THE VARIATION OF THE SPECIFIC HEAT OF SOLIDS WITH TEMPERATURE.

By Arthur H. Compton.

THE very considerable success of the quantum hypothesis in explaining the variations of the specific heat of solids with temperature has been taken as a strong confirmation of that hypothesis. Before this evidence can be considered as conclusive, however, it is necessary to see if there may not be some other satisfactory solution of the problem of specific heat, which does not involve the conception of quanta. It has been pointed out by several writers[1] that the sharp decrease of the specific heat of solids at low temperatures can be qualitatively explained if it is assumed that at these temperatures the atoms become so intimately associated that degrees of freedom are lost. In fact Benedicks[1] has been able to obtain an empirical expression on this assumption which, with properly chosen constants, fits the experimental data acceptably. In the present paper an assumption is introduced which leads directly to an expression for the variation of the specific heat with temperature which will be shown to agree at least as well with experiment as the expressions derived from the quantum hypothesis.

The assumption on which the following work is based is:

If the relative energy between two neighboring atoms in a solid falls below a certain critical value, the two atoms become agglomerated[2] so that the degree of freedom between them vanishes; but as soon as the energy increases again above the critical value, the degree of freedom reappears.

The defence of this assumption from various lines of evidence will form the subject of a later paper.

Derivation of a Formula for the Specific Heat.

The energy content of the unagglomerated degrees of freedom may be written, according to equipartition,

$$U_u = nRT,$$

---

[1] F. Richarz, Zeitschr. f. anorg. Chem., 58, 356; 59, 146. J. Duclaux, Compt. Rend., 155, 1015. C. Benedicks, Ann. d. Phys., 42, 133.

[2] The term "agglomeration," suggested by Benedicks, is used to indicate any state of association of the atoms on account of which degrees of freedom for thermal motion disappear.

where n is the number of unagglomerated degrees of freedom, R the gas constant for a single molecule, and T the absolute temperature. In the case of the chemical combination of two atoms, when a degree of freedom vanishes its energy is usually transmitted to the other degrees of freedom in the form of heat of formation. In the case of endothermic substances, however, the vanishing degree of freedom absorbs a certain amount of energy. We may assume provisionally, therefore, that when two atoms in a solid agglomerate they retain a certain amount of potential energy. The amount of this energy will be,

$$U_a = \gamma(3N - n),$$

where γ is the potential energy of each agglomerated degree of freedom, and $3N$ is the greatest possible number of degrees of freedom. The total energy content of the solid is therefore,

$$U = U_u + U_a = nRT + \gamma(3N - n).$$

If we call P the probability that a certain possible degree of freedom shall actually exist, $P = n/3N$, and

$$U = 3NRTP + 3N\gamma(1 - P). \tag{1}$$

In the case of a solid the kinetic energy of a degree of freedom is on the average equal to its potential energy. We may assume, therefore, that the probability for a certain value of the potential energy is equal to the probability for the same value of the kinetic energy. By Maxwell's distribution law, the probability that the relative velocity of two atoms along the line of their centers shall lie between $| u |$ and $| u + du |$ is

$$\frac{2}{\alpha\sqrt{\pi}} e^{-\frac{u^2}{\alpha^2}} du,$$

where

$$\alpha = 2\sqrt{\frac{RT}{m}}.$$

This is therefore also the probability that the relative kinetic energy shall lie between $\frac{1}{2}mu^2$ and $\frac{1}{2}m(u + du)^2$. Since the probability for the potential energy is equal to that for the kinetic energy, the probability that the relative potential energy shall lie between $\frac{1}{2}mv^2$ and $\frac{1}{2}m(v + dv)^2$ is similarly,

$$\frac{2}{\alpha\sqrt{\pi}} e^{-\frac{v^2}{\alpha^2}} dv.$$

Thus the probability that the total energy shall lie between $\frac{1}{2}m(u^2 + v^2)$ and $\frac{1}{2}m\{u^2 + v^2 + d(u^2 + v^2)\}$ is the product of these two expressions, or

$$\frac{4}{\alpha^2\pi} e^{-\frac{u^2}{\alpha^2}} e^{-\frac{v^2}{\alpha^2}} du dv.$$

