

**CLASS: III BSC CHEMISTRY**  
**SUBJECT: ANALYTICAL CHEMISTRY - I**

# ANALYTICAL CHEMISTRY-I

## UNIT-II

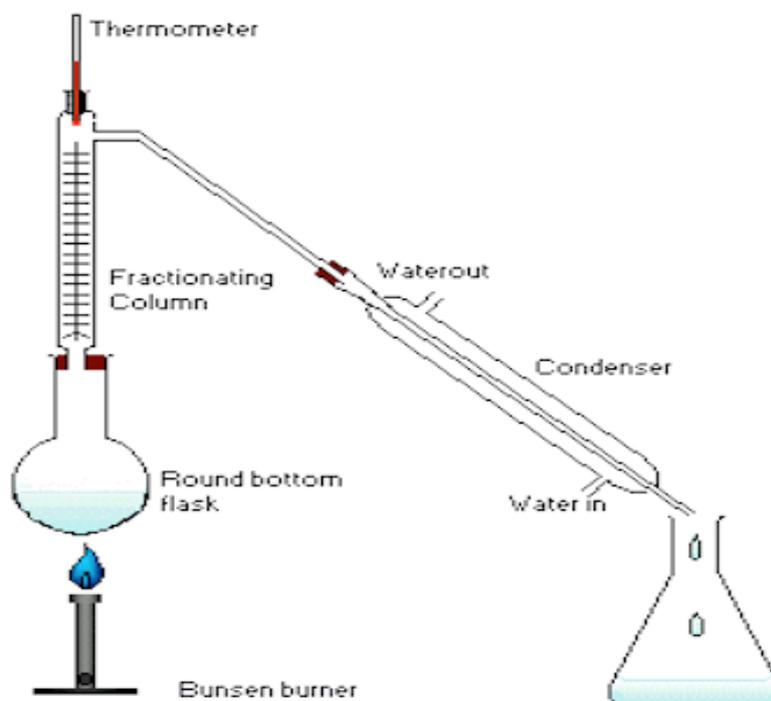
### 2.1 Purification of Liquid

Organic compounds in the **liquid** state are purified by distillation. Distillation involves the heating of a **liquid** to boiling and then collecting their vapours to condense them in **liquid** state

#### Fractional distillation

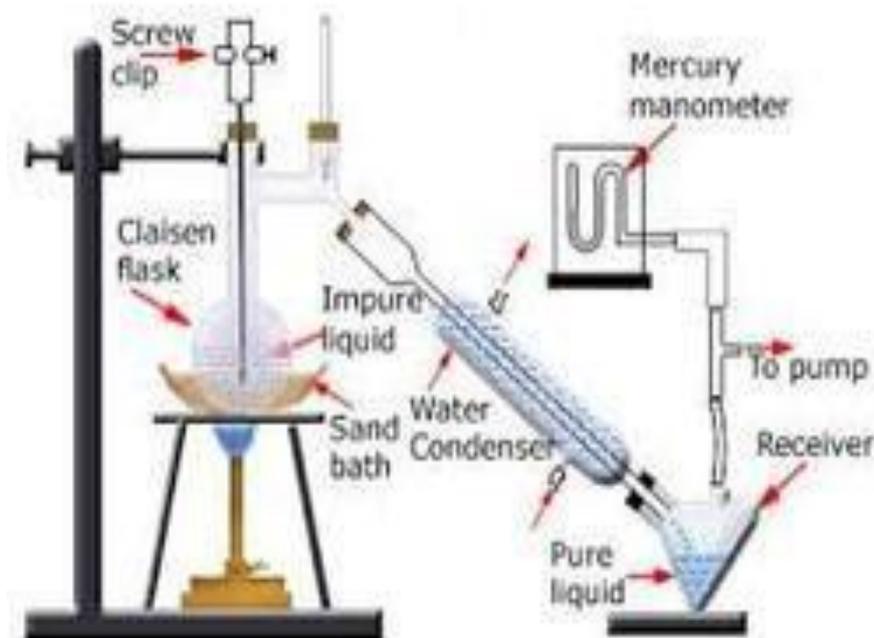
Fractional distillation is the process of taking a chemical mixture and using heat to separate out the various components in that mixture. When you think of this process, the first word that should come to mind is separation. In other words, as a chemist in the laboratory, you would use this process when you are interested in isolating one or more compounds present in a mixed sample containing as few as two and up to an endless number of compounds.

