6.1 Introduction:

Robert Boyle in the year 1663 gives explanation about acid. He said acid is substance whose aqueous solutions 1) Turned blue litmus red 2) Tasted sour 3) reacted with active metals liberating hydrogen 4) Neutralizes bases. Bases were defined by scientist Rouelle as it is substances whose aqueous solutions 1) Turned red litmus blue 2) Tasted bitter 3) Give soapy touch 4) Neutralizes acids. Also later Lavoisier in 1787 give “oxygen concept” of acids and proposed that acid is substance could be attributed to the presence of oxygen. Davy in 1811 showed that it was not necessary for an acid to contain oxygen (e.g. HCl, HF etc.) and many compounds like MgO, N₂O did not show acidic properties. Arrhenius theory, Lowry-Bronsted theory, Lewis acid–base theory, Lux-Flood theory are collectively very useful to identify Properties Of acids and bases.

6.2 Arrhenius Theory:

These definitions were formulated in late nineteenth century by Swedish chemist Svante Arrhenius as “An acid is a substance which gives H⁺ ions when dissolved in water”. e.g. HNO₃, HCl, etc.

e.g. HCl + water ⇌ H⁺(aq) + Cl⁻(aq)

HCl is acid because it gives H⁺ ions in its aqueous Solution aq. Indicate that the ions are hydrated i.e. associated with one or more molecules of water.

“A base is a substance which gives OH⁻ ions when dissolved in water e.g. KOH, NaOH, etc.

e.g. KOH + water ⇌ K⁺(aq) + OH⁻(aq)

KOH is base because it gives OH⁻ ions in its aqueous solution.

6.2.1 Advantages of Arrhenius Concept:

1. Gives idea about acid base properties in water solution.
2. It explains various concepts such as strength of acid and bases, neutralization etc.
6.2.2 Limitations of Arrhenius Theory:

1. It can be applied only to aqueous solutions i.e. it fails to explain behavior of acids and bases in solvent other than water i.e. non aqueous solvent e.g. liquid ammonia, liquid sulphur dioxide, liquid HF (hydrofluoride acid).
2. H\(^+\) ions do not exist in water solution. Proton reacts with water to form hydronium ions.
   \[ \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ \text{ (Hydronium ion)} \]
3. It does not explain the acidic character of inorganic salts such as AlCl\(_3\), in aqueous solution. Because it does not contain hydrogen.
4. This theory was also not applicable for to reaction in the gas phase where no solvent is present for example HCl remained unexplained as acid in gaseous phase.
5. According to theory base is considered as it should contain hydroxyl group unless base which do not have hydroxyl group not explained using this theory for example many substances ammonia and pyridine were known to exhibit basic properties although they do not contain hydroxyl group.

6.3 Lowry-Brosted Theory:

Arrhenius theory of acid and base apply only aqueous solution but the Bronsted – Lowry theory applies to aqueous as well as non-aqueous solutions. Definitions of acid and base given as- “Acid is a substance which has tendency to donate proton and base is a substance which has tendency to accept proton.”

\[
\text{Acid} \rightleftharpoons \text{H}^+ \text{ (proton)} + \text{Base}
\]

When an acid gives a proton, the residual part of it has a tendency to accept the proton

\[
\text{HCl} \text{ (aq)} \rightleftharpoons \text{H}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}
\]

Hydrochloric acid is a Bronsted acid because it donates proton in water. The proton exists in hydrated form as shown below-

\[
\text{HCl} \text{ (aq)} + \text{H}_2\text{O} \text{ (aq)} \rightleftharpoons \text{H}_3\text{O}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}
\]

Hydrated form of H\(^+\) is represented as H\(_3\)O\(^+\) is called hydronium ion.

It is evident that Hydrochloric acid donated a proton to water and thus it acts as acid while water accepts a proton and therefore, acts as a base. In the reverse reaction, hydronium ion (H\(_3\)O\(^+\)) donates proton to chloride ion acts as acid and chloride ion which accepts proton acts as
base. Consider ammonia (NH₃) in water classified as Bronsted base because it can accept an H⁺ ion.

\[
\text{NH}_3^{\text{(aq)}} + \text{H}_2\text{O}^{\text{(l)}} \rightleftharpoons \text{NH}_4^{\text{+}(aq)} + \text{OH}^{-}\text{(aq)}
\]

By considering above acid and base examples water possesses both basic and acidic properties. Thus water acts an acid (a proton donar) towards ammonia and base (a proton acceptor) towards hydrochloric acid such substances are said to be amphiprotic.

### 6.3.1 Conjugate acid base pairs:

In general ionization of acid in water may thus be represented as-

\[
\text{Acid}^{\text{(l)}} + \text{Base}^{\text{(2)}} \leftrightarrow \text{Acid}^{\text{(2)}} + \text{Base}^{\text{(1)}}
\]

Acid (1) and base (1) and so acid (2) and base (2) Is conjugate acid-base pairs. Consider ionization of acetic acid in water as-

\[
\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^{\text{+}(aq)} + \text{CH}_3\text{COO}^{-}\text{(aq)}
\]

Therefore CH₃COOH and CH₃COO⁻ are conjugate acid-base similarly also H₃O⁺ and H₂O are conjugate acid-base. Relative strength of acid-base pairs according to Lowry-Bronsted theory, the strength of acid depends upon its tendency to lose the proton and strength of base depends upon it tendency to gain proton. The hydrochloric acid considered as strong acid because it has strong tendency to donate proton.

