.

posite direction [1]). Now search which of the two currents preponderates, and vary the resistance in order to diminish the difference.

Soon we obtain that the secondary current first seems to preponderate and (after the primary current has passed some time) [2]) subsequently the compensative current seems to be stronger. In fact, the secondary current has diminished, in consequence of the occurring *galvanomagnetic difference of temperature* [3]).

We see f. i. the image of the graduated scale first deflect to the right, afterwards to the left. Now introduce somewhat less resistance in the compensative circuit, the deflection to the right will be smaller. Now still diminish the resistance somewhat (every time very little if great accuracy is desired), then we finally get to the point that the needle remains one moment at rest and afterwards wanders to the left. Then the compensation has been acquired as completely as possible, and the value read on the rheostat ought to be noted.

Now close the primary current in the opposite direction, neither touching the bridge of the mercury-cup II, nor reversing the magnetizing current, and determine the value of the resistance to be chosen in the compensative circuit.

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[1]) The direction, in which the compensative circuit is to be closed, must be rightly chosen with regard to the direction of the previously chosen magnetizing current. By preliminary experiments one should learn how to make the right choice.

[2]) We close the primary circuit every time only during one moment, in order not to produce needless thermo-electric currents.

[3]) See the Chapter „Sources of Errors" A 3.

This value having been noted, the magnetizing and the compensative current (mercury-cup II) should be reversed, whilst the primary current is open.

Determine also for this direction of the magnetic force the values, which are to be chosen in the rheostat.

This yields two numbers more, which with the two already found refer to one temperature.

For each temperature these four measurements are made and so the materials have been collected for calculating the variation of the Hall-constant with temperature.

Sources of errors, which may occur in measuring.

Group A. *Thermomagnetic phenomena.*

1. Differences of potential at the secondary electrodes arising in the magnetic field in the direction of the primary current. (Transversal thermo-magnetic effect of VON ETTINGSHAUSEN and NERNST) [1]).

For this one may give the law:

$$e = E_t M (t_1 - t_2),$$

e being the difference of potential at the secondary electrodes, $t_1 - t_2$ the difference of temperature at the primary electrodes, E_t a constant, M the magnetic force.

All dieffrences of temperature, which are independent of the direction of the primary current will cause differences of potential, which increase the Hall-effect for one direction of the primary current, and diminish it

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[1]) Wied. Ann. 29 p. 343. 1836.

for the opposite direction. Taking the mean of the two values for the two directions of the primary current, the error caused by this effect is eliminated.

For differences of temperature, caused by the Peltier-effect, this will not do. The difference of potential hereby arising may be put in the form

$$e = P E_t M I$$

P being a new constant, depending on the Peltier-effect, and I being the primary current. This difference of potential depends also on M and I in the same manner as the Hall-effect itself and is not separated from the Hall-effect in the methods used as yet.

The Peltier-effect however wanting some time for arising, the separation is performed by our momentary method.

2. Differences of potential at the secondary electrodes arising in the magnetic field by flows of heat in the direction of the secondary current. (Longitudinal thermomagnetic effect of VON ETTINGSHAUSEN and NERNST [1]).

For this one may give the law:

$$e = E_l M^2 (t_3 - t_4)$$

$t_3 - t_4$ is the difference of temperature at the secondary electrodes, E_l a constant.

The flow of heat, only arising if a difference of temperature does exist between the secondary electrodes, in which case also occurs a thermo-electric current, this effect may be considered as a variation of the thermoelectric current by the magnetic field. Measuring accord

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[1]) See NERNST, Thermomagnetische Ströme. Longitudinal effect. Wied. Ann. 31 p. 779.

ing to our method all influence falls away as we always close the magnetizing current before the primary current, thus acquiring a new point of rest with respect to which we determine the equivalence of the Hall-current and the compensative current.

Otherwise this effect would produce an apparent dissymmetry for the opposite directions of the magnetization.

3. Differences of temperature at the secondary electrodes, arising in the magnetic field by the primary current. (Galvanomagnetic difference of temperature of VON ETTINGSHAUSEN) [1]).

For this one may give the law:

$$t_3 - t_4 = E_e\, M\, I$$

E_e is a new constant.

This difference of temperature produces a thermo-electric current depending in the same way on M and I as the Hall-current itself, which therefore cannot be easily separated from it.

This error will show itself in its full magnitude, if using the former method of deflection. Our method however being momentary, we may judge of the strength of the Hall-current at the first moment. If we have introduced too much resistance in the compensative current, we shall first see the Hall-current preponderate. But after the primary current has passed a while, the deviation observed will change sign, the secondary current having diminished. By the deviation however, which has appeared the first moment, we know that too much

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[1]) Wied. Ann. 31 p. 737.

resistance had been introduced in order to compensate the Hall-current alone.

Group B. *Other errors.*

1. Variation of the primary current during the measurements.

As we always measure $\frac{e}{I}$, all influence falls away.

2. Variation of the magnetic field, in which the galvanometer-needle is moving, by accidental causes.

This produces a deviation of the point of rest, which causes errors in the former methods, the deflection to be measured needing some time to become constant, whilst in using our method the Hall-current is measured at the same moment it occurs.

3. Variation of the magnetic field in which the galvanometer needle is moving, by exciting and reversing the electromagnet. Even if a deviation of the point of rest has not been wholly avoided, yet all influence falls away, if we first close the magnetizing current and note the new point of rest. This also is applicable to the methods used by others.

The exciting and the reversing of the magnetic field generally will change the sensibility of the galvanometer; with our arrangement this happened to be even so in a high degree. Using however our method of measuring, we need not mind the sensibility, as the equivalence of the secondary and the compensative current may be observed at each sensibility. Only if the equivalence is not complete, the then appearing deviation will depend on the sensibility existing.

4. Variation of the magnetic field, in which the gal-

vanometer needle is moving, by exciting and reversing the primary current.

The deviation of the point of rest, as far as it arises by a wrong situation of that part of the primary circuit, which admits no reversing of the current, would bring about an apparent difference of the Hall-effect for the opposite directions of the magnetic field, apparently a dissymetry.

As far as it arises in that part of the primary circuit, which does admit reversing, the error may be eliminated by taking the mean of the values, obtained for the two directions of the primary current.

Variations of the sensibility of the galvanometer by this cause has no influence for the reasons explained in 3.

5. Variation of the magnetic field in which the plate of bismuth has been placed. This always will produce some error. The only remedy is to keep the magnetizing current as constant as possible, testing this with the aid of an Ammeter. The current having varied somewhat, one may regulate it again by somewhat increasing or diminishing the resistance.

6. Thermo-electric currents, which exist already by some difference of heat at the secondary electrodes. If the thermo-electric current is constant during the course of the measurement, it does not produce any error. Only the variations of it produce some errors. Our observation however being momentary, this error wholly falls away.

Moreover the constancy of the thermo-electric current is still favoured by the circumstance that the secondary circuit always may remain closed during the principal measurements (see n°. 9).

7. Thermo-electric currents, which arise by the passing of the primary current.

a. The heat, which develops at the contacts of the primary circuit according to JOULE's law may be propagated irregularly to the secondary electrodes. So a thermo-electric current arises. Since the primary current, if using our method, is closed only one moment, the thermo-electric current wants the necessary time to amount to a perceptible value.

The influence exercised upon the observations would produce a different value of the Hall-effect for the opposite directions to the primary current.

b. The heat, which develops at the contacts according to the law of PELTIER can also produce thermo-electric currents.

The same remarks may be made as in *a*, but the reversing of the primary current will not reverse this effect and the influence of it would produce a dissymmetry for the opposite directions of the magnetic field.

8. Differences of potential which may occur at the secondary electrodes even in a zero magnetic field, when the primary current passes.

These arise by not fastening the secondary electrodes to the plate at wholly symmetrical places. The error proceeding from it may be avoided in various manners.

a. By first closing the primary circuit, then determining the point of rest and after that closing the magnetizing current. The great objection however is that, in acting so, several other errors occur (See A 2).

b. By measuring the difference of potential with the aid of the compensative current, afterwards deducting the amount of it. This I performed sometimes, in order to control the method described in *d*.

c. By neutralizing the difference of potential with the aid of a branch-circuit, containing a DANIELL-element. The branch-current passes through the secondary wires. The objection to this method, is that we neutralize the difference of potential for only one fixed strength of the primary current.

d. By introducing the by-current according to the idea of BOLTZMANN, joining also the primary and the secondary electrodes by means of a great resistance, chosen exactly.

The last method was generally used.

9. Currents, induced by the variation of the magnetic force during an experiment.

These troubled the results of SHELFORD BIDWELL ¹), who used elements of GROVE in the magnetizing current. Therefore instead of one of the secondary electrodes he used a wire, divided into two parts (see the scheme II) ²).

Now we have the magnetic force sufficiently constant so that we need not fear the induction currents, but the arrangement with the double wire is very practical as the magnetic field may now be reversed, whilst the secondary current always remains closed, without producing any inconvenient shock.

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¹) Phil. Magaz. 5. 17. 1884. p. 249—265.

²) Engraving II.

10. Variation of the resistance of the secondary circuit in consequence of the temperature. As to the plate of bismuth the variation is not to be taken into consideration, as the resistance is but 0,0004 Ohm, the whole circuit having a resistance of 1 Ohm.

The resistance of the contacts at the two electrodes however amounts to 0,2 Ohm in the most disadvantageous case. It ought therefore to be measured at various temperatures.

11. Variation of the resistance by the magnetization is not to be taken into consideration, as it only influences the resistance of the plate of bismuth, which is very small.

12. Influence of the remanent magnetism.

The remanent magnetism will render it more implicate to determine the value of the resistance in the by-current, which ought to be chosen for a zero-magnetic field. We now determine the resistance for the remanent magnetism of the opposite directions, and take the mean of the two values acquired.

13. The magnetic force, which arises by the passing of the primary current alone, may yet bring about that after all the choice of the resistance in the by-current has been made not for a zero magnetic field, but for the magnetic field excited by the primary current itself. The arising Hall-effect does not change sign, if we reverse the primary current, as the magnetic force reverses also.

We however convinced ourselves that the effect is too small to be observed.

One might show the action existing by first using a very weak primary current in order to choose the resistance in the by-current. If we thereafter make the primary current stronger, then another choice of the resistance would be necessary. We however did not observe any difference.

Dr. A. LEBRET. *Dissymmetry of the Hall-effect in bismuth for the opposite directions of the magnetic field.*

In all the plates of bismuth I used, the Hall-current, proved not to be of the same strength for the two opposite directions of magnetization.

Always using the described method of observation, I was urged to introduce for one direction of magnetization (*A*) an amount of resistance, wholly different from that for the opposite direction (*B*).

(The amount of the resistance to be chosen for the opposite directions of the primary current differed but very little, and was independent of its strength) [1]).

If we trace the cause, which may produce this dissymmetry, we meet under *B* 7 *b* in the list of errors in the preceding communication thermo-electric currents, produced by the PELTIER-effect.

Since these only arise after the primary current ha passed a while, and as our method is a momentary one, it is not to be accepted that the right explanation should be found in them, chiefly on account of the great amount of the dissymmetry.

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[1]) The primary current could vary from 1.5 till 7 ampères. The strength of the magnetic field was about 3000 (c. g. s.).

Moreover we discussed the error, which might arise from not attending to the remanent magnetism, but which has been avoided according to B 12.

Further the influence of the magnetic force of the primary current also proved not to be the cause.

Now we still find under A 2 the longitudinal thermomagnetic effect, the influence of which however is avoided by closing in the first place the magnetizing current and then the primary current.

Finally under B 8 we find a difference of potential, which exists already without a magnetic field. In that place however, it has been shown how this difference of potential may be neutralized with the aid of the by-current. But can it be now, that the by-current produces the euqipotentiality for a zero magnetic field, but does not warrant it, if the resistance of the branch which passes through the plate of bismuth increases in consequence of the magnetic field? We examined this for the first plate which showed us the dissymmetry and it proved that an increase of the resistance would produce a dissymmetry of a direction opposite to the really observed.

The plate being very thick and consequently of small resistance, it was a priori improbable that this should be the right explanation. In order to exclude all mistakes however, the whole by-current was omitted, the error of the incomplete equipotentiality being eliminated by performing the experiment as was communicated in $B\,a$ 8 and 8 b. The dissymmetry arose exactly to the same amount as before, so that the cause is neither to be found in the by-current, nor in the variation of resistance of

the plate of bismuth according to the magnetic field.

We further made measurements, employing the usual method of deviation, which needs the correction for the different sensiblenesses according to the opponent directions of the magnetic field, but we found the dissymmetry as well as before.

Moreover we remark that by our method of compensation the difference of the sensibilities of the galvanometer for the two directions of the magnetization cannot have any influence.

The magnetic force was determined with the aid of a Rowland's proof-plate, and proved to be of the same amount for the opposite directions.

From all this it is plain that we have to do with a phenomenon, which cannot be explained with the aid of the phenomena already known.

Experiments with respect to the dissymmetry under various circumstances.

1. Turning the plate in such a manner that front and back change place.

We take the plate out of the vessel, turn it 180° about a vertical axis and put it back.

The dissymmetry proves now to be *reversed*, the Hall-effect, which before appeared to be stronger for the direction of magnetization B, now appearing to be stronger for the direction of magnetization A [1]. The

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[1] This was also found by van Aubel, as he communicates in the Archives des sciences physiques et naturelles de Genève 3. 33. 25 March 1895.

amount of the dissymmetry is the same. Hence it follows that there must be in the plate some difference, of what kind soever, the sign of which is determined by the normal, drawn to the outside from a previously fixed side of the plate.

2. Changing the primary and the secondary electrodes in such a manner that the primary current passes from C to D, A and B becoming the secondary electrodes, connected with the galvanometer.

The dissymmetry proves again to be *reversed*, the Hall-effect appearing stronger for the direction of magnetization A, when it was before stronger for the direction of magnetization B.

Again the amount of the dissymmetry was the same ¹).

Determination of an axis of symmetrie

Changing the primary and the secondary electrodes is theoretically the same as turning the plate in its plane round an angle of 90°.

The dissymmetry changing sign in turning 90° about the determining normal, must have passed the value of zero.

Therefore a round plate of bismuth was manufactured, to which the four electrodes could be fastened with

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¹) This experiment has properly been taken with regard to the possibility that the magnetic force, arising by the primary current itself, had rendered the determination of the equipotentiality in a zero magnetic field faulty. At that time I had not yet proved that this influence is too small to be measured. And we avoid the action of the magnetic force for the greater part by using the electrode divided into two parts. Instead of annulling the dissymmetry however, we found reversing.

the aid of small screws. These can easily be loosened and again be fastened after having somewhat turned the plate.

The dissymmetry appears again in this plate, changing sign after turning it in its own plane round an angle of 90°. And between these two positions we really found one, for which the dissymmetry had disappeared.

