Physics. — "*On the equation of state of a substance in the neighbourhood of the critical point liquid-gas. II. Spectrophotometrical investigation of the opalescence of a substance in the neighbourhood of the critical state*", by Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. Communication N°. 104*b* from the Physical Laboratory at Leiden.

§ 1. *Introduction.* The spectrophotometrical investigation [1]) of the opalescence will have to give an answer to the question how the intensity of the light of a certain wavelength scattered in a certain direction with respect to the incident light and included in a certain angle of vision, in connection with the polarisation state depends on the temperature and the density of the single substance in the neighbourhood of the critical point liquid-gas (cf. Comm. N°. 104*a* § 4). A first quantitative contribution to this investigation is given in this communication [2]).

We have confined ourselves in this first investigation to the determination of.

1. for different temperatures the ratio in which the rays of light of different wave lengths at the same temperature are scattered in a certain direction ;

2. the way in which the intensity of the light of definite wavelength scattered in a certain direction and included in a certain angle of vision changes with the temperature.

On the supposition *a*, that the light emitted by the blue mist is owing to the scattering of the incident light in consequence of part of the substance condensing to particles of the same size (e.g. spheres) round centres which are uniformly spread through the space, the results of the investigation mentioned under 1 will enable us to form an opinion on the size of these particles [3]), that under 2 on the way in which the total quantity of substance which has condensed, varies with the temperature.

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[1]) This investigation was carried out before the interesting article of SMOLUCHOWSKI Ann. d Phys. (4) 25 (Febr. 7, 1908) p. 205, appeared. We still had an opportunity, however, to compare it with some parts of the text (c.f. also the preceding Communication). [Added in the English translation].

[2]) The colorimetric determinations of FRIEDLANDER, ZS. physik. Chem. 38 (1901) p. 385 constitute such a contribution for a mixture of two liquids in the neighbourhood of the critical point of separation.

[3]) Already FRIEDLANDER loc. cit. p. 438 called attention to the importance of such an investigation for the knowledge of the internal structure of the critically turbid media

On the more general supposition *b*, that the opalescence is the
consequence of differences of density e.g. governed by the statistic
equilibrium, which extend over parts of the volume of irregular
shape and size, a distance can be pointed out which is connected
with the average size of these parts of the volume and so with the
substance being more or less coarse-grained in that state; and which
determines the optical phenomenon in a similar way as the size of
the particles on supposition *a*. The investigation mentioned under 1
will then enable us to judge about this distance. When in future
we speak of the size of the light-scattering particles, we shall refer
to this distance. In this case the investigation mentioned under 2
will teach us something about the mean deviation of the density in
these parts of the volume. This too will be implied in future in
"the quantity of condensed substance".

The measurements made by us can, however, be only considered
as preliminary ones. As, however, we have to put off the continuation
of these measurements for some time, we think that we must not
postpone the communication of these provisional results any longer.

§ 2. *The arrangement of the experiments* is represented in Pl. II
fig 1. After having passed through a layer of water the light emitted
by the luminous body of the NERNST-lamp *Ner* (70 HK) is concen-
trated by the lenses L_1 and L_2 (to an image of $\pm$ 1 c.M. height)
in the tube *Et* filled with ethylene [1]).

The light scattered upwards in the direction of the axis of the
tube [2]) by the cloud is concentrated by means of the system of

[1]) This was obtained by distilling over so much from the ethylene circulation
of the cryogenic laboratory into the glass tube with cock fused to it, which had
been cooled in liquid air, and rinsed with ethylene, that after the gas phase left
above the solid ethylene had been drawn off, and the tube was heated to the melting
point, $1/3$ of it was filled. Then with the cock closed the tube was removed from
the ethylene circulation, and fused together at a previously narrowed place while
still partially placed in liquid air. When the temperature rose to that of the room,
it appeared, when at 0° the rime cleared away, that in the gas space a thin white
deposit was visible on the wall, which evaporated some degrees below the critical
temperature of the ethylene. This deposit points to the presence of an admixture
which is slightly less volatile than ethylene (cf. VILLARD, Ann. de chim. et de phys.
(7) 10 (1897) p. 389). That it was not visible in the liquid space, probably points
to a small difference in refrangibility with liquid ethylene.
When we stirred, and then slowly cooled the tube to below the critical tempe-
rature, the meniscus appeared in the top of the tube.
[2]) The top of the tube is surrounded by a black cylindre in order to prevent
rays of light received by this part from being reflected upwards, and being thrown
into the spectroscope.

