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ARSENIC PENTAFLUORIDE EQUILIBRIA IN ANHYDROUS HYDROGEN FLUORIDE

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SUMMARY

Earlier work has indicated that arsenic pentafluoride when dissolved in anhydrous HF is present largely as the anion $As_2F_{11}^-$, particularly at temperatures much below ambient. Raman spectra and conductance measurements are used here to show that, at and near room temperature, there are significant concentrations of molecular AsF_5, AsF_6^- and $As_2F_{11}^-$ in equilibrium and that on reduction of temperature, $As_2F_{11}^-$ is formed at the expense of AsF_5 and AsF_6^-. The implications of the Lewis acid and oxidant strengths of AsF_5 are discussed as affecting synthetic procedures in anhydrous HF.

INTRODUCTION

A considerable amount of information has been accumulated on the behaviour of pentafluorides as Lewis acids in the anhydrous hydrogen fluoride (AHF) solvent system. Until about 1970 most of the reliable physico-chemical investigations had been of the SbF_5—HF system. Hyman and coworkers [1] observed that the electrical conductance of solutions of SbF_5 in AHF peaked at about 10 mole % (*i.e.* 5 molal) and then fell off sharply. They used vibrational spectroscopy to indicate some formation of SbF_6^- and interpreted their conductance data by postulating that SbF_5 was a relatively weak Lewis acid in 20 mole% solution and that a high degree of ion-pairing was occurring between H_2F^+ and SbF_6^- — the latter an unlikely postulate in a solvent of very high dielectric constant. Gillespie and Moss [2] effectively reproduced the earlier conductance data and then used ^{19}F nmr spectroscopy to show that at about 20 mole % SbF_5 in HF the dominant anionic species was $Sb_2F_{11}^-$. Up to about 10 mole % SbF_6^- is the principal anion and beyond about 30% $Sb_3F_{16}^-$ and more complex $Sb_nF_{5n+1}^-$ species are formed. Thus the conductance decreases with addition of SbF_5 as less ions per mole of

SbF_5 are produced, an effect enhanced by the size and reduced mobility of the polymeric anions. Subsequently crystal structures have been determined for compounds containing polymeric anions of Sb (V), e.g. for the closely chemically related compounds $I_2^+Sb_2F_{11}^-$ [3] and $Br_2^+Sb_3F_{16}^-$ [4].

An early investigation of the AsF_5—HF system [5] showed that at moderate concentrations, i.e. at about 0.1 molal, AsF_5—HF solutions at 0°C had about half the conductance of SbF_5—HF solutions at similar temperature and concentrations. In a later and much fuller study, Gillespie and co-workers [6] measured lowering of the freezing point of solutions of AsF_5 in HF up to about 0.5 molal and obtained a very reliable value of 1.0 for ν, the number of moles of particles produced in solution per mole of solute. The simplest interpretation of this result, namely that AsF_5 dissolves as single molecular units in HF, was known to be untenable in the light of the previously observed conductances of AsF_5—HF solutions.

Gillespie's group [6] then measured the conductances of SbF_5 and of AsF_5 at -83.6°C (very close to the freezing point of the solution) and established that for concentrations up to about 0.5 molal, AsF_5 solutions had almost exactly half the specific conductance of SbF_5 solutions of the same concentration. They explained their cryoscopic and conductance observations by postulating that at -83.6°C a dimeric anion is formed according to the equation.

$$2HF + 2AsF_5 \rightarrow H_2F^+ + As_2F_{11}^-,$$

i.e. ν is unity for 2 moles of ions per 2 moles of AsF_5, and for AsF_5 there are half the number of conducting ions per mole than is the case for SbF_5 in dilute solution in HF. They provided confirmatory evidence in HF solution by carrying out both cryoscopic and conductometric titrations of Et_4NAsF_6 against AsF_5 at -83.6 and -63.5°C respectively. They obtained maxima and minima respectively at a value of about 1.0 for the AsF_6^-/AsF_5 ratio, indicating the formation of $As_2F_{11}^-$. Additional support was obtained by recording the ^{19}F nmr spectrum for $Bu_4NAs_2F_{11}$ in SO_2ClF at -140°C. This spectrum had the same relative peak areas and coupling patterns as that obtained earlier for $Sb_2F_{11}^-$. The infra-red spectrum of solid $Et_4NAs_2F_{11}$ showed a weak band at 481 cm^{-1}. Such bands in the 480 to 500 cm^{-1} region are now known to be diagnostic for bridging F atoms in dimeric anions.