This fundamental position of the plate according to the primary electrodes may be indicated on it by a directrix. Turning from this position into both directions the appearing dissymmetry proved to be of different sign. The dissymmetry rose to the highest point after having turned round 45° (always in the plane of the plate), reckoning from that fundamental position. After having turned round an angle of 90° the dissymmetry again has disappeared, so that we might as well have chosen the latter position for the fundamental one. The only difference between these two positions is, that the dissymmetry appearing after turning in the same direction from each of these positions, acquires the other sign.

If the electrodes have not been fastened in the fundamental position, we obtain a dissymmetry changing sign also after turning about a vertical axis, i. e. after changing front and back. For, imagining the directrix indicated on the plate, we observe it acquiring a position exactly opposite to the position before the change. So the result of experiment I agrees entirely with the last result.

Modification of the Theory of the Hall-effect.

As has been shown by GOLDHAMMER ¹), the Hall-effect

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¹) WIED. Ann. 31 p. 370.

may be described by supposing that the metal used becomes aeolotropic by the magnetic field, in consequence of which the following relations of Maxwell concerning the current and the decrease of potential exist:

$$\frac{\partial p}{\partial x} = -K_{11}\ u - K_{12}\ v - K_{13}\ w$$

$$\frac{\partial p}{\partial y} = -K_{21}\ u - K_{22}\ v - K_{23}\ w$$

$$\frac{\partial p}{\partial z} = -K_{31}\ u - K_{32}\ v - K_{33}\ w.$$

Since two dimensions will suffice in order to explain the phenomenon, this becomes:

$$\frac{\partial p}{\partial x} = -\ K_{11}\ u - K_{12}\ v$$

$$\frac{\partial p}{\partial y} = -\ K_{21}\ u - K_{22}\ v.$$

Always however two perpendicular directions may be found, for which the equations become:

$$\frac{\partial p}{\partial x} = -\ K_{11}\ u - H v$$

$$\frac{\partial p}{\partial y} = H u - K_{22}\ v.$$

These directions we call the principal axes.

Goldhammer supposes there will be no reason to infer a difference between K_{11} and K_{22}, and so he equalizes these values. So the equations have been obtained, which Boltzmann introduced for describing the Hall-effect, which are in fact the same as those given by Lorentz [1]).

The difference of potential at the secondary electrodes really is:

$$e = H \frac{I}{d} \quad {}^{2})$$

so that we must consider H to be dependent on the used substance (coefficient of Hall) and of the magnetic force. Supposing that after reversing the magnetic force H only changes sign, retaining the same amount, the Hall-effect results symmetrical. And it is easily shown that the symmetry persists for all axes, as the equations remain the same after having turned the system of coordinates.

Supposing however that K_{11} and K_{22} are of a different value, we again can show that the resulting difference of potential is $e = H \frac{I}{d}$, if we fasten the primary electrodes to the plate in the direction of the principal axis, for which the equations have been given. It only changes sign, retaining the same amount, if we reverse the magnetic field. So for this principal axis the Hall-effect is symmetrical.

But now transforming the equations for another direction, the new axis making an angle x with the old ones, they become

$$\frac{\partial p}{\partial \xi} = u_1\,(-K_{11}\cos^2\alpha - K_{22}\sin^2\alpha) + v_1 \left\{-H + \sin\alpha\cos\alpha\,(-K_{22} + K_{11})\right\}$$

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[1]) Arch. Neérl. XIX p. 123.

[2]) d is the thickness of the plate.

$$\frac{\partial p}{\partial \eta} = u_1 \left\{ + H + \sin\alpha \cos\alpha\,(- K_{22} + K_{11}) \right\} + v_1\,(-\,K_{11} \sin^2\alpha - K_{22} \cos^2\alpha)$$

The difference of potential resulting at the secondary electrodes, the primary wires having been fastened in the direction of one of the new axes, is for one direction of magnetization:

$$e = \left\{ H + \tfrac{1}{2} \sin 2\alpha\,(- K_{22} + K_{11}) \right\} \frac{I}{d}$$

and for the opposite direction of magnetization

$$e = - \left\{ H - \tfrac{1}{2} \sin 2\alpha\,(- K_{22} + K_{11}) \right\} \frac{I}{d}$$

Hence it follows that the absolute values of the difference of potential are different, so that the dissymmetry is described by supposing the resistance of the plate of bismuth placed in the magnetic field, to be different in two perpendicular directions.

Variation of the dissymmetry with the strength of the magnetic field.

The dissymmetry now being ascribed to the difference of the resistance arising by the magnetic field, the question rises if the dissymmetry depends on the strength of the magnetic field just as the resistance itself.

The experiments, which will make this out, were performed in the position differing about 45° from the fundamental position [1]).

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[1]) These measurements were performed without the use of the by-current. Also it was determined (in accordance with *B* 8 *b* of the former communication) with the aid of the compensative current, how strong the secondary current for a zero magnetic field was, the amount being deducted from the currents arising for the various magnetic fields.

The dissymmetry observed proved to increase with the strength of the magnetic field, the increase for small values of the magnetic field being somewhat slower than that of the square of the magnetic force, and for great values of the magnetic field somewhat more than the increase of the magnetic force itself.

As it appears from the experiments of Drude and of Henderson [1]), that also the increase of the resistance of bismuth with the magnetic force follows the same law, this may be considered to confirm our explanation of the dissymmetry.

The following values result from calculating

$\frac{M}{\text{about } 1500}$	$H\,C$	$2.65\,(K_{11}-K_{22})\,C$	$H\,M\,C^1$
1	1	1	1
1.44	1.23	1.82	1.77
1.83	1.36	2.59	2.49
2.32	1.42	3.58	3.29

M, H and $K_{11}-K_{22}$ indicating in absolute measure the magnetic force, the Hall-effect and the dissymmetry, C and C^1 being constants of less importance.

The variation of $(K_{11}-K_{22})$ agreeing in some degree with the variation of the product $H\,M$, we have added an account of the relative value of this product.

We intend to examine the dissymmetry in a plate, cut out of a great crystal or an agglomeration of crystals all grown together in the same direction.

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[1]) Wied. Ann. 53, p. 912.

Dr. A. LEBRET. *The variation of the Hall-effect in Bismuth with temperature.*

(Including an investigation of the variation of the Electric Resistance of Bismuth with temperature).

The preliminary numbers have been communicated in n°. 15 of this series. The method, according to which the measurements have been performed, we described in this communication at p. 1 a. f.

For obtaining the low temperatures we used a solution of solid carbonic acid in alcohol, the high temperatures have been obtained with the help of a bath of liquid glycerine.

A vessel of hard soldered copper [1]), already briefly described on p. 4. , and more at large in my inaugural dissertation on p. 61 a. f., served to contain the liquid of the high as well as to contain that of the low temperatures.

I examined two plates of bismuth, originary from different sources. One has been made from the same bismuth as served us for the preliminary measurements, communicated in n°. 15. We call it bismuth I. The bismuth, from which the second plate has been made, we call bismuth II.

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[1]) See engraving I.

The following numbers have been obtained at different temperatures for the Hall-constant, compared to that at 21°, which we call R^{I}_{21} for the first plate, and R^{II}_{21} for the second.

Magnetic field about 3000 (c. g. s.)
Plate of Bismuth I.
α. Low temperatures.

Temperature.	Constant of Hall.	
— 74 °	1.256	R^{I}_{21}
— 72 °	1.250	
— 65.5°	1.245	
— 58.5°	1.246	
— 52.5°	1.244	
— 47.5°	1.241	
— 40.5°	1.211	
— 36 °	1.211	
— 27.5°	1.190	
— 23 °	1.180	
— 14 °	1.139	
— 7 5°	1.110	
0 °	1.056	
+ 7 °	1.050	
+ 11 °	1.046	

β. High temperatures.

21 °		R^{I}_{21}
246.5°	0.280	R^{I}_{21}
95 °	0.697	
157.5°	0.411	
198.5°	0.313	

124 °	0.532	
93 °	0.700	
76 °	0.784	
43.5°	0.927	
11.5°	1.052	

Plate of Bismuth II.

α. Low temperatures.

— 69 °	0.366	R^{II}_{21}
— 64 °	0.889	
— 59 °	0.915	
— 51 °	0.970	
— 47 °	0.985	
— 41.5°	1.007	
— 35.5°	1.016	
— 31.5°	1.030	
— 25 °	1.032	
— 19.5°	1.034	
— 12 °	1.040	
— 8 °	1.034	
— 4 °	1.034	
+ 0.5°	1.034	
+ 7.5°	1.028	
+ 21.5°	1.002	

β. High temperatures.

26.5°	0.980	R^{II}_{21}
203 °	0.288	
242.5°	0.175	
219 °	0.217	
124.5°	0.540	

105 °	0.634
84.5°	0.725
56.5°	0.869
22.5°	0.996
152 °	0.429

The numbers have been ranged in these tables in the same order, in which the measurements were performed.

In order to get an easy survey, they have been set out in curves in the engraving [1]) added.

The Hall-constant in bismuth I proves not to be a linear function of the temperature, as the preliminary measurements formerly communicated made presume. The deviation from the straight line however is not clearly perceptible at the temperatures above — 38°, the lowest at which a preliminary observation has been performed. The values formerly obtained, very sufficiently agree with the later. In judging this, one should attend to the Hall-constant at 21° now being taken as unit, and formerly that at 14°.

The variation of the Hall-constant in bismuth II agrees at the temperatures above 20° with that of the Hall-constant in bismuth I. On the contrary we perceive very distinctly at about — 20° a maximum, and at lower temperatures a sensibly smaller value of the Hall-constant.

For bismuth I the existence of a maximum probably would appear clearly, if we had experimented at still lower temperatures.

DRUDE and NERNST [2]) found a maximum of the Hall-

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[1]) See engraving III, curves 1 and 2.

[2]) WIED. Ann. 42. p. 568, 1891.

effect in bismuth at about 100°. The value however, which was found after cooling the plate was not the same as that observed before heating.

Leduc 1) found the maximum value at 29°.

Clough and Hall 2) found for nickel a maximum Hall-effect between 170° and 200°, and for steel a steady increase when heating to the highest temperature 319°, at which was observed. Hall 3) found this increase also for cobalt within the smaller limits, at which those measurements have been performed. As the Hall-coefficient appears to be zero for the melted state 4), these two metals must show a maximum Hall-effect at a certain temperature.

If yet for antimony a maximum value should be found which in this case probably would prove to lie at a low temperature at which for this metal no observations as yet have been performed, then it would be proved experimentally that the Hall-effect in all metals, for which it has a great value, shows at some temperature a maximum value, which is many times greater than the value at temperatures, far distant from that temperature.

The chemical analysis 5) of the two species of bismuth showed that in bismuth I traces of iron were

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1) C. R. 102. p. 358, 1886.

2) Proc. of the Americ. Acad. 20. p. 189, 1893.

3) Phil. Magaz. 15. p. 341. 1883; Sill. Journ. 29 p. 117, 1885.

4) See Wied. Ann. 42. p. 568, 1891.

5) This investigation has been kindly performed by Mr. F. H. Eydman at Delft, under the guidance of Professor Hoogewerff of the Polytechnic School there.

found too small to be weighed, in bismuth II noother substances were found.

The absolute value of the Hall-effect in bismuth I at 21° was about 7, that in bismuth II 13 1).

At last it may be mentioned here, that I have also examined the influence of the temperature on the resistance of bismuth I. I was induced to this investigation by the opinion expressed by Leduc 2), that the variation of the electric resistance of bismuth with temperature would be almost the same as that of the Hall-constant. Calling the specific resistance W, the Hall-constant R, then a new quantity $D = \frac{R}{W}$ would be almost independent of the temperature.

The contrary was proved by my measurements: when raising the temperature the resistance increases, the constant of Hall diminishes.

The method according to which the resistance was measured of a spiral wire of bismuth (obtained by infusing melted bismuth into a glass spiral), consists in this, that the differences of potential at the ends of the spiral wire in question are compared with those at the ends of a known resistance. If we join together the two ends of each of these resistances with the aid of a great resistance, so that each of the joining wires contains one of the two insulated windings of a differential galvanometer, the needle will remain at rest for a deter-

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1) Von Ettingshausen and Nernst give 10.1, Hall 8.6. The influence of the purity appeared before and also now from my measurements, to be very great.

2) See Lumière électrique 29, pag. 230, 1888.

Engraving I.

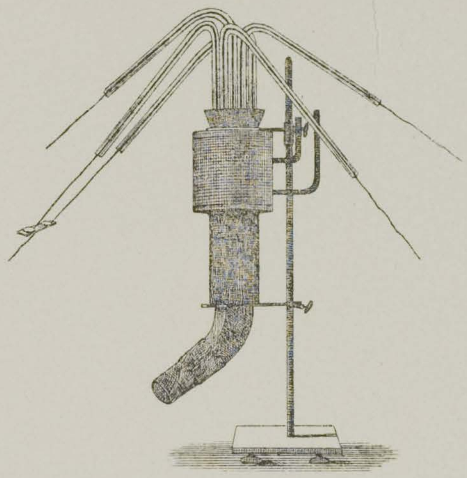


Fig. 1.