If we let ϵ be the critical value of the energy below which a degree of freedom remains agglomerated, the probability that the degree of freedom shall be agglomerated is:

$$P' = \int_0^{\frac{1}{2}m(u^2+v^2)=\epsilon} \frac{4}{\alpha^2\pi} e^{-\frac{u^2}{\alpha^2}} e^{-\frac{v^2}{\alpha^2}} du dv,$$

$$= \frac{4}{\alpha^2\pi} \int_0^{u^2=\frac{2\epsilon}{m}} e^{-\frac{u^2}{\alpha^2}} du \int_0^{v^2=\frac{2\epsilon}{m}-u^2} e^{-\frac{v^2}{\alpha^2}} dv,$$

or

$$= \frac{4}{\alpha^2\pi} \int_0^{\beta} e^{-\frac{u^2}{\alpha^2}} du \int_0^{\sqrt{\beta^2-u^2}} e^{-\frac{v^2}{\alpha^2}} dv;$$

where

$$\beta^2 = \frac{2\epsilon}{m}.$$

This integral may be determined by a series method, the solution being,

$$P' = \frac{\beta^2}{\alpha^2} - \frac{1}{2!}\frac{\beta^4}{\alpha^4} + \frac{1}{3!}\frac{\beta^6}{\alpha^6} - \cdots.$$

This is the probability that a possible degree of freedom shall be agglomerated. The probability that it shall actually exist is therefore:

$$\begin{aligned} P &= 1 - P' \\ &= 1 - \frac{\beta^2}{\alpha^2} + \frac{1}{2!}\frac{\beta^4}{\alpha^4} - \frac{1}{3!}\frac{\beta^6}{\alpha^6} + \cdots. \end{aligned}$$

But

$$e^{-\frac{\beta^2}{\alpha^2}} = 1 - \frac{\beta^2}{\alpha^2} + \frac{1}{2!}\frac{\beta^4}{\alpha^4} - \frac{1}{3!}\frac{\beta^6}{\alpha^6} + \cdots,$$

and by comparison of series,

$$P = e^{-\frac{\beta^2}{\alpha^2}}.$$

We may substitute for β^2/α^2 its equivalent,

$$\frac{\beta^2}{\alpha^2} = \frac{\frac{2\epsilon}{m}}{\frac{4RT}{m}} = \frac{\epsilon}{2RT} = \frac{\tau}{T}, \quad \text{where} \quad \tau = \frac{\epsilon}{2R},$$

then

$$P = e^{-\frac{\tau}{T}}. \tag{2}$$

Substituting this value of P in equation (1) we have:

$$U = 3NRTe^{-\frac{\tau}{T}} + 3N\gamma(1 - e^{-\frac{\tau}{T}}), \tag{3}$$

and the specific heat is:

$$C_v = \frac{dU}{dT} = 3NRe^{-\frac{\tau}{T}} + \frac{3NR\tau}{T} e^{-\frac{\tau}{T}} - 3N\gamma \frac{\tau}{T^2} e^{-\frac{\tau}{T}}. \tag{4}$$

Since there is a T^2 in the denominator of the last term, it is evident that as long as γ has a finite value, T can be made so small that C_v will become negative. This is impossible, as it implies a condition of instability, so we must place $\gamma = 0$, and

$$C_v = 3NRe^{-\frac{\tau}{T}}\left(\frac{\tau}{T} + 1\right). \tag{5}$$

If $T = \infty$, $C_v = 3NR = C_\infty$,

$$\therefore \frac{C_v}{C_\infty} = e^{-\frac{\tau}{T}}\left(\frac{\tau}{T} + 1\right). \tag{6}$$

This is the expression for the variation of the specific heat with temperature to which our assumption leads.

TESTING THIS EQUATION.

