UNIT-4

Photochemistry:

Photochemistry is a branches of chemistry that studies about chemical effects of light. It is concerned with chemical reaction, isomerization and physical behavior that may happen due to the influence of visible and ultraviolet light.

laws of photochemistry:

a).**Lambert's law:**

When a beam of monochromatic radiation passes through a homogeneous absorbing medium,the rate of decrease of intensity of the radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation.

b).**Lambert-beer's law**:

When a beam of monochromatic radiation is passed through a solution ,the rate of decrease of intensity of the radiation with the thickness of the solution is proportional to the intensity of incident radiation and the concentration of solution.

c).Grothus-Drapper law:

When light falls on matter ,it may be transmitted,reflected,refracted,scattered,or absorbed.There cannot be a photochemical reaction unless the radiation is absorbed.

d)**Einstein's law :**

Each molecule taking part in a photochemical reaction absorbs one quantum of radiation.

APPLICATIONS:

1.Photosynthesis:

It occurs in visible light for which both the reactant carbondioxide and water are transparent and takes place through absorptionof light energy by chlorophyll.

           hv

   $6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$
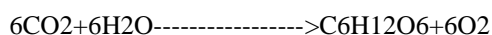
2.Photoelectric effect:

When some metals absorb light,electrons are ejected from the metals.This is known as photo electric effect.

3.Photography:

When silver bromide is exposed tosun light,silver ion to reduced to silver which for us the negative of photography.

A photochemical reactions differ from a thermal reaction.

A photo chemical reaction is caused by exposure to light of suitable wavelength only.

A photo chemical reaction does not depend upon temperature.

The temperature co-efficient of a thermal reaction is generally very large as compared with that of a photochemical reaction.

A thermal reaction is always accompanied by a decrease in free energy where as a large number of photochemical reactions are accompanied by increase of free energy.(e.g) photosynthesis.

Chromatography:

Chromatography is a laboratory technique for the separation of a mixture. The mixture is dissolved in a fluid called the mobile phase, which carries it through a structure holding another material called the stationary phase

Column Chromatography

Column chromatography is a technique which is used to separate a single chemical compound from a mixture dissolved in a fluid. It separates substances based on differential adsorption of compounds to the adsorbent as the compounds move through the column at different rates which allow them to get separated in fractions.

Principle:

Principle of involved in this technique is the separation of components by adsorption.

Applications:

- Column Chromatography is used to isolate active ingredients.
- It is very helpful in Separating compound mixtures.
- It is used to determine drug estimation from drug formulations
- It is used to remove impurities.
- Used to isolation metabolites from biological fluids

paper chromatography:

Paper Chromatography consists of two phases:

one mobile phase and one contiguous stationery phase. The stationery phase a paper and the mobile gas is solvent.

Paper chromatography is a chromatography technique used to separate mixture of chemical substances into its individual compounds. Paper used in paper chromatography is made of cellulose.

A suitable solvent (mobile phase) is moved along with a compound mixture through the paper according to the polarity and the degree of adhesion of each component on the stationery phase.

The ratio of the distance that the compound travelled and the distance that the solvent travelled is denoted as Rf.

Advantages:

- Paper Chromatography requires very less quantitative material.
- Paper Chromatography is Cheaper compared to other chromatography methods.
- Both unknown inorganic as well as organic compounds can be identified by paper chromatography method.
- Paper Chromatography do not occupy much space.compared to other analytical methods or equipments.

Thin layer chromatography:

Thin Layer Chromatography is a technique used to isolate non-volatile mixtures. The experiment is conducted on a sheet of aluminium foil, plastic, or glass which is coated with a thin layer of adsorbent material. The material usually used is aluminium oxide, silica gel.

