

SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT-1-Solutions-SCY1214

Introduction: Solid solution - Hume Rothery's rule. Types of solid solutions: Liquid solutions: Solubility of partially miscible liquids - Phenol-water system. Colligative properties: Lowering of vapour pressure. Raoult's law: Derivation - Osmotic pressure - Isotonic solution - Relationship between osmotic pressure and vapour pressure. Depression in freezing point - Derivation. Elevation in boiling point - Derivation - Problems.

INTRODUCTION

A solution is a single phase homogeneous system, containing two or more substances. Example common salt in water, alcohol in water, sugar in water, etc..The component of a solution forming the larger proportion is called as solvent. While the other component which is present in minor proportion in solution is called solute. A solution in water is called aqueous solution . while a solution in a solvent other than water is used is called non-aqueous solution. Modes of expressing concentration of solutions: Percentage of a solution can be expressed as Mass percentage, Volume percentage, Normality, Molarity, Molality ,Mole fraction,Mass fraction.

Solid solution: When in a solid, the atoms of a solutes are present in the lattice of the solvent, it is known as solid solution. Solid state solution contains one or more solutes in the solvent. The crystal structure of the solvent remains unchanged by addition of solutes.

Hume Ruther's rule:

- Rule 1:The solute must be smaller than the pores in the solvent lattice.
- Rule2:The solute and solvent have similar electro negativity.
- Rule3:Maximum solubility occurs when the solute and solvent have same valence.
- Rule4:The crystal structures of solute and solvent must match.

Types of solid solution:

a)SUBSTITUTIONAL SOLID SOLUTION

When the atoms of solute substitute for the atoms of the solvent in its lattice, the solution is known as substitutional solid solution. The solute may incorporate into the solvent crystal lattice substitutionally by replacing a solvent particle in the lattice.



Two types of solution (a) substitution solid in which particles of the solute replace interstitial solid, solution in which the solute particles fit in spaces between particles of the host lattice (the solvent)

b)**Interstitial solid solution**:when the atoms of the solute occupy the interstitial spaces in the lattice of the solvent it is known as interstitial solution.

Liquid solutions: It is a homogeneous mixture that compressed both the solute and solvent in the liquid formation.

Types:Solid-liquid,Liquid-liquid,Solid- gas

Liquid-liquid equilibria:

- Complete miscibility
- Immiscibility
- Partial miscibility

Types of partially miscible liquid-liquid systems have been observed are:

The partial miscibility increases on increasing temperature. at and above a certain temperature, the liquids become completely miscible.

The partial miscibility increases on lowering the temperature. at and below a certain temperature, the two liquids become completely miscible.

Critical solution temperature: The temperature above (or below)which pair of partially miscible liquids becomes miscible in all proportions is called critical solution temperature.

- Upper critical solution temperature(UCST)
- Lower critical solution temperature(LCST)

PHENOL-WATER SYSTEM:

As the temperature is raised, the solubility of phenol in water increases. Also at the same time that of water in phenol increases. This is shown by solubility curves AB(of phenol in water and CB(of water in phenol). At the point B, the two curves merge into one another and beyond this temperature, there is complete miscibility and no separation into layers takes place. thus the upper critical solution temperature or consulted temperature for this system, is 66.5 above 66.5 C, the two liquids are completely miscible.



Isotonic solution: Two solutions possessing same osmotic pressure at a given temperature are termed as isotonic solution. No osmosis occurs on isolation of these solutions when isolated through a semipermiable membrane.

colligative properties: are properties that depends upon the number of solute particles in solution and not on the nature of the solute particles. Physical properties can be divided into two categories. **Extensive properties** (such as mass and volume) depend on the size of the sample. **Intensive properties** (such as density and concentration) are characteristic properties of the substance; they do not depend on the size of the sample being studied. This section introduces a third category that is a subset of the intensive properties of a system. This third category, known as **colligative properties**, can only be applied to solutions. By definition, one of the properties of a solution is a *colligative property* if it depends only on the ratio of the number of particles of solute and solvent in the solution, not the identity of the solute.

Relative lowering of Vapor Pressure

Very few of the physical properties of a solution are colligative properties. As an example of this limited set of physical properties, let's consider what happens to the vapor pressure of the solvent when we add a solute to form a solution. We'll define P^o as the vapor pressure of the pure liquid — the solvent — and P as the vapor pressure of the solvent after a solute has been added.

 P^o = vapor pressure of the pure liquid, or solvent

P = vapor pressure of the solvent in a solution

When the temperature of a liquid is below its boiling point, we can assume that the only molecules that can escape from the liquid to form a gas are those that lie near the surface of the liquid.

When a solute is added to the solvent, some of the solute molecules occupy the space near the surface of the liquid, as shown in the figure below. When a solute is dissolved in a solvent, the number of solvent molecules near the surface decreases, and the vapor pressure of the solvent decreases.

This has no effect on the rate at which solvent molecules in the gas phase condense to form a liquid. But it decreases the rate at which the solvent molecules in the liquid can escape into the gas phase. As a result, the vapor pressure of the solvent escaping from a solution should be smaller than the vapor pressure of the pure solvent.

 $P < P^{o}$ vapor pressure vapor pressure of the solvent of the pure solvent above a solution

Between 1887 and 1888, Francois-Marie Raoult showed that the vapor pressure of a solution is equal to the mole fraction of the solvent times the vapor pressure of the pure liquid.

	Р	=	$C_{solvent} P^{o}$	
vapor pressure of the solvent	;		va pi	apor pressure of the ure solvent
above a solution				

This equation, which is known as **Raoult's law**, is easy to understand. When the solvent is pure, and the mole fraction of the solvent is equal to 1, P is equal to P^{o} . As the mole fraction of the solvent becomes smaller, the vapor pressure of the solvent escaping from the solution also becomes smaller.



Let's assume, for the moment, that the solvent is the only component of the solution that is volatile enough to have a measurable vapor pressure. If this is true, the vapor pressure of the solution will be equal to the vapor pressure of the solvent escaping from the solution. Raoult's law suggests that the difference between the vapor pressure of the pure solvent and the solution increases as the mole fraction of the solvent decreases. The *change in the vapor pressure* that occurs when a solute is added to a solvent is therefore a colligative property. If it depends on the mole fraction of the solute, then it must depend on the ratio of the number of particles of solute to solvent in the solution but not the identity of the solute.

Boiling Point Elevation and Freezing Point

The consequences of the fact that solutes lower the vapor pressure of a solvent. The solid line connecting points B and C in this phase diagram contains the combinations of temperature and pressure at which the pure solvent and its vapor are in equilibrium. Each point on this line therefore describes the vapor pressure of the puresolvent at that temperature. The dotted line in this figure describes the properties of a solution obtained by dissolving a solute in the solvent. At any given temperature, the vapor pressure of the solvent escaping from the solution is smaller than the vapor pressure of the pure solvent. The dotted line therefore lies below the solid line.



According to this figure, the solution can't boil at the same temperature as the pure solvent. If the vapor pressure of the solvent escaping from the solution is smaller than the vapor pressure of the pure solvent at any given temperature, the solution must be heated to a higher temperature before it boils. The lowering of the vapor pressure of the solvent that occurs when it is used to form a solution therefore increases the boiling point of the liquid.

When phase diagrams were introduced, the triple point was defined as the only combination of temperature and pressure at which the gas, liquid, and solid can exist at the same time. The figure above shows that the triple point of the solution occurs at a lower temperature than the triple point of the pure solvent. By itself, the change in the triple point is not important. But it results in a change in the temperature at which the solution freezes or melts. To understand why, we have to look carefully at the line that separates the solid and liquid regions in the phase diagram. This line is almost vertical because the melting point of a substance is not very sensitive to pressure.

Adding a solute to a solvent doesn't change the way the melting point depends on pressure. The line that separates the solid and liquid regions of the solution is therefore parallel to the line that serves the same function for the pure solvent. This line must pass through the triple point for the solution, however. The decrease in the triple point that occurs when a solute is dissolved in a solvent therefore decreases the melting point of the solution.

The figure above shows how the change in vapor pressure that occurs when a solute dissolves in a solvent leads to changes in the melting point and the boiling point of the solvent as well. Because the change in vapor pressure is a colligative property, which depends only on the relative number of solute and solvent particles, the changes in the boiling point and the melting point of the solvent are also colligative properties.

Thermodynamics derivation for elevation of boiling point and depression of freezing point: The derivation is bases on that if there are two phases in equilibrium, the chemical potential of substances must be same in both the bases.

We know $_T_f = T_f \circ - T_f$

The clauses chaperon which is applicable to phase equilibrium

Lnp2/p1 = AH/R[I/T1-1/T2]

AHV IS The latent heat of vaporization of one mole of the solvent from the solution.

Lnp0/ps = HV/r[ts-to/tots]

Lnpo/ps == AV/r[= V/tots]

A Dilute solutionTS~T0

According to raults law p0-ps/p0=x2

1 - ps/p0 = x2

ps/p0=1-x2 taking ln on both sides

 $Lnpo/ps=ln{1-x2}$

Lnpo/ps=- $ln\{1-x2\}$

```
X2 = n2/n1 + n2
```

X2=w2M1/w1M2



Relationship between osmosis and osmotic pressure:

A concentrated solution of alcohol in water expanded when it was immersed in water. The bladder acted as a *semipermiable membrane*, which allowed water molecules to enter the solution, but kept alcohol molecules from moving in the other direction. Movement of one component of a solution through a membrane to dilute the solution is called **osmosis**, and the pressure this produces is called the **osmotic pressure** (π).

Osmotic pressure can be demonstrated with the apparatus shown in the figure below. A semipermiable membrane is tied across the open end of a thistle tube. The tube is then partially filled with a solution of sugar or alcohol in water and immersed in a beaker of water. Water will flow into the tube until the pressure on the column of water due to the force of gravity balances the osmotic pressure driving water through the membrane.



The same year that Raoults discovered the relationship between the vapor pressure of a solution and the vapor pressure of a pure solvent, Jacobs Henricus vant's Hoff found that the osmotic pressure of a dilute solution (π) obeyed an equation analogous to the ideal gas equation.

$$\pi = \frac{nRT}{V}$$

This equation suggests that osmotic pressure is another example of a colligative property, because this pressure depends on the ratio of the number of solute particles to the volume of the solution -n/V — not the identity of the solute particles. It also reminds us of the magnitude of osmotic pressure. According to this equation, a 1.00 *M* solution has an osmotic pressure of 22.4 atm at 0°C.