The curves of Fig. 1 show how this formula compares with that of Debye for the specific heat.[1] The solid line is plotted from equation (6) and the broken one from Debye's equation,

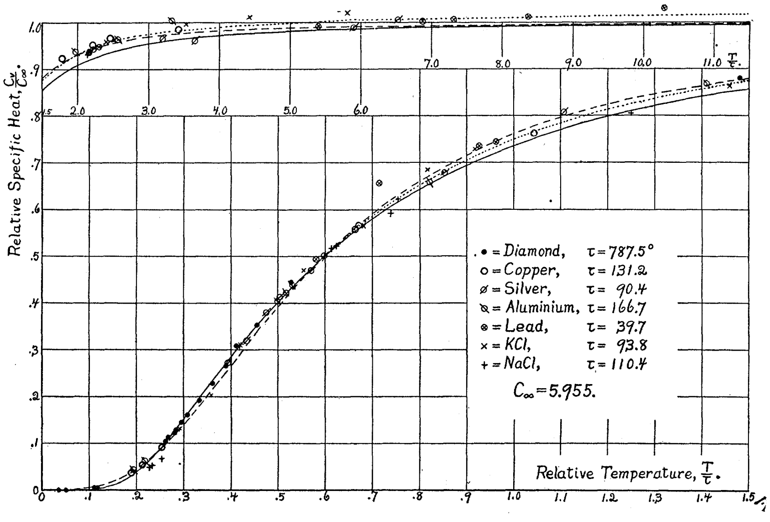

Fig. 1.

$$\frac{C_v}{C_\infty} = \frac{12}{x^3}\int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} - \frac{3x}{e^x - 1},$$

where $x = \Theta/T$. The two curves have been made to coincide at $C_v/C_\infty = 0.5$. That they are in general good agreement is evident at a glance.

---

[1] Debye, Ann. d. Phys., 39, 789. Debye's formula is used because his has been shown to be the most accurate of any of the existing expressions (cf. E. H. Griffiths and E. Griffiths, Proc. Roy. Soc., A, 90, 558).

Their comparative accuracy has been tested with the data used by Debye and by Nernst and Lindemann[1] in testing their own formulæ. I have taken their calculations of C_v from the observed value of C_p. The value of γ for each of the substances is chosen so as to bring the experimental values as near as possible to the two curves where they cross.[2]

At lower temperatures, though the curves are not far apart, there is an evident preponderance of experimental evidence in favor of the solid curve. Above $T/\tau = 0.6$, however, the experimental values gradually rise from the solid curve, cross the broken one at about 2.25, and continue approximately parallel to the solid curve but at a higher level. The dotted curve is drawn as an approximate experimental mean. It is evident that the data fit neither formula accurately for these temperatures, but that the values of C_v/C_∞ approach a limit some two per cent. higher than unity. That these high values of C_v are not due to proximity to the melting point is evident when one notices that none of the experiments are made at a temperature closer than 191° to the melting point, while in the case of KCl the value of C_v/C_∞ rises above unity when the temperature is only .40 as high as the melting point. A possible explanation of the high values of the specific heat at these temperatures is that there may be more degrees of freedom in a solid than indicated by Rayleigh's formula, $C_\infty = 3R$. Whatever the cause of this discrepancy, however, it is necessary on any theory that C_v shall never become greater than C_∞, so we must assume a value of C_∞ greater than $3R = 5.955$, which is the value used in calculating the values of C_v/C_∞ in Fig. 1. The value 6.081 has therefore been chosen as an experimental limit which C_v seems to approach.

Fig. 2 shows the same theoretical curves and the experimental data plotted with this new value of C_∞. The curves have here been made to coincide at $C_v/C_\infty = 0.65$, in order to show more clearly the differences between the two formulæ. It will be seen that this correction makes the observed specific heats conform very well with the curve plotted according to my expression, while they vary consistently from that of Debye. Thus while the data can in no way be made to conform at all temperatures with Debye's formula, by making a correction which would seem necessary in any case, the data may be made to fit well the equation

---

[1] Zeitschr. für Electrochemie, 17, p. 817.

