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7. Some further details concerning the apparatus may finally be given.

The mounting and the plates of the 5 m.m. étalon are by JOBIN. The inner surfaces of the plates are accurately flat. The outer surfaces need only ordinary flatness, they are inclined at an angle of  $1'$  to the inner ones. The plates of the étalon are vertical, and the whole apparatus is capable of the necessary adjustments in azimuth, while also a horizontal sliding motion parallel to the plates of the étalon was provided for.

An image of the vacuum tube was focussed upon the étalon by means of an achromatic lens of 12 cm. focus, the enlargement being four times. All optical pieces were mounted upon double *T*-pieces and therefore rigidly connected.

The figures clearly indicate that for the investigation of the magnetic separation of the yellow mercury lines, it would be of no value to use an étalon of greater optical thickness of the plate of air. On the contrary the effective width of the yellow mercury lines when under magnetic influence is rather large, so that the limits of the method in this case are being rapidly approached.

**Physics.** — *“Isotherms of monatomic gases and their binary mixtures.*

*I. Isotherms of helium between  $+100^{\circ}$  C. and  $-217^{\circ}$  C.”*

Communication N°. 102<sup>a</sup> from the Physical Laboratory at Leiden. By Prof. H. KAMERLINGH ONNES.

§ 1. On account of the important rôle, which VAN DER WAALS' theory plays in many chapters of thermodynamics, experimental data concerning the equation of state of a substance are of the greater value as the interaction of the molecules of this substance conforms the better to the hypotheses from which VAN DER WAALS started. The knowledge of the equation of state of the monatomic gases, whose molecules we must consider as the simplest for the present, is of the greatest importance from this point of view.

In Comm. N°. 69 (April 1901) on the isotherms of diatomic gases and their binary mixtures it was already observed that the investigation of the net of isotherms of argon and of helium promised still more important results than the completion of the net of isotherms of the gases formerly called permanent, particularly of hydrogen, at low temperatures, on which subject my attention had been chiefly fixed since the establishment of the cryogen laboratory (cf. Comm. N°. 14, Dec. '94). But the difficulty of obtaining argon and helium in so pure a state and in such quantities as are required for

the determination of isotherms, retarded the determination of the equation of state of helium and argon for a long time after Comm. N°. 69.

The investigations on the isotherms of hydrogen are in progress, and yielded already results laid down in communications N°. 78, 97<sup>a</sup>, 99<sup>a</sup> and 100<sup>a</sup>, which, I hope, will soon be followed by others. In the meantime, however, also the difficulty of obtaining pure helium has been quite, that of obtaining pure argon nearly overcome. The successful preparation of pure helium was chiefly due to the hydrogen circulation (Comm. N°. 94<sup>f</sup>) yielding the required liquid hydrogen. So the first measurements from the series which will refer to the monatomic gases and their binary mixtures, can already be communicated.

They concern the isotherms of helium, which have now taken the place occupied by the isotherms of hydrogen before the hydrogen was liquefied. Among others the isotherms must lead to the calculation of the critical quantities for helium. From the now communicated determinations of the compressibility along different isotherms at densities which are comparatively small and differ only slightly, the critical temperature can already be calculated by approximation.

## § 2. *Survey of the determinations.*

This investigation comprises some six determinations of isotherms. The temperatures at which they were made, were kept constant and determined in the same way as in the determinations of isotherms for hydrogen published in preceding Communications N°. 97<sup>a</sup> (April 1907), N°. 99<sup>a</sup> (Sept. 1907), N°. 100<sup>a</sup> (Jan. 1908). The readings of the hydrogen thermometer were reduced to the absolute scale by means of formula (4) of Comm. N°. 97<sup>b</sup> (Sept. 1907) with the new coefficients of § 2 of Comm. N°. 101<sup>b</sup>. The six temperatures thus reduced to which the isotherms refer, are:

$$+100^{\circ}.35, 20^{\circ}.00, 0^{\circ}, -103^{\circ}.57, -182^{\circ}.75 \text{ and } -216^{\circ}.56.$$

Besides the measurements at the two standard temperatures 0° C. and 100° C.<sup>1)</sup> and those at low temperatures a determination was made at 20° C. to obtain data for the calculation of the quantity of gas in the stem of the piezometer and in the other parts, which remain at the ordinary temperature during the measurements.

