

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## THE THERMAL ENERGY OF ELECTRONS IN METALS

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RECEIVED MARCH 4, 1924

The extent to which electrons in metals absorb energy when the metals are heated is a question of some interest which occurs in various phases of the study of the metallic state. The usual assumption has been that because the atomic heats of most metals are approximately  $3R$  at ordinary temperatures only an insignificant part of their heat capacity is due to their electrons. The specific heats of many metals are known to exceed  $3R$  considerably at high temperatures, but it has not been known how much of these large values is due to the work of expansion of the metal, that is, to  $C_p - C_v$ , the difference between the specific heats at constant pressure and constant volume. The calculations of Lewis<sup>1</sup> showed that  $C_p$  itself in the case of some of the alkali metals at least, was distinctly above  $3R$  even at  $20^\circ$ , and since then the same has been observed by other authors to be true in a number of isolated cases at higher temperatures. More systematic experimental studies of this question have been in progress in this Laboratory<sup>2,3</sup> for some years, and much valuable work which may be applied to the study has appeared elsewhere. It is our belief that the body of data which now exists is sufficiently extensive and reliable to permit general conclusions to be drawn with some confidence. Our purpose in this paper is to discuss the data and results of a general survey which we have made in this field.

**The Specific-Heat Data.**—The values of  $C_p$  upon which we base our discussion are given in Table I. They include all metals for which we have found measurements over any considerable temperature range. To obtain the figures of Table I, all values of the various observers of  $C_p$  for each metal have been plotted against the logarithm of the absolute temperature, and representative curves drawn, giving extra weight in some cases to individual researches which appear to us to be particularly reliable. The authors whose work we have considered are indicated by the reference numbers accompanying the symbols of the metals in the table. We find it necessary to mention that the extensive data of Wüst<sup>4</sup> seem to be frequently in error by rather large amounts. When unsupported by other work we have, therefore, used these measurements in only a very few cases in which approximate values could be obtained by correcting a recognizable and characteristic trend appearing in many of his results. Figures whose accuracy, for this or other reasons, we have thought not to be established

<sup>1</sup> Lewis, *THIS JOURNAL*, 29, 1165 (1907).

<sup>2</sup> Lewis, Eastman and Rodebush, *Proc. Nat. Acad. Sci.*, 4, 25 (1918).

<sup>3</sup> Eastman and Rodebush, *THIS JOURNAL*, 40, 489 (1918).

<sup>4</sup> Wüst, *Ver. deutsch. Ing. Forschungsarb.*, No. 204 (1918).

