DISORDER CONTRIBUTION TO FUSION ENTROPY

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Abstract Correlations of volume changes with fusion entropy for substances with spherical, linear and general molecules are presented. The separation of basic disorder and volume contributions has been explained by means of molecular degrees of freedom. A theoretical model of fusion for liquid metals is discussed.

1.Introduction

We have recently shown[1) that the correlation of relative volume change $\Delta V/V_s$ at fusion with associated entropy change S_f could give an insight into the mechanism of fusion. Fusion entropy contains several contributions given by

$$S_f = S_d + S_v + S_c + S_i \tag{1}$$

where S_d is the basic disorder term representing molecular motions and S_v the volume dependent term, while S_c and S_i are terms due to conformational and intermolecular changes at fusion, respectively[1).

2. Analysis of experimental data

Correlations of $\Delta V/V_s$ and S_f, both at normal and high pressure, for substances with effectively spherical and linear molecules, for which S_c and S_i are negligible, are shown in Fig.1.

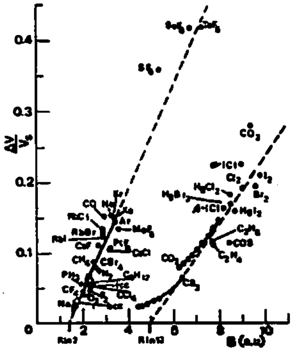

Fig.1 Correlations of volume change $\Delta V/V_s$ with fusion entropy S_f for substances with spherical and linear molecules. Data are taken from ref.2.

Effective sphericity of molecules in plastic crystals is achieved by quasi-free rotation in the high temperature phase of their solid state. In Fig.1 only halides of Rb and Cs are included[1), because for Li, Na and K halides change of the

Madelung constant is considerable[3], giving thus a non-zero contribution to the intermolecular term S_i. The experimental points in Fig.1 may well be approximated by means of straight lines. Extrapolation $\Delta V/V_s \rightarrow 0$ determines the basic disorder term S_d thus giving $\simeq R\ln 2$ for substances with spherical molecules[4] and $\simeq R\ln 12$ for linear ones. Substances with general molecules do not give a simple correlation at normal pressure. Nevertheless, S_d may be determined using $\Delta V/V_s$ or ΔV and S_f data under increased pressure. The diagram of each substance then independently gives its S_d. Fusion entropy is obtained by means of the Clausius-Clapeyron equation from T, P and ΔV data.

Fig.2a shows the considered correlations for chloroform and bromoform. Similarly, Fig.2b gives ΔV-S_f diagrams for benzene, $C_6H_5NO_2$ and compounds of Fig.2a. At the beginning of pressure increase, extrapolations $\Delta V/V_s \rightarrow 0$ or $\Delta V \rightarrow 0$ give $S_d \simeq R\ln 16$, except for benzene with $S_d \simeq R\ln 12$. At very high pressure, deviations to lower entropies occur, indicating a change in the fusion mechanism[5].

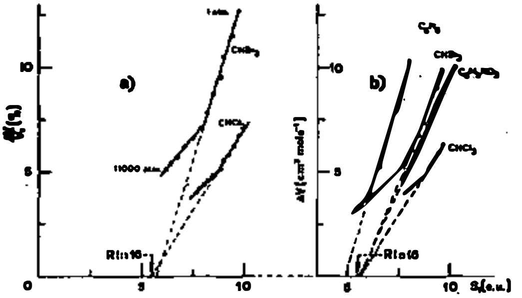

Fig.2 Correlations of $\Delta V/V_s$ (a) and ΔV (b) with S_f for some organic substances with general molecules. Data are taken from ref.2.

