

Physics. — “On the Equation of State of Liquids and Solid Bodies at High and at Low Temperatures”. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

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1. Introduction.

Some five years ago ¹⁾ I showed, that when in VAN DER WAALS' equation of state for liquids and gases, viz.

$$p + \frac{a}{v^2} = \frac{RT}{v-b}, \dots \dots \dots (1)$$

b is considered as a function of v (which VAN DER WAALS had already done in another way), and when the simple relation

$$b = \frac{b_g}{1 + \frac{b_g - b_0}{v}} \dots \dots \dots (2)$$

is assumed for this, a perfect agreement — not only a qualitative, but also a quantitative one — is reached between the values for different quantities derived from the equation of state, and the experimental results; which so far had either not been the case, or in a much smaller degree. All this has been set forth more at length and more systematically in my book on the equation of state ²⁾, to which I refer the interested reader. (Cf. in particular p. 74—79, 91 et seq., and further the Chapters II and III). I will only mention the following points here.

1. From (2) in connection with (1) follows the *almost-rectilinearity* of the locus $\frac{1}{2}(D_1 + D_2) = f(T)$, in which D_1 and D_2 represent resp. the densities of the coexisting liquid and gas phases.

2. The values derived e.g. for the coefficient of compressibility β_p , now become more than three times greater than on assumption of

¹⁾ Compare inter alia my two papers in the Recueil des Trav. Chim. des P. B. 39, 215—242 and 371—410 (1920).

²⁾ “Die Zustandsgleichung von Gasen und Flüssigkeiten, usw.”, Leipzig L. Voss (1924). Compare also a paper published recently: “Ueber die Flüssigkeitsdichten bei verschiedenen Temperaturen” in the Zeitschr. f. anorg. u. allg. Chemie 140, 52—60 (1924).

b constant, in perfect harmony with the values found experimentally for this coefficient.

3. The *critical* quantities, e. g. $r = v_k : b_k$, $s = RT'_k : p_k v_k$, the vapour-pressure coefficient f , are now in perfect agreement with the values found experimentally for them. Thus for ordinary substances r now becomes = 2,1 instead of 3, s becomes = 3,8 instead of 2 $\frac{1}{2}$, f becomes 7 instead of 4.

4. The coefficients of the general vapour-pressure equation $\log p = -\frac{A}{T} - B \log T + C - DT$, which may be calculated by means of the equation of state corrected by means of (2), agree again perfectly with the values found experimentally for them. Compare in the book cited particularly p. 296—304 (He, H₂, Ar, C, H₂), p. 287—296 (mercury and carbon), and p. 311—326 (the molten metals).

In this way I found in 1920 for *solid carbon* the theoretical vapour-pressure equation ¹⁾:

$$\log^{10} p_{atm.} = -\frac{47120}{T} + 9,4,$$

while in 1923 for the first time by an experimental way (method LANGMUIR) the equation

$$\log^{10} p_{atm.} = -\frac{47000}{T} + 9,3$$

was found by WERTENSTEIN and JEDRZEJEWSKI ²⁾.

A better agreement with theoretical calculation — which according to the formulæ derived by me was only based on the coefficient of expansion of graphite extrapolated to 4000°, in connection with the value of \sqrt{a} for carbon found from the additive fundamental values — could hardly be expected ³⁾.

And this was also found for the other above-mentioned substances, and wherever in other cases the equation of state supplemented by (2) was applied.

Probably a and b_g are still functions of T ; I have, however, found that these two *temperature*-dependences always almost entirely neutralize each other, so that the simple assumption

¹⁾ Recueil 39, 647—655 (1920).

²⁾ C.R. 177, 316—319 (1923).

³⁾ Compare also Recueil 43, 598—599 (1924), C.R. 23 June 1924, p. 2250—2252. Further VAN LIEMPT, "Het toestandsdiagram van koolstof", Chem. Weekbl. 21, No. 45 (1924), in particular the last two pages.

that *only* b is a function of the *volume* (for also the dependence of a on the volume may be neglected), which is rendered by (2), suffices in practice.

2. Significance of the found dependence on the volume of b .

When (2) is substituted in (1), the equation:

$$p + \frac{a}{v^2} = \frac{RT}{v-b_0} \left(1 + \frac{b_g - b_0}{v} \right), \quad \dots \quad (3)$$

is obtained after some reduction (Zustandsgl. p. 91). In this b_g represents the limiting value of b at $v = \infty$, and b_0 that at $v = v_0$. If $1,35 m$ is assumed for b_0 ($m =$ real dimension of the molecule imagined spherical; $1,35 = \frac{1}{2} \sqrt{2} : \frac{1}{6} \pi =$ coefficient in case of densest packing) and the theoretical value $4m$ for b_g , then b_g becomes $= 3b_0$, so that it is also allowed to write:

$$p + \frac{a}{v^2} = \frac{RT}{v-b_0} \left(1 + \frac{2b_0}{v} \right) \quad \dots \quad (3a)$$

The dependence of b on the volume represented by (2) is of course only an *apparent* one, ensuing from the necessity of applying a correction to the faulty equation of state $p + \frac{a}{v^2} = \frac{RT}{v-b}$ with b constant. For instead of the Virial equation

$$pv + \frac{a}{v} - RT \frac{b}{v-b} = RT,$$

which leads to $p + \frac{a}{v^2} = \frac{RT}{v-b}$, and in which $RT \frac{b}{v-b}$ represents the so-called Virial of repulsion ($b = 4m$), strictly speaking the equation

$$pv + \frac{a}{v} - RT \frac{b_g}{v-b_0} = RT \quad \dots \quad (3b)$$

ought to have been drawn up, which, with $b_g = 4m = 3b_0$, leads to the correct equation of state (3), which has been experimentally confirmed in every respect.