TABLE I

ATOMIC HEATS AT CONSTANT PRESSURE, IN CALORIES PER DEGREE, OF METALS AT VARIOUS TEMPERATURES

| Log T                          | 2.2  | 2.3  | 2.4    | 2.5    | 2.6    | 2.7    | 2.8    | 2.9    | 3.0    | 3.1    | 3.2    |
|--------------------------------|------|------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Na <sup>3,5,6,7,8</sup>        | 6.00 | 6.17 | 6.44   | 6.88   | ..     | ..     | ..     | ..     | ..     | ..     | ..     |
| Mg <sup>3,9,10,11</sup>        | ..   | 5.65 | 5.95   | 6.10   | 6.30   | 6.57   | 6.92   | 7.34   | ..     | ..     | ..     |
| Al <sup>4,9,10,11</sup>        | ..   | ..   | ..     | 5.88   | 6.18   | 6.48   | 6.82   | 7.20   | ..     | ..     | ..     |
| K <sup>3,5,6</sup>             | 6.38 | 6.58 | 6.87   | 7.32   | ..     | ..     | ..     | ..     | ..     | ..     | ..     |
| Ca <sup>11</sup>               | ..   | ..   | ..     | 6.22   | 6.57   | 7.00   | 7.50   | ..     | ..     | ..     | ..     |
| Cr <sup>4,9,12,13</sup>        | ..   | ..   | ..     | ..     | 5.85   | 6.15   | 6.55   | 7.12   | 7.85   | ..     | ..     |
| Fe <sup>4,7,9,14</sup>         | ..   | ..   | ..     | 6.05   | 6.60   | 7.20   | 7.90   | 8.60   | ..     | ..     | ..     |
| Co <sup>4,9,13,15,16</sup>     | ..   | ..   | ..     | 6.05   | 6.45   | 6.85   | 7.45   | 8.25   | 9.20   | ..     | ..     |
| Ni <sup>4,9,13,14,15</sup>     | ..   | ..   | ..     | 6.25   | 6.90   | 7.60   | 8.30   | ..     | ..     | ..     | ..     |
| Cu <sup>4,7,9,17</sup>         | ..   | ..   | 5.73   | 5.87   | 6.04   | 6.20   | 6.40   | 6.60   | 6.82   | ..     | ..     |
| Zn <sup>4,7,8,9,10,11</sup>    | ..   | ..   | 5.96   | 6.11   | 6.28   | 6.60   | 7.00   | ..     | ..     | ..     | ..     |
| Mo <sup>4</sup>                | ..   | ..   | ..     | (6.00) | (6.18) | (6.38) | (6.65) | (7.00) | (7.45) | (8.00) | (8.7)  |
| Ag <sup>4,7,9,11</sup>         | ..   | ..   | 5.96   | 6.07   | 6.20   | 6.36   | 6.55   | 6.79   | 7.10   | ..     | ..     |
| Cd <sup>4,7,17,18</sup>        | ..   | ..   | 6.05   | 6.27   | 6.47   | 6.75   | ..     | ..     | ..     | ..     | ..     |
| Sn <sup>4,7,8,9,13,15,19</sup> | ..   | 5.95 | 6.25   | 6.55   | 6.87   | ..     | ..     | ..     | ..     | ..     | ..     |
| Sb <sup>4,9,13,17,19</sup>     | ..   | ..   | ..     | 6.00   | 6.15   | 6.35   | 6.60   | 6.85   | ..     | ..     | ..     |
| W <sup>4,20</sup>              | ..   | ..   | ..     | (6.15) | ..     | (6.25) | ..     | (6.35) | (6.42) | (6.60) | (6.95) |
| Pt <sup>4,21</sup>             | ..   | ..   | 6.15   | 6.25   | 6.35   | 6.47   | 6.63   | 6.83   | 7.10   | 7.44   | 7.85   |
| Au <sup>4,13,18</sup>          | ..   | ..   | (6.10) | (6.15) | (6.20) | (6.27) | (6.35) | (6.45) | (6.60) | (6.8)  | ..     |
| Tl <sup>19</sup>               | 5.95 | 6.08 | 6.22   | 6.40   | ..     | ..     | ..     | ..     | ..     | ..     | ..     |
| Pb <sup>4,7,8,9,17</sup>       | 6.0  | 6.07 | 6.17   | 6.35   | 6.60   | 6.90   | ..     | ..     | ..     | ..     | ..     |
| Bi <sup>4,8,9,13,18,19</sup>   | ..   | ..   | 5.98   | 6.17   | 6.38   | 6.65   | ..     | ..     | ..     | ..     | ..     |

<sup>5</sup> Protz, *Ann. Phys.*, **31**, 127 (1910), quoting results of Thum, *Dissertation*, Zürich (1906).

<sup>6</sup> Rengade, *Compt. rend.*, **56**, 1879 (1913).

<sup>7</sup> Griffiths and Griffiths, *Trans. Roy. Soc. London*, **214A**, 319 (1914).

<sup>8</sup> Iitaka, *Sci. Reports Tohoku Imp. Univ.*, **8**, 99 (1919).

<sup>9</sup> Schübel, *Z. anorg. Chem.*, **87**, 81 (1914).

<sup>10</sup> Nernst and Lindemann, *Z. Elektrochem.*, **17**, 817 (1911).

<sup>11</sup> Eastman, Williams and Young, *This Journal*, **46**, 1178 (1924).

<sup>12</sup> Nordmeyer and Bernoulli, *Ver. physikal. Gesell.*, **9**, 175 (1907).

<sup>13</sup> Schimpf, *Z. physik. Chem.*, **71**, 257 (1910).

<sup>14</sup> Weiss and Beck, *J. physique*, **7**, 299 (1908).

<sup>15</sup> Pionchon, *Compt. rend.*, **103**, 1122 (1886); **106**, 1344 (1888).

<sup>16</sup> Kalmus and Harper, *J. Ind. Eng. Chem.*, **7**, 6 (1915).

<sup>17</sup> Naccarri, *Atti di Torino*, **23**, 107 (1887-88).

<sup>18</sup> Jaeger and Diesselhorst, *Wiss. Abh. physik.-tech. Reichsanstalt*, **3**, 269 (1900).

<sup>19</sup> Ewald, *Ann. Physik*, [4] **44**, 1226 (1914).

<sup>20</sup> Worthing, *Phys. Rev.*, **12**, 199 (1918).

<sup>21</sup> White, *ibid.*, **12**, 438 (1918).

within 1 or 2%, we have given in parentheses in Table I. It is our opinion, however, that none of the data of this table is seriously inaccurate.