\[
\text{HCl}^{\text{(aq)}} + \text{H}_2\text{O}^{\text{(aq)}} \rightleftharpoons \text{H}_3\text{O}^{\text{+}(aq)} + \text{Cl}^{-}\text{(aq)}
\]

An acetic acid on other hand has less tendency to take up proton, hence considered as weak acid.

\[
\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^{\text{+}(aq)} + \text{CH}_3\text{COO}^{-}\text{(aq)}
\]

It emphasis that stronger an acid the weaker must be it conjugate base and vice versa. If an acid HCl is strong its conjugate base Cl⁻ is weak. If base CH₃COO⁻ is strong its conjugate acid CH₃COOH is weak.
6.3.2 Advantages of Lowry-Bronsted theory:
1. Aqueous solutions not require identifying acid or base e.g. HCl is an acid because it can donate proton and NH₃ is base because it can accept proton.
2. The concept explains hydrolysis of salt in aqueous solution.

\[
\text{NaCl + H}_2\text{O} \rightleftharpoons \text{NaOH + HCl}
\]

6.3.3 Limitation of the Bronsted–Lowry theory:
1. Substances like AlCl₃, BF₃ etc. behave as acids but they do not have protons to loose or donate.
2. The extent to which a dissolved substance can act as acid or base depends upon largely on solvent. e.g.

\[
\text{HClO}_4 + \text{HF} \rightleftharpoons \text{H}_2\text{F} + \text{ClO}_4^- \quad \text{(HF acts as base)}
\]

Here HF act as base in HClO₄ while acts as acid when it in water.
3. The reaction between acidic oxides and basic oxides cannot be explained.

\[
\text{SO}_2 + \text{SO}_2 \rightleftharpoons \text{SO}_3^{2-} + \text{SO}^{2+} \\
\text{CO}_2 + \text{CaO} \rightleftharpoons \text{CO}_3^{2-} + \text{Ca}^{2+}
\]

6.4 Lewis theory:
One of the most useful definition was proposed by G.N. Lewis. According to Lewis theory “Acid is a substance which accept electron pair and base is a substance which donate electron pair”.

\[
\text{H}^+ + :\text{NH}_3 \rightarrow [\text{H} :\text{NH}_3]^+ \\
\text{Lewis acids} \quad \text{Lewis base}
\]

Here proton is Lewis acid and ammonia is a Lewis base which donates lone pair of electron to the proton. Similarly hydrogen chloride is a Lewis acid since it accepts a lone pair from the base such as water by ionization.

\[
\text{H}_2\text{O} + \text{HCl} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \\
\text{Lewis base} \quad \text{Lewis acid}
\]

The Lewis theory covers a great many systems where protons are not involves at all, consider reaction between NH₃ and BF₃ is an acid base reaction.

\[
:\text{NH}_3 + \text{BF}_3 \rightarrow \text{H}_3\text{N}:\text{BF}_3 \\
\text{Lewis Acid} \quad \text{Lewis Base}
\]
Therefore according to Lewis theory, all of the ligands can be regarded as bases and all metal ions can be regarded as acids. The degree of affinity of a metal ion for ligands can be termed its Lewis acidity and tendency of a ligand to become bound to a metal ion can be considered as a measure of its Lewis basicity.

Lewis acids include all substances which have vacant orbitals to take electron. Following types of substances is included

1) Allcations considered as Lewis acids because they can accepts electron. Big sizedcation such as Na\(^+\), K\(^+\),Ca\(^{2+}\) etc. behave as weak acids smaller cations such as H\(^+\), Ag\(^+\), Fe\(^{2+}\) etc. behave as strong Lewis acid.

\[ \text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ \]

2) Incomplete octet i.e. electron deficient compounds in which the central atoms can expand their valence shells are regarded as Lewis acids.

\[ \text{NH}_3 + \text{BF}_3 \rightarrow \text{H}_3\text{N}:\text{BF}_3 \]

3) Vacant d orbital molecules in which central atom considered as lewis acids.

\[ \text{SbF}_5 + \text{F}^- \rightarrow [\text{SbF}_6]^2- \]

4) Molecules in which the central atom attached to different electron negativity atom or attached to one or more multiple bonds behaves as Lewis acids.

\[ \text{O} \quad \text{C} \quad \text{O} + \text{OH}^- \rightarrow \text{O} \quad \text{C} = \text{O}^- \]

Strength of lewis acid and bases considering donar and acceptor species, acidity and basicity can be influenced greatly by the nature of the substituents electronic and steric effect influences mostly

1) The more electron withdrawing group can increase acidity of compounds and more electron donating group enhance basicity of compound. Consider following examples-

Basic strength \((\text{CH}_3)\text{N} > \text{NH}_3 > \text{NF}_3\)

Acid strength \((\text{CH}_3)\text{B} < \text{H}_3\text{B} < \text{F}_3\text{B}\)
2) Steric effect: Following compounds basic strength increase lightly from structure I to III to II

Structure II is more crowded therefore it is weak base than other two compounds.

6.4.1 Advantages of Lewis theory:
1) Using Lewis theory can explain wide variety of reactions including reactions with no proton transfer.
2) Lewis theory is the way it complements the model of oxidation reduction reaction oxidation reduction reactions involve a transfer of electron from one atom to another with net change in the oxidation number of atoms.
3) This theory is independent on the solvent.

