

Physics. — “On the Equation of State of Solid Substances (Metals) in connection with their Compressibility and with the Pressure and Temperature Coefficient of this Quantity.” By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of December 19, 1925).

I.

The Equation of State.

1. It is known that VAN DER WAALS's equation of state

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

holds for *gases* and *liquids* at higher temperatures. This equation may be imagined as having arisen from the Virial-equation (everything still to be multiplied by $\frac{3}{2}$)

$$pv + \frac{a}{v} - \frac{b}{v-b} RT = RT, \quad \dots \quad (2)$$

in which pv is the virial of the external forces (pressure), $\frac{a}{v}$ the so-called virial of attraction and $-\frac{b}{v-b} RT$ the virial of repulsion, which latter is proportional to RT , i.e. to the vis viva $L = \frac{3}{2} RT$ of the *progressive* motion of the molecules. Consequently it is immaterial for the equation of state whether the molecules contain only one or more atoms, as RT always refers to L , and *not* to $L +$ the energy of the atoms *in* the molecule.

In most cases the temperature functions of the quantities a and b , which about compensate each other, and also the small volume-function of a , may be neglected here. But this may by no means be done with the *very strong dependence on the volume* of b , which may be represented by the simple equation ¹⁾

$$b = \frac{b_g}{1 + \frac{b_g - b_0}{v}}, \quad \text{or} \quad v - b_0 = (v - b) \left(1 + \frac{b_g - b_0}{v} \right) \quad \dots \quad (3)$$

The second of equations (3) can be derived from the first by calculating $v - b$ from it. Then the virial equation (2) becomes:

¹⁾ Compare my book: „die Zustandsgleichung von Gasen und Flüssigkeiten”, Leipzig, L. Voss, 1924, especially p. 74–79 and 91. Also *Z. f. anorg. u. allg. Ch.* **140**, 58–60 (1924).

$$pv + \frac{a}{v} - RT \frac{b_g}{v - b_0} = RT, \quad \dots \quad (2^a)$$

and the equation of state (1), ensuing from it, becomes:

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

That the above equation for the dependence on the volume of b renders all the thermal quantities (compressibility, expansibility etc.) for liquids with great accuracy, I have shown before already more than once ¹⁾. If e.g. the quantity $1 + (b_g - b_0) : v$ is neglected, values 4 or 5 times too small are e.g. obtained for the coefficient of compressibility.

As for ordinary substances ($\gamma = 0,9$ to 1) the value $b_g : b_0$ lies in the neighbourhood of 3,8 to 4,8 at $T = \frac{1}{2} T_k$, $(b_g - b_0) : b_0$ will be 2,8 to 3,8, and $(b_g - b_0) : v$ will be $= 2,14$ to $2,85$, because v is $= 1,31$ to $1,33 b_0$ at temperatures in the neighbourhood of the solidifying point (T about $= \frac{1}{2} T_k$) ²⁾. Thus 2,5 is e.g. found for $(b_g - b_0) : v$ for mercury, 2,0 for C_2H_5Cl , 1,8 for ether, 2,0 for molten copper (see IV) ³⁾. Here T is, however, higher than $\frac{1}{2} T_k$ for ether and ethylchloride, hence $a_t : a_k < 1,5$, whereas mercury and molten copper belong strictly speaking to another category.

For the important quantity $\frac{v}{v - b}$ the following equation is found, when the external pressure is negligible by the side of $\frac{a}{v^2}$:

$$\frac{v}{v - b} = \frac{a/v}{RT} = \frac{fRT_k}{RT} = \frac{f}{m},$$

in which f is the known vapour pressure factor (still slightly variable with the temperature). For ordinary substances the value of 14 to 16 is found for $\frac{v}{v - b}$ at $m = \frac{1}{2}$ and with $f = 8 \gamma = 7$ to 8 . We may, therefore,

¹⁾ Compare inter alia pages 108—121 of the cited book.

²⁾ Compare also Z. f. anorg. u. allg. Ch. **149**, 349—350 (1925). At a temperature T the following relations are valid:

$$\frac{(b_g)_t}{b_0} = \frac{(b_g)_t}{(b_g)_k} \times \frac{(b_g)_k}{b_k} \times \frac{b_k}{b_0} = (1,5 \text{ à } 1,6) \times (\gamma + \frac{1}{2}) \times 2\gamma = (1,5 \text{ to } 1,6) \gamma (2\gamma + 1),$$

as at $T = \frac{1}{2} T_k$ $\frac{(b_g)_t}{(b_g)_k} = \frac{a_t}{a_k} = 1,5$ to $1,6$. Further from $d = d_0 - 2\gamma m$ follows

$$\frac{d}{d_0} = \frac{v}{v_0} = 1 - \frac{\gamma}{1 + \gamma} m, \text{ as } d_0 \text{ is } = 2(1 + \gamma). \text{ Hence with } \frac{T}{T_k} = \frac{1}{2} \text{ we get}$$

$$\frac{v}{v_0} = \frac{v}{b_0} = \frac{2(1 + \gamma)}{2 + \gamma}.$$

³⁾ Compare also Z. Gl. p. 114—115 and 156—162.

write for "ordinary" liquids in the neighbourhood of the solidifying point:

$$\frac{v}{v-b} \approx 15; \quad \frac{b_0 - b_0}{v} = \frac{p}{v} = \omega \approx 2.5. \quad (\text{liquid, } m = \frac{1}{2}).$$

2. For **solid substances** the equation of state

$$p + \frac{a}{v^2} - \frac{b}{v^n} = \gamma \frac{RT}{v}$$

has often been proposed (GRÜNEISEN and others), in which at very low temperatures PT^4 must be substituted for RT , in accordance with the expression for the Energy holding then. Here P is a volume function, which is still to be determined. It is, however, *not* equal to the coefficient of T^4 in the expression for E at very low temperatures.

But this equation cannot possibly be correct. For at very high pressures the first member would then approach to ∞ at a given temperature, whereas the second member remained finite. Hence here too $v-b$ must necessarily occur in the equation of state, and not v^n .

This is, however, not all. If the coefficient γ occurring in the above equation is calculated theoretically, $\frac{1}{3} \gamma = (3n+5):6$ is found for it¹⁾ (and not $(3n-1):6$, as GRÜNEISEN erroneously gives). But since for $\frac{1}{3} \gamma$ in different metals values are experimentally found between $\frac{4}{3}$ and $\frac{9}{3}$ (average 2; see II § 2), n would lie between 1 and 4, which is impossible. For in the first place n cannot be $= 2$, which would yet be the case with many metals; secondly it is inconceivable that in the term $b:v^n$, referring to the repulsive forces, the exponent of v should be different for every metal; and thirdly fractional exponents would frequently occur.

