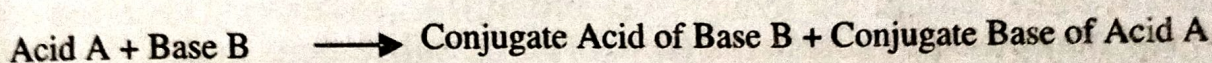
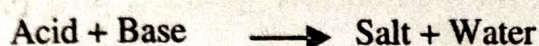


2.2. ACID-BASE TITRATION

In chemistry, acid-base titration is used for analysing the unknown concentration of an acid and base, quantitatively. The principle of acid-base titration is based on the **neutralisation reaction** occurring between acids and bases. Phenolphthalein is the most commonly used indicator for acid-base titrations.

Acid-base reactions involve transfer of protons, **for example**, base accepts protons from acids.



It is the most common neutralisation reaction.

At **equivalence point**, moles of H^+ are equal to the moles of OH^- .

During titration, one reactant (mostly an acid) is added progressively from the burette to the known volume of the other reactant (mostly base) in a conical flask. To mark the equivalence point (end point) of the titration, an indicator is used.

2.2.1. Theories

There are **three theories**, explaining the concept of acids and bases:

- 1) Arrhenius theory,
- 2) Bronsted-Lowry theory, and
- 3) Lewis theory.

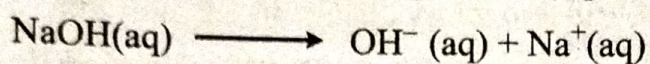
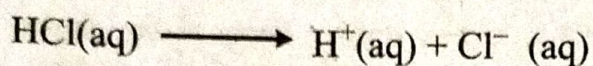
Figure 2.1: Overview of the Three Theories

Theory	Acid	Base
Arrhenius	H^+ producer	OH^- producer
Bronsted-Lowry	H^+ donor	H^+ acceptor
Lewis	Electron pair acceptor	Electron pair donor

2.2.1.1. Arrhenius Theory

The most commonly used concept of acids and bases was developed by **Savante Arrhenius** in **1884**, termed as **Arrhenius theory**. According to this theory, an **acid** is a substance which dissociates in aqueous solution and produces hydrogen

ion (H^+). On the other hand, a **base** is a substance which dissociates in aqueous solution to produce hydroxyl ion (OH^-). **For example**, HCl is an Arrhenius acid and $NaOH$ is an Arrhenius base.



Arrhenius theory was the first scientific theory that had given definitions for acids and bases, as well as classified them. It is the simplest theory and is useful in case of aqueous solutions.

Limitations

- 1) Chemical reactions can be studied well by using acid-base theory of Arrhenius but it has some limitations:
- 2) Acids and bases have been defined only in terms of solution and not as a solid substance.
- 3) This theory failed in elaborating the acidic and basic properties of a substance in non-aqueous solvents, e.g., NH_4NO_3 does not give H^+ ions but acts as an acid in liquid NH_3 .
- 4) This theory also failed to explain the neutralisation of acid and base in the absence of solvent.
- 5) There are many basic substances (few organic substances and NH_3) which do not have OH^- ions but are basic in nature. This fact could not be explained by Arrhenius theory.
- 6) Acidic properties of many salts ($AlCl_3$ in aqueous solution) could not be explained by this theory.

2.2.1.2. Bronsted-Lowry Theory

In 1923, **J.N. Bronsted** and **J.M. Lowry** independently introduced a broader concept of acids and bases. According to this theory, an **acid** is any molecule or ion that can donate a proton (H^+) and a **base** is any molecule or ion that can accept a proton, as shown in the **figure 2.1**.

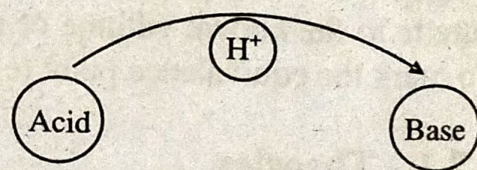
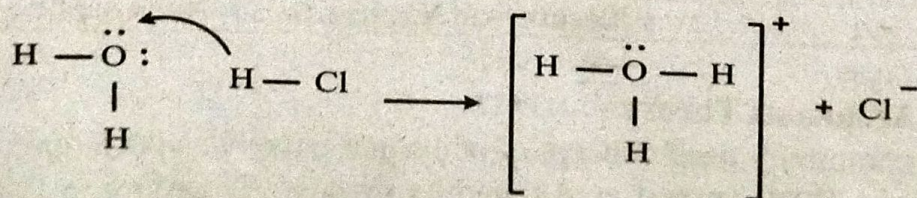