**The Calculation of  $C_p - C_v$ .**—In order to obtain specific heats at constant volume from the experimental values of  $C_p$ , it is necessary to use the thermodynamic relation,

$$C_p - C_v = \frac{\alpha^2 VT}{\beta} \quad (1)$$

$\alpha$  being the cubic expansion coefficient,  $V$  the atomic volume, and  $\beta$  the compressibility of the substance at the absolute temperature  $T$ . We have found values of both  $\alpha$  and  $\beta$ , over considerable temperature ranges, only for aluminum, iron, copper, silver and platinum. For these metals we have calculated the  $C_p - C_v$  corrections which, with the values of  $\alpha$  and  $\beta$ , are given in Table II. The expansion coefficients given there are based upon the work of the authors in the references <sup>22,23,24,25</sup> below. All of the compressibility data are due to Grüneisen.<sup>26</sup> The measurements of compressibility, unlike those of expansion, do not extend over the entire range of temperature desired. We have found, however, that nearly linear curves result when the compressibilities are plotted against the square of the absolute temperature. In addition, the temperature variation is usually fairly small, so we have felt justified in considerable extrapolation<sup>27</sup> in some cases. Extrapolated values and results depending upon them are given in parentheses in Table II.

The metals of Table II comprise a fraction only of those in which we have been interested. For the remaining metals some kind of an empirical equation is required for obtaining  $C_p - C_v$ , and the results in the fourth column of Table II have been of value principally in affording standards of comparison for testing various proposed equations. In particular, the formulas which we have tried are

$$C_p - C_v = k T^{3/2} \quad (2)$$

$$C_p - C_v = k T \alpha^2 \quad (3)$$

$$C_p - C_v = k T C_p^2 \quad (4)$$

The  $k$ 's of these equations are empirical constants determinable from known values of the other quantities at some one temperature. Equation 2 was proposed by Lindemann and Magnus<sup>28</sup> for use at low temperatures, and is in all cases less satisfactory than either (3) or (4). The latter are obtained from (1) by certain approximations and are discussed and used,

<sup>22</sup> Holborn and Day, *Ann. Physik*, [4] **4**, 104 (1901).

<sup>23</sup> Scheel, *Z. Physik*, **5**, 167 (1921).

<sup>24</sup> Dittenberger, *Z. Vern. deut. Ing.*, **46**, 1532 (1902).

<sup>25</sup> Le Chatelier, *Compt. rend.*, **129**, 331 (1899).

<sup>26</sup> Grüneisen, *Ann. Physik*, [4] **33**, 1239 (1918).

<sup>27</sup> Grüneisen's data extend to temperatures much lower than shown in the table, giving a more adequate basis of extrapolation than appears from the table itself.

<sup>28</sup> Lindemann and Magnus, *Z. Elektrochem.*, **16**, 269 (1910).



which prevent this procedure for obtaining  $C_v$  being completely satisfying. On the other hand, the difference between  $C_p$  and  $C_v$  fortunately is never very great, and relatively large percentage errors in it give rise to but small errors in  $C_v$ . We therefore believe that this feature also of our work is not open to serious objection.

The values of  $C_p - C_v$  at  $20^\circ$ , which we have used in determining the constants of Equation 5 for the various metals, are contained in the last column of Table III. In choosing the expansion and compressibility data upon which they are based, we have considered the following in addition to the references already cited: the tabulations of Richards<sup>30</sup> and the material in the International Tables,<sup>31</sup> together with the work of Protz<sup>5</sup> on compressibility of sodium and potassium and of Adams, Williamson and Johnston<sup>32</sup> for a number of other metals. We have ourselves determined by a dilatometric method the coefficient of expansion of calcium, using the block of metal which had previously been used in the specific-