Vant hoff theory for dilute solution

$$\pi = \frac{(1.00 \ mol)(0.08206 \ L \ atm/mol \ K)(273 \ K)}{(1.00 \ L)} = 22.4 \ atm$$

Electromagnetic spectrum, Absorption of radiation, electronic transition – Vibrational transition – Rotational transition – Intensities of spectral lines – Beer- Lambers law – Colorimetric analysis – Estimation of concentration of a solution by colorimetry – Flame photometry – Theory, Instrumentation(block diagram only) and application – UV-Visible spectroscopy – principles, instrumentation(block diagram only) and IR spectroscopy – simple application only.

Introduction

Analytical instrumentation plays an important role in the production and evaluation of new products and in the protection of consumers and environment. It is used in checking the quality of raw materials such as substances used in integrated circuit chips, detection and estimation of impurities to assure safe foods, drugs, water and air, process optimization and control, quality check of finished products and research and development. Most of the modern instruments are microprocessor/computer controlled with user friendly software for collection of data, analysis and presentation. This chapter deals with the different types of analytical instrumental methods that find use in a variety of industries. These include molecular spectroscopic methods, thermal methods of analysis, X-ray diffraction, scanning electron microscope and sensors.

> Spectroscopy:

- Spectroscopy It is the study of interaction of electromagnetic radiation with matter consisting of atoms and molecules.
- When a substance is irradiated with electromagnetic radiation, the energy of the incident photons may be transferred to atoms and molecules raising their energy from ground state level to excited state.
- 4 This process is known as absorption and the resultant spectrum is known as absorption spectrum.
- The process of absorption can occur only when the energy difference between the two levels E is exactly matched by the energy of the incident photons as given by the equation.
- = E = hθ = hc λ
- Where, h is Planck's constant (6.63 x 10-34Js), v is the frequency of incident radiation, c is the velocity of light and λ is the wavelength of the incident radiation.
- The excited state atoms and molecules then relax to the ground state by spontaneous emission of radiation. The frequency of the radiation emitted depends on E.
- The energy changes that occur in atoms and molecules during interaction with different regions of electromagnetic radiation.

UV-Visible spectroscopy

- The UV –Visible spectroscopy is also known as electronic absorption spectroscopy as molecules absorb radiation resulting in transitions between electronic energy levels.
- Absorption of radiation in the UV (wavelength range 190-400nm) and visible (wavelength 400–800nm) regions result in transitions between electronic energy levels.
- The principle of electronic transitions and the instruments required to record electronic transitions are common for both the regions.

The electronic transition occurs based on Franck Condon principle which states that electronic transition takes place so rapidly that a vibrating molecule does not change its inter-nuclear distance appreciably during the transition.

Laws of Absorption

The fraction of the photons absorbed by the molecule at a given frequency depends on

1. The nature of the absorbing molecules.

2. The concentration of the molecules (C). The higher the molar concentration, the higher is the absorption of photons.

3. The length of the path of the radiation through the substance or the thickness of the absorbing medium. Larger the path length (in cm), larger is the number of molecules exposed and greater is the probability of photons being absorbed.

Lambert's law: When a beam of monochromatic radiation passes through a transparent absorbing medium, the rate of decrease of intensity of radiation with the thickness of the absorbing medium is proportional to the intensity of incident radiation. It and Io are the intensities of the transmitted and incident beams of radiations, (x=b) b is the thickness of the absorbing medium and k is a constant

Beer's law: When a beam of monochromatic radiation passes through a solution containing an absorbing substance, the amount of light absorbed by a solution is proportional to the concentration of solution. Where, C is the molar concentration of the absorbing substance and k' is another constant. Beer-Lambert's law Where, C is the molar concentration of the absorbing substance and k' is another constant.

$$A = \log_{10} \frac{I_o}{I} = \varepsilon I c$$

When a monochromatic radiation passes through transparent absorbing medium, the amount of light absorbed is proportional to the concentration of the absorbing substance and the thickness of the absorbing material. $\varepsilon =$ molar absorption coefficient or extinction coefficient A = Absorbance or optical density.

Instrumentation of UV-Visible spectrophotometer

The instrument used to record the spectra of molecules is called a spectrometer.

The sophisticated double beam recording UV-Visible spectrophotometer covers the entire wavelength range of 190 - 800 nm.

The basic components are

- 1. Source of radiation
- 2. Monochromator
- 3. Sample cell
- 4. Detector

• 5. Display/ Recorder



1. Radiation source: Hydrogen discharge lamp or deuterium lamp is used as UV radiation source. For visible light, tungsten filament lamp is used.

2. Monochromator: It disperses the polychromatic radiation from the source to a narrow rangeof wavelength.

3.For UV and visible light, quartz prism or a grating is used. Two types of prisms, namely 600 Cornu quartz prism and 300 Littro prisms are employed. For visible light, a glass prism can be used.

4. Sample holder (Cells or cuvettes): Sample containers should be transparent to UV and visible radiation. Cuvettes made of quartz are used for both UV and Visible region, whereas for visible light, glass cuvettes are used. Standard path length of these cuvettes is usually 1 cm.

5. Sector mirror: The monochromatic beam of radiation is split into two parallel beams by the sector mirrors which pass through the sample and reference cells and reach the detector.

6. Solvents for UV region: Electronic absorption spectra are usually recorded for solutions. Solvent used should absorb in the same region as the solute.

Solvents used in the UV and visible region are water, methyl alcohol, ethyl alcohol, chloroform, hexane, etc. 95% ethyl alcohol is the most widely used solvent in UV region since it is a polar solvent, cheaper and transparent up to 210 nm.

7. Detectors: Photovoltaic cells or photo emissive cells or the more sensitive photomultiplier tubes are used to convert the incident photons into electric current.

8. Display/Recorder: The wavelength drive of the recorder and display unit are synchronized so that the detector signal converted into the transmittance or absorbance units is recorded as a function of wavelength of the incident beam of radiation.

9. In UV-visible spectrometer, a beam of light is split into two equal halves. One half of the beam (sample beam) is directed towards the sample cell containing the solution of the compound being analyzed and the other half (reference beam) through the reference cell that contains only the solvent.

The instrument is so designed that it can compare the intensities of both the beams at each wavelength of the region 190-800 nm. If the compound absorbs light at a particular wavelength, the intensity of the sample beam, I will be less than the intensity of the reference beam Io. An output graph, which is a plot of the wavelength (λ) versus the absorbance (A) at each wavelength obtained, is known as absorption spectrum.

FLAME PHOTOMETRY or flame spectrometry is an emission spectroscopic method. In this, a flame is used as the excitation source and an electronic photo detector is used as the measuring device. This is an sensitive method for qunatitative analysis of alkali and alkali earth metals and also a few other metals.



Block diagram:

Atomic spectroscopy is thought to be the oldest instrumental method for the determination of elements. These techniques are introduced in the mid of 19th Century during which Bunsen and Kirchhoff showed that the radiation emitted from the flames depends on the characteristic element present in the flame. The potential of atomic spectroscopy in both the qualitative as well as quantitative analysis were then well established. The developments in the instrumentation area led to the widespread application of atomic spectroscopy.

Atomic spectroscopy is an unavoidable tool in the field of analytical chemistry.

It is divided into three types which are absorption, emission, and luminescence spectroscopy. The different branches of atomic absorption spectroscopy are

(1) Flame photometry or flame atomic emission spectrometry in which the species is examined in the form of atoms

(2) Atomic absorption spectrophotometry, (AAS),

(3) Inductively coupled plasma-atomic emission spectrometry.

Photoelectric flame photometry, a branch of atomic spectroscopy is used for inorganic chemical analysis for determining the concentration of certain metal ions such as sodium, potassium, lithium, calcium, cesium, etc. In flame photometry the species (metal ions) used in the spectrum are in the form of atoms

- The basis of flame photometric working is that, the species of alkali metals (Group 1) and alkaline earth metals (Group II) metals are dissociated due to the thermal energy provided by the flame source.
- Due to this thermal excitation, some of the atoms are excited to a higher energy level where they are not stable.

- The absorbance of light due to the electrons excitation can be measured by using the direct absorption techniques.
- The subsequent loss of energy will result in the movement of excited atoms to the low energy ground state with emission of some radiations, which can be visualized in the visible region of the spectrum.
- The absorbance of light due to the electrons excitation can be measured by using the direct absorption techniques while the emitting radiation intensity is measured using the emission techniques. The wavelength of emitted light is specific for specific elements.
- The working of the flame photometer involves a series of steps which is discussed in the following sections.
- The solution of the substance to be analyzed is first aspirated into the burner, which is then dispersed into the flame as fine spray particles.

A brief overview of the process:

- 1. The solvent is first evaporated leaving fine divided solid particles.
- 2. This solid particles move towards the flame, where the gaseous atoms and ions are produced. 3. The ions absorb the energy from the flame and excited to high energy levels.
- 4. When the atoms return to the ground state radiation of the characteristic element is emitted. 5. The intensity of emitted light is related to the concentration of the element.
- Events occurring in the flame:
- Flame photometry employs a variety of fuels mainly air, oxygen or nitrous oxide (N2O) as oxidant.
- The temperature of the flame depends on fuel-oxidant ratio.
- Desolvation: The metal particles in the flame are dehydrated by the flame and hence the solvent is evaporated. •
- Vapourisation: The metal particles in the sample are dehydrated. This also led to the evaporation of the solvent. •
- Atomization: Reduction of metal ions in the solvent to metal atoms by the flame heat. •
- Excitation: The electrostatic force of attraction between the electrons and nucleus of the atom helps them to absorb a particular amount of energy. The atoms then jump to the exited energy state.
- Emission process: Since the higher energy state is unstable the atoms jump back to the stable low energy state with the emission of energy in the form of radiation of characteristic wavelength, which is measured by the photo detector.
- The intensity of the light emitted could be described by the Scheibe-Lomakin equation:

I=KXCⁿ



Applications:

- It is used in the analysis of biological fluids and tissues . some of the elements which are generally analysed are sodium , potassium calcium and iron.
- In solid analysis elements such as Na,K,Al,
- Ca ,Co and Fe are routinely determined.
- Metallurgical products and agronomic materials can also be analysed by the method.
- Flame photometry is very useful in medicine and agriculture.