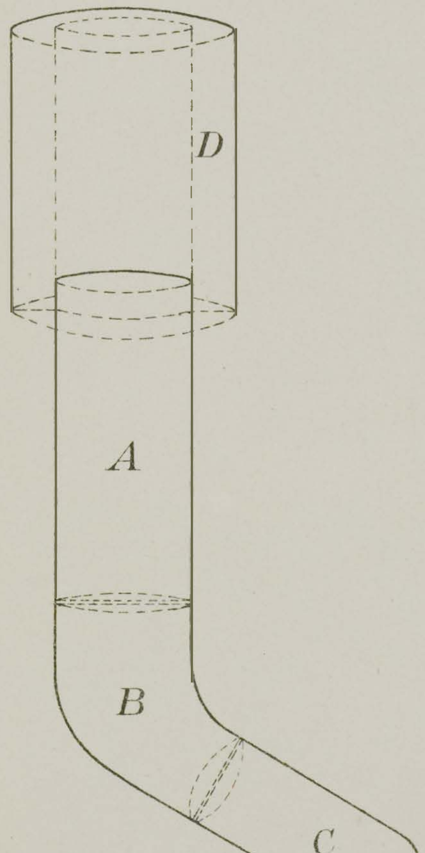
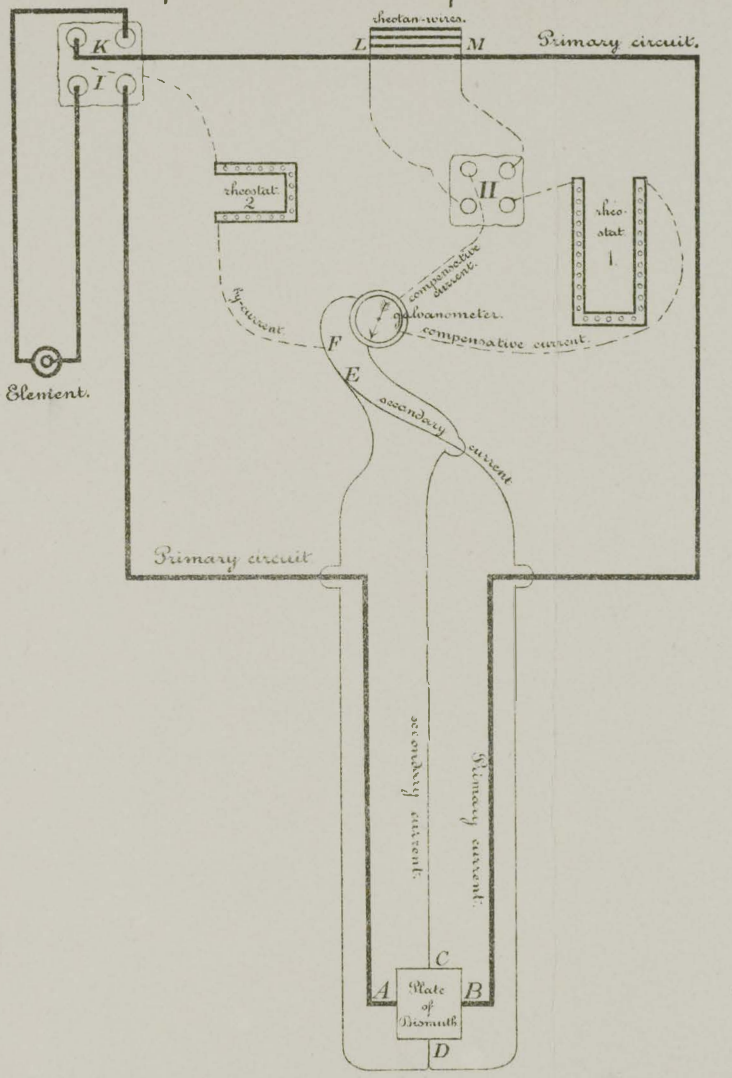


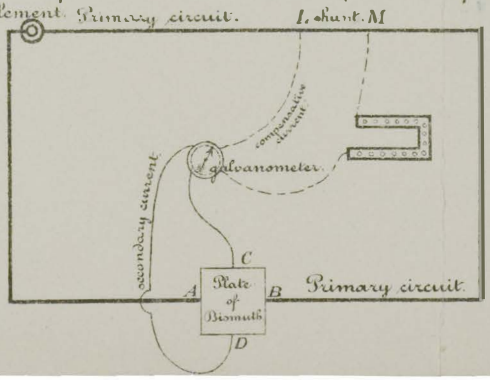
Fig. 2.

Engraving II.

Scheme II of the Method of Compensation.



Scheme I of the Method of Compensation.



Engraving III.

Variation of the Hall effect with temperature.
in Bismuth I.

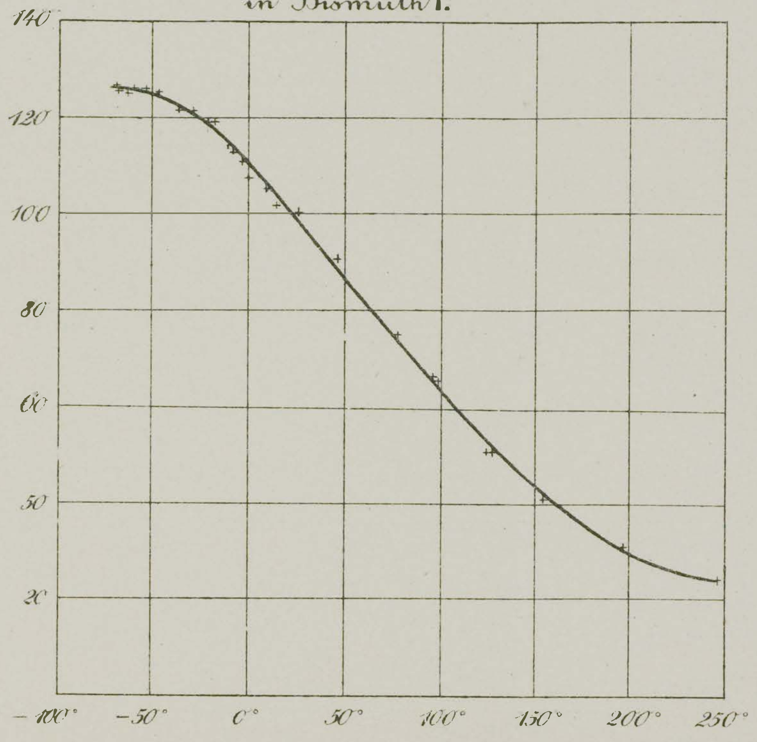


Fig.1

Variation of the Hall effect with temperature.
in Bismuth II

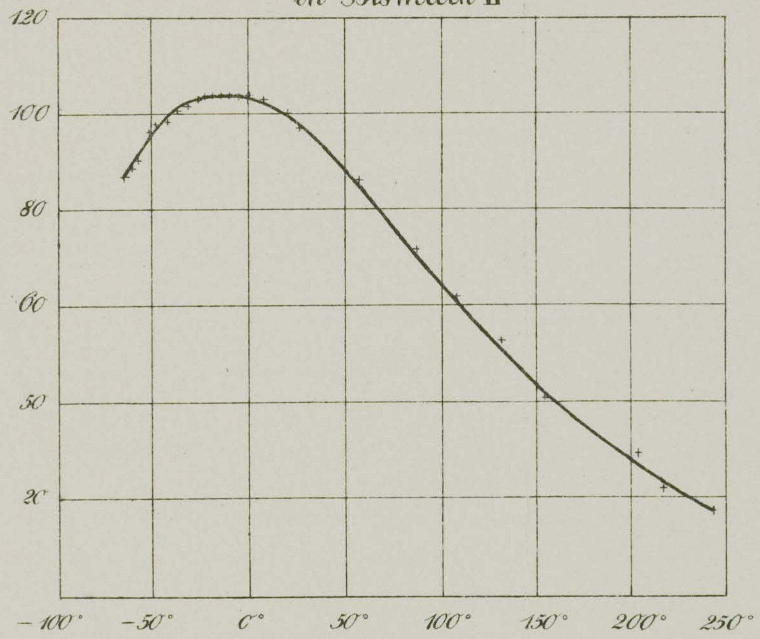


Fig.2.

Variation of the electric resistance of Bismuth I with temperature.

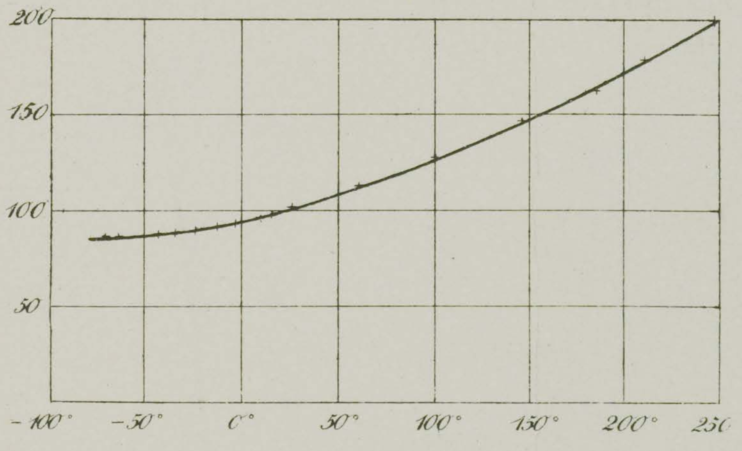


Fig.3.

minate choice of the resistance in one of the galvanometer-circuits.

If the resistance of the spiral wire of bismuth varies by cooling or heating, then another choice of the resistance in the galvanometer-circuit will be necessary to keep the needle at rest and from this the variation of the resistance of the bismuth can immediately be calculated.

We obtained the following values, expressed in the resistance at 18°, which we will call r_{18}.

Temperature.	Resistance.
— 76 °.	$r_{18} \times$ 0.88
— 71 °.	0.89
— 64 °.	0.895
— 44 °.	0.905
— 39 °.	0.91
— 25 °.	0.925
— 15,5°.	0.935
— 5 °.	0.955
+ 7,5°.	0.985
+ 10 °.	0.995
+ 20 °.	1.01
+ 51 °.	1.11
+ 99 °.	1.23
+ 147 °.	1.43
+ 174 °.	1.62
+ 217 °.	1 82
+ 246 °.	2.01

These numbers served to delineate the curve 3. 1)

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1) See engraving III.

20

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 20.

Dr. P. ZEEMAN. Measurement of the refractive index of incandescent pla~~n~~tinum.
(*Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen*, **28 September 1895**, *p.* 116—119).

1d

EDUARD IJDO — PRINTER — LEIDEN.

Dr. P. ZEEMAN. *Measurement of the refractive index of incandescent platinum.*

1. It is of much importance for the general theory of radiation of glowing bodies to know what rays may emanate from the interior of a body. If, at ordinary temperatures, the angle of incidence does not exceed a definite (relatively high) limit, they will by total reflexion not be prevented from emanating, because the refractive index is relatively low. Supposing, that with increasing temperatures the refractive index increases in a high degree, then at last only those rays can emanate which are nearly normal to the radiating surface.

Kolaček [1] by extrapolation, came to this conclusion from the experiments of Kundt [2] on the variation of the refractive indices of metal prisms with a temperature difference of about 90°.

On the other hand the observations of Sissingh [3],

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[1] Kolaček. *Wied. Ann.* Bd. 39. p. 236. 1890.

[2] Kundt. *Wied. Ann.* Bd. 36. p. 824. 1889.

[3] Sissingh. *Dissertatie* p. 133, Leiden 1885. *Communications* etc. Nr. 1.

who found it impossible to measure a variation of the optical constants of iron, when the temperature varied from 15° to 120° and those of DRUDE [1]), who found only very minute variations, when experimenting with platinum in cold and in warm water and with silver and gold up to 200°, lead to a different conclusion. I have extended the investigation to the temperature of glowing platinum (about 800°), endeavouring to measure the variation of the optical constants by means of BABINET's compensator.

2. It would result from the figures given by KUNDT that with an increase of temperature of 100° the refractive index n of platinum increases 27 %. Hence it follows that, the principal azimuth H remaining the same (7), the principal incidence I must increase about 2.5° for every 100° the temperature increases. With the apparatus used it was impossible to observe at an angle of incidence greater than 65°. At this angle, a diminution of 9° in the difference of phase Φ of the reflected rays, polarized resp. in and perpendicular to the plane of incidence corresponds to an increase of 2.5° in I. And this again corresponds to 36 divisions of the head of the screw of the compensator (the head being divided into 50 parts). Hence according to KUNDT's observations for every 100° degrees increase of temperature, a displacement of this order should be expected. At 800° n would be about 3 times as great as at an ordinary temperature and about 5.5 revolutions of the screw would be required for the compensation. On the other hand: if I remained constant, H would decrease 3.5° for every 100 degrees rise of temperature. The principal azimuth at 65° then rises 2,5°.

Now it is possible, to measure a difference of phase, corresponding to 4 divisions of the screwhead, and a variation, of the reestablished azimuth of 0.3° [1]) with the apparatus used, if only the mirror be sufficiently smooth.

3. It will be clear by the following how the experiment was made. The *mirror* of platinum was the middle part of a strip of flattened platinum, about 50 mm. in length, 5 mm. in breadth, and 1 mm. thickness treated with different kinds of amaril-paper, up to N°0000. In this manner a tolerably good mirror was obtained and though the image of the slit of the collimator left something to be desired, the central black band in the compensator of BABINET, (homogeneous light being used), was of sufficient definiteness. The strip was heated by the electric current so that the reflecting part obtained the highest temperature.

4. *Adjustment of the mirror.* On a wooden board two brass stiles are fastened. In the upper part of one of the stiles the end of the strip of platinum (3) is clamped.

To the other end of the strip has been clamped a piece, the cylindrical continuation of which passes

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[1]) DRUDE. *Wied. Ann.* Bd 39. p. 481. 1890.

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[1]) SISSINGH. *Dissertatie* pag. 70 and subs.

through an aperture in the other stile. A spiral spring surrounding this lengthening-piece, presses the end of it outwards and keeps the strip stretched at the high temperatures. The mirror then retains its position as is verified by observing the reflected image through the telescope. The wooden board is fastened above the spectrometer on an adjustable platform. In order to obviate the difficulties in adjusting the mirror which might be caused by the stiffness of the leads for the current, the latter are immersed into mercury cups with which are also connected the wires fastened to the two above mentioned stiles.

5. As to the *method of observation*, the disposition of the instruments, the means employed for getting homogeneous light etc., used in the determination of the optical constants, I refer to former publications [1]).

6. The optical observations being finished, I determined the *temperature of the mirror* by measuring the intensity of the current necessary for melting little crystals of different salts, placed on the mirror. The melting points I took from Landolt's and Börnstein's »Tabelle". It appeared that for a current of 80 Ampères the temperature was 800°. Then the central part of the strip was becoming red hot, but the emanating light did not yet interfere with the definiteness of the band in the compensator.

7. *Result.* It appeared that at this temperature and using red, yellow or blue light there was no ascertainable change in *position* or *darkness* of the band in the compensator. Yet with the same mirror a rotation of the screwhead for 6 divisions and of the analyser for less than 1°, gave a perceptible change. Hence the influence of temperature is below these values. From this it follows that also by increasing the temperature to 800° the refractive index does not undergo a variation, comparable to that, which has been derived (2) from Kundt's experiments on the behaviour of metal prisms in transmitted light (the temperature variation being only 90°). The precision of my observations is less than that of the observations mentioned in (2), but this only in a small degree can change our conclusion. I do not think, that it would now be of any use to investigate more closely the precise limits of the errors of measurement in this experiment resp. those in which I demonstrated the invariability of n. I intend to determine the value of the variation by making observations at the principal incidence and with a smoother mirror.

The investigation may also be extended to still higher temperatures by separating with the aid of a spectroscope behind the compensator the light emanated by the platinum from the homogeneous reflected light. However, with a view to the theories mentioned in (1) I think I may communicate already now the result concerning the insignificant change of I and H, or what comes to the same thing, of the coefficient of absorption ρ, and n. It is not to be doubted that at very high temperatures ρ as well as n must change: 1°. because according to the second low of thermo-

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[1]) Sissingh. *Archiv. Néerl.* T. XX p. 1. 1886.
Zeeman. *Archiv. Néerl.* T. XXVII p. 252. 1893.

dynamics a body [1]) absorbs those rays which it emits itself, 2°. because the distance of the molecules if there is a sufficient rise of temperature can undergo a sensible, and, if the body becomes liquid even a considerable change.

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[1]) Kolaček, l. c. p. 248.

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 21.

Prof. Dr. E. COHN and **Dr. P. ZEEMAN.** Observations concerning the propagation of electrical waves in water [1])

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam*, **28 September 1895**, *p.* 108—116).