TABLE III  
COEFFICIENTS OF EXPANSION, COMPRESSIBILITIES AND THE  $C_p - C_v$  CORRECTIONS FOR METALS AT  $20^\circ$

| Metal   | $\alpha \times 10^6$<br>$\frac{d \ln V}{dT}$ | $\beta \times 10^6$<br>$\frac{d \ln V}{dP}$ (megabars) | $C_p - C_v$<br>(Cal./deg./mole) |
|---------|--|--|---------------------------------|
| Na..... | 21.3   | 15.6   | 0.48                            |
| Mg..... | 7.7  | 2.9  | .20                             |
| Al..... | 7.4  | 1.32   | .29                             |
| K.....  | 24.3   | 37.0   | .50                             |
| Ca..... | 5.05   | 5.7  | .081                            |
| Cr..... | 2.5  | 0.9  | .037                            |
| Fe..... | 3.5  | .60  | .10                             |
| Co..... | 3.7  | (.5)   | .13                             |
| Ni..... | 3.9  | .43  | .16                             |
| Cu..... | 5.0  | .75  | .166                            |
| Zn..... | 8.7  | 1.74   | .28                             |
| Mo..... | 1.7  | 0.46   | .047                            |
| Ag..... | 5.7  | .97  | .242                            |
| Cd..... | 9.0  | 2.2  | .33                             |
| Sn..... | 6.5  | 1.9  | .25                             |
| Sb..... | 3.0  | 2.4  | .048                            |
| W.....  | 1.4  | 0.27   | .050                            |
| Pt..... | 2.7  | .38  | .117                            |
| Au..... | 4.23   | .60  | .214                            |
| Tl..... | 7.8  | 2.3  | .32                             |
| Pb..... | 8.6  | 2.2  | .43                             |
| Bi..... | 4.3  | 3.0  | .092                            |

<sup>30</sup> Richards, THIS JOURNAL, 37, 1646 (1915).

<sup>31</sup> "Tableaux Annuelles de Constantes et Donnés Numeriques," Gauthier-Villars et Cie., Paris, 1912 and 1921.

<sup>32</sup> Adams, Williamson and Johnston, THIS JOURNAL, 41, 12 (1919).

heat measurements of Eastman and Rodebush. The compressibility of cobalt we have estimated from the values for iron and nickel. These and the values of the constants for the remaining metals which we consider most representative are shown in the second and third columns of Table III. It should be mentioned that these are not in general the same as in Table II, since we are here interested in the best values of  $\alpha$  and  $\beta$  rather than in their variation with temperature.

**Specific Heats at Constant Volume.**—By using the methods and data of the preceding sections we have calculated  $C_v$  over wide temperature ranges for many metals. The results of these calculations are exhibited in Fig. 1,<sup>33</sup> where the specific heats are plotted against  $\log T/\theta$ .

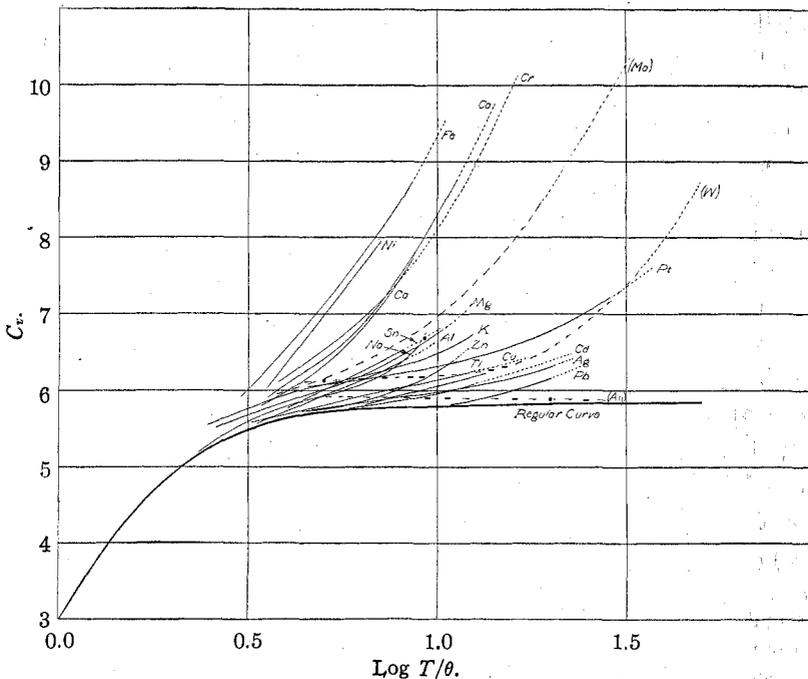


Fig. 1.—Heat capacities,  $C_v$ , of metals, in calories per degree per mole.

The definition of  $\theta$  will be recalled from the work of Lewis and Gibson<sup>34</sup> as the temperature, characteristic of each metal, at which  $C_v$  reaches  $3R/2$ . According to these authors the specific heats,  $C_v$ , of all crystalline elements of the cubic system (perhaps all monatomic elements) follow a single curve, at low temperatures at least, when plotted in this way. The upper portion

<sup>33</sup> A few values of specific heats which are not shown in Table I because of limited space are utilized in constructing Fig. 1 and the later graphs. This applies only to sodium and potassium, at low temperatures, and molybdenum and tungsten at high.

