

## **ESTIMATION OF ENTROPIES FOR INTERMETALLIC COMPOUNDS AND APPLICATIONS TO PHASE DIAGRAM CALCULATIONS**

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### **ABSTRACT**

A method was developed to estimate the standard entropies of intermetallic compounds from two contributions; a core-atom contribution and an interaction between atoms. The values calculated by the model agree with experimental data.

### **INTRODUCTION**

Estimation of the thermochemical properties of intermetallic compounds and alloy phases is often required when no experimental data are available. This can be done theoretically by statistical thermodynamics, but the lack of structural data limits the applicability of this approach. In most cases semi-empirical or empirical methods appear to be more practicable. Miedema et al. [1,2] have developed an 'atom model' to estimate the heats of formation of binary alloy phases, which described the energy effect on solid or liquid formation in terms of two atomic parameters, the cell boundary electron density and the electronegativity parameter. This model is very successful in predicting the enthalpy of binary alloy phases. Several other approaches have also been made by Machlin [3], Pasturel [4] and Watson [5]. In our earlier work [6], a model was proposed for estimating heat capacities for intermetallic compounds, in which the effect of interaction between atoms was taken into account, in addition to the contribution of the metal atom itself. It provides accurate estimates at different temperatures.

Very few entropy data for alloy phases and intermetallic compounds are available, so estimation is generally necessary, although few methods have been proposed. In this study we propose a method, based on our previous work, for estimating the standard entropies of intermetallic compounds at different temperatures.

## METHOD

As assumed previously [7], the entropy of an intermetallic compound may be expressed as the sum of two contributions

$$S^\ominus = \sum_i S_i^{\text{core}} + S_{ij} \quad (1)$$

where  $S_i^{\text{core}}$  is the contribution of the atom itself and  $S_{ij}$  represents the contribution due to the interaction between atoms in the compound.

In a metal crystal, atoms become core atoms by losing their valence electrons, partly or totally, and these electrons are not localized on any atom. In the case of intermetallic compounds, the compound is formed by chemical action with the type of bond formed depending on the difference between the electronegativities of the metal elements involved [8].

When only the interaction between different atoms is involved,  $S_{ij}$  may be related to the character of the bond by

$$S_{ij} = \frac{5}{2} R \frac{N}{2\bar{n}} \exp\left(-\frac{c}{4}(X_j - X_i)^2\right) \quad (2)$$

where  $X_j$  and  $X_i$  are the Pauling electronegativities [9],  $R$  is the gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $N$  is the number of atoms in the compound and  $\bar{n}$  denotes the average principal quantum number of valence electron of the atoms defined as

$$\bar{n} = \frac{1}{2}(n_i + n_j) \quad (3)$$

In eqn. (2) Pauling's expression for bond character [10] is used with a correction factor,  $c$ , included to account for other effects such as metallization. Here,  $c$  is set equal to 4 in all cases.

The core-atom entropy  $S_i^{\text{core}}$  may be related to the mass and electronic structure. In the Latimer scheme,  $S^\ominus$  of solid element varies only with the atomic mass, but this is not appropriate in the case of intermetallic compounds. Our aim here is to set up a model which is simple and can provide an accurate estimate, so we treat the core-atom entropy as a quantity derived from the available experimental data. The values of  $S_i^{\text{core}}$  can be determined by a least-squares fit of the experimental data to eqn. (1). This is done by minimizing the sum ( $E$ ) of squares of the errors  $\Delta S_i$  in the calculated values

$$E = \sum_i (\Delta S_i)^2 = \sum_i \left[ S - \left( \sum_i S_i^{\text{core}} + S_{ij} \right) \right]^2 \quad (4)$$

The optimum values  $S_i^{\text{core}}$  obtained are reported in Table 1.