On completion of the separation, each component appears as spots separated vertically. Each spot has a retention factor (Rf) expressed as:

Rf = dist. travelled by sample / dist. travelled by solvent

The factors affecting retardation factor are the solvent system, amount of material spotted, absorbent and temperature. TLC is one of the fastest, least expensive, simplest and easiest chromatography technique

Principle

  Thin layer chromatography (TLC) depends on the separation principle. The separation relies on the relative affinity of compounds towards both the phases. The compounds in the mobile phase move over the surface of the stationary phase. The movement occurs in such a way that the compounds which have a higher affinity to the stationary phase move slowly while the other compounds travel fast. Therefore, the separation of the mixture is attained. On completion of the separation process, the individual components from the mixture appear as spots at respective levels on the plates. Their character and nature are identified by suitable detection techniques.

Procedure: components required

Thin Layer Chromatography Plates – ready-made plates are used which are chemically inert and stable. The stationary phase is applied on its surface in the form of a thin layer. The stationary phase on the plate has a fine particle size and also has a uniform thickness.

Thin Layer Chromatography Chamber – Chamber is used to develop plates. It is responsible to keep a steady environment inside which will help in developing spots. Also, it prevents the solvent evaporation and keeps the entire process dust-free.

Thin Layer Chromatography Mobile phase – Mobile phase is the one that moves and consists of a solvent mixture or a solvent. This phase should be particulate-free. The higher the quality of purity the development of spots is better.

Thin Layer Chromatography Filter Paper – It has to be placed inside the chamber. It is moistened in the mobile phase.

Applications:

- The qualitative testing of Various medicines such as sedatives, local anaesthetics, anticonvulsant tranquilisers, analgesics, antihistamines, steroids, hypnotics is done by TLC.
- TLC is extremely useful in Biochemical analysis such as separation or isolation of biochemical metabolites from its blood plasma, urine, body fluids, serum, etc.
- Thin layer chromatography can be used to identify natural products like essential oils or volatile oil, fixed oil, glycosides, waxes, alkaloids, etc
- It is widely used in separating multicomponent pharmaceutical formulations.
- It is used to purify of any sample and direct comparison is done between the sample and the authentic sample
- It is used in the food industry, to separate and identify colours sweetening agent, and preservatives
- It is used in the cosmetic industry.
- It is used to study if a reaction is complete.

Emulsion:

An emulsion is a colloidal system in which both the dispersed phase and dispersion medium are liquids. An emulsion may be defined as a dispersion of finely divided liquid droplets in another.

Properties:

- Emulsions contain both a continuous and the dispersed with the boundary coming between the phases that are called "interface".
- Emulsions have a cloudy appearance due to many phase interfaces scattering light passing through the emulsions.
- Emulsions appear in white colour when the light is dispersed in equal proportions.
- If the emulsion is dilute, then higher-frequency and the low-wavelength type of light will be scattered in more fractions, and this kind of emulsion will appear in blue in colour. This is also referred to as the Tyndall effect.

Types:

1) Oil in water (O/W):

In this type of emulsion, the oil will be the dispersed phase and water will be the dispersion medium. The best example for o/w emulsion is milk. In milk, the fat globules (which act as the dispersed phase) are suspended in water (which acts as the dispersion medium).

2) Water in oil (w/o):

In this type, water will be the dispersed phase and oil will be the dispersion medium. Margarine (a spread used for flavouring, baking and working) is an example of water in oil emulsion.

Preparation:

An emulsion is a dispersion of one liquid into another liquid in the form of small globules. Emulsions are generally prepared by dispersion methods. Most emulsions are prepared by mixing the two liquids along with a suitable emulsifier and then passing the mixture through a colloid mill or a similar appliance. One of the liquids, mainly decided by the emulsifier, is broken down by the shearing forces into small globules and an emulsion results. The continental method is used to prepare the initial or primary emulsion from oil, water, and a hydrocolloid or "gum" type emulsifier (usual acacia). It can either be oil-in-water (O/W) or water-in-oil (W/O), be depending on whether the continuous phase is the water or the oil, respectively. In other methods, the liquid to be dispersed is forced through a narrow capillary and injected directly into the dispersion medium containing the emulsifier as shown in Figure.

Injection Method for preparation of Emulsion
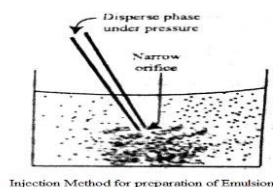
Under the pressure in the nozzle, the dispersed phase is broken down into small globules giving rise to an emulsion. The emulsifier could also be dissolved in the dispersed phase. The most common example of the emulsion is milk where small fat globules are dispersed in water, protein brings the principle stabilizer.