<sup>34</sup> Lewis and Gibson, *THIS JOURNAL*, 39, 2554 (1917).

of this curve, referred to as the regular curve, is indicated by the heavy line in Fig. 1. The values of  $\theta$  required for constructing the other curves of this diagram are taken mainly from Lewis and Gibson, though they also include a few of our own. That used for potassium is an approximation only. Broken lines are used in representing data uncertain for any reason to more than a few per cent.; and dotted lines in extrapolations which have been carried out wherever necessary to make the curves all extend to the melting point or to the lowest transition point<sup>35</sup> of the metal.

**Discussion.**—The striking feature of Fig. 1 is the departure, at the higher temperatures, of the curves of every metal for which reliable data exist from the uniformity found at low temperatures, and the ultimate rise of  $C_v$  in every case to values well above  $3R$ . We believe that this irregular behavior, observed previously in several individual cases, will be found to be entirely general. Nevertheless the curves of Fig. 1 do not appear to be wholly unrelated. Their character as a group convinces us that their divergence at high temperatures is due to differing deviations from a normal curve such as that of Lewis and Gibson, and justifies an inquiry into the causes of these deviations.

The explanations of high specific heats which seem to us most worthy of consideration are (1) that loosely bound electrons in the metal absorb appreciable quantities of energy, and (2) that some departure from harmonic oscillation of the atoms occurs which results in heat capacities larger than the normal limit. The contribution of the electrons to the specific heat of metals has been considered from the beginnings of the electron theory. Koenigsberger<sup>36</sup> appears to have been the first, however, to believe that this contribution might, in general, be large (he even considered it to be appreciable at quite low temperatures, where  $C_v$  is much lower than  $3R$ , in many metals). Protz<sup>5</sup> had previously inclined to the electronic explanation of the high specific heats of sodium and potassium. The same explanation in this case occurred independently also to Professor G. N. Lewis, upon whose suggestion the researches<sup>2,3</sup> of which the present studies are a continuation were initiated. The second explanation is briefly discussed by Langmuir.<sup>37</sup> Born and Brody<sup>38</sup> apply the quantum theory, and Schrödinger<sup>39</sup> classical mechanics to systems of oscillators whose potential energies are higher-than-quadratic functions of position.

<sup>35</sup> The transition of white to gray tin at  $20^\circ$  does not occur rapidly enough to influence specific-heat measurements. The only other case requiring comment from this standpoint is that of zinc. We have discussed questions concerning reported transition points in this metal in the preceding paper in which we conclude that no transition point exists which is susceptible of detection in specific-heat work or by cooling curves.

<sup>36</sup> Koenigsberger, *Z. Elektrochem.*, **17**, 289 (1911).

<sup>37</sup> Langmuir, *THIS JOURNAL*, **38**, 2236 (1916).

<sup>38</sup> Born and Brody, *Z. Physik*, **6**, 132 (1921).

<sup>39</sup> Schrödinger, *ibid.*, **11**, 170 (1922).

They conclude that in such cases approximately linear deviations in excess of the normal specific-heat curves may appear at high temperatures. Born and Brody also obtain certain approximate relations which indicate that, if this theory is correct, the effect should be larger, the lower the characteristic temperature,  $\theta$ , of the metal, and the higher its coefficient of expansion.

It is regrettable that at present no criterion exists by which these two very different effects may be differentiated from each other with certainty in any actual case. It must be admitted that the explanation which assumes deviation from Hooke's law is not without a certain degree of probability. It seems particularly well suited, for example, to account for the relatively rapid increase in specific heat which is found in some substances (such as sodium in Fig. 1) in the immediate neighborhood of the melting point. Such an effect is less likely, however, to be of importance over ranges of temperature as large as those in which the high specific heats of metals persist. Further light might be thrown on this question if the general behavior of substances which are both monatomic in their crystal structure and entirely nonmetallic in character were known. The only substance of this kind<sup>40</sup> for which we have found sufficiently complete data is sodium chloride. We calculate  $C_v$  (per mean gram atom) for it to be about 5.81, 5.87 and 5.87 at the three temperatures 143, 412 and 660°. <sup>41</sup> Its atomic heat capacity thus shows the normally expected tendency to approach but not to exceed  $3R$ , in contrast to most metals, and we believe its behavior to be typical. So far as the atoms alone are concerned, however, no reason is apparent why metals should not behave similarly. Further, the correspondence which Born and Brody expect between  $\theta$  and  $\alpha$  and the specific-heat effect, is not very well substantiated by the data. The method of plotting adopted in Fig. 1 compensates for differences in  $\theta$  among the different metals. Comparison of the excess of specific heats above the regular curve in this figure, with the values of  $\alpha$  (neglecting the temperature corrections to bring them to equal values of  $T/\theta$ ) in Table III, shows no general parallelism. We cite as instances of the frequent reversal of the expected relation the cases of calcium as

<sup>40</sup> The class referred to is rather limited in extent. Many of the substances having single atoms as the units of the space lattice are partially metallic in character, or contain loosely held electrons; for example; metallic sulfides and oxides like those of lead and silver, and the silver halides.