All these considerations completely condemn the equation of state in question. If on the contrary

$$\underline{\underline{p + \frac{a}{v^2} = \frac{\lambda + RT}{v-b} \dots \dots \dots \quad (4)}}$$

is written for solid substances at higher (i.e. at ordinary) temperatures, in which equation b is again a function of v , represented by a relation analogous to (3), all the discrepancies disappear, and also the discontinuity between the form of the virial of repulsion in liquids and that in solid bodies which is difficult to understand. At bottom it will, indeed, be pretty well immaterial whether the molecules move — as in liquids — along curvilinear „open” paths between the other molecules, frequently “colliding” (which may also take place “at a distance”; it is not neces-

¹⁾ Compare my earlier Paper in These Proceedings 27, 902—904 (1924).

sary that the molecules exactly touch¹⁾), or — as in solid substances — move in curvilinear „closed” paths round a certain state of equilibrium, without shifting from one molecule to another. This with reference to the so-called “dynamic” virial of repulsion, which accordingly, as in liquids in equation (2), keeps the form $-\frac{b}{v-b}RT$; this, added to RT in the second member, again yielding $\frac{RT}{v-b}$ after division by v .

But what distinguishes solid bodies from liquids (and gases), is that in consequence of the fact that the molecules are bound to definite positions of equilibrium, there must necessarily a term λ be present in the equation of state, which refers to the so-called “static” virial of repulsion. Hence this, no more than the static virial of attraction a/v , will contain the temperature as a factor, but it will, of course, contain $v-b$ in the denominator, as otherwise at $T=0$, $p=\infty$ equation (4) would lead to an absurdity.

Accordingly the virial equation has now the following form (everything still to be multiplied by $^{3/2}$):

$$pv + \left(\frac{a}{v} - \lambda \frac{v}{v-b} \right) - \frac{b}{v-b} RT = RT.$$

Here too, in the case of solid substances, it is quite indifferent whether the molecules are mon-atomic or pluri-atomic, because in both members RT refers again to the progressive energy of the molecules, now in closed paths (so that L is *half* the total energy of the path) instead of in open paths, as with liquids and gases.

In what follows we shall show that the equation (4), combined with a relation $b=f(v)$ of the form (3), represents the experimental results for metals perfectly accurately in every respect — not only the coefficient of compressibility and expansibility, but also the coefficients of pressure and temperature of the first-mentioned coefficient, which the earlier theories of GRÜNEISEN and others were entirely inadequate to do.

II.

Closer Consideration at Higher temperatures.

1. The quantity λ , occurring in the above equation (4), can be expressed in the volume v_0 , which the metal occupies at $T=0$ (PT^4 is then substituted for RT), when the external pressure $\underline{p=0}$ is retained, i. e. when the

¹⁾ In this we think e.g. of the molten electrolytes, where the molecules can remain at comparatively large distances apart from each other. Compare These Proceedings 28, 789—793 (1925), and also Z. f. anorg. u. allg. Ch. 149, 337—344 (1925), where we found about 2.7 for the ratio between the diameter of the molecules and the longitudinal dimension of the elementary cubes.

solid substance, as usually, is not under "strain". Then $\frac{a}{v_0^2} = \frac{\lambda}{v_0 - b_0}$, is obtained, hence $\lambda = \frac{a}{v_0^2} (v_0 - b_0)$.

In this b_0 is the value of b corresponding with v_0 , according to the equation

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

which corresponds to (3), or also, when we write $b_g - b_{00}$ for abbreviation $= \varphi$:

$$\underline{\underline{b = \frac{b_g}{1 + \varphi/v}, \quad \text{or} \quad \underline{\underline{v - b_{00}} = (v - b) \left(1 + \frac{\varphi}{v} \right)}}} \quad (5)$$

from which then follows $b_0 = b_g : \left(1 + \frac{\varphi}{v_0} \right)$. In this equation (5) b_g is evidently again the (fictitious) value of b , when v should be $= \infty$. The other limiting value $b_{00} = v_{00}$ is evidently the value of b , when in (5) we take $p = \infty$. This is, therefore, the smallest volume possible, that the solid substance can occupy at the utmost compression. Hence we distinguish *two* limiting volumes with the corresponding values of b , viz. v_0 and $b_0 < v_0$ at $T = 0$, $p = 0$, and $v_{00} = b_{00}$ at $p = \infty$.

The quantity $\frac{\varphi}{v}$ is much smaller in solid substances than in liquids, viz. $= 0,6$ in solid copper as we shall see in IV, as against an average value of $2,5$ in ordinary substances $\left(m = \frac{1}{2} \right)$, so that the variability of b is by no means so great.

2. The quantity $\frac{v}{v-b}$. From the equation of state (5) follows immediately:

$$s = \left(\frac{dp}{dt} \right)_v = \frac{R}{v-b} = \frac{R}{v} \times \frac{v}{v-b},$$

and as the coefficient of tension s according to a known identity is $= - \left(\frac{dv}{dt} \right)_p : \left(\frac{dp}{dt} \right)_t$, we may also write $s = \frac{\alpha}{\sigma}$, in which $\alpha = \frac{1}{v} \left(\frac{dv}{dt} \right)_p$ is the coefficient of expansion, and $\sigma = - \frac{1}{v} \left(\frac{dv}{dp} \right)_t$ is the coefficient of compressibility. Hence $\frac{\alpha}{\sigma} = \frac{R}{v} \times \frac{v}{v-b}$, i.e.

$$\underline{\underline{\frac{v}{v-b} = \frac{\alpha}{\sigma} \times \frac{v}{R}}} \quad (6)$$

from which the ratio $v : (v-b)$ can be calculated for every solid substance, when a and σ are known. Thus e.g. in copper at 20°C $a = 3 \times 17 \cdot 10^{-4}$, $\sigma = 0,73 \cdot 10^{-12}$ (p in dynes per cm^2), $v = 63,57 : 8,933 = 7,116$, and $R = 83,17 \cdot 10^6$ in ergs. Hence:

$$\frac{v}{v-b} = \frac{51 \cdot 10^{-6}}{0,73 \cdot 10^{-12}} \cdot \frac{7,116}{83,17 \cdot 10^6} = \frac{362,9}{60,7} = 5,98,$$

so that (see for $\frac{\varphi}{v} = \omega$ Chapter IV)

$$\frac{v}{v-b} = 6; \quad \frac{b_g - b_{00}}{v} = \frac{\varphi}{v} = \omega = 0,6 \text{ (solid copper } 20^\circ\text{C.)}$$

may be put. For other metals the following values are found in exactly the same way:

Cu	Ag	Au	Mg	Zn	Cd	Al	Sn	Pb	Ta	Bi	W	Fe	Ni	Pd	Pt
6	7	9	5	± 7	± 9	6	7	8	5	± 4	4	5	5	7	7

mean about 6.

