THERMO-ELECTRIC FORCE, THE ENTROPY OF ELECTRONS, AND THE SPECIFIC HEAT OF METALS AT HIGH TEMPERATURES

By WENDELL M. LATIMER

The conception of the specific heat of the electrons in a metal was first developed through the interpretation of thermo-electric phenomena. More recently the conception has been used in explaining the increase in the specific heat of metals above the "equipartition value" of $6/2\ R$. The purpose of this paper is to present evidence to show that these two ideas may be brought into quantitative agreement.

Many years ago Lord Kelvin pointed out that a thermo-electric circuit does work entirely at the expense of heat which is supplied from its surroundings and is, therefore, essentially a heat engine. Moreover, he was able to obtain valuable information about the thermo-electric circuit by the application of the principles of thermodynamics. The thermo-dynamical treatment of such a circuit must of course assume that the thermo-electric phenomena are strictly reversible. These phenomena are (1) the reversible absorption or evolution of heat at the junction of the metals, and (2) the reversible absorption or evolution of heat along the wires. The first of these, the Peltier effect, is the latent heat involved in the transfer of a unit quantity of electrons from one metal to the other at the temperature of the junction; the second, the Thomson effect, is the heat necessary to raise a unit quantity of electrons in the metal from the lower to the higher temperatures, and is the integral $\int_{T_1}^{T_2} \sigma\, dT$, where σ, the Thomson coefficient, is the specific heat of the electrons in the metal. In addition to these effects, any electrical current is accompanied, of course, by the non-reversible "Joule heating." However, this becomes very small as the current approaches zero and may therefore be neglected in these considerations.

In a circuit composed of two metals, 1 and 2, with junctions differing in temperature by $dT°$, the electrical energy generated by the flow of a unit quantity of electricity is equal to the heat absorbed minus the heat given out, according to the first law of thermodynamics,

$$dE = dq + (\sigma_2 - \sigma_1)dT \tag{1}$$

where dq is the difference in the Peltier effect for the two junctions, and σ_1 and σ_2 are the specific heats of the electrons in the two metals.

Applying the second law of thermodynamics, we obtain

$$\frac{dE}{dT} = \frac{q}{T} \tag{2}$$

Differentiating and combining with (1),

$$\frac{d^2E}{dT^2} = -\frac{1}{T}(\sigma_2 - \sigma_1) \tag{3}$$

or

$$\left(\frac{dE}{dT}\right)_{T_2} - \left(\frac{dE}{dT}\right)_{T_1} = -\int_{T_1}^{T_2}(\sigma_2 - \sigma_1)\frac{dT}{T}. \tag{4}$$

Many attempts have been made to confirm these equations by direct calorimetric measurements of the Peltier and Thomson effects. However, the experimental difficulties involved are so great that the accuracy attained is not sufficient to warrant definite conclusions. These equations are, however, thermodynamically accurate and any discrepancies which may be found must be due to the assumption of the complete reversibility of the thermo-electric phenomena.

Numerous attempts also have been made to justify these equations from kinetic and statistical considerations. Unfortunately, the assumption has commonly been made that there are "free electrons" in the metal which obey the gas laws and have a specific heat corresponding to the value demanded by the theory of the equipartition of energy for a monatomic gas.

It is possible, however, to approach the problem from an entirely different standpoint. G. N. Lewis[1] was the first to show that although the specific heat at constant volume of most metals at $25°$ is very close to the equipartition value of $6/2\ R$, it is, in the case of certain metals, clearly above this value. Since the ordinary deviations from the equipartition principle are such as to make the specific heat less than the theoretical value, he was led[2] to make the assumption that in the case of these metals the higher specific heat is due to the acquisition of thermal energy by the electrons. For example, the specific heat at constant volume for a mol of potassium at $298°$ K is 6.53 cal., or 0.56 cal. above $6/2\ R$. This difference of 0.56 cal. must then represent the thermal energy of the electrons. Now instead of assuming that this 0.56 cal. is due to a few electrons with a specific heat of a monatomic gas, $3/2\ R$, the postulate will be made that 0.56 cal. is the specific heat of a mol of electrons in potassium[3] so that $\sigma_K = 0.56$ at $298°$. It must be pointed out that it is the specific heat of the electrons at constant pressure which is involved in the thermo-

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[1] Lewis, THIS JOURNAL, 29, 1165 (1907).

