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THE SOLUTION THERMOCHEMISTRY OF ANTIMONY PENTAFLUORIDE AND SOME FLUOROANTIMONATES

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SUMMARY

From hydrolysis and solution measurements the enthalpies of formation of $SbF_5(\ell)$, $LiSbF_6(s)$, $NaSbF_6(s)$, $KSbF_6(s)$, $CsSbF_6(s)$, $AgSbF_6(s)$, and $SbF_6^-aq.$ are estimated to be -1324 ± 12, -2062 ± 5, -2060 ± 6, -2080 ± 3, -2082 ± 15, -1633 ± 3, and -1789 ± 4 kJ mol^{-1} respectively. Less precise estimates of the enthalpies of formation of O_2SbF_6 and of $CsSb_3F_{16}$ are also given. From the results the fluoride ion affinity of SbF_5, the single ion hydration enthalpy of $SbF_6^-(g)$, and the charge distribution within the SbF_6^- ion have been calculated.

INTRODUCTION

Antimony pentafluoride is known to be a very strong Lewis acid; it stabilises strongly oxidising cations such as NF_4^+ (in NF_4SbF_6),[1] O_2^+ (in O_2SbF_6 and $O_2Sb_2F_{11}$),[2] and Br_2^+ (in $Br_2Sb_3F_{16}$)[3] as well as carbonium cations in superacid solution.[4] However, quantitative data are restricted to the pioneer calorimetric studies carried out by Woolf in bromine trifluoride solution, from which estimates of the enthalpies of formation of the salts $KSbF_6$, $AgSbF_6$, $NaSbF_6$, and $Ba(SbF_6)_2$ were obtained.[5]

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EXPERIMENTAL

Compounds. SbF_5 was prepared from the elements in a flow system, and was purified by vacuum distillation. $NaSbF_6$, $KSbF_6$ and $AgSbF_6$ (I.C.N. Pharmaceuticals Inc.) were obtained from Alpha Inorganics. $CsSbF_6$ was prepared by the action of excess of BrF_3 on a stoichiometric mixture of CsCl and Sb_2O_3. $CsSb_3F_{16}$ was prepared by dissolving CsF in a large excess of warm SbF_5; the excess of solvent was removed by pumping at 25° to constant weight (3 days). $LiSbF_6$ was prepared a) by exchange from $AgSbF_6$ and LiCl in dry CH_3OH; the LiCl was filtered off and the $LiSbF_6$ recovered by pumping off the solvent b) by the action of BrF_3 on a stoichiometric mixture of LiCl and Sb_2O_3; the excess of BrF_3 was pumped off and the impure product, which still contains combined BrF_3, was recrystallised from dry methanol c) by the interaction of stoichiometric quantities of LiF and SbF_5 in liquid HF solution; the excess of solvent, in which $LiSbF_6$ is only slightly soluble, was pumped off at -80°, with the last traces being removed at room temperature. We are indebted to Professor N. Bartlett, FRS, for a sample of O_2SbF_6. The purity of all compounds was checked by infra-red and X-ray powder spectroscopy as appropriate.

Calorimetric Measurements. These were made in an LKB 8700 calorimeter with ancillary apparatus as described earlier.[6] The calorimeter's performance was checked periodically via determination of the enthalpy of solution of potassium chloride in water. Samples of between 10 and 40 mg were used, with 30 or 100 cm^3 of aqueous hydrolysing medium. The ranges of error reported in Tables 1, 2 and 4 refer to 90% confidence limits for the mean values given.