[2] In the following tables the values of C_v for Al, Pb, KCl and NaCl are taken from Nernst and Lindemann's paper (*loc. cit.*), those for Cu, Ag and diamond from that of Debye (*loc. cit.*). C_v is calculated from the observed values of C_p according to the formula, due to Nernst and Lindemann, $C_v = C_p - 0.0214 C_p^2 T/T_s$, where T_s is the melting point of the substance. C_∞ is taken to be 6.081 as explained in the text.

T	C_v Obs.	C_v Calc.
Diamond, $\tau = 794.0°$		
30°	0.00	0.00
42	0.00	0.00
88	0.03	0.01
92	0.03	0.015
205	0.62	0.63
209	0.66	0.67
220	0.72	0.75
222	0.76	0.80
232	0.86	0.87
243	0.95	0.98
262	1.14	1.18
284	1.35	1.41
306	1.58	1.60
331	1.83	1.87
358	2.11	2.13
413	2.64	2.62
1169	5.24	5.18
Copper, $\tau = 133.5°$		
23.5°	0.22	0.14
27.7	0.32	0.26
33.4	0.54	0.56
87	3.32	3.32
88	3.37	3.36
137	4.53	4.54
234	5.50	5.40
290	5.66	5.60
323	5.75	5.69
450	5.87	5.86
Lead, $\tau = 38.4°$		
23.0°	2.95	3.04
28.3	3.91	3.69
36.8	4.38	4.38
38.1	4.43	4.45
85.5	5.57	5.60
90.2	5.63	5.67
200	5.91	5.98
273	5.99	6.02
290	5.99	6.02
332	6.03	6.03
409	6.15	6.05
Silver, $\tau = 92.0°$		
35.0°	1.58	1.58
39.1	1.90	1.93
42.9	2.26	2.25
Silver (continued)		
45.5°	2.46	2.44
51.4	2.80	2.83
53.8	2.89	2.98
77.0	4.04	4.04
100	4.80	4.65
200	5.61	5.61
273	5.75	5.79
331	5.71	5.87
535	5.90	5.93
589	5.99	5.99
Aluminum, $\tau = 169.6°$		
32.4°	0.25	0.19
35.1	0.33	0.28
83.0	2.40	2.40
86.0	2.51	2.51
88.3	2.61	2.60
137	3.91	3.94
235	5.17	5.09
331	5.58	5.55
433	5.74	5.72
555	5.98	5.85
NaCl, $\tau = 113.5°$		
25.0°	0.29	0.36
25.5	0.31	0.38
28.0	0.40	0.52
67.5	3.05	3.04
69.0	3.12	3.10
81.4	3.52	3.60
83.4	3.72	3.71
138	4.79	4.87
235	5.55	5.57
KCl, $\tau = 96.1°$		
26.9°	0.76	0.78
33.7	1.25	1.35
39.0	1.83	1.80
52.8	2.79	2.78
63.2	3.34	3.34
76.6	4.08	3.91
86.0	4.33	4.22
137	5.18	5.15
235	5.73	5.69
331	5.93	5.87
416	6.02	5.95
550	6.09	5.99

just derived. In fact, all variations from the theoretical values seem to lie within the limits of experimental error.

Discussion of the Formula.

Some interesting aspects of formula (6) appear if the exponent of e is written in a different form. τ is defined as $\epsilon/2R$, where ϵ is the energy required to liberate an agglomerated degree of freedom. This quantity has the same dimensions as Planck's energy quantum $h\nu$, both being elementary units of energy. In fact Benedicks has shown,[1] from a consideration of the relation of hardness to the frequency of vibration of an atom, that ϵ is probably proportional to ν. If we call the factor of proportionality b, the probability becomes