[2] Lewis, Eastman and Rodebush, *Proc. Nat. Acad. Sci.*, 4, 25 (1918).

[3] The assumption that the potassium atoms possess their full quota of specific heat while the same number of electrons have only a very small fraction may at first thought seem unreasonable. It has, however, been thoroughly established [see Lewis and Adams, *Phys. Rev.*, 4, 331 (1914), and Latimer, THIS JOURNAL, 43, 818 (1921)] that the deviations from the equipartition conditions are greater, the smaller the mass of the atoms and the greater the constraints by which the atoms are held. Here the explanation is to be found in the very small mass of the electron.

electric equation, whereas here we are using the specific heat of electrons at constant volume. This discrepancy will exist in all the calculations which are to be made, but it is probably never greater than a few per cent.

We will first consider Equation 2. Since the quantity q is the heat absorbed or evolved when electrons pass reversibly from one metal to the other, q/T must represent the difference in entropy of the electrons in the two metals. Hence we may write

$$dE/dT = S_2 - S_1 = \Delta S \qquad (5)$$

Now from the third law of thermodynamics we may reason that at absolute zero the entropy difference will be zero. Experimental data to be considered later substantiate this conclusion. Then by the well-known thermodynamic relation for the change of entropy with temperature we obtain for the thermo-electric power at any temperature

$$\frac{dE}{dT} = \int_0^T \sigma_2 \frac{dT}{T} - \int_0^T \sigma_1 \frac{dT}{T} \qquad (6)$$

Although the verification of this relation involves a knowledge of the complete specific-heat curve of the electrons in the two metals, it seems worth while to attempt the calculation for sodium and potassium. In Fig. 1 the values of C_v for potassium and sodium given by Eastman and
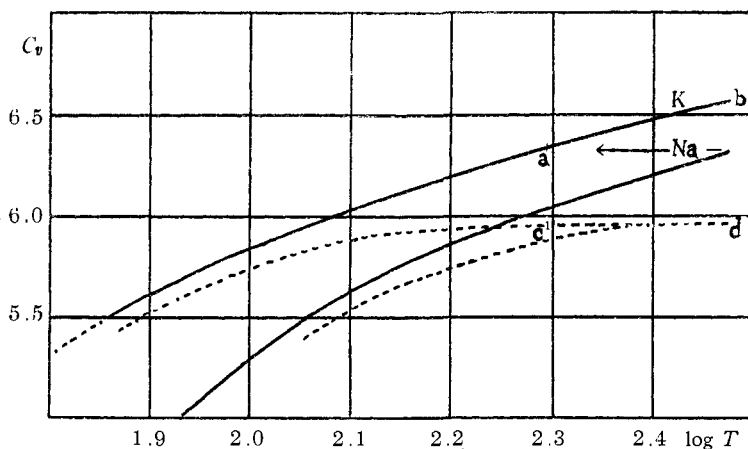

Fig. 1.

Rodebush[4] have been plotted against log T. In addition, the hypothetical curves for the metal atoms have been drawn, assuming the equipartition value at the higher temperature, so that the specific heat of the electron in each metal is given by the difference between the full and the dotted curves. Since the specific heat has been plotted against log T the value

[4] Eastman and Rodebush, THIS JOURNAL, **40**, 489 (1918).

of $\int \sigma \dfrac{dT}{T} = \int \sigma\, d\, ln\, T = 2.3 \int \sigma\, d\, \log\, T$ for each metal may be ob-

tained as the area between the two curves. If the sodium curves are dis-
placed to the left it is obvious that they will coincide with those of the po-
tassium. In the case of two such similar metals we may reasonably assume
that the unknown portions of the curves will also coincide, so that the
entropy of the electron in potassium at 25° C. will be greater by the area
abdc. By graphical methods this is found to be 0.18 entropy units. Broniew-
·ski and Hockspill[5] give for potassium against lead at 25°, $dE/dT = 12.26$
microvolts per degree, and for sodium against lead, $dE/dT = 4.52$ micro-
volts per degree. Hence for dE/dT of potassium against sodium, we
find 7.74 microvolts per degree. In order to convert volts per degree to
calories per degree per equivalent we must multiply by the factor 23074.
The result, 0.18, is in complete agreement with the value found from spe-
cific heat data.

