THERMAL PROPERTIES OF LIQUID AND SOLID METALS

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New generalized expressions for compressibility and thermal expansion of liquid and solid metals are presented.

The goal of this study is to demonstrate that a number of general relationships recently discovered for nonmetallic liquids hold true for liquid metals as well, and that these same principles are valid for the solid phase of metals in many cases.

It was established in [1] that for normal (nonmetallic, nonassociated) liquids the following expression for density on the saturation line is valid:

$$\omega \equiv \frac{\rho}{\rho_c} - 1 = B\vartheta^{\beta} + (B-1)\vartheta, \quad \vartheta \equiv \frac{T_c - T}{T_c} = 1 - \tau, \tag{1}$$

where the subscript c indicates the critical point. With the exponent $\beta = 0.323$ this expression describes inverse density over the entire extent of the binodal from the triple to the critical point, including states directly adjacent to the latter, where agreement exists with expressions known from scale theory. The single parameter B is simply related to the critical compressibility factor $z_c \equiv P_cV_c/RT_c$:

$$B = \frac{0{,}505}{z_c}. \tag{2}$$

There is also a fundamental relationship between B and the Ridel thermodynamic similarity criterion A_R [2, 3]:

$$B^{1/\beta} = A_R \equiv \left(\frac{d\ln P}{d\ln T}\right)_{T=T_c}, \tag{3}$$

where P is the saturated vapor pressure.

Equation (1) and similar expressions for the density of saturated vapor and for both branches of the spinodal were used in [4, 5] to develop methods for describing the thermal properties of liquids, including the metastable state range.

It has recently been established that Eqs. (1)-(3) are also valid for liquid metals over just as wide a range of states, but with $\beta = 1/2$. In addition an expression has been found for the change in $z \equiv PV/RT$ of a liquid along the saturation line:

$$-\frac{1}{B}\ln\frac{z}{z_c} = (1-\tau)^{1/2} + \ln\tau + 2\left(\frac{1}{\tau} - 1\right). \tag{4}$$

Simultaneous use of Eqs. (1), (2), (4) permits determination of the basic characteristic parameters of liquid metals T_c, P_c, ρ_c, and B using a minimum of empirical data (for example, from two density values and one saturated vapor pressure value).

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TABLE 1. Temperature Dependence of Molar Volume of Cesium and Lithium

T, K	Cs		Li	
	V [8, 9]	$V\vartheta^{1/2}$	V [10, 9]	$V\vartheta^{1/2}$
	cm³/mole			
200	68,7	65,2	12,81	12,45
250	69,5	65,1	12,92	12,46
300	70,5	65,1	13,03	12,42
310	72,58	66,9		
350	73,45	66,9	13,12	12,46
400	74,60	66,9		
450	75,82	67,0		
460			13,49	12,60
500	77,08	67,0	12,58	12,60
550			13,69	12,60
600			13,81	12,61
650			13,94	12,62
700			14,17	12,64

TABLE 2. Comparison of Expansion Coefficients of Liquid Metals (calculation by Eq. (7)) with Experimental Data for Solid Metals

Metal	T_c, K	B	$\alpha \cdot 10^{-4}$, K^{-1}	
			(7)	[11]
Cs	2050	2,26	2,90	2,91
Rb	2155	2,27	2,76	2,70
K	2300	2,37	2,60	2,52
Na	2660	2,55	2,28	2,16
Li	3600	2,9	1,72	1,80
Hg	2400*	1,36	1,75	1,82
Cu	7200	2,7	0,9	0,85
Sn	6700	2,7	0,9	1,0

*As is well known, the real critical temperature of mercury is significantly lower, due to the existence of a subcritical metal—nonmetal transition. The T_c value presented should be considered a characteristic parameter of metallic mercury.

TABLE 3. Parameter C in Eq. (4)

Metal	Cs	Rb	K	Na	Li
C (1)—(3)	1,03	0,97	1,00	0,80	0,5
C [14]	1,03	1,16	1,3	1,3	1,07

A very simple equation of state has also been found for liquid metals

$$\pi - \pi_s = C(\omega^3 - \omega_s^3),\ \pi \equiv P/P_c, \qquad (5)$$

where the subscript s refers to a reference line, the saturation line, $C \sim 1$. Equation (5) automatically includes the critical point, correctly conveys the configuration of the critical isotherm, quantitatively corresponds to results of study of the PVT-dependence of liquid cesium over a wide state range [6], and describes compressibility data for liquid metals given in [7].

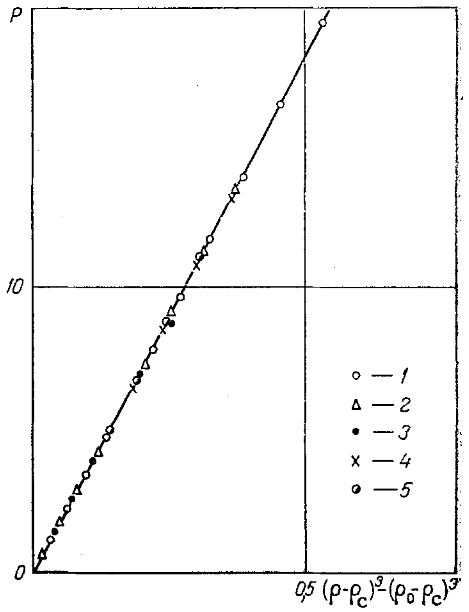

Fig. 1. Pressure P (kbar) vs variable $(\rho-\rho_c)^3-(\rho_0-\rho_c)^3$ for sodium: ρ_0, density at P = 0 for given isotherm; ρ_c, critical density (value ρ_c = 0.196 g/cm³ used). Liquid isotherms: 1) 493°K; 2) 453; 3) 433; solid phase isotherms: 4) 373; 5) 393°K.

