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Empirical equation for estimation of the enthalpies of formation of crystalline solvates containing water, methanol, ethanol, hydrogen peroxide or sulphur dioxide

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Abstract

The experimental data available on the standard enthalpy of formation $\Delta_f H^\ominus$ of crystalline solvates containing H_2O, CH_3OH, C_2H_5OH, H_2O_2 or SO_2 have been evaluated using the equation $\Delta\Phi = \Delta_f H^\ominus(M_aX_b \cdot nY) - \Delta_f H^\ominus(M_aX_b) = b_n n$.

This equation presents satisfactorily the data available on $\Delta_f H^\ominus$ for the above solvates. The unknown values of $\Delta_f H^\ominus$ for some crystalline solvates and unsolvated salts are predicted.

INTRODUCTION

The enthalpy of formation $\Delta_f H^\ominus$ of compounds is a very important thermodynamic characteristic. Theoretical prediction of the $\Delta_f H^\ominus$ values for crystalline solvates containing molecules of H_2O, CH_3OH, C_2H_5OH, H_2O_2 and adducts containing SO_2 is still impossible; moreover, in some cases, their experimental determination is also impossible depending on which empirical equations, considered in refs. 1–6, are used. These equations present well the available experimental data and are based on the assumption that $\Delta_f H^\ominus$ of the crystalline solvates can be represented as a sum of the $\Delta_f H^\ominus$ values for the unsolvated crystalline salt and a correcting term that accounts for the nature and number of the ligand molecules involved. The empirical equations can be represented by the expression

$$\Delta_f H^\ominus(MX \cdot nL) = \Delta_f H^\ominus(MX) + An^\alpha \tag{1}$$

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where $\Delta_f H^\ominus(\mathrm{MX} \cdot n\mathrm{L})$ is the enthalpy of formation of the crystalline solvate, $\Delta_f H^\ominus(\mathrm{MX})$ is the enthalpy of formation of the unsolvated salt, and n is the number of ligand molecules of a given kind involved in the solvate. A and α are constants which have different values.

In a previous paper [7] we have shown the possibility of additive prediction of standard thermodynamic functions $\Delta\Pi^\ominus$ for hydrofluorides on the basis of the equation

$$\Delta\Pi^\ominus(\mathrm{MF} \cdot n\mathrm{HF}) = \Delta\Pi^\ominus(\mathrm{MF}) + nb(n) \tag{2}$$

where n is the number of HF molecules in the hydrofluoride; $b(n)$ is the increment of an HF molecule and its value may depend on the succession of coordination. In the previous paper, it was shown that when $n \geqslant 2$, $b(n)$ is a constant.

It can be assumed that for crystalline solvates with $n \geqslant 1$, eqn. (2) can be written as

$$\Delta\Phi = b_n n \tag{3}$$

where $\Delta\Phi = \Delta_f H^\ominus(\mathrm{M_aX_b} \cdot n\mathrm{Y}) - \Delta_f H^\ominus(\mathrm{M_aX_b})$ and $b_n = b(n)$ is a constant.

This assumption is in agreement with the data in Ref. 8 according to which, when hydrates are formed from an anhydrous salt and liquid water, the bonding of the first water molecule is accompanied by a larger heat effect than that associated with each successive molecule.

The purpose of the present paper is to check whether there is an empirical equation describing the $\Delta_f H^\ominus$ values of the crystalline solvates containing the above ligands. In addition, the equation should take into account the nature and number of the ligands alone and not the succession of their coordination in the solvates. The assumption of the existence of this regularity is based on the fact that more noticeable deviations from the approximate monotony in the change of $\Delta_f H^\ominus$ for the crystalline solvates would occur only after essential changes in the coordination surroundings of the central ion, i.e. after the binding of the first molecule of the ligand. It is be expected that upon coordination of the successive molecules, deviations from the additivity would be small with respect to the $\Delta_f H^\ominus$ value of the crystalline solvate.

RESULTS AND DISCUSSION

In this paper, we have used the experimental data obtained in ref. 9 on $\Delta_f H^\ominus$ for unsolvated salts and crystalline solvates, and the data on peroxo hydrates given in refs. 10 and 11.

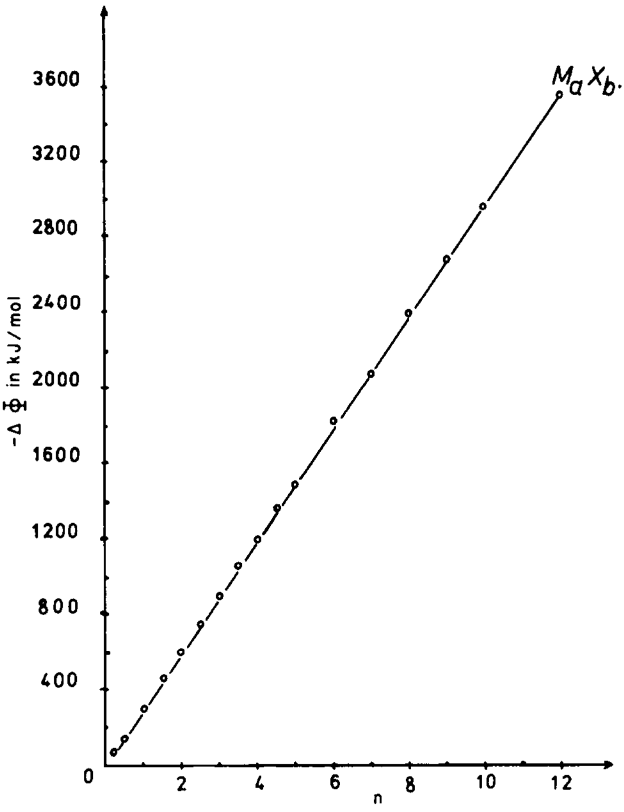

Fig. 1. Relationship between $\Delta\Phi$ for $M_aX_b \cdot nH_2O$ and n.