This method can be extended to the high temperature region. We suppose that  $S_{ij}$  is independent of temperature and that the core-atom entropy  $S_i^{\text{core}}$  at temperature  $T$  may be expressed as

$$S_{i,T}^{\text{core}} = S_{i,298}^{\text{core}} + a \ln T + b \times 10^{-3} T + c \times 10^5 T^{-2} + d \quad (5)$$

TABLE 1

Values of core-atom entropy and temperature coefficients

Atom	$S_{i,298}$	$a$	$b$	$c$	$d$
Ag	41.09	19.052	19.988	-0.687	-113.72
Al	23.30	37.718	-12.106	5.778	-217.78
Au	44.48	170.346	-215.342	41.626	-953.18
Ba	41.80	28.331	15.317	7.985	-174.96
Be	5.73	0.000	2.884	0.000	-0.70
Bi	52.34	21.738	4.314	-5.339	-119.12
Ca	24.98	-12.689	47.929	-12.856	72.49
Cd	51.84	17.406	15.482	-3.138	-100.24
Ce	66.90	32.864	3.366	4.636	-193.45
Co	29.79	60.486	-28.372	18.502	-356.97
Cr	21.71	24.646	8.979	1.859	-145.18
Cu	37.87	65.380	-66.598	10.912	-364.92
Fe	25.98	21.623	10.246	-0.930	-125.19
Ga	32.84	28.418	-4.897	0.106	-160.56
Ge	29.12	30.017	11.318	11.800	-187.67
In	43.68	19.523	7.752	-2.462	-110.76
K	47.86	9.380	33.413	-2.612	-60.45
La	57.36	71.140	-44.514	20.563	-415.18
Li	17.95	15.225	18.268	-2.220	-89.68
Mg	20.67	-5.506	23.773	-22.229	49.32
Mn	33.93	28.223	7.692	2.138	-165.49
Mo	28.07	14.773	13.463	-2.602	-85.25
Na	29.16	0.000	70.262	0.000	-20.55
Nb	36.99	14.986	13.780	-2.685	-86.46
Ni	25.48	29.559	1.134	3.858	-173.08
Pb	61.46	68.814	-67.340	6.320	-379.09
Pr	62.59	27.180	-1.282	0.967	-155.55
Re	38.07	15.551	16.450	-2.804	-90.34
Rh	31.84	21.173	10.458	-0.068	-123.67
Ru	18.41	22.297	4.644	0.284	-128.73
Sb	40.12	112.986	-89.708	39.688	-661.65
Si	15.40	36.814	-11.432	6.695	-213.86
Sn	43.93	13.849	4.350	-7.518	-71.73
Ta	42.80	15.409	13.178	-2.531	-88.86
Th	41.84	10.354	24.816	-4.424	-61.40
Ti	28.20	11.865	21.893	-4.257	-69.33
U	49.54	28.811	12.130	0.396	-168.20
V	27.74	-5.139	47.123	-11.705	28.42
W	35.98	12.195	17.070	-3.687	-70.41
Y	30.33	36.380	-10.509	4.245	-208.91
Zn	36.65	45.746	-22.823	6.722	-261.39
Zr	40.08	15.255	13.536	-2.612	-88.00

TABLE 2

Comparison of predicted and observed entropies <sup>a</sup> of intermetallic compounds

T (K)	FeTi			URh <sub>3</sub>			URu <sub>3</sub>		
	S <sub>obs</sub>	S <sub>cal</sub>	Diff.	S <sub>obs</sub>	S <sub>cal</sub>	Diff.	S <sub>obs</sub>	S <sub>cal</sub>	Diff.
298	52.72	55.42	2.70	148.11	146.70	-1.41	108.36	106.43	-1.93
300	53.01	55.78	2.77	148.75	147.40	-1.35	108.98	107.10	-1.88
400	67.25	71.15	3.90	179.41	178.22	-1.19	138.38	136.64	-1.74
500	79.13	83.01	3.88	204.54	203.13	-1.41	162.07	160.32	-1.75
600	89.26	92.96	3.70	225.90	224.29	-1.61	182.00	180.22	-1.78
700	98.09	101.72	3.63	244.56	242.86	-1.70	199.30	197.48	-1.82
800	105.94	109.65	3.71	261.21	259.53	-1.68	214.66	212.81	-1.85
900	113.01	116.98	3.97	276.29	274.75	-1.54	228.52	226.65	-1.87
1000	119.46	123.84	4.38	290.13	288.82	-1.31	241.19	239.31	-1.88
1100	125.41	130.34	4.93	302.96	301.97	-0.99	252.90	251.01	-1.89
1200	130.93	136.54	5.61	314.95	314.35	-0.60	263.81	261.93	-1.88