6.4.2 Limitations of Lewis concept:
1) Lewis theory is not helpful to find out relative strength of acids and bases.
2) Metal which is having zero oxidation state is termed as lewis acids in their complex, with pi acceptor ligands such as CO, cyclopentadiene and olefins.
3) Considering Lewis concept almost all reaction becomes acid base reaction.

6.5 Lux-flood Theory:
This concept given by Lux and extended by scientist flood. According to this theory “acid is substance which accepts the oxide ion and base is substance which donate the oxide ion.” i.e. acid is oxide ion acceptor and base is an oxide ion donar.

\[
\text{CaO + SiO}_2 \rightarrow \text{CaSiO}_2 \quad (1)
\]

Here CaO serves as base and SiO\(_2\) as acid.

\[
\text{CaO + CO}_2 \rightarrow \text{Ca [CO}_3^\text{]} \quad (2)
\]

Cao serves as acid while CO\(_2\) serves as a base.
System is very useful in dealing with anhydrous reaction fused melts of oxides, and other high temp reactions such as are found in metallurgy and ceramics. In above (1) and (2) reaction CaO acts as acid as well as base i.e. it is amphoteric in nature. Lux-Flood theory has inverse relationship to aqueous chemistry, since acids are oxides which react with water giving bases in water and bases react with water giving acids.

\[
\begin{align*}
\text{Na}_2\text{O} + \text{H}_2\text{O} & \rightarrow 2\text{NaOH} \\
\text{P}_4\text{O}_{10} + 6 \text{H}_2\text{O} & \rightarrow 4\text{H}_3\text{PO}_4
\end{align*}
\]

**6.6 Strength of acids and bases:**

Strength of acid is one which has a strong tendency to donate a proton. Comparison of acid strength is generally done by comparing proton donating ability of both acids to the same base. Generally water is used as the base. e.g. Acid HA donating a proton to the base following equilibrium is established in the aqueous solution –

\[
\begin{align*}
\text{HA} & + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-
\end{align*}
\]

Equilibrium constant \( K \) for this reaction is given as follows-

\[
K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}
\]

It measures the tendency of the acid HA to protonate H\(_2\)O. Since water is in large quantity, therefore its concentration is considered as constant.

\[
K\left[\text{H}_2\text{O}\right] = K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}
\]

\( K_a \) represent as dissociation constant or ionization constant or acidity constant for acid. Large \( K_a \) value indicates that the acid is strong and vice-versa. \( K_a \) for acetic acid at 25\(^\circ\)C is 1.8 \times 10^{-5} \text{ where as for hydrogen cyanide it is } 7.2 \times 10^{-10}. \text{ Here acetic acid is stronger acid than HCN. To avoid writing negative powers of } 10 \text{ the most convenient way to represent the acid strength is by using } P\text{Ka} = (- \log K_a), \text{ the larger the value of the } P\text{Ka} \text{ the weaker is the acid under dissociation.}

Similarly strength of base can be given by the following equilibrium,
\[ K = \frac{[BH^+][OH^-]}{[B][H_2O]} \]

\[ [H_2O] = \text{Constant, due to excess quantity therefore following equation obtained} \]

\[ K \times [H_2O] = Kb = \frac{[BH^+][OH^-]}{[B]} \]

The smaller value of \( Kb \), Stronger is the base. The strength of base conveniently expressed in terms of \( PKb \). (\( PKb = -\log Kb \)). Smaller the value of \( PKb \) Stronger is base.

### 6.7 Properties of solvent:

Large chemical reactions are carried out in a solvent. The properties of the solvent are crucial to the success or failure of any reaction. Water is very useful and most important solvents have been tried and found useful.

**Properties of solvent useful to determine its utility are as follows:**

1) The temperature range over which it is liquid (M.P-B.P range)
2) Dipole moment
3) Dielectric constant
4) Lewis acid base character

#### 1) The temperature range over which it is liquid (M.P-B.P range):

Most useful solvent is those solvent which are liquid at room temperature and 1- atm pressure which can be easily handled. Water is a good solvent in this regard. It is also desirable that measurement or reaction be feasible at temperatures well above and below room temperature. As table shows DMF, acetonitrile are especially good in this respect.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Formula</th>
<th>Liquid range °C</th>
<th>Dipole moment</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>0 to 100</td>
<td>1.84</td>
<td>82</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>CH₃CH</td>
<td>-45 TO 82</td>
<td>3.92</td>
<td>38</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>HC(O)N(CH₃)₂</td>
<td>-61 TO 153</td>
<td>----</td>
<td>38</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>(CH₃)₂SO</td>
<td>18 TO 189</td>
<td>3.96</td>
<td>47</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>CH₂Cl₂</td>
<td>-97 TO 40</td>
<td>1.60</td>
<td>9</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>-78 to -33</td>
<td>1.46</td>
<td>23</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H₂SO₄</td>
<td>10 TO 338</td>
<td>1.83</td>
<td>100</td>
</tr>
<tr>
<td>Hydrogen fluoride</td>
<td>HF</td>
<td>-83 TO 20</td>
<td>1.90</td>
<td>84</td>
</tr>
<tr>
<td>Hydrogen Cyanide</td>
<td>HCN</td>
<td>-14 to 26</td>
<td>----</td>
<td>107</td>
</tr>
</tbody>
</table>
2) **Dielectric constant:**

Dielectric constant $\varepsilon$ of a liquid is responsible for dissolve ionic solids. The force ($F$) of attraction between cation and anions gives dielectric constant in a medium. Force of attraction ($F$) is inversely proportional to dielectric constant $\varepsilon$, force of attraction between two charged bodies is given by expression.

$$F = \frac{(q^+ X q^-)}{(4 \pi \varepsilon r^2)}$$

Where $q^+$ and $q^-$ = charge on species,
$r$ = distance between centers of the charged species,
$\varepsilon$ = constant known as dielectric constant

higher dipole moment and dielectric constant is better solvent for dissolving ionic or polar compounds. e.g. water. It is clear that more polar a molecules the of a solvent the higher its dielectric constant at the same time the more polar a molecule the better able to use its negative & positive regions to solvate cations& anions respectively .

