

Physics. — “On the Equation of State of Solid Substances etc., in Connection with the General Expression for the Energy and the Entropy. Simple Derivation of the So-called Entropy Constant.”
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I

The Energy.

1. General Considerations.

In our foregoing paper we have made use of DEBYE's well-known expression for the Energy of a *solid substance*, viz. — with the addition of the terms referring to the potential Energy of the attractive and (static) repulsive forces:

$$E = \frac{9RT}{x_m^3} \int_0^{x_m} \left(\frac{1}{2} + \frac{1}{e^x - 1} \right) x^3 dx + \left(\frac{a}{v_{00}} - \frac{a}{v} \right) - \int_{\infty}^v \frac{\lambda/v}{v-b} dv, \quad (1)$$

in which x_m is $= \frac{\beta v_m}{T} = \frac{\theta}{T}$. The quantity θ occurring there (the so-called “characteristic” temperature) is given by equation (4) of the paper mentioned, viz.

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

in which C is $= 0,0025 f M^{-1/2}$. In this f is a factor containing the so-called POISSON modulus (to be replaced in gases and liquids by $\sqrt{c_p : c_v}$). Through $\sigma_1 = - \left(\frac{dv}{dp} \right)_t$ the value θ will, therefore, in general still be a function of T and v .

We have seen that as long as $p = 0$ for solid substances, the quantity θ varies but little between the absolute zero and the ordinary temperature. (for copper e.g. from 331 to 321; see § 5 of Chapter IV of the foregoing Paper). When p approaches to ∞ , in which the extreme limiting volume v_{00} is reached, θ will rapidly approach ∞ , because then the coefficient of compressibility $\sigma = - \frac{1}{v} \left(\frac{dv}{dp} \right)_t$ draws near to 0. Hence we have for solid substances (e.g. copper):

$$x_m = \frac{\theta}{T} = \frac{330 \left(\begin{smallmatrix} p=0 \\ v=v_0 \end{smallmatrix} \right) \text{ till } \infty \left(\begin{smallmatrix} p=\infty \\ v=v_{00} \end{smallmatrix} \right)}{T}.$$

At comparatively high temperatures (not too far below the meltingpoint) x_m will, therefore, be comparatively *small* at *ordinary* pressures, so that then the above formula (1) will fall, as regards the development into series, in the so-called RT -region $\left(E = 3RT \dots + \text{Pot.}; p + \frac{a}{v^2} = \frac{\lambda/v + RT \dots}{v-b}\right)$. (on the right of the line A in the subjoined Fig. 1). But at *very high*

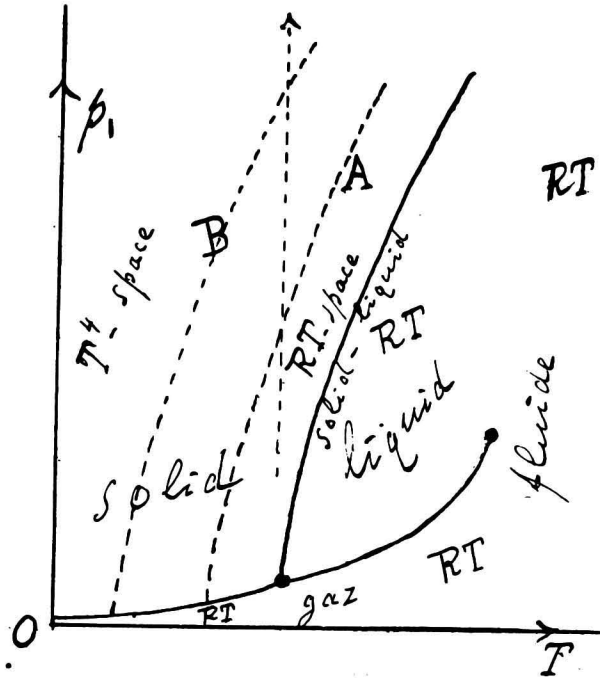


Fig. 1.

pressures x_m becomes great, and we shall gradually get, as regards the development into series, in the so-called T^4 -region:

$$\left(E = \frac{9}{8} R\theta_0 + \frac{3}{5} \frac{R\pi^4}{\theta_a^3} T^4 \dots + \text{Pot.}; p + \frac{a}{v^2} = \frac{\lambda/v + PT^4 \dots}{v-b}\right)^1)$$

(on the left of line B ; the part between A and B represents the intermediary region, in which neither the development into series for small values of x_m , neither that for large values of x_m is valid, so that there the general formula (1) would have to be used).

At *very low* temperatures we shall, of course, always be (in the solid state) in the T^4 -region (on the left of B), also at ordinary pressures.