lenses L_3, L_4 and L_5, L_6 and the totally-reflecting prism Pr to an -image of the beam of light crossing the ethylene tube on the slit of the spectroscope Sp (a direct-vision spectroscope of HILGER-CHRISTIE giving a spectrum of great intensity[1]), in which an eye-piece slit has been made in order to confine a certain portion of the spectrum; by means of the screw Scr_2 different portions of the spectrum may be brought into the field). A beam of the light emitted by the NERNST-lamp is thrown on the slit of the spectroscope by means of plane mirrors through the polarizing prisms Nic_1, Nic_2, Nic_3 (after having been first made parallel by lens L_7) and then through lens L_8 and a totally-reflecting prism. The prisms Nic_1 and $_rNic_3$ are rigid, which ensures that the light thrown into the spectroscope by the reflections on the mirrors with different positions of Nic_2 is reduced in the same proportion; the prism Nic_2 can turn round, and is provided with a graduated circle, which could be read up to $3'$. The plane of polarisation of Nic_3 is horizontal so that the condition of polarisation in the two beams thrown into the spectroscope agrees in the main[2]). The plane of polarisation of Nic_1 has been put parallel to that of Nic_3. After the tube of ethylene had been brought to the required temperature, and the temperature of the room had been regulated in such a way that the temperature of the tube of ethylene (read to $0°.01$) could be kept sufficiently constant (up to some hundredths of a degree) by the addition, when necessary, of some cold or hot water into the vacuum glass, the prism Nic_2 was adjusted by rotation so as to obtain equal intensity of the considered portions

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[1]) See ZEEMAN Comm. N°. 5, June '92, more detailed Arch. Néerl. 27 (1893) p. 259 and Pl. V. The "halfprism" was used in our experiments with a view to the intensity in the magnifying position (CHRISTIE, Proc. Roy. Soc. 26 (1877) p. 8). Moreover the dispersion is greater in this position, whereas the loss of purity in the spectrum is of no importance here.

[2]) Not too near the critical state the light emitted by the blue mist in a direction normal to the incident light, is polarized in the plane of incidence (RAMSAY, ZS. physik. Chem. 14 (1894) p. 486). It is to be expected that on approach to the critical state the light emitted in the direction mentioned becomes more and more partially polarized (cf. TYNDALL, Phil. Trans. 160 (1870) p. 348). It would be interesting to examine if then TYNDALL's residual blue (l. c.) could be observed (on the connection of this with the difference in refractivity of the scattering particles and the surrounding medium see RAYLEIGH, Phil. Mag. (4) 41 (1871) p. 454). Measurements on the condition of polarisation might also lead to an opinion on the size of the particles, see BOCK, Wied. Ann. 68 (1899) p. 674 (spectrophotometrical investigation of the light scattered by a jet of steam, measurement of the condition of polarisation, and determination of the size of the particles by means of diffraction rings) and PERNTER, Denkschr. Kais. Ak. d. Wiss. Wien 73 (1901) p. 301.

of the two spectra. With a view to this adjustment care had been taken that the two spectra were as close above each other as possible [1]) and had about the same height. The adjustment and reading were made in the four different positions of Nic_2 which gave equality of intensity.

§ 3. *Observations*. Only observations above the critical temperature have been communicated here; in order to get unambiguous data for the dependence of the intensity of the opalescence on the temperature and the density below the critical temperature, a stirring-apparatus, or an arrangement to keep the temperature constant till the thermo-dynamic equilibrium should have been reached, would have been required. The observations were made after the tube of ethylene had been kept at higher temperature for 15 hours or longer, and had then been slowly cooled down to the temperature of observation. The measurements have been made for two wavelengths, corresponding to D and F in the solar spectrum [2]). In order to give an idea of the degree of accuracy of the adjustments, we have communicated the data of an observation at a mean intensity of the scattered light in table I.

