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A computational study of Sb_nF_{5n} ($n = 1$–4) Implications for the fluoride ion affinity of nSbF$_5$

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Abstract

This contributions shows with a series of ab initio MP2 and DFT (BP86 and B3-LYP) computations with large basis sets up to cc-pVQZ quality that the literature value of the standard enthalpy of depolymerization of $\frac{1}{4}Sb_4F_{20(g)}$ to give $SbF_{5(g)}$ (+18.5 kJ mol^{-1}) [J. Fawcett, J.H. Holloway, R.D. Peacock, D.R. Russell, J. Fluorine Chem. 20 (1982) 9] is by about 50 kJ mol^{-1} in error and that the correct value of $\Delta_rH^\circ_{depoly.}$ ($\frac{1}{4}Sb_4F_{20(g)}$) is +68 ± 10 kJ mol^{-1}. We assign $\Delta_rH^\circ_{depoly.}$, Δ_rH°, Δ_rG° and Δ_rG° values for Sb_nF_{5n} with $n = 2$–4 and compare the results to available experimental gas phase data. Especially the MP2/TZVPP values obtained in an indirect procedure that rely on isodesmic reactions or the highly accurate compound methods G2 and CBS-Q are in excellent agreement with the experimental data, and reproduce also the fine experimental details at temperatures of 423 and 498 K. With these data and the additional calculation of $[Sb_nF_{5n+1}]^-$ ($n = 1$–4), we then assessed the fluoride ion affinities (FIAs) of $Sb_nF_{5n(g)}$, $nSbF_{5(g)}$, $nSbF_{5(l)}$ and the standard enthalpies of formation of $Sb_nF_{5n(g)}$ and $[Sb_nF_{5n+1}]^-{}_{(g)}$: FIA($Sb_nF_{5n(g)}$) = 514 ($n = 1$), 559 ($n = 2$), 572 ($n = 3$) and 580 ($n = 4$) kJ mol^{-1}; FIA($nSbF_{5(g)}$) = 667 ($n = 2$), 767 ($n = 3$) and 855 ($n = 4$) kJ mol^{-1}; FIA($nSbF_{5(l)}$) = 434 ($n = 1$), 506 ($n = 2$), 528 ($n = 3$) and 534 ($n = 4$) kJ mol^{-1}. Error bars are approximately ±10 kJ mol^{-1}. Also the related Gibbs energies were derived. $\Delta_fH^\circ([Sb_nF_{5n+1}]^-{}_{(g)}) = -2064 \pm 18$ ($n = 1$), -3516 ± 25 ($n = 2$), -4919 ± 31 ($n = 3$) and -6305 ± 36 ($n = 4$) kJ mol^{-1}.

Keywords: Fluoride ion affinity; Antimony; Ab initio; Compound methods; Thermodynamics

1. Introduction

Antimony pentafluoride is a reagent frequently used to generate salts containing highly reactive countercations [1,2]. Under ambient conditions, SbF_5 is a highly viscous liquid which contains polymeric macromolecules of the formula $(SbF_5)_x$ (x is very large) in which the octahedrally coordinated antimony atoms are connected via *cis*-bridging fluorine atoms. The X-ray structure showed that solid SbF_5 is a tetramer [3]. $SbF_{5(l)}$ acts as an oxidizing agent as well as a very strong Lewis acid and generates anions of the general formula $[Sb_nF_{5n+1}]^-$; salts with $n = 1$–4 were hitherto characterized in the solid state by X-ray diffraction. It was shown by electron diffraction [4] and vapor density measurements [5,6] that a mixture of mostly $Sb_3F_{15(g)}$ with little $Sb_4F_{20(g)}$ evaporates from $SbF_{5(l)}$ and the standard enthalpy Δ_rH° for the process (1)

$$Sb_3F_{15(l)} \xrightarrow{\Delta_rH^\circ} Sb_3F_{15(g)} \tag{1}$$

was 43.4 or 45.2 kJ mol^{-1} [7,8]. The depolymerization of gaseous Sb_4F_{20} to monomeric SbF_5 given in Eq. (2)

$$\frac{1}{4}Sb_4F_{20(g)} \xrightarrow{\Delta_rH^\circ} SbF_{5(g)} \tag{2}$$

was estimated to be $\Delta_rH^\circ = +18.5$ kJ mol^{-1} [6]. Both values are important in order to assess the fluoride ion affinity (FIA) of liquid SbF_5, which is, in turn, often used to predict the

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outcome of hitherto unknown reactions. The FIA of any Lewis acid A is defined as in Eq. (3)

$$A_{(g)} + F^{-} \xrightarrow{\Delta_r H^\circ = -\mathrm{FIA}} AF^{-} \qquad (3)$$

and FIA values for various Lewis acids have been assessed with lattice energy considerations [2,9,10] as well as quantum chemical calculations [11–15].

