

Physics. — “On the Maximum and Minimum Density and the Heat of Evaporation of Helium”. (First Part). By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

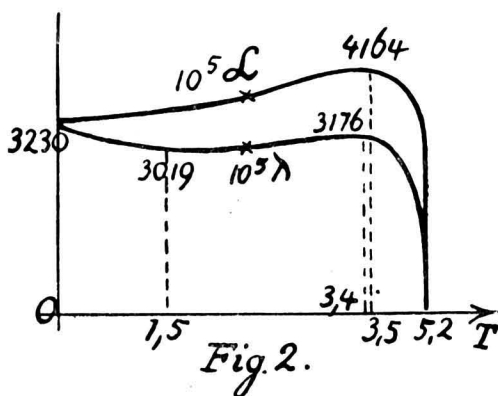
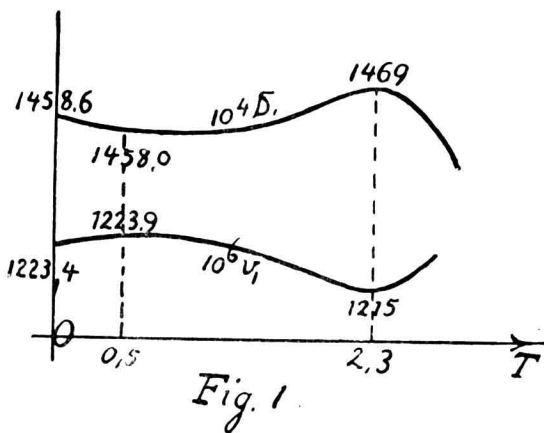
(Communicated at the meeting of September 25, 1926).

A. Theoretical Part.

1. Introduction.

It has become known through the investigations of KAMERLINGH ONNES (Comm. Leiden 119 (1911)), and later through those of KAMERLINGH ONNES and BOKS (Comm. 170^b (1924)), that the liquid density of Helium shows a *maximum* at 2°₃ abs. The course sketched in this latter paper leads us, however, to expect that, at still lower temperature, another *minimum* will appear; accordingly after this D_1 will again increase up to the absolute zero (See Fig. 1). The following simple theoretical considerations really confirm this supposition. We see from the values, calculated in § 3, that the minimum (at 0°₅₂) is exceedingly flat, and that the liquid density between $T=0$ and somewhat more than 1° abs. varies only very little — quite conformable to the diagram given p. 23 of Comm. 170^b.

Presently it will also appear theoretically, that the internal molecular heat of evaporation $\lambda = L - p(v_2 - v_1)$ does not only — like L itself —



present a *maximum* at 3°₄ (that of L lies at 3°₅), but that at lower temperature λ also passes through a *minimum*, and this at 1°₄₇. It can easily be shown that L does not pass through a minimum, but has a *point of inflection* in the neighbourhood of 2°₃. (Cf. Fig. 2; the values given there are expressed in “normal” units; multiplication by 542,63 yields L and λ in gr. cal.). The experiments of KAMERLINGH ONNES and DANA

recently published (These Proc. 29, 1051—1060 (1926)) only give the maximum of L at $3^{\circ},5$, for which we theoretically calculate 22,6 gr. cal.; experimentally also 22,6 is found, but at about 3° . The experiments are, however, not accurate enough to determine this temperature with certainty; compare on this point the Second Part of this Article.

The course of both, that of Fig. 1 and Fig. 2 — and to this is added the low temperature coefficient of the *constant* of EÖTVÖS (cf. VAN URK, KEESOM and KAMERLINGH ONNES, *ibid.* 28, 958 (1925)) and the too low values of the *specific heat* (DANA and KAMERLINGH ONNES, *ibid.* 29, 1061—1068 (1926)), but this we will treat in a later paper — is only accounted for by the fact, that in Helium below T_k the quantity a does not diminish with increasing temperature, as in all other substances, but *increases*. As secondary factor we have then the in itself *small value* of a in Helium. The quantity b *always* decreases with increasing temperature (this decrease is not to be confused with the increase of b with the *volume*, which may, however, be neglected in Helium at the lower temperatures, since then v_1 remains *practically* unchanged); and this, like the decrease of a , in consequence of exponential temperature functions occurring by the side of a and b (BOLTZMANN'S factors of distribution; c.f. among others "Zustandsgl.", p. 55-64). In all other substances the two decreases will counteract each other in the equation of state, and about neutralize each other, so that no special complications will appear, but in Helium the increase of a will act in the same direction as the decrease of b , and as we shall see, there the action of the two influences will give rise to the above-mentioned maxima and minima of D_1 and λ , in consequence of alternately stronger and weaker coöperation.