The calculations for potassium and sodium in Equation 6 are justi-
fiable not only because of the similarity of these two metals but also be-
cause of the extremely low temperature at which the C_v value for these
metals reaches $6/2\, R$. We may, however, test the validity of our postu-
late in regard to the specific heat of the electrons with any pair of metals
at high temperatures by means of Equation 4.

The Thermo-electric Diagram

In order to make these calculations the thermo-electric curves of a large
number of metals against silver have been plotted in Fig. 2. Silver was
chosen instead of lead, which is usually the standard, (1) because of its
much higher melting point, and (2) because the specific-heat data indicated
that σ for silver must be quite small. In constructing this diagram,
Dewar and Fleming's[6] values for E have been used for platinum, gold,
palladium, silver, copper, zinc, magnesium, tin, iron, nickel, aluminum
and cadmium between the temperatures −200° and 100°. For platinum,
iridium, gold, copper and palladium at high temperatures the values of
Holborn and Day[7] have been used. For nickel the values of Hevesy and
Wolff,[8] for tungsten up to 200° the values of Coblentz,[9] for cobalt the
values of Pecheux,[10] for iron at high temperatures the values of Burgess
and Scott,[11] for calcium the values of Swisher.[12] New experimental

[5] Broniewski and Hockspill, *Ann. chim. phys.*, 29, 455 (1912).
[6] Dewar and Fleming, *Phil. Mag.*, 40, 95 (1895).
[7] Holborn and Day, *Berl. Ber.*, 691 (1899); *Ann. Physik*, [4] 2, 505 (1900).
[8] Hevesy and Wolff, *Physik. Z.*, 11, 473 (1910).
[9] Coblentz, *Bur. Standards Bull.*, 6, 107 (1909).
[10] Pecheux, *Compt. rend.*, 143, 532 (1908).
[11] Burgess and Scott, *Bur. Standards Bull.*, 14, 15 (1918).
[12] Swisher, *Phys. Rev.*, [2] 10, 601 (1917).

data, Table I, have been obtained by the writer at high temperatures for zinc, aluminum, magnesium, lead, molybdenum and tungsten against silver. The sign of lead is taken as plus in respect to silver: at the warm junction electrons flow from the silver to the lead.
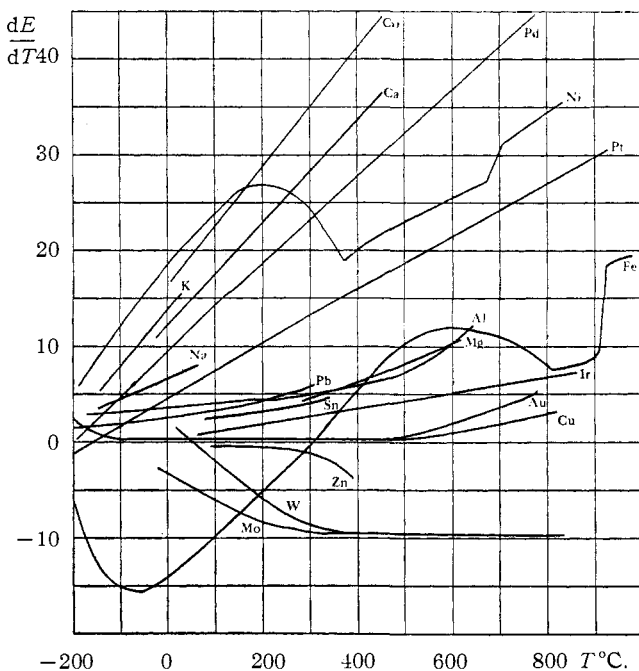

Fig. 2.—Thermo-electric power against silver in microvolts per degree.