Enthalpies of Hydrolysis

(a) Antimony Pentafluoride The reaction of $SbF_5(\ell)$ with KOHaq. is much cleaner and is more satisfactory from a thermochemical point of view than the reaction with NaOHaq.[8] In the latter case the hydrolysed SbF_5 is precipitated as slightly soluble $NaSb(OH)_6$, and there is the possibility that combined fluoride could be carried down in the precipitate. A value of -1324 ± 12 kJ mol^{-1} for $\Delta H_f(SbF_5(\ell))$ is calculated using the enthalpy of hydrolysis (Table 1) in M KOH combined with the ancillary data given in Table 3.

$$SbF_5(\ell) + 6OH^-aq. \rightarrow Sb(OH)_6^-aq. + 5F^-aq.$$

TABLE 1

ENTHALPIES OF HYDROLYSIS OF ANTIMONY COMPOUNDS AT 298K

Compound	Conditions	Enthalpy of Hydrolysis (kJ mol^{-1})
$SbF_5(\ell)$	M-KOH	-472 ± 4
$KSbF_6(s)$	M-KOH	-307 ± 3
$CsSbF_6(s)$	M-KOH	-293 ± 15
$O_2SbF_6(s)$	M-KOH	-587 ± 40
$CsSb_3F_{16}(s)$	M-KOH	-1150 ± 30
$SbCl_5(\ell)$	M-NaOH	-581 ± 8[a]

[a] Corrected for the enthalpy of solution of $NaSb(OH)_6$(+33 kJ mol^{-1}) [30]

(b) <u>$KSbF_6$ and $CsSbF_6$</u>. Hydrolysis data are reported in Table 1, and the calculated enthalpies of formation of the salts are reported in Table 4.

(c) <u>O_2SbF_6 and $CsSb_3F_{16}$</u>. With both these salts there is a large standard deviation in the hydrolysis measurements, and the results should be regarded as approximate.

<u>Enthalpies of Solution</u> Results are given in Table 2, and the calculated enthalpies in Table 4. It should be noted that $LiSbF_6$ is a particularly

difficult subject since it is very hygroscopic, but the results from all three preparative methods are substantially in agreement.

TABLE 2

ENTHALPIES OF SOLUTION OF FLUOROANTIMONATES AT 298K

Salt	ΔH_{soln}(kJ mol^{-1})
$LiSbF_6$	-6.0 ± 2.0
$NaSbF_6$	20.0 ± 3.0
$KSbF_6$	38.5 ± 0.7
$AgSbF_6$	-38.75 ± 0.16

Lattice Energy Calculations Structural parameters used in the calculations are listed in Table 5. The coulombic term was calculated using a program kindly provided by the late Professor T. C. Waddington. Values for the repulsion terms were calculated from the expression $Be^{-r/\rho}$, with $\rho = 0.345$ Å, making allowance for the changing basic radius of F with respect to ionic charge. The London energy was calculated using the procedure outlined in Phillips and Williams.[8] Results are given in Table 6.

TABLE 3

ANCILLARY DATA USED IN THE DERIVATION OF ENTHALPIES OF FORMATION AND FLUORIDE ION AFFINITIES

$\Delta H_f^\ominus$(kJ mol^{-1})	Ref.	$\Delta H_f^\ominus$(kJ mol^{-1})	Ref.
K^+aq -252.17	14	K^+(g) 514.6	16
F^-aq -335.35	15	Cs^+(g) 459.8	16
Cl^-aq -167.08	14	F^-(g) -250.7	31
OH^-aq -230.025	14	$SbCl_5(\ell)$ -440.2	17
$H_2O(\ell)$ -285.830	14	$SbF_5(\ell)$ -1328	9

DISCUSSION

The enthalpy of formation of liquid antimony pentafluoride, calculated from the new hydrolysis data is -1324 ± 12 kJ mol^{-1}. This is in excellent agreement with the most recent fluorine bomb calorimetry value of -1328 kJ mol^{-1},[9] and is within the experimental error of the earlier fluorine bomb calorimetric value of -1337 kJ mol^{-1}.[10] These values are to be preferred to our earlier figure of -1378 kJ mol^{-1} [11] (see Experimental above) and to Woolf's value of -1379 kJ mol^{-1},[5] which depended on solution measurements in bromine trifluoride and on assumptions which could not fully take account of the formation of the then unknown salt $Br_2Sb_3F_{16}$. In this paper we use $\Delta H_f^\ominus(SbF_5)(\ell)$ = -1328 kJ mol^{-1}.