Figure 2.1: Bronsted-Lowry Theory

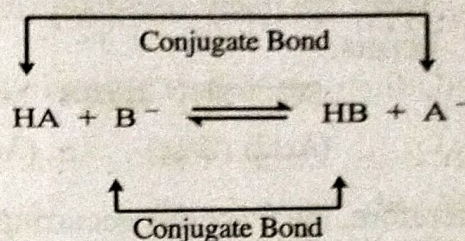
An acid is a proton donor while base is a proton acceptor. A **base** qualifying Bronsted-Lowry concept is termed as **Bronsted-Lowry base** or **Bronsted base**, whereas an **acid** qualifying Bronsted-Lowry concept is termed as **Bronsted-Lowry acid** or **Bronsted acid**. **For example**, on dissolving dry HCl gas in water, each molecule of HCl produces a hydronium ion (H_3O^+) by donating a proton to a water molecule.



Therefore, it can be concluded that water which accepts a proton is a **Bronsted base**, whereas HCl gas which donates a proton is a **Bronsted acid**.

Conjugate Acid-Base Pairs

The acid (HA) involved in an acid-base reaction produces a new base (A^-) by donating its proton (H^+). This new base is called the **conjugate base** which is related to the original acid. Similarly, after accepting a proton (H^+) the original base (B^-) produces a new acid (HB) known as the **conjugate acid**.

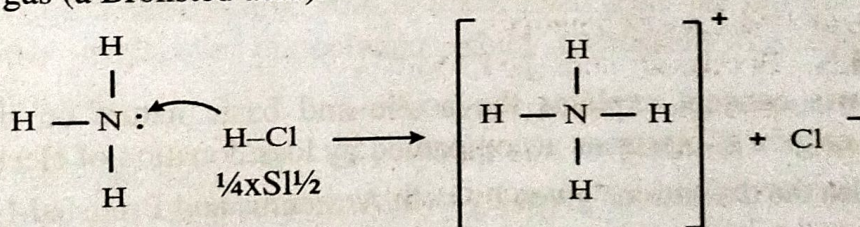


The acid (HA) and the conjugate base (A^-) together constitute a conjugate acid-base pair as they are related to each other by donating and accepting a single proton. The above acid-base reaction shows two pairs of conjugate acid-base, i.e., HA and A^- , and HB and B^- .

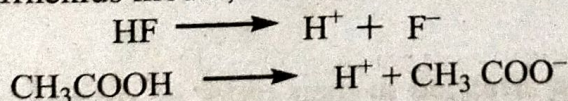
Advantages

The Bronsted-Lowry theory has many advantages over Arrhenius theory as given below:

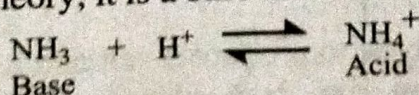
- 1) **Much Wider Scope:** Bronsted-Lowry concept of acids and bases covers wider range of molecules and ions accepting proton (bases) or donating proton (acids); whereas, Arrhenius concept of acids and bases involves only those substances which release H^+ or OH^- ions in aqueous solution.
- 2) **Not Limited to Aqueous Solutions:** Arrhenius concept is limited only to aqueous solutions but Bronsted-Lowry model not only covers aqueous solutions but also gas phase. **For example**, ammonium chloride is obtained by the reaction between gaseous ammonia (a Bronsted base) and hydrogen chloride gas (a Bronsted acid).



In this reaction, a proton donated by HCl is accepted by NH_3 . But according to Arrhenius model, this is not considered as an acid-base reaction.

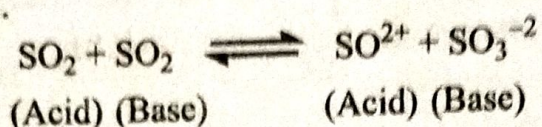


- 3) **Release of OH^- not Necessary to Qualify as a Base:** Bronsted base is a substance which accepts a proton, whereas Arrhenius base is a substance which releases OH^- ions in aqueous solution. **For example**, liquid ammonia (NH_3) is a base but does not release OH^- ions in water. But as per Bronsted-Lowry theory, it is a base as it forms NH_4^+ (an acid) by accepting a proton.



Limitations

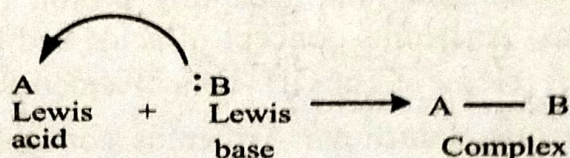
- 1) Bronsted-Lowry theory of acids and bases is based on transfer of protons. Commonly most of the acids are protonic in nature but some are not.
- 2) There are many acid-base chemical reactions in which proton transfer does not occur.