TABLE I.

Series VI, No. 3, 13 Nov 1907						
Wave length	Temperature	Adjustments of Nic_2				?
D	11° 69	63 48'	36°36'	154°36'	125° 9'	14°10'
	11 66	64 24	36 15	153 30	126 18	13 50
	11. 70	63 18	36 54	154 9	125	13 53
	11. 69					—
		temp. mean 11° 68				mean: 13°58'
F	11 66	155°45'	124°48'	65°18'	34°33'	15°15'.5
	11. 68	156 15	124 54	66 9	33 54	15 54
	11. 67	157 18	122 57	67 50	34 6	16 56
	11 61					—
		temp. mean 11°.66				mean: 16°5'

[1]) The use of a HÜFNER's prism would render more accurate adjustments possible.

[2]) When the experiments are repeated under circumstances which admit of a more accurate spectrophotometric adjustment, an extension of the measurements to more wavelengths will be desirable.

The last column contains the angle of the plane of polarisation of Nic_2 derived from the other columns, for the adjustment at equal intensity, with this plane of polarisation when Nic_3 crosses Nic_1 and Nic_1. In general the adjustment for the wavelength F was less accurate than for D on account of the slighter intensity in the spectrum for the former wavelength. The greater deviation which the latter angle φ shows for the wavelength F in table I from the preceding ones, may be explained from the difference in temperature.

The results thus obtained have been joined in table II.

T A B L E II.

Wavelength D		Wavelength F	
Temperature	φ	Temperature	φ
Series V, 12 Nov. 1907			
13°.53	8°27'	13°.59	10°11'
12 .55	9 45.5		
Series VI, 13 Nov. 1907			
12°.54	10°36'	12°.54	12°39'
11 .86⁵	12 37	11 .83	14 58.5
11 .68	13 58	11 .66	16 5
11 .42	17 52	11 43	18 24
11 .24	22 18		

The observations of series VI ceased after the adjustments for the wavelength D at 11.°24, because after this the temperature fell below the critical temperature, which was determined at 11.°18 [1]) (cf. § 3 beginning).

The difference between the angles φ for Series V 12.°55 and Series VI 12.°54, wavelength D, is owing to this that between these observations a slight modification in the position of the lenses L_7, L_8 has taken place. The observations mentioned here may serve

[1]) Comparison of this value of the critical temperature with that of other investigators indicates that the critical temperature of the admixture (cf. § 2, p. 612, note 1) does not lie much higher than that of ethylene.

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to bring connection between the series V and VI. The results of other series of observations are not communicated here, because for them all the precautions mentioned had not yet been taken.

From the data of table II the course of the intensity of the scattered light with the temperature ($\S$ 2 2nd) will be derived in the first place. Let us call $H_{D,t}$ the intensity in the spectrum of the light scattered by the cloud at the temperature t of the wave-length D for a certain arrangement of the apparatus, which is further thought to be unmodified, H_{Dcomp} the intensity in the comparison spectrum when Nic_2 is parallel with Nic_1 and Nic_3, then $i_{D,t} = H_{D,t}/H_{D,11.°68} = sin^4 \varphi_{D,t}/sin^4 \varphi_{D,11.°68}$. An investigation of the absolute intensity of the light scattered by the mist compared with that of the incident light (cf. $\S$ 6b) will have to reveal how to derive a quantity from $i_{D,t}$ which determines the intensity of the scattered light, independent of the particular circumstances of the arrangement. For an examination of the way in which the intensity of the scattered light depends on the temperature, the quantity $i_{D,t}$ is very suitable.

Table III contains the results obtained on this from table II:

TABLE III.

t	$i_{D,t}$	t	$i_{D,t}$
13°.53	0.190	11.°68	1
12. 54	·0.337	11. 42	2.61
11. 86⁵	0.671	11. 24	6.11

These results have been represented in Pl. II fig. 2, where also a curve has been traced through the points of observation (see further p. 620).