Very recently the enthalpy of the process $\frac{1}{4}(SbF_5)_4(g) \rightarrow SbF_5(g)$ has been estimated from vapour density measurements to be 18.4 kJ mol^{-1}.[12] Combining this with the known enthalpy of vapourisation of $SbF_5(\ell)$ (43.4 kJ mol^{-1}),[13] and the degree of association at the b.p. ($n \simeq 3.0$),[12] the enthalpy of the process $SbF_5(\ell) \rightarrow (SbF_5)(g)$ (monomer) is calculated to be approximately 27 kJ mol^{-1}. We hence derive $\Delta H_f^\ominus(SbF_5)(g)$ to be -1301 (±15) kJ mol^{-1}.

The enthalpies of formation of the fluoroantimonates, estimated from the hydrolysis and solution data, are in excellent agreement with those of Woolf,[5] after his data have been recalculated using the new value for $\Delta H_f^\ominus$ (SbF_5) (ℓ) as the baseline; a set of recommended (averaged) values is also given for some of the salts and for SbF_6^-aq. (Table 4).

A better indication of the chemical stabilities of the hexafluoroantimonates(V) is brought out in Table 5. For all except the NF_4^+ and O_2^+ salts the entropy change is small, so that the $\Delta H^\ominus$ figures are close to $\Delta G^\ominus$. The figures show the expected increase in stability from the Li to the Cs salts, and the large and favourable enthalpy change when $CsSbF_6$

TABLE 4

ENTHALPIES OF FORMATION OF FLUOROANTIMONATES (V) (kJ mol^{-1})

Compound	This work	Woolf[a] (recalculated)	Recommended Value	Calculated[c] (Kapustinskii)
$LiSbF_6$	-2062 ± 5^b	---	-2062	-2038
$NaSbF_6$	-2060 ± 6^b	-2058	-2054	-2054
$KSbF_6$	-2080 ± 3	-2092	-2086	-2086
$CsSbF_6$	-2082 ± 15^b	---	-2082	-2092
$AgSbF_6$	-1633 ± 3^b	-1622	-1628	-1616
$Ba(SbF_6)_2$	-	-4174	-4174	-4183
SbF_6^- aq[d]	-1789 ± 4	-1801	-1795	
O_2SbF_6	-1468 ± 40	---	---	
$CsSb_3F_{16}$	-4865 ± 30	---	---	

[a] Values from ref. 9 (no limits of error reported) recalculated for $\Delta H_f^{\ominus}(SbF_5)(\ell) = -1328$ kJ mol^{-1}

[b] Calculated from ΔH_{soln} and $\Delta H_f(KSbF_6)(s) = -2080$ kJ mol^{-1}

[c] Calculated from Kapustinskii's equation (ref 18) using $r_A = 1.94$ Å and ΔH_F (fluoride ion affinity) = -378 kJ mol^{-1} Cationic radii from ref.20

[d] Values calculated from $\Delta H_f(KSbF_6)(s)$ and $\Delta H_{soln}(KSbF_6) = 38.5$ kJ mol^{-1}

is converted to $CsSb_3F_{16}$. Even allowing for an unfavourable TΔS term (≃ 30 kJ mol^{-1}) it would appear that NF_4^+ salts are remarkably stable, much more so, in fact, than those of O_2^+, while the figures emphasise the marginal stability of XeF SbF_6.

TABLE 5

ENTHALPIES OF COMPLEXATION OF $SbF_5(\ell)$ WITH FLUORIDES/kJ mol^{-1}

Compound	$\Delta H^{\ominus}$
$LiSbF_6$	-116
$NaSbF_6$	-147
$KSbF_6$	-182
$CsSbF_6$	-217
$AgSbF_6$	-106
$Ba(SbF_6)_2$	-309
O_2SbF_6	-140 [a]
$CsSb_3F_{16}$	-304
$XeF\ SbF_6$ [21]	-32[d]
$XeF\ Sb_2F_{11}$ [11]	-99[b,d]
NF_4SbF_6 [22,23]	-218 [c]

a From $O_2(g) + \frac{1}{2}F_2(g) + SbF_5(\ell)$

b Recalculated using $\Delta H_f^{\ominus}\ (SbF_5)(\ell) = -1328$ kJ mol^{-1} (Ref.9)