¹⁾ θ_a denotes the value of θ at $T=0$; this is, accordingly, still a function of v ($\theta^2 = \theta_a^2 (1 + \varphi_1 T^4 \dots)$); cf. foregoing Paper p. 170). θ_0 is supposed independent of v .

For *liquids*, where Θ is smaller than for solid substances, and T higher, we shall always be in the RT -region, unless at very high pressures we should cross the line A , i.e. in the case that this line cuts the line of liquid-solid.

And finally for *gases* we shall *always* be in the RT -region, however low the temperature should become, and even at 0. This is very essential, because the opposite view has also been held, and the consequences of this, e.g. with regard to the Entropy are very far-reaching.

That what has been said is correct, will be clear on the following considerations. For gases the quantity θ is exceedingly small at the ordinary pressures, as at higher temperatures $\sigma_1^{-1} = - \left(\frac{dp}{dv} \right)_t = \frac{RT}{v^2}$ follows from $p = \frac{RT}{v}$, so that then the quantity θ becomes $= C \frac{\sqrt{RT}}{v^{1/3}}$

on account of (2), hence $x_m = \frac{\theta}{T} = \frac{C\sqrt{R}}{T^{1/2} v^{1/3}}$, in which T is great and v very great. And at *high pressures* the same thing holds for the *fluid* region as we have said before of the liquid phase.

How will all this be for gases at *very low temperatures*? Then the quantity θ will be either proportional to \sqrt{T} : $v^{1/3}$, or to T^2 : $v^{1/3}$, according as one supposes to be in the RT -region or in the T^4 -region.

Hence the quantity $x_m = \frac{\theta}{T}$ with $\frac{1}{T^{1/2} v^{1/3}}$ or with $\frac{T}{v^{1/3}}$. In the latter case, however, x_m would verge to 0 at T very small and v very great; i.e. one is then not in the supposed T^4 -region, but in the RT -region. And in the former case — as even on the saturation line solid-vapour it follows from the vapour-pressure-equation that v increases in a much greater degree (and that *exponentially*) with T than T decreases, so that even at $T=0$ x_m will still approach to 1: $(0 \times e^\infty)$, i.e. to 0 — this will be the case in a much greater degree *below* the said saturation line, where v is still much greater (∞ at $p=0$ on the T -axis).

We have, therefore, proved that in the *solid* state the T^4 -region exists only on the *left* of a certain line B , and that for *liquids* and *gases* we are *always* in the RT -region, even if the temperature (for gases) verges to 0. For in the first case x_m is comparatively *great*, so that the development into series with T^4 etc. is valid; in the second case x_m is comparatively *small*, so that the development into series with RT etc. will be applicable.

Hence, whether one has the first case or the other, does not depend only on T , but also on the quantity θ , which will depend in a pretty great degree on T and v . For it is after all only the value of $x_m = \theta:T$ that is decisive, and not that of T .

We will just remark that in the above equation (1) not λ has been written, but λ/v , in accordance with Note 1) to § 2 of Chapter II of the foregoing Paper, because otherwise the potential Energy of the

(static) repulsive forces would become infinite already for finite values of v . For gases, where (at ordinary pressures) v is very great, this term, like λ/v^2 , disappears naturally. For liquids and gases the expression for E must further still be divided by 2.

It may further still be mentioned that in the Figure we have assumed the possibility of an (exceedingly small) *zero-point pressure* at the equilibrium solid-vapour. This will be rendered probable in the following Paper.

2. Equation of Energy and Equation of State in the RT -Region (x_m small).

Though we already made some remarks on this subjects in our foregoing Paper, we will now come back to it to discuss, what was treated there, somewhat more at length.

For small values of x_m we may write for (1) (when nothing else is stated, it is supposed that we have to do with *solid* substances; the slight modifications for the liquid and gas state have already been indicated above):

$$E = \frac{9RT}{x_m^3} \left[\frac{1}{8} x_m^4 + \left(-\frac{1}{8} x_m^4 + \frac{1}{3} x_m^3 + \frac{1}{60} x_m^5 - \frac{1}{5040} x_m^7 \dots \right) \right] + \text{Pot. Energ.}$$

It is seen from this that the term corresponding to the zero-point energy $\frac{1}{8} x_m^4$ is cancelled by the term ensuing from the integration of the piece with $e^x - 1$, i.e. $-\frac{1}{8} x_m^4$, so that the zero-point energy will no longer occur in the expression for E at higher temperatures (i.e. small values of x_m), which comes to this that E will then duly approach to RT , without the addition of a constant term without T which remains *finite*. We, therefore, get simply with $x_m = \theta : T$:

$$E = 3RT \left[1 + \frac{1}{20} \frac{\theta^2}{T^2} - \frac{1}{1680} \frac{\theta^4}{T^4} \dots \right] + \text{Pot. Energ.}$$

