JOURNAL OF MATERIALS SCIENCE **39** (2004) 1535–1546

Review
Role of entropy of fusion in phase transformation and self-diffusion

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The present paper discusses the role of the entropy of fusion vis-à-vis the phase transformation characteristics and the self-diffusion behavior of crystalline matrices. The data correlating the entropy of fusion with these properties in metals, alkali halides and some other inorganic compounds are presented and analyzed. It is shown that the occurrence of a solid-solid state phase transformation decreases the magnitude of the entropy of fusion. In addition, the self-diffusion rates within any class of solids scale inversely with the entropy of fusion. The functional relationship of the entropy of fusion vis-a-vis the compressibility and the volume expansion coefficient is also discussed. The conclusion is that the entropy of fusion is not just a physical parameter describing the energy changes associated with the melting. It is, in fact, related in a substantial manner to the bulk properties of the solid and controls the phase transition characteristics and self-diffusion behavior within any group or class of solids in a uniform and consistent manner.

1. Introduction

Enthalpy and entropy are the two fundamental state properties of any substance. Between them, they govern the thermodynamic stability and the energetics of any process undergone by the substance. These are called state properties in the sense that they depend on thermodynamic state of the material defined by temperature, pressure, volume and composition. In the present article, we are concerned with the inter-relationships between the magnitude of entropy of fusion and the bulk properties of the matrix. The properties that we shall discuss vis-a-vis their relationships with the entropy of fusion are thermal expansion, bulk modulus, the structural transformation and self-diffusion behavior of the inorganic crystalline substances. The structural transformations of our present interest take place without any change in the composition of the matrix and involve only the changes in the coordination number of the atoms. The changes in entropy (S) and enthalpy (H) are related to each other as follows:

$$\partial S = \frac{\partial H}{T}, \tag{1}$$

where T represents the temperature at which such a change occurs. Fusion is a first order phase change and occurs at a constant temperature. In this case, Equation 1 is transformed as

$$\Delta S_\mathrm{m} = \Delta H_\mathrm{m}/T_\mathrm{m}. \tag{2}$$

Here ΔS_m, ΔH_m and T_m are respectively the entropy of fusion, enthalpy of fusion and fusion temperature. ΔS_m values as well as all other thermodynamic data for metals and inorganic substances used in this paper have been taken from Barin's latest compilations of thermochemical data of pure substances [1].

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Before dealing with the influence of entropy of fusion on phase transformation and diffusion, we will first discuss the relationship developed by Tallon [2, 3] between ΔS_{m} on the one hand and the volume thermal expansion coefficient and the compressibility on the other. Next, we will discuss the variation of the magnitude of the entropy of fusion in metals, alkali halides and some other inorganic compounds. It will be shown that the magnitude of entropy of fusion is controlled by phase changes in the solid state prior to the melting point. The overall effect of structural transformations in the solid state is to decrease the magnitude of the entropy of fusion although the transformation itself is accompanied by an increase in the entropy of the matrix. A discussion of the correlations discovered by Cho [4, 5] between the enthalpy and the entropy changes and the associated transformation temperatures is given. Reasons for anomalies in the magnitude of the entropy of fusion are also discussed. Finally, it will be shown that within any class of material having identical physical and chemical characteristics, the magnitude of the entropy of fusion governs the relative rates of self-diffusion. A lower value of the entropy of fusion is an indication of relatively higher diffusion rates and vice-versa. Thus, it turns out that a low value of ΔS_{m} is an indication of allotropy as well as high self-diffusion rates. The intention of present paper is to show that for any solid, the entropy of fusion is not merely a physical property defining the energy changes associated with its transformation into the liquid phase. Rather, it is related to its thermal behavior in a substantial manner.

2. Bulk modulus, thermal expansion coefficient and the entropy of fusion

Tallon [2, 3] has shown that the entropy change on melting, ΔS_{m}, can be related to compressibility and volume change (ΔV_{m}) as follows:

$$\Delta S_{\mathrm{m}} = \eta R \ln 2 + \alpha/\beta \cdot \Delta V_{\mathrm{m}} \qquad (3)$$

where η is the stoichiometry of the system, α the volumetric coefficient of thermal expansion, and β the compressibility. The first term containing η represents the zero volume change in entropy due to the fusion of solid. The value of η is 1 for metals and inert gas solids, 2 for alkali halides and its value is 3 for compounds like $CaCl_2$ and $SrCl_2$. Thus η represents the number of atoms in the system which become delocalised upon melting. According to Tallon [6], this term represents entropy acquired by the melt due to the localisation of the propagating shear modes. Alternatively, this is the entropy gained by the system, at the constant volume, due to the disappearance of the long range order on melting. The other term containing the thermal volume expansion coefficient and the compressibility represents the additional entropy gained due to the dilation of the matrix. This term relates ΔS_{m} with the bulk properties of the matrix. In Fig. 1, a plot of ΔS_{m} versus ΔV_{m} for a number of metals, including the alkalies, is shown. The value of the intercept is quite close to $R\ln 2$ for $\eta = 1$ for akali metals as well as for other common metals. However, the slopes are different in the two cases since these depend upon the values of the parameter α/β. The magnitude of the parameter α/β is markedly different for the alkali metals compared with other common metals [6]. Thus Fig. 1 lends further support to Tallon's model for ΔS_{m} by extending its validity to metals.

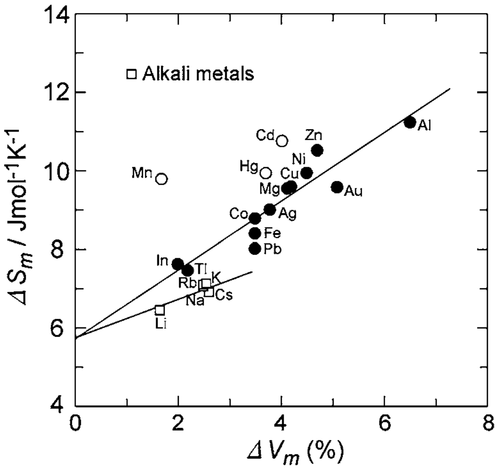

Figure 1 The plot of entropy change on melting (ΔS_{m}) against the corresponding change in volume (ΔV_{m}).

In Fig. 1, the metals Mn, Cd, Zn, Pb, Au and Hg show large deviations from the average line drawn for the other metals. These have been disregarded in drawing the least mean square line for the other metals. This deviation can be either due to variation in the value of parameter α/β or some anomalies in the behavior of molten state. This point is discussed later.

