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ABSTRACT

The heat capacity of a liquid metal is made up of several contributions: a kinetic term, an electronic term, a dilation term, and a configurational term due to interatomic forces. The theory of the radial distribution function is used to establish a corresponding states correlation of the configurational heat capacities of six low-melting metals. It is suggested that this correlation may be used to estimate the configurational contribution to the specific heats of other liquid metals. For instance, it might be used to decompose the abnormally high heat capacity of a molten transition metal in order to investigate its electronic energies. The theory is also used to explain the observed temperature dependence of liquid metal heat capacities.

INTRODUCTION

In recent years the application of liquid metals as heat transfer agents in nuclear reactors has caused increased interest in the heat capacities of these substances. Because of experimental difficulties the data have been so inexact that values reported to be constant with temperature were as well justified as any other representation. Generally, the values of C_p for most fused metals are found to be around 7 cal/mole-°K, which is close to the values for the solid metals at high temperatures. Conspicuous exceptions are the transition metals which have heat capacities as much as 40% higher than this average value. Some representative values of liquid metal heat capacities are given in Table 1.

Usually these observed values have been interpreted as indicating that the liquid near its melting point is structurally and thermodynamically quite similar to the solid. That is, the liquid is expected to possess a vibrational contribution to the heat capacity near $3R$. An additional portion of C_p is the dilation contribution which is given exactly by

$$C_p - C_v = \alpha^2 v T/k \quad (1)$$

where α is the coefficient of thermal expansion and k is the isothermal compressibility of the liquid. Any discrepancy between the sum of these two terms and the observed specific heat has been attributed to anharmonicity of the atomic vibrations and, particularly in the case

of the transition metals, to an electronic contribution.

Recently accurate heat capacities have become available over a wide range of temperatures for several low melting metals (1,2). These data are shown in Figure 1. It is seen that in each case C_p near the melting point initially decreases with increasing temperature. However, for four of the metals the heat capacity is found to reach a minimum and then to increase with temperature. Thus, a certain trend in the behavior of the heat capacity of the liquid is indicated by these data. The theoretical explanation of this behavior will be investigated here.

Rather than to emphasize the similarities between the solid and liquid metallic states one might find it fruitful to apply to liquid metals a statistical theory of liquids which not only takes into account the necessary short range order of the condensed phase but also allows for the fluidity of the liquid and the relatively high mobility of the particles. A general theory of fluids which does this is the one based on the radial distribution function (3), and this theory will be used here to interpret the liquid heat capacity data. Because of their monatomic nature the liquid metals should correspond quite well to the theoretical model, which assumes spherically symmetrical force fields.

THEORY

The internal energy of a monatomic fluid can be approximated by (4)

$$E = \frac{3}{2} RT + \frac{1}{2} \frac{N_0}{V} \int_0^{\infty} u(r)g(r) 4\pi r^2 dr. \quad (2)$$

The first term is the kinetic energy, and the second is the potential energy due to the pairwise molecular interactions in the system. Avogadro's number is denoted by N_0 , the molar volume by v , and $u(r)$ is the atomic pair potential energy function. The radial distribution function $g(r)$ represents the time-averaged relative configuration of the interacting particles. For a dense fluid the analytic expression of this function can be obtained only approximately (5). Nevertheless, the principles of statistical mechanics indicate the general form (6)

$$g(r) = \exp [-\omega(r)/kT] \quad (3)$$

where $\omega(r)$ is the potential of the mean force at a distance r from the central molecule due to the force fields of all the particles in the system. The potential of the mean force depends on the intermolecular potential energy function, the temperature, and the density. If the form of the potential energy function $u(r)$ for a group of substances is specified and depends on only two parameters, as does for example the Lennard-Jones potential, $\omega(r)$ can be written as a universal function of three dimensionless parameters which may be defined by

$$T^* \equiv kT/\epsilon, \quad V^* \equiv \frac{v}{N_0 \delta^3}, \quad r^* \equiv r/\delta. \quad (4)$$

The two parameters ϵ and δ are the energy and distance parameters of the potential energy function. Then $g(r)$

can be written as $g(r^*, T^*, V^*)$. Also $u(r)$ can be written as $\epsilon \cdot f(r^*)$ where $f(r^*)$ is some function of the reduced distance r^* .