It is known that LORENTZ has found $RT \frac{b_g}{v} = RT \frac{4m}{v}$ for the Virial of repulsion at $v = \infty$; it now appears that when v is no longer $= \infty$, the expression $RT \frac{b_g}{v-b_0}$ satisfies to the smallest volumes. In this $b_g = 4m$ might be called the "*kinetic*" co-volume, $b_0 = 1,35 m$ the *true* co-volume.

It is remarkable, that when it is tried to derive the equation of state by an entirely different way (see § 4), viz. from certain thermodynamic relations in connection with the assumption that at higher temperatures also for liquids (and gases) the quantity $\frac{3}{2} RT$ may be considered as the limiting value of the general expression for the kinetic energy, which has been derived quanta-theoretically e. g. by DEBYE — that *the same* expression (3^a) is then obtained, though in this derivation there has been no question of any dependence of b on the volume.

Putting generally for liquids:

$$p + \frac{a}{v^2} = \lambda \frac{L}{v-c},$$

in which c is an arbitrary *constant*, and L represents the general expression for the progressive energy of the molecules, the following value is found in the way mentioned (see § 4):

$$\lambda = \frac{2}{3} \left(1 + \frac{2c}{v} \right),$$

through which the equation of state for liquids (and gases) at higher temperatures ($L = \frac{3}{2} RT$) immediately passes into (3^a), when $c = b_0$ is taken. It will appear in the following paragraph from a single example that this equation of state is in perfect agreement with the experimental data.

3. Experimental confirmation of (3) or (3^a) for liquids at ordinary temperatures ($T = \frac{1}{2} T_k$).

We will derive from (3) the value of the coefficient of compressibility $\beta_p = -\frac{1}{v} \left(\frac{dv}{dp} \right)_t$. Differentiation with respect to p (T constant) yields, when $b_p - b_0 = \varphi$ is put in (3), from

$$p + \frac{a}{v^2} = \frac{RT}{v-b_0} \left(1 + \frac{\varphi}{v} \right)$$

the equation:

$$1 - \frac{2a}{v^3} \left(\frac{dv}{dp} \right)_t = \left[-\frac{RT}{(v-b_0)^2} \left(1 + \frac{\varphi}{v} \right) - \frac{RT\varphi}{(v-b_0)v^2} \right] \left(\frac{dv}{dp} \right)_t,$$

from which follows:

$$\beta_p = -\frac{1}{v} \left(\frac{dv}{dp} \right)_t = 1 : \left[-\frac{2a}{v^3} + \frac{RTv}{(v-b_0)^2} \left(1 + \frac{\varphi}{v} \right) + \frac{RT\varphi}{(v-b_0)v} \right].$$

When according to the equation of state $\frac{a}{v^2}$ is substituted in this

for $\frac{RT}{v-b_0} \left(1 + \frac{\varphi}{v}\right)$, in which, therefore, the external pressure is neglected, the following form results:

$$\frac{1}{\beta_p} = -\frac{2a}{v^2} + \frac{a}{v^2} \frac{v}{v-b_0} + \frac{a}{v^2} \frac{\varphi/v}{1+\varphi/v} = \frac{a}{v^2} \frac{v}{v-b_0} - \frac{2a}{v^2} \frac{1 + \frac{1}{2} \varphi/v}{1 + \varphi/v}.$$

Now $\frac{v}{v-b_0}$ is again $= \frac{a/v}{RT} : \left(1 + \frac{\varphi}{v}\right)$; hence finally:

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

or

$$\beta_p = \frac{\frac{RT}{a/v} \left(1 + \frac{\varphi}{v}\right)}{\frac{a}{v^2} \left[1 - 2 \frac{RT}{a/v} \left(1 + \frac{1}{2} \frac{\varphi}{v}\right)\right]} = \frac{\frac{m}{f} \left(1 + \frac{\varphi}{v}\right)}{\frac{a}{v^2} \left[1 - 2 \frac{m}{f} \left(1 + \frac{1}{2} \frac{\varphi}{v}\right)\right]}, \quad \dots \quad (4)$$

as $a/v = fRT_k$ ($f =$ vapour-pressure factor at T) and $m = T : T_k$.

Since for ordinary substances $f = 7$ at $m = \frac{1}{2}$, $\frac{m}{f}$ becomes $= \frac{1}{14}$, hence approximately with $\frac{\varphi}{v} = 2$:

$$\beta_p = \frac{\frac{1}{14}}{\frac{a/v^2 (1 - \frac{2}{14})}{a/v^2}} = \frac{0,3}{a/v^2}.$$

Without the factor $1 + \varphi/v$ in (3), i. e. if $b_0 = b_0$ had been put (b constant), the coefficient of compressibility would have therefore been at least $1 + \varphi/v$ times, i. e. **3 times smaller**. And now it actually appears from the following examples that values are found for β_p , which agree with (4); and *not* with the equation without $1 + \varphi/v$, hence with b constant, which equation would have had the simple

$$\text{form } \beta_p = \frac{m/f}{a/v^2 (1 - 2 m/f)}.$$

a. Mercury. (Cf. Zustandsgl. p. 114). Here $m = T : T_k = 295 : 1750 = 1 : 5,9$ at 22°C ., the value **4,1** being found for f from the vapour-tension at this temperature, so that m/f is $= \frac{1}{24}$. We assume the value **3** for $1 + \varphi/v = 1 + (b_0 - b_0)/v = 1 + 2b_0/v$, so that we obtain, when $10^6 a = 17140$ is assumed at 22° for a (from vapour-pressure observations; cf. Zust.gl. p. 101) and $10^6 v = 661$ (everything expressed in so-called "normal" units):

$$\beta_p = \frac{\frac{1}{24} \times 3}{39250 (1 - \frac{1}{12} \cdot 2)} = \frac{1}{261700} = 3,82 \cdot 10^{-6} \text{ (per atm/cm}^2\text{)}.$$

