

Synthesis and Characterization by Raman Spectroscopy of $\text{AsBr}_4\text{AsF}_6$; its Thermodynamic and Kinetic Stability and that of Related Salts †

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The thermodynamically and kinetically unstable salt $\text{AsBr}_4\text{AsF}_6$ was prepared by the reaction of stoichiometric quantities of AsBr_3 , Br_2 , and AsF_5 , and characterized by Raman spectroscopy at -196°C . It was shown by Raman spectroscopy that $\text{AsBr}_4\text{AsF}_6$ decomposes to AsF_3 and Br_2 via AsBr_3 . The energetics of the formation and decomposition have been estimated, and reaction pathways suggested. Simple estimates of the energetics of the formation of $\text{AsBr}_4\text{AlBr}_4$ showed it should have greater stability than that of $\text{AsBr}_4\text{AsF}_6$; it was subsequently prepared but shown to be in equilibrium at room temperature with AsBr_3 , Br_2 , and $\text{AsBr}_4\text{Al}_2\text{Br}_7$. The differences in thermodynamic stability of $\text{AsCl}_4\text{AsF}_6$ and $\text{AsBr}_4\text{AsF}_6$ have been accounted for, and reasons for the kinetic instability of $\text{AsBr}_4\text{AsF}_6$ proposed.

We have been able to estimate‡ the enthalpy of formation and relative stabilities of the hexafluoroarsenate salts of the simpler homopolyatomic cations of Groups 16 and 17,¹ MBr_3AsF_6 ($\text{M} = \text{S}$ or Se),^{2a} SeI_3AsF_6 ,^{2a} $\text{Se}_2\text{Br}_5\text{AsF}_6$,^{2b} and to account for the non-existence of $\text{Se}_2\text{I}_5\text{AsF}_6$,^{2b,c} using a simple model.^{1,2c} More recently we employed this approach as an aid to the synthesis of simple AsF_6^- salts, and estimated that $\text{AsBr}_4\text{AsF}_6$ might be preparable from stoichiometric quantities of AsBr_3 , Br_2 , and AsF_5 . The salt $\text{AsBr}_4\text{AsF}_6$ was subsequently prepared, and characterized by Raman spectroscopy at -196°C . It is unstable at room temperature; its decomposition was followed by Raman spectroscopy, and the intermediate AsBr_3 , and the final products AsF_3 and Br_2 , were identified. The model showed the decomposition to be thermodynamically favourable, and pathways to both the formation and the decomposition of $\text{AsBr}_4\text{AsF}_6$ have been suggested. We estimated the energetics of the formation of other AsBr_4^+ salts by various routes, and subsequently prepared $\text{AsBr}_4\text{AlBr}_4$, which is stable at room temperature but is in equilibrium with AsBr_3 , Br_2 , and $\text{AsBr}_4\text{Al}_2\text{Br}_7$.

The cation AsBr_4^+ is formally a derivative of the as yet unprepared AsBr_5 . In contrast to PCl_5 and SbCl_5 , which are stable at ambient temperature, AsCl_5 was prepared at -105°C and is stable for some days at -50°C .^{2d} Thus, the present absence of AsBr_5 , and the low stability of AsCl_5 , are examples of the tendency of the non-metals of the fourth row, As, Se, and Br, to be unstable in their maximum oxidation state,³ and AsBr_4^+ salts are of interest in this context. Although AsCl_5 is unstable, AsCl_4^+ and AsCl_6^- salts including $\text{AsCl}_4\text{AsF}_6$ have substantial stabilities at room temperature. In fact $\text{AsCl}_4\text{AsF}_6$ is prepared by the reaction of AsF_3 and Cl_2 at room temperature; in contrast $\text{AsBr}_4\text{AsF}_6$ decomposes to AsF_3 and Br_2 . We account for these differences by application of our simple energetics model. The salt PBr_4PF_6 is kinetically stable but thermodynamically unstable, in contrast to $\text{AsBr}_4\text{AsF}_6$, which is both kinetically and thermodynamically unstable. We suggest reasons for the kinetic stability of PBr_4PF_6 , and other related kinetically stable salts. Using a similar conceptual and experimental approach, one of us has recently prepared AsI_4^+ (in $\text{AsI}_4\text{AlCl}_4$),⁴ and PI_4^+ (in PI_4AsF_6).⁵ Thus, salts containing MX_4^+ ($\text{M} = \text{P}$ or As ; $\text{X} = \text{F}$, Cl , Br , or I , but excluding the species AsF_4^+)^{6,7} have been characterized. These salts are of interest as simple species and as members of the tetrahedral MX_4 class of compounds and ions. A preliminary communic-

ation of this work has been published,⁸ a full account of which is given below.

Experimental

General Procedures.—Techniques, except those listed below, have been described in ref. 9. The compounds AsBr_3 (Alfa), AlBr_3 (Merck), and AsF_5 (Ozak Mahoning) were used without further purification. Reactions were carried out in a 10-mm glass tube incorporating a Rotoflo valve and an attached 5-cm thin-walled (5 mm) n.m.r. tube (for Raman spectroscopy). Raman spectra were recorded in the solid state using a Spex Ramalab spectrometer with a Spectra Physics 2 W argon-ion laser exciting line 5145 Å, slit width 4 cm^{-1} , or an Ybin Yvon U 1000 spectrometer with a Spectra Physics krypton laser (exciting line 6471 Å), slit width 10 cm^{-1} ; Stokes radiation was analysed at a 90° angle to the exciting radiation at -196 or -100°C , respectively.

Preparation of $\text{AsBr}_4\text{AsF}_6$.—In a typical reaction AsF_5 (1.198 g, 7.05 mmol) was condensed at -196°C on to a mixture of Br_2 (0.376 g, 2.35 mmol) and AsBr_3 (1.479 g, 4.70 mmol) which had been held previously at room temperature (r.t.). The reaction mixture was warmed to -5°C until a clear solution was formed (1 min) and then recooled to -196°C . This process was repeated in excess of 10 times and a white solid formed (no Br_2 was present). The volatiles (AsF_3) were removed by pumping under a dynamic vacuum for 10 min at -5°C and after that, the vessel was cooled to -196°C . The Raman spectrum (5 145-Å excitation, -196°C) (Figure and Table 1) was indicative of $\text{AsBr}_4\text{AsF}_6$ (1.65 g, yield 60%).

Thermal Stability of $\text{AsBr}_4\text{AsF}_6$.—The solid salt decomposed within a few minutes at room temperature. At -78°C there was slow decomposition, and after 15 min at -50°C a significant fraction of the salt had decomposed (see Table 1). However, the compound appeared to be stable for several days at -196°C (Raman).

† Non-S.I. unit employed: cal = 4.184 J.

‡ We recognize that our approach employs an approximation for energy values that are not available, and therefore we use the term 'estimate'. In the text we compare our estimated values with those that have been more rigorously determined.