Substituting these expressions into equation (2) and differentiating with temperature at constant density yield an expression for the heat capacity at constant volume, namely,

$$C_v = \frac{3}{2} R + 2\pi \frac{R}{V^*} \int_0^\infty \frac{1}{T^*} \left(\frac{\partial g}{\partial T^*} \right)_{V^*} f(r^*) r^{*2} dr^* . \quad (5)$$

From this equation it can be seen that for a class of substances which obey the same intermolecular potential law C_v should be a universal function of the dimensionless variables T^* and V^* only since the dependence on r^* is eliminated by the definite integration.

APPLICATION OF THE THEORY TO LIQUID METALS

To investigate the validity of this conclusion in the case of the molten metals, it is necessary to obtain C_v from the measured C_p values. This is done by subtracting from C_p the dilation contribution given by equation (1). The compressibilities of all the metals in Figure 1 except lithium have been measured (7). The calculated C_v values are plotted versus temperature in Figure 2. The necessary compressibility data are available for very few other metals so that the conversion from C_p to C_v is not generally possible at this time.

It should be possible to represent the heat capacities

of the various metals by a single generalized plot if their interatomic potential energy functions are of the same form. This should be a reasonable approximation for the substances being considered here.

A comparison of the heat capacities which is based on equation (5) also requires that the electronic contribution to the C_p be eliminated from the data. According to the Fermi-Sommerfeld theory, the contribution C^{el} from the conduction electrons is given by

$$C^{el} = \gamma T \quad (6)$$

where γ is a constant for temperatures much smaller than the effective Fermi temperature (8). For the metals being considered here the Fermi temperature is on the order of 10^4 °K. Therefore equation (6) should give a good approximation of the electronic heat capacity of these simple metals even in the liquid state. The constant γ has been determined from very low temperature data. Values are given in Table 2. In the case of the transition metals there are the possibilities that the d electrons may contribute to C_v at high temperatures and that the melting temperatures are too high relative to the Fermi temperatures for linearity to persist. Therefore equation (6) may no longer be valid for these substances.

Finally, to demonstrate the existence of the universal function suggested by equation (5), it is necessary to estimate independently values for the parameters ϵ and

δ in such a manner that they have the proper physical significance. An appropriate distance parameter is assumed to be the interatomic spacing in the close-packed crystal at 0°K. This quantity will be introduced as δ in the definition (4) of the reduced volume V^* . In a previous paper (9) the author has developed an analogous corresponding states correlation for the viscosity of liquid metals. In that analysis the distance parameters were chosen to be the crystal spacings as suggested above. The energy parameters of nineteen metals were then determined from a generalized viscosity curve which was based on the effective Lennard-Jones parameters of sodium and potassium reported by Ling (10). The parameters obtained there have been used to define the reduced temperature for the heat capacity correlation. Values of these parameters are given in Table 3.

On the basis of the assumed parameters the reduced configurational heat capacity

$$C_v^* \equiv \frac{C_v}{R} - \frac{3}{2} - \frac{C_{el}}{R} \quad (7)$$

has been computed from the data for the six metals and the function $C_v^* \cdot V^*$ plotted versus reduced temperature T^* in Figure 3. The implicit effect of the parameter V^* on the integral in equation (5) has not been considered in the graphical representation of the function $C_v^* \cdot V^*(T^*)$ by the data because the reduced density does not vary greatly and one would therefore not expect $\left(\frac{\partial g}{\partial T^*}\right)_{V^*}$ to depend on V^* very much in this region. In spite of the various

assumptions made in the calculations, it is seen quite clearly in the figure that the data are all close to a single curve. In fact the maximum deviation of any point in Figure 3 from the mean value of $C_V^* \cdot V^*$ at a particular reduced temperature corresponds to less than 4% of the measured C_p value. The similarity in temperature dependence of the function for the six metals is particularly impressive. Thus it is concluded that the configurational heat capacities of these liquid metals obey a corresponding states law as predicted by the theory.

DISCUSSION

The steady decrease of C_V of the liquid metals with temperature seen in Figure 2 or, in particular, the decrease of C_V^* with temperature can be explained by the effect of temperature on the liquid structure. It has been found by x-ray diffraction analysis that the height of the first large peak of the radial distribution function, in the region where $u(r)$ is appreciable, decreases rapidly with temperature (11). For this reason the value of the integral in equation (2), which represents the configurational internal energy, also diminishes with increasing temperature. Because of the exponential form of $g(r)$, its temperature derivative decreases as well. Therefore one may expect the heat capacity due to intermolecular forces to decrease with increasing temperature as has been observed.