Initially, in the investigation of the behaviour of pentafluorides in HF it had been expected that Lewis acid/base interaction would be restricted to a reaction such as:

$2HF + AF_5 \rightleftharpoons H_2F^+ + AF_6^-.$

Gillespie had demonstrated unexpected behaviour in the SbF_5 system. SbF_5 is a strong Lewis acid yielding SbF_6^- with no detectable SbF_5 at low to moderate concentrations. At low concentrations of SbF_5 (up to 0.4 molal), cryoscopy had given a reliable value of 2.0 for v, i.e. the interaction of acid and solvent was best described as in the equation:

$2HF + SbF_5 \rightarrow H_2F^+ + SbF_6^-$

The unexpected feature was the formation of $Sb_2F_{11}^-$ at about 10 mole % of SbF_5. It was still more surprising that the weaker Lewis acid AsF_5 would form $As_2F_{11}^-$ predominantly even in quite dilute solution.

However it must be stressed that virtually all of Gillespie's reported observations on AsF_5—HF solutions were at very low temperatures, usually near -83.6°C. When AsF_5 is used as a Lewis acid in synthetic work, the solution is usually at or near room temperature. We have now shown that the situation is significantly different near room temperature from that indicated by the Gillespie work and this has important synthetic implications as will be shown towards the end of this paper. We have recorded conductances of AsF_5—HF solutions at 0°C as a convenient fixed temperature and in order to make our measurements directly comparable with those of other workers. We have used Raman spectroscopy to show significant concentrations of AsF_5 to be present in HF solutions near room temperature as well as both AsF_6^- and $As_2F_{11}^-$. Further the relative amounts of each species depend heavily on the absolute amount of AsF_5 present and on the temperature of the solution. Our conductance data are consistent with our spectral observations and with spectrometric and potentiometric measurements of the acidities of solutions of SbF_5 and of AsF_5 in HF.

EXPERIMENTAL

Manipulation of Fluorides

Air-sensitive solids were handled in an argon-filled glove box. Volatile fluorides, such as HF and AsF_5, were transferred **separately** through a vacuum line based on stainless steel Swagelok unions and Whitey valves, Bourdon and thermocouple gauges and KelF reaction traps. This vacuum line was essentially similar to those described previously [7,8a].

Conductance Cell

The simple conductance cell used for many of the measurements in this work has been described previously [8b].

Raman Spectroscopic Cell

A special cell, resistant to HF solutions of enhanced acidity and designed and constructed for this work, allowed simultaneous measurement of electrical conductance and recording of Raman spectra of the enclosed solutions under controlled temperature conditions. The only materials in contact with working solutions were platinum, KelF and synthetic sapphire. Mechanical strength was provided by having the components clamped together by brass fittings. The cell was provided with circulating cooling solutions and was thermally insulated by polyurethane foam, also enclosed within a brass envelope. The inner section of the cell was a thick-walled cylinder of KelF. Two 1 cm sapphire windows were self-sealed into recesses close to one end and these allowed passage of the laser source of the Raman spectrometer. A 3 cm sapphire window at that end enabled the transmission of the maximum possible amount of scattered radiation. Two bright platinum electrodes, 1 cm^2 in area, were located 1 cm apart at the other end of the cell. To one of those was fixed a Pt-Rh wire for solution temperature measurement. The three wires were sealed into the cell by Teflon compression fittings. That end of the KelF cylinder was gasketted and capped with a massive nickel disc faced with platinum sheet. This overcame the problem of the very slow thermal equilibration of the solution which occurs in equipment constructed entirely from KelF , a very poor thermal conductor. Cooling water was circulated from a bath containing ice and water for 0°C spectra or from 27% $CaCl_2$ solution cooled by dry ice for -20° spectra. Initially when the cell was in the spectrometer, fogging of the windows caused a serious problem, which was eliminated by constructing over the cell and the cell cavity of the instrument a canopy through which dried argon was passed.

Raman Spectrometer

Raman spectra were recorded on a Spex Ramalog 5, 14018 spectrometer with argon ion laser excitation (5145 A°). For most of the spectra reproduced in this paper, multiple spectral scans were computer averaged to improve the signal-to-noise ratios.