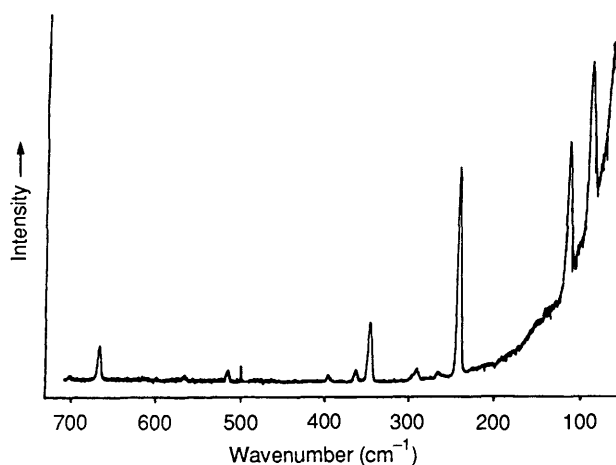


Figure. Raman spectrum of $\text{AsBr}_4\text{AsF}_6$ at -196°C . ^a Peak at 515 cm^{-1} attributable to the glass container

Table 1. Identification of $\text{AsBr}_4\text{AsF}_6$ by Raman spectroscopy (excitation line 5145 \AA , -196°C and of the decomposition products (time sequence)

Time, conditions	Identified species ^a	Identification				
		method	value ^b	assignment		
Immediately after preparation, vessel held at -196°C	$\text{AsBr}_4\text{AsF}_6$	Raman	88 (94)	$\text{AsBr}_4^+ \nu_2$		
			115 (74)	$\text{AsBr}_4^+ \nu_4$		
			244 (100)	$\text{AsBr}_4^+ \nu_1$		
			349 (28)	$\text{AsBr}_4^+ \nu_3$		
			370 (7)	$\text{AsF}_6^- \nu_5$		
			568 (5)	$\text{AsF}_6^- \nu_2$		
			671 (17)	$\text{AsF}_6^- \nu_1$		
		702 (1)	AsF_6^-			
		AsBr ₃ (traces)	Raman	266 (1)	$\text{AsBr}_3 \nu_1$	
		Br ₂ (traces)	Raman	292 (9)	Br ₂ ^c	
			Raman	396 (1)	Not assigned	
		After 15 min at -50°C ^d	$\text{AsBr}_4\text{AsF}_6$	Raman	113 (100)	$\text{AsBr}_4^+ \nu_4$ ^e
					244 (96)	$\text{AsBr}_4^+ \nu_1$
349 (38)	$\text{AsBr}_4^+ \nu_3$					
370 (25)	$\text{AsF}_6^- \nu_5$					
671 (32)	$\text{AsF}_6^- \nu_1$					
AsBr ₃	Raman				130 (59)	$\text{AsBr}_3 \nu_2$
					258 (24)	$\text{AsBr}_3 \nu_3$
Br ₂	Raman		268 (38)	$\text{AsBr}_3 \nu_1$		
	Raman		292 (70)	Br ₂		
				characteristic colour		
After 15 min at -50°C and 5 min at $+25^\circ\text{C}$ ^d	AsBr ₃		Raman	95 (23)	$\text{AsBr}_3 \nu_4$	
				105 (39)	$\text{AsBr}_3 \nu_4$	
				130 (37)	$\text{AsBr}_3 \nu_2$	
		258 (19)		$\text{AsBr}_3 \nu_3$		
		268 (100)		$\text{AsBr}_3 \nu_1$		
		282 (4)		$\text{AsBr}_3 \nu_1$		
		Br ₂		Raman	292 (15)	Br ₂
				characteristic colour		
	After 15 min at -50°C and 15 min at $+25^\circ\text{C}$	AsF ₃	i.r. (gas)	695s	$\text{AsF}_3 \nu_2$	
				750m	$\text{AsF}_3 \nu_1$	
		Br ₂			characteristic colour	

^a All species are in the solid state unless otherwise specified. ^b Raman and i.r. values (cm^{-1}). Intensities: i.r., s = strong, m = medium; Raman, intensities in parentheses (measured area under the peak) are relative to the strongest line given a value of 100. ^c Solid bromine (deep red) is a very weak Raman scatterer; the observed values for ν_1 are in agreement with those of a pure sample of Br₂ (s) the Raman spectrum of which we obtained in a separate experiment. ^d The sample was recooled to -196°C and the spectrum recorded. ^e Intensity may be too high, attributable to overlap with ν_4 AsBr₃.

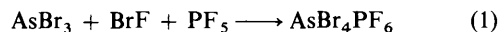
The final products of the decomposition reaction are Br₂ (Raman) and AsF₃ (i.r. spectroscopy); AsBr₃ was detected as an intermediate (see Table 1).

The preparation of $\text{AsBr}_4\text{AsF}_6$ in AsF₃ solution was carried out as described above, except that AsF₃ (ca. 2 cm^3) was condensed on to the mixture of Br₂ and AsBr₃ before addition of AsF₅. The reaction mixture was warmed to 0°C and thermally cycled 10 times ($-196 \leq T \leq -5^\circ\text{C}$). An insoluble solid was formed ($\text{AsBr}_4\text{AsF}_6$, Raman spectroscopy) which liberated bromine on standing in liquid AsF₃ at 0°C .

Reaction of AsF₅ with AsBr₃.—Arsenic pentafluoride (0.2561 g, 1.509 mmol) was condensed, at -196°C , on to AsBr₃ (0.9438 g, 2.999 mmol) in a Raman tube (5 mm). The reaction mixture was warmed to r.t. for 1 min and then recooled to -196°C . The Raman spectrum (5145-\AA excitation, -196°C) showed peaks attributable to AsBr₃, AsF₅, and $\text{AsBr}_4\text{AsF}_6$ (ν_1 and ν_3 of AsBr_4^+).

Attempted Synthesis of AsBr_4PF_6 .—(1) Stoichiometric amounts of AsBr₃, Br₂, and PF₅ were allowed to react in a manner similar to that described for $\text{AsBr}_4\text{AsF}_6$. Bromine was still present after thermal cycling, and AsBr₃ was the only solid identified (-196°C , Raman spectroscopy) after removal of the volatiles (PF₅, traces of OPF₃, i.r. spectroscopy) at 0°C .

(2) Arsenic tribromide (0.2004 g, 0.6369 mmol) was condensed on to PF₅ (0.0803 g, 0.6378 mmol) and BrF (ca. 0.64 mmol) in an attempt to prepare AsBr_4PF_6 according to equation (1). The BrF (not directly identified) was first prepared⁶ by condensing F₂ onto Br₂ which was frozen as a thin film on the surface of the Raman tube. After thermally

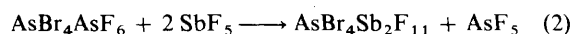


cycling ten times between -196 and -5°C the reaction mixture had the colour of elemental bromine and the gas-phase i.r. spectrum at r.t. showed only bands attributable to AsF₃ and PF₅ (and some POF₃). All the products were volatile and were readily removed under a dynamic vacuum.

(3) Arsenic trifluoride (5.66 g) and PF₃ (1.69 g) were added to Br₂ (0.54 g) in a Parr bomb (Monel 400, 40 cm^3) [i.e. AsF₃ and PF₃ were in excess relative to that needed for the reverse of equation (9) with X = Br, E = P, and M = As] and left at r.t. for 6 d. The volatile products were shown to contain PF₅, traces of OPF₃, PF₃, AsF₃ (i.r. spectroscopy), and Br₂ (appearance). The solid residue was identified as AsBr₃ (Raman spectroscopy m.p. $32\text{--}34^\circ\text{C}$).

Reaction of AsF₃ with AsBr₃.—Arsenic trifluoride (ca. 3 cm^3) was condensed on to AsBr₃ (0.4256 g, 1.3527 mmol) in a Raman tube at -196°C . At r.t. the mixture consisted of a liquid over a solid. The Raman spectrum (6471-\AA excitation) of the frozen liquid only showed two peaks (600 and 700 cm^{-1}), attributable to solid AsF₃; the solid showed much stronger peaks, attributable only to solid AsBr₃.

