

Citation:

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Physics. — “*Isothermals of monatomic substances and their binary mixtures. XV. The vapour pressure of solid and liquid argon, from the critical point down to -206° .*” By C. A. CROMMELIN. (Communicated by Prof. H. KAMERLINGH ONNES). Comm. N^o. 138c from the physical Laboratory at Leiden.

§ 1. In this paper the completed results are given of all the observations that I have so far made concerning the vapour pressure

T A B L E I.					
Date	N ^o .	θ (Celsius in Kelvin degrees)	$p_{\text{coex.}}$ in int. atm.	$p_{\text{coex.}}$ in cm. merc.	
1910. 14 Febr.	X	— 122.44	47.996	3645.1	critical point
14 "	IX	— 122.49	47.890	3637.1	liquid—vapour
12 "	VIII	— 122.70	47.503	3607.7	
9 "	II	— 125.49	42.457	3224.5	
9 "	III en IV	— 129.83	35.846	2722.4	
10 "	V	— 134.72	29.264	2222.5	
10 "	VI	— 140.80	22.185	1684.9	
1912. 29 May	XI	— 150.57	13.707	1041.0	
24 "	XIa	— 161.23	7.4332	564.53	
16 Dec.	XII	— 183.01	1.3369	101.53	
16 "	XIII	— 184.25	1.1794	89.574	
16 "	XIV	— 185.42	1.0451	79.371	triple point
16 "	XV	— 185.90	0.99379	75.475	
17 "	XVI	— 186.98	0.88575	67.270	solid—vapour
17 "	XVII	— 189.30	0.67896	51.565	
18 "	XIX	— 191.36	0.51917	39.429	
18 "	XX	— 194.58	0.33051	25.101	
18 "	XXI	— 197.62	0.21526	16.348	
18 "	XXII	— 206.04	0.088443	6.717	

For the boiling-point of argon under atmospheric pressure, by linear interpolation between observations XIV and XV we find:

$$\theta = -185.84.$$

of solid and liquid argon, besides some results which may be deduced from these observations.

The experimental material now at our disposal is put together in table I. (see p. 487).

The determinations in Febr. 1910 have already been published¹⁾, and are only included here to facilitate the complete survey of all the vapour pressure determinations, and because we shall need them in the following discussion of the results.

The observations in May 1912 were made on the occasion of the determinations of the straight diameter²⁾; as regards the apparatus we can therefore refer to the papers concerning this. We need only remark that the pressure determinations were made with an open standard manometer³⁾.

The measurements in Dec. 1912 were made with the apparatus already described⁴⁾ for the determination of vapour pressure at low pressures, which on this occasion also proved highly satisfactory.

As regards this last series of measurements we make the following remarks. Before we proceeded to a measurement we waited until the constancy of the pressure showed that the equilibrium between the phases was established. During this period the temperature was of course kept as carefully as possible constant. The measurement then consisted in reading the manometer and barometer several times alternately. As a rule the pressure in the apparatus remained almost completely constant during a measurement.

The values given for the temperature of the bath of liquid oxygen, boiling under atmospheric and under reduced pressure, in which these measurements were made, were based upon a new comparison of the standard platinum resistance thermometer P_{11} with the hydrogen and the helium thermometers, shortly to be published by KAMERLINGH ONNES and HOLST. This gives results that differ slightly from the former calibration⁵⁾ but for none of the temperatures are they more than 0.05 and they are of a completely systematic character. The cause of this difference is not yet clear. A direct determination of the difference between the boiling point of argon and of oxygen will throw more light upon it.

¹⁾ C. A. CROMMELIN, Proceedings May 1910, Comm. No. 115, and Thesis Leiden, 1910.

²⁾ E. MATHIAS, H. KAMERLINGH ONNES and C. A. CROMMELIN, Proceedings Oct. 1912, Comm. No. 131a.

³⁾ H. KAMERLINGH ONNES, Proceedings Nov. 1898, Comm. No. 44.

⁴⁾ H. KAMERLINGH ONNES and C. BRAAK, Proceedings Oct. 1908, Comm. No. 107a.

⁵⁾ H. KAMERLINGH ONNES and J. CLAY, Proceedings Sept. 1906, Comm. No. 95c and H. KAMERLINGH ONNES, C. BRAAK and J. CLAY, Proceedings Dec. 1907, Comm. No. 101a.

My thanks are due to Mr. G. HOIST, assistant at the Physical Laboratory, for making these temperature determinations, and for the calculations of the temperatures.