It is important to mention here that the term α/β in Equation 3 is approximately a constant for any material and practically independent of temperature [6, 7]. It is also related directly to the rate of change of the entropy of the matrix as follows:

$$\partial S/\partial V = \alpha/\beta \qquad (4)$$

3. Entropy of fusion and phase change

The entropy of fusion data for metals and compounds to be analyzed below are listed in Tables I–III and V–VII. In addition, the tables also list the solid state transformation temperature (T_{t}), melting point (T_{m}) and the cumulative entropy of fusion ($\Delta S_{\mathrm{m}}^{\mathrm{C}}$). This parameter is introduced later.

3.1. Metals

Table I lists the ΔS_{m} values of all the metals for whom this property is well established. Its variation due to the presence of solid state phase changes as well as the spread in the magnitude within any one class of material will be analyzed in this section.

A temperature-induced transformation such as melting or allotropic change in a closed or isolated system is brought about by the tendency of the system to attain a configuration of higher entropy. The occurrence of such changes is a manifestation of this tendency and hence a phase occurring at a higher temperature will always have relatively higher entropy and enthalpy than that of the low temperature phase. It will be seen that the net entropy change due to melting is reduced if it is preceded by one or more solid state phase transformations [8]. Smaller values of the entropy of fusion, therefore, can be regarded as being a consequence of the occurrence of solid state phase transformations.

Entropy of fusion values for the common metals are grouped in two categories in the Tables I and II. The first one, listed in Table I consists of non-allotropic metals. These exhibit ΔS_m values varying between 7.942 and 13.496 J·K^{-1} mol.$^{-1}$, the average being 9.778. In the Table II, the allotropic metals are listed where ΔS_m values lie between 3.116 and 9.845 with an average of 7.319. Thus on an average, values of the entropy of fusion are higher for non-allotropic metals than that for allotropic metals. Data for lanthanide elements are given in the Table III. The lanthanide elements are again divided into non-allotropic and allotropic classes. Lanthanide elements follow a similar correlation, as the common metals, between the incidence of allotropy and the magnitude of entropy of fusion.

TABLE I Melting point and entropy of fusion for non-allotropic metals

S. no	Structure	Metal	T_m (K)	ΔS_m (J mol^{-1}K^{-1})
1	FCC	Ag	1234	9.155
2		Al	933.5	11.475
3		Au	1337.6	9.384
4		Cu	1358	9.675
5		Ni	1726	10.123
6		Pb	600.6	7.942
7		Pd	1825	9.622
8		Pt	2045	9.616
9		Rh	2233	9.623
10		Ir	2716	9.623
11	HCP	Cd	594	10.424
12		Mg	922	9.711
13		Os	3300	9.623
14		Re	3453	9.623
15	BCC	Mo	2897	13.496
16		Cr	2130	7.95
17		W	3680	9.619
18		Nb	2740	9.623
19		Ta	3287	9.623
20		V	2175	9.622
				Av. 9.778

TABLE II Solid state phase transformation temperature (T_t), melting temperature (T_m), entropy of solid state phase transformation (ΔS_t), entropy of fusion (ΔS_m) and the cumulative entropy of fusion (ΔS_m^C) for allotropic metals

S. no	Structure	Metal	T_t (K)	T_m (K)	ΔS_t (J mol^{-1}K^{-1})	ΔS_m (J mol^{-1}K^{-1})	ΔS_m^C (J mol^{-1}K^{-1})
1	HCP	Ti	1166		3.578		
				1939		7.296	10.874
2		Zr	1135		3.539		
				2125		9.845	13.384
3		Hf	2013		3.346		
				2500		9.623	12.969
4		Mn	980		2.271		
			1360		1.560		
			1410		1.333		
				1517		7.949	13.113
5		Co	700		0.646		
				1768		9.158	9.804
6		Sc	1608		2.493		
				1812		7.779	10.272
7		Tl	507		0.744		
				577		7.179	7.923
8		Y	1752		2.849		
				1799		6.335	9.184
9		Th	1636		1.672		
				2028		7.949	9.621
10	BCC	Li		453.7		6.612	
11		Na		371		7.017	
12		K		336.4		6.966	
13		Cs		301		6.921	
14		Rb		312.7		6.985	
15		Fe	1184		0.760		
			1665		0.503		
				1809		7.632	8.895
16		U	941		2.966		
			1048		4.539		
				1405		6.063	13.568
17		Pu	395		8.473		
			480		1.221		
			588		0.925		
			730		0.115		
			753		2.44		
				913		3.116	16.290
						Av. 7.319	Av. 11.321

TABLE III Solid state phase transformation temperature (T_t), melting temperature (T_m), entropy of solid state phase transformation (ΔS_t), entropy of fusion (ΔS_m) and the cumulative entropy of fusion (ΔS_m^C) for lanthanides

S. no	Allotropy	Metal	T_t (K)	T_m (K)	ΔS_t (J mol^{-1}K^{-1})	ΔS_m (J mol^{-1}K^{-1})	ΔS_m^C (J mol^{-1}K^{-1})
1	Non-allotropic	Eu		1090		8.45	
2		Er		1765		11.09	
3		Tm		1818		9.62	
4		Lu		1936		9.29	
						Av. 9.61	
5	Allotropic	La	550		0.662		
			1134		2.752		
				1193		5.194	8.608
6		Ce	999		2.995		
				1071		5.098	8.093
7		Pr	1068		2.965		
				1204		5.720	8.685
8		Nd	1128		2.685		
				1289		5.508	8.193
9		Sm	1190		2.616		
				1345		6.408	9.024
10		Gd	1533		2.552		
				1585		6.343	8.895
11		Tb	1560		3.219		
				1630		6.623	9.842
12		Dy	1657		2.512		
				1682		6.574	9.086
13		Ho	1701		2.757		
				1743		6.988	9.745
14		Yb	1033		1.693		
				1097		6.980	8.673
						Av. 6.144	Av. 8.884

The alkali metals have been included in Table II among allotropic metals because some of them (Li and Na) undergo transformations to the closed packed structures at low temperatures [9]. The other alkali metals (K, Rb and Cs) undergo phase transformation on application of pressure [10] and have nearly same values of ΔS_m.

It should be pointed out that the differences between the values of ΔS_m for the two categories of metals in Tables I–III are real since the average error in ΔS_m is 1.5% whereas the observed difference between the two groups are in the range of 20% or more. Thus ΔS_m is consistently smaller, beyond the limits of precision in the measurements, for metallic elements that exhibit allotropy.

The validity of a correlation of this nature can be evaluated on the basis of two considerations. Firstly, within a group of metals showing identical physical and chemical behavior, the proposed correlation should not be violated. Secondly, among different classes of solids, there should not be any gross violations which cannot be properly explained.

