

*Citation:*

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field, we get the combinations 2.3, 1.3, 1.2 for the vibrations normal to the field. Experiment shows that the divergences of the pairs of doublets in these three cases are very different. Thus for a band of spectrum 1, the vibration being normal to the field, the magnetic doublet is different according as the direction normal to the field has the principal direction 2 or 3. The phenomenon is clearly seen in the figure which represents the group of bands in the orange for neodymium sulphate at  $-259^{\circ}$ . Fig. 7 Pl. V gives a survey of the phenomena of the changes with the temperature and the magnetic field in the blue of neodymium sulphate. According to theory it follows from this that each of the three different directions has a different magnetic constant, and that therefore the vibrating system presents three different masses for the three kinds of vibrations.

As the corresponding bands in the two spectra occupy the same or only slightly different places, it follows that in first approximation the constant of the quasi-elastic force in each of the three directions must be proportional to the mass in that direction.

**Physics.** — *“On the equation of state of a substance in the neighbourhood of the critical point liquid-gas. I. The disturbance function in the neighbourhood of the critical state.”* By Prof. KAMERLINGH ONNES and Dr. W. H. KEESOM. Communication N<sup>o</sup>. 104<sup>r</sup> from the Physical Laboratory at Leiden.

§ 1. The great compressibility of a substance in the neighbourhood of the critical point liquid-gas and the properties connected with this, (such as the small variation of the thermodynamical potential at isothermal compression etc.) — which are derived from VAN DER WAALS' original equation of state and better still from his latest considerations about the compressibility of a molecule<sup>1)</sup> — render it necessary that in deriving conclusions from observations in the neighbourhood of that condition we must take into account various circumstances, otherwise unnecessary for the experimental investigation of the equation of state of a homogeneous substance consisting of one component, which investigation includes that of the quantities of saturation etc.

It is well-known that owing to the great compressibility the thermodynamic equilibrium is difficult to attain, in fact it has often

<sup>1)</sup> Comp. VAN DER WAALS, Proceedings June '03,

happened that phenomena<sup>1)</sup> at the critical point have been described as abnormal and as being at variance with the views of ANDREWS-VAN DER WAALS, in cases where the thermodynamic equilibrium had not yet been attained either because small differences in composition had remained owing to the slow diffusion of very small quantities of admixture (KUENEN Comms. N°. 8, Oct. '93, N°. 11, May and June '94), or because differences of temperature resulting from variations of volume in different portions of the substance during the passage from one condition of temperature and pressure to the next had not yet been equalized (KAMERLINGH ONNES, Comm. N°. 68, March and April '01 and KAMERLINGH ONNES and FABIUS, N°. 98, May '07).

When the thermodynamical equilibrium is obtained either by keeping the substance in the neighbourhood of the critical point during a long time at a constant temperature or by repeated reversals of the sealed tube containing the substance (GOUY), or by stirring it electromagnetically (KUENEN) we must pay regard to the gravitation which on account of the great compressibility of the substance in that condition becomes of great influence<sup>2)</sup> and also to small quantities of admixture which may occur and of which the nature and the quantity are known<sup>3)</sup>.

The consideration of these influences and those of capillarity and absorption phenomena near the walls of the vessel<sup>4)</sup>, things which in other cases are hardly to be considered, is indispensable at the critical point liquid-gas for the determination of the *experimental equation of state of a substance*, i. e. the relation between  $p$ ,  $v$  and  $T$  for a substance consisting of one component in thermodynamic equilibrium subject to no other external forces than the pressure on the walls of the vessel.

§ 2. In this communication we intend to bring into connection some peculiarities in the experimental equation of state in the neighbourhood of the critical state with the great compressibility

<sup>1)</sup> For a survey of these phenomena comp. GRAETZ, WINKELMANN's Handbuch, III, 2te Aufl. p. 837.

<sup>2)</sup> GOUY. C. R. 115 (1892) p. 720 and 116, p. 1289. J. P. KUENEN, Comm. N°. 17 May '95.

