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Correlation between the Entropies of Fusion and of Allotropic Transitions of Metals

S.-A. CHO*

Department of Metallurgy and Materials Science, Instituto Venezolano de Investigaciones Científicas (IVIC), Caracas, Venezuela

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The relations between the heats of fusion A_2(BCC) → liquid, A_1(FCC) → liquid, and A_3(HCP) → liquid, and the fusion temperatures of allotropic metals were established:

$$A_2 \rightarrow L: \Delta H_{f_1} = 1.74\, T_{f_1} \quad \text{and} \quad \Delta S_{f_1} = 1.74$$
$$A_1 \rightarrow L: \Delta H_{f_2} = 2.25\, T_{f_2} \quad \text{and} \quad \Delta S_{f_2} = 2.25$$
$$A_3 \rightarrow L: \Delta H_{f_3} = 2.42\, T_{f_3} \quad \text{and} \quad \Delta S_{f_3} = 2.42.$$

The results reveal that enthalpies and entropies of fusion of these metals are merely dependent upon the ultimate structural type of the modification of the solid phase at the fusion temperature. The differences of energy and entropy between the solid and liquid states at the fusion point are termed "structural energy change" and "structural entropy change" of fusion.

Introduction

The relations between the changes in entropies and the associated phase transition of a substance have been a subject of scientific interest (*1–3*) since the establishment of the well-known Richards' rule for fusion and Trouton's rule for vaporization (both in the late nineteenth century). Very recently, Cho (*4*) established similar empirical relations for allotropic transitions: $A_3 \rightarrow A_1$, $A_1 \rightarrow A_2$ and $A_3 \rightarrow A_2$, of the allotropic metals. The entropies of the transitions were

$$A_3(\text{HCP}) \rightarrow A_1(\text{FCC}),\ \Delta S_{t_1} = 0.17 \text{ eu} \qquad (1a)$$
$$A_1(\text{FCC}) \rightarrow A_2(\text{BCC}),\ \Delta S_{t_2} = 0.51 \text{ eu} \qquad (1b)$$
$$A_3(\text{HCP}) \rightarrow A_2(\text{BCC}),\ \Delta S_{t_3} = 0.68 \text{ eu} \qquad (1c)$$

and the ratios of the enthalpies and entropies of the transitions, $A_3 \rightarrow A_1 : A_1 \rightarrow A_2 : A_3 \rightarrow A_2$, have been deduced, respectively,

$$\Delta H_{t_1} : \Delta H_{t_2} : \Delta H_{t_3} = T_{t_1} : 3T_{t_2} : 4T_{t_3} \qquad (2)$$
$$\Delta S_{t_1} : \Delta S_{t_2} : \Delta S_{t_3} = 1 : 3 : 4. \qquad (3)$$

The energy and entropy of the phases concerned were termed "structural energy" and "structural entropy" since the total differences of the enthalpies and entropies between the allotropic phases appear to be merely dependent on the structural difference of the phases across the transition points (*4*). In this paper, an attempt has been made to establish an empirical relation between the heat of fusion (ΔH_f) and the fusion temperature (T_f) of the various metals with structural types of A_1, A_2, and A_3 at their fusion points and deduced the entropies of fusion (ΔS_f) of different types of metals. The ΔH_f and ΔS_f are then

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* Adjunct Associate Professor, School of Metallurgical Engineering and Material Science, Universidad Central de Venezuela, Caracas, Venezuela.

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TABLE I

DATA ON THE HEAT OF FUSIONS (ΔH_f) AND THE FUSION TEMPERATURES (T_f)[a]

