REDOX REACTIONS IN FLUOROSULPHURIC ACID
Oxidation reduction reactions in aqueous solutions have been studied for many years and quantitative thermodynamic treatments have been applied to the subject. The aqueous chemistry of any element can be studied quantitatively in terms of the standard redox potentials. The overall treatment is, however, thermodynamic in itself and cannot account for any activation effects. Thus, although potassium permanganate should oxidise water under acid conditions, yet the aqueous solution is stable for all practical purposes. This is because of the high overvoltage necessary to liberate oxygen which makes the rate of the reaction exceedingly slow. With a change in the reaction medium, it is very likely that the various redox potentials may also change. Thus all the values for various non-aqueous media have to be reported again. Most of the available information relating to these systems is empirical so far.

Due to the difference of redox potentials in aqueous and non-aqueous solutions for a particular element, it is possible to reduce an element in non-aqueous solutions to a state unknown in aqueous solutions. It is very likely
that a suitable solvent for this will be one, which is less acidic than water i.e. with a lower concentration of the hydrogen ions. Thus the alkali metals dissolve in liquid ammonia at -33°C, to form highly reducing solutions. These solutions have been used very extensively for reduction purposes (171) e.g., tetracyano nickelate (II) and hexacyano cobaltate (II) ions are reduced to nickel (I) and cobalt (I) cyanometallates respectively (172, 173). Further reduction to nickel (0) and cobalt (0) also takes place, but is very slow. However, zinc, cadmium and mercury (II) salts are directly reduced to the metal.

Apart from liquid ammonia, redox reactions have also been carried out in liquid sulphur dioxide which acts merely as an inert medium. Iodine oxidises tetramethyl ammonium sulphite very rapidly to the corresponding sulphate, whereas a solution of ferric chloride, oxidises potassium iodide to iodine. Even antimony pentachloride is known to oxidise potassium iodide to iodine. Also, in liquid sulphur dioxide the azides are reduced to nitrogen and the nitrosyl compounds oxidise various iodides to elemental iodine.

Acetic acid is another solvent where redox reactions
have been investigated in detail (174, 175). These reactions have also been used for various synthetic purposes. Anhydrous acetates of cobalt (III) and nickel (III) are prepared by the anodic oxidation of the metals in an electrolyte consisting of a mixture of an alkali metal acetate and acetic acid (176).

The discharge of metallic antimony, arsenic and bismuth from solutions of their chlorides in glacial acetic acid has also been reported (177), but the studies on electrochemical reductions in acetic acid are still far from complete. Acetic acid, in fact, is more useful for studying oxidation than the reduction reactions. This is especially applicable to the compounds which get solvolysed in other solvents. Thus stannic iodide is prepared by the oxidation of stannous chloride with iodine.

Recently, the redox reactions have been extended to highly acidic media (loc.cit.) such as hydrochloric and fluorosulphuric acids (178). Waddington and coworkers (179) have successfully used nitrosyl chloride, iodine monochloride, chlorine and bromine as the oxidising agents and have oxidised various compounds of phosphorous (III) arsenic (III) and metal carbonyls to their respective higher oxidation states.
in liquid HCl (180). Gillespie and coworkers (loc.cit.) have used peroxydisulphuryl difluoride as an oxidising agent in fluorosulphuric acid. Metals and non-metals have been oxidised to various unusual cations in this strongly acidic medium. Very recently, Paul and coworkers (181) have carried out redox reactions in formamide using lead tetraformamide as an oxidising agent. Potassium dichromate has also been used to oxidise As(III), Sb(III) and Sn(II) to their corresponding higher oxidation states.

Lack of systematic knowledge about redox behaviour in non-aqueous solvents makes the oxidation reduction studies in fluorosulphuric acid comparatively simple. In the present investigations, only those entities have been oxidised as would give simple known products. The basic redox behaviour in this solvent may be represented as:

\[ 2\text{SO}_3F^- \rightarrow \text{S}_2\text{O}_6F_2 + 2e^- \]  
\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \]

where \( E \) represents the standard electrode potential.

