

Citation:

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Physics. — “*Isothermals of di-atomic substances and their binary mixtures. XIX. A preliminary determination of the critical point of hydrogen*”. By H. KAMERLINGH ONNES, C. A. CROMMELIN and P. G. CATH (Communication N°. 151c from the Physical Laboratory at Leiden).

(Communicated in the meeting of June 24, 1916).

1. *Introduction. Apparatus and method.*

The results so far obtained by different observers in the determination of the critical data for hydrogen show a wide divergence. DEWAR ¹⁾ found $T_k = 29^\circ \text{K}$, 30°K and 32°K respectively, $p_k = 15$ atm., OLZEWSKI's ²⁾ latest values were $T_k = 32^\circ.3 \text{K}$ and $p_k = 13$ atm., BULLE ³⁾ found $T_k = 31^\circ.4 \text{K}$ and $p_k = 11$ atm. It will appear from this communication that all these results differ very considerably ⁴⁾ from those which we consider to be the correct ones, viz. $T_k = 33^\circ.2 \text{K}$, $p_k = 12.8$ atm. In view of the great difficulty of the problem this is not to be wondered at.

We ourselves had repeatedly been compelled to defer the accurate investigation regarding the critical condition of hydrogen, because we were unable to get over the difficulty of keeping temperatures such as those, at which the experiments had to be carried out, sufficiently constant. As soon as this difficulty had been conquered by the construction of our hydrogen-vapour cryostat ⁵⁾ we were enabled to avail ourselves of this material improvement in order to arrive at a first determination of the critical temperature of neon ⁶⁾ and also a more accurate measurement of the critical data of hydrogen.

¹⁾ J. DEWAR. Inaug. Adress Brit. Ass. Adv. Sc Belfast 1902.

²⁾ K. OLSZEWSKI, Ann. d. Phys. (4) 17 (1905) pg. 986, Ann. de chimie et de phys 8 (1906) pg. 193.

³⁾ F. BULLE, Physik. ZS. 14 (1913) pg. 860.

BULLE's results differ a good deal more from ours than OLSZEWSKI's much earlier results.

⁴⁾ With the exception of DEWAR's p_k and ours (Note added in the translation). In fact the weaker point in OLSZEWSKI's work will have been probably the determination of the temperature.

⁵⁾ H. KAMERLINGH ONNES, Proc. XIX (2) p. 1049. Comm. N°. 151a.

⁶⁾ H. KAMERLINGH ONNES, C. A. CROMMELIN and P. G. CATH, Proc. XIX (2) p. 1058. 1917. Comm. N°. 151b.

On the whole the same apparatus were used for both substances; as regards these we may therefore refer to the communication on neon just quoted. Only the pressures were measured in a different way. The readings on the closed manometer M_{60} , which was used in the case of neon, do not begin before 20 atm. and the critical pressure of hydrogen being smaller than that, we had to use the open standard-gauge of the laboratory ¹⁾ for the purpose.

The hydrogen which had been purified by distillation was free from all admixture as shown by the heterogeneous parts of the isothermals in the pressure-density diagram being straight lines running parallel to the density-axis (comp. fig. 1). At the same time we wish our results to be considered as preliminary ones. In the first place because a larger number of observations than we have made (comp. fig. 1) will be needed to smooth out certain small irregularities which our observations still show and thus draw with sufficient certainty the set of isothermals which have to serve the purpose of settling in a perfectly satisfactory manner physical constants of so fundamental a character as the critical data of hydrogen. But even more because in our opinion it is necessary for definite determinations to be able to follow the critical phenomena by eye which we have not been able to do as yet, no more than in the

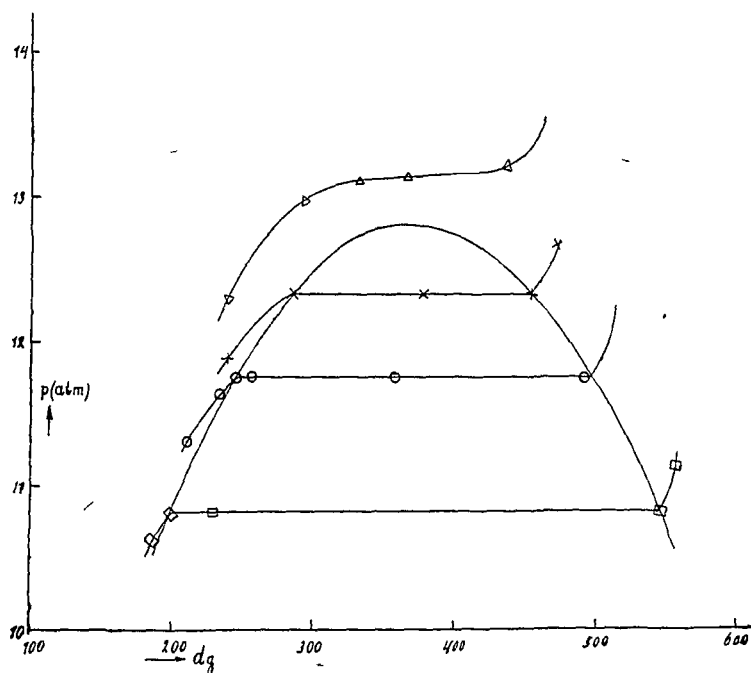


Fig. 1.