Applications:

- Usually used in cosmetics, pharmaceuticals, personal hygiene.
- Microemulsions are used to deliver vaccines to kill various microbes.
- It is used in chemical synthesis mainly in the manufacture of polymer dispersions.

- It is used in firefighting.

Gel:

A gel is a jelly-like colloidal system in which a liquid is dispersed in a solid medium.When a hot solution of gelatin is cooled it sets to a semi- solid mass.

Examples: jellies,gelatine,agar-agar,aluminium hydroxide etc.

Preparation:

1)by cooling:Gels are prepared by dissolving them in hot water and allowing the solution to cool.

2)by coagulation:Adding a coagulating agent to the colloidal solution gives a gel.Gels of Al(OH)3 and Fe(NO)3 may be prepared by adding salts as coagulating agents to their solutions.

3)by double decomposition:

When dilute acid is added to sodium silicate,silicic acid is obtained.

Na2SiO3 +2HCl ---------->H2SiO3+2NaCl
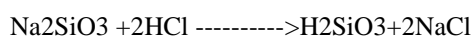
4)by exchange of solvent:Gels may be formed by changing suddenly the solvent in which the substance is insoluble.

Classification:Dry gels are called xerogels.(examples)gelatin sheets and cellophane.Gels are classified in to two types:elastic gels,non-elastic gels.

Properties:Hydrations ,swelling,syneresis,thixotropy.

Applications:

- It can be used as a dehydrating agent.
- It is used in laboratories for making liquid junctions in electrochemistry.
- Curds and eatable jellies are forms of gels.
- Protected gels are used in food preparations.
- Boot polishes and animal tissues have gel structures.
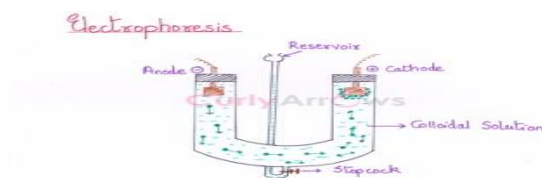
 electrophoresis:.

The colloidal particles carry specific charge.When current is passed through colloidal solution the colloidal particles migrate and when the dispersion medium

doesnot migrate the phenomenon is known as electrophoresis.

Burton tube experiment:

The colloidal solution is taken in a U tube such that level in the two limbs are same.Two platinum electrodes are dipped in electrolytic solution.When current is passed,the

colloidal particles move towards the electrodes.The charge of the particles can be ascertained from the direction of the movement of the boundary.

Applications:

- Electrophoresis is an important industrial process.It is useful.
- To classify colloids as positive or negative colloids.
- For the removal of smoke from chimney gases.
- For the removal of suspended impurites.
- Electro-deposition of rubber on metal surfaces from latex

UNIT-5

specific conductivity.

Specific conductivity (better known as conductivity) is the measure of the ability of that electricity. It is represented by the symbol "K". It is represented by the symbol "K".

equivalent conductivity.

It is defined as the conducting power of all the ions produced by dissolving one gram equivalent of the solution. where C is the concentration in gram equivalent per litre (or Normality). This term has earlier been quite frequently used.

Cell constant:

The ratio of distance between conductance-titration electrodes to the area of the electrodes, measured from the determined resistance of a solution of known specific conductance.

kohlrauschs law:

It States that the equivalent conductivity of an electrolyte at infinite dilution is equal to the sum of the conductances of the anions and cations.

Kohlrausch's law of independent migration of ions:
At infinite dilution, each ion migrates independently of its co-ion and makes its own contribution to the total molar conductivity of an electrolyte irrespective of the nature of other ion with which it is associated.

