

Physics. — “On the Equation of State of Solid Substances in Connection with the General Expression for the Energy.” II. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

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I

The Equation of Energy at Higher Temperature.

1. After having established in our preceding paper ¹⁾, that the equation of state of solid substances at *higher temperatures* must possess the form

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

in which

$$b = \frac{b_g}{1 + \frac{b_g - b_{00}}{v}} = \frac{b_g}{1 + \frac{\varphi}{v}}, \quad \text{or} \quad \underline{v - b_{00} = (v - b) \left(1 + \frac{\varphi}{v} \right)}, \quad \dots (2)$$

we now proceed to the solution of the more general problem, what will be the form of the equation of state at somewhat lower temperatures, when the progressive energy of the molecules slowly begins to “degenerate”, so that $L = \frac{3}{2}RT$ must be replaced by the expression of DEBYE:

$$L = \frac{3}{2}RT \left(1 + \frac{1}{20} \frac{\theta^2}{T^2} - \frac{1}{1680} \frac{\theta^4}{T^4} + \dots \right), \quad \dots \dots (3)$$

which holds at *comparatively high* temperatures (the development into series at low temperatures will be treated in Chapter IV).

This progressive Energy is half the total energy of path for *solid* substances (kinetic + potential energy in the paths round the positions of equilibrium of the different molecules). In the above expression the so-called *zero-point energy* is included. For in the general expression

$$L = \frac{9}{2} \frac{RT}{x_m^3} \int_0^{x_m} \left(\frac{1}{2} + \frac{1}{e^x - 1} \right) x^3 dx,$$

in which x is $= \frac{\beta v}{T} \left(\beta = \frac{h}{k} \right)$, and ν_m represents the maximum frequency given by

$$\nu_m^3 = \frac{3 \bar{c}^3 N}{4\pi v},$$

¹⁾ These Proceed. 29, 95 (1926).

so that x_m is $= \frac{\beta v_m}{T}$, the term $1/2$ within the integral sign refers to the zero point energy, as immediately appears from the derivation. Execution of the integration then gives:

$$L = \frac{9/2 RT}{x_m^3} \left[\frac{1}{8} x_m^4 + \left(-\frac{1}{8} x_m^4 + \frac{1}{3} x_m^3 + \frac{1}{60} x_m^5 - \frac{1}{5040} x_m^7 + \dots \right) \right],$$

in which the first $\frac{1}{8} x_m^4$ refers to the term $\frac{1}{2}$ (hence to the zero point energy) and the form between () to the integral with $e^x - 1$. In consequence of this L becomes:

$$L = \frac{3}{2} RT \left(1 + \frac{1}{20} x_m^2 - \frac{1}{1680} x_m^4 + \dots \right),$$

which is in harmony with (3), when also

$$\theta = \beta v_m = \beta \bar{c} \sqrt[3]{\frac{3N}{4\pi v}}$$

is introduced, so that x_m becomes $= \theta : T$.

2. In the above expression for θ (the so-called "characteristic" temperature) c is the mean velocity of propagation of the elastic waves, given for solid substances by

$$\bar{c} = \frac{f}{(\sigma D)^{1/2}},$$

in which f is a pretty complicated factor containing the so-called POISSON modulus μ (into which we shall not enter any further here), σ the coefficient of compressibility $= -\frac{1}{v} \left(\frac{dv}{dp} \right)_t$, and $D = \frac{M}{v}$ the density. Then we get the following equation:

$$\theta = \beta \sqrt[3]{\frac{3N}{4\pi}} \times f \sigma^{-1/2} M^{-1/2} v^{1/2} v^{-1/3}.$$

In this $\beta = h : k = 4,77 \cdot 10^{-11}$, $\sqrt[3]{\frac{3}{4\pi}} = 0,6203$, $N = 0,6060 \cdot 10^{24}$, hence $N^{1/3} = 0,8462 \cdot 10^8$, therefore

$$\theta = 0,00250 f \cdot M^{-1/2} \sigma^{-1/2} v^{1/6}.$$

When in this $\sigma_1 = -\left(\frac{dv}{dp} \right)_t$ is substituted for $\sigma = -\frac{1}{v} \left(\frac{dv}{dp} \right)_t$, we get

$$\theta = 0,00250 f \cdot M^{-1/2} \sigma_1^{-1/2} v^{2/3},$$

in which for different metals f may lie between 0,96 ($\mu = 0,20$) and 0,37 ($\mu = 0,45$). In many cases $\mu = 1/3$, and then $f = 0,69$. If we write

$$\theta = C v^{2/3} \sigma_1^{-1/2},$$

in which therefore

$$\underline{C = 0,0025 f M^{-1/2}},$$

then becomes

$$\theta^2 = C^2 v^{4/3} \sigma_1^{-1} \dots \dots \dots (4)$$

From this formula (valid for *all states of aggregation*; for liquids and gases $f=1$ in C, but then the known factor $\sqrt{c_p : c_v}$ must be added in the expression for the velocity of propagation, hence $c_p : c_v$ in C^2) θ may be successfully calculated for different metals; these values are in excellent harmony with the values calculated for them.

3. When now σ or σ_1 is calculated from the equation of state, it will at once appear that θ^2 in any case (i. e. at comparatively high temperatures) can be represented by

$$\theta^2 = \theta_a^2 \left(1 + \varphi_1 T + \frac{\varphi_2}{T} + \dots \right), \dots \dots \dots (5)$$

in which $\theta_a, \varphi_1, \varphi_2$, etc. are still functions of v . In this it is of importance noteworthy, that θ^2 contains still a *term* with T , so that the above equation (3) for L after all does not give a development into series with $\frac{1}{T^2}, \frac{1}{T^4}$, etc., but with $\frac{1}{T}, \frac{1}{T^2}, \frac{1}{T^3}$, etc., in consequence of which a term without T will occur in L .

Substituting (5) in (3), and leaving the terms with $1 : T^3$ etc., which contain φ_2 , out of account, we get:

$$L = \frac{3}{2} RT \left(1 + \frac{A}{T} + \frac{B}{T^2} + \dots \right), \dots \dots \dots (6)$$

in which

$$A = \frac{1}{20} \theta_a^2 \varphi_1 \quad ; \quad B = \frac{1}{20} \left(\theta_a^2 - \frac{1}{84} \theta_a^4 \varphi_1^2 \right), \dots \dots \dots (6a)$$

Hence the term in question without T is $\frac{3}{2} RA$.

II.

The Equations of Energy and of State at Higher Temperatures.