Reagents

Anhydrous Hydrogen Fluoride

Commercial HF (Matheson, 99.5%) was purified by three trap-to-trap distillations in well conditioned KelF apparatus, collecting the liquid at -45°C. The solvent used had a specific conductance of about 10^{-4} ohm^{-1} cm^{-1}.

Arsenic Pentafluoride

The gas was used as supplied by the Ozark-Mahoning Company and showed no spectroscopic impurities.

Sodium Hexafluoroarsenate (V)

A.R. NaCl was dried at 600°, treated with liquid AHF and HCl was pumped off. Equimolar AsF_5 was metered into a solution of NaF in HF from a bulb of known volume containing AsF_5 at known temperature and pressure. Finally HF was pumped off.

Solution Preparation

Where appropriate, as in the case of $NaAsF_6$, a solid reagent was added in a glove box to a KelF reaction tube, previously weighed while evacuated; the tube was re-evacuated and weighed. Anhydrous HF was condensed into the tube which was re-weighed. AsF_5 was added quantitatively from a bulb by p-V-T metering. Such solutions were diluted progressively with weighed amounts of HF. Alternatively, additions of AsF_5 were made by quantitative metering. Prior to recording of spectra, all solutions were treated with a small partial pressure of fluorine, in order to quench fluorescence, a common problem in Raman spectroscopy, particularly of HF solutions in or from KelF containers.

RESULTS

Figure 1 shows a Raman spectrum, obtained by computer addition of 40 spectral scans for a solution 0.1 molal in AsF_5. The peak at 732 cm^{-1} corresponds

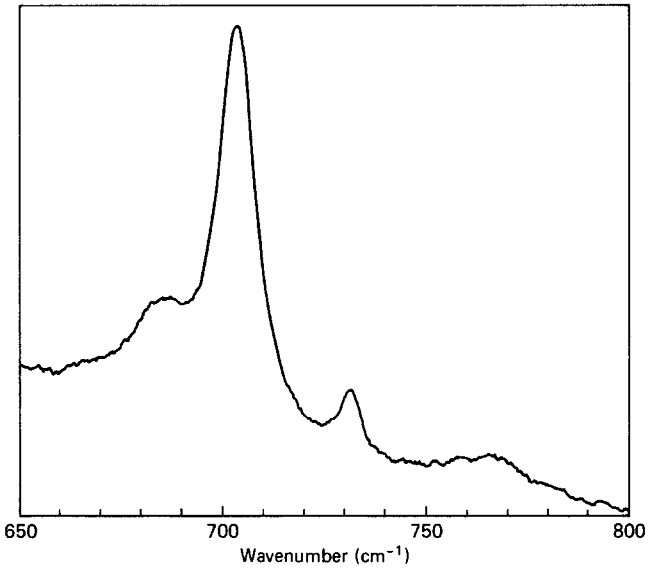

Fig. 1. The Raman spectrum of 0.1 molal AsF_5 in HF at room temperature.

with that at 733 cm^{-1}, previously reported as the strongest peak in the Raman spectrum of liquid AsF_5 [9]. The broader peak around 685 cm^{-1} can be related to that reported at 685 cm^{-1} in solid $CsAsF_6$ [10] and at 680 cm^{-1} in $ClF_6^+AsF_6^-$ [11], a compound in which the coordinately-saturated cation would have little distorting influence on the symmetry of the fluoroanion. The largest peak at 703 cm^{-1} would then be associated with $As_2F_{11}^-$.

These assignments were confirmed by carrying out the series of experiments shown in Figure 2, where again computer addition techniques were used in order to obtain 'cleaner', more reliable spectra. Each of the spectra in Figure 2 is based on 5 to 10 spectral scans. The peak marked with an asterisk in Fig. 2 (c) is due to sapphire. Very careful alignment of the cell was found to be necessary to avoid this complication. For $NaAsF_6$ in HF a single peak at 686 cm^{-1} was observed. The anion AsF_6^- is the dominantly stable one in a solution of $NaAsF_6$ in HF. Any proposed formation of AsF_5 or $As_2F_{11}^-$ would generate F^- and produce a basic solution. When AsF_5 equimolar to $NaAsF_6$ was added, the solution would have