If, \( E_{\text{red}} > E_{\text{oxi}} \) as in water, then the substances having \( E < E_{\text{red}} \) will reduce the solvent and those with \( E < E_{\text{oxi}} \) will oxidise it. Thermodynamically, therefore, the strongest
oxidising agent stable in this solvent will be its oxidised product i.e. $S_2O_6F_2$. Apart from it (Chapter III) the conventional oxidising agents such as chlorine, bromine, iodine monochloride and nitrosyl chloride have been used here.

Before studying the redox reactions, behaviour of various oxidising agents has been investigated in fluorosulphuric acid solvent. At room temperature chlorine is fairly soluble in fluorosulphuric acid, the colour of the solution being yellow. There is no change in the conductance of the solution, even when left overnight. Bromine behaves similarly and the solutions are fairly stable. It may be pointed out here that only dilute solutions of these oxidising agents could be obtained in fluorosulphuric acid.

Phosphorous trichloride dissolves in fluorosulphuric acid without effecting the conductance. When a solution of known concentration of chlorine is added to it, there is a sudden increase in the conductance of the solution and the colour of the chlorine solution disappears. The rise in the conductance continues (Fig.24-A) till the molar ratio $Cl_2/FCl_3$ reaches 1:1. After that, further addition of the chlorine solution does not change the conductance and the solution
FIG. 24-A OXIDATION OF PHOSPHORUS(III) COMPOUNDS

MOLAR RATIO OXIDANT/REDUCTANT

SP. CONDUCTANCE \( \times 10^{-3} \) ohm\(^{-1}\) cm\(^{-1}\)

- \(\text{NOCl} \) vs \(\text{PCl}_3\)
- \(\text{ICl} \) vs \(\text{PCl}_3\)
- \(\text{Br}_2 \) vs \(\text{PCl}_3\)
- \(\text{Cl}_2 \) vs \(\text{PCl}_3\)
develops a yellowish tinge. The oxidation reduction reaction can be followed both conductimetrically and visually. When this solution is evaporated under reduced pressure a viscous liquid is left behind which corresponds to the composition \( \text{PCl}_{4}\cdot\text{SO}_3\text{F} \) (found chlorine 52.00\% and \( \text{SO}_3\text{F}^- \) 36.23\%).

Infrared spectrum of the compound is given in Table VIII. From the bands given therein the \( \text{PCl}_4^+ \) cations and the \( \text{SO}_3\text{F}^- \) anions have been characterised.

\( \text{PCl}_4^+ \) has a tetrahedral structure with a \( \text{Td} \) symmetry and should have six fundamental i.r. active bands; the available data of six bands shows that the compound isolated has the structure \( \text{PCl}_4^+\cdot\text{SO}_3\text{F}^- \). Its ionic nature has been confirmed by studying it in disulphuric acid. From cryoscopic and conductimetric studies, the solvolytic reaction may be represented as:

\[
\text{PCl}_4\cdot\text{SO}_3\text{F} + 2\text{HS}_2\text{SO}_7 \rightarrow \text{PCl}_4^+ + \text{HSO}_3\text{F} + \text{HS}_3\text{O}_{10}^- + \text{H}_2\text{SO}_4
\]

\( (\gamma = 1, \nu = 3, \text{ and } c = 1) \)

Fluorosulphuric acid produced in the reaction behaves as a non-electrolyte.

It is also evident from Fig. 24A that bromine oxidises
**TABLE VIII**

<table>
<thead>
<tr>
<th>PCl$_4^+$SO$_3$F$^-$</th>
<th>PCl$_3$Br$^+$SO$_3$F$^-$</th>
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phosphorous trichloride. When bromine is added, the solution develops some brown colour and the conductance of the solution increases. The increase in the conductance is due to the formation of the following ions:

$$\text{PCl}_3 + \text{Br}_2 + \text{HSO}_3^F \longrightarrow \text{PCl}_3\text{Br}^+ + \text{SO}_3^F^- + \text{HBr}$$

