COMMUNICATIONS

FROM THE

LABORATORY OF PHYSICS

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 1–12.
March 1885 — Juny 1894.

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(*Versl. Kon. Akad.* **Januari 1894**).

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(*Versl. Kon. Akad.* **Juni 1894**).

For insertion in the Volume No. **1—12**.

Erratum Communication N°. 6.

p. 6 l. 8 from the top: for "103.8°" read "193°.8".

Erratum Communication N°. 11.

title-page l. 3 from the bottom: for "Keunen" read "Kuenen".

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No. 1.

Dr. R. SISSINGH. Measurements concerning the Elliptic Polarization of Light.

(Short account of my dissertation, published under the same title, Leiden **March 1885**. Appeared afterwards: Archives Néerlandaises. T. **20**. p. 171—258.

EDUARD IJDO — PRINTER — LEIDEN.

Dr. R. SISSINGH. *Measurements concerning the elliptic polarisation of light.*

In the dissertation the method, first used by Jamin in his careful observations on the light reflected from metals and afterwards several times by Quincke, has been as much as possible refined.

The method has been applied to the subjects indicated briefly in the titles of the various chapters.

I. *Method of observation.* The chief changes made in Jamin's method of measurement by means of Babinet's compensator are:

1. Arrangements to the compensator for the precise adjustment of the various pieces.

2. Combination of the observations in order to eliminate the remaining errors and those arising from faults in the Nicols.

3. Dispositions made in order to cause that the beam of light is always reflected by the same part of mirror and

4. to determine precisely the angle of incidence.

I refer to the original for a description of the means by which a parallel beam was obtained and the principal position of the Nicols were determined. If the principal planes of the wedges of quartz of the compensator are not carefully adjusted by means of the above mentioned mechanism so that they are perpendicular, anomalous phenomena are observed, which are elaborately treated.

The error of the perpendicular positions amounted in the measurements to about 5′.

The errors are completely eliminated by means of the used method of measurement. By means of a flint prism the light of the sun or of the electric arc was developed into a pure spectrum.

The homogeneousness of the beam of light was $^{2}/_{72}$ of the spectrum between B and G, the divergency 2.3′, the accuracy of the

	reflexion from metal mirror	reflexion from flint glass (coeff. of ellipticity 0,08)
determination of the phases.	$0.05\frac{\lambda}{4}$	0.005λ
» of the reestablished azimuths . .	6′	3′
angle of incidence. . . .	1′	1′.

The part of the mirror used in the observations was 2.7×0.57 m.m².

2. *Reflexion from silver in air.* The observations made with 3 silver mirrors in order to verify Cauchy's formulae gave for angles of incidence, corresponding to:

A difference of phase of about	Difference of phase observed—calculated.	Mean.	Ratio of amplit. Observed—calcul.	Mean.
$\frac{3}{8}\lambda$ (Wavelength)	+ 0.016, + 0,013, + 0.013 + 0.003	$+ 0.011\frac{\lambda}{4}$	—2′, +19′, +2′ +1′	+5′
$\frac{1}{4}\lambda$	+ 0.004, — 0.003, + 0.007 — 0.007, + 0 002, + 0.008 + 0.004, + 0.003	$+0.001^{5}\frac{\lambda}{4}$	—4′, —5′, +16′ +0′, —12′, +12′ +2′. —1′	+1′
$\frac{1}{8}\lambda$	+ 0.016, — 0.003, + 0.006	$+ 0.006\frac{\lambda}{4}$	—7.5′, +6′, —6′.5	—3′

These values, especially the reestablished azimuths are in better agreement with the formulae of Cauchy than those observed by Jamin and Quincke. The formulae of Neumann and Voigt for metallic reflexion give precisely the same nnmerical values for the difference of phase and the ratios of the amplitudes, hence it is impossible to decide experimentally between the rival theories.

3. Also in the case of *reflexion from silver in water* the theory of Voigt gives the same values as that of Cauchy.

4. *Reflexion from soft iron.* The formulae of Cauchy were derived from the electromagnetic theory of light by Prof. H. A. Lorentz supposing that $\frac{1 + 4\pi\theta_1}{1 + 4\pi\theta_2}$ may be put 1, θ_1 and θ_2 being the components of the magnetic polarization in air and in the metal. In the case of strongly magnetisable metals however this supposition is not allowed. Hence one should expect in the case of iron a deviation from the laws of reflexion. However it appeared, that the reflexion from soft iron is represented by Cauchy's formulae with the same degree of accuracy in the case of iron as in that of silver.

5. *The variation of optical constants with temperature.* In the electromagnetic theory of light the optical constants of a metal are dependent on its resistance. Now the resistance changes with temperature, hence one should suppose that also the optical constants must vary with temperature.

Observations, however, made at ordinary temperature and up to 120°, gave no evidence as for a variation of the optical constants with temperature [1]).

6. *Influence of a change of the surface of transparent media on the reflexion.* Observations with a prism made by STEINHEIL were undertaken in the first place with a view to test more accurately as had been done till now CAUCHY's reflexion formula; the agreement was very good. However the refractive index, calculated according to CAUCHY's theory from the angle of principal incidence and the principal azimuth, differed no less than 6 % from the value determined by the minimum deviation method. This difference pointed to the presence of a surface-layer, formed on the old prism, long out of use. It was found impossible to remove the layer by WAIDELE's process (using heated coalpulver), hence it did not exist of condensed gases. The prism being however recently polished, a satisfactory agreement between the refractive index as calculated from theory and as determined by the refraction was observed.

Remarkable enough CAUCHY's and GREEN's formulae represent fairly well the reflexion from transparent bodies with a transparent surface-layer, the refractive index being calculated from the angle of principal incidence and the principal azimuth. This may be seen from the following table in which the results are entered for angles of incidence corresponding to:

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[1]) Cf. ZEEMAN. Communications etc. No. 20.

		Observed—Calculated difference of phase according to CAUCHY.	Mean		Observed—Calculated reestablished azimuth according to CAUCHY.	Mean	
			CAUCHY.	GREEN.		CAUCHY.	GREEN.
A difference of phase of nearly.	$\frac{15}{32}\lambda$	—0.013,	—0.013	—0.024	—10′,	—10′	—5′
	$\frac{7}{16}\lambda$	—0.007, —0.005;	—0.006	$—0.018^5$	—2′, +6′,	+2′	+8′
	$\frac{3}{8}\lambda$	—0.005, —0.007, —0.003, +0.002;	—0.003	—0.012	—1′.5. —4′, +7′, +6′;	+2′	+7′
	$\frac{1}{4}\lambda$	—0.000, —0.000; —0.000, +0.008; +0.010. —0.002, +0.007; —0.003. —0.006, +0.024: —0.000, +0.010;	0.000	0.000	—1′.5, +1′.5; —0′, +2′; +3′. —4′.5, +4′; —2′, —3′, +8′: —0′, —0′;	—0′	0′
	$\frac{1}{8}\lambda$	+0.003, —0.001, —0.002, —0.000;	0.000	—0.010	—1′, —1′, —2′, +4′,	+0′	—4′.5
	$\frac{1}{16}\lambda$	—0.004, —0.004;	—0.004	—0.022	—6′, —10′;	—8′	—14′.5
	$\frac{1}{32}\lambda$	—0.013, —0.009;	0.010^5	$—0.032^5$	—5′, —4′;	—4′.5	—10′.5

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No. 2.

Dr. L. M. J. STOEL. Measurements on the influence of temperature on the viscosity of fluids between the boiling-point and the critical state.

(*Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Academie van Wetensch. te Amsterdam. van* **28 Februari 1891**).

EDUAR IJDO — PRINTER — LEIDEN.

Dr. L. M. J. STOEL. *Measurements on the influence of temperature on the viscosity of fluids between the boiling-point and the critical state.* [1])

Most investigations hitherto made on the viscosity of liquids deal with the influence of substances in solution. In a few cases only the effect of temperature and pressure was examined. WARBURG and VON BABO [2]) excepted, who investigated the viscosity of carbonic acid about the critical temperature, there are no observations, as far as I know, about the viscosity of liquids above the boiling-point.

The aim of my investigation was to ascertain the change of viscosity of a liquid between the boiling-point at the atmospherical pressure and the critical temperature; in order to fill up the gap between the examinations of the liquid state below the ordinary boiling-point, as made by several investigators on one side and those of the critical state by WARBURG and VON BABO on the other. The liquid I chose was methyl chloride, which boils at — 23° C under the pressure of the atmosphere, and the critical temperature of which is 143° C.

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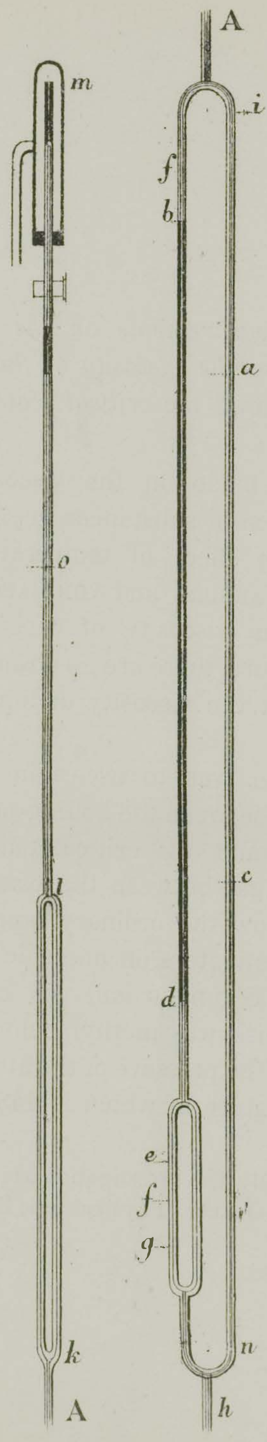
[1]) Dissertation, Leiden, Febr. 1891. The investigation has been published in extenso also by prof. GRAETZ, Physikalische Revue I, p. 513, 1892.

[2]) Wied. Ann. 17, pag. 390, 1882.



The apparatus consists chiefly of two vertical glass tubes *b g* and *i n* (as shown in the fig.) at a small distance from each other, connected at the top and at the bottom forming thus a long-drawn *O*. The whole apparatus is made of thick glass, the inner diameter of the branch *i n* being about 2,5 mM. while the other branch contains a wide reservoir *e g* of 7 mM. diameter and a capillary tube *b d* of 0,2 mM. bore and 55 cM. length. From *h* downward goes a tube, the open end of which is fitted into the pressure-cilinder of a Cailletet-apparatus, so that mercury can be forced into the instrument from below. To this purpose the just mentioned pressure-cilinder is connected with a second vessel containing mercury, on the surface of which a high pressure can be applied by means of compressed carbonic acid or air; the use of compressed air necessary as the pressure of saturated vapour of methyl chloride near the critical point amounts to 65 atmospheres.

From the top of the *O*-shaped tube upwards goes a vertical tube *k l m*, which is at first left open and provided with a special arrangement *o m* for cleaning purposes and for exhausting the air and distilling methyl chloride into the apparatus (the tube being cooled by a mixture of solid carbonic acid and alcohol) but afterwards is closed by melting it at *o*.

The part *k l* has the same diameter as *e g*, its bulk being about twice that of the whole *O*-shaped apparatus, as it must be able to contain the whole quantity of liquid in the apparatus.

The apparatus described is placed within a glass cylinder of the same height, which forms part of a circulation-arrangement in which absolute alcohol, cooled within a spiral by a mixture of solid carbonic acid and alcohol, is made to circulate, or water of the desired temperature or finally heated glycerine. By this method experiments could be made between — 23° C. and + 123° C.

At the beginning of an experiment the level of the mercury stands just below the *O*-tube, that of the liquid methyl chloride stands a little way in the reservoir *k l*, while the upper part of the apparatus contains only the vapour of the liquid. Now, when the mercury is forced up, it soon rises into the tube *i n*; by regulating the supply of mercury, its level is kept at one of the marks *a* or *c*, while the mercury introduced from below slowly forces up the methyl chloride from the reservoir *e g* through the capillary tube to *k l*.

At *e*, *f* and *g* marks have been engraved to which reading-microscopes with cross-wires are focused; with the aid of a registering-instrument the moments are recorded at which the rising mercury-level reaches these marks; tenths of seconds can thus be measured with accuracy and even hundredths can be estimated.

As in the upper part of the apparatus always remains a space filled with vapour, the pressure at the top of the capillary tube is only a little greater than the maximum vapour-pressure at the temperature of the experiment. The excess of pressure at the bottom is measured by the height of the mercury-column in the tube *in*.

In the manner, indicated by Warburg for his experiments on carbonic acid, I investigated the influence which the compressibility of the methyl chloride and the variation of viscosity with change of density can possibly have in my experiments and the corrections required by them. In this investigation it became clear to me that by neglecting these corrections an error can be made of 0,5 % at the utmost. The formula by which, taking no account of these corrections, the coëfficient of viscosity can be calculated, is as follows:

$$\mu = \frac{g \pi r^4 (\sigma - s_0) T \log e}{8 q l A},$$

in which g = acceleration of gravitation.
r = radius of the capillary tube.
σ = density of mercury.
s = „ of methyl chloride.
T = time of passage of the liquid.
e = base of the Nep. log.
q = cross-section of the reservoir *e f g*.
l = length of the capillary tube.
$A = l \frac{a_A}{a_B} = l \frac{H - h_1}{H - h_2}$, if we denote

by H the constant height of the mercury in the branch *in* during each experiment and by h_1 and h_2, the height of the marks g and e, measured from an arbitrary horizontal plane.

The expression here given for μ must be corrected for the differences which the pressures show from the values they should have according to Poiseuille's law. By the great difference in diameter of the reservoir *e f g* and the tube *in* there remains an uncertainty in the recorded pressures, caused by capillary depression, so that the difference of the pressures from those following from Poiseuille's law cannot accurately be determined from my experiments. If this were the case, it would be possible to calculate absolute values for the coëfficient of viscosity from the recorded times of passage and the dimensions of the apparatus. These we might also obtain by using the same tube for experiments with a fluid of known viscosity.

But even without this, the non-corrected times of passages T give a sufficient idea of the variations of the internal friction with temperature.

Expressed in seconds they can with sufficient accuracy be represented by the empirical formula:

$$\log T = \frac{896 - T}{250}$$

in which T denotes the absolute temperature. This appears from the following table, taken from my dissertation.

$T - 273$	T (observed)	T (calculated)	Difference in percents.
— 28°	408.50	401.79	+ 1.7 p.Ct.
— 20.75	379.91	375.84	+ 1.1
— 11.3	339.41	344.51	— 1.5
+ 0.75	305.72	308.32	— 0.8
10.8	280.21	281.06	— 0.3
19.0	259.81	260.62	— 0.3
27.8	236.17	240.33	— 1.7
35.9	220.995	223.05	— 0.9
45.2	204.595	204.74	— 0.1
55.8	186.58	185.69	+ 0.5
66.6	169.99	168.11	+ 1.1
75.2	157.59	155.31	+ 1.5
85.1	143.46	141.78	+ 1.2
93.15	133.38	131.64	+ 1.2
104.3	120.88	118.80	+ 1.8
110.7	112.68	112.00	+ 0.6
122.95	97.06	100.04	— 3.0

The times of passage I observed also satisfy approximately the relation:

$$\mu \, p^{\frac{1}{3}} = \text{Const.},$$

in which μ is the coëfficient of viscosity when the liquid is under the pressure of its own vapour and p the vapour-pressure.

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No. 3.

Dr. R. SISSINGH. On Kerr's Magnetooptic Phenomenon in the case of Equatorial Magnetization of Iron.

(*Translated from:* Natuurk. Verhandel. Kon. Akad. v. Wetensch. Amsterdam. Deel **28. 1890.**)

Because there appeared a translation of the somewhat abridged paper (Wied. Ann. Bd. **42** p. 115. (1891)) in Phil. Mag. (5). Vol. **31.** p. 293. 1891, a reprint seems unnecessary.

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No. 4.

Dr. J. P. KUENEN. Measurements concerning the surface of VAN DER WAALS for mixtures of carbonic acid and methyl chloride [1]).

(*Translated from: Verslagen en Mededeelingen der Afdeeling Natuurkunde der Kon. Akademie van wetensch. te Amsterdam.* *van* **29 April 1892** 9. *p.* 422—424.)

Dr. J. P. KUENEN. On retrogade condensation and the critical phenomena of mixtures of two substances.

(*Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Akademie van wetensch. te Amsterdam van* **25 Juni 1892,** *p.*15—19.)

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[1]) Short account of my dissertation, published under the same title, Leiden 1892. Appeared enlarged afterwards: Archives Néerlandaises de la Soc. Holl. des science à Harlem 26 p. 354—422; an abstract of it: Zeitschr. Phys. Chem. 11. p. 38—48.

EDUARD IJDO — PRINTER — LEIDEN.

Dr. J. P. KUENEN. *Measurements concerning the surface of* van der Waals *for mixtures of carbonic acid and methyl chloride.*

The appearing of van der Waals's theory [1], for the application of which experimental material is wanting, suggested to me to determine a series of isothermal lines for three mixtures of carbonic acid and methyl chloride between 25° C. and 160° C. in order to calculate the constants, which van der Waals uses, and with them to execute the construction of the surface of free energy, which was introduced by him. However it was impossible to use the characteristic equation of van der Waals, which. as is well-known, can, with simple substances even, represent the observations within narrow limits only. With the first equation of Clausius [2] the isothermals for methyl chloride and one of the mixtures could be rendered very well, for the other two approximately only. The constants calculated are the following (the letters are those of Clausius) [3]:

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[1] Arch. Néerl. 24 p. 1—56. Zeitschr. Phys. Chem. 5. p. 133—173.

[2] Wied. Ann. 9. p. 14.

[3] The values are slightly modified according to later results;

	K	β	b	R
CH_3Cl	6.555	0.00165	0.00135	0.003750
$\frac{3}{4}CH_3Cl$	(4.94)	0.00138	0.00110	0.003738
$\frac{1}{2}CH_3Cl$	4.020	0.00163	0.00098	0.003721
$\frac{1}{4}CH_3Cl$	(2.86)	0.00117	0.00085	0.003705
CO_2	2.116	0.00095	0.00087	0.003684

The values in brackets for two of the mixtures are only mean values of those, which hold good for the different temperatures [1]).

By using these equations we can calculate the lines of free energy for the different temperatures and so execute approximately the construction of van der Waals's surface; in order to obtain some accuracy it will be necessary to extend the observations over further intervening mixtures, since the manner in which in Clausius's equation the constants depend upon the constitution of the mixture is not known. The knowledge of such a thermodynamical surface for a mixture is of the greatest importance for the study of the coëxistence of two or three phases. These phenomena (condensation) were studied qualitatively only as yet; the results partly agree with those of former investigators, Andrews and others.

The great influence of retardation, also in the homogeneous condition (imperfect mixing), was investigated at large and at last for the greater part neutralised by the application of a stirring-apparatus, consisting in a small piece of iron within the tube, in which the mixtures were investigated, which piece could be moved during the experiments by an electromagnet gliding round the tube. Thus agreeing results were obtained and the experiments did not take more time than was necessary.

The flattening and disappearing of the liquid surface, which at definite temperatures was observed by former experimenters, was also seen by me. However from van der Waals's theory we may conclude another way of condensation, which must take the place of the disappearing of the liquid surface and which may be called *retrograde condensation;* with it the quantity of the denser phase at first increases till a maximum is attained, and then diminishes and at length disappears. The fact, that observation has given the disappearing of the surface instead of this retrograde condensation till now, can be explained by the retardation, which in the case of two phases becomes of important influence. I am going to test this explanation by aid of my stirring-apparatus mentioned above, and, as independent from this theoretical reasoning I sometimes observed the diminishing of the fluid phase by compression, I soon hope to be able to obtain all the successive stages of the phenomenon as described above.

The critical temperatures of the mixtures investigated do not agree with Pawlewski's law, as indeed was not to be expected.

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cf. Arch. Néerl. 26 p. 61, 68, 69. In the equations for methyl chloride and for carbonic acid some more small modifications have been made.

[1]) See my treatise in Arch. Néerl. l. c.

The following values were found:

	Obs.	Calc.
CH_3Cl	143.0	143.0
$\frac{3}{4}\,CH_3Cl$	123.0	117.8
$\frac{1}{2}\,CH_3Cl$	97.1	90.9
$\frac{1}{4}\,CH_3Cl$	65.4	62.0
$\frac{1}{9}\,CH_3Cl$	46.0	45.1
CO_2	31.0	31.0

At last from the equations some Tables were calculated for the deviations from DALTON's law and for the increase of pressure by mixing at constant volume.

Dr. J. P. KUENEN. *On retrograde condensation and the critical phenomena of mixtures of two substances.*

In my dissertation „Measurements concerning the surface of VAN DER WAALS for mixtures of carbonic acid and methyl chloride. Leiden 1892" [1]) I discussed a case, which occurs pretty often with mixtures of two substances, namely that by compression during the condensation, i. e. in those conditions, in which two phases are in equilibrium, the surface between the two phases gradually becomes flatter and at length disappears entirely. This is the well-known phenomenon, which was successively observed by CAILLETET [2]), VAN DER WAALS [3]), ANDREWS [4]) and others and also during my investigations under certain circumstances. I succeeded by aid of VAN DER WAALS's theory in discovering the probable cause of it and to open the prospect of an early experimental confirmation. The following

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[1]) cf. the above communication.

[2]) Compt. Rend. 90, p. 210.

[3]) The continuity of the liquid and gaseous states. Phys. Memoirs etc. I 3, p. 472.