The first one of these criterion can be tested using the entropy of fusion data for the lanthanide elements listed in Table III. It is seen that in the case of Group IIIB lanthanides namely, Eu, Er and Lu, which do not exhibit allotropy, the entropy values are higher than 8.45 J·K^{-1} mole^{-1}. For the other elements that do show allotropy, the entropy values are lower by about 20–60%. The data for lanthanide elements, which are so similar in their physical and chemical behavior, provide significant support for the validity of the present correlation.

As regards the second test, there are no gross violations of the proposed correlation. The three exceptions are cobalt, chromium and lead. Cobalt with $\Delta S_m =$ 9.158 J·K^{-1} mol^{-1} undergoes a phase transformation from hcp to fcc slightly above room temperature. However, this particular phase change does not involve a change in the coordination number. It can be achieved by a change in the stacking sequence of (111) planes from AB to ABC type. In contrast, the other phase changes concerned in this paper are from a close packed to a more open structure, i.e., fcc or hcp to bcc on heating. As a result, the entropy changes involved in the hcp → fcc transformation in cobalt is only 0.646 J·K^{-1} mol^{-1} and influences the value of ΔS_m only marginally. At 7.95 JK^{-1} mol^{-1}, the value of ΔS_m for chromium is considered low and we believe that it does not represent its true value. It has been pointed out by Miodownik [11], Cho [5] as well as Kubaschewski and Alcock [12] that the entropy of fusion for metals having same crystal structure scales with the melting point. Thus a relatively lower value of ΔS_m and low melting point for lead appear to be intrinsic in nature and related to its own electronic structure.

3.2. Cumulative entropy of fusion

Richard's rule states that the entropy of fusion is a constant for true metals and equal to 9.20 J·K^{-1} mol^{-1} [8]. However, a survey of the entropy of fusion for the metals shows that this rule is not strictly followed [4, 5, 8, 11–15]. Elements which do not obey Richard's rule have been classified as anamolous by Grimvall [14]. Data for metals and lanthanides listed in Tables I–III show that in general the occurrence of phase transformation reduces the entropy of fusion. However, it is observed that if the changes in entropy at all the transformation

TABLE IV Cumulative entropy of fusion for metals

S. no	Element	Cumulative entropy of fusion (J mol^{-1}K^{-1})
1	Co	$9.158 + 0.646 = 9.804$
2	Fe	$7.632 + 0.503 + 0.76 = 8.895$
3	Mn	$7.949 + 1.333 + 1.56 + 2.271 = 13.113$
4	Sc	$7.779 + 2.493 = 10.272$
5	Y	$6.335 + 2.849 = 9.184$
6	Ti	$7.296 + 3.578 = 11.874$
7	Zr	$9.845 + 3.539 = 13.384$
8	Hf	$9.623 + 3.346 = 12.969$
9	La	$5.194 + 2.752 + 0.662 = 8.608$
10	Ce(γ)	$5.098 + 2.995(\gamma \rightarrow \delta) = 8.093$
11	Pr	$5.72 + 2.965 = 8.685$
12	Nd	$5.508 + 2.685 = 8.193$
13	Sm	$6.408 + 2.616 = 9.024$
14	Gd	$6.343 + 2.552 = 8.895$
15	Tb	$6.623 + 3.219 = 9.842$
16	Dy	$6.574 + 2.512 = 9.086$
17	Ho	$6.988 + 2.757 = 9.745$
18	Yb	$6.98 + 1.693 = 8.673$
19	Th	$7.649 + 1.672 = 9.621$
20	U	$6.063 + 4.539 + 2.966 = 13.568$
21	Pu	$3.116 + 2.445 + 0.115 + 0.925$ $+ 1.221 + 8.473 = 16.295$

The entropy changes are sequentially recorded starting from melting point to 0 K. Thus for Fe, entropy of fusion and entropy changes at $\gamma \rightarrow \delta$ and $\alpha \rightarrow \gamma$ transformation temperatures are 7.632, 0.503 and 0.76, respectively.

temperatures (T_t) and the melting point (T_m) are added together, the value obtained is approximately a constant for each group. This is shown in Table IV for metals. This parameter is termed as the cumulative entropy of fusion, ΔS_m^C [8]. Obviously, the cumulative entropy of fusion can be defined only for allotropic matrices. Table IV shows that the cumulative entropy of fusion and the standard entropy of fusion for normal metals is nearly same.

The close proximity in the values of the cumulative entropy of fusion for allotropic metals and the entropy of fusion for non-allotropic metals suggests that the total entropy change due solely to structural phase transitions for metals from 0 K up to the transition to the liquid state is nearly a constant. Thus Richard's Rule should be modified to state that the cumulative entropy of fusion is nearly a constant for each group of solids. As shown in the next section, the principle of cumulative entropy of fusion holds for alkali halides and for other inorganic compounds as well. Therefore, the modified Richard's rule based on cumulative entropy of fusion has a wider and general applicability. Further, the constancy of the entropy of fusion and the cumulative entropy of fusion for any group of solids having identical physical and chemical characteristics shows that it is a specific bulk property characterizing the matrix, like density, melting point and compressibility etc.

Instead of the phrase, cumulative entropy, Cho [5] described this parameter as "structural entropy change." It is felt that the phrase cumulative entropy of fusion is more appropriate designation for this parameter because primarily, it concerns only the entropy changes at the transformation point and is not related to the changes in the matrix that take place in the lattice between 0 K and the fusion temperature. Moreover, representing the sum of more than one entropy change, it is cumulative in nature.

Empirical correlations between the entropy changes associated with the solid state phase transformations and melting have been independently discovered by Cho [4] as well. Cho showed that the entropies of phase transformations in metallic lattices are as follows:

HCP to FCC	. . .	0.17 entropy units
FCC to BCC	. . .	0.51 "
HCP to BCC	. . .	0.64 "

As a consequence, the ratios of transition entropy for the three transformations are approximately in the ratio of 1:3:4. Cho also suggested that the fusion entropy for metals scales linearly with the fusion temperature for all these three lattices. Cho's plot between ΔH_m and T_m is reproduced in Fig. 2. This figure shows that average value of the fusion entropy for each class of lattice considered by Cho is nearly same. The lines drawn in Fig. 2 are not the least–square-fit lines but starting from the origin, they are carefully drawn to represent the data point and differentiate between metals belonging to hcp, fcc and bcc structures. Using Fig. 2 and the entropy ratios for solid state phase changes mentioned above, Cho showed that the cumulative entropy of melting for HCP, FCC and BCC lattices are same.

A difficulty with Cho's analysis is that it completely disregards the effect of the nature of chemical bonding on the magnitude of the entropy of fusion. The importance of this factor is brought about by a comparison of the value of ΔS_m for Mo, Na and Cu. Mo and Na both possess bcc structure. Na is polymorphous while Mo is not and their ΔS_m values are 7.017 and 13.496 entropy units respectively. According to Cho's analysis, the ΔS_m values for Mo and Na should be the same.