1. It is now our task to calculate from (6) and (6a) the coefficients P and Q in the general equation of state (the quantity λ , which refers to the so-called „static” virial of repulsion (see our first Paper) appears only in solid substances)

$$p + \frac{a}{v^2} = \frac{\lambda + RT \left(1 + \frac{P}{T} + \frac{Q}{T^2} + \dots \right)}{v - b}, \dots \dots \dots (7)$$

in which the development into series will also contain $\frac{1}{T}, \frac{1}{T^2}$, etc. We

shall see, that P , Q , etc. are related in an exceedingly simple way with A , B , etc. in the equation (6) for L , but are *by no means equal* — in contradiction with what has often been supposed.

For the calculation of P we make use of the general formula for the Energy E , viz. (the lower limits ∞ for T and v have been arbitrarily chosen, but are rational in view of the higher temperatures we are now considering)

$$E = \int_{\infty}^T c_v dT + \int_{\infty}^v \left(T \left(\frac{dp}{dt} \right)_v - p \right) dv + E_{T=\infty, v=\infty}, \dots \dots (8)$$

in which the quantity under the second integral sign (with regard to v) must be taken at $T=\infty$, i.e. at the lower limit of the *first* integral (with regard to T)¹⁾.

2. We now calculate further the quantities occurring in the second

¹⁾ For, if in general

$$du = \frac{\partial u}{\partial x} dx + \frac{\partial u}{\partial y} dy = A_{x,y} dx + B_{x,y} dy,$$

in which u is a function of x and y , du being a total differential (as is here the case with dE), we shall prove that it follows from this that

$$u_{x,y} - u_{a,b} = \int_a^x A_{x,y} dx + \int_b^y B_{a,y} dy,$$

in which, therefore, in the *second* integral x has been replaced by the *lower* limit a of the first integral. For from this latter equation follows by *total* differentiation with regard to x and y :

$$du = \frac{\partial}{\partial x} \left[\int_a^x A_{x,y} dx + \int_b^y B_{a,y} dy \right] dx + \frac{\partial}{\partial y} \left[\int_a^x A_{x,y} dx + \int_b^y B_{a,y} dy \right] dy,$$

or also

$$du = (A_{x,y} + 0) dx + \left[\int_a^x \frac{\partial A_{x,y}}{\partial y} dx + B_{a,y} \right] dy,$$

as $\frac{\partial}{\partial x} \int_b^y B_{a,y} dy = \int_b^y \frac{\partial B_{a,y}}{\partial x} dy = 0$, because $B_{a,y}$ (in which x has been substituted by a)

is independent of x . Now, however, $\frac{\partial A_{x,y}}{\partial y} = \frac{\partial B_{x,y}}{\partial x}$, according to a known property of total differentials, so that

$$du = A_{x,y} dx + \left[\int_a^x \frac{\partial B_{x,y}}{\partial x} dx + B_{a,y} \right] dy$$

hence

$$du = A_{x,y} dx + \left[(B_{x,y} - B_{a,y}) + B_{a,y} \right] dy = A_{x,y} dx + B_{x,y} dy,$$

integral of (8) from the equation of state (7). As regards c_v , as $(a, b$ and λ independent of $T)$

$$E = 2L + f(v) = 2 \cdot \frac{3}{2} RT \left(1 + \frac{A}{T} + \frac{B}{T^2} + \dots \right) + \mu \cdot RT + f(v)$$

(the factor 2 only for solid; μ for multi-atomic mol.), we have immediately :

$$c_v = 2 \cdot \frac{3}{2} R \left(1 - \frac{B}{T^2} - \dots \right) + \mu R.$$

When $a, b,$ and λ are supposed independent of T (see above),

$$\left(\frac{dp}{dt} \right)_v = \frac{R}{v-b} - \frac{R}{T^2} \frac{Q}{v-b} - \dots$$

follows from (7), hence :

$$\begin{aligned} T \left(\frac{dp}{dt} \right)_v - p &= \left(\frac{RT}{v-b} - \frac{R}{T} \frac{Q}{v-b} \right) - \left(-\frac{a}{v^2} + \frac{\lambda}{v-b} + \frac{RT}{v-b} + R \frac{P}{v-b} + \frac{R}{T} \frac{Q}{v-b} \right) \\ &= \frac{a}{v^2} - \frac{\lambda}{v-b} - R \frac{P}{v-b} - \frac{R}{T} \frac{2Q}{v-b}. \end{aligned}$$

Hence extrapolated to $T = \infty$, we have

$$\left(T \left(\frac{dp}{dt} \right)_v - p \right)_{T=\infty} = \frac{a}{v^2} - \frac{\lambda}{v-b} - R \frac{P}{v-b},$$

so that, neglecting the term μRT , the following equation may be written for (8):

$$E = 2 \cdot \frac{3}{2} R \left[(T - T_\infty) + \frac{B}{T} \right] + \left[-\frac{a}{v} - \int_\infty^v \frac{\lambda}{v-b} dv - R \int_\infty^v \frac{P}{v-b} dv \right] + E_{T=\infty}.$$

But in this $E_{T=\infty}$ is evidently $= \left[2 \cdot \frac{3}{2} RT_\infty + 2 \cdot \frac{3}{2} RA_{v=\infty} \right] + \frac{a}{v_{00}}$, be-

cause the potential energy of the attractive forces is $\frac{a}{v_{00}}$ for $v = \infty$ (for liquids and gases v_0 may be simply written), the first part referring to $2L_\infty$. (the potential energy of the ("static") repulsive forces will disappear in solid substances at $v = \infty$).

Now $A = \frac{1}{20} \theta_a^2 \varphi_1$ (see above), and as we shall see presently (in Chapter III),

g. e. d. (It can, likewise, be proved that from $du = A_{x,y} dx + B_{x,y} dy$ follows $u_{x,y} - u_{a,b} = \int_a^x A_{x,b} dx + \int_b^y B_{x,y} dy$, in which inside the first integral y has been replaced by the lowest limit b of the second integral).