TABLE 4. Compressibility of Cesium, Constancy of Complex $\beta_T\omega^2(\omega + 1)$

T, K	β_T	$\beta_T\,\omega^2(\omega+1)$	T, K	β_T	$\beta_T\,\omega^2(\omega+1)$
	10^{-11} m²/N			10^{-11} m²/N	
Solid			Liquid		
0	46,5	280	303	65,5	291
50	47,6	281	400	73,6	293
100	48,8	282	500	85,2	301
150	50,0	280	600	98	306
200	52,9	284	700	113	310
250	56,8	294	800	130	313
300	61,3	300	90	150	313
			1000	170	302
			1100	197	295

Below we will show that the relationships presented above may also be used for the solid phase.

1. In describing the temperature dependence of density of the solid and liquid phases near the fusion point we will use the following variant of Eq. (1):

$$\rho = \rho^{x}\vartheta^{1/2},\ \rho^{x} = \rho_c[2(B-1)^{1/2} + B]. \tag{6}$$

This expression can be obtained from Eq. (1) by replacing the sum $1 + (B-1)\vartheta$ by the mean geometric value.

Table 1 presents values of the product $V\vartheta^{1/2}$ (where V is the molar volume) of cesium and lithium, which, according to Eq. (6), should be constant. It is evident from the table that for alkali metals Eq. (6) describes the temperature dependence of density of the solid and liquid phases in the ϑ interval from 0.94 to 0.75. At lower temperatures deviations from Eq. (1) commence, related to a more rapid decrease in the expansion coefficient due to the role of quantum effects.

2. The same question can be treated by considering the thermal expansion coefficient. We write for $\alpha \equiv \frac{1}{V}\left(\frac{dV}{dT}\right)_P$ an expression analogous to Eq. (6):

$$\alpha = \frac{(B-1)^{1/4}}{2\vartheta^{3/4}} \frac{1}{T_c}. \tag{7}$$

Table 2 compares calculations with this expression to experimental data for the solid phase near the fusion temperature.

3. Use of Eq. (4) for isotherms of liquid and solid metals is illustrated by Fig. 1, which presents data on sodium from [12]. The straight line dependence in the variables used indicates the validity of Eq. (4). Points of the liquid isotherms from 493 to 373°K and solid phase points from 433 to 373°K fall on a single curve. The data of [13] for low-temperature (to 20°K) isotherms of solid sodium are very close to those presented.

Similar constructions for other alkali metals not only confirm the fact established in [12] of similarity of the equations of state for solid and liquid phases, but convincingly indicate that Eq. (4) can serve as such an equation. For liquid cesium the range of validity of Eq. (4) extends from 0°K in the solid phase to 1900°K ($0.93T_c$) in the liquid.

For relatively low changes in volume $\Delta V/V$ Eq. (4) is close to the known empirical expression

$$P = \Pi\left[\left(\frac{V_0}{V}\right)^n - 1\right] \tag{8}$$

for n = 3. Then

$$\Pi = CP_c\left(\frac{\rho_0}{\rho_c}\right)^3 \tag{9}$$

(in [8] n = 2.84 for cesium). Of course Eq. (8) cannot be applied to liquids at high temperatures.

Equation (4) can be used to calculate isotherms from characteristic parameters and a single value of volume under pressure, the latter being required to define C. To generalize, values of C for metals of different groups are required. Table 3 presents C values for alkali metals. In the calculations experimental data were used for compressibility with P_c and ρ_c determined with Eqs. (1)-(7), as well as values recommended in [14] (second row of table). According to the table, for heavy alkali metals we may take C = 1, while the data for Na and Li require refinement (for which data on Gruneisen parameters may be used).

4. For the isothermal compressibility $\beta_T = -\frac{1}{V}\left(\frac{dV}{dP}\right)_T$ of liquid and solid metals, from Eq. (4) we have the expression

$$\beta_T^{-1} = 3CP_c\omega^2(\omega+1). \tag{10}$$

According to Eq. (10), the isothermal compressibility on an isochore should be temperature independent. Data for β_T of sodium from [12] demonstrate that this consequence of Eq. (4) is satisfied to a very good approximation. For the liquid phase of Na for molar volumes of 19.9-25.5 cm^3/mole in the temperature interval 493-393°K the changes in β_T with temperature lie within the limits ± 0.6%, while for the solid phase from 20.5 to 24 cm^3/mole in the temperature range 433-373°K they are within 0.1%.

The degree to which Eq. (10) is satisfied can be judged from Table 4, presenting data for solid [8] and liquid [9] cesium.

We will note that the data presented are based on ρ_c values obtained from data for the coexistence curve, and selection of an optimal ρ_c value will reduce the inconstancy of $\beta_T\omega^2(\omega+1)$ by a factor of several times.

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