TABLE I

THERMO-ELECTRIC FORCE, dE/dT, AGAINST SILVER

In microvolts per degree

T °C.	Pb	Zn	Mg	Al	Mo	W
100	3.0	−0.5	3.5	3.7	−6.3	−2.5
200	4.0	−0.6	4.2	4.4	−8.0	−6.0
300	5.4	−1.0	5.0	5.0	−9.2	−8.5
400	...	−4.6	6.2	5.9	−9.6	−9.2
500	...	...	8.0	7.5	−9.7	−9.5
600	...	...	10.4	10.1	−9.8	−9.7
700	...	...	..	..	−9.8	−9.8

The measurements were made with the metals in the form of wire except for magnesium, in which case magnesium ribbon was used. The metals were presumably of high purity; however, no analyses were made, nor were the wires tested for inhomogeneities. As a rule, the curves of Dewar and Fleming joined admirably with the various determinations at higher

temperatures. In certain cases the values of Noll,[13] who measured nickel, cadmium, aluminum, tin, magnesium, lead and iron against copper from 0° to 200° C. were used in adjusting slight differences between the various investigators. Swisher measured the thermo-electric force of calcium against platinum and calculated his results in terms of calcium against lead. In making these calculations differences were added instead of subtracted. Corrections have been made for this obvious error.

It is important to bear in mind in interpreting the thermo-electric diagram that it is also an entropy diagram. The value of dE/dT in volts per degree corresponding to any point on the curves when multiplied by the factor 23074 gives the difference between the entropy of 1 mol of electrons in that particular metal and 1 mol of electons in silver at the same temperature. The electrons flow, of course, from the metal of lower entropy to that of the higher at the junction which is absorbing heat.

Entropy Changes of the Electrons in Metals at High Temperatures

In Fig. 3 curves of C_v against log T are given for a number of metals. Since the values are all $6/2 R$ or above, we may assume as in the case of
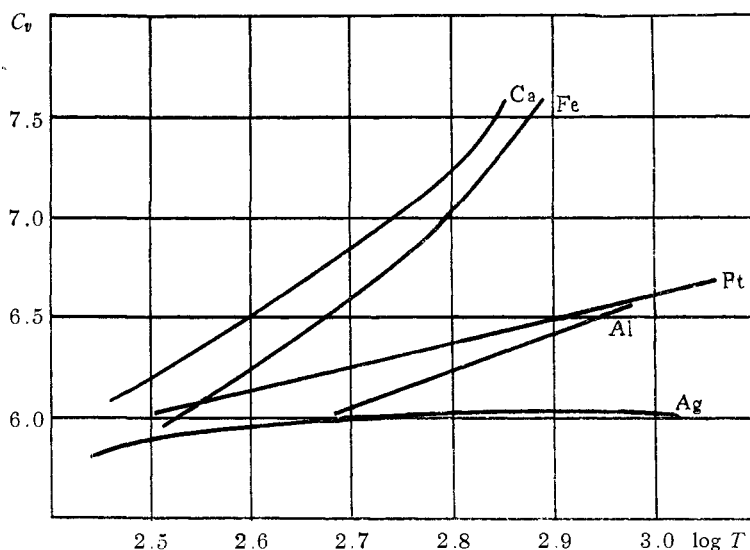

Fig. 3.—Experimental values for C_v at high temperatures.

sodium and potassium that C_v for the atoms of the metals has the equipartition value, and the increase above that is due to the specific heat of the electons. Hence, for any pair of metals the quantity $\sigma_2 - \sigma_1$ in Equation 4 is the difference in the values of C_v for those metals and $\int_{T_1}^{T_2} \left(\sigma_2 - \sigma_1 \right) \frac{dT}{T}$ may be obtained from the area between two C_v curves.

[13] Noll, *Wied. Ann.*, **53**, 874 (1894).

Platinum and Silver.—White's[14] determination of the specific heat at constant pressure of platinum is certainly the most careful piece of work that has been done at high temperatures. The calculation of the specific heat at constant volume from these values depends, of course, upon the coefficients of compressibility and expansion. These calculations for platinum, as for all other metals, involve extrapolations far above the temperatures at which these coefficients have been determined, and are therefore subject to considerable error. We have, however, accepted the values which White calculates for C_p. Schübel[15] and Eastman and Williams[16] have measured C_p for silver and calculated C_v. Schübel finds C_v practically constant at 5.70 from 0° to 600° C. We will accept, however, the higher values of Eastman and Williams as more probable. Then for $\int_{200}^{900} \left(\sigma_2 - \sigma_1 \right) \frac{dT}{T}$ we find 0.42 cal./deg. For $dE/dT_{900} - dE/dT_{200}$ we have 29.0 − 11.5 = 17.5 microvolts per degree, or 0.40 cal./deg.