The value found was $3,9 \cdot 10^{-6}$ (per kg/cm^2), so that the agreement may be considered good. (It follows really from BRIDGMAN'S observations, that $1 + \varphi/v$ is somewhat greater than 3). But *without* the factor $1 + \varphi/v$ the value $\frac{1}{39250(1-1/12)} = \frac{1}{863500} = 1,16 \cdot 10^{-6}$ would have been calculated, hence *3,3 times too small!*

b. *Ether*. (Zust.gl. p. 115). At 20° $\frac{5}{8} : 7 = \frac{1}{11}$ is found for m/f . ($RT : a/v$ gives $1,073 : (2413 \times 4618 \cdot 10^{-6})$, as a/v_2 is $= 2413$ (loc. cit. p. 103), i. e. $1 : 10,4$. From BRIDGMAN'S experiments I calculated $8405 \cdot 10^6 : 4618 \cdot 10^6 = 1,82$ for φ/v , so that $1 + \varphi/v$ becomes $= 2,82$. Hence we have:

$$\beta_p = \frac{1/10,4 \times 2,82}{2413(1-1/12 \cdot 1,91)} = 178 \cdot 10^{-6},$$

while from 176 to 185 has been found (average 180), which is again in excellent harmony with the calculated value. The uncorrected value $\frac{1/10,4}{2413(1-1/5,2)}$ would have been $= 49 \cdot 10^{-6}$, hence *3,6 times too small!*

c. *Ethylchloride* (Zust.gl. p. 115). We refer to the book cited, and will only mention that the calculated value of β_p is $135 \cdot 10^{-6}$, while AMAGAT likewise found $135 \cdot 10^{-6}$. The uncorrected value would have been $34 \cdot 10^{-6}$, i. e. *4 times too small!*

4. Derivation of the equation of state from thermodynamic relations.

From the well-known thermodynamic formula

$$T \left(\frac{d^2 p}{dt^2} \right)_v = \left(\frac{dc_v}{dv} \right)_t \dots \dots \dots (5)$$

follows:

$$\left(\frac{dp}{dt} \right)_v = \int \frac{1}{T} \left(\frac{dc_v}{dv} \right)_t dt - \psi(v), \dots \dots \dots (a)$$

in which the meaning of $\psi(v)$ will appear from what follows.

In order to be able to integrate the above equation quite generally at all temperatures, we apply the following expedient. According to DEBYE'S well-known expression c_v is only a function of $x_m = hv_m/kT$: $kT = \theta : T$, in which the characteristic temperature θ will, in general, still be a function of v and T . For according to the well-known expression

$$\theta = \frac{3,61}{\omega} 10^{-3} M^{1/3} D^{-1/6} \beta_p^{-1/2},$$

in which ω is a numerical factor related to Poisson's coefficient σ (which is absent with liquids), θ can be represented by

$$\theta = Av^{1/6} \beta_p^{-1/2} = Av^{2/3} \beta^{-1/2}$$

when the coefficient $\beta = - \left(\frac{dv}{dp} \right)_t$ is introduced instead of

$\beta_p = - \frac{1}{v} \left(\frac{dv}{dp} \right)_t$, which will prove to be more convenient. Hence

$$x_m = Av^{2/3} \beta^{-1/2} T^{-1}$$

is obtained for $x_m = \theta : T$.

From this follows, as β is still a function both of v and T :

$$\frac{1}{x_m} \left(\frac{dx_m}{dv} \right)_t = \frac{2}{3} \frac{1}{v} - \frac{1}{2} \frac{1}{\beta} \left(\frac{d\beta}{dv} \right)_t = - \frac{1}{v} \left[-\frac{2}{3} + \frac{1}{2} \frac{v}{\beta} \left(\frac{d\beta}{dv} \right)_t \right];$$

$$\frac{1}{x_m} \left(\frac{dx_m}{dt} \right)_v = - \frac{1}{T} - \frac{1}{2} \frac{1}{\beta} \left(\frac{d\beta}{dt} \right)_v = - \frac{1}{T} \left[1 + \frac{1}{2} \frac{T}{\beta} \left(\frac{d\beta}{dt} \right)_v \right].$$

In consequence of this we get:

$$\left(\frac{dx_m}{dv} \right)_t = \frac{T}{v} \left(\frac{dx_m}{dt} \right)_v \times \frac{-2/3 + 1/2 \beta'_v}{1 + 1/2 \beta'_t} = \gamma \times \frac{T}{v} \left(\frac{dx_m}{dt} \right)_v,$$

in which γ is a numerical coefficient, which will in general still be a function of v and T ; β'_v being substituted for $\frac{v}{\beta} \left(\frac{d\beta}{dv} \right)$ and

β'_t for $\frac{T}{\beta} \left(\frac{d\beta}{dt} \right)_v$ for brevity's sake.