A_2 (BCC) → liquid				A_1 (FCC) → liquid				A_3 (HCP) → liquid			
Metal	T_f (°K)	ΔH_f (cal/g-atom)	ΔS_f (eu)	Metal	T_f (°K)	ΔH_f (cal/g-atom)	ΔS_f (eu)	Metal	T_f (°K)	ΔH_f (cal/g-atom)	ΔS_f (eu)
Li	453.7	717.0	1.58	Co	1768.0	3900.0[d]	2.21	Mg	922.0	2200.0[c]	2.39
Na	371.0	621.0	1.67	Rh	2233.0	(5136.0)	2.30	Tc	(2400.0)[c]	(5688.0)	2.37
K	336.4	558.0	1.66	Ir	2716.0	(6247.0)	2.30	Re	3308.0[a]	(7898.5)[a]	2.39
Rb	312.0	524.0	1.68	Ni	1726.0	4060.0[k]	2.35	Ru	2523.0	(6100.0)[c]	2.42
Cs	301.6	500.0	1.66	Pd	1825.0	(4197.0)	2.30	Os	3000.0[j]	(7590.0)	2.53
Be	1560.0	(2919.0)	1.87	Pt	2045.0	(4696.0)	2.30	Zn	692.7	1750.0	2.53
Ca	1112.0	2040.0	1.84	Cu	1357.0	3100.0[d]	2.28	Cd	594.0	1480.0	2.49
Sr	1041.0	(1978.0)	1.85	Ag	1234.0	2700.0	2.19	Er	1795.0	4757.0	2.65
Ba	1002.0	1852.0	1.85	Au	1336.0	3000.0	2.25	Lu	1925.0	4600.5	2.39[b]
Sc	1812.0	3369.0	1.86	Al	933.0	2300.0[k]	2.47				
Y	1799.0	2724.0	1.51	Pb	600.6	1297.0[b]	2.16				
Ti	1943.0	3161.0[f]	1.63	Ac	(1090.0)[c]	(2500.0)[c]	2.29				
Zr	2134.0[i]	(4038.0)	1.89	Am	1268.0	2900.0	2.30				
Hf	2500.0	(5199.0)[a]	2.08								
V	2175.0	4136.0[f]	1.90								
Nb	2770.0[e]	(5800.0)[c]	2.09								

Ta	3253.0[d]	5900.0[d]	1.81
Cr	2173.0[c]	3500.0[c]	1.61
Mo	2883.0[c]	(5800.0)[c]	2.01
W	3698.0[g]	8089.0[b]	2.19
Mn	1517.0[e]	2368.0[e]	1.56
Fe	1809.0	3300.0	1.82
Tl	577.0	990.0	1.72
La	1193.0	2030.0[d]	1.70
Ce	1077.0[e]	2120.0[e]	1.97
Pr	1204.0	1646.0	1.36
Nd	1289.0	1707.0	1.32
Gd	1585.0	2403.0	1.52
Tb	1630.0	2580.0	1.59
Tm	1818.0	4025.0	2.22
Yb	1097.0	1830.0	1.67
Th	2173.0[c]	(3740.0)[e]	1.72
U	1408.0[i]	2500.0[h]	1.78
Sm	1345.0	2130.0[d]	1.58
Eu	1090.0	2202.0	2.02
Dy	1682.0	2643.0	1.57
Ho	1743.0	(2911.0)	1.67

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[a] Letters denote: a, Ref. (*6*); b, Ref. (*7*); c, Ref. (*9*); d, Ref. (*12*); e, Ref. (*13*); f, Ref. (*14*); g, Ref. (*15*); h, Ref. (*16*); i, Ref. (*17*); j, Ref. (*18*); k, Ref. (27). Values given in parentheses are estimated values.

correlated with the aforementioned ΔH_t and ΔS_t of the allotropic transitions.

Empirical Derivation

Since the Gibbs free energy change (ΔG) of the thermodynamic relation, $\Delta G = \Delta H - T\Delta S$, is zero for any phase change process at the transition point at constant pressure, the relation between the ΔH and T at the transition points becomes

$$\Delta H_f = T_f \cdot \Delta S_f \qquad (4a)$$

$$\Delta H_t = T_t \cdot \Delta S_t, \qquad (4b)$$

where the subscripts f and t represent, respectively, for fusion and allotropic transitions. From these simple formulations and employing available experimental data for ΔH_f, ΔH_t, T_f, and T_t we can formulate simple empirical relationship for ΔH_f as a function of T_f as well as for ΔH_t of T_t, and we also get the information on empirical values of ΔS_f and ΔS_t. The empirical relationship of the latter (Eq. (4b)) has been established in the previous paper (*4*). The former relation was established in the late ninteenth century and is widely known as Richard's Rule, which states that the entropy of fusion of metals should be nearly constant. The average value was redetermined to be approximately 2.2 eu by Tammann (*5*). Since then, the problem has been reexamined by Ubbelohde (*1*) and Chalmers (*3*). Both of them have been able to show a difference in the average values of ΔS_f between two main structural groups: A_2 and $A_1 - A_3$, among the A_1, A_2, and A_3 type metals. The present paper reexamines the problem using the more recent data on the values of ΔH_f and T_f, and on the allotropic information from the broad reference sources in the hope of revealing three different H_f versus T_f relations for the three distinctive structural types of metals, A_1 (FCC), A_2 (BCC), and A_3 (HCP), at their respective fusion temperatures. The result is to be correlated with the relation ΔH_t versus T_t of the allotropic transition of these metals.