Attempted Synthesis of $\text{AsBr}_4\text{Sb}_2\text{F}_{11}$.—The salt $\text{AsBr}_4\text{AsF}_6$ was prepared as described above. At -78°C SbF₅ (2.2501 g, 10.3815 mmol) was condensed onto solid $\text{AsBr}_4\text{AsF}_6$ (ca. 2.92 g, 5 mmol) [see equation (2)], followed by thermal cycling between -5 and -196°C ten times. The i.r. spectrum of the



solid, and its weight (2.3268 g), was consistent with SbF₃·SbF₅¹⁰ (5.88 mmol) and some other material (perhaps occluded SbF₅).

Preparation of $\text{AsBr}_4\text{AlBr}_4$ (i) and $\text{AsBr}_4\text{Al}_2\text{Br}_7$ (ii).—(i) Bromine (0.707 g, 4.42 mmol) was condensed on to a mixture

Table 2. Raman bands (excitation line 6 471 Å, -100 °C) of 'AsBr₄AlBr₄' and 'AsBr₄Al₂Br₇'

Sample ^a	Raman ^b	Assignment ^c
AsBr ₄ AlBr ₄ prepared according to equation (4), (i), equilibria at 45 °C, quenched to -100 °C	96 (78)	AlBr ₄ ⁻ ν ₂
	115 (80)	AlBr ₄ ⁻ ν ₄
		AsBr ₄ ⁺ ν ₄
	201 (64)	AlBr ₄ ⁻ ν ₁
		Al ₂ Br ₇ ⁻ d
	233 (100)	AsBr ₄ ⁺ ν ₁
	258-289 (vb)	AsBr ₃ ν ₁ and ν ₃
AsBr ₄ AlBr ₄ prepared according to equation (4), (i), equilibrium frozen from 5 to -100 °C	300 (69)	Br ₂ e
	344 (70)	AsBr ₄ ⁺ ν ₃
	116 (73)	AsBr ₄ ⁺ ν ₄ /AlBr ₄ ⁻ ν ₄
	202 (57)	AlBr ₄ ⁻ ν ₁
		Al ₂ Br ₇ d
	233 (100)	AsBr ₄ ⁺ ν ₁
	260-285 (vb)	AsBr ₃ ν ₁ and ν ₃
AsBr ₄ Al ₂ Br ₇ prepared according to equation (5), (ii), equilibrium frozen from 20 to -100 °C	298 (71)	Br ₂ e
	344 (62)	AsBr ₄ ⁺ ν ₃
	116 (78)	AsBr ₄ ⁺ ν ₄ /AlBr ₄ ⁻ ν ₄
	201 ^f (77)	AlBr ₄ ⁻ ν ₁
		Al ₂ Br ₇ ⁻ d
	233 ^f (100)	AsBr ₄ ⁺ ν ₁
	302 ^f (86)	Br ₂ e
AsBr ₄ AlBr ₄ prepared according to equation (4), (iii), equilibrium frozen from 20 to -100 °C	344 ^f (90)	AsBr ₄ ⁺ ν ₃
	76 (9)	—
	88 (10)	AsBr ₄ ⁺ ν ₂
	114 (4)	AsBr ₄ ⁺ /AlBr ₄ ⁻ ν ₄
	200 (1)	AlBr ₄ ⁻ ν ₁
	231 (6)	AsBr ₄ ⁺ ν ₁
	266 (1)	AsBr ₃ ν ₁
298 (100)	Br ₂ e	
342 (3)	AsBr ₄ ⁺ ν ₃	
596 (1)	AlBr ₃ ν ₃	

^a All species in the solid phase unless otherwise specified. ^b In cm⁻¹. Raman intensities in parentheses (measured area under the peak) are relative to the strongest line (100); the baseline was off-scale at 90 cm⁻¹. ^c cf. D. H. Brown and D. T. Stewart, *Spectrochim. Acta, Part A*, 1970, **26**, 1344. ^d A sample of pure KAl₂Br₇ made from KBr and AlBr₃ showed only one peak at 205 cm⁻¹ (excitation 5 145 Å). ^e See footnote c in Table 1. ^f Broad lines.

Table 3. Raman bands (cm⁻¹) with intensities in parentheses of AsBr₄⁺ (in AsBr₄AsF₆), AsCl₄⁺ (in AsCl₄AsF₆), and GeBr₄

AsBr ₄ ⁺ ^a	AsCl ₄ ⁺ ^b	GeBr ₄ ^c	Assignment
88 (94)	156 (78)	75	ν ₂
115 (74)	187 (92)	111	ν ₄
244 (100)	422 (100)	236	ν ₁
349 (28)	500 (35)	332	ν ₃

^a This work. ^b See refs. 11 and 12. ^c See refs. 13 and 14.

of AsBr₃ (1.380 g, 4.39 mmol) and AlBr₃ (1.175 g, 4.40 mmol) at -78 °C. On warming to r.t. an intense red viscous solution was obtained. In one case the reaction mixture was warmed to 45 °C, in the other case it was recooled to 5 °C. Both solutions were then quickly frozen to -196 °C and Raman spectra (6 471-Å excitation) were obtained at -100 °C. Both Raman spectra were very similar and consisted of peaks attributable to AsBr₄⁺, AlBr₄⁻/Al₂Br₇⁻, AsBr₃, and Br₂ (see Table 2).

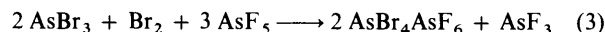
(ii) In another similar reaction, designed to give AsBr₄Al₂Br₇, a very viscous liquid was formed and very similar species were identified in the Raman spectrum (see Table 2), with the exception of the absence of a peak due to AsBr₃.

(iii) In another similar reaction, designed to give AsBr₄AlBr₄, a large excess of bromine (5.1885 g, 32.437 mmol) was condensed onto a mixture of AsBr₃ (0.6872 g, 2.1861 mmol) and

AlBr₃ (0.5870 g, 2.1981 mmol) at -78 °C. On warming to r.t. an intense red liquid was obtained. The solution was quickly frozen to -196 °C and the Raman spectrum (6 471-Å excitation) obtained at -100 °C. The spectrum consists of peaks attributable to AsBr₄⁺, AlBr₄⁻, AsBr₃, AlBr₃, and a very intense line attributable to Br₂ (s) (see Table 2).

Results and Discussion

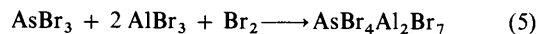
Preparation of AsBr₄AsF₆.—A white solid, AsBr₄AsF₆, was prepared by the oxidation of AsBr₃ and Br₂, by AsF₅, between -5 and -196 °C according to equation (3). The salt AsBr₄AsF₆



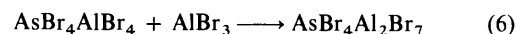
was unambiguously identified by its Raman spectrum (see Figure, Table 1).

There was no evidence (Raman spectrum) for AsBr₃ in freshly prepared AsBr₄AsF₆, and thus the reaction appeared to be quantitative. The isolated yield was only 60%, because decomposition products (AsF₃, Br₂) had been removed under dynamic evacuation.

Preparation of AsBr₄AlBr₄ and AsBr₄Al₂Br₇.—The preparation of these compounds was attempted by reaction of stoichiometric amounts of AsBr₃, Br₂, and AlBr₃ according to equations (4) and (5). In both cases viscous liquids were formed.



