UNUSUAL CATIONS OF ANTIMONY AND ARSENIC
In the past few years considerable interest has been shown in the high acidity of fluorosulphuric acid and the solutions of antimony pentafluoride therein. The high acidity of this system can be further increased by the addition of sulphur trioxide (67). These highly acidic media are weakly nucleophilic and provide good conditions for the stabilisation of various electrophilic cations, such as nitronium (156), carbonium (74) and oxocarbonium (157). Homoatomic cations of chlorine (84) bromine (83) and iodine (79, 158) have also been stabilised in fluorosulphuric acid.

Gillespie and coworkers (159) have shown that by using varying amounts of an oxidising agent viz. $S_2O_6F_2$, the solutions of iodine in fluorosulphuric acid can be oxidised quantitatively to a number of different oxidation states. By means of cryoscopic, conductimetric, spectrophotometric and magnetic susceptibility measurements; it has been shown that the following reactions take place quantitatively:

$$5I_2 + S_2O_6F_2 \rightarrow 2I_5^+ + 2SO_3F^-$$
$$3I_2 + S_2O_6F_2 \rightarrow 2I_3^+ + 2SO_3F^-$$
$$2I_2 + S_2O_6F_2 \rightarrow 2I_2^+ + 2SO_3F^-$$
$$I_2 + 3S_2O_6F_2 \rightarrow 2I(SO_3F)_3$$
When dissolved in disulphuric acid, iodine gives a blue coloured solution (158, 160). This blue colour has been characterised due to the $I_2^+$ cation as:

$$2I_2 + 6H_2S_2O_7 \rightarrow 2I_2^+ + 2H_3S_2O_7^- + 5H_2SO_4 + S_O_2$$

The existence of cations $I_3^+$ and $I_5^+$ has also been established in sulphuric acid (161); iodine being oxidised by iodic acid as:

$$HI0_3 + 7I_2 + 8H_2SO_4 \rightarrow 5I_3^+ + 3H_2SO_4^- + 8HSO_4^-$$

Attempts to isolate solid compounds with unusual configurations ($I_2^+$, $I_3^+$ and $I_5^+$) have not met with much success.

Selenium when oxidised with $S_2O_6F_2$, forms green and yellow coloured solutions (80). The green colour which was previously attributed to the compound $Se.SO_3$ has now been shown to be due to the species $Se_8^{2+}$, which is formed in the solution according to the following reaction:

$$8Se + S_2O_6F_2 \rightarrow Se_8^{2+} + 2SO_3F^-$$

The yellow coloured solution, previously thought to be one of the varieties of the adduct $Se.SO_3$ (162), is now considered to be due to the $Se_4^{2+}$ ions formed according to the equation:

$$4Se + S_2O_6F_2 \rightarrow Se_4^{2+} + 2SO_3F^-$$
Similar type of cations have also been reported in sulphuric and disulphuric acids.

Unusual cations in case of Tellurium have also been reported (82). A red species is formed by the oxidation of Te with $S_6O_6F_2$ in fluorosulphuric acid. This has been attributed to the $Te_4^{2+}$ ions. Similar cations in sulphuric and disulphuric acids have also been established. The ion formation has been formulated:

$$4Te + S_6O_6F_2 \rightarrow Te_4^{2+} + 23O_3F^-$$

$$4Te + 6H_2S_2O_7 \rightarrow Te_4^{2+} + 2HS_3O_10^- + 5H_2SO_4 + SO_2$$

Very recently, some unusual cations of sulphur viz. $S_{16}^{2+}$, $S_8^{2+}$ and $S_4^{2+}$ (81, 163) have also been reported.

