The Thermochemistry of Inorganic Solids
IV. Enthalpies of Formation of Compounds of the Formula MX_aY_b

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It is found that the standard enthalpies of formation $\Delta_f H^\circ_{298}$ of double salts of the type MX_aY_b are related by a simple additivity relation to $\Delta_f H^\circ_{298}$ of their binary salts MX_c and MY_d. For divalent metals M this relation takes the form, $\Delta_f H^\circ_{298}(MXY) = \frac{1}{2}\Delta_f H^\circ_{298}(MX_2) + \frac{1}{2}\Delta_f H^\circ_{298}(MY_2) + C$, with $C = -13.4$ or -17.6 kJ/mol giving equally good fits to the data. From a lesser number of data for trivalent and tetravalent metals M, one finds again a simple additivity relation of the form $\Delta_f H^\circ_{298}(MX_aY_b) = (ax/z)\Delta_f H^\circ_{298}(MX_{z/x}) + (by/z)\Delta_f H^\circ_{298}(MY_{z/y}) + C$, where x, y, and z are the formal valences of X, Y, and M, respectively, so that $z = ax + by$, and $C = 0$. For 16 divalent metal compounds average deviations are 5.5 kJ/mol with a maximum deviation of 10.7 kJ/mol. For eight trivalent metal compounds the average deviations are 13.9 kJ/mol with a maximum of 50.6 kJ/mol. For five tetravalent compounds, the average deviations are 3.5 kJ/mol with a maximum of 6.3 kJ/mol.

Key words: additivity; average deviation; binary salts; di-, tri-, and tetravalent metals; double salts; maximum deviation; relation; standard enthalpies of formation.

Contents

List of Tables

1. Introduction

Accurate values for the enthalpies of formation of solid compounds are of great utility for many applications[1] such as calculating equilibrium mixture compositions in a system where solid compounds are present and in predicting the stability of the solid compounds. There are several reliable methods[2,3] available for estimating enthalpies of formation of gaseous and liquid compounds, but methods for the estimation of enthalpies of formation of solid compounds to within a few kJ/mol are lacking. General formulas for the derivation of enthalpies of formation of oxides, sulfides, and halides from consideration of position in the periodic table have been given independently by Sue, Trombe, and Kapustinski, and are summarized by Kubachewski and Alcock.[4] Kapustinski suggests the use of Eq. (1) to correlate enthalpies of formation of binary compounds:

$$\log Z_A = \Delta_f H^\circ(AB)/n_A + \text{const.} \qquad (1)$$

A is an element selected from a vertical or horizontal column of the periodic table combined with a common element B, Z_A is its atomic number, n_A is its valency, and $\Delta_f H^\circ(AB)$ is the standard enthalpy of formation of the solid compound of A and B. However, large errors can be encountered when these methods are used. For example, use of the above equation for vanadium oxides can give errors in $\Delta_f H^\circ$ of up to 85 kJ/mol per metal atom.

In a recent paper,[5] we have presented evidence that for solid–metal oxyhalide compounds of different valence states, the standard enthalpies of formation of these compounds can be correlated quantitatively with the enthalpies of formation of the corresponding oxides and halides of the

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same oxidation states by using

$$\Delta_f H^\circ_{298}(\mathrm{MO}_x\mathrm{X}_y) = a\left(\frac{2x}{z}\Delta_f H^\circ_{298}(\mathrm{MO}_{z/2}) + \frac{y}{z}\Delta_f H^\circ_{298}(\mathrm{MX}_z)\right) + C, \quad (2)$$

where $z = 2x + y =$ the formal oxidation state of the metal. $\mathrm{MO}_x\mathrm{X}_y$ is the oxyhalide, $\mathrm{MO}_{z/2}$ and MX_z are the corresponding oxide and halide of the same oxidation state z of the metal. C is a correction factor and a is a constant.

For main group and first transition metal compounds	$a = 1$ and $C = 0$
For trivalent state lanthanides	$a = 2.155$ and $C =$ either 1078.6 or 1047.7 kJ/mol
For tetravalent oxychlorides	$a = 1$ and $C = 20.9$ kJ/mol
For penta- and hexavalent compounds	$a = 1$ and $C = 0$

We have also discovered[6–9] quantitative relations that exist between the standard enthalpies of formation of various types of solid–metal compounds such as polyvalent binary compounds, hydrated compounds, etc.