Relation (4a) has been applied to various metallic elements of the types, A_1, A_2, and A_3, at the fusion points. The employed ΔH_f and T_f values are presented in Table I for each structural type of the metals. The extensive phase relations and the structural infor-

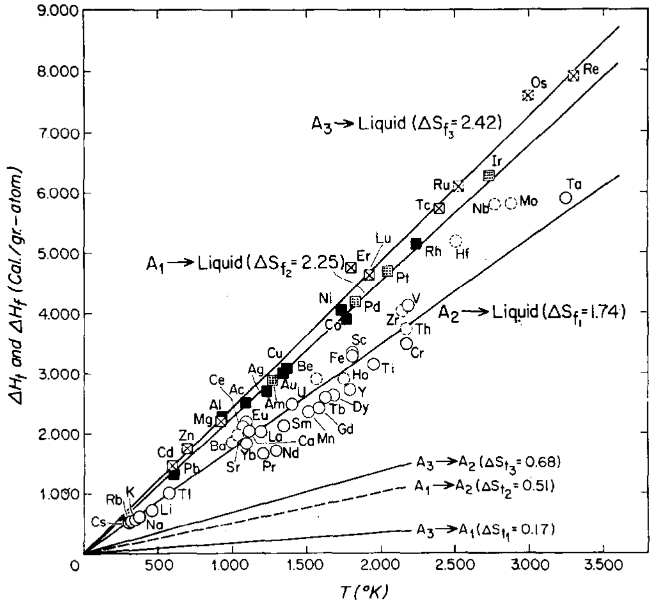

FIG. 1. The plot of ΔH_f versus T_f. The three lines at the bottom are for the ΔH_t versus T_t from Ref. (*4*).

mation near fusion temperatures were given in various sources (*6–11*). The ΔH_f and T_f values reported by various authors (*6–10, 12, 13*) differ by only a few percent; for some elements the reported values differ greatly. In the latter case, the values used are the ones that are more frequently reported and, in a few cases, the ones that provide values closer to the empirical relations sought. About half of the data were obtained from the selected values of Hultgren et al (*8*). Other metals whose data are not from the reference mentioned above are identified with additional references in the table, and the values in the parentheses represent the estimated values. The plots of data in ΔH_f versus T_f is represented in Fig. 1 along with the previous plots (*4*) of ΔH_t versus T_t of the allotropic metals for further correlation between ΔS_f and ΔS_t. The dotted squares and the broken circles and squares in Fig. 1 represent the estimated values of the data. Considering the possible errors present in the data, the ΔH_f and T_f values used appear to lie along the three distinctive straight lines for the fusion transitions, $A_1 \rightarrow$ liquid, $A_2 \rightarrow$ liquid, and $A_3 \rightarrow$ liquid. Although the data points for the metals of the type $A_2 \rightarrow$ liquid are rather scattered compared to the other types of the metals, the data fitting seems, however, reasonable. The present plots cover a large number of metallic elements from various parts of the periodic table and a wide range of ΔH_f and T_f values. By considering the conceivable reasons for the sattering of the data values due to the experimental uncertainity involved with either the divergence in purity or the measurement errors, or both, the scheme of the present data fitting is, in general, reasonable and definite, and the two lines for the transitions, $A_1 \rightarrow$ liquid and $A_3 \rightarrow$ liquid, are now clearly separated.

Discussion

As has been mentioned earlier, the purpose of the present paper is in seeking an empirical relation between the heat of fusion and the fusion temperature of the various metals with structural types of A_1, A_2, and A_3 at the fusion points, and is further to show the correlation between the entropies of fusion and of allotropic transitions. Because of this, the three lines for the three different types of metals for the fusion shown in Fig. 1 are not the least-squares fit lines of the data points. The lines are rather carefully drawn so that the lines follow reasonably well with the data points and the lines would maintain the relative intervals of corresponding allotropic transitions which are shown at the bottom of the figure. Figure 1 shows the systematic relationship between the ΔH_f and ΔH_t against T. This systematic relationship can be represented more clearly by a schematic presentation of the entropies of transitions of the states. This schematic relation is presented diagrammatically in Fig. 2.