Figures 1 and 2 shows relationships between $\Delta\Phi$ and n. They are obviously linear, the straight lines having different slopes and no intercepts. The data in Figs. 1 and 2 confirm that eqn. (3) is valid for hydrates, methylates, ethylates, peroxy hydrates and for adducts of salts containing SO_2. The values of the constant b_n for the above solvates are summarized in Table 1. It can be seen that for all the ligands mentioned, the constant b_n has negative values. It should also be pointed out that the b_n values for the hydrates and the ethylates are close.

We have established that eqn. (3) for estimating $\Delta_f H^\ominus$ values of the crystalline solvates under consideration, presents satisfactorily the available data on $\Delta_f H^\ominus$. The maximum error reaches 5%, while the mean error is 2.2%. In our opinion, this allows this equation to be used for estimating unknown $\Delta_f H^\ominus$ values for the crystalline solvates and, if necessary, also for unsolvated crystalline salts whose thermodynamic stability has been demonstrated in the literature [9, 10]. Table 2 shows some predicted $\Delta_f H^\ominus$ values.

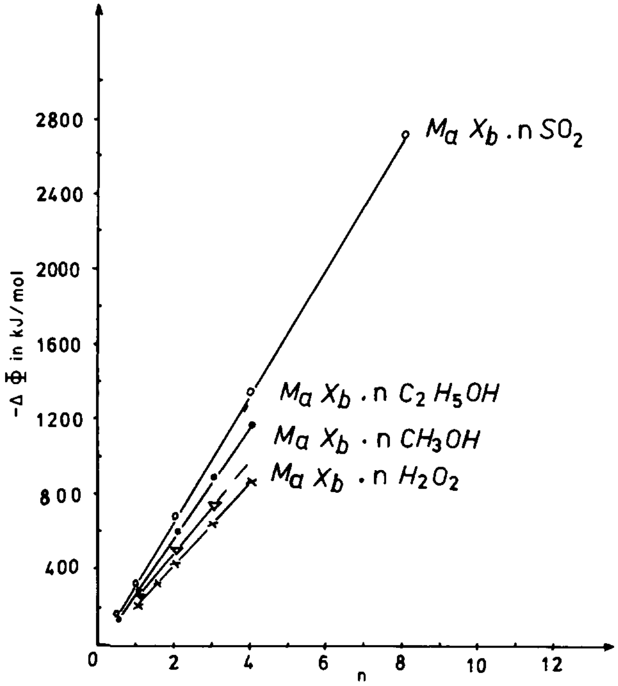

Fig. 2. Relationship between $\Delta\Phi$ for $M_aX_b \cdot n$L and n (where L is CH_3OH, C_2H_5OH, SO_2 and H_2O_2).

In conclusion, the validity of eqn. (3) for the crystalline solvates under investigation has been established. We shall continue our studies in order to determine whether this equation is also valid for other crystalline solvates, i.e. whether it is generally valid.

TABLE 1

Values for b_n in eqn. (3)

$M_aX_b \cdot n$L	$-b_n$	M_aX_b
$M_aX_b \cdot nH_2O$	298.3 ± 1.5	Valid for all salt hydrates
$M_aX_b \cdot nCH_3OH$	252.9 ± 5.2	$CuCl_2$,$CuSO_4$, $CoBr_2$, $MnCl_2$, $Ca(NO_3)_2$, NaI
$M_aX_b \cdot nC_2H_5OH$	296.4 ± 6.8	$CuCl_2$, $CoCl_2$, $CoBr_2$, $MnBr_2$, $CaCl_2$, $SrBr_2$
$M_aX_b \cdot nSO_2$	340.2 ± 1.4	LiI, NaI, NaCNS, KI, KCNS, NH_4CNS, SrI_2, BaI_2, $AlCl_3$
$M_aX_b \cdot nH_2O_2$	214.5 ± 7.6	Li_2O, Na_2CO_3, Na_2HPO_4, $Na_4P_2O_7$, KF, $Ca(OH)_2$, BaO_2

TABLE 2

Some predicted $\Delta_f H^\ominus$ values using eqn. (3)

Compound	$-\Delta_f H^\ominus$/ kJ mol^{-1}	Ref. and remarks
$CdC_2O_4 \cdot 3H_2O$	1807	9
$NiF_2 \cdot 4H_2O$	1885	9
FeC_2O_4	886	9 using $\Delta_f H^\ominus$ for $FeC_2O_4 \cdot 2H_2O$
MnI_2	246	9 using $\Delta_f H^\ominus$ for $MnI_2 \cdot nH_2O$ ($n = 2, 4$)
$NaAl(SO_4)_2$	2436	9 using $\Delta_f H^\ominus$ for $NaAl(SO_4)_2 \cdot nH_2O$ ($n = 2, 5, 6, 12$)
$TlBr_3$	209	9 using $\Delta_f H^\ominus$ for $TlBr_3 \cdot 4H_2O$
GdF_3	1656	10 using $\Delta_f H^\ominus$ for $GdF_3 \cdot H_2O$
$La(ClO_4)_3$	956	10 using $\Delta_f H^\ominus$ for $La(ClO_4)_3 \cdot 4H_2O$
RbCNS	226	10 using $\Delta_f H^\ominus$ for $RbCNS \cdot 0.5SO_2$
$Na_2SO_4 \cdot 3H_2O_2$	2031	10
$RbF \cdot 2H_2O_2$	985	10
$CsF \cdot H_2O_2$	768	10

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