SUMMARY
Fluorosulphuric acid is a highly acidic solvent and most of the solutes behave as bases in it. Even organic compounds such as phenol, diethyl carbonate etc. behave as fully ionised bases therein. Effects of substitution of electron withdrawing group (-I effect) on the basicity of these compounds has been determined. Compounds such as m-dinitrobenzene, 2-chloro-4-nitroaniline, o-chloroaniline, p-chloroaniline, p-nitroaniline, p-anisidine, glycine and phenyl hydrazine behave as weak bases. From the extent of protonation of these weak bases, a comparative study with other strong protonic acids has been made where it has been observed that fluorosulphuric acid is a better proton donor than sulphuric acid. Basicities of compounds containing S=O and S-S groups have also been determined. Sulphoxides behave as strong bases whereas sulphones behave as weak bases. It is interesting to note that in some compounds S-S bond does not undergo cleavage or oxidation in fluorosulphuric acid and a triprotonated disulphide has been visualised e.g.
The relative strength of various simple protonic acids has been determined by studying their behaviour in fluorosulphuric acid. Chlorosulphuric acid behaves as a nonelectrolyte whereas perchloric acid, sulphuric acid, selenic acid, methanesulphuric acid and difluorophosphoric acid behave as weak bases in it. From the extent of their ionisation, relative order of their basicity has been determined e.g.

\[
\text{H}_2\text{SeO}_4 < \text{H}_2\text{SO}_4 < \text{HClO}_4 < \text{HSO}_3\text{Cl} < \text{HPO}_2\text{F}_2
\]

Hydrazoic acid behaves as a weak electrolyte whereas hydrocyanic acid is not soluble in it. Hydrogen sulphide forms colloidal sulphur in it. Iodic acid gets dehydrated and forms unionised polymeric iodosylfluorosulphate.

Behaviour of diketones, both aliphatic and aromatic has been investigated in fluorosulphuric and chlorosulphuric acids. It is observed that benzil behaves as a weak electrolyte. Anthraquinone is diprotonated whereas p-benzoquinone and alizarin are only monoprotonated. Acetyl acetone, acetonyl acetone, benzyl acetone and dibenzoylmethane behave as bases in fluorosulphuric acid. A comparative study with super acid, where these are diprotonated
suggests that fluorosulphuric acid is weaker than super acid.

Hydrochloric acid is only slightly soluble in fluorosulphuric acid and behaves as a nonelectrolyte. This behaviour is confirmed by studying the ionisation of tetrabutylammonium chloride and triphenyl chloromethane in fluorosulphuric acid. However, hydrochloric gas behaves as a base in super acid and a compound of composition $H_2^+Cl\left[SbF_2(SO_3F)_4\right]$ has been isolated. Hydrobromic acid also behaves as a nonelectrolyte. Compounds such as $PCl_5$, $TeCl_4$, $SeCl_4$, $ICl_3$, $S_4N_3Cl$ and $S_4N_3F$ get solvolysed in fluorosulphuric acid and form cations of the type:

$$TeCl_4 + HSO_3F \rightarrow TeCl_3^+ + SO_3F^- + HCl$$
$$SeCl_4 + HSO_3F \rightarrow SeCl_3^+ + SO_3F^- + HCl$$
$$PCl_5 + HSO_3F \rightarrow PCl_4^+ + SO_3F^- + HCl$$
$$ICl_3 + HSO_3F \rightarrow ICl_2^+ + SO_3F^- + HCl$$
$$S_4N_3X + HSO_3F \rightarrow S_4N_3^+ + SO_3F^- + HX$$

The presence of these cations in solutions has been confirmed by conductance and spectral studies. Trihalides of phosphorus and arsenic get solvolysed in fluorosulphuric acid and form
trifluorosulphates e.g.

\[ \text{AsX}_3 + \text{HSO}_3\text{F} \rightarrow \text{As(SO}_3\text{F)}_3 + 3\text{HX} \]

which behave as nonelectrolytes in fluorosulphuric acid.

Acid halides behave as strong bases; from the conductance and spectral studies it is observed that acetyl chloride and bromide form acyl ions and nitryl chloride and fluoride form nitryl ions in fluorosulphuric acid. Phosphoryl chloride and bromide, thiophosphoryl chloride and bromide and selenyl chloride simply get protonated and behave as simple bases therein.