IR SPECTROSCOPY:

It is the spectroscopy which deals with the infrared region (700nm to 1000μ m) of the electromagnetic spectrum with a longer wave length and lower frequency than visible light.

Principle:

An IR spectrum is produced by the absorption of energy by a molecule in the infrared region and the transitions occur between vibrational levels.

Hence IR spectroscopy is also known as vibrational spectroscopy.

It is divided into three regions.

(i) Near IR -12500 to 4000 cm-1

- (ii) Middle IR -4000 to 670 cm-1
- (iii) Far IR -670 to 50 cm-1 The most useful IR region lies between 4000 to 670 cm-1.

Theory of IR absorption

IR radiation does not have sufficient energy to induce electronic transitions like UV-Visible spectroscopy. It causes only vibrational and rotational changes. For a molecule to absorb IR radiation, two conditions must be satisfied.

- a. There must be change in the net dipole moment of the molecule during the vibration.
- b. The energy of the IR radiation must match the energy difference between two vibrational levels.

c. The bonds of a molecule experience various types of vibrations. The atoms are not stationary and fluctuate continuously. Vibrational motions are defined by stretching and bending modes.

- There are two types of vibrations.
- 1. Stretching Vibration Symmetric and Asymmetric
- 2. Bending Vibration (a) Inplane bending Rocking, Scissoring,
- (b) Outplane bending Wagging and Twisting.
- Application: a) Identification of functional group and structure elucidation
- Entire IR region is divided into group frequency region and fingerprint region. Range of group frequency is 4000-1500 cm-1 while that of finger print region is 1500-400 cm-1. In group frequency region, the peaks corresponding to different functional groups can be observed. According to corresponding peaks, functional group can be determined. Each atom of the molecule is connected by bond and each bond requires different IR region so characteristic peaks are observed. This region of IR spectrum is called as finger print region of the molecule. It can be determined by characteristic peaks.
- b) Identification of substances
- IR spectroscopy is used to establish whether a given sample of an organic substance is identical with another or not.

This is because large number of absorption bands is observed in the IR spectra of organic molecules and the probability that any two compounds will produce identical spectra is almost zero. if two compounds have identical IR spectra then both of them must be samples of the same substances. IR spectra of two enantiomeric compound are identical. So IR spectroscopy fails to distinguish between enantiomers.

For example, an IR spectrum of benzaldehyde is observed as follows. C-H stretching of aromatic ring - 3080 cm-1 C-H stretching of aldehydes - 2860 cm-1 and 2775 cm-1 C=O stretching of an aromatic aldehydes - 1700 cm-1 C=C stretching of an aromatic ring - 1595 cm-1 C-H bending - 745cm-1 and 685 cm-1.

(c) Studying the progress of the reaction Progress of chemical reaction can be determined by examining the small portion of the reaction mixture withdrawn from time to time. The rate of disappearance of a characteristic absorption band of the reactant group and/or the rate of appearance of the characteristic absorption band of the product group due to formation of product is observed.

(d) Detection of impurities IR spectrum of the test sample to be determined is compared with the standard compound. If any additional peaks are observed in the IR spectrum, then it is due to impurities present in the compound.

(e) Quantitative analysis The quantity of the substance can be determined either in pure form or as a mixture of two or more compounds. In this, characteristic peak corresponding to the drug substance is chosen and log I0/It of peaks for standard and test sample is compared. This is called base line technique to determine the quantity of the substance.

Limitation :

- i. Molecular weight cannot be predicted.
- ii. It is frequently non- adherence to Beers law of complexity spectra.
- iii. Relative position of different functional group on a molecule.

Colorimetric analysis

Colorimetric analysis is a method of determining the concentration of a chemical element or chemical compound in a solution with the aid of a color reagent. It is applicable to both organic compounds and inorganic compounds. colorimetry, measurement of the wavelength and the intensity of electromagnetic radiation in the visible region of the spectrum. It is used extensively for identification and determination of concentrations of substances that absorb light.



Estimation of concentration of a solution by colorimetry

colorimeter (colourimeter) measures the absorption of light of a specific wavelength (λ) by a solution. The colorimeter records this as the absorbance. In order to determine the concentration of a solution, we will need to obtain the absorbances for a range of different concentrations of the same solution using the same wavelength of light (same filter).

We use the absorbance of each of these solutions of known concentration to draw a calibration curve. We can then measure the absorbance of our solution of unknown concentration and use the calibration curve to determine its concentration.

If, for example, we have an aqueous solution of copper sulfate, $CuSO_{4(aq)}$, and we want to determine its concentration colorimetrically, we would first prepare a stock solution of aqueous copper sulfate. We then use this stock solution to prepare a number of dilute copper sulfate solutions, calculating the concentration of each solution.

Note that we should visually check the colour of our unknown solution against the colour of each of the prepared solutions in order to ensure that the colour of our solution lies between the colour of the most concentrated and most dilute solution we have prepared.

Next we use the colorimeter (colourimeter) to measure the absorbance of each of these solutions of known concentration.

UNIT – III–Chemical kinetics-SCY1214

Introduction, Basic Concepts, Factors affecting reaction rates, rate equations for different orders – Derivation of Zero order, First order, Second order (A+A and A+B) reactions, Half life, problem based on First order and second order kinetics. Methods for the determination of the order of a reaction, Steady state hypothesis, Arrhenius Equation, Energy of activation, complex reactions – kinetics of opposing, parallel and consecutive reactions, Theories of reaction rates – Collision theory, Absoulte reaction rate theory

Introduction

Chemical kinetics also called reaction kinetics helps us understand the rates of reactions and how it is influenced by certain conditions. It further helps to gather and analyze the information about the mechanism of the reaction and define the characteristics of a chemical reaction.

Factors affecting reactions rates

chemical kinetics - area of chemistry dealing with speeds/rates of reactions

rates of reactions affected by four factors

- concentrations of reactants
- temperature at which reaction occurs
- presence of a catalyst
- surface area of solid or liquid reactants and/or catalysts

Specific Rotation =
$$[\alpha] = \frac{\alpha}{c \times l}$$

 $[\alpha] = specific rotation$

$$\alpha = observed rotation$$

 $c = concentration \left(rac{gm}{mL}
ight)$
 $l = path length (dm)$

half-life: The half-life of a reaction is the time required for the reactant concentration to decrease to one-half its initial value. The half-life of a first-order reaction is a constant that is related to the rate constant for the reaction:

$$t_{1/2} = 0.693/k.$$

• It is a first order reaction and also independent of the concentration medium.

Steady state hypothesis: When a reaction involves one or more intermediates, the concentration of one of the intermediates remains constant at some stage of the reaction. The concentration of one of the intermediates, [Int], varies with *time*. At the start and end of the reaction, [Int] does vary with time.

d[Int]/dt=0

Effect of catalyst on energy of activation:

- Activation Energy: The activation energy is defined as the energy that can be provided in a chemical reaction. sometimes it is called as potential barrier energy. The activation energy (*E*_a) of a reaction is measured in joules per mole (J/mol), <u>kilojoules per mole</u> (kJ/mol) or <u>kilocalories per mole</u> (kcal/mol). At the chemical reaction will raise the temperature by the way also activation energy also increases. We are using catalyst in this case, it can stimulate the rate of the reaction but it does not change the reactants or products.
- Calculation of E_a using Arrhenius Equation: As temperature increases, gas molecule velocity also increases (according to the <u>kinetic theory of gas</u>). This is also true for liquid and solid substances. The (translational) kinetic energy of a molecule is proportional to the velocity of the molecules ($KE = 1/2 \text{ mv}^2$). Therefore, when temperature increases, KE also increases; as temperature increases, more molecules have higher KE, and thus the fraction of molecules that have high enough KE to overcome the energy barrier also increases. The fraction of molecules with energy equal to or greater than E_a is given by the exponential term e–Ea/RT in the Arrhenius equation:

► k is the rate constant

:

- E_a is the activation energy
- ► R is the gas constant
- ► T is temperature in Kelvin

A is frequency factor constant or also known as pre-exponential factor or Arrhenius factor. It indicates the rate of collision and the fraction of collisions.



Transition state: The transition state of a <u>chemical reaction</u> is a particular configuration along the <u>reaction</u> <u>coordinate</u>. It is defined as the state corresponding to the highest potential energy along this reaction coordinate. It is often marked with the <u>double dagger</u> ‡ symbol.

Transition state for a substitution reaction between hydroxide and chloromethane:

$\rm CH3Cl{+}HO{-}{\rightarrow}\rm CH3OH{+}Cl{-}$

Transition state theory (TST) describes a hypothetical "transition state" that occurs in the space between the reactants and the products in a chemical reaction. The species that is formed during the transition state is known as the activated complex. TST is used to describe how a chemical reaction occurs, and it is based upon collision theory. If the rate constant for a reaction is known, TST can be used successfully to calculate the standard enthalpy of activation, the standard entropy of activation, and the standard Gibbs energy of activation. TST is also referred to as "activated-complex theory," "absolute-rate theory," and "theory of absolute reaction rates."**Transition state theory**The activated complex, which a kind of reactant-product hybrid, exists at the peak of the reaction coordinate, in what is known as the transition state.

Postulates of Transition State Theory: According to transition state theory, between the state in which molecules exist as reactants and the state in which they exist as products, there is an intermediate state known as the transition state. The species that forms during the transition state is a higher-energy species known as the activated complex. TST postulates three major factors that determine whether or not a reaction will occur.

These factors are:

- 1. The concentration of the activated complex.
- 2. The rate at which the activated complex breaks apart.
- 3. The mechanism by which the activated complex breaks apart; it can either be converted into products, or it can "revert" back to reactants.

Intermediate: A **reaction intermediate** is formed from the reactants in a chemical reaction, and reacts further to produce the products observed after the reaction is complete.



Activation Energy:

The activation energy is defined as the energy that can be provided in a chemical reaction. sometimes it is called as potential barrier energy. The activation energy (E_a) of a reaction is measured in joules per mole (J/mol), <u>kilojoules per mole</u> (kJ/mol) or <u>kilocalories per mole</u> (kcal/mol). At the chemical reaction will

raise the temperature by the way also activation energy also increases. We are using catalyst in this case ,it can stimulate the rate of the reaction but it does not change the reactants or products .