¹⁾ H. KAMERLINGH ONNES, Proc. I p. 213. Comm. N^o. 44.

case of neon, although we hope before long to be in a position to carry out this purpose.¹⁾

As regards the method of deducing the critical data from the observations we have in our Communication on the critical condition of neon referred to the similar case of hydrogen, which is the subject of our present communication. In this case we are able to illustrate our method of procedure by means of a suitable diagram²⁾.

This figure gives the main features of the pressure-density diagram, drawn during the observations to keep a graphical record of the results already obtained, in order to guide us, as we went along, in the choice of the conditions under which the next observations had to be made.

In representing an observation we used as abscissa the quantity of gas³⁾ that was at that moment present in the part of the vapour-pressure apparatus which was at the temperature of the observation⁴⁾.

The observations relating to one isothermal are each time indicated by one and the same of the signs \square , \circ , \times and \triangle . The determination of the points of beginning and completed condensation had been preceded by tentative readings in the neighbourhood of the observations recorded in the diagram. The fact that the heterogeneous

¹⁾ Compare, besides the paper already quoted on the hydrogen-vapour cryostat (151a), particularly H. KAMERLINGH ONNES, Proc. XVIII. pg. 507. Comm N^o. 147c, where a cryostat is discussed working with neon boiling under enhanced pressure to be used amongst others for this object.

²⁾ The corresponding diagram of neon being somewhat modified owing to impurities would necessitate an elaborate discussion.

³⁾ The quantity is given in cc. of gas measured in the normal condition.

⁴⁾ The volume of this part is approximately 1.0J cc. Our apparatus, being a simple vapour-pressure apparatus, was not suitable either for the accurate measurement of this volume or of the quantity of substance which enters this volume. In consequence of this the uncertainty as regards the accurate value of the volume which is at the observational temperature as also the value of the temperature of certain other parts of the apparatus whose volume cannot be neglected is such that the accuracy of the density-determinations cannot be guaranteed beyond a limit of a few percentagés.

Owing to the uncertainty of the correction for the "waste" space, the figure may deviate in a systematic manner from the correct pressure-density diagram to the same degree: in order to obtain the correct figure the chords of the boundary curve i. e. the heterogeneous parts of the isothermals will have to be shifted without any change in length, each by an amount about proportional to the pressure; the uncertainty about the part of the volume which has the low observational temperature causes the value of the unit of density which is assumed in setting off the density on the axis of abscissae in fig. 1 to be only approximately known.

parts of the isothermals are accurately parallel to the axis of abscissae proves on the one hand that the hydrogen was absolutely pure and on the other that the temperature could be kept constant to .01 of a degree ¹⁾. It proved possible to connect the points which give the beginning and the completion of the liquefaction by means of an ordinary parabola. The pressure corresponding to the top of this parabola was taken as the critical pressure. The temperature corresponding to the critical pressure thus found was obtained by extrapolation from the measurements of the vapour-pressure at the temperatures immediately below the critical temperatures.

Beside the observations just mentioned on the isothermals which show a heterogeneous part, an isothermal will be found plotted in the figure which was determined at a slightly higher temperature and where a similar part parallel to the density-axis (heterogeneous condition) is no longer found. The tangent to the point of inflexion is inclined to the axis of densities and this isothermal thus appears to belong to a temperature higher than the critical temperature. It is clear, that by means of this figure an upper and a lower limit may be fixed for the critical pressure and a probable value of the critical pressure may be established, from which in their turn follow an upper and a lower limit and a probable value of the critical temperature. The degree of certainty with which the latter determination may be effected is fairly satisfactory. For hydrogen the two limiting values just mentioned as regards the temperature differ by less than .4 of a degree. The figure further shows that in the manner described the temperature itself may be considered to be determinable with a certainty of .1 of a degree.

§ 2. *Results.*

In the following table of vapour-pressures the absolute temperature as well as that on the centigrade scale have been corrected to the KELVIN-scale by means of the table of corrections published on former occasions ²⁾.

The pressure is given in international ³⁾ cms mercury and in

¹⁾ To make this result possible the distribution of the temperature must also have been a very uniform one throughout the experimental space. We are glad to express once more our thanks to Mr. J. M. BURGERS, phil. cand. for his careful assistance in the regulation of the temperatures.

²⁾ H. KAMERLINGH ONNES, Proc. X, p. 589. Comm. N^o. 102b, and H. KAMERLINGH ONNES and G. HOLST, Proc. XVII, 1, pg. 501. Comm. N^o. 141a.