It has already been pointed out earlier (Chapter II) that HBr like HCl behaves as a non-electrolyte in fluorosulphuric acid. After complete oxidation at the molar ratio PCl$_3$:Br$_2$ of 1:1, further addition of bromine does not result in any change in the conductance of the solution. When the solutions are evacuated under reduced pressure, a white compound of composition PCl$_3$BrSO$_3$F separates out (found chlorine 33.4% and SO$_3$F$^-$ 31.25%). It is an extremely hygroscopic compound and fumes in moist air. The molar conductance value in nitromethane suggests that it is an ionic compound. When dissolved in disulphuric acid, the solvolysis takes place like a normal fluorosulphate as:

$$\text{PCl}_3\text{BrSO}_3^F + 2\text{H}_2\text{SO}_2\text{O}_7 \rightarrow \text{PCl}_3\text{Br}^+ + \text{HSO}_3^F + \text{HS}_3\text{O}_10^- + \text{H}_2\text{SO}_4$$

The cation PCl$_3$Br$^+$ does not seem to get solvolysed in
disulphuric acid otherwise it would have resulted in complicated products. This finds support from the investigation of the oxidation of phosphorus trichloride with bromine in HCl where the cation does not get solvolysed in hydrochloric acid (loc. cit.). I.r. spectrum confirms the ionic nature of the compound. All the characteristic bands corresponding to $\text{PCl}_4^+$ and $\text{PCl}_3\text{Br}^+$ cations along with the fluorosulphate ions are reported in Table VIII.

Oxidation of phosphorus trichloride with iodine monochloride is quite interesting as the end point corresponds to the composition $\text{ICI} : \text{PCl}_3$, 2:1. During the course of the reaction, iodine is liberated and sometimes it gets deposited on the electrodes of the conductance cell. That explains the reason for getting some of the points off the curve. The various equations that can be written for the above reaction are:

$\text{HSO}_4^- + \text{PCl}_3 + 2\text{ICI} \rightarrow \text{PCl}_4^+ + \text{I}_2 + \text{SO}_3\text{F}^- + \text{HCl} \quad \ldots \quad (a)$

$\text{PCl}_3 + 3\text{ICI} \rightarrow \text{PCl}_4^+ + \text{I}_2 + \text{ICI}_2^- \quad \ldots \quad (b)$

Both, conductance and infrared spectral studies support the equation (a) as the value for equation (a) has been found to be equal to one. Moreover, the i.r. evidence for $\text{PCl}_4^+$ and
SO₃F⁻ ions is conclusive in the concentrated solutions obtained from the reaction (a). Equation (b) can be ruled out as the molar ratio does not correspond to this particular formulation; also the solutions are highly conducting which is contrary to the properties of the equation (b). As the isolated compound PCl₄⁺SO₃F⁻ is always contaminated with iodine, therefore, it has not been possible to get the analysis of the compound. Though Waddington and coworkers (loc. cit.) have been able to isolate a compound of composition PCl₄⁺ICI₂⁻ during the studies of redox reaction in liquid HCl, yet, in the present investigation, highly nucleophilic anions such as ICI₂⁻ cannot be stabilised as the medium is weakly nucleophilic. Figure 24 gives the titration curve for the above reaction.

Nitrosyl chloride has also been used as an oxidising agent. Waddington and coworkers have successfully oxidised metal carbonyls (180) to form very interesting class of compounds. In the present investigation, it is observed that nitrosyl chloride is fairly soluble in fluorosulphuric acid, it oxidises phosphorous trichloride which is evident
from the conductimetric titrations. The break in the conductance composition curve is at the molar ratio NOCl:PCl₃ or 2:1. The reaction may be represented as:

\[ \text{PCl}_3 + 2\text{NOCl} + \text{HSO}_3\text{F} \rightarrow \text{PCl}_4^+ + 2\text{NO} + \text{HCl} + \text{SO}_3\text{F}^- \]

When the solvent is removed under reduced pressure, a compound of composition PCl₄SO₃F is obtained which has been characterised by studies as discussed earlier.