In these calculations, as in the case of sodium and potassium, the assumption has been made that there is one electron per atom which possesses an appreciable amount of thermal energy. Since these elements have several valence electrons the justification of such an assumption is not as obvious as it is for sodium or potassium. However, the potential necessary to ionize a second electron from an atom is so much greater than that necessary to ionize the first that the thermal energy of the second electron is probably negligible in respect to the first. The excellent agreement which has been found seems to justify the assumption.

Iron.—The most peculiar thermo-electric curve to be considered is that of iron. The transition of β- to γ-iron at 900° is definite and takes place with a considerable increase in the entropy of the electron. On the other hand, the transition of α to β takes place with a decrease in entropy of the electron, and although there is a break in the curve at about 800°, the transition seems to be spread out over several hundred degrees. The curves for both β and γ are much flatter than the α curve, which shows that the values of C_v for these forms are considerably less than those for the α form. Although we do not have sufficient data to calculate C_v for the β and γ forms, the data of Wüst[17] for C_p, Fig. 4, indicates that these conclusions are correct. His specific heat curve, however, does not show that the transition of α to β takes place over as large a temperature difference as that observed for the thermo-electric effect. From the values of Schübel for C_v, Fig. 3, we calculate 0.47 cal./deg. for the increase in the entropy of the electron in α iron over that for silver between the temperatures of 200° and 500°. For the change in the ther-

[14] White, *Phys. Rev.*, **12**, 436 (1918).

[15] Schübel, *Z. anorg. Chem.*, **87**, 81 (1914).

[16] Eastman and Williams, a paper to be published shortly from this Laboratory.

[17] Wüst, *Ver. deutsch. Ing. Forschungsarb.*, No. 204 (1918).

mo-electric force between these temperatures, we find 15.5 microvolts, or 0.36 entropy units. Again, the agreement is quite satisfactory.

Nickel.—The thermo-electric curve for nickel also decreases considerably before the first transition is reached. Although data on C_v are not available, Wüst, Fig. 4, finds C_p for nickel at 300° higher than for any other metal, a fact which agrees with the high thermo-electric force of nickel. The decrease in the slope of the dE/dT curve for the β form also indicates a lower specific heat which is in agreement with Wüst's values. He does not, however, note a second transition.

Cobalt.—The thermo-electric data for cobalt are not very satisfactory; a transition apparently occurs in the neighborhood of 500°. Drawing a smooth curve through Pecheux's points, we find for the difference in dE/dT between 200° and 450° 20 microvolts, or 0.46 entropy units. Schübel gives C_v equal to 6.50 at 200° and 7.36 at 450°, from which we calculate 0.38 entropy units.

Palladium.—We have no data for C_v for palladium. Violle[18] found the average C_p between 0° and 1265° to be 7.62. Although no great reliability can be attached to his work, it would seem that C_v must be high, which fact is in agreement with the thermo-electric power.

Gold and Copper.—All the available specific-heat data for gold and copper indicate that their C_v curves are practically identical with that for silver. This is verified by the thermo-electric data; but above 400° the thermo-electric forces of gold and copper increase appreciably above that of silver.

Tungsten and Molybdenum.—The thermo-electric force of these metals is below that of silver. However, d^2E/dT^2 is zero between 300° and 900°, and we therefore conclude that between these temperatures their C_v curves coincide with that for silver. Since Wüst finds C_p for tungsten 6.17 at 100° and 6.72 at 1500°, C_v must obviously be very close to 6 over the whole range. His data for molybdenum, however, are not in agreement with the thermo-electric data. For C_p he finds 6.11 at 100° and 7.80 at 900°. It seems doubtful that the difference between C_p and C_v is sufficient to reduce the values of C_v to 6.[19]

Calcium.—Eastman and Williams give C_v equal to 6.01 at 0° and 7.46 at 400°, from which we may calculate 0.59 entropy units as the change

[18] Violle, *Compt. rend.*, **27**, 981 (1878).