When this is applied to the well-known equation $dE = c_v dT + \left[T \left(\frac{dp}{dt} \right)_v - p \right] dv$, equation (8) ensures naturally.

this is $= 0$ at $v = \infty$ (on account of the factor $v^{-2/3}$; see (14) and (15)). Hence we have finally:

$$E = \left(\frac{a}{v_{00}} - \frac{a}{v} \right) - \int_{\infty}^v \frac{\lambda}{v-b} dv + 2 \cdot \frac{3}{2} RT \left(1 + \frac{B}{T^2} \right) - R \int_{\infty}^v \frac{P}{v-b} dv.$$

But according to (6) is also:

$$E = \left(\frac{a}{v_{00}} - \frac{a}{v} \right) - \int_{\infty}^v \frac{\lambda}{v-b} dv + 2 \cdot \frac{3}{2} RT \left(1 + \frac{A}{T} + \frac{B}{T^2} \right), \quad (9)$$

where $2L$ has been increased by the potential energy of the attractive forces and (in solid substances) by that of the „static” repulsive forces¹⁾, so that

$$2 \cdot \frac{3}{2} RA = -R \int_{\infty}^v \frac{P}{v-b} dv$$

1) To prevent the potential energy from becoming $= \infty$ at finite values of v , it would be better to substitute $\frac{\lambda}{v}$ for λ in the equation of state. The expression

$$\begin{aligned} \int_{\infty}^v \frac{\lambda}{v-b} dv &= \int_{\infty}^v \frac{\lambda}{v-b_{00}} \left(1 + \frac{\varphi}{v} \right) dv = \lambda \left(\log(v-b_{00}) + \frac{\varphi}{b_{00}} \log \frac{v-b_{00}}{v} \right) \Big|_{\infty}^v = \\ &= \lambda \left(\log \frac{v-b_{00}}{\infty} + \frac{\varphi}{b_{00}} \log \frac{v-b_{00}}{v} \right) = \lambda \left[\log \frac{(v-b)(1+\varphi/v)}{\infty} + \right. \\ &\quad \left. + \frac{\varphi}{b_{00}} \log \left(\frac{v-b}{v} \left(1 + \frac{\varphi}{v} \right) \right) \right], \end{aligned}$$

which would be $= -\infty$ for all finite values of v , becomes with $\frac{\lambda}{v}$:

$$\begin{aligned} \int_{\infty}^v \frac{\lambda}{v(v-b)} dv &= \int_{\infty}^v \frac{\lambda}{v(v-b_{00})} \left(1 + \frac{\varphi}{v} \right) dv = \\ &= \lambda \left[\frac{1}{b_{00}} \log \frac{v-b_{00}}{v} + \varphi \int_{\infty}^v \left(-\frac{1}{b_{00}v^2} + \frac{1}{b_{00}^2} \left(\frac{1}{v-b_{00}} - \frac{1}{v} \right) \right) dv \right] = \\ &= \lambda \left[\frac{1}{b_{00}} \log \frac{v-b_{00}}{v} + \frac{\varphi}{b_{00}^2} \left(\frac{b_{00}}{v} + \log \frac{v-b_{00}}{v} \right) \right], \end{aligned}$$

which now remains finite for finite values of v , as it should.

In consequence of the substitution of $\frac{\lambda}{v}$ for λ (which has practically very little influence for solid substances (at $p = 0$) on the different calculations, because v varies only little between the melting-point of solid substances and $T = 0$), not λ stands next to RT , in (1), but $\frac{\lambda}{v}$, in consequence of which $-RT$ being of the dimensions of $\frac{a}{v} - \lambda$ now becomes analogous to a , and not to $\frac{a}{v}$.

must be found. A will, therefore, have to disappear for $v = \infty$ (see above), and we have for the quantity P in the equation of state (7):

$$\underline{P = -2 \cdot \frac{3}{2} (v-b) \frac{dA}{dv} \dots \dots \dots (10)}$$

In this A is $= \frac{1}{20} \theta_a^2 \varphi_1$ according to (6^a), and we shall therefore have to calculate $\theta_a^2 \varphi_1$ (in Chapter III). It may still be mentioned, that the quantities λ and a can never be determined by means of thermodynamic relations; these quantities can only be calculated on the basis of molecular-theoretical considerations.

3. For the calculation of Q, S, U etc. in (7) we start from the well-known equation

$$T \left(\frac{d^2 p}{dt^2} \right)_v = \left(\frac{dc_v}{dv} \right)_t \dots \dots \dots (11)$$

In this is, according to (7):

$$\left(\frac{dp}{dt} \right)_v = \frac{R}{v-b} - \frac{1R}{T^2} \frac{Q}{v-b} - \frac{2R}{T^3} \frac{S}{v-b} - \frac{3R}{T^4} \frac{U}{v-b} - \dots$$

hence

$$T \left(\frac{d^2 p}{dt^2} \right)_v = \frac{1.2R}{T^2} \frac{Q}{v-b} + \frac{2.3R}{T^3} \frac{S}{v-b} + \frac{3.4R}{T^4} \frac{U}{v-b} + \dots$$

Further follows from $c_v = 2 \cdot \frac{3}{2} R \left(1 - \frac{1B}{T^2} - \frac{2C}{T^3} - \frac{3D}{T^4} - \dots \right)$:

$$\left(\frac{dc_v}{dv} \right)_t = -2 \cdot \frac{3}{2} R \left(\frac{1}{T^2} \left(\frac{dB}{dv} \right)_t + \frac{2}{T^3} \left(\frac{dC}{dv} \right)_t + \frac{3}{T^4} \left(\frac{dD}{dv} \right)_t \right).$$

We find, therefore, immediately:

$$\underline{Q = -2 \cdot \frac{3}{2} \frac{v-b}{2} \frac{dB}{dv}}; \underline{S = -2 \cdot \frac{3}{2} \frac{v-b}{3} \frac{dC}{dv}}; \underline{U = -2 \cdot \frac{v-b}{4} \frac{dD}{dv}}, \quad (12)$$

which expressions are in perfect harmony with (10). The factor 2 disappears for liquids and gases.

The quantities P, Q, S, U , etc. in the equation of state

$$p + \frac{a}{v^2} = \frac{1}{v-b} \left[\lambda + RT \left(1 + \frac{P}{T} + \frac{Q}{T^2} + \frac{S}{T^3} + \frac{M}{T^4} + \dots \right) \right],$$

in which the quantity λ only appears in solid substances, are therefore *not equal* to the corresponding quantities A, B, C, D , etc. of the equation of Energy

$$E = 2 \cdot \frac{3}{2} RT \left(1 + \frac{A}{T} + \frac{B}{T^2} + \frac{C}{T^3} + \frac{D}{T^4} + \dots \right) + \text{Pot. Energy,}$$

but there is a simple relation between them (expressed by 10) and (12) ¹⁾.

III.

Calculation of $A = \frac{1}{20} \theta_a^2 \varphi_1$ and $\frac{dA}{dv}$ at Higher Temperatures.

