

Published just before the condensed matter paradigm shifting measurements on Hg... Concentrating on the phase diagram of argon.

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BY
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**H. KAMERLINGH ONNES and C. A. CROMMELIN.**  
„Isotherms of monatomic substances and of their binary mixtures. IX. The behaviour of argon with regard to the law of corresponding states”. (*With a plate.*)

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**H. KAMERLINGH ONNES and C. A. CROMMELIN.** — *“Isotherms of monatomic substances and of their binary mixtures. IX. The behaviour of argon with regard to the law of corresponding states.”*

§ 1. *The mean reduced surface of state for monatomic substances.*

A difficulty which is by no means small is introduced into theoretical investigations dealing with the equation of state by the fact that, for every substance, and, in particular, for substances of simple molecular construction, the region that has been experimentally investigated extends over a small range of reduced pressure and of reduced temperature. If the law of corresponding states were strictly obeyed, this difficulty could be obviated by reducing and then combining with each other the regions investigated for the various substances. In this way the mean reduced equation of state has been synthesized in the form VII. 1 <sup>1)</sup>. It has been obtained from AMAGAT's observations on hydrogen, oxygen, and nitrogen, YOUNG's on isopentane and AMAGAT's and RAMSAY and YOUNG's on ether. In this way the equation of state has been obtained for an imaginary substance which, if further amplified by the disturbance function <sup>2)</sup> for the neighbourhood of the critical point, is suitable for all calculations in which the validity of the law of corresponding states is assumed. And this equation is of particular use in tracing deviations from the law of corresponding states, for it affords a suitable means of easily comparing individual results, which cannot be satisfactorily represented by a special equation of state, with results obtained for other substances, and, particularly, with results obtained for those substances which have served for the calculation of equation VII. 1. When deviations of some particular substance from the imaginary substance in the same reduced state have been cal-

<sup>1)</sup> Suppl. N<sup>o</sup>. 19 (May 1908).

<sup>2)</sup> Comm. N<sup>o</sup>. 104.

culated, then, the far more concise deviations from VII. 1. may replace the actual results of the experiments themselves. Such deviations were determined for each of the substances used in the synthesis of equation VII. 1. with respect to whose reduced surfaces of state that of VII. 1. plays the part of a quasi-enveloping surface. The critical temperatures of the substances can greatly influence the differences existing between the separate surfaces; the peculiarities of the molecules, however, can influence them, too, in another way.

The object we had in view in our research upon the isotherms of monatomic substances was to obtain, in the same manner as that in which equation VII. 1. was obtained, a mean reduced equation of state in the synthesis of which observations on monatomic substances should exclusively be used. Unless in the structure of the various atoms of the monatomic substances further peculiarities are discovered which influence the equation of state, then, the only influence exerted upon the form of the reduced surface is that of the critical temperature. This influence will manifest itself in the deviations of the special equations from the mean equation undisturbed by other possible factors. And it is to be expected that the special surfaces of state for the various monatomic substances should systematically differ from the enveloping surface and from each other in such a manner that a gradual transformation would change the xenon <sup>1)</sup> surface into those for krypton, argon, and neon, to finally assume a limiting shape in the case of helium <sup>2)</sup>. From the sequel, in which is given a first, but very small, step in the desired direction, it is evident that the mean reduced equation of state for monatomic substances which we desire to obtain, and which we shall indicate by  $VII_{mon.}$ , will exhibit important characteristic differences from the general mean equation VII. 1.

<sup>1)</sup> We shall, for the present, leave out of consideration substances of higher critical temperature

<sup>2)</sup> It was remarked in 1881 that a separate equation of state would have to be applied to each group of substances having similar molecules. (H. KAMMERLINGH ONNES. Verh. Kon. Akad. 1881, Arch. Néerl. 30, p. 101). The group of monatomic substances has been made a subject of special study from this point of view by H. HAPPEL, see Ann. d. Phys. (4). 13. 340. 1904.