Figure 1 shows the ratios of enthalpy and entropy changes of the fusion transformations

$$(A_2 \rightarrow \mathrm{L}):(A_1 \rightarrow \mathrm{L}):(A_3 \rightarrow \mathrm{L})$$

as:

$$\Delta H_{f_1}^{A_2\rightarrow \mathrm{L}}:\Delta H_{f_2}^{A_1\rightarrow \mathrm{L}}:\Delta H_{f_3}^{A_3\rightarrow \mathrm{L}} = \mathrm{T}_{f_1}:1.30T_{f_2}:1.40T_{f_3} \quad \text{(5a)}$$

$$\Delta S_{f_1}^{A_2\rightarrow \mathrm{L}}:\Delta S_{f_2}^{A_1\rightarrow \mathrm{L}}:\Delta S_{f_3}^{A_3\rightarrow \mathrm{L}} = 1:1.30:1.40 \quad \text{(5b)}$$

and the empirical relational schemes shown in both Figs. 1 and 2 reveal the following entropy relations between the different struc-

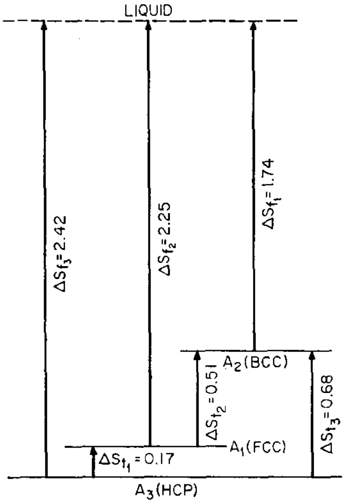

FIG. 2. Schematic entropy difference diagram of allotropic and fusion transitions of the allotropic metals.

tural groups of the metals involved with their fusion processes:

$$A_2(\text{BCC}) \rightarrow \text{liquid},\ \Delta S_{f_1}^{A_2\rightarrow \text{L}} = 1.74\ \text{eu} \tag{6}$$

$$A_1(\text{FCC}) \rightarrow \text{liquid},\ \Delta S_{f_2}^{A_1\rightarrow \text{L}} = 2.25\ \text{eu} \tag{7}$$

$$A_3(\text{HCP}) \rightarrow \text{liquid},\ \Delta S_{f_3}^{A_3\rightarrow \text{L}} = 2.42\ \text{eu}. \tag{8}$$

Through the algebraic manipulation of Eqs. (6), (7), and (8), one obtains

$$A_3(\text{HCP}) \rightarrow A_1(\text{FCC}),\ \Delta S_{t_1}^{A_3\rightarrow A_1} = 0.17\ \text{eu} \tag{9}$$

$$A_1(\text{FCC}) \rightarrow A_2(\text{BCC}),\ \Delta S_{t_2}^{A_1\rightarrow A_2} = 0.51\ \text{eu} \tag{10}$$

$$A_3(\text{HCP}) \rightarrow A_2(\text{BCC}),\ \Delta S_{t_3}^{A_3\rightarrow A_2} = 0.68\ \text{eu}. \tag{11}$$

This result, Eqs. (9)–(11), is exactly corresponding to the empirical data obtained previously for the allotropic transformations (*4*). The schematic entropy diagram of Fig. 2 and the mathematical relations (5a, b) show that the enthalpies and entropies of fusion of these metals are merely dependent upon the ultimate structural types of the modifications of the solid phases at their fusion temperatures. The differences of energy (enthalpy) and entropy between the solid and liquid states at the fusion point may thus be termed "structural energy change" and "structural entropy change" of fusion. The structural entropy changes for the fusion processes are greater than those of allotropic transitions (*4*) by about an order of magnitude. The relative magnitudes of the structural entropy changes of both transition processes are well represented in Fig. 2. From the figure it is of interest to note that the total changes in entropies involved in both allotropic and fusion processes with respect to the state of A_3(HCP) is constant by 2.42 eu:

$$\begin{aligned}&\Delta S_{t_1}^{A_3\rightarrow A_1} + \Delta S_{t_2}^{A_1\rightarrow A_2} + \Delta S_{f_1}^{A_2\rightarrow \text{L}}\\ &= \Delta S_{t_3}^{A_3\rightarrow A_2} + \Delta S_{f_1}^{A_2\rightarrow \text{L}} = \Delta S_{t_1}^{A_3\rightarrow A_1} + \Delta S_{f_2}^{A_1\rightarrow \text{L}}\\ &= \Delta S_{f_3}^{A_3\rightarrow \text{L}} = 2.42\ \text{eu}.\end{aligned}$$

Since the entropy is physically related to the degree of disorder, Fig. 2 reveals the very important fact that the total changes in the degree of disorder involved in the changes of phase of these metals en route to the liquid states at the fusion points are the same.

The combination of the implications of this empirical relation of the present work and the recent studies on the theoretical interpretation of the melting phenomena of solids (*19–26*) may further the understanding of the physical behavior of fusion transition of matter as well as of the physical state of a liquid at the fusion point. The result could also lead to a physical correlation between the atomistic behaviors involved in both allotropic and fusion transitions of metals.

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