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[1]) The greater part of the measurements were made at the laboratory of physics of Strassburg.

Eduard IJdo — Printer — Leiden.

Prof. Dr. E. COHN *and* Dr. P. ZEEMAN. *Observations concerning the propagation of electrical waves in water.*

The greater part of the following observations were made by us jointly in Strassburg in the summer of 1893. One of us (P. Z. in Leiden) has filled up a blank in the observations then made by some new series of observations. According to the original plan the investigations made were preliminary, being introductions to questions, relating to the behaviour of *conductors*, and as yet not treated. We infer however from some publications made of late that also the results obtained for *pure water* may be useful.

Method.

The method is closely related to the one exposed in the paper ,,on the propagation of electrical vibrations in water" [1]). It is necessary to refer to this paper for the disposition of the experiments. We desired to make the method as accurate as possible. Our attention was especially directed to three points, viz: In the first place it is assumed in the calculation of the

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[1]) E. Cohn, *Berliner Berichte*, 3 December 1891; *Wied. Ann.* 45 p. 370 (1892).

refractive indices, that the waves are travelling through a medium unlimited on either side. However in the first place a lateral boundary is practically necessary. If this boundary has the form of two concentric cylinders, it is yet possible to solve the resulting mathematical problem: it appears, that for the required frequencies and geometrical relations, the electrical forces are almost normal to the axis of the cylinder, and that the velocity of the waves is sensibly equal to that of the wave in the infinite medium. One may infer, that the same holds good if the waves are propagated along two parallel metallic wires, and if the only lateral boundaries, besides these wires, of the traversed dielectric (the water) are *metallic* plates, parallel to the axes of the wire. If however for the latter is substituted a different insulator (the material of the basin and then the air), only the experiment can decide, to what degree the case of the infinite wave is realized. Our first experiments were undertaken with the view to decide this question. They related to waves, half a wavelength being $l_0 = 188$ cm. The water was contained [1]) in a basin, the length of which was 66 cm. and the breadth 39 cm., filled in different sets of experiments to the height

$$h = 18,\ 22,\ 28.5 \text{ cm.}$$

the wires being always 10 cm. above the bottom. A

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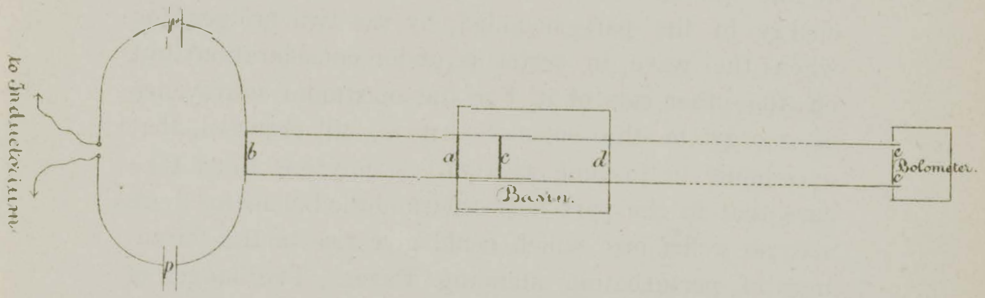
[1]) The following numbers refer to *all* the series of observations, series 1 of the table given below excepted; in the last the dimensions were: length 51 cm., breath 35.5 cm., height of the water 28 cm., height of the wires 15 cm.

systematic variation of the apparent refractive index dependent on the hulk of the mass of water was not found. Accordingly we desisted from the use of a metallic enclosure, which would have complicated the method of observation. However we must confess, that the totality of the data now given seems to evince a slight variation of the apparent refractive index in the expected direction [1]).

Secondly it was questionable whether by the method of observation used before one was sure of the existence in water of *one pure* vibration, determined by the wirelength *ab* in air [2]).

Accordingly [3]) we made the first part *p b p* of the "secondary conductor" congruent to the "primary", *fastened the bridge b*, and determined *the position of a* by resonance.



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[1]) Vide the end!

[2]) Cf. figure and substance of the cited paper.

[3]) Cf. for the following the subjoined figure.

Nevertheless it appeared sometimes from an exploration of the vibrations on the other side of *a* in air, (before the basin was in its place), that here several waves were superposed. We did not succeed in every instance to find the cause of the disturbance; we have however made measurements in water only for these waves, which gave a pure vibration with a sharply defined maximum.

A last objection relates to the disturbances, which the regular shape of the waves must necessarily undergo through the outer coats and the leads of the little "Leiden jars" which collect the energy of the vibrations and transmit it to the bolometer. It is possible to avoid the jars and *to remove entirely the measuring apparatus from the wave to be measured,* by arranging the parrallel wires, along which the wave is propagated, and their prolongation so, that they terminate directly in the bolometer. Now, one does not measure the energy in the part bounded by the two bridges, (*ac* when the wave in water is under consideration) but on the other side of it. For the maximum conveyance of energy to the bolometer it is still required, that *ac* schould be in tune with *ba*, -- only one must take care that in the part between *c* and the bolometer there are no reflexions, which could give rise to the formation of perturbating standing waves. The danger of such reflections exists in two places: First at the bolometer itself. If it is used in the manner generally adopted, according to the statements in the literature of the subject, it collects energy from the vibrations travelling through space, entirely independent of the

leads connected with the wires. We did not obtain suitable results before we had put the bolometer in a metallic enclosure; however at *e*, where the (insulated) leads pass through this enclosure, there now occur strong reflections of the incident waves. The reflected wave is again reflected at *c*. The delivery of energy in the bolometer is then generally determined not only by the length *ac*, but also by *ce*. These reflexions are however rendered harmless according to BJERKNES' principle by the introduction between *c* and the bolometer of sufficiently long pieces of wire (varying according to the wavelength to 100 M.), so that on account of the powerful damping of the vibrations the resonance of the end *c e* is of no consequence.

Secondly there is on account of the high refractive index of water a powerful reflexion at *d* where the wave passes from the water into the air. This reflexion may, as with the former method of observation, prevent us from finding the maximum sought for, if to the length *cd* corresponds *nearly* the same period, as to *ac* and *ab* (or a multiple), h. e. if the oscillation period for the whole length traversed in water *ad* is *nearly* a multiple of the oscillation period for the chosen air length *a b*. However there is reversal of the phase, if the reflection takes place at the bridge *a*, if the reflection takes place in the water from air there is no reversal of the phase of the electric intensity; hence follows: *full* resonance exists between *ab* and *cd*, if *ad* is $^1/_2$, $^3/_2$, $^5/_2$. . . . . . half wavelengths.

Consequently half wavelengths *ab*, which would suffice *approximately* to these conditions are to be avoided.

(This had escaped us in one of the series of observations in 1893, $l_o = 188$ cm.; this series has been replaced by the new series 1 and 2).

If the measurements without the jars were undertaken with the here mentioned precautions, and if on the other hand coats of the jars of sufficient smallness, were chosen, it was impossible to establish a measurable difference in the results of the two methods of observation.

Of the comparative measurements, relating as well to the waves in air, as to the waves in water, one of the latter has been entered in the table under n⁰. 3. The jars were glass tubes 0,1 cm. in thickness, closely surrounding the parallel wires, thick 0,2 cm., and distant 7 cm.; the coats were $1\,^3/_4$ turns *at most* of 0,05 cm. thick copper wire.

SUMMARY OF THE RESULTS OF THE OBSERVATIONS ¹).

Series N⁰.	Place a. Time.	l_o	l_w	n	h	θ	with or without jars.
1	Leiden 1895	155.5 (3)	17.4 (0.4) 17.5 (1.2) 17.3 (1.5)	8.98	v. pag. 2	19.2	with
		155.2 (3)	17.7 (0.6) 17.4 (0.8) 17.4 (1.0)	8.90	18	18.7	with.
2	d⁰.	»	17.4 (0.6) 17.4 (0.8) 17.4 (1.0)	8.95	22	18.7	with.
		»	17.3 (0.6) 17.3 (0.8) 17.3 (1.0)	8.99	28.5	18.2	with.
3	Strassburg 1893	341.5 (4)	38.7 (0.6)	8.89	22	20.2	without.
		»	39.0 (0.6)	8.86	»	22.0	with.
4	d⁰.	376.0 (4)	42.9 (0.6)	8.85	18	21.2	without.
		»	42.7 (0.6)	8.89	22	21.3	without.
		»	42.5 (0.6)	8.93	28.5	21.1	without.
5	d⁰.	562.0 (4)	63.9 (0.6)	8.89	18	22.0	without.
		»	63.6 (0.6)	8.94	22	22.3	without.
		»	63.4 (0.6)	8.97	28.5	22.3	without.

The table has been calculated in the following manner: Let *b* denote the position of the bridge in air, *a* the boundary of the water and the bridge in that place; *c*, *c′ c″* the bridges in water (only *one* being present at a time); then the parts *b a*, *a c*, *a c′*, *a c″*

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¹) All lenghts in cm.

are directly observed, the exact position of the bridge being at every turn found in this manner: one compares the deflections of the bolometer for three aequidistant positions, and varies these positions, always making the distances as small as possible, until the deflections for the two exterior positions are equal inter se and yet distinctly smaller than the deflection for the medium position. In the columns l_o and l_w are in parenthesi ( ) the values of the used lateral displacements.

From the measured lengths follows.

$$l_o = ba + \delta \quad l_w = ac + \delta = cc' = c'\,c''$$

δ being the wire length ‘equivalent’ to the bridge. This can be determined for waves in water from each of the sets of observations in brackets $\}\{$ of the series 1 and 2. The values entered under l_w in these sets are always calculated successively as

$$ac + 4.5,\ cc',\ c'c''.$$

In the same manner δ has been determined for a great many air waves, l_o between 200 and 600 cm., from

$$l_o = ba + \delta = aa' = a'a'',$$

a, a', a'' being the several positions of the bridge, giving resonance. Always δ was found between 4 and 5 cm. Hence for *all* wavelengths has been accepted:

$$\delta = 4.5$$

Further follows the refractive index at the temperature ϑ of the water

$$n' = {}^{l_o}\!/_{l_w}$$

Thence we have calculated the refractive index n *at* 17° C by means of the temperature coefficient determined by Heerwagen [1])

$$n = n' + 0.0201\ (\vartheta - 17).$$

The conductivity of the water was in all series of observations 5 to 10.10^{-10} (mercury = 1); the single values being of no consequence [2]) have not been entered in the table.

Discussion.

From the results of the observation an answer to both the following queries can be abstracted:

1. is the refractive index in the domain of the used frequencies a constant? and if this is the case,
2. is this constant equal to the square root of the specific inductive capacity, resulting from experiments with *stationary* electric fields?

The third of the series of observations 1 to 5 of the table must serve as an example, that the two methods of measurement, with and without jars, give identical results. In fact the difference of the measured wavelengths, the difference of temperature being taken into

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[1]) *Wied. Ann.* 49. p. 279. 1893.

[2]) Vide E. Cohn. l. c.

account, only amounts to 0.15 cm. Besides the series is in full harmony with the middle set of series 4, to which belongs the same h and nearly the same l_o, though it was made at another time and with another primary vibration. — The series 1, differing from the others by different dimensions of the bulk of the water, (approximately the same as the *last* sets of the series 2, 4, 5) must support the result of series 2, and especially the value of the bridge correction $\delta = 4.5$.

For answering the above questions then remain the series 2, 4, 5, of each of which are made three sets under otherwise equal circumstances for the frequencies.

$\nu = 97,\ 40,\ 27$ millions of entire vibrations. The three sets differ by the depths of the water:

$$h = 18,\ 22,\ 28.5 \text{ cM.}$$

Summarising the values of n are for

	h		
$\nu/10^6$	18	22	28.5
97	8.90	8.95	8.99
40	8.85	8.89	8.93
27	8.89	8.94	8.95

Allowing first the possibility, in accordance with the remark on pag. 2, that the velocity of propagation depends on the value of h, we have for answering the first question to regard the numbers of the several columns separately.

Taking $h = 18,\ 22,\ 28.5$ and for each ν the mean value: $n = 8.87,\ 8.92,\ 8.94$, all errors in the observed l_w appear to be inferior to 0.15 cM. Accidental errors of this value cannot be considered as non-existing; hence it follows:

1°. In the region of frequencies between 27 and 97 millions *dispersion cannot* be demonstrated. The greatest difference between the observed refractive indices becomes 0.06, equal to $^2/_3$ per cent.

Seeking to represent *all* observations by *one* value of n, the most favourable value is found to be

$$n = 8.91 \text{ at } 17^\circ\ C,$$

with this the errors in the observed l_w are calculated:

$$\begin{array}{ccc} +\,0.0 & -\,0.1 & -\,0.2 \\ +\,0.3 & +\,0.1 & -\,0.1 \\ +\,0.1 & -\,0.2 & -\,0.3. \end{array}$$

Also these deviations *may* be accidental. However in all the three lines the values of the n's rise with ascending h, and this suggests the suspicion, that the systematic error mentioned on pag. 2 has become effectual. If it exists, and if it is the only one, the real value of n must lie *above* the observed one. Then however this error is not inherent to our special method of observation, but according to the geometrical dimensions in a yet *higher* degree to *all* other methods in which refractive indices and specific inductive capacities are determined from lengths of electrical waves. According to the statical method and with an accuracy unattainable in the measurement of velocities of propagation, HEERWAGEN [1]) has found the square root of the specific inductive capacity

$$n = 8{,}99 \text{ at } 17° \, C.$$

We believe, that it is allowed to conclude:

2°. the refractive index of water for vibrations the frequency of which is less than 100 millions per second, is equal to the square root of the specific inductive capacity — as may be stated with the highest degree of certainty, hitherto attained. If this certainty seems insufficient, the method may be improved according to what has been said on pag. 2; in the other case we should consider as the most accurate value of the refractive index, as well as of the spec. induct. capacity, the one obtained by the statical method.

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[1]) l. c.

22

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

N°. 22.

Dr. P. ZEEMAN. Measurements concerning the Absorption of Electrical Vibrations in Electrolytes.

(*Translated from:* Verslagen der Afdeeling Natuurkunde der Kon. Academie van **26 October 1895.** p. 148—152.)

Dr. P. ZEEMAN. Measurements of the Absorption of Electrical Vibrations in different Electrolytes.

(*Translated from the same:* **30 November 1895.** p. 188—192.)

EDUARD IJDO — PRINTER — LEIDEN.