If in (4) $\frac{2}{3}L$ is substituted for RT ¹⁾, then $\frac{2}{3}c'_v$ is to be substituted for R , in which c'_v represents the specific heat referring to the pure progressive energy (= half the total energy of path) of the molecule (atom) at constant volume. We then get:

$$\frac{\alpha}{\sigma} = \frac{2/3c'_v}{v-b},$$

from which it therefore follows, that as $v-b$ does not approach 0 at $T = 0$ and $p = 0$, but approaches the *finite* value $v_0 - b_0$ (see above), and also σ remaining *finite*, the coefficient of expansion α will always run parallel with c'_v , and will, therefore, also approach 0 at very low temperatures, where c'_v approaches 0; and this about proportional to T^4 . In this way this property of α is proved in an independent way, and *not* in the way indicated by NERNST and others on the ground of perfectly wrong formulae. (compare my Paper in These Proc. 27, 911–913 (1924) already cited).

According to the earlier equation of state $p + \frac{a}{v^2} - \frac{b}{v^n} = \gamma \frac{RT}{v}$, $\gamma \frac{R}{v}$ would have been found for $\left(\frac{dp}{dt}\right)_v = \frac{\alpha}{\sigma}$, instead of $\frac{R}{v} \times \frac{v}{v-b}$. It is seen from this that the earlier γ (determined by $\frac{1}{3}\gamma = \frac{3n+5}{6}$) is nothing else than the ratio $\frac{v}{v-b}$ in the new equation of state. And it is very plausible that

¹⁾ This is not *perfectly* correct. We shall see later on that there is a difference. At higher temperatures this difference approaches, however, to 0, but at very low temperatures P and A are *not* equal to each other in $L = AT^4$, and PT^4 in the equation of state.

this ratio will assume different values at e.g. 20° according to circumstances (different values of a and of $T:T_k$, etc.), whereas the older equation of state would lead to great absurdities with regard to n (see I).

As regards the quantity λ in the equation of state (4), it follows immediately from $\lambda = \frac{a}{v_0^2} (v_0 - b_0) = \frac{a}{v_0} \frac{v_0 - b_0}{v_0}$, that λ is about $= \frac{1}{6} \frac{a}{v_0}$, as $\frac{v_0 - b_0}{v_0}$ will hardly differ from $\frac{v - b}{v} = \frac{1}{6}$. If we assume that $\frac{a}{v_0}$ (solid) is practically $= \frac{a}{v_0}$ (liquid), which is quite fulfilled with respect to a as we shall see soon, and with great approximation with respect to v_0 , then $\frac{a}{v_0} = 7\gamma \cdot RT_k$ will follow from $RT_k = \frac{2}{7} \frac{a}{b_k} = \frac{1}{7\gamma} \frac{a}{b_0}$ (liquid), because $b_k = 2\gamma \cdot b_0$ and $b_0 = v_0$ (γ is here the coefficient of direction of the straight joining line between d_k and $1/2 d_0$). Now γ is $= 1,76$ for copper ¹⁾ according to our formula $2\gamma = 1 + 0,038\sqrt{T_k}$, with $T_k =$ about 4400°; hence $\frac{a}{v_0} = 12,3 RT_k$ and $\lambda = 2 RT_k$. We have therefore (for copper):

$$\lambda = \frac{1}{6} \frac{a}{v_0}, \quad \text{or} \quad = \underline{2 RT_k}.$$

3. We shall now calculate the different values of v and b , both for solid and (by way of comparison) for liquid copper. For solid copper at 20° C. we found already above $v = 63,57 : 8,933$, i.e. $v_{20} = 7,116$. From this the value $v_0 = 7,046$ is easily calculated at $T = 0$, $p = 0$. For the coefficient of expansion between 16° and -191° is $3 \times 14,28 \cdot 10^{-6}$ (HENNING), in consequence of which v_{-191° becomes $= 7,052$. And between -193° and -253° $\alpha = 3 \times 3,9 \cdot 10^{-6}$ (LINDEMANN), which yields $v_{-253^\circ} = 7,047$, so that $v_{-273^\circ} = v_0$ will be $= 7,046$.

Now $b_{20} = \frac{5}{8} v_{20}$ follows further from $\frac{v}{v-b} = 6$ at 20°, from which we get $b_{20} = 5,930$. And as according to (5) $v_{20} - b_{00} = (v_{20} - b_{20}) \left(1 + \frac{\varphi}{v_{20}}\right)$, in which $\frac{\varphi}{v_{20}} = 0,6$ (see IV), $v_{20} - b_{00}$ becomes $= 1,186 \times 1,6 = 1,898$, hence $b_{00} = v_{00} = 5,218$. Then $v_0 - b_0 = 1,828 : 1,606 = 1,138$ is found according to (5) from $(v_0 - b_{00}) = (v_0 - b_0) \left(1 + \frac{\varphi}{v_0}\right)$, with $\frac{\varphi}{v_0} = \frac{\varphi}{v_{20}} \times \frac{v_{20}}{v_0} = 0,6 \times 1,01$, which yields $b_0 = 5,908$. As regards the (fictitious) value of b_g (at $v = \infty$), the value $7,116 \times 0,6 = 4,270$ follows for $\varphi = b_g - b_{00}$ from $\frac{\varphi}{v_{20}} = 0,6$, which yields $b_g = 9,488$. (Also from $b_{20} = b_g : \left(1 + \frac{\varphi}{v_{20}}\right)$ the value $b_g = 5,930 \times 1,6 = 9,488$ would have followed).

¹⁾ From $T_s \times 1,7 = 2578^\circ \times 1,7 = 4383^\circ$ abs.