[4]) Phil. Trans. 178, p. 53.

may serve to recall these facts and to complete them.

Examining how, according to the theory, the condensation must take place, and ascribing to the first plait 1) the peculiar form, which it must probably have for temperatures between the critical temperatures of the two ingredients 2), I concluded, that at a given temperature we can arrange the mixtures in three groups according to the nature of the condensation: for the first group, consisting of those mixtures, which contain the largest quantity of the substance of the lower critical temperature, a separation in two coëxisting phases is impossible. For a second group the condensation has the ordinary aspect, that is to say, the relative quantity of the denser phase regularly increases with decreasing volume, till the other phase has disappeared; these mixtures contain the largest quantity of the substance possessing the highest critical temperature. Between these groups there is a third, for which the relative quantity of the denser phase at first increases by compression, attains a maximum and then again diminishes and disappears: with expansion the same phenomena but in opposite order are to be observed. This kind of condensation I proposed to call „*retrograde condensation*". The limits, within which this group of mixtures in contained, may be easily indicated: one limit is formed by a mixture, in which the proportion of the ingredients

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1) For the names used here compare: Communications etc. n⁰. 7, p. 4.

2) vid. VAN DER WAALS l. c. The case of other possible cases is discussed in my paper Arch. Néerl. l. c., Zeitschr. Phys. Ch. l. c.

is that of the plaitpoint, the other limit by a mixture, whose plane parallel to the ψ, v plane touches the connode curve. From this we may derive, how on the other hand for one given mixture the nature of the condensation must alter with the temperature. Above a definite temperature, the *critical temperature* or rather the *temperature of the critical point of contact*, separation is impossible; beneath another lower temperature, which I call the *plaitpoint-temperature* of the mixture, the condensation is normal; between these we must find retrograde condensation. If we consider the difference in density and proportion of the coëxisting phases we find, that this difference will be very slight at the end of the condensation close to the plaitpoint-temperature, both above and beneath it and that, according as the temperature diverges from it, this difference will increase. So the very small quantity of liquid, which is formed close by the critical temperature may show a considerable difference from the vapour-phase: a flat surface is not to be expected there. The well-known property of the critical temperature of simple substances, that above it no two phases can coëxist, here belongs to the temperature of the critical point of contact and in this respect the critical point of contact is to be compared with the critical point of simple substances. In the plaitpoint however we meet with the property of the coëxisting of two identical phases 1). Consequently with mixtures

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1) The phenomena described here are modified a little by the influence of gravitation, as in the case of simple substances was first pointed out by Gouy (Compt. Rend. 115, p. 720.

the properties of the critical point are so to say divided over two points, the plaitpoint and the critical point of contact.

The observations were partly in contradiction with all this; especially retrograde condensation had never been observed: instead of it the flattening and disappearing of the liquid surface. As the cause of this deviation from theory I suggested the influence of retardation, which with mixtures may already modify the phenomena in the gaseous state and shows itself clearer still, when two phases are present. This retardation, the result of slow diffusion, is not to be mistaken for the thermodynamical retardation, which may delay for a time the appearing of the first small quantity of a new phase [1]).

It is possible to point out a little clearer, why retardation may have such a great influence under the given circumstances, and thereby render the explanation more accurate. We may best express the influence of retardation by saying, that with increasing pressure the two phases are compressed separately and that then by interchange at the surface and by diffusion equilibrium will be slowly occasioned. In the case, we are referring to, a particularity shows itself, namely that both the phases, when compressed, remain in stable

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cf. Communications etc. n°. 8, p. 10). The flattening and disappearing of the surface will not be possible exactly at the plaitpoint-temperature only, but also at temperatures a little above and beneath it, the limits of which will depend a. o. upon the length of the tube employed.

[1]) cf. Blümcke, Wied. Ann. 36, p. 916.

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equilibrium, because the corresponding points of the connode curve are both situated at the liquid side of the plait, and therefore pass into the stable part of the surface. As the phases are not in equilibrium with each other, probably a continuous transition between them will be formed, which reveals itself in the disappearing of the surface observed. Of course this reasoning holds good for temperatures lying not too far beneath the plaitpoint-temperature as well as for temperatures ranging between it and the critical temperature. The disappearing of the surface with insufficient mixing may therefore not only take the place of retrograde but also of normal condensation. The fact, that, if one of the two points is situated at the vapour-side of the plait, this point with compression must enter the semi-stable or even the unstable part of the surface and so immediately give rise to a new separation and an increase of the liquid phase, must be considered as the reason, why retardation causes less marked abnormalities there. It is also to be borne in mind, that here the difference between the phases becomes greater as a rule.

Some days ago I have succeeded, by aid of my stirring-apparatus mentioned before, entirely to confirm the theoretical predictions and the explanation of the ordinary phenomena. With the utmost care a new mixture was prepared: the process was conducted in such a manner, that the possibility of decomposition of the methyl chloride during the closing of the tube by the blow-pipe was excluded. Moreover the apparatus was made of glass and copper only, so that probably the gases were very pure. The proportion of the carbonic acid in the mixture amounted to 0.41.

If, during the condensation, I did not stir and only waited some time before the readings were taken, between varying limits of temperature, depending upon the time of waiting, (circa 100° C—107° C) the separating surface could be effaced by pressure. The movement of the piece of iron within the tube changed the phenomenon entirely, as the theory had predicted. Beneath 102° C the condensation was normal. At 102.5° C and 103° C the observations were dubious; at 103.5° C retrograde condensation was already discernible, though very indistinct still. The difficulty of the observations in this neigbourhood is caused by the nearly complete similarity of the phases. A small change of temperature may cause considerable deviations and a too sudden change of pressure, which often occurred with my regulator of pressure, was sufficient to make the line of demarcation disappear at once against my intention. In these cases I succeeded far better in producing the opposite phenomenon, which occurs with expansion. Though exact numbers were not to be obtained at 103.5° C, the existence of the retrograde condensation at that temperature was not doubtful [1]). At 104° C the phenomenon could be followed entirely, also at 105° C and 106° C. The critical temperature was fixed at 106.5°. The difference between the phases close to 106.5° C was very marked: the focal lines, which are to be observed in a glass tube, had a different breadth

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[1]) 103° C = plaitpoint-temperature.

in the two phases and the surface was much more curved than at lower temperatures, entirely in accordance with theory. The following numbers were obtained at 105° C; the volumes are expressed in an arbitrary unit, the pressures in atmosferes.

Vol.	Vol. of the liquid.	Pressure.
117.9	0	73.3
99.6	3.9	77.2
81.2	8.2	81.8
81.0	8.6	81.8
78.6	7.6	82.4
77.3	4.3	83.1
75.3	4.7	83.3
75.4	2.8	83.5
74.3	2.5	83.8
74.0	0	83.8

We may call the succession of volumes and pressures pretty regular, considering the great difficulties of the observations.

The limits, between which retrograde condensation takes place, are much narrower than those of the ordinary phenomenon (disappearing of the liquid surface). This agrees with what was pointed out before, viz. that the limits become wider by the influence of retardation.

The results of former experimenters especially of Andrews, who describes his experiments most accurately, are also quite in accordance with the explanation laid down here. That an investigator like ANDREWS has not seen the true state of affairs is due to his want of a theory, without which the critical phenomena of mixtures would not have been disentangled easily.

5

COMMUNICATIONS

FROM THE

LABORATORY OF PHYSICS

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 5.

Dr. P. ZEEMAN. Measurements on KERR'S phenomenon in the case of reflexion from the polar surface of a magnet made of iron, cobalt and nickel.

Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Akademie te Amsterdam van **25 Juni 1892,** *p.* 19; *published in extenso Archives Néerlandaises, T.* 27. *p.* 252. 1893.

Dr. P. ZEEMAN. Measurements on KERR'S phenomenon in the case of reflexion from the polar surface of a magnet made of cobalt at different angles of incidence.

Translated from the same **29 October 1892,** *p.* 58; *published in extenso with subsequent investigations in the Archives Néerlandaises referred to above.*

Dr. P. ZEEMAN. On a subjective phenomenon in the eye,

Translated from the same **25 Februari 1893,** p. 155.

EDUARD IJDO — PRINTER — LEIDEN.

Dr. P. ZEEMAN. *Measurements on Kerr's phenomenon in the case of reflexion from the polar surface of a magnet made of iron, cobalt and nickel.*

Dr. Sissingh measured the amplitude and the phase of the new magnetic component, which appears when light falls obliquely upon an iron mirror, magnetized tangentially (aequatorial reflexion). In order to avoid further complications the incident light was polarized either in or at right angles to the plane of incidence

The comparison with Prof. Lorentz's theory taught him that at different angles of incidence existed a constant difference amounting to about 85° between the observed and calculated phases. I will call this difference of phase Sissingh's phase S. In the continuation of the inquiry it seemed indicated to consider (*a*) in the first place whether the reflexion from a normally magnetized mirror (polar reflexion) can be described by this theory.

(*b*) Further, to examine the existence of the relation required by the theory between polar and aequatorial reflexion.

(*c*) The influence of the colour of the reflected light on the phenomena was in the last place a point of research. Although these researches are not yet (June '92) closed, it may be perhaps of interest to give a preliminary communication.

As to point (*a*) there is something to be learned from Kaz's en Righi's observations calculated by Dr. Sissingh. It follows from the observations of Kaz, accepting values for the ordinary optical constants, that there exists a difference of phase between theory and experiment amounting to about 68°. This value is derived from the observations at the angles of incidence 80°, 68°, 60°, these giving the most accurate result.

A difference of phase S = 75° follows from Righi's observations at 6 angles between 44°18′ and 87°, likewise accepting values of the optical constants.

From the experiments of both these observers result very irregular oscillating values of the quotient of the calculated and observed amplitudo's.

As to the second point (*b*) it is impossible to draw any conclusion from a comparison of the aequatorial and the polar observations of Kaz and Righi, as they give not the magnetizations made use of in their experiments which are moreover insufficient as follows from the just named anomalies.

We have referred to the third point (*c*). Observations made by Righi, but they cannot be exactly compared with the theory as there is no statement of the optical constants of his mirror for the not accurately defined rays.

Hence the desirableness of new measurements. Therefore I have made experiments on the reflexion from the *pole* of an *iron* mirror; I have found that also in this case there exists a Sissingh's phase S, the preliminary value of which is about 80°.

This follows from measurements relating to 3 mirrors, the optical constants, I and H, of which were found for light of refrangibility D:

A.	$I = 76^\circ\,20'$	$H = 27^\circ\,40'$
B.	$73^\circ\,59'$	$28^\circ\,45'$
C.	$76^\circ\,13'$	$27^\circ\,39'$

The difference of phase just named following from our measurements is:

in the case of mirror A, $S = 80^\circ\,47'$
B. $79^\circ\,58'$
C. $80^\circ\,30'$

As to our second point (b) the relation between aequatorial and polar reflexion, I have found till now what follows.

According to theory, at $i = 51^\circ\,22'$ the magnetization being the same, the amplitudo's μ_{aeq} and μ_{pol} have the following relation:

$$\frac{\mu_{aeq}}{\mu_{pol}} = 0{,}194.$$

From SISSINGH's aequatorial and my polar measurements follows:

$$\frac{\mu_{aeq}}{\mu_{pol}} = 0{,}294.$$

In SISSINGH's case the magnetization was 1400. C.G.S. and in my measurements 850 C.G.S. hence:

$$\frac{\mu_{aeq}}{\mu_{pol}} = 0{,}179.$$

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by the proportionality of μ and magnetization, as proved by DU BOIS.

The difference is about 8%.

Point (c): the dispersion of the phenomenon is investigated for 3 colours at an angle of incidence $i = 51^\circ\,22'$ and polar reflexion. The light was made monochromatic bij means of a Hilger-Christie spectroscope. The optical constants of the iron-mirror were determined for the same colours. Variations of the mirror-surface were controlled by repetitions of this determination. Also the invariability of the light used was especially controlled. In this manner it was found (m being the phase):

	$m - 180^\circ$	
	from observations.	from theory.
for red light w. l. $\lambda_1 = 0{,}618\,\mu$	$39^\circ\,8'$	$-\ 29^\circ\,58'$
» blue » w. l. $\lambda_2 = 0{,}460\,\mu$	$53^\circ\,10'$	$-\ 24^\circ\,58'$.

According to theory the dispersion ought to be $+ 5^\circ$, the calculation being made with the determined optical constants. Hence it follows that SISSINGH's phase has a different value for various colours and hence results the existence of *a magneto-optic dispersion of the phase;* the dispersion of the phase from blue to red is $+ 14^\circ\,2'$.

To the present time measurements on reflexion from magnetized cobalt from which phase and amplitude might be calculated did not exist. Therefore I commenced with measurements on light reflected from the pole of a magnet made from a solid piece of cobalt. For 3 colours the optical constants were found as follows.

$\lambda_1 = 0{,}618\ \mu$	$I = 76^0\ 33'$	$H = 30^0\ 49'$
$\lambda_2 = 0{,}540\ \mu$	$75^0\ 20'$	$31^0\ 23'$
$\lambda_3 = 0{,}460\ \mu$	$73^0\ 44'$	$31^0\ 27'$

At $i = 60^0$ my measurements again give a *magneto-optic dispersion of the phase;* the change of the magneto-optic amplitude with colour may be called *magneto-optic dispersion of the amplitude.*

The results are the following:

	$m - 180^0$		μ			
colour	observed	calculated	observ.	calcul.	S.	$\dfrac{\mu \text{ observ.}}{\mu \text{ calcul.}}$
λ_1	$22^0\ 33'$	$-18^0\ 39'$	$2{,}30 \times 10^{-3}$	$2{,}77\ A$	$41^0\ 12'$	$0{,}83 \times \dfrac{10^{-3}}{A}$
λ_2	$32^0\ 30'$	$-16^0\ 53'$	$2{,}41 \times 10^{-3}$	$2{,}44\ A$	$49^0\ 23'$	$0{,}99 \times$ „.
λ_3	$33^0\ 55'$	$-16^0\ 56'$	$2{,}18 \times 10^{-3}$	$2{,}03\ A$	$50^0\ 51'$	$1{,}07 \times$ „

For the constant $A = \frac{2\pi}{T}\, \varepsilon_1\ h\ N$. vide theory. The hitherto given and yet following amplitudes relate to the intensity of magnetization $I = 700$ C.G.S.

Inferior in exactness is a determination at $i = 50^0$:

λ_2	$25^0\ 9'$	$-22^0\ 21'$			$47^0\ 30'$	

At $i = 72^0$, phase not very exact:

λ_2	$45^0\ 5'$	$-6^0\ 44'$	$1{,}96 \times 10^{-3}$	$2{,}02\ A$	$51^0\ 49'$	$0{,}97 \times \dfrac{10^{-3}}{A}$

On a mirror of electrolytically deposed *nickel* was found at $i = 50^0$:

$\lambda = 0{,}589\ \mu$	$11^0\ 40'$	$-19^0\ 30'$	$1{,}20 \times 10^{-3}$		$31^0 10'$	$0{,}52 \times \dfrac{10^{-3}}{A}$

Dr. P. ZEEMAN. *Measurements on Kerr's phenomenon in the case of reflexion from the polar surface of a magnet made of cobalt at different angles of incidence.*

Not long ago appeared a theory of KERR's phenomenon by GOLDHAMMER (Wied. Ann. Bd. 46).

He introduces into his theory the difference of phase S, the existence of which Dr. SISSINGH deduced from his observations on light reflected from tangentially magnetized iron. GOLDHAMMER's δ is $= -S$. The formulae arrived at are the same as those given in LORENTZ's theory; only the expression for the phase differs with a constant quantity $-\delta$. Somewhat later also DRUDE gave a very comprehensive memoir on the same subject (Wied Ann. Bd. 46). DRUDE also communicated at the same occasion some observations made by him, on the reflexion from tangentially magnetized cobalt and iron (aequatorial reflexion). I calculated as well from these observations as from LORENTZ's theory the phase and amplitude of the magneto-optical component. The values adopted for the optical constants, the principal incidence and principal azimuth are for cobalt those determined by DRUDE; for nickel the usually given ones. From DRUDE's observations on aequatorial reflexion on cobalt and nickel I deduce, m being the phase and μ the amplitude at the angle of incidence i:

Cobalt.

	$m - 180^0$		μ			
i	observ.	calcul.	observ.	calcul.	$S.$	$\frac{\mu \text{ observ.}}{\mu \text{ calcul.}}$
35^0	$-77^0\,24'$	$-89^0\,3'$	$2{,}80 \times 10^{-3}$	$0{,}450\,A$	$11\ \ 39'$	$6{,}20 \times \frac{10^{-3}}{A}$
60^0	$-25^0\,27'$	$-79^0\,42'$	$0{,}56 \times 10^{-3}$	$0{,}629\,A$	$54^0\,15'$	$0{,}90 \times$ „
75^0	$-12^0\,56'$	$-67^0\,1'$	$0{,}54 \times 10^{-3}$	$0{,}574\,A$	$54^0\,5'$	$0{,}95 \times$ „
83^0	$-12^0\,57'$	$-54^0\,9'$	$0{,}50 \times 10^{-3}$	$0{,}389\,A$	$41^0\,12'$	$1{,}30 \times$ „
			Nickel.			
60^0	$-48^0\,22'$	$-79^0\,14'$	$0{,}65 \times 10^{-3}$	$0{,}595\,A$	$30^0\,52'$	$1{,}08 \times$ „
65^0	$-46^0\,3'$	$-76^0\,16'$	$0{,}84 \times 10^{-3}$	$0{,}592\,A$	$30^0\,12'$	$1{,}42 \times$ „
75^0	$+11^0\,41'$	$-66^0\,19'$	$0{,}30 \times 10^{-3}$	$0{,}512\,A$	78^0	$0{,}59 \times$ „
80^0	$-\ 8^0\,42'$	$-58^0\,11'$	$0{,}17 \times 10^{-3}$	$0{,}420\,A$	$49^0\,29'$	$0{,}40 \times$ „

A being the constant from Lorentz's theory.

The results of this calculation don't show anything of a constancy of S.

At first sight one would rather think that these observations contradict that constancy. However Drude's observations are so called minimum-rotations, whereby the errors of measurement influence to a much higher degree on the value of Sissingh's phase, than when null-rotations are made. Yet the discordances among the results might give rise to some doubt as to the exactness of my preliminary conclusions communicated to the Academy, June 25, '92. The continuation of the investigation however has wholly convinced me of the constancy of S, in the case of polar reflexion from cobalt. For my purpose I have made measurements with *white light* at 3 angles of incidence, always controlling the invariability of the mirror and eliminating the errors, that might arise from deviations of the light by the passing through the Nicols; besides I ever employed the method of the null- as well as that of the minimum-rotations. A sufficient accordancy of the result of both methods was always found. For the calculation of the result in every especial case that method was used, which gives for the required quantity the result least affected by errors of measurements.

The final results, reduced concerning the amplitude, at the magnetization $I = 430$ C.G.S. are the following with our usual notation.

Reflexion from the pole of cobalt mirror $I = 430$ C.G.S.

	$m - 180^0$		μ			
i	observ.	calcul.	observ.	calcul.	$S.$	$\frac{\mu \text{ observ.}}{\mu \text{ calcul.}}$
45^0	$20^0\,34'$	$-28^0\,47'$	$1{,}58 \times 10^{-3}$	$2{,}76\,A$	$49^0\,21'$	$0{,}57 \times \frac{10^{-3}}{A}$
60^0	$27^0\,40'$	$-21^0\,49'$	$1{,}50 \times 10^{-3}$	$2{,}71\,A$	$49^0\,29'$	$0{,}56 \times$ „
73^0	$37^0\,55'$	$-11^0\,43'$	$1{,}17 \times 10^{-3}$	$2{,}18\,A$	$49^0\,38'$	$0{,}54 \times$ „

Hence it follows that Sissingh's difference of phase is nearly constant within wide limits of the angle of incidence. Also they wholly confirm the value formerly given (Comm. to the Academy of June 25 '92. p. 2. supra). The theory of Kerr's phenomenon also requires the exact numerical value of Sissingh's phase. According to Drude's theory, containing only one magneto-optical constant in the differential-equations, contrary to Goldhammer's theory with two constants, one might calculate (as was remarked by Goldhammer) Sissingh's phase from $2\,o - \delta = \pi$ etc. In this formula $-\delta = S$ and o is the quantity first introduced by EISENLOHR and called τ in LORENTZ'S theory. For cobalt GOLDHAMMER employed the preliminary value $S = 50^0$ with which I furnished him (Wied. Ann. Bd. 47, p. 347). He calculates that according to DRUDE'S theory this should be 60^0 and accordingly concludes that DRUDE'S theory is in error. This conclusion is wholly confirmed by the now given measurements.

Dr. P. **ZEEMAN**. *On a subjective phenomenon in the eye.*

When being engaged in measurements on KERR'S magneto-optic phenomenon, I noticed, observing with the compensator of Babinet, a phenomenon, the cause of which lies in the eye. Since the phenomenon seems yet to be unknown in physiology, I wish to communicate it here.

Soon I noticed that the complicated apparatus, with which I at first saw the appearance, is not necessary for the observation. The light needs not to be polarized, only a slit is wanted intensely illuminated, while the surrounding of the field is dark na-light being very efficacious

When observing with a telescope one sees, especially during the first moments after suddenly bringing the eye before the eye-piece, not only the illuminated slit but also a blue-violet line of light soon fading.

The phenomenon may be observed as well by looking suddenly with unassisted eye at the slit. The line resembles to the outline of a pear, the axis of which is perpendicular to the centre of the slit. To the right eye the pointed part of the line, i. e. the stem of the pear appears at the right side of the slit, the curved part falling somewhat at the other side.