Theories of reaction rates

Collision theory, theory used to predict the rates of <u>chemical reactions</u>, particularly for <u>gases</u>. The collision theory is based on the assumption that for a reaction to occur it is necessary for the reacting species (<u>atoms</u> or <u>molecules</u>) to come together or collide with one another.

The concepts of collision frequency can be applied in the laboratory:

(1) The temperature of the environment affects the average speed of molecules. Thus, reactions are heated to increase the reaction rate.

(2) The initial concentration of reactants is directly proportional to the collision frequency; increasing the initial concentration will speed up the reaction. For a successful collision to occur, the reactant molecules must collide with enough kinetic energy to break original bonds and form new bonds to become the product molecules. This energy is called the activation energy for the reaction; it is also often referred to as the energy barrier.

LINDEMANN / LINDEMANN-HINSHELWOOD THEORY

- This is the simplest theory of unimolecular reaction rates, and was the first to successfully explain the observed first-order kinetics of many unimolecular reactions.
- **4** The proposed mechanism actually consists of a second-order bimolecular collisional activation step, followed by a rate-determining unimolecular step.

 $4 \qquad A + M \rightarrow A^* + M$

 $4 \qquad A^* \rightarrow k2 \ \mathbb{R} \ P$

↓ Applying the steady-state approximation to the concentration of A* gives

 $4 \qquad [A^*] = k1[A][M] / k - 1[M] + k2$

 \downarrow so that the overall rate is

 $\circ \quad d[P]/dT = k2[A^*] = k1k2[A][M]/k-1[M] + k2$

 \blacksquare This is often written as

- 4 d[P]/dT = keff[A]
- 4 where keff = k1k2[M] /k-1[M] + k2 is an effective first-order rate constant.
- keff is, of course, a function of pressure. At high pressures, collisional deactivation of A* is more likely than unimolecular reaction, keff reduces to k1k2/k-1 and the reaction is truly first order in A.
- **4** At low pressures, bimolecular excitation is the rate determining step;
- \downarrow once formed A* is more likely to react than be collisionally deactivated.

 \downarrow The rate constant reduces to keff=k1[M] and the reaction is second order.



1/[A]

Lindemann theory breaks down for two main reasons:

i) The bimolecular step takes no account of the energy dependence of activation; the internal degrees of freedom of the molecule are completely neglected, and the theory consequently underestimates the rate of activation.

ii) The unimolecular step fails to take into account that a unimolecular reaction specifically involves one particular form of molecular motion (e.g. rotation around a double bond for cis-trans isomerization.

Absolute reaction rate:

- Absolute reaction rate theory is a theory that aims to provide explanations for both the 'activation energy' and the pre-exponential factor A (the 'frequency factor') in the rate equation from first principles.
- > Its underlying theories are quantum mechanics and statistical mechanics.
- The success of the theory depends on an accurate calculation of the potential energy surface of the reaction, as well as a detailed consideration of the initial and final states of the molecules.
- > The theory also introduces a precise concept of a transition state which is like a 'normal' molecule.
- > The transition state has a definite structure, mass, and so forth.
- > The only exception is that there is one particular direction of motion (the 'reaction coordinate') which causes the molecule to 'break up' into the end products of the reaction.

Zeroth -order reaction:

It is one whose rate is independent of concentration; its differential rate law is rate = k. We refer to these reactions as zeroth order because we could also write their rate in a form such that the exponent of the reactant in the rate law is 0:

rate=
$$-\Delta[A]\Delta t = k[reactant]0 = k(1) = k$$

An example is the decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2 , which occurs at temperatures ranging from 200°C to 400°C:

$$2N_2O(g) \rightarrow Pt 2N_2(g) + O_2(g)$$

The reaction rate is as follows:

$$rate = -12(\Delta[N_2O]\Delta t) = 12(\Delta[N_2]\Delta t) = \Delta[O_2]\Delta t = k[N_2O]_0 = k$$

First-Order Reactions:

In a first-order reaction, the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form $A \rightarrow$ products. The differential rate for a first-order reaction is as follows:

rate=
$$-\Delta[A]\Delta t = k[A]$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds (s^{-1}).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

where $[A]_0$ is the initial concentration of reactant A at t = 0; k is the rate constant; and e is the base of the natural logarithms, which has the value 2.718 to three decimal places.

Recall that an integrated rate law gives the relationship between reactant concentration and time. the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and *t*:

$$\ln[A] = \ln[A] - kt f_0[A] = \ln f_0[A] - kt$$

Because has the form of the algebraic equation for a straight line, y = mx + b, with $y = \ln[A]$ and $b = \ln[A]_0$, a plot of $\ln[A]$ versus *t* for a first-order reaction should give a straight line with a slope of -k and an intercept of $\ln[A]_0$. Either the differential rate law or the integrated rate law can be used to determine whether a particular reaction is first order.



Second-Order Reactions:

The simplest kind of **second-order reaction** is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form $2A \rightarrow \text{products}$. A second kind of second-order reaction has a reaction rate that is proportional to the product of the concentrations of two reactants. Such reactions generally have the form $A + B \rightarrow \text{products}$. An example of the former is a dimerization reaction, in which two smaller molecules, each called a monomer, combine to form a larger molecule (a dimer).

The differential rate law for the simplest second-order reaction in which $2A \rightarrow$ products is as follows:

rate=
$$-\Delta[A]/2\Delta t = k[A]2$$

Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse ($M^{-1} \cdot s^{-1}$). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as L(mol·s). For the reaction 2A \rightarrow products, the following integrated rate law describes the concentration of the reactant at a given time:

$$1/[A]=1/[A]0+kt$$

Methods for Determination of Order of a reaction:

Integration method

- (1) Substitution method in integrated rate equation: (Hit and Trial method)
- (i) The method can be used with various sets of a, x, and t with integrated rate equations.
- (ii) The value of k is determined and checked for all sets of a, x and t.
- (iii) If the value of k is constant, the used equation gives the order of reaction.
- (iv) If all the reactants are at the same molar concentration, the kinetic equations are : 10 (For first order reactions)

$$k = 2.303 / t \log 10 (a/a - x)$$

Graphical Method

This method can be used when there is only one reactant.

If the plot of log [A] vs t is a straight line, the reaction follows first-order .

If the plot of 1/[A] vs t is a straight line, the reaction follows second order.

If the plot of $1/[A]^2$ is a straight line, the reaction follows third order.

Generally, for a reaction of nth order, a graph of $1/[A]^{n-1}$ vs t must be a straight line. Here [A] is the concentration of reactant at any given time of the reaction (other t =0). [A] = (a-x) where a is the initial concentration and x is the extent of reaction at time t. Half Life Method

This method is used only when the rate law involved by only one concentration term.

 $\begin{array}{l} t_{(1/2)} \ \infty \ a^{1-n} \\ t_{(1/2)} = k' \ 1/a^{n-1} \\ log \ t_{(1/2)} = log \ k' + (1-n)a \end{array}$

Graph of logt 1/2 vs log a, gives a straight line with slope (1-n), where 'n' is the order of the reaction.

Determining the slope we can find the order n.

If half life at different concentrations is given then.

$$(t_{1/2})_1 \alpha \frac{1}{a_1^{n-1}} \text{ and } (t_{1/2})_2 \alpha \frac{1}{a_2^{n-1}} \\ \therefore \frac{(t_{1/2})_1}{(t_{1/2})_2} = (\frac{a_2}{a_1})^{n-1}$$

Taking logarithm and rearranging

$$n = 1 + \frac{\log(t_{1/2}) - \log(t_{1/2})_2}{\log a_2 - \log a_1}$$

Plots of half-lives concentration $(t_{1/2} \propto a^{1-a})$:



This relation can be used to determine order of reaction 'n'

Van't Hoff Differential Method

As we know that, the rate of a reaction varies as the nth power of the concentration of the reactant where 'n' is the order of the reaction.

Thus, for two different initial concentrations C_1 and C_2 , equations can be written in the form

$$log(\frac{dC_1}{dt}) = logk + nlogC_1 \dots (i)$$

and

$$log(\frac{dC_2}{dt}) = logk + nlogC_2$$
....(ii)

Taking logarithms,

Subtracting Eq. (ii) from (i),

$$log(\frac{dC_1}{dt}) - log(\frac{dC_2}{dt}) = n(logC_1 - logC_2)$$

or

$$n = [\log(-(dC_1)/dt) - \log((dC_2)/dt)] \div [\log C_1 - \log C_2] \qquad \dots (iii)$$

 $-dc_1/dt$ and $-dc_2/dt$ are determined from concentration vs. time graphs and the value of 'n' can be determined.

Complex reactions

Parallel or Competing Reaction

The reactions in which a substance reacts or decomposes in more than one way are called parallel or side reactions.



If we assume that both of them are first order, we get.

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A] = k_{av}[A]$$

 k_1 = fractional yield of $B \times k_{av}$

 k_2 = fractional yield of C × k_{av}

If $k_1 > k_2$ then

 $A \rightarrow B$ main and

 $A \rightarrow C$ is side reaction

Let after a definite interval x mol/litre of B and y mol/litre of C are formed.

 $\frac{x}{y} = \frac{k_1}{k_2}$
i.e

$$\frac{\frac{d[B]}{dt}}{\frac{d[C]}{dt}} = \frac{k_1}{k_2}$$

This means that irrespective of how much time is elapsed, the ratio of concentration of B to that of C from the start (assuming no B and C in the beginning) is a constant equal to k_1/k_2 .



Consecutive or Sequential Reactions

This reaction is defined as that reaction which proceeds from reactants to final products through one or more intermediate stages. The overall reaction is a result of several successive or consecutive steps.