Arsenic and antimony form coloured solutions in fluorosulphuric acid when oxidised with potassium persulphate or peroxydisulphuryl difluoride. The coloured solutions of these metals have been attributed to the various positive oxidation states. From u.v., conductance and magnetic susceptibility measurements of these solutions, following types of cations have been postulated for both the metals:

\[
\begin{align*}
3\text{Sb} + \text{S}_2\text{O}_6\text{F}_2 & \rightarrow \text{Sb}_8^{2+} + 2\text{SO}_3\text{F}^- \quad \text{(green)} \\
4\text{Sb} + \text{S}_2\text{O}_6\text{F}_2 & \rightarrow \text{Sb}_4^{2+} + 2\text{SO}_3\text{F}^- \quad \text{(yellow)} \\
4\text{As} + \text{S}_2\text{O}_6\text{F}_2 & \rightarrow \text{As}_4^{2+} + 2\text{SO}_3\text{F}^- \quad \text{(red)} \\
2\text{As} + \text{S}_2\text{O}_6\text{F}_2 & \rightarrow \text{As}_2^{2+} + 2\text{SO}_3\text{F}^- \quad \text{(yellow)}
\end{align*}
\]
In case of antimony, a yellowish brown needle shaped compound of composition $\text{Sb}_4(\text{SO}_3\text{F})_2$ separates out which has been characterised by studies in disulphuric acid and also by i.r. studies. In case of arsenic a white compound separates out which could not be fully characterised.

Redox reactions have been carried out in pure fluorosulphuric acid. These reactions have been followed both conductimetrically and visually. $\text{Cl}_2$, $\text{Br}_2$, $\text{ICl}$ and NOCl have been used as oxidising agents whereas phosphorus(III) and arsenic (III) compounds have been used as reductants. It is observed that phosphorus (V) compounds are quite stable both in solution as well as in the solid state whereas arsenic (V) compounds are stable only in the solutions.

During the course of these redox titrations, quite a few new compounds have been isolated and characterised.

Behaviour of anhydrides of both organic and inorganic acids has been investigated in fluorosulphuric acid. Investigation of phosphorus pentoxide in fluorosulphuric acid has led to the standardisation of a new convenient method for the preparation of disulphuryl fluoride and trisulphuryl fluoride. Nitric and nitrous oxides behave as neutral
oxides whereas dinitrogen pentoxide, dinitrogen tetroxide
and dinitrogen trioxide form nitronium and nitrosyl ions as:

\[
\begin{align*}
N_2O_5 + 3HSO_3F & \rightarrow 2NO_2^+ + H_3O^+ + 3SO_3F^- \\
N_2O_4 + 3HSO_3F & \rightarrow NO^+ + H_3O^+ + 3SO_3F^- \\
N_2O_3 + 3HSO_3F & \rightarrow 2NO^+ + H_3O^+ + 3SO_3F^- 
\end{align*}
\]

Compounds of composition NO$_2$SO$_3$F and NO$_3$SO$_3$F have been isolated and characterised. Arsenic trioxide forms unionised polymeric solvolysed product As(SO$_3$F)$_3$. Antimony oxides behave in a similar way, whereas bismuth trioxide is not soluble in it.

Acetic anhydride and isobutyric anhydride behave as strong bases in fluoroosulphuric acid and are monoprotonated whereas monochloroacetic anhydride behaves as a weak base. Phthalic, succinic and maleic anhydrides also behave as weak bases. From the extent of their protonation, it is observed that, as compared to sulphuric acid, they are more ionised in fluorosulphuric acid.

From the phase diagram of HSO$_3$F–H$_2$O system, hydrates of fluorosulphuric acid having composition HSO$_3$F.H$_2$O (m.p. -34°C), HSO$_3$F.2H$_2$O (m.p. -6°C) and HSO$_3$F.4H$_2$O (m.p. 14°C) have been indicated. Conductance and i.r. spectral studies of these hydrates show them to be ionic in nature.
A new method for the preparation of periodyl fluoride, by refluxing a mixture of fluorosulphuric acid and potassium periodate (2:1) has been suggested.

When chromyl chloride is refluxed with fluorosulphuric acid in a dry atmosphere, chromyl fluorosulphate is obtained. This also contributes a new method for the preparation of this compound.

Conductimetric investigations of various solutes in methane-sulphuric acid have been carried out to prove its autoionisation. Acids and bases specific to its autoionisation have been explored. The behaviour of weak bases and nonelectrolytes of the system has been discussed. From the molar conductance values of strong bases, Grothuss chain mechanism for conductance has been suggested. Disulphuric acid, fluorosulphuric acid, chlorosulphuric acid, sulphuric acid and selenic acids behave as acids in it and the order of relative acid strength has been established as:

\[ \text{H}_2\text{S}_2\text{O}_7 > \text{H}_2\text{SO}_3\text{F} > \text{H}_2\text{SO}_3\text{Cl} > \text{H}_2\text{SO}_4 > \text{H}_2\text{SeO}_4 \]