The above equation (a) now passes into

$$\left(\frac{dp}{dt} \right)_v = \int \frac{1}{T} \left(\frac{dc_v}{dv} \right)_t = \int \frac{1}{T} \frac{dc_v}{dx_m} \left(\frac{dx_m}{dv} \right)_t = \int \frac{\gamma}{v} \frac{dc_v}{dx_m} \left(\frac{dx_m}{dt} \right)_v dt - \psi(v),$$

i. e.

$$\left(\frac{dp}{dt} \right)_v = \int \frac{\gamma}{v} \left(\frac{dc_v}{dt} \right)_v dt - \psi(v), \dots \dots \dots (b)$$

through which — in consequence of the substitution of $\left(\frac{dc_v}{dv} \right)_v$ by $\left(\frac{dc_v}{dt} \right)_t$, which has been effected by the aid of x_m and the introduced coefficient γ — the integration with respect to T has been rendered possible; since the dependence of γ on the temperature will pract-

ically entirely disappear from the result, as will be shown in § 5. The integration of (b) gives:

$$\left(\frac{dp}{dt}\right)_v = \frac{\gamma_1}{v} c_v - \psi(v), \dots \dots \dots (c)$$

which, once more integrated with respect to T (c_v being $= \left(\frac{dE_t}{dt}\right)_v$), leads to

$$p + f(v) = \frac{\gamma_2}{v} E_t - T\psi(v), \dots \dots \dots (d)$$

in which according to § 5 γ_1 and γ_2 will differ only exceedingly little from the limiting value at $T = \infty$ of the coefficient γ above introduced, viz. from

$$\gamma = \frac{-\frac{3}{2} + \frac{1}{2}\beta'_v}{1 + \frac{1}{2}\beta'_t}, \dots \dots \dots (6)$$

which limiting value will appear to contain the factor $\frac{v}{v-b_0}$ for liquids.

The integration constant $f(v)$ remains thermodynamically undetermined, and can be determined only by considerations of a kinetic nature. (is $= a/v^2$ for liquids).

With regard to $T\psi(v)$ it may be stated that this is evidently $= \frac{\gamma_2}{v} (\mu - \frac{3}{2})RT$, as in the equation for p according to the usual kinetic derivation (e.g. by means of the Virial theorem) *not* the whole energy will occur in the second member, but only the *progressive* part of the energy of the molecules (L) — i. e. with exclusion of the potential energy of the forces acting between the atoms in the molecule. Hence $(\mu - \frac{3}{2})RT$, which relates to the said potential energy, must be subtracted from E_t . For mon-atomic substances μ is therefore $= \frac{3}{2}$, for di-atomic substances $= \frac{5}{2}$, etc. Hence we may write instead of (d):

$$p + f(v) = \frac{\gamma_2}{v} L \dots \dots \dots (7)$$

The considerations given in this paragraph are namely not only valid for solid substances, but also for liquids and gases; when it is only assumed, that the value of L then depends on $x_m = \theta : T$ (according to the relation of DEBYE) in quite the same way as for solid bodies. But according to the formula holding for θ this quantity has then

a much smaller value than for solid bodies. That the degeneration of the progressive energy L may be assumed to take place in an entirely analogous way in liquids and in gases as in solid bodies, has, indeed, already been assumed by many physicists (among others by KEESOM in many of his papers).

5. Determination of γ_2 (or λ) for liquids and gases.

We shall now proceed to the determination of the value of γ_2 , or rather — starting from the known form of the equation of state for liquids and gases, viz.

$$p + \frac{a}{v^2} = \frac{\lambda}{v-b_0} L, \quad \dots \dots \dots (8)$$

of the value of the quantity $\lambda = \gamma_2 \frac{v-b_0}{v}$, in which λ will be in the neighbourhood of 2, and in which the quantity $v : (v-b_0)$ will no longer occur directly as a factor.

At not too low temperatures the expansion into series

$$L = \frac{3}{2} RT \left(1 + \frac{1}{20} \frac{\theta^2}{T^2} - \frac{1}{1680} \frac{\theta^4}{T^4} + \frac{1}{90720} \frac{\theta^6}{T^6} - \text{etc.} \right) \quad \dots (a)$$

holds for L , at least when the zero-point energy is also taken into account in the expression

$$L = \frac{1}{2} RT \int_0^{x_m} \left(\frac{1}{2} + \frac{1}{e^x - 1} \right) x^2 dx.$$

($\frac{1}{2} x^2 dx$ under the integral sign). For otherwise L would become $= \frac{3}{2} RT \left(1 - \frac{3}{8} \frac{\theta}{T} + \frac{1}{20} \frac{\theta^2}{T^2} - \text{etc.} \right)$, which would not approach to $\frac{1}{2} RT$ even at the highest temperatures, but which would always remain the finite value of $\frac{1}{16} R\theta$ distant from it.

The quantity θ can be represented as function of T by

$$\theta^2 = \theta_0^2 \left(1 + \varphi_1 T + \frac{\varphi_2}{T} + \dots \right),$$

in which $\theta_0, \varphi_1, \varphi_2$, etc. are still functions of v . For in $\theta^2 = A^2 v^{4/3} \beta^{-1}$ (see § 4) β^{-1} will have the form $a + bT + \frac{c}{T} + \dots$ (see § 6). With regard to λ we may write:

$$\lambda = \lambda_0 \left(1 + \frac{\alpha}{T^2} + \dots \right),$$

in which terms with $1/T$ and $1/T^2$ must be omitted, as it will at once appear, that when the expansion into series of L is not pursued further than θ^3/T^3 , the expansion into series of λ must be continued to α/T^3 . But since only two equations will then be obtained for the two unknown quantities λ_0 and one coefficient, there can occur only one coefficient in the expansion into series of λ . If the expansion of L is carried up to θ^3/T^3 , that of λ must go to α'/T^4 , and there will be one equation more for the determination of the new coefficient α' . Etc. It is, therefore, clear that in the expansion into series of λ the terms with $1/T$ and $1/T^2$ will be absent.