 $A \rightarrow B \rightarrow C$ and so on

• Decomposition of ethylene oxide $(CH_2)_2O \xrightarrow{k_1} CH_3CHO$ $CH_3CHO \xrightarrow{k_2} CO + CH_4$

For the reaction

$$A \xrightarrow{k_1} B \xrightarrow{K_2} C$$

$$-\frac{d[A]}{dt} = k_1[A]$$
.....(i)

$$\frac{d[B]}{dt} = k_1[A] - K_2[B]$$
....(ii)

$$\frac{d[C]}{dt} = k_2[B]$$
.....(iii)

Integrating equation (i), we get

t

$$[A] - [A]_o e^{-k_1}$$

Now we shall integrate equation (ii) and find the concentration of B related to time t.

$$\frac{d[B]}{dt} = k_1 [A] - k_2 [B] \Rightarrow \frac{d[B]}{dt} + k_2 [B] = k_1 [A]$$

substituting [A] as $[A]_0 e^{-k_1 t}$
 $\Rightarrow \frac{d[B]}{dt} + k_2 [B] = k_1 [A]_0 e^{-k_1 t} \qquad \dots (iv)$

Integration of the above equation is not possible as we are not able to separate the two variables, [B] and t. Therefore we multiply equation (4) by an integrating factor $e^{-k_1 t}$, on both the sides of the equation.

$$\left(\frac{d[B]}{dt} + k_2[B]\right) e^{k_2 t} = k_1[A]_{Q} e^{(k_2 - k_1)t}$$

We can see that the left hand side of the equation is a differential of $[B]e^{k_2 t}$

$$\therefore \frac{\mathrm{d}}{\mathrm{dt}} \left([\mathsf{B}] \, \mathrm{e}^{k_2 t} \right) = k_1 [\mathsf{A}]_0 \, \mathrm{e}^{(k_2 - k_1)t}$$
$$d\left([\mathsf{B}] \, \mathrm{e}^{k_2 t} \right) = k_1 [\mathsf{A}]_0 \, \mathrm{e}^{(k_2 - k_1)t} \, \mathrm{dt}$$

Integrating with in the limits 0 to t.

$$\left(\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} + k_2[\mathrm{B}]\right) \mathrm{e}^{k_2 t} = k_1[\mathrm{A}]_{\mathrm{Q}} \mathrm{e}^{(k_2 - k_1)t}$$

We can see that the left hand side of the equation is a differential of $[B]e^{k_2 t}$

$$\therefore \frac{\mathrm{d}}{\mathrm{dt}} \left([\mathbf{B}] \mathbf{e}^{k_2 t} \right) = \kappa_1 [\mathbf{A}]_0 \mathbf{e}^{(k_2 - k_1)t}$$
$$d\left([\mathbf{B}] \mathbf{e}^{k_2 t} \right) = \kappa_1 [\mathbf{A}]_0 \mathbf{e}^{(k_2 - k_1)t} \mathrm{dt}$$

Now in order to find [C], substitute equation (vi) in equation (iii), we get

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A]_0}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right]$$

$$\therefore \ d[C] = \frac{k_1 k_2 [A]_0}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right] dt$$

On integrating

$$\int d[C] = \frac{k_1 k_2 [A]_0}{(k_2 - k_1)} \int_0^t \left[e^{-k_1 t} - e^{-k_2 t} \right] dt$$

$$\Rightarrow [C] = \frac{k_1 k_2 [A]_0}{(k_2 - k_1)} \left[\left(\frac{e^{-k_1 t}}{-k_1} \right)_0^t - \left(\frac{e^{-k_2 t}}{-k_2} \right)_0^t \right] \Rightarrow [C] = \frac{k_1 k_2}{(k_2 - k_1)} [A]_0 \left[\left(\frac{e^{-k_1 t} - 1}{-k_1} \right) - \left(\frac{e^{-k_2 t} - 1}{-k_2} \right) \right]$$

$$\Rightarrow [C] = \frac{k_1 k_2}{k_2 - k_1} [A]_0 \left[\left(\frac{1 - e^{-k_1 t}}{k_1} \right) - \left(\frac{1 - e^{-k_2 t}}{k_2} \right) \right]$$

$$[C] = \frac{[A]_0}{k_2 - k_1} \left[k_2 (1 - e^{-k_1 t}) - k_1 (1 - e^{-k_2 t}) \right]$$

UNIT – IV–Surface chemistry and catalysis-SCY1214

Adsorption – types of adsorption – Adsorption of gases on solids – adsorption isotherm – Freundlich, Langmuir isotherms – Adsorption of solutes from solutions – applications – Role of adsorption in catalytic reactions - Ion exchange adsorption - basic principles in adsorption chromatography - catalysis - classification - characteristic of catalysts - Auto catalysis - Enzyme catalysis - Michaelis - Menten equation - Acid - base catalysis

Adsorption: The phenomenon of concentration or assimilation of a gas (or liquid) at the surface of a solid (or liquid) with which it is in close proximity or contact, is called adsorption. The material providing the surface upon which adsorption occurs ,known as adsorbent. The substance adsorbed or attached, is called the adsorbate. Examples of adsorbents are charcoal, silica gel, clay, fullers earth, alumina gel...



Difference between adsorption and absorption:

(1)	
Adsorption	Absorption
 (a) It is a surface phenomenon. Adsorbate molecules are held at the surface of adsor- bent 	Absorption occurs in the bulk of absorbing substance.
(b) Initially, rate of adsorption is rapid.	Absorption occurs at uniform rate.
(c) The concentration of the adsorbent surface is much more than that in the bulk.	Absorbed material is uni- formly distributed throught the bulk means concentra- tion is same throughout.
(d) E.g., water vapours on silica gel.	E.g., Water vapours are absorbed by anhydrous CaCl ₂ .

Types of adsorption:

- Physical adsorption(or physisorption) or vander waals adsorption: When a gas is adsorbed on the surface of a solid by the weak intermolecular forces of attraction (van der waals forces) without the formation of any chemical bond between the adsorbate and the adsorbent, it is called physical adsorption.
- Chemical adsorption or chemisorption or activated adsorption: When the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond, the process is called Chemical adsorption or chemisorption. Chemisorption takes place with formation of unilayer of adsorbate on adsorbent. It has high enthalpy of adsorption. It can take place at all temperature and With the increases in temperature, Chemisorption first increases and then decreases.



Difference between physosortion and chemisorption

ll	Physisorption	Chemisorption
1	Occurs due to van der Waals' force	Chemical Bond
2	Reversible	Irreversible
3	Not specific	Specific
4	Enthalpy of adsorption is low	Enthalpy of adsorption is high
5	More liquefiable gases are adsorbed readily	Gases which form compounds with adsorbent alone undergo chemisorption
6	Decreases with increase of temperature	Increases with increase of temperature
7	Low temperature is favorable.	High temperature is favorable
8	High pressure favors physisorption and decrease of pressure causes desorption	High pressure is favorable but decreases of pressure does not cause desorption
9	Results in multimolecular layers	Only unimolecular layer are formed
10	No activation energy is needed	High activation energy is needed
11	It is instantaneous	It is a slow process

Adsorption of gases on solids:The adsorption of the gases on solid surfaces of finely divided metals like Fe,Ni,Pt,Pd etc are affected the following factors.

1.Nature of gases:

• Easily liquefiable gases like(Hcl,NH3,Cl2)are adsorbed more easily than the permanent gases like H2,O2,N2 etc.

• The higher the critical temperature the more easily the gas is liquefied and consequently, more readily it is adsorbed.

2.Nature of adsorbent:

- The gas is observed that a gas is adsorbed to different extent by different solid adsorption material at the same temperature.
- Moreover, the greater the surface area of the adsorbent, greater is its adsorption capacity.
- Eg: Charcoal and silica gel are excellent adsorbents, since their structure is highly porous and hence large surface areas.

3.Effect of pressure:

• The extent of adsorption (x/m)where x is the mass of adsorbate , gas and m is the mass of the adsorbent)depends upon the pressure.



4.Effect of temperature:

- Physical adsorption: exothermic –increasing temperature, x/m decrease.
- Chemical adsoption: x/m initially increased after that decreased.



5. Activation of adsorbent:

- Mechanical rubbing of metallic adsorbents,
- Subjecting to some chemical reactions of metallic adsorbents.
- Sub-dividing the solid adsorbents into finer particles and hence ,increasing surface area.
- Strong heating in superheated steam of some adsorbents,

Adsorption of solutes from solutions

(1) The process of adsorption can take place from solutions also.

(2) In any solution, there are two (or more) components ; solute and solvent. The solute may be present in the molecular or ionic form.

(3) The extent of adsorption from solution depends upon the concentration of the solute in the solution, and can be expressed by the Freundlich isotherm.

(4)The Freundlich adsorption isotherm for the adsorption from solution is $x/m=kc^{1/n}$, where, x is the mass of the solute adsorbed, m is the mass of the solid adsorbent, c is the equilibrium concentration of the solute in the solution, n is a constant having value greater than one, k is the proportionality constant, (The value of k depends upon the nature of solid, its particle size, temperature, and the nature of solute and solvent etc.)

(5) The plot of x/m against c is similar to that Freundlich adsorption isotherm.

$$\log \frac{x}{m} = \log k + \frac{1}{n}\log c$$

Applications of adsorption:

- Activated charcoal is used for Removing coloring matter of sugar solution and the decolorating of vinegar.
- Silica and alumina gels are used as adsorbent for removing moisture and for controlling humidities of room.Charcoal adsorption filters are used for removing organic matter for drinking water drinking water

Langmuir Adsorption Isotherm:

In 1916, Irving Langmuir proposed another Adsorption isotherm which explained the variation of Adsorption with pressure. Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

Assumptions of Langmuir Isotherm

- Langmuir proposed his theory by making OF
- 1. Fixed number of vacant or adsorption sites are available on the surface of solid.
 - 2. All the vacant sites are of equal size and shape on the surface of adsorbent.

3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.

4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules allowing assumptions

$$A(g) + B(S) \xrightarrow{Adsorption} AB$$

- Where K_a represents equilibrium constant for forward reaction and K_d represents equilibrium constant for backward direction.
- According to Kinetic theory,
- Rate of forward reaction = K_a [A] [B]
- Rate of backward reaction = K_d [AB]

 $K_a [A] [B] = K_d [AB]$

Or,
$$\frac{K_a}{K_d} = \frac{\begin{bmatrix} AB \end{bmatrix}}{\begin{bmatrix} A \end{bmatrix}}$$

 $K = \frac{K_a}{K_a} = \frac{[AB]}{[A][B]}$

•

- At equilibrium, Rate of forward reaction is equal to Rate of backward reaction
- The above equation represents the equilibrium constant for distribution of adsorbate between the surface and the gas phase.
- Langmuir Equation which depicts a relationship between the number of active sites of the surface undergoing adsorption (i.e. extent of adsorption) and pressure.
- To derive Langmuir Equation and new parameter ' θ ' is introduced. Let θ the number of sites of the surface which are covered with gaseous molecules. Therefore, the fraction of surface which are unoccupied by gaseous molecules will be (1θ) .
- Now, Rate of forward direction depends upon two factors: Number of sited available on the surface of adsorbent, (1θ) and Pressure, P. Therefore rate of forward reaction is directly proportional to both mentioned factors

Rate of forward reaction $\propto P(1 - \theta)$

Rate of adsorption $\propto P(1 - \theta)$

- Or, Rate of adsorption = $K_a P (1 \theta)$
- Similarly, Rate of backward reaction or Rate of Desorption depends upon number of sites occupied by the gaseous molecules on the surface of adsorbent.