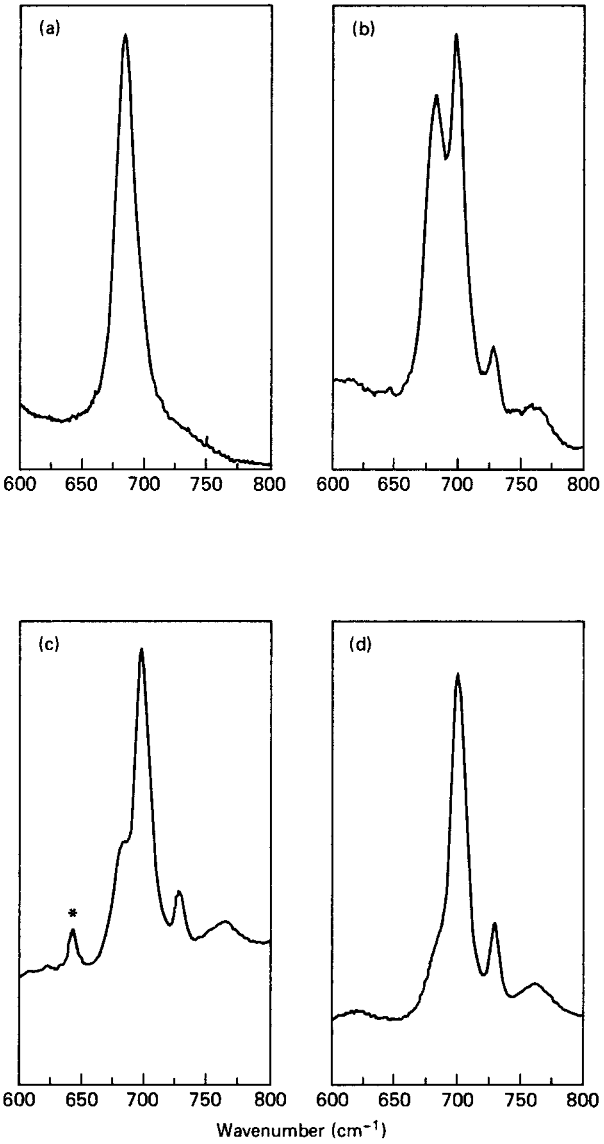

Fig. 2. Raman spectra of AsF_5, AsF_6^- and $As_2F_{11}^-$ in HF at room temperature.

(a) $NaAsF_6$

(b) $NaAsF_6$: AsF_5, 1:1

(c) $NaAsF_6$: AsF_5, 1:3

(d) $NaAsF_6$: AsF_5, 1:7

become acidic and three new peaks were observed in the region 600 to 800 cm^{-1} in addition to a marked diminution in the size of the AsF_6^- peak. There was a small peak at 736 cm^{-1}, indicating the presence of free AsF_5 and a strong sharp peak at 702 cm^{-1}. This can all be interpreted in terms of an equilibrium in acidic HF,

$$AsF_6^- + AsF_5 \rightleftharpoons As_2F_{11}^-.$$

The broad peak in the 760-770 cm^{-1} region is a feature of all Raman spectra of HF solutions containing $As_2F_{11}^-$ but is not the most diagnostic one for the dimeric anion. Increase in the ratio AsF_5:AsF_6^- as in Figures 2 (c) and 2 (d), shows a marked decrease in the AsF_6^- with an increase in the peak due to molecular AsF_5. It should be noted that, even with a seven-fold excess of AsF_5 over AsF_6^- there is still a shoulder indicating the presence of some AsF_6^- in HF at room temperature.

In another series of experiments HF containing no $NaAsF_6$ was made 2, 4, 6 and 8 molal in AsF_5. Spectra, recorded at room temperature, gave little or no evidence for AsF_6^- but the height of the AsF_5 peak rose steadily being approximately 27%, 35%, 50% and 90% that of the $As_2F_{11}^-$ peak in each case as the total molality was increased. While this shows that there is a marked increase in the concentration of molecular AsF_5 in solution as the total molality of arsenic pentafluoride is increased, no attempt has been made in this work to use the spectra quantitatively because of the great difficulty of relating peak heights in Raman spectroscopy to concentrations of solutes.