The Raman spectrum of the product of equation (4) showed unambiguously that AsBr₄AlBr₄ and Br₂ were present; it was also consistent with the presence of AsBr₃ and Al₂Br₇⁻. It is therefore likely that reaction (4) did not go to completion (*i.e.* both reactants and products were in equilibrium with one another) and a second equilibrium occurred also [equation (6)]. Adding an excess of Br₂ did not remove AsBr₃ and AlBr₃ by displacing the equilibrium to the right.



The attempted preparation of AsBr₄Al₂Br₇ also resulted in an equilibrium mixture (see Table 2), as Br₂ was unambiguously identified. It is possible that the corresponding AsBr₃ was also present but that it was not detected (broad lines, low resolution).

Raman Spectrum of AsBr₄⁺.—The best Raman spectrum of AsBr₄⁺ was obtained from solid AsBr₄AsF₆ at -196 °C (Figure). The AsBr₄⁺ portion of the spectrum consists of four bands with similar relative intensities to those of AsCl₄⁺ in AsCl₄AsF₆,^{11,12} but with similar frequencies to those of (the isoelectronic) GeBr₄.^{13,14} (see Table 3). The value of the symmetric stretch, ν₁, increases in the series GaBr₄⁻, GeBr₄, AsBr₄⁺ (210, 236, 244 cm⁻¹), as do related values of ν₁ for other related isoelectronic partners in Table 4.

The value of ν₁(AsBr₄⁺) (244 cm⁻¹) is slightly less than ν₁(PBr₄⁺) (254 cm⁻¹), as are all ν₁(MX₄) values of row 4, relative to their row 3 counterparts. Thus all the data are consistent with the new species being tetrahedral AsBr₄⁺.

Thermal Decomposition of AsBr₄AsF₆.—The salt is stable at -196 °C, decomposes slowly at -78 °C, and rapidly at room temperature according to equation (7). Both final

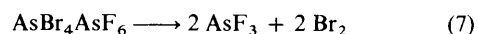


Table 4. Vibrational spectroscopic data (ν , cm^{-1}) for tetrahedral species

AlCl_4^-	348 ^a
SiCl_4	423 ^b
PCl_4^+	458 ^c
AlBr_4^-	212 ^d
SiBr_4	247 ^b
PBr_4^+	254 ^e
GaCl_4^-	343 ^f
GeCl_4	397 ^b
AsCl_4^+	422 ^g
GaBr_4^-	210 ^h
GeBr_4	236 ^b
AsBr_4^+	244 ⁱ

^a E. Rytter and H. A. Oye, *J. Inorg. Nucl. Chem.*, 1973, **35**, 4311. ^b Refs. 13 and 14. ^c P. Van Huong and B. Desbat, *Bull. Soc. Chim. Fr.*, 1972, 2631. ^d D. H. Brown and D. T. Stewart, *Spectrochim. Acta, Part A*, 1970, **26**, 1344. ^e M. Delahaye, P. Dhameincourt, and J. C. Merlin, *C.R. Acad. Sci., Ser. B*, 1971, **272**, 370. ^f H. A. Oye and W. Bues, *Inorg. Nucl. Chem. Lett.*, 1977, **8**, 31. ^g Refs. 11 and 12. ^h L. A. Woodward and A. A. Nord, *J. Chem. Soc.*, 1955, 2655. ⁱ This work.

Table 5. Heats of formation and reaction enthalpies for the formation of MX_4EF_6 (M = P or As; X = Cl, Br, or I; E = P or As) according to equation 8 and their decomposition by equation (9). All values correspond to 1 mol of MX_4EF_6

Compound	$\Delta H_f^{a,b}$	$\Delta H(8)^{a,c}$	$\Delta H(9)^{a,c}$
$\text{AsBr}_4\text{AsF}_6$	-433	-113	-25
AsI_4AsF_6	-360	-33	-98
$\text{AsCl}_4\text{AsF}_6$	-483	-161	+25
AsBr_4PF_6	-509	+2	+60
PBr_4AsF_6	-423	-91	-26
PBr_4PF_6	-499	+24	+59

^a All values in kcal mol^{-1} . ^b Estimated by Scheme 1. ^c $\Delta H(8)$ and $\Delta H(9)$ calculated, using the following heats of formations (kcal mol^{-1}): ²³ PBr_3 (l), -48; AsBr_3 (s), -47; AsCl_3 (l), -73; AsI_3 (s), -14; AsF_5 (g), -296; PF_5 (g), -382; AsF_3 (l), -229; and PF_3 (g) = -220.

Table 6. Heats and enthalpies of formation of AsX_4AlX_4 (X = Br or I) calculated from equation (10)

Compound	$\Delta H_f^{a,b}$	$\Delta H(10)^a$
$\text{AsBr}_4\text{AlBr}_4$	-191	-23 ^c
AsI_4AlI_4	-67	+21 ^d

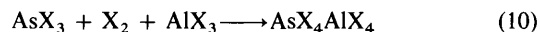
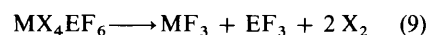
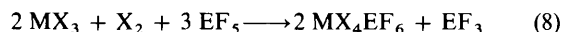
^a Values in kcal mol^{-1} . ^b Estimated by Scheme 2. ^c $\Delta H_f^\circ[\text{AsBr}_3(\text{s})] = -47.1 \text{ kcal mol}^{-1}$. ^d $\Delta H_f^\circ[\text{AsI}_3(\text{s})] = -13.9 \text{ kcal mol}^{-1}$.

decomposition products were identified by Raman spectroscopy, as was the reaction intermediate AsBr_3 .

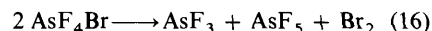
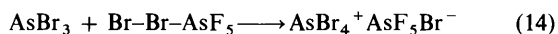
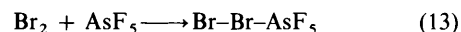
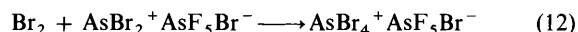
Thermodynamics and Kinetics of Formation of $\text{AsBr}_4\text{AsF}_6$ and $\text{AsBr}_4\text{AlBr}_4$.—Our estimate of a favourable reaction enthalpy for the formation of $\text{AsBr}_4\text{AsF}_6$ by equation (3) [$\Delta H(3) = -113 \text{ kcal mol}^{-1}$; see Table 5, equation (8) with M = As, X = Br, E = As] motivated us to carry out this reaction. The subsequent successful preparation of $\text{AsBr}_4\text{AsF}_6$, by this route, shows that $\Delta H(3)$ must, at least, be substantially negative to offset the unfavourable entropy term, and illustrates the usefulness of the simple thermodynamic model in guiding chemical syntheses of hitherto unknown salts. The estimate for the formation of $\text{AsBr}_4\text{AlBr}_4$ by equation (4) (see Table 6) of $\Delta H(4) -23 \text{ kcal}$

* An ionic formulation is written here and elsewhere for simplicity. However, there will be significant cation-anion interactions, especially in $\text{AsBr}_2^+ \text{AsF}_5\text{Br}^-$.

mol^{-1} is of the same order of magnitude as the entropy at room temperature, and is consistent with the observed equilibrium mixture of products and reactants, and the presence of $\text{AsBr}_4\text{Al}_2\text{Br}_7$ as given by equation (6).

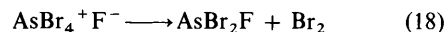


The formation of $\text{AsBr}_4\text{AsF}_6$ may proceed by equations (11) and (12), and/or (13) and (14), followed by (15) and (16).