1. For the calculation of $\theta_a^2 \varphi_1$ in (5), viz. $\theta^2 = \theta_a^2 (1 + \varphi_1 T)$, we must determine $\theta^2 = C^2 v^{4/3} \sigma_1^{-1}$ according to (4). But for this it is necessary in the first place to know the value of $\sigma_1 = -\left(\frac{dp}{dv}\right)_t$. Taking (10) into account, the equation of state becomes:

$$p = -\frac{a}{v^2} + \frac{\lambda + RT}{v - b} - 2 \cdot \frac{3}{2} R \frac{dA}{dv} \dots = -\frac{a}{v^2} + \frac{\lambda + RT}{v - b_{00}} \left(1 + \frac{\varphi}{v} \right) - 2 \cdot \frac{3}{2} R \frac{dA}{dv} \dots$$

from which follows:

$$\left(\frac{dp}{dv}\right)_t = \frac{2a}{v^3} - (\lambda + RT) \left(\frac{1 + \varphi/v}{(v - b_{00})^2} + \frac{\varphi/v^2}{v - b_{00}} \right) - 2 \cdot \frac{3}{2} R \frac{d^2 A}{dv^2} \dots$$

hence

$$\sigma_1^{-1} = -\left(\frac{dp}{dv}\right)_t = \left[-\frac{2a}{v^3} + 2 \cdot \frac{3}{2} R \frac{d^2 A}{dv^2} + \frac{\lambda}{(v - b_{00})^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi v - b_{00}}{v} \right) \right] + \frac{RT}{(v - b_{00})^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi v - b_{00}}{v} \right),$$

so that from $\theta^2 = C^2 v^{4/3} \sigma_1^{-1} = \theta_a^2 (1 + \varphi_1 T)$ follows:

$$\theta_a^2 = C^2 v^{4/3} \left[-\frac{2a}{v^3} + 2 \cdot \frac{3}{2} R \frac{d^2 A}{dv^2} + \frac{\lambda}{(v - b_{00})^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi v - b_{00}}{v} \right) \right],$$

and

$$\theta_a^2 \varphi_1 = C^2 R \frac{v^{4/3}}{(v - b_{00})^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi v - b_{00}}{v} \right). \quad \dots \quad (13)$$

From $A = \frac{1}{20} \theta_a^2 \varphi_1$ follows therefore:

$$\frac{dA}{dv} = \frac{1}{20} C^2 R \left[\left(\frac{4}{3} \frac{v^{1/3}}{(v - b_{00})^2} - 2 \frac{v^{4/3}}{(v - b_{00})^3} \right) \left(1 + \frac{\varphi}{v} + \frac{\varphi v - b_{00}}{v} \right) - \frac{v^{4/3}}{(v - b_{00})^2} \left(\frac{\varphi}{v^2} + \frac{\varphi v - b_{00}}{v^2} + \frac{\varphi}{v} \left(\frac{v - b_{00}}{v^2} - \frac{1}{v} \right) \right) \right],$$

¹⁾ Expressions, as among others have been drawn up by K. BENNEWITZ, Z. f. phys. Ch. 110, p. 725 (1924), i. e. (for ideal gases) $pv = RT \left(1 + \frac{U}{E_0} \right)$, and by many others, must therefore be absolutely rejected.

or

$$\frac{dA}{dv} = \frac{1}{20} C^2 R \frac{v^{1/3}}{(v-b_{00})^2} \left[\left(\frac{4}{3} - 2 \frac{v}{v-b_{00}} \right) \left(1 + \frac{\varphi}{v} + \frac{\varphi}{v} \frac{v-b_{00}}{v} \right) - 2 \frac{\varphi}{v} \frac{v-b_{00}}{v} \right],$$

or also with $\frac{v-b_{00}}{v} = z'$ and $\frac{\varphi}{v} = \omega$:

$$\frac{dA}{dv} = \frac{1}{20} C^2 R \frac{v^{1/3}}{(v-b_{00})^2} \left[\left(\frac{4}{3} - \frac{2}{z'} \right) + \omega \left(\left(\frac{4}{3} - \frac{2}{z'} \right) (1+z') - 2z' \right) \right],$$

i.e.

$$\frac{dA}{dv} = \frac{1}{20} C^2 R v^{-2/3} \frac{v}{(v-b_{00})^2} \left[\left(\frac{4}{3} - \frac{2}{z'} \right) - \omega \left(\frac{2}{3} + \frac{2}{z'} + \frac{2}{3} z' \right) \right].$$

With $v - b_{00} = (v - b) (1 + \omega)$ and $\frac{v-b}{v} = z$ we get $z' = z (1 + \omega)$,

hence

$$\frac{dA}{dv} = \frac{1}{20} C^2 R v^{-2/3} \frac{v}{(v-b)^2 (1+\omega)^2} \left[\frac{4}{3} - \frac{2}{z} \frac{1}{1+\omega} - \omega \left(\frac{2}{3} + \frac{2}{z} \frac{1}{1+\omega} + \frac{2}{3} z (1+\omega) \right) \right],$$

or

$$\frac{dA}{dv} = \frac{1}{20} C^2 R v^{-2/3} \frac{v^2}{(v-b)^3 (1+\omega)^3} \left[\frac{4}{3} z (1+\omega) - 2 - \omega \left(\frac{2}{3} z (1+\omega) + 2 + \frac{2}{3} z^2 (1+\omega)^2 \right) \right].$$

so that we get with $-2 - 2\omega = -2(1 + \omega)$:

$$-(v-b) \frac{dA}{dv} = \frac{1}{10} \frac{C^2 R v^{-2/3}}{z^2 (1+\omega)^2} \left(1 - \frac{1}{3} z (2-\omega) + \frac{1}{3} z^2 \omega (1+\omega) \right). \quad (\alpha)$$

From this we see, that the calculation of $\frac{d^2 A}{dv^2}$, occurring in θ_a^2 , will become very complicated, so that we will omit the calculation of Q , in which $\frac{dB}{dv}$ occurs, because B contains θ_a^2 according to (6^a). And the same thing applies to the following coefficients in a still greater degree, where, besides, the coefficients φ_2 etc. would have to be calculated according to (5). For $A = \frac{1}{20} \theta_a^2 \varphi_1$ we found above according to (13):

$$A = \frac{1}{20} C^2 R v^{-2/3} \frac{v^2}{(v-b_{00})^2} \left(1 + \omega + \omega \frac{v-b_{00}}{v} \right),$$

or with $v - b_{00} = (v - b) (1 + \omega)$, $\frac{v-b}{v} = z$:

$$A = \frac{1}{20} \frac{C^2 R v^{-2/3}}{z^2 (1+\omega)} (1 + \omega z). \quad (\beta)$$

Putting

$$\underline{A_0 = \frac{1}{20} \frac{C^2 R v^{-2/3}}{z^2 (1+\omega)^2} \dots \dots \dots (14)}$$

we get according to (α), (β) and (10):

$$\underline{A = A_0(1+\omega)(1+\omega z) ; P = 2.3 A_0 \left(1 - \frac{1}{3} z(2-\omega) + \frac{1}{3} z^2 \omega(1+\omega) \right)} . \quad (15)$$

through which the quantity P of the equation of state

$$\left(p + \frac{a}{v^2} \right) (v-b) = \lambda + RT \left(1 + \frac{P}{T} \right)$$

is expressed in the quantity A of the equation of Energy

$$E = 2 \cdot \frac{3}{2} RT \left(1 + \frac{A}{T} \right) + \text{Pot. Energy.}$$

As we already remarked in Chapter II: P is *by no means equal to* A , and this will also apply to the following coefficients. Only in the case of ideal gases (see further below) the different coefficients would become equal to each other ($z = 1$, $\omega = 0$), thus $A = P = A_0$ (the factor 2 in P (and E) appears only in solid substances).