The present computations suggest that the enthalpy of depolymerization $\Delta_r H^\circ$ of +18.5 kJ mol^{-1} for $\frac{1}{4}Sb_4F_{20}$ as in Eq. (2) is by about 50 kJ mol^{-1} in error, based on a series of quantum chemical calculations at various levels and with increasingly larger basis sets. We also calculated the structures of the gaseous $[Sb_nF_{5n+1}]^-$ anions at various levels and include the most accurate calculation of the FIAs of $nSbF_{5(g)}$ and $Sb_nF_{5n(g)}$ currently available. The revised $\Delta_r H^\circ$ of gaseous Sb_nF_{5n} was then included to extract the FIAs of $nSbF_5$ in the liquid state and to establish standard enthalpies of formation $\Delta_f H^\circ$ of Sb_nF_{5n} as well as for $[Sb_nF_{5n+1}]^-$ (n = 1–4).

2. Results and discussion

The strategy adopted in this paper is to address some accuracy considerations and then select a suitable model for our calculations giving a brief description of the global minimum geometries. Using the selected model, we then analyze the thermodynamics of the system with regard to the depolymerization and interconversion of Sb_nF_{5n} as well as the fluoride ion affinities of various antimony fluorides. We conclude this section with the assessment of the standard enthalpies of formation of Sb_nF_{5n}, as well as those for the anions $[Sb_nF_{5n+1}]^-$.

2.1. Selection of the model: basis set and correlation effects

Modeling fluorine-containing molecules is known to represent a difficult computational challenge. We consider first how satisfactory the different levels and basis sets available to us are able to describe a simple test reaction (4):

$$\frac{1}{2}\underset{D_{2h}}{Sb_2F_{10(g)}} \xrightarrow[\text{direct value}]{\Delta_r H^\circ = ?} \underset{D_{3h}}{SbF_{5(g)}} \qquad (4)$$

This provides a convenient and relatively computationally fast test reaction, due to the high local symmetry of both, Sb_2F_{10} (D_{2h}) and SbF_5 (D_{3h}). Since the *direct* calculation of $\Delta_r H^\circ$ of reaction (4) is non isodesmic, an additional approach was required in order to independently assess this quantity indirectly. Here we use an isodesmic reaction in conjunction with a highly accurate compound method (G2 and CBS-Q were selected) and reaction (5) was chosen for the indirect calculation:

$$AlF_3 + \frac{1}{2}Sb_2F_{10} \xrightarrow{\text{isodesmic}} SbF_5 + \frac{1}{2}Al_2F_6 \qquad (5a)$$

$$\frac{1}{2}Al_2F_6 \xrightarrow[(\text{G2+CBS-Q})/2]{\text{non isodesmic}} AlF_3 \qquad (5b)$$

$$\frac{1}{2}Sb_2F_{10(g)} \xrightarrow[\text{indirect calc.}]{\Delta_r H^\circ = ?} SbF_{5(g)} \qquad (5)$$

Eq. (5a) represents an isodesmic process and its computation is likely to be accurate and any errors are likely to cancel. The second reaction (5b) is a non-isodesmic process which utilizes the average of the values calculated by the G2 and CBS-Q compound methods, which are reported [16–18] to reproduce experimental quantities with an accuracy of better than ±8 kJ mol^{-1}. The latter computation was taken from our earlier work, in which G2 gave $\Delta_r H^\circ$ of Al_2F_6 to be 204.4 kJ mol^{-1} while CBS-Q gave the value 195.2 kJ mol^{-1}. We have adopted the average: (G2 + CBS-Q)/2 = 199.8 kJ mol^{-1} to indirectly establish $\Delta_r H^\circ$ of Eq. (5). A table with necessary G2 and CBS-Q data is deposited.

Table 1 summarizes values of $\Delta_r H^\circ$ and $\Delta_r G^\circ$ based on the direct and indirect computational routes above and obtained using pure DFT (BP86), hybrid HF-DFT (B3-LYP) and ab initio (MP2) calculations and with increasing the basis set size from SVP (double zeta quality, one d polarization function) through TZVPP (triple zeta quality, two d and one f polarization functions) to cc-pVQZ (quadruple zeta quality, three d, two f and one g polarization functions). A TZVPP basis is reported to be already close to the basis set limit of the DFT and HF-DFT calculations while the quadruple zeta basis cc-pVQZ is close to the basis set limit of MP2.

The values collected in Table 1 show consistent trends throughout and both the free energy and the enthalpy of depolymerization differ by a maximum of 42 kJ mol^{-1}. Analyzing firstly the non-isodesmic *direct* values (labeled ‘a’ in Table 1). Increasing the basis set size from SVP through TZVPP to cc-pVQZ lowers the direct values (of both $\Delta_r H^\circ$ and $\Delta_r G^\circ$) by up to 31 kJ mol^{-1}. The *direct* values obtained using the TZVPP and the cc-pVQZ basis sets agree more closely than those generated using SVP and are within 7–13 kJ mol^{-1}. BP86 and B3-LYP give almost

Table 1
$\Delta_r H^\circ$ (Eq. (4)) and $\Delta_r G^\circ$ (Eq. (4)) values in kJ mol^{-1} obtained with pure DFT (BP86), hybrid HF-DFT (B3-LYP1) and ab initio (MP2) calculations with increasing basis set sizes from SVP to TZVPP and cc-pVQZ