<sup>a</sup> All values in J K<sup>-1</sup> mol<sup>-1</sup>.

The constants *a*, *b*, *c* and *d* have been evaluated and are also listed in Table 1.

In general, the error for entropy estimation by this method is about 4%. We have also predicted the entropies of FeTi, URh<sub>3</sub> and URu<sub>3</sub> at different temperatures and compared these predicted values with experimental data taken from the Inorganic Thermochemistry Data Base [11] (see Table 2).

#### PHASE DIAGRAM CALCULATION

Phase diagrams are used widely in metallurgy, material science, geology and ceramics. Since the introduction of computers, phase-diagram calculations have developed rapidly.

There are two approaches for relating phase diagrams to thermodynamics; either extracting thermodynamic data from the phase diagram, or constructing phase diagrams from the thermodynamic data. There has been much interest in the estimation of activities from phase diagrams and we now show how this can be done from the thermodynamic data estimated by our model.

Hauffe and Wagner [12], Zhou Yuanxi [13], and Zhou Guozhi and Wang Jianjun [14] have proposed formulae for calculating activities for systems containing compounds. Here we quote only Zhou Guozhi's formula

$$d \ln \gamma_A = - \frac{1}{T_0(\eta X_B - \xi X_A)} \left[ \frac{X_B \Delta S_f^\ominus}{R} + \xi(X_A \ln X_A + X_B \ln X_B) \right] dT - d \left( \frac{T}{T_0} \ln X_A \right) \quad (6)$$

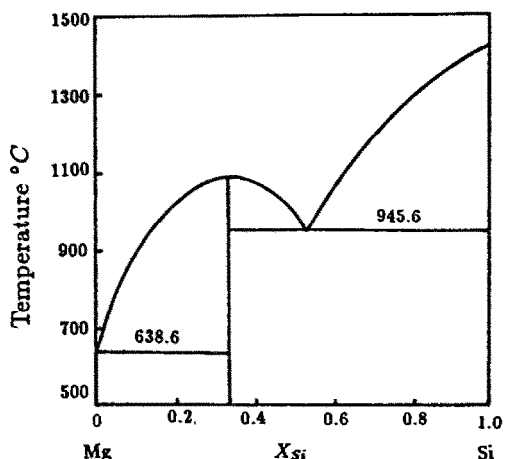


Fig. 1. Phase diagram of the magnesium–silicon system [15].

where  $T_0$  is the assigned temperature,  $T$  is the liquidus temperature,  $X_A$  and  $X_B$  are mole fractions of components A and B, respectively,  $\gamma$  is the activity coefficient of component A at the liquidus temperature and  $\Delta S_f^\ominus$  is the standard entropy of compound  $A_\eta B_\xi$ .

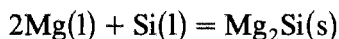
Consider the Si–Mg system as an example (see Fig. 1; data from ref. 15). The entropy of formation of the intermediate phase  $\text{Mg}_2\text{Si}$  was estimated by our model as follows

$$S_T^\ominus = -48.13 + 25.802 \ln T + 36.114 \times 10^{-3}T - 37.763 \\ \times 10^5 T^{-2} \text{ J K}^{-1} \text{ mol}^{-1} \quad (7)$$