§ 2. Comparison of argon isotherms <sup>1)</sup> with those of isopentane (YOUNG) <sup>2)</sup>, ether (RAMSAY and YOUNG) <sup>3)</sup> and carbon dioxide (AMAGAT) <sup>4)</sup> between the reduced temperatures 1.0000 and 1.1323.

In order to obtain a systematic comparison from the point of view of the law of corresponding states between the results obtained for argon and those for other substances, we have in the manner indicated in § 1, calculated the differences between the observed data for the various substances and the values obtained from VII. 1 <sup>5)</sup>. To begin with, the critical temperature and pressure already published <sup>6)</sup> were used in the calculation of the virial coefficients for argon according to VII. 1, and, with the aid of these coefficients, deviations from VII. 1 were obtained. It appeared to be most suitable to work with percentage deviations of  $pv$  from values of  $pv$  given by equation VII. 1 <sup>7)</sup>.

The virial coefficients are given in table I and the deviations in table II.

The deviations for isopentane, ether and carbon dioxide from VII. 1. were calculated a considerable time ago; they form part of an extensive research upon the differences between the empirical equations of state for these substances as expressed by their deviations from the general mean reduced equation, of which only a very small part has yet been published. From amongst these, deviations are taken which can be compared with the argon isotherms between  $-100^{\circ}$  C. and the critical point, that is, those which lie in the same region of reduced temperature as the argon isotherms. The deviations for all four substances were then united

<sup>1)</sup> Comm. N<sup>o</sup>. 118<sup>b</sup> and C. A. CROMMELIN. Thesis for the doctorate, Leiden, 1910.

<sup>2)</sup> S. YOUNG, Proc. phys. soc. London, 1894/95, p. 602.

<sup>3)</sup> W. RAMSAY and S. YOUNG Phil. Trans. 178. 57. 1887.

<sup>4)</sup> E. H. AMAGAT, Ann. de chim. e d. phys. (6) 29, June and Aug. 1893.

<sup>5)</sup> For a critical examination of the observations it is also very desirable to substitute deviations from VII. 1. for the actual observations so as to eliminate experimental error, and to reduce to one common substance the results obtained by different observers. Our results for argon were treated in this fashion before being placed upon the diagram.

<sup>6)</sup> Comm. N<sup>o</sup>. 115.

<sup>7)</sup> For the method by which these calculations are made, cf. Comm. N<sup>o</sup>. 71.

TABLE I.

| Virial coefficients for argon according to VII. 1. |                  |                  |                     |                     |                     |
|----------------------------------------------------|------------------|------------------|---------------------|---------------------|---------------------|
| $t$                                                | $B_A \cdot 10^3$ | $C_A \cdot 10^6$ | $D_A \cdot 10^{12}$ | $E_A \cdot 10^{18}$ | $F_A \cdot 10^{24}$ |
| + 20.39 C.                                         | -0.61763         | + 2.21916        | + 4.32836           | + 7.6045            | - 4.35430           |
| 0.00 C.                                            | -0.77633         | + 2.21208        | + 3.09635           | + 8.7321            | - 4.98937           |
| - 57.72 C.                                         | -1.30816         | + 2.40067        | - 0.67139           | + 10.5255           | - 5.02409           |
| - 87.05 C.                                         | -1.66571         | + 2.73556        | - 2.83014           | + 10.5566           | - 3.93044           |
| - 102.51 C.                                        | -1.89979         | + 3.04873        | - 4.10121           | + 10.4013           | - 3.10842           |
| - 109.88 C.                                        | -2.02794         | + 3.25078        | - 4.76310           | + 10.3251           | - 2.69045           |
| - 113.80 C.                                        | -2.10156         | + 3.37635        | - 5.13599           | + 10.2947           | - 2.47655           |
| - 115.86 C.                                        | -2.14498         | + 3.44818        | - 5.35020           | + 10.2837           | - 2.35600           |
| - 116.62 C.                                        | -2.15723         | + 3.47581        | - 5.41531           | + 10.2806           | - 2.31432           |
| - 119.20 C.                                        | -2.21026         | + 3.57411        | - 5.67996           | + 10.2759           | - 2.17669           |
| - 120.24 C.                                        | -2.23230         | + 3.61597        | - 5.78950           | + 10.2764           | - 2.12239           |
| - 121.21 C.                                        | -2.25318         | + 3.65616        | - 5.89340           | + 10.2783           | - 2.07246           |
| - 130.38 C.                                        | -2.46836         | + 4.10021        | - 6.96374           | + 10.3966           | - 1.66293           |
| - 139.62 C.                                        | -2.72584         | + 4.69951        | - 8.27734           | + 10.8045           | - 1.42979           |
| - 149.60 C.                                        | -3.06753         | + 5.59972        | - 10.15136          | + 11.8440           | - 1.53961           |