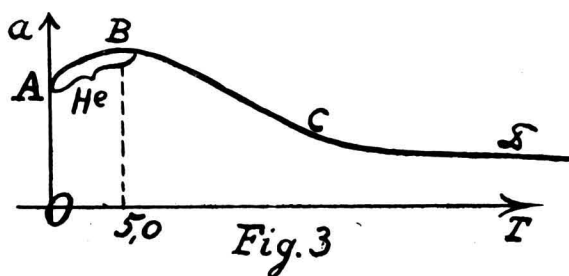
It need scarcely be stated, that in the fact of the relatively *too small* liquid density at low temperatures lies also the key to the phenomenon that Helium cannot become solid at the ordinary vapour pressures. Not until the *external* pressure is raised, through which the too small internal pressure a/v^2 (in consequence of the decrease of a at fall of temperature) is compensated, there can be question of solidification. Which has, indeed, proved to be true through KEESOM'S recent experiments.¹⁾

That the phenomenon of the maximum density is a consequence of the decrease of a with falling temperature, I showed already in 1920 (Recueil Tr. Chim., 34, 382), though at the time I still shared KAMERLINGH ONNES' (erroneous) view, that the liquid density could again diminish to a very small value at very low temperature, in other words might give rise to a second vapour phase. This would be the consequence of KAMERLINGH ONNES' assumption (Comm. 119 (1911); cf. particularly § 6, p. 15—19), that a would be $= cT^2$ (loc. cit. p. 17), in other

¹⁾ Cf. on this subject my article in the N. Rott. Ct. of July 21th (Evening paper A. p. 1) and (without the numerous confusing printer's errors that occur in the N. R. Ct.) in the Journal de Genève of July 26th 1926. Cf. also Chem. Weekbl. of July 31st (under "Personalia").

words would become $=0$ at $T=0$. The later, above-mentioned investigations of KAMERLINGH ONNES and BOKS have contradicted these, in fact pretty improbable, assumption. We shall see in § 2 that $10^6 a$, which quantity has the value of 67,4 at T_k , approaches to 39,5 at $T=0$, hence by no means $=0$. The assumption $a = cT^2$ would not be able to explain the minimum at $0^{\circ},5$, nor that of λ at $1^{\circ},5$. No more is the so-called „energy-degeneration” at lower temperatures, on which e.g. VERSCHAFFELT (see the cited paper by DANA and KAMERLINGH ONNES) refers, able to do so. I, therefore, disputed this view already in the paper of 1920 mentioned before (p. 382 under: “L’effet des “quanta” n’y est pour rien, etc.”). Later on I worked out the theory on a better basis (L’Hydrogène et les gaz nobles, Leiden, Sijthoff, 1921, p. 39—41), and this theory is the same as will be developed in what follows (with only slight modification as regards db/dt).

Through my researches on the equation of state I have, of late, entirely relinquished the idea that in the case of *liquids* there could be question of “energy-degeneration”, even at the lowest temperatures.¹⁾ Not only that all the phenomena of ordinary substances, and even the so greatly diverging ones of Helium can be explained qualitatively and quantitatively by the dependence of a and b on the temperature, and the dependence of b on the volume; this being *not* the case on assumption of energy-degeneration (the coefficient of expansion, inter alia, would simply rapidly approach to 0 without maximum nor minimum volume; the minimum for λ remained unexplained, etc.) — but in principle I protest against applying PLANCK’s and DEBYE’s considerations, which are especially valid for “oscillators” moving round fixed positions of equilibrium, to liquids (and even to gases!), where the molecules can move freely with regard to each other. Especially in Germany, where, in spite of all that has been written about it — even by VAN DER WAALS himself already —



a and b are still almost universally considered as constant, physicists have recourse to the assumption of energy degeneration for liquids, in imitation of NERNST c. s. (vapour-pressure equations with $+1,75 \log T$, even at the highest temperatures, etc.).

With regard to this decrease of a in Helium at fall of temperature it may be pointed out, that this is a *quite general* phenomenon. There is (see Fig. 3) between B and D , i. e. almost over the total course of a ,

¹⁾ PALACIOS MARTINEZ and KAMERLINGH ONNES (Comm. 164 (1923)) showed already for H_2 and He that — in contradiction to the opinion of some authors — there is not yet question of any quantum effect in the gaseous state at very low temperatures ($20^{\circ},5$ abs.).

a decrease with increasing temperature (see above: BOLTZMANN'S distribution factor); only at *very* low temperatures there will be found decrease after a maximum on further fall of the temperature (Cf. on this point also my considerations in These Proc. 21, 19 (1918)). As a is practically independent of v , the results found there for large volumes may also be applied to small volumes.

What is now the case? For almost all substances the region *between melting point and critical temperature* lies in the descending part, e. g. in the neighbourhood of C ; only for hydrogen the part left of B is encroached on a little. Helium is, however, the only substance where the region between 0° and $5^\circ,2$ lies *almost entirely* between A and B . (The maximum lies at exactly 5° , so that T_k lies slightly on the right of B). Also for ordinary substances deviating phenomena would make their appearance at very low temperatures, but this is prevented by the appearance of the *solid* state long before the time.

2. The maximum of density at $2^\circ,3$. Formulae for a and b .

As $\left(\frac{dv}{dt}\right)_p = \left(\frac{dp}{dt}\right)_v; -\left(\frac{dp}{dv}\right)_t$, and the coefficient of compressibility $-\frac{1}{v}\left(\frac{dv}{dp}\right)_t$ always remains finite, hence never becomes 0 or ∞ , $\left(\frac{dv}{dt}\right)_p$ will necessarily become 0 (maxima and minima of v) at the same time with $\left(\frac{dp}{dt}\right)_v$ or $T\left(\frac{dp}{dt}\right)_v$. From $p = \frac{RT}{v-b} - \frac{a}{v^2}$ follows:

$$T\left(\frac{dp}{dt}\right)_v = \frac{RT}{v-b} - \frac{Ta'}{v^2} + \frac{RT^2 b'}{(v-b)^2} = \frac{a-Ta'}{v^2} + \frac{RT^2 b'}{(v-b)^2} + p,$$

when for shortness a' is written for $\left(\frac{da}{dt}\right)_v$ and b' for $\left(\frac{db}{dt}\right)_v$.

