Acid-Base Concept
ACID-BASE CONCEPT

Earlier definitions of acids and bases lay much emphasis on their empirical properties rather than on any theoretical considerations. Arrhenius theory of electrolytic dissociation was the most striking success in the field of acids and bases. According to this theory solutes which on dissociation in solution give hydrogen ions are called acids and the compounds which furnish hydroxyl ions in solutions are called bases. This definition of acids and bases also provides a method to compare their strength. But soon it was discovered that the organic compounds such as pyridine, ketones and amines have distinctly basic properties but do not give hydroxyl ions in solution. So the presence of hydroxyl ion was no longer considered to be essential criterion of a base while ionisable hydrogen ion was still regarded to be an essential constituent of an acid.

In 1923 Bronsted (100) and Lowery (101) independently developed an acid base theory based on the central role of the proton. They defined acid as a proton donor and base as a proton acceptor. Thus an acid base reaction is one in which proton transfer occurs:

\[
\text{Acid} \rightleftharpoons \text{Base} + H^+ 
\]
This theory of acids and bases also accounts the acidic properties of cations, anions or neutral molecules such as:

\[
\begin{align*}
\text{NH}_4^+ & \rightleftharpoons \text{NH}_3 + \text{H}^+ \\
\text{H}_2\text{PO}_4^- & \rightleftharpoons \text{HPO}_4^{2-} + \text{H}^+ \\
\text{H}_2\text{O} & \rightleftharpoons \text{OH}^- + \text{H}^+
\end{align*}
\]

Cations, anions and neutral molecules after donating a proton become proton acceptor and act as bases. The acids and bases so related can be expressed as:

\[A \rightleftharpoons B + \text{H}^+\]

where \(A\) and \(B\) are termed as conjugate acid-base pair. This definition places no restriction on the sign or magnitude of the charge on \(A\) and \(B\), but \(A\) must be more positive than \(B\) by one unit.

The nature of the solvent plays an important role in deciding the acidic or basic properties of a solute. Urea behaves as a base when dissolved in formic acid but acts as an acid in liquid ammonia. Although, Bronsted-Lowery theory explains the basic properties of a wide variety of substances like hydroxyl ions, pyridine and amines yet the term acid is restricted only to the proton donor substances. This theory does not explain the acidic character of compounds like tin(IV) chloride, antimony(V) chloride etc., which are otherwise known to act as acids.
in non-protonic solvents.

The theory of solvent system was proposed by Franklin (102) with due importance to the role of the solvent. Water ionises to produce hydronium and hydroxyl ions, similarly liquid ammonia gives ammonium and amide ions:

\[
\begin{align*}
2\text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \\
2\text{NH}_3 & \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-
\end{align*}
\]

The production of hydronium ions is the characteristic property of the acids in water. On similar lines it may be envisaged that ammonium ion is the characteristic ion for acidic properties in liquid ammonia. So the compounds like ammonium chloride, ammonium nitrate etc., which furnish ammonium ions may act as acids and compounds like sodamide, potassium amide etc., may act as bases in liquid ammonia. The neutralisation reaction of ammonium chloride and sodamide in liquid ammonia is similar to the neutralisation of hydrochloric acid and sodium hydroxide in water.

\[
\begin{align*}
\text{HCl} + \text{NaOH} & \rightarrow \text{NaCl} + \text{H}_2\text{O} \\
(\text{acid}) & (\text{base}) & (\text{salt}) & (\text{solvent}) \\
\text{NH}_4\text{Cl} + \text{NaNH}_2 & \rightarrow \text{NaCl} + 2\text{NH}_3 \\
(\text{acid}) & (\text{base}) & (\text{salt}) & (\text{solvent})
\end{align*}
\]

The use of Franklin theory of solvent system has also been extended to include non-protonic solvents. Jander (103) has studied the acid base neutralisation reactions in liquid
sulphur dioxide, which has been proposed to ionise as:

\[ 2SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-} \]

Substances like thionyl chloride, thionyl bromide etc., which give cations characteristic of the solvent will act as acids and soluble sulphites will behave as bases in it. The conductometric titrations confirm the neutralisation of the base by an acid and the neutralisation reaction has been represented as:

\[ \text{SOCl}_2 \rightleftharpoons SO^{2+} + 2\text{Cl}^- \]  
(ionisation of the acid)

\[ \text{Cs}_2\text{SO}_3 \rightleftharpoons 2\text{Cs}^+ + \text{SO}_3^{2-} \]  
(ionisation of the base)

\[ 2\text{Cs}^+ + \text{SO}_3^{2-} + \text{SO}^{2+} + 2\text{Cl}^- \rightarrow 2\text{CsCl} + 2\text{SO}_2 \]  
(neutralisation reaction)

Later, it was observed that thionyl chloride labelled with \( ^{33}\text{S} \) when dissolved in liquid sulphur dioxide exchanged very slowly with \( ^{32}\text{S} \). This is contrary to expectations, if the solvent and the thionyl chloride both were to give \( \text{SO}^{2+} \) ions. The ionisation of thionyl chloride may be, therefore, as \( \text{SOCl}^+ + \text{Cl}^- \) which seems to be more probable. However, when tetramethylammonium chloride or rubidium chloride is added to a solution of thionyl chloride in labelled sulphur dioxide, sulphur exchange occurs readily.
This can be explained on the basis of the conversion of SO$^{2+}$ ions formed by sulphur dioxide to SOCl$^+$ by the presence of excess of chloride ions.