<sup>41</sup> From the results of Magnus [*Physik. Z.*, **14**, 5 (1913)] the mean  $C_p$  per mole may be calculated to be 12.64 cal./deg. in the range 18° to 268°, 13.43 from 268° to 556°, and 14.02 from 556° to 763°. Baxter and Wallace, [*THIS JOURNAL*, **38**, 259 (1916)] give the average cubic coefficient of expansion between 0° and 25° as  $12.5 \times 10^{-6}$ , and Adams, Williamson and Johnston, Ref. 32, give the compressibility as  $4.12 \times 10^{-6}$ .  $C_p - C_v$  at ordinary temperatures is then about 0.7 cal./deg./mole. Assuming that Equation 5 is approximately applicable we may calculate values at the midpoints of the above ranges and so obtain the values of  $C_v$  at these points given above.

compared with sodium, or potassium or silver; magnesium as compared with calcium or zinc, and so on. For these reasons it seems to us that the electronic explanation of the high specific heats of metals remains the more probable one if restricted to temperatures not too near the melting (or transition) point, yet high enough so that  $C_v$  should normally be nearly equal to  $3R$ . We shall therefore proceed to the discussion of this hypothesis.

The particular way in which the electrons may absorb or cause the absorption of energy depends of course upon the conditions which obtain in the interior of the metal. Just how the electrons of the outermost shells of the atoms are disposed in the metallic crystal is not at present known. They may for the most part occupy positions or participate in motions relative to the rest of the atom not fundamentally different from electrons on atoms in the vapor state. Some may be "free" in the sense that they move on paths through the atomic lattice over much of whose lengths the potential energy of the electron is nearly independent of position. Or perhaps some or all of the valence electrons may themselves occupy equilibrium positions in the crystal lattice. These conditions are not mutually exclusive, and no one of them necessarily represents the state in all metals or in one metal under all circumstances.

Whatever the state may be in the metal, we believe that the total rate of gain of energy by the system may be justifiably considered in two parts, associated with the changes in motion and positions of the electrons and the nuclei, respectively. We think of the rate of absorption associated with the nuclei of the atoms as that which the system would possess if all the electrons were rigidly fixed in the structures about the nuclei, at the same time leaving all of the conditions affecting the motions of the atoms themselves exactly as in the actual system. Representing this quantity as  $\left(\frac{\partial E_A}{\partial T}\right)_v$ , or  $C_A$ , we then equate the rate of absorption by electrons,  $\left(\frac{\partial E_e}{\partial T}\right)_v$ , or  $c_e$ , to the specific heat of the actual system,  $C_v$ , minus  $C_A$ . When  $C_v$  is found to exceed the value according to the regular curve for the metal, which we shall designate  $C_R$ , it is not possible to say with certainty how much of this excess is due to  $C_A$  and how much to  $c_e$ . It is our opinion, however, that at moderately large values of  $T/\theta$ ,  $C_A$  may be regarded as sensibly equal to  $C_R$ . If this is true,  $c_e$  is obviously equal to  $C_v - C_R$ . Whether this equality is closely approached or not, the more general conclusion that loosely bound electrons in some way cause the large values of  $C_v$  remains possible. By either assumption the extent of the difference  $C_v - C_R$  should in any given case depend, in part at least, upon the differences in energy levels which electrons in periodic motion may assume, and upon the number of free electrons. The latter quantities also determine in a general way the electropositive character of metals.

We are led to look, therefore, for increasing values of  $C_v - C_R$  as the positiveness of the metal increases, other things being equal.

The procedure best suited to disclose any relations of this kind which may exist among the metals will depend again upon the state of the electrons in them. If, for example, the valence electrons are the determining factors in holding the atomic lattice together, comparisons of  $C_v - C_R$  might be most significant at the same values of  $T/\theta$ ; in other cases equal values of  $T$  might better be chosen. Fig. 1 suffices for the first of these comparisons: for the second, reference should be made to Fig. 2. In the latter  $C_v - C_R$  for each metal<sup>42</sup> is plotted against  $\log T$ . By this method of plotting some correspondence with electropositive character is seen to