But as $\theta^2 = \theta_a^2 \left(1 + \varphi_1 T + \frac{\varphi_2}{T} + \dots \right)$, in which φ_1, φ_2 etc. are still functions of v (see the foregoing Paper, Chapter I § 3), the above development into series with exclusively even powers of T^{-1} will pass into one with all whole powers of T^{-1} , i.e. it will be of the form:

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

in which A will be $= \frac{1}{20} \theta_a^2 \varphi_1$; $B = \frac{1}{20} \left(\theta_a^2 - \frac{1}{84} \theta_a^4 \varphi_1^2 \right)$; etc. The quan-

tities θ_a, φ_1 , etc. can be calculated from the coefficient of compressibility occurring in the equation (2) of § 1. And this coefficient can in its turn be derived from the equation of state. It is, therefore, of the highest importance accurately to know the form of this latter equation in connection with (3). All this has already been set forth at length in our preceding Paper, but we wish to give some more generality and extension to it here.

As it is known, the following purely *thermodynamic* relation holds for E :

$$E = \int_{\infty}^T c_v dT + \int_{\infty}^v \left(T \left(\frac{dp}{dt} \right)_v - p \right) dv + E_{T=\infty, v=\infty}, \dots \quad (4)$$

in which we have, of course, chosen ∞ for the lower limit of T , and not 0, because (3) is only valid for small values of x_m (high values of T). With regard to v , we might also have chosen $v = v_{00}$ for lower limit; $E_{T=\infty, v=\infty}$ would then have become $E_{T=\infty, v=v_{00}}$. We draw attention to this, that according to a theorem proved in our foregoing Paper (chapter II, § 1, Note 1) concerning the integration between definite limits of *total* differentials (here dE), either at the limit of the *first* integral what stands under it must be taken at the lower (constant) limit of the *second* integral; or inversely at the second integral what stands under it at the lower (constant) limit of the *first* integral.

For c_v the following equation evidently holds according to (3):

$$c_v = \left(\frac{dE}{dt} \right)_v = 3R \left(1 - \frac{B}{T^2} - \frac{2C}{T^3} \dots \right),$$

so that $c_{v=\infty}$ becomes $= 3R$, as the coefficients B, C , etc. (see our preceding Paper) all become $= 0$ at $v = \infty$.

We may, therefore, write for p :

$$p = -\frac{a}{v^2} + \frac{\lambda/v}{v-b} + \frac{RT}{v-b} \left(1 + \frac{P'}{T} + \frac{Q'}{T^2} + \frac{S'}{T^3} \dots \right),$$

or also:

$$p = -\frac{a}{v^2} + \frac{\lambda/v}{v-b} + \frac{RT}{v-b} + R \left(P + \frac{Q}{T} + \frac{S}{T^2} \dots \right), \dots \quad (5)$$

in which the coefficients P, Q, S , etc. are in general still functions of v , and can be expressed from the above thermodynamic relation (4) in A, B, C , etc. We now get:

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

hence

$$T \left(\frac{dp}{dt} \right)_v - p = \frac{a}{v^2} - \frac{\lambda/v}{v-b} - RP - 2R \frac{Q}{T} - 3R \frac{S}{T^2} \dots$$

so that we may now write:

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

In this the quantity $E_{T=\infty}$ is evidently $= 3RT_\infty + \frac{a}{v_{00}}$ (the potential energy of the (static) repulsive forces disappears at $v = \infty$), so that the following equation is obtained:

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

If this is compared with (3), the following equations follow immediately:

$$\underline{P = -3 \cdot \frac{dA}{dv}}; \quad \underline{Q = -3 \cdot \frac{1}{2} \frac{dB}{dv}}; \quad \underline{S = -3 \cdot \frac{1}{3} \frac{dC}{dv}}; \quad \text{etc.,} \quad (6)$$

(all the differentiations with respect to T const.), through which the additional terms at $\frac{RT}{v-b}$ in the equation of state (5) have been brought in connection with the corresponding additional terms at $3RT$ in the Energy equation (3). If, therefore, A, B, C , etc. are functions of v — and this is the case in the theory of DEBYE, because θ depends, besides on T , in a great degree on v — also the equation of state will necessarily contain terms of “degeneration”. It appears from the above that those terms with P, Q, S etc. will in general not be equal to those with A, B, C etc. This is only the case with ideal gases; then P becomes $= A, Q = B$, etc., as may be read in my preceding Paper.

