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Physics. — “On the Fundamental Values of the Quantities b and \sqrt{a} for Different Elements, in Connection with the Periodic System. III. Discussion of the Different Groups of Elements Separately.” By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of May 27, 1916).

1. In the preceding Paper¹⁾ in § 3 we saw that b_k can be obtained from the liquid volume v_1 (at such a low temperature that the vapour density may be neglected) through the formula

$$b_k = v_1 \times 2\gamma \left[1 - \frac{\gamma}{1 + \gamma} m_1 \right], \quad \dots \dots (1)$$

in which γ represents the (reduced) coefficient of direction of the straight diameter between D_1 and D_k in a D, T -diagram, and m_1 is the reduced (absolute) temperature $T_1 : T_k$.

We might even continue to use this formula, when v_1 represents the volume in *solid* state — when namely the law of the variability of v with T does not deviate too much from that holding for the liquid state. But in case v_1 is only known for the solid state, we can also first reduce v_1 to the value of v at the triple point (by means of the experimentally determined formulae for the expansivity), and then apply the above formula (1) starting from that point.

A great difficulty is experienced for elements the melting point of which lies very high, and for which the value of γ is perfectly unknown; besides — when also that of v at the melting point is unknown — the value of γ can in many cases no longer be calculated from the empiric formulae of expansion in the solid state, seeing that mostly these are only valid for temperatures far below the melting point. In such cases there is often nothing left but to apply formula (1) as a first approximation also to the solid state, and determine the value of γ from other data. In many cases the formula (valid for the liquid state)

$$2\gamma = 1 + 0,038 \sqrt{T_k} \quad \dots \dots (2)$$

can be used for it, which formula was lately derived by me²⁾. It will be remembered that 2γ is also $= b_k : b_0$, and therefore expresses the degree of the variability of b .

¹⁾ Denoted by II in what follows; cf. These Proc. of March 25, 1916. Paper I appeared in These Proc. of Jan. 29, 1916.

Cf. also Journal de Chimie physique, T. 14, N^o. 1 (March 31, 1916).

²⁾ Cf. the series of papers, cited by me already in I (Footnote 3) on p. 1221, particularly the 3^d paper of May 29, 1914, p. 1051.

It is to be expected that probably the value of $b_1 : v_1$ at the *triple point* will possess the same value for certain groups of elements. *That in other words the solid state then occurs when the molecular volume shall have become a definite fraction of the total volume.*

To investigate this we shall determine the general value of $b_1 : v_1$ from the equation of state (when, namely, at the triple point p can be neglected)

$$\frac{a_1}{v_1^2} (v_1 - b_1) = RT_1,$$

from which follows:

$$\frac{v_1 - b_1}{v_1^2} = \frac{RT_1}{a_1} \cdot \frac{a_k}{a_1}.$$

Now $RT_k = \frac{8}{27} \lambda \frac{a_k}{b_k}$, in which λ lies between 1 and $27/28$ (for substances with high critical temperature). For most substances with which we shall occupy ourselves in what follows, we may put $RT_k = \frac{2}{7} \frac{a_k}{b_k}$, hence $a_k = 7 RT_k \cdot b_k$. In consequence we get:

$$\frac{v_1 - b_1}{v_1^2} = \frac{2 a_k m_1}{7 a_1 b_k} = \varphi \frac{m_1}{b_k},$$

in which (a_k and a_1 not differing much) the factor φ will never be far from $2/7$. Hence we find:

$$\frac{v_1 - b_1}{v_1} = \varphi \frac{v_1}{b_k} m_1.$$

If therefore $b_1 : v_1$ or $(v_1 - b_1) : v_1$ has a constant value, also the value of $v_1 : b_k \times m_1$ must be constant. In this $b_k : v_1$ is the factor of the above formula (1), which we shall call f_1 , so that

$$f_1 = 2\gamma \left[1 - \frac{\gamma}{1 + \gamma} m_1 \right] \dots \dots \dots (a)$$

Hence

$$\frac{v_1 - b_1}{v_1} = \varphi \frac{m_1}{f_1} \dots \dots \dots (3)$$

If e.g. $f_1 : m_1 = 6$, then $(v_1 - b_1) : v_1 = 2/7 \times 1/6 = 1/21$, so that then the solid state would occur, when the free (available) space between the molecules has become $1/21$ of the total volume.

