CHAPTER-II

BEHAVIOUR OF LEWIS ACIDS IN FUSED PHENOL
Organic polar molecules are well known to form addition compounds with a number of acceptor molecules. A study of the physico-chemical properties of these compounds or their solutions in the parent compound has been reported to be very helpful to investigate their nature.

In order to study the constitution of various addition compounds, Sugdon and Waloff (1) prepared the complexes of boron trifluoride with organic acids and esters and studied their parachor. Gerrard and his coworkers (2) prepared the addition compound of boron trifluoride and ethyl acetate in order to study the donor properties of esters. Greenwood and Martin (3) prepared the addition compound of boron trifluoride and ethyl acetate and determined the reduced conductivity, dynamic viscosity and density of the compound in the molten state and determined the degree of dissociation of the adduct. Antimony trichloride and antimony pentachloride are known to form solvates with acetyl chloride (4), phosphoryl chloride (5) and nitrosyl chloride (6). The assumption regarding the existence of solvates of Lewis acids and bases in acid halides solution is supported by the isolation and characterisation of a few solvates (7). However, the structures of these solvates in the solid state do not always conform to the assumption that they are comprised of ionic species.

Acetic acid forms addition compounds with a large variety
of organic and inorganic compounds. In many cases such complexes have been isolated as crystalline solids, in others, the evidence for compound formation is based upon indirect physicochemical measurements. Lewis acids are known to form solvates with acetic acid. Usanovich and his coworkers (8) have reported an addition compound of acetic acid and tin(IV) chloride of composition \( \text{SnCl}_4 \cdot 2\text{CH}_3\text{COOH} \) which is a strong acid of composition \( (\text{H}^+)_2 \left[ \text{SnCl}_4(\text{OAc})_2 \right]^2^- \). Tin(IV) bromide also forms an adduct of composition \( \text{SnBr}_4 \cdot 2\text{CH}_3\text{COOH} \) which again is a strong acid of composition \( \text{H}_2 \left[ \text{SnBr}_4(\text{OAc})_2 \right] \) (9). Boron(III) fluoride reacts with acetic acid to give two addition compounds of composition \( \text{BF}_3 \cdot \text{AcOH} \) and \( \text{BF}_3 \cdot 2\text{CH}_3\text{COOH} \) (10,11) which is ionised in the molten state and is formulated as \( \text{H}^+ \left[ \text{BF}_3\cdot\text{OOCCH}_3 \right]^- \). Similar reactions were observed with antimony(III) chloride (12). Two compounds of composition \( 2\text{SbCl}_3 \cdot \text{CH}_3\text{COOH} \) and \( \text{SbCl}_3 \cdot \text{CH}_3\text{COOH} \) have been reported with respective structures as \( \left[ \text{SbCl}_2 \cdot \text{CH}_3\text{COOH} \right]^+ \text{SbCl}_4^- \) and \( \left[ \text{SbCl}_2 \cdot \text{CH}_3\text{COOH} \right]^+ \text{Cl}^- \). Physico-chemical study of \( \text{SnCl}_4\cdot\text{HCOOH} \) system indicates the formation of addition compound \( \text{SnCl}_4 \cdot 3\text{HCOOH} \) (8). Antimony(V) chloride also forms 1:1 addition compound with formic acid (13). Meerwein and Pannurtz (14) report the formation of two addition compounds of composition \( \text{BF}_3 \cdot \text{HCOOH} \) and \( \text{BF}_3 \cdot 2\text{HCOOH} \) between boron trifluoride and formic acid.

Methanol is more basic than carboxylic acids. It readily dissolves many acceptor halides such as antimony(V) chloride, titanium(IV) chloride, tin(IV) chloride, aluminium(III) chloride,
aluminium(III) bromide and solvates may be isolated from the solutions. Solvates are also known for many other salts such as magnesium bromide, magnesium iodide or calcium chloride which contain solvated cationic species. Boron trifluoride forms solvates of composition $\text{BF}_3 \cdot \text{CH}_3\text{OH}$ and $\text{BF}_3 \cdot (\text{CH}_3\text{OH})_2$ with methanol which have been formulated as $\text{H}^+(\text{BF}_3 \cdot \text{OCH}_3^-)$ and $\text{CH}_3\text{OH}^+ \text{BF}_3 \cdot \text{OCH}_3^-$ in the molten state (15). Since phenol is also acidic in nature and can also act as a donor molecule, it is worthwhile to study the possibility of the formation of solvates with a number of acceptor molecules.

Trichlorides and tribromides of phosphorus, arsenic and antimony are very soluble in phenol at $50^\circ$C. The solutions so formed are fairly conducting (more conducting than either of the components). If the temperature of the solution is kept constant the conductance of the solution does not change with time even when the solutions were left for longer hours. It indicates that there are no side reactions between these halides and phenol. The conductance of the solution increases as the concentration of these solutes increases. There is a break in the conductance-composition curve at the molar ratio $\text{MX}_3$/phenol (where $M$ is P, As and Sb) of 1:1 which corresponds to the existence of the solvates of composition $\text{PCl}_3 \cdot \text{C}_6\text{H}_5\text{OH}$, $\text{PBr}_3 \cdot \text{C}_6\text{H}_5\text{OH}$, $\text{AsCl}_3 \cdot \text{C}_6\text{H}_5\text{OH}$, $\text{AsBr}_3 \cdot \text{C}_6\text{H}_5\text{OH}$, $\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{OH}$ and $\text{SbBr}_3 \cdot \text{C}_6\text{H}_5\text{OH}$ in solutions respectively. Further addition of the solute does not bring about any change in the conductance of the solutions. No solid
compound separated out during the course of measurements of the conductance of the solutions. No compound separated out even when petroleum spirit was added to the solution of trihalides of phosphorus and arsenic while a liquid layer separated out in the case of trihalides of antimony which has been characterised to be solvates of composition SbX$_3$.C$_6$H$_5$OH. But when antimony(V) chloride was added to phenol, a black compound separated out of the solution. The conductance measurements of the solution had to be abandoned. In the case of phosphorus(V) chloride, the solutions formed were not very stable as the conductance of the solution changed with time. Though the solutions formed are more conducting than the parent components yet the solutions are not very stable. There is a variation in the conductance of the solution with time. Possibly a solvolytic reaction takes place and hydrogen chloride so formed is responsible for the variation of conductance of the solution. A possible solvolytic reaction may be proposed as:

$$\text{PCl}_5 + n\text{C}_6\text{H}_5\text{OH} \rightarrow \text{PCl}_5(\text{C}_6\text{H}_5\text{OH})_n \rightarrow \text{PCl}_5-n(\text{OC}_6\text{H}_5)_n + n\text{HCl}$$

The conductance measurements of the solutions had to be abandoned.

When anhydrous niobium(V) and tantalum(V) chlorides were added to fused phenol, they changed their colours and the solutions developed straw colour and it was accompanied by a change in the conductance of the solutions. Again there was a
continuous increase in the conductance of the solution when the solutions were left over for some time. Possibly a solvolytic reaction took place and because of hydrogen chloride so liberated, there was a continuous change in the conductance of the solutions. Similarly in the case of aluminium(III) chloride, thallium(III) chloride, iron(III) chloride and titanium(IV) chloride, there was a continuous change in the conductance of the solution, therefore, the conductance measurements of the solutions so formed had to be abandoned. When the solutions containing these solutes were filtered, in most of the cases, partially solvolysed products were obtained and were characterised. In the case of pentachlorides of niobium and tantalum, solvolysed products of composition TaCl$_4$(OPh) and NbCl$_4$(OPh) were obtained. In the case of aluminium(III) chloride and iron(III) chloride, no definite composition could be assigned to the isolated products. It is interesting to note that in the case of tin(IV) chloride, there are two breaks in the conductance-composition curves corresponding to the formation of solvates of composition SnCl$_4$.2PhOH and SnCl$_4$.PhOH. But in the case of tin(IV) bromide and tin(IV) iodide, again the solutions formed were not very stable which suggests that Sn-Cl bond is less polar as compared to Sn-Br or Sn-I bond. Since the solutions are more conducting than each of the components, it implies that the ions are present in the solution. By analogy with the ions present in the solvates of tin(IV) chloride in acetic acid (8), possible
ions present in the solutions of tin(IV) chloride and phenols are:

\[
\text{SnCl}_4 + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{SnCl}_4\cdot\text{C}_6\text{H}_5\text{OH} \rightleftharpoons \text{H}^+ \text{(solvated)} + \left[ \text{SnCl}_4\cdot \text{OC}_6\text{H}_5 \right]^2-
\]

\[
\text{SnCl}_4 + 2\text{C}_6\text{H}_5\text{OH} \rightarrow \text{SnCl}_4\cdot 2\text{C}_6\text{H}_5\text{OH} \rightleftharpoons 2\text{H}^+ \text{(solvated)} + \left[ \text{SnCl}_4\cdot \text{OC}_6\text{H}_5 \right]^2-
\]

No solid solvate of tin(IV) chloride with phenol has been isolated.