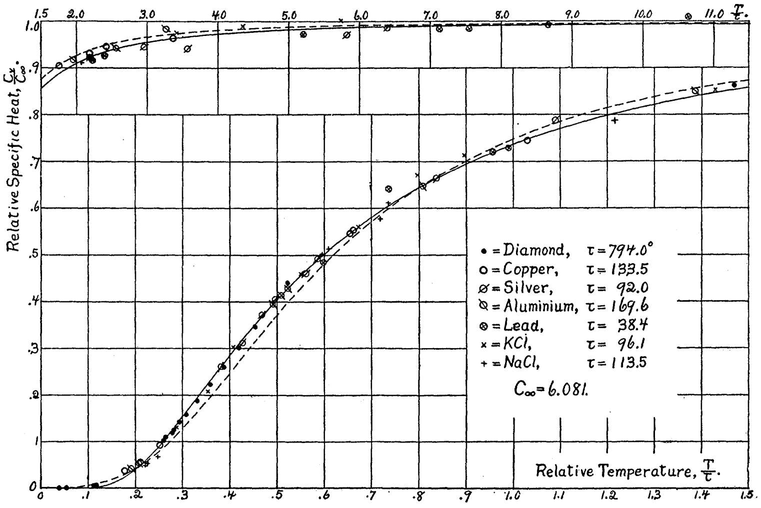

Fig. 2.

$$P = e^{-\frac{\tau}{T}} = e^{-\frac{\epsilon}{2RT}} = e^{-\frac{b\nu}{2RT}} = e^{-\frac{\beta\nu}{T}}\,, \tag{7}$$

where

$$\beta = \frac{b}{2R}.$$

The value of β can easily be determined from the expression $\beta = \tau/\nu$, which follows from equation (7). The values of τ for the different substances considered are determined by their specific heats as shown in Fig. 2. The values of ν may be taken as those assigned by Nernst and Lindemann's formula for the specific heat, since their values of ν have been shown to be in very accurate agreement with the characteristic

---

[1] *Loc. cit.*

frequencies of those substances whose reststrahlen can be obtained. The different values of β as thus determined are given in the following table.

Substance.	τ	$\nu \times 10^{-12}$	$\beta \times 10^{11}$	Difference from Mean.
Lead	38.4	1.9	2.02	+0.3%
Silver	92.0	4.5	2.04	+1.4
KCl	96.1	4.73	2.03	+0.6
NaCl	113.1	5.8	1.96	−2.9
Copper	133.5	6.6	2.02	+0.3
Aluminium	169.6	8.3	2.04	+1.4
Diamond	794.0	40.0	1.98	−1.4

β is thus determined just as accurately as ν is known, and since it remains constant over so great a range of frequencies, equation (7) may be considered valid, even though its derivation is not rigid.

It is interesting to see how the quantity b in this equation compares with the similar quantity h of Planck's expression. b is determined by the equation $b = 2R\beta$, in which the accepted value of R is about 1.35×10^{-16} erg deg.$^{-1}$, and $\beta = 2.01 \times 10^{-11}$ deg. sec. Thus

$$b = 5.44 \times 10^{-27} \text{ erg sec.},$$

while Planck's constant h has the value

$$h = 6.55 \times 10^{-27} \text{ erg sec.}$$

The value for b found here is in excellent agreement with certain values of h as determined by photoelectric methods: Richardson and Compton[1] 5.4×10^{-27}; Hughes[2] 5.6×10^{-27}; Cornelius[3] 5.7×10^{-27}; though Kadesch[4] and Millikan[5] very recently have obtained photoelectric values of h more nearly 6.55×10^{-27}.

Now that equation (7) has been established we are in a position to make a new application of Debye's theory which interprets the heat energy of solids in terms of their elastic vibrations. He considers a whole spectrum of frequencies, the number of vibrations between the frequencies ν and $\nu + d\nu$ being

$$dn = \frac{9N}{\nu_m^3}\nu^2 d\nu, \tag{8}$$

---

[1] Phil. Mag., 24, 574.

[2] Phil. Trans. Roy. Soc., 212, 205.

[3] K. T. Compton, PHYS. REV., 1, 382.

[4] PHYS. REV., 3, 367.