2. In *ordinary liquids* (e.g. in benzene) $z = \frac{1}{14}$ and $\omega = 2 \frac{1}{7}$ in the neighbourhood of the point of solidification ($5,5^\circ \text{C}$.), hence

$$A = 3,624 A_0 ; P = 3,045 A_0.$$

In *molten copper* $z = \frac{1}{38,2}$, $\omega = 2$ at 1083°C ., through which A and P become:

$$A = 3,157 A_0 ; P = 3,004 A_0.$$

And in *solid copper* $z = \frac{1}{6}$, $\omega = 0,6$, (20°C .), hence

$$A = 1,760 A_0 ; P = 5,587 A_0.$$

Accordingly in the two liquids mentioned, P is only slightly smaller than A , whereas in solid copper P is more than 3 times as great as A .

Let us now determine the different values of A_0 according to the above expression (14). C being $= 0,0025 f \times M^{-1/2}$ (see I, § 1), $C^2 v^{-2/3} = 6 \frac{1}{4} \cdot 10^{-6} \cdot M^{-5/3} D^{2/3}$ with $f=1$, because $v = M:D$. Therefore in *liquid benzene* ($5,5^\circ \text{C}$.):

$$C^2 R v^{-2/3} = 6 \frac{1}{4} \cdot 10^{-6} \times 83,17 \cdot 10^6 \times (78,05)^{-5/3} \times (0,9)^{2/3} = 519,8 : 1425 \times \\ \times 0,9322 = 0,3400.$$

Hence

$$A_0 = \frac{1}{20} \times 0,3400 \times (14)^2 : \left(3 \frac{1}{7} \right)^2 = 0,3373.$$

In *molten copper* at 1083°C . we have:

$$C^2 R v^{-2/3} = 519,8 \times (63,57)^{-5/3} \times (8,40)^{2/3} = 519,8 : 1013 \times 4,132 = 2,121,$$

so that we get:

$$A_0 = \frac{1}{20} \times 2,121 \times (38,23)^2 : 3^2 = 17,22.$$

In *solid copper* (20° C.) evidently

$$C^2 R v^{-2/3} = 2,121 \times \left(\frac{8,933}{8,40} \right)^{2/3} = 2,121 \times 1,042 = 2,210.$$

in consequence of which becomes

$$A_0 = \frac{1}{20} \times 2,210 \times (6)^2 : (1,6)^2 = 1,554.$$

We then get finally:

<i>liquid Benzene</i> (5°5 C.)	$A = 1,22^2$	$P = 1,02^7$	$\frac{A}{T} = \frac{1}{228}$	$\frac{P}{T} = \frac{1}{271}$
<i>molten Copper</i> (1083° C.)	$A = 54,3^6$	$P = 51,7^3$	$\frac{A}{T} = \frac{1}{25}$	$\frac{P}{T} = \frac{1}{26}$
<i>solid Copper</i> (20° C.)	$A = 2,73^5$	$P = 8,68^2$	$\frac{A}{T} = \frac{1}{107}$	$\frac{P}{T} = \frac{1}{34}$

In substances as *benzene* the correction in the equation of state is accordingly only about **0,4** % at $T = \frac{1}{2}$, but in liquid $\left(T = \frac{1}{3} T_k \right)$ and in solid $\left(T = \frac{1}{15} T_k \right)$ copper already resp. **4** % and **3** %, hence about 10 or 8 times greater. But in the calculation of *C* we took above the factor $f = 1$. In liquid benzene and copper $f^2 = c_p : c_v$ is only slightly greater than the unit, but in solid copper f^2 will become = 0,4 (with $\mu = 0,36$, $f = 0,63$). Consequently $\frac{P}{T}$ becomes only = $\frac{1}{85}$, i.e. **1,2** % instead of $\frac{1}{34} = 3$ %.

In gases, where v is so many times greater than in liquids, the correction $P : T$ will appear to be a great many times smaller at the same temperature, and even approach 0. The quantity $\omega = \varphi : v$ can be put = 0, whereas z becomes = $(v - b) : v = 1$. In consequence of this we get for gases simply:

$$A = A_0; \quad P = 3A_0 \left(1 - \frac{1}{3} \cdot 2 \right) = A_0.$$

If in benzene vapour v is taken 1000-times greater than in liquid benzene, A_0 becomes:

$$A_0 = \frac{1}{20} C^2 R v^{-2/3} = \frac{1}{20} \times 0,3400 : (1000)^{2/3} = 0,00017;$$

hence at $T = \text{about } 280^\circ \text{ absolute}$ the correction quantity $\frac{P}{T}$ will become $= 0,6 \cdot 10^{-6}$, i. e. perfectly negligible. And the following terms with Q will appear to be still much smaller.

IV.

The Equations of Energy and State at very Low Temperatures.

The development into series (3) is now replaced by the DEBYE development holding only at very low temperatures

$$E_t = \frac{9}{8} R \theta_0 + \frac{3}{5} \frac{R\pi^4}{\theta^3} T^4 - \dots \quad (16)$$

when by E_t we represent the temperature part of the Energy. For the total Energy the potential energy of the attractive and repulsive forces of static nature (see Chapter II) have to be added. The expression (16) applies to *solid* substances; the question in how far it is also applicable to liquids and gases at *very low* temperatures, and whether in these cases we have to do with open or closed paths (in the former case we should have still to divide by 2) may be left undecided for the present.

Now the zero point energy $\frac{9}{8} R \theta_0$ remains *outside* the terms with T^4, T^8 etc. Of course θ_0 should be put in it and not θ , because with the cor-

responding term $\frac{9RT}{x_m^3} \int_0^{x_m} \frac{1}{2} x^3 dx = \frac{9}{8} RT x_m$ the quantity $T x_m = \beta \nu_m = \theta$

will refer to $T=0$ according to the definition (since this term must represent the energy at $T=0$). The quantity ν_m , hence also θ , however, remains a function of ν .