In order to explore the possibility of the formation of phenoxides of these metals, conductometric titrations between metal halides against phenoxides of sodium, potassium and lithium have been carried out in phenol at 50 ± 0.1°C. In the case of aluminium(III) chloride and aluminium(III) bromide, the conductance-composition curves show two breaks at the composition \(\text{NaOPh/AlX}_3\) of 1:1 and 1:2. There is no break in the conductance-composition curve corresponding to the composition \(\text{NaOPh/AlX}_3\) of 1:3. It does not mean that third halogen atom has not undergone any replacement. It simply suggests that there is not much difference in the conductance of solutions due to either \(\text{AlCl(OPh)}_2\) or \(\text{Al(OPh)}_3\). If it were not so, further addition of sodium phenoxide might have resulted in an increase in the conductance of the solution. But after reaching the molar ratio \(\text{NaOPh/Al(OPh)}_3\) of 1:3, further addition of NaOPh results in an increase in the conductance of the solution due to the formation of a double salt. Possible reactions in solutions may be
postulated as:

\[
\begin{align*}
&\text{AlX}_3 + \text{NaOPh} \rightarrow \text{AlX}_2\text{OPh} + \text{NaX} \\
&\text{AlX}_2\text{OPh} + \text{NaOPh} \rightarrow \text{AlX(0Ph)}_2 + \text{NaX} \\
&\text{AlX(0Ph)}_2 + \text{NaOPh} \rightarrow \text{Al(0Ph)}_3 + \text{NaX} \\
&\text{Al(0Ph)}_3 + \text{NaOPh} \rightarrow \text{Na[Al(0Ph)]}_4
\end{align*}
\]

Three breaks in the conductance-composition curve are quite apparent in the case of iron(III) chloride which suggest that in the case of iron(III) chloride, all the chlorine is lost and there is indication of the formation of the phenoxides of composition \(\text{FeCl}_2\text{(0Ph)}, \text{FeCl(0Ph)}_2\) and \(\text{Fe(0Ph)}_3\). Further addition of sodium phenoxide results in an increase in the conductance of solution but there is no indication of the formation of any double phenoxide of composition \(\text{Na[Fe(0Ph)]}_4\). This behaviour of iron(III) chloride is different from that of aluminium(III) chloride wherein there is an indication of the formation of double salt of composition \(\text{Na[Al(0Ph)]}_4\). Possible displacement reaction in the case of iron(III) chloride may be postulated as:

\[
\begin{align*}
&\text{NaOPh} + \text{FeCl}_3 \rightarrow \text{FeCl}_2\text{(0Ph)} + \text{NaCl} \\
&\text{FeCl}_2\text{(0Ph)} + \text{NaOPh} \rightarrow \text{FeCl(0Ph)}_2 + \text{NaCl} \\
&\text{FeCl(0Ph)}_2 + \text{NaOPh} \rightarrow \text{Fe(0Ph)}_3 + \text{NaCl}
\end{align*}
\]
Since iron(III) phenoxide does not form any double salt, it appears that as compared to aluminium(III) phenoxide, iron(III) phenoxide is a poor acceptor. All these titrations are given in Fig. 16.

Tetrahalides of tin, titanium, zirconium and hafnium are known to form addition compounds of stoichiometric composition 1:1, 1:2 and rarely of 1:4 with various donor molecules but the most general stoichiometric composition is that of 1:2 where the central atom acquires a coordination number of six. Some 1:1 adducts of these tetrahalides with monodentate ligands have been rationalised through a coordination number of five. But sometimes in these 1:1 adducts, the central metal atom acquires a coordination number of six through halogen bridging. The relative acceptor strength of these tetrahalides is of the order: Sn > Ge > Si and F > Cl > Br > I which agrees very well with simple electronegativity consideration or from calculations of d orbital contraction. Stereochemistry and thermal stability of the adducts MX₄.2L present a unique series for studying cis-trans isomerism and its relation to thermal stability.

Solutions of titanium(IV) chloride in fused phenol are fairly conducting and stable. On the addition of sodium or potassium phenoxides, there is a continuous decrease in the conductance of the solutions which is accompanied by the formation of a precipitate. There are two breaks in the conductance-
FIG.16. CONDUCTOMETRIC TITRATIONS BETWEEN LEWIS ACIDS AND SODIUM PHENOXIDE IN PHENOL AT 50 ± 0.1°C

![Graph showing conductometric titrations between Lewis acids and sodium phenoxide in phenol at 50 ± 0.1°C. The graph includes data for AlCl₃, AlBr₃, FeCl₃, TiCl₄, and ZrCl₄ across different molar ratios of base to acid.]
composition curves corresponding to the molar ratio NaOPh/TiCl$_4$ of 1:1 and 2:1. After the said molar ratio, further addition of sodium phenoxide does not result in any change in the conductance of the solution. Possible reaction may be postulated as:

$$\text{TiCl}_4 + 2\text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_6\text{H}_5\text{OH}_2^+ + \left[\text{TiCl}_4(\text{OC}_6\text{H}_5)\right]^-$$

$$\text{NaOC}_6\text{H}_5 \rightarrow \text{Na}^+ + \text{OC}_6\text{H}_5^-$$

$$\text{C}_6\text{H}_5\text{OH}_2^+ + \text{Na}^+ + \text{OC}_6\text{H}_5^- + \left[\text{TiCl}_4(\text{OC}_6\text{H}_5)\right]^- \rightarrow \text{Na}^+ + \left[\text{TiCl}_4(\text{OC}_6\text{H}_5)\right]^- + 2\text{C}_6\text{H}_5\text{OH}$$

Further addition of sodium phenoxide results in the formation of less conducting species i.e.

$$\text{TiCl}_4 + 2\text{C}_6\text{H}_5\text{OH} \rightarrow 2\text{C}_6\text{H}_5\text{OH}_2^+ + \left[\text{TiCl}_4(\text{OC}_6\text{H}_5)_2\right]^{2-}$$

$$2\text{NaOC}_6\text{H}_5 \rightarrow 2\text{Na}^+ + 2\text{OC}_6\text{H}_5^-$$

$$2\text{C}_6\text{H}_5\text{OH}_2^+ + \left[\text{TiCl}_4(\text{OC}_6\text{H}_5)_2\right]^{2-} + 2\text{Na}^+ + 2\text{OC}_6\text{H}_5^- \rightarrow$$

$$2\text{Na}^+ + \left[\text{TiCl}_4(\text{OC}_6\text{H}_5)_2\right]^{2-} + 4\text{C}_6\text{H}_5^-$$

After the molar ratio, NaOPh/TiCl$_4$ of 2:1, further addition of sodium phenoxide should result in an increase in the conductance of the solution as sodium phenoxide is a base of the system fused phenol but on the contrary it is observed that there is no change in the conductance of the solution on the addition of sodium phenoxide. Possibly there is displacement reaction rather than
acid-base reaction in the beginning which yields sodium chloride as:

\[
\begin{align*}
[TiCl_4(OC_6H_5)_2]^{2-} + NaOC_6H_5 & \rightleftharpoons [TiCl_3(OC_6H_5)_3]^{2-} + NaCl \\
[TiCl_3(OC_6H_5)_3]^{2-} + NaOC_6H_5 & \rightleftharpoons [TiCl_2(OC_6H_5)_4]^{2-} + NaCl \\
[TiCl_2(OC_6H_5)_4]^{2-} + NaOC_6H_5 & \rightleftharpoons [TiCl(OC_6H_5)_5]^{2-} + NaCl \\
[TiCl(OC_6H_5)_5]^{2-} + NaOC_6H_5 & \rightleftharpoons [Ti(OC_6H_5)_6]^{2-} + NaCl
\end{align*}
\]

Since sodium chloride formed is insoluble in phenol, there is no significant change in the conductance of the solution on the addition of a base. A similar trend in the conductance-composition curve is observed in the case of reaction of sodium phenoxide and zirconium(IV) chloride in fused phenol. Zirconium(IV) chloride has a limited solubility in phenol and the solutions formed are conducting. On the addition of alkali metal phenoxide, there is a break in the conductance-composition curve at the molar ratio base/ZrCl\textsubscript{4} of 1:1 and 2:1. Further addition of the base does not result in any change in the conductance of the solution. Similar reactions can be proposed for the formation of ions as in the case of titanium(IV) chloride solutions.

\[
\begin{align*}
ZrCl_4 + 4C_6H_5OH & \rightarrow 2C_6H_5OH^+ + \left[\text{ZrCl}_4(OC_6H_5)_2\right]^{2-} \\
NaOC_6H_5 & \rightarrow \text{Na}^+ + OC_6H_5^-
\end{align*}
\]
These titrations are presented in Fig. 16. A perusal of the graph suggests that the solutions finally formed are not highly conducting. It is in agreement with the earlier observations that in a solvent of low dielectric constant, there is extensive ion-pair formation.