in one diagram in which the deviations were plotted as functions of  $\log \lambda v$  in which  $\lambda = \frac{p_k v_k}{T_k}$  and  $v = \frac{v}{v_k}$ .

Hence, the critical volume does not appear in the expression  $\lambda v = \frac{p_k}{T_k} v$ ; only the critical temperature and pressure are used in the calculation of  $\lambda v$ , while, when different substances are being compared with each other a single but undetermined value is ascribed to  $\lambda$  for all substances. This method which has already

been adopted on former occasions <sup>1)</sup> has the great advantage that it is not necessary to use the critical magnitude which is most uncertain, viz. the critical volume, and only well defined magnitudes are employed. To make  $\lambda$  the same for all substances, although it varies distinctly for the various substances <sup>2)</sup>, may well appear somewhat strange at first sight. The systematic deviations of the various equations from VII. 1 revealed in the different values of  $\lambda$  are not, however, the only systematic deviations to which expression will here be given. There is, therefore, no danger in uniting this one kind of deviation with the other ones in the common representation which we try to obtain for them. According to the method we followed it appears to be possible to unite all deviations from the law of corresponding states in a single representation as definite as can be desired for the present; but, of course, we do not mean to say that it might not be found more suitable in a more extended and more searching study of the deviations from the law of corresponding states to adopt a different method of summarising these deviations.

In order to be able to ascribe the same value to  $\lambda$  in every case, all the volumes must be expressed in the same unit. This was not the case with the observations which are now being dealt with, so that some reductions were found necessary. The volumes in the argon isotherms and in the carbon dioxide isotherms, viz  $v_A$ , are expressed in terms of the experimental normal volume, while those in the isopentane and ether isotherms, viz  $v_Y$ , are expressed in terms of the number of cubic centimetres per gram of the substance. Since we wished to express  $\lambda v$  in terms of the theoretical normal volume for all the substances we calculated its values according to the following expressions:

$$\text{for argon and carbon dioxide: } \lambda v = \frac{p_k}{T_k A_{A0}} v_A;$$

$$\text{for isopentane and ether: } \lambda v = \frac{p_k \gamma}{T_k A_{A0}} v_Y^3).$$

<sup>1)</sup> Comm. No. 71.

<sup>2)</sup> Suppl. No. 14.

<sup>3)</sup> Arch. néerl. (2) 6, 874. 1901, Comm. No. 74.

percentage deviations of  $pv_A$  from  $pv_A$  (C) of the general mean reduced equation VII. 1.