[19] Tolman [THIS JOURNAL, **43**, 1592 (1921)] in his calculation of the entropy of electron gas from the vapor pressure of electrons in equilibrium with these metals neglected the entropy of the electrons in the metals. Now although the thermo-electric diagram does not give us the absolute value of the entropy of the electrons, the fact that the entropy of the electrons in these metals is even lower than in silver indicates that no great error was made in his calculations. In the case of platinum, however, at 1500°, such an assumption would doubtless lead to serious discrepancies.

in dE/dT between those temperatures. From thermo-electric data we find 21 microvolts, or 0.49 entropy units.[20]

Zinc and Cadmium.—The presence of transition points slightly above room temperature, together with the low melting points of these metals, renders both the specific-heat and thermo-electric data of doubtful value.

Aluminum.—Both the specific heat and thermo-electric curves indicate that the electrons in aluminum start to pick up energy very rapidly at about 200°. From the specific heat data of Eastman and Williams (Fig. 4) we calculate $dE/dT_{650} - dE/dT_{200}$ equal to 0.20 cal. per deg. The corresponding value from thermo-electric data is 8.2 microvolts per degree, or 0.19 cal. per deg.

Magnesium.—Eastman and Williams find C_v to be 6.24 at 200 and 6.87 at 600°, from which the value of $dE/dT_{650} - dE/dT_{200}$ is 0.33 cal. per deg. From the thermo-electric curve we find 7.5 microvolts per degree, or 0.18 cal. per deg. Although this discrepancy is fairly large, doubtless it is within the uncertainties of the $C_p - C_v$ correction for magnesium.

Lead.—Schübel calculates that C_v for lead is 6.21 at 200° and 6.23 at 300°. His values for C_p, however, are somewhat higher than those given
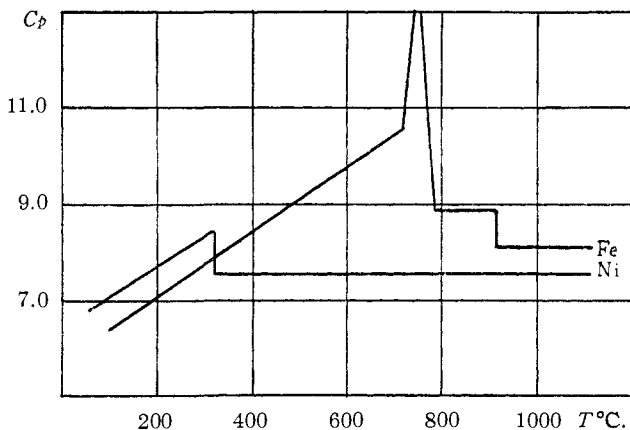

Fig. 4.

by Griffith and Griffith.[21] Although the temperature difference is hardly great enough to make a calculation worth while, we obtain 0.04 cal. per deg. for the change in dE/dT from his specific-heat values between 200° and 300°. The corresponding value from the thermo-electric curve is 1.4 microvolts, or 0.03 cal. per deg.

[20] These calculations are somewhat doubtful due to the uncertainty of the sign of Swisher's value for calcium against platinum. It seems unlikely that the sign is negative; if so, the thermo-electric power of calcium is somewhat less than that of silver and disagrees completely with the specific-heat data.

[21] Griffith and Griffith, *Trans. Roy. Soc. London*, **214A,** 319 (1914).

The metals which have been considered exhaust the cases for which there are data on both C_v and thermo-electric effects. The results of the various calculations are summarized in the following table.

TABLE II

ENTROPY CHANGES IN METAL ELECTRONS (1) FROM THERMO-ELECTRIC DATA (2) FROM SPECIFIC-HEAT DATA

Metal against silver	T_1 to T_2 °C.	$\Delta S_{T_2} - \Delta S_{T_1}$ From thermo-electric data	From specific-heat data
Platinum.....................	200–900	0.40	0.42
Iron........................	200–500	0.36	0.47
Cobalt......................	200–450	0.46	0.38
Nickel......................	0–200	high	high
Gold........................	200–500	0.0	0.0
Copper......................	200–500	0.0	0.0
Tungsten....................	250–900	0.0	0.0
Molybdenum................	250–900	0.0	?
Calcium.....................	100–400	0.49	0.59
Aluminum...................	200–600	0.19	0.20
Magnesium..................	200–650	0.18	0.33
Lead........................	200–300	0.03	0.04