Tin(IV) chloride, tin(IV) bromide and tin(IV) iodide are highly miscible or soluble in fused phenol and the solutions are moderately conducting. Unlike titanium(IV) chloride and zirconium(IV) chloride, there is a continuous increase in the conductance of the solution on the addition of sodium, potassium or lithium phenoxides in fused phenol which suggests that unlike titanium(IV) chloride, tin(IV) halides do not act as solvo acids in fused phenol and does not furnish \( \text{CrH}_2\text{OH}^- \) ions in solutions. On the addition of \( \text{Na}^+ + \text{OPh}^- \), there should have been removal of \( \text{C}_6\text{H}_5\text{OH}^+ \) and there should have been a fall in the conductance of the solutions. Possible displacement reaction may be postulated as:

\[
\text{SnCl}_4 + \text{NaOC}_6\text{H}_5 \rightarrow \text{SnCl}_3(\text{OC}_6\text{H}_5^-) + \text{NaCl}
\]
SnCl$_3$(OPh) $\rightarrow$ NaOPh $\rightarrow$ SnCl$_2$(OPh)$_2$ + NaCl

Here SnCl$_2$(OPh)$_2$ so formed behaves as a solvo acid and the possible reaction may be postulated as:

SnCl$_2$(OPh)$_2$ + 4PhOH $\rightarrow$ 2C$_6$H$_5$OH$^+$ + $\left[\text{SnCl}_2(\text{OPh})_4\right]^{2-}$

On the addition of sodium/potassium phenoxide, acid-base neutralisation reaction takes place, which is evident from a decrease in the conductance of the solution after 2:1 molar ratio.

NaOPh $\rightarrow$ Na$^+$ + OPh$^-$

Na$^+$ + OPh$^-$ + 2C$_6$H$_5$OH$^+$ + $\left[\text{SnCl}_2(\text{OPh})_4\right]^{2-}$ $\rightarrow$

C$_6$H$_5$OH$^+$ + Na$^+$ + $\left[\text{SnCl}_2(\text{OPh})_4\right]^{2-}$ + 2C$_6$H$_5$OH

Na$^+$ + OPh$^-$ + C$_6$H$_5$OH$^+$ + Na$^+$ + $\left[\text{SnCl}_2(\text{OPh})_4\right]^{2-}$ $\rightarrow$

2Na$^+$ + $\left[\text{SnCl}_2(\text{OPh})_4\right]^{2-}$ + 2C$_6$H$_5$OH

Similar observations have been made in the case of tin(IV) bromide and tin(IV) iodide solutions.

In the case of silicon(IV) chloride, there is a continuous increase in the conductance of the solution on the addition of sodium phenoxide. There is no break in the conductance-
composition curve and no solid compound separated out during the course of the titrations. It suggests that silicon-chlorine bond is more covalent in nature and is not readily replaced by silicon-oxygen bond. The increase in the conductance of the solution is only due to the increase in the concentration of OPh\textsuperscript{-} ions in the solutions. All these titrations presented as graphs are included in Fig. 17.

When potassium phenoxide is added to a suspension of niobium(V) chloride or tantalum(V) chloride, there is a continuous increase in the conductance of the solution and a fine solid separated out of the solution till the molar ratio KOPh/TaCl\textsubscript{5} reaches a value of 3:1. Further addition of potassium phenoxide in the solution results in a decrease in the conductance of the solution which continues till the molar ratio KOPh/TaCl\textsubscript{5} reaches a value of 4:1. Any further addition of potassium phenoxide results in again rise in the conductance of the solution. The conductance continuous to increase on the adduction of potassium phenoxide (though not very much). It appears that the replacement reaction takes place which may be postulated as:

\[ \text{NbCl}_5 + 3\text{KOPh} \rightarrow \text{NbCl}_2(\text{OPh})_3 + 3\text{KCl} \]

\[ \text{TaCl}_5 + 3\text{KOPh} \rightarrow \text{TaCl}_2(\text{OPh})_3 + 3\text{KCl} \]

In case if these pentachlorides had behaved as acids, there
IG.17. CONDUCTOMETRIC TITRATIONS BETWEEN LEWIS ACIDS AND POTASSIUM PHENOXIDE IN PHENOL AT 50°C
would have been a decrease in the conductance of the solution on the addition of potassium phenoxide. But after the molar ratio $KOPh/TaCl_5$ reaches a value of 3:1, further addition of the phenoxide results in a decrease of the conductance which may be explained in terms of acid-base reactions as:

$$TaCl_2(0Ph)_3 + 2C_6H_5OH \rightleftharpoons C_6H_5OH^+ + [TaCl_2(0Ph)_4]^-$$

$$KOC_6H_5 \rightarrow K^+ + OC_6H_5^-$$

and the neutralisation reaction is

$$K^+ + OC_6H_5^- + C_6H_5OH^+ + [TaCl_2(0Ph)_4]^- \rightarrow 2C_6H_5OH + K^+ + [TaCl_2(0Ph)_4]^-$$

Further addition of potassium phenoxide provides the ions $K^+ + OC_6H_5^-$ and there is again rise in the conductance of the solutions. The trend of the acid-base reactions presented as graphs is reported in Fig. 17. The trend of the reaction between potassium phenoxide and niobium(V) chloride in fused phenol is also included in Fig. 17. It is exactly the same as observed in the case of tantalum(V) chloride. A possible reaction may be represented as:

$$NbCl_2(OPh)_3 + 2C_6H_5OH \rightarrow C_6H_5OH^+ + [NbCl_2(OPh)_4]^-$$

$$KOC_6H_5 \rightarrow K^+ + OC_6H_5^-$$
When tungsten(VI) chloride is dissolved in fused phenol at 50°C, the solution develops reddish brown colour. On the addition of potassium phenoxide, there is no significant change in the conductance of the solution till the molar ratio $\text{KOFPH/WWC}_6$ reaches a value of 4:1 suggesting that a replacement reaction takes place. Further addition of potassium phenoxide results in a decrease in the conductance of the solution till the molar ratio $\text{KOFPH/WWC}_6$ reaches a value of 6:1. After this molar ratio, further addition of potassium phenoxide results in an increase in the conductance of the solution. The possible reaction may be postulated as:

$$\text{WCl}_6 + \text{KOC}_6\text{H}_5 \rightarrow \text{WCl}_5(\text{OC}_6\text{H}_5) + \text{KCl}$$

$$\text{WCl}_5(\text{OC}_6\text{H}_5) + \text{KOC}_6\text{H}_5 \rightarrow \text{WCl}_4(\text{OC}_6\text{H}_5)_2 + \text{KCl}$$

$$\text{WCl}_4(\text{OC}_6\text{H}_5)_2 + 2\text{KOC}_6\text{H}_5 \rightarrow \text{WCl}_2(\text{OC}_6\text{H}_5)_4 + 2\text{KCl}$$

$$\text{WCl}_2(\text{OC}_6\text{H}_5)_4 + 2\text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_6\text{H}_5\text{OH}^+ + \text{WCl}_2(\text{OC}_6\text{H}_5)_5$$

Acidic solutions

$$\text{KOC}_6\text{H}_5 \rightarrow \text{K}^+ + \text{OC}_6\text{H}_5^-$$
\[ C_6H_5OH^+ + OC_6H_5^- + K^+ + WCl_2(OPh)_5^- \rightarrow K^+ + WCl_2(OPh)_5^- + 2C_6H_5OH \]

Neutralisation reaction

Tungsten(VI) chloride does not act as a solvo acid and the replacement of chlorine by phenoxide group proceeds but on the formation of \( WCl_2(OC_6H_5)_4 \), further addition of the base does not replace chlorine, rather it is used in the neutralisation reaction. But in the case of \( WOCl_4 \) again there is no acid-base reaction and replacement reaction takes place as:

\[ WOCl_4 + KOPh \rightarrow WOCl_3(OPh) + KCl \]
\[ WOCl_3(OPh) + KOPh \rightarrow WOCl_2(OPh)_2 + KCl \]
\[ WOCl_2(OPh)_2 + KOPh \rightarrow WOCl(OPh)_3 + KCl \]
\[ WOCl(OPh)_3 + KOPh \rightarrow WO(OPh)_4 + KCl \]

After the formation of \( WO(OPh)_4 \), further addition of \( KOPh \) results in an increase in the conductance of the solution suggesting that \( WO(OPh)_4 \) does not act as a solvo acid of the system which is unlike \( WCl_2(OPh)_4 \).

