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THERMOCHEMISTRY OF INORGANIC COMPOUNDS. PART 1. ESTIMATION OF ENTROPIES OF A_xB_y TYPES OF SOLIDS

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ABSTRACT

A model for estimation of standard entropies of inorganic solid compounds A_xB_y at 298 K has been developed, which divides the entropy into two contributions, the ionic entropy and the reorganization entropy. The entropy values of 112 compounds have been investigated and the average deviation is about 3.54 J $K^{-1}mol^{-1}$.

INTRODUCTION

The entropy of an inorganic compound can be theoretically estimated by statistical thermodynamics, but this requires a detailed knowledge of structure which is not always available, especially for solid compounds. Many attempts to obtain estimates of the entropies of solid inorganic compounds have been made by empirical or semi-empirical methods. The most commonly used formula was developed by Latimer [1], which regards the standard entropy of a compound A_xB_y as the sum of individual contributions. Xu et al. [2] recently made some modifications to Latimer's scheme and successfully extended it to the high temperature region in the case of binary oxides. Latimer's formula is simple, but it appears to be unsatisfactory when applied to compounds which contain *d* or *f* electrons [3]. A volumetric formula was suggested by Westrum and co-workers [4] for estimating the heat capacities or entropies of lanthanide compounds, which involves linear interpolation on the basis of the molar volumes of the compounds. Based on Latimer's [1] and Westrum's [4] formulae, Zhang [5] proposed another approximate method, in which the lattice entropy is related to the effects of both cation mass and molar volume of the compound. Zhang's method has good accuracy, but is limited to the rare-earth compounds and accurate spectral data are required in the magnetic entropy estimation. The entropies of compounds are important thermochemical data; it is desirable to develop some new estimation methods which can be applied broadly and reliably.

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Based on previous work [6], we here develop a new model for estimating the entropy of an inorganic solid compound A_xB_y.

MODEL

For an inorganic solid compound A_xB_y, we make the following assumptions:

(1) Entropy contributions are assigned to each ion which can be termed ionic entropy. The entropy of a compound with pure ionic character is simply taken as the sum of ionic entropies.

(2) When ions combine into a compound, a chemical bond (or bonds) forms. The energy levels of ions in the compound will change with the redistribution of electrons. This effect results in the change of entropies since the thermochemical features of a compound are related to the state of the chemical bonding [7]. We may define the change of entropy caused by redistribution of electrons as "reorganization entropy", which also makes a contribution to the entropy of the compound.

According to the above postulate, we can then write S, the entropy of inorganic solid, as the sum of two contributions if only the nearest neighbouring reactions are considered

$$S = \sum_i S_\mathrm{i} + S_\mathrm{r} \tag{1}$$

where S_i is the ionic entropy and S_r the reorganization entropy.

Determination of ionic entropy

According to the lattice dynamic theory, the standard entropy at 298.15 K is [8]

$$S = (3rR/2)\ \ln\ Me + 3rR\left[1 + \ln(k_\mathrm{B}T'/\hbar\beta)\right] + (3rR/24)(\hbar/k_\mathrm{B}T')^2\ \langle w^2\rangle + \cdots \tag{2}$$

Latimer devised that S of element solids varies only with the atomic mass M, and is of the form

$$S = (3R/2)\ \ln\ M + c \tag{3}$$

This is a good approximation only when the masses are not too small and the interatomic forces not too strong [8]. In order to get an agreement with the experimental results, Latimer himself adjusted it. Obviously, if we try to calculate the ionic entropy theoretically, a vast amount of complexity may be introduced. Since our aim is to set up a model which is simple and can provide an accurate estimate, here we only treat the ionic entropy as a quantity which can be derived from the experimental data. Thus we take

