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Short Communication

Additive Prediction of Thermodynamic Functions of Hydrofluorides

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Summary. The experimental data available on the thermodynamic functions $\Delta\Pi^0$ for $M\mathrm{F} \cdot n\mathrm{HF}$ hydrofluorides [M = Li, Na, K, Rb, Cs, NH_4, Ag(I) and Tl(I); n = 1–3] have been evaluated additively. The unknown values of $\Delta\Pi^0$ for $n = 0 \div 7$ are predicted.

Keywords. Hydrofluorides; Thermodynamic functions; Additive prediction; Increments of HF molecules.

Additive Voraussagen der thermodynamischen Funktionen von Hydrogenfluoriden (Kurze Mitt.)

Zusammenfassung. Die vorhandenen experimentellen Daten über die thermodynamischen Funktionen $\Delta\Pi^0$ von Hydrogenfluoriden $M\mathrm{F} \cdot n\mathrm{HF}$ [M = Li, Na, K, Rb, Cs, NH_4, Ag(I) und Tl(I); n = 1–3] werden linear ausgeglichen und die fehlendenden Werte für $\Delta\Pi^0$ mit $n = 0 \div 7$ vorausgesagt.

A series of hydrofluorides of alkali metals, ammonia, silver and thallium with the composition $M\mathrm{F} \cdot n\mathrm{HF}$ (n = 1 to 7) are described [1–3]. The values of the standard thermodynamic functions denoted as $\Delta\Pi^0$ are experimentally determined for some hydrofluorides containing 1–3 HF molecules.

The possibility of additive prediction of standard thermodynamic functions of crystalline hydrates has been established in Refs. [4–8]. It may be expected that the additive approach to the estimation and prediction of $\Delta\Pi^0$ would also be applicable to hydrofluorides in view of the important part played by hydrogen bonds in the formation of hydrates and hydrofluorides.

Maslov [9] has additively presented known values of the enthalpy of formation $\Delta_f H^0$ for potassium hydrofluorides ($\mathrm{KF} \cdot n\mathrm{HF}$, n = 1–3), suggesting the value of −319.2 kJ/mol for each HF molecule. However, this author adds the increment to the value of −602.5 kJ/mol which differs from $\Delta_f H^0$ = −562.6 kJ/mol given in the reference book [10] for anhydrous KF. Presenting $\Delta_f H^0$ for KF hydrates and for more complex KF-containing compounds, the same researcher adds the increments of the water molecules to $\Delta_f H^0$ = −562.6 kJ/mol for anhydrous KF.

In the literature there are no data which would allow the prediction of unknown $\Delta\Pi^0$ values for hydrofluorides. On the other hand, the application of some compounds of this group in the practice requires looking for other possibilities of prediction of $\Delta\Pi^0$ values for hydrofluorides.

The purpose of the present paper is to check the additive presentation of experimental data on the $\Delta\Pi^0$ values of hydrofluorides, which would allow deducing the increments of the HF molecules and predicting the $\Delta\Pi^0$ values.

Experimental data presented in Ref. [11] on $\Delta\Pi^0$ for anhydrous *M*F fluorides and hydrofluorides were used in the study.

The following correlation between the experimental data on $\Delta\Pi^0$ for hydrofluorides, the $\Delta\Pi^0$ values for the corresponding anhydrous fluorides and the number *n* of coordinated HF molecules were obtained,

$$\Delta\Pi^0\,(M\mathrm{F}\cdot n\mathrm{HF}) = \Delta\Pi^0\,(M\mathrm{F}) + n\cdot b(n),$$

where $b(n)$ is the increment of a HF molecule.