It has been reported in literature that bismuth on treatment with bismuth trichloride in the fused state forms certain unusual cations (164). Existence of $Bi_8^{2+}$ (165) in KCl-AlCl$_3$ melts has been reported recently. It has, therefore, been of some interest to study the oxidation and to explore the possibility of the formation of such unusual cations of the elements of group VB in fluorosulphuric acid.
Arsenic, antimony and bismuth dissolve slowly in sulphur trioxide free fluorosulphuric acid to give transparent solutions. Woolf (166) has reported that the dissolution is accompanied by no change in the conductance of the solution. However, we have found that at room temperature, in the presence of potassium persulphate or peroxydisulphuryl difluoride, antimony forms blue coloured solutions. In presence of excess of the oxidising agent, the blue colour changes to green and finally to yellow. In concentrated solutions, the final colour of the solution is orange. Solutions with an excess of oxidising agent when allowed to stand overnight become colourless. The yellow solutions turn blue when hydrazine sulphate is added. Antimony metal separates out on pouring these solutions on crushed ice. It may, therefore, be concluded from the above observations that the coloured antimony species are positive oxidation states of the metal and that the yellow is a higher oxidation state than the blue one. Coloured solutions could not be obtained with oxidising agents such as sulphur trioxide, perchloric acid, periodic acid and ceric sulphate. It is for the first time that the above mentioned observations have been made.
In order to make a comparative study of the coloured solutions in other protonic acids, attempt has been made to prepare such solutions in sulphuric and disulphuric acid also. Antimony does not dissolve in 100% sulphuric and disulphuric acids. This suggests that sulphur trioxide is a weaker oxidising agent than potassium persulphate.

Coloured solutions of antimony in sulphuric acid have been prepared by oxidising the metal with the requisite amount of potassium persulphate. In case of disulphuric acid, the coloured solutions have been first prepared in 100% sulphuric acid and then the necessary amount of sulphur trioxide has been distilled to make disulphuric acid of exact composition. This technique has already been used by Symons and coworkers (167) in the stabilisation of carbonium ions in 65% oleum.

Unlike the blue coloured solutions of iodine and sulphur in oleum (168, 169) and fluorosulphuric acid (81), the blue coloured solutions of antimony are diamagnetic. The yellow solutions are also diamagnetic. This rules out the possibility of the presence of any cations having unpaired electrons.
The absorption spectra of the blue and the yellow coloured solutions of antimony is exactly the same in all three solvents indicating the similarity in nature of the cations formed. The u.v. and visible spectra of the blue solution is shown in Fig. 20. A look at the figure shows that the blue species have peaks at 280 nm (intense) and at 460 nm (weak) and a broad band at 680 nm. It may be mentioned here that the blue species are not very stable and there is always a possibility of oxidation to yellow species in the presence of even a slight excess of the oxidising agent. This is indicated by the existence of a slight absorption band at 390 nm (green solutions). This difficulty can be dealt with by keeping the amount of the oxidising agent to a bare minimum and keeping the temperature low.

The spectrum of the pure blue solution has been recorded by careful addition of hydrazine sulphate until there was no trace of the 390 nm peak. The blue solutions are stable and obey Lambert-Beer Law. The values for the extinction coefficients for various maxima in the curve are given in Table VII. The similarity in the molar extinction
### TABLE VII

Molar Extinction coefficients for the various species of antimony and arsenic in fluorosulphuric acid

<table>
<thead>
<tr>
<th>Antimony (Fig. 20 &amp; 21)</th>
<th>$\lambda_{\text{nm}}$</th>
<th>$E_{\text{max}}$</th>
<th>Arsenic (Fig. 23)</th>
<th>$\lambda_{\text{nm}}$</th>
<th>$E_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Blue solution)</td>
<td>280</td>
<td>1050</td>
<td>A (Red solution)</td>
<td>520</td>
<td>1980</td>
</tr>
<tr>
<td></td>
<td>460</td>
<td>420</td>
<td></td>
<td>440</td>
<td>390</td>
</tr>
<tr>
<td></td>
<td>680</td>
<td>620</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B (Yellow solution)</td>
<td>390</td>
<td>2030</td>
<td>B (Yellow solution)</td>
<td>480</td>
<td>1850</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>340</td>
<td></td>
<td>330</td>
<td>1640</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>260</td>
<td>1250</td>
</tr>
</tbody>
</table>
FIG. 20 ABSORPTION SPECTRUM OF BLUE SOLUTION OF ANTIMONY.
coefficients in various solvents show that the species formed are the same. The extinction coefficients are quoted in terms of antimony concentration in g.atom/litre. However, it may be made clear that these cations like those of selenium and tellurium are unlikely to be present in monoatomic form but this is the most simple method of comparing the strength of various solutions and will be used throughout the chapter.