[5] PHYS. REV., 4, 73.

where $3N$ is the total number of degrees of freedom in the solid, and ν_m is the maximum possible frequency, determined by the equation:

$$\frac{1}{\nu_m^3} = \frac{4\pi V}{9N}\left\{2\left(\frac{2\rho(1+\sigma)\chi}{3(1-2\sigma)}\right)^{\frac{3}{2}} + \left(\frac{2\rho(1+\sigma)\chi}{3(1-\sigma)}\right)^{\frac{3}{2}}\right\}, \tag{9}$$

where V is the volume, ρ the density, χ the compressibility, and σ Poisson's ratio, for the substance considered. The average energy of a degree of freedom of frequency ν is, by equations (3) and (7),

$$\frac{3NRTe^{-\frac{\beta\nu}{T}}}{3N} = RTe^{-\frac{\beta\nu}{T}}; \tag{10}$$

so the total energy in the solid is

$$U = \int_0^{\nu_m} \frac{9N}{\nu_m^3}\nu^2 \cdot RTe^{-\frac{\beta\nu}{T}},$$

$$= \frac{9NRT}{\nu_m^3}\left\{\frac{2T^3}{\beta^3} - e^{-\frac{\beta\nu_m}{T}}\left(\frac{T}{\beta}\nu_m^2 + \frac{2T^2}{\beta^2}\nu_m + \frac{2T^3}{\beta^3}\right)\right\}.$$

Substituting $\tau = \beta\nu_m$,

$$U = 9NRT\left\{\frac{2T^3}{\tau^3} - e^{-\frac{\tau}{T}}\left(\frac{T}{\tau} + \frac{2T^2}{\tau^2} + \frac{2T^3}{\tau^3}\right)\right\}.$$

According to Debye's assumptions ν_m, and hence also τ, are not functions of T, so the specific heat is:

$$C_v = \frac{dU}{dT} = 9RN\left\{8\frac{T^3}{\tau^3} - e^{-\frac{\tau}{T}}\left(8\frac{T^3}{\tau^3} + 8\frac{T^2}{\tau^2} + 4\frac{T}{\tau} + 1\right)\right\},$$

and

$$\frac{C_v}{C_\infty} = 3\left\{8\frac{T^3}{\tau^3} - e^{-\frac{\tau}{T}}\left(8\frac{T^3}{\tau^3} + 8\frac{T^2}{\tau^2} + 4\frac{T}{\tau} + 1\right)\right\}. \tag{11}$$

Fig. 3 shows how this expression compares with equation (6). The solid line as before represents the first equation derived, while the broken one represents equation (11). Although the difference between these two curves is not large, it is evident, particularly at low temperatures, that this new formula does not represent the facts accurately. It is necessary to conclude, therefore, either that the energy of each degree of freedom is not accurately expressed by equation (10) or that some of the assumptions on which Debye's theory is based are not valid.

It is evident that if equation (11) is to be valid, ν_m must not vary with the temperature. That is, by equation (9), the quantities σ and χ must be independent of the temperature. While there is no evidence of any considerable variation in the value of σ, Grüneisen has shown[1]

---

[1] Ann. d. Phys., 33, 1239. Some of Grüneisen's results indicating such a variation of the compressibility with the temperature may be given:

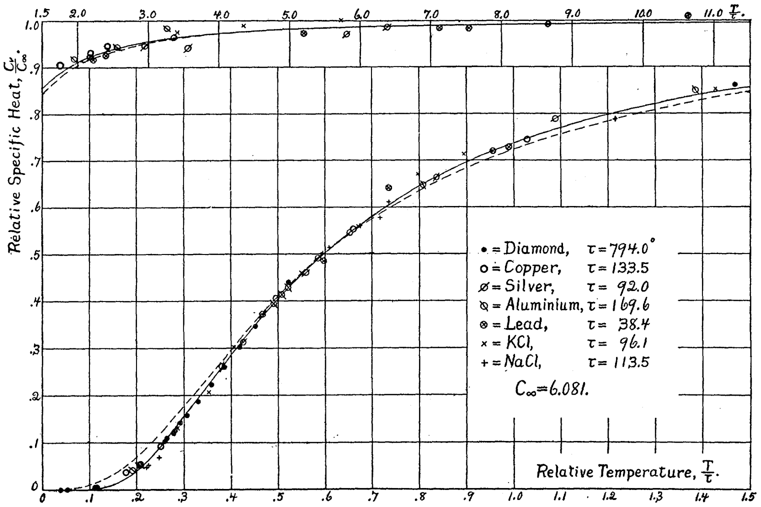

Fig. 3.