Because of the complex nature of the liquid state,

the heat capacity of liquids in general has not received extensive theoretical treatment, and the representation of the data has been purely empirical. However, it has been pointed out that accurate values of liquid heat capacities at constant volume might be used to investigate the types of motion executed by molecules in the liquid state (12). Heat capacities of various substances have been analyzed for this purpose by assuming that the contribution due to the motion of the center of gravity of a molecule in the liquid near the melting temperature is $3R$ (13). An attempt is then made to interpret the additional portion of C_v in terms of the internal modes of molecular energy. It is seen in Figure 2 that the assumption of $3R$ for the "lattice" C_v of K, Na, In, Sn, Hg and Pb is a poor estimate for these monatomic liquids. It is suggested that a better approximation to the molecular interaction heat capacity contribution can be obtained, at least for simple liquids, through the application of a semi-empirical corresponding states correlation such as that presented in Figure 3. For example, if one wished to determine the electronic energy of a transition metal by investigating its abnormally high heat capacity, one could use Figure 3 to estimate the configurational contribution; thus, the behavior of the electronic contribution could be inferred from the appropriate C_v values by the use of equation (8).

SUMMARY

The specific heat of a liquid is made up of several contributions: a kinetic term, a dilation term, a configurational term due to intermolecular forces, and possibly an electronic term or some intramolecular energy contribution. In order to gain information about either of these last two phenomena from heat capacity measurements, one must have reasonable estimates of the other contributions. The kinetic and dilation terms are known. It has been shown here that for several low-melting liquid metals the configurational term obeys a corresponding states law based on atomic interaction parameters and can be represented by a generalized correlation. This correlation may be useful in estimating the configurational contribution to the heat capacities of other liquid metals.

By decomposing the heat capacities of the liquid metals in this way it has been possible to use the theory of the radial distribution function to explain the temperature dependence of C_p which has recently been observed.

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Table 1. Heat capacities of liquid metals at their melting points. (1)

Metal	C_p (cal/mole-°K)
Hg	6.81
Na	7.61
K	7.68
Sn	7.10
In	7.05
Pb	7.32
Mg	7.80
Al	7.00
Ca	7.4
Ti	8.0
V	9.5
Cr	9.40
Mn	11.00
Fe	10.50
Co	9.0
Ni	9.20
Cu	7.5
Ag	7.3
Zn	7.5
Ga	6.65

Table 2. Temperature coefficient of
electronic heat capacity γ . (1)

Metal	$\gamma \times 10^4$ (cal/mole($^{\circ}$ K) 2)
Hg	4.5
Na	3.3
K	5(± 2)
Sn	4.2
In	3.6
Pb	7.5(± 4.0)
Cu	1.64
Mn	28
Fe	12.0

Table 3. Goldschmidt atomic radii and energy parameters of the metals.

Metal	$\delta(\text{\AA})$ (14)	$\epsilon/k(^{\circ}\text{K})$ (9)
Hg	3.10	1250
Na	3.84	1970 (10)
K	4.76	1760 (10)
Pb	3.50	2800
Sn	3.16	2650
In	3.14	2500

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FIGURE CAPTIONS

Figure 1. Heat capacity at constant pressure of liquid metals.

Figure 2. Heat capacity at constant volume of liquid metals.

Figure 3. Reduced configurational heat capacity of liquid metals.