<sup>3)</sup> Cf. Comm. N°. 75, Nov. '01, N°. 79, March '02, N°. 88 Nov. '03 (KEESOM), N°. 81, June and Sept. '02, Suppl. N°. 6, Febr. and May '03, N°. 18, Dec '04, N°. 12, Jan. '07 (VERSCHAFFELT). On the influence of gravity a small quantity of admixture being present, cf. KUENEN, Comm. N°. 17, May '95 and KEESOM, Comm. N°. 88 VI, Nov. '03.

<sup>4)</sup> Comp. VAN DER WAALS, l.c. p. 106 and 107.

in this area. Therefore we compare the experimental equation of state of a substance near the critical point liquid-gas with an equation of state which we shall call *the special undisturbed equation of state for that substance* and which is derived by adjusting interpolation formulae to observations in areas where no disturbances occur such as in the neighbourhood of the critical point.

For we presume to be able to derive from the results of data at our disposal that the experimental equation of state differs from the special undisturbed one by the presence of terms which for the accuracy reached in the observations meant only deserve notice in the neighbourhood of the critical point, and which are intimately connected with the great compressibility in this area. We shall call the compound of these terms *the disturbance function in the equation of state in the neighbourhood of the critical point*.

In order to be able to derive from the special undisturbed equation of state and the disturbance function at the critical state the conditions of coexistence, vapour pressures, liquid and vapour densities, we must have investigated whether in that condition MAXWELL's criterium for a substance consisting of one component may be applied unmodified or not.

For the present we must include in this disturbance function the disturbances caused by admixtures which chemically may have an existence of their own, but which it was not possible to remove and which always occur in definite quantities, as long as the nature and the quantity of these admixtures are unknown. The investigation of substances with small quantities of admixture<sup>1)</sup> may help us towards a better judgment of the question whether this disturbance function may be entirely ascribed to admixtures which may exist separately. As long as this has not yet been decided it will be indispensable to pay regard also to admixtures which can have no existence of their own but which may always occur as electrically charged particles, or as portions of the substance of greater density which may give rise to differences of density distributed as nebulous drops and which in this area might be kept up by capillary force. It will also be necessary to take into account differences of density depending on the statistic equilibrium.

In order to arrive at some knowledge of such a disturbance

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<sup>1)</sup> Comp. p. 604 note 3. For the influence of small quantities of admixture of substances of small volatility the following investigations are important: M. CENTNERSZWER, ZS. physik. Chemie 46 (1903) OSTWALD Jubelb. p. 427, 61 (1907) p. 356; M. CENTNERSZWER and A. PAKALNEET, *ibid.* 55 (1906) p. 303, M. CENTNERSZWER and A. KALNIN, *ibid.* 60 (1907) p. 441.

function, observations of greater accuracy are required over an area which comprises the critical state and also approaches it sufficiently. These observations must be accurate to within  $\frac{1}{50000}$ , as is usual in the Leiden laboratory in the investigations of bi- and monatomic substances and their binary mixtures, while the nature and the quantity of the separable admixtures ought to be known to  $\frac{1}{10000}$  of the whole mass <sup>1)</sup>.

§ 3. Our conclusion about the existence of a disturbance function in the equation of state in the neighbourhood of the critical point liquid-gas is based on the following data which may be arranged into three groups.

a. In Comm. N°. 74 (Arch. Néerl. (2) 6 (1901) livre jub. BOSSCHA p. 874) has been pointed out that AMAGAT's observations of the isothermals of carbon dioxide near the critical point show systematic deviations from the values derived from the special undisturbed equation of state. This equation of state was derived from the empiric equation of state introduced in Comm. N°. 71, June '01, by choosing the virial coefficients so (Comm. N°. 74 § 4) that the agreement with the observations over the whole area of observations is as good as possible while the agreement with the general reduced equation of state at a reduced temperature lying far outside the area of observation was retained.