With the left eye one sees a figure symmetrical to the described one and observing with both eyes the two figures may be seen simultaneously. The inner part of the line is dark as a rule. It is very remarkable that not only yellow light but all colours of the spectrum give the same violet line. It is even possible to observe the appearance, looking at either of the 3 hydrogenium-lines, and only using a common spectroscope of Desaga, the slit being sufficiently widened With the red line the experiment is easy, but with the other rather difficult. The observation succeeds very well with yellow or with white light. We can even observe the phenomenon, though somewhat indistinctly, if we look at a slit made between our two stretched hands, while a lamp is placed behind.

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COMMUNICATIONS
FROM THE
PHYSICAL LABORATORY
AT THE
UNIVERSITY OF LEIDEN
BY
PROF. DR. H. KAMERLINGH ONNES.

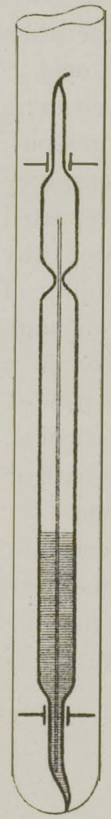
No. 6.

Dr. E. C. DE VRIES. Measurements on the influence of temperature on the capillary elevation of ether between the critical state and the boiling-point of ethylene.

(*Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen.* **25 Februari 1893.**)

EDUARD IJDO — PRINTER — LEIDEN.

Dr. E. C. DE VRIES. *Measurements on the influence of temperature on the capillary elevation of ether between the critical state and the boiling-point of ethylene* [1]).



Taking into account the law of corresponding states and denoting by ϑ VAN DER WAALS's reduced temperatures, these observations give approximately the rate of variation of the surface-tension for all substances between $\vartheta = 0{,}366$ and $\vartheta = 0{,}9772$. The measurements of the elevations were made by means of a thick glass tube, closed by melting, and filled in a vacuum with such a quantity of ether that at the critical temperature the disappearance of the meniscus could be observed about the middle of the tube. In the closed tube is placed a thin cappillary tube in which the rise of the liquid is measured. In order to keep it in a central position the thick wider tube is narrowed in fit places. The

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[1]) Short account of my dissertation published under the same title. Leiden, 1893.

bottom by which the capillary tube is supported is inclined, so that the tube is open below. The thick tubes with which at first several auxiliary apparatuses are connected by melting them together and the capillary tubes they contain are cleaned with the utmost care, for which purpose they are repeatedly rinsed and boiled with various liquids which are carefully made dust-free in apparatuses purposely constructed and which can only arrive into the principal tube and accessory auxiliary tubes connected with them by melting.

The cleanness obtained in this way was so great that by the retardation of ebullition, shown by water and alcohol, more tubes burst by overheating the water than when boiling them with concentrated sulphuric acid.

The result of all the precautions taken in cleaning the glass-walls and in getting rid of every (also gaseous) foreign admixture in the ether was a complete constancy of the capillary elevation in this tube even after repeated heating and for months afterwards, in the same way as Eötvös obtained in his method the invariability of the capillary constants by closing his tubes in a vacuum. The tube destined for the experiment was placed in a wider one containing methyl-salicylate which is suspended in a vapour-bath heated by the vapours of ethyl-alcohol, amyl-alcohol, terebene or aniline or in a liquid-bath or finally in an apparatus for boiling liquid ethylene.

The utmost care was taken in maintaining a constant temperature during a very long time, because otherwise drops of liquid settle easily in the capillary tube or vapour-bubbles are formed by which all observation is rendered impossible.

The arrangement for maintaining a constant temperature also permits the capillary tube to be seen in an illuminated part of the field of the telescope, the small meniscus being otherwise difficult to observe. The arrangement for the observations at higher temperatures is described in the academical thesis; about the contrivance for the observation in the ethylene which boils at — 102°, I shall ask permission for a following communication to your Section.

The capillary tube being placed in a wider tube which would give a capillary elevation itself, it is necessary to correct the observed rise, a correction however for which only an approximate value could be given.

The results of the measurements, corrected as well as possible, are

$\rho_v - \rho_d$	temperature	VAN DER WAALS's reduced temperature	Capillary rise (relative)	Surface-energy (relative)
0	193°.6	1	0	0
1.61	182.92	0.9772	2.81	4.52
2.38	159.31	0.9265	8.59	20.45
2.96	125.58	0.8542	16.09	47.54
3.505	71.8	0.754	26.10	91.48
3.965	19.56	0.627	38.44	152.41
4.57	—102.	0.366	63.69	291.07

From —100° to + 160° the capillary rise h can be satisfactorily represented by a linear function of the temperature, according to

$$h = 1 - 0{,}004960\, t$$

in which the rise at 0° is put 1, while the curve by which *h* is graphically represented as a function of the temperature evidently ends logarithmically near the critical temperature. The walls of the tube were found to be wetted at all temperatures, in opposition to RAMSAY's statement. By using RAMSAY and YOUNG's data on the density of the liquid ρ_v and of the vapour ρ_d above 0° (for the critical temperature they found also ~~103.0~~, which agrees perfectly) and an interpolation-formula deduced from PIERRE's formule and a determination of the density at —71,°5 by Dr. KUENEN

H193,°0

$$\frac{\rho^\circ}{\rho} = 1 + 15172 \times 10^{-7} t + 22.55 \times 10^{-7} t^2 + 0,2119 \times 10^{-7} t^3 + 0,00470 \times 10^{-7} t^4$$

by which the density at —102° can be found by extrapolation, we can calculate the relative value of the surface-energy *H* given in the last column. EÖTVÖS's formula (Wied. Ann. 27) does not agree with these results. From the data in his paper we can calculate the relative value of the surface-tension of ether at 120°, 62°, 0°, which he determined by another method not dependent on the angle of contact. If we were allowed (the density of the vapour ρ_v and the way in which the influence of the vapour is taken into account not being mentioned at all) to multiply this surface-tension by $\rho_v - \rho_d$ his measurements would approach nearer to those of ours. If *H* is graphically represented as a function of θ, the curve, near the critical temperature, proves to turn its convex side to the *T*-axis in

such a way that by a regular continuation of this part it might end touching the *T*-axis. Undoubtedly an accurate knowledge of its form in this part is of high theoretical importance. An investigation thereof is now being undertaken.

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COMMUNICATIONS
FROM THE
LABORATORY OF PHYSICS
AT THE
UNIVERSITY OF LEIDEN
BY
PROF. DR. H. KAMERLINGH ONNES.

No. 7.

Dr. J. P. KUENEN. Some experiments about the connection between the two plaits in the surface of VAN DER WAALS for mixtures
(*Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Akademie te Amsterdam, van* **24 Juni 1893**, *p.* 28).

Dr. L. H. SIERTSEMA. The dispersion of the magnetic rotation in oxygen.
(*Translated from the same p.* 31.)

EDUARD IJDO — PRINTER — LEIDEN.

Dr. J. P. KUENEN. *Some experiments about the connections between the two plaits in the surface of* VAN DER WAALS *for mixtures.*

As a continuation of my researches about the critical phenomena of mixtures of two substances 1) some new experiments were made. During my observations of the mixture of $^3/_5$ methyl chloride and $^2/_5$ carbonic acid, occasionally on the fluid, which appears with small volumes, a small quantity of a second fluid phase had become visible, which was separated from the former by an indistinct and gradually (by stirring even immediately) disappearing meniscus. This gave rise to the question, whether it might be possible to acquire such circumstances of temperature and volume, wherein methyl chloride and carbonic acid should show three coëxisting stable phases. The possibility thereof was not excluded: for Prof. VAN DER WAALS in this treatise on the theory of mixtures 2) laid particular stress on

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1) Arch. Néerl. 26. p. 369—390; Zeitschr. Phys. Chem. 11. p. 38—48; Comm. Lab. of Physics. Leiden n°. 4.

2) Arch. Néerl. 24. p. 54—56; Zeitschr. Phys. Chem. 5. p. 172—173.

the connection between the situation of the plaitpoint 1) of the gas-fluid plait in the surface on the side of the small volumes and the existence of the second plait, which indicates the not mixing of the substances in the liquid state. In fact this plaitpoint P_2 would properly speaking belong to the second plait, which would in this case constitute one whole with the first plait, whereas the plaitpoint of the first plait P^1 would but become visible on the binode curve 2), when the temperature had neared the critical temperature of the most volatile component. (conf. the figure in Prof. V. D. WAALL's treatise 3), where the form of the spinode curve indicates the approach of a second plaitpoint i. e. of P_1). Below that temperature therefore two plaitpoints might be found, that is to say the possibility of three phases for al mixtures the ratio's (x) of which are contained within the triangle formed by the three phases. When the temperature sinks below the critical temperature of the above mentioned component and accordingly the plaitpoint P_1 falls outside the surface, still a coëxistence of three phases for mixtures within certain limits will remain possible, if only the plaitpoint P_1 has not likewise fallen outside the surface or disappeared altogether. In this way we have got the case of two substances, which do not mix in the liquid state within certain limits of quantity (as ether and water) and will probably do so even less at lower temperatures.

In orde to investigate whether this is the case with methyl chloride and carbonic acid the afore mentioned mixture was accurately observed. The results obtained in my former paper prove that the surface for these two substances has at any rate no two plaitpoints in the neighbourhood of the critical temperature (100° C.—106.5° C.) The mixture was now investigated at lower temperatures nearing the critical temperature of carbonic acid, but here two stable liquid phase were not obtained either. The fact that no three phases were found is no proof at all of the non-existence of the triangle, because it is very probable that by the large quantity of CH_3Cl in the mixture its ψ-v plane does not pass through the triangle. But even after a great part of the CH_3Cl had been removed from the mixture nothing like a dividing into two liquids appeared. Besides the non-existence of the triangle is rendered probable by observations at low temperatures down to — 35° C which always showed complete mixing in the liquid state.

So with methyl chloride and carbonic acid the plaitpoint P_2 would appear not to exist above — 35° C and the existing plaitpoint (above 31° C) should be considered as actually belonging to the first plait (so as P_1), whilst according as the temperature falls towards 31° it moves to the side of the large volumes and at 31° coïncides with the critical point of carbonic acid.

In connection with the question here investigated

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1) Plaitpoint = tacnodal point; cf. KORTEWEG, Arch. Néerl. 24. p. 57. Wien. Sitz. Ber. 98. IIa, p. 1154; MAXWELL, Theory of Heat. p. 205—206.

2) Binode curve = condode curve = node-couple curve cf. KORTEWEG l.l. c.c.; MAXWELL l. c.; V. D. WAALS l. c.

3) V. D. WAALS l.l. c.c.

it seemed that great importance was to be attached to an observation of WROBLEWSKI [1]) with a mixture of $^5/_6$ carbonic acid and $^1/_6$ air (the same mixture, which was olso investigated by CAILLETET [2])); at compression and subsequent expansion at 0° C he observed two liquid and one gaseous phase [3]). If this observation were correct, the surface for these two substances would contain the above mentioned triangle at 0° C (at this temperature air may be considered as a simple substance). The same mixture was now investigated by me with the aid of my electro-magnetic stirring-apparatus [4]) and produced in the first place entire confirmation of previous results about the critical plenomena of mixtures in general. For the critical temperature I obtained 19° C, for the plaitpoint-temperature 15°6 C, between both *retrograde condensation.* CAILLETET found at first [5]) 20° C as the critical temperature, afterwards [6]) there still was condensation at 25° C. The reason of these considerable differences between the two numbers is to be found in the phenomena of retardation, the influence of which was discussed in my treatise already cited [7]).

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[1]) a. o. Wied Ann. 26. p. 134—135.

[2]) Compt. Rend. 90. p. 210.

[3]) WROBLEWSKI observed the same phenomenon with liquid air.

[4]) Arch. Néerl. 26. p. 372; Zeitschr. Phys. Chem. 11 l. c.; Comm. etc. n° 4.

[5]) Compt. Rend. 90. p. 210.

[6]) JAMIN, Compt. Rend. 96. p. 1451.

[7]) Arch. Néerl. 26. p. 371. sqq; Zeitschr. Phys. Chemie 11. p. 40. sqq.

The efforts in consequence of WROBLEWSKI's investigation to obtain the three phases near 0° C were in vain however; though very often a second, even a third meniscus was formed, it soon appeared that these states were transient and disappeared by stirring. This proves that the triangle does not exist at the chosen temperatures.

In order to find a case at last, in which the fluidplait might be expected and would make its influence felt even between the critical temperatures, a treatise of DEWAR [1]) was referred to, who compressed carbonic acid in the presence of several substances. One case, in which DEWAR states that liquid carbonic acid was clearly visible on the other fluid was that of carbon disulphide: no particulars are given about the quantity used. I began by repeating this experiment. In a tube filled with pure carbonic acid a thin layer of CS_2 was brought. By a treatment with mercury and distillation the CS_2 had been purified to a colourless fluid of an agreeable smell, which did not attack the mercury at all. When the mixture was compressed the second layer of liquid showed itself on the CS_2: at low temperatures especially the phenomenon was very clear; as soon however as the small piece of iron, within the tube, was moved, it became evident, that equilibrium did not exist, and the substances mixed completely; in fact in the vicinity of the meniscus mixing-phenomena were to be observed from the be-

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[1]) Proc. R. S. of L. 30. p. 538.

ginning. THILORIER [1], as I found out afterwards, already states in opposition to DEWAR that CO_2 and CS_2 are miscible in all proportions.

The investigations into the connection between the two plaits are now being carried on with carbonic acid and water.

The results communicated here show clearly, how great the influence of retardation may be and of how great a significance careful stirring is for those experiments.

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[1] Ann. Ch. et Phys. 60. p. 430.

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

The dispersion of the magnetic rotation follows in most substances pretty much the same law that governs the natural rotation, viz. that the rotation varies inversily as the square of the wave-length. The strongly magnetic substances form an exception to this law. In solutions of iron-salts and a few others the dispersion is, according to BECQUEREL [1], much greater, the rotation varies inversely as the fourth power of the wave-length. In iron, nickel and cobalt the rotation, according to KUNDT [2] and LOBACH [3], increases with the wave-length. Also with the phenomenon of KERR, which is closely connected with the foregoing, KUNDT [2], RIGHI [4], DU BOIS [5] and ZEEMAN [6] found anomalous

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[1] H. BECQUEREL, C. R. 83. p. 125 (1876); Ann. de Ch. et de Ph. (5) 12. p. 68 (1877).

[2] KUNDT, Wied. Ann. 23. p. 228 (1884).

[3] LOBACH, Wied. Ann. 39. p. 347 (1890).

[4] RIGHI, Ann. de Ch. et de Ph. (6) 9. p. 136 (1886).

[5] DU BOIS, Wied. Ann. 39. p. 25 (1890).

[6] ZEEMAN, Dissertatie Leiden (1893); Verslag Kon. Akad. v. Wetensch. Amsterdam Oct. 1892 en Febr. 1893.

dispersion. Oxygen seems to stand between these two groups. BECQUEREL [1]) found the dispersion in this case to be very slight; the rotation for red was somewhat larger than for green, but he himself thinks the measured angles of rotation too small to establish this with sufficient certainty. With other measurements of the magnetic rotation in oxygen made by KUNDT and RÖNTGEN [2]) no dispersion was determined.

This peculiar bearing of oxygen deserves to be more accurately investigated, not only for the fact itself, but also because several theories have been published of late, explaining all optical phenomena with the electromagnetic theory of light. For when in this way the optical properties of a substance are brought into connection with the magnetic, it is by the very deviations, which the strongly magnetic substances show, that we can test these theories.

When, as VON HELMHOLTZ [3]) proves, the ordinary dispersion in the electro-magnetic theory of light can be explained by introducing into the formulae quantities which are related to the molecules (electric moment, friction), it is probable that these considerations, when we take the magnetic properties of the molecules into account, can also explain the magnetic rotatory dispersion. In this case the optical behaviour of a magnetic gas, whose molecular structure is certainly much more simple than that of a metal, will be of great importance to the theory.

For this reason it is very desirable, that the magnetic rotatory dispersion of oxygen should be more narrowly investigated. Some preliminary results of such an investigation will be communicated here.

The arrangement of the apparatus resembles, in its main features, that of KUNDT and RÖNTGEN. The gas is enclosed with a polarisator and an analysator in a long tube under high pressure, and the rotation is obtained by fixing one end of the tube, and turning the other, so that torsion is given to the tube. The tube lies in a long bobbin, through which circulates the magnetising current.

The apparatus differs from that of KUNDT and RÖNTGEN in so far that instead of tourmalines nicols are used for polarisator and analysator, and that monochromatic light is used sufficiently intense to point at the black line, which can be observed in the field of two nicols with perpendicular principal planes [1]). Moreover the magnetic potential difference at the extremities of the bobbin with a current of 70 amp. is 315000 C. G. S. units, whereas this quantity only reached 90000 C. G. S. with the bobbins of KUNDT and RÖNTGEN. This apparatus not only shows greater rotations than those of KUNDT and RÖNTGEN but also enables them to be measured much more accurately.

The copper tube, which contains the gas, is 2 M. long,

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[1]) H. BECQUEREL, Ann. de Ch. et de Ph. (5) 21 p. 289 (1880); Journ. de Ph. (1) 8. p. 198 (1879); 9 p. 265 (1880).

[2]) KUNDT und RÖNTGEN, Wied. Ann. 8. p. 278 (1879); 10. p. 257 (1880).

[3]) VON HELMHOLTZ, Wied. Ann. 48. p. 389 (1893).

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[1]) LIPPICH, Wien. Sitz.-Ber. 85. II. p. 269 (1882).

3 cM. wide. To the ends are fastened large pieces of coquille-bronze, in which are placed the nicols. These pieces are closed by flanges, in which a piece of glass is inclosed by a nut. The thickness of the walls is calculated for a pressure of 200 atm., with threefold certainty. The tightness of the joints is obtained by rings of lead, which caused no peculiar difficulties. Only at the glass-pieces we had to take care, by means of a little paper ring, that metal and glass did not come in contact with each other. In order to obtain the greatest intensity of light, the nicol which is used as analysator must be so large, that all the light, proceeding from the tube, can pass through it. Owing to this the endpiece at this side of the tube assumes rather great dimensions. When, as will be shown hereafter, iron and steel are excluded, the best material for the construction of these pieces is coquille-bronze, which excels by its peculiar toughness and homogeneity. The described pieces were constructed in the utmost perfection in the cannon-foundery of the Hague by the friendly care of the concerned authorities.

The endpieces are lodged in supports of bronze, so that the greater one is fixed in a six-angled frame, and the smaller one can be turned. To the latter piece is fastened a long rod, by means of which rotations can be given to this piece with the aid of cords and little pullies. The angles of rotation were measured with mirror and scale.

The nicols are provided with perpendicular ends, and are chosen so as to show the black line very distinctly. They are fixed in tubes, so that the gas can pass very

easily on all sides. When this was not attended to, the nicols were observed to move at the entering of the gas. The black line remains very distinct at high pressures. Only once, when the apparatus had been left filled during 4 to 5 days, under a pressure of 100 atm., in order to try the tightness, the nicols had ceased to transmit the light, and an examination showed that the layer of Canada-balsam had become untransparent. When this had been repaired, the gas was let out after every experiment, and never remained longer than half a day in the apparatus; in this way the nicols remained perfectly transparent. The tubes in which the nicols are held, can turn in a ring, which can be adjusted with screws in the endpiece, in such a manner that it is exactly perpendicular to the ray of light.

The nicols are carefully adjusted in perpendicular positions before closing the apparatus.

Through the tube passed parallel monochromatic light, proceeding from an arch-lamp of 30 amp., or from the sun. In a telescope behind the tube is observed the image of the slit in the collimator, which makes parallel the monochromatic light. In a spectroscope of DESAGA, placed behind the tube, instead of the telescope, the light covers 3 to 4 divisions, whereas the whole visible spectrum covers 90 divisions. There were also made some observations according to another method, in which is sent parallel white light through the tube; this was resolved into a spectrum after leaving it. By this method the absorption-bands, observed by LIVEING and DEWAR [1]), could be used to determine the wavelength.

The magnetising bobbin consists of two equal parts, placed one behind the other, each part 1 M. long. They consist of a brass tube, 6 cM. wide, provided with flanges, on which are wound 12 to 13 layers of copper wire, of 6 mM. thick. The total number of windings on both bobbins is 3600, the total resistance nearly 1 Ohm. The current of 70 amp. which can circulate through this bobbin was produced by a dynamo of 75 Volt. The space between the bobbin and the tube enables us to prevent the transition of heat. Without this precaution the heating is soon great enough to excite currents in the gas in the tube, which render the image confused; and all subsequent pointings impossible. All the parts of these bobbins, as well as the whole apparatus, which contains the gas, are made of copper or bronze, and wholly free from iron. The magnetic field is in this way proportional to the intensity of the current, which is of great importance for its calculation and measurement. We find for the magnetic potential-difference with 70 amp., calculated by the known formula $4\pi in$ 320000 C. G. S., whereas from a determinations of the rotation in water is deduced 314000 C. G. S.

With this apparatus were made some preliminary experiments with oxygen out of the commercial iron cylinders, at a pressure of about 100 atm., which gas appeared to contain 94% pure oxygen. From these

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[1]) LIVEING and DEWAR, Phil. Mag. (5) 26. p. 286 (1888).

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experiments it follows that, contrary to the result of BECQUEREL mentioned before, the constant of magnetic rotation in oxygen decreases regularly with increasing wave-lengths, and that for violet it is twice as large as for red. It agrees tolerably well with the constant, which can be deduced from the determinations of KUNDT for white light.