Thus, $\Lambda_0 = \lambda_{+0} + \lambda_{-0}$

Here,
Λ_0= the molar conductivity of the electrolyte at zero concentration
λ_{+0}= the molar conductivity of cation at zero concentration
λ_{-0}= the molar conductivity of anion at zero concentration

For example, $\Lambda_0(HCl) = \lambda_0(H_+) + \lambda_0(Cl_-)$

Here,
$\Lambda_0(HCl)$= the molar conductivity of HCl at zero concentration
$\lambda_0(H_+)$= the molar conductivity of protons at zero concentration
$\lambda_0(Cl_-)$= the molar conductivity of chloride ions at zero concentration

Application:

(i)   Determination of conductance for weak electrolytes : The molar conductivity of a weak electrolyte at infinite dilution cannot be determined by extrapolation method.

(ii)   Determination of the degree of ionisation of a weak electrolyte:

          Kohlrauscs equation the degree of ionisation at any concentration can be determined.

(iii)   Determination of the ionisation constant of a weak electrolyte : Weak electrolytes in aqueous solutions ionise to a very smallextent. Such an equilibrium can be described by a constant called ionisation constant.

(iv)   Determination of the solubility of a sparingly soluble salt : The solubility of a sparingly soluble salt in a solvent is quite low.

(v)   The molar concentration of the sparingly soluble salt in its saturated solution. Thus, is equal to the solubility of the sparingly soluble salt in the mole per litre units. The solubility of the salt in gram per litre units can be obtained by multiplying with the molar mass of the salt.

Ostwald's dilution law :

 It relates the dissociation constant of the weak electrolyte with the degree of dissociation and the concentration of the weak electrolyte. K a =dissociation constant of weak acid α = degree of dissociation. Ostwald's dilution law states that the weak electrolyte undergoes complete ionisation at infinite dilution only.

Ostwald's dilution law relates the dissociation constant of the weak electrolyte with the degree of dissociation and the concentration of the weak electrolyte.
$Ka = 1 - \alpha$ $K a \alpha 2 c$
=dissociation constant of weak acid
α= degree of dissociation.
Ostwald's dilution law states that the weak electrolyte undergoes complete ionisation at infinite dilution only.

Limitations:.

 The law holds good only for weak electrolytes and fails completely in the case of strong electrolytes. The value of 'α' is determined by conductivity measurements by applying the formula $\Lambda/\Lambda\infty$. The value of 'α' determined at various dilutions of an electrolyte when substituted in Eq. (i) gives a constant value of K only in the case of weak electrolytes like CH_3COOH, NH_4OH, etc. the cause of failure of Ostwald's dilution law in the case of strong electrolytes is due to the following factors"

(i)   The law is based on the fact that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution. Strong electrolytes are almost completely ionized at all dilutions and $\Lambda/\Lambda\infty$ does not give accurate value of 'α'.

(ii) When concentration of the ions is very high, the presence of charges on the ions appreciably effects the equilibrium. Hence, law of mass action its simple form cannot be strictly applied in the case of string electrolytes.

PH:

pH is a measure of hydrogen ion concentration, a measure of the acidity or alkalinity of a solution. The pH scale usually ranges from 0 to 14. Aqueous solutions at 25°C with a pH less than 7 are acidic, while those with a pH greater than 7 are basic or alkaline

Importance of PH:

• Soils of specific pH are required for optimum group growth and better yields of crops.
• Specific pH values are to be maintained for the biological process and industrial process to occur.
• Specific pH is also to be maintained by the blood.
• PH plays an important role in chemical analysis

.Buffer solutions

Buffers **are** solutions **th**at resist a change in pH on dilution or on addition of small amounts of acids or alkali. A lot of biological and chemical reactions need a constant pH for the reaction to proceed. Buffers are extremely useful in these systems to maintain the pH at a constant value.

.Importance of buffer solution:

- Blood as a Buffer Solution. Blood itself tends to be a buffer solution by keeping its pH value...
- Role of Buffers in Human Body. Reactions inside the human body take place in the blood plasma.
- The importance of Buffer Solutions to Human Body.
- The action of Buffers in Blood Plasma..

Conductometric Titration :

strong acid and strong base Strong Acid is an acid that is totally ionized in aqueous solution. This means when the strong acid is positioned in a solution such as water, all of the strong acids will detach into its ions, as contrasting to a weak acid.