Phosphorous tribromide behaves as a non-electrolyte when dissolved in fluorosulphuric acid. It has also been oxidised by chlorine, bromine, iodine monochloride and nitrosyl chloride. The reactions have been followed conductimetrically, in Fig. 25 are given the oxidation reactions of phosphorous tribromide. The sharp breaks in the conductance composition curves are quite significant, and the various oxidising reactions may be represented as follows:

\[ \text{PBr}_3 + \text{Cl}_2 + \text{HSO}_3\text{F} \rightarrow \text{PBr}_3^+\text{Cl} + \text{SO}_3\text{F}^- + \text{HCl} \]
\[ \text{PBr}_3 + \text{Br}_2 + \text{HSO}_3\text{F} \rightarrow \text{PBr}_4^+ + \text{SO}_3\text{F}^- + \text{HBr} \]
\[ \text{PBr}_3 + 2\text{NOCl} + \text{HSO}_3\text{F} \rightarrow \text{PBr}_3^+\text{Cl} + \text{SO}_3\text{F}^- + \text{HCl} + 2\text{NO} \]

When these solutions are evaporated under reduced pressure, no solid compound could be obtained, only highly viscous liquids
FIG. 25A OXIDATION OF PHOSPHORUS (II) COMPOUNDS
SP. COND. IN HSO₃F AT 25°C.
are left behind. Elemental analysis shows the presence of chlorine, bromine, sulphur etc. but all attempts to assign a particular stoichiometric composition through spectral as well as quantitative analysis have failed.

It is quite interesting to note that PCl₃Br⁺ is quite stable whereas its analogous ion PBr₃Cl⁺ does not exist in the solid state. Similar observations have already been made by Waddington and coworkers (loc.cit.). May be, that the cation PCl₃Br⁺ is quite stable to solvolysis whereas PBr₃Cl⁺ may not be that stable in fluorosulphuric acid. However, the oxidation of PBr₃ has been shown to take place completely by the titration curves.

Triphenyl phosphine has also been titrated conductimetrically against chlorine, bromine and iodine monochloride. Unlike phosphorus trichloride and bromide, triphenyl phosphine is highly conducting in fluorosulphuric acid (Chapter I). When the oxidising agents are added, there is a slight decrease in the conductance of the solution. After the molar ratio (Cl₂/C₆H₅)₃P of 1:1, there is no change in the conductance of the solution, indicating complete
oxidation. Though there has been a decrease in the conductance of the solution after oxidation, yet the solutions are highly conducting indicating that the oxidised product is also ionised. Similar oxidation taken place in case of bromine and the reaction may, in general, be visualised as:

\[ \text{HSO}_3\text{F} + (\text{C}_6\text{H}_5)_3\text{P} + X_2 \rightarrow (\text{C}_6\text{H}_5)_3\text{PX}^+ + \text{HX} + \text{SO}_3\text{F}^- \]

When the solvent is removed under reduced pressure, the compounds of the composition \((\text{C}_6\text{H}_5)_3\text{PCl}\cdot\text{SO}_3\text{F}\) and \((\text{C}_6\text{H}_5)_3\text{PBr}\cdot\text{SO}_3\text{F}\) are obtained.

The compounds triphenylphosphine chlorofluorosulphate and triphenylphosphine bromofluorosulphate are fairly stable in dry atmosphere and do not fume in moist air. Their molar conductance values in nitrobenzene and nitromethane suggest that these compounds are fairly ionic in nature. Infrared studies of the compound show bands corresponding to the fluorosulphate ion. A new band at 538 cm\(^{-1}\) which is originally absent is observed. This is consistent with the P-Cl vibration in a cation of the type \((\text{C}_6\text{H}_5)_3\text{PCl}^+\) (192). Similar types of absorptions have also been reported for P-Cl stretching vibration in \(\text{PCl}_4^+\); where
it is present either at 694 or 650 cm\(^{-1}\). Even in phosphorus pentachloride in gaseous state this band is observed at 592 cm\(^{-1}\). Therefore, it may be safely concluded that triphenylphosphine forms triphenylphosphine dichloride and triphenylphosphine dibromide when oxidised with chlorine and bromine respectively. Triphenylphosphine gets oxidised by iodine monochloride to form triphenylchlorophosphonium ion \((C_6H_5)_3\text{PCl}\) rather than triphenyliodophosphonium ion \((C_6H_5)_3\text{PI}\), as two moles of iodine monochloride are required per mole of triphenylphosphine (Figure 25-A).