The determination of the triple point was made difficult by the undercooling phenomena which constantly appeared. If, while the temperature was just above the triple point, the temperature was slowly allowed to fall, it repeatedly happened that the whole mass of liquid argon crystallized out. By allowing the temperature to rise and fall with extreme slowness, and waiting patiently for the establishment of the equilibrium, I at last succeeded in establishing a temperature at which the three phases remained in equilibrium with each other for nearly two hours. During this period, the triple point was determined with an admirably constant pressure and temperature. This also gave me an opportunity of observing that the piece of solid argon sank in the liquid, and remained lying at the bottom of the tube, so that *in the triple point the density of solid argon is greater than that of liquid argon*. We shall presently be able to make use of this observation, although I had no opportunity to make a quantitative determination of the density of solid argon. Concerning the calculation of the observation there is nothing particular to remark. An atmosphere in Leiden is reckoned at 75.9488 cm. mercury.

2. Representation of the observations by formulae.

In order to get a useful representation of the observations by a formula, I first made use of RANKINE and BOSE's formula

$$\log p_{\text{KOEX}} = a_{\text{RB}} + b_{\text{RB}} T^{-1} + c_{\text{RB}} T^{-2} + d_{\text{RB}} T^{-3}$$

for the field of liquid-vapour as well as for that of solid-vapour. The result of the testing of the values of the pressure calculated from these formulae by the values observed, are found in table II.

As can be seen in the table, the correspondence is fairly satisfactory, especially in the part liquid-vapour, while it might be further improved for instance by the application of the method of least squares.

In the second place I have tried to apply to my observations NERNST's¹⁾ vapour pressure formula. We may regard it as a purely empirical formula with 4 coefficients, written in the form

$$\log p = \frac{A}{T} + BT + D \log T + C$$

and then calculate the coefficients which correspond best to the observations, without troubling about the theoretical significance of

¹⁾ W. NERNST, Göttinger Nachr. 1906, p. 1.

the coefficients. The result of a calculation of this kind is found in table III. The correspondence is considerably better than with RANKINE and BOSE's formula.

In the field of liquid-vapour the correspondence is less good, so that we have omitted the calculation of the results.

TABLE II.				
Liquid-vapour. $a_{RB} = +4.85033$. $b_{RB} = -634.391$. $c_{RB} = +30769.09$. $d_{RB} = -1076464$.				
θ	$p_{\text{koex. (O)}}$	$p_{\text{koex. (C)}}$	O-C abs.	O-C in %
-122.44	47.996	67.886	+ 0.110	+ 0.23
122.49	47.890	47.797	+ 0.093	+ 0.19
122.70	47.503	47.422	+ 0.081	+ 0.17
125.49	42.457	42.646	- 0.189	- 0.45
129.83	35.846	35.908	- 0.062	- 0.17
134.72	29.264	29.264	0.000	0.00
140.80	22.185	22.289	- 0.104	- 0.47
150.57	13.707	13.707	0.000	0.00
161.23	7.4332	7.3961	+ 0.0371	+ 0.50
183.01	1.3369	1.3397	- 0.0028	- 0.21
184.25	1.1794	1.1825	- 0.0031	- 0.26
185.42	1.0451	1.0470	- 0.0019	- 0.18
185.90	0.99379	0.99492	- 0.00113	- 0.11
186.98	0.88575	0.88473	+ 0.00102	+ 0.12
189.30	0.67896	0.67896	0.00000	0.00
Solid-vapour. $a_{RB} = +8.48993$ $b_{RB} = -849.4767$. $c_{RB} = -4204.71$. $d_{RB} = +122.3163$.				
- 189.30	0.67896	0.68126	- 0.00230	- 0.34
191.36	0.51917	0.51105	+ 0.00812	+ 1.56
194.58	0.33051	0.32861	+ 0.00190	+ 0.58
197.62	0.21526	0.22016	- 0.00490	- 2.28
206.04	0.088443	0.088028	+ 0.000415	+ 0.45

For practical use in the field of liquid-vapour therefore in our case, RANKINE-BOSE'S formula is preferable to NERNST'S. At the same

TABLE III. Solid—vapour.			
$A = + 9034.32. B = - 1.42112. C = - 1014.0278.$			
$D = + 533.0275.$			
θ	$p(O)$	$p(C)$	$O-C$ in %
-189.30	0.67896	0.67764	+0.19
191.36	0.51017	0.51809	+0.21
194.58	0.33051	0.33197	-0.45
197.62	0.21526	0.21526	0.00
206.04	0.088443	0.087942	+0.57

time the following calculation will show that NERNST'S formula, also in the field of liquid-vapour is capable of representing the observations as far as the critical point in a fairly satisfactory way, and in many cases, where the accuracy required is not so very great, may be a convenient help in calculation. I wrote the formula in the more usual form

$$\log p = - \frac{\lambda}{4.571 \cdot T} + 1.75 \log T - \frac{\varepsilon}{4.571} T + C$$

and took for the chemical constant C in accordance with SACKUR¹⁾ the value 0.35, so that there now only remain two constants that are to be determined by the observations. With the value of the constants

$$\lambda = + 1385 \quad \text{and} \quad \varepsilon = + 0.01446$$

we get a fairly good correspondence from the critical point down to the triplepoint, in which the deviations in p are all less than 2%.