We get a similar series of observations if we compare the observations of carbon dioxide in the neighbourhood of the critical point — described in Comm. N°. 88 (Jan. '04) — with the special undisturbed equation of state, while using the reduced virial coefficients V s. 1 (Comm. N°. 74, p. 884) and the critical temperature and pressure found in Comm. N°. 88.

It really appeared in Suppl. N°. 14, Jan. '07 (KAMERLINGH ONNES and Miss JOLLES) that the critical quantities, derived according to  $\partial p / \partial v = 0$ ,  $\partial^2 p / \partial v^2 = 0$  from the special undisturbed equation of state V s. 1, show great deviations from those derived experimentally.

A similar difference was found by AMAGAT (Journ. de phys. (3) 8 (1899) p. 353) when he derived the densities of saturated liquid and vapour from the equation of state (containing 10 constants) formed by him for carbon dioxide. The curve which represents the densities calculated thus as a function of the temperature, at lower tempera-

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<sup>1)</sup> For such an investigation carbon dioxide would be fittest owing to the comparably small difficulties in preparing it perfectly pure and keeping its temperature sufficiently constant, and also because much is already known about its equation of state over a large area.

tures coincides almost with the curve given by the observations: according as we approach the critical temperature the calculated curve shows a displacement towards the small densities with regard to the observed curve. That this displacement is much larger than follows from the calculation of Suppl. N<sup>o</sup>. 14 mentioned above must be ascribed at least partly to the circumstance that AMAGAT probably did not derive the liquid and vapour densities from his equation of state by means of the criterium of MAXWELL, but for shortness' sake calculated by means of his equation of state the densities for which  $p$  has the value for the saturation pressure furnished by experiment.

b. In Comm. N<sup>o</sup>. 75 Nov. '01 attention was directed to the difference between the  $C_s = \left[ \frac{T}{p} \left( \frac{\partial p}{\partial T} \right)_v \right]_k$  derived from AMAGAT's net of isothermals and the  $C'_s = \left[ \frac{T}{p} \frac{dp_{\text{sat.}}}{dT} \right]_k$  resulting from his determinations of the saturated vapour pressure, which values must be equal for the undisturbed equation of state<sup>1)</sup>. One of the reasons to undertake the observations about carbon dioxide of Comm. N<sup>o</sup>. 88, Jan. '04, was the wish to obtain more certainty about these peculiarities in the behaviour of the substance in the neighbourhood of the critical point (comp. l.c. p. 566). The same difference viz.  $C_s = 7.12$ ,  $C'_s = 6.71$  followed from these determinations. BRINKMAN (Thesis for the doctorate, Amsterdam 1904, p. 43) confirmed this difference not only for carbon dioxide, but he also found it for methyl chloride, while MILLS (Journ. phys. Chem. 8 (1904) p. 594, 635; comp. also 9 (1905) p. 402) for ethyl oxide (RAMSAY and YOUNG), isopentane and normal pentane (YOUNG) finds differences of 10 percent between  $C_s$  derived by means of the formula of BIOT for the saturated vapour pressures and  $C'_s$  which with regard paid to the regular variation of  $b$  with temperature<sup>2)</sup>, follows from the data collected by RAMSAY and YOUNG (ethyl oxyde), YOUNG (isopentane) and ROSE-INNES and YOUNG (normal pentane) in order to judge of the equation of isochors  $p = bT - a$ .

c. In Comm. N<sup>o</sup>. 88, Jan. '04, p. 575 table XXII the saturated vapour pressures of carbon dioxide between 25°.55 C. and the critical temperature (30°.98 C.) are compared with the formula  $\log \frac{p}{p_k} = f \frac{(T - T_k) T_k}{T^2}$  which was obtained by keeping in the develop-

<sup>1)</sup> M. PLANCK, Wied. Ann. 15 (1882) p. 457; comp. also Comm. N<sup>o</sup>. 75 § 3. The quantities  $C_s$  and  $C'_s$  are both obtained by an extrapolation,  $C_s$  at  $v = v_k$  of a higher temperature to  $T_k$ ,  $C'_s$  along the vapour pressure curve of lower  $T$  to  $T_k$ .