Examination of the existing data on the standard enthalpies of formation of solid–metal compounds of the formula $\mathrm{MX}_a\mathrm{Y}_b$ [where X and Y are atoms, and $\mathrm{X} \neq \mathrm{Y} \neq 0$ (except in Fe(O)(OH)], reveals an interesting feature concerning the enthalpies of formation of these compounds and the corresponding binary compounds of the same oxidation states. Unless otherwise stated, thermochemical data used here are taken from NBS Tables,[10] and values are given for standard enthalpies of formation $\Delta_f H^\circ_{298}$ per metal atom at 298 K in kJ/mol.

2. Divalent Compounds

Data for 18 compounds are available; all are compounds of main group metals, while X and Y are mainly monovalent species such as halides, hydrides, and hydroxides. $\Delta_f H^\circ_{298}$ of these compounds may be compared with the average of the enthalpies of formation of the corresponding binary compounds of the same oxidation states of the metal by the simple additivity relation illustrated below for some compounds.

$$\begin{aligned}
\text{(i) } \Delta_f H^\circ_{298}(\mathrm{MgOHCl}) &= \tfrac{1}{2}\Delta_f H^\circ_{298}[\mathrm{Mg(OH)_2}] \\
&\quad + \tfrac{1}{2}\Delta_f H^\circ_{298}(\mathrm{MgCl_2}) \\
&= \tfrac{1}{2}(-924.5) + \tfrac{1}{2}(-641.3) \\
&= -782.9,\ (\text{obs}) \\
&= -799.6,\ \Delta(\Delta H) = -16.7
\end{aligned}$$

$$\begin{aligned}
\text{(ii) } \Delta_f H^\circ_{298}(\mathrm{SrBrH}) &= \tfrac{1}{2}\Delta_f H^\circ_{298}(\mathrm{SrBr_2}) \\
&\quad + \tfrac{1}{2}\Delta_f H^\circ_{298}(\mathrm{SrH_2}) \\
&= \tfrac{1}{2}(-717.6) + \tfrac{1}{2}(-180.3) \\
&= -449.0,\ (\text{obs}) \\
&= -464.4,\ \Delta(\Delta H) = -15.4
\end{aligned}$$

$$\begin{aligned}
\text{(iii) } \Delta_f H^\circ_{298}(\mathrm{BaClH}) &= \tfrac{1}{2}\Delta_f H^\circ_{298}(\mathrm{BaCl_2}) \\
&\quad + \tfrac{1}{2}\Delta_f H^\circ_{298}(\mathrm{BaH_2}) \\
&= \tfrac{1}{2}(-858.6) + \tfrac{1}{2}(-178.7) \\
&= -518.7,\ (\text{obs}) \\
&= -536.0,\ \Delta(\Delta H) = -17.3
\end{aligned}$$

$$\begin{aligned}
\text{(iv) } \Delta_f H^\circ_{298}(\mathrm{CdBrOH}) &= \tfrac{1}{2}\Delta_f H^\circ_{298}(\mathrm{CdBr_2}) \\
&\quad + \tfrac{1}{2}\Delta_f H^\circ_{298}[\mathrm{Cd(OH)_2}] \\
&= \tfrac{1}{2}(-316.2) + \tfrac{1}{2}(-560.7) \\
&= -438.5,(\text{obs}) \\
&= -454.8,\ \Delta(\Delta H) = -16.3
\end{aligned}$$

Except for CdIOH, in all other cases the observed values are lower than the calculated values using simple additivity relations and the differences vary from 6 to 32 kJ/mol.