The ratio $r_{F:D,t} = \dfrac{H_{F,t}/H_{F\,comp.}}{H_{D,t}/H_{D\,comp.}} = \dfrac{sin^4\varphi_{F,t}}{sin^4\varphi_{D,t}}$ yields data for the inquiry mentioned in $\S$ 2 1st. into the ratio in which the light of different wavelengths is scattered. Table IV contains the results.

T A B L E IV.

t	$r_{F:D,t}$	t	$r_{F:D,t}$
13°.59	2.00	11°.68	1.66
12. .54 ·	2.01	11 .43	1.18
11 .56⁶	1.85		

To this purpose the angles φ for D and F have been reduced to the same temperature by interpolation.

Above $12°.54$ the ratio of the intensities of D and F seems to be constant. The fact already observed by several earlier observers that on approach of the critical temperature the mist changes from blue to almost white, is clearly set forth in the table. Measurements on this change of colour, however, have been communicated here for the first time.

§ 4. *On the size of the light-scattering particles* [1]). To be able to derive from $r_{F:D}$ the ratio of the intensities F and D of the light scattered in a certain direction by the mist compared with the ratio of the intensities F and D of the incident light on the mist, we must bear in mind : 1st that the two beams of light which are compared with each other in the spectroscope are subjected to different reflections and absorptions outside the spectroscope, which might bring about a change in the ratio of the intensities D and F, 2nd that the optical apparatus for observation of the scattered light not being perfectly achromatic might cause a similar change in the ratios of intensities, 3[td] that if the condition of polarisation of the two beams is not exactly the same on their arrival in the spectroscope, the reflections in the spectroscope may also give rise to such a change [2]).

The influences mentioned under 1 and 2 may be determined and eliminated by measurements of the scattered light when the substance in the neighbourhood of the critical state has been replaced by a suspension for which the ratios of intensities of the scattered light are known [3]). Then it will have to appear in how far the deviation of the values $2,00$ found in table IV at the higher temperatures from that which according to RAYLEIGH (Phil. Mag. (4) 41 (1871) p. 107) would be found if the scattering were brought about by non-conducting particles the dimensions of which are small with

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[1]) Cf. § 1 p. 612.

[2]) Cf. CHRISTIE loc. cit.

[3]) Suspensions for which the intensity of the transmitted light is: according to

RAYLEIGH $I = I_0 e^{-k\lambda^{-4}x}$: mastic, Ag Cl, $Cu_2 S$ in water, emulsion of lemon-essence in water: ABNEY and FESTING, Proc. Roy. Soc. 40 (1886) p. 378, LAMPA, Wien. Sitz. ber. [2a] 100 (1891) p. 730, HURION, C.R. 112 (1891) p. 1431, COMPAN,

C.R. 128 (1899) p. 1226; according to CLAUSIUS $I = I_0 e^{-k\lambda^{-2}x}$: Ba SO_4 in a mixture of glycerin and water, etc.: COMPAN loc. cit. To ensure that in this experiment the light is subjected to the same reflections as in the experiments with the mist we should have to take a suspension in ethylene of the critical density.

respect to the wavelength: $\lambda^4{}_D/\lambda^4{}_F = 2.129$, is to be explained in this way [1].

About the influence of what was mentioned under 3 we have made a separate measurement. See for this § 5.

After the corrections indicated in this § have been applied, the data of table IV may serve to give an idea of the size of the particles by the aid of developments such as are given by LORENZ [2]. From the change of $r_{F:D}$ in table IV on approach to the critical temperature may already be deduced that the light-scattering particles must no longer be considered as small with regard to the wavelength at and below 11°.86⁵ (i.e. 0°.5 above T_k).

§ 5. *On the quantity of substance which is condensed in the light-scattering particles at different temperatures* [3]. To get to know the intensity of the scattered light at different temperatures, only a correction has to be applied to table III on account of the circumstance mentioned p. 617 under 3. Therefor the condition of polarisation of the scattered light at different temperatures must first be known (cf. p. 613 note 2). An upper limit for this correction may already be given as follows.