Dr. P. ZEEMAN. *Measurements concerning the Absorption of Electrical Vibrations in Electrolytes.*

On the occasion of our joint investigation, the results of which were communicated to the Academy last month 1), Prof. Cohn of Strassburg proposed me to verify Maxwell's theory as to one of its consequences on the propagation of electrical oscillations in conductors, according to the following scheme:

The oscillations are absorbed in the conductor. The magnitude of the absorption is determined generally by the *conductivity* and the *specific inductive capacity* of the conductor, and by the *frequence* and the *logarithmic decrement* of the vibrator. If, the frequency being given, and the spec. induc. capacity being known approximatively, one chooses the conductivity high enough, it is possible to diminish indefinitely the influence of the specific inductive capacity. Now electrolytes of so high a conductivity were to be examined, that of their two electrical constants, only the easily measured conductivity was of importance. Frequency and logarithmic decrement of the oscillator were to be determined by Bjerknes's method. Further the diminution of the energy of the vibrations in the electrolyte was to be

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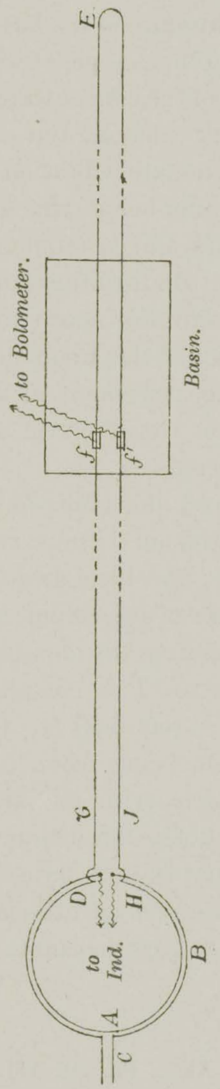
1) Cohn and Zeeman. Verslagen Kon. Akad. Amsterdam. Zitting 28 Sept. 1895. Communications etc. nº. 21.

measured by moving along two parallel wires in the interior of the fluid little Leyden jars, transferring the energy to a bolometer. The general course of the absorption, determined in this manner, was to be compared with the one calculated according to MAXWELL's theory from the three mentioned data.

I have now commenced this investigation in the Physical Laboratory of Leiden. The favourable results obtained by the method as described in the above mentioned publication, led me to think that it would be suited immediately for the investigation of the absorption. In this respect however the result did not answer to my expectation.

Nevertheless I found it possible to maintain the following: 1°. measuring in separate experiments the wavelength and decrement of the vibrations in air, 2°. measuring the energy with *little Leyden jars in the fluid.* But for the rest I was obliged to modify the disposition of the experiments. The preliminary determination of the coefficient of absorption for Hertzian vibrations in an electrolyte seems to me to be of sufficient interest to communicate it already now.

2. *Method.* The disposition of the experiments is given in the subjoined figure. *B* is an oscillator of BLONDLOT, to which a RUHMKORFF was used as induction coil. The primary of the coil was interrupted by a rotating commutator. The interruptor had been fastened at the axis of an electromotor. The frequency was 2400 per minute. The regularity of the vibrations exceeds that which is obtained by means of the Foucault-interrupter. The double-wire circuit *A H J E G D*, along which the Hertzian waves are allowed to propagate, is



made of wires about 1 m.m. in diameter, the distance of the wires being 7 cm. According to BJERKNES's principle between A and the basin containing the electrolyte, are about 60 M. of the wires, and the double-wire circuit, being run through the basin, still continues for about 34 M. and is closed at *E*. *f* and *f'* are the little Leyden jars (6 turns of very fine wire), which are connected with the bolometer [1]) and by which the energy *in the electrolyte* is measured. They are attached to a frame work which is moved easily along the wires. The position of the tubes is to be read on a scale at the border of the basin.

The length of the wires was chosen in accordance with BJERKNES's principle. The wave train generated by the vibrator, being partially reflected from the surface of the electrolyte, returns to *A* only when the oscillations of the vibrator have died away. There is *no bridge* at the surface of the electrolyte, contrary to the experiments with pure

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[1]) Communications l. c. pag. 6.

water [1]). In this manner the oscillations of the vibrator are undisturbed by the presence or absence of the basin.

That part of the train which is *not* reflected penetrates *into the basin.* By a suitable choice of the concentration of the electrolyte may be obtained, that at the end of the basin the energy of a determinate vibration is completely absorbed. That vibration, not being reflected, will pass only once by the little jars and no standing waves of the given period will occur. On the other hand the absence of a special stationary vibration shows that the energy, belonging to the vibration of this frequency, is really absorbed at the end. The measurement of the *wavelength* and the *decrement* of the vibrations *in air* I made according to BJERKNES's precepts. [2])

Of course the basin is then removed and a horizontal part of the circuit (10 M. in length in our case) serves for the displacement of the bridge; the little Leyden jars (6 turns) take the place of BJERKNES's electrometer.

The curve of interference resulting from the measurements was a fine damped sinuscurve. The complete wavelength of the incident vibrations was 6.40 M., the logarithmic decrement, γ of BJERKNES, being 0,34.

The measurements in the electrolyte with the little jars were taken for successive positions, the distances between them being 2.5 cM. At every turn 2 series of these observations were taken; in the one the little jars were moved away from the oscillator, in the other up to it.

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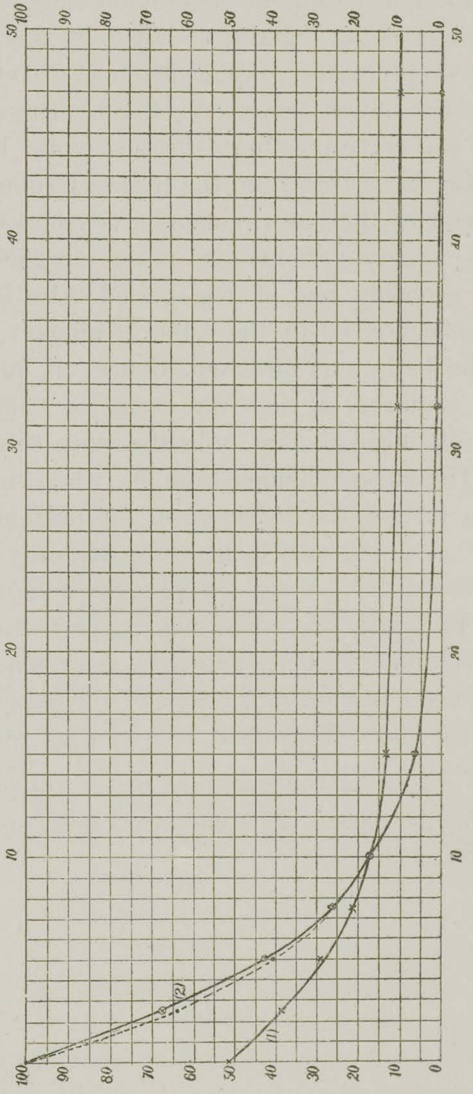
[1]) Communications l. c. pag. 6.

[2]) BJERKNES, Bihang till K. Sv. Vet. Akad. Bd. 20. Afd. I. n°. 5. p. 7. 1895.



3. *Result.* For a solution of common salt, the conductivity being $\lambda = 3200.10^{-10}$ that of mercury, the results are represented graphically in (1). The abscissae represent the layer traversed of the electrolyte, the ordinates the corresponding deflection of the bolometer.

The latter is derived from the mean of 3 double-series. At the end of the basin remains a constant deflection, due to a superponed motion of the electricity in the vibrator, probably one of long period. Also *behind* the basin a deflection about the same in amount as at the end of the basin was observed. Hence, till further evidence is acquired, it does not seem too bold a procedure, to diminish all the ordinates with this constant amount. The curve obtained from (1), when this is done and when further the deflection at the beginning is put 100, the other values being proportionally reduced, is represented in the fig. by (2). The following table contains the data on which the curve is founded. In the first column has been entered the thickness of the traversed layer in cm., in the second the reduced deflections, in the third the values derived from the formula $100. e^{-2pz}$, z being the thickness of the traversed layer and p being $= 0.0884$. This curve has been represented by the dotted line.

Traversed layer.	Observed deflection.	Calcul. deflection.
0	100	100
2.5	67	64
5	42	41
7.5	26	27
10	17	17
12.5	11	11
15	7	7
31	1	0
47	0	0

Hence it would follow: 1°. that the intensity of the vibrations, travelling through an electrolyte, decreases within the limits of the errors of measurements, in the logarithmic ratio; 2°. that the vibrations now used decrease to $^1/e$ their initial intensity, when they travel through a layer of 5,7 cm. of a solution of common salt, the coductivity of which is $\lambda = 3200.10^{-10}$. This, I believe, is the first measurement of a coefficient of absorption for electrical vibrations. It is hardly necessary to mention that the above demonstration is far from complete and especially that the supposition concerning the constant deflection requires further investigation. However I intend soon to investigate the subject more closely, and to consider at the same time the agreement between the value of p, deduced from theoretical considerations, with the observed one.

Dr. P. ZEEMAN. *Measurements of the Absorption of Electrical Vibrations in different Electrolytes.*

1. For the determination of a coefficient of absorption of electrical vibrations in an electrolyte, communicated to the Academy last month [1], I was obliged to postulate, that it is allowed [2] to diminish the deflections of the bolometer with the constant amount observed at the end of the basin. It would certainly require considerable labour to demonstrate that this supposition was really permitted.

However I succeeded in arranging the experiment in such a manner that considerable perturbations were excluded and I could make disappear almost completely the mentioned constant deflection at the end of the basin. Now the energy, at the end of the basin is really quite absorbed. [3]

It appeared to me, that there are several causes capable of producing such a constant deflection, to wit 1°. insufficient polishing of the balls between which the spark passes; 2°. too great viscosity of the isolating fluid used; 3°. great resistances in the wires connecting the induction coil with the balls; 4°. capacity in these wires; 5°. conductors attached to LECHER's wires; 6°. induced currents in the wires connecting the little jars with the bolometer.

In my experiments 1 and 2 were the chief disturbing causes.

As soon as this had appeared to me, it was easy to avoid these errors. As for the rest the disposition of the experiments remained the same as described in the preceding communication.

2. For a solution of common salt of about the same concentration as that used earlier, I have again, under the more favourable circumstances, measured the absorption. The results are in accordance with those found on a former occasion. However the results now found are of more importance, not only because of the improvement (1), but also on account of the improved technics of the method of observation.

It appeared to me of some interest to compare the absorption of a solution of chloride of natrium with that of another of the same conductivity. I have chosen for that second solution one of sulfate of copper

Both the solutions were of a conductivity 3340.10^{-10} that of mercury, the temperature during the observations being $\theta = 18^{\circ}.0$.

The following table, relating to the observations on copper sulfate, may serve as an example of the experiments.

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[1] ZEEMAN. Verslagen Kon. Akad. Zitting 26 October 1895. This Communication. pag. 3.

[2] l. c. pag. 8.

[3] l. c. pag. 6.

Traversed layer.	Observed deflection.			Mean.	Deviation from mean.		
0	47	47	47	47	0	0	0
2.5	27	30	27	28	− 2	+ 2	− 1
5	16	24	17	19	− 3	+ 5	− 2
7.5	14	10	15	13	+ 1	− 3	+ 2
10	7	11	9	9	− 2	+ 2	0
15	0	7	5	4	− 4	+ 3	+ 1
20	3	0	2	1.7	+ 1.3	− 1.7	+ 0.3
47	0	0	0	0	0	0	0

The second column contains the deflections, observed in 3 series, of the bolometer, the third the mean of the deflections, the fourth the deviations from the mean. Altogether 18 series of observations were made with copper sulfate. In order to point out that by combination of the observations the accuracy is increased, I have combined the result of 6 series and I have again compared the 3 series, obtained in this manner, with their mean. This mean may be considered as representing the result for copper sulfate.

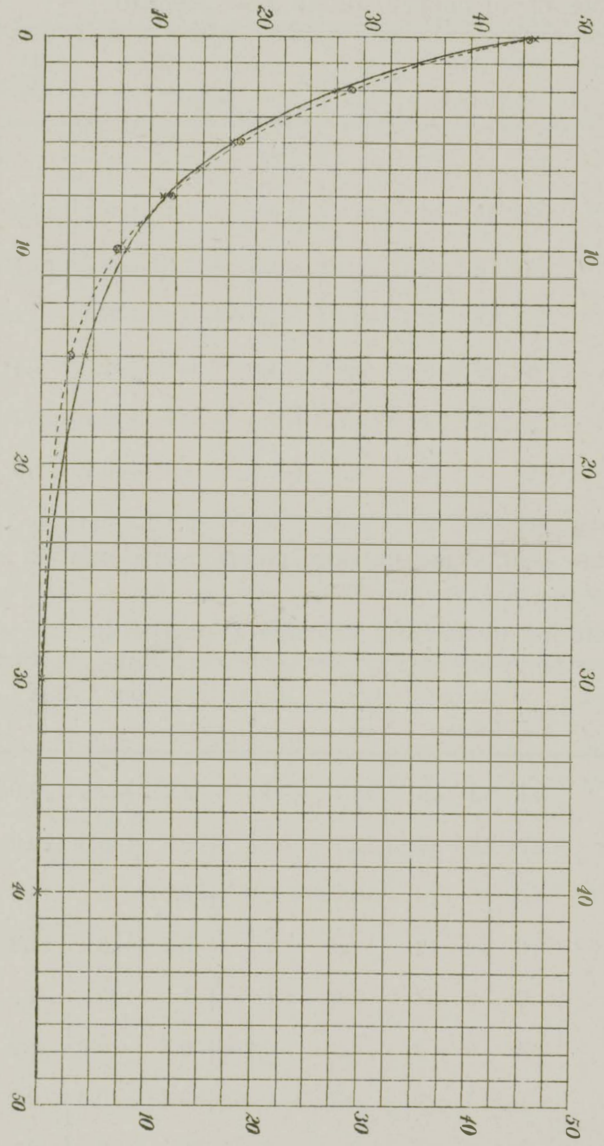
Solution of copper sulfate $\lambda = 3340.10^{-10}$.

Traversed layer.	Observed deflection.			Mean.	Deviation from mean.			Calc.	Observ. —calcul.
0	47	47	47	47.0	0	0	0	47.0	0
2.5	30	28	30	29.3	+ 0.7	− 1.3	+ 0.7	30.0	− 0.7
5	16	18	18	17.3	− 1.3	+ 0.7	+ 0.7	19.1	− 1.8
7.5	11	13	12.5	12.1	− 1.1	+ 0.9	+ 0.4	12.2	− 0.1
10	8	9	10	9.0	− 1.0	0.0	+ 1.0	7.8	+ 1.2
15	6	4	4	4.7	+ 1.3	− 0.7	− 0.7	3.2	+ 1.5
20	2	0	2	1.3	+ 0.7	− 1.3	+ 0.7	1.3	0
47	0	0	0	0	0	0	0	0	0

The results for natrium chloride are entered in the same manner.