Method	$\Delta_r H^\circ$ (Eq. (4))			$\Delta_r G^\circ$ (Eq. (4))		
	SVP	TZVPP	cc-pVQZ	SVP	TZVPP	cc-pVQZ
BP86	62[a]/45[b]	41[a]/51[b]	31[a]/**43**[b]	37[a]/23[b]	15[a]/29[b]	7[a]/**20**[b]
B3-LYP	66[a]/43[b]	42[a]/47[b]	33[a]/**41**[b]	40[a]/21[b]	16[a]/25[b]	9[a]/**17**[b]
MP2	73[a]/46[b]	57[a]/54[b]	44[a]/**46**[b]	48[a]/25[b]	31[a]/32[b]	21[a]/**21**[b]

Values in bold are considered being the most accurate ones.

[a] Direct calculation, non-isodesmic.

[b] Indirect calculation via Eq. (5); isodesmic or (G2 + CBS-Q)/2.

identical values in all cases. We infer from this that the low $\Delta_r H^\circ$ (Eq. (4)) and $\Delta_r G^\circ$ (Eq. (4)) values obtained with the BP86 and B3-LYP levels with the largest basis set are at the basis set limit of the respective methods and therefore represent the "best" direct DFT values of approximately 31 ($\Delta_r H^\circ$ (Eq. (4))) and 7 kJ mol^{-1} ($\Delta_r G^\circ$ (Eq. (4))). In contrast, the MP2 method at the basis set limit gives values about 10–15 kJ mol^{-1} higher for $\Delta_r H^\circ$ (Eq. (4)) and $\Delta_r G^\circ$ (Eq. (4)). Thus, there is only moderate agreement between DFT and MP2 calculations when using the *direct* values. Turning now to the *indirect* values calculated according to the procedure in Eq. (5). As expected, direct and indirect values differ more (up to 27 kJ mol^{-1}) with the smaller SVP basis. With the larger basis sets, the maximum deviation between direct and indirect values is much reduced, 12 kJ mol^{-1} being typical. Regardless of the basis set, all indirect values ($\Delta_r H^\circ$ (Eq. (4)) lie in the narrow range of 41–54 and of 17–21 kJ mol^{-1} ($\Delta_r G^\circ$ (Eq. (4)). The "best" *indirect* values with the largest cc-pVQZ basis are marked in bold in Table 1 and agree to within 3–5 kJ mol^{-1} both for $\Delta_r H^\circ$ (Eq. (4)) and $\Delta_r G^\circ$ (Eq. (4)) due to error cancellation. The more accurate depolymerization values are thus the *indirect* ones. Since the difference between the indirect values calculated with a TZVPP and a cc-pVQZ basis is at most 8 kJ mol^{-1}, we use the computationally much more economic TZVPP basis and the indirect procedure as in Eq. (5) for all further computations. BP86 and B3-LYP give almost identical values and, therefore, we use the less demanding BP86 method for further work.

2.2. Molecular structures

The molecular structures of the optimized compounds are shown in Fig. 1 (neutrals) and Fig. 2 (anions), the calculated structural parameters are collected in Table 2 and are compared to available experimental data. Readers interested in the finer structural details of the optimized compounds are referred to the supplementary information, where *xyz* orientations of each compound are deposited.

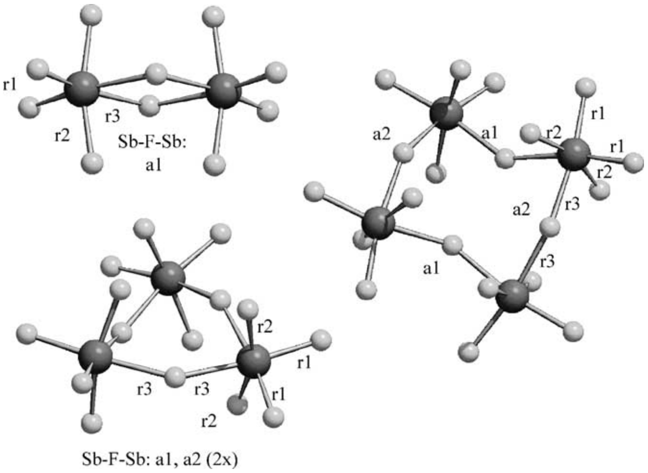

Fig. 1. Molecular structures of Sb_nF_{5n} with $n = 2$–4. The structural parameters at the BP86/TZVPP and MP2/TZVPP levels are collected in Table 2.