And now the corresponding values for liquid copper. But as at 1083° C. (the melting-point of copper) the coefficient of expansion is, indeed, known to a certain extent, but not the compressibility, we must know the value of a for the calculation of $\frac{v}{v-b}$ at 1083°. For from the equation of state follows (see I, §1) $\frac{v}{v-b} = \frac{a/v}{RT}$. Now we shall calculate the value $a = 32,63 \cdot 10^{12}$ for a in III from measurements of the vapour pressure. We find for v at 1083° the value 63.57 : 8.40, i.e. $v_{1083} = 7,568$. Hence we have:

$$\frac{v}{v-b} = \frac{32,63 \cdot 10^{12} : 7,568}{83,17 \cdot 10^6 \times 1356} = \frac{4,312 \cdot 10^{12}}{0,1128 \cdot 10^{12}} = \underline{38,23}.$$

This value is considerably greater than for solid copper (= 6) and for ordinary liquids (± 15), but all the same perfectly plausible. For from $\frac{v}{v-b} = \frac{f}{m}$ (see I, § 1) with $m = T : T_k = 1356 : 4400 = 0,3082$ follows for f the value $38,23 \times 0,3082 = 11,8 =$ about 12. From our formula $f_k = 8\gamma = 8 \times 1,76$ (see above § 2) the value 14,1 = 14 would follow for f_k . And as f_{1083} will be somewhat smaller than f_k as it usually is, this value agrees very well.

In IV we shall find the value $2,017 = \underline{2}$ for $\frac{\varphi}{v}$ (at 1083°), hence about the same as for ordinary liquids ($\frac{\varphi}{v} = 2,5$; zie I, § 1). For solid substances (copper) this was only = 0.6. And knowing this value, we can easily calculate the different values of v and b .

From $v : (v-b) = 38,23$ and $v = 7,568$ (at 1083°) follows immediately $v-b = 0,198$, hence $b_{1083} = \underline{7,370}$. And then the value $0,198 \times 3,017 = 0,597$ follows for $v-b_0$ at 1083° from (3), i.e. $v-b_0 = (v-b) \left(1 + \frac{\varphi}{v}\right)$, so that (fictitiously) we find $b_0 = v_0 = \underline{6,971}$. And from $b_g = b \left(1 + \frac{\varphi}{v}\right)$ the value $7,370 \times 3,017$ is found for b_g , hence $b_g = \underline{22,24}$.

Taking all that has been found together, we get the following summary, in which we have also added the results for "ordinary" substances for a comparison.

The values for "ordinary" liquids ($\gamma = 0,9$ to 1) are :

$$\left\{ \begin{array}{lll} v_0 & v_{1/2T_k} = 1,3 v_0 & v = \infty \\ b_0 = v_0 & b_{1/2T_k} = \frac{14}{15} v_{1/2T_k} & (b_g)_{1/2T_k} = 4,3 b_0 \end{array} \right. \left| \begin{array}{l} \left(\frac{v}{v-b}\right)_{1/2T_k} = 15 \\ \left(\frac{\varphi}{v}\right)_{1/2T_k} = 2,5. \end{array} \right.$$

The values for molten copper ($\gamma = 1,7$) are:

$$\left\{ \begin{array}{lll} (v_0 = 6,97) & v_{1083} = 7,57 & v = \infty \\ (b_0 = 6,97) & b_{1083} = 7,37 & (b_g)_{1083} = 22,2 \end{array} \right. \left| \begin{array}{l} \left(\frac{v}{v-b} \right)_{1083} = 38 \\ \left(\frac{\varphi}{v} \right)_{1083} = 2. \end{array} \right.$$

The values for *solid copper* (v_{20} is at 20° C.) are:

$$\left\{ \begin{array}{llll} v_{00} = 5,22 & v_0 = 7,05 & v_{20} = 7,12 & (v = \infty) \\ b_{00} = 5,22 & b_0 = 5,91 & b_{20} = 5,93 & ((b_g)_{20} = 9,5) \end{array} \right. \left| \begin{array}{l} \left(\frac{v}{v-b} \right)_{20} = 6 \\ \left(\frac{\varphi}{v} \right)_{20} = 0,6. \end{array} \right.$$

If the limiting volume $v_{00} = 5,22$ for solid copper is assumed to be $= 1,91m$ (in the case of cubic distribution; m is the *real* volume of the molecule or atom thought spherical), then we have $\underline{m = 2,73}$, from which it follows that at 1083° $\underline{b_g = 8,14m}$ for liquid copper, i.e. $= 4m \times$ BOLTZMANN'S factor of distribution, which is accordingly about $= 2$ at the temperature mentioned. Also for ordinary liquids $(b_g)_{1/2 T_k}$ lies on an average in the neighbourhood of $4,3 \times 1,9m = 8,17m$, so that BOLTZMANN'S factor is again $= 2$. At the absolute zero, but $p = 0$, we find further $\underline{b_0 = v_0 = 2,6m}$ for liquid copper, and $\underline{b_0 = 2,2m}$ for solid copper, so that in both cases some space is left (in consequence of the repulsive forces), which space does not vanish before $p = \infty$ ($b_{00} = v_{00} = 1,9m$).

III.

Calculation of $\frac{a}{v^2}$ in Copper.

We will now calculate the value of a in *liquid* copper, which value, as will appear in what follows, may be applied to the solid state unchanged. The value of a seems therefore to be the same for all the three states of aggregation. This is not the case with b , as appears very clearly from the survey in § 3 of II.

Many years ago I drew up a theory of the solid state — without the very essential quantity λ however — in which $v-b$ was retained, a passed unchanged from one state to another, and also b was supposed variable, not only in each of the two states of aggregation separately, but also at the transition from the liquid into the solid state. I did not ascribe this variability, however, to the true cause at the time, but to the so-called “quasi-association”, which was then the fashion. Then another state of association was assumed by me to exist in the solid state than in the liquid state, and also the degrees of association in the two states could differ according to T and v . This hypothesis could account for much, but by no means for everything, and at present this theory may be considered as entirely discarded.

According to RUFF and BERGDAHL¹⁾ we have, for molten copper, the subjoined values of p , at the values of T standing above them. According to the shortened formula

$$\log_{10} p^{mm} = -\frac{A_{10}}{T} + C_{10},$$

the values of C_{10} can be determined from the values of $T \log_{10} p = -A_{10} + C_{10} T$ by subtraction. If for this purpose the values at the lowest and at the highest temperature are taken for the sake of accuracy (with the exclusion of that of the very lowest temperature, which in spite of the redetermination by RUFF and MUGDAN²⁾ is not yet quite certain), C_{10} is found from

$$C_{10} = \frac{T_2 \log_{10} p_2 - T_1 \log_{10} p_1}{T_2 - T_1}.$$

$t = 1875$	2105	2175	2215	2245	2300
$T = 2148$	2378	2448	2488	2518	2573
$p^{mm} = 20$	124	209	300	404	752
<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
$\log_{10} p^{mm} = 1,3010$	2,0934	2,3201	2,4771	2,6064	2,8762
$T \log_{10} p^{mm} = 2795$	4978	5680	6163	6563	7401

From this follows for C_{10} averagely $C_{10} = \frac{7401 - 4978}{2573 - 2378} = \frac{2423}{195} = 12,43$.