3) **Dipole moment:**

It`s measure polarity of bond & denoted as $(\mu)$ it is a product of the charge $(q)$ and the distance $r$ between charges,

$$\mu=q \times r$$

Where, $q$ is the charge, $r$ is the distance between two charges.

The solvent which have higher dipole moment is responsible for dissolution of polar solute non polar solute not dissolved in polar solvent.

4) **Lewis acid-base properties:**

For ionic solute there are both anions & cations are solvated, normally cations are smaller so solvation of cationis easily happen. The solvation process is essential for formation of complex where ligands are solvent molecules. The order of coordinating ability toward typical cations for some common solvent is -

DMSO $> \text{H}_2\text{O} > \text{acetone} \approx \text{CH}_3\text{CN} > \text{CH}_3\text{NO}_2 > \text{CH}_2\text{Cl}_2$

The positive ends of the solvent molecule dipoles will orient themselves towards anions. Cations like $\text{Cu}^{+2}$, $\text{Ca}^{+2}$, $\text{Fe}^{+3}$, etc. are solvated to a greater extent than anions like $\text{Cl}^-$, $\text{Br}^-$, $\text{I}^-$ due to smaller size of it. Here metal ion acts as an acceptor of electrons i.e. Lewis acid & the solvent molecule acts as donar of electrons lewis base coordinate bond formed between a metal ion and solvent ions. Energy liberated during process is salvation when water is used as solvent then energy
involved is termed as hydration energy. The solvation of cation can take place due to the interaction between an ion and the negative end of the solvent molecules as shown below-

\[ \ce{H_2O} \rightarrow \ce{B^{n+}} :\ce{OH_2} \]

**Fig. 6.1 Solvation of Cation**

Similarly solvation of ion can take place due to the interaction of anion and the +ve end of the solvent molecules as shown below.

**Fig. 6.2 Solvation of anion**

5) **Protonic acidity or basicity:**

**Types of solvent:**

The solvent may be classified as - I) Protonic solvent II) Non-protonic solvent
I) Protonic or protic solvents:
Solvent which lose protons or gain proton or can show both the tendencies these solvent divided into three parts- 

a) A acidic of protogenic solvents: These solvent can lose protons easily e.g. HCN, HF, H₂SO₄, CH₃COOH etc.

b) Basic or protophilic solvent :These solvent can accepts proton e.g. NH₃, NH₂OH, N₂H₄, amines etc.

c) Amphi-protic or amphoteric solvents: These solvent shows both character i.e. it can lose as well as accept protons depending upon nature of the reacting substance e.g. H₂O, alcohols, liquid NH₃, etc are amphoteric solvents undergoes self-ionization in which proton transfer between two similar neutral molecule can takes place and cation anion pair of the solvent is obtained .

\[
\begin{align*}
H₂O + H₂O & \rightarrow H₃O^+ + OH^- \\
\text{Acid} & \quad \text{Base} & \quad \text{Acid} & \quad \text{Base}
\end{align*}
\]

II)-protonic solvents: These solvent neither gain or lose protons e.g. CCl₄, C₆H₆, BF₃ etc.

There are 3 classes of non protonic solvents-

1) Non polar or weak polar, non-dissociates liquids: They have usually ions dielectric constant and low dipole moments. They cannot go self-ionization. Non-ionic reactions occur in these solvents. It dissolves non-ionic compounds and cannot initiate ionic reactions.

2) Non-ionized but strongly solvating solvents : N,N-dimethyl formamide (DMF) , dimethyl sulfoxide (DMSO), sulfur dioxide (SO₂) are aprotic solvent which not show auto dissociation but they can solvate ions mostly they solvate cations best by using negatively charged oxygen atoms, pair and solvate anions and lewis bases effectively.
3) Highly polar, auto ionizing solvents: these solvents are high polarity and high dielectric constant. They can dissolve ionic compounds and initiate ionic reactions. Ionic reaction takes place in these solvents. They can undergo auto ionization e.g. Ammonia, sulfur dioxide etc.

\[
\text{IF}_5 + \text{IF}_5 \rightarrow \text{IF}_4^+ + \text{IF}_6^-
\]

\[
\text{NH}_3 + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NH}_2^-
\]

6.8 Trends in strength of hydracids and oxyacids:

Hydracids are acids containing hydrogen and another nonmetallic element other than oxygen e.g. Fluorine, chlorine etc. and are shown by general formula HX e.g. HCl, HF, etc.

Oxyacids are compounds containing Hydrogen, oxygen and another central element. The formulas of oxyacids are usually written with the H first followed by the central element and then oxygen general formula XOH or XOm(OH)H e.g. HNO\(_3\), HClO\(_3\) etc.