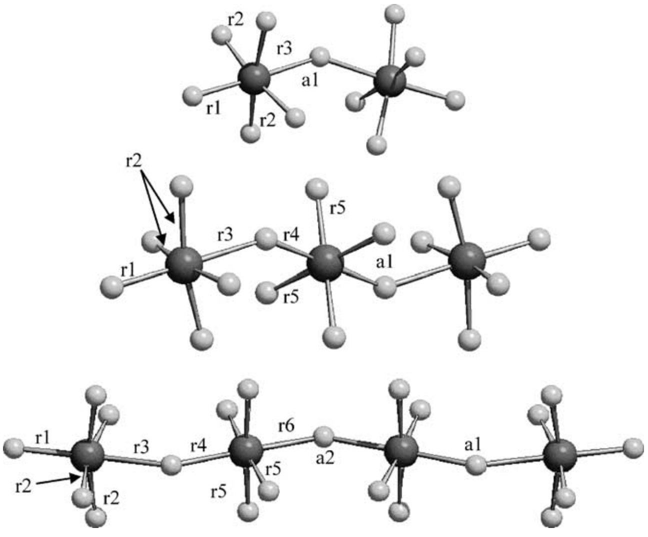

Fig. 2. Molecular structures of $[Sb_nF_{5n+1}]^-$ with $n = 2$–4. The structural parameters at the BP86/TZVPP and MP2/TZVPP levels are collected in Table 2.

The calculated and available experimental data displayed in Table 2 are in good qualitative agreement. The MP2 derived geometries are particularly close to experiment. However, many of the experimental structures are hampered by the lack of librational correction of the bond lengths and bond angles and, therefore, consistently give too short bond distances and bond angles that are too wide. Therefore, we believe that the correct structural parameters of these antimony fluorine compounds are likely to be intermediate between the MP2 values and the experimental values collected in Table 2.

2.3. Depolymerization and interconversion of Sb_nF_{5n} ($n = 2$–4)

We now turn to the question, as to whether the literature value of the experimentally derived [6] enthalpy of depolymerization $\Delta_r H^\circ$ (Eq. (2)) of +18.5 kJ mol^{-1} is correct or in error. Our starting point for this discussion shall be the assessment of $\Delta_r G^\circ$ (Eq. (2)) based on the experimental standard depolymerization enthalpy $\Delta_r H^\circ$ (Eq. (2)) of +18.5 kJ mol^{-1}: $\Delta_r G^\circ$ (Eq. (2)) was obtained as −15.1 kJ mol^{-1} based on the estimation of the reaction entropies and associated thermal contributions to the enthalpy at 298 K, as calculated with the help of the BP86/SVP derived vibrational frequencies for SbF_5 and Sb_4F_{20}. Since $Sb_3F_{15(g)}$ and $Sb_4F_{20(g)}$ were shown to be in equilibrium in the gas phase, we assume that they are thus close in energy. Further the depolymerization of $\frac{1}{3}Sb_3F_{15}$ and of $\frac{1}{4}Sb_4F_{20}$ to give monomeric SbF_5 are expected to be almost equal in energy and therefore a similar value of $\Delta_r G^\circ$ ($\frac{1}{3}Sb_3F_{15}$) of approximately −15 kJ mol^{-1} can be anticipated. If these values of $\Delta_r G^\circ$ are correct, then one would

Table 2
The structural parameters of Sb_nF_{5n} as well as $[Sb_nF_{5n+1}]^-$ (n = 2–4) at the BP86/TZVPP and MP2/TZVPP levels

	Sb_2F_{10}			Sb_3F_{15} [4]			Sb_4F_{20} [3]		
	Exp.	BP86	MP2	Exp.	BP86	MP2	Exp.	BP86	MP2
r1 (pm)	–	187	185	181	187–188	184–185	182	187–188	184–185
r2 (pm)	–	188	185	181	187–188	184–185	182	187–188	184–185
r3 (pm)	–	210	206	204	208–209	204–205	203	208	204
a1 (°)	–	108	109	150	153	154	141	154–155	151
a2 (°)	–	–	–	150	152	153	170	148–149	150
	$[Sb_2F_{11}]^-$ [19]			$[Sb_3F_{16}]^-$ [20]			$[Sb_4F_{21}]^-$ [21]		
r1 (pm)	185	191	187	181–184	190	187	184–185	189	186
r2 (pm)	185	190	187	181–184	190	187	184–185	189–190	186–187
r3 (pm)	202	210	204	210	216	210	210	220	214
r4 (pm)	–	–	–	197	203	198	198	200	196
r5 (pm)	–	–	–	181–184	189	186	184–185	188–189	185–186
r6 (pm)	–	–	–	–	–	–	201	208	203
a1 (°)	Flexible	147	160	146	150	150	–	149	149
a2 (°)	–	–	–	–	–	–	–	150	150

Labeling according to Figs. 1 and 2.

