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Correlation of Heat Capacity, Absolute Temperature and Entropy

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Correlation of heat capacity, absolute temperature and entropy: Starting with the two assumptions that at very low temperature the heat capacity is proportional to the entropy, and that at relatively high temperature it approaches a limiting value (C_∞), very simple relations are obtained between the heat capacity and the absolute temperature, and between the entropy and the absolute

temperature of a given substance, by the introduction of a simple algebraic function which satisfies the two assumptions. The validity of these relations is substantiated by the excellent agreement of the observed and the calculated values for the heat capacities and for the entropies of a considerable number of substances, ten of which are given in this paper.

IN establishing the relation of heat capacity, absolute temperature and entropy of a given substance at constant pressure, two assumptions are made: first, the heat capacity C is proportional to the entropy S as the absolute temperature approaches zero; second, the heat capacity C approaches a limiting value C_∞ at relatively high temperature. These assumptions may be expressed analytically as follows:

- (a) $(\partial C/\partial S)_p = K(T \rightarrow 0)$,
and
(b) $(\partial C/\partial S)_p = 0(T \rightarrow \infty)$.

Making use of the thermodynamic equation,

$$(\partial S/\partial T)_p = C_p/T,$$

gives

$$\left(\frac{\partial C}{\partial S}\right)_p = \left(\frac{\partial C}{\partial T}\right)_p \cdot \left(\frac{\partial T}{\partial S}\right)_p = \left(\frac{\partial C}{\partial T}\right)_p \cdot \frac{T}{C_p}. \quad (1)$$

Arithmetical experience with a large number of heat capacity data shows that the left-hand member of Eq. (1) may be replaced by a very simple function, namely,

$$(\partial C/\partial S)_p = K(1 - C/C_\infty), \quad (2)$$

so that Eq. (1) becomes,

$$(\partial C/\partial T)_p = K(1 - C/C_\infty)C/T. \quad (3)$$

The right-hand member of Eq. (2) obviously satisfies the two assumptions (a) and (b).

The integrated form of Eq. (3) is,

$$\log C/(C_\infty - C) = K \log T + \log k, \quad (4)$$

which may also be written in the forms,

$$C = C_\infty k T^K / (1 + k T^K) \quad (5)$$

or,

$$C = C_\infty k e^{K \log T} / (1 + k e^{K \log T}). \quad (6)$$

In testing the validity of Eq. (4), the following method was used.

First, the experimental values for C were plotted against the corresponding logarithms of the absolute temperatures, and the curves representing Eq. (6) sketched in.

Second, the best value for C_∞ was in each case located on the curve. This was easily attained, since the curve is symmetrical with respect to the inflection point, as may be readily shown by placing the second derivative of C with respect to $\log T$, of Eq. (6) or (7), equal to zero; at this point, $C = C_\infty/2$.

Third, the best values for K and for $\log k$ were obtained from the straight line plot of Eq. (4), where K is the slope and $\log k$ is the intercept on the $\log C/(C_\infty - C)$ axis.

Fourth, with the aid of these quantities, the values for C "calculated" may be readily obtained by means of Eq. (4).

DISCUSSION OF C_∞

From the analogy of the specific heat of a "perfect monatomic gas," the older school of physical chemists reached the conclusion that C_∞ for all solids at constant volume should be $3R$ (5.966), calories per gram atom of substance. Any excess of this value was attributed to the work done by virtue of the expansion of the