Strong Base is a base that is totally ionized in aqueous solution. This means when the strong base is positioned in a solution such as water, all of the strong bases will detach into its ions.

In water, one mole of a strong acid HA dissolves yielding one mole of H^+ (as hydronium ion H_3O^+) and one mole of the conjugate base, A^-. Fundamentally, none of the non-ionized acid HA remains.

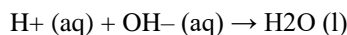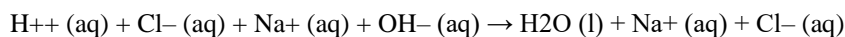Strong acid: $HA + H_2O \rightarrow A^-(aq) + H_3O^+(aq)$

Strong base: $BOH + H_2O \rightarrow B^+(aq) + OH^-(aq)$

An example of this would be the titration of hydrochloric acid (strong acid) and sodium hydroxide (strong base) to form sodium chloride and water.
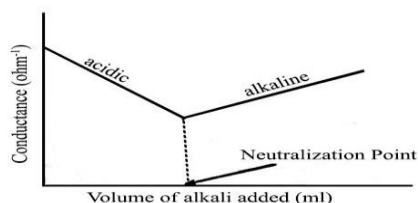
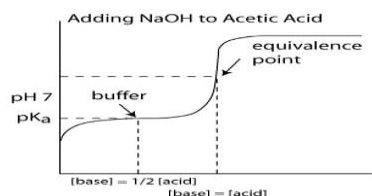Let us consider the titration of a solution of HCl by NaOH solution. Before NaOH is added, the conductance is high due to the existence of highly mobile hydrogen ions. The net reaction in this neutralization reaction is the production of water from H^+ and OH^-. The neutralization reaction is

$H^{++} (aq) + Cl^- (aq) + Na^+ (aq) + OH^- (aq) \rightarrow H_2O (l) + Na^+ (aq) + Cl^- (aq)$

$H^+ (aq) + OH^- (aq) \rightarrow H_2O (l)$

However, H^+ ion of the acid is gradually replaced by Na^+ as NaOH is added to the acid solution. Since the ionic conductance of H^+ is much higher than that of Na^+ there will be a decrease in the conductance as the addition of NaOH continues. This will go on until all the acid is neutralized.
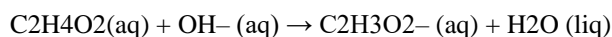
weak acid and strong base:

. For conductometric titration experiments, a known volume of the solution to be titrated is placed in a beaker and a conductivity cell dipped into it. The conductivity cell is now connected to one end of the Wheatstone's bridge.

Let us consider that ethanoic acid is titrated against NaOH. The initial conductance of the acid solution is very low because of the low ionization of the weak acid. However, as NaOH is gradually added to the acid solution a salt, CH3COONa, will be formed which ionizes readily to form Na+ and CH3COO– ions.

The titration of a weak acid with a strong base involves the direct transfer of protons from the weak acid to the hydroxide ion. The reaction of the weak acid, acetic acid, with a strong base, NaOH, can be seen below. In the reaction the acid and base react in a one to one ratio.

$C_2H_4O_2(aq) + OH^-(aq) \rightarrow C_2H_3O_2^-(aq) + H_2O(liq)$

In a titration of a Weak Acid with a Strong Base the titrant is a strong base and the analyte is a weak acid.

Conductometric titration:

Advantages:

- This process is very useful in the titrations of very dilute solutions and weak acids.
- The end-point of this method of titration is very sharp and accurate when compared to a few other titration processes.
- This type of titration is applicable for solutions that are coloured or turbid, and for which the endpoint of the titration with normal indicators cannot be observed easily by the human eye.
- Conductometric titration has numerous applications in acid-base titrations, redox titrations, precipitation titrations, and complex titrations.

Disadvantages :

- Only a few specific redox titrations can be done with the help of this process. This is because the conductivity of the solution is masked by relatively high hydronium ion concentration.
- The accuracy of conductometric titration is low when the concentrations of the electrolyte are high, making the titration process unsatisfactory.