Table 1 contains the increments for the 1st–3rd HF molecules. The increments of the first molecule are calculated by averaging 6–7 values with a confidence level

Table 1. Increments *b* (*n*) of 1st to 3rd HF molecules for $\Delta\Pi^0$ of hydrofluorides (kJ/mol, J/mol grd)

No.	$-\Delta_f H^0$	$-\Delta_f G^0$	$-\Delta_f H_0^0$	$H^0 - H_0^0$	S^0	C_p^0
1	350.1	312.3	347.1	5.7	41.9	32.1
2	320.8	282.4	317.4	5.4	38.4	28.2
3	320.8	282.4	317.4	5.4	38.4	28.2

Table 2. Predicted $\Delta\Pi^0$ values for hydrofluorides (kJ/mol, J/mol grd)

Compounds	$-\Delta_f H^0$	$-\Delta_f G^0$	$-\Delta_f H_0^0$	$H^0 - H_0^0$	S^0	C_p^0
NaF · 3 HF	1564.5	1419.7	1552.3	25.0	169.9	135.3
NaF · 4 HF	1885.3	1702.1	1869.7	30.4	208.3	163.5
KF · 2.5 HF	1397.4	1272.3	1387.8	23.8	166.0	123.4
KF · 4 HF	1878.6	1695.9	1863.9	31.9	223.6	165.7
RbF · 2 HF	1226.7	1120.6	1219.2	22.0	158.1	110.9
RbF · 3 HF	1547.5	1403.0	1536.6	27.4	196.5	139.1
RbF · 4 HF	1868.3	1685.4	1854.0	32.8	234.9	167.3
CsF · 2 HF	1224.4	1120.4	1217.6	22.9	173.3	111.4
CsF · 3 HF	1545.2	1402.8	1535.0	28.3	211.7	139.6
CsF · 6 HF	2507.6	2250.0	2487.2	44.5	326.9	224.2
NH_4F · 3 HF	1455.3	1225.6	1430.9	27.6	190.7	153.8
NH_4F · 4 HF	1776.1	1508.0	1748.3	33.0	229.1	182.0
NH_4F · 7 HF	2738.5	2355.2	2700.5	49.2	344.3	266.6
TlF · HF	677.1	618.5	–	–	[a]	[a]
TlF	[a]	[a]	–	12.3[b]	[a]	[a]
AgF · HF	555.9	500.2	–	–	[a]	80.2

[a] The value is known and no prediction is needed

[b] The value is estimated on the basis of $H^0 - H_0^0 = 18.0$ kJ/mol for TlF · HF and the increment 5.7 for the first HF molecule

of 95%. The increments for the second and third HF molecules are obtained by averaging the values for thre hydrofluorides ($NaF \cdot 2\,HF$, $KF \cdot 2\,HF$ and $KF \cdot 3\,HF$).

The increments for the first HF molecule, which are higher in absolute value than those for the 2nd and 3rd molecules of the ligand, are not unexpected and show good agreement with the data according to which the strongest bond in hydrates is formed between the central ions and the first water molecule.

The differences between additively estimated $\Delta\Pi^0$ values and available experimental data established for the enthalpies of formation ($\Delta_f H^0$), the Gibbs energies ($\Delta_f G^0$) and enthalpies of formation at 0 K ($\Delta_f H_0^0$) are below 3%. The differences found for $H^0-H_0^0$, the entropy S^0 and the specific heat C_p^0 are larger and reach, in some cases, 6–8.8%.

The $\Delta\Pi^0$ values expected for a series of hydrofluorides are given in Table 2. They are calculated on the basis of the values for the corresponding anhydrous fluoride and the deduced increments, supposing the increments for the 2nd and the 3rd molecules to be valid for the 4th to 7th molecules. We have predicted $\Delta\Pi^0$ only for hydrofluorides which are known to be really existing phases because the possibility of evaluating $\Delta\Pi^0$ does not prove the existence of a hydrofluoride.

The data given in Ref. [12] concerning $KF.4\,HF$, i.e. $\Delta_f H^0 = -1877.4$ and $\Delta_f G^0 = -1\,709.8$ kJ/mol, confirm the values predicted by us: $-1\,878.6$ and $-1\,695.6$ kJ/mol, respectively.

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