COMMUNICATIONS

FROM THE

LABORATORY OF PHYSICS

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 8.

Dr. P. ZEEMAN. Comparison of measurements on the reflexion of light from the polar surface of a magnet with the theories of GOLDHAMMER and DRUDE.

(*Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Akademie te Amsterdam*, *van* **29 October 1893,** *p.* 82.)

Dr. J. P. KUENEN. On the abnormal phenomena near the critical point.

(*Translated from the same p.* 85.)

EDUARD IJDO — PRINTER — LEIDEN.

Dr. P. ZEEMAN. *Comparison of measurements on the reflexion of light from the polar surface of a magnet with the theories of* GOLDHAMMER *and* DRUDE.

According to DRUDE (Wied. Ann. Bd. 49, p. 696. 1893) the formulae of his theory on the magneto-optic phenomena are a particular case of the results of GOLDHAMMER's theory [1]), that is to say, that GOLDHAMMER's complex constant b is in DRUDE's theory a real quantity. Hence it follows, that SISSINGH's phase [2]) may be calculated in the manner given by GOLDHAMMER and also followed by DRUDE [3]).

It was communicated to the Academy 29 October 1892, that my measurements on the reflexion of polarised light from the polar surface of a magnetized cobalt-mirror [4]) are not in accordance with this view.

DRUDE's theory gives the following values of SISSINGH's phase for.

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[1]) GOLDHAMMER, Wied. Ann. Bd. 46, p. 72. 1892.

[2]) ZEEMAN, Archiv. Néerl. T. XXVII. p. 254, 1893 and Diss. Leiden 1893. p. 3.

[3]) DRUDE, Wied. Ann. Bd. 48, p. 124. 1893.

[4]) Vide also ZEEMAN, l. c. p. 296.

	iron (D-light)	cobalt (red light)	nickel (D-light)	
	76°16′	61°26′ [1]	60°	
I have found	80°	45°32′	30°	(preliminary determination).

It is wholly impossible to attribute the discordances to errors of measurement.

It seems however that DRUDE is not convinced by the calculation of SISSINGH's phase from the observations and still prefers to calculate the rotations with mean values of the magneto-optic constants, deduced from the observed rotations. In the following communication I will make use of the latter manner of calculation. The refutation of DRUDE's remarks on my measurements (Wied. Ann. Bd. 49 p. 490. 1893) is hereby simplified.

DRUDE himself pays in his theory a particular attention to the angles of incidence, whereby, the incident light being polarised *perpendicular* to the plane of incidence, the so-called null rotation of the polarisator is = 0. ($\psi^0{}_{ip} = \psi^0{}_{ia} = 0$) [2]. At angles of incidence, greater or smaller than those just named, the sign of the rotations is opposite. The value of that particular angle is indeed a very suitable criterium for the exactness of the proposed theories.

From DRUDE's theory in the case of polar reflexion

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[1] In a communication to the Academy of Amsterdam 29 Oct. '92 this value was erroneously given 80°.

[2] Vide for notation. SISSINGH. Phil. Mag. April 1891.
ZEEMAN, l. c. p. 262.

it follows, when the calculations are made with the values of the optical constants as given by him, that a reversal in the sign of the rotations may be expected

for iron at the angle of inc. $i = 67°6'$ (D. light)
» cobalt » » » » » $i = 64°50'$ »
» nickel » » » » » $i = 60\ 35'$ »

Wholly different GOLDHAMMER's theory gives a reversal of sign

for iron at $i = 64°$ ($S = 80°$)
» cobalt » $i = 50°$ ($S = 49°5°$)
» nickel » $i = 35°$ ($S = 36°$).

In the calculation the values of SISSINGH's phase closed in brackets were made use of. In the case of iron the value of S is known from SISSINGH's measurements on the reflexion from the aequatorial and from my measurements from the polar surface of a magnet. In the case of cobalt my polar measurements give the value; whereas for nickel, accepting according to analogy that also in this case the value of SISSINGH's phase will be found nearly constant within wide limits, I determined a preliminary value of $S = 30°$ (deduced from observations at the angle of incidence $i = 50°$). If the value of S were $= 32°$, then there must be at an angle of incidence of 10° a reversal of the null rotations, whereas for values of S, less than 31°, there cannot be according to GOLDHAMMER's theory a reversal, when the incident light is polarised perpendicular to the plane of incidence.

An accurate determination of SISSINGH's phase for nickel was therefore much wanted. Some measurements made by Mr. WIND in the Leiden laboratory, point to the fact, that S is nearly equal to 36° and that $\psi^0_{lp} = 0$ at about 35°. This result confirms GOLDHAMMER's theory, but it is impossible to account for it by DRUDE's

For D-light ψ^0_{lp} must be = 0 for

	iron	cobalt
according to DRUDE's theory at	67°6′	64°50′
whereas observations gave	63° (RIGHI)	51°,5 (ZEEMAN).

What has been said above wholly confirms my former [1]) result about DRUDE's theory.

Not only that particular rotation, treated above, but also the rotations at other angles, are duly predicted by GOLDHAMMER's theory. No doubt there is a misunderstanding on the part of DRUDE in his considerations [2]) on this point.

He makes the supposition, that the rotations as observed by me, were made at the same magnetisation. The contrary was however l. c. [3]) expressly stated. I have, using the proper magnetisations, recalculated the rotations according to DRUDE's and GOLDHAMMER's theories. The tables exhibit the rotations, reduced to the same magnetization in minutes, the result of the 2 theories

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[1]) ZEEMAN, l. c. p. 296.

[2]) DRUDE, Wied. Ann. Bd. 49. p. 690. 1893.

[3]) ZEEMAN, Dissertation p. 40 and p. 43 and Archiv. Néerl. p. 288, 293.

(G and D) and the differences between observation and theory. The notation of the minimum and null rotations is the same as that used and quoted in the beginning. The angle of incidence is indicated by ϕ.

	ψ^m_{la}			$-\psi^m_{lp}$			$-\psi^0_{lp}$			ψ^0_{la}		
ϕ	obverv.	D	diff.	observ.	D	diff.	observ.	D	diff.	observ.	D	diff.
45°	+ 15.0	+ 13.9	+ 1.1	+ 11.8	+ 10.6	+ 0.8	— 1.4	— 13.4	+ 12.0	+ 17.5	+ 28.6	— 11.1
60°	+ 16.2	+ 14.2	+ 2.0	+ 10.3	+ 8.9	+ 1.4	+ 3 2	— 2.2	+ 5.4	+ 13.4	+ 17.3	— 3.9
73°	+ 11 2	+ 14.1	— 2.9	+ 6.1	+ 6.1	+ 0.8	+ 5.3	+ 3.0	+ 2.3	+ 9.5	+ 12.3	— 2.8

GOLDHAMMER's theory gives:

	ψ^m_{la}			$-\psi^m_{lp}$			$-\psi^0_{lp}$			ψ^0_{la}		
ϕ	observ.	G	diff.	observ.	G	diff.	observ.	G	diff.	observ.	G	diff.
45°	+ 15.0	+ 15.6	— 0.6	+ 11.8	+ 12.1	— 0.3	— 1.4	— 1.4	— 0.0	+ 17.5	+ 17.1	+ 0.4
60°	+ 16.2	+ 16.7	— 0.5	+ 10.3	+ 10.5	— 0.2	+ 3.2	+ 3.0	+ 0.2	+ 13.4	+ 12.9	+ 0.5
73°	+ 11.2	+ 12.5	— 1.3	+ 6.9	+ 7.2	— 0.3	+ 5.3	+ 5.8	— 0.5	+ 9.5	+ 10.1	— 0.6

Again it follows, that great differences remain between DRUDE's theory and observation. With GOLDHAMMER's theory there is no discrepancy between theory and observation, especially when it is considered, that the measurements were made in the first place for the determination of the phase, whereby there is no influence of possible errors in the determination of the magnetization [1]).

Undoubtedly now the determination of the phase at

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[1]) ZEEMAN, l. c. p. p. 14 and 27.

normal incidence from a normally magnetized mirror becomes of great interest, in order to decide whether SISSINGH's phase has the same value at all incidences. This investigation, of great importance to judge on the exactnes of the description of the phenomena by GOLDHAMMER's theory, is therefore prepared in the physical Laboratory of the Leiden University.

Dr. J. P. KUENEN *On the abnormal phenomena near the critical point.*

Various phenomena are seemingly opposed to ANDREWS's clear conception of the connection between the liquid and the gaseous states of matter and the signification of the critical point [1]. In the first place the disappearing and reappearing of the liquid surface at other volumes than the critical volume, the explanation of which phenomenon STOLETOW [2]) finds in the smallness of the difference between the indices of refraction. Accurate observation of the phenomenon suffices to render this hypothesis improbable: at a given moment independent of the illumination the surface is seen to lose its clearness and to change into a layer of transition, as with two liquids mixing. Moreover the disappearing-temperature would not alter with the volume, which on the contrary it does (vid. below).

CAILLETET et HAUTEFEUILLE [3]) and CAILLETET et COLARDEAU [4]) conclude from their experiments with a solution of iodine in carbonic acid, that the liquid and vapour

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[1]) cf. RAMSAY Pr. R. S. of L. 30 p. 323.

[2]) Physik. Revue II Juli 1892. p. 44. 73.

[3]) C. R. 92 p. 840, 1086.

[4]) C. R. 108 p. 1280.

still exist above Andrews's critical temperature, but acquire the property of mixing together. However the fact is sufficiently explained by the slow diffusion of the iodine through the carbonic acid; there is no necessity of adopting the influence of differences of temperature as Stoletow [1]) does.

They confirmed the experiment by another with an O-tube,[2]) on which Pellat [3]) based his distinction between the real critical temperature, at which the densities agree and the lower temperatures, at which the surface disappears. The problem was further examined experimentally by Zambiasi, [4]) who began by confirming the experiment with the O-tube with ether. Then he found, that the disappearing temperature increased according as the quantity of liquid was smaller. De Heen [5]) on the contrary finds that the temperature is higher the smaller the quantity of vapour is.

New light has been thrown upon the problem by Gouy's [6]) extensive and accurate investigation, in which he shows that a distinction should be made between the *état final* of the substance and the *états variables*, differing from it. He furthered the establishment of equilibrium by repeatedly turning the Natterer-tubes filled with CO_2 and thus found that the disappearing

of the surface in the état final is observed within very narrow limits of density only (0.438 and 0.470; critical density = 0.464 Amagat) and that with densities outside these limits, the disappearing is possible only when the equilibrium has not yet been attained. [1]) the fact, that even in the état final the surface disappears at different volumes and not merely at the critical volume, as follows from Andrews's theory, Gouy [2]) ascribes to the influence of gravitation. The truth of this conclusion is evident: it will easily be seen, that within certain narrow limits near the critical volume the surface may disappear at different heights in the tube and always exactly *at the critical temperature*, [3]) whilst there, where the surface is disappearing, we find the critical pressure and the critical density.

Two earlier observations by de Heen [4]) are in accordance with Gouy's experiments. One tube in which the surface had disappeared was reversed and then cooled, whereas another tube remained in its former position. In the latter the surface reappeared nearly at the same point, where it had formerly disappeared, in the former however a cloud spread through the tube. In

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[1]) l. c. p. 63.

[2]) C. R. 108 p. 1284.

[3]) Journ. de Ph. (3) 1. p. 225.

[4]) Atti Acc. Linc. (5) I. 2. p. 423.

[5]) Bull. Ac. R. des Sc. de Belg. (3) 24. p. 96.

[6]) C. R. 116 p. 1289. June 1893.

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[1]) The limits of the phenomenon are very wide in this case, as with the experiments with ether. Here it was observed by Zambiasi and de Heen within the volumes 2,6 and 6,2, whereas the critical volume amounts to 4,0 (ccm per gram).

[2]) l. c. and C. R. 115 p. 720.

[3]) The disappearing-temperatures seem indeed to have shown but minimal differences in Gouy's experiments too; vid. the final points of the two curves.

[4]) l. c. 24 p. 277 and 25 p. 14,15.

a second experiment a tube was heated at 35° C. for 24 hours: at cooling a cloud spread through the tube, which was dissolved into a thin liquid layer upon the mercury, though the surface had disappeared at a much higher point. In the former case the état final was brought about by reversion of the tube, in the latter by time.

Before being acquainted with GOUY's work and DE HEEN's last experiments I had concluded from the experiments which were known at that time, that with the disappearing of the surface we had to do with retardation [1]), and have succeeded in showing in a way different from GOUY's that the deviations from theory vanish if the substance is well mixed. To this end I made use of my electromagnetic stirring-apparatus, employed by me in my investigation of mixtures [2]). As I pointed out in my treatise and was also shown by DE HEEN's experiments, the cooling (resp. expansion) proves an excellent means to distinguish homogeneous from not homogeneous states. The critical volume of the carbonic acid investigated by me amounted to ± 35, expressed in an arbitrary unit. When the volume was less than 34 and the substance was rendered homogeneous bij stirring above 31° C., slow decrease of temperature produced at about 31° C. a cloud through the tube and then the liquid surface at the top of the tube, with volumes larger than 36 also a cloud and then the surface close to the mercury. The limits within which the surface could disappear in case of stability, are therefore no wider than 34 and 36, which distance about agrees with GOUY's.

No doubt the same result will be attained with ether, if care is taken to establish stability.

How to explain this retardation? Theoretically in a simple substance retardation may be admitted only, if one of two possible phases is entirely wanting or forms itself with difficulty, whereas observation shows, that as soon as the phase begins to form the most stable equilibrium is established in a very short time, sometimes even in the manner of an explosion. Here however we have to deal with the fact that the evaporation or condensation regularly lag behind, which reminds us of phenomena of diffusion of two substances. No doubt therefore we may assume retardation as soon as we ascribe some influence to the slight impurities of our so-called pure substances. [1])

Indeed from this point of view the phenomena may be easily explained. Only it should be borne in mind, that the amount of retardation and the direction in

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[1]) With the volume 2.9 ZAMBIASI saw the meniscus rise slowly, which is typical for a retarded process; when the O-tube was cooled an equal quantity or an unequal was observed in the branches, according as the temperature fell at once or after being raised to 196 C. etc. The influence of time was already noticed by RAMSAY l. c.

[2]) vid. Arch. Néerl. 26 p 354—422. Z. Phys. Ch. 11 p. 38.

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[1]) As regards ether, vid. TAMMANN. W. A. 32 p. 683. GOUY says l. c.: „Il y a lieu d'examiner si ces différences entre l'état final et les états variables ne sont pas dues à la présence d'un peu d'air mélangé au CO_2" cf. HANNAY, Pr. R. S. of L. 30, p. 478—489.

which it works depend on the nature of the impurities, in as much as some will for the greater part be found in the liquid other in the vapour. Moreover the special circumstances of the experiments (as width of the tubes rate of change of temperature, mobility of the tubes) will influence the results, so much that agreement of the results of different experimentators is not even probable (vid. ZAMBIASI and DE HEEN) [1].

Suppose for instance some air is mixed with the ether: it will for the greater part be present in the vapour. If the volume is below v_k, the liquid will increase at rise of temperature partly because it expands partly because the vapour condenses. The latter process will now be retarded by the presence af air. Slowly according as the air is absorbed by the liquid and spreads through it by diffusion equilibrium will be attained. The liquid remains beneath its normal quantity; the densities also lay behind. Meanwhile the tube is heated above the temperature, at which all should be homogeneous; this may call forth a condition, in which the free surface between the phases is impossible. We may say, that the separating surface disappears, as soon as we attain a continuous transition between the two phases without unstable states, as the latter occasion the formation of a free surface. [2] It is clear that a similar state of continuous transition will be attained as we approach an ordinary case of diffusion of gases.

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[1] Consequently it is impossible to draw PELLAT's line (l. c.)

[2] vid. V. D. WAALS. Thermodynamical theory of capillarity etc. Kon Acad. Amsterdam I, n⁰ 8. 1893.

It should be remembered in the first place, that by impurities mixed with the liquid the evaporation of the liquid will be chiefly retarded (with volumes larger than v_k); in the second place that as a rule the impurities will be so slight, that the deviations of the disappearing-temperature will be small, and even that the final state after diffusion need not necessarily differ considerably from the state of the pure substance. If we keep all this well in mind, the facts, which can be decuded from the retardation of diffusion occasioned by impurities, agree so well with observation, that we have a right to maintain this explanation as long as its insufficiency has not been proved otherwise. [1] New theories about simple substances seem to me at present superfluous for the explanation of the critical phenomena.

Now that the great influence of retardation has once been established, we should be very careful in the acceptance of results, which have not been proved to be exempt from that influence. DE HEEN's [2] conclusion, that vapour-density is a quantity dependent on the quantity of liquid in contact with the vapour, cannot be accepted as proved. In the first place we point out, that the vapour-densities calculated especially when they turn out so much greater, are obtained by the division of two small magnitudes and therefore must of necessity be uncertain. Besides the retardation in

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[1] The details of the experiments with the O-tube and the other experiments mentioned are likewise in accordance with the explanation laid down here.

[2] l. c. 24 p. 267—285.

those cases must have diminished the quantity of liquid and will so have caused a too great value for the density. The experiment with the U-tube[1]) too proves nothing but that absolute homogenity is very slow in coming: from the experiments we may only conclude, that the influence of the retardation is perceptible even at temperatures far below the critical.

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[1]) l. c. 24 p. 278. sq.

COMMUNICATIONS

FROM THE

LABORATORY OF PHYSICS

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 9.

Dr. C. H. WIND. Measurements regarding the SISSINGH magneto-optical phase difference in the case of polar reflexion from Nickel.

(*Translated from: Verslagen en Mededeelingen der Kon. Akad. v. Wetenschappen te Amsterdam*, **27 Januari 1894**, *p.* 116.)

EDUARD IJDO — PRINTER — LEIDEN.

Dr. C. H. WIND. *Measurements regarding the Sissingh magneto-optical phase difference in the case of polar reflexion from Nickel.*

Through SISSINGH's experiments [1]) concerning equatorial reflexion on iron magnets, attention has been drawn, for the first time, to the fact, that there is a difference between the phase of the magneto-optical component in the KERR effect, as deduced from observation, and that derived from the theory of LORENTZ [2]), which difference is nearly constant within ample limits of the angle of incidence. GOLDHAMMER [3]) has inserted it in his theory. On the other hand ZEEMAN [4]) has shown that the same constant phase difference occurs in the case of polar reflexion on iron too, and that it also exists in polar reflexion on cobalt. My investigation shows, or makes it at least very probable, that this is likewise the case for nickel and consequently confirms the opinion, that SISSINGH's phase difference has a physical meaning.

For my experiments the apparatus as composed and

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[1]) SISSINGH, Phil. Mag. 1891; Arch. Néerl. 27. 1893.

[2]) LORENTZ. Versl. en Meded. Kon. Akad. v. Wetensch., Amst. II, 19; Arch. Néerl., 19. Cf. VAN LOGHEM, Dissertation, Leiden.

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

[4]) Vid. Communications N^r. 5, 8, 10, and citation 1) p. 3.

described by ZEEMAN [1]) was made use of — only a few alterations of minor importance were made.

As to the electro-magnet the core ending in a truncated cone, to the top of which the mirror was attached by means of canadian balm, had a diameter of 12 mM.; a special experimental examination [2]), made beforehand, had proved this thickness to be the most desirable. The mirror (a circular little disc, $1\frac{1}{2}$ mM. thick, 5 mM. diam.), though no doubt the best among a great number manufactured for the purpose of pure nickel (as it is produced in cubes by Trommsdorff at Erfurt), was not quite flat; with the aid of a microscope there could be discerned scratches, porous spots, and furrows of a more or less regular shape, which to a certain extent suggested a crystalline and fibrous structure of the metal. As long as the surface was unimpaired its optical constants were nearly equal to those given by DRUDE [3]) for pure nickel; during the experiments, however, they were subject to continual changes, which, in some instances, when the mirror was too much heated, became very considerable. This was what especially occurred during the first series of observations (the angle of incidence α being 39°4′); in the second and third series ($\alpha = 55°$ and $\alpha = 75°$) the intervals between the separate observations were taken so long, that the temperature of the mirror could not rise higher than 60°,

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[1]) ZEEMAN. Dissertation. Leiden, 1893; Arch. Néerl. 27, p. 252. 1893.

[2]) cf. ZEEMAN. Diss., p. 10.

[3]) DRUDE. Wied. Ann. 39, p. 522. 1890.

resp. 40° Celsius, and here the above changes of the optical constants, which were continually watched during the experiments, proved of no importance. As for the rest the mean of the optical constants at the beginning and at the end of the observations was made use of for the calculation of the results, the influence of the changes in the surface of the mirror may be taken to be sufficiently eliminated. In this respect the first series left much to be desired.

In the first and the third series of observations, null- and minimum-rotations were measured at every one of the eight combinations of principal positions of the nicols, which are possible[1]), as was in some cases done by Sissingh; in the second series only at four of them, two in which the plane of polarisation was parallel, two in which it was perpendicalar to the plane of incidence. Whether all systematic faults, which may be caused by imperfect condition of the nicols and other parts of the apparatus, are really quite eliminated, even when the observations are made at the eight combinations mentioned above, is a quaestion, which cannot be taken as to have entirely been settled by Sissingh's examination on this head[2]). I should rather think a very elaborate investigation to be required in order to state the degree, in which this elimination may be considered as to be attained by the method of observation.

All the measurements have been made with yellow

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[1]) Sissingh. l. c.; Kaz. Dissertation. Amsterdam, 1884.