| 1)          | O-C<br>in % | $d_A$   | O-C<br>in % | $d_A$   | O-C<br>in % | $d_A$   | O-C<br>in % | $d_A$   | O-C<br>in % | $d_A$   | O-C<br>in % | $d_A$ |
|-------------|-------------|---------|-------------|---------|-------------|---------|-------------|---------|-------------|---------|-------------|-------|
| 0°-39 C.    |             |         |             |         |             |         |             |         |             |         |             |       |
| 0° 00 C.    |             |         |             |         |             |         |             |         |             |         |             |       |
| -57° 72 C.  |             |         |             |         |             |         |             |         |             |         |             |       |
| -87° 05 C.  |             |         |             |         |             |         |             |         |             |         |             |       |
| -102° 51 C. |             |         |             |         |             |         |             |         |             |         |             |       |
| -109° 88 C. |             |         |             |         |             |         |             |         |             |         |             |       |
| 99          | 0.0         | 20.877  | 0.0         | 23.509  | +0.1        | 25.152  | +0.3        | 25.571  | +0.5        | 26.242  | +0.6        |       |
| 99          | 0.0         | 26.581  | -0.1        | [28.575 | -0.2]       | 34.467  | +0.1        | 35.077  | +0.4        | 34.807  | +0.8        |       |
| 90          | 0.0         | 32.302  | -0.1        | 33.793  | -0.2        | 55.822  | -0.1        | [47.893 | +0.9]       | 65.142  | +0.8        |       |
| 99          | 0.0         | 37.782  | -0.2        | 48.116  | -0.3        | 71.444  | -0.2        | [53.752 | +0.9]       | 87.176  | +0.8        |       |
| 99          | 0.0         | 51.840  | -0.5        | 64.948  | -0.4        | 94.625  | -0.7        | 62.240  | +0.4        | 102.76  | +0.5        |       |
| 90          | -0.1        | 65.325  | -0.7        | 90.695  | -0.9        | 119.84  | -1.0        | [69.954 | +0.9]       | 125.56  | +0.2        |       |
|             |             |         |             |         |             |         |             | 84.002  | +0.2        | 148.32  | -0.2        |       |
|             |             |         |             |         |             |         |             | 95.802  | 0.0         | 180.84  | -1.0        |       |
|             |             |         |             |         |             |         |             | 115.88  | -0.4        |         |             |       |
|             |             |         |             |         |             |         |             | 135.65  | -0.7        |         |             |       |
|             |             |         |             |         |             |         |             | 158.01  | -1.2        |         |             |       |
| 13° 80 C.   |             |         |             |         |             |         |             |         |             |         |             |       |
| -115° 86 C. |             |         |             |         |             |         |             |         |             |         |             |       |
| -116° 62 C. |             |         |             |         |             |         |             |         |             |         |             |       |
| -119° 20 C. |             |         |             |         |             |         |             |         |             |         |             |       |
| -120° 24 C. |             |         |             |         |             |         |             |         |             |         |             |       |
| -121° 21 C. |             |         |             |         |             |         |             |         |             |         |             |       |
| 78          | +1.0        | 69.947  | +1.1        | 26.480  | +0.9        | 26.871  | +1.0        | 72.627  | +1.7        | 27.326  | +1.1        |       |
| 89          | +1.0        | 91.308  | +1.2        | 34.939  | +0.8        | 34.965  | +1.2        | 82.816  | +2.0        | 35.283  | +1.3        |       |
| 8           | +0.7        | 108.02  | +0.9        | 68.630  | +1.2        | 70.314  | +1.4        | 99.246  | +2.0        | 71.459  | +1.8        |       |
| 7           | +0.5        | 131.51  | +0.6        | 90.563  | +1.2        | 70.481  | +1.0        | 118.51  | +1.8        | 85.580  | +2.0        |       |
| 1           | 0.0         | 155.12  | +0.1        | 110.19  | +0.9        | 83.257  | +1.1        | 136.31  | +1.7        | 100.33  | +1.8        |       |
| 0           | 0.0         | 179.94  | -0.5        | 133.69  | +0.7        | 96.834  | +1.5        | 165.79  | +0.9        | [123.85 | +1.9]       |       |
| 3           | -0.5        | [183.35 | +1.8]       | 159.71  | +0.2        | 98.863  | +1.0        | 206.57  | +0.1        | 148.95  | +1.6        |       |
| 2           | -0.7        | 235.47  | -1.7        | 161.75  | 0.0         | 124.97  | +0.6        | 280.25  | -0.7        | 170.05  | +0.9        |       |
| 9           | -1.1        | 319.52  | -2.9        | [186.15 | -0.4]       | [143.71 | +0.9]       | 338.95  | -0.5        | 234.13  | -0.2        |       |
|             |             |         |             | 210.02  | -0.9        | 156.36  | -0.1        |         |             | 333.75  | -0.1        |       |
|             |             |         |             | [260.61 | -2.0]       | [172.25 | +0.6]       |         |             |         |             |       |
|             |             |         |             | 331.29  | -2.8        | 222.69  | -1.8        |         |             |         |             |       |
|             |             |         |             |         |             | 275.02  | -2.8        |         |             |         |             |       |
|             |             |         |             |         |             | 336.89  | -3.4        |         |             |         |             |       |
| 30° 38 C.   |             |         |             |         |             |         |             |         |             |         |             |       |
| -139° 62 C. |             |         |             |         |             |         |             |         |             |         |             |       |
| -149° 60 C. |             |         |             |         |             |         |             |         |             |         |             |       |
| 94          | +1.7        | 28.122  | +2.4        | 29.183  | +3.8        |         |             |         |             |         |             |       |
| 83          | +1.2        | 35.573  | +2.9        | 34.646  | +4.4        |         |             |         |             |         |             |       |
| 26          | +2.0        |         |             |         |             |         |             |         |             |         |             |       |
| 07          | +2.9        |         |             |         |             |         |             |         |             |         |             |       |
| 25          | +3.2        |         |             |         |             |         |             |         |             |         |             |       |
| 21          | +4.2        |         |             |         |             |         |             |         |             |         |             |       |
| 1           | +3.3        |         |             |         |             |         |             |         |             |         |             |       |