In the measurement mentioned in § 4 it appeared that light polarized normal to the slit was weakened to a greater degree in the spectroscope than light polarized parallel to the slit, in such a way that the ratio of the intensities in the spectrum is [4]:

$$H_{D\perp}/H_{D//} = 0.82, \quad H_{F\perp}/H_{F//} = 0.70.$$

If we now suppose that at 13°.53 all the light of wavelength D scattered in a direction normal to the incident light is polarized in the plane of incidence, and that at 11°.24 this light would be totally unpolarized, it follows from this measurement, that at 11°.24 the weakening of the D-light in the spectroscope would be 1.10 times the weakening of the D-light at 13°.53.

To be able to derive from the intensity of the scattered light at different temperatures how the quantity of condensed substance depends on the temperature, we should have to get a somewhat complete insight into the way in which the light is scattered by such

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[1] Also the fact that the light scattered by the mist must pass through a layer of a certain thickness (± 2 cM.) in the direction of propagation, may cause a deviation in the same direction.

[2] L. LORENZ. Vidensk. Selsk. Skr. Copenhagen 6 (1890). Oeuvres Scientifiques 1 p. 405.

[3] Cf. § 1 p. 612.

[4] Cf. with this the calculations of CHRISTIE Proc. Roy. Soc. 26 (1877) p. 24.

particles, and hence be acquainted with the structure of the particles (cf. § 1), in which also the origin (cf. Comm. N°. 104^a, § 4) would come in for discussion. However, it is to be expected that when the particles, are small compared with the wavelength of the light, the intensity of the scattered light will increase proportional to the square of the quantity of condensed substance, whereas when the particles are no longer so small, the increase will take place more slowly.

To whatever cause we may attribute the occurrence of the differences in density, the great compressibility of the substance in the neighbourhood of the critical state will have a preponderating influence on it. Thus e.g. the mean deviation in density governed by the statistic equilibrium (SMOLUCHOWSKI)[1] will be proportional to $\sqrt{\partial p/\partial \varrho}$ (ϱ = density). If we assume that the substance condenses round centres of attraction which exert forces on the surrounding particles of the substance which per unit of mass are only dependent on the distance, the quantity which is condensed round every centrum of attraction is proportional to[2] $\partial p/\partial \varrho$.

In order to examine what information the data in table III give on a connection between the intensity of the scattered light and the compressibility, we notice that in the neighbourhood of the critical point $\partial p/\partial \varrho = q_{11} (T - T_k)$, if the average density of the substance differs so little from ϱ_k that the following term $3q_{30} (\varrho - \varrho_k)^2$ may be neglected (so $T - T_k$ not too small).

TABLE V.

t	i_{DtO}	i_{DtC}	$O-C$ in % of O
13.°53	0.190	0 213	— 12
12. 54	0.337	0.368	— 9
11. 86⁵	0.671	0.730	— 9
11. 68	1	1	
11. 42	2.61	2.08	+ 20
11. 24	6.11	8.33	— 36

[1] M. v. SMOLUCHOWSKI, Ann. d. Phys. (4) 25 1908 p. 205.

[2] In this it is supposed that the condensation is so insignificant that ϱ in a condensed part remains sufficiently near ι_k.

In table V the data of table III have been compared with the formula: $i_{D,t} = \dfrac{0.5}{T-T_k}$ ($t_k = 11°.18$, see p. 615).

The — — — — — curve in Pl. II fig. 2 represents $i_{D,C}$.

The differences $O — C$ are of two kinds:

1. The deviation at $11°.24$: this was to be expected in the immediate neighbourhood of the critical temperature, as the formula for T_k would give an infinite intensity; here the influence makes itself felt of following terms in the development of $\partial p/\partial \varrho$, or of the intensity of the scattered light as function of the quantity of substance (see p. 619);

2. also at temperatures further from the critical temperature there is a systematic deviation: the observed curve of intensity ascends here more rapidly than the calculated one. This might among others be in connection with the observation of TRAVERS and USHER [1]), who found that the maximum of the intensity of the opalescence should not lie at T_k, but for SO_2 $0°.05$ above T_k.

Leaving these deviations out of account we may conclude that on the main the observations conform to the mentioned equation. The deviations from a formula $i_{D,t} = \dfrac{0.25}{(T-T_k)^2}$ would have been much larger. The correction mentioned in the beginning of this § will not affect this conclusion.