Uranium(VI) chloride when dissolved in fused phenol forms straw pale conducting solutions. The solutions formed are quite stable. But has a limited solubility in fused phenol. On the addition of potassium phenoxide, there is a gradual increase in the conductance of the solution with the formation of sodium.
chloride. The increase in the conductance of the solution continuous on the addition of potassium phenoxide till the molar ratio KOPh/UCl\(_6\) reaches a value of 2:1, but after that molar ratio, further addition of potassium phenoxide results in a decrease of the conductance of the solution suggesting that the compound UCl\(_4\)(OPh)\(_2\) so formed behaves as an acid of the system

\[\text{UCl}_6 + 2\text{KOPh} \rightarrow \text{UCl}_4(\text{OPh})_2 + 2\text{KCl}\]

Further addition of potassium phenoxide results in an increase in the conductance of the solutions. Uranyl chloride, UO\(_2\)Cl\(_2\), on the other hand is sparingly soluble in phenol due to its polymeric nature. The solutions in phenol so formed are low conducting. Addition of potassium phenoxide does not result in any significant change in the conductance of the solution but when the molar ratio KOPh/UO\(_2\)Cl\(_2\) reaches a value of 2:1, further addition of KOPh in fused phenol results in a slight decrease in the conductance of the solution. The reaction may be postulated as:

\[\text{UO}_2\text{Cl}_2 + 2\text{KOPh} \rightarrow \text{UO}_2(\text{OPh})_2 + 2\text{KCl}\]
Uranyl phenoxide so formed behaves as an acid of the system and combines with potassium phenoxide to form a salt. All these reactions are presented as graphs and are reported in Fig. 18.

\[
\text{UO}_2(\text{OPh})_2 + 2\text{KOPh} \rightarrow K_2\left[\text{UO}_2(\text{OPh})_4\right]
\]

Acid-base neutralisation reactions between a number of Lewis acids such as aluminium(III) chloride, aluminium(III) bromide, tin(IV) chloride and tin(IV) bromide, titanium(IV) chloride and antimony(V) chloride and organic tertiary bases such as pyridine, quinoline, α-picoline etc. have been carried out in acetyl chloride (16,17), thionyl chloride (18), selenoyl chloride (19,20), acetic acid (21,22), ethyl acetate (23,24), acetamide (25,26), dimethylformamide (27,28) etc. The acid-base reactions in these solvents have been explained in terms of the formation of ions specific to the autoionisation of these solvents and role played by the autoionisation is also emphasized. In the case of the solvo system acetyl chloride, Paul and his coworkers (16) have explained the reaction of pyridine and aluminium(III) chloride as:

\[
\text{CH}_3\text{COCl} \rightleftharpoons \text{CH}_3\text{CO}^+ + \text{Cl}^-
\]

\[
\text{CH}_3\text{COCl} + \text{C}_5\text{H}_5\text{N} \rightarrow \text{CH}_3\text{COCl.C}_5\text{H}_5\text{N} \rightleftharpoons \text{CH}_3\text{CO.C}_5\text{H}_5\text{N}^+ + \text{Cl}^- \quad \text{Solvo base}
\]

\[
\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{COCl.AlCl}_3 \rightleftharpoons \text{CH}_3\text{CO}^+ + \text{AlCl}_4^- \quad \text{Solvo acid}
\]
FIG. 18. CONDUCTOMETRIC TITRATIONS BETWEEN LEWIS ACIDS AND SODIUM PHENOXIDE IN PHENOL AT 50 °C

- ○ WCl₆
- △ UCl₆
- ○ WOCl₄
- △ UO₂Cl₂
Similarly in the case of ethyl acetate, acid-base reaction may be explained in ethylacetate ions as (29):

\[
\text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{CH}_3\text{CO}^+ + \text{OC}_2\text{H}_5^- \\
\text{Self ionisation}
\]

\[
\text{C}_5\text{H}_5\text{N} + \text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{C}_5\text{H}_5\text{N}\cdot\text{CH}_3\text{COOC}_2\text{H}_5 \\
\text{CH}_3\text{COC}_5\text{H}_5\text{N}^+ + \text{OC}_2\text{H}_5^- \\
\text{Solvo base solution}
\]

\[
\text{AlCl}_3 + \text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5\cdot\text{AlCl}_3 \\
\text{CH}_3\text{CO}^+ + \text{AlCl}_3\text{OC}_2\text{H}_5^- \\
\text{Solvo acid solution}
\]

\[
\text{CH}_3\text{CO}^+ + \text{AlCl}_3\text{OC}_2\text{H}_5^- + \text{CH}_3\text{CO}\cdot\text{C}_5\text{H}_5\text{N}^+ + \text{OC}_2\text{H}_5^- \rightarrow \\
\text{CH}_3\text{COOC}_2\text{H}_5 + \text{CH}_3\text{COOC}_2\text{H}_5\cdot\text{AlCl}_3\cdot\text{C}_5\text{H}_5\text{N}
\]

Since phenol has been shown to be self ionised as \(2\text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_6\text{H}_5\text{OH}^+ + \text{OC}_6\text{H}_5^-\), therefore, it is of interest to investigate the reactions between tertiary organic bases and various Lewis acids in fused phenol. These reactions have been followed conductometrically.
When pyridine is added to a conducting solutions of aluminium(III) chloride in fused phenol, there is a continuous increase in the conductance of the solution till the molar ratio \( C_5H_5N/AlCl_3 \) reaches a value of 1:1. Further addition of the base results in an increase of the conductance of the solution though the trend in the slope of the conductance of the solution is different. A possible explanation of the acid-base reaction may be put forward as:

\[
AlCl_3 + C_6H_5OH \rightarrow AlCl_3\cdot C_6H_5OH \rightleftharpoons C_6H_5OH^+ + AlCl_3\cdot OC_6H_5^- \\
\text{Solvo acid}
\]

\[
Base + C_6H_5OH \rightarrow Base\cdot C_6H_5OH \rightleftharpoons BaseH^+ + OC_6H_5^- \\
\text{Solvo base}
\]

Acid-base neutralisation reaction is

\[
C_6H_5OH^+ + AlCl_3\cdot OC_6H_5^- + BaseH^+ + OC_6H_5^- \rightarrow 2C_6H_5OH + AlCl_3\cdot OC_6H_5^- + BaseH^+
\]

\[
AlCl_3\cdot OC_6H_5^- + BaseH^+ \rightarrow C_5H_5N\cdot AlCl_3\cdot C_6H_5OH \rightarrow C_5H_5N\cdot AlCl_3 + C_6H_5OH
\]

The compound isolated has the composition \( C_5H_5N\cdot AlCl_3 \) and there is no solvent molecule attached. Nevertheless, the reactions have been followed conductometrically and the existence of the formation of ions is indicated which can be explained in terms
of the formation of ions. Similar types of ions can be postulated in the case of aluminium(III) bromide which exhibits the same type of curves. But in the case of acid-base reaction of iron(III) chloride, there are two breaks in the conductance-composition curves at the molar ratio Base/FeCl$_3$ of 1:1 and 2:1 respectively. Trends of these conductance-composition curves have been explained as follows:

Base + C$_6$H$_5$OH $\rightarrow$ Base.C$_6$H$_5$OH $\rightarrow$ Base H$^+$ + OC$_6$H$_5^-$

Solvo base

FeCl$_3$ + 2C$_6$H$_5$OH $\rightarrow$ FeCl$_3$.2C$_6$H$_5$OH $\rightarrow$ C$_6$H$_5$OH$^+$ + FeCl$_3$.OC$_6$H$_5^-$

Solvo acid

Acid-base reaction can be explained as:

BH$^+$ + OC$_6$H$_5^-$ + C$_6$H$_5$OH$^+$ + FeCl$_3$.OC$_6$H$_5^-$ $\rightarrow$

BH$^+$ + FeCl$_3$.OC$_6$H$_5^-$ + 2C$_6$H$_5$OH

The compound isolated has the composition B.FeCl$_3$. Possibly the solvated solvent molecule is lost in the process of drying of the compound. A similar trend is obtained in the conductance-composition curves when iron(III) chloride is titrated against quinoline and triethylamine. All these titrations are presented as graphs in Fig. 19.