expect $SbF_{5(l)}$ to evaporate exclusively to give monomeric $SbF_{5(g)}$. However, this is clearly not the case and indicates that the published Δ_rH° (Eq. (2)) of +18.5 kJ mol^{-1} is wrong. This conclusion and the BP86/SVP calculated thermal and entropic corrections to the free energy at 298 K (which sum to −33.6 kJ mol^{-1}) then allow us to estimate that the experimental Δ_rH° (Eq. (2)) should at least amount to 60 ± 15 kJ mol^{-1} and thus that Δ_rG° (Eq. (2)) should be about 26 ± 15 kJ mol^{-1} in order to allow for the exclusive presence of Sb_3F_{15} and Sb_4F_{20} in the gas phase at the temperatures corresponding to those of the electron diffraction studies [4] (423 K). With these values in mind, we further studied the standard enthalpy and free energy changes on depolymerization of $\frac{1}{n}\cdot Sb_nF_{5n(g)}$ to give $SbF_{5(g)}$, the values of which are given in Table 3. To enable a direct comparison with the conditions of the electron diffraction [4] and vapor density measurement [5,6] studies also the $\Delta_rG^{423\,K}_{depoly.}$ and $\Delta_rG^{498\,K}_{depoly.}$ values were calculated and these are included in Table 3. At 423 K the vapor above liquid SbF_5 consists of mostly Sb_3F_{15} with little Sb_4F_{20} while at 498 K the major component is Sb_2F_{10}. Only the more reliable *indirect* values obtained by procedures related to Eq. (5) are given. The enthalpies and free energies for the interconversion of Sb_nF_{5n} in Eqs. (9)–(11) reflect the gas-phase behavior of the Sb_nF_{5n} molecules as well as the degree of association in the gas phase that was determined [5,6] experimentally. Therefore, Δ_rH° and Δ_rG° were also studied. The latter reactions are isodesmic and thus the computations made should be accurate.

The depolymerization enthalpies Δ_rH° in Eqs. (6)–(8) lie in the range of 59 ± 9 kJ mol^{-1} and are thus close to the value predicted above based on experimental considerations (60 ± 15 kJ mol^{-1}). On inspection of Eqs. (9)–(11), one realizes that *only the MP2/TZVPP calculations* describe the experimental electron diffraction and vapor density measurement results adequately (much Sb_3F_{15} and little Sb_4F_{20} at 423 K and much Sb_2F_{10} at 498 K in the gas phase). Thus, in agreement with the experiment, the interconversion of the slightly less favorable Sb_4F_{20} into the slightly more favorable Sb_3F_{15} in Eq. (11) is at 298 and 423 K slightly exergonic by 1.5 and 3.5 kJ mol^{-1}. By contrast, the BP86/TZVPP values would suggest that in the gas phase at 423 K only Sb_2F_{10} is (exclusively) formed (i.e. Eqs. (9) and (10) are already exergonic at 298 K by 3.9 or 9 kJ mol^{-1} and at

Table 3
Standard enthalpies and free energies for the depolymerization of $1/n\cdot Sb_nF_{5n(g)}$ to give $SbF_{5(g)}$ and for the interconversion of Sb_nF_{5n} with differing n

Eq.	Reaction	Δ_rH°		Δ_rG°		$\Delta_rG^{423\,K}$		$\Delta_rG^{498\,K}$	
		BP86	MP2	BP86	MP2	BP86	MP2	BP86	MP2
(6)	$\frac{1}{2}Sb_2F_{10} \rightarrow SbF_5$	50	53	29	32	20	22	14	17
(7)	$\frac{1}{3}Sb_3F_{15} \rightarrow SbF_5$	54	65	25	36	12	23	4.7	15
(8)	$\frac{1}{4}Sb_4F_{20} \rightarrow SbF_5$	54	68	20	34	5	19	−3.4	11
(9)	$\frac{1}{3}Sb_3F_{15} \rightarrow \frac{1}{2}Sb_2F_{10}$	4.2	12	−3.9	3.8	−7	0.5	−9	−1.5
(10)	$\frac{1}{4}Sb_4F_{20} \rightarrow \frac{1}{2}Sb_2F_{10}$	2.6	14	−9	2.3	−14	−2.9	−17	−6
(11)	$\frac{1}{4}Sb_4F_{20} \rightarrow \frac{1}{3}Sb_3F_{15}$	−0.4	3.2	−5.1	−1.5	−7	−3.5	−8	−4.6

Only the (more reliable) indirect values are included (in kJ mol^{-1}) (using a TZVPP basis).

423 K by 7 and 14 kJ mol^{-1}). This does not correspond to the situation found in the experiment. However, in agreement with the experiment, at 498 K also the MP2/TZVPP predicted $\Delta_r G^{498\,K}_{\text{interconv.}}$ suggests that the most favored species in the gas phase is Sb_2F_{10} (Eq. (9) is now exergonic by -1.5 kJ mol^{-1}). Since the MP2 results appear to predict the experimental outcome best, we exclude the BP86/TZVPP values from further discussion and use exclusively the MP2/TZVPP values in order to establish the FIAs and other properties.

2.3.1. Assignment of error bars

Due to the excellent agreement of the MP2/TZVPP values with available experimental data, we estimate error bars to be at most ±10 kJ mol^{-1} for the calculations (enthalpies, free energies and FIAs). For the assignment of the enthalpies of formation below, the experimental $\Delta_f H(SbF_5(g))$ with an uncertainty of ±15 kJ mol^{-1} has to be used. For the assessed enthalpies of formation, the error bars, therefore, add up to $\sqrt{10^2 + 15^2} = \pm 18$ kJ mol^{-1} (enthalpies of formation below).