For all these isotherms the densities, at which the pressure was observed, lie about between the same limits which were set by the

<sup>1)</sup> The results at 0° C. and 100° C. are incompatible with those of RAMSAY and TRAVERS, which, indeed, show strange deviations.

dimensions of the piezometer and by the manometer. The utmost limits of the density are 25 and 54 times the normal one. The piezometer and further auxiliary apparatus were perfectly the same as have served for the determinations of C. BRAAK and me (see Comm. N°. 100<sup>b</sup> Jan. 1908) with hydrogen at 0° C. and 100° C. The satisfactory results obtained then, enhance at the same time the reliability of the measurements considered now.

### § 3. *Results for $pv_A$ .*

The subjoined table contains the results of the determinations. The first column gives the number of observation, the second the temperature measured above 0° C. on the absolute scale, the third the pressure in atmospheres, the two following ones the product  $pv_A$ , and the density  $d_A$ , in which the volume of the gas  $v_A$  is expressed in the normal volume (that at 0° C. and 1 atmosphere) and the density  $d_A$  in the normal density (that at 0° C. and 1 atmosphere). (Compare the corresponding tables of the above mentioned determinations of isotherms of hydrogen).

The calculation of these results was made as follows:

First the points of the isotherm of 20° C. were calculated, (cf. also § 8 of Comm. N°. 79 (April 1902)) and the coefficients  $A_A$  and  $B_A$  of the curve

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{v_A^2} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

were determined by the 3 points by the aid of the method of least squares. For  $C_A$  a definite value was assumed, the densities being too small for this coefficient to be determined with sufficient certainty. If we write VAN DER WAALS' equation with the second correction for the size of the molecules in the form:

$$pv = RT + \frac{RTb-a}{v} + \frac{5}{8} \frac{RTb^2}{v^2},$$

where  $v$  is the volume of the gas under the pressure  $p$  at the absolute temperature  $T$ , expressed in the theoretical normal volume (see Comm. N°. 71 § 3) and if we put the value of  $A_A$  at 0°,  $A_{A_0} = 1$ , which approximation is allowed for our purpose, we find (cf. Comm. N°. 71 § 3) for the value  $C_{A_T}$  of  $C_A$  at  $T$

$$C_{A_T} = \frac{1}{8} RT b^2,$$

where  $R = 0.0036619$ . The value of  $b$  was first estimated at 0.0005 (cf. the note to § 6 of Comm. N°. 96<sup>c</sup> Jan. 1907), afterwards at 0.000432, see § 4. With the coefficients  $A_A$  and  $B_A$  obtained for 20°

TABLE I. He. Values of $pv_A$ .				
Nº.	$\theta$	$p$	$\bar{pv}_A$	$d_A$
1	+ 100°.35	42 574	1 38725	30.689
2		54 459	1 39314	39.091
3		66 590	1 39929	47.589
4	+ 20°.00	27.539	1.08664	25.343
5		36.303	1.09028	33.297
6		53.708	1.09918	48 862
7	0°	26.634	1.01392	26.268
8		38.565	1.01851	37 864
9		50 240	1 02521	49 004
10	— 103° 57	20.580	0 63135	32 597
11		24.100	0 63296	38.075
12		29.185	0.63597	45.891
13	— 182° 75	53 383	0 63845	52 288
14		13 751	0.33787	40 699
15		16 019	0.33898	47.257
16	— 216° 56	18.189	0 34025	53.457
17		9 564	0.21132	45 259
18		10.502	0 21171	49.606
19		11.448	0 21219	53.951

in this way, the reductions to 0° for the gas which is outside the reservoir at a temperature of 20° and for a small part at the temperature of the room, were carried out in first approximation. With the three points which were thus found on the isotherm of 0°, the virial coefficients  $A_A$  and  $B_A$  were then calculated also for this temperature.

From this follows  $A_{A_0}$ , the value of  $pv_A$  for  $d=0$  by means of the formula:

$$A_{A_0} = 1 - B_{A_0} - C_{A_0}.$$

With the pressure coefficient from 0° C. for the state of AVOGADRO, 0.0036619 (cf. § 1 of Comm. N°. 101<sup>b</sup>) follows for 20°:

$$A_{A_{20^\circ}} = A_{A_0} (1 + 0.0036619 \times 20),$$

so that on the isotherm of 20° a fourth point is acquired, which renders the slope of the  $pv_A$  line a great deal more certain (cf. the conclusion of § 1 of Comm. N°. 101<sup>b</sup>). Then the calculation of  $A_A$  and  $B_A$  was repeated, and by the aid of these corrected coefficients the isotherm of 0° C. was again calculated, and this calculation by approximation was continued till it caused no longer any change. In this way we found for 20° C. (for  $b=0.000432$ ):

$$pv_{A,20} = 1.07273 + 0.0005337 d_{20} + 0.000000125 d_{20}^2 \dots (3)$$

With this formula the corrections have been calculated for the determinations of isotherms. For the rest the latter were treated as in the preceding communications.