If instead of $m_1 = T_1 : T_k$ the reciprocal quantity $\mu_1 = T_k : T_1$ is introduced, then becomes:

$$\frac{v_1 - b_1}{v_1} = \frac{\varphi}{f_1 \mu_1} \dots \dots \dots (3a)$$

in which:

$$f_1 = 2\gamma \left[1 - \frac{\gamma}{1+\gamma} \frac{1}{\mu_1} \right], \dots \dots \dots (\beta)$$

hence

$$f_1 \mu_1 = 2\gamma \left[\mu_1 - \frac{\gamma}{1+\gamma} \right] \dots \dots \dots (\gamma)$$

For the verification of the possible constancy of the ratio $(v_1 - b_1) : v_1$ at the *triple point* we shall try to determine in what follows the value of $f_1 \times \mu_1$ for every group of homologous elements. It will then appear at the same time what law the ratio $\bar{\mu} = T_k : T_1$ obeys, about which ratio we now only know that it can vary between $5^{1/3}$ and $1^{1/3}$.

Let us now proceed to examine the different groups of the periodic system separately.

II. The Hydrogen-Helium group.

a. Hydrogen.

If d_1' may be neglected at the triple point, it follows from $\frac{1}{2} d_1 = 1 + \gamma(1 - m_1)$, as $d_1 = D_1 : D_k$, that:

$$2\gamma = \frac{d_1 - 2}{1 - m_1} = \frac{T_k}{D_k} \cdot \frac{D_1 - 2D_k}{T_k - T_1}$$

With $T_k = 31,95$, $D_k = 0,03025$, $T_1 = 13,95$, $D_1 = 0,07709$ we find:

$$2\gamma = 1056 \times \frac{0,01659}{18,0} = 0,9734, \text{ accordingly } \gamma = 0,487,$$

so that we have according to (a) with $m_1 = 0,437$:

$$f_1 = 0,973 \left[1 - \frac{0,487}{1,487} \times 0,437 \right] = 0,973 (1 - 0,143) = 0,834.$$

As v_1 (expressed in normal units) is $= 58,3 \times 10^{-5}$ according to the subjoined table A, it would follow from this that $b_k = 58,3 \times 10^{-5} \times 0,834 = 48,7 \times 10^{-5}$.

The value $48,5 \times 10^{-5}$ has been found directly from T_k and p_k (see I).

We find 2,29 for $\mu_1 = T_k : T_1$, hence we have here:

$$f_1 \times \mu_1 = 0,834 \times 2,29 = 1,91.$$

b. Helium.

As the value of γ cannot be calculated here yet with certainty from the few data concerning d_1 and d_2 (from them a theoretically impossible value of γ would namely follow, much smaller than 0,5), I have calculated the theoretical value from (2). We find $2\gamma = 1 + 0,038 \sqrt{5,2} = 1 + 0,038 \times 2,28 = 1,0866$, hence $\gamma = 0,543$.

19,

[For H_2 we should have found $2\gamma = 1,2148$, $\gamma = 0,607$ by means of this formula, with $\sqrt{31,95} = 5,65$. With $D_1 = 0,07709$ ($v_1 = 58,3 \times 10^{-5}$) this value would, however, have yielded much too high a value for b_k].

For He with $m = 1,48 : 5,20 = 0,285$ ($T = 1,48$ lies above the triple point temperature, but is the lowest temperature at which a density determination has as yet been made) we get:

$$f = 1,087 \left[1 - \frac{0,543}{1,543} \times 0,285 \right] = 1,087 (1 - 0,100) = 0,978.$$

As $v = 122,1 \times 10^{-5}$ is found from $D = 0,146$, we find the value 119×10^{-5} for b_k , 105×10^{-5} having been found directly from T_k and p_k . Hence the given value of D at $1^\circ,48$ (absolute) is probably somewhat too low.