With this values of C_{10} the values

$$A_{10} = 23880 \mid 24560 \quad 24720 \quad 24740 \quad 24710 \quad 24560$$

are further found from $A_{10} = C_{10} T - T \log_{10} p$, hence on an average $A_{10} = 24530$. It is seen that the first value (calculated from p at 1875°) does not fit in with the others. VAN LIEMPT³⁾ gave the somewhat smaller value 23600. For $A = A_{10} \times 2,3026$ we find therefore $A = 56480$, hence AR becomes $= 4,698 \cdot 10^{12}$ with $R = 83,17 \cdot 10^6$.

As in $\log p = -\frac{A}{T} + C = -\frac{AR}{RT} + C$ the numerator AR is the *extrapolated* heat of evaporation at the absolute zero⁴⁾, viz. $= \frac{a}{v'_0}$ (strictly

¹⁾ Z. für anorg. u. allg. Chemie **106**, 76–94 (1919). GREENWOOD, Z. f. physik. Ch. **76**, 484–490 (1911).

²⁾ Z. für anorg. u. allg. Ch. **117**, 147 (1921).

³⁾ Z. f. anorg. u. allg. Ch. **114**, 105–116 (1920).

⁴⁾ For in the general formula $\log p = -\frac{a/v}{RT} + C'$ $\frac{a}{v}$ has been developed into a series, viz. $= \frac{a_0}{v_0} + \alpha T + \dots$, in which the term with T joins the constant C' after division by RT , through which it becomes $= C$.

speaking $\frac{a_0}{v_0}$, but a is supposed independent of T), we get

$$\frac{a}{v_0} = 4,698 \cdot 10^{12}.$$

If for the coefficient of expansion of liquid copper at 1083° the value $65 \cdot 10^{-6}$ is assumed¹⁾, the value 9,153 follows for D_0' , i. e. the *extrapolated* value of D at $T=0$ (which we want here, as appears from the derivation of the formula for $\log p$ (cf. note 2), from the density 8.40 at 1083°). And from this the value $63,57 : 9,153 = 6,945$ is calculated for v_0' . (This value v_0' , calculated from the expansibility at 1083° , is therefore *slightly* smaller than the real value of $v_0 = b_0$, which we have found above in II, § 3, viz. 6.97).

In virtue of this a finally becomes for liquid, hence according to the hypothesis also for *solid* copper:

$$a = 4,698 \cdot 10^{12} \times 6,945 = \underline{\underline{32,63 \cdot 10^{12}}},$$

in which a/v^2 is expressed in dynes per cm^2 . For this quality the following value is found for solid copper with $v_{20} = 7,116$:

$$\frac{a}{v_{20}^2} = 0,6444 \cdot 10^{12} \text{ (solid copper } 20^\circ \text{ C.)}$$

IV.

The Coefficient of Expansion (Solid).

We start from (4) combined with (5), viz.

$$p + \frac{a}{v^2} = \frac{\lambda + RT}{v-b} = \frac{\lambda + RT}{v-b_{00}} \left(1 + \frac{\varphi}{v}\right),$$

which equation we shall differentiate with respect to T (p constant). Then we get:

$$-\frac{2a}{v^3} \left(\frac{dv}{dt}\right)_p = (\lambda + RT) \left(-\frac{1 + \varphi/v}{(v-b_{00})^2} - \frac{1}{v-b_{00}} \frac{\varphi}{v^2}\right) \left(\frac{dv}{dt}\right)_p + \frac{R}{v-b},$$

when both a and b_g (in $\varphi = b_g - b_0$) are supposed independent of T . Hence we get further:

$$\frac{1}{v} \left(\frac{dv}{dt}\right)_p \left[-\frac{2a}{v^2} + \frac{(\lambda + RT)v}{(v-b_{00})^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi}{v} \frac{v-b_{00}}{v}\right) \right] = \frac{R}{v-b}.$$

If in this for $\lambda + RT$ its value from the equation of state is substituted, in which p is put $= 0$, we get:

¹⁾ Between 1083° and 1200° PASCAL and JOUNIAUX gave the formula $v = v_{1083} (1 + 62 \cdot 10^{-6} (t - 1083) - 560 \cdot 10^{-9} (\text{ibid.})^2 + 5600 \cdot 10^{-12} (\text{ibid.})^3)$, of which the coefficients of the 2nd and the 3rd powers of $t - 1083$ are much too great. Close to 1083° the coefficient of expansion is $= 62 \cdot 10^{-6}$. But if v_{1200} is calculated according to this formula, v becomes $= 7.633$ ($D = 8,328$ and not 8,32 as is given). And this would give $\alpha = 73 \cdot 10^{-6}$. As most probable value we take 65, somewhat greater than 62.

$$\alpha \left[-\frac{2a}{v^2} + \frac{a}{v^2} \frac{v(v-b)}{(v-b_{00})^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi}{v} \frac{v-b_{00}}{v} \right) \right] = \frac{R}{v-b},$$

i.e. after substitution of $v-b_0 = (v-b) \left(1 + \frac{\varphi}{v} \right)$:

$$\alpha \frac{a}{v^2} \left[-2 + \frac{v}{v-b} \frac{1}{1 + \varphi/v} \left(1 + \frac{\varphi}{v} \frac{v-b}{v} \right) \right] = \frac{R}{v} \frac{v}{v-b},$$

or finally

$$\alpha \frac{a}{v^2} \left[-2 \frac{v-b}{v} + \frac{1 + \frac{\varphi}{v} \frac{v-b}{v}}{1 + \frac{\varphi}{v}} \right] = \frac{R}{v}.$$

If $\frac{v-b}{v} = z$, $\frac{\varphi}{v} = \omega$, the equation becomes:

$$\alpha \frac{a}{v^2} \left(\frac{1 + \omega z}{1 + \omega} - 2z \right) = \frac{R}{v},$$

i.e.

$$\alpha = \frac{R}{a/v} \frac{1 + \omega}{1 - (2 + \omega)z} \dots \dots \dots (7)$$

and this equation for α will evidently also be valid for the liquid state ($p=0$). It is true that then in the equation of state λ is absent by the side of RT , but this quantity λ is eliminated during the calculation. Only, φ is then not $= b_g - b_{00}$, but simply $= b_g - b_0$.