These illustrations suggest the following revised relation:

$$\Delta_f H^\circ_{298}(\mathrm{MXY}) = \tfrac{1}{2}\Delta_f H^\circ_{298}(\mathrm{MX_2}) + \tfrac{1}{2}\Delta_f H^\circ_{298}(\mathrm{MY_2}) + C. \quad (3)$$

As shown in Table I, with $C = -13.4$ or -17.6 kJ/mol, the expression shows good agreement with observed values for each compound. However, there are two exceptions. CdIOH gives deviations of 19.7 and 23.1 kJ/mol depending upon the value of C, and BaClF also gives a deviation of 18.1 kJ/mol when $C = -13.4$ kJ/mol. Excluding these two compounds, when $C = -13.4$ the average deviation is only 5.5 kJ/mol with the maximum deviation 10.7 kJ/mol. With $C = -17.6$ kJ/mol, the same average deviation is obtained with the maximum deviation of 15 kJ/mol.

3. Trivalent Compounds

In this category limited experimental data make detailed analysis difficult to make. Equation (3) may be replaced for this series as

$$\Delta_f H^\circ_{298}(\mathrm{MX}_a\mathrm{Y}_b) = (ax/z)\Delta_f H^\circ_{298}(\mathrm{MX}_{z/x}) + (by/z)\Delta_f H^\circ_{298}(\mathrm{MY}_{z/y}) + C, \quad (4)$$

where x, y, and z are the formal valences of X, Y, and M, respectively, so that $z = ax + by$. When $C = 0$, as shown in Table I, the compounds FeO(OH), $\mathrm{FeBrCl_2}$, $\mathrm{UClBr_2}$, and $\mathrm{UCl_2Br}$ give good agreement with observed values. However, $\mathrm{Sc(OH)_2Cl}$ and $\mathrm{CrIBr_2}$ show deviations of 50.6 and 21.3 kJ/mol, respectively.

For Tl, two trivalent compounds are available. However, the experimental values given are for the hydrated compounds. We have recently found[8] that $\Delta_f H^\circ_{298}$ for hydrated compounds can be correlated quantitatively by Eq. (5) given below:

$$\Delta_f H^\circ(\mathrm{MX}_n \cdot n\mathrm{H_2O}) = An^\alpha + \Delta_f H^\circ(\mathrm{MX}_n), \quad (5)$$

where n is the number of water molecules involved in the hydrated compounds. $\Delta_f H^\circ(\mathrm{MX}_n \cdot n\mathrm{H_2O})$ and $\Delta_f H^\circ(\mathrm{MX}_n)$ are the standard enthalpies of formation of

TABLE I. Deviations between the observed and calculated values using Eqs. (3) and (4)

Parameter Z	Compound	$\Delta_f H^\circ_{298}$ (obs) (kJ/mol)	Dev (calc − obs)/kJ/mol $C = 13.4$ kJ/mol	$C = -17.6$ kJ/mol
$Z = 2$ (divalent compounds)	MgOHCl	799.6	3.3	−0.9
	CaClH	504.2	−0.2	−4.4
	CaBrH	443.5	−4.4	−8.6
	CaIH	366.1	7.3	11.5
	SrClH	525.1	7.1	2.9
	SrFCl	1046.0	10.0	5.8
	SrBrH	464.4	2.1	−2.2
	SrIH	385.8	3.2	−1.0
	BaClH	536.0	3.9	−0.3
	BaBrH	487.0	5.6	1.4
	BaIH	410.5	6.7	2.5
	BaClF	1064.4	18.1	13.9
	$1/2[Ba_2NCl]$	308.2[a]	−10.7	−14.9
	$1/2[Ba_2NBr]$	286.6[a]	−6.9	−11.1
	$1/6[Ba_6NI_9]$	488.8[a]	6.4	10.6
	CdOHCl	497.9	8.4	4.2
	CdBrOH	454.8	2.9	−1.3
	CdIOH	375.7	−19.7	−23.9

Parameter Z	Compound	$-\Delta_f H^\circ_{298}$ (obs) (kJ/mol)	Dev (calc − obs) $C = 0$
$Z = 3$ (trivalent compounds)	FeO(OH)	559.0	9.9
	$FeBrCl_2$	348.9	−6.8
	$UClBr_2$	751.0	−1.9
	UCl_2Br	812.5	5.8
	$TlCl_2Br$	262.9[b]	−11.4
	$TlClBr_2$	229.8[b]	−3.6
	$Sc(OH)_2Cl$	1268.0	50.6
	$CrICl_2$	418.0	−21.3
$Z = 4$ (tetravalent compounds)	UCl_3Br	967.8	2.8
	UCl_2Br_2	908.3	−2.6
	$UClBr_3$	852.7	−4.0
	UCl_3I	898.7	6.3
	UBr_3I	728.0	1.9

[a] The values given for these compounds are per metal atom.