Because heat is used in this separation technique, boiling points play a very important role in fractional distillation. Essentially, you are able to determine what given component is separated out from the mixture by its boiling point. Remember that **boiling point** is a physical property. Specifically, it is the temperature where a phase change occurs from liquid to vapour. Before we go over the process of fractional distillation, let's look at some examples where this process is commonly used.



## Vacuum distillation

Vacuum distillation is **distillation** performed under reduced pressure, which allows the purification of compounds not readily **distilled** at ambient pressures or simply to save time or energy. This technique separates compounds based on differences in boiling points.



### The typical process steps involved are as follows:

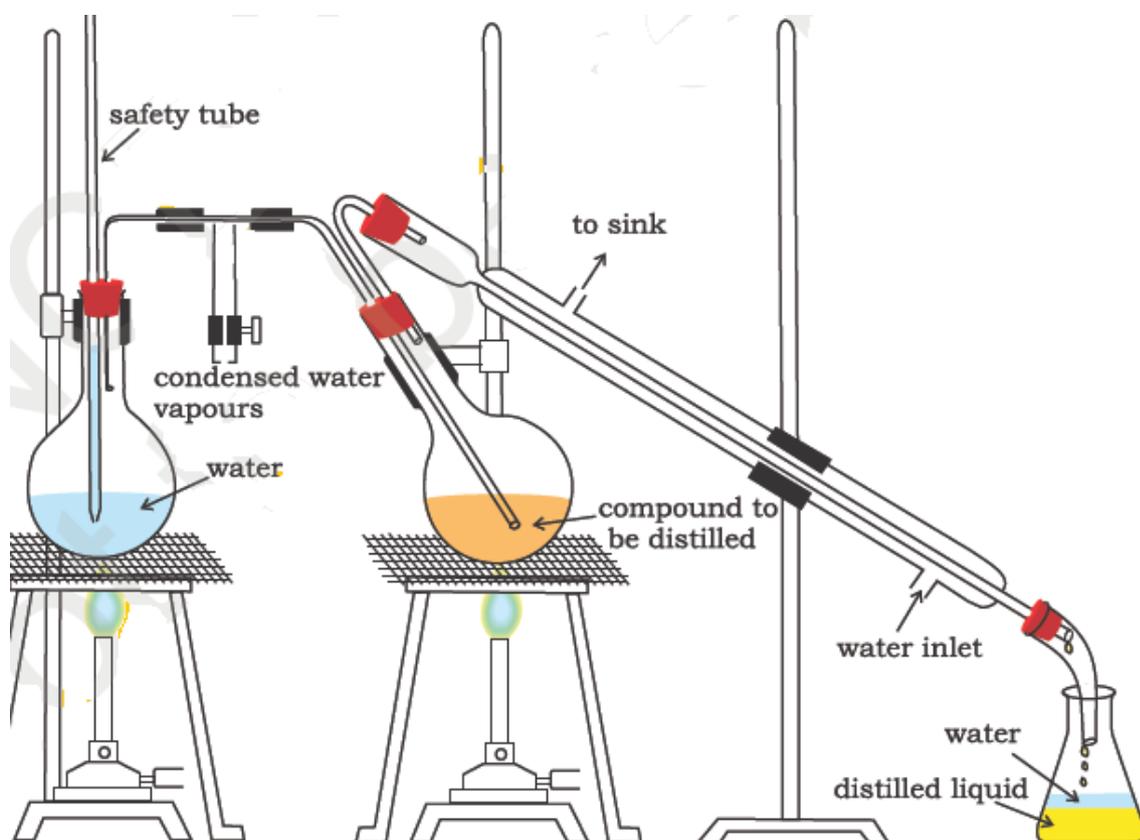
1. The reduced crude oil is pumped through a series of heat exchangers and a crude furnace until reaching the desired temperature (350°C – 390°C)
2. The reduced crude oil is flashed to separate the desired fractions. Light vapors rise to the top and heavier hydrocarbon liquids fall to the bottom.
3. Steam injection at the bottom of the column improves the separation of lighter boiling components
4. The vacuum column uses a series of pump arounds to maintain temperature at the correct level at certain points along the tower
5. Light vapour gases are removed at the top of the tower, condensed and recycled back to the column as reflux. Light Naphtha is drawn off and excess gases sent to flare.
6. Vacuum gas oil (VGO) and lubricating oils are drawn off and routed for further treatment in Hydrotreating units

7. Vacuum residue from the bottom is sent to intermediate storage or typically to be further processed in a FCC or delayed coking unit.

### Steam distillation

Steam Distillation is a separation process for temperature sensitive substances. It is a particular type of distillation. Another way round it is a method for separating miscible liquid base depending upon their volatilities. For instance aromatic compounds. It plays a vital role in some industrial regions.