Reaction sequences related to those given in equations (11)–(14), but with AlBr_3 replacing AsF_5 , likely represent the reaction steps leading to $\text{AsBr}_4\text{AlBr}_4$ formation.

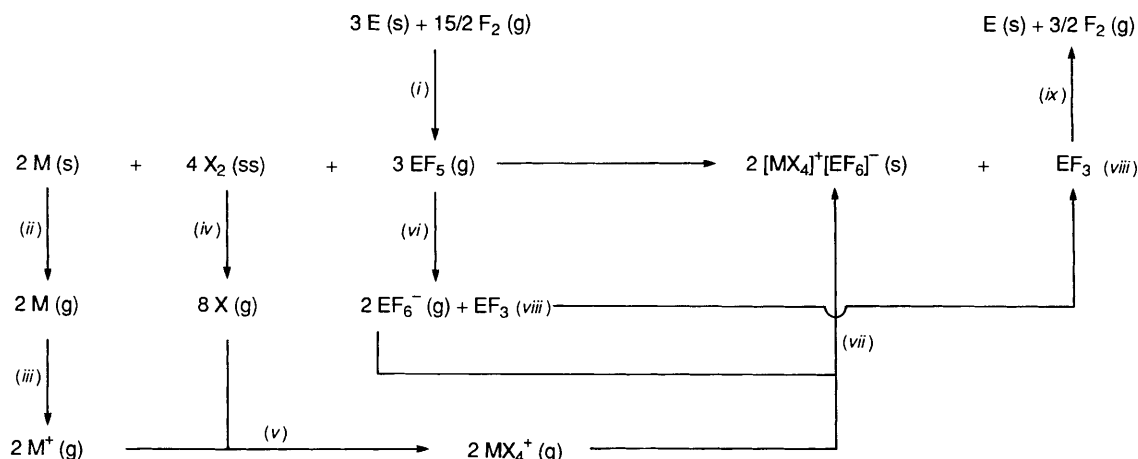
Thermodynamics and Kinetics of Thermal Decomposition of $\text{AsBr}_4\text{AsF}_6$.—The enthalpy of decomposition of $\text{AsBr}_4\text{AsF}_6$ [equation (7) or equation (9) (M = E = As, X = Br)] is estimated as $-25 \text{ kcal mol}^{-1}$ (Table 5) and is also favoured by entropy. Possible steps in the decomposition are shown in equations (17)–(20).



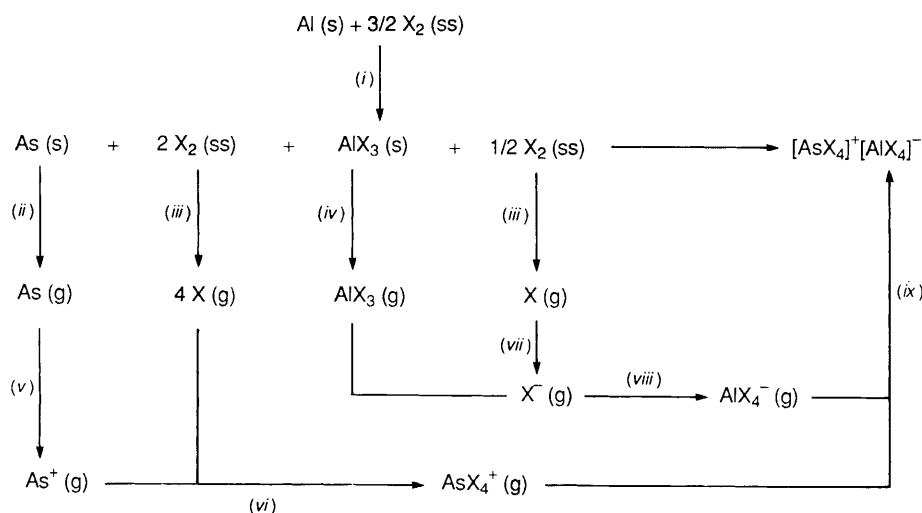
In one experiment SO_2 was added to $\text{AsBr}_4\text{AsF}_6$ and the mixture held at -20°C for 1 h. The reaction products included Br_2 and AsF_3 , but not SO_2BrF (i.r., Raman, spectroscopy), showing BrF was unlikely as an intermediate in the decomposition.¹⁵

Rather surprisingly, AsBr_3 , but not AsBr_2F or AsBrF_2 , was detected as a reaction intermediate (Raman).[†] Consistently we only detected AsBr_3 and AsF_3 in the Raman spectrum of AsF_3 (l) and AsBr_3 (s). Arsenic pentafluoride was not detected, either because it is a weaker Raman scatterer than AsBr_3 and Br_2 , or much more likely because it immediately reacts with AsBr_3 and/or AsBr_2F . In a separate reaction, AsF_5 was treated with AsBr_3 and proceeded according to equation (21). It could

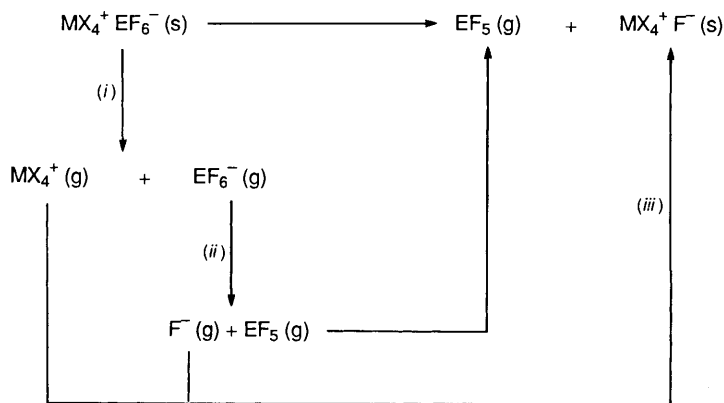
[†] Halogen-exchange reactions which are observed in phosphorus trihalide systems^{16–19} are not favoured in the arsenic system.^{18–20} Only a few examples of mixed arsenic trihalides have been completely characterized. For example, mixed species were found in a study of a mixture of AsCl_3 and AsF_3 .²⁰ However, the equilibrium constants for the exchange reactions ($2 \text{AsF}_3 + \text{AsCl}_3 \longrightarrow 3 \text{AsF}_2\text{Cl}$, $K_1 = 5 \times 10^{-3}$; $2 \text{AsCl}_3 + \text{AsF}_3 \longrightarrow 3 \text{AsFCl}_2$, $K_2 = 5 \times 10^{-3}$) are very low. This probably explains why these species were not detected in the Raman study.¹⁸ There is strong intermolecular association in both liquid and solid AsF_3 .^{7,21} This may be one reason for the entropy-disfavoured 'dissociation' of mixed arsenic(III) fluorohalides into AsF_3 and AsX_3 (X = halide).