Rate of desorption $\infty \theta$

- Or, Rate of desorption = $K_d \theta$
- At equilibrium, rate of adsorption is equal to rate of desorption

 $K_a P (1 - \theta) = K_d \theta$

$$\theta = \frac{K_a P}{K_d + K_a P}$$
$$\theta = \frac{\frac{K_a}{K_d} P}{\frac{K_d}{K_d} + \frac{K_a}{K_d} P}$$

This is known as Langmuir Adsorption Equation.

$$K = \frac{K_a}{K_a}$$
$$\theta = \frac{KP}{1 + KP}$$

Catalysis:

Catalyst is defined as a substance ,a small amount of which alters (increases or decreases)the velocity of a chemical reaction by its mere presence ,without itself undergoing any change in mass and composition at the end of the reaction. This phenomenon of altering the velocity of a chemical reaction by the presence of catalyst, is called catalysis.

Positive catalyst

Negative catalyst

Auto catalyst: When a product formed in the course of reaction enhances the velocity of the reaction (or act as catalyst)the phenomenon, is called auto-catalysis. Thus the HYDROLYSIS of an ester by water is an auto catalytic process, since the acid is liberated.

 $RCOOR'+H_2O \rightarrow RCOOH+R'OH$

TYPES OF CATALYST:

Homogeneous catalyst:

The catalyst is present in the same phase as the reacting substances.

Heterogeneous catalyst:

The catalyst is present in a different phase from the reacting substances.

Characteristics of catalyst:

1) A catalyst remains unchanged in mass and chemical composition at the end of the reaction.

(2) A small quantity of the catalyst is generally sufficient to catalyses almost unlimited reactions

(i) For example, in the decomposition of hydrogen peroxide, one gram of colloidal platinum can catalyses litres of hydrogen peroxide.

(ii) In Friedel craft's reaction, anhydrous aluminium chloride is required in relatively large amount to the extent of 30% of the mass of benzene,

(3) The catalyst can not initiate the reaction: The function of the catalyst is to alter the speed of the reaction rather than to start it.

(4) The catalyst is generally specific in nature: A substance, which acts as a catalyst for a particular reaction, fails to catalyse the other reaction, different catalysts for the same reactant may for different products.

(5) **The catalyst can not change the position of equilibrium :** The catalyst catalyse both forward and backward reactions to the same extent in a reversible reaction and thus have no effect on the equilibrium constant.

\

ROLE OF ADSORPTION:

Catalyst is used to increase rate of reaction. Heterogeneous catalyst is used to increase rate of reaction in which catalyst is not in phase with reactants and products.

Role of adsorption in heterogeneous catalysis are

(i) Diffusion of reactants to the surface of the catalyst.

(ii) Reactants are adsorbed on the catalyst surface.

(iii) Occurrence of chemical reaction at catalyst surface.

(iv) Desorption

(v) Diffusion of reaction produsts away from the catalysts surface.



Ion exchange process: Ions of positive charge (cations) or negative charge (anions) in a liquid solution replace dissimilar and displaceable ions of the same charge contained in a solid ion exchanger •

- Ion exchanger contains immobile, insoluble, and permanently bound co-ions of the opposite charge
- • Water softening by ion exchange $Ca2+(aq) + 2NaR(s) \ll CaR 2(s) + 2Na + (aq)$

Adsorption chromatography:

- Adsorption chromatography is the oldest types of chromatography technique.
- It makes use of a mobile phase which is either in liquid or gaseous form.
- The mobile phase is adsorbed onto the surface of a stationary solid phase.

Basic principles of adsorption chromatography:

- Adsorption Chromatography involves the analytical separation of a chemical mixture based on the interaction of the adsorbate with the adsorbent.
- The mixture of gas or liquid gets separated when it passes over the adsorbent bed that adsorbs different compounds at different rates.
- Adsorbent A substance which is generally porous in nature with a high surface area to adsorb substances on its surface by intermolecular forces is called adsorbent.
- Some commonly used adsorbents are Silica gel H, silica gel G, silica gel N, silica gel S, hydrated gel silica, cellulose microcrystalline, alumina, modified silica gel, etc.

Michaelis -menton equation:

The general reaction scheme of an enzyme-catalyzed reaction is as follows:

$$\mathsf{E}{+}\mathsf{S}{-}{\rightarrow}\mathsf{k}1[\mathsf{ES}]{-}{\rightarrow}\mathsf{k}2\mathsf{E}{+}\mathsf{P}$$

The enzyme interacts with the substrate by binding to its active site to form the enzyme-substrate complex, ES. That reaction is followed by the decomposition of ES to regenerate the free enzyme, E, and the new product, P.

To begin our discussion of enzyme kinetics, let's define the number of moles of product (P) formed per time as V. The variable, V, is also referred to as the rate of catalysis of an enzyme. For different enzymes, V varies with the concentration of the substrate, S. At low S, V is linearly proportional to S, but when S is high relative to the amount of total enzyme, V is independent of S. Concentrations is important in determining the initial rate of an enzymecatalyzed reaction. A more thorough explanation of enzyme rates can be found here: Definition of Reaction Rate.

To understand Michaelis-Menten Kinetics, we will use the general enzyme reaction scheme shown below, which includes the back reactions in addition the the forward reactions:

$$E+S \longrightarrow k_1[ES] \longrightarrow k_2E+P$$
$$E+S \longleftarrow k_3[ES] \longleftarrow k_4E+P$$

Substrate Complex:

$$E+S \longrightarrow k_1 ESE+S \longrightarrow k_1 ES v_0$$

$$ES \longrightarrow k_2 E+SES \longrightarrow k_2 E+S v_0]$$

$$ES \longrightarrow k_3 E+PES \longrightarrow k_3 E+P v_0$$

$$E+P \longrightarrow k_4 ESE+P v_0=k_4[E][P]=0$$

The ES complex is formed by combining enzyme E with substrate S at rate constant k_1 . The ES complex can either dissociate to form E_F (free enzyme) and S, or form product P at rate constant k_2 and k_3 , respectively.

E, S, and the ES complex can equilibrate very rapidly. The instantaneous velocity is the catalytic rate that is equal to the product of ES concentration and k_2 the catalytic rate constant.

$$v_0 = k_2[E-S]$$

The total enzyme concentration (E_T) is equal to the concentration of free enzyme E (E_F) plus the concentration of the bound enzyme in ES complex:

 $[E]_{T}=[EF]+[ES](5)$ $K_{s}=k_{2}k_{1}=[E][S][ES](6)$ $K_{s}([E_{0}]-[ES])[S][ES](7)$ $[ES]=[E_{0}][S]K_{s}+[S](8)$ $v_{0}=(dPdt)_{0}=k_{3}[ES](9)$ $v_{0}=(dPdt)_{0}=k_{3}[E0][S]K_{s}+[S](10)$

At high substrate concentrations, $[S] >> K_s$

$$v_0 = (dPdt)_0 = k_3[E_0] = V_{max}$$



↓ We can then substitue $k_2[E_T]$ with V_{max} to get the **Michaelis Menten Kinetic Equation:** ↓ $v_o = (v_{max}[S])(k_M+[S])$



Acid-base catalysis:

acid-base reactions the addition or removal of a proton does not bring about any drastic change in the structure of the molecule or in its stability or reactivity.

It is a characteristic of reactions catalyzed by acids or bases, however, that the addition or removal of a proton either makes the substrate unstable, so that it decomposes or rearranges, or that it causes the substrate to become reactive toward some other species present in the system.

In cases of rearrangement, the regeneration of the catalyst often involves the removal or addition of a proton at a site other than that at which the initial addition or removal took place.

It is not necessary that the substrate in an acid- or base-catalyzed reaction should itself have marked acid-base properties, since even a very small extent of initial acid-base reaction may be enough to bring about the subsequent change.

Acid-catalyzed reaction:

Unsaturated compound frequently rearrange reversibly under the influence of acids to give products in which the double bond occurs in a new location. The interconversion of 2-butene and 1-butene is shown here:

 $\begin{array}{c} CH_{3}CH = CHCH_{3} + H_{3}O^{\dagger} \longleftrightarrow CH_{3}CH_{2}\overset{\dagger}{C}HCH_{3} + H_{2}O\\ CH_{3}CH_{2}\overset{\dagger}{C}HCH_{3} + H_{2}O \rightleftharpoons CH_{3}CH_{2}CH = CH_{2} + H_{3}O^{\dagger}. \end{array}$

Reversible dehydration of alcohols, acid-catalyzed. Under the influence of acids, alcohols generally undergo loss of water to give olefinic products. The dehydration of ethanol to ethylenene occurs as follows:

$$\begin{aligned} \mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{OH} + \mathrm{H}_{3}\mathrm{O}^{*} &\rightleftharpoons \mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{OH}_{2}^{*} + \mathrm{H}_{2}\mathrm{O} \\ \mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{OH}_{2}^{*} &\rightleftharpoons \mathrm{CH}_{3}\mathrm{CH}_{2}^{*} + \mathrm{H}_{2}\mathrm{O} &\rightleftharpoons \\ \mathrm{CH}_{2} &= \mathrm{CH}_{2} + \mathrm{H}_{3}\mathrm{O}^{*}. \end{aligned}$$

Base catalyzed reaction:

Self-condensation of aldehydes, the so-called aldol condensation, occurs readily, when catalyzed by bases, to give β -hydroxy aldehydes. The prototypeof this reaction is the conversion of acetaldehyde to β -hydroxybutyraldehyde, or aldol. The first step of this reaction is the production of an enolate ion (as in formation of the keto–enol tautomeric mixture), but this anion then reacts with a second molecule of acetaldehyde to give the product as shown below:

$$\begin{split} & \operatorname{CH}_3\operatorname{CHO} + \operatorname{OH}^- \rightleftharpoons \operatorname{[CH}_2\operatorname{CHO]}^- + \operatorname{H}_2\operatorname{O} \\ & \operatorname{CH}_3\operatorname{CHO} + \operatorname{[CH}_2\operatorname{CHO]}^- \rightleftharpoons \operatorname{CH}_3\operatorname{CH}(\operatorname{O}^-)\operatorname{CH}_2\operatorname{CHO} \\ & \operatorname{CH}_3\operatorname{CH}(\operatorname{O}^-)\operatorname{CH}_2\operatorname{CHO} + \operatorname{H}_2\operatorname{O} \rightleftharpoons \operatorname{CH}_3\operatorname{CHOHCH}_2\operatorname{CHO} + \operatorname{OH}^- \\ & \text{aldol} \end{split}$$

Distillation techniques: Fractional distillation - Steam distillation - Vacuum distillation. Chromatography: Elution analysis - Paper chromatography - Thin layer chromatography - Liquid chromatography - High performance liquid chromatography (HPLC) - Gas chromatography (GC).