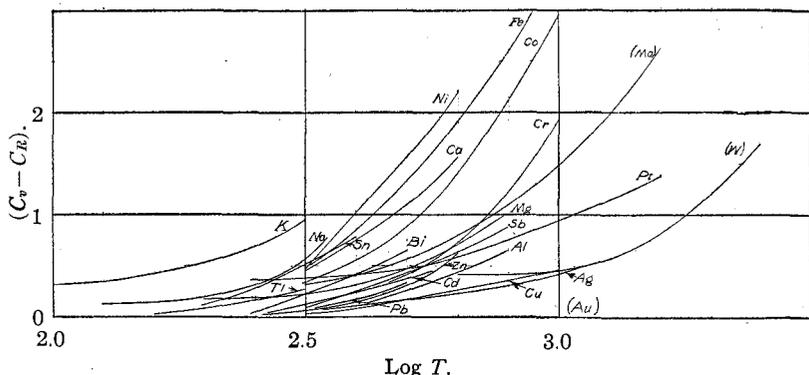


Fig. 2.—Supposed electronic heat capacities,  $C_v - C_R$ , per mole of metal, in calories per degree.

be developed, since the strong metals usually reach given values of  $C_v - C_R$  at lower temperatures than the others.

While this tendency is quite general, it will nevertheless be seen to be far from universal. For aside from small irregularities which may be traceable to minor uncertainties in  $C_v$  or in  $\theta$ , a number of metals, such as iron, cobalt, nickel, antimony, bismuth and platinum appear to be out of order compared to the neighboring metals. If any closer insight into this situation than is afforded by the preceding considerations is to be obtained, it will obviously be necessary to have more information concerning the number of electrons involved in the effect. At present it may be said that in certain simple cases, such as the alkali metals, there is only one

<sup>42</sup> Antimony and bismuth, which are represented in this and the following figure do not appear in Fig. 1 because they are not regular. For both of these metals  $C_R$  is, taken simply as 5.90 at all temperatures considered. In these figures also the position of the curve for gold has been taken as coincident with the axis, since the values of  $C_v - C_R$  are no larger than the possible errors in  $C_v$  in this case.

It should also be noted that in Figs. 2 and 3 the extrapolations of the curves made in Fig. 1 have been omitted.

electron per atom which is likely under any realizable conditions to absorb independently appreciable quantities of energy. When elements which have two or more valence electrons are considered, there is no definite evidence that these electrons are all equivalent to one another in that they may absorb equal amounts of energy. In those elements which exhibit the same valence in all their compounds, such as magnesium or aluminum, we believe it likely though not necessary that the electrons are all equivalent in this sense. For elements having two or more valences, such as chromium, iron, copper or platinum, it is more likely that there is an unequal division of energy between the valence electrons. In elements having many electrons in the valence shell, and in those of "variable

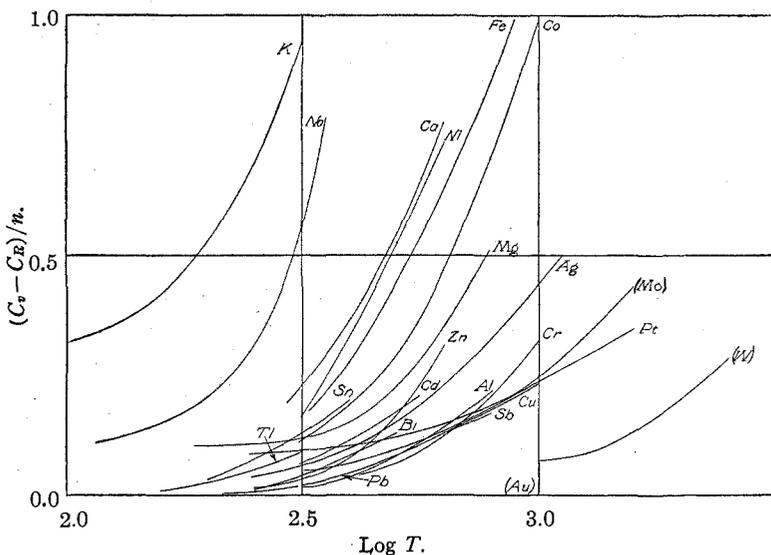


Fig. 3.—Electronic heat capacities per mole of valence electrons per mole of metal  $(C_v - C_R)/n$ , in calories per degree.

kernel,"<sup>43</sup> another factor enters, that is, the possibility that a relatively large number of electrons in the valence or sub-valence shell are able to acquire amounts of energy individually small but appreciable in the aggregate as compared with the valence electrons themselves. As examples of metals which may be of these types, chromium, iron and nickel may be cited.