c From $NF_3(g) + F_2(g) + SbF_5(\ell)$

d From $XeF_2(s) + SbF_5(\ell)$

Approximate values for the enthalpies of formation of some of the salts (Table 4) have been calculated. These are based on the known enthalpies of the Na and K fluoroantimonates; if Kapustinskii's equation[18]

$$U = \frac{1214\ z_1z_2}{r_c + r_A}\left(1 - \frac{0.345}{r_c+r_A}\right) \text{kJ mol}^{-1}$$

is used to estimate the lattice enthalpy, U, then arbitrary values of r_A, the thermochemical radius of the anion, and of ΔH_F, the fluoride ion affinity, (see Figure 1) may be determined which fit the known data (Table 4) and which may be used to estimate enthalpies of formation of other hexafluoroantimonates(V).

TABLE 6

CRYSTAL DATA FOR LiSbF$_6$ AND KSbF$_6$

LiSbF$_6$ [24]	Hexagonal (R$\bar{3}$) a_o = 5.18, c_o = 13.60Å Li at 0, 0, $\frac{1}{2}$; Sb at 0, 0, 0 F at .3186, .0540, -.0799
KSbF$_6$ [25]	Tetragonal (P$\bar{4}$2m) a_o = 5.16(1), c_o = 10.07(2) Å K(1) at $\frac{1}{2}$, $\frac{1}{2}$, 0; K(2) at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$; Sb at 0, 0, ·2504; F(1) at ·1876, ·1876, ·1280; F(2) at ·1745, ·1745, ·3825; F(3) at ·2529, -·2529, ·2630

We have also calculated more realistic values of the lattice enthalpies of the SbF$_6^-$ salts and of other quantities together with the charge distribution within the anion, from the known structures of LiSbF$_6$ and KSbF$_6$ (Table 6) and the thermochemical cycles in Figure 1 (cf. ref. 19). The graphical plot of the single ion hydration enthalpy of SbF$_6^-$(g), calculated for various charge distributions within the ion, against the charge on the Sb atom, is shown in Figure 2. The point of intersection gives a measure both of q(Sb) (about + 1.7) and of the single ion hydration enthalpy (-1316 kJ mol^{-1}) relative to S.I.H.E. (H$^+$)(g) = 0. It should be noted that q(Sb) is sensitive to small changes in the data especially for LiSbF$_6$, but the single ion hydration enthalpy value is not. Combined with the hydration enthalpy of the proton (-1091 kJ mol^{-1}), a value of -225 kJ mol^{-1} is obtained for the absolute hydration enthalpy of SbF$_6^-$(g). The lattice enthalpies of KSbF$_6$ and LiSbF$_6$ are -585 and -740 kJ mol^{-1} respectively.