[2]) Sissingh. Dissertation. Leiden, 1885.

light (wave-lengths from 564 to 614 $\mu\mu$). The strength of the magnetic field was determined by the same method as applied by Zeeman[1]). To derive from this the intensity of magnetization of the mirror, a special magnetic examination of the nickel used would have been necessary, for which there was at the moment no opportunity and no time. With the known data regarding the magnetie qualities of nickel, it would ensue from my observations, that the way, in which the amplitude of the magnetic component in the Kerr effect depends upon the angle of incidence is not correctly described by the theories of Lorentz or Goldhammer. It may be mentioned here, that the measurements of Sissingh and Zeeman seem to show a deviation from these theories in the same sense as mine. As, however, the determination of the intensity of magnetization is no easy matter and becomes especially very incertain for nickel, this deviation must not be considered of much importance for the present, though we might feel inclined to refer it to the crystalline structure of the metal, suggested above. If it had been my intention to compare theory and experiments with respect to the *amplitude* of the magnetic component, I should have preferred leaving the position of the »submagnet,” as well as the current power in the magnetic coil unaltered at different angles of incidence, in order to avoid the difficulties just mentioned as much as possible. However, at this examination as at Zeeman's the Sissingh phase difference was prominent, and to

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[1]) Zeeman. l. c.

determine it no knowledge of proportions of magnetisations at different angles of incidence is required, seeing that the value of this difference is deducted from the proportion of rotations at one and the same α. In order to determine this proportion as minutely as possible the magnetization at each angle of incidence should be raised as much as possible. This end could be reached only in a different degree for each separate angle of incidence, seeing that when this angle decreased, the distance of the sub-magnet, that is the width of the air-gap in the magnetic circuit, had to be made larger. Though in this way comparison of the amplitudes was rendered rather valueless, it had to be sacrificed, in order that greater precision for the determination of the phase might be acquired.

In communicating my measurements I make use of the notations, as employed by SISSINGH and ZEEMAN [1]).

I.

Angle of incidence $\alpha = 39° \, 4'$; Strength of magnetic field 2190 C.G.S.:

$$\psi^{\circ}_{lp} = 1',96 \pm 0,22; \quad \psi^{\circ}_{la} = -10',11 \pm 0,35^{5};$$

$$\psi^{\circ}_{ia} = 0',50 \pm 0,15; \quad \psi^{\circ}_{ip} = 12',90 \pm 0,16;$$

$$\psi'''_{lp} = 9',95 \pm 0,21; \quad \psi'''_{la} = -12',50 \pm 0,23^{5};$$

$$\psi'''_{ia} = -9'88, \pm 0,18^{5}; \quad \psi'''_{ip} = 12',31 \pm 0,30.$$

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[1]) SISSINGH. l. c.; ZEEMAN. l. c.

Mean values:

$$\psi^{\circ}_{ia} = -0,'73^{1)} \pm 0,13^{5}; \quad \psi^{\circ}_{ip} = 11',25 \pm 0,19^{5};$$

$$\psi^{m}_{ia} = -9',91 \pm 0,14; \quad \psi'''_{ip} = 12',40 + 0,19.$$

Before KERR-observations:

Principal angle incidence $I = 75°32'$,
Principal azimut $H = 31°26'$;

After KERR-observations: $I = 73° \, 13'$, $H = 34°9'$.

The formulae for the calculation of m_i become:

$$\text{tg. } m'''_i = -3.589 - 3,274 \frac{\psi'''_{ip}}{\psi^{m}_{ia}},$$

$$\text{cotg. } m^{\circ}_i = 3,589 - 4,238 \frac{\psi^{\circ}_{ia}}{\psi^{\circ}_{ip}}.$$

So we derive from the ψ''': $m'''_i = 26° \, 56' \pm 3° \, 52'$,
$10^3 \, \mu'''_i = -1,339 \pm 0.37^{5}$;

and from the ψ°: $m^{\circ}_i = 14° \, 30',5 \pm 11'$,
$10^3 \, \mu^{\circ}_i = -1,276 \pm 0,023^{5}$.

Most probable values, as resulting from this series of observations:

$$m_i = 14° \, 32' \pm 11', 10^3 \, \mu_i = -1,293^{5} \pm 0,020.$$

The circumstance that so little weight is to be attached to the final values resulting from the minimum-rotations agrees with the fact, that a variation of only 0',8 in

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[1]) ψ°_{lp} being positive the sign of the mean value of ψ°_{ia} should be, according to the relation $\psi_{ia} == -\psi_{lp}$ (ZEEMAN. Arch. Néerl., p. 268, 286. 1893).

the value of one of the minimum-rotations would transfer m^{m}_{i} into m^{o}_{i}. Besides this, on recently developed grounds the null-rotations should be preferred to determine the phase.

Calculated after Prof. LORENTZ's theory:

$$m_i = -23^{\circ}\,30',5.$$

II.

$\alpha = 55^{o}$, Strength of magnetic field 9560 C.G.S.

$\psi^{o}_{lp} = 5',37 \pm 0,26$; $\psi^{o}_{la} = -7',39 \pm 0,46$;

$\psi^{o}_{ia} = -5',35^{5} \pm 0,32^{5}$; $\psi^{o}_{ip} = 7',78^{5} \pm 0,32^{5}$;

$\psi^{m}_{lp} = 10',09 \pm 0,23$; $\psi^{m}_{la} = -14',54 \pm 0,31^{5}$;

$\psi^{m}_{ia} = 10',48^{5} \pm 0,23^{5}$; $\psi^{m}_{ip} = 13',22 \pm 0,20.$

Mean values:

$\psi^{o}_{ia} = -5',36 \pm 5,21^{5}$; $\psi^{o}_{ip} = 7'59 \pm 0.29$;

$\psi^{m}_{ia} = -10',29 \pm 0,17$; $\psi^{m}_{ip} = 13'88 \pm 0,19^{5}.$

Mean values: $I = 74^{\circ}\,34',5$; $H = 31^{\circ}\,53'$.

The formulae for the calculation of m_i become:

$$\text{tg. } m^{m}_{i} = -1,470 - 1,348\,\frac{\psi^{m}_{ip}}{\psi^{m}_{ia}},$$

$$\text{cotg. } m^{o}_{i} = 1,470 - 2,351\,\frac{\psi^{o}_{ia}}{\psi^{o}_{ip}}.$$

Derived from the ψ^{m}:

$$m^{m}_{i} = 19^{\circ}\,0',5 \pm 2^{\circ}\,1'; \quad 10^{3}\,\mu^{m} = -1,368 \pm 0,014^{5}.$$

Derived from the ψ^{o}:

$$m^{o}_{i} - 17^{\circ}\,43' \pm 28',5; \quad 10^{3}\,\mu^{o}_{i} = 1,333^{5} \pm 0,035.$$

Most probable values, derived from the observations:

$$m_i = 17^{\circ}\,47' \pm 28'; \quad 10^{3}\,\mu_i = -1,359 \pm 0,013.$$

Calculated after the theory:

$$m_i = -18^{0}\,36'.$$

III.

$\alpha = 75^{0}$, Strength of magnetic field 12470 C.G.S.

$\psi^{0}_{lp} = 6',16 \pm 0,13$; $\psi^{0}_{la} = -6',44^{5} \pm 0,19^{5}$;

$\psi^{0}_{ia} = -6',09 \pm 0,19^{5}$; $\psi_{ip} = 6',61 \pm 0,15^{5}$;

$\psi^{m}_{lp} = 6',25 \pm 0,15$; $\psi^{m}_{la} = -8',12 \pm 0,25^{5}$;

$\psi^{m}_{ia} = -6',28 \pm 0,15$; $\psi^{m}_{ip} = 8',01 \pm 0,27^{5}.$

Mean values:

$\psi^{o}_{ia} = -6',12 \pm 0,12$; $\psi^{o}_{ip} = 6',53 \pm 0,12^{5}$;

$\psi^{m}_{ia} = -6',26^{5} \pm 0,10^{5}$; $\psi^{m}_{ip} = 8',07 \pm 0,19.$

Mean values: $I = 75^{\circ}58'$; $H = 30^{\circ}57',5.$

The formulae for the calculation of m_i become:

$$\text{tg. } m^{m}_{i} = -0,0881 - 0,6038\,\frac{\psi^{m}_{lp}}{\psi^{m}_{ia}},$$

$$\text{cotg. } m^{o}_{i} = 0,0881 - 1,669\,\frac{\psi^{o}_{ia}}{\psi^{o}_{ip}},$$

Derived from the ψ^{m}:

$$m^{m}_{i} = 34^{\circ}\,34' \pm 50'; \quad 10^{3}\,\mu^{m}_{i} = -1,039^{5} \pm 0,014^{5}$$

Derived from the ψ^o:

$$m^o_i = 31^0\,10 \pm 37',5;\ 10^3\,\mu^o_i = -1,031 - 0,016.$$

Most probable values, derived from the observations.

$$m_i = 32^0\,24',5 \pm 30';\ 10^3\,\mu_i = -1,035^5 \pm 0,011.$$

Calculated after the theory:

$$m_i = -4^0\,44'$$

Resuming the results we have:

Angle of incidence.	m duduced from observations	theory.	$\frac{m_{obs.} - m_{theor.}}{\overline{S_{Ni}}}$
$30^0\,4'$	$14^0\,32' \pm 11'$	$-23^0 30,'5$	$38^0 2,'5 \pm 11'$
55^0	$17^0\,47' \pm 28'$	$-18^0 36'$	$36^0 23' \pm 28'$
75^0	$32^0\,24,'5 \pm 30'$	$-\ 4^0\,44'$	$37^0 8,'5 \pm 30'$

Taking into consideration that the observations at 39° 41′ have been influenced by considerable variations of the optical constants and that for that reason the values taken into account for them are certainly not exact, there are sufficient grounds to conclude from the above measurements to the probability of the existence of a Sissingh phase difference, which is nearly constant within ample limits for the angle of incidence. The experiments agree so much the better with the assumption of a constant phase difference as in the method of determining the optical constants (calculating them according to Drude's approximating formulae from Φ and h measured at an angle of incidence not very much differring from I) the theoretically calculated phase may easily deviate 10′ from the value which would have been found with the aid of correct optical constants, and the coefficients in the equations, which serve to derive μ and m from the rotations observed, are likewise not very exact.

If in determining the numerical value of the Sissingh phase difference we don't take into account the results of the observations at 39°4′, which are by far the least reliable, also because the "Sub-magnet" was not so well centred during these experiments as during the other series, we find:

$$S_{Ni} = 36^0 44' \pm 20,'5 \text{ for } D\text{-light,}$$

whereas Zeeman had derived a preliminary value of 30° from measurements on a nickel mirror, electrolytically plated on Kundt's platined glass. The most probable error given at the value of S_{Ni}, as only calculated from the single orientations of the Nicols, cannot give an exact measure for the accuracy of the results obtained. By reason of the sources of error mentioned above, the degree of accuracy obtained is somewhat less.

The conclusions, which Zeeman 1) derived from the numerical value of S_{Ni} after his preliminary determination, hold good at the value more carefully determined by me.

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1) Zeeman. Arch. Néerl., 27, p. 296. 1893.
Vid. also: Communications 5, 8 and 10.

10

COMMUNICATIONS

FROM THE

LABORATORY OF PHYSICS

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 10.

Dr. P. ZEEMAN. The phase in the case of polar reflextion from cobalt and nickel and the angle of reversal of the null rotation $\psi^0{}_{lp}$ according to theory and experiment, (*with a diagram*).

(*Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Akademie te Amsterdam van* **21 April 1894,** *p.* 174.)

EDUARD IJDO — PRINTER — LEIDEN.

Dr. P. ZEEMAN. *The phase in the case of polar reflexion from cobalt and nickel and the angle of reversal of the null-rotation ψ°_{lp} according to theory and experiment, (with a diagram).*

In a former communication [1]) I pointed out the great difference between DRUDE's theory and my observations on cobalt, especially as to the angle of incidence at which the null rotation $\psi^{\circ}_{lp} = \psi^{\circ}_{la}$ is $= 0$ and the direction of rotation is reversed. Now $\psi^{\circ}_{lp} = 0$ only means that the phases of the magneto-optical component (m) and of the metallic reflexion (Φ) are of the same numerical magnitude. Let a line be drawn representing the phase of the metallic reflexion at every angle of incidence. Let also lines be drawn representing the phase of the magneto-optical component according to observation and theory, then the intersections of these lines give us the observed and calculated angles of the reversal of the sign.

Besides, the diagram gives a very clear representation of the whole course of the phase in the rival theories, clearer indeed than any table can give. Therefore, I thought important the actual drawing of these curves

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[1]) Verslagen Afd. Natuurkunde, 29 Oct. 1893. These communications n°. 8.

for cobalt and nickel, partially using the already known data, partially now determining what was wanted.

Experiments on cobalt and nickel are best fitted to distinguish between the rival theories, because the value of SISSINGH's phase for these metals is much lower than for iron.

Cobalt. Fig. 1 represents:

1. The phase Φ of metallic reflexion, calculated according to the formulae of CAUCHY.
2. The phase $m_b + S$ of the magneto-optical component [1]) as calculated according to GOLDHAMMER's [2]) theory.
3. The phase m according to DRUDE's theory. As this theory immediately gives the rotations [3]), I calculated those ones in the first place and hence derived the phases according to known relations.
4. The observed phases, as determined by my former observations [4]). This line in the case of cobalt so nearly coincides with line 2, that it is not drawn in the figure.

The data for the construction of the diagram are given in the following table:

i	Φ	$m_b + S$ (GOLDHAMMER)	m_w (Observ.)	m (DRUDE)
45°	18°38′	20°43′	20°34′	11°39′
60°	36°42′	27°31′	27°40′	29°44′
73°	75°18′	37°47′	37°55′	94°48′

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[1]) ZEEMAN. Arch. Néerl. T. 27. p. 296. 1893.

[2]) GOLDHAMMER. Wied. Ann. Bd. 46. p. 72. 1892.

[3]) DRUDE. Wied. Ann. Bd. 46. p. 401. 1892.

[4]) ZEEMAN. l. c. p. 293.

I have adopted for S the value 49°30′, which I have given on a former [1]) occasion.

According to the figure the said reversal according to DRUDE takes place at i about 64°,5.

According to observation and GOLDHAMMER's theory the result identically is $i = 49°24'$.

The course of the phase wholly differs according to GOLDHAMMER and DRUDE, but as was already remarked, the observed line of the phases coincides with that one derived from GOLDHAMMER's theory.

The theory of Prof. LORENTZ, of which GOLDHAMMER's is a modified form, gives a line for the phases, quite parallel to GOLDHAMMER's line, but with ordinates differing to the amount of SISSINGH's phase.

In fig. 2 and 3 I have yet given the representation of a table, in my former communication [2]), showing the observed null- and minimum-rotations and those derived from GOLDHAMMER's and DRUDE's theories. Evidently from these figures we find the same values of the point at which the reversal takes place.

Nickel. The observations of Mr. WIND on the reflexion from nickel don't extend to the region, wherein ψ°_{lp} becomes null. Hence for my purpose an extension of his measurements was necessary; also it was desirable to repeat the observations at $i = 39°4'$, because, according to the communication of Mr. WIND, different causes of error may have falsified his results obtained as that angle of incidence.

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[1]) ZEEMAN. l. c. p. 293.

[2]) Verslagen Afdeel. Natuurk. 29 Oct. '93, Communication n°. 8.

Now I will communicate the results of my measurements on white light, using my former notations. For different particulars as to the precautions used, the method of observations etc., I refer to the publication cited in n° 5.

I.

angle of incidence $i = 39° 4'$ intensity of the field $H = 2190$ C. G. S.

Mean: $\psi^{\circ}_{lp} = + 2{,}9' \pm 0{,}24'$ $\psi^{\circ}_{la} = -- 6{,}1' \pm 0{,}24'$.
Mean $I = 75° 26'$ $H = 31°43'$ for light of refrangibility D.

The formula for determining m_l becomes

$$\text{cotg } m_l = 2{,}194—4{,}614 \frac{\psi^{\circ}_{lp}}{\psi^{\circ}_{la}}$$

Most probable value derived from the observations

$m = 9° 17' \pm 24'$ $10^3 \mu = - 0{,}975 \pm 0{,}050$.

Prof. Lorentz's theory gives:

$$m^l = - 26° 44'.$$

II.

angle of incidence $i = 25°$ intensity of the field $H = 2190$ C. G. S.

Mean: $\psi^{\circ}_{lp} = + 0{,}5' \pm 1{,}0'$ $\psi^{\circ}_{la} = - 8{,}6' \pm 0{,}9'$.
Mean: $I = 75°16'$ $H = 31°15'$ for light of refrangibility D.

The formula for determining m_l becomes:

$$\text{cotg m}_l = 10{,}445 - 10{,}997 \frac{\psi^{\circ}_{lp}}{\psi^{\circ}_{la}}$$

Most probable value derived from the observations

$m = 5° 9' \pm 43'$ $10^3 \mu = - 1{,}00 \pm 0{,}12$.

According to Prof. Lorentz's theory.

$$m_l = - 30° 29'.$$

I also endeavoured to perform null rotations at smaller angles of incidence. However I did not finish these series, because at $i = 22°$ the probable error of the mean

of ψ°_{la} amounts to about ± 3,1′
» ψ°_{lp} » » » ± 2,7′.

Hence a determination of the phase in this manner is of no value for the determination of Sissingh's phase.

Resuming the now obtained results and those found by Dr. Wind at the angles 55° and 75° we have:

angle of incidence.	m observed.	m_b calcul.	S
25°	5°9′ ± 43′	— 30°29′	35°38′ ± 43′
39°4′	9°17′ ± 24′	— 26°44′	36°1′ ± 24′
55°	17°47′ ± 28′	— 18°36′	36°23′ ± 28′
75°	32°25′ ± 30′	— 4°44′	37°9′ ± 30′.

The final result for Sissingh's phase becomes, if the different weights of the observations are taken into account.

$$S_{Ni} = 36°21' \pm 15' \text{ for } D\text{-light}.$$

In fig. 4 the same 4 curves for nickel are drawn, which were given above for cobalt.

The circles, the centres of which are on the curve 4 give the probable error in m.

Fig.I.

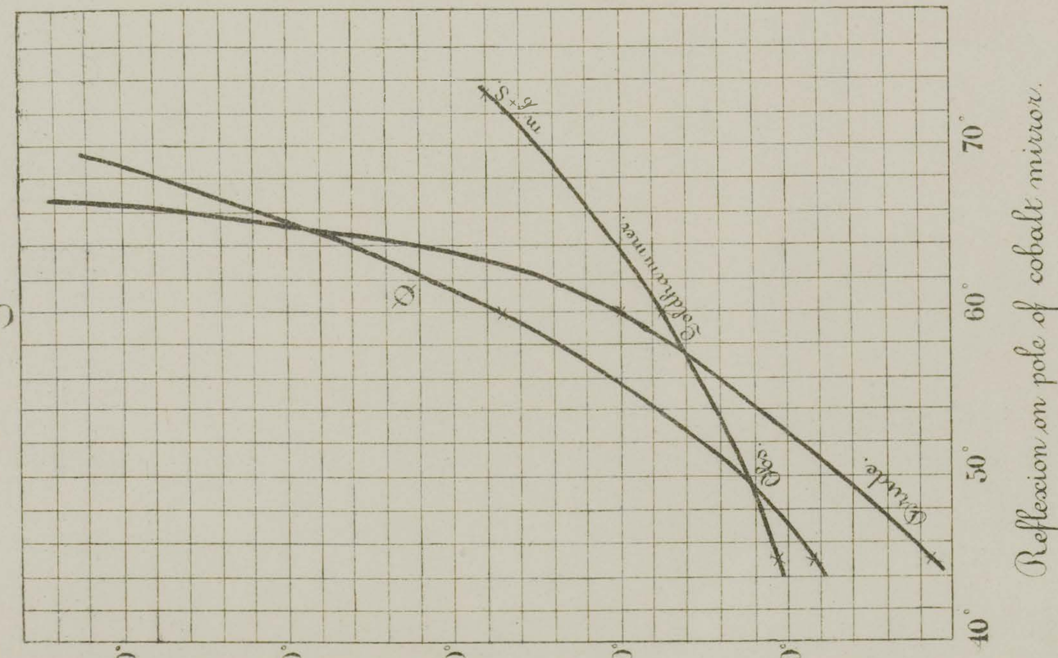


Fig.II.

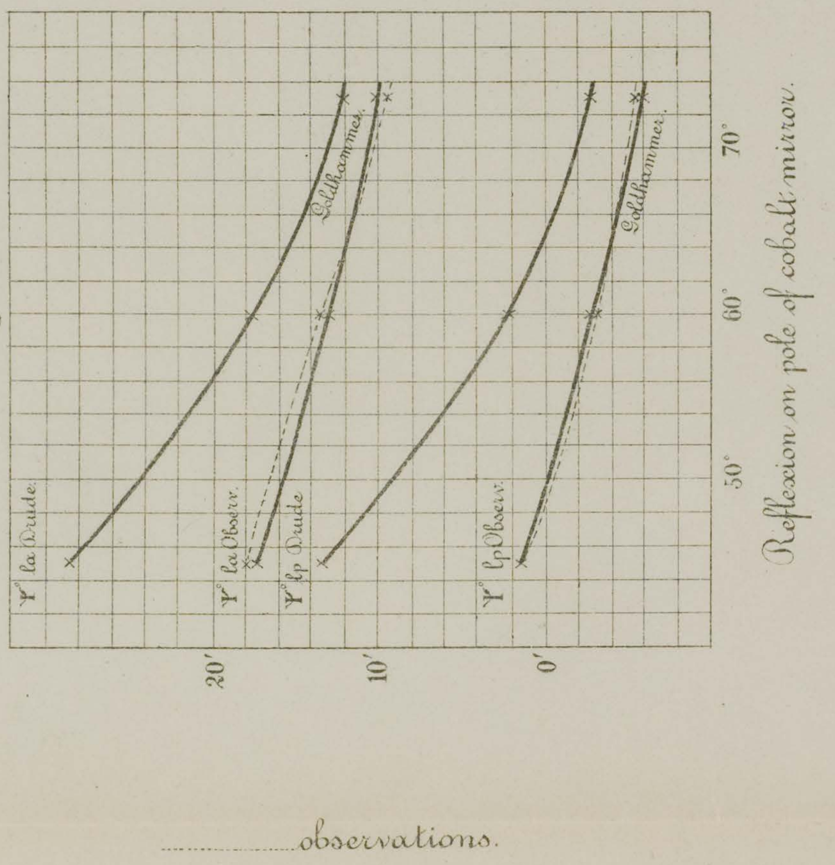


Fig.III.