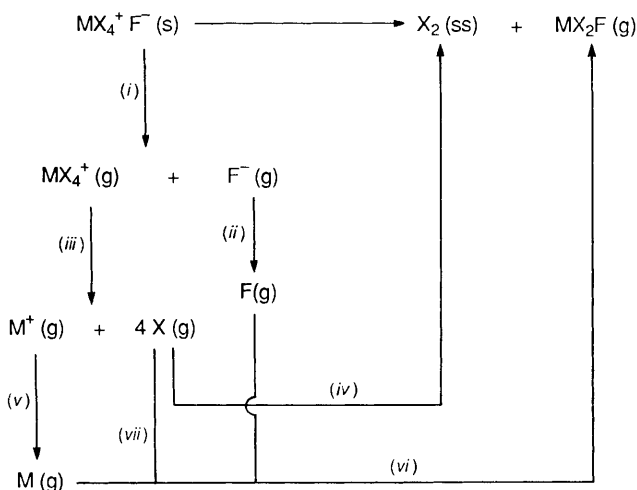
Scheme 1. Energy cycle for the formation of $[\text{MX}_4]^+[\text{EF}_6]^-$ ($\text{M} = \text{P}$ or As ; $\text{X} = \text{Cl}, \text{Br}$ or I ; $\text{E} = \text{P}$ or As). (i) $\Delta H_f^\circ(\text{PF}_5, \text{g}) = -381.8$, $\Delta H_f^\circ(\text{AsF}_5, \text{g}) = -295.6 \text{ kcal mol}^{-1}$.^b (ii) atomization energy: $+75.3$ (P)^a or $+72.4 \text{ kcal mol}^{-1}$ (As).^a (iii) First ionization potential of gaseous P : $+241.8$ and As : $+226.2 \text{ kcal mol}^{-1}$.^c (iv) Atomization energy of X_2 in its standard state, $\text{X} = \text{Cl}$ ($+29.1$), Br ($+26.8$), or I ($+25.6 \text{ kcal g-atom}^{-1}$).^a (v) $\text{M}^+ - \text{X}$ bond energy in MX_4^+ (i.e. $\text{MX}_4^+ \longrightarrow \text{M}^+ + 4 \text{X}$), estimated as $\text{M}-\text{X}$ bond energy in $\text{MX}_3^a + 5\%$ (calibrated on: $2 \text{AsF}_3 + 2 \text{Cl}_2 \longrightarrow [\text{AsCl}_4]^+ [\text{AsF}_6]^-$ with $\Delta H = -25 \text{ kcal mol}^{-1}$). This gives: PBr , -66.2 ; AsCl , -77.6 ; AsBr , -64.1 ; and AsI , $-45.8 \text{ kcal mol}^{-1}$. N.B. The $+5\%$ estimate for stronger bonds in the cationic species is in good agreement with the estimate of Jenkins *et al.*,^d e.g. $\Delta H_f^\circ(\text{PCl}_4^+, \text{g}) + 110.6 \text{ kcal mol}^{-1}$, cf. our estimate $+110.3 \text{ kcal mol}^{-1}$ from $\frac{1}{4} \text{P}_4 \text{ (s)} \longrightarrow \text{P (g)}$, $+75.3$, $2 \text{Cl}_2 \text{ (g)} \longrightarrow 4 \text{Cl (g)}$, $+116.4$, $\text{P (g)} \longrightarrow \text{P}^+ \text{ (g)}$, $+242.1$, and $\text{P}^+ + 4 \text{Cl (g)} \longrightarrow \text{PCl}_4^+ \text{ (g)}$, $4 \times (77.0 + 3.85) \text{ kcal mol}^{-1}$.^a (vi) Calculated as shown in ref. 2, Fluoride affinity of AsF_5 , -111 , PF_5 , $-101 \text{ kcal mol}^{-1}$.^c $\Delta H[3 \text{AsF}_5 \text{ (g)} + 2 \text{e}^- \longrightarrow 2 \text{AsF}_6^- \text{ (g)} + \text{AsF}_3 \text{ (l)}] = -284.7$, $\Delta H[3 \text{PF}_5 \text{ (g)} + 2 \text{e}^- \longrightarrow 2 \text{PF}_6^- \text{ (g)} + \text{PF}_3 \text{ (g)}] = -169.5 \text{ kcal mol}^{-1}$. (vii) Crystal-lattice energy ($U/\text{kcal mol}^{-1}$), calculated from the molecular volume ($V_M/\text{\AA}^3$), using linear relationship: $U = 556.3 (V_M)^{-0.33} + 26.3$.^{e,f} $V_M(\text{AsF}_6^-) = 105$,² $(\text{PF}_6^-) = 103$,^g $(\text{AsCl}_4^+) = 133$,^h $(\text{AsBr}_4^+) = 178$, and $(\text{AsI}_4^+) = 223$. (The volumes of AsBr_4^+ and AsI_4^+ were taken to be equal to the volumes of GeBr_4 and GeI_4 .)^b (viii) AsF_3 (l), PF_3 (g). (ix) $\Delta H_f^\circ(\text{PF}_3, \text{g}) = -219.8$, $\Delta H_f^\circ(\text{AsF}_3, \text{l}) = -228.8 \text{ kcal mol}^{-1}$.^a (x) The salt is written as $[\text{MX}_4]^+[\text{EF}_6]^-$ (s) to stress that the anion and cation carry full negative and positive charges respectively. In the text and in equations in the text it is written as MX_4EF_6 for brevity. A similar protocol is used for related salts. ^a D. A. Johnson, 'Some Thermodynamic Aspects of Inorganic Chemistry,' 2nd edn., Cambridge University Press, 1982, appendix. ^b I. Barin, O. Knackle, and O. Kubaschewski, in 'Thermodynamic Properties of Inorganic Substances,' Springer, New York, 1977, supplement. ^c E. Fluck and K. Heumann, 'Periodic Table of the Elements,' VCH, Weinheim, 1985. ^d H. D. B. Jenkins, K. P. Thakur, A. Finch, and P. N. Gates, *Inorg. Chem.*, 1982, **21**, 423. ^e T. E. Mallouk, G. L. Rosenthal, G. Müller, R. Brusasco, and N. Bartlett, *Inorg. Chem.*, 1984, **23**, 3167. ^f T. J. Richardson, F. L. Tarzella, and N. Bartlett, *J. Am. Chem. Soc.*, 1986, **108**, 4937. ^g H. Bode and H. Clausen, *Z. Anorg. Allg. Chem.*, 1951, **265**, 229. ^h H. Preiss, *Z. Anorg. Allg. Chem.*, 1971, **380**, 45.



Scheme 2. Energy cycle for the formation of $[\text{AsX}_4]^+[\text{AlX}_4]^-$ salts ($\text{X} = \text{Br}$ or I). (i) $\Delta H_f^\circ(\text{AlBr}_3, \text{s}) = -121$, $\Delta H_f^\circ(\text{AlI}_3, \text{s}) = -74.2 \text{ kcal mol}^{-1}$.⁶ (ii) Atomization energy of As : $+72.4 \text{ kcal mol}^{-1}$.^b (iii) Atomization energies: Br , 26.8 ; I , $25.6 \text{ kcal g-atom}^{-1}$.^b (iv) Sublimation energies: AlBr_3 , 20 ; AlI_3 , 19 kcal mol^{-1} .^d (v) First ionization potential of As : $+226.2 \text{ kcal mol}^{-1}$.^c (vi) $\text{As}^+ - \text{X}$ bond energies [see Scheme 1, (v)]: $\text{X} = \text{Br}$, -64.1 ; I , $-45.8 \text{ kcal mol}^{-1}$. (vii) Electron affinities: Br (g) , -82.7 ; I (g) , $-72.6 \text{ kcal mol}^{-1}$.^b (viii) $\text{Al}^- - \text{X}$ bond energies in AlX_4^- , estimated as $\text{Al}-\text{X}$ bond energy in $\text{AlX}_3^a - 5\%$: $\text{X} = \text{Br}$, -81.7 ; I , $-83 \text{ kcal mol}^{-1}$.^b (ix) Crystal lattice energy ($U/\text{kcal mol}^{-1}$), calculated from the molecular volume ($V_M/\text{\AA}^3$), see Scheme 1, (vii). $V_M(\text{AsBr}_4^+) = 178$, $(\text{AsI}_4^+) = 223$ [see Scheme 1, (vii)]; $(\text{AlBr}_4^-) = 218$, $(\text{AlI}_4^-) = 223$ [estimated by using the volumes of Al_2Br_6 (335\AA^3) and Al_2I_6 (341\AA^3)].^f ^a W. Klemm and E. Tanke, *Z. Anorg. Allg. Chem.*, 1931, **200**, 364. ^b D. A. Johnson, in 'Some Thermodynamic Aspects of Inorganic Chemistry,' 2nd edn., Cambridge University Press, 1982, appendix. ^c W. Fischer and O. Ralfs, *Z. Anorg. Allg. Chem.*, 1932, **205**, 32; 34. ^d W. Fischer and O. Ralfs, *Z. Anorg. Allg. Chem.*, 1932, **205**, 37. ^e E. Fluck and K. Heumann, 'Periodic Table of the Elements,' VCH, Weinheim, 1985. ^f R. C. Weast, 'Handbook of Chemistry and Physics,' 54th edn., CRC Press, Boca Raton, Florida, 1973—1974, B-63.