For purposes of comparison with the AsF_5—HF system, Raman spectra were recorded at room temperature for SbF_5—HF solutions with SbF_5 concentrations up to 2 molal. Raman peaks were observed for SbF_6^- but there was no strong Raman spectroscopic evidence over this solute concentration range for significant concentrations of $Sb_2F_{11}^-$ or SbF_5. This is consistent with previous reports [1,2,6] that SbF_5 is a very strong Lewis acid and that the monomeric anion is the predominant species in solutions that are reasonably dilute. Currently, Raman spectra are being recorded for solutions of SbF_5 in HF more concentrated than 2 molal and at temperatures below room temperature. We expect to report this work shortly.

It was stressed in the Introduction that Gillespie's excellent experimental evidence [6] for the predominance of the $As_2F_{11}^-$ anion in HF-AsF_5 systems applied to solutions at low temperatures. The Raman cell specially designed for this work was used to give information on the effect of temperature on the equilibrium written above. Because of the experimental difficulties in recording spectra of HF solution at low temperatures, the spectra in Figure 3 are all single-pass spectra and therefore not of the quality of those in Figures 1 and 2. However the spectra in Figure 3, recorded on the same solution at 20°, 0° and -20°C, provide very good evidence for shift of the equilibrium in favour of $As_2F_{11}^-$ with decrease in temperature. There is clear spectroscopic evidence for AsF_5 at 20° but no AsF_5 detectable spectroscopically at -20°C. It should be noted that the enhancement of the Raman signal in passing from +20° to -20° should favour the possibility of observing free AsF_5 at -20°. For AsF_6^- the evidence is not so clear cut. A separate peak at 20° becomes a shoulder at lower temperatures.

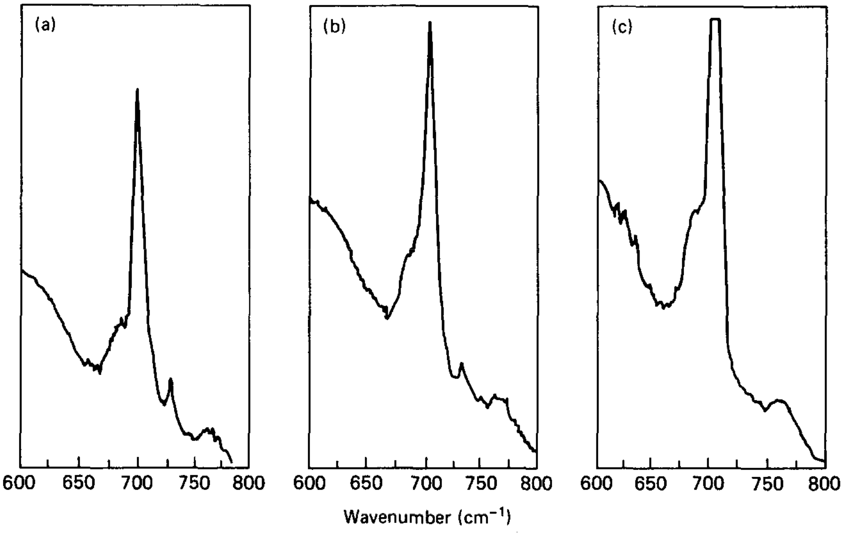

Fig. 3. Raman spectra of 0.18 molal AsF_5 in HF at (a) 20°C (b) 0°C and (c) -20°C.

In this work electrical conductances of HF solutions containing AsF_5 up to 2 molal were measured at 0°C. With increase in the amount of AsF_5, specific conductances became very much less than one-half of the conductances at corresponding concentrations of SbF_5 at 0°C — the values that would be expected if the species in solution were H_2F^+ and $As_2F_{11}^-$ in the former case and H_2F^+ and SbF_6^- in the latter. In fact there was little increase in specific conductance in the HF—AsF_5 system between 1 molal and 2 molal.

Only the comparative values up to 0.1 molal will be presented in this paper for the following reasons. Firstly, the Raman spectra presented are in that range and it is typical of the amount of AsF_5 that would be used in synthetic work in HF — a point that will be developed towards the end of the paper. Secondly there have been earlier suggestions [5,6] that even in relatively dilute solution much of the AsF_5 could be in the vapour phase. We measured additive vapour pressures for HF-AsF_5 solutions and made the assumption — not necessarily valid — that ideal vapour pressure additivity applies. For experimental systems in which the volumes of the solution and of the vapour were comparable, we found about 96.0% of AsF_5 in solution at 18° when the total molality was 3.25 and about 95% when the molality was 5.57. It can be assumed that, for AsF_5—HF solutions up to 0.1 molal at 0°C, the errors in measured conductances because of loss of AsF_5 to the vapour phase will be slight — probably negligible.