For *solid* copper (20° C.) α is now $= 3 \times 17 \cdot 10^{-6} = 51 \cdot 10^{-6}$. We have, therefore, for the calculation of ω (for z we found already the value $1/6$ in II) with $v_{20} = 7,116$, $\frac{a}{v_{20}} = 4,585 \cdot 10^{12}$ and $R : 83,17 \cdot 10^6$:

$$\frac{1 + \omega}{1 - 1/6(2 + \omega)} = \frac{51 \cdot 10^{-6} \times 4,585 \cdot 10^{12}}{83,17 \cdot 10^6} = 2,812,$$

from which $\omega = 0,596 = 0,6$, of which we have already made use in II, § 3. For ordinary substances the mean value 2,5 was found for this (see I, § 1).

In *molten* copper at 1083° $\alpha = 65 \cdot 10^{-6}$ (see III); there we get, therefore, with $a : v_{1083} = 32,63 \cdot 10^{12} : 7,568 = 4,312 \cdot 10^{12}$ and $z = 1 : 38,23$ (see II, § 3):

$$\frac{1 + \omega}{1 - 1/38,23(2 + \omega)} = \frac{65 \cdot 10^{-6} \times 4,312 \cdot 10^{12}}{83,17 \cdot 10^6} = 3,370,$$

from which $\omega = 2,017 = 2$, which value is, therefore, in the neighbourhood of that of ordinary liquids (see I, § 1 and II, § 3).

At *very low* temperatures (but $p=0$) the value

$$\alpha = \frac{4PT^3}{a/v_0} \frac{1 + \omega_0}{1 - (2 + \omega_0)z_0}$$

is evidently found instead of (7), as everything remains the same; only

PT^4 is now substituted for RT , which, differentiated with respect to T , yields $4PT^3$. Now ω_0 is $=\varphi : v_0$ and z_0 is $=(v_0-b_0) : v_0$, which values will differ only little from those at 20° C. e.g. for solid copper (see the summary in II, § 3). Hence the coefficient of expansion α will become proportional to T^3 at very low temperatures, just as c_v , with which it runs parallel.

V.

The Coefficient of Compressibility (Solid).

Now that both $z=(v-b):v$ and $\omega=\varphi:v$ are known, the calculated coefficient of compressibility, after substitution of these values, must agree with the coefficient determined experimentally. For according to

$$(6) \frac{\alpha}{\sigma} = \frac{R}{v} \times \frac{1}{z}, \text{ from which we have determined the value of } z (= 1/6).$$

When, therefore, the value of α comes right (and in IV this has been effected by the assumption of $\omega=0,6$), σ must naturally also be in harmony. Only in VI and VII with the pressure and temperature coefficients of the coefficient of compressibility there can be question of a verification of our hypotheses.

Now $\sigma^{-1} = \frac{R}{v} \times \frac{1}{\alpha z}$, follows immediately from the above equation, hence according to (7) for α , we have:

$$\sigma^{-1} = \frac{a}{v^2} \times \frac{1}{z} \frac{1-(2+\omega)z}{1+\omega}, \dots \dots \dots (8)$$

which might also easily have been derived directly from the equation of state by differentiation with respect to v (T constant), in entirely the same way as in IV for α . However, in VI and VII we cannot make use of this result, because in this $\lambda + RT$ has been replaced by its value from the equation of state, in which $p=0$ was put.

If in (8) the value $0,6444 \cdot 10^{12}$, found in III, is substituted for $\frac{a}{v^2}$, the value 6 for $\frac{1}{z} = \frac{v}{v-b}$, the value 0,6 determined just now in IV from the coefficient of expansion (everything at 20° C.), we get:

$$\sigma^{-1} = 0,6444 \cdot 10^{12} \times 6 \times \frac{1-(2,6:6)}{1,6} = 3,866 \cdot 10^{12} \times 0,3542 = \underline{1,369 \cdot 10^{12}}.$$

The value $\underline{1,370 \cdot 10^{12}}$ was found by BRIDGMAN at 20° C., so that the agreement of course is perfect. For BRIDGMAN¹⁾ found for pure copper (loc.

¹⁾ Compare his exceedingly important and comprehensive paper in the Proceedings of the American Acad. of Arts and Sciences 58, No. 5, p. 165-242 (1923): The compressibility of thirty metals as a function of pressure and temperature. Also in numerous other papers BRIDGMAN has considerably enriched our knowledge in this and allied regions after RICHARDS. We are greatly indebted to this investigator for his extensive and very accurate researches.

cit. p. 192) for $-\frac{1}{v_a} \frac{\Delta v}{p} = \sigma'$, which is practically $= \sigma$, in which v_a represents the volume at t^0 and $p=0$:

$$\left. \begin{aligned} \sigma'_{30^\circ} &= 10^{-6} (0,719 - 2,6 \cdot 10^{-6} p) \\ \sigma'_{75^\circ} &= 10^{-6} (0,734 - 2,7 \cdot 10^{-6} p) \end{aligned} \right\} p \text{ in } \text{KG/cm}^2.$$

If p is expressed in Dynes/cm² (in which then e. g. 0,719 must be multiplied by $1,02 \cdot 10^{-6}$ and 2,6 by $(1,02 \cdot 10^{-6})^2$), the expression becomes:

$$\left. \begin{aligned} \sigma'_{30^\circ} &= 10^{-12} (0,7334 - 2,704 \cdot 10^{-12} p) \\ \sigma'_{75^\circ} &= 10^{-12} (0,7487 - 2,808 \cdot 10^{-12} p) \end{aligned} \right\} p \text{ in } \frac{\text{dynes}}{\text{cm}^2}.$$

From this follows by extrapolation:

$$\underline{\sigma'_{20} = 10^{-12} (0,7300 - 2,681 \cdot 10^{-12} p)},$$

so that σ_{20} becomes $= 0,7300 \cdot 10^{-12}$ at $p=0$, hence $\sigma_{20}^{-1} = 1,370 \cdot 10^{12}$, as we gave above.

VI.

The Coefficient of Pressure of σ^{-1} .