For the above oxidation process the following reactions may be written:

\[
\text{HSO}_3^F + (C_6H_5)_3\text{P} + \text{ICl} \rightarrow (C_6H_5)_3\text{PI}^+ + \text{SO}_3\text{F}^- + \text{HCl} \quad (Y = 1)
\]

\[
\text{HSO}_3^F + (C_6H_5)_3\text{P} + 2\text{ICl} \rightarrow (C_6H_5)_3\text{PCl}^+ + \text{SO}_3\text{F}^- + \text{HCl} + I_2 \quad (Y = 1)
\]

\[
(C_6H_5)_3\text{P} + 2\text{ICl} \rightarrow (C_6H_5)_3\text{PI}^+ + \text{ICl}_2^- \quad (Y = 0)
\]

However, only the second equation seems to hold good, others being ruled out on conductimetric and visual observations. The mode of oxidation represented by the second equation is further confirmed as iodine is formed during the course of the reaction. The stoichiometric composition of the compound
FIG. 25A OXIDATION OF PHOSPHORUS (III) COMPOUNDS
SP. COND. IN HSO₃F AT 25°C.

\[10^3 \times k \text{ (ohm}^{-1} \text{ cm}^{-1})\]

\(-25\)
\(-20\)
\(-15\)
\(-10\)
\(-5\)

\(-2\)
\(-1.0\)
\(-0.0\)
\(-1.0\)
\(-2.0\)
\(-2.6\)

\(\bullet \bullet \) \((C_6H_5)_3P\) Vs ICl
\(\triangle \triangle \) \((C_6H_5)_3P\) Vs Br₂
\(\square \square \) \((C_6H_5)_3P\) Vs Cl₂
which could be isolated by the removal of the solvent under reduced pressure, could not be determined as it was always contaminated with free iodine. The presence of P—Cl bond in the cation and the fluorosulphate anion in the compound has been confirmed by infrared spectral studies which also supports the reaction represented by second equation.

Further light on the ionic nature of this compound has been thrown by investigating the behaviour of these compounds in various aprotic and non-protonic solvents. Molar conductance values in nitrobenzene and acetonitrile for the compound \((\text{C}_6\text{H}_5)_3\text{PCl}.\text{SO}_3\text{F}\) are fairly high. It means that it is a fairly ionic compound and the possible ions may be \((\text{C}_6\text{H}_5)_3\text{PCl}^+\) and \(\text{SO}_3\text{F}^-\). When this is dissolved in disulphuric acid, it results in the formation of a clear and highly conducting solution. From the cryoscopic and conductimetric investigations, it is evident that the mode of solvolysis in disulphuric acid is as follows:

\[
(\text{C}_6\text{H}_5)_3\text{PCl}.\text{SO}_3\text{F} + 2\text{H}_2\text{S}_2\text{O}_7 \rightarrow (\text{C}_6\text{H}_5)_3\text{PCl}^+ + \text{HSO}_3\text{F} + \text{H}_3\text{SO}_4^{-} + \text{H}_2\text{SO}_4
\]

This further lends support to the ionic nature of the compound.
It may further be pointed out that because of high acidic character of the solvent, the cations of the type PC\textsubscript{14}\textsuperscript{+}, PC\textsubscript{3}.Br\textsuperscript{+}, (C\textsubscript{6}H\textsubscript{5})\textsubscript{3}PCl\textsuperscript{+} etc. have been stabilised as these cations are strongly electrophilic in nature and hence can be stabilised in weakly nucleophilic media. It may be interesting to note that the cation (C\textsubscript{6}H\textsubscript{5})\textsubscript{3}PCl\textsuperscript{+} seems to be more stable than the cation (C\textsubscript{6}H\textsubscript{5})\textsubscript{3}PH\textsuperscript{+}. It is very difficult at the present to assign any reason for such a behaviour.