This theory of solvent system has been further simplified by Gady and Elsey (104). The acid is defined as a solute which furnishes the cations characteristic of the solvent and the base that gives anions characteristic of the solvent. According to this theory the presence of a polar solvent is essential for acid-base neutralisation reactions. But it has been observed that the presence of the solvent for neutralisation reactions is not necessary and the acid-base neutralisation reaction can take place even in the vapour state (105). The ionisation of the solvent is also not a prerequisite for these reactions. Some typical acid-base neutralisation reactions have been carried out successfully in non-polar solvents like carbon tetrachloride and benzene (106).

Electronic theory of acids and bases put forward by Lewis (107) has broadened the field of acids and bases. The acid is defined as a substance which can accept an electron pair and a base as capable of donating it. Thus neutralisation reactions result in unifying the two molecules through a coordinate bond. The neutralisation reaction between aluminium chloride and pyridine may be represented as:
Electronic theory of Lewis completely ignores the role of the solvent. There is also no provision for the quantitative treatment of relative strength of acids, whereas earlier theories of Arrhenius and Bronsted provided.

Smith (308) reconciled the theories of Lewis and Franklin and defined a solute to be an acid when its molecule neutral or charged is an electron pair acceptor towards the molecule or the ion of the solvent, while a solute has been defined as a base when its molecule (neutral or charged) is an electron pair donor towards the molecule or ion of the solvent. Thus the solvent has a major role to play in acid-base neutralisation reactions. The solvent reacts with the solute as such or in the form of ions. The Lewis acids react with the basic solvent and increase the concentration of the cations and vice versa. The extent to which these acids and bases react with the solvent to form solvo acids and solvo bases is a measure of their acidic and basic strengths. These solvo acids and bases subsequently may undergo ionisation. Neutralisation reaction thus is an exchange reaction between the ions that already exist in the solution. The neutralisation reaction between antimony(V)chloride and pyridine in seleninyl chloride has been represented as:

\[ \text{Cl} \quad \text{N} \quad + \quad \text{Al} : \text{Cl} \quad \rightarrow \quad \text{Cl} \quad \text{N} : \text{Al} : \text{Cl} \quad \text{Cl} \]
Smith's ideas regarding acids and bases have been used to explain the neutralisation reactions in polar solvent like benzoyl chloride (109), nitrosyl chloride (110), acetyl chloride (111) and phosphoryl chloride (112). The above mechanism is best applicable in polar solvents and may not hold good in relatively non-polar solvents.

A new type of acids like LiAlH₄ etc., have been discussed by Jander and coworkers (113) in diethyl ether and acetone. These workers have proposed that ether ionises as:

$$C_2H_5OC_2H_5 \leftrightarrow (C_2H_5)^+ + (OC_2H_5)^-$$

and the compounds LiAl[(C₄H₁₀)₂OH]₄ and LiAl[(CH₃)₂COH]₄ have been isolated with these acids.

From the study of acids and bases Usanovich (114) has developed a very broad concept of acids and bases. He has
defined acids as substances which form salts with bases through neutralisation, give up cations or combine with anions or electrons. The base has been defined as a substance which neutralises acids, gives up anions or electrons or combines with cations. Although, the underlined concept is the same i.e. the salt formation, yet the scope of this definition is very wide and it covers all theories of acids and bases so far considered. It also embraces the oxidation reduction process as representative of acid-base neutralisation reactions. Though, this theory has classified all examples of acidity and basicity, yet its scope is very wide and includes reactions which are better considered from other point of view, such as oxidation-reduction phenomena.

It is quite evident from the above discussion that no single theory is adequate to explain all types of acid-base reactions. Each theory has its own field of applicability. Lewis concept of acids and bases is more comprehensive and can explain certain phenomena but this is not the only criterion for usefulness.

The modified solvent theory of Smith has been applied in the present work to understand the acid-base reactions in formamide. It has been proposed in the present work that formamide ionises to give proton and \((\text{HCONH})^-\) ion. Substances which increase the concentration of proton would act as acids and those which increase the concentration of
(HCONH)\textsuperscript{-} ions would act as bases in this solvent. Lewis acids such as aluminium chloride, tin(IV)chloride and antimony(V)chloride act as the solvo acids in formamide. The addition compounds of the Lewis acids with formamide ionise to give proton as:

\[
\text{AlCl}_3 + \text{HCONH}_2 \rightarrow \text{AlCl}_3\cdot\text{HCONH}_2 \rightleftharpoons [\text{AlCl}_3(\text{HCONH})]^- + \text{H}^+ \\
\text{SnCl}_4 + 2\text{HCONH}_2 \rightarrow \text{SnCl}_4\cdot2\text{HCONH}_2 \rightleftharpoons [\text{SnCl}_4(\text{HCONH})_2]^{2-} + 2\text{H}^+ \\
\text{SbCl}_5 + \text{HCONH}_2 \rightarrow \text{SbCl}_5\cdot\text{HCONH}_2 \rightleftharpoons [\text{SbCl}_5(\text{HCONH})]^- + \text{H}^+
\]

The organic tertiary bases like pyridine, aniline etc., act as the solvo bases in this solvent as they indirectly increase the concentration of (HCONH)\textsuperscript{-} ions as:

\[
\text{B} + \text{HCONH}_2 \rightarrow \text{B.HCONH}_2 \rightleftharpoons \text{BH}^+ + (\text{HCONH})^-
\]

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