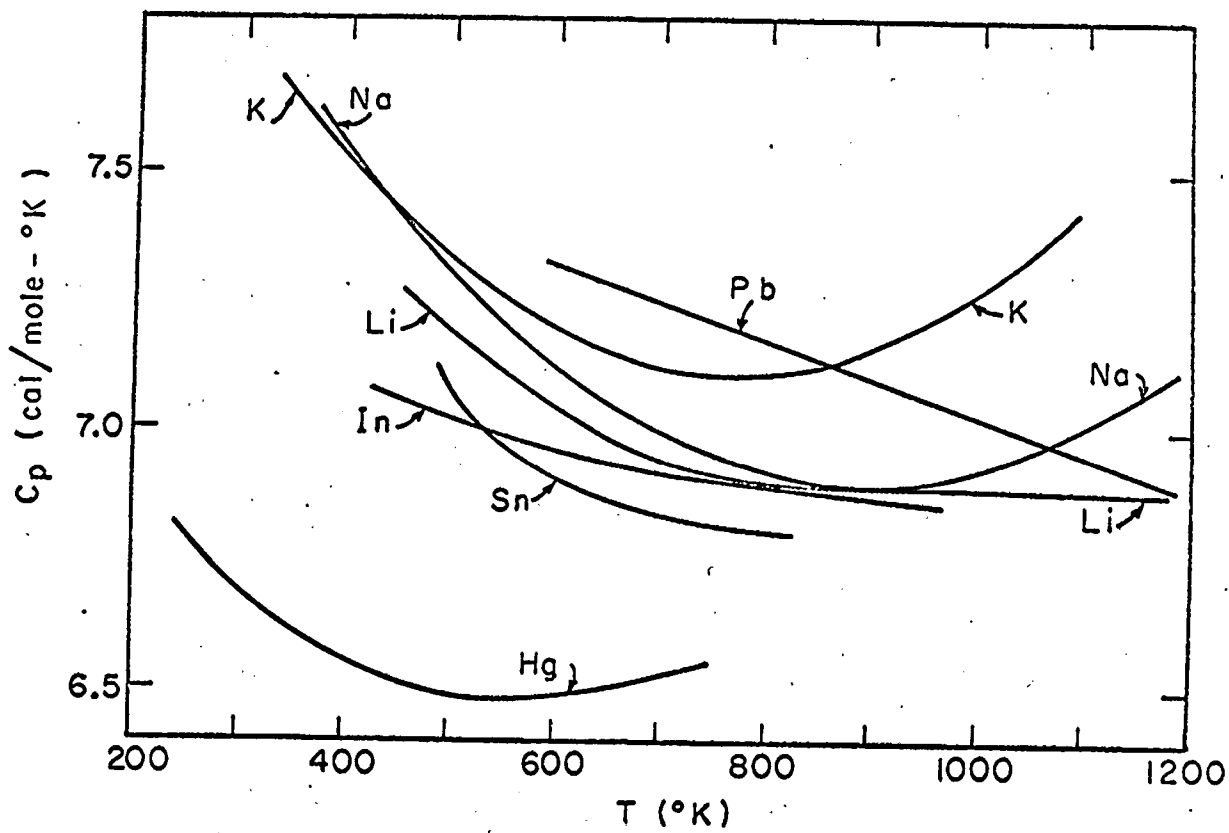
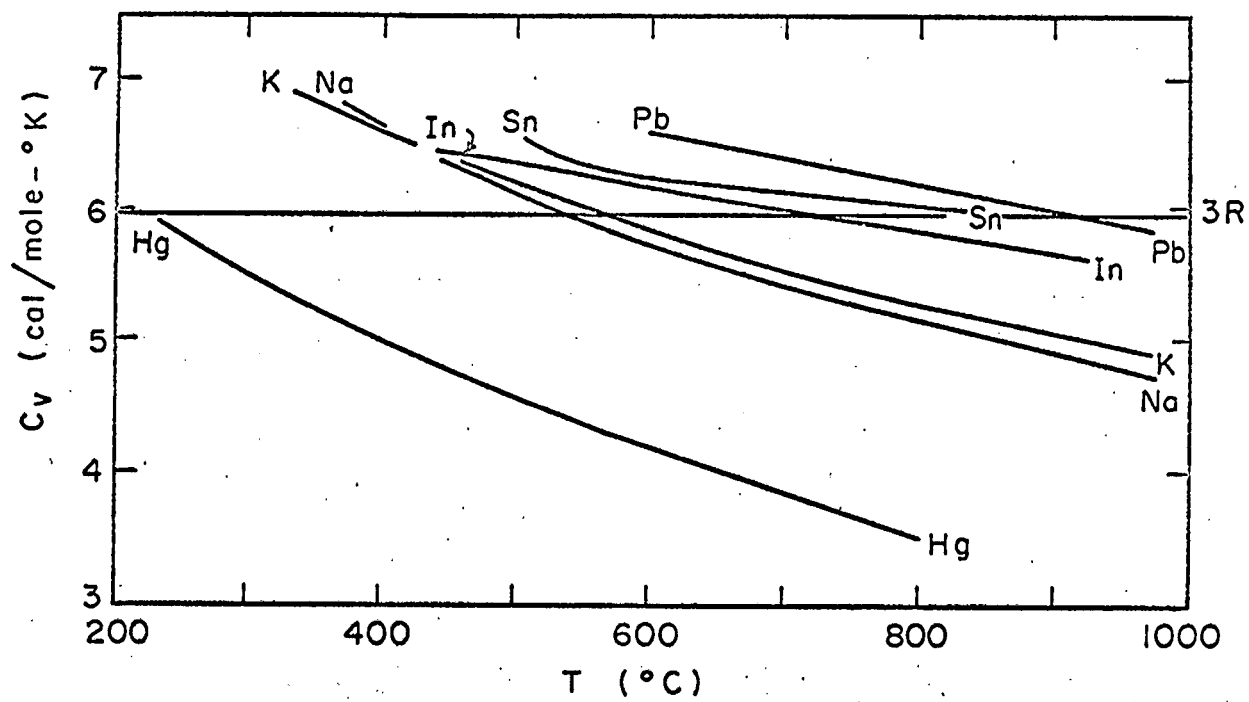