Arsenic trichloride is fairly miscible in fluorosulphuric acid and unlike arsenic trifluoride where it forms AsF\textsubscript{2}+.SO\textsubscript{3}F\textsuperscript{−}(loc.cit.), it behaves as a non-electrolyte. However, when it is oxidised by chlorine, the solutions become highly conducting (Fig.26). On concentrating these solutions nothing separates out indicating that AsCl\textsubscript{4}\textsuperscript{+} ion is stable only in solution. These findings are in agreement with those of earlier workers (133), where it has been found that arsenic pentachloride does not exist but its salts, where it is present as AsCl\textsubscript{4}\textsuperscript{+} have actually been indicated by conductimetric studies and by the isolation of the compound in the solid state. Though it has not been possible to
isolate any compound of composition AsCl$_4^+$·SO$_3$F$^-$, yet it is evident from the conductimetric studies that As(III) has undergone oxidation in fluorosulphuric acid to As(V).

Arsenic trichloride also gets oxidised with bromine and iodine monochloride Fig. 26. After the oxidation of As(III) to As(V), further addition of the oxidising agent does not result in any change in the conductance and the colour of the solution persists. Though the oxidation is evident from the conductimetric and visual titrations, yet, when an attempt is made to recover the oxidised products by evaporating the solvent, nothing is left behind indicating that the salts containing AsCl$_4^+$ or AsBr$_3$Cl$^+$ ions are not stable in the solid state.

The existence of the ions AsCl$_4^+$ and SO$_3$F$^-$ in the concentrated solutions has been confirmed exactly as in case of PCl$_4^+$·SO$_3$F$^-$.

In case of iodine monochloride, since the break in the conductance-composition curve is at the molar ratio ICl/AsCl$_3$ of 2:1 and iodine is liberated during the course of the titration, the mode of oxidation may be safely assumed to be:

$$\text{HSO}_3\text{F} + \text{AsCl}_3 + 2\text{ICl} \rightarrow \text{AsCl}_4^+ + \text{HCl} + \text{I}_2 + \text{SO}_3\text{F}^-$$
FIG. 27 OXIDATION OF ARSENIC (III) COMPOUNDS

$\text{FIG. 27 OXIDATION OF ARSENIC (III) COMPOUNDS}$

$\text{MOLAR RATIO OXIDANT/REDUCTANT}$

$\text{ICl Vs } (\text{C}_6\text{H}_5)_3\text{As}$

$\text{Cl}_2 \text{Vs } (\text{C}_6\text{H}_5)_3\text{As}$

$\text{Br}_2 \text{Vs } (\text{C}_6\text{H}_5)_3\text{As}$

$K \times 10^3 \text{ (ohm}^{-1}\text{cm}^{-1})$
Since the solutions are highly conducting, therefore, the possibility of the existence of the following reaction

\[ \text{AsCl}_3 + 3\text{ICI} \rightarrow \text{AsCl}_4^+ + \text{ICl}_2^- + \text{I}_2 \]

can be ruled out. Unfortunately, no solid compound other than iodine separates out when the solvent is evaporated.

Triphenylarsine forms a fairly conducting solution in fluorosulphuric acid. Waddington and coworkers (179) have shown that it gets oxidised in hydrochloric acid by chlorine and bromine but with iodine monochloride it forms a compound of composition \((\text{C}_6\text{H}_5)_3\text{AsI}^+.\text{ICl}_2^-\) which is quite stable in hydrochloric acid. Here triphenylarsine has been oxidised by chlorine, bromine, and iodine monochloride in fluorosulphuric acid. The oxidation reaction has been followed conductimetrically and the conductance curves are given in Fig. 27. Like triphenyl phosphine, triphenylarsine forms highly conducting solutions though to a lesser extent. It gets oxidised and there is a slight increase in the conductance of the solution which is different from the trend of triphenylphosphine. This is attributed to the difference in the basicities of the two compounds in the pure solvent.
Fig. 27 Oxidation of Arsenic (III) Compounds