If for the present — for the calculation of different quantities — we confine ourselves to the minimum of v at $2^\circ,3$, we shall have there:

$$a - Ta' = -\left(\frac{v}{v-b}\right)^2 RT^2 b' - pv^2 \quad (2^\circ,3).$$

From the equation of state follows, however;

$$\frac{v}{v-b} = \frac{a/v + pv}{RT} = \frac{a/v}{RT} \left(1 + \frac{p}{a/v^2}\right),$$

so that we may also write:

$$a - Ta' = -\left(\frac{a^+}{v}\right)^2 \frac{b'}{R} - pv^2,$$

where, accordingly, a^+ means $a(1 + p : a/v^2)$. We shall see that for Helium at $2^\circ,3$ the different correction quantities may not be neglected.

Putting now

$$a = a_0 + \alpha T - \gamma T^2 \quad ; \quad b = b_0 - \beta T + \delta T^2,$$

we have the following equation at 2°3, with $a-Ta' = a_0 + \gamma T^2$:

$$a_0 + \gamma T^2 = \frac{\left(\frac{a^+}{v}\right)^2 \beta - 2 \delta T}{R} - p v^2 \quad (2^\circ, 3) \quad . . . \quad (1)$$

This is already a *first* relation between a_0, a, γ and $-b' = \beta - 2 \delta T$, when v is experimentally known.

A *second* relation is found from (for a is practically independent of v , and the above expression for a is, therefore, certainly valid up to T_k)

$$a_k = a_0 + a T_k - \gamma T_k^2,$$

i.e. with $T_k = 5^\circ, 19$ and $10^6 a_k = 67,42$ (to be calculated from T_k and p_k)

$$a_0 + 5,19 a - 26,94 \gamma = 67,42 \cdot 10^{-6} \quad . . . \quad (2)$$

A *third* relation follows from the theoretical value of the internal molecular heat of evaporation λ . For this, as the difference of two energies, the following equation is evidently valid — when, as we suppose, no energy degeneration occurs in liquids:

$$\lambda = \int_{v_1}^{v_2} \left(T \left(\frac{dp}{dt} \right)_v - p \right) dv,$$

which, accordingly, yields with the above-found value of $T \left(\frac{dp}{dt} \right)_v$ 1):

$$\lambda = \int_{v_1}^{v_2} \left(\frac{a-Ta'}{v^2} + \frac{RT^2 b'}{(v-b)^2} \right) dv = \frac{a-Ta'}{v_1} + \frac{RT^2 b'}{v_1-b} - \text{corr. } v_2,$$

when we may consider b and b' as independent of v in Helium, at least on the liquid branch. When we again substitute $a^+/v : RT$ for $v:(v-b)$ (see above), we get (substituting v for v_1):

$$\lambda v = (a-Ta') + \frac{a^+}{v} T b' - \text{corr. } v_2. \quad . . . \quad (a)$$

The value of λ in this equation can be calculated from the experimental values of p, v_1 and v_2 . (Cf the Second Part of this paper).

In this equation $b' = -(\beta - 2 \delta T)$ can be eliminated at 2°3 by means of (1). We then obtain:

$$\lambda v = (a_0 + \gamma T^2) - \frac{a_0 + \gamma T^2 + p v^2}{a^+/v} RT - \text{corr. } v_2,$$

i. e.

$$\lambda v \left(1 + \frac{v_1}{v_2} \right) = (a_0 + \gamma T^2) \left(1 - \frac{RT}{a^+/v} \right) - p v^2 \frac{RT}{a^+/v} \quad (2^\circ, 3), \quad . . . \quad (3)$$

1) For ordinary substances, where the terms with a' and b' about cancel each other, this expression becomes simply $\lambda = \frac{a}{v_1} - \frac{a}{v_2}$, which relation was first derived by BAKKER in his Thesis for the Doctorate (1885).

in which with regard to the very slight correction for v_2 it has been taken into account, that both in (a) and in (3) the principal term is $(a_0 + \gamma T^2)$, so that in approximation λ will be $= (a_0 + \gamma T^2) : v_1 - \text{ibid} : v_2$,

which leads to $\lambda v_1 = (a_0 + \gamma T^2) \left(1 - \frac{v_1}{v_2}\right)$ or $\lambda v_1 \left(1 + \frac{v_1}{v_2}\right) = a_0 + \gamma T^2$,

i. e. — with the addition of the other terms — to (3).