$d_A$  means the density, expressed in terms of the normal density.

In these expressions  $A_{A_0} = \frac{1}{v_N}$  is the ratio of the experimental to the theoretical normal volume, and  $\gamma$  is the specific mass<sup>1)</sup> in grams per c.c. at normal temperature and pressure.

Values of  $\log \lambda v$  were marked off as abscissae, and as ordinates values of the common logarithms of the reduced temperatures. Lines parallel to the  $\log \lambda v$  axis represent the course of the equation VII. 1, while deviations are marked off from these lines, (positive above, negative below) in such a way that a 1 % deviation corresponds to 5 mm. on the accompanying diagram. We shall call this method of exhibiting the deviations in a diagram "arranging according to  $\log t$  the deviations expressed as functions of  $\log \lambda v$ ." From this drawing which, since it contains the deviations for the various substances at the different reduced temperatures (the observation temperatures of the isotherms), has been somewhat abridged, the deviations for each substance for successive values of  $\log \lambda v$  were now read off, and the values thus obtained were then graphed as functions of  $\log t$ , arranged according to  $\log \lambda v$ . By reading from the graphs thus deduced, the deviations for the various substances were brought to the same reduced temperature. For these reduced temperatures were chosen the temperatures of the argon isotherms, viz.

|          |           |                  |             |
|----------|-----------|------------------|-------------|
| 1.00816, | for argon | corresponding to | -121° 21 C. |
| 1.01460, | "         | "                | " -120° 24  |
| 1.02151, | "         | "                | " -119° 20  |
| 1.03863, | "         | "                | " -116° 62  |
| 1.04368, | "         | "                | " -115° 86  |
| 1.05735, | "         | "                | " -113° 80  |
| 1.08337, | "         | "                | " -109° 88  |
| 1.13229, | "         | "                | " -102° 51  |

And finally, the deviations were graphed as functions of  $\log \lambda v$ , and all reduced to the same temperatures. This diagram is reproduced on the Plate accompanying this Communication. The deviation curves for the reduced temperatures 1.01460 and

<sup>1)</sup> In all these considerations we may neglect the difference between the specific mass and the density (number of grams pro m. L.).