Like λ , the coefficient α is again a function of v .

Finally, as will appear in § 6, the quantity γ in (6) will be represented by

$$\gamma = \gamma_0 \frac{1 + \sigma_1 T}{1 + \sigma_2 T},$$

in which further terms with $1/T$ may be omitted, and in which γ_0 , σ_1 , and σ_2 will still be functions of v .

We may now write:

$$\frac{\theta^2}{T^2} = \theta_0^2 \left(\frac{\varphi_1}{T} + \frac{1}{T^2} + \frac{\varphi_2}{T^3} \right); \frac{\theta^4}{T^4} = \theta_0^4 \left(\frac{\varphi_1^2}{T^2} + \frac{2\varphi_1}{T^3} \right); \frac{\theta^6}{T^6} = \theta_0^6 \frac{\varphi_1^3}{T^3},$$

when in what follows one restricts oneself to terms with $1/T^3$. This lowering of the degree with respect to T has of course been brought about by the term with T in the above expression for θ^2 . Hence we have according to (a):

$$L = \frac{3}{2} R \left[T + \frac{1}{20} \theta_0^2 \left(\varphi_1 + \frac{1}{T} + \frac{\varphi_2}{T^2} \right) - \frac{1}{1680} \theta_0^4 \left(\frac{\varphi_1^2}{T} + \frac{2\varphi_1}{T^2} \right) + \frac{1}{90720} \theta_0^6 \left(\frac{\varphi_1^3}{T^3} \right) \right] = \frac{3}{2} R \cdot Q,$$

and from this:

$$\begin{aligned} c_v &= \left(\frac{dE_t}{dt} \right)_v = \left(\frac{d(L + (\mu - \frac{1}{2}) RT)}{dt} \right)_v \quad (\text{cf. § 4}) = \\ &= \frac{3}{2} R \left[1 + \frac{1}{20} \theta_0^2 \left(-\frac{1}{T^2} - \frac{2\varphi_2}{T^3} \right) - \frac{1}{1680} \theta_0^4 \left(-\frac{\varphi_1^2}{T^2} - \frac{4\varphi_1}{T^3} \right) + \right. \\ &\quad \left. + \frac{1}{90720} \theta_0^6 \left(-\frac{2\varphi_1^3}{T^3} \right) \right] + \left(\mu - \frac{3}{2} \right) R, \end{aligned}$$

hence:

$$\begin{aligned} \left(\frac{dc_v}{dt} \right)_v &= \frac{3}{2} R \left[\frac{1}{20} \theta_0^2 \left(\frac{2}{T^3} + \frac{6\varphi_2}{T^4} \right) - \frac{1}{1680} \theta_0^4 \left(\frac{2\varphi_1^2}{T^3} + \frac{12\varphi_1}{T^4} \right) + \right. \\ &\quad \left. + \frac{1}{90720} \theta_0^6 \left(\frac{6\varphi_1^3}{T^4} \right) \right]. \end{aligned}$$

With $\lambda = \lambda_0 \left(1 + \frac{\alpha}{T^2}\right)$ we get:

$$\lambda L = \lambda_0 \cdot \frac{3}{2} R \left(Q + \frac{\alpha Q}{T^2}\right) = \lambda_0 \cdot \frac{3}{2} R \left(Q + \frac{\alpha(T + \dots)}{T^2}\right),$$

from which it appears that the expansion into series for λ need not go further than α/T^2 , when Q is not continued further than $1/T^2$ (see above). From the equation of state (8) follows, as $\frac{d^2}{dt^2} \left(\frac{3}{2} RQ\right)_v = \left(\frac{d^2 L}{dt^2}\right)_v = \left(\frac{dc_v}{dt}\right)_v$, according to the above:

$$\left(\frac{d^2 p}{dt^2}\right)_v = \frac{\lambda_0}{v - b_0} \left[\left(\frac{dc_v}{dt}\right)_v + \frac{3}{2} R \frac{6\alpha}{T^4} \right].$$

Now according to the thermodynamic relation (5), in connection with our transformation of $\left(\frac{dc_v}{dv}\right)_t$ into $\left(\frac{dc_v}{dt}\right)_v$ by means of γ , which we developed in § 4, the following equation ensues:

$$\left(\frac{d^2 p}{dt^2}\right)_v = \frac{1}{T} \left(\frac{dc_v}{dv}\right)_t = \frac{\gamma}{v} \left(\frac{dc_v}{dt}\right)_v,$$

so that

$$\frac{\lambda_0}{v - b_0} \left[\left(\frac{dc_v}{dt}\right)_v + \frac{3}{2} R \frac{6\alpha}{T^4} \right] = \frac{\gamma}{v} \left(\frac{dc_v}{dt}\right)_v = \frac{\gamma_0}{v} \frac{1 + \delta_1 T}{1 + \delta_2 T} \left(\frac{dc_v}{dt}\right)_v.$$

According to the above, the following form may be written for $\left(\frac{dc_v}{dt}\right)_v$:

$$\begin{aligned} \left(\frac{dc_v}{dt}\right)_v = \frac{3}{2} R \left[\frac{1}{T^2} \left(\frac{1}{10} \theta_0^2 - \frac{1}{840} \theta_0^4 \varphi_1^2 \right) + \right. \\ \left. + \frac{1}{T^4} \left(\frac{3}{10} \theta_0^2 \varphi_1 - \frac{1}{140} \theta_0^4 \varphi_1 + \frac{1}{15120} \theta_0^6 \varphi_1^3 \right) \right], \end{aligned}$$

or also

$$\left(\frac{dc_v}{dt}\right)_v = \frac{3}{2} R \left(\frac{A}{T^2} + \frac{B}{T^4} \right).$$