If in general

$$E = \omega + \text{Pot. Energ.}; \quad p = -\frac{a}{v^2} + \frac{\lambda/v}{v-b} + \varphi,$$

in which, therefore, ω and φ are two different functions of T , it appears from the above derivation that generally $\left(\varphi' \text{ means } \left(\frac{d\varphi}{dt} \right)_v \right)$ must be:

$$T\varphi' - \varphi = \left(\frac{d\omega}{dv} \right)_t \dots \dots \dots (6^a)$$

This follows, of course, also from the well-known relation $\left(\frac{dc_v}{dv} \right)_t = T \left(\frac{d^2p}{dt^2} \right)_v$, yielding $\left(\omega' \text{ means } \left(\frac{d\omega}{dt} \right)_v \right) \left(\frac{d\omega'}{dv} \right)_t = T\varphi''$, i.e. $\left(\frac{d\omega}{dv} \right)_t = T\varphi' - \varphi$.

We now have for c_v :

$$c_v = 4AT^3 + 8PT^7 \dots, \text{ hence } c_{v_0} = 4A_0T^3 + 8B_0T^2 \dots,$$

in which, therefore, A_0, B_0 etc. represent the values of A, B etc. at $v=v_0$. Further

$$T \left(\frac{dp}{dt} \right)_v = 4PT^4 + 8PT^8 \dots,$$

hence

$$T \left(\frac{dp}{dt} \right)_v - p = \frac{a}{v^2} - \frac{\lambda/v}{v-b} + 3PT^4 + 7QT^8 \dots,$$

and therefore:

$$E = (A_0T^4 + B_0T^8 \dots) + \left[\left(\frac{a}{v_0} - \frac{a}{v} \right) - \int_{v_0}^v \frac{\lambda/v}{v-b} dv + 3T^4 \int_{v_0}^v P dv + 7T^8 \int_{v_0}^v Q dv \dots \right] + E_{T=0}.$$

In this $E_{T=0}$ is evidently $= E_0 - \int_{\infty}^{v_0} \frac{\lambda/v}{v-b} dv$ (now the potential energy of the attractive forces disappears at $v=v_0$), so that we get:

$$E = E_0 + \left(A_0 + 3 \int_{v_0}^v P dv \right) T^4 + \left(B_0 + 7 \int_{v_0}^v Q dv \right) T^8 \dots + \left(\frac{a}{v_0} - \frac{a}{v} \right) - \int_{\infty}^v \frac{\lambda/v}{v-b} dv.$$

And from this follows immediately by comparison with (7):

$$\underline{P = \frac{1}{3} \frac{dA}{dv}}; \quad \underline{Q = \frac{1}{7} \frac{dB}{dv}}; \text{ etc.} \dots \dots \dots (9)$$

(the differentiations with respect to v again to be taken at T constant),

for then becomes e.g. $A_0 + 3 \int_{v_0}^v P dv = A_0 + 3 \cdot \frac{1}{3} (A - A_0) = A$; etc.

Also at low temperatures (large values of x_m) the coefficients P, Q etc. in the equation of state depend, therefore, in a very definite way on the coefficients A, B , etc. of the equation of Energy; in which in general (comp. § 2) $\left(\frac{d\omega}{dv} \right)_t$ will again be $= T\varphi' - \varphi$, they again *not* being equal to each other.

Recapitulating, we have for the Energy ($x_m = \Theta : T$):

$$\left\{ \begin{array}{l} E = 3RT \left(1 + \frac{A}{T} + \frac{B}{T^2} \right) + \text{Pot. Energ. } (x_m \text{ small : } RT\text{-region}). \\ E = \frac{9RT}{x_m^3} \int_0^{x_m} \left(\frac{1}{2} + \frac{1}{e^x - 1} \right) x^3 dx + \text{Pot. Energ. (general)}. \\ E = E_0 + (AT^4 + BT^8 \dots) + \text{Pot. Energ. } (x_m \text{ great : } T^4\text{-region}). \\ \text{(Occurs only for solid substances at low temp.; cf. Fig. 1).} \end{array} \right.$$

In this A , B , etc. are still functions of v , and the Pot. Energ. is everywhere $= \left(\frac{a}{v_{00}} - \frac{a}{v} \right) - \int_{\infty}^v \frac{\lambda/v}{v-b} dv$. The coefficients P , Q , etc. of the equations of state (5) and (8) are dependent on A , B , etc. by means of the simple relations (6) and (9).

II

The Entropy.

1. The Entropy in the T^4 -region (x_m great).

In the calculation of the Entropy greater difficulties, chiefly on account of the so-called "Entropy constant", are to be surmounted than in that of the Energy. What we have found above in Chapter I concerning the equation of Energy, is now required for the calculation of the Entropy from the *thermodynamic* relation holding for it, because we cannot draw up the expression for the Entropy — as was the case with the Energy in equation (1) — in an independent way outside statistic, i.e. thermodynamic considerations.