For the elements Mg and Si, the data needed are

$$\begin{array}{ll} \text{Mg} & C_p = 21.389 + 11.778 \times 10^{-3}T \text{ J K}^{-1} \text{ mol}^{-1} \\ & S_{298}^\ominus = 32.68 \text{ J K}^{-1} \text{ mol}^{-1} \quad S_m = 9.71 \text{ J K}^{-1} \text{ mol}^{-1} \\ \text{Si} & C_p = 22.824 + 3.858 \times 10^{-3}T - 1.77 \times 10^5 T^{-2} \text{ J K}^{-1} \text{ mol}^{-1} \\ & S_{298}^\ominus = 18.82 \text{ J K}^{-1} \text{ mol}^{-1} \quad S_m = 30.0 \text{ J K}^{-1} \text{ mol}^{-1} \end{array}$$

With this data, the entropy of the reaction



is calculated as

$$\Delta S_f^\ominus = 204.60 - 39.8 \ln T + 8.7 \times 10^{-3}T - 39.533 \times 10^5 T^{-2} \text{ J K}^{-1} \text{ mol}^{-1} \quad (8)$$

The results are shown in Fig. 2 and the agreement with experimental values [16] may be regarded as satisfactory.

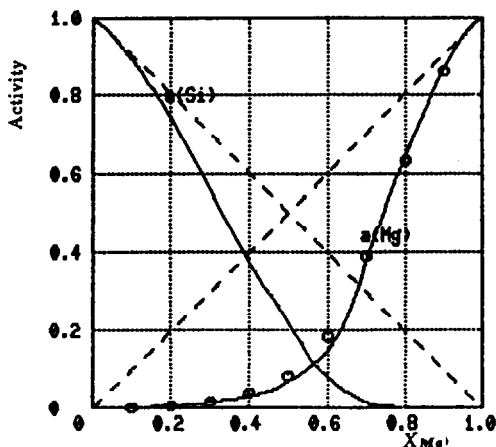


Fig. 2. Activities of Mg and Si in the Mg-Si system at 1350 K. o, Experimental values [16]; —, calculated values (this work).

These results indicate that our model should provide a useful means for prediction of standard entropies of intermetallic compounds. Also, it will be possible to incorporate other computational methods so as to derive activity data or to construct phase diagrams.

## REFERENCES

- 1 A.R. Miedema, R. Boom and F.R. de Boer, *J. Less-Common Met.*, 41 (1975) 283.
- 2 A.R. Miedema, *J. Less-Common Met.*, 46 (1976) 67.
- 3 E.S. Machlin, *Acta Metall.*, 22 (1974) 95.
- 4 A. Pasturel, P. Hicter and F. Cryrot-Lackmann, *J. Less-Common Met.*, 86 (1982) 181.
- 5 R.E. Watson and L.H. Bennett, *Calphad*, 5 (1981) 25.
- 6 Huang Guosheng and Xu Zhihong, *Chinese Sci. Bull.*, 34 (1989) 574.
- 7 Huang Guosheng and Xu Zhihong, *J. Thermochim. Acta*, 136 (1988) 133.
- 8 Gou Qingquan, *A Course in Solid Physics*, Peoples Education Press, Beijing, 1978.
- 9 J.J. Lagowski, *Modern Inorganic Chemistry*, Marcel Dekker, New York, 1973.
- 10 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, 1960.
- 11 Xu Zhihong and Wang Leshan, *Eng. Chem. Metall.*, 5 (1980) 88.
- 12 K. Hauffe and C. Wagner, *Z. Elektrochem.*, 46 (1940) 160.
- 13 Zhou Yuanxi, *Acta Metall. Sinica*, 7 (1964) 123.
- 14 Zhou Guozhi and Wang Jianjun, *Metall. Trans., Sect. A*, 18 (1987) 323.
- 15 R. Geffken and E. Miller, *Trans. Metall. Soc. AIME*, 239 (1967) 775.
- 16 Y.R. Rao and G.R. Belton, in A. Gokeen (Ed.), *Chemical Metallurgy*, The Metallurgical Society of AIME, New York, 1981, pp. 75-96.