If molecules are assumed to be rigid, then only changes of translational and rotational motions could be responsible for S_d at fusion. Relation of S_d to molecular degrees of freedom may be concieved using the Boltzmann equation[1,5]

$$S_d = R\ \ln(n_l/n_s) \qquad (2)$$

where n_l and n_s are numbers of states of disorder in liquid and solid. We take n_s=1 representing all possible vibrations and librations of a molecule around its equilibrium position in a crystal lattice. Consequently, n_1 has to be 2 for spherical molecules, 12 for linear and 16 for general ones. Following mainly the idea of Eyring's significant structures6), but specifying now each possible kind of motion, we introduce a number of various states which we expect to be responsible for the entropy of fusion. It is supposed that a molecule in liquid may be subjected to one-, two- or three-dimensional translations. Similarly, one expects the same for rotations. Furthermore, all combinations of translations and rotations would be possible. In Table I, the numbers before T (translation) and R (rotation) define the dimensionality of motions, and all possible 16 states including various additional motions are represented. The first state characterizes a molecule in liquid, which remains in the solid state conditions. For general molecules there are 16 possible states. For linear molecules 3R is missing and so there remain only 12 states in agreement with the experimental evaluation. In Fig.2b benzene has $S_d \simeq R\ln 12$. This indicates a possibility of molecular rotations around the axis normal to the molecular plane already in the solid state5). Thus benzene would behave like a linear molecule at fusion. It is surprising that substances with spherical molecules have $S_d \simeq R\ln 2$ indicating that in liquid only one new additional state appears.

TABLE I

No. of state	1T	2T	3T	1R	2R	3R
1	-	-	-	-	-	-
2	1	-	-	-	-	-
3	-	1	-	-	-	-
4	-	-	1	-	-	-
5	-	-	-	1	-	-
6	-	-	-	-	1	-
7	-	-	-	-	-	1
8	1	-	-	1	-	-
9	-	1	-	1	-	-
10	-	-	1	1	-	-
11	1	-	-	-	1	-
12	-	1	-	-	1	-
13	-	-	1	-	1	-
14	1	-	-	-	-	1
15	-	1	-	-	-	1
16	-	-	1	-	-	1

3. Theoretical model of fusion for simple metals

The simplest substances, for studying the single new state in liquid, are metals. It may be sopposed that, in solid, atoms vibrate around equilibrium lattice sites according to the Einstein model. In liquid, besides the similar vibrations, an atom is subjected to additional onedimensional translation of distance $(V/N)^{(1/3)}$, where V is molar volume and N Avogadro's number.

The starting point is the classical partition function for an atom

$$q = h^{-3}\iiint e^{-\frac{p_x^2+p_y^2+p_z^2}{2mkT}}\,dp_x\,dp_y\,dp_z \iiint e^{-\frac{\phi(x,y,z)}{kT}}\,dx\,dy\,dz \tag{3}$$

The symbols have their usual meaning. If ϕ_l is an equilibrium potential energy of an atom in liquid, then the partition function for the harmonic oscillator, using eq.(3), will be

$$q_v' = e^{-\phi_l/kT}(kT/h\nu)^3 = e^{-\phi_l/kT}(T/\Theta_l)^3 = e^{-\phi_l/kT}q_v^3 \tag{4}$$

where Θ_l is the characteristic temperature of the liquid. The partition function for translational motions in volume V/N is

$$q_t' = e^{-\phi_l/kT}(2\pi mkT/h)^{3/2}(V/N) = e^{-\phi_l/kT}q_t^3 \tag{5}$$

One may assume that one-dimensional translations appear at melting, above energy level

$$\varepsilon = 3RT_f + \Delta H_f \tag{6}$$

determined by the fusion temperature T_f and the heat of fusion ΔH_f. Then it is possible to divide atomic motions in liquid into two parts, defined by partition functions $q_s = q_v'$ and

$$q_l = e^{-\phi_l/kT}\,3q_v^2\,(1-e^{-\varepsilon/kT})^2 q_t\,e^{-\varepsilon/kT} \tag{7a}$$

Function q_s represents the solid-like motions, while q_l represents a combination of two-dimensional oscillations with energy levels below ε and the one-dimensional translations with energies above ε [7]. Factor 3 means three possible orientations of one-dimensional translations.

