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Note

THERMOCHEMISTRY OF INORGANIC COMPOUNDS.
PART 2. ESTIMATION OF HEAT CAPACITIES OF A_xB_y-TYPE SOLIDS

HUANG GUOSHENG and XU ZHIHONG

Institute of Chemical Metallurgy, Chinese Academy of Sciences, Beijing (China)

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ABSTRACT

An ion-bonding model proposed previously was extended to estimate the heat capacities of inorganic solid compounds A_xB_y at 298.15 K. Good agreement was found between the calculated and experimental values.

INTRODUCTION

Additive methods are often used to estimate the standard entropy or heat capacity of a compound with predominantly ionic character. Examples include Latimer's method [1] for entropy estimation and Kellogg's method [2] for heat capacity estimation which has been revised by Kubaschewski and Unal [3]. The quantity of compound is obtained from values of its components

$$P = \sum_i n_i P_i \tag{1}$$

Unfortunately these methods cannot be expected to be reliable when they are applied to predominantly covalent compounds. Other methods, such as the volumetric method proposed by Westrum and Chirico [4], are limited, although they may give good results in some cases.

In a recent paper [5], an ion-bonding model was developed to estimate the entropies of solid compounds which seemed to give satisfactory results for both predominantly ionic and predominantly covalent compounds. In this paper, this model is extended to calculate the heat capacity of solid compounds.

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RECOMMENDED METHOD

As assumed previously [5], the heat capacity of the inorganic solid compound A_xB_y can be defined as the sum of two contributions

$$C_p = \sum_i C_{p_i} + C_{p_r} \tag{2}$$

where the ionic heat capacity C_{p_i} is the heat capacity contribution assigned to each ion in the compound. The quantity can be derived from the experimental data. A typical ionic compound, caesium fluoride CsF, is taken as the reference compound, and it is supposed that the heat capacity of CsF is only the sum of the ionic heat capacities of the components. If we suppose that the anion F^- has a heat capacity of 19.00 J K^{-1} mol^{-1}, then the values of the ions can be determined as described previously [5]. Some ionic heat capacity values are listed in Table 1.

TABLE 1

Values of ionic heat capacity for ions (J K^{-1} mol^{-1})

Ion	C_p	Ion	C_p	Ion	C_p	Ion	C_p
Ag^+	28.60	Hg^{2+}	28.82	Sb^{3+}	28.14	As^{3-}	17.80
Al^{3+}	18.68	Ho^{3+}	28.24	Sc^{3+}	24.50	Br^-	23.33
As^{3+}	27.00	In^{3+}	28.20	Se^{4+}	30.00	C^{4-}	8.32
Au^+	26.76	Ir^{4+}	27.95	Si^{4+}	8.23	Cl^-	21.53
B^{3+}	5.11	K^+	28.82	Sm^{3+}	34.85	F^-	19.00
Ba^{2+}	31.83	La^{3+}	31.70	Sn^{2+}	30.32	H^-	1.38
Be^{2+}	12.93	Li^+	22.03	Sn^{4+}	28.40	I^-	22.54
Bi^{3+}	28.40	Mg^{2+}	26.52	Sr^{2+}	30.91	N^{3-}	8.51
Ca^{2+}	29.13	Mn^{2+}	27.80	Ta^{4+}	25.49	O^{2-}	12.65
Cd^{2+}	31.38	Mn^{3+}	30.62	Ta^{5+}	32.08	P^{3-}	14.00
Ce^{3+}	31.80	Mo^{3+}	24.94	Te^{4+}	34.60	S^{2-}	16.91
Co^{2+}	34.18	Mo^{6+}	27.34	Ti^{2+}	27.89	Se^{2-}	20.00
Cr^{3+}	39.02	Na^+	29.67	Ti^{3+}	26.48	Te^{2-}	20.18
Cs^+	30.63	Nb^{4+}	28.76	Ti^{4+}	27.53		
Cu^+	25.92	Nb^{5+}	29.43	Ti^{5+}	27.77		
Cu^{2+}	26.49	Nd^{3+}	33.60	Tl^+	28.80		
Dy^{3+}	31.12	Ni^{2+}	26.56	Tm^{3+}	34.50		
Er^{3+}	32.38	Os^{4+}	26.50	V^{2+}	29.98		
Fe^{2+}	31.10	Pb^{2+}	30.69	V^{3+}	31.41		
Fe^{3+}	29.37	Pb^{4+}	31.52	W^{4+}	26.03		
Ga^{3+}	25.20	Pr^{3+}	31.50	W^{6+}	26.36		
Gd^{3+}	29.54	Pt^{4+}	43.50	Y^{3+}	28.18		
Ge^{2+}	32.00	Rb^+	30.10	Yb^{3+}	37.28		
Ge^{4+}	22.38	Re^{4+}	27.34	Zn^{2+}	23.41		
Hf^{3+}	31.34	Rh^{3+}	25.80	Zr^{3+}	30.08		
Hf^{4+}	25.00	Ru^{4+}	25.11	Zr^{4+}	26.94		