1.04368 could not be drawn on it, as in order to do this distinctly the scale would have to be made too great. The rectangle on the right hand lower portion of the diagram borders the immediate neighbourhood of the critical state. It is best, while employing this method of critically examining the deviations, to leave this region out of account provisionally, as otherwise one would have to allow for the influence of the disturbance function <sup>1)</sup>. A description of the information afforded by this plate concerning the deviations of the various substances seems to us unnecessary; it speaks for itself, and gives clear expression to the systematic deviations of argon from the other substances in this region.

§ 3. *Calculation of certain data which are of importance in the discussion of deviations from the law of corresponding states.*

To get an idea of deviations from the law of corresponding states, certain data are usually calculated, and we are now able to obtain their values for argon from our former experiments <sup>2)</sup>.

a. By substituting values of argon vapour pressures in the well known VAN DER WAALS vapour pressure equation <sup>3)</sup>:

$$\log \frac{p}{p_k} = f \frac{T - T_k}{T}$$

and using common logarithms we get the following values for  $f$ :

| $t$         | $p$ in atm. | $f$   |
|-------------|-------------|-------|
| -140°.80 C. | 22.185      | 2.415 |
| -134°.72 C. | 29.264      | 2.421 |
| -129°.83 C. | 35.846      | 2.457 |
| -125°.49 C. | 42.457      | 2.577 |

A cursory comparison of these values of  $f$  with those for other substances shows us that the value for argon is closer to

<sup>1)</sup> Comm. No. 104.

<sup>2)</sup> Comm. No. 115; Comm. No. 118a; Comm. No. 118b.

<sup>3)</sup> J. D. VAN DER WAALS, Cont. I. p. 158.

the theoretical value of  $f$  at the critical point deduced from VAN DER WAALS's equation (1.737) than the values belonging to by far the greater number of other substances; this is what one would expect for monatomic substances. For carbon dioxide between  $-63^\circ$  C. and the critical point  $f$  goes from 2.84 to 2.97 <sup>1)</sup>; for isopentane <sup>2)</sup> between  $130^\circ$  C. and the critical point  $f$  assumes a value between 2.75 and 2.95, while it further appears from the list published by KUENEN <sup>3)</sup>, that, with the exception of monatomic substances and a few others such as hydrogen, oxygen, and carbon monoxide, values of  $f$  are always still greater.

b. From the critical data already published, and from the weight in grams of one litre of argon at normal temperature and pressure which, according to RAMSAY and TRAVERS <sup>4)</sup> is 1.782, we found for the critical virial quotient

$$K_4 = \frac{RT_k}{p_k v_k} = 3.283.$$

This value is also closer to the theoretical value deduced from VAN DER WAALS's equation, 2.67, than those of almost all other substances, as is evident from the table of values given by KUENEN <sup>5)</sup>. Hence, D. BERTHELOT's <sup>6)</sup> estimate is probably much too low.

c. Let us write the equation of the rectilinear diameter of CAILLETET and MATHIAS <sup>7)</sup> in the form

$$\frac{\rho_{\text{liq}} + \rho_{\text{vap}}}{2} = \rho_k - \alpha (T_k - T),$$

in which  $\rho_{\text{liq}}$ ,  $\rho_{\text{vap}}$  and  $\rho_k$  are the liquid, vapour and critical

<sup>1)</sup> J. P. KUENEN, Die Zustandsgleichung, p. 101, supplemented by KEESOM's measurements, Comm. No. 88.

<sup>2)</sup> S. YOUNG l. c.

<sup>3)</sup> J. P. KUENEN, l. c. p. 142.

<sup>4)</sup> W. RAMSAY and M. W. TRAVERS, Proc. R. S. 67. 329. 1900.

<sup>5)</sup> J. P. KUENEN, Die Zustandsgleichung, p. 60.

<sup>6)</sup> D. BERTHELOT, Journ. de phys. (3) 10. 611. 1901.