If we calculate the value of f_1 , which would correspond with the probable triple point ($\pm 1^\circ$ absolute), we find with $m_1 = 0,192$:

$$f_1 = 1,087 [1 - 0,352 \times 0,192] = 1,087 (1 - 0,0677) = 1,013.$$

As $\mu_1 = 5,20$, we find for He (approximately):

$$f_1 \times \mu_1 = 1,013 \times 5,20 = 5,27.$$

c. Neon.

We again calculate the coefficient of direction of the straight diameter from formula (2), giving with $\sqrt{45} = 6,708$ for 2γ the value $1,2549$, hence $\gamma = 0,627$.

We then find for f_1 with $m_1 = 24,42 : 45 = 0,543$:

$$f_1 = 1,255 \left[1 - \frac{0,627}{1,627} \times 0,543 \right] = 1,255 (1 - 0,209) = 0,992$$

For b_k (from $D_1 = 1,251$, $v_1 = 72,1 \times 10^{-5}$) this gives the value $71,5 \times 10^{-5}$, 71×10^{-5} being found directly from T_k and p_k .

For μ_1 we find $1,84$, so that we get for $f_1 \times \mu_1$:

$$f_1 \times \mu_1 = 0,992 \times 1,84 = 1,83.$$

d. Argon.

Experimentally $\gamma = 0,745$ has been found (formula (2) would have yielded $2\gamma = 1,4663$, $\gamma = 0,733$ with $\sqrt{150,65} = 12,27$), so that we find with $m_1 = 83,79 : 150,65 = 0,556$:

$$f_1 = 1,490 \left[1 - \frac{0,745}{1,745} \times 0,556 \right] = 1,49 (1 - 0,237) = 1,136.$$

The density at the triple point is $1,413$, from which follows $v_1 = 126,1 \times 10^{-5}$. Hence $b_k = v_1 \times f_1$ becomes $= 143 \times 10^{-5}$. (Directly from T_k and p_k was found 144×10^{-5}).

Further is

$$f_1 \times \mu_1 = 1,136 \times 1,80 = 2,04.$$

e. Krypton.

Formula (2) yields with $\sqrt{210,6} = 14,51$ the value $2\gamma = 1,5514$, $\gamma = 0,776$, giving:

$$f_1 = 1,551 \left[1 - \frac{0,776}{1,776} \times 0,494 \right] = 1,551 (1 - 0,216) = 1,216,$$

as $m_1 = 104,1 : 210,6 = 0,494$.

Now RAMSAY and TRAVERS¹⁾ give the density 2,155 for 127°,1 abs. ($m = 0,6035$). The factor f corresponding with this temperature is

$$f = 1,551 (1 - 0,437 \times 0,6035) = 1,551 (1 - 0,264) = 1,142.$$

With $D = 2,155$ corresponds $v = 171,7 \times 10^{-5}$, so that b_k would become $= 196 \times 10^{-5}$, while 177×10^{-5} was found directly from T_k and p_k . The given density is therefore too small.

We find for the product $f_1 \times \mu_1$:

$$f_1 \times \mu_1 = 1,216 \times 2,02 = 2,46.$$

f. Xenon.

From the experiments of PATTERSON, CRIPPS and WHYTLAW GRAY (1912) follows $\gamma = 0,780$, while from (2) is calculated $2\gamma = 1,6468$, $\gamma = 0,823$, as $\sqrt{289,7} = 17,02$.

With $\gamma = 0,780$ we find from $\frac{1}{2} d_1 = 1 + \gamma(1 - m_1)$, in which $m_1 = 133,1 : 289,7 = 0,459$, for d_1 the value 2,843. Hence the value²⁾ 3,281 is found for D_1 with $D_k = 1,154$, hence $v_1 = 177,1 \times 10^{-5}$.