<sup>2)</sup> S. YOUNG, Proc. Phys. Soc. London 1894/95, p. 602; comp. also Comm. Phys. Lab. Leiden No. 88 p. 54 note 1, KEESOM Thesis p. 86.

ment of  $\log p$  in ascending powers of  $T^{-1}$  the second power<sup>1)</sup>. While for the other temperatures in the table mentioned the deviations did not exceed 0.01 atm., a deviation of Obs.—Comp. = 0.05 atm. was found for 30°.82 C.<sup>2)</sup>. Although it was then held probable that this deviation was to be ascribed to an accidental error of observation, we have afterwards found that a deviation in the same sense and of about the same size also occurs in the results of other observers about saturated vapour pressures of carbon dioxide near the critical point.

A comparison of the results of BRINKMAN's observations (Thesis Amsterdam 1904 pp. 41 and 42) of saturated vapour pressures of methyl chloride and carbon dioxide with the pressures derived by him according to a formula of the same form as the one mentioned above, yields the following differences:

for methyl chloride ( $t_k = 143.^\circ 12$ ):

$$\begin{aligned} &\text{at } t = 137.^\circ 54, 138.^\circ 92, 140.^\circ 26, 141.^\circ 66, 142.^\circ 02 \\ O-C &= +0.02, -0.01, -0.02, +0.03, +0.08; \end{aligned}$$

for carbon dioxide ( $t_k = 31.^\circ 12$ ):

$$\begin{aligned} &\text{at } t = 24.^\circ 24, 26.^\circ 08, 28.^\circ 46, 29.^\circ 86, 30.^\circ 40 \\ O-C &= +0.02, -0.02, +0.03, +0.08, +0.07. \end{aligned}$$

In both substances investigated one finds below the critical temperature an obvious deviation resembling that found in Comm. N°. 88.

The observations of AMAGAT, Journ. de phys. (2) 1 (1892) p. 288, of the saturated vapour pressure of carbon dioxide fail to give any definite indication about the question treated here because AMAGAT has rounded off the pressures to 0.1 atm. In connection with the preceding statements, however, it deserves attention that TSURUTA, Journ. de phys. (3) 2 (1893) p. 272, when comparing these data with the formula  $p = 34.3 + 0.8739t + 0.01135t^2$ , also there found an obvious difference  $O-C$  at 31.°25 which exceeds by 0.06 atm. that at 31.°35 (crit. temp. according to AMAGAT).

From the data mentioned here one might draw the conclusion that for carbon dioxide and methyl chloride the curve of the saturated vapour pressures, continued to near the critical point, with extrapolation to this point would lead us to expect a  $p_k$  somewhat larger than the critical pressure found experimentally. From the very careful

<sup>1)</sup> In Physik. ZS. 8 (1907) p. 944, Bose went still farther and kept the third power in this development which had been given by RANKINE, Misc. Scientif. Papers pp. 1 and 410,

<sup>2)</sup> As it appears from the columns Obs. and Comp. all the numbers in the column  $O-C$  have wrong signs.

observations of YOUNG of isopentane Proc. Phys. Soc. London 1894/95, p. 613, however, a deviation as found above for carbon dioxide cannot be derived.

It may be that some connection exists between the above mentioned disturbance in the saturation pressure in the immediate neighbourhood of the critical point of carbon dioxide and a disturbance in the observations of Comm. N°. 88 of the densities of saturated liquid and vapour of carbon dioxide. Plate I represents these densities