2.4. Fluoride ion affinities of nSbF$_5$ and Sb$_n$F$_{5n}$ in the gas phase (n = 1, 2, 3, 4)

We now assess the FIAs of nSbF$_5$ and Sb$_n$F$_{5n}$ (n = 1, 2, 3, 4) in the gas phase. The case for n = 1 is simple and the same isodesmic reaction as was initially introduced by Christe and Dixon may be used, i.e. Eq. (12) [13]:

$$A + OCF_3^- \xrightarrow{\text{isodesmic}} AF^- + OCF_2$$

$$OCF_2 + F^- \xrightarrow{\text{experimental value}} OCF_3^-$$

$$A + F^- \xrightarrow{-\Delta_r H^\circ = \text{FIA}} AF^- \qquad (12)$$

However, when fluoride-bridged Sb$_n$F$_{5n}$ or [Sb$_n$F$_{5n+1}$]$^-$ species are involved, the situation is more complicated and Eq. (12) becomes non-isodesmic and thus less reliable. Accordingly, we introduce an alternative scheme in order to assess the FIAs of fluoride-bridged species reliably that is shown exemplarily for Sb$_2$F$_{10}$ in Eq. (13) and for nSbF$_5$ in Eq. (14).

$$Sb_2F_{10} + Al_2F_7^- \xrightarrow{\text{isodesmic}} Sb_2F_{11}^- + Al_2F_6$$

$$Al_2F_6 + OCF_3^- \xrightarrow[\text{(G2+CBS-Q)/2}]{\text{non-isodesmic}} Al_2F_7^- + OCF_2$$

$$OCF_2 + F^- \xrightarrow{\text{experimental value}} OCF_3^-$$

$$Sb_2F_{10} + F^- \xrightarrow{-\Delta_r H^\circ = \text{FIA}} Sb_2F_{11}^- \qquad (13)$$

All non-isodesmic reactions were calculated by the very accurate compound methods G2 and CBS-Q and, therefore, the addition of the isodesmic reaction with the average of the enthalpies calculated by G2 and CBS-Q as in Eq. (13) gives very reliable values of the FIAs of Sb$_n$F$_{5n}$. A table with the G2 and CBS-Q data is deposited. To further obtain the FIAs of n monomeric SbF$_5$ molecules, one simply has to add the best indirect $\Delta_r H^\circ$ values in Table 3 to the FIAs of Sb$_n$F$_{5n}$, i.e. Eq. (14):

$$\text{FIA}(nSbF_{5(g)}) = \text{FIA}(Sb_nF5_{n(g)}) + \Delta_r H^\circ_{\text{depoly.}}\ (\text{Table 3}) \qquad (14)$$

All FIA values are included in Table 4 and compared to available literature data.

The data included in Table 4 is in good agreement with existing literature data, however, we are able to estimate a more complete set of FIA values and the first values for Sb$_4$F$_{20}$ and 4SbF$_4$. One realizes that the Lewis acidity of Sb$_n$F$_{5n}$ increases with increasing n more slowly and that the Lewis acidity of Sb$_4$F$_{20}$ is only little higher than that of Sb$_3$F$_{15}$. This accords with experimental experience [2].

2.5. Fluoride ion affinity of nSbF$_5$ liquid (n = 1–4)

Having established the FIAs of gaseous antimony fluorides, we now turn to the FIA of n liquid SbF$_5$ molecules, since liquid SbF$_5$ itself is frequently used as a reaction medium. Comparison of melting point (m.p.), boiling point (b.p.) and $\Delta_r H^\circ_{\text{vap.}}$ of SbF$_5$ with those of several related binary halides having a similar liquid state temperature range as SbF$_5$ (Table 5) leads us to the conclusion that the experimental standard enthalpy of

Table 4
Fluoride ion affinities of nSbF$_5$ and Sb$_n$F$_{5n}$ (n = 1–4) in the gas-phase (MP2/TZVPP)

FIA of	FIA [13] (Dixon)	FIA [10] (Jenkins)	$-\Delta_r H^\circ$ = FIA (this work)	$-\Delta_r G^\circ$ (this work)
$SbF_{5(g)}$	503	506 ± 63	514	512
$Sb_2F_{10(g)}$	556[a]	–	559	521
$Sb_3F_{15(g)}$	570[a]	–	572	543
$Sb_4F_{20(g)}$	–	–	580	561
$2SbF_{5(g)}$	–	671 ± 63	667	585
$3SbF_{5(g)}$	–	728 ± 39	767	651
$4SbF_{5(g)}$	–	–	855	697

Comparison to available literature data (in kJ mol^{-1}).

[a] Not yet published. Cited as personal communication to H.D.B.J. in Ref. [10].

Table 5
Comparison of the melting point (m.p.), boiling point (b.p.) and $\Delta_r H^\circ_{vap.}$ of SbF_5 with those of several binary halides with a similar liquid state range as SbF_5

Binary halide	m.p. (°C)	b.p. (°C)	$\Delta_r H^\circ_{vap.}$ (kJ mol^{-1})
SbF_5	8.3	141	43.4/45.2
$AsCl_3$	−16	130	43.5
$TiCl_4$	−25	136	41.0
$SiBr_4$	5.2	154	41.8
PBr_3	−40	173	45.2

vaporization $\Delta_r H^\circ_{vap.}$ (averaging to 44 kJ mol^{-1} as in Eq. (1)) appears to be reasonably consistent with $\Delta_r H^\circ_{vap.}$ values for all other related halides and, therefore, is considered to be accurate.