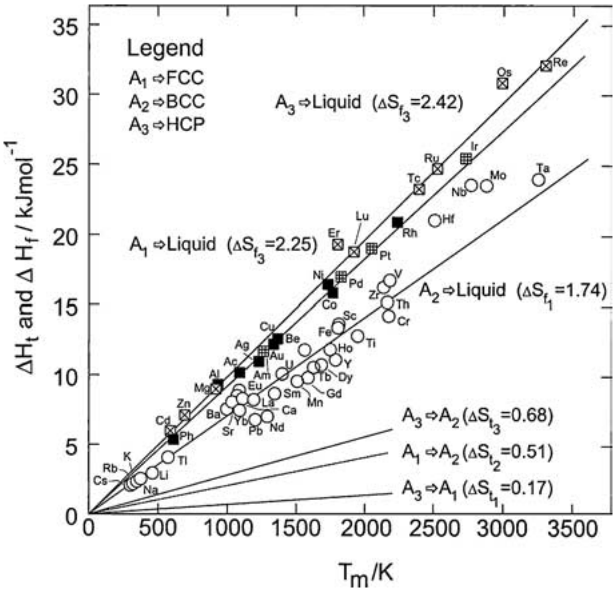

Figure 2 Cho's plot between the enthalpy of fusion (ΔH_m) and the melting point (T_m) for metals.

Further, the ΔS_{m} values for Mo should be lower than that of Cu. In fact, at 9.675 entropy units, the ΔS_{m} for Cu is lower than that of molybdenum. While Cho is right in suggesting that within any group of solids, ΔS_{m} tends to increase with the melting point, the neglect of the nature of cohesive forces gives rise to distortions in his analysis. In sodium, the bonding is purely metallic in character and d-shell electrons do not take part in bonding. The reverse is true for Mo. All five of its d-electrons take part in bonding. Although the outer shell of Cu has the $d^{10}s^{1}$ structure, it exhibits a variable valency and at least one d-shell electron takes part in the formation of inter-atomic bonds. This example shows that while analyzing the magnitude of the entropy of fusion, the crystal structure as well as the nature of chemical bonding must be taken into the consideration.

Miodownik [11] has given a simple explanation for the entropy of fusion of elements which obey Richard's rule and designated as normal by Grimvall [14]. Increase in entropy can be equated to increase in disorder and the structural changes within the matrix constitute an important contribution to the overall entropy of melting. According to Miodownik [11], the structural contribution to the entropy of fusion ($\Delta S_{\mathrm{m}}^{\mathrm{C}}$) can be written as:

$$\Delta S_{\mathrm{m}}^{\mathrm{C}} = [R(\ln Z'_{\mathrm{liq}} - \ln Z'_{\mathrm{solid}})] \tag{5}$$

where Z' is defined as the effective coordination number for solid as well as liquid. Following Bernal, $Z' = 14$ was taken for liquid metals and Kubaschewski's formulation for effective co-ordination was employed to obtain the Z' for solid metals. The latter is defined as the number of atoms lying within a distance of $(2d)^{1/2}$ where d is the distance of closest approach. This is different from the geometrical coordination numbers (fcc $= 12$, bcc $= 8$, etc.) and varies between 4–12 for common metals. The Equation 5 yields a value of R per atom for the entropy of fusion where R is the universal gas constant. This is fairly close to that predicted by the Richard's rule.

Break-down of Richard's rule and the occurrence of anomalies in the entropy of fusion have been discussed by several authors [8, 11–15]. In the previous section, we have discussed how allotropy can cause the failure of Richard's rule. This situation can be corrected by the use of cumulative entropy of fusion in place of the standard entropy of fusion. Grimvall has analysed the situation where the break-down of Richard's rule and anomalies in the magnitude of entropy of fusion occur even in the absence of solid-solid phase transformation. For non-magnetic solid, after Grimvall [14],we may write

$$\Delta S_{\mathrm{m}} = \Delta S_{\mathrm{m}}^{\mathrm{vib}} + \Delta S_{\mathrm{m}}^{\mathrm{an}} + \Delta S_{\mathrm{m}}^{\mathrm{el}} \tag{6}$$

where $\Delta S_{\mathrm{m}}^{\mathrm{vib}}$, $\Delta S_{\mathrm{m}}^{\mathrm{an}}$ and $\Delta S_{\mathrm{m}}^{\mathrm{el}}$ signify vibrational, anharmonic and electronic contributions to the entropy of fusion respectively. From the difference between the specific heats of solid and liquid, Grimvall deduced that the anharmonic component of the entropy in two states is nearly same. On this basis it was concluded that in case of iron, cobalt and nickel, the magnetic moments persist in the liquid state in directionally disordered manner. It is to be noted that all the three elements obey Richard's rule and undergo an increase in volume upon melting. Hence the main contribution to the entropy of fusion in Fe, Co and Ni comes from the structural factor. On the contrary, silicon, germanium, gallium, antimony and bismuth suffer contraction upon melting. At the same time all these elements exhibit entropy of fusion far in excess of the value predicted by Richard's rule. Hence, the structural considerations do not appear to play an important role during melting in these cases.

Silicon and germanium undergo semi-conducting to metallic transition upon melting. According to Grimvall, existence of metallic character is an indication of reduction in the Debye temperature caused by decrease of cohesive strength. Grimvall showed that this factor can account for nearly 50% of the entropy of fusion in Si and Ge. The remaining part may be coming from structural factor and electronic factor.

Sb, Bi and Ga retain metallic character in the molten state as well and hence the arguments based on Debye theory of specific heat cannot be applied to account for their excessive entropy of fusion. From qualitative considerations, one may speculate that the entropy of fusion in these elements is chiefly contributed by the electronic factors [14]. Grimvall's Equation 6 does not contain any term to account for change in the entropy of fusion which may arise from change in atomic configuration after melting. However, the work of several authors [2, 3, 11–16] shows that structural and configurational factors are indeed important when there is a volume increase upon melting.

There are two additional factors which can give rise to anomolously low values of the entropy of fusion. One of these is the delocalization of the anions in certain halides [17–19]. The examples are AgI [19], $SrCl_2$, and $CaCl_2$ [17, 18]. This phenomenon occurs much below the melting point and has been variously described as massive disorder or the presence of a molten sublattice within the rigid lattice formed by cations [20]. The other one is clustering by like as well as unlike atoms in the melt. Memories of solid-phase lattice symmetry in the liquid state have been seen in case of Hg, Ga, Sb, Ge and Sn [21]. Metallographic evidence for clustering in eutectic melts in case of alloys has been provided by Kumar and his co-workers [22, 23]. According to these authors, clusters constitute nearly 10 percent of the volume fraction near the melting point In the absence of a proper theory of liquid state [14, 24], an in-depth analysis of the deviations from the Richard's rule for the entropy of fusion is not feasible.