Finally I have tried to calculate all the terms of the formula, which SACKUR deduces from the heat theorem of NERNST, from the available calorimetric data, as SACKUR has done for some vapour pressure determinations by RAMSAY and TRAVERS²⁾.

SACKUR writes the vapour pressure formula in the following form

¹⁾ O. SACKUR, Ann. d. Physik (4) 40 (1913) p. 80.

²⁾ W. RAMSAY and M. W. TRAVERS, Phil. Trans. (A) 197 (1901) p. 47.

$$\log p = -\frac{\lambda}{2.3 RT} + \frac{c_p}{R} \log T - \frac{1}{2.3} \int_0^T \frac{c}{T} dT + C + \frac{c_p}{2.3 R}$$

in which λ means the heat of evaporation at the temperature T , c the specific heat of liquid or solid, c_p the specific heat of the vapour and R the gas constant (all for a grammolecule of the substance).

I have only made calculations from this formula for the field of solid-vapour. The reason for this will be seen presently.

The measurements of DITTENBERGER²⁾ and PIER³⁾ both give the value of 4.91 for the molecular specific heat at constant pressure, of gaseous argon at higher temperatures. As in many cases it has been shown that this quantity is conspicuously independent of the temperature, we shall make use of it also for low temperatures.

For R we assume the value 1.985.

Concerning the value of c nothing is known experimentally. In order to arrive at a rational estimation, in spite of this, of the integral

$\int_0^T \frac{c}{T} dT$ I calculated the frequency ν from LINDEMANN'S⁴⁾ formula.

$$\nu = 2.80 \times 10^{13} \sqrt{\frac{T_0}{Mv_0^{2/3}}}$$

(in which the index 0 refers to the melting point) and then values for c at the various temperatures by the formulae of NERNST-LINDEMANN⁵⁾ and of DEBIJE⁶⁾. In the field of temperature with which we have to deal, it makes no difference which of the two formulae we use⁷⁾.

Finally the values of the integral were determined by the graphic method.

Naturally these calculations could only be made for solid argon, as NERNST-LINDEMANN'S and DEBIJE'S formulae only apply to solid substances.

¹⁾ l. c. p. 80.

²⁾ W. DITTENBERGER, In. Diss. Halle 1897.

³⁾ M. PIER, Zeitschr. f. Electrochemie 15 (1909) p. 536.

⁴⁾ F. A. LINDEMANN, Physik. Zeitschr. 11 (1910) p. 609 and W. NERNST and F. A. LINDEMANN, Berl. Sitz. Ber. 1911 p. 494.

⁵⁾ l. c.

⁶⁾ P. DEBIJE, Ann. der Physik. (4) 39 (1912) p. 789.

⁷⁾ Tables for the calculation of c are published: for the formula of NERNST-LINDEMANN by F. POLLITZER, Die Berechnung chemischer Affinitäten nach dem NERNST'schen Wärmetheorem, Enke, Stuttgart, 1912, p. 162 sqq; for the formula of DEBIJE by W. NERNST, Berl. Sitz. Ber. 1912 p. 1172.

If we take the value 1630 for the molecular heat of evaporation for all the temperatures in the field considered, a value which is chosen with a view to obtaining the best correspondence, and which is not contrary to an extrapolation of the values of λ for the liquid given below then we find the following.

TABLE IV.			
θ	$p(O)$	$p(C)$	O-C in % of O
- 189.30	0.6790	0.6433	+ 5.3
191.36	0.5192	0.5050	+ 2.7
194.58	0.3305	0.3385	- 2.4
197.62	0.2153	0.2351	- 9.2
206.04	0.0884	0.0617	+30.0

The correspondence obtained in this way, may be considered on the whole satisfactory.

I have to thank Mr. W. H. KEESOM for many useful suggestions in connection with these calculations.

§ 3. The triple point.

The triple point constants as observed are given in Table I. Calculation showed that the break of the two curves in argon is in the usual direction. In order to determine the values of $\left(\frac{dp}{dT}\right)_{\text{coex vap liq}}$ and $\left(\frac{dp}{dT}\right)_{\text{coex vap sol}}$ at the triple point as sharply as possible, I calculated for the triple point and for the two points lying immediately above and below it, the constants in the formula of WREDE-RANKINE-KEESOM $\log p_{\text{coex}} = a_{\text{RK}} + b_{\text{RK}} T^{-1} + c_{\text{RK}} T^{-2}$ and by differentiation of this formula, the values of the differential coefficients.