Hence, when both members of the above equation are divided by $\frac{3}{2} R$, and multiplied by $1 + \delta_2 T$, the following equation is obtained:

$$\lambda_0 \frac{v}{v - b_0} (1 + \delta_2 T) \left[\frac{A}{T^2} + \frac{B + 6\alpha}{T^4} \right] = \gamma_0 (1 + \delta_1 T) \left(\frac{A}{T^2} + \frac{B}{T^4} \right),$$

i.e.

$$\lambda_0 \frac{v}{v-b_0} \left[\frac{\sigma_2 A}{T^2} + \frac{A}{T^2} + \frac{\sigma_2 (B+6\alpha)}{T^2} \right] = \gamma_0 \left[\frac{\delta_1 A}{T^2} + \frac{A}{T^2} + \frac{\sigma_1 B}{T^2} \right].$$

Equalizing the terms with $1/T^2$ and $1/T^2$ in the two members now gives the two conditional equations for λ_0 and α , which were referred to above, viz.

$$\lambda_0 \frac{v}{v-b_0} \sigma_2 A = \gamma_0 \sigma_1 A \quad ; \quad \lambda_0 \frac{v}{v-b_0} [A + \sigma_2 (B + 6\alpha)] = \gamma_0 (A + \sigma_1 B).$$

The former leads immediately to

$$\lambda_0 = \frac{v-b_0}{v} \gamma_0 \frac{\sigma_1}{\sigma_2}, \dots \dots \dots (9)$$

while then from

$$\gamma_0 \frac{\sigma_1}{\sigma_2} [A + \sigma_2 (B + 6\alpha)] = \gamma_0 (A + \sigma_1 B)$$

ensues:

$$\sigma_1 [A + \sigma_2 (B + 6\alpha)] = \sigma_2 (A + \sigma_1 B),$$

i.e.

$$\sigma_1 \sigma_2 \cdot 6\alpha = (\sigma_2 - \sigma_1) A,$$

the whole term with B disappearing, and with it the coefficient σ_1 in the expression for θ^2 (see above). And we get:

$$\alpha = \frac{1}{6} \frac{\sigma_2 - \sigma_1}{\sigma_1 \sigma_2} A = \frac{1}{6} \frac{\sigma_2 - \sigma_1}{\sigma_1 \sigma_2} \left(\frac{1}{10} \theta_0^2 - \frac{1}{840} \theta_0^4 \varphi_1^2 \right), \dots (10)$$

by which the two coefficients λ_0 and α in $\lambda = \lambda_0 \left(1 + \frac{\alpha}{T^2} \right)$ are, therefore, expressed in a simple way in γ_0 , δ_1 and δ_2 of

$$\gamma = \gamma_0 \frac{1 + \delta_1 T}{1 + \delta_2 T} = \gamma_0 \frac{\sigma_1 (1 + 1/\delta_1 T)}{\sigma_2 (1 + 1/\delta_2 T)}$$

and φ_1 of $\theta^2 = \theta_0^2 (1 + \varphi_1 T)$. With regard to λ_0 it may be said that $\gamma_0 \frac{\delta_1}{\delta_2}$ is evidently the limiting value, to which γ approaches for great values of T .

6. Further calculation of λ_0 from β and γ .

We must now determine the value of γ , but for this the knowledge of $\beta = \left(\frac{dv}{dp} \right)_t$ and of the two differential quotients β'_0 and β'_t

is required (see § 4). With regard to β it may be stated that from (8), viz.

$$p + \frac{a}{v^2} = \frac{\lambda L}{v - b_0} = \lambda_0 \frac{^{3/2} RT}{v - b_0} \left(1 + \frac{1}{20} \frac{\theta^2}{T^2} - \dots \right),$$

with neglect of α/T^2 in $\lambda = \lambda_0 (1 + \alpha/T^2)$, and even of the term θ^2/T^2 , as having no influence on the result, follows:

$$1 - \frac{2a}{v^2} \left(\frac{dv}{dp} \right)_t = - \lambda_0 \frac{^{3/2} RT}{(v - b_0)^2} \left(\frac{dv}{dp} \right)_t,$$

from which

$$\beta = - \left(\frac{dv}{dp} \right) = 1 : \left[- \frac{2a}{v^2} + \lambda_0 \frac{^{3/2} RT}{(v - b_0)^2} \right] = 1 : N.$$

When determining $\beta'_v = \frac{v}{\beta} \left(\frac{d\beta}{dv} \right)_t$ and $\beta'_t = \frac{T}{\beta} \left(\frac{d\beta}{dt} \right)_v$ from this, a grave error would be committed, if e. g. $\lambda_0 \frac{^{3/2} RT}{v - b_0}$ was substituted for a/v^2 according to the equation of state, with neglect of p . For though p may safely be neglected with regard to a/v^2 , this is *not* the case with $\left(\frac{dp}{dv} \right)_t = - \frac{1}{\beta}$, which quantity runs into thousands (and for solid bodies into millions). For β must be differentiated with respect to v with T constant. In the same way the dependence on the temperature of β , v constant, would be estimated quite wrongly, when the substitution mentioned was executed. For $\left(\frac{dp}{dt} \right)_v$ is likewise very great. Such substitutions may only be made *after* the necessary differentiations described have been carried out (in which certain quantities must remain constant). A most elementary truth, but which is frequently overlooked!