3.3. Compounds and halides

Tables V–VII contain data on the entropy of fusion for halides and some other compounds. Also included is the information regarding the solid state transformation temperature (T_{t}), melting point (T_{m}) and the magnitude of entropy changes associated with these transformations. To begin with, fluorides are excluded

TABLE V Solid state phase transformation temperature (T_t), melting temperature (T_m), entropy of solid state phase transformation (ΔS_t), entropy of fusion (ΔS_m) and the cumulative entropy of fusion (ΔS_m^C) for halides

S. no	Element	Compound	T_t (K)	T_m (K)	ΔS_t (J mol^{-1}K^{-1})	ΔS_m (J mol^{-1}K^{-1})	ΔS_m^C (J mol^{-1}K^{-1})
1	Ag	AgCl		730		16.879	
2		AgBr		700		12.134	
3		AgI		831		11.329	
4	Cd	$CdCl_2$		841		37.810	
5		$CdBr_2$		841.15		39.643	
6		CdI_2		661.15		31.326	
7		CdF_2		1345		16.799	
8	Ce	$CeCl_3$		1080		49.201	
9		$CeBr_3$		1005		51.624	
10		CeI_3		1033		50.225	
11		CeF_3		1710		32.542	
12	Ca	$CaCl_2$		1045		27.314	
13		$CaBr_2$		1015		28.649	
14		CaI_2		1052		39.772	
15		CaF_2	1424		3.350		
				1691		17.567	20.917
16	Cu	CuCl	685		7.115		
				696		10.718	17.833
17		CuBr	657		7.005		
			741		2.880		
				759		6.725	16.61
18		CuI	642		4.822		
			680		3.894		
				868		9.139	17.855
19	Eu	$EuCl_3$		897		56.906	
20		$EuBr_3$		956		26.303	
21		EuF_3		920		6.959	

TABLE VI Solid state phase transformation temperature (T_t), melting temperature (T_m), entropy of solid state phase transformation (ΔS_t), entropy of fusion (ΔS_m) and the cumulative entropy of fusion (ΔS_m^C) for alkali halides

S. no	Element	Compound	T_t (K)	T_m (K)	ΔS_t (J mol^{-1}K^{-1})	ΔS_m (J mol^{-1}K^{-1})	ΔS_m^C (J mol^{-1}K^{-1})
1	Li	LiF		1121		24.157	
2		LiCl		883		22.450	
3		LiBr		823		21.453	
4		LiI		742		19.736	
5	Na	NaF		1269		26.277	
6		NaCl		1074		23.426	
7		NaBr		1020		25.596	
8		NaI		933		25.293	
9	K	KF		1130		24.067	
10		KCl		1044		25.176	
11		KBr		1007		25.345	
12		KI		954		25.174	
13	Rb	RbCl		996		23.818	
14		RbF		1068		23.995	
15		RbBr		965		24.150	
16		RbI		929		23.735	
17	Cs	CsF		976		23.274	
18		CsCl	743		5.069		
				918		17.319	22.388
19		CsBr		909		25.960	
20		CsI		900		28.451	

from discussion because, as a group, they (except the alkali metal fluorides) seem to constitute an exception. In their case, the values of ΔS_m are always significantly smaller than all the other halides. Such a behavior could arise from the clustering of atoms in the melt [21–23]. In compounds where polar and covalent bonding predominates, clustering may play an important role in deciding the magnitude of the entropy of fusion. One more exception is calcium iodide. Its value at 39.772 J·K^{-1}mol^{-1} is significantly higher than those of $CaCl_2$ (27.314 J·K^{-1}mol^{-1}) and $CaBr_2$ (28.649 J·K^{-1}mol^{-1}).

Barring the exceptions discussed above, the general pattern of behavior of ΔS_m within any group of halides follows the same general features as observed for the metals and lanthanide elements. For every group of solids in the Tables V–VII, the entropy of fusion has nearly the same value. For silver halides (Table V), the variation ranges from 11.329 (AgI) to 16.879 (AgCl) entropy units. In case of potassium halides (Table VI), the ΔS_m values for different halides are the closest. A similar pattern of behavior is exhibited by cadmium and cerium halides. The case of copper (Table V) and

TABLE VII Solid state phase transformation temperature (T_t), melting temperature (T_m), entropy of solid state phase transformation (ΔS_t), entropy of fusion (ΔS_m) and the cumulative entropy of fusion (ΔS_m^C) for some alkali compounds

S. no	Compound	T_t (K)	T_m (K)	ΔS_t (J mol^{-1}K^{-1})	ΔS_m (J mol^{-1}K^{-1})	ΔS_m^C (J mol^{-1}K^{-1})
1	$LiSO_4$	848		33.551		
			1132		7.577	41.128
2	Na_2SO_4	458		0.557		
		514		21.222		
			1157		20.613	42.392
3	K_2SO_4	857		9.862		
			1342		25.627	35.489
4	Rb_2SO_4	928		4.509		
			1343		28.599	33.108
5	Cs_2SO_4	940		4.585		
			1278		27.926	32.511
6	Na_2MoO_4	724		32.362		
		858		2.34		
		908		10.045		
			961		23.336	68.083
7	Na_2WO_4	864		39.854		
			969		24.56	64.414

Cesium (Table VI) is different from other halides. All three copper mono-halides listed in the Table V undergo phase transitions in the solid phase. When the entropy changes at the transformation temperature are added to the fusion entropy, the resulting cumulative entropy of fusion gives similar results as for metals. The cumulative entropy of fusion for CuCl, CuBr and CuI are 17.833, 16.61 and 17.855 entropy units respectively. In case of cesium, its chloride undergoes a solid state transformation. This is the only alkali halide which shows allotropy. Table VI shows that the cumulative entropy of fusion for cesium chloride and the entropy of fusion for all other alkali halides are of the same order.

Table VII lists the entropy of fusion as well as the entropy of solid state phase transitions for sulfates of alkali metals and molybdate and tungstate of sodium. All these compounds are polymorphic in nature. Taken as a group, the cumulative entropy of fusion are practically the same for sulphates of (a) lithium and sodium and (b) potassium, rubidium and cesium. The values of cumulative entropy of fusion for sodium molybdate and sodium tungstate are of the same order. Thus the data in Tables V–VII demonstrate that the same general pattern, as seen for metals and lanthanide elements, follows but their application becomes much more restricted due to the increased complexity in the nature of chemical bonding with increase in the number and type of atoms. Considering the conceivable reasons for the scatter in the data due to uncertainties arising either from the specimen purity or the inherent error in the experimental procedures, it would be fair to conclude that the concept of the cumulative entropy of fusion is validated by the data listed in the Tables I–VII. Further, the type of correlation discussed above could have universal validity.