We now start with the T^4 -region, because this presents no difficulties. This region is — see Fig. 1 — exclusively assigned to the *solid* state. As we have shown, it does not occur for liquids and gases, unless at exceedingly high pressures. As

$$dS = \frac{dQ}{T} = \frac{dE + p dv}{T} = \frac{dE}{T} + \frac{p}{T} dv,$$

in which $dE = c_v dT + \left(T \left(\frac{dp}{dt} \right)_v - p \right) dv$, we have also

$$dS = \frac{c_v}{T} dT + \left(\frac{dp}{dt} \right)_v dv,$$

and hence

$$S = \int_0^T \frac{c_v}{T} dT + \int_{\nu_{00}}^{\nu} \left(\frac{dp}{dt} \right)_v d\nu + S_{T=0, \nu=\nu_{00}}$$

in which we have chosen the natural limits 0 and ν_{00} as lower limits for the two integrals, and have further taken what stands under the second integral at the *lower* limit of the first integral, according to a theorem proved by me in the foregoing Paper. (See also above with the Energy). We might also inversely have taken the first integral at $\nu = \nu_{00}$, but this would have been more complicated; the result remains, of course, exactly the same.

From $c_v = 4AT^3 + 8BT^7 \dots$ and $\left(\frac{dp}{dt} \right)_v = 4PT^3 + 8QT^7 \dots$ (comp. § 3 of Chapter I) follows therefore:

$$S = \int_0^T (4AT^2 + 8BT^3 \dots) dT + \int_{\nu_{00}}^{\nu} 0 \cdot d\nu + 0,$$

because $\left(\frac{dp}{dt} \right)_v$ disappears at $T=0$, and also the Entropy at the absolute zero and at the extreme limiting volume must necessarily disappear, as then the probability of the appearance of a molecule or atom in the elementary limiting space $\nu_{00} : N$ has become the unit, and accordingly the log. of it = 0. Hence there remains simply:

$$S = \underline{\underline{\frac{4}{3} AT^3 + \frac{8}{7} BT^7 \dots}} \left(\begin{matrix} T^4\text{-region} \\ x_m \text{ great} \end{matrix} \right), \dots \dots \dots (10)$$

which, therefore, duly becomes = 0 for $T=0$. As long as T is not yet absolutely = 0, S will still be dependent on ν through A and B , though in a very small degree.

2. The Entropy in the RT -region (x_m small).

This case comprises the entire gas- and liquid states, and besides also part of the solid state at comparatively higher temperatures (Fig. 1, right of A). Let us now write:

$$S = \int_{\infty}^T \frac{c_v}{T} dT + \int_{\nu_{00}}^{\nu} \left(\frac{dp}{dt} \right)_v d\nu + S_{T=\infty, \nu=\nu_{00}}$$

then with $c_v = 3R \left(1 - \frac{B}{T^2} - \frac{2C}{T^3} \dots \right)$ and $\left(\frac{dp}{dt} \right)_v = \frac{R}{\nu-b} - R \frac{Q}{T^2} - 2R \frac{S}{T^3} \dots$

(see § 2 of Chapter I) the equation becomes:

$$S = \int_{\infty}^T \left(\frac{3R}{T} - 3R \frac{B}{T^3} - 3R \frac{2C}{T^4} \right) dT + \int_{\nu_{00}}^{\nu} \frac{R}{\nu-b} d\nu + S_{T=\infty, \nu=\nu_{00}}$$

because at $T = \infty$ the terms with \propto/T^2 etc. all disappear. Hence, as $S_{T=\infty}$ will evidently be of the form $3R \log \frac{T_\infty}{\tau} + S_a$, in which τ represents a constant temperature to be defined later, and S_a a possible additional constant:

$$S = 3R \left(\log \frac{T}{T_\infty} + \frac{1}{2} \frac{B}{T^2} + \frac{2}{3} \frac{C}{T^3} \dots \right) + R \log \frac{v-b}{v_{00}-b_{00}} + \left(3R \log \frac{T_\infty}{\tau} + S_a \right),$$

i.e.

$$S = 3R \log \frac{T}{\tau} + 3R \left(\frac{1}{2} \frac{B}{T^2} + \frac{2}{3} \frac{C}{T^3} \dots \right) + R \log \frac{v-b}{\omega} + S_a \dots \quad (a)$$

in which ω is the exceedingly small elementary volume $v_{00} - b_{00}$, which does not become $= 0$ (even at the absolute zero there is always left the small space of the zero-point paths round the states of equilibrium), but remains $= (b_{00} + \omega) - b_{00} = \omega$.