Solution of natrium chloride $\lambda = 3340.10^{-10}$. $\vartheta = 18^{0}.0$

Traversed layer.	Observed deflection.			Mean.	Deviation from mean.			Calc.	Observ. calcul.
0	46	43	48	45.7	+ 0.3	− 2.7	+ 2.3	46.0	− 0.3
2.5	27	28	28	27.7	− 0.7	+ 0.3	+ 0.3	29.0	− 1.3
5	16	20	18	18.0	− 2.0	+ 2.0	0	18.3	− 0.3
7.5	10	12	12	11.3	− 1.3	+ 0.7	+ 0.7	11.6	− 0.3
10	7	9	8	8.0	− 1	+ 1	0	7.3	+ 0.7
15	4	5	4	4.3	− 0.3	+ 0.7	− 0.3	2.9	+ 1.4
31	0	1	0	0.3	− 0.3	+ 0.7	− 0.3	0.2	+ 0.1
47	0	0	0	0	0	0	0	0	0



The general course of the deflections appears to be the same for the two solutions within the limits of the errors of the observations. In the fig. is given the curve for common salt. The dotted line represents the formula $46.e^{-2pz}$, $p = 0{,}092$ being the value most closely approaching the observations. In order to make it clear how far goes the representation of the observations by the exponential formula, I have entered under »calculated", the computed values and in the last column the deviations from the observed deflections. The yet remaining deviations surpass a little the limit of the errors of observations and therefore require further investigation.

In order to avoid confusion in the figure the observations relating to copper sulfate are not graphically represented. They are represented in the same manner by $47.e^{-2pz}$, p being $= 0{,}090$. Hence the values of p calculated in this manner are the same in the two cases within the limits of the errors of observation. If other salts offer no deviations, we have for Hertzian waves in dilute aqueous solutions the law: *solutions of equal conductivity absorb in the same manner vibrations of the same period.*

Prof. COHN [1]) has already remarked that for the vibrations which constitute light, there does not exist such a law. The great difference existing between the absorption of light- and electrical-waves, may also be expressed in another way. According to the theory of electrolytic dissociation dilute solutions containing

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[1]) COHN. Wied. Ann. Bd. 45, pag. 59. 1892.

aequivalent quantities of a coloured ion absorb equally strongly the light of this colour. This is confirmed by Ostwald's experiments. Aequivalent solutions of different combinations however may have *totally different* conductivities, hence the different behaviour of solutions with respect to the two kinds of vibrations is evident.

3. By the value of p and the data given in our last publication, sufficient data are known, to compare the observed absorption with that derived from theory. It is proposed to return to the subject on a future occasion.

The results obtained till now may be summed up as follows:

1. The intensity of electrical vibrations travelling through a layer 5,1 cm. in thickness of a solution of common salt, the conductivity of which is $\lambda = 3340.10^{-10}$ that of mercury decreases to $^1/e$ of the original value. This result is now independent of a supposition necessary in my last communication.

2. In dilute solutions of equal conductivity vibrations of the same period are equally absorbed. cf. § 2.

23

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 23.

Dr. H. KAMERLINGH ONNES. Remarks on the liquefaction of hydrogen, on thermodynamical similarity and on the use of vacuum vessels.

(*Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen.* **25 Januari 1896.**)

Eduard IJdo — Printer — Leiden.

place pressure, surface, volume, temperature (kinetic energy of the centrum of a molecule), energy of the molecular forces, together with the quantities derived from these like coefficient of dilatation, isothermic compressibility, isothermic surface tension etc. Further viscosity and conduction of heat by the progressive motion of the molecules.

We will now consider the quantities which occur when production of work is accompanied by change of temperature. The change of temperature in these cases depends on the quantity of heat that can be given out by the molecule. In the demonstration of the theorem mentioned above only the kinetic energy of the centre of mass of the molecule is taken into account. An adiabatic change of temperature will therefore only take place with two substances in a corresponding manner, if in both cases the same proportion exists between the kinetic energy of progressive motion of a molecule and the total energy contained in it. Otherwise expressed: the number of degrees of freedom (the number of atoms in the molecule) must be the same to make heating and cooling go on in corresponding manner. For normal substances with the same number of atoms in the molecule the corresponding states are at the same time thermodynamically corresponding.¹) A

classification of the substances in groups according to the number of atoms in the molecule is therefore very suitable.

That the number of atoms in the molecule influences the adiabatic phenomena appears very elegantly from the calculations made by v. d. Waals in 1878.¹) As early as that v. d. Waals indicated that the superheating of ethervapour when adiabatically expanded, contrary to what happens to watervapour, is to be ascribed to the great number of atoms in the ethermolecule. He further pointed out that the formation of visible vapour say by oxygen in the tube of Cailletet, regarded by many scientists as an obvious consequence of oxygen being liquefiable, could only take place to such extent, because this possibility coïncides with a very limited number of atoms in the oxygen molecule.

From the considerations developed above on the thermodynamical similarity or non similarity of normal

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¹) Riecke (Ann. d. Phys. und Chem. 53 p. 388, 1894) has introduced in the entropy and the thermodynamic potential, calculated from the isothermal of v. d. Waals the reduced values of pressure, volume and temperature and remarks that there remain functions of the indivudual properties of substances in the thermodynamic potential. If according to a friendly remark of prof. Lorentz as zero of entropy is taken the entropy in the critical state, then Riecke's formulae also give for all substances with the same number of atoms in the molecule the same functions of reduced pressure, volume and temperature for the entropy and the reduced thermodynamic potential or what comes to the same, Riecke finds the surface of Gibbs expressed in the reduced quantities the same for all substances with the same number of atoms in the molecule. For the calculation of the reduced thermodynamic potential the energy has to be reckoned from the critical state and the thermodynamic potential to be divided by the critical temperature.

The deduction given above is independent of the special form of the isothermal.

¹) v. d. Waals, On specific heat of saturated vapour. Versl. en Med. d. Kon. Akad. Amsterdam, 1878.

substances the inference is obvious that the reserving point of the sign of the specific heat of saturated vapour will not be found in general at corresponding temperatures in different groups of substances.[1] According to a friendly communication by prof. v. d. Waals, this consequence as well as the whole consideration of thermodynamically similar and non similar states, were given by himself in his lectures a long time ago. /v /s

But let us return to the thermodynamically corresponding substances. If two such substances are brought in corresponding engines and if these engines are set in motion with corresponding velocities, then they will run correspondingly as long as there is given off a corresponding quantity of heat in the corresponding times by the walls of the machine.

If then in a model, working with oxygen, after a given time a given volume of liquid oxygen is obtained, there will be obtained in the corresponding hydrogen apparatus after the corresponding time a corresponding volume of liquid hydrogen.

There are some difficulties in the application of this rule to an actual apparatus. For instance gravity is no corresponding force for two substances in corresponding states. The mutual accelerations by the effect of the molecular forces of two pairs of molecules of substances in corresponding states when these pairs of molecules are in conform situations will be expressed for each pair by the same number, when measured with the unit of acce-

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[1] In opposition to the hypothesis of Natanson, Bull de l' Acad. d. Sc. de Cracovie, 1895, p. 141.

leration proper to the system. But the acceleration of gravity will in general be represented by different numbers, when measured in the two cases by the said units and the similarity in the motion will be disturbed. The theorem therefore can only strictly be applied if the influence of gravity (and accordingly also the influence of convectional transport of heat) is to be neglected.

The condition of heat by the motion of the atomes in the molecule is a non similar process to which we wished to draw the attention on pag. 5 by speaking of that conduction that takes place by the progressive molecular motion only. /uc

And lastly it will not be possible in general without special artifices to obtain walls of such conductive power and such specific heat, that these can give off corresponding quantities of heat in corresponding times.

Still with these restrictions it can be of use in the questions we have in view to consider the gas in the machine as part of the machine itself.

An important example of thermodynamically corresponding operations gives the method sagaciously devised by Olszewski for the determination of the critical pressure, which enabled him to find the long sought for critical constants of hydrogen[1] with extremely small appliances — probably less in different respect, than those which are at my disposal.

4. The method by which I intended to reach the low temperatures necessary for the liquefaction of hydrogen, relied upon the possession of the permanent liquid oxygen

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[1] Bullet. Intern. Cracovie 1891. S. 192, 1895 Juin, S. 192.

bath. When hydrogen is expanded in a tube of CAILLETET the low temperature exists for a moment only in reason of the extremely small water equivalent of the compressed gas in comparison with that of the walls of the vessel in which it is enclosed. Repeated expansions with continuously supplied fresh quantities of hydrogen, cooled in the oxygen bath, as can be realised in a motor, will make the temperature of the walls fall, until the hydrogen is streaming out at a temperature nearly in accordance with the degree of expansion chosen. I wished to hasten and to continue this process by cooling the supplied hydrogen with the blown off hydrogen. What the problem comes to therefore is: to withdraw in a given time a maximum of work from a gas with the aid of a motor of minimum volume and to insert this motor in a regenerative process. I supposed that a solution of this problem might be arrived at in the following manner.

The compressed and cooled hydrogen is conveyed by a copper coil to a little, fast running motor (0,1 Liter volume of cylinder) driven by the hydrogen. The inner wall of the cylinder and the piston are coated with isolating substances. The piston in the case of a double acting and the plunger in the case of a single acting motor is ground accurately in the cylinder and moves therein without friction.[1]) The expansion is regulated by valves, moved by rods, working without conduction of heat and the packings of which are out of reach of the

cold, in the same manner as the packings of the non conduction stopcock in my oxygen boiling glass (l. c. § 8).

The packings of the piston-rod or plunger are isolated in a similar manner from the walls of the cylinder and are removed from the working gas by prolonging tubes. The shaft and gearing which must take work from the engine if the latter will run properly, is isolated from the working parts. The exhaust-hydrogen is lead away round a second copper hydrogen-supplying coil provided at the end with a cock, and escapes through an india rubber tube which encloses both coils.

In the first place the difficulties of mechanical kind were to be overcome. In order to study the mechanical working a little motor with regenerative coil had to be made, that would cool itself, working with compressed air.

The coils in an isolating cover for the exhange of heat 7ch were easily made, and also a wooden cylinder with piston was connected with a shaft and gearing, very imperfect indeed, in order to try the experiment, but the experiment has not been carried out. Friction of the piston could not be avoided without considerable leaking. The only possibility in this respect which remained was to run the motor very fast, and this the gearing did not admit. But especially I did not succeed well in regulating the expansion. Since the beginning of 1892 I have consulted different constructors in order to obtain a self cooling motor, or otherwise a motor for working under ordinary circumstances with 10fold or even 5fold expansion by valves and with a cylinder volume of 0,1 Liter, in order to work out after this example a self cooling motor, fit for the laboratory. But I have not succeeded in obtaining such an engine.

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[1]) A similar contrivance has been executed in the case of the auxiliary compressor (l. c. § 3) and satisfies well.

If a little self cooling motor could be made after my design (and then of course easily also a cascade) it would become an important appliance for laboratories, for compressed air can be easily stored 1) and will probably soon become a cheap article of trade.

It appears now that Solvay before me developed the idea of a self cooling motor from an industrial point of view, but has no more arrived to a satisfactory result, though he obtained temperatures (—95°) very desirable for a laboratory.

If we suppose the fall of temperature obtained by Solvay to be further extended in the direction of the lower temperatures, it has to be taken into account also that the regenerative process will become more defective as the gas approaches the critical state. In general only *a cascade of theoretically perfect cooling apparatus* will prove able to withdraw at extremely low temperatures quantities of heat, that come in comparison with those, which we might deduce from the work spended, when utilized in a reversible cycle.

If we suppose that we have also taken up in this cascade evaporating fluids, the motor mentioned is again required in the character of the »Speise cylinder" to which attention was drawn by Zeuner many years ago. Indeed this Speisecylinder serves to neutralize the theoretically important loss that occurs, because in a circulation of evaporating liquid, the jet of liquid coming from the condensator enters by a regulation valve into the refrigerator where a much lower pressure prevails. With a cascade such as has been brought about at Leiden this disadvantageous deviation from the theoretical process repeats itself in every circulation. Oxygen gives in this case the most important factor in the product.

The problems treated in this § without doubt will more and more occupy practical engineers and perhaps the preceding remarks may be of some use in the repetition of experiments in the manner of Solvay. If an apparatus for liquefying oxygen according to this principle has been found, the theorem of § 3 gives the corresponding hydrogen apparatus.

For collecting liquid hydrogen according to the expansion principle there remains provisionally the following method. We have to introduce into a cylinder with piston or plunger (for which purpose a thick walled tube as used by Wroblewski and Olszewski in liquefying oxygen may be used) compressed hydrogen by the aid of handworked cocks, and to blow it off through a regenerator after sufficient expansion. For the supply of hydrogen the well known steel capillaries may be used (Cf. l. c. § 3). The thick walled expansion tube ought to be protected against supply of heat by a narrowly enclosing vacuum tube of Dewar as I have prepared for similar purposes.

5. After the difficulties I met with in the execution of the project of a self cooling motor treated in the preceding §, it was quite natural to ask as soon as the ingenious invention of Linde became known, whether this method could be applied to the liquefaction of hydrogen.

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1) Than especially in view in this respect the so well adapted Brotherhood compressors (l. c. §10).

In Linde's method[1] gas flows from a compressor under high pressure along a regenerative coil and through a reducing valve where it does work against the molecular forces and is accordingly cooled, and then returns by the regenerative coil to the compressor.

The part that in my project and in Solvay's apparatus is played by the motor, in Linde's apparatus is taken by the reducing valve.

Theoretically this gives a loss. The use of the reducing valve has the effect that power is sacrificed that could have been used for cooling. If afterwards it will be sought to make in the method of Linde the loss by friction as little as possible, one will come to the addition of a motor as treated in § 4.

Theoretically the regenerator of Linde's apparatus also is defective by the very nature of the molecular forces as will be further elucidated at the end of this §. So far as I can form an opinion on the method of Linde, in order to make the regenerator a perfect one, there would have to be added to Linde's apparatus a cooling machine, withdrawing at every temperature as much heat from the supplied gas, as it must give off between two temperature grades more than the gas flowing back can take in. But the case of liquefying hydrogen the utmost compendiousness of the apparatus is of the greatest importance and to friction and non reversible transfers of heat may be sacrificed what is economised on the disadvantageous supply of heat to the apparatus.

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[1] M. Schröter, Linde's Verfahren der Sauerstoffgewinnung mittelst verflüssigter Luft. Ztschr. d. Ver. deutscher Ingenieure 28 Sept. 1895. Bd. 39; 1157.

The most important question is without doubt this one: are the molecular forces on which the experiment of Joule and Thomson and therefore also the method of Linde depends, sufficient to get noticeable cooling by the flowing through the reducing valve and to give within a not too long interval of time the wished for low temperature. Under ordinary circumstances these temperature variations are very small for hydrogen. At ordinary temperature and at 90° Joule and Thomson in their 1862 experiments found even a heating effect. In fact if in the formula by which v. d. Waals in 1873 first calculated the variations measured by Joule and Thomson (v. d. Waals, Continuity etc. p. 110) are substituted the values of the molecular constants given else where in the same work, a negative value is found for the cooling. When all this is correct, then a Linde apparatus put in working with hydrogen under ordinary circumstances far from giving a cooling would give a progressive heating of the gas streaming through the reducing valve.