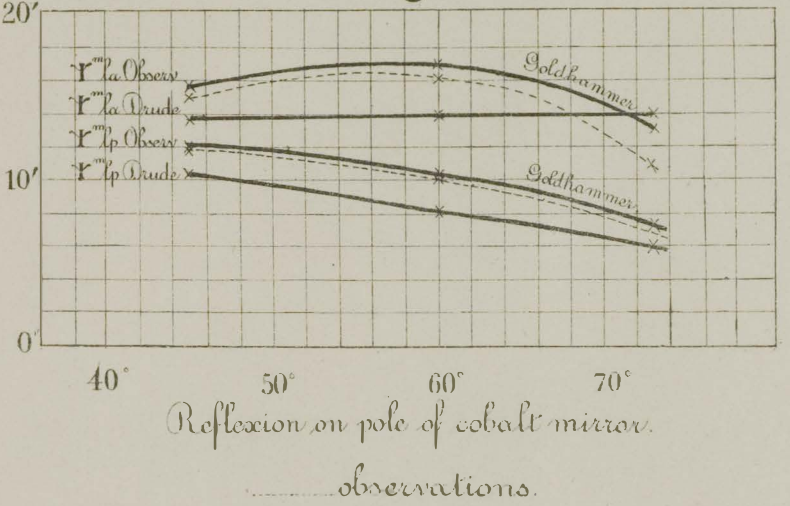
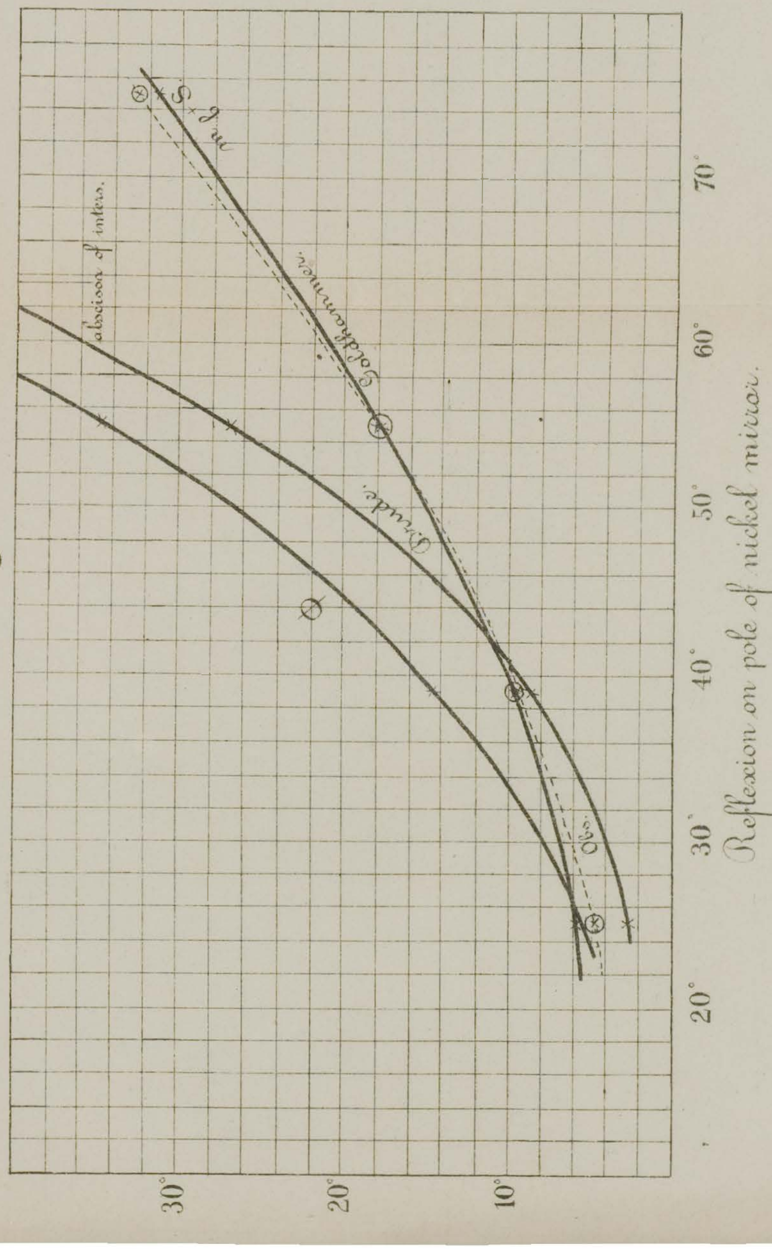


Fig.IV.



man, Kerr's phenomenon 1893/94.

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The points of the curves are determined by the numbers given in the following table.

i	Φ	$m_b + S$ (Goldhammer)	m_w (Observ.)	m (Drude)
25°	5°30′	5°52′	5°9′ ± 43′	2°58′
39°4′	14°19′	9°17′	9°17′ ± 24′	8°45′
55°	34°14′	17°45′	17°47′ ± 28′	26°58′
75°	84°58′	31°37′	32°25′ ± 30′	115°7′.

The intersection of DRUDE's line with the line Φ gives the reversal of the rotations at $i = 63°30'$. ¹)

Observation however gives this reversal at about $i = 24°$.

According to GOLDHAMMER's theory this should be at about $i = 26°$. The difference between the 2 last numbers however does not surpass the limits of the errors of observation, because at $i = 25°$ was found $\psi^{\circ}_{lp} = +0{,}5' \pm 1',0$. Hence ψ°_{lp} may very well become null at 26°.

The investigation which I am carrying on, concerning the light normally reflected from the polar surface, will decide this point and also the constancy of SISSINGH's phase. But, whatever may be the result of this inquiry, now already we may state that GOLDHAMMER's final formulae describe the phenomena in a very satisfactory way, the remaining differences being of a different order of magnitude than the differences between observation and DRUDE's formulae.

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¹) This value differs somewhat from that given in the assembly of the Acad. of 29 Oct. '93, then being made use of DRUDE's more severe formulae.

This difference of course does not influence our results.

11

COMMUNICATIONS

FROM THE

LABORATORY OF PHYSICS

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 11.

Dr. J. P. KUENEN. Some experiments regarding the anomalous phenomena near the critical point. (With a plate).

(*Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Akademie te Amsterdam, van* **26 Mei 1894**, *p.* 19–34).

UE **Dr. J. P. KEUNEN**. Further experiments regarding the anomalous phenomena near the critical point.

(*Translated from the same* **30 Juni 1894**, p. 57–62).

EDUARD IJDO — PRINTER — LEIDEN.

Dr. J. P. KUENEN. *Some experiments regarding the anomalous phenomena near the critical point*

In a former communication on the same subject ¹) I was led to the conclusion, that the phenomena near the critical point observed by different experimenters do not lead to the accepting of a new theory about vapour and liquid of a simple substance, that the ordinary theory, which may be called the ANDREWS-VAN DER WAALS theory, is in harmony with all observations, if only the influence of impurities, of retardation, connected with it, and gravitation is taken into account. Since then some new investigations about the critical point have been published, of which especially those of BATTELLI ²), GALITZINE ³) and WESENDONCK ⁴) deserve to be mentioned. For the greater part these observations are the same or of the same kind as those described by ZAMBIASI, DE HEEN, GOUY etc. before, and to those therefore refer the considerations laid down in my

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¹) Verslagen Kon. Akad. van Wet. Afd. Natuurkunde 1893/1894 Oct. p. 85—90. Communications etc. n⁰. 8.

²) Ann. Ch. et Phys. (6) 29 p. 400—432.

³) Wied. Ann. 50. p. 521—545.

⁴) Naturw. Rundschau 9. 209—212.

former paper [1]). In the meantime an important note has appeared by RAMSAY and YOUNG [2]), in which depending on experimental labour of years they unreservedly declare, that the anomalies do not belong to the real conduct of bodies and can be entirely explained by disturbing circumstances (differences of temperature, impurities etc.). The importance of this note is still more enhanced by the fact, that RAMSAY had been the first, starting from observed irregularities, to set up a new theory [3]) and now, with his collaborator YOUNG, declares his observations to have been caused by the presence of impurities.

In the 5th paragraph of his paper GALITZINE describes a new experiment, which he supposes to confirm, what he calls »die neueren Anschauungen über die Molekularvorgänge in Flüssigkeit und Dampf" having in view the theories as brought forward by DE HEEN [4]),

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[1]) In WESENDONCK's paper for instance an observation is described, the explanation of which seems to be easy. A Natterer-tube heated quite above the critical temperature and therefore apparently quite homogeneous, showed mixing-phenomena (striae, cloudy appearance) by being turned at constant temperature. When it is considered, that in consequence of gravitation the density and, if some impurity is present, also the composition of the mixture varies regularly with the height in the tube, the observed fact can but appear quite natural.

[2]) Phil. Mag. (5) 37 p. 215—218. Vid. Young, Trans. Chem. Soc. 59, p. 128.

[3]) Pr. R. Soc. of L. 30 p. 323.

[4]) Physique Comp. 1888. Bull. Ac. r. de Belg. passim. o. a. 24 p. 281.

BATTELLI [1]) a. o. Into an U-shaped tube he introduces two quantities of ether separated from each other by a column of mercury; one is entirely liquid at ordinary temperature, the other in part vapour. This tube is heated beyond the critical temperature and the volumes occupied by both quantities are measured. With three tubes investigated in this manner GALITZINE finds large differences of density between both branches of the tube, diminishing with rising temperature, but at 15° or 20° C above the critical temperature still amounting to 20%; the larger density he always finds at the liquid-side of the tube independently from the relative height of the mercury in the two branches of the tube. These differences were not of a transitory nature, but did not change in the course of $1^1/_2$ hour, and are supposed by GALITZINE not to be connected with the presence of air, as he derives from the fact, that admittance of air at the vapour-side of the tube did not change the phenomena to a large extent. It does not seem to me to be superfluous in connection with this experiment rigorously to formulate the »neueren Anschauungen" and to see, which form they must assume, in order not to be inconsistent with GALITZINE's and other experiments. This is necessary, because the theories of DE HEEN, BATTELLI a. o. cannot be said to have been developed very precisely, so much so that, as will appear, they lead to results contradictory to observed facts, which they are supposed to explain. If starting from GALITZINE's experiment we accept his

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[1]) Ann. Ch. et Ph. (6) 25 p. 38. 26 p. 394. 29 p. 239, 400.

explanation of his observations as right, we are led to the hypothesis, that at least two different kinds of ethermolecules exist, of which one is lighter and chiefly present in the vapour, the other denser and for the greater part existing in liquid ether. We may now make two different suppositions. The first is, that these two kinds of ethermolecules (liquid- and vapourmolecules) can pass into each other, that is to say that the liquidmolecules are to be considered as compounds of vapourmolecules, as is also admitted by De Heen 1). The hypothesis in this form we will call Hypothesis I. This Hypothesis I is not inconsistent with the Andrews-van der Waals's theory taken in a general sense. Many observations of late show the probability, that in many cases the transformation of a vapour into a liquid consists for a part in the formation of such complexes of molecules. The formation of these complexes can commence in the homogeneous state already and will especially take place to a large extent quite above the critical temperature, where the density changes so rapidly. Unattacked however remains, if not the form and the derivation of van der Waals's formula, still the existing of a system of unambiguously determined isothermal lines, the property that one point of the p-v-diagram represents only one state of equilibrium with determined p, v, and T, in which exists a definite proportion between the number of simple molecules and complexes of molecules. In this way it at once appears, that the hypothesis I is unable to perform, what it is meant to do, viz. to explain

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1) l. c. „molécules liquidogènes”.

Galitzine's experiment and on the other hand, that his experiment cannot confirm the hypothesis, taken in this manner. For according to this theory differences of density as found by Galitzine in the homogeneous state at the same temperature and pressure, ought to disappear gradually, as the stable condition is attained, in which the same proportion of simple and compound molecules is found at both sides. The contrary has been observed by Galitzine, as was mentioned above. We come to the same conclusion as to other anomalous phenomena, which are supposed to be explained by hypothesis I, as for instance the small slope of the lines, which indicate the coëxistence of two phases in the p-v-diagram, a well-known phenomenon, recently again observed by Battelli 1), who even from his observations calculates the relative number of compound molecules. The application of the thermodynamical rule for deriving the possible phases from the system of isothermal lines (Gibbs) must in this case take place in the ordinary way and at definite temperature only one pressure and one possible composition of both coëxisting phases is found. In absolute contradiction with this same conclusion is one of de Heen's 2) experimental results, viz. the difference of density of saturated vapour in the presence of more or less liquid, which fact he maintains to be entirely explained by the new theory! A clearer

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1) Ann. Ch. et Ph. (6) 25 p. 66. 29 p. 242. Battelli's opinion, that the curvature of the straight line at the end is connected with the course of the theoretical isothermal line (J. J. Thomson), also arises from a misconception.

2) l. c. 24 p. 281.

proof of the unsatisfactory way in which the theoretical question has been treated by the originators of the »neueren Anschauungen" is hardly possible [1]).

If therefore it is thought necessary as by de Heen and others for the explanation of the anomalous phenomena observed to call to assistance the hypothesis of the compound molecules, only one way lies open viz. to suppose, that the two different kinds of molecules are different in nature and cannot pass into each other. We call this: Hypothesis II. According to this supposition vapour-molecules issuing from the vapour of ether might solve into liquid ether and perhaps be condensed into the fluid state, but the liquid originating thus would not be liquid ether but only condensed vapour of smaller density than real liquid ether. On the other hand ether might evaporate, but this vapour would not be vapour of ether, but evaporated liquid of larger specific gravity than real vapour and other properties, which the experimenter should learn to distinguish from those of ordinary vapour. Between these extremes in both liquid and vapour different modifications would be possible, formed

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[1]) Independently from the questions discussed here it might be asked, whether this Hypothesis I would not have the advantage of explaining the retardation without the influence of impurities being admitted: the dividing of the liquid-molecules into the vapour-molecules might take some time. It is to be observed however, that this time ought to be extremely long (Gouy sometimes had to keep his tubes at constant temperature during a whole week!) for which supposition no analogue exists; whereas the fact cannot astonish us, if we regard the phenomenon as caused by diffusion.

by mixing the two sorts of ether-molecules, for which therefore the *laws of mixtures* would hold good. The hypothesis in this form, which admits two kinds of ether, which must be called chemically different, would perhaps succeed in explaining some observed facts and Galitzine's result among them, but who would like to accept it with its consequences stated above? Of these two kinds of ether (and the same would be the case with many other substances) with properties differing so widely nothing has ever been discovered in the most trustworthy experiments [1]) and Ramsay and Young therefore do not hesitate to declare in their note, that the experiments, which compel to the accepting of such an hypothesis (as Galitzine's experiment) must be ascribed to experimental errors, a statement against which Galitzine and de Heen [2]) have protested without delay.

However with regard to Galitzine's experiment, which is perhaps the most surprising, we may not content ourselves with doubt, however justified it may be; immediately after the publication of Galitzine's paper I set myself to repeat the investigation, in order to find out, under what circumstances such results could be obtained. For discovering differences of density, as found by Galitzine, his method being a differential-method seems to be very fit.

It seemed of high importance to follow Galitzine's method as faithfully as possible and to take all precautions

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[1]) Regnault's observation (Mém. de l'ac. 26, p. 375, 824) has not been confirmed.

[2]) Phil. Mag. (5). 27. p. 423, 424.

necessary for making a pure experiment. GALITZINE states, that in his tubes in consequence of his manner of filling them some air was probably left. This quantity will probably not have been very small 1° because the liquid at the liquid-side never divided (at least nothing of the kind is mentioned) not even when the mercury was higher at that side, 2° because the phenomena did not alter by the admitting of a large quantity of air. In order to avoid the presence of air and other impurities as much as possible, the following disposition was chosen[1]). The *U*-shaped tube *F* (vid. Plate) (inner diameter ± 3.5 mm.) is closed at one end (liquid-branch of the tube); the other end is connected to a *T*-tube a small sphere *E* being between them. Both open ends of the *T*-tube are provided with conical glass ground joints: by aid of one (*A*) at the end of the long horizontal tube the apparatus may be connected to a mercury-pump: to the other joint *B* a sphere *C* filled with ether may be connected. This joint is made tight by aid of the small globe *D*, which is filled with mercury: in this way the use of grease is avoided. The direction of the *U*-tube is nearly perpendicular to the *T*-piece and therefore horizontal; in this way by turning the apparatus round the first joint (*A*) the *U*-tube undergoes small changes of position near the horizontal direction without the sphere *C* deviating too much from the vertical position; the turning of the tube is necessary during the boiling of the mercury and the ether. The liquid-branch and a part of the vapour-branch are now filled with the quantity of pure mercury required, and the mercury is made to boil in an atmosfere of nitrogen at the mercury-pump. The sphere is then provided with a quantity of pure ether distilled from pure sodium; and some fresh sodium is added: then the ether is cooled to —80° C, made to boil at the air-pump and then distilled into the *U*-tube by cooling this until the whole tube and the sphere *E* are full. Then it is made to boil again, until the vapour-bubbles formed can be made to disappear entirely in a moment and at last the tube is sealed under the surface of the ether at *G*; the quantity of liquid remaining in the tube was chosen so that it nearly occupied its critical volume at the critical temperature, which I succeeded pretty well in doing as a rule. In the tubes, which were filled by cooling with solid carbonic acid, it sometimes happened, that some ether was found between the mercury and the glass. It soon appeared that the cause was to be looked for in the freezing of the mercury, which contracts in solidifying. Afterwards the temperature of the cooling liquid was kept above — 40° C and the phenomenon did not show itself any more.

The *U*-tube being ready the quantity of ether in the vapour-branch was measured. All measurements at ordinary temperature were made the tube being placed in a vessel with water. The readings were taken with a cathetometer. The perpendicular position of the tube

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[1]) The description given here pertains to the last tube examined, the results of which will be given further on. The treatment of former tubes only differed in details; where it seemed to be necessary experience obtained with other tubes has been added to the description.

was controlled continually [1]) and the glass vessel was especially chosen so, that errors arising from the refraction of the glass might not influence the results too much.

In order to make the tube ready for the measurements a part of the liquid must be transported to the liquid-branch. Notwithstanding the care, with which the glass, mercury and ether had been treated, it sometimes happened, that this operation did not go on very easily because of a sort of sticking of the mercury to the glass. This was very troublesome, because the utmost care had to be taken, lest a part of the vapour should also be introduced into the liquid-branch. Probably the reason of it was to be looked for in the surface of the glass, which by repeated heating, cleaning, boiling of the mercury etc. was perhaps decomposed a little and therefore obtained other capillary properties, which supposition was confirmed by a faint bluish colour in the wide part of the tube, as is sometimes observed in old bottles. Nothing like a chemical action between the ether and the mercury could be discovered.

An important fact, which appeared without exception, consists in the presence of some permanent gas in the vapour-branch of the tube. The ether introduced into the liquid-branch remained undivided at first notwithstanding the greater level of the mercury on that side, in consequence of the ether being almost absolutely without gas: by hitting the tube or heating it the ether

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[1]) To a slope of 2.4° corresponds an error of 0.001 in a measurement of a vertical distance: the error cannot have amounted to that in my experiments.

could be made to divide and then at the vapour-side a pressure of 5 or more mm. became manifest. While by inclining the tube the ether at the liquid-side could be reunited in a moment, the same could not be done at the vapour-side, without warming the tube at the other side, though before the sealing of the tube the vapour-bubbles disappeared in a moment. The hypothesis I cannot explain this, because the difference of pressure did not disappear of itself. Moreover the wole of the ether is got from boiled liquid ether and therefore cannot contain many vapour-molecules (speaking in the language of the IInd Hypothesis). Should not decomposition of the ether be supposed to be the reason of this phenomenon? As far as I know, this probability has not been taken into account till now, though in many and manifold experiments the same thing must have happened [1]). Chemical analysis might perhaps decide this question (cf. p. 26, 27). The quantities of gas as calculated from the differences of pressure expressed in weight-proportion are exceedingly small, and do not exceed 0.00002 or 0.00003.

The ether being transported, the quantities on both sides were measured at ordinary temperature, first with undivided, then with divided liquid, by means of which a calibration of the ends of the tube was obtained.

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[1]) For instance with Natterer-tubes filled with ether. The products of the decomposition of ether by conduction through a glowing tube are: ethylene, aldehyde, hydrogen, water, methane. The decomposition of methylchloride by the sealing of the tube was formerly established by myself by means of a deposit of carbon. (Arch. Néerl. 26. p. 360.)