In order to get a closer indication about the nature of the constants τ and S_a , we take, instead of the function of DEBIJE for E_t , which in general cannot be integrated (i.e. the part of E that bears relation to the temperature, hence outside the potential Energy), the simpler PLANCK-EINSTEIN function $E_t = E_0 + 3RT \frac{x}{e^x - 1} = E_0 + \frac{3R\theta}{e^x - 1}$, which can be integrated; in which now in $x = \frac{\theta}{T}$ the characteristic temperature $\theta = \beta v$ is a constant, independent of T and v . Then we get $c_v = \left(\frac{dE}{dT} \right)_v = 3R \frac{x^2 e^x}{(e^x - 1)^2}$, because $\frac{dx}{dT} = -\frac{\theta}{T^2} = -\frac{x}{T}$. Consequently, as x becomes $= \infty$ for $T = 0$, and $\frac{dT}{T}$ is $= -\frac{dx}{x}$:

$$\int_0^T \frac{c_v}{T} dT = - \int_\infty^x \frac{c_v}{x} dx = - 3R \int_\infty^x \frac{x e^x}{(e^x - 1)^2} dx = 3R \left[\frac{x e^x}{e^x - 1} - \log(e^x - 1) \right]_x$$

i.e.

$$\int_0^T \frac{c_v}{T} dT = 3R \left[\frac{x e^x}{e^x - 1} - \log(e^x - 1) \right],$$

because $[\]$ becomes $= x - x = 0$ for $x = \infty$. We may, therefore, also write:

$$\int_0^T \frac{c_v}{T} dT = 3R \left[\frac{x e^x}{e^x - 1} - \log \frac{e^x - 1}{x} \right] - 3R \log x,$$

so that finally (see above, as regards the term with v):

$$S = 3R \left[\frac{xe^x}{e^x - 1} - \log \frac{e^x - 1}{x} \right] + 3R \log x \frac{T}{\theta} + R \log \frac{v-b}{\omega}, \quad (b)$$

as $S_{T=0}$ is again $= 0$ (see § 1).¹⁾ This would therefore represent the quite general value of S , if the PLANCK-EINSTEIN function were valid. At low temperatures this is certainly not the case, but at high temperatures the DEBIJE function almost coincides with that of PLANCK-EINSTEIN, and when, therefore, we determine S at *higher* temperatures (in any case *small* values of x) from (b), we shall obtain the right expression. Then we find ($x = 0$):

$$S = 3R + 3R \log \frac{T}{\theta} + R \log \frac{v-b}{\omega} \quad (x \text{ small}), \quad \dots \quad (c)$$

because the expression between [] becomes $= \frac{x(1+x)}{x + \frac{1}{2}x^2} - \log \frac{x + \frac{1}{2}x^2}{x} = (1 + \frac{1}{2}x) - \frac{1}{2}x = 1$.

Comparing (c) with (a) we accordingly see that the quantity τ introduced there is nothing but θ , for which in the DEBIJE theory of course its constant limiting value θ_0 at $T=0$, $v=v_0$ must be substituted, the constant S_a appearing to be $= 3R$: We may, therefore, finally write:

$$S = 3R \log \frac{T}{\theta_0} + 3R \left(\frac{1}{2} \frac{B}{T^2} \dots \right) + 3R + R \log \frac{v-b}{\omega} \left(\begin{array}{l} RT\text{-region} \\ x_m \text{ small} \end{array} \right), \quad (11)$$

in which now everything is determined, for also ω (see below § 3) can be easily calculated. The quantities B, C , etc. are the volume functions in the Energy equation (3), which we can determine by means of the equation of state (see preceding Paper).

For ideal gases $v = \infty$ or very great; then B, C , etc. are $= 0$, and we get, substituting $\frac{1}{2}R$ for R in the temperature part:

$$S = \frac{3}{2}R \log \frac{T}{\theta_0} + \frac{3}{2}R + R \log \frac{v-b}{\omega} \quad (\text{ideal gases}), \quad \dots \quad (11^a)$$

in which v may now also be written for $v-b$.

¹⁾ As we have used the general function, valid for *all* values of T and v , we have, purposely, chosen the lower limits, so that $S_{T=0}$ occurs, of which we *know* that it is $= 0$. Now the quantity $\left(\frac{dp}{dt} \right)_v$ under the second integral sign must, however, be taken at $T=0$. But we have already seen in I, § 2, that on assumption of the PLANCK-EINSTEIN function $\left(\frac{dp}{dt} \right)_v$ is always $= \frac{RT}{v-b}$, without additional degeneration-terms (hence $P = Q = S = \text{etc.} = 0$).