From the equation of state (see further below) the following equation will follow as an analogon to (5):

$$\theta^2 = \theta_0^2 (1 + \varphi_1 T^4 \dots), \dots \quad (17)$$

so that we get:

$$E_t = \frac{9}{8} R \theta_0 + \frac{3}{5} \frac{R\pi^4}{\theta_0^3 (1 + \varphi_1 T^4 \dots)^{3/2}} T^4 - BT^8 \dots$$

i. e.

$$E_t = \frac{9}{8} R \theta_0 + \frac{3}{5} \frac{R\pi^4}{\theta_0^3} \left(1 - \frac{3}{2} \varphi_1 T^4 \dots \right) T^4 - BT^8 \dots$$

Confining ourselves, therefore, to terms with T^4 , the following equation remains:

$$E_t = \frac{9}{8} R \theta_0 + \frac{3}{5} \frac{R\pi^4}{\theta_0^3} T^4 = \frac{9}{8} R \theta_0 + AT^4 \quad (18)$$

Instead of (7) we may write for the equation of state:

$$p + \frac{a}{v^2} = \frac{\lambda + PT^4 \dots}{v-b}; \dots \dots \dots (19)$$

in which we shall try to express P in A . For this purpose we start again from the formula

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

giving

$$\frac{12 PT^3}{v-b} = \frac{d}{dv} (4 AT^3)_t = 4 T^3 \left(\frac{dA}{dv} \right)_t$$

from which follows:

$$P = \frac{1}{3} (v-b) \left(\frac{dA}{dv} \right)_t \dots \dots \dots (20)$$

2. As A depends on v through θ_0 , we must again determine the quantity $\theta^2 = C^2 v^{4/3} \sigma_1^{-1}$, i.e. $\sigma_1^{-1} = - \left(\frac{dp}{dv} \right)_t$. From (19), i.e. $\left(\text{with } \frac{1}{v-b} = \frac{1}{v-b_0} \left(1 + \frac{\varphi}{v} \right) \right)$

$$p = - \frac{a}{v^2} + \frac{\lambda + PT^4}{v-b_0} \left(1 + \frac{\varphi}{v} \right).$$

follows

$$\left(\frac{dp}{dv} \right)_t = \frac{2a}{v^3} - \frac{\lambda}{(v-b_0)^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi}{v} \frac{v-b_0}{v} \right) + T^4 \frac{d}{dv} \left(\frac{P}{v-b} \right)_t$$

which (with (20)) passes into

$$\left(\frac{dp}{dv} \right)_t = \frac{2a}{v^3} - \frac{\lambda}{(v-b_0)^2} \left(\quad \right) + \frac{1}{3} T^4 \left(\frac{d^2 A}{dv^2} \right)_t$$

so that we get:

$$\theta^2 = C^2 v^{4/3} \left[- \frac{2a}{v^3} + \frac{\lambda}{(v-b_0)^2} \left(\quad \right) - \frac{1}{3} T^4 \left(\frac{d^2 A}{dv^2} \right)_t \right],$$

consequently

$$\theta_0^2 = C^2 v^{4/3} \left[- \frac{2a}{v^3} + \frac{\lambda}{(v-b_0)^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi}{v} \frac{v-b_0}{v} \right) \right] \dots \dots (a)$$

As according to (18) $A = \frac{3}{5} \frac{R\pi^4}{\theta_0^3}$, we have $\left(\frac{dA}{dv} \right)_t = - \frac{9}{5} \frac{R\pi^4}{\theta_0^4} \left(\frac{d\theta_0}{dv} \right)_t$;

But from (a) follows:

$$2\theta_0 \left(\frac{d\theta_0}{dv} \right)_t = C^2 \left[\frac{10}{3} \frac{a}{v^{8/3}} + \lambda \frac{d}{dv} \left(\frac{v^{4/3}}{(v-b_0)^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi}{v} \frac{v-b_0}{v} \right) \right)_t \right].$$

The last differentiation has already been carried out in § 1 of Chapter III

in the expression (a), when this is divided by $-\frac{1}{20} C^2 R (v-b)$. Hence we get :

$$2\theta_0 \left(\frac{d\theta_0}{dv} \right) = C^2 \left[\frac{10}{3} \frac{a}{v^{5/3}} - 2\lambda \frac{v^{-2/3}}{(v-b)z^2(1+\omega)^2} \left(1 - \frac{1}{3} z(2-\omega) + \frac{1}{3} z^2\omega(1+\omega) \right) \right],$$

or also

$$2\theta_0 \left(\frac{d\theta_0}{dv} \right)_t = \frac{C^2}{v^{5/3}} \left[\frac{10}{3} \frac{a}{v} - 2\lambda \frac{\lambda}{z^3(1+\omega)^2} \left(1 - \frac{1}{3} z(2-\omega) + \frac{1}{3} z^2\omega(1+\omega) \right) \right],$$

as $\frac{v-b}{v} = z$. We have, therefore :

$$\left(\frac{dA}{dv} \right)_t = \frac{9}{5} \frac{R\pi^4}{\theta_0^5} \frac{C^2}{v^{5/3}} \left[-\frac{5}{3} \frac{a}{v} + \frac{\lambda}{z^3(1+\omega)^2} \left(\quad \right) \right].$$

In this θ_0^2 has been given by (a), consequently (cf. § 1 of Chapter III) by

$$\theta_0^2 = C^2 v^{4/3} \left[-\frac{2a}{v^3} + \frac{\lambda}{(v-b)^2(1+\omega)} (1+\omega z) \right],$$

i. e.

$$\theta_0^2 = \frac{C^2}{v^{2/3}} \left[-\frac{2a}{v} + \lambda \frac{1+\omega z}{z^2(1+\omega)} \right] \dots \dots \dots (21)$$

We find, therefore, for P according to (20):

$$P = \frac{3}{5} \frac{R\pi^4}{\theta_0^5} C^2 \frac{v-b}{v^{5/3}} \left[-\frac{5}{3} \frac{a}{v} + \frac{\lambda}{z^3(1+\omega)^2} \left(1 - \frac{1}{3} z(2-\omega) + \frac{1}{3} z^2\omega(1+\omega) \right) \right].$$

And as

$$\underline{A = \frac{3}{5} \frac{R\pi^4}{\theta_0^3} \dots \dots \dots (22)}$$

(see above), we finally get with $(v-b) : v = z$ and θ_0^2 according to (21):

$$P = Az \frac{-\frac{5}{3} \frac{a}{v} + \frac{\lambda}{z^3(1+\omega)^2} \left(1 - \frac{1}{3} z(2-\omega) + \frac{1}{3} z^2\omega(1+\omega) \right)}{-2 \frac{a}{v} + \frac{\lambda}{z^2(1+\omega)} (1+\omega z)} \dots \dots \dots (23)$$

If, therefore, A is known through (22), combined with (21), P can be calculated from (23). Again — no more than at high temperatures — the coefficient P of the equation of state is *not* equal to the corresponding coefficient A of the equation of energy.