6.8.1 Trends in strength of hydracids (HX):

i) Trends in strength of hydracids (HX) depend on Electronegativity of X, bond length, bond energy. Consider following table with its pka value.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pka</th>
<th>Compound</th>
<th>Pka</th>
<th>compound</th>
<th>Pka</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_3)N</td>
<td>35</td>
<td>H(_2)O</td>
<td>16</td>
<td>HCl</td>
<td>-7</td>
</tr>
<tr>
<td>H(_3)P</td>
<td>27</td>
<td>H(_2)S</td>
<td>7</td>
<td>H(_2)Te</td>
<td>3</td>
</tr>
<tr>
<td>H(_2)Se</td>
<td>4</td>
<td>HBr</td>
<td>-9</td>
<td>HF</td>
<td>3</td>
</tr>
<tr>
<td>HI</td>
<td>-10</td>
<td>HF</td>
<td>3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Considering hydracids HX with increasing electronegativity of X there is strength of hydracid increasing across, in horizontal series in period as from left to right as-

\[
\text{Li} \ > \ \text{Be} \ < \ \text{B} \ < \ \text{C} \ < \ \text{N} \ < \ \text{O} \ < \ \text{F}
\]

Here HF is more acidic than NH\(_3\) because nitrogen is less electronegative but for group acidity decreases as decrease in electronegativity of X Thus acidity shows following order-

\[
\text{F} \ < \ \text{Cl} \ < \ \text{Br} \ < \ \text{I}
\]

This is depend on also Bond length and bond energy consider following table

<table>
<thead>
<tr>
<th></th>
<th>Bond energy in K/mol(^{-})</th>
<th>Bond length m A(^{0})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>13527</td>
<td>1.01 A(^{0})</td>
</tr>
<tr>
<td>HI</td>
<td>6890</td>
<td>1.70 A(^{0})</td>
</tr>
</tbody>
</table>
In aqueous solution acidity is primarily associated with ease with which an acid release H\(^+\) ions into the solution. It is favored by a weakening of hydrogen and non-metallic i.e. H-X bond due to small bond energy and large bond length. Therefore due to larger bond length and less bond energy the HI is more acidic than HF. Acid strength of increasing order of oxo acid of chlorine also depends upon oxidation of central atom which shown below:

<table>
<thead>
<tr>
<th>Oxidation number of Cl</th>
<th>HCl</th>
<th>&lt; HClO(_2)</th>
<th>&lt; HClO(_3)</th>
<th>&lt; HClO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pka value</td>
<td>7.52</td>
<td>1.94</td>
<td>-3</td>
<td>-10</td>
</tr>
</tbody>
</table>

### 6.8.2 Trends in strength of oxy acids:

-Oxyacid represented as formula XO\(_n\) (OH), n= number of non-hydrogenated oxygen atom, m= number of –OH (hydroxyl group), Oxyacid may be pictured as

\[
\begin{array}{c}
E \\
\mid \ \\
O \\
\mid \\
H
\end{array}
\]

E-represent central atom

Strength of oxyacid calculated by electronegativity and size of the central atom. Highly electronegative E shifting both electron pairs towards the central atom. Therefore bond between oxygen and hydrogen weakened and proton easily goes away.

\[
\begin{array}{c}
O \\
\mid \ \\
X \\
\mid \\
OH
\end{array}
\]

High electronegativity atom pulls electron towards itselfs.

Consider H\(_2\)SO\(_4\) and H\(_2\)SeO\(_3\), sulfur is more electronegative than Se. Therefore H\(_2\)SO\(_4\) is more acidic than H\(_2\)SeO\(_3\).

**Rule (I)** – The strength of oxyacid’s is also depends upon the number of oxygen atom present in oxyacid’s other than (OH). As number of oxygen atom increases acidity of oxyacid’s increase other than (OH). By considering n from formula XO\(_n\) (OH) of oxacids.

<table>
<thead>
<tr>
<th>No.of ‘ n’</th>
<th>Acid strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Very strong</td>
</tr>
<tr>
<td>2</td>
<td>Strong</td>
</tr>
<tr>
<td>1</td>
<td>Medium</td>
</tr>
<tr>
<td>0</td>
<td>Weak</td>
</tr>
</tbody>
</table>
Consider HNO₃, the more negative charge of the anion can be spread out and thus more stable is anion. As shown below -

Fig.6.3 Conjugate base of HNO₃
In case where there are many oxygen atoms and only a single proton e.g. HClO₄ Here delocalization of the negative charge in the conjugate base is very effective and removal of proton is favorable. Consider e.g. Acidity increases in following order and series-

\[ \text{HCl} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4 \]

Thus in NaOH molecule the central atom is electropositive and so it will acts as base. In case of hydrated cation acids the strength of an acid depends on the size of the central ion and magnitude of its charge. e.g. (Fe (H₂O)₆)⁴⁺ is fairly acidic since Fe⁴⁺ is small and carries a high charge.

Rule2) The ratio of successive dissociation constant \((K_n/K_{n-1})\) is \(10^{-4}\) to \(10^{-5}\). Conclusion is drawn as more the number of non hydrogenated oxygen atoms greater is the dissociation and stronger is the acid.

6.9 Hard and Soft acids and bases:

**Hard acids** i.e. cation are those which fulfill the following conditions-
1) Cation of smaller size or lighter element.
2) Cation of higher charge.
3) Not easily polarizable.
4) Molecules or ions which lesser number of valence electron.e.g. alkali metal ions and alkaline earth metal ions Al, Si ions lighter transition metal ions i.e. Fe⁴⁺, Co²⁺ etc.