Thus the total partition function of one mole of liquid is[7]

$$Q_l = (N!/N_s!\,N_l!)\,q_s^{N_s}\,q_l^{N_l} \tag{7b}$$

and the Helmholtz free energy $F = -kT\ln Q_l$ gives the entropy of liquid from $S_l = -(\partial F_l/\partial T)_V$, i.e.

$$S_l = 2R(\ln q_v + 1) + R\ln[q_v + 3q_t(1-e^{-\varepsilon/kT})^2] + \tag{8}$$

$$+\{RT/[q_v + 3q_t(1-e^{-\varepsilon/kT})^2]\}\{(\partial q_v/\partial T) + 3[(1-e^{-\varepsilon/kT})^2(\partial q_t/\partial T) - (2q_t\varepsilon/kT^2)(1-e^{-\varepsilon/kT})e^{-\varepsilon/kT}]\}$$

For calculating S_l by eq.(8), it is necessary to know the following parameters: heat of fusion ΔH_f, molar volumes V_s and V_l of solid and liquid, respectively, and characteristic temperature Θ_s of solid, all near the known fusion temperature T_f. Θ_s can be obtained from the solid state entropy S_s in the Einstein model

$$S_s = 3R[1 + \ln(T_f/\Theta_s)] \tag{9}$$

if the experimental values of S_s are known. For fcc metals, the characteristic temperature of the liquid is determined by the Grüneisen law[7)]

$$(\theta_l-\theta_s)=\Delta\theta=-\gamma\,\theta_s\,\Delta V/V_s. \tag{10}$$

The Grüneisen constant γ is known for metals[8)]. For bcc metals the characteristic temperature θ_l for the liquid is higher than θ_s of the corresponding solid, and in order to determine $\Delta\theta$ or θ_l, the entropy of liquid at T_f must be known from experiment. Using experimental data[9)], it is possible to determine the entropy within the whole temperature interval of the liquid state. In Table II, the entropy of liquid copper is given for various temperatures and for other metals only at fusion temperatures T_f.

TABLE II

Metal	T(K)	θ_s(K)^a	$\Delta\theta$(K)	θ_l (K)	S_l (exp.)^b	S_l (calc.)^b	
					x 4,18 J/mol·K)		
Cu	1357	195	-16^c	179	19.82	19,78	
	1600	"	"	"	21.04	21.29	
	2000	"	"	"	22.64	22.94	fcc
	2500	"	"	"	24.23	24.21	and
Ag	1234	131	-12	119	21.67	21.68	hcp
Au	1336	118	-16	102	23.06	23.40	metals
Al	932	242	-35	208	16.71	16.45	
Ni	1725	243	-25	218	20.04	19.97	
Zn	693	145	-15	130	17.84	17.70	
Cd	594	96	-8	88	19.27	19.27	
Li	454	265	35^d	278	10.76	10.79	
Na	371	104	10	114	15.23	15.21	
K	337	61	5	66	17.86	17.87	
Rb	312	40	4	44	19.98	19.95	bcc
Cs	302	29	3	32	21.71	21.64	metals
Be	1556	660	60	720	12.86	12.91	
Ca	1123	122	13	135	20.96	20.85	
Tl	577	57.7	3	60.7	21.40	21.38	

a) θ_s is determined from eq.(9); b) the electron gas contribution to the total entropy of liquid is substructed; c) eq. (10) is used; d) these values are fitted from known S_l at fusion.

Negative or positive values of $\Delta\theta$ for corresponding crystal structures might be expected, because the coordination number diminshes from 12 to ≃10 for fcc and hcp metals at melting, but increases from 8 to ≃lo for bcc metals[10)].

4. Conclusion

It may be stated that at normal pressure liquid metals may well be described by oscillations of atoms around their equilibrium positions in a quasi-crystalline lattice and by additional one-dimensional translations of the order of $(V/N)^{(1/3)}$. But an extrapolation to high pressure (or temperature) is not possible at present. Namely, it is still unknown how the characteristic temperature depends on pressure near fusion. Thus S_d cannot be evaluated. However, the assumption that one-dimensional translations are essential in liquid metals seems to be supported by very good agreement between the calculated and experimental entropy values presented in Table II. For more complicated substances like Cl_2, $CHCl_3$, etc., all possible molecular motions or states, as suggested by Table I, should be included. These dynamical states of a disordered liquid may be connected with the number of static sublattices in generalized Lennard-Jones and Devonshire, and Pople and Karasz theories[11]. Investigations of this connection and introduction of an appropriate extended partition function for complex systems are under way.

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