Now

$$f_1 = 1,560 \left[1 - \frac{0,78}{1,78} \times 0,459 \right] = 1,560 (1 - 0,201) = 1,246.$$

Hence b_k becomes $= 221 \times 10^{-5}$, while the value 228×10^{-5} has been directly found from T_k and p_k .

We have further:

$$f_1 \times \mu_1 = 1,246 \times 2,18 = 2,71.$$

g. Niton (Radium-emanation).

We can again calculate the value of γ from $\sqrt{T_k} = \sqrt{377,6} = 19,43$, which gives $2\gamma = 1,738$, $\gamma = 0,869$. For the boiling point, where $D = 1 : 0,2281 = 4,384$, hence $v = 226,3 \times 10^{-5}$ has been found by RUDOLF (1910) (all the other recorded values

¹⁾ Zeitschr. f. physik. Ch. 38, 674 (1901).

²⁾ Some time ago RAMSAY and TRAVERS (loc. cit.) found $D = 3,52$ at 171°,1 abs. As for the boiling point (166°,2 abs.) the liquid density was found only $= 3,06$ by P., C., W.G., D must be found somewhat smaller than 3,06 for 171°,1. In his interesting study on the periodic system (Zeitschr. für physik. Ch. 76, 577 (1911)) BAUR is very near the truth, when he surmises that the much too high value 3,52 must be replaced by about 3,07.

TABLE A.
The Hydrogen-Helium Group.

	A	$\frac{A}{N}$	D_1	$\frac{A}{D_1}$	$v_1 = \text{id.}$ 22412	γ	γ'	m_1	f_1	$b_k \cdot 10^5$ calculated	$b_k \cdot 10^5$ found	$\sqrt{a_k} \cdot 10^2$ id.
1 H ₂	1,008	1,01	0,07709 (K. O., Cr)	13,07	58,3 · 10 ⁻⁵	0,487	0,607	0,437	0,834	48,7	48,5	3,2 (1,6)
2 He	3,994	2,00	0,146 (K. O.) ¹⁾	27,36	122,1	—	0,543	0,192	1,013	119	105	0,8
10 Ne	20,200	2,02	1,251 (Cr.)	16,15	72,1	—	0,627	0,543	0,992	71,5	71	2,7
18 Ar	39,945	2,22	1,413 (K. O., Cr.)	28,27	126,1	0,745	0,733	0,556	1,136	143	144	5,2
36 Kr	82,92	2,30	2,155 (R., Tr) ²⁾	38,48	171,7	—	0,776	0,494	1,216	196	177	6,9
54 X	130,22	2,41	3,281 (P, Cr, W.G.)	39,69	177,1	0,780	0,823	0,459	1,246	221	228	9,1
86 Ni (Eman.)	222,4	2,59	4,384 (RUDORF) ³⁾	50,73	226,3	—	0,869	0,535	1,305	291	277	11,5

¹⁾ For 1°48 abs.

²⁾ For 127°1 abs. RUDORF (Das periodische System, 1904) gives the somewhat higher value 2,185 (p. 317).

³⁾ For 211°1 abs.

have been found by RAMSAY and GRAY, Z. f. ph. Ch. **70**, p. 121) this yields the equation.

$$f = 1,738 \left[1 - \frac{0,869}{1,869} \times 0,559 \right] = 1,738 (1 - 0,260) = 1,286.$$

For T_s we have namely $m = 211,1 \quad 377,6 = 0,559$. We therefore calculate $b_k = 291 \times 10^{-5}$, whereas $b_k = 277 \times 10^{-5}$ is directly found from T_k and p_k ¹⁾.

At the triple point $m_1 = 202,1 \quad 377,6 = 0,535$, through which f_1 becomes $= 1,738 (1 - 0,249) = 1,305$, and further:

$$f_1 \times \mu_1 = 1,305 \times 1,87 = 2,44.$$

If we summarize the values found and used in what precedes in the Hydrogen-Helium group, we get the following survey. (See Table A p. 292).