**Soft acids** e.g. Cations are those which fulfill the following condition
1) Cation large size or heavier element.
2) Cation of less charge.
3) Easily polarizable.
4) Molecules or ions which are having large number of valence electron
e.g. Hg²⁺, Pd²⁺, Cu⁺, Ag⁺⁺, Hg⁺ etc.
**Hard Bases and soft bases:**

Hard bases fulfill the following condition
1) Donor atoms of higher electronegativity.
2) Donor atoms with low polarizability.
   e.g. NH₃, F⁻, ROH etc.

Similarly soft bases fulfill the following conditions-
1) Donor atom of lower electronegativity
2) Donor atoms of higher polarizibility
   e.g. R₃P, R₂S, etc.

Therefore hard acid and hard base is smaller sized, slightly polarizable substance while soft base and soft acid is larger and more polarizable substance. I⁻ ion a soft base which is having a very high polarizability. Cu⁺² ions behave as a harder acid than Mn⁺² ions because of smaller size of the Cu⁺² ions. NH₃ is harder base than C₆H₆NH₂ which is harder when compared with (C₆H₅)₂NH.

**HSAB Principle:**

For formation of coordination complexes hard acids prefers to combine with hard bases while soft acid prefer to combine with soft bases. This is known as HSAB principle.

**6.10 Reactions in non aqueous solvents:**

Inorganic reactions are generally carried out in aqueous system since water is known as best solvent. Many non aqueous solvents have been investigated. The usefulness of a solvent is determined by its parameter i.e. m.p., b. p., viscosity, dipole moment and dielectric constant. Here we discuss few representative non aqueous solvents like ammonia and hydrogen fluoride. Liquid NH₃ and liquid HF is resembles with H₂O as solvent.

**6.10.1 Liquid ammonia:**

Some characteristic of liquid ammonia exhibits similarity with water. Ammonia molecules show a high degree of polarity resulting from its pyramidal structure.
Fig 6.4 pyramidal structure of ammonia

Liquid ammonia also undergoes auto ionization like water. Dielectric constant of water is higher than ammonia. Therefore liquid ammonia acts as poorer solvent for ionic substances but it is better solvent than water for molecules containing many electrons like iodine compounds and for non-polar substances like hydrocarbons. The solubility of halides decreases from iodides to fluorides.

6.10.2 Alkali metals in liquid ammonia:

The alkali metals except beryllium dissolve in liquid ammonia gives homogeneous solutions. Dilute metal ammonia gives homogeneous solution. Dilute metal ammonia solution are blue but when concentration of metal increases a bronze phase separate and float on the blue solution. The alkali metal may be recovered by evaporating the solvent.

\[
M + NH_3 \rightarrow MNH_2 + \frac{1}{2} H_2
\]

Where \( M \) = Alkali metal

All the metal ammonia solutions have high electrical conductivity which changes with concentration of solution. At large dilution the conductivity of these solutions is higher than that of fully ionized salt in water. While in the higher concentrated solutions the value approaches that for a pure metal. It shows that they contain solvated metal cation and solvated electrons.

\[
M \rightleftharpoons M^+ + e^- \quad \text{Or}
M + (x + y) NH_3 \rightarrow M(NH_3)_x + e^- (NH_3)_y
\]

Fig 6.5 Graph of equivalence conductance Vs metal concentration
The blue colour of solutions of metal in liquid ammonia are unique as they conduct an electric current and proves presence of free electrons. The dilute solutions are paramagnetic in nature. With increase in concentration of solution the solution become diamagnetic and shows minimum conductance. The decrease in paramagnetism with increasing metal concentration shows that the electrons which is solvated undergo a pairing process.

\[ 2e(NH_3) - x = e_2(NH_3)_{2-x} \]

The solvated electrons and solvated metal ions also get associated to form non conducting paramagnetic ion pair.

### 6.10.3 Reactions in liquid ammonia:

Other interesting reactions in liquid ammonia are- 1) Acid – Base reactions 2) Precipitation or Metathesis reactions 3) Complex formation reactions 4) Solvolysis

#### 1) Acid – Base reactions:

Liquid NH\(_3\) behaves like water in respect of autoionization as follows-

\[ 2H_2O \rightleftharpoons H_3O^+ + OH^- \]

Acid Base

\[ 2NH_3 \rightleftharpoons NH_4^+ + NH_2^- \]

Acid Base

In water H\(_3\)O\(^+\) is the strongest possible acid and OH\(^-\) is strongest possible base. In liquid ammonia, NH\(_4\)\(^+\) is the strongest possible acid and NH\(_2\)\(^-\) is the strongest possible base. Typical neutralization reactions are feasible in which NH\(_4\)\(^+\) salts acts as acids and both soluble and insoluble amides, imides and nitrides as bases in liquid NH\(_3\).

\[
\begin{align*}
\text{NH}_4\text{Cl} & + \text{KNH}_2 \rightleftharpoons \text{KCl} \text{ salt} + 2\text{NH}_3 \text{ solvent} \\
\text{NH}_4\text{NO}_3 & + \text{NaNH}_2 \rightleftharpoons \text{NaNO}_3 + 2\text{NH}_3 \\
2\text{NH}_4\text{I} & + \text{PbNH} \rightleftharpoons \text{PbI}_2 + 3\text{NH}_3 \\
3\text{NH}_4\text{I} & + \text{BiN} \rightleftharpoons \text{BiI}_3 + 4\text{NH}_3
\end{align*}
\]