3. We will now carry out the calculation for the case of *solid* copper at very low temperatures. We know that the quantity λ is determined by

$$\lambda = \frac{a}{v_0^2} (v_0 - b_0) = \frac{a}{v_0} \frac{v_0 - b_0}{v_0} = \frac{a}{v_0} z_0,$$

as immediately appears from the equation of state (19), when (at $p = 0$) v approaches to v_0 . In the neighbourhood of $T = 0$ z and z_0 , ω and ω_0 , v and v_0 may be put equal to each other without the slightest hesitation. For already at comparatively high temperatures, e. g. at 20°C. , the difference is inappreciable; at 20°C. $v = 7,12$ and $v_0 = 7,05$; $z = (v - b)$: $v = 1,18^6 : 7,11^6 = 1 : 6,00$ and $z_0 = 1,13^8 : 7,04^6 = 1 : 6,19^2$ (see Chapter II of our first Paper), so that the differences between these quantities at T in the neighbourhood of T_0 and at T_0 itself will no doubt be quite negligible.

If, therefore, we write simply $\lambda = \frac{a}{v} z$ with omission of the indices 0, then

$$\left. \begin{aligned} \theta_0^2 &= \frac{C^2 a}{v^{2/3} v} \frac{1 - z(2 + \omega)}{z(1 + \omega)} \\ P &= A \frac{1 - \frac{1}{3} z(2 - \omega) - \frac{1}{3} z^2(1 + \omega)(5 + 4\omega)}{(1 + \omega)(1 - z(2 + \omega))} \end{aligned} \right\} \dots \dots (24)$$

With $z = 1 : 6,19^2$, $\omega = 0,6 \times (7,116 : 7,046) = 0,6060$ this becomes:

$$\left. \begin{aligned} \theta_0^2 &= 2,233 \frac{C^2 a}{v^{2/3} v} \\ P &= 0,8830 A \end{aligned} \right\}$$

In this $C^2 : v^{2/3} = 6 \frac{1}{4} \cdot 10^{-6} \times (63,57)^{-1} \times (7,046)^{-2/3} \times 0,3969$, because in C^2 the factor f^2 is $= (0,63)^2 \cdot 0,3969$ (see § 2 of Chapter III). Hence $C^2 : v^{2/3} = 0,01062 \cdot 10^{-6}$ is found. Further $\frac{a}{v} = 32,63 \cdot 10^{12} : 7,046 = 4,631 \cdot 10^{12}$, so that for θ_0^2 is found:

$$\theta_0^2 = 2,233 \times 0,01062 \cdot 10^{-6} \times 4,631 \cdot 10^{12} = 0,1098 \cdot 10^6,$$

so that $\theta_0 = 331,3$, $\theta_0^3 = 36,38 \cdot 10^6$.

Therefore, according to (22):

$$A = \frac{3}{5} \frac{83,17 \cdot 10^6 \times 97,41}{36,38 \cdot 10^6} = \underline{133,6}; \quad P = \underline{118,0}.$$

According to (16) and (19) we have therefore for solid copper in the neighbourhood of $T = 0$:

$$\left. \begin{aligned} E_t &= \frac{9}{8} R\theta_0 + 134 T^4 \\ p + \frac{a}{v^2} &= \frac{\lambda + 118 T^4}{v - b} \end{aligned} \right\}$$

In this the zero-point energy $\frac{9}{8} R\theta_0 = \frac{9}{8} \times 83,17 \cdot 10^6 \times 331,3 =$

$$= 0,03100 \cdot 10^{12}, \lambda \text{ being } = \frac{a}{v} \times z = 4,631 \cdot 10^{12} : 6,192 = 0,7479 \cdot 10^{12}.$$

Hence we have:

$$\left. \begin{aligned} E_t &= 0,031 \cdot 10^{12} + 134 T^4 \\ \left(p + \frac{a}{v^2}\right)(v-b) &= 0,75 \cdot 10^{12} + 118 T^4 \end{aligned} \right\} \text{Solid copper. } \quad (25)$$

$T = 0$

If $T = 20^\circ$ absolute, the equations become:

$$\left. \begin{aligned} E_t &= 0,031 \cdot 10^{12} + 21,4 \cdot 10^6 \\ \left(p + \frac{a}{v^2}\right)(v-b) &= 0,75 \cdot 10^{12} + 18,9 \cdot 10^6 \end{aligned} \right\} (T = 20^\circ \text{ abs.})$$

so that the first terms are then still resp. 1450 and 40000 times greater than the terms with T^4 . Hence at 20° abs. the temperature energy is already almost equal to the zero point energy, the temperature exercising hardly any influence in the equation of state, so that the coefficient of expansion has become exceedingly small.

4. For the calculation of the *coefficient of expansion* in the neighbourhood of $T = 0$ we start from the known expression

$$\left(\frac{dp}{dt}\right)_v = - \left(\frac{dp}{dv}\right)_t \times \left(\frac{dv}{dt}\right)_p = v \sigma_1^{-1} \times \frac{1}{v} \left(\frac{dv}{dt}\right)_p$$

From this follows:

$$\alpha = \frac{1}{v} \left(\frac{dv}{dt}\right)_p = \frac{\left(\frac{dp}{dt}\right)_v}{v \sigma_1^{-1}}$$

In this $\left(\frac{dp}{dt}\right)_v$ is according to (19) $= \frac{4PT^3}{v-b} = \frac{471,9}{1,138} T^3 = 414,7 T^3$. And θ_2^0 being $= C^2 v^{4/3} \sigma_1^{-1}$, $v \sigma_1^{-1} = \theta_2^0 : C^2 v^{1/3}$. For $C^2 : v^{2/3}$ we found above the value $0,01062 \cdot 10^{-6}$, so that $C^2 v^{1/3}$ becomes $= 0,01062 \cdot 10^{-6} \times v = 0,01062 \cdot 10^{-6} + 7,046 = 0,07483 \cdot 10^{-6}$. Hence we calculate $0,1098 \cdot 10^6 : 0,07483 \cdot 10^{-6} = 1,467 \cdot 10^{12}$ for $v \sigma_1^{-1}$. Thus

$$10^6 \alpha = \frac{414,7 T^3}{1,467 \cdot 10^6} = \underline{282,6 \cdot 10^{-6} T^3} \quad (T = 0).$$

For the *specific heat* follows from (25):

$$c_v = 534,4 T^3 \text{ abs. units.}$$

But as 1 gr. cal. $= 41,86^3 \cdot 10^6$ Ergs, c_v becomes

$$c_v = \underline{12,77 \cdot 10^{-6} T^3} \text{ gr. cal. } (T = 0).$$

According at very low temperatures the coefficient of expansion runs entirely parallel with the atomic heat, but is *numerically* (i. e. $10^6 \alpha$) 22,14 times greater than c_v expressed in gr. cal.