The quantitative checks which have been obtained substantiate in a large measure the postulates made in regard to the reversibility of the thermo-electric effects and the significance of the increase of the specific heats of metals above the equipartition values at high temperatures. Where there is a tendency toward the formation of a molecular structure, as may be the case in bismuth and certain alloys, large discrepancies may possibly exist. This would be the case if in the metal molecule the number of electrons possessing thermal energy were not equal to the number of atoms, or if the specific heat of the substance involved a gradual transition from one molecular structure to another.[22] Even for bismuth there is a qualitative agreement. Although the thermo-electric force is very high, it is so unreproducible that a definite value cannot be chosen. Wüst finds C_p for bismuth 6.96 at 200° which agrees with the high thermo-electric power. In addition to sodium and potassium, Broniewski and Hockspill determined the thermo-electric force of rubidium and cesium. Their value for rubidium is slightly less than that for potassium, while their value for cesium is quite low. Although the C_v curve for cesium has not been determined, it would be very surprising to find it lower than that for potassium, as their measurements indicate.

[22] Langmuir [THIS JOURNAL, **38**, 2236 (1916)] has pointed out that if the vibrations of the atoms are not harmonic the average potential energy may be greater than the average kinetic energy and the specific heat of the solid greater than $^6/_2 R$ even under conditions in which the kinetic energy is determined by the equipartition principle. It is quite possible that such a condition may exist in metals of low constraints or in the neighborhood of transition points.

The Entropy of the Metallic Electrons at Low Temperatures

The most striking fact about the thermo-electric diagram is its agreement with the third law of thermodynamics. Onnes and Holt[23] have investigated certain couples which possess appreciable thermo-electric force at the temperature of liquid hydrogen. In every case the values were zero when the couples were cooled to the still lower temperatures of liquid helium. However, some of their results are very interesting. At 15° K the entropy difference for the silver-gold couple amounts to 4.6 microvolts, or 0.11 entropy unit. It would be surprising indeed if such entropy differences really exist, for even though a decrease in the entropy occurs at still lower temperatures, the specific-heat data indicate that the total entropy of a mol of gold at 15° K is hardly more than 0.11 entropy unit.

The thermo-electric curve of iron at low temperatures offers more interesting considerations. It seems obvious that below —100° C. the thermal
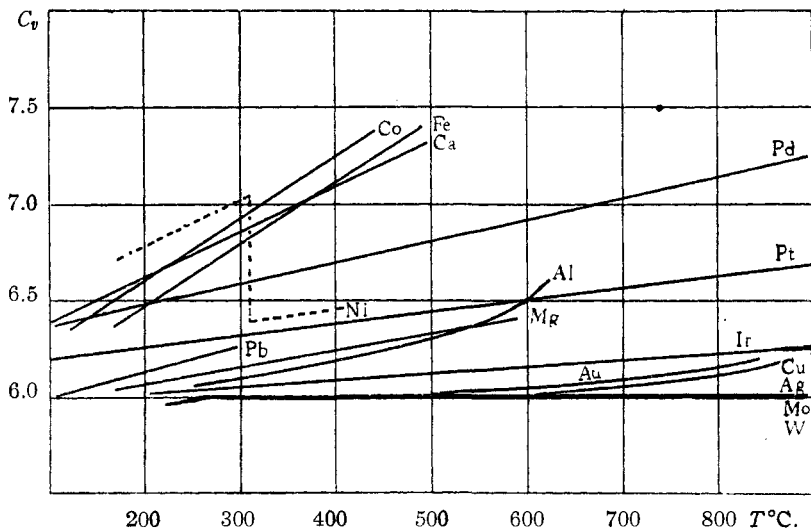

Fig. 5.—Specific heats calculated from thermo-electric force. Compare Fig. 3.

energy of the electrons in iron is very low, and that in the neighborhood of that temperature the electrons suddenly start to gain energy very rapidly. The interesting point, however, is the conclusion that at —100° the entropy of the electrons in silver must be at least 0.35 entropy unit. This is larger than could be expected in view of the low value of σ at high temperatures. It is possible, however, that the specific heat of the electron in some cases is greater at low than at high temperatures. For example, if at low temperatures an electron is held in equilibrium between 2 atoms, the thermal motion of the 2 atoms would in itself tend to create thermal