The second term in eqn. (2) is a quantity which represents the contribution due to the interaction between ions. It can be calculated as follows

$$C_{p_r} = cmR\frac{Z}{2n}(\Delta X_{\mathrm{CsF}} - \Delta X) \tag{3}$$

in which

$$\Delta X = X_j - X_i \tag{4}$$

where m is the bond number ($= xy/2$), R is the gas constant ($= 8.314$ J K^{-1} mol^{-1}), Z is the charge of the cation, n is the principal quantum number of the outermost electrons of the cation, X_i is the Pauling electronegativity [6] and c is the modified factor

$$c = \frac{1}{2}\frac{xy}{x+y} \tag{5}$$

If $c = 1$, eqn (3) is the same as the formula used in the previous paper [5]. With eqn. (4), eqn (5) and $\Delta X_{\mathrm{C_sF}} = 3.19$, eqn. (3) becomes

$$C_{p_r} = \frac{x+y}{4}R\frac{Z}{2n}(3.19 - \Delta X) \tag{6}$$

The heat capacities of the solid compounds can be calculated using eqn. (2), eqn. (6) and the data in Table 1.

DISCUSSION

We applied the above model to calculate the heat capacities of 126 compounds. Good agreement between the calculated and experimental values is obtained as shown in Table 2. The average deviation from the experimental data is about 1.78 J K^{-1} mol^{-1}. This is superior to the results of Kubaschewski's method (with an average deviation of 3.14 J K^{-1} mol^{-1}) which are also listed in Table 2. The experimental data used were taken from JANAF tables [7].

As demonstrated in our earlier paper [8], the properties of a compound are not the simple summation of the properties of its constituents, particularly in the case of covalent compounds. It can be seen from the results of Kubaschewski's method that the deviation for the compounds with predominantly covalent character, such as carbides and nitrides, is larger than those with predominantly ionic character.

It is of interest to compare C_{p_r} with the reorganization entropy S_r, which is given by [5]

$$S_r = \frac{xy}{2}R\frac{Z}{2n}(3.19 - \Delta X) \tag{7}$$

TABLE 2

Comparison of the errors of two methods (J K^{-1} mol^{-1})

Compounds	Number of compounds	Average deviation	
		This work	Kubaschewski and Unal [3]
Fluorides	16	2.62	3.34
Chlorides	22	1.25	1.98
Bromides	11	1.77	2.56
Iodides	14	2.71	2.89
Oxides	32	1.55	3.28
Sulphides	12	0.87	3.44
Hydrides	4	3.07	3.33
Carbides	6	2.19	4.96
Nitrides	9	1.41	4.50
All	126	1.79	3.14

The ratio of S_r to C_{p_r}

$$\frac{S_r}{C_{p_r}} = \frac{xy}{\frac{1}{2}(x+y)} \tag{8}$$

reveals that the contribution of the interaction term to the heat capacity is less than that to entropy. This implies that the additive method may be more accurate for the estimation of heat capacity than for the estimation of entropy.

The results of our calculations indicate that the heat capacity of the inorganic solid A_xB_y can be estimated with accuracy with our model, especially in cases where some of the data are missing. This may be very helpful to the thermodynamic calculation.

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