4. Correlation of fusion entropy with self-diffusion

In the previous section, it is shown that the magnitude of the entropy of fusion influences the phase transition characteristic of any crystalline solid. In this section it is shown that the entropy of fusion has a remarkable influence on the relative rates of self-diffusion among any class or sub-group of materials as well.

Arrhenius plots for self-diffusion in metals are shown in Fig. 3. The data for self-diffusion coefficients in metals have been taken from Smithells Metals Reference Hand Book [25]. The numbers in parentheses in Fig. 3 and in all subsequent similar plots shown in Figs. 4–6 indicate the magnitude of the entropy of fusion. The data shows that a higher value of entropy of fusion is associated with smaller diffusion rate and vice-versa. Thus the relative diffusion rates of metals scale inversely with the entropy of fusion and the gradation in increasing diffusion rates with decreasing values of entropy of fusion is apparent. In Fig. 4 data for lanthanide elements are plotted. The self-diffusion behavior of

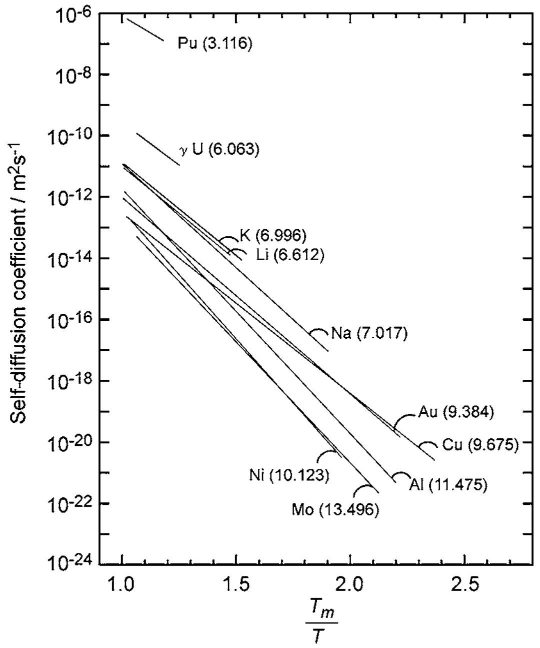

Figure 3 Self-diffusion coefficient in metals plotted against the homologous temperature (T_m/T). The numbers in parentheses represent the entropy of fusion. The figure shows that the self-diffusion rates scale inversely with the entropy of fusion.

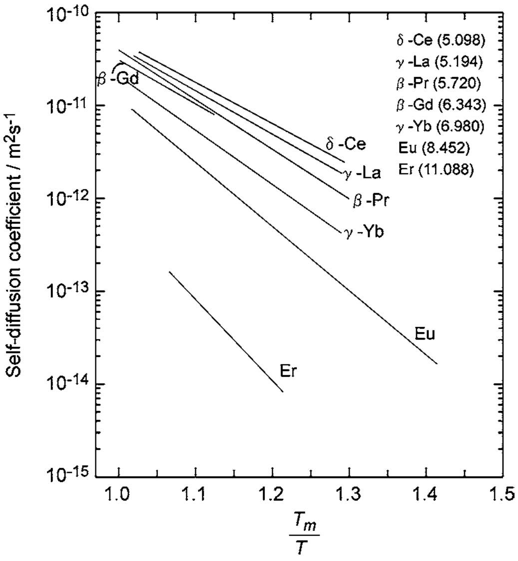

Figure 4 Same as Fig. 3 for lanthanide elements.

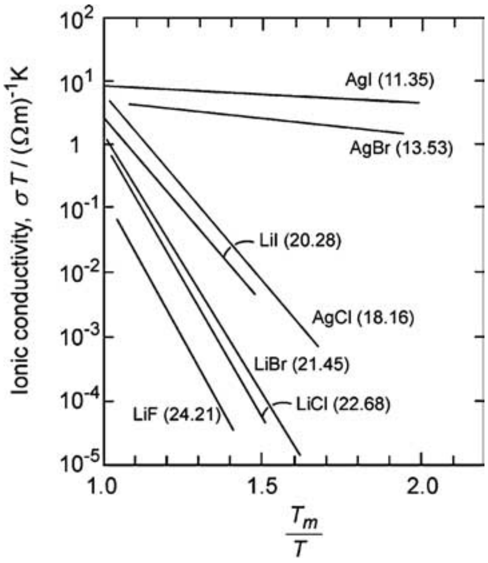

Figure 5 Logarithmic plot of ionic conductivity multiplied by temperature as a function of homologous temperature (T_m/T) for silver and lithium halides. Entropy of fusion is indicated by numbers in parentheses. The product σT is directly proportional to the self-diffusion rates.

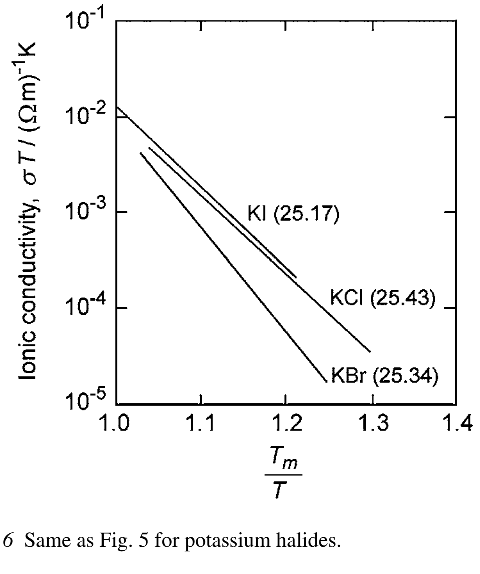

Figure 6 Same as Fig. 5 for potassium halides.

lanthanide elements with respect to the entropy of fusion is exactly similar to that of the metals plotted in Fig. 3. The plots for alkali and silver halides are shown in Figs. 5–6. The data shown in these figures are taken from Ref. [17]. In case of halides, the intrinsic ionic conductivity (σ) is used in place of self-diffusion; the two quantities being directly related by the Nernst-Einstein relationship [26]. An explanation for the relationship between the entropy of fusion and the self-diffusion coefficient depicted in Figs 3–6 is given below.