$d_{liq}$  and  $d_{vap}$ , expressed in the theoretical normal density.  $\frac{1}{2}(d_{liq} + d_{vap})$

is also represented. The straight line is the line which was drawn for the determination of the critical volume after the method of the rectilinear diameter of CAILLETET and MATHIAS in Comm. N°. 88 (comp. Comm. N°. 88 p. 574). The middle of the chord belonging to 30.8 lies clearly below this line. If for the determination of the rectilinear diameter only the three points at lower temperature are used, the difference is much larger. If this deviation cannot be ascribed to an error of observation, it would follow hence that the diameter of CAILLETET and MATHIAS for carbon dioxide shows a curvature in the immediate neighbourhood of the critical point<sup>1)</sup>.  $K_{98}$  indicates the critical density which in Comm. N°. 98 (KAMERLINGH ONNES and FABUS) was derived from determinations less than 0.002 deg. below the critical temperature. If we might assume that the carbon dioxide of Comm. N°. 98 and that of N°. 88 possessed the same degree of purity, an assumption to which the agreement between the critical temperatures entitles, and also that the difference in the methods of density determination has not given rise to a systematic difference, then the situation of the point  $K_{98}$  would confirm the curvature of the diameter in the neighbourhood of the critical point.

A similar disturbance as we remarked above for the saturation volumes of carbon dioxide in the immediate neighbourhood of the critical point, cannot be derived either from YOUNG's observations of isopentane (comp. Proc. Phys. Soc. London 1894/95 p. 636) or from those of normal pentane (Trans. Chem. Soc. 71 (1897) p. 455),

<sup>1)</sup> This curvature is in another sense than the curvature found by KUENEN and ROBSON, (Phil. Mag. (6) 3 p. (1902) p. 624) at lower temperatures in the diameter for carbon dioxide and which agrees with the general rule given by YOUNG (Phil. Mag. (5) 50 (1900) p. 291) about this curvature at lower temperatures in connection with the value of  $\frac{RT_k}{p_k v}$  and the slope of the diameter as compared with the temperature axis.



which are continued down to  $0^{\circ}.05$  below the critical temperature <sup>1)</sup>. It would be very desirable to investigate more closely in how far the disturbances mentioned sub c are connected with a disturbance in the equation of state, or must be ascribed to special circumstances of those experiments themselves (such as the difficulty to determine the moment at which begin condensation occurs).

§ 4. The disturbances mentioned in § 3 apparently point to the fact that the substance in the neighbourhood of the critical point occupies a smaller volume than would be expected according to the special undisturbed equation of state. In Comm. N<sup>o</sup>. 88 p. 555 the possibility is mentioned that these disturbances are connected with differences of density which occur in the substance near the critical state, as it is indicated by the mist (the blue opalescence) in the neighbourhood of that state. The question was left aside whether those differences of density are to be interpreted either as condensations round condensation centres with an existence of their own (dust according to KONOWALOW <sup>2)</sup>), electrically charged particles <sup>3)</sup> a third phase separated in small drops and for the greater part consisting of an admixture), or simply as spontaneously formed differences of density, either as accidental aggregations caused by molecular motion and governed by the statistic equilibrium (SMOLUCHOWSKI <sup>4)</sup>), or because small drops still have a positive surface tension at temperatures at which larger drops are no longer stable (DONNAN <sup>5)</sup>).

Whatever may be the cause of the blue mist, in all cases we may expect a close relation between the compressibility and the occurrence of it. In order to form a better judgment about this matter it was considered to be desirable to start an investigation of the conditions of existence of this mist in a substance consisting of one component in the neighbourhood of the critical point liquid-gas. For an optical research of these conditions of existence we refer to the next communication.

<sup>1)</sup> Nor can a similar disturbance be derived with certainty from BRINKMAN's observations of carbon dioxide and methyl chloride, which observations, however, are not continued so near to the critical point as those of comm. N<sup>o</sup>. 88.

<sup>2)</sup> D. KONOWALOW. Ann. d. Phys. (4) 10 (1903) p. 360.