#### 2) Precipitation or metathesis reactions:

Because difference in solubilities of various substances in liquid ammonia and water, a large number of reactions, which do not occur in water have been reported to be carried out in ammonia.
e.g. 1) Lithium chloride may be precipitated by reaction of ammonium chloride and lithium nitrate in ammonia –

\[ \text{NH}_4\text{Cl} + \text{LiNO}_3 \xrightleftharpoons{\text{NH}_3(\text{l})} \text{NH}_4\text{NO}_3 + \text{LiCl} \]

2) When solution of potassium iodide and ammonium chloride in liquid ammonia are brought together a white ppt of KCl obtained.

\[ \text{KI} + \text{NH}_4\text{Cl} \xrightarrow{\text{liq. NH}_3} \text{KCl} + \text{NH}_4\text{I} \]

3) The precipitation of barium sulphide occurs from ammonium solution of barium nitrate and ammonium sulphide.

\[ \text{Ba(NO}_3)_2 + (\text{NH}_4)_2\text{S} \xrightarrow{\text{liq. NH}_3} \text{BaS} + 2\text{NH}_4\text{NO}_3 \]

4) Precipitation of LiCl from ammonical solutions of LiNO\textsubscript{3} and ammonium chloride.

\[ \text{NH}_4\text{Cl} + \text{LiNO}_3 \rightarrow \text{LiCl} + \text{NH}_4\text{NO}_3 \]

3) **Complex formation reaction:**

Some reactions which have been studied are quite similar complex formation occurring in the water system e.g. the zinc ion is precipitated as insoluble zinc amide which dissolves in excess of amide to form the ammonozincate.

\[ \text{Zn(NO}_3)_2 + 2\text{KNH}_2 \xrightarrow{\text{liq. NH}_3} \text{Zn(NH}_3)_2 + 2\text{KNO}_3 \]

Metal amides, imides and nitrides with NH\textsubscript{2}\textsuperscript{-} shows analogous reactions in liquid ammonia to form corresponding amido complexes, as

\[ \text{AlNH} + \text{KNH}_2 + 2\text{NH}_3 \rightarrow \text{K[Al(NH}_2)}_4 \]

\[ \text{BeNH} + \text{KNH}_2 + \text{NH}_3 \rightarrow \text{K[Be(NH}_2)_3} \]

\[ \text{AgNH}_2 + \text{KNH}_2 \xrightarrow{\text{liq NH}_3} \text{K[Ag(NH}_2)_2} \]

4) **Solvolysis:**

In solvolysis, the solvent molecule is split into two parts and one or both parts get attached to a solute molecule or ion reaction between halides and water of the non-metals. Normally leads to replacement of the halogen by hydroxyl groups.
e.g. In water

\[
\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}_3\text{O}^+ + \text{Cl}^- \\
\text{POCl}_3 + 6\text{H}_2\text{O} \rightarrow \text{PO(OH)}_3 + 3\text{H}_3\text{O}^+ + \text{Cl}^- \\
\text{phosphoric acid}
\]

In ammonia

\[
\text{Cl}_2 + 2\text{NH}_3 \rightarrow \text{NH}_4\text{Cl} + \text{NH}_4^+ + \text{Cl}^- \\
\text{POCl}_3 + 6\text{NH}_3 \rightarrow \text{PO(\text{NH}_2)}_4 + 3 \text{NH}_4^+ + \text{Cl}^- \\
\text{phosphoramide}
\]

Some other examples are-

\[
\text{SiCl}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{HCl} \\
\text{SiCl}_4 + 4\text{NH}_3 \rightarrow \text{Si(\text{NH}_2)}_4 + 4\text{HCl}
\]

In manner analogous to that used in water, a PH scale can be set up for ammonia PH = 0 \[ 1 \text{ mol dm}^{-3}\text{NH}_4^+ \]; PH = \[ 13.5 \text{ (}[\text{NH}_4^+] = [\text{NH}_2^-]) \], neutrality therefore PH = 27(1 mol dm^{-3}\text{NH}_2^-).

Likewise oxidation – Reduction potentials may be obtained based on the hydrogen electrode-

\[
\text{NH}_4^+ + \text{e}^- = \text{NH}_3 + \frac{1}{2}\text{H}_2 \quad \varepsilon^o = 0
\]

Therefore the chemistry of ammonia solutions is remarkably parallel to that of aqueous solutions. The principal difference are in the increased basicity of ammonia and its decreased dielectric constant.

6.10.4 Liquid HF:

Anhydrous HF has low specific conductance its high dielectric constant make it an excellent ionising solvent i.e. it shows good solvent properties. Anhydrous HF is very reactive and many compounds decompose during dissolution. Hydrogen fluoride undergoes autoionization as –

\[
3\text{HF(l)} \rightleftharpoons \text{H}_2\text{F}^- + \text{HF}_2^-
\]

It is strongly acid solvent. Many organic compounds are soluble in liquid HF. It dissolves water, ethers, ketones, aliphatic acids and even nitric acid all of them acts as bases which are protonated and dissolved.

\[
\text{H}_2\text{O} + \text{HF} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^- \\
\text{HNO}_3 + \text{HF} \rightleftharpoons \text{H}_2\text{NO}_3^+ + \text{F}^- \\
\text{R}_2\text{O} + 2\text{HF} \rightleftharpoons \text{R}_2\text{OH}^+ + \text{HF}_2^- \\
\text{H}_2\text{SO}_4 + \text{HF} \rightleftharpoons \text{H}_3\text{SO}_4^+ + \text{F}^-
\]
Some non metal fluorides dissolve to give acid solutions. It accept fluorides ions and behaves as acids in HF forms super acid. e. g.