The self-diffusion coefficient in any cubic crystalline lattice [27] is expressed as

$$D = fa^2\upsilon \exp\left(-\frac{G_d}{RT}\right) \tag{7}$$

or

$$D = fa^2\upsilon \exp\left(\frac{S_d}{R}\right)\exp\left(-\frac{Q}{RT}\right) \tag{8}$$

where D = Diffusion Coefficient, f = correlation factor, υ = vibration frequency, a = lattice parameter, G_d = Free energy of activation for diffusion, Q = Activation enthalpy for diffusion, and S_d = Activation entropy of diffusion

Also,

$$G_d = Q - TS_d \tag{9}$$

R and T have their usual meaning. Introduction of a numerical factor in Equations 7 and 8 is necessary for diffusion in non-cubic crystalline lattices.

According to Dienes [28] and Nachtrieb *et al.* [29], the relationship between diffusion and melting owes its origin to the fact that the saddle-point around the diffusing atom is akin to the liquid phase of the matrix. Mathematically, this statement can be written as

$$G_d = KG_l \tag{10}$$

where G_l is the Gibbs energy of the liquid state and K is a numerical constant [28, 30].

Further,

$$G_l = \Delta H_m - T\Delta S_m \tag{11}$$

Multiplication of both sides of Equation 11 by K and substitution from Equation 10 yields

$$G_d = K\cdot\Delta H_m - K\cdot T\Delta S_m \tag{12}$$

Comparing the temperature independent and temperature dependent terms in Equations 9 and 12, we have

$$Q = K\Delta H_m \tag{13}$$

and

$$\Delta S_d = K\Delta S_m \tag{14}$$

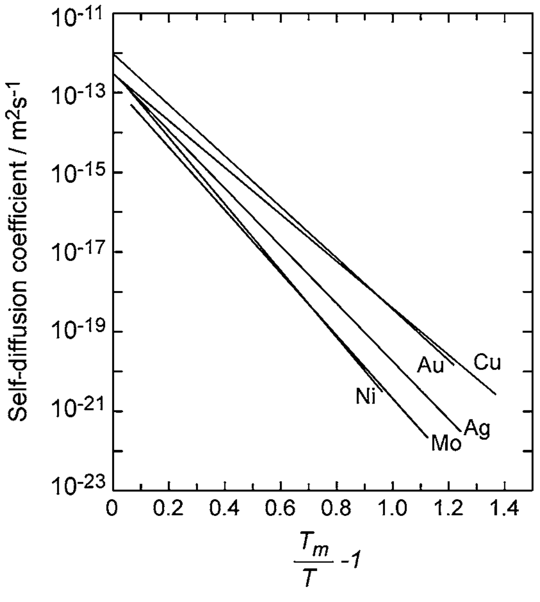

Figure 7 Self-diffusion coefficient in some common metals against the parameter ($T_m/T - 1$). The linearity of the plot demonstrates the validity of the relation between self-diffusion and the entropy of fusion as given by the Equation 16.

We now substitute for Q and S_d from Equations 13 and 14 in the Equation 8 to obtain

$$D = fa^2 \upsilon \exp\left(\frac{K \Delta S_m}{R}\right) \exp\left(-\frac{K T_m \Delta S_m}{RT}\right) \quad (15)$$

In writing the Equation 15, the identity represented in Equation 2 has been used. This equation can be simplified as

$$D = fa^2 \upsilon \exp\left(-\frac{K \Delta S_m}{R}\right)\left(\frac{T_m}{T} - 1\right) \quad (16)$$

According to Equation 16, the logarithm of self-diffusion coefficient should scale inversely with the entropy of fusion. A plot of the self-diffusion coefficients for some metals based on Equation 16 is shown in Fig. 7. The linearity of the plot justifies the assumption made in the derivation of Equation 16, namely the Equation 10.

5. Interrelationship between diffusion and allotropy

It is an established fact that at the corresponding fraction of melting point, the relative diffusion rates in allotropic metals as against those in non-allotropic metals are higher [31–33]. This is also evident from the fact that the self-diffusion rates within any group of solids scale inversely with the entropy and allotropic materials have relatively smaller values of entropy of fusion. An explanation to this phenomenon can be found on the basis of interrelationship of the entropy of fusion with the allotropy and the diffusion characteristics discussed earlier. In effect, the entropy of fusion connects these two physical attributes of the matrix. In the present section, we analyze how the allotropy when present, per se, influences the diffusion characteristics.

It has been stated earlier in Section 4 that the basis of the correlation between the melting parameter and the diffusion characteristics is the hypothesis that the saddle point configuration of the diffusing atom is similar to the molten state of the matrix. This hypothesis provides a rationale only for the relationship between the diffusion and melting parameter for non-allotropic matrices. For a matrix undergoing phase transformation, the saddle-point configuration can be like that of liquid phase for the phase which exists just below the melting point. For the other phases occuring further down in the temperature range, saddle-point configuration can adopt the configuration of a liquid phase or that of any other phase which manifests in the system. However, the configuration adopted will be the one which will have the lower Gibbs energy.

On the basis of above arguments, the saddle point configurations during diffusion in any phase, α, will be based on the liquid phase L and the Gibbs energy required for the formation of the saddle point configuration based on the liquid phase is PQ. This situation is depicted in Fig. 8 and represents the case of non-allotropic matrices. The situation in polymorphous matrices is shown in Fig. 9 where, in addition to the phase α, we have another phase β existing below T_m. Considering the diffusion in the α phase, the saddle-point configuration can adopt either the structure of β or the liquid phase, L. However, the configuration based on β phase will be preferred because of the lower free energy, PQ, needed for it's formation. The free energy required for saddle-point configuration based liquid phase is PR and will not be energetically favored. Hence for the non-polymorphic matrices, shown in Fig. 8, the correlation between the diffusion and melting parameter will be valid. However, such correlations will not be valid for polymorphic case represented in Fig. 9.

The reason for comparatively faster self-diffusion rates in polymorphic matrices can be understood with reference to Fig. 10. We consider the diffusion at any

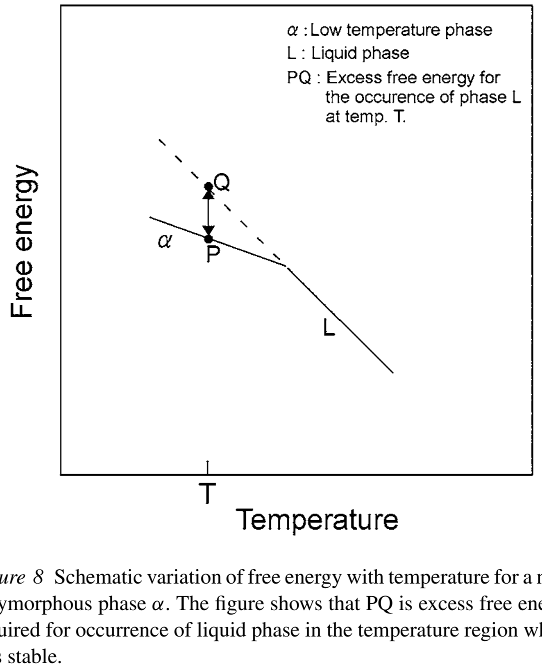

Figure 8 Schematic variation of free energy with temperature for a non-polymorphous phase α. The figure shows that PQ is excess free energy required for occurrence of liquid phase in the temperature region where α is stable.