Sulphur dioxide is not evolved when antimony is oxidised by \( \text{S}_2\text{O}_6\text{F}_2 \) in fluorosulphuric acid, therefore, the sharp peak at 280 nm cannot be attributed to the absorption due to sulphur dioxide. Even in case of sulphuric acid where the oxidation is effected by potassium persulphate, pumping out the liberated sulphur dioxide has no effect on the intensity of the 280 nm peak.

In the presence of an excess of the oxidising agent \( \text{S}_2\text{O}_6\text{F}_2 \), the blue solutions change to yellow with an absorption maximum at 390 nm and a weak absorption at 310 nm. The absorption spectrum of the yellow solution is given in Fig. 21. The extinction coefficients of the 390 nm and 280 nm peaks as a function of the ratio of antimony to
FIG. 21  ABSORPTION SPECTRUM OF YELLOW SOLUTION OF ANTIMONY
peroxydisulphuryl difluoride are given in Table VII. The intensity of the 390 nm peak of the yellow solution is maximum at 4:1, Sb: \( \text{Sb}_2 \text{O}_6 \text{F}_2 \). On the addition of more of antimony the intensity of the 390 nm peak decreases and there is an increase in the intensity of 280 nm peak, suggesting that antimony forms a blue solution on reaction with the yellow species. Finally at the molar ratio Sb: \( \text{Sb}_2 \text{O}_6 \text{F}_2 \) of 8.5:1, a blue solution is obtained which has no trace of the 390 nm peak.

From the spectroscopic data it is evident that the yellow solution corresponds to an oxidation state of +\( \frac{5}{2} \) of antimony while the blue solution has an oxidation state less than +\( \frac{5}{2} \), it may be +\( \frac{4}{2} \).

An oxidation state of +\( \frac{4}{2} \) cannot be explained in terms of the known compounds of antimony. Moreover, no compounds analogous to thiosulphate or polythionate can give the required oxidation state and such type of the anions are unstable in highly acidic media. The most feasible hypothesis is that antimony is oxidised to polyatomic cations of the type \( \text{Sb}_n^{+\frac{4}{n}} \), e.g. \( \text{Sb}_2^+ \), \( \text{Sb}_4^{2+} \) and \( \text{Sb}_6^{3+} \) etc.
The cations with an odd number of electrons can easily be rejected as these solutions are diamagnetic. Such type of polymeric homoatomic cations as above have already been established in case of iodine, selenium and tellurium.

Similarly an oxidation state of $+$ cannot be explained in terms of the known compounds of antimony, but most probably it can be explained in terms of various polyatomic cations of the type $\text{Sb}_n^{++}$, e.g. $\text{Sb}_4^+$, $\text{Sb}_8^{2+}$, $\text{Sb}_{16}^{4+}$, $\text{Sb}_{12}^{3+}$, $\text{Sb}_{20}^{5+}$, $\text{Sb}_{24}^{6+}$ and $\text{Sb}_{28}^{4+}$ etc. The possible cations of the type $\text{Sb}_4^+$, $\text{Sb}_{12}^{3+}$, $\text{Sb}_{20}^{5+}$ can be ruled out as the blue solutions are also diamagnetic.

Nature of these cations can be further elaborated with the help of conductimetric studies. Conductance measurements on the solutions of antimony and peroxydisulphuryl difluoride have been carried out in fluorosulphuric acid at $25^\circ\text{C}$ ($\text{Sb}:\text{S}_2\text{O}_6\text{F}_2$, 4:1). In order to be sure that no further oxidation of antimony takes place, change in the conductance has been recorded with time and has been extrapolated to zero time. Sticking to the above procedure, for each addition only one observation could be made. In Fig. 22 are given the
FIG. 22. CONDUCTANCE CURVES OF Sb IN HSO$_3$F
AT 25°C.