Compressibility × 10⁶.

T	Al	Fe	Cu	Ag	Pt	Sn	Pb
83°	1.32	0.606	0.718	0.709	0.374	2.1	2.5
290	1.46	0.633	0.773	0.763	0.392	3.1	3.2
373	1.70	0.652	0.801	0.820	0.398	—	—

that there is a general and decided increase in the compressibility χ with the temperature. It is evident, therefore, that account must be taken of the variation of ν_m with the temperature. If this is done, equation (11) becomes:

$$\frac{C_v}{C^\infty} = 3\left\{8\frac{T^3}{\tau^3} - e^{-\frac{\tau}{T}}\left(8\frac{T^3}{\tau^3} + 8\frac{T^2}{\tau^2} + 4\frac{T}{\tau} + 1\right)\right.$$
$$\left. - \left[6\frac{T^4}{\tau^4} - e^{-\frac{\tau}{T}}\left(6\frac{T^4}{\tau^4} + 6\frac{T^3}{\tau^3} + 3\frac{T^2}{\tau^2} + \frac{T}{\tau}\right)\right]\frac{d\tau}{dT}\right\}.$$

The order of magnitude of $d\tau/dT$ is 5×10^{-4}, so the last term is negligible except at high temperatures; but instead of considering τ to be constant, its particular value which corresponds to the temperature for which C_v/C_∞ is evaluated must be employed in order to make equation (11) valid. In the case of aluminum, for example, the compressibility at 373° is 29 per cent. greater than at 83°. This corresponds to a difference in ν_m, and hence also in τ of 13.5 per cent., and in the specific heat at the lower temperature of about 45 per cent. Thus if the specific heat of aluminum at 83° is calculated from its elastic constants at 373°

the resulting value is some 45 per cent. greater than if calculated from its constants at the lower temperature. This shows conclusively that equation (11) is not valid if τ is considered independent of the temperature.

That the same argument applies to Debye's formula for the specific heat is shown by the form of his equation at low temperatures,

$$\frac{C_v}{C_\infty} = 77\cdot93\frac{R^3T^3}{h^3\nu_m{}^3}.$$

In this equation the value of the ratio C_v/C_∞ for aluminum varies 46 per cent. according as the value of ν_m is calculated from the elastic constants at 373° or at 83°. It is thus evident that the error introduced by Debye's assumption that ν_m is independent of the temperature is much too large to be neglected.

It can be shown, moreover, that the fundamental assumption on which Debye's theory is based, that the heat energy of a solid lies in the elastic vibrations of the body as a whole, does not represent the truth. It may be shown that the velocity of propagation of a thermal disturbance in a solid is directly proportional to the diameter of the elementary vibrator. If, as Debye assumes, the whole substance is capable of vibrating as a unit in its heat motion, the thermal conductivity should therefore be very great. This may be shown more clearly in the following manner. Consider two infinite parallel planes in an elastic medium, at one of which the medium is maintained with vibrational energy greater than at the other corresponding to a difference in temperature of one degree. The thermal conductivity, or rate at which energy is transmitted from the hotter to the colder plane per unit area will then be equal to the product of the difference in the energy content of the medium at the two planes by the velocity of transmission of the vibrational disturbance; *i. e.*:

$$\text{thermal conductivity} = V\cdot C(t_1 - t_2) = V\cdot C,$$

where C is the heat capacity per unit volume of the medium, and V is the mean velocity of propagation of a vibrational disturbance. For aluminum C is about 0.5 calories cm.$^{-3}$ deg.$^{-1}$, and V may be taken as about 5×10^6 cm. sec.$^{-1}$, so the thermal conductivity should be of the order of magnitude of 2.5×10^5 calories cm.$^{-2}$ sec.$^{-1}$ deg.$^{-1}$. This is wholly out of accord with the experimental value, which is 0.5 calories cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$. In fact the dimensions themselves are different, the rate of heat transmission according to this assumption being independent of the distance apart of the two parallel planes. It is evident, therefore, that the heat energy of solids is not contained in the elastic vibrations of the body as a whole, but is contained in the motion of very much smaller elements. Since the lower limit of the frequencies which enter into Debye's theory is determined by the dimensions of the vibrator, the range of frequencies in which thermal motion occurs is thus limited. If the elementary vibrator is of atomic dimensions, the only frequencies to be considered are the natural frequencies of the atoms themselves.[1] Thus the assumption that thermal motion occurs in all the possible frequencies from o to ν_m cannot be accepted.