TABLE 1

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

Ion	S	Ion	S	Ion	S	Ion	S
Ag^+	58.00	Hf^{3+}	40.15	Rb^+	55.20	As^{3-}	38.00
Al^{3+}	6.95	Hf^{4+}	42.30	Rh^{3+}	24.00	Br^-	49.00
As^{3+}	33.50	Hg^{2+}	61.11	Se^{4+}	41.20	C^{4-}	0.17
Au^+	59.50	Ho^{3+}	41.39	Si^{4+}	12.80	Cl^-	36.02
B^{3+}	0.05	In^{3+}	35.40	Sn^{2+}	53.00	F^-	20.52
Ba^{2+}	56.73	K^+	46.80	Sn^{4+}	35.50	H^-	3.22
Be^{2+}	0.40	La^{3+}	44.46	Sr^{2+}	44.80	I^-	53.50
Bi^{3+}	54.20	Li^+	16.40	Ta^{4+}	39.22	N^{3-}	7.62
Ca^{2+}	31.50	Mg^{2+}	18.00	Ta^{5+}	40.81	O^{2-}	7.94
Cd^{2+}	43.88	Mn^{2+}	47.67	Te^{4+}	42.50	P^{3-}	25.50
Ce^{3+}	49.50	Mn^{3+}	31.60	Ti^{2+}	17.34	S^{2-}	21.71
Co^{2+}	38.42	Mo^{3+}	14.50	Ti^{3+}	20.80	Se^{2-}	37.73
Co^{3+}	23.50	Mo^{6+}	39.56	Ti^{4+}	32.56	Te^{2-}	44.80
Cr^{3+}	23.10	Na^+	35.40	Ti^{5+}	28.56		
Cr^{4+}	34.40	Nb^{4+}	34.11	Tl^+	73.80		
Cs^+	67.78	Nb^{5+}	25.80	Tm^{3+}	49.80		
Cu^+	43.60	Nd^{3+}	53.20	V^{2+}	29.63		
Cu^{2+}	33.00	Ni^{2+}	25.34	V^{3+}	29.88		
Dy^{3+}	44.40	Os^{4+}	31.70	W^{4+}	28.76		
Fe^{2+}	39.66	Pb^{2+}	61.90	W^{6+}	38.85		
Fe^{3+}	24.59	Pb^{4+}	50.12	Y^{3+}	40.20		
Ga^{3+}	22.50	Pr^{3+}	60.60	Yb^{3+}	51.44		
Ge^{2+}	41.02	Pt^{3+}	29.20	Zr^{3+}	29.38		
Ge^{4+}	30.00	Pt^{4+}	27.40	Zr^{4+}	25.70		

caesium fluoride CsF, a typical ionic compound, as the reference compound, and suppose its reorganization entropy $S_r = 0$. The standard entropy of CsF then is divided into the individual ion contributions. We suppose $S_{F^-} = 20.52$ (J K^{-1} mol^{-1}); then the entropies of other ions in solid compounds at 298 K can be determined from the experimental values which have been listed in Table 1. It should be noted that the values of ionic entropy defined here are relative values which refer to the value of anion F^{-1}.

Determination of reorganization entropy

As the reorganization entropy S_r represents the contribution resulting from the redistribution of electrons when binding happens, it may be related to the character of the bond, I, in the compound

$$S_r = a\, I \qquad (4)$$

If the Gordy form [9]

$$I = \tfrac{1}{2}(X_B - X_A) \qquad (5)$$

is used, eqn. (4) becomes

$$S_r = a\tfrac{1}{2}(X_B - X_A) = a\tfrac{1}{2}\Delta X \tag{6}$$

where X_A and X_B are the electronegativities of atom A and atom B. Since we have taken CsF as reference compound, eqn. (6) may be written

$$S_r = \frac{a}{2}(\Delta X_{CsF} - \Delta X) \tag{7}$$

We found that the parameter a is related to the charge Z and the principal quantum number n of outermost electrons of the cation if the differences among s, p and d electrons are ignored

$$a = R\frac{Z}{n} \tag{8}$$

With eqns. (7), (8) and $\Delta X_{CsF} = 3.19$, the reorganization entropy is represented by

$$S_r = mR\frac{Z}{2\,n}(3.19 - \Delta X) \tag{9}$$

where ΔX is the difference of electronegativity of the ions (in Pauling's scale [10]), n is the principal quantum number of the cation, and m is the bond number ($m = xy$).

DISCUSSION

The standard entropies of 112 compounds were investigated by our model. The deviations from experimental data are shown in Table 2. All the experimental values used are taken from JANAF tables [11]. In order to

TABLE 2

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

Compounds	This paper		Latimer's [1]	
	Number of compounds	Average deviation	Number of compounds	Average deviation
Fluorides	15	4.09	15	7.14
Chlorides	21	4.53	21	7.83
Bromides	8	2.78	8	9.28
Iodides	8	6.00	8	9.95
Oxides	31	2.91	26	6.92
Sulfides	12	2.87	12	10.57
Hydrides	4	0.64		
Carbides	5	4.99		
Nitrides	8	2.04		
All	112	3.54	90	8.14

compare Latimer's scheme, the calculation errors obtained by Latimer's method are also listed in Table 2. The average deviation for the calculated values of our model is about 3.54 J K^{-1} mol^{-1}. The improvement over Latimer's method is clearly significant.

The entropy of solid Nd_2Se_3 at 298 K was given as 185.3 J K^{-1} mol^{-1} in the literature [12]. This may be a mistaken or misprinted number, according to the value of 230.7 J K^{-1} mol^{-1} estimated by our model which is consistent with the value of 224.1 J K^{-1} mol^{-1} quoted by Mills [13].

In conclusion, we have set up a model based on the concept of the chemical bond, which can be applied to the compounds with predominant ionic character or with predominant covalent character. For the latter type of compounds Latimer's method often failed. The preliminary investigation enables us, with some confidence, to estimate or evaluate the standard entropy values of inorganic solid compounds.

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