At 20°

$$10^6 \alpha = \underline{2,261} \quad ; \quad c_v = \underline{0,1021} (T = 20^\circ \text{ abs.})$$

would be according to the above. At $20^{\circ},7$ abs. $c_v = 0.122$ has been found according to KEESOM and K. ONNES ¹⁾. This is in pretty good agreement, for c_v must be $= 0.102 \times \left(\frac{20,7}{20}\right)^3 = 0.102 \times 1.11 = 0.113$ at $20^{\circ},7$. Also the coefficient of expansion can be right, for $3 \times 3,9 = 11,7$ has been found by LINDEMANN between 20° and 80° abs., while $10^6 \alpha = 3 \times 6,8 = 20,4$ at 85° (there the T -law is no longer valid), so that duly 11.7 lies intermediate between 2.26 and 20.4 (the mean value would be 11.3).

We remark that at 20° C. ($T = 293$) $10^6 \alpha = 3 \times 17 = 51$, and c_v is $= 5.8$. The coefficient of expansion $10^6 \alpha$ is at these higher temperatures numerically only 8.8 times greater than c_v in gr. cal., against 22.1 times at very low temperatures (see above).

5. Above in (24) we found for θ_0^2 an expression, which is quite identical with that found by us in our first paper (see chapter V, equation (8) for $\sigma^{-1} = v\sigma_1^{-1}$) at higher temperatures for $\theta^2 = C^2 v^{4/3} \sigma_1^{-1}$. This is self-evident, because, as appears from the derivation, at higher temperatures $\lambda + RT$ has been replaced by its value $\frac{a}{v^2} (v-b)$ from the equation of state ($p=0$), the same thing having been done above with ($p=0$) $\lambda = \frac{a}{v_0^2} (v_0 - b_0)$, while $T=0$ was put. Through this the expressions for θ^2 (with T) and θ_0^2 (with $T=0$) have become identical; with this difference, however, that the values of v will be slightly different in the two cases. Consequently at 20° C. with $z = 1 : 6,00$, $\omega = 0,6$ is obtained

$\theta^2 = 2,125 \frac{C^2 a}{v^{2/3}}$ instead of $2,233 \times \text{ibid}$ (see above). We have therefore:

$$\theta^2 : \theta_0^2 = \frac{2,125}{(7,116)^{5/3}} : \frac{2,233}{(7,046)^{5/3}} = \frac{2,125}{2,233} \times \left(\frac{7,046}{7,116}\right)^{5/3},$$

i.e.

$$\theta^2 (T=0) = \theta^2 (20^{\circ} \text{ C.}) \times 1,051 \times (1,010)^{5/3} = \theta_{(20^{\circ} \text{ C.})}^2 \times 1,068.$$

And as $\theta_0 (T=0) = 331.3$ was found (see § 3), θ will be $331.3 : 1.034 = 320.6$ at 20° C ($= 293^{\circ}$ abs.) ²⁾. The difference in value at $T=0$ and $T=293^{\circ}$ is therefore small.

And the same thing will be the case with the coefficient of compressibility σ . As $\theta^2 = C^2 v^{4/3} \sigma_1^{-1} = C^2 v^{1/3} \times v\sigma_1^{-1}$, the values of $v\sigma_1^{-1} = -v \frac{dp}{dv}$

will be to each other as those of $\theta^2 : v^{1/3}$, i. e. those of $\sigma = -\frac{1}{v} \frac{dv}{dp}$ as those of $v^{1/3} : T^2$. Hence

$$\sigma : \sigma = (1,010)^{1/3} \times 1,068 = 1,072.$$

(20° C.) (T=0)

¹⁾ Comm. 147a, p. 8 (1915).

²⁾ KEESOM and KAMERLINGH ONNES (Comm. 143, 1914) have found between 15° and 22° abs. the value 323.5. Later on (Comm. 147a, 1915) the somewhat smaller value 315 was found between 14° and 90° abs.

As at 20°C σ is found = $0,730 \cdot 10^{-12}$ (see Chapter V of the previous paper), the value of σ will only be $0,681 \cdot 10^{-12}$ at $T = 0$, again not very different. Hence we have:

$$\begin{array}{l|l} T = 0 \text{ (abs.)} & \theta = 331; \sigma = 0,68 \cdot 10^{-12} \\ T = 293 \text{ (20}^{\circ}\text{C.)} & \theta = 321; \sigma = 0,73 \cdot 10^{-12}. \end{array}$$

The differences are so small, that it may safely be said that (p supposed = 0) the values of θ and σ practically vary little between the absolute zero and the ordinary temperatures.

And as the values of the coefficients of expansion have been given by (see § 4)

$$a = \left(\frac{dp}{dt} \right)_v \times \sigma,$$

the values of a (σ = constant) will about vary with those of $\left(\frac{dp}{dt} \right)_v$; i.e. the values of a at ordinary temperatures will be to those at very low temperatures as $\frac{R}{v-b} \sigma$ to $\frac{4PT^3}{v-b} \sigma$, hence (the values of $v-b$ being resp. = 1,186 and 1,138) as $\frac{R}{4PT^3} : 1,042 \times 1,072$ (see above).

We have accordingly:

$$a = (20^{\circ}\text{C.}) : a (20^{\circ}\text{C. abs.}) = 83,17 \cdot 10^6 : (471,9 \times 20^3) \times 1,029 = 22,7.$$

In § 4 we found about this ratio $51 : 2,261 = 22,6$.

In a concluding article we will briefly discuss the calculation of the *heat of melting* and the *heat of evaporation* for solid substances, and also the derivation of the equation of the vapour pressure at higher and lower temperatures. Besides, the dimensions of the closed paths round the positions of equilibrium will be treated; and then there only remains to test the equation of state drawn up by us by all other metals of which BRIDGMAN has determined the coefficients of compressibility and their coefficients of pressure and temperature with so great accuracy. By the aid of these two papers this can now easily be done, and may, if need be, be left to others.

N.B. It is self-evident, that in all that precedes there is only question of solid substances, which with regard to the three principal directions show identical properties. Otherwise the quantities b_g , b_{00} , and λ will have different values in the said directions, and properly speaking there are three equations of state, or, as it may also be expressed, one mean equation of state.

Tavel sur Clarens, Suisse, Dec. 1925.