Debye's formula for the specific heat must therefore be considered to be largely empirical. In order to compare the results of this agglomeration hypothesis with those of the quantum hypothesis, equation (6) should be compared rather with Einstein's formula,[2]

$$\frac{C_v}{C_\infty} = \frac{h^2\nu^2}{R^2T^2}\,\frac{e^{h\nu/RT}}{(e^{h\nu/RT}-1)^2},$$

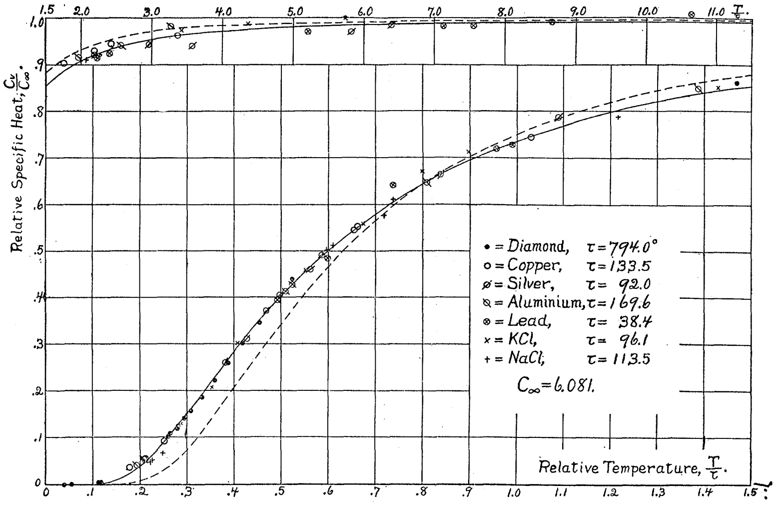

Fig. 4.

which is a valid deduction from the quantum hypothesis. Fig. 4 shows how these two expressions compare. The solid line represents my

---

[1] The great increase in thermal conductivity at low temperatures may be shown to indicate that the diameter of the elementary vibrator becomes comparatively large at low temperatures. Under these circumstances Debye's assumption of a whole spectrum of frequencies may be valid. This may account for the fact that at extremely low temperatures, $T/\tau = 0$ to 0.22, the observed specific heats are slightly larger than indicated by equation (6). If this be true, equation (11) should hold at these temperatures, and Debye's "third power law" would still be true.

[2] Einstein, Ann. d. Phys., 22, 180.

formula and the broken one that of Einstein. The experimental values are the same as in Fig. 2. It is evident that Einstein's expression is much the less accurate of the two. Thus from the standpoint of the variation of specific heat with temperature the assumption is strongly supported that at sufficiently low temperatures many of the atoms of a solid become so intimately associated that they lose degrees of freedom.

Summary.

The assumption has been made that a possible degree of freedom between two atoms in a solid actually exists only as long as the relative energy between the two atoms is greater than a certain critical value.

An expression for the variation of the specific heat of solids with temperature has been derived from this assumption, which seems to agree more satisfactorily with experiment than any of the existing formulæ.

Debye's expression for the variation of the specific heat with temperature has been found to be largely empirical; so to compare this agglomeration hypothesis with the quantum hypothesis my formula is rather to be compared with that of Einstein.

The strong support of experimental evidence in this case seems to indicate that this agglomeration hypothesis represents more accurately the condition of the atoms in a solid than does the quantum hypothesis.

I wish to express my thanks to Professor Adams and Professor Magie for their continued interest in this study.

Palmer Physical Laboratory,
Princeton, N. J.,
May 5, 1915.