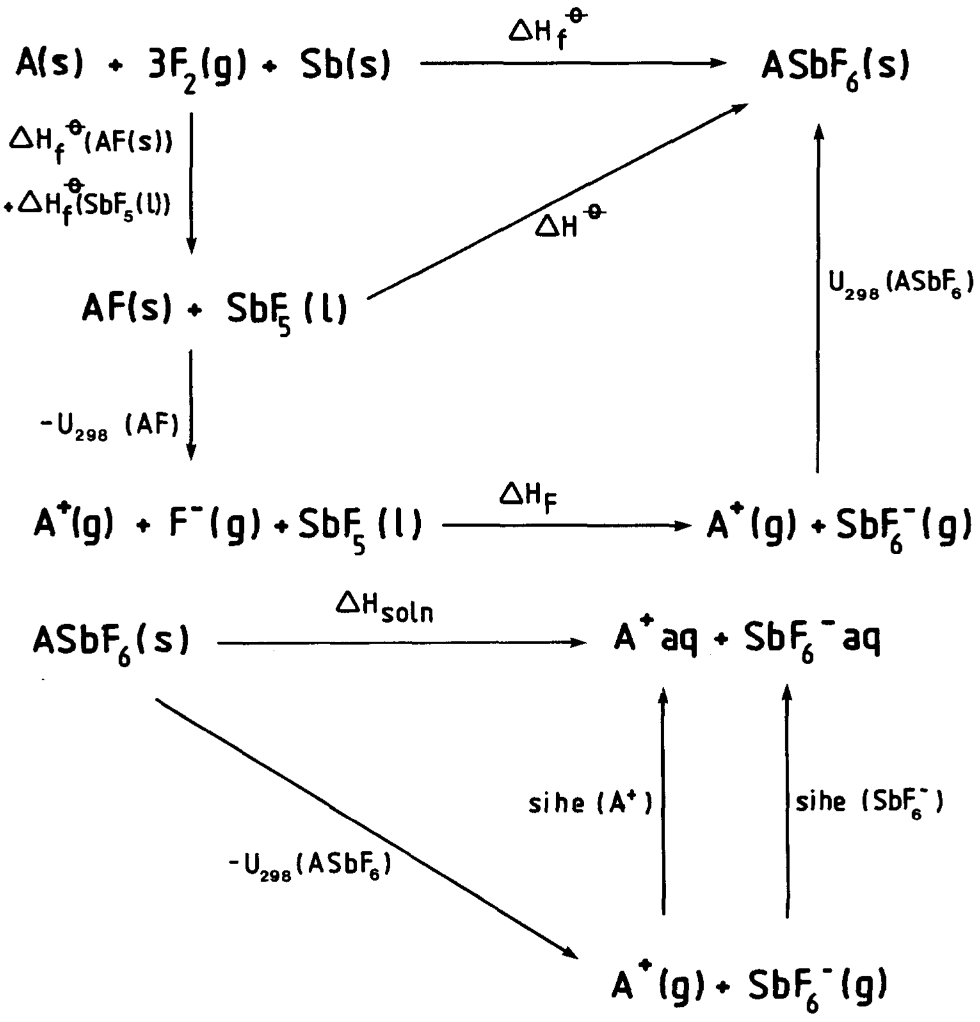

FIG. 1. THERMOCHEMICAL CYCLES FOR HEXAFLUOROANTIMONATES (V).

The fluoride affinity of $SbF_5(\ell)$, (i.e. the enthalpy of the reaction $SbF_5(\ell) + F^-(g) \rightarrow SbF_6^-(g)$) is calculated to be -418 kJ mol^{-1}, whilst that of $SbF_5(g)$ is -390 kJ mol^{-1}. For the preparative chemist it is the value of ΔH_F based on $SbF_5(\ell)$ which is chiefly of interest. This figure of -418 kJ mol^{-1} is to be compared with estimates of -450 kJ mol^{-1} for $WF_5(s)$,[26,27] and of -387

TABLE 7

LATTICE ENERGY CONTRIBUTIONS IN $LiSbF_6$ AND $KSbF_6$ CALCULATED AT VARIOUS CHARGE DISTRIBUTIONS (kJ mol^{-1})

	Charge on Antimony (q_{Sb})			
$LiSbF_6$	-1	0	1	2
U_c	-646.0	-699.8	-752.0	-811.0
U_R	41.6	46.5	56.2	69.2
U_L	-6.7	-6.7	-6.7	-6.7
U_o	-611.6	-660.0	-702.5	-748.5
U_{298}	-616.6	-665.0	-707.5	-753.5
$KSbF_6$				
U_c	-552.2	-572.6	-596.7	-630.5
U_R	26.9	40.2	47.6	64.0
U_L	-18.9	-18.9	-18.9	-18.9
U_o	-544.2	-551.3	-568.0	-585.4
U_{298}	-549.2	-556.3	-573.0	-590.4

kJ mol^{-1} for TaF_5(s),[28] assuming the lattice enthalpies of the three potassium salts to be the same. It is also interesting to compare the above estimated charge on Sb and the hydration enthalpy of the SbF_6^- anion with values for analogous ions. The most studied anion of this type is SiF_6^{2-}, for which a variety of approaches suggest q(Si) to lie within the range +1.3 to +1.9; the hydration enthalpy of SiF_6^{2-} is estimated to be -960 to -990 kJ mol^{-1} (relative to -1091 kJ mol^{-1} for H^+).[19] The most recent value for the hydration enthalpy of F^- is -502 kJ mol^{-1}.[29] The relative values for SbF_6^-, SiF_6^{2-} and F^- conform satisfactorily to the general