A *fourth* relation follows from (a), when $T=0$ is put. Then follows

$$\lambda_0 v_0 = a_0, \quad (4)$$

in which λ_0 and v_0 are known from experimental data. For we have from the vapour-pressure equation $\log^{10} p = -A/T + \text{etc.}$, in which $2.3026 A = 3.8308 \times 2.3026 = \gamma_0/R$ (see § 1 of the Second Part), with $R = 1 : 273.09 = 0.0036618$:

$$\lambda_0 = 3.8308 \times 0.0036618 \times 2.3026 = \underline{0.03230} \text{ (in norm. units).}$$

To reduce this to gr. cal. 15° , it must be multiplied by $273.09 \times 1.9866 = 542.63$, R being $= 1 : 273.09$ in normal units, and $= 1.9866$ in gr. cal. Then $\lambda_0 = L_0 = \underline{17.53}$ gr. cal. is obtained, and not $4 \times 3.5 = 14$ gr. cal., as VERSCHAFFELT calculated on the ground of in my opinion unfounded suppositions.

Now from $\underline{D_0 = 0.1458^6}$ (this value will be found in § 3) follows in normal units:

$$v_0 = \frac{4}{22416 D_0} = \frac{0.000178444}{D_0},$$

so that $10^6 v_0$ becomes $= \underline{1223.4}$, and further according to (4):

$$a_0 = 0.03230 \times 1223.4 \cdot 10^{-6} = \underline{39.515 \cdot 10^{-6}},$$

against $a_k = \underline{67.42 \cdot 10^{-6}}$; in consequence of which $a_0 : a_k$ becomes $= 0.5861 = 0.6$. For ordinary substances this relation is about 1.6.

With this value of a_0 we can now determine α and γ from (2) and (3). According to table IX in the Second Part λ is at $2^\circ,3 = 0.03060$, $v_1 = 1215 \cdot 10^{-6}$, hence $\lambda v_1 = 37.18 \cdot 10^{-6}$. And $v_1 : v_2$ being $= 1 : 93$ at $2^\circ,3$, $\lambda v_1 (1 + v_1/v_2)$ becomes $= 37.58 \cdot 10^{-6}$.

At $2^\circ,3$ the correction term $p v_1^2 (RT : a^+ / v_1)$ is $= 0.06959 (1215)^2 \cdot 10^{-12} \times (0.008422 \times 1215 \cdot 10^{-6} : 59.41 \cdot 10^{-6})$, in which p is expressed in atm. (Table V), while for a at $2^\circ,3$ presently $59.31 \cdot 10^{-6}$ will be found, to which then $0.10 \cdot 10^{-6}$ is added as correction on a , viz. (see before (1)) $p v_1^2 = 0.06959 \times (1215)^2 \cdot 10^{-12} = 0.06959 \times 1.476 \cdot 10^{-6} = 0.1027 \cdot 10^{-6}$.

We then find for the correction term in question:

$$0.103 \cdot 10^{-6} \times (10.233 \cdot 10^{-6} : 59.41 \cdot 10^{-6}) = 0.103 \cdot 10^{-6} \times 0.172 = \\ = 0.0177 \cdot 10^{-6} = 0.02 \cdot 10^{-6}.$$

Hence (3) becomes:

$$37,58 \cdot 10^{-6} + 0,02 \cdot 10^{-6} = \\ = (39,515 \cdot 10^{-6} + 5,29 \gamma) \left(1 - \frac{0,008422 \times 1215 \cdot 10^{-6}}{(39,515 \cdot 10^{-6} + 2,3a - 5,29 \gamma)^+} \right).$$

Now according to (2) $5,19 \cdot 10^6 a - 26,94 \cdot 10^6 \gamma = 67,42 - 39,515 = 27,905$, hence $10^6 a - 5,19 \cdot 10^6 \gamma = 5,3767$, and therefore $2,3 \cdot 10^6 a = 12,366 + 11,94 \cdot 10^6 \gamma$. Substituting this in the above equation, the result is

$$37,60 = (39,515 + 5,29 \cdot 10^6 \gamma) \left(1 - \frac{10,233}{(51,881 + 6,65 \cdot 10^6 \gamma)^+} \right),$$

in which the correction factor at a^+ amounts to $= 0,103 : 59,31 = 0,00173 = 1 : 600$ of the value, according to the above.

In consequence of this we get:

$$39,515 + 5,29 \cdot 10^6 \gamma = \frac{37,60}{1 - \frac{10,233}{51,971 + 6,661 \cdot 10^6 \gamma}},$$

i.e.

$$(39,515 + 5,29 \cdot 10^6 \gamma) (41,738 + 6,661 \cdot 10^6 \gamma) = 37,60 (51,971 + 6,661 \cdot 10^6 \gamma),$$

leading to

$$35,237 (10^6 \gamma)^2 + 233,54 \cdot 10^6 \gamma - 304,8 = 0,$$

or $(10^6 \gamma)^2 + 6,622 \cdot 10^6 \gamma - 8,650 = 0$, yielding $10^6 \gamma = 1,1177$; and further (see above) $10^6 a = 5,3767 + 5,19 \times 1,1177 = 11,178$. We then finally find for a :

$$\underline{10^6 a = 39,515 + 11,178 T - 1,1177 T^2} \text{ (valid to a little further than } T_k), \quad (5)$$

in which accidentally the coefficient of T^2 is exactly $= 0,1$ of that of T . Hence for a the formula gives a maximum at exactly 5° , i.e. $= 67,46 \cdot 10^{-6}$. After this a will decrease, approaching a limiting value at $T = \infty$ (see Fig. 3), which is, of course, not rendered by (5). Now the following values for a are calculated from (5).