But if one will form an opinion of what happens if hydrogen is brought at low temperatures into the apparatus, one must take into account the variation of the molecular effects with temperature. In view of these changes v. d. Waals has given a new value for the molecular attraction instead of the original constant value, namely $a_k \, e^{\frac{T_k - T}{T_k}}$ where a_k again is a constant, T the absolute temperature of the substance in question, so that a increases when the temperature decreases.

In fact the theory of the dynamical similarity of corresponding states (§ 3) includes that the molecular energy in all normal substances varies with great approximation in corresponding manner with temperature. According to this theorem we shall find with hydrogen at lower temperatures the normal behaviour in the experiment of JOULE and THOMSON. Hence according to the 1862 experiments there must be a reversing point in the phenomenon of JOULE and THOMSON from which follows that this must occur with all normal substances at the corresponding i. e. a sufficient high temperature. Further we have to expect with hydrogen at sufficiently low temperatures a relatively great molecular potential energy, so that we have to expect a sensible cooling in the experiment of JOULE and THOMSON and therefore also a good working of the LINDE apparatus.

As soon as I became acquainted with LINDE's original method, it therefore seemed to me that it gave the appropriated method to liquefy hydrogen. The hydrogen liquefied in this manner can be taken off from the apparatus into a boiling glass like that described l. c. § 8.

From OLSZEWSKI's critical data for hydrogen and from the theorem of § 3 follows, that if we can dispose in a LINDE apparatus of hydrogen supplied at a temperature of — 210°, an apparatus, operating with oxygen cooled to — 20° can be used as model to study the most economical working. To this apparatus in 2.33 units of time the same number of oxygen molecules must be supplied that we intend to supply to the hydrogen apparatus in the unit of time. In the hydrogen apparatus the pressure can be 2.54 times less and the inner

dimensions can be 1.164 times less than they are in the oxygen apparatus. In a given interval in the hydrogen apparatus a volume of liquid hydrogen will be obtained 1.58 times less than the volume of liquid oxygen produced in the model in a 2.33 times longer interval.

We did not have to take special notice of the law of variation of the molecular energy with the temperature as long as we were treating the question if LINDE's method is fit to be used in liquefying hydrogen. If we are satisfied with the working of the oxygen model, we shall also be content with the corresponding hydrogen apparatus. As the first finds its application now in industry, the last may perhaps soon be admired by us.

It is another question in how far we may be satisfied from a theoretical point of view with our model working with oxygen, apart from the reducing valve, that has been treated already. To judge in how far the regenerator in LINDE's apparatus deviates from a perfect regenerator the law of variation of molecular energy with temperature is a most important factor. Indeed this variability will reveal itself in the difference of specific heat at different pressures increasing with decreasing temperature, a given weight of returning gas, being under low pressure between two temperatures giving off less heat than the same quantity of supplied gas under higher pressure requires to undergo the temperature-changes between the same temperatures in reversed direction. When the liquefying apparatus has come to stationary working conditions there must be cooled beside a quantity of supplied gas equal to the returning quantity so much fresh gas as is poured out in liquid state from the apparatus. And for this cooling is only disposable the gas returning from the second apparatus wherein the liquid has been poured out, which gas is again at a lower pressure and gives consequently a greater deficiency of the regenerative process. The increase of the molecular potential energy with decreasing temperature, which in one respect promotes the success of LINDE's method by increasing the THOMSON-JOULE-effect, in another respect therefore necessarily lessens the output of liquefied gas by increasing the deficiency of the regenerative process at decreasing temperatures.

An essential part of LINDE's method is that for saving power the gas is only a little expanded and that in view of this saving the most advantageous beginning and finishing pressure have been sought for. A process with the second power of this expansion can be considered as two successive processes of LINDE in which the second and also therefore the total is less advantageous than the first. The process with expansion until the gas has the ordinary atmosferic pressure, which is used in LINDE's oxygen apparatus, is therefore very disadvantageous. If we start in this less appropriate manner with the same disposable power and the same liquefying apparatus as we had in view before, we shall have to wait much longer before we get liquid. Accordingly we have to take more care to prevent that heat finds its way to the apparatus.

6. DEWAR beginning with much higher pressures than LINDE expands in his spray the condensed gas immediately until it has the ordinary pressure. By going further in the wasting of power disposable for cooling

than LINDE even in his oxygen apparatus he departs yet further from the theoretically most favourable cooling process. But the water equivalent of his apparatus divided by the waterequivalent of the quantity of gas passing in the unit of time being much smaller he proceeds in this manner in order to get for a little part of the substance in a very short time an extreme lowering of temperature.

In my boiling glass just as in DEWAR's apparatus the supply-coil has a cock at the end and is wound round the cock-supporter. This part of my apparatus is also immersed in the gas flowing away (l. c. § 8). What is blown away from the jet as liquid and mist serves to cool the supply coil and further to take away heat, that would otherwise find its way to the bath of liquid oxygen. But in the supply-coil the oxygen is already in liquid state. As soon as no more liquid issues from the needle regulating cock, this cock is shut (l. c. pag. 178) and this is done in order to avoid wasting of gas as much as possible. In previous constructions of my boiling glass, I had supply-coils of greater cooling surface immersed in the gas flowing away for the sake of making a liquid jet with gas cooled to little below the critical temperature or even to temperatures in the neighbourhood of the critical. It proved more effective for the construction of the permanent liquid oxygen bath, to reckon upon the oxygen being intensely cooled before it is tranported to the boiling glass. The spiral was therefore shortened to only such length as seemed necessary to catch the liquid blown away and to utilize the evaporation ot this liquid to cool the adducing coil. Dewar on the contrary has not been discouraged by the less economical employment of gas and armed with his vacuum vessel that leaves the returning gas wholly disposable to cool the coming gas has directed his attention exclusively to the lowering of the temperature.

He succeeded in this manner even in freezing oxygen by means of his hydrogen-spray, a splendid outcome of his prosperous researches.

Let us apply the theorem of § 3 also to the experiments of Dewar. Dewar proceeds indeed according to this theorem as far as the choice of the temperatures is concerned. The apparatus giving by means of a spray a sufficient quantity of liquid oxygen, can serve as the model to build an hydrogen apparatus. The same ratios as those, which we have given in treating the Linde liquefying apparatus are applicable here for the choice of the dimensions, pressures and temperatures. The percentage of the hydrogen used, that will be reduced to the liquid state after a certain time, will be the same as the percentage, that after a 2.33fold longer time becomes liquid in the oxygen model.

The theorem of § 3 may not be applied to the quantity of liquid that will be collected on the bottom of a corresponding vessel. For the acceleration of gravity is expressed in the system of units derived from the molecules by a 3.43 times greater number in the case of oxygen than in the case of hydrogen, and one would have to go with the oxygen model to a place where gravity was 3.43 times less, to deduce from the quantity of liquid that collects in that case on the bottom, how much we may expect with hydrogen in the ordinary circumstances. It is obvious that the oxygen spray under these circumstances would give off liquid oxygen with more difficulty. It will therefore probably be necessary to give the compressed hydrogen the opportunity to liquefy in a special cylindrical or coil shaped vessel under the cooling effect of the spray. This liquid may then flow out under less pressure than the spray into a vessel, constructed in the main part as the boiling glass with boiling case, described by me for liquid oxygen (cf. l. c. § 8). In this boiling case the regenerative coil would find an appropriate place [1]).

7. In the same degree as it becomes of more importance to effectuate adiabatic processes at very low temperatures, the importance of the vacuum vessels of Dewar will increase. It seems to me that they are the most important addition since 1883 to the appliances for low temperature research.

The perfection of these vacuum jackets was again made evident in the experiments treated in the preceding §.

The vacuum jackets make it easy to work with liquid oxygen in a different room from where the cryogenic apparatuses are placed and enable one to do this even in other laboratories. On one occasion when paying a visit to show the properties of liquid oxygen, I took a vacuum vessel filled with liquid oxygen with me in my hand and after returning to the laboratory there was a rest of liquid oxygen left which I could pour

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[1]) To liquefy hydrogen it appears from a communication of Ramsay that Olszewski has cooled a little quantity by the expansion of another quantity.

again into my boiling glass. To transport liquid oxygen from my boiling glass into a vacuum glass, a little glass bucket is used, hanging from a glass rod, that can be pushed up and down through an india rubber stopper, fitting on the boiling glass. In withdrawing the bucket this stopper is replaced temporarily by another.

In many cases vacuum jackets can also be used to improve the construction of my boiling glass in making the evaporation of the bath less still than it is without this appliance. I have prepared for this purpose a cup shaped vacuum vessel just fitting round the lower part of the boiling glass, where the liquid gas is accumulated. Only when measurements are to be made exclusively across parallel walls, this auxiliary appliance is of no avail. (l. c. § 8.)

In § 4 I mentioned the application of a vacuum vessel in the form of a long double test tube to furnish a thick walled tube with a vacuum jacket.

Even if the vacuum glasses are not prepared with the same painful care as the most beautiful ones of DEWAR have been, they are apt to render great services. To judge of this it is sufficient to consult the table of KUNDT and WARBURG in their research on the conduction of heat in high vacua [1].

To isolate objects of greater size, one can pile up straight, egg-shaped, ring-shaped or otherwise shaped exhausted and sealed tubes of convenient dimensions (incandescent lamp glasses) and unite these by parafine, wool, paper and varnish as shape giving substances in order to get continuous walls preventing convection. In this manner vessels of arbitrary form and bulk can be built up, with very badly conducting walls of very little water equivalent the cells of which consist of vacuum tubes. These walls recall the covering, that protects my ethylene boiling flask. (l. c. § 2.)

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[1] Monatsber. Kön. Akad. Berlin, 25 Febr. 1875, pag. 171.

If it is wished to have an exhausted space between two metal walls isolated from each other, it may be profitable to build the walls that are to be isolated with strengthening ribs in the manner followed in the construction of the very thin walled ethylene boiling flask (l. c. § 5) and oxygen boiling case (l. c. § 8.).

It is a rejoicing prospect that practical engineers will doubtless soon feel the want of such non conducting mantles. For as soon as this stage is reached number of heads and hands are disposed to take over the problem from the scientific researcher.

24

COMMUNICATIONS

FROM THE

PHYSICAL LABORATORY

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

Director of the Laboratory.

No. 24.

(REPRINT.)

Dr. L. H. SIERTSEMA. Measurements on the magnetic rotatory dispersion in gases (*with a plate*).

(*Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam van* **28 Maart 1896,** *pag.* 294).

Dr. L. H. SIERTSEMA. Measurements on the magnetic rotatory dispersion in gases.

(*Translated from the same* **18 April 1896,** *pag.* 317.)

EDUARD IJDO — PRINTER — LEIDEN.

Dr. L. H. SIERTSEMA, *Measurements on the magnetic rotatory dispersion in gases.*

The observations with the apparatus described in the former communications[1]) are continued, and the magnetic rotatory dispersion is measured in nitrogen, carbonic acid and nitrogen monoxide.

The construction of the apparatus and the method of observation have undergone no further changes of any importance. A plate is added of the whole apparatus and some details, as an illustration to the formerly given description.

On this plate Fig. 1 represents the whole apparatus, seen from above. In this figure *A* is the collimator, *B* the smaller nicol-bearer. *C* and *D* the two coils[2]), *E* the greater nicol-bearer, *F* the prism with the telescope, in which the spectrum is observed. The pointing of the smaller nicol is obtained by the screw *G* and the steel-wire *HH*[3]). Fig. 4 shows the handle to which the wire is fixed, seem from the collimator. At *J* (Fig. 1) a weight is hanging at the wire. The rotation of the nicol is measured with the telescope *K*, the vertical glass scale *L*, and the mirrors *M* and *N*.

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[1]) Communications etc. N⁰. 7, 15.

[2]) „ „ N⁰. 7, p. 14.

[3]) „ „ N⁰. 15, p. 18.

Fig. 2 represents the greater nicol-bearer [1]) on a larger scale. The upper part of the figure is drawn in section, the lower part in aspect. In this figure *a* is the nicol, which is held in a ring with adjusting-screws *b*, *c* the glass-plate fixed in the flanges by the nut *d*. The packings are here and at other places indicated by black lines. The gas can enter the apparatus by a tube which is fastened to the nut *e*, and to which also the manometer is connected. *f* is the experimental tube, which is fixed to the nicol-bearer by the nut *g*, *h* is the section of the level on the greater nicol-bearer, *i* are the tubes through which water circulates for equalizing the temperature, *k* the supply-tube thereof with the thermometer *l*. A similar tube with thermometer serves for the outlet of the water. In fig. 1 both tubes are visible. Between the experimental tube and the water-tubes we find a layer of indiarubber.

Fig. 3 represents the smaller nicol-bearer, drawn in the same way as fig. 2. The meaning of *a—d*, *f*, *g*, *i* is the same as in the former figure; *e* is the beam to which the steel wire is fixed (see also fig. 4.)

The wave-length is always determined by a calibration of the spectrum with lines of FRAUNHOFER.

The gases are taken from commercial steel and iron cylinders, and are analysed by HEMPEL's pipetts.

With carbonic acid and nitrogen monoxide only a moderate pressure could be used. Close to the condensing point the image of the slit was too much confused to admit good pointings, a consequence of the great variability of density with temperature. With these gases it became necessary to envelop the ends of the experimental tube and the nicol-bearers in cotton-wool. At these moderate pressures the manometer-readings were found not to be sufficiently accurate. The measurements shall be repeated with better determinations of the pressures; the now obtained results are to be considered as preliminary ones.

Now the method of observation and of calculation shall be explained more detailed.

The measurements of the rotations are always divided in sets of four pointings. At the beginning of each set the direction of the ray of light was corrected. Then the telescope was pointed to that part of the spectrum, at which a determination should be made, and its position read on a divided circle. Then readings were made on the manometer, the thermometers which give the temperatures of the gas, and those from galvanometer and shunt. Hereafter follow four pointings, with current-directions which can be represented by (+ — — +), which pointings are made in this manner, that the black band in the spectrum, which already is made visible by a preliminary turning of the nicol, now by more turning is adjusted exactly on the vertical wire in the telescope, after which immediately the galvanometer is read, and the current is opened. Then follow readings of the zero of the galvanometer, the position of the nicol, and the level. After such a set of four pointings the manometer and thermometers are read again, and then a new set begins with another wave-length.

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[1]) Communications etc. N⁰. 7, p. 12.

At the beginning and the end of the observations the reducing factor of the galvanometer is usually determined, and also the distance of the mirror which serves for the measurement of the rotation of the nicol.

At the beginning of the calculations corrections are added to the four mirror-readings, which determine the position of the nicol, in order to obtain quantities proportional to the rotations, and then corrections for the rotation of the greater nicol, which is measured with the level. When we call the so obtained quantities Φ_1, Φ_2, Φ_3, Φ_4, and the corresponding galvanometer-deflections a_1, a_2, a_3, a_4, it will easily be seen that the two quantities $\frac{\Phi_1 - \Phi_2}{a_1 + a_2}$ and $\frac{\Phi_4 - \Phi_3}{a_4 + a_3}$ ought to be equal, and proportional to the constant of rotation for the given pressure, temperature and wave-length.