For the determination of the FIA of liquid SbF_5, we therefore adopt the average value $\Delta_r H^\circ_{vap.} \approx 44$ kJ mol^{-1} and develop a thermochemical cycle from which this quantity may be assessed; a suitable cycle is shown in Eq. (15):

$$\begin{tikzcd}
n/3\ Sb_3F_{15\,(g)} + F^-_{(g)} \arrow[r, "+\Delta_r H^\circ_{interconv.}"] & Sb_nF_{5n\,(g)} + F^-_{(g)} \arrow[d, "\Delta_r H^\circ = -FIA(Sb_nF_{5n\,(g)})"] \\
n\ SbF_{5\,(l)} + F^-_{(g)} \arrow[u, "+ n/3\ \Delta_r H^\circ_{vap.}"] \arrow[r, "-\Delta_r H^\circ = FIA(n\ SbF_{5\,(l)})"] & {[Sb_nF_{5n+1}]^-_{(g)}}
\end{tikzcd} \quad (15)$$

All quantities in the peripheral cycle are known and therefore the FIAs of nSbF$_5$(l) can be established (Table 6) based on the MP2/TZVPP values in Tables 3 and 4 and the experimental $\Delta_r H^\circ_{vap.}$ verified above. The values in Table 6 are compared to available literature data.

Naturally, the calculated FIAs of n liquid SbF_5 molecules are much lower than those of the gaseous compounds. Again the same trend as for gaseous antimony fluorides is evident. The higher the n, the higher is the FIA, however, the increase in FIA is slowing down for increasing n. The large difference to the published values arises from adoption of too low a value for the enthalpy of depolymerization of Sb_4F_{20} giving $\frac{1}{4}SbF_5$ (+18.5 kJ mol^{-1} instead of 68 kJ mol^{-1} in Table 3). When the published values are corrected for this error, i.e. lowered by 49.5 kJ mol^{-1} per SbF_5, then present and corrected literature values are in good qualitative agreement.

Table 6
Fluoride ion affinities FIA(nSbF$_{5(l)}$) of nSbF$_5$ as a liquid according to Eq. (15) (n = 1–4) (in kJ mol^{-1})

FIA of	FIA(nSbF$_{5(l)}$) (Jenkins) [10]	$-\Delta_r H^\circ$(Eq. (15)) = FIA(nSbF$_{5(l)}$) (this Work)
$SbF_{5(l)}$	475 ± 63 (425 ± 63)	434 ± 18
$2SbF_{5(l)}$	609 ± 63 (510 ± 63)	506 ± 18
$3SbF_{5(l)}$	635 ± 39 (487 ± 39)	528 ± 18
$4SbF_{5(l)}$	–	534 ± 18

Comparison to available literature data. The literature values in parentheses were corrected for the wrong enthalpy of depolymerization (see text).

Table 7
$\Delta_f H^\circ$ values of $Sb_nF_{5n(g)}$ and $[Sb_nF_{5n+1}]^-_{(g)}$ calculated according to Eqs. (16) and (17) (in kJ mol^{-1})

n	$\Delta_f H^\circ(Sb_nF_{5n(g)})$ (this work)	$\Delta_f H^\circ([Sb_nF_{5n+1}]^-_{(g)})$ (this work)	$\Delta_f H^\circ([Sb_nF_{5n+1}]^-_{(g)})$ (Jenkins) [10]
1	−1301 ± 15 [10]	−2064 ± 18	−2075 ± 52
2	−2708 ± 21	−3516 ± 25	−3520 ± 63
3	−4098 ± 26	−4919 ± 31	−4874 ± 39
4	−5476 ± 30	−6305 ± 36	–

Comparison to available literature data.

2.6. *Standard enthalpies of formation of Sb_nF_{5n} and $[Sb_nF_{5n+1}]^-$ (n = 1–4)*

The standard enthalpies of formation $\Delta_f H^\circ$ of SbF_5(g) (−1301 ± 15 kJ mol^{-1}) and F$^-$ (−249 kJ mol^{-1}) are known and thus $\Delta_f H^\circ$ of $Sb_nF_{5n(g)}$ and $[Sb_nF_{5n+1}]^-_{(g)}$ can be calculated from $\Delta_r H^\circ$ (Table 3) and the FIAs of $Sb_nF_{5n(g)}$ (Table 4). Thus

$$\Delta_f H^\circ(Sb_nF_{5n(g)}) = n \cdot \Delta_f H^\circ(SbF_{5(g)}) - \Delta_f H^\circ_{depoly.}(Sb_nF_{5n(g)}) \quad (16)$$

$$\Delta_f H^\circ([Sb_nF_{5n+1}]^-) = \Delta_f H^\circ(Sb_nF_{5n(g)}) + \Delta_f H^\circ(F^-) - FIA(Sb_nF_{5n}) \quad (17)$$

All $\Delta_f H^\circ$ values calculated by this approach are collected in Table 7 and compared to available literature data.