At a very high sustained temperature, few of organic compounds may decompose. It would be difficult to separate by a distillation process at a certain boiling point. Steam will be introduced into an apparatus (distillation).



*Steam distillation. Steam volatile component volatilizes, the vapours condense in the condenser and the liquid collects in conical flask.*

### Principal

Miscibility is a characteristic of a mixture that would mix well in right proportion leading to the formation of homogeneous mixtures. When such immiscible mixtures are heated and it starts arousing the to unmask the surface to a phase that involves the conversion of liquid to vapour phase.

Here vapour pressure is extracted independently by an individual constituent on its own. Vapour pressure of the system increases consequently. The two immiscible liquids starts to boil when the vapour pressure of these liquids outplace the atmospheric pressure.

Many organic compounds are insoluble in water. They can purified at an absolute temperature that is below the point where decomposition occurs.

## Applications

Steam distillation are widely used in the manufacturing of essential oils, for instance perfumes. This method uses a plant material that consists of essential oils. Mainly orange oil is extracted on a large scale in industries using this method.

Application of steam distillation can be found in the production of consumer food products and petroleum industries. They are used in separation of fatty acids from mixtures.

**purity testing:** methods include titration, infrared spectroscopy, paper chromatography, and optical rotation, among others. These are some of the strategies used in **testing** the presence of impurities in **chemical** compound,boiling point, melting point

## 2.2 GRAVIMETRIC ANALYSIS

**Gravimetric analysis** describes a set of methods used in analytical **chemistry** for the quantitative **determination** of an analyte (the ion being analyzed) based on its mass.

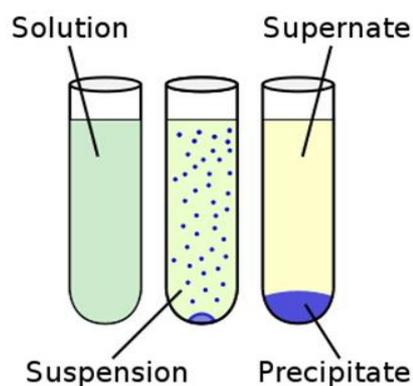
### Precipitation

precipitation is any form of liquid or solid water particles that fall from the atmosphere and reach the surface of the Earth.

An ideal world, an analytical **precipitate** for **gravimetric analysis** should consist of perfect crystals large enough to be easily washed and filtered.

## Precipitation

is the formation of a **solid** in a **solution** or inside another solid during a **chemical reaction** or by **diffusion** in a solid. When the reaction occurs in a liquid, the solid formed is called the **precipitate**, or when compacted by a **centrifuge**, a **pellet**. The liquid remaining above the solid is in either case called the **supernate** or **supernatant**.



## Conditions for analytical precipitation

In an ideal world, an analytical precipitate for gravimetric analysis should consist of perfect crystals large enough to be easily washed and filtered. The perfect crystal would be free from impurities and be large enough so that it presented a minimum surface area onto which foreign ions could be adsorbed.

The precipitate should also be "insoluble" (i.e. be of such slight solubility that losses from dissolution would be minimal).

## Characteristics of precipitation reagents

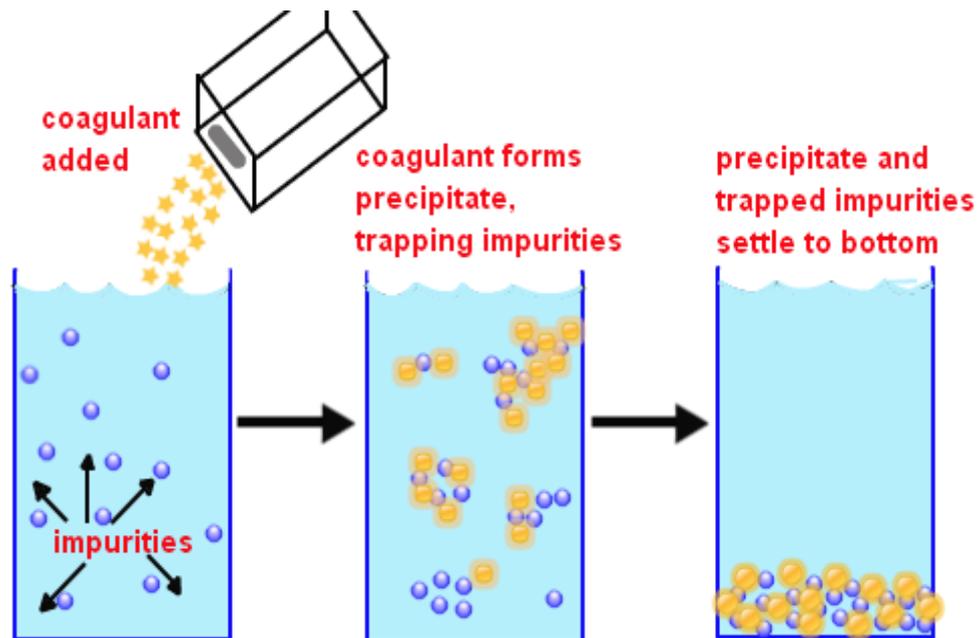
- i) Be free of contaminants and easily filterable;
- ii) Produce a **precipitate** that is sufficiently insoluble that it will not dissolve during washing;
- iii) The **precipitate** needs to be chemically stable;
- iv) The **precipitate** needs to be of known composition after drying or even calcination