For the observations at high temperatures a combination of a vapour- and a liquid-bath was made use of viz. glycerine being heated by purified methylic salicylate boiling under different pressures. The bath resembles that of Galitzine and is in principle the same as the one used before by myself 1) and by Dr. E. C. de Vries 2) for his experiments on the capillarity of ether. It seems superfluous to describe it more extensively. The U-tube was fixed to a glass rod which was put into the glycerine and fixed in a stand. In this way no inequality of temperature by conduction of heat was to be dreaded, as with a metal bar. Moreover the position of the tube was now independent from the small displacements of the liquid-bath resulting from changes of pressure in the vapour-bath. The thermometers used (0.2° C) have been compared to a standard-thermometer, which has been controlled by the Phys. Techn. Reichsanstalt in Berlin.

During the heating the following difficulty arose: Galitzine does not mention the dividing of the liquid in the liquid-branch of the tube and it seems as if during the heating such a thing did not take place, not even with the tube in which the level of the mercury was highest at the liquid-side. With my tubes however the liquid always divided at a temperature far below the critical temperature though hardly any gas was present in the liquid-branch. Happily this point does not seem to be of high interest: for, as the

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1) c. f. Arch. Néerl. 26. p. 363 sqq.

2) Dissertation. Leiden 1893. p. 17 sqq., 31.

deviations found by Galitzine have been proved by himself not to depend on retardation, the condition of the ether in both branches can only depend upon their original contents and not upon the history of the substance between the original and the final condition: therefore it cannot make any difference, whether the ether has divided or not during the heating. But in order to anticipate the objection, that here at least a difference between Galitzine's and my experiments exists, by means of the following device the liquid at the liquid-side was kept undivided. Through a thin copper tube situated quite above the liquid-branch of the tube within the glycerine bath a stream of water is conducted. By this means the glycerine above and around the ether cools a little and the small difference of temperature arising from that is sufficient to prevent the dividing of the liquid. Comparison of readings, with or without dividing liquid, proves the validity of the above reasoning; the readings do not differ more than must be ascribed to the uncertainty of the method.

Example: volume of the ether in the vapour-branch v_v, in the liquid-branch v_l (expressed in mm. of the tube at 15° C.)

		liquid undivided	divided
at 223.3° C.	v_v	40.46	40.50
	v_l	44.32	44.24
at 206.5° C.	v_v	40.73	40.70
	v_l	44.24	44.25

The agreement is even better than might be expected. Henceforth it appeared unnecessary to prevent the liquid from dividing and the tube was left alone during the heating.

It therefore appears (as GALITZINE found) that the condition of the substance above the critical temperature in the circumstances of the experiment is not much influenced by retardation and so does not change much with time. This I proved separately by putting a small stirring-rod within the vapour-branch of the tube and by testing the influence of stirring [1]. Here again no changes could be established with certainty. Observation of the position of the surfaces during a long time confirmed this result. Only in the beginning after the temperature had been reached now and then a small displacement of the mercury was observed, but it is very probable, that this displacement must be ascribed not to retardation but to the time wanted for the establishment of a stable condition within the bath. Moreover the displacements were much smaller at least at high temperatures than the differences to be discovered by this investigation.

Tracing the different sources of errors I find

1° the differences of temperature. Approaching the critical temperature from above, the position of the mercury becomes more and more susceptible to variations. At one or two degrees above the critical temperature a mean value may be given in the Tables, but the exact value is uncertain. This is the effect of small variations of temperature in the glycerine-bath, which sometimes under unfavourable circumstances could be

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[1] c. f. Arch. Néerl. 26. p. 372. Communications etc. n°. 4. p. 5.

observed with the thermometer, though as a rule the thermometer throughout the whole bath at different heights did not show any differences. In order to get an idea of the influence of a difference of temperature between the two branches, I have calculated for some temperatures by the aid of CLAUSIUS's formula [1] for ether the difference of temperature corresponding to a definite difference of volume at constant pressure, the volume being nearly equal to the critical volume. Thus I found:

At 10° above the critical temp. for 1% diff. of vol. 0.17° diff. of temp.
» 5° » » » » » 1% » » » 0.11° » » »
» 1° » » » » » 3% » » » 0.05° » » »

It is evident, how sensitive a differential-thermometer a GALITZINE-tube is near the critical point. During my experiments at 5° above the critical temperature sometimes variations of 1% occurred, but generally they were not larger than 0.5%. At higher temperatures changes of the position of the surfaces could not be established with certainty. Near the critical point variations of 3% and 4% occurred; all these variations correspond to differences of temperature of 0.05° — 0.1° C. As a rule however even at these lower temperatures the mean values obtained at one temperature agree pretty well. Moreover the observations were always made in two positions of the tube, differing 180°, by means of which possible constant differences of temperature between the two sides of the bath could be

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[1] Wied. Ann. 14. p. 701.

eleminated. There existed some chance of such constant differences, as the inner tube, in consequence of the continual low pressure within the vapour-bath and the giving way of the rubber stopper, had shifted a little from its coaxial position and the stream of the vapour consequently had not the same strength on all sides.

2°. The uncertainty of the form of the liquid surfaces. The form of the surfaces was not to be observed easily in the glycerine. The heights measured on different occasions above the critical temperature lay between 1.17 and 1.26, by which in the correction ($= {}^1/_3$ of the height) an error of 0.02 is possible i. e. of less than 0.1 % in the volumes. The influence is more important at ordinary temperature. Not only the readings were as changeable as at high temperatures, but besides the influence on the small columns of ether to be measured is much greater: an error of ${}^1/_2$ % is not impossible there.

3°. Enclosing of drops of liquid between the mercury and the glass. It was impossible entirely to collect the liquid or to determine by eye the quantity enclosed; but the size of the vapour-bubbles formed at high temperature was very small. A part of the small differences between the volumes read at different time proceeds from this source of errors.

4°. Variation of the section of the tube. From a provisional calibration it appears that the mean value of the section on both sides differed 0.8 %. The variations on one side are smaller, but must have had some influence on readings at different heights of the tube.

5°. Besides we must recall here the error arising from the walls of the glass tubes used as baths on the lengths measured, together with the errors of reading, dependent from different illumination and different pointing of the telescope. The influence of these causes together may have amounted to 0.5 mm. in a single reading: it was eliminated as well as possible by repeating the measurements with different positions of the tube.

From the foregoing we conclude, that errors of ${}^1/_2$ and 1 % can be entirely explained by the errors of the method, but that the deviations especially in the final values will be smaller as a rule.

The results obtained with my last tube will be communicated here completely: they agree qualitatively with those afforded by former tubes. The volumes are expressed in the volume of 1 mm. of the tube at 15°. Corrections have been applied for the quantity of vapour, for the liquid surfaces, for the expansion of the glass, for the volume of the two ends of the tube, for the errors of the thermometers, for the expansion of the ether.

v_v = volume in the vapour-branch.
v_l = » » » liquid-branch.
$V = v_v + v_l$.

I. Volume of the ether at 15° C, before the transport of a part of the liquid to the liquid-branch.

$$v_v = V = 29.75 \text{ mm.}$$

II. Volume of the ether at 15° C, after a small quantity having been transported to the liquid-branch:

$v_v = 23.68$ $v_l = 6.10$ $V = 29.78$ (undivided liquid in liq. br.)
$v_v = 23.64$ $v_l = 6.09$ $V = 29.73$ (divided » » » »)
Mean value: $v_v = 23.66$ $v_l = 6.09$.

III. Volume of the ether at 15° C, after a larger quantity having been transported to the liquid-branch:

$v_v = 14.18$ $v_l = 15.72$ $V = 29.90$ (undivided)
$v_v = 14.06$ $v_l = 15.68$ $V = 29.74$ (divided)
Mean value: $v_v = 14.12$ $v_l = 15.70$

IV. Volume of the ether at 15°.C, again with a small quantity in the liquid-branch:

$v_v = 23.04$ $v_l = 6.68$ $V = 29.72$ (undivided)
$v_v = 22.97$ $v_l = 6.68$ $V = 29.65$ (divided)
Mean value: $v_v = 23.01$ $v_l = 6.68$

The proportion of v_v and v_l represents the proportion of the quantity of ether present in both branches. The differences between the corresponding volumes may give an idea about possible errors.

Before communicating the complete results obtained at high temperatures, we must say a word about the expansion of the glass and the mercury. This expansion is revealed by the fact, that the sum of the entire volumes at both sides (outside the mercury) is different at high and low temperature. We found for this volume outside the mercury:

I. Before the transport of liquid at 15° C 86.69

II. 1st series at 15° C 86.76, 86.56 mean: 86.66
at 222° C 84.22
Difference for 207° C 2.44

III. 2nd series at 15° C 86.90, 86.66 mean: 86.78
at 223° C 84.45

Difference for 208° C 2.33
IV. 3rd series at 15° C 86.71, 86,77 mean: 86.74
at 223° C 84.11

Difference for 208° C 2.63
Mean difference for 208° C 2.47

This diminution of length contains the apparent expansion of the mercury, diminished by the linear expansion of the glass. By calculation I obtain for this quantity circa 2.50, agreeing very well with the quantity derived from observation.

The results obtained with the tube are laid down in the following Tables, in which:

v_v = volume at the vapour-side expressed in mm of the tube at 15° C.
v_l = » » » liquid-side » » » » » » » »

▲ = difference of pressure between v and l expressed in mm. of mercury.

σ_v and σ_l = calculated densities on both sides.

A = their difference expressed in percents.

I. 1st series. At high temperatures pressure higher at the vapour-side (△ positive).

Temp.	v_v	v_l	$\frac{v_v}{v_l}$	∠	σ_v	σ_l	A (%)
194.5	66.79	18.00	3.71	17.2	0.255	0.244	—4.5
198.9	67.34	17.43	3.86	18.5	0.253	0.252	—0.6
203.0	67.40	17.31	3.89	18.6	0.253	0.253	+0.2
207.6	67.46	17.21	3.92	18.8	0.252	0.255	+0.9
221.6	67.31	17.22	3.81	18.7	0.253	0.255	+0.6
15.0	23.66	6.09	3.88	+7.4	0.72	0.72	—

II. 2nd series. At high temperatures pressure higher at the liquid-side (Δ negative).

Temp.	v_v	v_l	$\frac{v_v}{v_l}$	Δ	σ_v	σ_l	A (%)
194.7	47.74	37.50	1.273	—20.9	0.213	0.301	+35
195.0	45.53	39.67	1.148	—25.3	0.223	0.285	+24
196.7	41.80	43.19	0.968	—32.5	0.240	0.262	+8
202.4	40.80	44.14	0.924	—34.5	0.249	0.256	+2.8
206.5	40.71	44.24	0.920	—34.6	0.250	0.255^5	+2.3
223.3	40.48	44.28	0.914	—35.1	0.251	0.255	+1.7
15.0	14.12	15.70	0.900	+ 3.4	0.72	0.72	—

III. 3^d series. At high temperatures pressure higher at the vapour-side (Δ positive).

Temp.	v_v	v_l	$\frac{v_v}{v_l}$	Δ	σ_v	σ_l	A (%)
194.5	65.48	19.25	3.40	15.1	0.253	0.250	—1.3
196.1	65.74	18.90	3.48	15.5	0.252	0.254^5	+1.0
199.1	65.71	18.98	3.46	15.3	0.252	0.253	+0.5
205.9	65.67	18.96	3.46	15.4	0.252	0.254	+0.6
222.7	65.52	18.90	3.47	15.2	0.253	0.254^5	+0.6
15.0	23.01	6.68	3.44	+9.3	0.72	0.72	

For the critical temperature I found circa 194.3° C

While intending to discuss the above results in another paper, I wish to give here the general conclusion to be drawn from the foregoing tables.

While GALITZINE finds large differences of density between the two branches of the U-tubes, which at 15° C above the critical temperature sometimes amount to 20 %, such differences here only occur in II and

even there only quite near to the critical temperature. At 3° C above the critical temperature the differences are beneath 8 % already, at 10° C above the critical temperature beneath 3 %, at 15° C beneath 2%. In the other cases I and III the differences are very small. Moreover GALITZINE always finds the density largest in the liquid-branch of the tube whereas the density is here found largest in the vapour-branch in I and III near to the critical temperature. The differences therefore found here are of a different magnitude and sometimes of a different direction to those in GALITZINE'S experiments.

Dr. J. P. KUENEN. *Further experiments regarding the anomalous phenomena near the critical point.*

In inspecting the three Tables I, II and III of my former communication [1]) one is struck at once by the difference between the Tables I, III on one and II on the other side. While in II the values of A, i. e. the differences of density expressed in percents, are always positive and proportionally large, in I and III these differences are small and in the beginning negative. The fact, that Δ i. e. the difference of pressure has a different sign in II from that in I and III leads to the supposition that these quantities A en Δ are connected together. But one glance is sufficient to see, that the explanation of the differences of density in this way cannot be complete. The value of A in proportion to that of Δ is much too high for that in the second series compared with the 1st and 3d series, while besides the positive values of A in I and III don't agree with that suppositon [2]). Closer inspection shows

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[1]) p. 20—21.

[2]) These positive values are smaller than 1 percent; as the possible errors in my results were estimated to be as large as that, I do not think much worth ought to be attached to these positive numbers.

us, that an influence must have existed to make the density at the liquid-side too large. It lies at hand to look for that influence in the presence of the permanent gas, which was discussed in the above communication. In order to test this idea I transported the greater part of the gas to the liquid-branch and repeated the measurements (v and l indicate the same sides of the tube as in I, II and III).

IV. 4th series. At high temperature pressure higher at the vapour-side (Δ positive).

Temp.	v_v	v_l	$\frac{v_v}{v_l}$	Δ	σ_v	σ_l	$A(\%)$
195.0	64.65	20.09	3.22	13.1	0.264	0.218	—19
196.0	66.09	18.65	3.54	16.2	0.258	0.235	—9.5
198.0	66.67	18.03	3.70	17.5	0.256	0.243	—5
207.6	67.21	17.33	3.88	18.6	0.254	0.253	—0.5
223.0	67.14	17.21	3.90	18.7	0.254	0.254	+0.1
15.0	23.70	6.08	3.90	—6.6	0.72	0.72	—

Taken on itself the Table now obtained confirms the general conclusion, stated at the end of the former paper, i. e. that the differences of density become imperceptible at 10° C above the critical temperature. What regards the influence of the gas, the meaning of this Table becomes most evident bij comparing it to I. Accidently the quantities at ordinary temperature were exactly the same in I and IV and the differences between the A's must therefore entirely be ascribed to the fact, that in I the gas was for the greater part present at the vapour-side, in IV at the liquid-side of the tube: hence it appears, that a small quantity of gas, especially quite above the critical temperature, has a great influence upon the volume viz. increases it very remarkably [1]. This conclusion is confirmed by comparison with II. In both II and IV the gas was in that branch of the tube, where the pressure at high temperature was smallest. Both causes (difference of density and gas) therefore acted in the same direction and accordingly the values of A are large (naturally of different sign).

In order to show how small the quantities of gas are, that can produce differences as those between I and IV, I have, admitting that in III no gas was present at the liquid-side of the tube, calculated from the values of Δ at ordinary temperature the proportion of the gas to the ether expressed in the volume of the vapour and I have found:

	I	II	III	IV
x_v	0.000086	0.0000138	0.000095	0.000029
x_l	0.000026	0.0000015	0.000000	0.000247

Solution of the gas into the ether is not taken into account here.

I have not succeeded in calculating from the Δ's observed and the x's given above numerical values of A agreeing with those observed. This may for a part have been caused by disturbing circumstances in the experiments (viz. a small impurity of a different kind etc.) but by the uncertainty of the calculations as well,

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[1] The Δ's were smaller in IV than in I; hence the A's ought to have been smallest in IV; the conclusion about the influence of the air is thereby strengthened still more.

for which use had to be made of Clausius's formula for ether and of Dalton's law for the mixtures. It is improbable that the course of the isorthermal lines quite above the critical temperature should be rigorously rendered by Clausius's formula. It is a known fact that this formula, though in a less degree than van der Waals's equation, generally gives wrong values for the critical volume, which fact of course is very nearly connected with the course of the isothermal lines. It is equally doubtful, whether Dalton's law holds good for these small impurities quite near the critical point. I must therefore be content with the following conclusion: Galitzine's *experiment executed with nearly gasless ether, furnishes differences of density for the greater part to be explained by the differences of pressure and the gas still present. The remaining differences are of uncertain origin and at 10° C above the critical temperature amount to nearly 2 % in one case only, to less than 1 % in the other cases.*

We must add a word about the origin of the permanent gas and its influence on the determinations of volume. In the former communication I ventured to bring forward the hypothesis, that the gas is originated by the sealing of the tube. The same opinion is expressed by Ramsay and Young in a recent note in the Philosophical Magazine [1]. I have since been able to confirm this by direct experiment: a tube of Galitzine, of which the glass had been drawn into a very thin point in consequence of which it had to be heated only a small

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[1] Phil. Mag. (5). 37. p. 503—504.

time during the sealing, was filled in the manner explained before. This time in fact the quantity of gas appeared to be very small: the difference of pressure amounted to 1.4 mm. only. Now the point of the tube was heated for some time, in consequence of which the difference of pressure had now increased to circa 5 mm. It does not seem possible to explain this otherwise than by decomposition of the ether.

The result obtained above as to the large influence of small quantities of gas is highly important for different experiments near the critical point. It cannot be derived fom these experiments, how large the influence is of a definite quantity of gas in case of a *direct* determination of the critical volume. It is a remarkable fact however, that the direction of the slow movement of the liquid surface in the neighbourhood of the critical temperature as also observed by GALITZINE [1]) from which he concludes: »In der Nähe des kritischen Punktes sind δ und ρ keine constanten Gröszen: ρ nimmt mit der Zeit und nach mehrmaligem Erwärmen über τ_c hinaus ab und δ zu" (ρ density of the liquid, δ of the vapour) agrees, with what might be expected from the results obtained here, if this movement was to be explained by a slow solution of some gas from the vapour-phase into the liquid-phase. This circumstance gives aid to the opinion, expressed in my former papers on this subject [2]),

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[1]) Wied. Ann. 50 p. 540.

[2]) Communications etc. n°. 8, n°. 11. This opinion is also confirmed by some recent experiments of VILLARD, C. R. 118. p. 1096.

that the anomalous phenomena near the critical point depend on the presence of some permanent gas.

In connection with the result obtained above we are led to suppose, that large differences of density, as obtained by GALITZINE, may be the consequence of a large quantity of a gas in the vapour-branch of the tube. It was mentioned before [1]) that the presence of much gas in the tubes, investigated by GALITZINE, was very probable, because his observations did not change by admitting air into the tube. In order to establish this point with certainty the new tube, mentioned above, was investigated at high temperature; afterwards the point was broken, a large quantity of air was admitted by cooling the tube, the point was closed again and the measurements were repeated. The values of A are laid down in the following Tables.

a. Before adm. of air.

Temp.	Δ	A (%)
197.3	—8.6	+2.3
199.6	– 8.9	+1.4
202.3	—9.6	—0.2
204.1	—9.2	+0.5
223.5	—9.4	+0.2
15	+1.4	—

b. After adm. of air.

Temp.	Δ	A (%)
197.9	—6	+32
207.3	0	+18
223.2	+4	+ 8.8
15.0	?	—

In table *a* x_v amounts to 0.000014, a very small value. In *b* x_v cannot be determined in the same way because Δ is unknown. Table *a* entirely confirms our former

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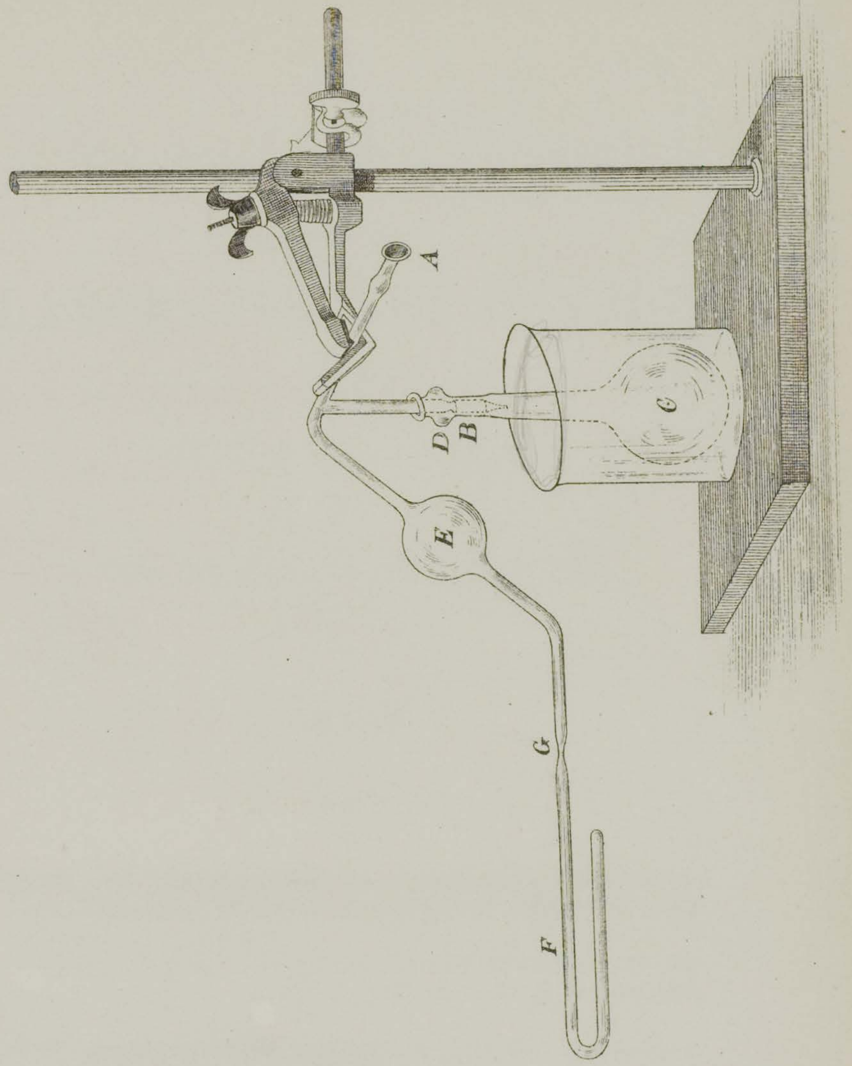
[1]) c. f. the former communication p. 9.

result; Table *b* proves our supposition about the influence of a large quantity of air to have been right. As by accident Δ was very small in this case, the large values of it must entirely be derived from the influence of the air. This result justifies the supposition, that Galitzine's numbers, being of the same magnitude and the same direction, must at least for the greater part be explained by the presence of gas (air?) in the vapour-branch of his tubes.