In Figure 4 a comparison is made between specific conductances at 0°C of SbF_5 [2] and our values for AsF_5 in HF at 0°C for concentrations up to 0.1 molal. Earlier measurements [6], also shown in Figure 4, are very similar to those in the present work. The coincidence of our AsF_5 conductances with the earlier ones [6] adds considerable weight to the argument that virtually all of the AsF_5 is in solution at low concentrations at 0°C. It is highly probable that there would have been differences between the two research groups in the methods used in preparing AsF_5—HF solutions and transferring them to conductance cells. Certainly, we know that "dead-space" was minimized in our procedures. The similar results suggest very strongly that negligible amounts of AsF_5 were lost to the vapour phase.

By comparing the curve through the experimental points for AsF_5 with that constructed through points which are half the value of the SbF_5 conductances at the same concentrations (broken line), it is clear that, even in relatively dilute solution at 0°C, much arsenic pentafluoride is in solution other than as $As_2F_{11}^-$ presumably as

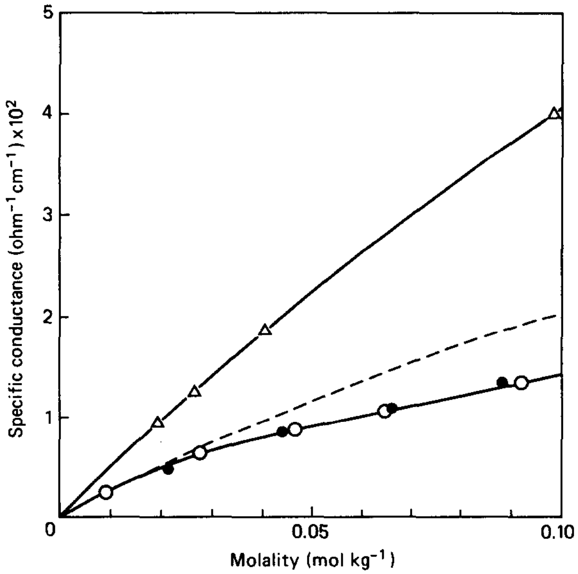

**Fig. 4. Specific conductances of SbF_5 and AsF_5 in HF at 0°C.
△ SbF_5 (ref. 2), ● AsF_5 (ref. 6) , o AsF_5 (this work)**

molecular AsF_5 as indicated by the Raman spectra. Were it to be present as AsF_6^-, of course, AsF_5 conductance points would be greater than half of the SbF_5 points. It would be difficult to try to deal with these differences in conductances quantitatively , because the limiting ionic mobility of $As_2F_{11}^-$ will be less than that of SbF_6^-. On the other hand, the H_2F^+ cations in each system will have a greater effect on observed conductances than that of the anions, whether monomeric or dimeric.

DISCUSSION

There is little doubt from the 1971 work of Gillespie and colleagues [6] that at very low temperatures, approaching the freezing point of anhydrous HF, arsenic pentafloride is present in solution in HF predominantly, perhaps almost exclusively as $As_2F_{11}^-$. It is to be expected that as solutions approach extreme dilution the dimeric ion, and indeed any molecular AsF_5, will give place to AsF_6^-. Hyman, Lane and O'Donnell [5] demonstrated this with the experimental points given in Table 1.

The conductances listed here show that AsF_5 is a much weaker conductor (i.e. weaker Lewis acid) than SbF_5 at about 0.1 molar but as solutions become very dilute both solutions approach the same limiting conductance.

TABLE 1

Molar Conductances (ohm^{-1} cm^2 $mole^{-1}$) of SbF_5 and AsF_5 in HF at 0°C

SbF_5 Molarity	Molar conductance	AsF_5 molarity	Molar conductance
0.1570	396	0.0953	197
0.0348	538	0.0319	317
0.0248	557	0.0062	502
0.0247	559	0.0036	579
0.0002	614	0.0022	605

However the main thrust of this paper is to shed further light on the speciation in an anhydrous HF solution containing about 0.1 M of total arsenic pentafluoride at room temperature. This would be a typical situation in synthetic work in HF when AsF_5 was being used deliberately as a moderately strong Lewis acid. The Raman spectra show clearly that an equilibrium exists:

$$AsF_6^- + AsF_5 \rightleftharpoons As_2F_{11}^-$$

Lowering of the temperature favours the formation of $As_2F_{11}^-$ as does increasing the pentafluoride concentration; but increasing the absolute amount of arsenic pentafluoride also increases the concentration of molecular AsF_5 in solution. As indicated earlier in the paper, no attempt has been made to provide a quantitative basis for this equilibrium. It is very difficult to use peak sizes in Raman spectroscopy to determine concentrations; but the data presented give good qualitative evidence for the effects of arsenic pentafluoride concentration and of temperature on the equilibrium.