## TYPES OF PRECIPITATION

1. The phenomenon of the **precipitation** of a **colloidal** solution by the addition of the excess of an electrolyte is called coagulation or flocculation. This reduces the charge on the particles and ultimately they settle down to form a **precipitate**.
2. A **precipitation** process is characterized by the rapid formation of a solid from an oversaturated solution creating an **crystalline** or amorphous solid.

Colloidal suspensions· whose tiny particles are invisible to the naked eye (  $< 1 \mu\text{m}$  in diameter).· Colloidal particles show no tendency to settle from solution· not easily filtered.

Crystalline suspension· particles with dimensions on the order of tenths of a millimeter or greater.· The temporary dispersion of such particles of a tend to settle spontaneously,· easily filtered.



### Co-precipitation

- It is the precipitation that occurs simultaneously by more than one soluble component in a single solution. Mixed crystals appear after co-precipitation.
- This impurity occurs either by adsorption, occlusion or entrapment.
- It is helpful for the separation of tracer in radioisotopes.
- Magnitude of contamination is less.

### Post-precipitation

It is the precipitation that occurs as a layer upon the already formed precipitate. It is a surface based contamination/impurity that occurs due to high primary adsorption and supersaturated solution. Magnitude of impurity is higher.

## Impurities In Precipitates

Occurred in two ways:

- **Co-Precipitation**

Known as absorbed and adsorbed impurities.

Co-precipitation is a process where the impurity is precipitated along with the desired precipitate, even though the solubility of the impurity has not been exceeded.

- **Post Precipitation**

Foreign compound precipitates on top of the desired precipitate. For example, post precipitation of magnesium oxalate occurs if a precipitate of calcium oxalate is allowed to stand too long before being filtered.

### Example for co-precipitation

- When estimating barium



- The contaminants will go and get occluded inside the crystal lattice of  $\text{BaSO}_4$ .
- Co-precipitation can cause erroneous results.
- In order to minimise this co-precipitation we digest the precipitate.
- Digesting the precipitate in suitable solvent and reprecipitation gives good yield.

## Post-precipitation



- If  $\text{Mg}^{2+}$  is present as an impurity in  $\text{Ca}^{2+}$ , then we can have a post precipitation of  $\text{MgC}_2\text{O}_4$  over  $\text{CaC}_2\text{O}_4$ . The post precipitation can be avoided by keeping a high pH.

### PRECIPITATION OF HOMOGENEOUS SOLUTION

If a precipitating agent is produced over a long period of time in a **homogeneous solution** the level of supersaturation remains low and compact crystal **precipitates** usually result instead of coagulated colloids.

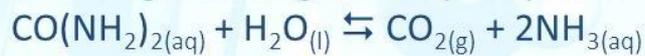
The procedure is accurate and very simple. The **precipitate** is of definite composition and can be weighted directly and the reagent shows to be selective under special conditions.

#### 12A-6 Precipitation from Homogeneous Solution

➤ **Homogeneous precipitation:** A process in which a precipitate is formed by slow generation of a precipitating reagent homogeneously throughout a solution.

- Solids formed by homogeneous precipitation are generally purer and larger size particles.

Example 1: For generating  $\text{OH}^-$  as precipitant



\* Generation rate can be controlled by temperature

Example 2: For generating  $\text{SO}_4^{2-}$  as precipitant



\* Generation rate can be controlled by pH

## IGNITION OF PRECIPITATE

High temperature drying, called **ignition**, is used for the lyophilic (solvent liking) **precipitates**. The thing to remember is that drying or **ignition** may change the chemical composition of the **precipitate**. The dried or **ignited** is solid cooled prior to weighing.