We now get:

$$\beta'_v = \frac{v}{\beta} \left(\frac{d\beta}{dv} \right)_t = - \frac{v}{N} \left(\frac{dN}{dv} \right)_t = \frac{- \frac{6a}{v^3} + 2 \lambda_0 \frac{^{3/2} RT v}{(v - b_0)^2}}{- \frac{2a}{v^3} + \lambda_0 \frac{^{3/2} RT}{(v - b_0)^2}},$$

and for β'_t :

$$\beta'_t = \frac{T}{\beta} \left(\frac{d\beta}{dT} \right)_v = - \frac{T}{N} \left(\frac{dN}{dt} \right)_v = \frac{- \lambda_0 \frac{^{3/2} RT}{(v - b_0)^2}}{- \frac{2a}{v^3} + \lambda_0 \frac{^{3/2} RT}{(v - b_0)^2}}.$$

This yields according to (6):

$$\gamma = \frac{-\frac{2}{3} \left(-\frac{2a}{v^3} + \lambda_0 \frac{^{3/2}RT}{(v-b_0)^2} \right) + \frac{1}{2} \left(-\frac{6a}{v^3} + 2\lambda_0 \frac{^{3/2}RTv}{(v-b_0)^2} \right)}{\left(-\frac{2a}{v^3} + \lambda_0 \frac{^{3/2}RT}{(v-b_0)^2} \right) + \frac{1}{2} \left(-\lambda_0 \frac{^{3/2}RT}{(v-b_0)^2} \right)},$$

or

$$\begin{aligned} \gamma &= \frac{-\frac{5}{3} \frac{a}{v^3} + \lambda_0 \frac{^{3/2}RT}{(v-b_0)^2} \left(\frac{v}{v-b_0} - \frac{2}{3} \right)}{-\frac{2a}{v^3} + \frac{1}{2} \lambda_0 \frac{^{3/2}RT}{(v-b_0)^2}} = \\ &= \frac{5}{6} \frac{1 - \frac{1}{5} \lambda_0 \frac{^{3/2}RT}{a/v} \frac{v^2}{(v-b_0)^2} \frac{v+2b_0}{v-b_0}}{1 - \frac{1}{4} \lambda_0 \frac{^{3/2}RT}{a/v} \frac{v^2}{(v-b_0)^2}}. \end{aligned}$$

Also in this case we have not replaced α/v^3 by its value from the equation of state with neglect of p , because in formula (9) derived above the quantities δ_1 and δ_2 in $\gamma = \gamma_0 \frac{1 + \delta_1 T}{1 + \delta_2 T}$ are the *pure* coefficients of T , calculated from an equation, in which only v and T occur.

Now the formula (9) mentioned yields immediately:

$$\lambda_0 = \frac{v-b_0}{v} \gamma_0 \frac{\delta_1}{\delta_2} = \frac{v-b_0}{v} \cdot \frac{5}{6} \left(\frac{4}{5} \cdot \frac{v+2b_0}{v-b_0} \right) = \frac{2}{3} \left(1 + \frac{2b_0}{v} \right), \quad (11)$$

so that (8), with neglect of α/T^2 in $\lambda_0 (1 + \alpha/T^2)$, passes into

$$p + \frac{a}{v^2} = \frac{^{3/2}L}{v-b_0} \left(1 + \frac{2b_0}{v} \right), \quad \dots \dots \dots (12)$$

i. e. our equation (3^a) in § 2, as at higher temperatures $L = ^{3/2}RT$. Hence — making use of the thermodynamic relation (5) and of the general expression for E_t or L (DEBYE) at higher temperatures, where the expansion into series (a) of § 5 is valid — a value, which is *in perfect agreement* with the coefficient found by us in § 2 by an entirely different way, has been found for the coefficient λ , which had remained quite undetermined in (8). We may point out that (12) might also have been written in the form

$$p + \frac{a}{v^2} - RT \frac{3b_0}{v(v-b_0)} = \frac{RT}{v},$$

in which $RT \frac{3b_0}{v-b_0}$ may be interpreted as repulsive Virial (cf. § 2).

Accordingly at *higher* temperatures the equation of state

$$v + \frac{a}{v^2} = \frac{3}{2} L \left(1 + 2 \frac{b_0}{v}\right) = \frac{RT \left(1 + \frac{1}{20} \frac{\theta^2}{T^2} - \dots\right)}{v - b_0} \left(1 + 2 \frac{b_0}{v}\right)$$

holds for *liquids* (and *gases*); which approaches to

$$p + \frac{a}{v^2} = \frac{RT}{v - b_0} \left(1 + 2 \frac{b_0}{v}\right) = \frac{3 RT}{v - b_0} \left(1 - \frac{2}{3} \frac{v - b_0}{v}\right)$$

at sufficiently high temperature. As we have seen, this equation of state with the factor $1 + 2 \frac{b_0}{v}$ at RT is in harmony with the experimental data concerning the straight diameter, coefficient of compressibility, critical quantities, vapour-pressure equation, etc. It immediately ensues from the dependence on the volume of b in $p + \frac{a}{v^2} = RT : (v - b)$ found by us, but also from the thermodynamic formula $T \left(\frac{d^2 p}{dt^2}\right)_v = \left(\frac{dc_v}{dv}\right)_t$ in connection with DEBYE'S quanta-theoretical expansion into series for L .

For gases we have $v = \infty$, and λ becomes $= \lambda_0 = \frac{3}{2}$, so that simply $p = RT : v$.