The value N placed on the lefthand of the sign for the element denotes the value of the "core charge", in connection with the frequencies of the so-called high frequency spectra of the elements (MOSELEY). N is also sometimes called the *atom number* of the elements concerned. We shall later on make a few more remarks on the ratio A (atomic weight): N .

The coefficients of direction γ refer to the values of D and D' determined experimentally, the quantities γ' have been calculated from formula (2).

We subjoin the values T_h, T_s, T_k etc. used, and also the above determined products $f_1 \times \mu_1$, which are a measure for the ratio $(v_1 - b_1) : v_1$ at the triple point.

¹⁾ From $b_k = RT_k \cdot 8p_k$ we, namely, calculate with $p_k = 62,43$ atm. $b_k = 276,8 \times 10^{-5}$. And from $a_k = RT_k \times b_k \times (27 : 8\lambda)$ we find further ($\lambda = 0,98$) $b_k = 131,8 \times 10^{-4}$, hence $\sqrt{a_k} = 11,5 \times 10^{-2}$. In the 5th series of the periodic system a value for b_k is expected somewhat greater than 275×10^{-5} , which would be valid for Supra-iodine (277×10^{-5} satisfies this demand), and for $\sqrt{a_k}$ a value $= \pm 11 \times 10^{-2}$, as was found among others for Hg (see I and II). Also this last expectation is again very nearly fulfilled.

We point out here, that when for *Neon* not the critical temperature estimated last by K. ONNES, viz. $\pm 45^\circ$ abs., but the somewhat higher value found before by K. O. and CROMMELIN (1911), viz. some degrees below 55° abs. — or the value found by RANKINE also in 1911, viz. $61^\circ,1$ abs., or the value found by RAMSAY and TRAVERS in 1900, viz. $< 68,1$ is taken, we find somewhat higher values for a_k and b_k than the before given values $b_k = 71 \times 10^{-5}$, $\sqrt{a_k} = 2,0 \times 10^{-2}$. If we assume $T_k = 60^\circ$ abs., $p_k = 29$ atm., then with $\lambda = 0,998$ b_k becomes $= 94,7 \times 10^{-5}$, $a_k = 7,035 \times 10^{-4}$, $\sqrt{a_k} = 2,65 \times 10^{-2}$. This latter value for $\sqrt{a_k}$ fits in already a good deal better with the system drawn up by us than the too low value 2,0, where a value 3 or slightly smaller than 3 was expected. With $T_k = 65^\circ$ abs. we should have found $b_k = 102,6 \times 10^{-5}$, $\sqrt{a_k} = 2,9 \times 10^{-2}$, which would be still more satisfactory.

	T_{tr}	T_S	T_k	p_k	D_k	$\frac{T_k}{T_S}$	$\mu_1 = \frac{T_k}{T_{tr}}$	$f_1 \times \mu_1$	Authors
H ₂	13,95	20,33	31,95	15,0	0,03025	1,57	2,29	1,91	K.O., Km., Dew.
He	±1	4,20	5,20	>2,26	0,066	1,24	5,20	5,27	K.O.
Ne	24,42	27,17	45?	29	—	1,66	1,84	1,83	K.O.; Cr.
Ar	83,79	87,25	150,65	48,0	0,531	1,73	1,80	2,04	Cr.; M., K.O., Cr.
Kr	104,1	121,4	210,6	54,3	—	1,73	2,02	2,46	R.; R., Tr.
X	133,1	166,2	289,7	58,2	1,154	1,74	2,18	2,71	R.; P., C., W.G.
Ni	202,1	211,1	377,6	62,4	—	1,79	1,87	2,44	Gr., R.