\[
\begin{align*}
\text{AsF}_5 + \text{HF} & \rightarrow \text{H}^+ + \text{AsF}_6^- \\
\text{SbF}_5 + \text{HF} & \rightarrow \text{H}^+ + \text{SBF}_6^-
\end{align*}
\]

Many salt are converted into fluorides by action of liquid HF and some of these are soluble in HF. The fluorides of alkali metals, silver, thallium, ammonia and some of alkaline earth metals get dissolve in hydrogen fluoride and yield their ions e. g.

\[
\begin{align*}
\text{KF} + \text{HF} & \rightarrow \text{K}^+ + \text{HF}_2^-
\end{align*}
\]

### 6.11 Levelling Effect:

The effect of solvent on the properties of acids and base i.e. the strength of strong acid is limited (leveled) by the basicity of the solvent. Similarly strength of a strong base is leveled by the acidity of the solvent.

**Ionization equilibrium of different strong acids in water represented as:**

\[
\begin{align*}
\text{HCl} + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \\
\text{HCO}_4^- + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{ClO}_4^- \\
\text{HBr} + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{Br}^- \\
\text{HNO}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^-
\end{align*}
\]

All the acids mentioned in the above series, therefore react almost completely with water to form hydronium ion H$_3$O$^+$. Therefore all strong acid in aqueous solutions appears almost equally strong. This phenomenon is called as the leveling effect. These acids completely leveled (or converted) to the characteristic cation H$_3$O$^+$ of the solvent and thus behave equally strong. Therefore water is acts as leveling solvent. Other way said that strength of all acids stronger than H$_3$O$^+$ becomes equal to that of H$_3$O$^+$. If any acid e.g. Acetic acid weaker than hydronium ion is, then two acids will coexist i.e. large number of undissociated molecules of acetic acid and H$_3$O$^+$. 
\[
\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^- \\
\text{Acid} \quad \text{Base} \quad \text{Acid} \quad \text{Base}
\]

In this case there is no leveling equilibrium shifted towards left hand side because CH3COO\(^-\) has greater tendency to combine H\(^+\). Similarly HF, HCN behaves as weak acids in water.

In bases it is represented as,

\[
\begin{align*}
\text{H}^- & + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}^- \\
\text{NH}_2^- & + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{OH}^- \\
\text{C}_2\text{H}_5\text{O}^- & + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{OH}^- 
\end{align*}
\]

Strong bases accept proton from water and their basicity is decreased to the level of hydroxide ion. When very strong bases like NaH, NaNH\(_2\), NaOC\(_2\)H\(_5\) when dissolved in water are leveled to the same strength of OH\(^-\) ions when added to water.

![Fig. 6.6 Leveling effect of water on strong bases](image_url)
Differentiating solvents: In differentiating solvent, various acids dissociates to different degrees and have different strength. In a levelling solvent, several acids are completely dissociated and show the same strength. The tendency of a solvent to accept or donate protons determines the strength of a solute base or acids dissolved in it. For example, hydrochloric acid and perchloric acid are strong acids in water. Acetic acid a weaker proton acceptor than water is taken as solvent, neither of these acids undergoes complete dissociation. In acetic acid perchloric acid dissociates 500 times greater than hydrochloric acid. Therefore perchloric acid is stronger than hydrochloric acid.

\[
\text{CH}_3\text{COOH} + \text{HClO}_4 \rightleftharpoons \text{CH}_3\text{COOH} + \text{ClO}_4^- \]

Here thus acetic acid acts as a differentiating solvent toward the two acids by showing the differences in dissociations. On the other hand, water is leveling solvent for perchloric, nitric, hydrochloric acids due to it completely dissociates in it and show no difference in strength. Similarly is true for base. Water is levelling solvent for bases like KOH, NH_4OH which are completely ionised in water. However solvent like ammonia is a differentiating solvent for them because their different dissociation in ammonia.
Exercise

1. Answer the following
2. Explain Bronsted – Lowry theory of acids and bases. Give its assumptions? What are its merits and demerits?
3. Explain the Lewis concept of acids and bases. What are its assumptions? What are its merits and demerits?
5. What are merits and demerits of Bronsted – Lowry concept compared to Arrhenius theory?
6. Give the general formula of oxyacid. Comment on the relation between the strength of oxyacids and the number of non –hydrogenated oxygen atoms.
8. Compare Arrhenius and Bronsted theory of acids and bases?
9. What are properties of solvents that determine the utility of it ? Explain any two properties of solvent.
10. Explain with suitable example concept of hard and soft acid base.
11. BF3 is stronger acid than BH3. Explain.
12. Give the comparison between Arrhenius theory and Bronsted – Lowery theory of acids and bases.
13. Identify Lewis bases from the following:
   H2O, AlCl3, Ag++, CN-
14. Explain the concept of acid- base according to Lewis theory . Give types of Lewis acids with suitable examples?
15. What is oxyacid? Discuss trends in strength of oxyacids?
17. Why HClO4 is stronger acid than HClO3 ?
18. Explain the concept of acid- base according to Lux- Flood concept.
19. What are properties of usefull solvent ? Discuss each property in brief.
20. Write two examples of protic solvents.