On the supposition that at least when the dimensions of the volume elements in which appreciable condensations or rarefactions are found, are small with respect to the wavelength, the intensity of the scattered light is proportional to the square of the quantity of substance which has condensed round every centrum, or to the square of the mean deviation in density governed by the statistic equilibrium, it follows that our observations rather support the hypothesis of the condensations and the rarefactions caused by the molecular movement and governed by the statistic equilibrium, than the hypothesis of centres of attraction whose number remains constant with varying temperature.

If it appears from further investigations that the absolute value of the intensity of the light scattered by the mist is in harmony with what is to be expected according to the distribution law of BOLTZMANN (cf. SMOLUCHOWSKI, loc. cit.) a connection may be formed between the observations of the intensity of the light scattered by the mist and the disturbance function in the equation of state in

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[1]) M. W. TRAVERS and F. L. USHER. Proc. Roy. Soc. A. 78 (1906), p. 247.

the neighbourhood of the critical point through considerations on the increase of the virial of attraction in consequence of the differences of density [1]).

§ 6. *Remarks on further experiments on the mist in the neighbourhood of the critical state.*

a. When through measurements as treated in § 3 the way in which the intensity of the light scattered by the mist depends on temperature and density, will have been sufficiently brought to light, the determination of this intensity at different heights in a CAGNIARD-LATOUR tube may be substituted for the method of the floating bulbs for the determination of the density at different heights in the tube (See Comm. N°. 98, Sept. '07). If the establishing of the thermodynamic equilibrium is effected by keeping the temperature for a long time sufficiently constant, the determination of the intensity of the scattered light as function of the height in the tube would supply a method for the accurate determination of the experimental equation of state in the immediate neighbourhood of the critical state (cf. Comm. N°. 98 § 1 p. 218).

b. Besides the before-mentioned measurements on the condition of polarisation (§ 2) and the measurements for the sake of the corrections mentioned in § 4, measurements on the ratio between the intensity of the scattered light and that of the incident light would also be desirable. (Cf. § 3 p. 616 and § 5 p. 620). For this purpose measurements might serve in which the ethylene is replaced by a silver mirror forming an angle of 45° with the axis of the tube [2]).

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[1]) Cf. M. v. SMOLUCHOWSKI, BOLTZMANN Festschrift 1904, p. 626

[2]) We have in the meantime made a preliminary measurement of the absolute intensity of the scattered light by comparing it with the light reflected from a silver mirror (reflection constants for light polarized perpendicular and parallel to the plane of incidence calculated according to QUINCKE, Pogg. Ann. 128 (1866) p. 541 from determinations of the principal angle of incidence and the principal azimuth by JAMIN, Ann. chim. phys. (3) 22 (1848) p. 311). For this measurement the comparison spectrum had to be intensified by replacing the systems of lenses L_7 and L_8 by stronger combinations. From the angles $\wp_{Ag} = 31°33'$ and $\wp_{Et} = 5°4.'5$ we derive that at $t = 11°.93$ the intensity of the light of wavelength D scattered by 1 cM.[3] of ethylene perpendicular to the direction of incidence per unit angle of vision is $s_D = 0,0007$, if the intensity of the incident (unpolarized) light $= 1$.

If we calculate according to RAYLEIGH, Phil. Mag. (5) 12 (1881) p. 86—88, LORENZ, Oeuvres Scientif. I p. 496, $s = \dfrac{2\pi^2}{N\lambda^4} \dfrac{(\Delta\mu)^2}{\mu_0^2}$ ($N =$ number of light-scattering

c. If would be of interest to investigate whether for a single substance in the neighbourhood of the critical point an increase of viscosity is found as has been noted by OSTWALD [1]) for a liquid mixture in the neighbourhood of the critical point of separation from measurements of STEBUTT, and has been further determined by FRIEDLÄNDER (see p. 611). Perhaps the increase of the viscosity and the size of the light-scattering particles (§ 1) might be brought into relation, and so also the colour of the scattered light.