A - O-PHENYLENE DIAMINE
B - KSO$_3$F
C - Sb/S$_2$O$_6$F$_2$ (4:1)
D - Sb/S$_2$O$_6$F$_2$ (8:1)

10$^{-4}$xK (ohm$^{-1}$ cm$^{-1}$)

MOLALITY

-500
-400
-300
-200
-100
0

0.10
0.20

MOLALITY
conductance curves for antimony and S$_2$O$_6$F$_2$ mixtures in the ratio 4:1 and 8:1. These have been compared with potassium fluorosulphate. The solutions are fairly conducting and the equivalent conductance values have been determined, $\lambda_{nm}$ value has been found to be 65.4 for the blue solution, but for yellow solutions it is 128.4 ($\lambda_{nm}$K$_3$O$_3$F = 262 at 25°C).

This implies that (4:1) molar ratio solution produces half the conducting ions whereas the 8:1 solution produces $\frac{1}{4}$ of the conducting ions as produced by potassium fluorosulphate.

The value of $\gamma$ (the number of fluorosulphate ions produced per gm. atom of antimony) has been calculated by the conventional method of comparing the concentration of a base with that of the unknown required to produce the same conductance. For the yellow solution, the value of $\gamma$ has been found to be 0.48. The lower value of $\gamma$ may be due to the fact that we have compared the conductance due to the doubly charged cations with that of potassium fluorosulphate. On comparison with o-phenylenediamine a strong diprotonated base, the $\gamma$ value has been found to be 0.49–0.50 at 25°C.

The reaction in case of blue and yellow coloured solutions
can thus be written as:

\[
\begin{align*}
\text{nSb + } n/4 \text{S}_2\text{O}_6\text{F}_2 & \rightarrow \text{Sb}^{\frac{1}{n}+} + n/2 \text{SO}_3\text{F}^- \\
n\text{Sb + } n/8 \text{S}_2\text{O}_6\text{F}_2 & \rightarrow \text{Sb}^{\frac{1}{n}+} + n/4 \text{SO}_3\text{F}^- 
\end{align*}
\] (Yellow\')

For the yellow solutions, where the visible and u.v. absorption spectra is similar to that of Se\textsubscript{4}\textsuperscript{2+} and Te\textsubscript{4}\textsuperscript{2+} and the \( \gamma \) value is only 0.5; the value of \( n \) may be 4. This agrees very well with the experimental results:

\[
4\text{Sb + S}_2\text{O}_6\text{F}_2 \rightarrow \text{Sb}_4^{2+} + 2\text{SO}_3\text{F}^-
\]

In case of blue solutions the value of \( n \) when eight, fits in very well with the conductimetric factor of 0.25 and from the following equation it may be inferred that the blue colour is due to the Sb\textsubscript{5}\textsuperscript{2+} cation:

\[
8\text{Sb + S}_2\text{O}_6\text{F}_2 \rightarrow \text{Sb}_5^{2+} + 2\text{SO}_3\text{F}^-
\]

When a saturated solution of antimony (2M) in fluorosulphuric acid is allowed to stand for over a week, a pale brown needle shaped crystalline compound separates out. It was filtered in a dry atmosphere and washed free of the solvent by disulphuryl fluoride. It is an extremely hygroscopic compound and fumes in moist air. Elemental
analysis of the compound confirms the stoichiometric composition as $\text{Sb}_2(\text{SO}_3\text{F})_2$.

It is not soluble in nitrobenzene but slightly soluble in nitromethane. Molar conductance values could not be determined because the conductance changed with time and the solution developed some colour indicating that a side reaction had taken place. The nature of this compound has been investigated by studying it in disulphuric acid where the ionic fluorosulphates are solvolysed as:

$$\text{MSO}_3\text{F} + 2\text{H}_2\text{S}_2\text{O}_7 \rightarrow M^+ + \text{HSO}_3\text{F} + \text{HS}_3\text{O}_10^- + \text{H}_2\text{SO}_4$$