Chromatography

Definition:

- Chrome colour, Graphy Technique
- It was invented by Russian Botanist Michael Tswet.
- They employed the technique to separate plant pigments like chlorophyll and xanthophyll using a column of calcium carbonate.
- The separated components appeared as coloured bands on the columns and hence the name chromatography.

Principle:

- It is based on the general principle of phase distribution.
- This method involves the removal of components of one phase from that phase when it flows to a secondary stationary phase.
- The stationary phase is always fixed in a column.
- The mobile phase is the solvent flow.
- Separation of two or more components is possible when the equilibrium constant for the distribution of these components vary between the two phases.
- i.e) the substance which interact with the stationary phase strongly will move slowly through the column, where as the substance which does not interact with the stationary phase will move rapidly.
- This results in the migration of components into separate regions and appearing as bands in the fixed phase.
 <u>Types:</u>
- ✤ Adsorption Chromatography
- Partition Chromatography
- Ion exchange Chromatography

Gas Liquid Chromatography:

It is also called as gas liquid partition chromatography.

Definition:

Gas chromatography is a common type of chromatography used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition.

Principle:

The sample solution injected into the instrument enters a gas stream which transports the sample into a separation tube known as the "column." (Helium or nitrogen is used as the so-called carrier gas.)

Fixed phase- liquid

Mobile phase- Gas

Process:

- ▶ In GLC the mixture to be separated is vaporized and sent through a column by flowing a inert gas such as He or H₂.
- The inert gas is called carrier gas which carries the gaseous mixture in the mobile phase.
- ▶ The column is packed with a solid, on the surface of which is adsorbed a liquid of very low volatility .
- ► The liquid serves as the stationary phase.
- The components of the mixture moves through the column at different rates due to selective phase distribution between their two phases and get separated.
- ▶ In general low boiling and high volatile compounds will move through the column faster than low volatile components because higher the vapour pressure of a gas, the lower will be its solubility in a liquid.
- Apart from volatility polar interactions will also affect the solubility of a solute in a solvent.
- The basic components of GLC is shown below.



- ▶ The column is kept in an oven whose temperature is controlled by thermostat and heating elements.
- The sample is introduced into the flow system at the injection pore.
- ▶ This unit is individually heated to facilitate the vaporization of the sample.
- As the sample is vapourised and swept into the column by carrier gas and its component is separated into individual bands in the carrier gas and passes into the detector.
- A simple detector system consist of a instrument called "katherometer" which measures the changes in the thermal conductivity of the gas stream.
- The instrument consist of an electrically heated wire which forms one arm of a wheatstone bridge.
- ► The wire assumes a steady temperature and resistance when the pure carrier gas flows over it as the separated components reaches the wire and its temperature increases as a result of the decrease in thermal conductivity of its surroundings.
- The consequent change in the system is measured by wheat stone bridge.
- The change in resistance is proportional to the concentration of the component.
- The bridge is coupled to a pen recorder and chromatogram consist of a plot of concentration of the components in the carrier gas Vs time.
- A typical gas liquid chromatogram is shown below.



High Performance/Pressure Liquid Chromatography(HPLC)

Definition:

► It is a chromatographic technique that can separate a mixture of compounds and to identify, quantify and purify the individual compounds of the mixture.

Principle:

- ▶ The separation is based on the analytes relative solubility between the two liquid phases.
- ▶ HPLC utilizes different types of stationary phase and analyte through the column.
- The detector provides a characteristic retention time for the analyte.

Components:

▶ It consists of a reservoir of mobile phase, a pump, a injector, a separation column and a detector.

Working:

- It is a type of liquid chromatography used to separate compounds that are dissolve in solution.
- A reservoir holds the solvent that is to be injected into the column.
- Compounds are separated by injecting a sample mixture onto the column.
- The different components in the mixture passes through the column at different rates due to their difference in their partition behaviour between the mobile phase and stationary phase.
- The mobile phase must be degassed to eliminate the formation of air bubbles.
- An injector is used to introduce the sample into the HPLC column.
- The column contains the chromatographic packing material needed to effect the separation process.
- This packing of materials is called the stationary phase.
- An injector is needed to collect the separated compound bands as they elute from the column.
- The mobile phase exist the detector and can send the waste or collected as a desired products.
- The detector generate the signals needed to generate the chromatogram on its display and to identify quantitatively the concentration of the sample constituents.
- The flow rate is adjusted of about 0.01 to 10 cm^3 per minute using the pump.
- Application:
- Used in both quantitative and qualitative applications.
- Used for molecular weight determination.
- Used in environmental chemistry.
- Used in green chemistry.
- Used in polymer chemistry for identification of nature of the polymer



Column Chromatography

It is an example for solid-liquid adsorption chromatography.

• Fixed phase- solid Mobile phase- liquid

Principle:

• A solid which is insoluble in the solvent is choosen as fixed phase.

• The mode of interaction between the components of the mixture and the fixed phase is adsorption.

• Hence this is called as adsorption chromatography.

Process:

• The basis of separation is selective adsorption of the components present in the liquid phase on the solid.

• A long thin column with few millimetre to several centimetre in diameter is used for effective separation.

• The column is made up of fused silica glass.

• The column is packed with an active solid such as silica gel or alumina, charcoal, calcium carbonate, magnesia, starch, sucrose, etc., are also used as solid adsorbents. For effective separation the solid adsorbent should be of uniform size particle with high specific area which can contribute to rapid equilibrium of the solute between the two phases.

• The column has to be filled with suitable adsorbent carefully to avoid air gaps.

• The adsorbent is usually made into a paste using solvent like petroleum ether poured into the column and allow to settle .

• During the packing continuous tapping of column with glass rod is required for uniform packing.

• After packing the column with adsorbent a small liquid sample is poured on the top.

• The sample gets adsorbed on the top of the column and eluting solvent is allowed to flow through the column.

• This solvent carries the component of the mixture with it because of the selective adsorption capacity of the solid phase.

• These component moves down the column at different rates.

• The separated components may be recovered from the column by two ways.

1. The solvent can be sent through the column until the bands are eluted from the bottom of the column and collected in different containers.

2. If the solid can be extruded from the column in one piece, the portion of the solid containing different bands may be cut out separately and extracted with appropriate solvents. This method is difficult than the earlier method. The eluting power of the solvent is given as, n-C6H14 < CCl4 < C6H6 < CHCl3 < C2H5OC2H5 < CH3COCH3 < C2H5OH < H2O

Applications:

•Used to remove small amount of impurities whose structure differ widely from that major component. •Used for separation of structurally similar components . Homogeneity of coloured compounds can be tested easily.

Thin Layer Chromatography

It is an example for solid-liquid adsorption chromatography.

Principle:

•A solid which is insoluble in the solvent is chosen as fixed phase.

•The mode of interaction between the components of the mixture and the fixed phase is adsorption. •Hence this is called as adsorption chromatography.

Nature of phases: Stationary Phase- Solid

Mobile phase- Liquid Process: Preparation of TLC plates:

•The solid adsorbents like silica gel or alumina are used in TLC.

•A thin layer plate is prepared by spreading an aqueous slurry(paste) of the finely ground solid adsorbent on the clean surface of a glass or plastic plate.

•A small of binder such as plaster of paris, CaSO4, starch etc., is incorporated into the slurry to increase adhesion of the solid property to the glass and to one another.

• The plate is heated in an oven for half an hour and cooled inside the oven itself

. • Care should be taken to avoid the exposure of surface to the atmosphere because the moisture get adsorbed on the plate present in the atmosphere. Plate Development:

• A drop of the solution mixture to be separated is placed in one edge of the plate and its position is marked with a pencil.

• The plate is then placed in a container and the chamber is closed in along with the glass plate. • The solvent migrates up in the plate carrying the mixture and the components of the mixture is developed on the plate at different rates.

• Once the solvent has reached the top edge, the plate is removed and dried.

- Coloured material appeared as dots in the chromatogram.
- A number of methods are available for coating the spot of the colourless material.

• There are some detecting agents which sprayed on the chromatogram make the spot coloured.

• Eg., Sulphuric acid and KMnO4 solution. Iodine is also used as another detecting agent.

• Iodine is adsorbed by many organic compounds and consequently brown spots appear on the chromatogram. • Sometimes the location of the spots can be exhibited by fluorescent spectroscopy.

• Under a given set of conditions the rate of movement of a compound w.r.to the rate of movement of the solvent front is a characteristic property of a compound.

• This property is denoted by a symbol "Rf".

• Rf = Retardation / Retention factor.

• It is obtained by dividing the distance travelled by the solvent front from the original spot. \therefore Rf = A/B.Applications

: •The individual ion present in the mixture can be easily identified by this technique. •It is used to find out the best eluting agent for column chromatography.

•The technique is easy and can be done rapidly for analysis of mixture of composition. •Only a small quantity of the sample is required. Paper Chromatography It is an example for liquid –liquid partition chromatography.

Paper Chromatography:

•The fixed phase may be a solid on which liquid is adsorbed to form a stationary phase.

•Distribution of component of a mixture could occur between the adsorbed liquid and the flowing liquid due to difference in their solubility.

•The adsorbed liquid should be immiscible with the flowing solvent.

•This technique is called partition chromatography.

•Eg., Paper chromatography.