d. We could not ascertain an influence of RÖNTGEN-rays on the blue mist in ethylene. An investigation might be made as to whether the a-rays or the emanation of radium exert an influence on the mist.

e. FÜCHTBAUER [2]) investigated a mixture of iso-butyric acid and water in the neighbourhood of the critical point of separation ultramicroscopically ; he did not succeed in dissolving the cone of light. Nor could we ascertain [3]) the presence of separate light-scattering particles in the mist for a mixture of amylene-aniline with the objective Homog. Imm. $\dfrac{1}{12}$, eye-piece 4, condenser AA (ZEISS) and as source of light an electric arc lamp (30 Ampère) or solar light (10 Dec. '07), We consider a repetition of this experiment with more intense solar light and with more precautions taken to keep the temperature of the mixture that is ultramicroscopically examined,

particles per cM^3, Δ_μ deviation from the average refractive index μ_0), and if we express Δ_μ in terms of the deviation in density according to LORENTZ-LORENZ, and

if according to SMOLUCHOWSKI we write $\bar{\delta}^2 = -\dfrac{RT_0}{\nu v_0{}^2\left(\frac{\partial p}{\partial v}\right)_0}$ ($\nu=$ number of

molecules in the light-scattering particle), in which $\left(\dfrac{\partial p}{\partial v}\right)_0$ for $v_0 = v_k$ can be

developed as $\dfrac{p_0}{v_0 T_0}\, \mathfrak{p}_{11}\,(T-T_k)$ (Suppl. N°. 6, May '03), we find at $T-T_k=0.75$ for ethylene $s_D = 0.00075.$

Although our measurement is but preliminary, it leads us to conclude that, at least as far as the order of magnitude is concerned, the intensity of the light scattered by the blue mist in a single substance in the neighbourhood of the critical state agrees with the hypothesis of SMOLUCHOWSKI, that light is due to differences in density caused by molecular motion and governed by statistical equilibrium. [Note added in the English translation].

[1]) W. OSTWALD. Lehrbuch der allgemeinen Chemie II 2 (2te Aufl. p. 684).

[2]) CHR. FÜCHTBAUER, Zeitschr. physik. Chem. 48 (1904) p. 552.

[3]) We express our hearty thanks to Prof. M. DE HAAS of Delft for his kindness to lend us his ultramicroscopic apparatus,