As we already remarked in V, it is not allowed to start from (8), where $p=0$ is put, for the differentiation with respect to p , but from the equation for σ^{-1} derived directly from the equation of state

$$p = -\frac{a}{v^2} + \frac{\lambda + RT}{v-b} = -\frac{a}{v^2} + \frac{\lambda + RT}{v-b_{00}} \left(1 + \frac{\varphi}{v}\right).$$

We find then (see also IV):

$$\left(\frac{dp}{dv}\right)_t = \frac{2a}{v^3} - \frac{\lambda + RT}{(v-b_{00})^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi}{v} \frac{v-b_{00}}{v}\right),$$

so that

$$\sigma^{-1} = -v \left(\frac{dp}{dv}\right)_t = -\frac{2a}{v^2} + \frac{\lambda + RT}{(v-b_{00})^2} \left(v + \varphi + \varphi \frac{v-b_{00}}{v}\right). \quad (a)$$

From this follows (T constant):

$$\begin{aligned} \frac{d\sigma^{-1}}{dp} &= \left[\frac{4a}{v^3} + (\lambda + RT) \right] \left\{ -\frac{2 \left(v + \varphi + \varphi \frac{v-b_{00}}{v} \right)}{(v-b_{00})^3} + \frac{1 + \varphi \left(-\frac{v-b_{00}}{v^2} + \frac{1}{v} \right)}{(v-b_{00})^2} \right\} \frac{dv}{dp} \\ &= \frac{1}{v} \frac{dv}{dp} \left[\frac{4a}{v^2} - \frac{(\lambda + RT)v^2}{(v-b_{00})^3} \right] \left\{ 2 \left(1 + \frac{\varphi}{v} + \frac{\varphi}{v} \frac{v-b_{00}}{v} \right) - \frac{v-b_{00}}{v} \left(1 + \frac{\varphi}{v} - \frac{\varphi}{v} \frac{v-b_{00}}{v} \right) \right\}. \end{aligned}$$

If the value $\left(p + \frac{a}{v^2}\right)(v-b)$ is substituted here for $\lambda + RT$, and the value $(v-b) \left(1 + \frac{\varphi}{v}\right)$ for $v-b_{00}$, we get ($p=0$):

$$\frac{d\sigma^{-1}}{dp} = \frac{1}{v} \frac{dv}{dp} \frac{a}{v^2} \left[4 - \frac{v^2}{(v-b)^2} \frac{1}{(1+\frac{v}{v})^2} \right] \left\{ 2 \left(1 + \frac{\varphi}{v} \frac{v-b}{v} \right) - \frac{v-b}{v} \left(1 + \frac{\varphi}{v} \right) \left(1 - \frac{\varphi}{v} \frac{v-b}{v} \right) \right\}$$

i.e. with $\frac{\varphi}{v} = \omega$ and $\frac{v-b}{v} = z$:

$$\frac{d\sigma^{-1}}{dp} = \frac{1}{v} \frac{dv}{dp} \frac{a}{v^2} \frac{1}{z^2 (1+\omega)^2} \left[4 z^2 (1+\omega)^2 - \left\{ 2 (1+\omega z) - z (1+\omega) (1-\omega z) \right\} \right],$$

or

$$\frac{d\sigma^{-1}}{dp} = (-\sigma) \frac{a}{v^2} \frac{1}{z^2 (1+\omega)^2} \left(-2 + (1-\omega) z + (4 + 7\omega + 3\omega^2) z^2 \right).$$

According to (8) σ is $= \left(1 : \frac{a}{v^2} \right) \times z \frac{1+\omega}{1-(2+\omega)z}$, so that we finally obtain:

$$\frac{d\sigma^{-1}}{dp_{(p=0)}} = \frac{1}{z} \frac{2 - (1-\omega)z - (4 + 7\omega + 3\omega^2)z^2}{(1+\omega)(1-(2+\omega)z)} \dots \dots \dots (9)$$

We will now compare this with BRIDGMAN's experimental values written above.

With $z = \frac{1}{6}$, $\omega = 0,6$ (at 20° C.) the above becomes:

$$\frac{d\sigma^{-1}}{dp} = 6 \frac{2 - (0,4 : 6) - (9,28 : 36)}{1,6 (1 - (2,6 : 6))} = \frac{60,32}{5,44} = 11,1 (p=0).$$

According to us $\sigma = \frac{1}{v} \frac{dv}{dp}$, whereas in $\sigma_1 = \frac{1}{v_a} \frac{dv}{dp}$ v_a is constant with respect to p (see V). We have, therefore:

$$\begin{aligned} \frac{d\sigma^{-1}}{dp} &= \frac{d}{dp} \left(-v \frac{dp}{dv} \right) = v \frac{d}{dp} \left(-\frac{dp}{dv} \right) - \frac{dp}{dv} \frac{dv}{dp} = \\ &= \frac{v}{v_a} \frac{d}{dp} \left(-v_a \frac{dp}{dv} \right) - 1 = \frac{d\sigma_1^{-1}}{dp} - 1 \end{aligned}$$

at $p=0$, where $v_a = v$. Hence we find theoretically:

$$\frac{d\sigma_1^{-1}}{dp} = \underline{12,1} (p=0).$$

According to BRIDGMAN (see V) $\sigma' = -\frac{\Delta v}{v_a p}$ is of the form of $\alpha - \beta p$, i.e.

$$\frac{v_a - v}{v_a} = \alpha p - \beta p^2.$$

From this follows therefore:

$$\sigma_1 = -\frac{1}{v_a} \frac{dv}{dp} = \alpha - 2\beta p, \text{ hence because } \frac{d\sigma_1^{-1}}{dp} = -\frac{1}{\sigma_1^2} \frac{d\sigma_1}{dp}$$

$$\frac{d\sigma_1^{-1}}{dp} = \frac{2\beta}{a^2} (p=0).$$

Accordingly at 20° C is *experimentally* (with $a = 0,73 \cdot 10^{-12}$, $\beta = 2,681 \cdot 10^{-24}$) (see V):

$$\frac{d\sigma_1^{-1}}{dp} = \frac{2 \times 2,681 \cdot 10^{-24}}{0,5329 \cdot 10^{-24}} = \underline{10,1} (p=0).$$

The difference between 10 and 12 as differential coefficient with respect to p of a quantity which is $= 1,37 \cdot 10^{12}$ itself, may be called very small. Not only is the order of magnitude the same, but there is even almost *numerical* agreement; this was impossible with the earlier theories of GRÜNEISEN, BORN and others (BRIDGMAN, loc. cit. p. 233 et seq.). Even the order of magnitude is already wrong there in many cases, up to a ratio of $1 : \frac{1}{4} \cdot 10^{-16}$!! In comparison with this it is seen how unexpectedly well our theoretical value 12 harmonizes with the value 10 found experimentally, taking note that it would be easy through a very small modification in the value of a , which was transferred from the liquid phase to the solid phase, hence also of the value of ω , to obtain a perfect harmony.

VII.

The Coefficient of the Temperature of σ^{-1} .