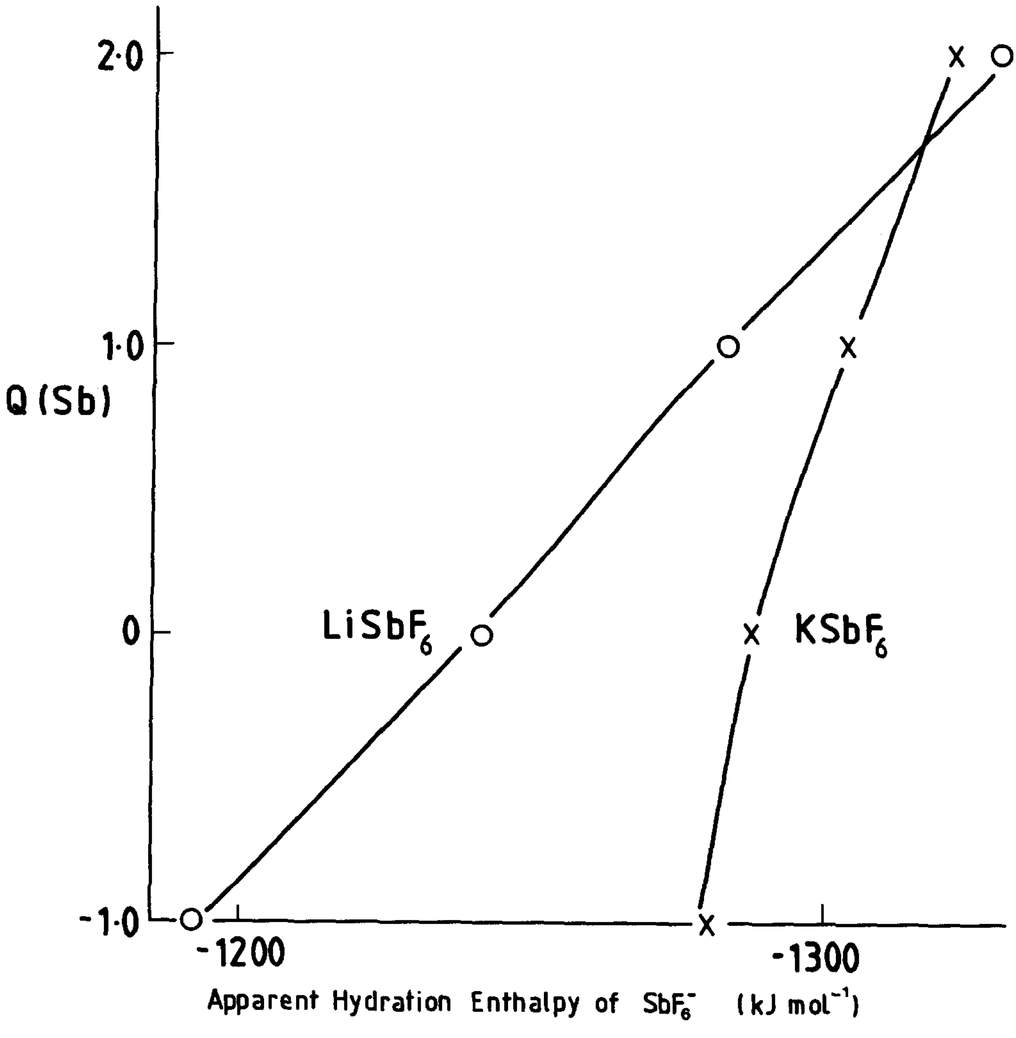

FIG. 2. HYDRATION ENTHALPY OF SbF_6^-.

expectation from relative sizes and charges. The single ion hydration enthalpy for the $Sb(OH)_6^-$ ion, -124 kJ mol^{-1},[30] is much smaller numerically than that of SbF_6^-, but this was based upon a lattice enthalpy obtained from a simple Born-Mayer calculation assuming q(Sb) = -1.

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