Fluorosulphuric acid formed in the reaction behaves as a non-electrolyte. The compound $\text{Sb}_4(\text{SO}_3\text{F})_2$ when dissolved in disulphuric acid forms a yellow coloured solution. U.V. and visible spectra of these solutions is exactly the same as that of the $\text{Sb}_4^{2+}$ cation. From the molar extinction coefficient of the maxima at 390 nm, it is found that the compound is completely ionised in disulphuric acid. From the values of $\gamma$, $\nu$ and $c$
the reaction may be written as:

\[
\text{Sb}_4(\text{SO}_3\text{F})_2 + 4\text{H}_2\text{SO}_4 \rightarrow \text{Sb}_4^{2+} + 2\text{HSO}_3\text{F} + 2\text{HSO}_4^- + 2\text{H}_2\text{SO}_4
\]

From these observations, it may be concluded that \(\text{Sb}_4(\text{SO}_3\text{F})_2\) is an ionic compound. Further support to the ionic structure of the compound comes from the i.r. spectroscopy. The fluorosulphate ion has a \(C_{3v}\) symmetry and all the six i.r. active absorption bands have been observed at 1290, 1276, 1070, 732, 580 and 560 cm\(^{-1}\). These bands confirm the ionic nature of the compound. Infrared studies have been confined only to the anionic part, as the characterisation of the \(\text{Sb}_4^{2+}\) is extremely difficult; partly due to the complicated lattice effects and partly due to the overlapping bands from the anion. Apart from the investigation of the cations of antimony in fluorosulphuric acid, interest has been extended to explore the possibility of formation of the cations of arsenic and bismuth.

Arsenic metal dissolves in fluorosulphuric acid to form colourless solutions without effecting the conductance (166). When sulphur trioxide is distilled into
the cell containing the above solutions, there is still no change in the conductance. However, when oxidation is effected by potassium persulphate or peroxydisulphuryl difluoride, metallic arsenic dissolves giving a red coloured solution. In the presence of excess of the oxidising agent, the solution changes to yellow. The time required for the change to yellow is dependent upon the amount of arsenic and the oxidising agent. Unlike antimony, yellow solution could not be further oxidised to a transparent state even after keeping the solution as such for over two weeks. The yellow species on reduction with hydrazine sulphate regenerate the red colour. When these coloured solutions are poured on crushed ice, the metal is recovered quantitatively. From all these observations, it is inferred that in these solutions, the metal exists in positive oxidation states and the yellow is a higher oxidation state than the red one. No colours could be obtained with oxidising agents like potassium periodate and ceric sulphate.

The ultraviolet and visible absorption spectra of the red and yellow solutions is given in Fig. 23. The absorption spectra of the red solution shows peaks at 520 nm (strong)
FIG. 23 ABSORPTION SPECTRA OF As-S₂O₆F₂ MIXTURES IN HSO₃F.

A - RED SOLUTION
B - YELLOW SOLUTION
and 440 nm (weak). The intense band at 520 nm has been considered as a reference band and the solution has been found to obey Lambert-Beer Law. The molar extinction coefficients for the 520 nm and 440 nm peaks are given in Table VII. Here also, the molar extinction coefficients are quoted in terms of arsenic concentration in gm. atom/litre. This, however, should not imply that the possibility of existence of these cations in polymeric nature has been ruled out.

In the presence of excess of potassium persulphate or peroxydisulphuryl difluoride, the red colour changes to yellow with an intense absorption band at 480 nm, the other weak absorption bands being at 380 and 260 nm. Figure 23-A gives the molar extinction coefficients for 520 nm and 480 nm peaks as a function of ratio of arsenic to peroxydisulphuryl difluoride. The intensity of the 520 nm peak of the red species reaches a maxima at the molar ratio of 4:1, As: $S_2O_6F_2$.

On addition of more of $S_2O_6F_2$ with time, the intensity of the 480 nm peak increases and that of the 520 nm peak decreases; confirming that red is being oxidised to yellow.
FIG. 23-A PHOTOMETRIC TITRATION OF ARSENIC VS $S_2O_6F_2$. 