Fig. 1

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Fig. 2

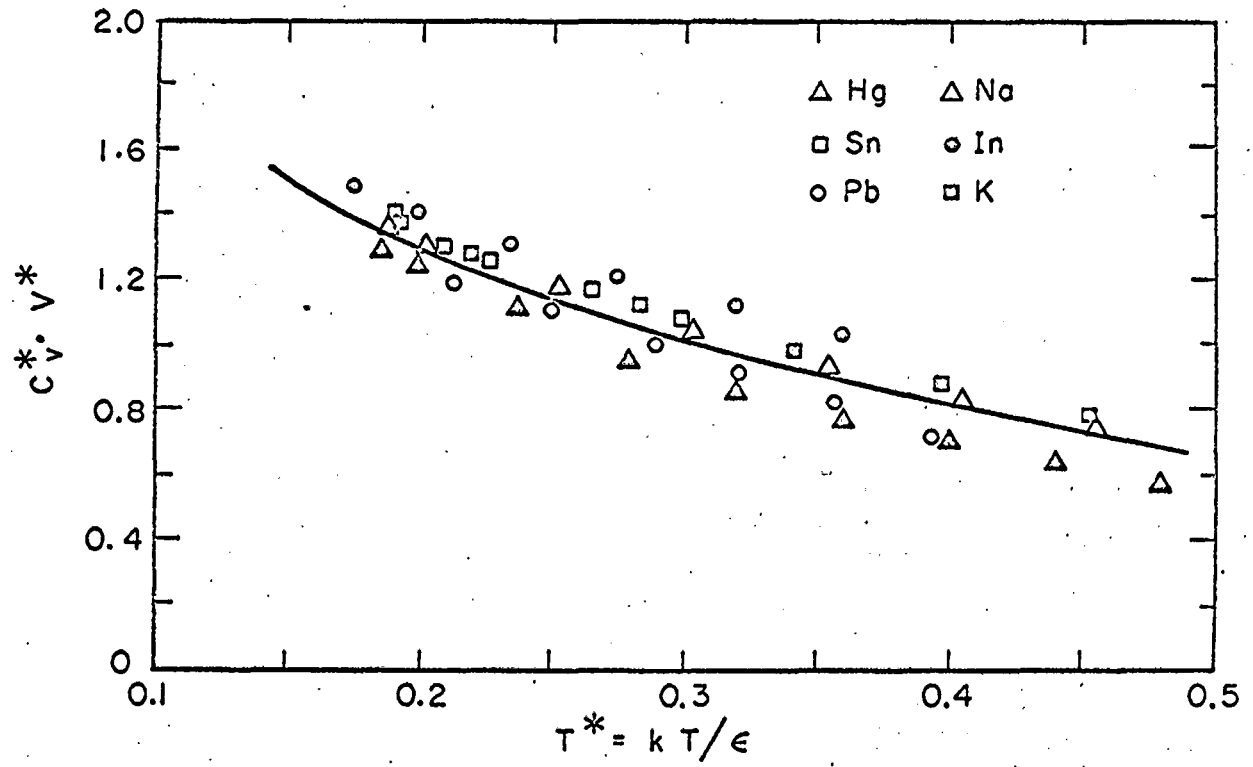


Fig. 3

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