[23] Onnes and Holt, *Comm. Phys. Lab. Univ. Leiden*, **1914**, No. 142.

energy in the electron, due to the pull first in one direction and then in the other. However, as the thermal motion becomes large the electron may not be able to maintain its equilibrium position between the two atoms, but may be shifted to a more stable position where it is no longer subject to the vibrations of both atoms. In such a case its specific heat would be smaller. In addition to iron, it would seem that some such explanation must be offered to account for the decrease in the thermo-electric force of tungsten and molybdenum against silver. It may also be pointed out, of course, that it is the partial molal specific heat of electrons with which we are concerned, and that in some cases this quantity may even be negative.

Thermo-electric Force as a Method of Determining C_v At High Temperatures

If the postulates which have been made in regard to the relation between thermo-electric force and the specific heat of metals are accepted, we then have at our command a very easy and direct method for the determination of the specific heat of metals at high temperatures. As an illustration, the curves in Fig. 5 have been constructed in agreement with the thermo-electric data (by means of Equation 4) and the experimental values of C_v at the lower temperatures. In the case of certain metals too much emphasis should not be laid upon a definite value for either the thermo-electric force or the specific heat, since both are altered by any mechanical or thermal treatment which affects the constraints operating between the atoms. From the quantitative checks which have been secured it seems probable that the determinations of C_v from thermo-electric data are to be preferred to the values calculated from the often questionable direct determination of C_p.

Summary

1. The thermo-electric force of a circuit of 2 metals has been expressed in terms of the entropy of the electrons in the 2 metals.

2. The postulate has been made that the specific heat of a mol of electrons in a metal is given by the increase in the specific heat at constant volume of a mol of the metal above the equipartition value of $6/2\ R$.

3. On this assumption the absolute value of the thermo-electric force of the potassium-sodium couple has been calculated at 25° from values of the specific heats of these metals.

4. The changes in thermo-electric force of 12 metals against silver have been calculated from specific-heat data for temperature differences of 100° to 700°. Satisfactory agreement has been obtained between the calculated and observed values.

5. In order to make these calculations the existing data on the thermo-electric force have been collected; new data for the thermo-electric force

of 6 metals against silver have been obtained, and all these values have been summarized in a thermo-electric diagram.

6. The entropy of the metal electrons at low temperatures has been discussed.

7. The possibility of using thermo-electric data as a means of determining C_v for metals at higher temperatures has been pointed out, and the C_v curves for 15 metals have been drawn in agreement with existing thermo-electric data.

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THE ELECTROMETRIC TITRATION OF DICHROMATE WITH FERROUS SULFATE

BY MARION EPPLEY AND WARREN C. VOSBURGH

It has been shown by Forbes and Bartlett[1] that, due to the peculiar relationship between electromotive force and amount of ferrous salt added in the electrometric titration of dichromic acid, end-points could be determined without plotting curves. This method of titration has been applied by Kelley and collaborators[2] in several analytical methods. It has been assumed that the point at which the great change in electromotive force occurs represents the point at which an amount of ferrous salt equivalent to the dichromate present has been added. The accuracy of this assumption apparently has not been determined. In the present investigation the conditions affecting the electrometric titration of dichromate with ferrous sulfate were investigated and the relation determined between the quantities of each reacting.

It was found that, although it was possible to determine accurately the point at which the great change in electromotice force occurs by the method of Forbes and Bartlett and to duplicate results very well under constant conditions, the ratio of ferrous ion to dichromate ion varied with the concentration of the dichromate. Under certain conditions dichromic acid appeared to oxidize more than an equivalent amount of ferrous ion, the error being about 0.4%. Therefore, the method is to some extent empirical and its accuracy is dependent on the care taken to standardize the experimental conditions.

Experimental

Effect of Acidity on the End-point.—The effect of acidity of the solution on the shape of the titration curve and on the end-point was deter-

[1] Forbes and Bartlett, THIS JOURNAL, **35**, 1535 (1913).

[2] Kelley and Conant, *J. Ind. Eng. Chem.*, **8**, 719 (1916). Kelley, Adams and Wiley, *ibid.*, **9**, 781 (1917). Kelley and Wiley, *ibid.*, **13**, 1053 (1921).