Scheme 3. (i) Crystal lattice energy $U/\text{kcal mol}^{-1}$: PBr_4PF_6 , -112 ; PBr_4AsF_6 , -112 ; AsBr_4PF_6 , -111 ; $\text{AsBr}_4\text{AsF}_6$, -111 ; $\text{AsCl}_4\text{AsF}_6$, -116 . For calculation see Scheme 1, (v). (ii) Fluoride affinity (kcal mol^{-1}): AsF_5 , -111 ; PF_5 , -101 .^a (iii) Crystal lattice energy $U/\text{kcal mol}^{-1}$ [for calculation see Scheme 1, (v)]. $V_M(\text{F}^-) = 10 \text{ \AA}^3$; V_M (cations), see Scheme 1. U : PBr_4F , -125 ; AsBr_4F , -123 ; AsCl_4F , -133 .^a T. E. Mallouk, G. L. Rosenthal, G. Müller, R. Brusasco, and N. Bartlett. *Inorg. Chem.* 1984, **23**, 3167.



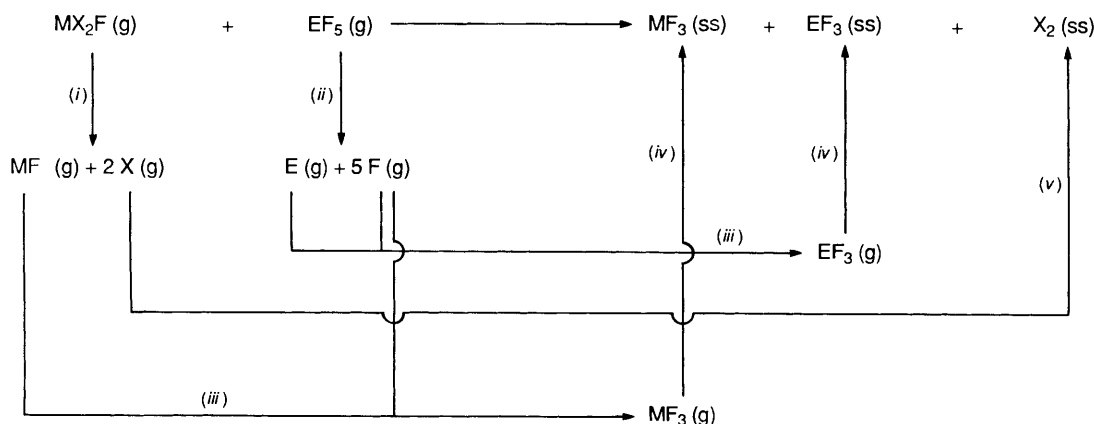
Scheme 4. (i) Crystal lattice energy, see Scheme 3. (ii) Electron affinity of F (g): $-83.6 \text{ kcal mol}^{-1}$.² (iii) $\text{M}^{\text{V}+}\text{-X}$ bond energy: see Scheme 1. (iv) Atomization energies of Cl_2 (g), Br_2 (l), and I_2 (s): see Scheme 1. (v) Ionization potentials of P and As: see Scheme 1. (vi) $\text{M}^{\text{III}}\text{-F}$ bond energies: M = P, 117; As, 117 kcal mol^{-1} .^a (vii) $\text{M}^{\text{III}}\text{-X}$ bond energies: P-Br, 63; As-Cl, 74; As-Br, 61 kcal mol^{-1} .^a D. A. Johnson in 'Some Thermodynamic Aspects of Inorganic Chemistry,' 2nd edn., Cambridge University Press, 1982, appendix.



be that without this $\text{AsBr}_4\text{AsF}_6$ regeneration step the salt would be very much more difficult to identify.

The first step in the decomposition of $\text{AsBr}_4\text{AsF}_6$ is, reasonably, fluoride-ion transfer with formation of $\text{AsBr}_4^+\text{F}^-$ [equation (17)]. The analogues PBr_4^+F^- and $\text{AsCl}_4^+\text{F}^-$ have both been observed as products of the thermal decomposition of PBr_4AsF_6 and $\text{AsCl}_4\text{AsF}_6$, respectively²². This step is endothermic, $\Delta H(17) \equiv \Delta H(22) = +99 \text{ kcal mol}^{-1}$ (see Table 7 with M = As, X = Br, E = As). However, the decomposition reaction (18) is exothermic ($-78 \text{ kcal mol}^{-1}$) and may take place almost simultaneously, substantially reducing the activation barrier [equation (17)]. Inclusion of the enthalpy of the subsequent reaction (20) [$\Delta H(20) \equiv \Delta H(24) = -73 \text{ kcal mol}^{-1}$; M = As, X = Br, E = As] renders the decomposition sequence substantially exothermic ($-29 \text{ kcal mol}^{-1}$) in agreement with observations and the estimated overall enthalpy of $-24 \text{ kcal mol}^{-1}$ (see Tables 5 and 7).

Differences in Thermodynamic Stability of $\text{AsBr}_4\text{AsF}_6$ and $\text{AsCl}_4\text{AsF}_6$: a Criterion for the Kinetic Stability of Thermodynamically Unstable Salts of Complex anions; the Search for New Stable AsBr_4^+ and AsI_4^+ Salts.—The low stability of $\text{AsBr}_4\text{AsF}_6$ contrasts with that of $\text{AsCl}_4\text{AsF}_6$,¹² which can be prepared by the reaction of AsF_3 (l) and Cl_2 (g) at room

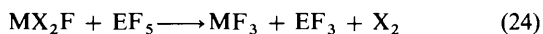
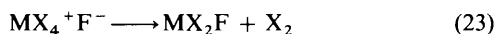
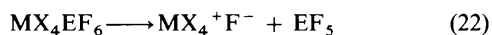


Scheme 5. (i) $\text{M}^{\text{III}}\text{-X}$ bond energies (kcal mol^{-1}): P-Br, 63; As-Cl, 74; As-Br, 61.^a (ii) $\text{M}^{\text{V}}\text{-F}$ bond energies (kcal mol^{-1}): P-F, 110;⁷ As-F, 92.6, ref.², Scheme 1.³ (iii) $\text{M}^{\text{III}}\text{-F}$ bond energies (kcal mol^{-1}): P-F, 117; As-F, 117.^a (iv) Heat of vaporization of AsF_3 (l): 9 kcal mol^{-1} .² (v) Atomization energies: see Scheme 1. ^a D. A. Johnson, in 'Some Thermodynamic Aspects of Inorganic Chemistry,' 2nd edn., Cambridge University Press, 1982, appendix.