At *very low* temperature in the neighbourhood of $T = 0$ we must use another expansion into series for L . The further development of this case will be treated in the sequel to this paper, in which also the equation of state will be derived for *solid* substances both at high and at low temperatures.

7: Concluding remark. (A thermo-dynamic sophism).

According to (c) of § 4 $\left(\frac{dp}{dt}\right)_v$ will be $= \frac{\gamma_1}{v} c_v$, when $\psi(v) = 0$ may be put, i. e. when $\left(\frac{dp}{dt}\right)_v$ at $T = 0$ converges to zero, parallel to c_v . But then the *coefficient of expansion* will also converge to 0 parallel to c_v . For from the known relation

$$\left(\frac{dv}{dt}\right)_p = - \left(\frac{dv}{dp}\right)_t \times \left(\frac{dp}{dt}\right)_v \quad \text{or} \quad \alpha_t = \beta_p \times s, \dots \quad (13)$$

in which $\alpha_t = \frac{1}{v} \left(\frac{dv}{dt}\right)_p$ is the coefficient of expansion, $\beta_p = \frac{1}{v} \left(\frac{dv}{dp}\right)_t$ the coefficient of compressibility, and $\left(\frac{dp}{dt}\right)_v$ the coefficient of tension, then follows immediately:

$$\alpha_t = \beta_p \times \frac{\gamma_1}{v} c_v, \dots \dots \dots (13a)$$

in which β_p will remain finite down to the lowest temperature, and γ_1 is a numerical coefficient, so that α_t will approach 0 proportional to c_v .

This property is, however, proved by some¹⁾ quasi-thermodynamically in the following wonderful way.

It is known that the general equation

$$dQ = c_p dt + l_p dp$$

leads to the equation

$$dS = \frac{c_p}{T} dt + \frac{l_p}{T} dp$$

for the entropy, when T and p are chosen as independent variables, in which $l_p = \left(\frac{dQ}{dp}\right)_t = -T \left(\frac{dv}{dt}\right)_p$, just as the quantity l_v is $= T \left(\frac{dp}{dt}\right)_v$ in $dQ = c_v dt + l_v dv$. In consequence of this we have:

$$dS = \frac{c_p}{T} dt - \left(\frac{dv}{dt}\right)_p dp,$$

hence, according to well-known rules of integration, in which e.g. T must be kept constant in the second integral, and equal to the lowest limit of the first integral:

$$S = \int_0^T \frac{c_p}{T} dt - \int_0^p \left(\frac{dv}{dt}\right)_p dp, \dots \dots \dots (a)$$

because S_0 disappears in $S = S_0$ at $T = 0, p = 0 (v = v_0)$.

This expression is sometimes shortened into

$$S = \int_0^T \frac{c_p}{T} dt, \dots \dots \dots (b)$$

which is correct, when the coefficient of expansion $\left(\frac{dv}{dt}\right)_p$ is assumed to approach 0 with c_v at $T = 0$ (see above). But now the shortened formula thus obtained is used to prove, that e.g. $\left(\frac{dv}{dt}\right)_p$ approaches 0 at $T = 0!!$

This marvellous reasoning runs as follows. From (cf. (b))

¹⁾ Cf. inter alia PLANCK, Thermodynamik (1921), p. 276.

$$\left(\frac{dS}{dp}\right)_t = \int_0^T \frac{1}{T} \left(\frac{dc_p}{dp}\right)_t dt = \int_0^T - \left(\frac{d^2v}{dt^2}\right)_p dt = - \left(\frac{dv}{dt}\right)_p + \left(\frac{dv}{dt}\right)_p \Big|_{(T=0)}$$

follows immediately, $\left(\frac{dS}{dp}\right)_t$ being $= - \left(\frac{dv}{dt}\right)_p$, that $\left(\frac{dv}{dt}\right)_p$ must necessarily be $= 0$ at $T=0$ (PLANCK, loc. cit.)!!

In reality *nothing* has been proved; for the formula, on which the reasoning is based, is only correct if it is assumed *beforehand*, that the thesis that is to be proved, *has already been proved*.

When, however, the second integral in (a) is *not* neglected, the following equation ensues:

$$\left(\frac{dS}{dp}\right)_t = \left[- \left(\frac{dv}{dt}\right)_p + \left(\frac{dv}{dt}\right)_p \Big|_{(T=0)} \right] - \left(\frac{dv}{dt}\right)_p \Big|_{(T=0)}$$

hence

$$\left(\frac{dS}{dp}\right)_t = - \left(\frac{dv}{dt}\right)_p$$

a known thermodynamic formula, which of course might much quicker be written down directly from the original equation

$$dS = \frac{c_p}{T} dt - \left(\frac{dv}{dt}\right)_p dp!$$

The *valid* proof, that $\left(\frac{dv}{dt}\right)_p$ really approaches to 0 parallel to c_v for solid substances, can only be furnished when it is *assumed* (see above), or proved in an independent way, that $\psi(v) = 0$ in (c) of § 4, in other words that $\left(\frac{dp}{dt}\right)_v$ converges to 0 at $T=0$. And inversely, when the approach of $\left(\frac{dv}{dt}\right)_p$ is assumed to be known, the approach of $\left(\frac{dp}{dt}\right)_v$ to 0 can be derived from (13), from which it then *follows*, that $\psi(v)$ must be $= 0$.

But "proofs" like the above, which are no proofs at all, should be guarded against. Unfortunately in many books from a certain school, recently published on these subjects, various new, often very questionable curtailed "thermodynamic" formulae are found; of which the elder generation never dreamt, and which — the above proves it — should be treated with the greatest caution.

Tavel sur Clarens, Suisse,

December 1924.