Conductometric titrations between pyridine, quinoline and
FIG. 19 CONDUCTOMETRIC TITRATIONS BETWEEN LEWIS ACIDS AND ORGANIC BASES IN PHENOL AT 50°C

- ○ AlCl₃ VS PYRIDINE
- × AlCl₃ VS QUINOLINE
- • AlCl₃ VS TRIETHYL AMINE
- △ FeCl₃ VS PYRIDINE
- □ FeCl₃ VS QUINOLINE
- ◦ FeCl₃ VS TRIETHYL AMINE
α-picoline and tin(IV) chloride and titanium(IV) chloride have been carried out in phenol at 50 ± 0.1°C. These titrations are presented as graphs in Fig. 20. It is evident from the graphs that there are two breaks in the conductance-composition curves at the molar ratio base/SnCl₄ of 0.5:1 and 1:1 suggesting that tin(IV) chloride acts as a dibasic acid. The acid salt so formed is less conducting than the neutral salt possibly because of low solubility. The conductance-composition curve may be explained as:

\[
\text{SnCl}_4 + 2\text{C}_6\text{H}_5\text{OH} \rightarrow \text{SnCl}_4.2\text{C}_6\text{H}_5\text{OH} \quad \rightarrow \quad \text{Excess of phenol}
\]

\[
2\text{C}_6\text{H}_5\text{OH}^+ + \left[\text{SnCl}_4(\text{OC}_6\text{H}_5)_2\right]^{-2}
\]

Solvo acid

\[
\text{C}_5\text{H}_5\text{N} + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_5\text{H}_5\text{N.C}_6\text{H}_5\text{OH} \rightarrow \text{C}_5\text{H}_5\text{NH}^+ + \text{OC}_6\text{H}_5^-
\]

The formation of the normal salt may be visualised as:

\[
\text{SnCl}_4(\text{OC}_6\text{H}_5)_2^{2-} + 2\text{C}_6\text{H}_5\text{OH}_2^+ + 2\text{BH}^+ + 2\text{C}_6\text{H}_5\text{O}^-
\]

\[
\left[\text{BH}^+\right]_2 \cdot \text{SnCl}_4(\text{OC}_6\text{H}_5)_2 + 4\text{C}_6\text{H}_5\text{OH}^{-}
\]

and the formation of the acid salt can be explained as:

\[
(\text{BH})_2 \cdot \text{SnCl}_4(\text{OC}_6\text{H}_5)_2 + \text{H}_2\left[\text{SnCl}_4(\text{OC}_6\text{H}_5)_2\right] \rightarrow
\]

\[
2\text{C}_6\text{H}_5\text{OH} + 2\text{BH}^+ + 2\text{H}\left[\text{SnCl}_4(\text{OC}_6\text{H}_5)_2\right]^{-}
\]
FIG. 20. CONDUCTOMETRIC TITRATIONS BETWEEN LEWIS ACIDS AND ORGANIC BASES IN PHENOL AT 50°C

- SnCl₄ VS PYRIDINE
- SnCl₄ VS QUINOLINE
- SnCl₄ VS α-PICOLINE
- TiCl₄ VS PYRIDINE
- TiCl₄ VS QUINOLINE
- TiCl₄ VS α-PICOLINE

SPECIFIC CONDUCTANCE x 10⁵ (ohm⁻¹ cm⁻¹)

MOLAR RATIO BASE/ACID
Similarly titrations of quinoline and o-picoline against diphenoxytin(IV) chloride and diphenoxytin(IV) bromide in phenol have been carried out. These titrations are also included in Fig. 21. The trends of that titrations are exactly the same as in the case of tin(IV) chloride. These titrations have been explained in terms of the formation of ions which may be formulated as:

\[
SnX_2(0Ph)_2 + 4C_6H_5OH \rightarrow [SnX_2(0Ph)_4]^{2-} + 2C_6H_5OH^+
\]

\[
2B + 2C_6H_5OH \rightarrow (B.C_6H_5OH)_2 \leftrightarrow 2BH^+ + 20C_6H_5^-
\]

\[
2C_6H_5OH^+ + [SnX_2(0Ph)_4]^{2-} + 2BH^+ + 20C_6H_5^- \rightarrow [BH]^+ [SnX_2(0Ph)_4]^{2-} + 4C_6H_5OH
\]

The normal salts have actually been prepared and characterised by analysis (Table VI). It is found that in the case of base complexes, no solvent molecules are retained by the complexes. Possibly the solvent molecules are lost during washing and drying.

Titanium(IV) chloride has been used as a solvo acid in a number of the solvents such as nitryl chloride (30,31), acetyl
FIG. 21. CONDUCTOMETRIC TITRATIONS BETWEEN SnCl₂(OPh)₂, SnBr₂(OPh)₂ AND ORGANIC BASES IN PHENOL AT 50°C.
TABLE-VI: Analytical results of the adducts of Lewis acids with organic tertiary bases

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour and physical state</th>
<th>m.p. (°C)</th>
<th>Elemental analysis</th>
<th>M</th>
<th>X</th>
<th>OPh</th>
<th>% Found</th>
<th>% Reqd.</th>
<th>M</th>
<th>X</th>
<th>OPh</th>
<th>% Reqd.</th>
<th>Molar conductance of 10⁻³M solution in nitrobenzene (ohm⁻¹ cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl₃ · py</td>
<td>White solid</td>
<td>118</td>
<td></td>
<td>12.48</td>
<td>49.64</td>
<td>-</td>
<td>12.71</td>
<td>50.12</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.8</td>
</tr>
<tr>
<td>AlCl₃ · pic</td>
<td>White solid</td>
<td>96</td>
<td></td>
<td>12.08</td>
<td>48.14</td>
<td>-</td>
<td>11.92</td>
<td>47.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.4</td>
</tr>
<tr>
<td>AlBr₃ · py</td>
<td>White solid</td>
<td>126</td>
<td></td>
<td>8.14</td>
<td>68.82</td>
<td>-</td>
<td>7.80</td>
<td>69.36</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.6</td>
</tr>
<tr>
<td>SnCl₄ · 2py</td>
<td>White solid</td>
<td>144</td>
<td></td>
<td>28.36</td>
<td>34.14</td>
<td>-</td>
<td>28.35</td>
<td>33.92</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.2</td>
</tr>
<tr>
<td>SnCl₄ · 2pic</td>
<td>White solid</td>
<td>136</td>
<td></td>
<td>26.62</td>
<td>32.23</td>
<td>-</td>
<td>26.57</td>
<td>31.79</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.8</td>
</tr>
<tr>
<td>SnCl₂(OC₆H₅)₂ · 2py</td>
<td>White solid</td>
<td>125</td>
<td></td>
<td>22.28</td>
<td>13.62</td>
<td>34.12</td>
<td>22.24</td>
<td>13.30</td>
<td>34.85</td>
<td>1.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnCl₂(OC₆H₅)₂ · 2pic</td>
<td>White solid</td>
<td>106</td>
<td></td>
<td>21.38</td>
<td>12.46</td>
<td>33.28</td>
<td>21.13</td>
<td>12.64</td>
<td>33.11</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnBr₂(OC₆H₅)₂ · 2py</td>
<td>White solid</td>
<td>116</td>
<td></td>
<td>19.16</td>
<td>25.42</td>
<td>30.18</td>
<td>19.06</td>
<td>25.69</td>
<td>29.87</td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiCl₄ · 2py</td>
<td>White solid</td>
<td>138</td>
<td></td>
<td>13.86</td>
<td>41.26</td>
<td>-</td>
<td>13.79</td>
<td>40.80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.2</td>
</tr>
<tr>
<td>TiCl₄ · 2(CH₃)₃N</td>
<td>White solid</td>
<td>156</td>
<td></td>
<td>15.46</td>
<td>42.24</td>
<td>-</td>
<td>15.58</td>
<td>46.10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.4</td>
</tr>
</tbody>
</table>
chloride (16,17,32), benzoyl chloride (33,34) and thionyl chloride (18,35) and acetic anhydride (36) and acid-base neutralisation reactions have been carried out in these solvents laying emphasis on the role played by the autoionisation of the solvent. In the present studies, acid-base conductometric studies have been carried out in fused phenol against pyridine, α-picoline, trimethylamine and benzylamine. All these titrations are included in Figs. 20 and 21. It is apparent from these curves that like tin(IV) chloride, diphenoxytin(IV) halides, titanium(IV) chloride behaves as a dibasic acid and there are two breaks in the conductance-composition curves at the molar ratio base/acid of 1:1 and 2:1. Possibly ions present in the solution are:

\[
\begin{align*}
\text{SnX}_2(\text{OPh})_2 + 4\text{PhOH} & \rightarrow 2\text{PhOH}^+ + \text{SnX}_2(\text{OPh})_4^{2-} \\
\text{B} + \text{C}_6\text{H}_5\text{OH} & \rightarrow \text{B.C}_6\text{H}_5\text{OH} \rightleftharpoons \text{BH}^+ + \text{OC}_6\text{H}_5^- \\
2\text{PhOH}^+ + \text{SnX}_2(\text{OPh})_4^{2-} + \text{BH}^+ + \text{OC}_6\text{H}_5^- & \rightarrow \\
2\text{C}_6\text{H}_5\text{OH} + \text{PhOH}_2^+ + \text{BH}^+ + \left[\text{SnX}_2(\text{OPh})_4\right]^{2-} & \text{Acid salt} \\
\text{PhOH}_2^+ + \text{BH}^+ + \text{SnX}_2(\text{OPh})_4^{2-} + \text{BH}^+ + \text{OPh}^- & \rightarrow \\
2\text{BH}^+ + \left[\text{SnX}_2(\text{OPh})_4\right]^{2-} + 2\text{PhOH} & 
\end{align*}
\]

In most of these titrations, the breaks in the conductance-
composition curves are slightly deviated from that of the exact position of molar ratio 2:1 and 1:1 because of the solvolytic reaction which these Lewis acids may suffer in phenol. All these salts have been isolated and characterised and are included in Tables VII and VIII.

As discussed in Chapter I, the pure solvent has the specific conductance of $3.6 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ (37,38). By analogy with the mode of ionisation of acetic acid, methyl alcohol (39), the possible mode of ionisation of phenol is:

$$2\text{C}_6\text{H}_5\text{OH} \rightleftharpoons \text{C}_6\text{H}_5\text{OH}^+ + \text{OH}^-$$

Accordingly to the solvent system concept, the solutes which directly or indirectly increase the concentration of the cations characteristic of the autoionisation of phenol will be the solvo acid of the system and the solutes which increase the concentrations of the anions characteristic of its autoionisation will be the bases of the solvo system phenol. Accordingly phenoxides of alkali metals and quaternary ammonium phenoxides will be the bases of the system while the phenoxides of group III and group IV elements will be the acids of the system and that a particular solute acts as an acid of the system or not is established by the fact that there is a decrease in the conductance of the solution on the addition of alkali metal phenoxides.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour and physical state</th>
<th>m.p. (°C)</th>
<th>Elemental analysis</th>
<th>Molar conductance of 10⁻³M solution in nitrobenzene (ohm⁻¹cm²mol⁻¹)</th>
<th>Molecular weight in nitrobenzene (Found</th>
<th>Req'd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂[Ti(OC₆H₅)₆]</td>
<td>Orange solid</td>
<td>148</td>
<td>7.62 - 88.2⁺ 7.7⁴ - 90.00 16.4</td>
<td>226 620</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂[Ti(OC₆H₅)₆]</td>
<td>Red solid</td>
<td>162</td>
<td>7.18 - 84.2 7.36 - 85.58 13.6</td>
<td>242 652</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂[Ti(OC₆H₅)₆]</td>
<td>Red solid</td>
<td>178</td>
<td>7.21 - 82.1 7.02 - 81.58 18.2</td>
<td>286 684</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂[Ti(OC₆H₄NO₂)₆]</td>
<td>Orange solid</td>
<td>146</td>
<td>5.46 - 90.18 5.21 - 89.90 24.8</td>
<td>326 922</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂[Ti(OC₆H₄NO₂)₆]</td>
<td>Orange solid</td>
<td>182</td>
<td>5.16 - 88.2 5.03 - 86.79 32.6</td>
<td>342 954</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂[Ti(OC₆H₄Cl)₆]</td>
<td>Orange solid</td>
<td>192</td>
<td>5.62 - 89.18 5.59 - 89.06 28.3</td>
<td>302 859</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂[Ti(OC₆H₄Cl)₆]</td>
<td>Red solid</td>
<td>186</td>
<td>5.46 - 84.9 5.39 - 85.86 26.4</td>
<td>296 891</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Color</td>
<td>#1</td>
<td>#2</td>
<td>#3</td>
<td>#4</td>
<td>#5</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>-----------</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Na[1(IOC_6H_5)_4]</td>
<td>Orange</td>
<td>112</td>
<td>4.38</td>
<td>24.82</td>
<td>70.62</td>
<td>4.41*</td>
</tr>
<tr>
<td>K[1(IOC_6H_5)_4]</td>
<td>Orange</td>
<td>124</td>
<td>7.18</td>
<td>22.92</td>
<td>68.84</td>
<td>7.25*</td>
</tr>
<tr>
<td>(CH_3)_4N[1(IOC_6H_5)_4]</td>
<td>Orange</td>
<td>98</td>
<td>-</td>
<td>21.86</td>
<td>65.12</td>
<td>-</td>
</tr>
<tr>
<td>(C_4H_9)_4N[1(IOC_6H_5)_4]</td>
<td>Orange</td>
<td>102</td>
<td>-</td>
<td>16.38</td>
<td>48.92</td>
<td>-</td>
</tr>
</tbody>
</table>

* Here metal means alkali metal.
TABLE-VIII: Analytical results of the double phenoxyides of tin(IV) and diphenoxytin(IV)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour and physical state</th>
<th>m.p. (°C)</th>
<th>Elemental analysis (%)</th>
<th>Molar conductance in nitrobenzene (ohm(^{-1}\text{cm}^2\text{mol}^{-1}))</th>
<th>Molecular weight in nitrobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Na}_2\left[\text{Sn(OC}_6\text{H}_5\right]_6]</td>
<td>White solid</td>
<td>158</td>
<td>M 15.92 X 78.38 OPh 16.45</td>
<td>24.6</td>
<td>264 722.7</td>
</tr>
<tr>
<td>(\text{Li}_2\left[\text{Sn(OC}_6\text{H}_5\right]_6]</td>
<td>White solid</td>
<td>142</td>
<td>M 16.38 X 81.64 OPh 17.18</td>
<td>21.8</td>
<td>238 690.7</td>
</tr>
<tr>
<td>(\left[\text{C}_4\text{H}_9\right]_2\text{Sn(OC}_6\text{H}_5\right]_6]</td>
<td>White solid</td>
<td>164</td>
<td>M 10.82 X 48.26 OPh 10.23</td>
<td>28.6</td>
<td>406 1160.7</td>
</tr>
<tr>
<td>(\text{K}_2\left[\text{SnBr}_2(\text{OC}_6\text{H}_5\right]_4]</td>
<td>Yellow solid</td>
<td>192</td>
<td>M 17.34 X 22.40 OPh 48.64</td>
<td>20.6</td>
<td>286 728.7</td>
</tr>
<tr>
<td>(\text{K}_2\left[\text{SnI}_2(\text{OC}_6\text{H}_5\right]_4]</td>
<td>Yellow solid</td>
<td>162</td>
<td>M 14.68 X 29.64 OPh 44.82</td>
<td>28.4</td>
<td>336 822.7</td>
</tr>
<tr>
<td>(\text{Na}_2\left[\text{SnBr}_2(\text{OC}_6\text{H}_5\right]_4]</td>
<td>Yellow solid</td>
<td>172</td>
<td>M 17.64 X 21.86 OPh 52.92</td>
<td>23.8</td>
<td>312 696.7</td>
</tr>
<tr>
<td>(\text{Na}_2\left[\text{SnI}_2(\text{OC}_6\text{H}_5\right]_4]</td>
<td>Yellow solid</td>
<td>148</td>
<td>M 14.72 X 31.82 OPh 46.42</td>
<td>29.8</td>
<td>318 790.7</td>
</tr>
</tbody>
</table>
Phenoxides of alkali metals and tetrabutylammonium phenoxide, tetraethylammonium phenoxide and tetramethylammonium phenoxide are highly soluble in phenols and the solutions so formed are highly conducting. Possible ions may be formulated as:

\[
\begin{align*}
(C_{4}H_{9})_{4}NOC_{6}H_{5} & \rightarrow Phenol \quad (C_{4}H_{9})_{4}N^{+} + OC_{6}H_{5}^{-} \\
(CH_{3})_{4}NOC_{6}H_{5} & \rightarrow Phenol \quad (CH_{3})_{4}N^{+} + OC_{6}H_{5}^{-} \\
KOC_{6}H_{5} & \rightarrow K^{+} + OC_{6}H_{5}^{-}
\end{align*}
\]