Now by an entirely different way the following form has been found for mon-atomic gases (LORENTZ, PLANCK, TETRODE, and many others):

$$S = \frac{3}{2} R \log T + R \log (v-b) + \left[\frac{3}{2} R + R - R \log R + R \log \frac{k^{5/2} (2 \pi m)^{3/2}}{h^3} \right],$$

which we may also write in the more homogeneous form:

$$S = \frac{3}{2} R \log \frac{T}{\theta_0} + \frac{3}{2} R + R \log (v-b) + R \log \frac{e k^{3/2} \theta_0^{3/2} (2 \pi m)^{3/2}}{N h^3},$$

for $R = R \log e$ and $-R \log R = -R \log Nk$. This is, therefore, in perfect harmony with (11^a), if only we assume for the elementary volume $\omega = v_{00} - b_{00}$:

$$\omega = \frac{N h^3}{e (k \theta_0)^{3/2} (2 \pi m)^{3/2}} \dots \dots \dots (12)$$

That this really represents a *volume*, is easy to see. For the dimensions of the different quantities are $h = \text{erg. sec.}$, $k = \text{erg.} : T$, hence $k \theta_0 = \text{erg.}$, so that the dimensions of ω will be (N is the number of molecules in a Gr. mol).:

$$\frac{\text{erg}^{3/2} \text{sec}^3}{m^{3/2}} = \left(\frac{\text{erg}^{1/2} \text{sec}}{m^{1/2}} \right)^3 = \left[\left(\frac{m l^2}{t^2} \right)^{1/2} t : m^{1/2} \right]^3 = l^3.$$

3. Calculation of ω from the cyclic movement round the states of equilibrium in connection with the zero-point energy.

That the elementary volume ω — which will, of course, be the same for all states of aggregation — is really equal to the above expression (with a difference of a numerical factor, which is near 1), so that we might have immediately written this value for it, even without statistic and other considerations — and through which the Entropy-constant would come into our possession without any difficulty — may appear from what follows.

In the neighbourhood of the absolute zero the molecule centres in solid substances (which we choose for convenience sake) will still describe paths with exceedingly small distances round the positions of equilibrium in consequence of the periodically acting attractive and repulsive forces ¹⁾.

The vis viva of this movement is $2 \times \frac{1}{2} m u^2$, when u is the velocity with which the path is passed through. Now $u = 2 \pi r \nu$, when ν represents the number of revolutions per second, which quantity is evidently identical with the frequency ν of the elastic waves introduced by DEBYE, the quasi-linear vibrations of which may be considered as projections of the said revolutions round the positions of equilibrium on the path-diameters ($= 2 r$). Thus we have:

$$4 \pi^2 r^2 m \nu^2 = \frac{9}{8} k \theta_0 + a T^4 \dots$$

¹⁾ Cf. also These Proceedings 21, 1184 (1919), 23, 887 (1920) and especially These Proceedings 24, 294 (1921).

as the zero-point energy according to DEBYE is $= \frac{9}{8} R \theta_0$: $N = \frac{9}{8} k \theta_0$ for one molecule. The terms with aT^4 , etc. ($a = A : N$, etc.) remain, so long as T has not yet become $= 0$. (In this the coefficients a etc. are still functions of v). As further $\beta v = \theta$, we may write — now passing to the limit $T = 0$:

$$4\pi^2 r_0^2 m \frac{\theta_0^2}{\beta^2} = \frac{9}{8} k \theta_0.$$

i.e.

$$r_0^2 = \frac{9}{32\pi^2} \frac{k \beta^2}{m \theta_0} = \frac{9}{32\pi^2} \frac{h^2}{k m \theta_0} = \frac{9}{16\pi} \frac{h^2}{k \theta_0 \cdot 2\pi m},$$

because $\beta = h : k$. (Accordingly the quantity h appears here for the first time in consequence of the equation $\theta = \beta v$). The volume of the space thought spherical, which the molecule centres thus leave in their circular paths (in all possible planes) round the positions of equilibrium, will be $= \frac{4}{3} \pi r_0^3$, so that for the limiting space indicated above by $\omega = v_{00} - b_{00}$ (ω refers to 1 Gr. mol. $= N$ molecules) we get:

$$\omega = N \times \frac{4}{3} \pi \left(\frac{9}{16\pi} \right)^{3/2} \left(\frac{h^2}{k \theta_0 \cdot 2\pi m} \right)^{3/2},$$

i.e.

$$\omega = \frac{9}{16} \frac{N}{\sqrt{\pi}} \frac{h^3}{(k \theta_0)^{3/2} (2\pi m)^{3/2}}, \dots \dots \dots (12^a)$$

which in fact — except for a numerical factor — is in harmony with the value (12) found in an entirely different way¹⁾. Instead of $\frac{1}{e} = \frac{1}{2,72}$ there stands $\frac{9}{16\sqrt{\pi}}$ as fore-factor, i.e. $\frac{1}{1,78 \times 1,77} = \frac{1}{3,15}$, which is 1,16 times smaller. But this does not greatly affect the matter itself in my opinion, seeing that there is no absolute agreement in the statistic theory either, concerning the numerical factors which occur in the proportionality of ω to h^3 . Our considerations form a bridge, so to say, between the Entropy constant and the theory of the cyclic movements in the sense of HELMHOLTZ.