Plate II

Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. On the equation of state of a substance in the neigbourhood of the critical point liquid-gas. II. Spectrophotometrical investigation of the opalescence of a substance in the neigbourhood of the critical state.
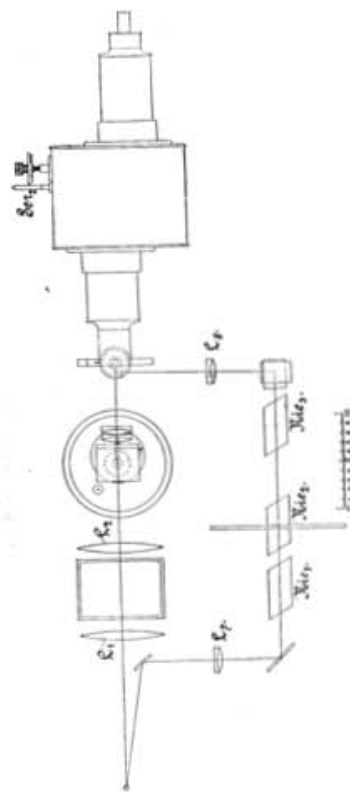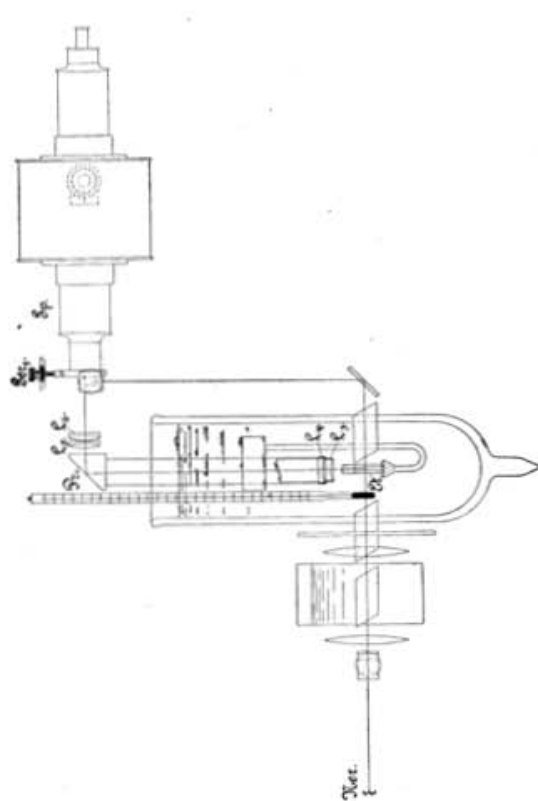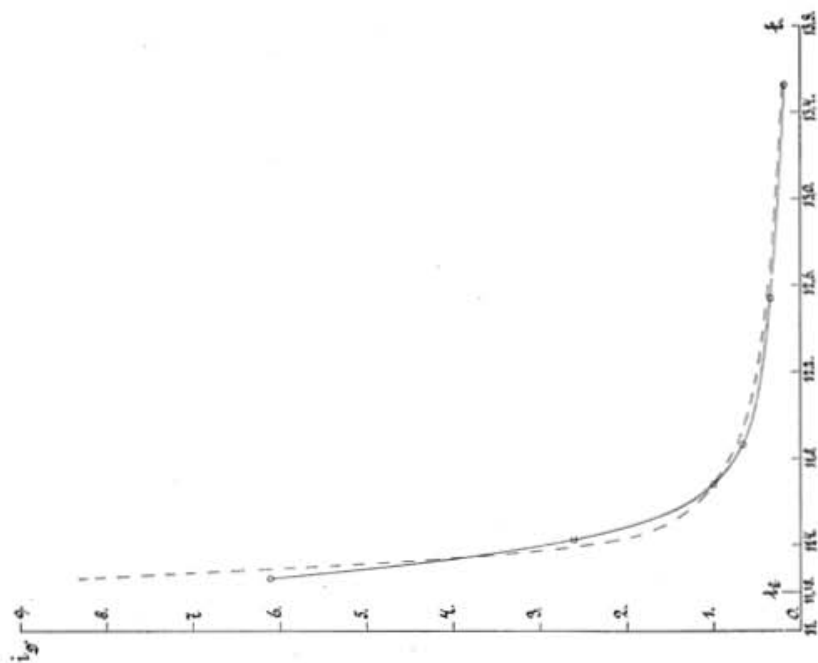

Fig. 2.

Fig. 1.

at a constant temperature near the critical temperature of separation, desirable, and also such an investigation for a single substance in the neighbourhood of the critical point gas-liquid [1]).

This investigation in connection with what follows (see § 4) from measurements as mentioned in § 3 on the size of the light-scattering particles might give us an idea of the velocity of motion of the light-scattering particles or of the mean time of existence of definite aggregations governed by the statistic equilibrium.

Chemistry. — *"On the form-analogy of Halogene-derivatives of Hydro-carbones with open chains"*. By Dr. F. M. JAEGER. (Communicated by Prof. A. P. N. FRANCHIMONT).

(This paper will not be published in these Proceedings).

ERRATA.

In the Proceedings of the meeting of March 30, 1907:

Plate II belonging to the Communication of Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM: for $\tau = 1.18$ read $\tau = 1.08$; for $\tau = 1.05$ read $\tau = 1.035$.

p. 798 l. 4 from the bottom: for 0.966 read 0.996.

In the Proceedings of the meeting of September 28, 1907:

p. 211 l. 12 from the bottom: for 0.16822 read 0.25234.

In the Proceedings of the meeting of December 28, 1907:

p. 414 l. 7 from the bottom: for 28.955 read 29.030.

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[1]) The possibility is namely not excluded that then the light-scattering particles have larger dimensions and a greater mutual distance than at the critical point of separation of two liquids. To form an opinion on this point a spectrophotometric investigation for a liquid mixture, in the same way as we have made for a single substance (§ 3) would be useful.

(March 27, 1908).