Aluminium(III) phenoxide has a limited solubility in fused phenol and the solutions formed are fairly conducting. Phenoxides of thallium(III) and indium(III) also have a limited solubility and the solutions are conducting. Since these elements have a tendency to increase their coordination to four, possible ions may be formulated as:

\[
\begin{align*}
Al(OC_{6}H_{5})_{3} + C_{6}H_{5}OH & \rightarrow H[Al(OC_{6}H_{5})_{4}] \quad Phenol \quad H_{2}OC_{6}H_{5} + Al(OC_{6}H_{5})_{4}^{-} \\
Tl(OC_{6}H_{5})_{3} + C_{6}H_{5}OH & \rightarrow H[Tl(OC_{6}H_{5})_{4}] \quad Phenol \quad C_{6}H_{5}OH^{+} + Tl(OPh)_{4}^{-}
\end{align*}
\]

On the addition of a base solution to the solution of aluminium (III) phenoxide, there is a continuous decrease in the conductance
of the solution till the molar ratio base/Al(0Ph)$_3$ reaches a value of 1:1. Further addition of a base solution results in an increase in the conductance of the solution due to the presence of excess of OC$_6$H$_5^-$ ions. Neutralisation reaction may be proposed as:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{OH}^+ + \text{Al}(0\text{Ph})_4^- + \text{Na}^+ + \text{OC}_6\text{H}_5^- &\rightarrow \text{Na}^+ + \text{Al}(0\text{Ph})_4^- + 2\text{C}_6\text{H}_5\text{OH} \\
\text{C}_6\text{H}_5\text{OH}^+ + \text{Tl}(0\text{Ph})_4^- + \text{Bu}^+.\text{N}^+ + \text{OC}_6\text{H}_5^- &\rightarrow \\
&\quad \text{Bu}^+.\text{N}^+ + \text{Tl}(0\text{Ph})_4^- + 2\text{C}_6\text{H}_5\text{OH}
\end{align*}
\]

Conductometric titrations between tetraethylammonium phenoxide and aluminium trinitrophenoxide and tetraethylammonium phenoxide and aluminium trichlorophenoxide have been carried out in fused phenol. The trend of the conductance-molar ratio curve are the same as reported for pure phenoxides. Similar types of ions can be proposed for these reactions. All these titrations are given as graphs in Fig. 22.

Tetraphenoxides of titanium has a very high solubility in fused phenol and the solutions formed are highly conducting. Tetrachlorophenoxides and tetranitrophenoxides of titanium form fairly conducting in phenol. Possible ions present in these solutions may be postulated as:

\[
\text{Ti}(\text{OC}_6\text{H}_4\text{Cl})_4 + 2\text{C}_6\text{H}_5\text{OH} \rightarrow \text{H}_2\left[\text{Ti}(\text{OC}_6\text{H}_4\text{Cl})_4(\text{OC}_6\text{H}_5)_2\right] \quad \text{Excess of phenol}
\]

\[
2\text{C}_6\text{H}_5\text{OH}^+ + \left[\text{Ti}(\text{OC}_6\text{H}_4\text{Cl})_4(\text{OC}_6\text{H}_5)_2\right]^{2-}
\]
FIG. 22. CONDUCTOMETRIC TITRATIONS BETWEEN ARYLOXIDES OF Al(III) Ti (III) AND In (III) AGAINST BASIC PHENOXIDES IN PHENOL AT 50°C.

- ○ Al(OPh)₃
- X Ti(OPh)₃
- O - In(OPh)₃
- △ Al(OC₆H₄NO₂)₃
- X X Al(OC₆H₄Cl)₃

MOLAR RATIO BASE/ACID
On the addition of a base solution, there is a continuous decrease in the conductance of the solution till the molar ratio base/Ti(OCH₃)₄ reaches a value of 1:1. Further addition of a base solution results in an increase in the conductance of the solution and the rise in the conductance of the solution continues till the molar ratio base/acid reaches a value of 2:1. After this molar ratio further addition of the base solution results in a change in the rise of the conductance of the solution. First break in the conductance-composition corresponds to the formation of acid salt while the second break corresponds to the formation of the normal salt. Possible reaction may be proposed as:

\[
\text{Ti(OCH₃)₄ + 2C₆H₅OH} \rightarrow \text{H₂[Ti(OCH₃)₄(NO₂)₄(OC₆H₅)₂]} \xrightarrow{\text{phenol}} 2\text{C₆H₅OH}^+ + \left[\text{Ti(OCH₃)₄(NO₂)₄(OC₆H₅)₂}\right]^{2-}
\]

\[
\text{KOC₆H₅} \rightarrow \text{K}^+ + \text{OC₆H₅}^-
\]

\[
\text{K}^+ + \text{OC₆H₅}^- + 2\text{C₆H₅OH}^+ + \left[\text{Ti(OCH₃)₄(NO₂)₄(OC₆H₅)₂}\right]
\]

\[
\text{K}^+ + \text{C₆H₅OH}^+ + \left[\text{Ti(OCH₃)₄(NO₂)₄(OC₆H₅)₂}\right]^{2-}
\]

\[
\text{Acid salt}
\]

\[
\text{K}^+ + \text{C₆H₅OH}^+ + \left[\text{Ti(OCH₃)₄(NO₂)₄(OC₆H₅)₂}\right] + \text{K}^+ + \text{OC₆H₅}^-
\]

\[
2\text{K}^+ + 2\text{C₆H₅OH} + \left[\text{Ti(OCH₃)₄(NO₂)₄(OC₆H₅)₂}\right]^{2-}
\]
The neutral salt $K_2\left[\text{Ti} (\text{OC}_6\text{H}_5)_6\right]$ has actually been isolated and characterised. Similarly in the case of tetranitrophenoxydes of titanium and tetrachlorophenoxydes of titanium, neutral salts of composition $K_2\left[\text{Ti} (\text{OC}_6\text{H}_4\text{NO}_2)_6\right]$ and $K_2\left[\text{Ti} (\text{OC}_6\text{H}_4\text{Cl})_6\right]$ have actually been isolated and characterised. All these salts have been listed in Table VII. All these conductometric titrations are included in Fig. 23.

Tin(IV) phenoxide has a limited solubility in fused phenol and the solutions are fairly conducting. On the addition of tetrabutylammonium phenoxide, there is a gradual decrease in the conductance of the solution till the molar ratio base/Sn(OC_6H_5)_4 reaches a value of 1:1. Further addition of the base solution gives an increase in the conductance of the solution. Possible acid-base reaction may be proposed as:

$$\text{(C}_2\text{H}_5)_4\text{NOC}_6\text{H}_5 \xrightarrow{\text{Phenol}} (\text{C}_2\text{H}_5)_4\text{N}^+ + \text{OC}_6\text{H}_5^-$$

$$\text{Sn(OC}_6\text{H}_5)_4 + 2\text{C}_6\text{H}_5\text{OH} \rightarrow \text{H}_2\left[\text{Sn(OC}_6\text{H}_5)_6\right] \xrightarrow{\text{Phenol}} 2\text{C}_6\text{H}_5\text{OH}^+ + \left[\text{Sn(OC}_6\text{H}_5)_6\right]^{2-}$$

$$2\text{C}_6\text{H}_5\text{OH}^+ + \left[\text{Sn(OC}_6\text{H}_5)_6\right]^{2-} \rightarrow (\text{C}_2\text{H}_5)_4\text{N}^+ + \text{OC}_6\text{H}_5^-$$

$$2\text{C}_6\text{H}_5\text{OH}^+ + (\text{C}_2\text{H}_5)_4\text{N}^+ + \text{C}_6\text{H}_5\text{OH}^+ \rightarrow 2\text{C}_6\text{H}_5\text{OH} + (\text{C}_2\text{H}_5)_4\text{N}^+ + \left[\text{Sn(OC}_6\text{H}_5)_6\right]^{2-}$$

$$\left[\text{C}_2\text{H}_5\right]_4\text{N}^+ + \text{OC}_6\text{H}_5^- + (\text{C}_2\text{H}_5)_4\text{N}^+ + \text{C}_6\text{H}_5\text{OH}^+ \rightarrow \left[\text{C}_2\text{H}_5\right]_4\text{N}^+ + \left[\text{Sn(OC}_6\text{H}_5)_6\right]^{2-} + 2\text{C}_6\text{H}_5\text{OH}$$
FIG. 23 CONDUCTOMETRIC TITRATIONS BETWEEN SOLVO ACIDS AND SOLVO BASES IN PHENOL AT 50°C