In undertaking to allow for the number of electrons involved, in making our comparisons we have seen nothing better to do than to consider the number of electrons per atom which may be available to absorb energy as equal to the maximum positive valence,  $n$ , commonly shown by the

<sup>43</sup> Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Company, New York, 1923.

respective elements in their compounds, and to assume all valence electrons in a metal to be approximately equivalent to each other in this sense. On the basis of this assumption, the rates of gain of energy per available electron are compared in Fig. 3 where we have plotted the quotient  $(C_p - C_R)/n$  against  $\log T$ . Some of the apparent inconsistencies of fact and our theory are removed or lessened by this procedure, and it is our belief that those which remain are to be explained in so far as they are real, on the basis of inadequate knowledge as to the number of electrons concerned. The criteria upon which ideas as to the positiveness of a metal are usually based, besides often depending partly on the properties of other substances (as in the electrode potentials, where the degree of solvation of the ion is often a large factor), no doubt rest mainly upon the behavior of valence electrons only. The effect we have been investigating, on the other hand, must include all "loosely held" electrons. It is thus our belief that it constitutes a unique criterion of the "freedom" of electrons in metals, and we expect other estimates of this freedom to do nothing more than roughly parallel it. The relations shown in Fig. 3, particularly among the metals of simple type and those which fall in any one group of the periodic system, make it appear probable that the hypothesis we have been guided by is essentially correct in a good many cases, and perhaps in all.

The relation between  $C_p - C_R$  as defined above and the "specific heat of electricity," or Thomson effect, in thermo-electric phenomena is a question which has been discussed by Latimer.<sup>45</sup> Since the adequate presentation of the conclusions we have reached in the study of this phase of the problem involves many considerations which are far removed in character from the material presented here, we shall reserve their discussion for a later paper.

### Summary

1. Specific heats,  $C_p$ , at high temperatures of a number of metals have been collected and critically compared, and representative values tabulated.

2. A study has been made of the dependence of  $C_p - C_v$  upon temperature in ranges above  $0^\circ$ . It has been found that the empirical equation  $C_p - C_v = kT$  represents within the limits of error all the data (which are unfortunately limited in extent and accuracy) by which it may be tested.

3. The  $C_p$  vs.  $\log T$  curves of metals in general are far from identical in form over wide ranges at high temperatures.

4.  $C_p$  for all metals for which data were found attains values which exceed  $3R$  by amounts unmistakably beyond experimental error in most cases and probably so in all.

<sup>45</sup> Latimer, THIS JOURNAL, 44, 2136 (1922).

5. It is inferred that those explanations of the excess of  $C_p$  for metals over  $3R$  which assume departure by the atoms from simple harmonic oscillation, are probably not valid at all temperatures. This inference is based upon the apparent failure of  $C_p$  for typical non-metals to exceed  $3R$ , and upon the unexplained lack of generality in certain anticipated relations between the excess heat capacity and other properties of the metals.

6. A correspondence between electropositive character and the "excess" heat capacity is shown to exist for many of the metals. This is taken as support for the hypotheses that the excess heat capacities are due to the presence in the metals of loosely bound electrons, and that at moderately high temperatures this excess represents approximately the rate of gain of thermal energy by the electrons. Variation among the metals of the number of electrons involved in the effect is assumed to be responsible for some of the apparent exceptions to the correspondence mentioned above.

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## THE DETERMINATION OF SURFACE TENSION WITH VERY SMALL VOLUMES OF LIQUID, AND THE SURFACE TENSIONS OF OCTANES AND XYLENES AT SEVERAL TEMPERATURES

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RECEIVED MARCH 5, 1924

Occasionally it is necessary to determine the surface tension of a liquid of which only a very small volume is available. This determination may be most conveniently carried out in a small U-tube of which one arm is a fine capillary, and the other a somewhat wider tube, not much over 2 mm. in internal diameter.<sup>1</sup> The method requires special precautions, and has special advantages, which are discussed below.

In 1910 the capillary constants of octanes and xylenes were thus measured by the late Clarence L. Speyers under the direction of one of us. The results have not heretofore been published, because of question as to the precise magnitude of the correction to be applied to the height of liquid in the wider of the tubes. Very narrow tubes are adequately treated by

<sup>1</sup> This method was perhaps first used by Frankenheim [*Pogg. Ann.*, **72**, 177 (1847)]. Later it was also used by Schiff [*Ann.*, **223**, 47 (1884)], who perceived some of its advantages. Neither of these experimenters applied satisfactory corrections to the results. The description in Ostwald-Luther's "Physiko-Chemische Messungen," 1910, vol. 3, pp. 235-237 is also incomplete. Very recently a modification of the method has been used by Y. L. Shekhtman, *Bull. acad. sci. russie* [VI] **13**, 657-662 (1919); see also *C. A.*, **17**, 1909 (1923).