[b] These values are obtained from the corresponding hydrated compounds using Eq. (5).

hydrated compound $MX_n \cdot H_2O$ and the corresponding anhydrous salts MX_n, respectively. A and α are constants.

Using Eq. (5) the values obtained for the compounds $TlCl_2Br$ and $TlClBr_2$ are -262.9 and -229.8 kJ/mol, respectively. Comparison of these values with the values obtained from the additivity relation given by Eq. (4) shows very good agreement, and the results are summarized in Table I.

4. Tetravalent Compounds

Sufficient data exist for only five compounds of uranium. As shown in Table I the calculated values using Eq. (4) with $C = 0$ are in very good agreement with observed values. The maximum absolute deviation is only 6.3 kJ/mol for the entire group.

5. Discussion

The simple additivity type relation given in Eq. (4) appears to relate $\Delta_f H^\circ$ of mixed salts of the same metal to $\Delta_f H^\circ$ of the binary salts with good accuracy. There is no simple way of ascertaining the absolute accuracy of the data listed in the NBS Tables so we cannot comment on the magnitudes of the deviations observed. All of the Sr and Ba salts show positive deviations in the divalent metal group of a magnitude to suggest that $C = -17.6$ kJ/mol would give a better fit to the group in terms of balancing positive and negative deviations. With $C = -17.6$ kJ/mol the average absolute deviation for the 16 compound is also 5.4 kJ/mol and the maximum is -23.9 kJ/mol for CdIOH. This latter value is so far out of line in comparison with the other members of the group that we would regard it with some skepticism. In a similar vein the $Sc(OH)_2Cl$ value appears far out of line compared to the generally good agreement shown by the other trivalent species. We would think its value might be reexamined.

The rather surprising additivity type relations exhibited by the mixed salts would not be anticipated from any simple crystal models. They suggest that bonding in the salt is short range and that next-nearest neighbor interactions are of minor importance. The observation that for the binary group, C is negative implies that the mixed salts are always more stable than their binary derivatives. This is a consequence of the fact that entropies are expected to be very close to additive and hence, ΔS of disproportionation will be very small.

Tardy[11–14] and Sverjensky[15,16] have also shown the existence of empirical relations between Gibbs free energies of formation and enthalpies of formation in the case of phosphates, oxides, and aqueous ions.[13] Unfortunately for the prediction of $\Delta_f H^\circ$ of phosphates, deviations from data of up to 84 kJ/mol are found for $Mg_3(PO_4)_2$ and $Ba_3(PO_4)_2$. Average deviations for most orthophosphates quoted are about 50 kJ/mol. Such large deviations make their correlation virtually useless for chemical purposes.

A more useful empirical relation has recently been proposed by Bratsch and Lagowski[17] for predicting $\Delta_f H^\circ$ of solid lanthanides, MX_n. It relates $\Delta_f H^\circ(MX_n,cr)$ to $\Delta_f H^\circ(M^{z+},g)$ and the radius of the metal lanthanide ion, $r_M(z+)$. Here $z+$ is the valence of the ion M^{z+}. The relation is a four parameter equation of the form

$$\Delta_f H^\circ(MX_n,cr) = \Delta_f H^\circ(M^{z+},g) + A/(r_{M^{z+}} + r_X) + B,$$

where r_X is the radius of the anion. A, B, and r_X will vary with crystal class (cubic, etc.) and valence type. Despite the large number of input data and some uncertainties in some of the values for $\Delta_f H^\circ(M^{z+},g)$ for the gas phase ions, calculated values appear to be within ± 12 kJ/mol for most of the simple halides, sulfides, arsenides, and oxides, but show deviations up to 30 kJ/mol. They do not attempt to examine the type of mixed salts considered here.

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