$T = 0^\circ$	$0^\circ,5$	$1^\circ,4$	$2^\circ,3$	$5^\circ,0$	$5^\circ,2 \text{ abs.}$
$10^6 a = 39,515$	$44,82\bar{5}$	$52,973$	$59,311$	$67,46$	$67,42$

The value $59,31$ at $2^\circ,3$ has already been used above for the calculation of the small correction term.

From (1) the value of $-b' = \beta - 2 \delta T$ at $2^\circ,3$ can now be calculated. We find:

$$-b' = \frac{(a_0 + \gamma T^2 + \rho v^2) R}{(a^+ / v)^2} = \frac{(39,515 + 5,913 + 0,103) 10^{-6} \times 0,0036618}{(59,414 : 1215)^2}.$$

For at $2^\circ,3$ $10^6 a$ is $= 59,311$, which becomes $= 59,414$ with the correction $0,103$ (see above). Hence we get:

$$-10^6 b' = 0,16673 \times (20,450)^2 = \text{ibid.} \times 418,20 = \underline{69,73} (2^\circ,3).$$

Thus from the fact of the maximum density at $2^{\circ},3$, and making use of the values of λ_0 and $\lambda_{2,3}$ to be calculated from the experimental material, we have determined the whole course of a , and have succeeded at the same time in finding out something about the quantity b , viz. $-b' = \beta - 2\delta T$.

Assuming again $10^6 v_0 = 1223,4$, the coefficients β and δ in $b = b_0 - \beta T + \delta T^2$ can easily be determined, now that a is known, from two observations of the liquid density, e.g. at $1^{\circ},4$ and at $2^{\circ},3$. Of course we might also have determined $b_0 = v_0$, β and δ from three such observations, but — now that the value of v_0 has once been established (see § 3) — we prefer the method of calculation indicated, the more so because we then also possess a means to test the value of $-10^6 b'$ at $2^{\circ},3$ found just now, i. e. about 70.

From the equation of state follows:

$$\left. \begin{array}{l} T=1^{\circ},4 \quad \left| \quad 0,003822 + \frac{52,973 \cdot 10^{-6}}{(1222,5)^2 \cdot 10^{-12}} (1222,5 - 10^6 b_{1,4}) 10^{-6} = 0,005127 \right. \\ T=2^{\circ},3 \quad \left| \quad 0,06959 + \frac{59,311 \cdot 10^{-6}}{(1215)^2 \cdot 10^{-12}} (1215 - 10^6 b_{2,3}) 10^{-6} = 0,008422 \right. \end{array} \right\}$$

in which the values of a were determined just now, those of p and v (calculated from D) having been experimentally given (Table V and VII). This yields therefore:

$$\begin{aligned} (0,004 + 35,445) (1222,5 - 10^6 b_{1,4}) &= 5127 \\ (0,070 + 40,178) (1215 - 10^6 b_{2,3}) &= 8422 \end{aligned}$$

from which $1222,5 - 10^6 b_{1,4} = 144,63$, $1215 - 10^6 b_{2,3} = 209,25$, hence

$$10^6 b_{1,4} = 1077,87 \quad ; \quad 10^6 b_{2,3} = 1005,75.$$

From this, and with $10^6 b_0 = 1223,4$, follows immediately:

$$\underline{10^6 b = 1223,4 - 118,45 T + 10,356 T^2} \quad (\text{valid to } \pm 2^{\circ},3) \quad . \quad . \quad (6)$$

From this follows, therefore, $10^6 b'_{2,3} = 118,45 - 20,71 \times 2,3 = 70,82$, against 69,73 above, or round 71 against 70. Hence the maximum of density lies possibly not *exactly* at $2^{\circ},3$; it is also possible that the slight dependence of b on the volume at $2^{\circ},3$, which has been neglected in the beginning, is already perceptible¹⁾.

3. The minimum of density at $0^{\circ},52$. Formula for D_1 .

From the equation for $T \left(\frac{dp}{dt} \right)_v$ in the beginning of § 2, after substi-

¹⁾ In this connection we remark that from the above formulae, which of course remains valid to T_k , when only the volume is kept $= v_0$, it would follow that $10^6 (b_{v_0})_k = 888$, $10^6 b_k$ being $= 1051$ (from T_k and p_k). It would then follow from this, according to a formula derived by me (Zeitschr. f. anorg. u. allg. Chem. **149**, p. 349 (1925)), that $(b_{\infty})_k : b_k$ is $= \frac{1}{2} \left(\frac{1051}{888} + 1 \right) = 1,09$, hence $10^6 (b_{\infty})_k = 1146$. From this it is possible, at least at T_k , to judge to some extent about the variability of b with the volume. Between $v = v_0$ and $v = \infty$ the value of b then varies from 888 to 1146, i. e. in the ratio of 1 : 1,3.

tution of the value for $\left(\frac{v}{v-b}\right)^2$, follows:

$$T\left(\frac{dp}{dt}\right)_v v^2 = a_0 + \gamma T^2 + pv^2 - \left(\frac{a^+}{v}\right)^2 \frac{\beta - 2 \delta T}{R}$$

At $T=0$ this becomes:

$$a_0 - \left(\frac{a_0}{v_0}\right)^2 \frac{\beta}{R} = a_0 \left(1 - \frac{a_0}{v_0^2} \frac{\beta}{R}\right)$$