The standard enthalpies for the formation of $Sb_nF_{5n(g)}$ and $[Sb_nF_{5n+1}]^-_{(g)}$ increase with increasing n and are in good agreement with available literature data. They may be used to assess the thermodynamics of known and unknown reactions (see, e.g. [2]).

3. Conclusion

We have shown that the literature value for the enthalpy of depolymerization of $Sb_4F_{20(g)}$ to give $SbF_{5(g)}$ was by about 50 kJ mol^{-1} in error. This error contributes n times to the previously established FIAs of nSbF$_{5(l)}$ such that the reported literature values [10] were by up to 148.5 kJ mol^{-1} (n = 3) in error. The present enthalpies of depolymerization of $\frac{1}{n}\cdot Sb_nF_{5n(g)} \rightarrow SbF_{5(g)}$ are the most accurate values currently available and are in agreement with the experimental results obtained by electron diffraction [4] and vapor density measurements [5,6]. All subsequently derived quantities such as FIAs of $Sb_nF_{5n(g)}$, nSbF$_{5(g)}$, nSbF$_{5(l)}$ and the standard enthalpies of formation of $Sb_nF_{5n(g)}$ and $[Sb_nF_{5n+1}]^-_{(g)}$ are considered to be equally accurate and thus will be very useful to assess the thermodynamics of known as well as hitherto unknown reactions (see [2]).

Table A.1
Total energies $U^{0\ \mathrm{K}}$, ZPEs, H°, G°, $G^{423\ \mathrm{K}}$ and $G^{498\ \mathrm{K}}$ at the MP2/TZVPP level (in [Hartree])

Species	$U^{0\ \mathrm{K}}$	ZPE	H°	G°	$G^{423\ \mathrm{K}}$	$G^{498\ \mathrm{K}}$
$[SbF_6]^-$	−604.08481	0.01107	−604.06364	−604.10534	–	–
$[Sb_2F_{11}]^-$	−1108.30383	0.02389	−1108.26188	−1108.32708	–	–
$[Sb_3F_{16}]^-$	−1612.50431	0.03547	−1612.44068	−1612.53135	–	–
$[Sb_4F_{21}]^-$	−2116.69761	0.04671	−2116.61317	−2116.72908	–	–
SbF_5	−504.15798	0.01035	−504.13911	−504.17942	−504.19727	−504.20882
Sb_2F_{10}	−1008.35997	0.02233	−1008.32038	−1008.38331	−1008.41175	−1008.43060
Sb_3F_{15}	−1512.55457	0.03375	−1512.49428	−1512.57936	−1512.61821	−1512.64425
Sb_4F_{20}	−2016.74506	0.04551	−2016.66391	−2016.77018	−2016.81902	−2016.85200
AlF_3	−541.43589	0.00764	−541.42281	−541.45452	−541.46837	−541.47717
$[AlF_4]^-$	−641.35103	0.00998	−641.33457	−641.36816	–	–
Al_2F_6	−1082.95014	0.01758	−1082.92197	−1082.96753	−1082.98787	−1083.00117
$[Al_2F_7]^-$	−1182.87235	0.01928	−1182.84069	−1182.89245	–	–
OCF_2	−312.62546	0.01380	−312.60740	−312.63690	–	–
$[OCF_3]^-$	−412.43652	0.01542	−412.41593	−412.44745	–	–

The ZPEs and thermal corrections to the enthalpy and entropy at 298, 423 and 498 K were taken from the BP86/SVP frequency calculation.

4. Computational details

All computations – except the G2 and CBS-Q calculations – were performed using the program TURBOMOLE [22]. The geometries were optimized at the (RI)-BP86 [23,24], B3LYP [24–26] and/or (RI)-MP2 [27,28] level with the SV(P) [29] and the TZVPP basis set [30]. Additionally, single point calculations of SbF_5 and Sb_2F_{10} using the Method/TZVPP geometry and Dunning's larger cc-pVQZ basis set [31] were performed to analyze the basis set dependence of the methods. Frequency calculations [32] of all compounds were performed at the BP86/SV(P) level and all species represent true minima without imaginary frequencies on the respective potential energy surface (deposited). The G2 [17] and CBS-Q [16,18] calculations were done with Gaussian'98 [33]. For all calculations zero point energies (BP86/SVP quality) and thermal corrections to the enthalpy at 298, 423 and 498 K as calculated with the program FreeH included with TURBOMOLE on the basis of the BP86/SVP geometries and frequencies are included. The good agreement found between the thermochemically derived literature values and the computationally derived thermodynamic parameters reported here firmly establishes these numbers.

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Appendix A

Table A.1 contains the total energies and corrections to standard and non-standard conditions (298, 423 and 498 K with 1 atm pressure) of all species included in this article. They may be used for further computations.

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2004.09.016.

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