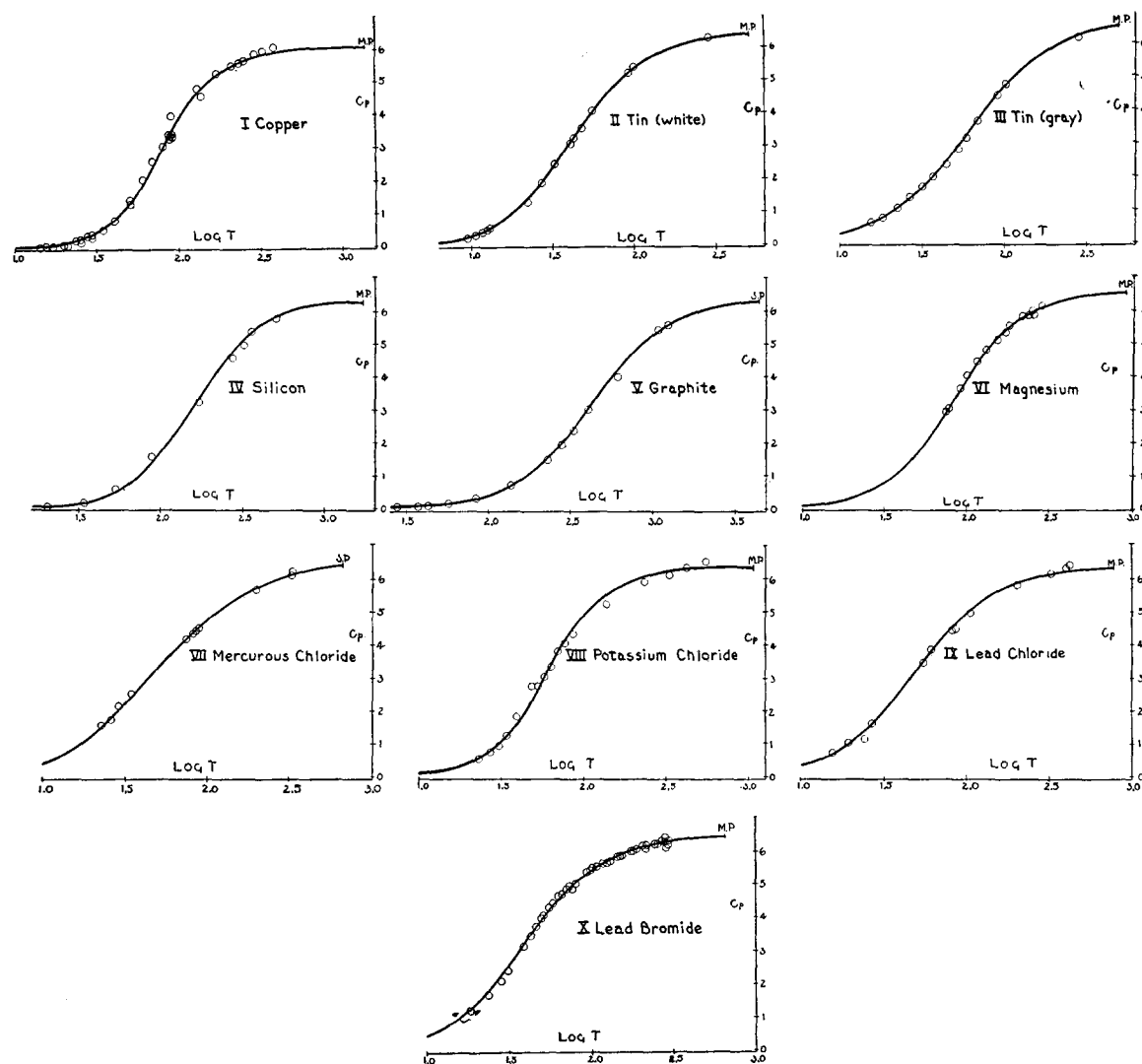


FIG. 1.

substance. Modern investigators have found, however, that the rather large excess of $3R$ calories near the melting point cannot be accounted for in this manner. Some suggest that at the upper temperature, or near the melting point of the substance, the electrons themselves may acquire an appreciable heat capacity; but the specific heat data in the region of the melting point are still meager and of insufficient accuracy to warrant calculation of the heat capacity of the electrons. Investigations in this field are now being conducted by Jaeger and Bottema,¹

¹ Jaeger and Bottema, Proc. Acad. Sci. (Amsterdam), 1932.

and their results will very likely lead to definite conclusions.

Similar investigations in the neighborhood of the absolute zero are now being carried on by Keesom and his associates.² When sufficient data have been accumulated in these two fields they will be analyzed in a similar manner.

THE GRAPHS

The graphs are self-explanatory. The letters M.P. denote the melting point; the letters S.P. denote the sublimation point. It is of interest

² Keesom, Proc. Acad. Sci. (Amsterdam), 1932.

TABLE I. *Summary of entropies from 0 to 298° absolute, and constants.*

	S_p		C_∞	K	$\log k$
Copper	8.10	8.18	5.97	2.900	-5.49550
Tin (white)	12.22	11.17	6.40	2.074	-3.41445
Tin (gray)	10.82	9.23	6.70	1.700	-3.03844
Silicon	4.25	4.70	6.30	2.316	-5.15068
Graphite	1.45	1.30	6.40	1.820	-4.79222
Magnesium	8.55	8.30	6.60	2.050	-3.94848
Mercurous chloride	23.88	23.20	6.50	1.480	-2.52140
Potassium chloride	20.50	19.70	6.40	2.380	-4.23445
Lead chloride	34.86	33.20	6.40	1.769	-2.99838
Lead bromide	39.02	39.75	5.50	1.840	-2.96575

to note that the experimental points follow the calculated curves very closely, and that the average deviations do not exceed the average experimental variations.

CONCLUSION

In conclusion it may be mentioned that the heat capacities of all substances, measured by the thermoelectric method, conform statistically to Eq. (6). The ten substances given in this paper were taken at random from a group of about three times that number. It is also interesting to find that the entropies calculated from the integrated form of Eq. (2) between 0 and 298° absolute are practically identical with those given in the thermodynamic literature, which have been obtained by the mechanical integration of the areas under the $C - \log T$

curves. A comparison of these values is given in Table I. In the second column are given the values for the entropies from 0 to 298° absolute calculated from the integrated form of 2,

$$S = 2.3(C_\infty/K) \log C_\infty/(C_\infty - C), \quad (7)$$

and in the third column are given the values as recorded in the thermodynamic literature; these have been obtained by mechanical integration.

It is seen that in every one of the ten substances the observed values agree with the calculated values within experimental error.

Note: References to the data used in this paper may be found in the International Critical Tables, Vol. V. The data recorded in that volume are not, however, the original values and are therefore not suitable for investigational purposes. For an extensive and interesting discussion of specific heat data at constant volume, the reader is referred to an article by F. Schwes, Phys. Rev. **8**, 117 (1916).