This work correlates well with measurements of the relative acidities at room temperature of solutions containing SbF_5 and AsF_5. If, as is approximately correct for SbF_5, it were in solution only as SbF_6^-, and AsF_5 predominantly as $As_2F_{11}^-$, the acidities of the solutions would be expected to differ by a factor of about 2. Spectrophotometric Hammett Acidity Function measurements [12] and potentiometric methods based on the chloranil electrode [13] show the difference to be greater than a power of ten in each case. Obviously AsF_5 is a much weaker Lewis acid than SbF_5, being present in solution to a large extent as molecular AsF_5.

This has very great implications for synthetic work in anhydrous HF. By contrast, the more acidic SbF_5—HF system containing SbF_6^-, a weaker oxidant than SbF_5, will be a weaker oxidizing system than AsF_5—HF which contains a relatively large equilibrium concentration of molecular AsF_5, a much stronger oxidant than AsF_6^-. Also $As_2F_{11}^-$ will readily dissociate to give AsF_5.

There has been an extensive Melbourne programme of preparation of solutions in HF of cations of *d*- and *f*- transition metals in a wide range of oxidation states and subsequent recording of UV-visible spectra of the solvated cations in HF. Although AsF_5 is a weaker Lewis acid than SbF_5,[12,13] there can be advantages in using it in preference to SbF_5 in some synthetic progammes e.g. HF—AsF_5 usually gives solutions that have very much higher concentrations of cations than does the HF—SbF_5 system. Solids isolated from HF—AsF_5 solution usually contain the monomeric AsF_6^- ion, whereas HF—SbF_5 yields $Sb_2F_{11}^-$ and more complex anions. Our experience has been that salts of cations and AsF_6^- are very much more soluble in acidic HF solutions than corresponding compounds containing the anion $Sb_2F_{11}^-$.

AsF_5 is very much more volatile than SbF_5. The relative volatilities and Lewis acid strengths of AsF_5 and SbF_5 probably account for the common observation that, even though the dominant anion in dilute AsF_5—HF is $As_2F_{11}^-$, solids isolated from AsF_5—HF almost invariably contain the AsF_6^- anion whereas for the SbF_5—HF system the anion in dilute solution is SbF_6^- but the solids isolated usually contain $Sb_2F_{11}^-$.

Much judgement must be exercized in selection of the appropriate Lewis acid used to enhance HF acidity. We have accumulated a considerable amount of evidence during the generation of cations in low oxidation states to show that AsF_5, a weaker Lewis acid than SbF_5, is a stronger oxidant in HF, for the reasons given above. Metallic Cr, when treated with a concentrated (5 M) solution of SbF_5 in HF, yielded solvated Cr^{2+} and H_2, whereas when AsF_5 was the Lewis acid there was no H_2 evolution and Cr (III) was produced, AsF_3 being presumed to be the reduction product [14]. 3 M SbF_5—HF reacted with metallic Ti to give orange-yellow solutions containing $Ti^{2+}_{(solv)}$ but AsF_5 gave blue or green solutions with spectra indicating the presence of Ti^{3+}[15].

Other, more complex, synthetic systems may also be rationalized in terms of relative Lewis acid and oxidant strengths of the reagents AsF_5 and SbF_5. For example, AsF_5 in solvents such as SO_2, has been very effective in producing unusual and unstable polyatomic cations such as Cl_3^+ which was isolated as $Cl_3^+AsF_6^-$ [16]. In reactions such as this, the pentafluoride was used as an oxidant, and additionally to provide a very weakly basic reaction medium and to be a source of the counter-anion AsF_6^-. Not only is the reduction product AsF_3 weakly basic and sufficiently volatile to be removed easily from the reaction mixture — unlike SbF_3 — but the system can be more effective in oxidation reactions than the SbF_5 counterpart.

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