In the following paper the element groups of the Halogens, of the Oxygen and Nitrogen group, and also those of the Carbon group will be treated. For the Hydrogen-Helium group considered here we have not found anything special — for the following groups, however, we shall find the remarkable fact that everywhere where (specially for metals) the molecules of the elements consist only of one atom at T_k , the value of $\sqrt{a_k}$ becomes *much greater* than the normal one, calculated by us in I. These are only valid when two or more atoms are bound to each other in the molecule; so that the attraction cannot make itself *fully* felt in consequence of the mutually shadowing action. What we have found there ($\sqrt{a_k} = \text{resp. } 1, 3, 5, 7, 9, 11 \times 10^{-2}$) must be considered as a kind of **rest attraction**. If, namely, N₂ were entirely dissociated to N₁, the attraction found by us for N₂, viz. $\sqrt{a_k} = 2,9 \cdot 10^{-2}$, would at once rise to about **30** ($\times 10^{-2}$), hence to the *tenfold* value.

We shall even have an opportunity to ascertain, that where in compounds as TeCl₄ and TeCl₂, the shadowing action gradually decreases, the value of $\sqrt{a_k}$ will already increase. Thus $\sqrt{a_k}$ for TeCl₄ has the normal rest value 9. But for TeCl₂, $\sqrt{a_k}$ will already have risen to the value 13. The *non-saturate valencies*, therefore, already make their influence felt. If, however, also the last chlorine atoms have been removed, the attraction of the Tellurium rises still more, and reaches the value 26.

We shall find back this remarkable phenomenon for all metals; the exceedingly high values of melting point, boiling point, and critical temperature for many metals are owing to the high values of $\sqrt{a_k}$ in consequence of the monatomic state, from which ensues that the *valence-attraction* can make itself felt freely towards the outside.

That for the Helium group, where the molecules also consist of only one atom, only the ordinary rest attraction asserts itself, and not the so much greater valence-attractions, is owing to this that the noble gases mentioned are *valenceless*.

Clarens, May 1916.

Physics. — “*On the Fundamental Values of the Quantities b and \sqrt{a} for Different Elements, in Connection with the Periodic System. IV. The Elements of the Halogen- Oxygen- and Nitrogen Groups.*” By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ.)

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

I. The Halogen Group.

After the treatment of the valenceless eighth group of the periodic system, i.e. of the group of the noble gases (to which we have added the hydrogen for convenience, sake)¹⁾, we shall now discuss the seventh group, that of the Halogens. We remind the reader that our chief aim is now to determine the values of $\sqrt{a_k}$ of the *elements themselves*, independent of the values calculated before in I and II²⁾ from their *compounds*.

a. Fluor. The critical temperature is unknown; I find somewhere stated $-170^\circ \text{C.} = 103^\circ \text{abs.}$, but this cannot possibly be true, as the boiling point temperature lies already at $-187^\circ \text{C.} = 86^\circ \text{abs.}$ according to MOISSAN and DEWAR (1903). Now for the Halogens the ratio $T_k : T_b$ (Cf. the table in II on p. 18) is resp. 1,72 for I_2 , 1,73 for Br_2 , and 1,75 for Cl_2 . If, therefore, for F_2 we also assume 1,75 for it, T_k would become $=151^\circ \text{abs.}$ To this corresponds $2\gamma = 1 + 0,038\sqrt{151} = 1,467$, hence $\gamma = 0,733$. If, therefore, the triple point temperature lies at $-223^\circ \text{C.} = 50^\circ \text{abs.}$ (MOISSAN and DEWAR, 1903)³⁾, then $m_1 = 50 : 151 = 0,331$, and the factor $f_1 = b_k : v_1$ becomes:

$$f_1 = 1,467 \left[1 - \frac{0,733}{1,733} \times 0,331 \right] = 1,467(1 - 0,140) = 1,262.$$

Hence to find $b_k = 55 \cdot 10^{-5}$ for 1 Gr. atom Fluor, the atomic volume at the triple point must be $= (55 : 1,262) 10^{-5} = 43,6 \cdot 10^{-5}$. Now for -200°C. MOISSAN and DEWAR (1897) found $D = 1,14$,

¹⁾ See III, These Proc. p. 287.

²⁾ These Proc. of Jan. 29 and March 25, 1916; p. 1228 and 2.

³⁾ In the “Chemisch Jaarboekje” for 1915–1916, I find -233°C. given.