In conclusion we may still remark that our equations (11) and (11^a) are now also perfectly homogeneous: S has the dimensions of R . Under the log sign there stands, below T , duly another (constant) temperature θ_0 ; below $v - b$ another (constant) volume ω .

¹⁾ This derivation was already found by me many years ago, and is inserted in my book on the thermodynamic functions of simple substances and of mixtures with a number of new things. But for various reasons the completion of it has been much delayed, so that I avail myself of this opportunity to make these considerations public, which, I believe, are new.

As appears from the derivation, (11) holds of course only for the RT -region. Hence for gases (see fig. 1) $T=0$ and $v = v_{00}$ can never occur simultaneously, but $T=0$ and $v = \infty$ (at very low temperatures), or $T = \infty$ (great) and v arbitrary (in the so-called fluid region). For the T^4 -region, which occurs only for *solid* substances (Fig. 1, left of B), formula (10) of § 1 is valid, and *this* gives $S=0$ at $T=0$. But for gases S can *never become* $=0$. Here follow some limiting values.

a) $T=0, v = \infty$ (Fig. 1, at O): $S = \frac{3}{2} \log 0 + R \log \infty = \infty,$

as v then varies $\therefore e^{1/T}$ (on the saturation line), or (below it) in a still greater degree, so that $\log v$ becomes $\therefore \frac{1}{T}$. The first term of S ($\therefore \log T$) will accordingly be very small with regard to the second term, which is $\therefore \frac{1}{T}$. Hence the volume is predominant.

b) $T = \infty, v = \infty$ (Fig. 1 on the T -axis, quite on the right):
 $S = \infty + \infty = \infty.$

c) $T = \infty, v = \omega$ (Fig. 1 quite on the right above at $p = \infty$):
 $S = \infty + 0 = \infty.$

Just as in Chapter I for E we give in conclusion the following summary for S^1).

$$\left\{ \begin{array}{l} S = 3R \log \frac{T}{\theta_0} + 3R \left(\frac{1}{2} \frac{B}{T^2} \dots \right) + 3R + R \log \frac{v-b}{\omega} \quad (x_m \text{ small: } RT\text{-region}). \\ S = 3R \left[\frac{x e^x}{e^x - 1} - \log \frac{e^x - 1}{x} \right] + 3R \log \frac{T}{\theta} + R \log \frac{v-b}{\omega} \quad (\text{in general, according to PLANCK-EINSTEIN}). \\ S = \int_0^T \frac{c_v}{T} dT + \int_{v_{00}}^v \left(\frac{dp}{dt} \right)_v dv \quad (\text{in general, according to thermodynamics}). \\ S = \frac{4}{3} A T^3 + \frac{8}{7} B T^4 \dots \quad (\text{according to DEBIJJE}) \quad (x_m \text{ great: } T^4\text{-region}). \end{array} \right.$$

1) It is self-evident that for the temperature part of S in general $3R$ must be replaced by c , when by c is represented the specific heat at constant infinitely great volume. For mon-atomic solid substances c is then $3R$, for multi-atomic substances $> 3R$; for mon-atomic gases $c = \frac{3}{2} R$, for multi-atomic gases $> \frac{3}{2} R$; etc. The R before $\log \frac{v-b}{\omega}$ always remains R , because it results from the RT of the equation of state and only the progressive Energy plays a part here, but ω is modified. It is further noteworthy that for convenience we have always put here $\log (v-b)$ for $\int \frac{dv}{v-b}$, neglecting the volume variability of b . If this is taken into account, the term with $\log (v-b)$ becomes somewhat more intricate. (See the note concerning $\int \frac{\lambda}{v-b} dv$ in § 2 of Chapter II of our foregoing Paper).

And now we have completed our considerations on Entropy and the Entropy-constant, and in a fourth (concluding) Paper we can draw up the *vapour-pressure equations*, both for the equilibrium liquid-vapour and for solid-vapour, the latter up to the absolute zero-point — making use of the expressions for E found now (required for the calculation of the melting-point and evaporation heats) and for S (required for the vapour pressure constants). At the same time the question concerning the so-called “zero-point vapour pressure” will then be discussed.

Tavel sur Clarens, 1926.