Table 7. Enthalpies of steps in the decomposition of MX_4EF_6 ($\text{M} = \text{P}$ or As , $\text{X} = \text{Cl}$ or Br , $\text{E} = \text{P}$ or As) calculated from equations (22)–(24)

Compound	$\Delta H(22)^{a,b}$	$\Delta H(23)^{a,c}$	$\Delta H(24)^{a,d}$	ΔH_1^a
$\text{AsBr}_4\text{AsF}_6$	+99	-55	-73	-29
$\text{AsCl}_4\text{AsF}_6$	+94	-22	-50	+22
AsBr_4PF_6	+89	-55	+24	+58
PBr_4AsF_6	+98	-65	-59	-26
PBr_4PF_6	+88	-65	+37	+60

^a Values in kcal mol^{-1} . $\Delta H_1 = \Delta H(22) + \Delta H(23) + \Delta H(24)$. ^b Estimated by Scheme 3. ^c Estimated by Scheme 4. ^d Estimated by Scheme 5.



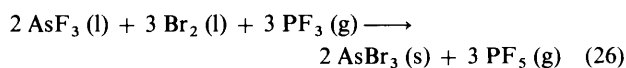
temperature. The positive enthalpies of the first steps [equation (22)] in the decomposition of $\text{AsBr}_4\text{AsF}_6$ [$\Delta H(22) \equiv \Delta H(17) = +99 \text{ kcal mol}^{-1}$; $\text{M} = \text{As}$, $\text{X} = \text{Br}$, $\text{E} = \text{As}$] and $\text{AsCl}_4\text{AsF}_6$ [$\Delta H(22) = +94 \text{ kcal mol}^{-1}$; $\text{M} = \text{As}$, $\text{X} = \text{Cl}$, $\text{E} = \text{As}$] are both very similar. However, the enthalpies of reactions (23) and (24) are significantly less favourable for $\text{AsCl}_4\text{AsF}_6$ [$\Delta H(23) = -22$, $\Delta H(24) = -50 \text{ kcal mol}^{-1}$] than for $\text{AsBr}_4\text{AsF}_6$ [$\Delta H(23) = -55$, $\Delta H(24) = -73 \text{ kcal mol}^{-1}$]. Thus the overall decomposition of $\text{AsBr}_4\text{AsF}_6$ is favourable ($-29 \text{ kcal mol}^{-1}$), whereas that of $\text{AsCl}_4\text{AsF}_6$ is not ($+22 \text{ kcal mol}^{-1}$). These differences arise because the As^+-Cl bond ($-77.6 \text{ kcal mol}^{-1}$) is stronger than the As^+-Br bond ($-64.1 \text{ kcal mol}^{-1}$).

The enthalpy for fluoride loss is greater in the order $\text{AsF}_6^- < \text{SbF}_6^- < \text{Sb}_2\text{F}_{11}^-$; therefore on this basis $\text{AsBr}_4\text{Sb}_2\text{F}_{11}$ is expected to be significantly more stable to decomposition than $\text{AsBr}_4\text{AsF}_6$. Our attempts to prepare this salt by the reaction of $\text{AsBr}_4\text{AsF}_6$ and SbF_5 were unsuccessful. If $\text{AsBr}_4\text{Sb}_2\text{F}_{11}$ were formed, it may have decomposed according to equation (25).

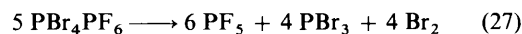


The enthalpy of formation of AsI_4AsF_6 by equation (8) is estimated (see Table 5) as favourable [$\Delta H(8) = -33 \text{ kcal mol}^{-1}$; $\text{M} = \text{E} = \text{As}$, $\text{X} = \text{I}$] and is approximately the same as the enthalpy of formation of $\text{AsBr}_4\text{AsF}_6$ by the same reaction [$\Delta H(8) = -113 \text{ kcal mol}^{-1}$; $\text{M} = \text{E} = \text{As}$, $\text{X} = \text{Br}$]. However the estimate of the decomposition enthalpy of AsI_4AsF_6 ($\Delta H = -98 \text{ kcal mol}^{-1}$; $\text{M} = \text{E} = \text{As}$, $\text{X} = \text{I}$) is substantially greater than that of $\text{AsBr}_4\text{AsF}_6$ [$\Delta H(9) = -25 \text{ kcal mol}^{-1}$]. Our attempts to prepare AsI_4AsF_6 were unsuccessful and are consistent with this. However, using a similar experimental and conceptual approach, one of us has succeeded in preparing the thermodynamically more stable AlCl_4^- salt of the AsI_4^+ cation.⁵

The enthalpy of formation of AsBr_4PF_6 by equation (8) [$\text{M} = \text{As}$, $\text{X} = \text{Br}$, $\text{E} = \text{P}$; $\Delta H(8) = +2 \text{ kcal mol}^{-1}$] is about zero, and not surprisingly attempts to prepare the salt by this method were unsuccessful. The estimated enthalpy of decomposition of AsBr_4PF_6 to PF_3 , AsF_3 , and Br_2 was significantly positive [$\Delta H(9) = +60 \text{ kcal mol}^{-1}$; $\text{M} = \text{As}$, $\text{X} = \text{Br}$, $\text{E} = \text{P}$], showing that the salt is substantially more thermodynamically stable than those decomposition products. However, our attempts to prepare AsBr_4PF_6 by this route [see Table 5, equation (8)], proceeded instead by equation (26), which is even more exothermic [$\Delta H(26) = -122 \text{ kcal mol}^{-1}$]; $\Delta H_f(\text{AsF}_3, \text{l}) = -229$, $(\text{PF}_3, \text{g}) = -220$, $(\text{AsBr}_3, \text{s}) = -47$, and $(\text{PF}_5, \text{g}) = -382 \text{ kcal mol}^{-1}$.²³



The salt PBr_4PF_6 is stable up to 125°C .^{24–26} However, we estimated that it is only marginally stable ($\Delta H = +11 \text{ kcal mol}^{-1}$) with respect to the products given in equation (27).



Thus PBr_4PF_6 is likely to be kinetically stable, but $\text{AsBr}_4\text{AsF}_6$ is both kinetically and thermodynamically unstable. We therefore suggest that the criterion for salts of this kind to have kinetic stability is simply that the products after halide transfer must retain kinetic stability in their new environment. In the PBr_4PF_6 system [see equations (26) and (27)] PF_5 is both kinetically and thermodynamically stable and PBr_4^+F^- is kinetically stable up to 85°C .^{24–26} This contrasts with the $\text{AsBr}_4\text{AsF}_6$ system; AsF_3 is likely to react rapidly with any AsBr containing species, and $\text{AsBr}_4^+\text{F}^-$ is very probably kinetically labile, even if it did not react with AsF_5 . A number of related salts [e.g. $\text{S}_4(\text{AsF}_6)_2$,¹ $\text{SeBr}_3\text{AsF}_6$,^{2c} and SBr_3AsF_6 ^{2c}] may also be only kinetically stable.

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The authors thank Professor R. Steudel (TU Berlin) for providing us with the use of the laser-Raman facilities, the Natural Sciences and Engineering Research Council of Canada and the University of New Brunswick for financial support, the Humboldt Foundation for a Fellowship (to J. P.) and for a Lynen Fellowship (to T. K.), and Dr. A. J. Banister (Durham University) for help improving the manuscript.

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