We again start from the equation (a) in VI:

$$\sigma^{-1} = -\frac{2a}{v^2} + \frac{\lambda + RT}{(v-b_{00})^2} \left(v - \varphi + \varphi \frac{v-b_{00}}{v} \right), \quad \dots \quad (a)$$

and must differentiate this now with respect to T (p constant). This calculation runs almost parallel with that in VI, but is somewhat longer. We can, however, obtain the result more easily by the following consideration. According to (a) is $\sigma^{-1} = f(T, v)$, hence $\left(\frac{dx}{dp} \right)_t = \frac{\partial x}{\partial v} \left(\frac{dv}{dp} \right)_t$, when for shortness we write x for σ^{-1} . Likewise $\left(\frac{dx}{dt} \right)_p = \frac{\partial x}{\partial t} + \frac{\partial x}{\partial v} \left(\frac{dv}{dt} \right)_p$.

Hence we have:

$$\left(\frac{dx}{dt} \right)_p = \frac{\partial x}{\partial t} + \left(\frac{dx}{dp} \right)_t \left(\frac{dp}{dv} \right)_t \left(\frac{dv}{dt} \right)_p = \frac{\partial x}{\partial t} - \left(\frac{dx}{dp} \right)_t \left(\frac{dp}{dt} \right)_v.$$

We have, therefore, according to (a) and (9):

¹⁾ Thus in an extensive theoretical discussion of his experimental results BRIDGMAN found the value $8,5 \cdot 10^{-40}$ (p. 230), calculated from the experiments for a certain quantity β (p. 232), whereas on p. 232 the quantity $1,04 \cdot 10^{-40}$ is found for it, which he all the same calls "the same order of magnitude" (8,5 and 1). But on p. 235 the value of $2,03 \cdot 10^{-56}$ would ensue from the coefficient of pressure, which is not less than $\frac{1}{4} \times 10^{-16}$ of the first-mentioned value!

$$\left(\frac{dx}{dt}\right)_p = \frac{R\left(v + \varphi + \varphi \frac{v-b_{00}}{v}\right)}{(v-b_{00})^2} - \frac{1}{z} \frac{2-(1-\omega)z-(4+7\omega+3\omega^2)z^2}{(1+\omega)(1-(2+\omega)z)} \times \frac{R}{v-b},$$

as $\left(\frac{dp}{dt}\right)_v = \frac{R}{v-b}$ immediately follows from the equation of state. With

$v-b_{00} = (v-b)(1+\omega)$ and $\frac{\varphi}{v} = \omega$ this becomes, when σ^{-1} is again written for x and the indication $p = \text{constant}$ is omitted:

$$\frac{d\sigma^{-1}}{dt} = \frac{Rv}{(v-b)^2} \frac{1+\omega z}{1+\omega} - \frac{Rv}{(v-b)^2} \frac{2-(1-\omega)z-(4+7\omega+3\omega^2)z^2}{(1+\omega)(1-(2+\omega)z)},$$

as $\frac{1}{z} = \frac{v}{v-b}$.

We have therefore finally:

$$\frac{d\sigma^{-1}}{dt} = - \frac{Rv}{(v-b)^2} \frac{(2-(1-\omega)z-(4+7\omega+3\omega^2)z^2) - (1+\omega z)(1-(2+\omega)z)}{(1+\omega)(1-(2+\omega)z)},$$

or

$$\frac{d\sigma^{-1}}{dt_{(p=0)}} = - \frac{R}{v} \frac{1}{z^2} \frac{1+(1+\omega)z-(4+5\omega+2\omega^2)z^2}{(1+\omega)(1-(2+\omega)z)} \quad \dots \quad (10)$$

With $z = \frac{1}{6}$, $\omega = 0,6$, $R = 83,17 \cdot 10^6$, $v = 7,116$ (all this at 20°C.) this becomes:

$$\frac{d\sigma^{-1}}{dt} = - 11,69 \cdot 10^6 \times 36 \frac{1+(1,6:6)-(7,72:36)}{1,6(1-(2,6:6))},$$

i. e.

$$\frac{d\sigma^{-1}}{dt} = - 11,69 \cdot 10^6 \times 36 \times \frac{37,88}{6 \times 1,6 \times 3,4} = - 70,14 \cdot 10^6 \times \frac{37,88}{5,44} = - 488 \cdot 10^6$$

at $p = 0$. We have therefore *theoretically*:

$$\frac{d\sigma^{-1}}{dt} = - \underline{490 \cdot 10^6} \quad (p = 0).$$

The following value has been found by BRIDGMAN for pure copper ($p = 0$) (see V):

$$\sigma_{300}^{-1} = \frac{10^{12}}{0,7334} = 1,3635 \cdot 10^{12}; \quad \sigma_{750}^{-1} = \frac{10^{12}}{0,7487} = 1,3357 \cdot 10^{12}.$$

Per degree this gives an increase of $- 0,0278 \cdot 10^{12}:45 = - 618 \cdot 10^6$.

But in another specimen BRIDGMAN found a much smaller value for $\Delta\sigma$, i.e. (in his units) against $(0,734-0,719) 10^{-6} = 15 \cdot 10^{-9}$, on which we based the above calculation, also $(0,737-0,729) 10^{-6} = 8 \cdot 10^{-9}$. On an average therefore $11,5 \cdot 10^{-9}$, and not $15 \cdot 10^{-9}$, so that we must also take only the $\frac{23}{30}$ of the above value $- 618 \cdot 10^6$ referring to σ^{-1} (the pressure coefficients are exactly the same in the two specimens; only

the temperature coefficients are different). Accordingly we get *experimentally* on an average:

$$\frac{d\sigma^{-1}}{dt} = - \underline{475 \cdot 10^6} (p = 0),$$

which is again in very good harmony with the above theoretical value $- 490 \cdot 10^6$,

Summarizing we may, therefore, say that — at least in copper — our equation of state (4), which has now again (with the exception of λ) the VAN DER WAALS' type, accurately represents, combined with $b = f(v)$ according to (5), all the thermic quantities, and — as far as the coefficients of pressure and temperature of the compressibility coefficient are concerned — it does so with sufficient accuracy, not only as regards the order of magnitude, but also as regards the numerical value. None of the equations of state proposed earlier, were in any way adequate to do so (even apart from the inner inconsistencies contained in them; see I).

When in a following Communication we shall first have discussed further the question of the degeneration of RT in the equation of state in connection with the degeneration of the Energy, we will determine the values of $z = \frac{v}{v-b}$, $\omega = \frac{p}{v}$ and a for *all* the metals of which a and σ are known (and this is by far the majority), and so doing again verify the said coefficients of pressure and temperature of σ .

Tavel sur Clarens, Suisse, 1924—1925.