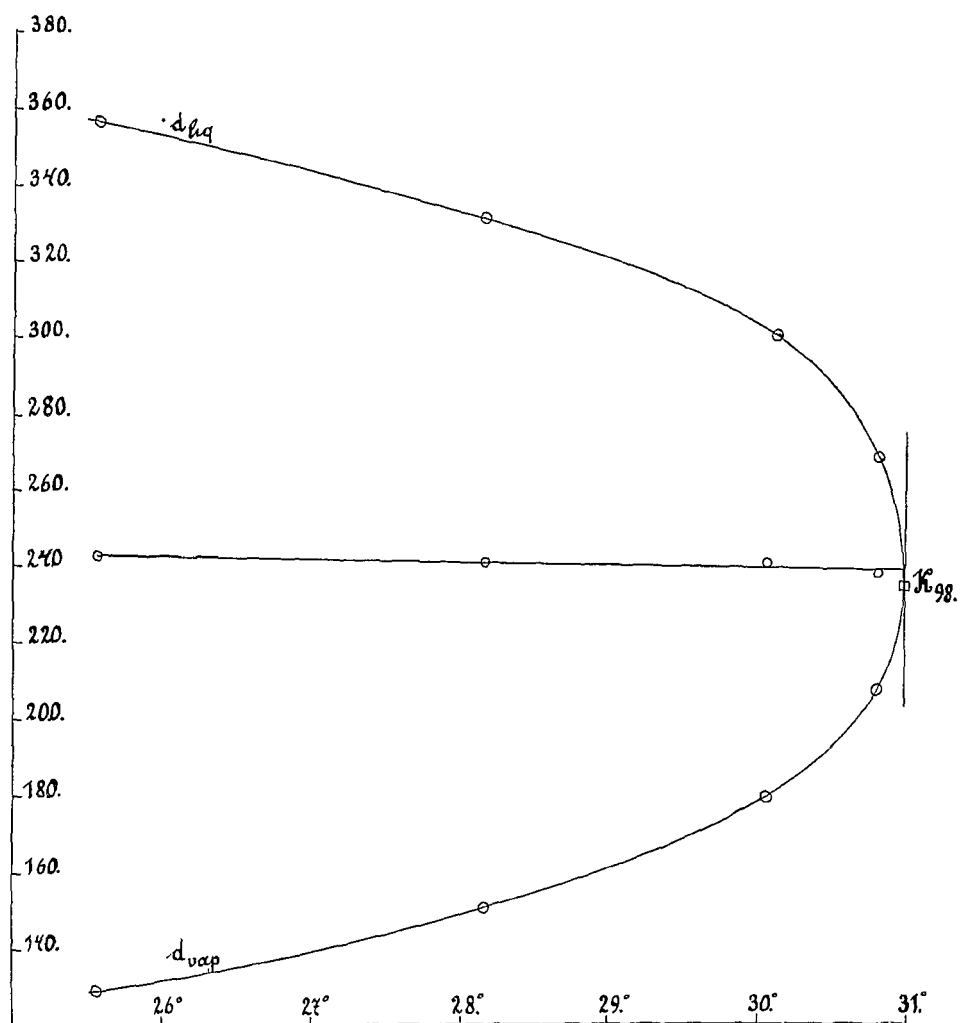
<sup>3)</sup> Owing to the highly penetrating radiation from the radio-active portions of the crust of the earth (EVE, Phil. Mag. (6) 12 (1906) p. 189) in the atmosphere (STRONG, Physik. ZS. 9 (1908) p. 170), or in the surroundings of the building where the experiments are made, these particles would always be present to almost the same amount. In the mean time it follows from the experiment of FRIEDLÄNDER ZS physik. Chem. 38 (1901) p. 385, on the stability of the mist in an electric field, that the particles which cause the opalescence are not charged.

<sup>4)</sup> M. v. SMOLACHOWSKI, Ann. d. Phys. (4) 25 (1908) p. 205.

<sup>5)</sup> F. G. DONNAN. Chem. News 90 (1904) p. 139.

Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. On the equation of state of a substance in the neighbourhood of the critical point liquid-gas. I. The disturbance function in the neighbourhood of the critical state.

Plate I.



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