Types: •Ascending chromatography- The technique goes with its name as the solvent moves in an upward direction

•Descending chromatography- The movement of the flow of solvent due to gravitational pull and capillary action is downwards .

It is performed in the same way as thin layer chromatography.

Fixed phase- liquid

Mobile phase- liquidProcess:

•Specially prepared papers which are reproducible with respect to porosity and thickness are used. •Such paper contains sufficient porosity for adsorption and hence paper chromatography is classified as liquid-liquid chromatography.

•A milligram mixture of solution is spotted on the paper which is then dipped into the developing solvent.

•The paper is hanged vertically within a wide mouth bottle which contains one centimetre layer of solvent

The solvent rises by capillary action and the components are carried along with it at different rates. •When solvent reaches at most the top edge of the paper, the paper is removed and dried in an oven. •If the spots are colourless it may be rendered visible by treating with a n appropriate reagent.

•The paper is made up of cellulose acetate, starch, agar-agar etc.Applications:

•It is suitable for rapid analysis of reaction mixture because the method is very simple.

•Compounds may be identified by comparing the Rf values because the Rf values produced by paper chromatography are more reproducible than Rf values by TLC.Paper Electrophoresis

• It is a process in which separation of amino acids can be carried out.

• Ascending chromatography cannot be applied for substances having high molecular weight such as proteins or peptides since the separation are very slow.

• In such cases paper electrophoresis is the alternative method.

Process:

• A strip of paper is held horizontally between two container filled with a buffer solution.

• The paper is soaked with buffer and the sample to be separated is placed at the centre of the strip.

• A DC potential of 100-1000 volts is applied across the electrode which is dipped in the buffer solution. • The components of the mixture is separated by moving at different speeds in the applied electric field. • The paper acts as porous supporting material which prevents remixing by diffusion of the separated compounds.

• After passing the current for a suitable for a suitable period paper is removed and dried.• The separated zones are rendered visible by spraying a suitable detecting agent.

• This method is applicable only to the substances such as acids, bases, amino acids and proteins which carry charge in a buffer of a suitable pH.

• Careful choice of buffer is n essential requirement of electrochromatography.

• In general the pH of the buffer should be roughly in the middle of a Pka range of the components to be separated.

• This technique is applied for water soluble substances if the aqueous buffer can be replaced by organic buffer such as pyridine acetic acid or trimethyl amine formic acid.

Applications:

• Used in clinical diagnosis.

• Used in separation of large molecules such as protein present in the serum such as spinal fluid, gastric juice and other body fluids.

• Inorganic ions can also be separated by this method.

• It is also a valuable tool for the separation of carbohydrates, amino acids, vitamins etc.

Distillation:

Definition:

It is the process of separating the components or substances from a liquid mixture by using selective boiling and condensation.

Principle:

- A liquid present in a closed space will evaporate giving off vapour until the vapour attains a definite pressure.
- This pressure depends on the temperature and the vapour pressure of a liquid in contact with its own liquid is a constant at given temperature.
- It is independent of the absolute amount of liquid and vapour pressure in the system.

The distillation apparatus consists of,

- Distillation flask
- Thermometer
- Round bottom flask
- Liebig condenser

- Funnel
- Condenser tube

Process:

- The liquid is boiled in the distillation flask, condensing the vapour produced by means of a Liebig condenser.
- The condensed pure liquid is collected in a receiver.
- All the joints in the distillation unit must be interchangeable standard joints.
- A small amount of silicone grease may be used at the joints so that dismantling will be easy.
- Sometimes lubrication may contaminate the liquid.
- Bumping of the liquid during boiling may be avoided by adding unglazed porcelain bits.
- These bits should be added before the boiling process and never to be a heated liquid.

Aspects to be followed while distilling a liquid,

- A round bottom flask should be used and not the flat bottom flask.
- Heating must be slow and uniform using a bunsen flame or electric heater.
- The distillate should be collected separately.
- Reject the last portion of the liquid in the flask itself.
- The clamp should hold the coolest part of the neck of the flask.
- The bulb of the thermometer should be below the position where the side tube is fused into the neck of the flask.
- The thermometer tube should not be immersed inside the liquid.
- The glass units must be assembled tightly to avoid loss of vapour or liquid.
- The distillation should be stopped when some liquid is left in the flask.
- Flammable liquids like ethanol, benzene, carbon disulphide etc., should never be heated with a bunsen burner.
- They must be distilled with a steam-bath or controlled electric heating mantle.



Fig.5.1. Distillation Apparatus

Vapor Pressure vs Temperature of Water



Fractional Distillation:

Definition:

It is a method of separating two or more liquids having different boiling points.

Principle:

When a mixture of two liquids is boiled, the vapour phase is richer in the more volatile component than the boiling liquid with which it is in equilibrium at any given temperature.

Eg: If the component A is more volatile than B then,

Partial pressure of A/ Partial pressure of B > 1

or

mole fraction of A in the V.P/ mole fraction of B in the V.P >

mole fraction of A in the L.P/ mole fraction of B in the L.P

 \therefore it is a method used to separate liquids which are miscible with one another

and the boiling point of two liquids should be far from each other.

Eg: A mixture of benzene and toluene have boiling point at 80° C and 110° C can be separated by fractional distillation.

Procedure:

- The mixture of liquids is distilled by heating the flask electrically.
- Care should be taken that the condensed liquid does not drop into the receiver at rapid rate than one drop per second.
- In this distillation a special type of fractionating column is attached to the top of the distillation flask.
- As a mixture of vapour of the two liquids rises in the column the vapours of the higher boiling liquid will condense and fall back into the flask.
- Whereas the vapours of the lower boiling liquid will alone go the top of the column and escape into the condenser.

- The process will proceed slowly and eventually.
- Separate fractions are collected at 3 or 5°C.
- Any distillate passing over between 80.2°C and 81.2°C will be rich in benzene.
- Pure toluene will distills at 110.6°C.
- Each component must be collected at closed temperature ranges as possible.
- Complete separation is not possible at one distillation process.
- The fractionalized liquid should be separately distilled for effective purity of a component.
- Repeated fractionations will give pure component.

Conditions for good fractionation:

- There should be large amount of liquid continuously running through the column.
- Thorough mixing of liquid and vapour should occur.
- A large effective surface area between liquid and vapour should be available.
- There should not be excess cooling in the column.



Steam Distillation:

Definition:

It is a process in which the separation and purification of volatile organic compounds which are immiscible in water is distilled by steam distillation.

Principle:

In this method a current of steam is blown through the substances to be distilled.

The steam escapes from the substance carrying with it only the volatile component which is being separated from the impurities.

Eg: Mixture of benzene and water.

As the temperature is raised the sum of the two pressures reaches the atmospheric pressure and at this temperature the mixture boils.But this temperature is less than 80°C which is the boiling point of the benzene.Actually the temperature is 69.3° C and partial pressure of benzene is 533mm and for water is 227 mm.: a mixture of benzene and water distills at 69.3° C until one or the other material is exhausted in the distillation flask.Thus passing steam through the benzene will remove as a distillate and this operation is called steam distillation.

Process:

- The organic compound to be distilled is placed in a round bottom flask with a claisen head, which is equipped with a head connected to a water cool condenser?
- The claisen head prevents splattering of the mixture into the condenser during distillation.
- Steam is produced externally in a steam generator and passed through a long tube reaching almost the bottom of the distillation flask.
- Water may condense in the distillation flask filling into the inconvenient levels.
- This problem is avoided by heating the flask gently using bunsen burner or connecting with a bent adapter.
- Instead of passing through the liquid water can be added to the organic compound to be distilled in the distillation flask. This mixture is heated directly to generate steam inside and it is best suitable for steam distillation of small amount of soft liquids.

Precautions:

Steam should be turned off only after opening the pinch clamp on the bent adapter exit tube otherwise due to the development of vacuum in the distillation flask the distilled liquid from the receiver will go back into track.

Uses:

- > Used in chemical industries for separating turban oil from crude pine oil.
- > Used for separating volatile components of several classes.
- Provides a method of separation of volatile liquids and volatile solids which are insoluble in water from non-volatile substance under mild conditions.



Definition:

It is technique for distilling organic liquids having high boiling temperature.

Principle:

The boiling point of the liquid is that the temperature at which the total vapour pressure is equal to the atmospheric pressure from this it follows that when the external pressure increases the pressure above the liquid is reduced. Hence the boiling point will be decreased. When vacuum is applied(no pressure) the boiling point should be minimum at intermediate pressure... the boiling will be intermediate and hence normal distillation is effective under diminished pressure.

Need to adopt under diminished pressure:

- A certain liquids have high boiling points ... distillation of these under vacuum is easy.
 In many cases boiling temperature at atmospheric pressure ae too high because the compound being distilled may get oxidised or decompose or undergo molecular rearrangements.
- Sometimes impurities present in the liquid may catalyse some reactions at high temperature.



Fig. 1.12. Vacuum Distillation Apparatus

Process:

- For distillation under reduced pressure the distillation apparatus consists of a distillation unit having provision for as aspirator(water pump) or a mechanical oil pump.
- An aspirator commonly reduces the pressure to above 25mm and oil pump to below 1mm.
- The flask should be made up of stout glass otherwise low pressure due to insight it may collapse.
- The distillation apparatus should be tightly assembled with no leakage or loose joints.
- The ground glass joints surfaces of the distillation unit may be lubricated using vaseline or silicon grease.
- Bumping is much more pronounced in distillation under diminished pressure than in ordinary distillation this is avoided by the introduction of a bit of porcelain materials.

- Another way of avoiding bumping is to have a glass tube fitted to the neck of the flask.
- This tube drawn out at its lower end to a capillary which dips into the liquid and closed using a piece of rubber and small screw clamp at its upper end.
- With this arrangement the passage of air into the distilling flask is easily regulated.
- The pressure inside can be read using manometer which is connected to the system between the pump and the distillation unit.

Approximation need to follow for vacuum distillation:

- ➤ When the pressure is reduced from 760mm to 25mm, the boiling of a high boiling liquid(250-300°C) is reduced by about 100-125°C.
- Below 25mm,each time the pressure is halved, the boiling point is reduced by about 10°. The exact boiling points at different pressures can also be calculated using the Clausius-Clapeyron equation.

REFERENCE:

Puri Sharma and pathaniya., physical chemistry

j.laidler.,chemical kinetics

atkins.P.W.,Physical chemistry