Kuenen. Critical point (25 Mei 1894).
Commun. Labor. of Physics Leiden N°. 11.

12

COMMUNICATIONS

FROM THE

LABORATORY OF PHYSICS

AT THE

UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES.

No. 12.

Dr. M. DE HAAS. Measurements concerning the coëfficient of viscosity of methyl chloride in absolute measure between the boiling-point and the critical state.

(*Translated from: Verslagen der Afdeeling Natuurkunde der Kon. Akademie van Wetensch. te Amsterdam van* **27 Januari 1894,** *p.* 123.

Dr. H. KAMERLINGH ONNES. The coëfficients of viscosity for fluids in corresponding states.

(*Translated from the same, p.* 126).

Dr. H. KAMERLINGH ONNES. On the coëfficient of viscosity of liquids in corresponding states according to calculations by Dr. M. DE HAAS.

(*Translated from the same*, **30 Juni 1894,** *p.* 62).

EDUARD IJDO — PRINTER — LEIDEN.

Dr. M. DE HAAS. *Measurements concerning the coëfficient of viscosity of methyl chloride in absolute measure between the boiling point and the critical state.* [1]

Although the change of the coëfficient of viscosity of methyl chloride with the temperature between the boiling point and the critical state has been examined by Dr. L. M. J. STOEL [2], yet only relative numbers were found. My intention was to derive in two ways absolute values for the coëfficient of viscosity from the times of discharge then obtained. In the first place by determining the dimensions of the apparatus, and deriving from them the constants in the formula for μ (with which we design the coëfficient of viscosity), calculated for his experiments by Dr. STOEL [3]. Secondly by using the same apparatus for experiments with a liquid whose coëfficient is known from other experiments. The execution of this purpose however was rendered impossible by the breaking of the original apparatus. Nevertheless the knowledge of the absolute values was

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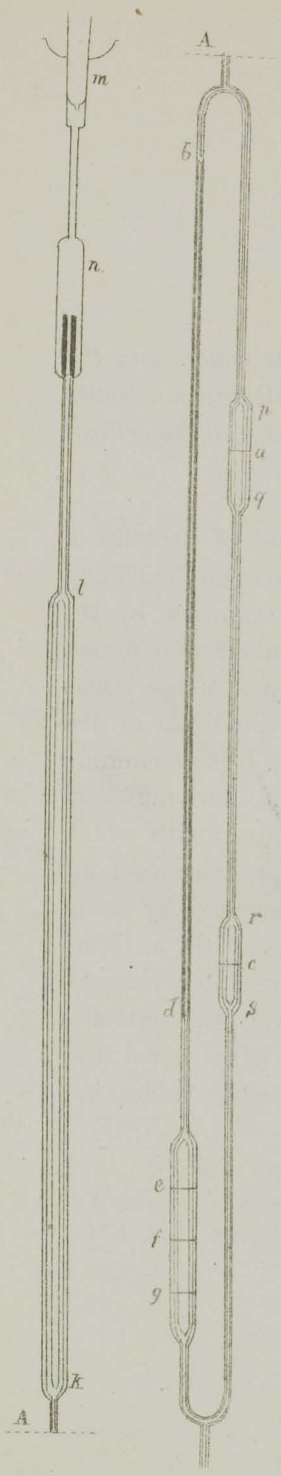
[1] Published in extenso Dissertation, Leiden, 1894.

[2] Dissertation, Leiden, 1891. Verslagen Kon. Acad. van Wet. Amsterdam, 28 Febr. 1891. Physikalische Revue 1892, N°. 5. Comm. Lab. of Physics Leiden, N°. 2.

[3] Communications etc. N°. 2, p. 6.



particularly desirable for testing the law of corresponding states. This is the reason why I repeated Dr. STOEL's observations in such a way, that the absolute values of the coëfficient of viscosity might be established. In constructing another apparatus I avoided at the same time a difficulty in the method applied by Dr. STOEL [1]). As the tube in which the methyl chloride was pressed upward and the other branch of the O-shaped tube, had a different diameter, it was impossible to find the pressure, under which the methyl chloride was really pressed through the capillary tube, unless a most uncertain correction for the capillarity was applied, which appears having been rather considerable in Dr. STOEL's experiments. So I constructed the tube in such a manner that the parts pq and rs whereon the marks a and c are engraved, obtained the same diameter as eg. With this remodelled apparatus, measurings were done with water as discharging liquid, which were extended beyond 100°. The results

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[1]) Communications etc. N°. 2. p. 7.

were compared with those obtained by SLOTTE [1]) for the temperatures between 20° and 90°, and with those of MÜTZEL [2]) and others for the ordinary temperature. Sufficient agreement being found it appeared that the apparatus was fit for absolute determinations. The following results we obtained from the experiments with water beyond 100° C.:

Temp.	μ
124°.0	0.002232
142°.2	0.001925
153°.0	0.001805

The experiments on methyl chloride were now repeated, and some modifications were made in the manner of cleaning and filling the tube, as well as in the circulation of the bath. Dr. STOEL already mentioned that his results had still to be corrected for the deviation of the observed pressures from the law of POISEUILLE. In repeating his experiments I paid particular attention to the influence of the deviations and in calculating the results I took it into account.

First of all it is found by the application of the formula of REYNOLDS [3]) that the velocity of the methyl chloride in the capillary tube does not reach the »critical" value (at which the motion in the whole tube ceases to be in accordance with the suppositions, which are made in deducing POISEUILLE's law) in

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[1]) Wied. Ann. 20 p. 257, 1883; Ofversigt of Finska Vetensk. Soc. Forhandl. 32, p. 116, 1890, vide also Beibl. 16, p. 182, 1892.

[2]) Wied. Ann. 43, p. 15, 1891.

[3]) Phil. Trans. 1886, p. 167.

the observations below 130°, while according to WILBERFORCE [1]) this should not be the case in any of my experiments. The greatest velocity attained in the experiments was 80 c.M. a second.

The correction, which should be applied here, is caused by the loss of energy, in consequence of irregular motion at the ends of the capillary tube. The complete discussion of this correction is impossible in the absence of a solution of the equations of motion of a viscous fluid for this case. HAGENBACH [2]), REYNOLDS [3]), HOUBA [4]), COUETTE [5]), WILBERFORCE [6]) and others [7]) have given different expressions for the deviation of the pressure from the law of POISSEUILLE: all of them agree in this, that, in order to find the pressure, that should exist if the law of POISEUILLE was fulfilled, they diminish the pressure really measured with an amount proportional to the square of the mean strength of current and to the density of the liquid. In accordance with the principle of the mechanical similarity the hypothesis was made, that for my experiments the deviation would in the same way depend on the strength of current and the density. As with this apparatus the pressure

and consequently the strength of current changes every moment, the correction of the pressure must be inserted into the equation of motion; after integration we obtain the following result, that in order to find the true coëfficient the uncorrected coëfficient of viscosity has to be diminished by a term inversely proportional to the time of discharge and proportional to the density and a constant C′ [1]). By making two observations at each temperature with different pressure, we get the same number of values for C′. The fact, that C′ was found almost constant at different temperatures, shows us that we are entitled to the hypothesis mentioned above.

In this way we found:

Temp.	C′
50°	0.00367
60°	0.00349
70°	0.00374
80°	0.00336
90°	0.00340
100°	0.00325

As the greatest value, the correction attains in these experiments, amounts to about 3 percent, this result is sufficient to calculate the correction. By means of graphic interpolation the following values [2]) of μ were derived from 120 times of discharge observed,

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[1]) Phil. Mag. 31, 5e Ser. 407, 1891.

[2]) Pogg. Ann. 109, p. 385, 1860.

[3]) Phil. Trans. 1883, p. 981.

[4]) Dissertation, Leiden 1883, p. 96.

[5]) Ann. de Chim. et de Phys. 6e Série, T. 21, p. 500, 1890.

[6]) l. c. pag. 408.

[7]) Vide for instance the theoretical investigations of BOUSSINESQ, C. R. 113, p. 9 and 49.

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[1]) This quantity is not really constant but may still be a function of REYNOLD's number $\left(\frac{D\rho v}{\mu}\right)$ as is supposed by WILBERFORCE.

[2]) The values differ slightly from those given in the Reports of the Academy of Amsterdam according to later results.

while STOEL'S numbers for the density of methyl chloride were made use of:

Temp.	*Uncorr.* $\mu \times 10^6$.	*Corr.* $\times 10^7$.	*Corr.* $\mu \times 10^6$.
10°	2032	86	2023
20°	1833	93	1834
30°	1671	100	1661
40°	1532	107	1521
50°	1411	113	1400
60°	1301	120	1289
70°	1196	126	1183
80°	1097	133	1084
90°	1001	140	987.4
100°	911.1	148	896.3
110°	822.8	156	807.2
120°	736.4	163	720.1
130°	651.6	172	634.4
136°.8	590.6	168	573.8

The formula $\mu = C e^{-\frac{T}{B}}$ (in which T represents the absolute temperature, and C and B are constants) given by Dr. STOEL as an approximate formula, not differing too much from his uncorrected observations [1], represents with the same differences the corrected values I found; only beyond 120° greater deviations are found.

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[1] Communications etc. No. 2 p. 7.

Dr. H. KAMERLINGH ONNES. *The coëfficient of viscosity for fluids in corresponding states.*

The foregoing communication gives the coëfficient of viscosity of methyl chloride in absolute value. These results enable us to test near the critical temperature the relation between the coëfficiënts of viscosity of two fluids at corresponding temperatures, which I have deduced [1]) from the theorem, that corresponding states are to be considered as mechanically similar forms of motion. [2])

This relation is:

$$\mu_1 : \mu_2 = \frac{\sqrt{M_1}}{\sqrt[3]{m_1^2}}\sqrt{T_{k_1}} : \frac{\sqrt{M_2}}{\sqrt[3]{m_2^2}}\sqrt{T_{k_2}},$$

where μ represents the coëfficient of viscosity, M the molecular weight, m the volume of the molecules and T_k the critical temperature, while the indices 1

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[1]) Theorie der vloeistoffen, Verh. der Kon. Acad. v. Wetensch. Amsterdam, 1881, tweede stuk, pag. 8. Beibl. 5, p. 718, 1881.

[2]) Compare for further applications of this theorem: VAN DER WAALS, Thermodynamische Theorie der Kapillarität unter Voraussetzung stetiger Dichteänderung. Ztschr. f. phys. Chemie XIII. 4. Zusatz 2, 3, 4.

and 2 refer to the different fluids. As in this case we may put:

$$m = \text{const.} \times \frac{T_k}{p_k},$$

(p_k representing the critical pressure), we have:

$$\mu_1 : \mu_2 = \frac{\sqrt{M_1}}{\sqrt[6]{\dfrac{T_{k_1}}{p^4_{k_1}}}} : \frac{\sqrt{M_2}}{\sqrt[6]{\dfrac{T_{k_2}}{p^4_{k_2}}}}.$$

The latter formula is more fit for calculation, because the values given for critical pressures are generally better to be relied upon then those for critical volumes.

It follows from the consideration on which this relation is founded, that it will probably be best realised near the critical state.

Beside methyl chloride there is but one liquid of which the coëfficiënt of viscosity near the critical state is known, viz. carbonic acid, by the investigations made by WARBURG and VON BABO [1]). If we call μ_c and μ_m the coefficient of viscosity for carbonic acid and methyl chloride, we ought to have according to the above mentioned relation:

$$\mu_c : \mu_m = 44.63 : 42.01$$

or:

$$\frac{\mu_c}{44,63} = \frac{\mu_m}{42,01} = \text{const.}$$

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[1]) Wied. Ann. 17, p. 390, 1882.

According to the experiments and calculations of Dr. M. DE HAAS we find: [1])

Corresp. Temp.		μ'_c	μ'_m	$\frac{\mu'_c}{44.63}$	$\frac{\mu'_m}{42,01}$
Carbon. ac.	Methyl chl.				
5°	107°0	5,099	4,589	0,114	0,109
10°	113°8	4,697	4,267	0,105	0,102
15°	120°6	4,222	3,887	0,097	0,093
20°	127°5	3,925	3,628	0,088	0,086
25°	134·3	3,444	3,302	0,077	0,079

It results from this, that near the critical temperature the agreement is sufficient, and that the differences are not greater than with other applications of the law of the corresponding states.

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[1]) In this table μ'_c and μ'_m denote the „specific” coëfficient of viscosity, i. e. they are expressed in the $\frac{1}{100}$ th. part of the coëff. of visc. of water at 0°, taken as unit.

Dr. H. KAMERLINGH ONNES. *On the coëfficient of viscosity of liquids in corresponding states according to calculations by* Dr. M. DE HAAS.

Continuing the investigation, the results of which were communicated in the session of 27 January 1894, Dr. M. DE HAAS has calculated the coëfficient of viscosity for a number of substances at the corresponding temperatures 0.58 T_k (T_k denoting the critical temperature) and besides the quantities $C = \mu \frac{\sqrt[6]{p^4_k}}{M^3 T_k}$ (in which μ denotes the coëfficient of viscosity, p_k the critical pressure, M the molecular weight of the substance) and $C' = \mu \frac{\sqrt[3]{m^2_k}}{\sqrt{M T_k}}$ (in which m_k represents the critical molecular volume) which according to the thesis: that corresponding states are mechanically equivalent for all substances, should have the same value in corresponding states. The result of the calculations is laid down in the following table:

Hydrocarbons.		$0.58 T_k - 273$	p_k	m	μ	C	C′
Benzene	$C_6 H_6$	52.7	47.9	92.2	23.6	0.58	2.3
Toluene	$C_7 H_8$	71.4	40.1	114.5	18.8	0.48	1.9
Metaxylene	$C_8 H_{10}$	85.3 (H)	38.0	134.5	18.5	0.48	1.8
Halogen Compounds.		$0,58\ T_k - 273$	p_k	m	μ	C	C′
Methyl chloride	CH_3Cl	—31.7	65.0	50.1	16.2	0.38	1.5
Methyl iodide	CH_3J	33.2 (H)		67.4	26.0		1.6
Ethyl bromide	C_2H_5Br	22.2		76.7	21.3		1.6
Propyl chloride	C_3H_7Cl	13.5	49.0	89.6	20.9	0.50	2.1
Propyl iodide	C_2H_7J	65.3 (H)	44.8	103.0	23.4	0.44	1.6
Butyl iodide	C_4H_9J	85.0 (H)	39.8	125.0	27.3	0.50	2.0
Benzene chloride	C_6H_5Cl	94.5 (H)	44.7	109.4	21.5	0.47	1.9
Benzene bromide	C_6H_5Br	117.1 (H)		114.7	25.4		1.9
Allyl chloride	C_3H_5Cl	24.9		82.3	19.0		1.8
Ethylene chloride	$C_2H_4Cl_2$	52.6	53.0	82.3	30.7	0.62	2.4
Ethylidene chloride	$C_2H_4Cl_2$	30.3	50.0	86.0	25.9	0.54	2.2
Chloroform	$CH\ Cl_3$	38.5	54.9	82.1	26.5	0.48	1.9
Tetra-chlormethane	$C\ Cl_4$	49.5	45.0	99.8	37.2	0.68	2.7
Ether	$C_4H_{10}O$	— 2.2	35.6	102.1	16.1	0.48	1.8
Ethyl sulphide	$C_4H_{10}S$	37.3 (H)		113.2	20.5		2.2
Ethereal salts.							
Ethyl formate	$C_3H_6O_2$	20.5	48.7	80.1	22.5	0.55	2.2
Propyl formate	$C_4H_8O_2$	36.6	42.7	99.0	24.0	0.60	2.4
Isobutyl formate	$C_5H_{10}O_2$	46.7 (H)	38.3	123.3	27.0	0.67	2.8
Methyl acetate	$C_3H_6O_2$	20.4	57.6	79.5	22.9	0.57	2.2
Ethyl acetate	$C_4H_8O_2$	29.5	41.1	98.7	22.4	0.57	2.2
Propyl acetate	$C_5H_{10}O_2$	49.1	34.8	118.9	22.2	0.59	2.2
Normal butyl acetate	$C_6H_{12}O_2$	62.7		139.0	24.7		2.5
Isobutyl acetate	$C_6H_{12}O_2$	54.7	31.4	140.0	24.7	0.66	2.5
Methyl propionate	$C_4H_8O_2$	35.7	39.9	97.9	22.9	0.60	2.2
Ethyl propionate	$C_5H_{10}O_2$	43.3	34.6	117.9	25.3	0.67	2.5
Norm. propyl prop.	$C_6H_{12}O_2$	62.1		139 0	25.3		2.6
Isobutyl propionate	$C_7H_{14}O_2$	70.2		124.4	25.2		2.3
Methyl butyrate	$C_5H_{10}O_2$	46.6	36.0	117.1	22.9 (R)	0.59	2.3
Ethyl butyrate	$C_6H_{12}O_2$	58.5	30.2	138.0	23.0	0.63	2.4
Norm.propyl butyrate	$C_7H_{14}O_2$	74.7		147.0	24.7		2.5
Methyl isobutyrate	$C_5H_{10}O_2$	44.0		118.1	24.2		2.1
Ethyl isobutyrate	$C_6H_{12}O_2$	50.8	30.1	139.7	24.8	0.68	2.6
Norm. prop. isobutyr.	$C_7H_{14}O_2$	68.6		160.0	25.5		2.7
Ethyl valerate	$C_7H_{14}O_2$	55.7		156.6	26.7		2.8
Amyl valerate	$C_{10}H_{20}O_2$	71.6 (H)	21.3	214.7	36.4 (R)	1.04	4.1

		$0.58\,T_k—273$	p_k	m	μ	C	C′
Acetic aldehyde	C_2H_4O	— 9.4 (H)		53.6	19.2		1.9
Acetone	C_4H_6O	24.2	52.2	74.3	21.2	0.56	2.1
Water	H_2O	99.9	195.5	18.7	16.0	0.33	1.0
Bisulphide of carbon.	$C\,S_2$	44.9	77.0	62.0	17.0(W)	0.31	1.3
Fatty acids.							
Formic acid	$C\,H_2O_2$	81.5	115.1	41.2	37.9 (R)	0.68	2.6
Acetic acid	$C_2H_4O_2$	71.8 (H)	76.4	59.1	35.3	0.73	2.8
Propionic acid	$C_3H_6O_2$	82.4	58.2	80.4	31.3	0.71	2.8
Butyric acid	$C_4H_8O_2$	81.5	48.0	99.0	38.3	0.91	3.5
Isobutyric acid	$C_4H_8O_2$	76.7	46.6	100.0	34.7	0.82	3.2
Valeric acid	$C_5H_{10}O_2$	80.4	40.1	117.0	47.2 (R)	1.2	4.0
Capronic acid	$C_6H_{12}O_2$	113.0	37.2	140.0	44.3 (R)	1.1	4.3
Alcohols.							
Methyl alcohol	$C\,H_4O$	24.5	73.7	40.5	33.7 (R)	0.96	3.1
Ethyl alcohol	C_2H_6O	26.6	64.5	58.5	61.9 (R)	1.61	6.0
Normal propyl alcohol	C_3H_8O	34.2	51.7	75.9	95.8	2.53	9.7
Isopropyl alcohol	C_3H_8O	21.4	53.0	77.0	130.3	3.37	13.5
Normal butyl alcohol	$C_4H_{10}O$	51.8		96.0	80.0		8.2
Isobutyl alcohol	$C_4H_{10}O$	39.0	48.3	96.0	129.0	3.2	13.5
Allyl alcohol	C_3H_6O	43.0		70.9	54.7		5.3

The critical temperature has been taken from the Annuaire du Bureau des Longitudes and from HEILBORN (H). Under μ are given the specific [1]) coëfficients of viscosity calculated from the results of PRIBRAM and HANDL, RELLSTAB (R) and WYKANDER (W) and from the formula of GRAETZ; under m the quotient of the molecular weight and the density in corresponding states, partially calculated with the aid of VAN DER WAALS's law.

Remarkable is the large deviation shown by the fatty acids and still more by the alcohols. In these anomalous series of bodies we also remark a tendency to reach higher values for C and C' with greater molecular weight and this the more as the class diverges more itself. With water and bisulphide of carbon however, we find a value which differs in a direction opposite to the fatty acids and alcohols.

The logarithmic gradients of the coëfficient of viscosity are dealt with in Dr. DE HAAS's dissertation. They show the desirableness of further determination of frictional coefficient above the boiling-point.

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[1]) Vide note on p. 11.