Now

$$1 - \frac{a_0}{v_0^2} \frac{\beta}{R} = 1 - \frac{39,515 \cdot 10^{-6}}{(1223,4)^2 \cdot 10^{-12}} \times 118,45 \cdot 10^{-6} \times 273,09,$$

i.e. with $(1,2234)^2 = 1,4967$:

$$1 - 26,401 \times 118,45 \cdot 10^{-6} \times 273,09 = 1 - 0,854 = 0,15.$$

And $\left(\frac{dv}{dt}\right)_v$ always having the same sign as $\left(\frac{dp}{dt}\right)_v$ (see § 2), hence also as $T\left(\frac{dp}{dt}\right)_v \cdot v^2$, with Helium $\left(\frac{dv}{dt}\right)_p$ will be **positive** at the absolute zero. And since there is a minimum at $2^\circ,3$, there will *necessarily* be also a maximum volume at lower temperature, i.e. a **minimum density** (See Fig. 1), and this in the neighbourhood of $0^\circ,52$, as we shall presently see.

In general it follows from the above relation, that $\left(\frac{dv}{dt}\right)_p$ will be *positive* at $T=0$, when

$$\frac{\beta}{b_0} < \frac{R}{a_0/b_0} \dots \dots \dots (7)$$

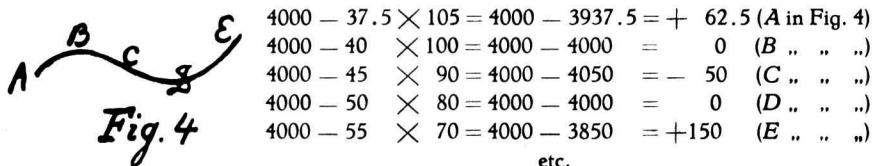
This is fulfilled in Helium, owing to the small value of a (low critical temperature). But how is this with ordinary substances with comparatively high critical temperature? For such substances $a_0 = 1,6 a_k$, $b_0 = 0,5 b_k$, hence $a_0 : b_0 = 3,2 (a_k : b_k)$. With $\lambda = \frac{27}{28}$ it follows from $RT_k = \frac{8}{27} \lambda a_k/b_k$, that $a_k : b_k$ is $= \frac{7}{2} RT_k$, so that for ordinary substances $a_0 : b_0$ will be about $= 11 RT_k$. For a positive initial course $\beta : b_0$ must, therefore, be $< 1 : 11 T_k$, which would yield $\beta : b_0 < 1 : 6000$ with e.g. $T_k = 550^\circ$ abs.

Now it is, of course, *possible* that β is so small, and then v will immediately increase, without maximum or minimum, however. For if this were the case, it would follow that $(a_0 + \gamma T^2) - \text{etc.}$ could become $= 0$, which with such small values of β is evidently impossible.

But generally β will, no doubt, be greater. And then v begins with a *decrease*, because then $\left(\frac{dv}{dt}\right)_p$ is negative. But because v must of course, increase later on, there must necessarily be a minimum volume (maximum density) in this (most frequently occurring) case. Accordingly, the

phenomenon of a maximum density would not remain restricted to Helium, but would have to be found for any substance (provided β be not too small) at low temperature — without the minimum, however, at still lower temperature. But unfortunately an “ordinary” substance becomes solid long before the temperature, at which this phenomenon could appear, is reached. And above the melting-point, a just as b decreases with the temperature, so that then the phenomenon cannot possibly be realized (see below).

The possibility of a maximum and a minimum in Helium can very simply be represented in a diagram in the following way. If the terms γT^2 and $p\nu^2$, whose values are small compared with the other terms, are disregarded, the sign of $\left(\frac{dv}{dt}\right)_v$ is chiefly determined by that of $a_0 - q \times r$, in which for Helium $q = (a/\nu)^2$ is an *increasing* quantity owing to $a = a_0 + aT \dots$ (ν varies then exceedingly little), and $r = (\beta - 2 \delta T) : R$ is a *decreasing* quantity. This may e. g. give rise to what follows (the figures are entirely arbitrary).



Here the quantity b itself must, of course, also decrease (β positive). For else we should get (see above) $a_0 + q \times r$ (instead of $a_0 - q \times r$), which of course, could never become = 0. Nor can the phenomenon, of course, be found with a diminishing at the same time with b (e. g. for ordinary substances above the melting-point, (see above), since $\left(\frac{dv}{dt}\right)_p$ being once positive, becomes then greater and greater positive (q and r both decrease).

Let us now examine *where* the minimum of density in Helium lies. For this purpose T must be solved from

$$(a_0 + \gamma T^2) - \left(\frac{a}{\nu}\right)^2 \frac{\beta - 2 \delta T}{R},$$

where a is $a = a_0 + aT - \gamma T^2$, the correction term $p\nu^2$ being certainly negligible at $0^\circ,5$ ($p = 0,073$ atm.!). After some trials the following value is soon found:

$$\underline{T_{\min.} = 0^\circ,521.}$$

For then the above expression becomes:

$$(39,515 + 0,304) 10^{-6} - \left(\frac{45,039 \cdot 10^{-6}}{1223,9 \cdot 10^{-6}}\right)^2 (118,45 - 10,79) \cdot 10^{-6} \times 273,09,$$

or after division by 10^{-6} :