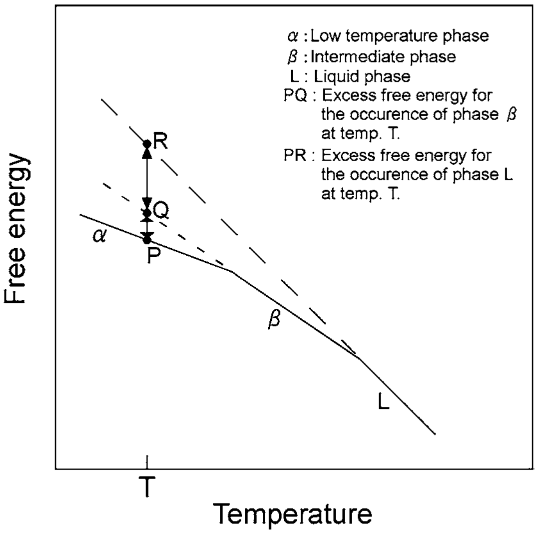

Figure 9 Schematic variation of free energy with temperature for the polymorphous phases α, β and the liquid phase L. The figure shows the excess free energy required for the occurrence of phases β and L in the temperature region where α is stable.

temperarure T under two different situations, one when the system exhibits allotropy and the other when it does not. When the system undergoes phase transition, it follows α-β-L route in the free energy-temperature regime. For self-diffusion in β phase, the energy needed for the formation of saddle-point configuration is YZ. In the absence of phase transformation, the system follows α'-L path in the free energy versus temperature regime and the energy required for the formation of a saddle-point configuration during diffusion is represented by XZ. Since at all temperatures $XZ > YZ$, the introduction of phase transformation will enhance the relative diffusion rate in matrix at all temperatures. A more detailed discussion of the relationship between the diffusion behavior and phase transition characteristics is given elsewhere [32].

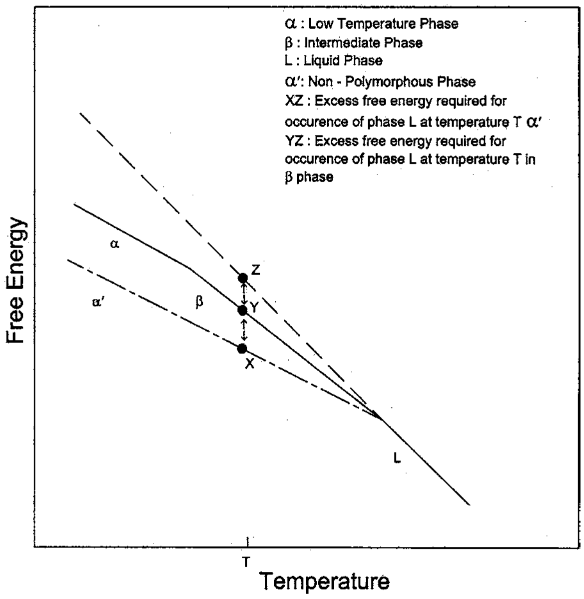

Figure 10 Schematic comparison of free energies for the occurrence of liquid phase in polymorphous and non-polymorphous systems. The figure shows that in comparison to phases α and β, the occurrence of liquid phase in α' (a non-polymorphous system having the same melting point as the polymorphous system formed by the phases α and β) will always require higher free energy for the formation of the liquid phase.

6. Anomalies in the magnitudes of the entropy of fusion

It has been seen earlier in the Section 3 that the presence of a phase transition in the system lowers the magnitude of the entropy of fusion. However, sometimes the changes in the entropy (either a decrease or an increase) occur even in the absence of phase transition. The reasons for change in fusion entropy arise from the discontinuous changes in the thermodynamic parameter at the time of melting. The possible reasons for such changes are listed below:

(a) Higher vibrational entropy of atoms in the melt as seen in case of silicon and germanium [14].

(b) In some elements such as Ga and Bi, it is essential to invoke electronic considerations to explain very large magnitudes of the entropy of fusion [14].

(c) Sub-lattice transition prior to melting due to the de-localization of one of the matrix constituents [17–20].

(d) Formation of clusters in the melt. Clustering in the liquid phase of eutectic type of metallic systems has been experimentally demonstrated by Kumar and co-workers [22, 23].

7. Summary

The present survey includes metals and some inorganic compounds for which reliable self-diffusion and fusion entropy data are available. As a group, these materials exhibit a widely varying nature of chemical bonding. Irrespective of the nature of chemical bonding, the consistent manner in which the entropy of fusion corelates with the phase transition characteristics and self-diffusion behavior of the solids is significant. In this context it is to be noted that the magnitude of the entropy of fusion, per se, is not important. What is important is its relative magnitude among a class or sub-group of materials having identical physical and chemical characteristics.

The general features of variation of ΔS_m for metals and inorganic compounds listed in Tables I–III and V–VII can be summed up as follows:

1. In any class of materials which are structurally analogous and exhibit identical physical and chemical characteristics, the magnitude of entropy of fusion is nearly same and the variations within the group are significantly smaller than the variations from one group to another.
2. The incidence of phase transformation below the melting point lowers the entropy of fusion.
3. In allotropic matrices, when the changes in the entropy at the solid state transition temperature/s are added to the entropy of fusion, the sum is very nearly a constant for the group. This parameter has been designated as the cumulative entropy of fusion. If the group

of solids under consideration contains allotropic as well as non-allotropic members, then the cumulative entropy of fusion for allotropic constituents and the entropy of fusion for non-allotropic members are very nearly the same.

4. The above generalizations are closely followed by the pure metals as well compounds. The variety of elements and compounds for which the above generalizations are true is impressive. This fact holds the promise for their universal validity.

5. In the absence of a formal theory of liquid state, it is difficult to assign reasons for the anomalies in the entropy of fusion. However, on the basis of qualitative and semi-quantitative arguments, one may state that vibrational and electronic factors are responsible for the deviations from the Richard's rule in pure elements. In the case of compounds, clustering in the liquid state appears to be the main reason for the variations in the entropy of fusion within any class of solid compounds having similar physico-chemical characteristics.

Acknowledgement

The authors appreciate the assistance of Mr. R. Nakamura in the preparation and Dr. R. S. Mehrotra for critical reading of the manuscript.

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Received 28 March
and accepted 29 September 2003