Therefore, the reactions occurring in non-protonic solvents (e.g., COCl_2 , SO_2 , N_2O_4 , etc.) cannot be explained by the protonic definitions.

2.2.1.3. Lewis Theory of Acids and Bases

A more general model of acids and bases was given by G.N. Lewis in the early 1930s. He defined **acid** as an electron-pair acceptor and **base** as an electron-pair donor. In this theory, the **Lewis acid** and **Lewis base** shares an electron pair given by base resulting in the formation of a covalent or coordinate bond between them. This resultant compound bonded with a covalent bond is known as a **complex**. If the Lewis acid is denoted by A and the Lewis base by B, the fundamental equation of the Lewis theory can be represented as:



According to this concept:

- 1) Lewis bases are anions or molecules having a lone pair of electron, and
- 2) Lewis acids are cations or molecules lacking an electron-pair.

Advantages

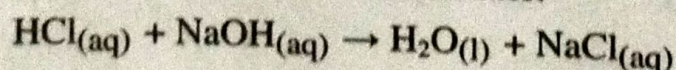
- 1) The Lewis concept explains the acidic and basic nature on the basis of transfer or gain of electrons accompanied by loss/donation of electron pair.
- 2) It includes the definitions given by both Arrhenius and Bronsted-Lowry.
- 3) It overcame the disadvantages of Bronsted-Lowry theory; CO_2 could now encompass within the definition of an acid.

Limitations

- 1) Lewis acids and bases cannot be arranged in their order of strength as their strength depends on the reaction type.
- 2) Lewis acids and bases reactions are expected to be very fast due to the involvement of electrons, but some of these reactions are slow.

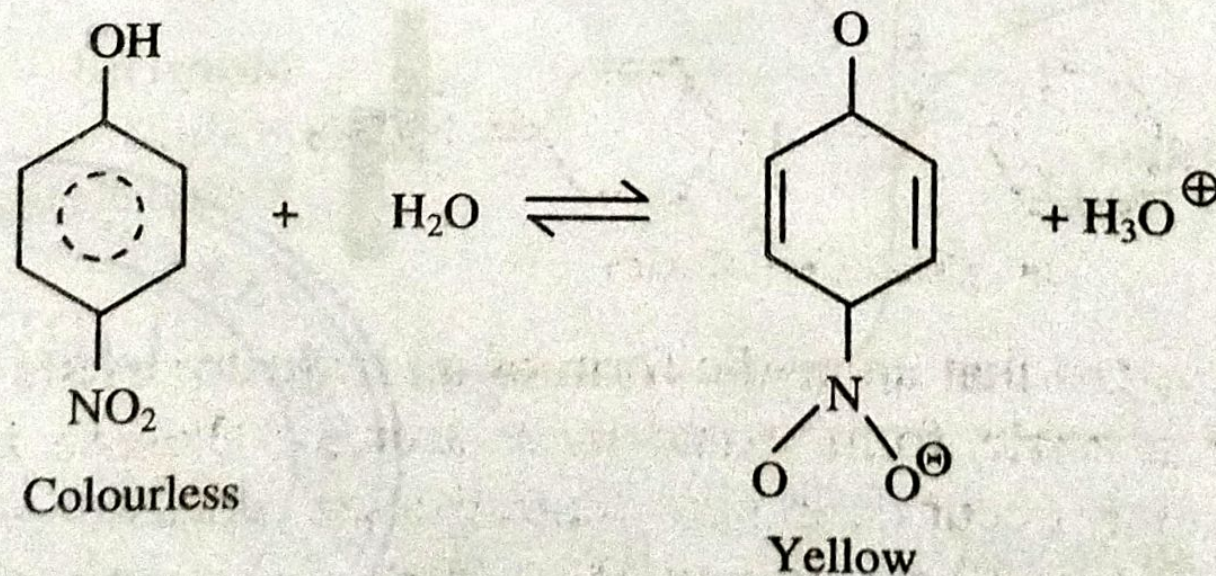
2.2.2. Neutralisation Curves

A reaction in which an acid reacts with a base to produce a salt and a neutralised base, is known as **neutralisation reaction**, e.g., hydrochloric acid reacts with sodium hydroxide to form sodium chloride and water:



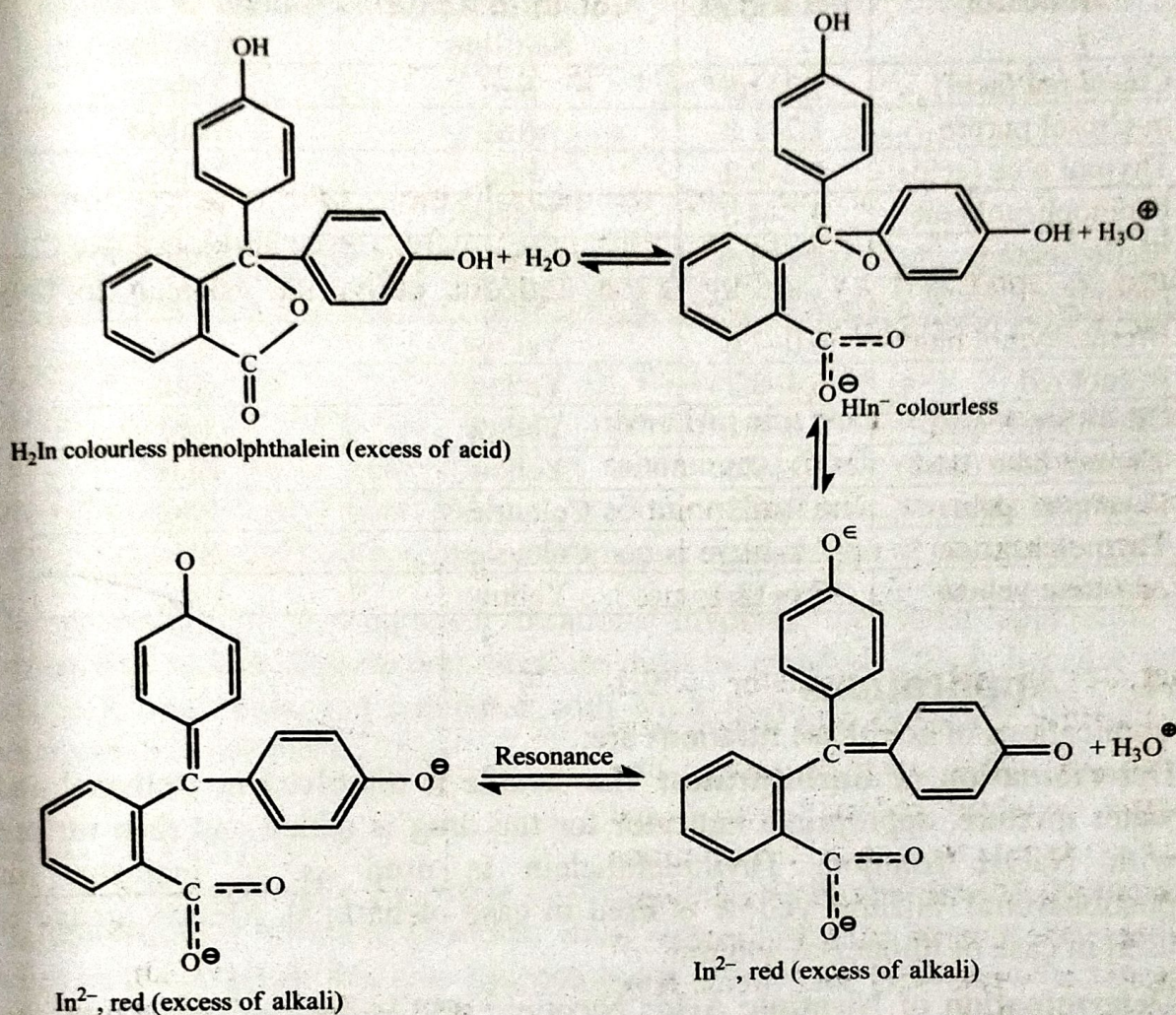
2.2.3. Acid-Base Indicators

Acid base indicators (weak organic acids or bases) having different colours depending upon the concentration of H^+ ions in the solution are available. These indicators exhibit a colour change from an acidic colour to an alkaline colour. Although, this colour change does not occur suddenly or rapidly, but takes place within a small pH range (usually about two pH units) which is the **indicator range**. The position of the colour change on the pH scale is different for different indicators.