**Sequestering agent** is a dyeing auxiliaries which is used during dyeing for removing hardness of water. **Sequestering agents** combine with calcium and magnesium ions and other heavy metal ions in hard water. They form molecules in which the ions are held so securely (**sequestered**) that they can no longer react.

### Type of commercial sequestering agents

There are some main type of commercial sequestering agents are:

1. Aminocarboxylic acid base products
2. Phosphates and Phosphonates
3. Hydroxy carboxylates
4. Polyacrylates
5. Sugar acrylates

## SPECIFIC PRECIPITANTS

These substances are haptenes, but the word "haptene " is also used for the simpler substances which inhibit reactions. A term is needed for a substance which, though not the true antigen, will form a precipitate, more or less specifically, with an antiserum, and with some hesitation the word " **precipitant** " is used

### EXAMPLE:

DMG, oxine, ethylene di ammine etc.....

# Spectroscopy

## **Definition:**

The study of the interaction between radiations and matter as a function of wavelength  $\lambda$ .

Interactions with particle radiation or a response of a material to an alternating field or varying frequency  $\nu$ .

## **Spectrum:**

A plot of the response as a function of wavelength or more commonly frequency is referred to as a spectrum.

## **Spectrometry:**

It is the measurement of these responses and an instrument which performs such measurements is a **spectrometer or spectrograph**, although these terms are more limited in use to the original field of optics from which the concept sprang.

Spectroscopy is often used in physical and analytical chemistry for the identification of substances through the spectrum emitted from or absorbed by them. Spectroscopy is also heavily used in astronomy and remote sensing. Most large telescopes have spectrometers, which are used either to measure the chemical composition and physical properties of astronomical objects or to measure their velocities from the Doppler Shift of their spectral lines.

## **ENERGY STATE OF MOLECULES**

The energy states and spectra of molecules are much more complex than those of isolated atoms. In addition to the energies associated with molecular electronic states, there is kinetic energy associated with vibrational and rotational motions. The total energy,  $E$ , of a molecule (apart from its translational and nuclear energy) can be expressed as the sum of three terms:

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} \quad (9.6.1)$$

Absorption of electromagnetic radiation by molecules occurs not only by electronic excitation of the type described for atoms, but also by changes in the vibrational and rotational energies.

Both rotations and vibrations of molecules are quantized. This means that only particular values of rotational angular momentum or vibrational energy are possible. We speak of these permitted values of the energies as the vibrational and rotational energy levels.

Translational energy is not very important in connection with spectroscopy and will not be considered here

## Common types

- Fluorescence spectroscopy
- X-ray spectroscopy and crystallography
- Flame spectroscopy
  - 1- Atomic emission spectroscopy
  - 2- Atomic absorption spectroscopy
  - 3- Atomic fluorescence spectroscopy
- Plasma emission spectroscopy
- Spark or arc emission spectroscopy
- UV/VIS spectroscopy
- IR spectroscopy
- Raman spectroscopy
- NMR spectroscopy
- Photo thermal spectroscopy
- Thermal infra-red spectroscopy
- Mass Spectroscopy

Name of Spectroscopy	Type of Radiation Used	Wavelength	Relative Energy	What it does to the molecule/atom	What it tells us about the atom/molecule
Photoelectron Spectroscopy (PES)	X-rays	0.01 to 10 nm	Very high	Removes core electrons	- Atomic Structure - how tightly the electrons are held by the nucleus - identity of an element
UV-Visible Spectroscopy	Ultraviolet	50-400 nm	High	Excites valence electrons	- identity of a molecule or element
UV-Visible Spectroscopy	Visible Light	400-800 nm	Medium	Excites valence electrons	- concentration of a molecule
IR (vibrational) spectroscopy	Infrared	2.5 – 50 $\mu\text{m}$	Low	Changes the vibrations in covalent bonds	- types of bonds / atoms / functional groups within a molecule
Microwave (rotational) spectroscopy	Microwave	0.3mm – 0.5m	Very Low	Changes the rotations of the atoms in covalent bonds	- location of hydrogen atoms within a molecule

## BORN-OPPENHEIMER APPROXIMATION

The **Born-Oppenheimer Approximation** is the assumption that the electronic motion and the nuclear motion in molecules can be separated. The **Born-Oppenheimer** (named for its original inventors, Max **Born** and Robert **Oppenheimer**) is based on the fact that nuclei are several thousand times heavier than electrons.

## **REFERENCES:**

A Text book of analytical chemistry by R. gopalan

Basic concept of physical chemistry by puri and sharma

Basic concept of spectroscopy by Banwell