³⁾ In the original paper the pressures were given in local cms mercury and in international atmospheres. [Note added in the translation].

international atmospheres, the international atmosphere being taken equal to a mercury column of 75.9488 cms at Leiden.

T	θ	$p_{koex.}$ (int. cm.)	$p_{koex.}$ (int. atm.)
32.02° K.	— 241.07° C.	822.7	10.825
32.60	— 240.49	893.2	11.752
32.93	— 240.16	936.5	12.322

Above θ_k the following point was measured :

T	θ	p (int. cm.)	p (int. atm.)
33.28° K	— 239.81° C.	999.5	13.151

The critical quantities derived from the above figures are as follows :

T_k	θ_k	p_k (int. cm.)	p_k (int. atm.)
33.18° K.	— 239.91° C.	973	12.80

The deviation of BULLÉ's result from ours may, as we think, be partly explained from his having used a resistance-thermometer which was only calibrated by means of hydrogen- and oxygen-temperatures and on the other hand perhaps also from the arrangement of his apparatus. Possibly owing to the rapidity with which he had to conduct the experiment the flask in which the hydrogen was compressed had not yet assumed the temperature of the resistance-thermometer when the measurement was made.

§ 3. Estimation of the critical density.

By means of the above value of the critical temperature, of the

liquid-densities ¹⁾ and vapour-pressures ²⁾ published on former occasions and finally of the values of the constant B ³⁾, it is now possible to make a calculation of the critical density of hydrogen assuming the diameter of CALLETET and MATHIAS to be a straight line for hydrogen; there is all the more reason for the latter supposition as according to the figure the inclination of the diameter in the neighbourhood of the critical point cannot deviate much from that at the lower temperatures where the expansion of the liquid has been determined.

For this purpose, using the vapour-pressures and the value of B , by means of the relation ⁴⁾ $d_A = \frac{p}{A_A} \left\{ 1 - \frac{B_A}{A_A^2} p \right\}$ the vapour densities are calculated at the same temperatures at which the density of the liquid has been measured. The constant A_{A_0} is taken equal to .99939.

In this manner the ordinates of the diameter are obtained and by means of these the equation of the diameter. In the following table $\rho_{\Gamma vap}$ and $\rho_{\Gamma liq}$ denote the densities of the saturated vapour and the liquid respectively in gr. per cm³ and y the ordinate of the diameter. The two points through which the diameter is laid are indicated by an asterisk.

θ .	$\rho_{\Gamma liq}$	$\rho_{\Gamma vap}$.	y (W).	y (R).	W-R
- 252.68	.07081	.00135	.03608	.03604	+ .00004
- 253.24	7137	116	3627	3626	+ 1
* - 253.76	7192	101	3647	3647	0
- 255.19	7344	0.00064	3704	3704	0
- 255.99	7421	49	3736	3735	+ 1
* - 256.75	7494	38	3766	3766	0
- 257.23	7538	31	3784	3785	- 1
- 258.27	7631	20	3826	3826	0

¹⁾ H. KAMERLINGH ONNES and C. A. CROMMELIN, Proc. XVI, 1, pg. 245, Comm. No. 137a.

²⁾ H. KAMERLINGH ONNES and W. H. KEESOM, Proc. XVI, 1, pg. 440, Comm. No. 137d.

³⁾ H. KAMERLINGH ONNES and W. J. DE HAAS, Proc. XV, 1, p. 405, Comm. No. 127c. The values of B were smoothed in the manner as given in this paper.

⁴⁾ B_A was found by graphical interpolation; C_A does not come into account.

The equation of the diameter becomes

$$y = - .06453 - .000398 \theta.$$

or in the more usual form

$$y = + .04416 - .000398 T.$$

Substituting in this equation our value for the critical temperature $\theta = - 239.91^\circ \text{C}$. the critical density is found to be

$$\rho_{\Gamma_k} = .0310.$$

In 1904 DEWAR¹⁾ published an estimate of the density viz. .033, calculated from a couple of liquid densities as determined by himself.²⁾

¹⁾ J. DEWAR, Proc. R. S. 73 (1904) pg. 251.

²⁾ If the critical density is derived using the quantities d_g in the small flask as read from fig. 1, the weight of a cc. of hydrogen measured under normal conditions and the volume of the flask as given in note 4 on page 180 the result is $\rho_{\Gamma_k} = .033$. If the diameter is truly a straight line and thus $\rho_{\Gamma_k} = .031$ as given in the text, a comparison of ρ' from the figure and ρ from the diameter would provide a means of correcting fig. 1 for the systematic deviation (see the note mentioned) from the true pressure density diagram. It is found that the direction of the diameter in the neighbourhood of the critical point in the corrected figure still coincides within the limits of accuracy with the direction holding for lower temperatures according to the above table.