- Ti(OPh)_4 VS KOPh
- Ti[(OC_6H_4Cl)_4] VS KOPh
- Ti[(OC_6H_4NO_2)_4] VS KOPh
- Sn(OPh)_4 VS (C_6H_5)_4N.OPh
- Sn Br_2(OPh)_2 VS KOPh
- SnI_2(OPh)_2 VS KOPh

SPECIFIC CONDUCTANCE x 10^5 (ohm^-1cm^-1)

MOLAR RATIO BASE/ACID

300 280 260 240 220 200 180 160 140 120 100 80 60 40 20

MOLAR RATIO BASE/ACID
In the case of diphenoxyltin(IV) bromide and diphenoxyltin(IV) iodide, the titration curves are reported in Fig. 23. The acid-base reaction may be proposed as:

\[
\begin{align*}
KOPh & \rightarrow K^+ + OC_6H_5^- \\
SnX_2(OC_6H_5)_2 + 4C_6H_5OH & \rightarrow 2C_6H_5OH^+ + \left[SnX_2(OC_6H_5)_4\right]^{2-} \\
K^+ + OC_6H_5^- + 2C_6H_5OH^+ + \left[SnX_2(OC_6H_5)_4\right]^{2-} & \rightarrow 2C_6H_5OH + K^+ + C_6H_5OH^+ + \left[SnX_2(OC_6H_5)_4\right]^{2-}
\end{align*}
\]

On the addition of excess of base, neutral salts are formed as:

\[
\begin{align*}
K^+ + OC_6H_5^- + K^+ + C_6H_5OH^+ + \left[SnX_2(OC_6H_5)_4\right]^{2-} & \rightarrow 2K^+ + \left[SnX_2(OC_6H_5)_4\right]^{2-} + 2C_6H_5OH
\end{align*}
\]

Most of the salts have been isolated and characterised and are included in Table VIII.

It has been shown by Mehrotra and his coworkers (40) that when metal alkoxides are treated with acetyl chloride, the original metal chlorides could be regenerated. However, in some of the cases only a part of the alkoxide group could be replaced. The ester so formed would be added up to the metal chloride so generated. When niobium(V) or tantalum(V) alkoxides are refluxed with excess of acetyl chloride, niobium(V) or tantalum(V) chloride would be formed as:
In the present studies, when acetyl chloride is added to the solution of aluminium phenoxide in phenol, there is a gradual decrease in the conductance of the solution which continues till the molar ratio AcCl/Al(O\text{Ph})_3 reaches a value of 1:1. Any further addition of acetyl chloride does not result in any change of the conductance of the solution. Possible reaction may be postulated as:

\[
\text{Al(O\text{Ph})}_3^{-} + C_6H_5\text{OH}^{+} + CH_3\text{CO}^{+} + Cl^- \rightarrow \text{Al(O\text{Ph})}_2\text{Cl}.CH_3\text{COOC}_6\text{H}_5 + HCl + C_6H_5\text{OH}
\]

Since hydrogen chloride so formed is not soluble in phenol at 50 ± 0.1°C, it escapes from the solution. The compound isolated from the reaction mixture has the composition Al(O\text{Ph})_2ClCH_3COOC_6H_5. But when aluminium(III) phenoxide is refluxed with excess of acetyl chloride in benzene a complex of composition AlCl_3·CH_3COOC_6H_5 is obtained % Al = 10.03(10.02), % Cl = 39.48 (39.52); Found(Calcd). Similarly when diphenoxotin(II) halides are titrated against acetyl chloride, there is again a decrease in the conductance of the solution. There are two breaks in the conductance-composition curves corresponding to the molar acetyl chloride/SnX_2(O\text{Ph})_2 of 1:1 and 2:1. Finally, a compound
of composition SnX₂(0Ph)₂.2CH₃COOC₆H₅ could be obtained. Possible reaction may be postulated as:

\[
\text{SnX}_2(0\text{Ph})_2^2- + 2C_6H_5OH^+ + CH_3CO^+ + Cl^- \rightarrow \text{SnX}_2(0\text{Ph})_3^-\cdot CH_3COOC_6H_5 + HCl + C_6H_5OH^2 + \cdot CH_3CO^+ + Cl^- \rightarrow \text{SnX}_2(0\text{Ph})_2.2CH_3COOC_6H_5 + HCl
\]

All these titrations are shown in Fig. 24. When diphenoxytin(II)₆ are refluxed with excess of acetyl chloride, compound of composition SnCl₄.2CH₃COOC₆H₅ has been isolated and characterised as Sn = 22.24(22.28), Cl = 26.61(26.66); Found(Calcd).

Iodine(III) chloride is known to be slightly self ionised as \( \text{ICl}_3 \rightleftharpoons \text{ICl}^+ + \text{ICl}^- \) in the molten state (41). It is known to form addition compounds with a number of acceptor molecules which have been formulated as \( \text{ICl}_2^+\cdot\text{MCl}_4^- \) (42) and \( \text{ICl}_2^+\cdot\text{MCl}_6^- \) (43). It is also known to form addition compounds with a number of organic tertiary bases (44). Iodine(III) phenoxide has been prepared from iodine(III) chloride and sodium phenoxide. It is highly soluble in phenol and the solutions formed are fairly conducting. Possible ions may be formulated as:

\[
\text{I(0Ph)}_3 \rightleftharpoons \text{I(0Ph)}_2^+ + \text{OPh}^- \]

Base
FIG. 24. CONDUCTOMETRIC TITRATIONS BETWEEN ACETYL CHLORIDE AND METAL PHENOXIDES

- O - Al(0Ph)₃
- X - SnBr₂(0Ph)₂
- △ - SnI₂(0Ph)₂

SPECIFIC CONDUCTANCE x 10⁶ ohm⁻¹cm⁻¹

MOLAR RATIO ACETYL CHLORIDE/M.PHENOXIDE
In order to ascertain whether iodine(III) phenoxide acts as an acid or a base in fused phenol, a solution of the base was added. In case there is an increase in the conductance of the solution then iodine(III) phenoxide behaves as a base but when there is a decrease in the conductance of the solution, then iodine(III) phenoxide behaves as an acid. On the addition of potassium phenoxide to the solution of iodine(III) phenoxide in fused phenol, there is a slight decrease in the conductance of the solution. The decrease in the conductance of the solution continues as the addition of potassium phenoxide is continued. After the molar ratio KOPh/I(OPh)\(_3\) reaches a value of 1:1, further addition of potassium phenoxide results in an increase of the conductance of the solution. The reaction may be postulated as:

\[
I(\text{OPh})_3^+ + \text{C}_6\text{H}_5\text{OH}^+ + K^+ + \text{OPh}^- \rightarrow K^+ + I(\text{OPh})_4^- + 2\text{C}_6\text{H}_5\text{OH}
\]

This titration curve is included in Fig. 25. Conductometric titrations between iodine(III) phenoxide and sodium phenoxide, lithium phenoxide and tetrabutylammonium phenoxide have also been carried out in fused phenol and these curves are also included in Fig. 25. All these compounds have been isolated and characterised and given in Table VII. From the trends of the curves of acid-base reactions in phenol, it is apparent that the phenoxides of metals such as aluminium, tin, titanium,
FIG. 25. CONDUCTOMETRIC TITRATIONS BETWEEN I(OPh)$_3$ AND BASIC PHENOXIDES

- O KOPh
- • NaOPh
- (C$_4$H$_4$)$_2$N.OPh

SPECIFIC CONDUCTANCE x 10$^{-4}$ (ohm$^{-1}$ cm$^{-1}$)

MOLAR RATIO BASE/ACID
antimony etc. behave as an acid of the system while phenoxides of alkali metals and tetraalkylammonium phenoxide behave as bases as both type of solutes produce on dissolution in phenol, cation and anion characteristics of its autoionisation. From the above observations and on the analogy of the mode of ionisation of methyl alcohol (loc cit) and acetic acid (loc cit), possible mode of ionisation of phenol may be proposed as:

\[ 2C_6H_5OH \rightleftharpoons C_6H_5OH^+ + OC_6H_5^- \]