A - 520 nm
B - 480 nm

MOLAR RATIO $\text{As}/S_2O_6F_2$
At the ratio \( \text{As:SeO}_4 \) of 2:1, there is a maximum intensity at 480 nm peak and it is found that at this stage most intense peak due to the red solution has completely disappeared. From these observations, it may be inferred that the red species correspond to an oxidation state of \( +\frac{1}{2} \) for arsenic while the yellow solution corresponds to a cation with an oxidation state of either +1 or lower than that.

As suggested in case of the cations of antimony, an oxidation state of \( +\frac{1}{2} \) of arsenic cannot be explained in terms of the known compounds of arsenic. Analogous to the behaviour of selenium, tellurium and antimony, the most feasible hypothesis is that arsenic may also exist as polyatomic cations of the type \( \text{As}_n^{+\frac{1}{2}n} \), e.g. \( \text{As}_4^{2+} \), \( \text{As}_6^{3+} \) etc. Since the solutions are diamagnetic in character, the cations with unpaired electrons cannot exist. Similarly, +1 oxidation state of arsenic cannot be explained in terms of the known compounds of arsenic and it may be safely assumed that in these solutions arsenic exists in homoatomic polymeric cations. Further light on the nature of these
cations is thrown by the conductimetric measurements of their solutions. Conductimetric titrations of the solutions of arsenic in fluorosulphuric acid have been carried out against peroxydisulphuryl difluoride. The measurements have been made at different molalities in each case. In order to be sure that conductance does not change with time, values at different time intervals have been recorded and extrapolated to zero time. In Fig. 24 are given the conductance curves for the red and the yellow solutions at various molalities. Comparing the curve for o-phenylene diamine, a strong diprotonated base, the $Y$ value in case of red solutions has been found to be equal to 0.49 to .51 at various molalities and 0.94 –1.06 in case of the yellow solutions. The overall reaction in the respective cases may be written as:

$$n \text{As} + \frac{n}{4} \text{S}_2\text{O}_6\text{F}_2 \rightarrow \text{As}_n^{\frac{1}{2}n^+} + \frac{n}{2} \text{SO}_3\text{F}^- \quad \text{(red)}$$

$$n \text{As} + \frac{n}{2} \text{S}_2\text{O}_6\text{F}_2 \rightarrow \text{As}_n^{n^+} + n\text{SO}_3\text{F}^- \quad \text{(yellow)}$$

The value of $n$ in case of red solution is four and the reaction may be written as:

$$4\text{As} + \text{S}_2\text{O}_6\text{F}_2 \rightarrow \text{As}_4^{2^+} + 2\text{SO}_3\text{F}^-$$
FIG. 24 SP. CONDUCTANCE OF ARSENIC SPECIES IN HSO₃F AT 25°C.

A - Yellow solution \((\text{As}^{2+}_2)\)
B - Red solution \((\text{As}^{2+}_4)\)
C - KSO₃F

\(10^2 \times K \) (ohm\(^{-1}\) cm\(^{-1}\))

MOLALITY

0.00
0.10
0.20
The conductimetric factor of 0.5 can best be explained in terms of the above equation. For the yellow solution the spectrum is exactly the same as in case of Te_2^{2+}. The reaction in this case may be written as:

$$2\text{As} + S_2O_6F_2 \rightarrow \text{As}_2^{2+} + 2\text{S}_3O_3^{F^-}$$

The above reaction is supported by conductimetric studies.

Like the solutions of antimony, it has been possible to isolate a white compound of unknown composition from the solution of arsenic and S_2O_6F_2 in fluorosulphuric acid. Investigations to characterise it are in progress.

It is very difficult, at the moment with limited data, to assign any structure to the cations As_4^{2+} and Sb_4^{2+} etc. But by analogy with the structure of Se_4^{2+} cations, the possible structure for Sb_4^{2+} and As_4^{2+} cations may be written in a square planar form with delocalised electrons. Similarly, a possible structure for the cation Sb_8^{2+} may be assigned by analogy with the structure of Se_3^{2+} in Se_3(AlCl_4)_2 (170) which are similar to those of Se_3 and S_4N_4. However, nothing at the moment can be said about the structure of As_2^{2+} cation where all attempts to isolate any compound have failed.