$$39,819 - (36,801)^2 \times 107,66 \cdot 10^{-6} \times 273,09 = 39,819 - 1354,3 \times \text{etc.},$$

hence

$$39,819 - 39,820, \text{ i.e. } 39,82 - 39,82 = 0.$$

If, now, at low temperatures the liquid density is represented by the quadratic formula $D = D_0 - \varepsilon T + \varphi T^2$, already $\varepsilon : 2\varphi$ is $= 0,521$ on account of the minimum at $0^\circ,521$. If, further, we assume the experimental values $D_{1^\circ,2} = 0,1459$ and $D_{1^\circ,9} = 0,1462$, we find easily from

$$D = D_0 - 1,042 \varphi T + \varphi T^2:$$

$$10^4 \varphi = 2,0825, \quad 10^4 D_0 = 1458,605, \quad \text{and further } 10^4 \varepsilon = 2,1700,$$

so that at low temperatures the liquid densities may be represented by

$$\underline{10^4 D_1 = 1458,6 - 2,170 T + 2,082 T^2} \quad (\text{valid up to } \pm 2^\circ). \quad (8)$$

It is the above value of D_0 , that we have assumed in our calculations in § 2. If we had assumed a slightly different value, the value found now would *not* have been in perfect harmony with it. Through some repeated new calculations the right value, which leads to a value in (8) identical with it, is finally found. This formula gives the following values of D_1 and $v_1 = 178,444 \cdot 10^{-6} : D_1$ (see § 2).

TABLE A.

T	$10^4 D_1$	$10^6 v_1$	T	$10^4 D_1$	$10^6 v_1$
0	1458.61	1223.39	1.2	1459.00	1223.1
0.5	1458.04	1223.86	1.3	1459.30	1222.8
0.6	1458.05	1223.85	1.4	1459.65	1222.5
0.7	1458.11	1223.80	1.5	1460.04	1222.2
0.8	1458.20	1223.7	1.6	1460.46	1221.8
0.9	1458.34	1223.6	1.7	1460.93	1221.4
1.0	1458.52	1223.5	1.8	1461.45	1221.0
1.1	1458.74	1223.3	1.9	1462.00	1220.5

At 2° the formula gives 1462,6; experimentally round 1463 has been found. (At $1^\circ,6$ the value according to the formula is 1460,5, round 1460 having been found experimentally). Hence the minimum of density at $0^\circ,52$ is $= 0,1458$; we know that D_1 at $2^\circ,3$ reaches the maximum 0,1469. The values of D_1 between 0° and 1° , therefore, do not differ much, they are always in the neighbourhood of 0,1458; only after this they begin to rise somewhat. The course is then *quite conformable* to the graphical representation given in Comm. 170^b.

4. The minimum of λ at $1^{\circ},5$.

Also the molecular internal latent heat λ , which passes through a maximum at $3^{\circ},4$, will again pass through a *minimum* at about $1^{\circ},5$, as does not only follow from the values of λ calculated from $\frac{dp}{dt}$ and $v_2 - v_1$ (see Table IX), but can also be demonstrated theoretically.

We saw above in § 2, that

$$\lambda = \frac{a_0 + \gamma T^2}{v} - \frac{a}{v^2} T (\beta - 2 \delta T),$$

when the corrections are omitted, which disappear at very low temperatures, and of course at $T=0$. Then it follows from this, when we suppose v along the saturation line to be constant, which is about fulfilled in the neighbourhood of $T=0$, that

$$\frac{d\lambda}{dT} = \frac{2\gamma T}{v} - \frac{a + Ta'}{v^2} (\beta - 2\delta T) + \frac{aT}{v^2} 2\delta.$$

Hence at $T=0$, $a + Ta' = a_0 + 2aT - 3\gamma T^2$ then being $= a_0$, we have:

$$\left(\frac{d\lambda}{dT}\right)_0 = -\frac{\beta a_0}{v_0^2}, \dots \dots \dots (9)$$

which is, accordingly, **always negative**. (See Fig. 2).

For *ordinary* substances, where the variability of v cannot be neglected, there is, besides, still a term $-\frac{a_0}{v_0^2} \left(\frac{dv}{dt}\right)_0$. This is then even the principal term, as β is then small in comparison with $\left(\frac{dv}{dt}\right)_0$. It now follows from the equation of state, that when a and b are constant (ideal substances), this term is $= -R$, and *greater negative*, when the substances are not ideal. λ , therefore, decreases continually, from $T=0$ to T_k , without minimum or maximum, as in Helium (see further).

As regards $L = \lambda + RT$ (at low temperatures $p(v_2 - v_1) = RT$), this will be $\left(\frac{dL}{dt}\right)_0 = -R + R = 0$ for ordinary substances, when they are ideal substances, and *negative* when they are not ideal substances.