In this way I found

$$\left(\frac{dp}{dT}\right)_{\text{coex vap liq}} = 0.08162; \left(\frac{dp}{dT}\right)_{\text{coex vap sol}} = 0.08623.$$

As may be seen from these values there is a break in the usual direction although very slight.

From the observation already mentioned, that in the triple point

the density of solid argon is greater than that of liquid argon, we may conclude, upon the ground of the general thermodynamical rules¹⁾, about the triple point, that the melting curve from the triple point and in the immediate neighbourhood of it will run in the direction of the higher temperatures and pressures.

4. Calculation of the heat of evaporation at different temperatures.

As the density of the liquid and of the saturated vapour is known along by far the greater part of the vapour pressure curve²⁾, we were able to calculate the heat of evaporation for a number of temperatures by the well known equation of CLAPEYRON-CLAUSIUS:

$$\lambda_{\text{liq. vap}} = T \left(\frac{dp}{dT} \right)_{\text{coex.}} (v_{\text{vap.}} - v_{\text{liq.}})$$

For the simplification of the calculations those temperatures were chosen at which the vapour pressure determinations were made. The derivation of the liquid and vapour densities to these temperatures was made by the aid of the formulae that KEESOM³⁾ has given for the curve of these densities. They are

$$\begin{aligned} \rho_{\text{liq}} &= \rho_k \{1 + A(1-t) + B(1-t)^2\} \\ \rho_{\text{vap}} &= \rho_k \{1 + A(1-t) - B(1-t)^2\}. \end{aligned}$$

With the constants

$$A = + 0.744537; B = + 1.76408; \lambda = 0.341571$$

and the critical density $\rho_{\text{crit}} = 0.53078$ ³⁾ they give a very satisfactory correspondence with the observations, except for the vapour densities at the lowest temperatures, where the percentual deviations become very large. As, however, at these temperatures the vapour densities can be calculated by the ordinary gaslaws, this gives no difficulty.

The values of $\left(\frac{dp}{dT} \right)_{\text{coex.}}$ were calculated by the formula of RANKINE-BOSE already mentioned.

All quantities were expressed in *C. G. S.* units, and then the whole expression for the heat of evaporation divided by the mechanical equivalent, in order to get the result in calories per degree. The results are shown in table III.

¹⁾ Cf. H. W. BAKHUIS ROOZEBOOM, Die heterogenen Gleichgewichte, erstes Heft, p. 94.

²⁾ E. MATHIAS, H. KAMERLINGH ONNES and C. A. CROMMELIN, Proceedings Oct. and Dec. 1912 and Jan. 1913. Comm. No. 131a.

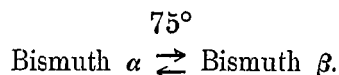
³⁾ W. H. KEESOM, Proceedings April 1902. Comm. No. 79. See also J. E. VERSCHAFFELT, Zittingsversl. June 1896, Comm. No. 25 and Proceedings April 1900, Comm. No. 55.

TABLE V. Heat of evaporation of argon.			
θ	$q_{\text{Fvap.}}$	$q_{\text{Flq.}}$	$\lambda_{\text{liq. vap. in cal.}}$
— 125.49	0.28727	0.78303	12.916
— 129.83	0.21451	0.88342	17.821
— 134.72	0.16621	0.96258	21.014
— 140.80	0.12115	1.04134	24.105
— 150.57	0.06854	1.13680	29.672
— 161.23	0.03723	1.22414	33.005
— 183.06	0.00814	1.37338	35.001

In conclusion I offer my hearty thanks to Prof. KAMERLINGH ONNES for the interest which he has taken in my work.

Chemistry. — “*The Allotropy of Cadmium.*” I. By Prof. ERNST COHEN and W. D. HELDERMAN.

1. In a paper which will be published in the *Zeitschrift für physik. Chemie* one of us (C.) proved in collaboration with Mr. A. L. TH. MOESVELD, that bismuth is capable of existing in more than one allotropic modification and that there is a transition temperature at 75° of the enantiotropic transformation



In that paper we mention that we had found in a publication of MATTHIESSEN and VON BOSE¹⁾ (on the electric conductivity of metals, published in 1862) certain indications which justified the presumption that other metals which till now are only known in one modification would show the same behaviour as bismuth (and tin). The following clauses may be quoted from MATTHIESSEN and VON BOSE's paper as referring specially to the metal cadmium:

“Die nach mehrtägigem Erhitzen auf 100° erhaltenen Veränderungen in der Leitungsfähigkeit der Drahte, sind unglücklicher Weise verloren gegangen. Es mag bemerkt werden, dass die Veränderungen sehr gering waren und dass eine Abnahme in der

¹⁾ POGGENDORFF's Ann. **115**, 353 (1862).