<sup>7)</sup> L. CAILLETET and E. MATHIAS, Journ. d. phys. (2). 5. 549. 1886.

densities in terms of the density of water of 4° C. respectively and  $\alpha$  is the slope of the diameter; calling

$$a_M = -\alpha \frac{T_k}{\rho_k}$$

the reduced slope, we can, with the liquid densities published by Baly and DONNAN<sup>1)</sup> and the value of the critical density already published, deduce from the isotherms

$$\alpha = -0.003050$$

$$a_M = 0.9027.$$

The inclination of the diameter for argon is, therefore, unusually great — greater than has ever yet been found for any other substance since  $\alpha$  for most substances lies between  $-0.0005$  and  $-0.0023$ <sup>2)</sup>.

In connection with the foregoing, it is of interest to note that YOUNG<sup>3)</sup> discovered an intimate relationship for substances of higher critical temperature between the diameter's inclination and curvature and the values of the critical volume deduced from the law of the diameter. Representing the curved diameter by

$$d = a_d + b_d t + c_d t^2$$

in which

$$d = \frac{1}{2} \left( \frac{1}{v_{\text{liq}}} + \frac{1}{v_{\text{vap}}} \right),$$

then we obtain the following corresponding relations

$$\begin{aligned} -b_d < 0.93 & \quad K_{4d} < 3.77 & \quad c_d > 0 \\ -b_d = 0.93 & \quad K_{4d} = 3.77 & \quad c_d = 0 \\ -b_d > 0.93 & \quad K_{4d} > 3.77 & \quad c_d < 0. \end{aligned}$$

On a former occasion<sup>4)</sup> the diameter was considered to be straight for argon, and the assumption was then justified; we must, there-

<sup>1)</sup> E. C. C. Baly and F. G. DONNAN, Journ. chem. Soc. 81. 911. 1902.

<sup>2)</sup> E. MATHIAS, Le point critique des corps purs, p. 9 and 10.

<sup>3)</sup> S. YOUNG, Phil. Mag. (5). 50. 291. 1900.

<sup>4)</sup> Comm. No. 118a.

fore put  $c_d = 0$ . But we have just found a value for  $K_4$ , and, since  $K_4 = K_{4d}$ <sup>1)</sup> it follows that

$$K_{4d} = 3.283 \text{ and } -b_d = a_M = 0.9027.$$

From this we may conclude either that argon is an exception to YOUNG's rule, or, as is not impossible, that its diameter is somewhat curved, in which case it would belong to the first group given by YOUNG. An accurate experimental research upon the diameter for argon would probably lead to important results bearing not only upon this point, but also upon the question of the value of the critical density of argon.

For oxygen MATHIAS and KAMERLINGH ONNES<sup>2)</sup> found

$$-b_d = 0.813, \quad K_{4d} = 3.346. \quad c_d = 0.$$

It appears, therefore, as if values of  $K_{4d}$  in YOUNG's criterion become smaller and smaller the lower the critical temperature of the substance.

d. We can, in the meantime, say nothing definite about the function

$$\left( T \frac{\partial p}{\partial T} - p \right) v^2$$

investigated by REINGANUM<sup>3)</sup> and by VOGEL<sup>4)</sup>. An investigation of this point is, however, in progress.

<sup>1)</sup> The subscript  $d$  in  $K_{4d}$  is used to indicate the fact that the value of the critical volume with which this number is calculated has been obtained from the diameter. Although the value here given for the critical virial quotient has been obtained from a value of  $v_k$  calculated from the isotherms, we have, nevertheless, assumed that we may write  $K_4 = K_{4d}$ , seeing that probably the two values of  $v_k$  obtained by the two different methods differ but little from each other. (See Comm. No. 118a).

<sup>2)</sup> 1911. Comm. No. 117.

<sup>3)</sup> M. REINGANUM, Diss. Göttingen 1899. Ann. d. Phys. (4). 18. 1008. 1905. Phys. Ztschr. 11. 735. 1910

<sup>4)</sup> G. VOGEL, Diss. Freiburg (Baden) 1910, Ztschr. f. phys. Chem. 73 429. 1910.

..... Ramsay-Young  
- - - - -  $CO_2$  (Amagat)