These two quantities are therefore calculated, and when they differed more than 2%, which did not often happen, the set was cancelled. Usually they differed less than 1%, and the mean of both was taken. The reducing factor of the galvanometer and the density of the gas were calculated, with due regard to the deviations from the laws of BOYLE and GAY-LUSSAC. Also from the dimensions of the apparatus a preliminary factor was calculated, by which the rotations were expressed in minutes, for unity of length and magnetic force, and for a pressure of 100 KG. pro cM².

In this manner the following numbers were obtained In the first place the measurements with air and oxygen are once more communicated, on account of a better

determination of some constants, which till now were only preliminarily measured.

The wave-lengths λ are expressed in $\frac{1}{1000}$ mM., the rotations n in minutes.

Air (100 KG., $t = 7.°0$). During the observations the pressure was 91.5 KG.

λ	$n.10^6$	λ	$n.10^6$	λ	$n.10^6$
0.678	441	0.519	731	0.445	994
627	508	500	787	434	1038
583	587	477	857	423	1103
549	658	460	924		

Oxygen (100 KG., $t = 7.°0$). Admixtures 1.4%, probably nitrogen. Pressure during the observations 88.5—97.8 KG.

λ	$n.10^6$	λ	$n.10^6$	λ	$n.10^6$	λ	$n.10^6$
0.684	484	0.604	547	0.507	696	0.450	818
667	484	603	542	506	690	446	838
666	485	578	590	505	690	445	840
664	483	578	582	503	698	439	870
660	493	578	580	477	755	433	875
630	515	578	577	477	756	423	922
630	512	578	577	477	760	423	918
630	515	549	624	477	757	423	922
630	516	539	635	460	797	423	926
606	543	538	635	460	803		
604	545	527	653	456	818		

Nitrogen (100 KG., $t = 14.°0$). Composition: N 93.95 %, O 4.80 %, CO_2 1.25 %. Pressure during the observations 90.0—109.2 KG.

λ	n.10⁶	λ	n.10⁶	λ	n.10⁶	λ	n.10⁶
0.656	448	0.583	585	0.517	728	0.431	1069
656	444	554	626	517	723	431	1068
656	440	554	619	486	836	431	1072
643	486	554	624	486	833	423	1102
620	488	543	667	486	821	423	1115
619	496	527	702	477	849	423	1085
619	497	527	705	456	938	423	1110
589	563	527	695	455	950		
589	557	518	732	454	944		
589	554	517	731	436	1033		

From the results for those wave-lengths, which are nearly equal, the means are taken, and with these are calculated formulae for interpolation of the formerly announced form, in which a weight p is given to each number equal to the number of set, from which it is deduced. At the same time the rotations calculated with these formulae are compared with the observed rotations.

Air (100 KG., 7.°0).

$$n.10^6 = \frac{200.2}{\lambda} + \frac{47.68}{\lambda^3} = \frac{200.2}{\lambda}\left(1 + \frac{0.238}{\lambda^2}\right)$$

λ	n.10⁶ Calculated	n.10⁶ Observed	Diff.
0.678	448	441	7
627	513	508	5
583	584	587	—3
549	653	658	—5
519	727	731	—4

λ	n.10⁶ Calculated	n.10⁶ Observed	Diff.
500	782	787	—5
477	859	857	2
460	925	924	1
445	991	994	—3
434	1044	1038	6
423	1103	1103	0

Oxygen (100 KG., 7.°0).

$$n.10^6 = \frac{274.5}{\lambda} + \frac{20.04}{\lambda^3} = \frac{274.5}{\lambda}\left(1 + \frac{0.0730}{\lambda^2}\right)$$

λ	p	n.10⁶ Calculated	n.10⁶ Observed	Diff
0.684	1	464	484	—20
664	4	482	486	—4
630	4	516	514	2
604	4	545	544	1
578	5	579	581	—2
549	1	621	624	—3
538^5	2	638	635	3
527	1	658	653	5
505	4	699	693	6
477	4	760	757	3
460	2	803	800	3
453	2	821	818	3
455^5	2	843	839	4
436	2	871	872	—1
423	4	914	922	—8

If the admixture is supposed to be only nitrogen, we find for pure oxygen:

$$n.10^6 = \frac{275.7}{\lambda} + \frac{19.52}{\lambda} = \frac{275.7}{\lambda}\left(1 + \frac{0.0708}{\lambda^2}\right)$$

Nitrogen (100 KG., 14.°0).

$$n.10^6 = \frac{177.9}{\lambda} + \frac{52.18}{\lambda^3} = \frac{177.9}{\lambda}\left(1 + \frac{0.293}{\lambda^2}\right)$$

λ	p	$n.10^6$ Calculated	$n.10^6$ Observed	Diff.
0.656	3	456	444	12
643	1	473	486	— 13
619	3	507	494	13
587^5	4	560	565	—5
554	3	628	623	5
543	1	654	667	— 13
527	3	694	701	—7
517	4	722	728	— 6
486	3	821	830	—9
477	1	854	849	5
455	3	945	944	1
432	4	1059	1060	—1
423	4	1110	1103	7

For pure nitrogen we find:

$$n.10^6 = \frac{172.5}{\lambda} + \frac{53.45}{\lambda^3} = \frac{172.5}{\lambda}\left(1 + \frac{0.310}{\lambda^2}\right).$$

If we reduce the results for nitrogen to 7.°0 and then calculate the formula for air from those for oxygen and nitrogen, we find:

$$n.10^6 = \frac{198.0}{\lambda} + \frac{47.51}{\lambda^3} = \frac{198.0}{\lambda}\left(1 + \frac{0.240}{\lambda^2}\right).$$

which formula agrees sufficiently with that which was found above.

The observations with carbonic acid, and with nitrogen monoxide lead to the following formulae:

Carbonic acid (1 atm., 6°.5). Pressure during the observations 18.9—24.7 KG.

$$n.10^3 = \frac{284.3}{\lambda} + \frac{87.68}{\lambda^3} = \frac{284.3}{\lambda}\left(1 + \frac{0.308}{\lambda^2}\right).$$

Nitrogen monoxide (1 atm. 0°.0). Pressure during the observations 25.0—32.9 KG.

$$n.10^8 = \frac{228.6}{\lambda} + \frac{68.46}{\lambda^3} = \frac{228.6}{\lambda}\left(1 + \frac{0.300}{\lambda^2}\right).$$

Dr. L. H. SIERTSEMA. *Measurements on the magnetic rotatory dispersion in gases.*

With the apparatus and method of observation, described in the former communications [1]), and in the first part of the present one, the rotatory dispersion is now measured in hydrogen, and the following results are obtained:

Hydrogen (85.0 KG., $t = 9°.5$). Admixtures 1.7 %, without oxygen, which admixture is the most important on account of its small dispersion. Pressure during the observations 77.7—93.7 KG.

λ	$n.10^6$	λ	$n.10^6$	λ	$n.10^6$	λ	$n.10^6$
0.656	370	0.589	472	0.517	606	0.431	896
»	365	0.555	527	0.486	683	»	898
»	362	»	526	»	688	»	900
»	361	»	526	»	695	0.423	921
0.619	414	»	527	»	691	»	938
»	417	0.527	593	0.454	803	»	935
»	408	»	589	»	801	»	939
0.589	468	»	582	»	796		
»	466	0.517	614	0.431	897		
»	460	»	614	»	889		

Calculating a formula for interpolation in the same manner as for the other gases, and comparing it with the observations, we find:

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[1]) Communications etc. N°. 7, 15.

Hydrogen (85.0 KG., $t = 9°.5$).

$$n.10^6 = \frac{140.3}{\lambda} + \frac{45.82}{\lambda^3} = \frac{140.3}{\lambda}\left(1 + \frac{0.326}{\lambda^2}\right)$$

λ	p	$n.10^6$ Calculated	$n.10^6$ Observed	Diff.
0.656	4	376	364	12
619	3	412	413	—1
589	4	462	466	—4
555	4	521	526	—5
527	3	579	588	—9
517	3	603	611	--8
486	4	688	689	—1
454	3	799	800	—1
431	5	898	896	2
423	4	937	933	4

The rotation is positive, as with the other gases.

Dr. L. H. SIERTSEMA. Measurements on the magnetic rotatory dispersion in gases.

Fig 1. ($\frac{1}{16}$).

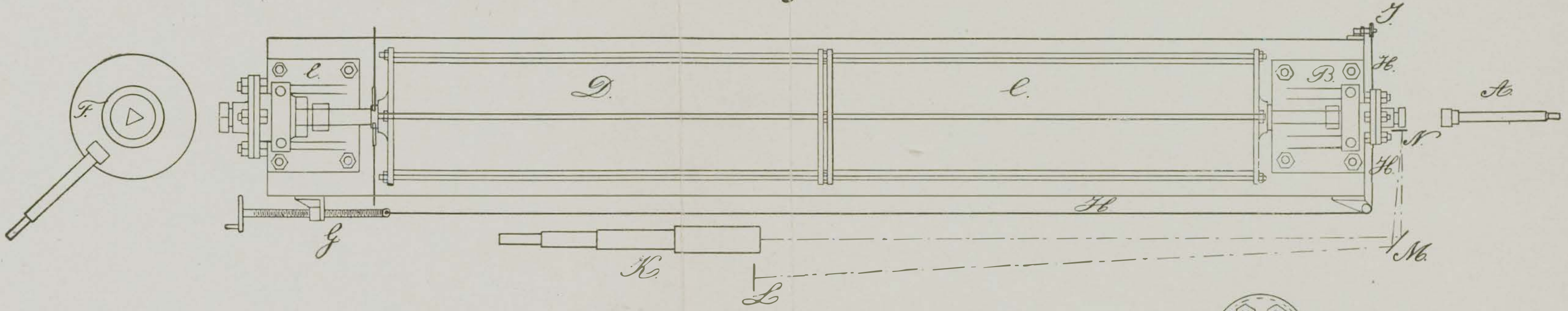


Fig 4. ($\frac{1}{10}$).

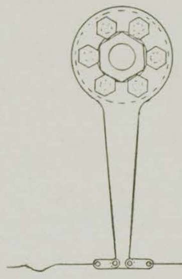


Fig 2. ($\frac{1}{4}$).

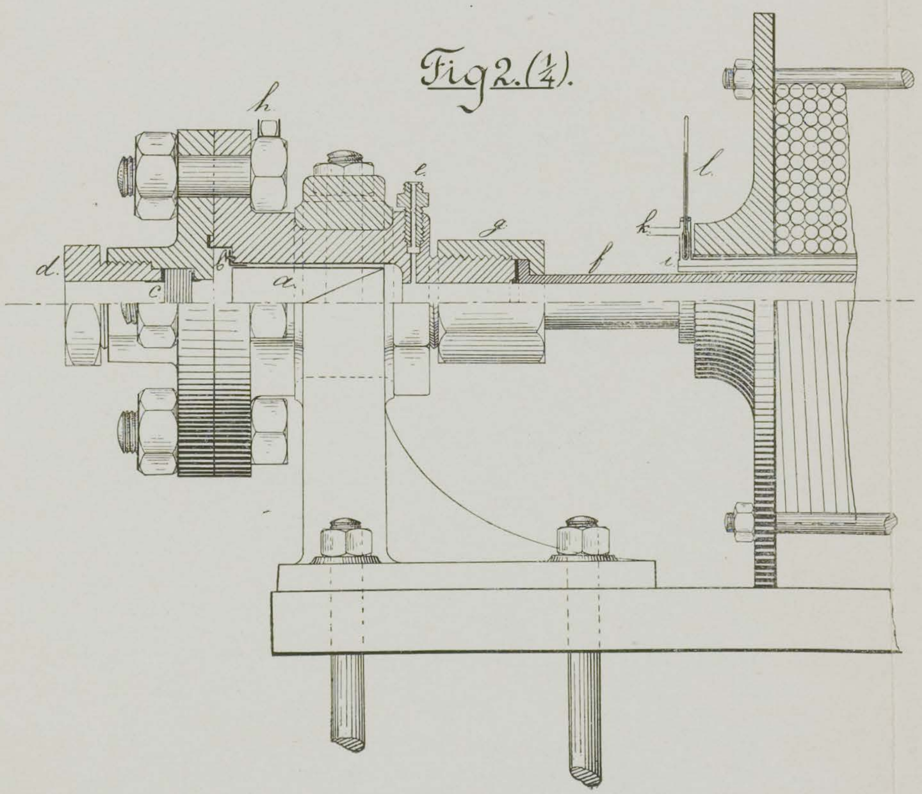
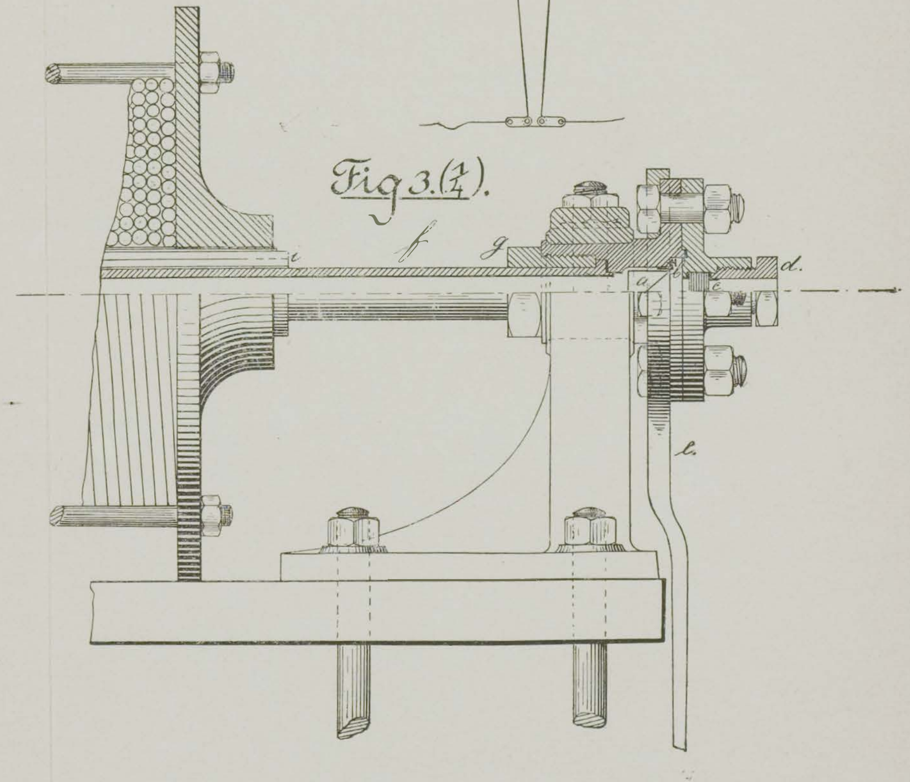


Fig 3. ($\frac{1}{4}$).



Communication No. 24.