#### § 4. *Individual virial coefficients.*

We may avail ourselves of the data of table I in order to derive the coefficients  $A_A$  and  $B_A$  by the aid of the method of least squares.  $C_A$  was assumed according to formula (2) of the preceding §. For every isotherm  $pv_{A,d=0}$  was calculated, and this value was added to the others as if it concerned a new observed point. This calculation was effected by the aid of the value  $A_{A_0} = 0.99949$ , which may be derived from the value for the coefficients  $B_A$  and  $C_A$  for 0° finally obtained in the calculation by approximation from the conclusion of the preceding §. Table II contains the virial coefficients and at the same time the differences between the given  $pv_A$ 's and the calculated ones. These differences are arranged according to the ascending densities. So the first column of differences refers to  $pv_{A,d=0}$ , the others to the data of table I in the above succession.

The calculation of the  $B_A$ 's is still uncertain, because for  $C_A$  estimated values have been assumed. Determinations of  $pv_A$  at greater densities, which will render an independent determination of  $C_A$  possible, are in preparation.

That the estimations of  $C_A$  are not too inaccurate, may be made probable as follows. For 100° follows from table II  $B_{A,100} = 0.000673$ . On the suppositions on which VAN DER WAALS' equation rests, the value of  $b$  may be derived from the value for two temperatures of  $B = RTb - a$  with  $B = B_A(A_{A_0})$  and then  $b = 0.000432$  is found, which does not differ much from the value 0.0005, which was first assumed by way of estimation on other grounds. Though the calculation followed here is very uncertain, yet the found value was preferred to the first estimated one, and for this reason the calculations which were first made with 0.0005, have been repeated with this new estimation. The differences of the results lie within the limit of errors of observation.

TABLE II. He. Individual virial coefficients.  
Deviations of the  $p v_A$  from the calculated ones.

$\theta$	$A_A$	$10^4 B_A$	$10^6 C_A$	$10^5 (O-C)$			
+100° 35	1.26667	+0.673	+1.16	+10	-21	-10	+22
+20° 00	1.07273	+0.534	+0.13	-3	+31	-36	+8
0°	0.90970	+0.512	+0.12	-20	+80	-75	+15
-103° 57	0.62026	+0.337	+0.07	+11	-7	-32	0 +27
-182° 75	0.33066	+0.176	+0.04	1	-1	-8	+8
-216° 56	0.20693	+0.096	+0.02	0	+1	-3	+3

§ 5. *Determination of the critical temperature of helium.*

From the data of table II we may arrive at a first estimation concerning the critical temperature of helium, which will be found from determinations of isotherms within the now accessible region of temperatures.

Extrapolation proves that the Boyle-point will lie in the neighbourhood of  $-250^\circ \text{C}$ . For hydrogen  $-166^\circ$  was found for this. (cf. Comm. N°. 100<sup>re</sup>). If we assume  $30^\circ \text{K}$ . for the critical temperature of hydrogen, then follows from this for helium

$$T_{kHe} = 6^\circ \text{K}.$$

If this value of  $T_k$  is adopted, the region of temperature  $-217^\circ$  to  $-183^\circ$  for helium corresponds with that of  $0^\circ$  to  $+200^\circ$  for hydrogen. By applying the law of the corresponding states to the slopes of the  $p v_A$ -lines for the two substances in the neighbourhood of these equivalent limits of temperature, we arrive at a slightly lower value of the critical temperature viz.

$$T_{kHe} = 5^\circ.3 \text{K}.$$

This value too I think I may still consider as a highest limit for the critical temperature of He, as it seems probable to me, that He with respect to  $\text{H}_2$  will deviate from the law of the corresponding states in this sense that the critical temperature will be found lower than would follow from the application of this law to corresponding states for values of the reduced temperatures many times larger than 1.

Now there can only be question of a first estimation based on determinations of isotherms. The determination of the isotherms of  $-253^\circ$  and  $-259^\circ$ , which is in progress, will, I hope, soon lead to a more reliable estimation.

In conclusion I gladly express my thanks to Mr. C. BRAAK for his assistance in this investigation.

(January 23, 1908).