Now from (9) follows for *Helium*:

$$\left(\frac{d\lambda}{dT}\right)_0 = -\frac{118,45 \cdot 10^{-6} \times 39,515 \cdot 10^{-6}}{(1223,4)^2 \cdot 10^{-12}} = \underline{\underline{-0,003127}},$$

theoretically. Experimentally the following value is found (see Table IX) between 0° and $0^{\circ},5$:

$$(0,03091 - 0,03230) : 0,5 = -0,0028.$$

This is the chord between the said temperatures. Hence for the tangent a somewhat greater (negative) value must be found (see Fig. 2), so that

— 0,0031 may be right. If to this $R = 0,0036618$ is added, then the following value holds for Helium:

$$\left(\frac{dL}{dT}\right)_0 = + 0,000535,$$

i.e. **positive**. Also this value proves to be in good agreement. For according to Table IX $(0,03274 - 0,03230) : 0,5 = 0,00088$ is found for it between 0° and $0^\circ,5$, and $(0,03399 - 0,03274) : 0,5 = 0,00250$ between $0^\circ,5$ and 1° (which points to a *point of inflection* between $T = 0$ and the maximum at $3^\circ,5$; see Fig. 2). The value of $10^5 \left(\frac{dL}{dT}\right)_0$ will, therefore, be pretty considerable smaller than 88, so that again 53,5 may be correct.

L increases, therefore, at first, and as this quantity will necessarily rapidly approach to 0 in the neighbourhood of T_k , in consequence of the factor $\frac{1}{v_1} - \frac{1}{v_2}$, there must also necessarily be a **maximum** at L , which is, indeed, found at $3^\circ,5$ (cf. Table IX).

Now it follows from the experimental data, that not only L presents a *maximum*, but also λ , and this at $3^\circ,4$ (Table IX). And because λ at first *decreases*, there must *necessarily*, besides this maximum, be also present a **minimum** for λ at low temperature. This, too, is confirmed experimentally. According to Table IX this minimum lies between $1^\circ,4$ and $1^\circ,5$, but nearer to $1^\circ,5$. *Theoretically* $1^\circ,47$ is found for it, as appears from what follows.

At this temperature

$$(2,2354 \cdot 10^{-6} \times 1,47 \times 1222,3 \cdot 10^{-6}) - (a_0 + 2\alpha T - 3\gamma T^2) \times \\ \times (118,45 - 20,71 \times 1,47) 10^{-6} + (a_0 + \alpha T - \gamma T^2) \times 1,47 \times 20,71 \cdot 10^{-6}$$

is found for

$$v^2 \frac{d\lambda}{dT} = 2\gamma T v - (a_0 + 2\alpha T - 3\gamma T^2) (\beta - 2\delta T) + (a_0 + \alpha T - \gamma T^2) T \cdot 2\delta.$$

Now $10^6 (a_0 + \alpha T - \gamma T^2) = 39,515 + 11,178 \times 1,47 - 1,1177 \times (1,47)^2 = 39,515 + 16,432 - 2,415 = 53,532$. And $10^6 (a_0 + 2\alpha T - 3\gamma T^2) = 39,515 + 32,864 - 7,245 = 65,134$. Hence, multiplying by 10^{12} , the above becomes, with $118,45 - 30,444 = 88,006$:

$$10^{12} v^2 \frac{d\lambda}{dT} = 4016,5 - 5732,2 + 1629,9 = - 85,8.$$

To this should be added 101,2 of a correction term with $\frac{dv}{dt}$, viz.

$$\left[-\frac{a_0 + \gamma T^2}{v^2} + \frac{2\alpha T(\beta - 2\delta T)}{v^3} \right] \frac{dv}{dT} \times 10^{12} v^2,$$

i.e.

$$\left[(a_0 + \gamma T^2) - \frac{2\alpha T(\beta - 2\delta T)}{v} \right] \times \left(-\frac{dv}{dT} \right) \times 10^{12}.$$

Now $-\frac{dv}{dt}$ is at $1^{\circ},47$ (see Table A in § 3, or formula (8) for D_1) $= 3,307 \cdot 10^{-6}$. With $10^6(a_0 + \gamma T^2) = 39,515 + 2,415 = 41,93$ this correction term, therefore, becomes:

$$\left[41,93 - \frac{2 \times 53,532 \times 1,47 \times 88,006}{1222,3} \right] \times 3,307,$$

or

$$(41,93 - 11,33) \times 3,307 = 30,60 \times 3,307 = 101,2.$$

Hence we get at $1^{\circ},47$:

$$10^{12} v^2 \frac{d\lambda}{dT} = -85,8 + 101,2 = +14,4.$$

At $1^{\circ},48$ we would have found in the same way:

$$(4043,7 - 5729,5 + 1643,2) + (-100) = +57.$$

And at $1^{\circ},4$ we get $(3826 - 5747 + 1536) + (-90) = -295$, from which it is therefore seen, that at slightly below $1^{\circ},47$ $\frac{d\lambda}{dT}$ passes through 0. At $1^{\circ},46$ this quantity is already about -30 ; all this in perfect harmony with Fig. 2 in connection with the values of λ , calculated from the experimental data (Table IX).

We once more point out how accurate the results are (also quantitatively) to which the formulae for a and b , determined from observations at $2^{\circ},3$, lead; also in the neighbourhood of $T=0$ and at very low temperatures (minimum D_1 and λ resp. at $0^{\circ},5$ and $1^{\circ},5$). We may, therefore, safely put aside the value $L_0 = \lambda_0 = 14$ gr. cal. of VERSCHAFFELT (based on NERNST's quite erroneous theory), and accept the value 17,5, following necessarily from the different data; which value, indeed, is in much better harmony with the observations of DANA and KAMERLINGH ONNES, whereas the value 14 would be in conflict with them. (See § 4 of the Second Part).