Graph showing the relationship between the molar ratio of oxidant to reductant and the rate constant ($k \times 10^3$ ohm$^{-1}$ cm$^{-1}$) for different reactions:

- ICl vs. $\left(\text{C}_6\text{H}_5\right)_3\text{As}$
- Cl$_2$ vs. $\left(\text{C}_6\text{H}_5\right)_3\text{As}$
- Br$_2$ vs. $\left(\text{C}_6\text{H}_5\right)_3\text{As}$

The graph is plotted with the molar ratio of oxidant to reductant on the x-axis and the rate constant ($k \times 10^3$ ohm$^{-1}$ cm$^{-1}$) on the y-axis.
In case of triphenylarsine, the mode of oxidation is exactly the same as that in case of triphenylphosphine:

\[(C_6H_5)_3As + 2ICI + HSO_3F \rightarrow (C_6H_5)_3AsI^+ + I_2 + HCl + SO_3F^-\]

This mode of oxidation by ICI in fluorosulphuric acid is different from that in hydrochloric acid where triphenylphosphine and arsine form the compounds of composition \((C_6H_5)_3PI^+\), \(ICI_2^-\) and \((C_6H_5)_3AsI^+\). \(ICI_2^-\) respectively. May be that \(ICI_2^-\) ion cannot be stabilised in fluorosulphuric acid due to its very high acid strength.

Considering the feasibility of redox reactions in fluorosulphuric acid, it was felt worthwhile that certain oxidation processes should be undertaken using the usual oxidising agents like \(K_2CrO_4\) and \(K_2Cr_2O_7\).

Potassium dichromate is a strong oxidising agent, and forms highly conducting and stable solutions in fluorosulphuric acid. In the present case potassium dichromate has been used to oxidise arsenic (III), antimony (III), tin (II) and iron (II) chlorides. The course of oxidation reduction reactions has been followed potentiometrically.

The e.m.f. versus concentration curves are given
in Fig. 28. As the titrant is added to the solution of arsenic (III) chloride, the yellow colour of potassium dichromate changes to green in the cell but there is no appreciable change in the potential of the system. However, a sharp potential jump appears at $\text{K}_2\text{Cr}_2\text{O}_7/\text{AsCl}_3$ molar ratio of 3:1. Further addition of the dichromate solution results in a gradual change in the e.m.f. of the system and the curve flattens out at higher concentrations. No solid product separates out during the course of the titration and the reduction of dichromate is marked by the appearance of green colour in the solution. The nature of the anions formed in the solution is not certain. However, in view of the various molar ratios, the following reactions may be postulated:

$$2\text{Cr}^6+ + 3\text{Sn}^2+ \rightarrow 2\text{Cr}^3+ + 3\text{Sn}^4+$$
$$2\text{Cr}^6+ + 3\text{As}^3+ \rightarrow 2\text{Cr}^3+ + 3\text{As}^5+$$
$$2\text{Cr}^6+ + 3\text{Sb}^3+ \rightarrow 2\text{Cr}^3+ + 3\text{Sb}^5+$$
$$\text{Cr}^6+ + 3\text{Fe}^2+ \rightarrow \text{Cr}^3+ + 3\text{Fe}^3+$$

Visual titrations were not tried as the end points were not very sharp.
FIG. 28 REDOX POTENTIOMETRIC TITRATIONS IN FLUOROSULPHURIC ACID.
It may be concluded that sulphur trioxide free fluorosulphuric acid is an excellent medium for carrying out redox reactions. The purpose of fluorosulphuric acid is simply to provide a medium and to stabilise the oxidised products. It has been elaborated that P(V) compounds are fairly stable even in the solid state whereas As(V) compounds are indicated only in the solution and are unstable in the solid state.