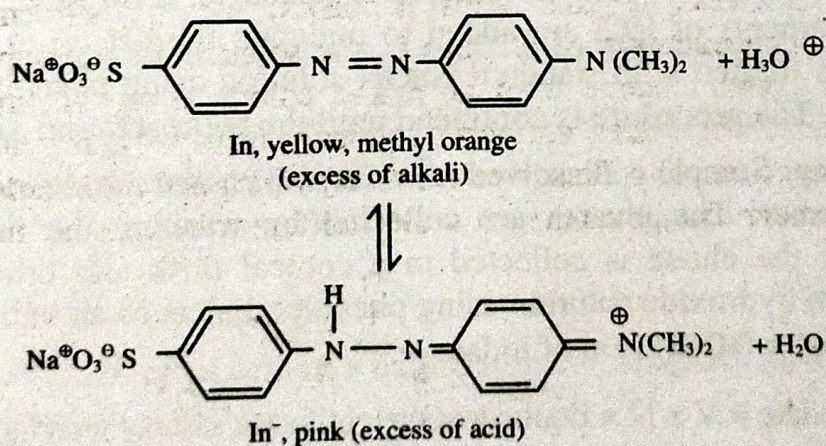


The acid-base indicators are also known as **visual indicators**, e.g., **p-nitrophenol** (simplest acid-base indicator) is a weak acid that undergoes dissociation as follows:

Phenolphthalein (most popular indicator) is colourless and a **diprotic acid**. When it loses the first proton it gives a colourless solution, but when loses another proton, it produces a red colour by forming an anion with the conjugated system.



Methyl orange (second most widely used indicator) is yellow coloured in its molecular form and is a base. On addition of a proton it gives a pink coloured cation.



Thus, it can be concluded that an acidic form of an indicator exists in a strongly acidic solution and a basic form exists in a strongly alkaline solution. The following **two cases** may occur during the neutralisation process:

- 1) When a strong acid and base in equivalent quantities react with each other, $pH = 7$.
- 2) Hydrolysis of the salt (sodium carbonate) results in $pH > 7$, while, the hydrolysis of salt (ammonium chloride) results in $pH < 7$.

Examples

The examples of acid-base indicators are mentioned in the table 2.2:

Table 2.2: Acid-Base Indicators

Indicator	pH Range	Colour in Acidic Solution	Colour in Alkaline Solution
Cresol red (acid)	1.2-1.8	Red	Yellow
m-Cresol purple	1.2-1.8	Red	Yellow
Thymol blue (acid)	1.2-2.8	Red	Yellow
Bromophenol blue	3.1-4.6	Yellow	Purple
Methyl orange	3.1-4.5	Red	Yellow
Methyl red	4.2-6.3	Red	Yellow
Bromothymol blue	6.0-7.6	Yellow	Blue
Phenol red	6.4-8.2	Yellow	Red
Cresol red (base)	7.0-8.1	Yellow	Red
Thymol blue (base)	8.1-9.6	Yellow	Blue
Phenolphthalein	8.0-9.8	Colourless	Pink
Thymolphthalein	9.3-10.5	Colourless	Blue
Alizarine yellow	10.1-12.1	Yellow	Lilac

2.2.4. Applications

The applications of acid-base titrations are:

- 1) **Determination of Barbiturates:** The sample is dissolved in methanol and water mixture, appropriate indicator for the drug is added and then titrated with NaOH solution. Thymolphthalein is used as an indicator for phenobarbital. Nizarin yellow is used in case of barbital. Methyl orange is used in case of thiopental sodium.
- 2) **Determination of Nicotinic Acid:** Nicotinic acid is analysed mainly by the titrimetric method based upon the acid-base titration principle. Nicotinic acid is titrated with standard alkali like NaOH using phenolphthalein as an indicator.
- 3) **Determination of Amino Acids:** Sample is added to 25ml distilled water and small increments of HCl are added to maintain the pH up to 1.5. The solution is then titrated with standard NaOH solution using phenolphthalein as an indicator. The procedure is continued until the pH reaches to 12.
- 4) **Periodate Assay:** Sample is dissolved in water and passed through the cation exchange chamber. The eluates are collected by washing the resin with water. 10ml of the eluate is collected in a conical flask and titrated with standard sodium hydroxide solution using phenolphthalein as an indicator.

$$1\text{ml of NaOH} \equiv 0.01011\text{gm of iodate}$$

$$\text{Percentage of iodate} = V \times N \times \text{Equivalent weight factor/sample weight in grams}$$

- 5) **Determination of Aspirin:** Sample is dissolved in ethanol and 2-3 drops of phenolphthalein is added as an indicator. The resulting solution is titrated with standard NaOH solution until pink colour is obtained.
- 6) **Assay of Benzoic Acid:** Sample is dissolved in ethanol and water. To this, 2-3 drops of phenolphthalein is added as an indicator. The solution obtained is titrated with standard NaOH. Then the percentage of benzoic acid is determined by the following equation: