Unit-I

Chapter-1-General Chemistry

Introduction to Chemical Sciences:

Chemical Science: It is the branch of science that deals with the composition, structure and properties of matter. Chemical science is called the science of atoms and molecule and very commonly we say it Chemistry.

Branches of Chemistry

| Branch	Area of Emphasis	Examples
Organic chemistry	most carbon-containing chemicals	pharmaceuticals, plastics
Inorganic chemistry	in general, matter that does not contain carbon	minerals, metals and nonmetals, semi-conductors
Physical chemistry	the behavior and changes of matter and the related energy changes	reaction rates, reaction mechanisms
Analytical chemistry	components and composition of substances	food nutrients, quality control
Biochemistry	matter and processes of living organisms	metabolism, fermentation
Theoretical chemistry	use of mathematics and computer to understand the principles behind observed chemical behaviors	Research laboratories often at universities

Basic concepts of the chemical sciences include the following areas:

1) **Periodicity:** It is the repeating patterns of chemical and physical properties. The properties of the elements are a periodic function of their atomic weights.

The periodic table:

i) The development of the periodic table took many years and involved scientists from several countries.

ii) Mendeleev grouped the known elements into families on the basis of their relative atomic masses and their chemical properties.

iii) He left gaps where no known elements fitted in and predicted the physical and chemical properties of these missing elements.

iv) In the modern periodic table the elements are arranged in order of increasing atomic number (Z).

v) Elements with similar chemical and physical properties are placed underneath each other in vertical columns called groups. The groups are numbered 1-18.

vi) Certain groups have their own names:- alkali metals- alkaline earth metals-pnictogens-chalcogens-halogens- noble gases.

vii) The period number is equal to the principal quantum number, n, of the highest occupied energy level in the elements of the period.

viii) Some chemical elements are called **metals**. They are the majority of elements in the periodic table. These elements usually have the following properties:

    i)   They can conduct electricity and heat.

    ii)   They can be formed easily.

    iii)   They have a shiny appearance.

    iv)   They have a high melting point.

ix) **Nonmetal**, substance that does not exhibit such characteristic properties of metals as hardness, mechanical adaptability, or the ability to conduct electricity. This classification is generally applied to the chemical elements carbon, nitrogen, phosphorus, oxygen, sulfur, selenium, fluorine, chlorine, bromine, iodine, and the noble-gas elements. These elements have few physical properties in common; most are gases, one (bromine) is liquid, and others are solids.

x) **Metalloid**, a chemical element with properties intermediate between those of typical metals and nonmetals. Usually considered under this classification are the chemical elements boron, silicon, germanium, arsenic, antimony, and tellurium. The rare elements polonium and astatine are also sometimes included. Most of these elements are important industrial materials, being used to make transistors and other semiconductor devices, ceramics, solar batteries, and certain polymers.

xi) **Transition metal**, they have very similar chemical and physical properties, relatively high melting point, high boiling point and high densities, they form more than one stable cation, and they often have colored compounds and colored solutions.

Figure 1: The periodic table
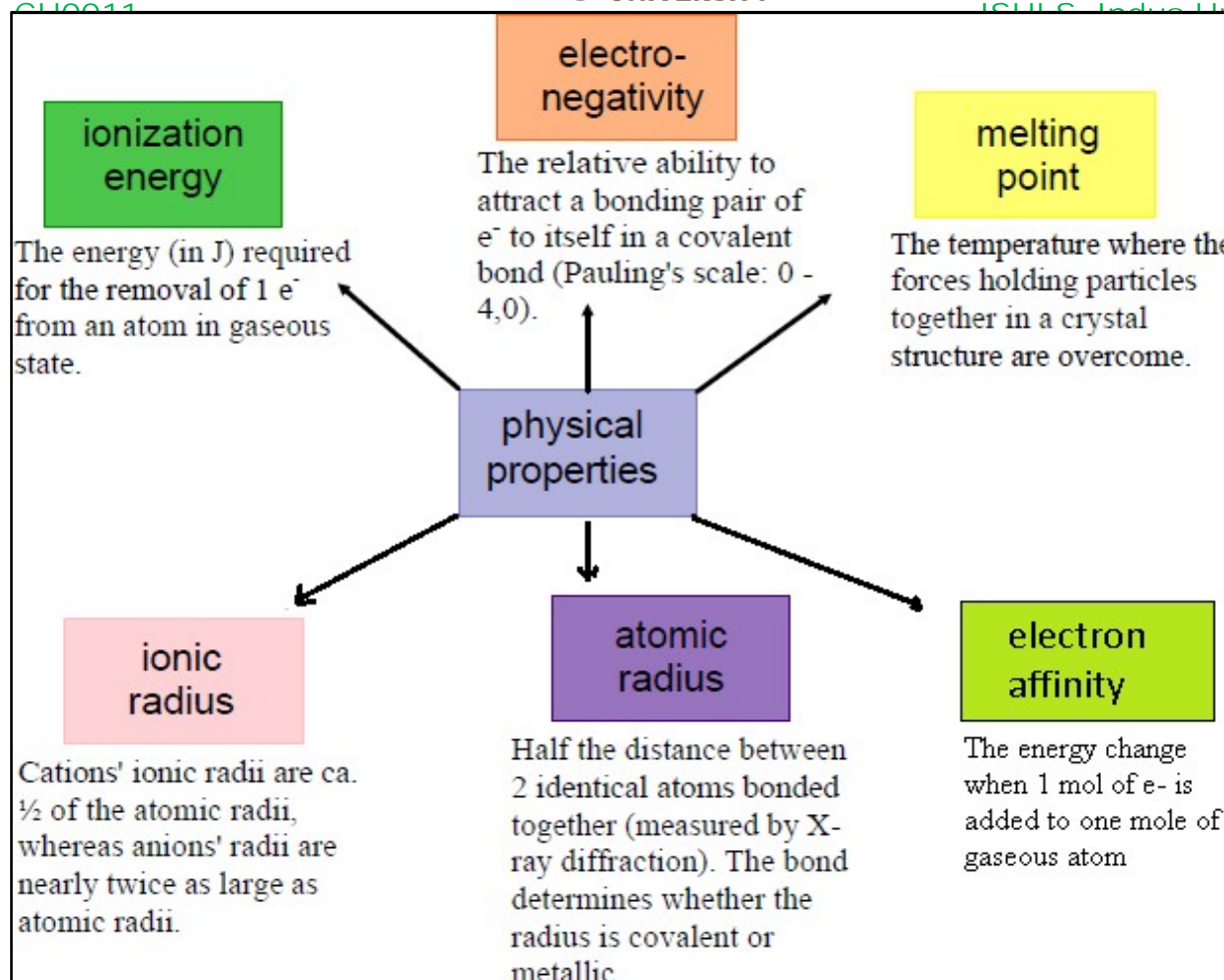
Figure 2: The physical properties of the elements
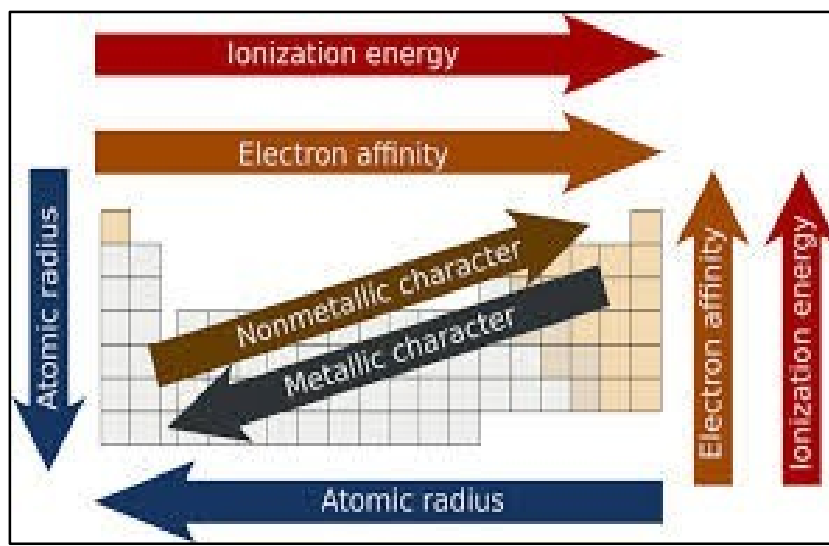
Figure 3: The trends of physical properties of the elements

Matter cannot be created or destroyed - That's why we must balance chemical
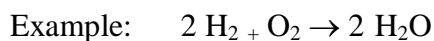
reactions

Types of reactions:-

The good news-there are only five main types of chemical reactions

1. ## Synthesis/Combination
   A type of reaction in which an element or compound combines with another element or compound to form a new compound

   Example: $2 H_2 + O_2 \rightarrow 2 H_2O$

2. ## Decomposition
   A type of reaction in which a compound breaks down into two or more elements or compounds

   Example: $CaCO_3 \rightarrow CaO + CO_2$

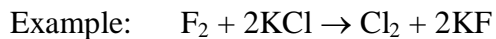3. ## Combustion
   A type of reaction in which a hydrocarbon reacts with oxygen to form carbon dioxide and water

   Example: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

4. ## Single displacement
   A type of reaction in which a compound and an element react to form a new element and a new compound

   Example: $F_2 + 2KCl \rightarrow Cl_2 + 2KF$

5. ## Double displacement
   A type of reaction in which two compounds react to form two different compounds.
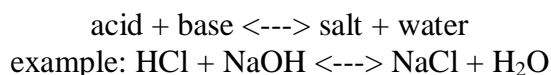
   Example: $AgNO_3 + KCl \rightarrow AgCl + KNO_3$

Various Acid Base Concepts:

Definitions of acids and bases:-
Arrhenius:- Acid: generates in [H^+] solution. Base: generates [OH^-] in solution.
Normal Arrhenius equation:
$$acid + base <---> salt + water$$
$$example: HCl + NaOH <---> NaCl + H_2O$$
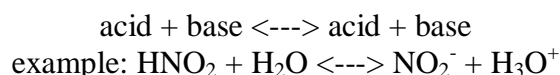
Bronsted-Lowery: The Brønsted/ Lowry Defintions: Specifies an acid as a proton donor and a base as a proton acceptor which applies to aqueous systems.

Acid: anything that donates a $[H^+]$ (proton donor). **Base:** anything that accepts a $[H^+]$ (proton acceptor)
Normal Bronsted-Lowery equation:

$$acid + base \longleftrightarrow acid + base$$
$$example: HNO_2 + H_2O \longleftrightarrow NO_2^- + H_3O^+$$

Each acid has a conjugate base and each base has a conjugate acid. These conjugate pairs only differ by a proton. In this example: HNO_2 is the acid, H_2O is the base, NO_2^- is the conj. base, and H_3O^+ is the conj. acid.
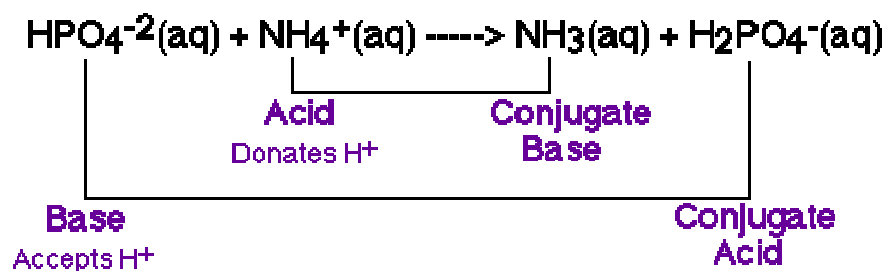

Acid-Base Character:-

For a molecule with a H-X bond to be an acid, the hydrogen must have a positive oxidation number so it can ionize to form a positive +1 ion. For instance, in sodium hydride (NaH) the hydrogen has a -1 charge so it is not an acid but it is actually a base. Molecules like CH_4 with nonpolar bonds also cannot be acids because the H does not ionize. Molecules with strong bonds (large electronegativity differences), are less likely to be strong acids because they do not ionize very well. For a molecule with an X-O-H bond (also called an oxyacid) to be an acid, the hydrogen must again ionize to form H^+. To be a base, the O-H must break off to form the hydroxide ion (OH^-). Both of these happen when dealing with oxyacids.

Strong Acids: These acids completely ionize in solution so they are always represented in chemical equations in their ionized form. There are only seven (7) strong acids:

$$HCl, HBr, HI, H_2SO_4, HNO_3, HClO_3, HClO_3, HClO_4$$

Strong Bases: Like strong acids, these bases completely ionize in solution and are always represented in their ionized form in chemical equations. There are only seven (7) strong bases:

$$LiOH, NaOH, KOH, RbOH, Ca(OH)_2, Sr(OH)_2, Ba(OH)_2$$
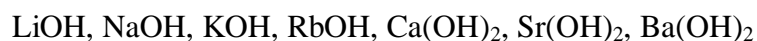
Acid Bases in Water:-

Proton transfer equilibria in water

We typically talk about acid-base reactions in aqueous-phase environments that is, in the presence of water. The most fundamental acid-base reaction is the <u>dissociation</u> of water:

$$H_2O \xleftrightarrow{\hspace{1cm}} H^+ + OH^-$$
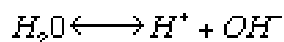
In this reaction, water breaks apart to form a hydrogen ion (H^+) and a hydroxyl ion (OH^-). In pure water, we can define a special equilibrium constant (K_w) as follows:

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$$

Where K_w is the equilibrium constant for water (unitless) $[H^+]$ is the molar concentration of hydrogen
$[OH^-]$ is the molar concentration of hydroxide. Equilibrium constant less than one (1) suggests that the reaction prefers to stay on the side of the reactants in this case, water likes to stay as water. Because water hardly <u>ionizes</u>, it is a very poor conductor of electricity.

pH:-

What is of interest in this reading, however, is the acid-base nature of a substance like water. Water actually behaves both like an <u>acid</u> and a <u>base</u>. The acidity or basicity of a substance is defined most typically by the <u>pH</u> value, defined as below:

$$pH = -\log[H^+]$$

At equilibrium, the concentration of H^+ is 10^{-7}, so we can calculate the pH of water at equilibrium as:

$$pH = -\log[H^+] = -\log[10^{-7}] = 7$$

Solutions with a pH of seven (7) are said to be neutral, while those with pH values below seven are defined as acidic and those above pH of seven (7) as being basic.

<u>pOH</u> gives us another way to measure the acidity of a solution. It is just the opposite of pH.

A high pOH means the solution is acidic while a low pOH means the solution is basic.

$$pOH = -\log[OH^-] \quad pH + pOH = 14.00$$

Salts:-

A salt is formed when an acid and a base are mixed and the acid releases H^+ ions while the base releases OH^- ions. This process is called hydrolysis. The pH of the salt depends on the strengths of the original acids and bases:

Acid	Base	Salt pH
strong	strong	pH = 7
weak	strong	pH > 7
strong	weak	pH < 7
weak	weak	depends on which is stronger

This is because the conjugate base of a strong acid is very weak and cannot undergo hydrolysis. Similarily, the conjugate acid of a strong base is very weak and likewise does not undergo hydrolysis.

Electrochemistry

INTRODUCTION

- **Electrochemistry is a branch of chemistry that studies chemical reactions which** take place in a solution at the interface of an electron conductor (the electrode: a metal or a semiconductor) and anionic conductor (the electrolyte).
- These reactions involve electron transfer between the electrode and the electrolyte or species in solution.
- If a chemical reaction is driven by an externally applied voltage, as in electrolysis, or if a voltage is created by a chemical reaction as in a battery, it is an electrochemical reaction.
- In contrast, chemical reactions where electrons are transferred between molecules are called oxidation /reduction (redox) reactions. In general, electrochemistry deals with situations where oxidation and reduction reactions are separated in space or time, connected by an external electric circuit**.**

Definitions

- **Electrolysis:** The chemical decomposition of an electrolyte caused by the passage of electricity is called electrolysis.
- **Electrolyticcells:** The cells used for the process of electrolysis are known as Electrolytic cells.
- **Galvanicorvoltaic cells:** The cells used for generation of electric energy from chemical reactions are called Galvanic or voltaic cells.
- **Saltbridge:** The salt bridge is the bridge placed between the two half cells of the galvanic cell. (A saturated soln. of KCl or NH4NO3 in agar-agar gel is used as salt bridge.)
- **EMF:** The difference of potential which causes the flow of current from one electrode which is higher potential to the other electrode which is a lower potential is called electromotive force.
- **ElectrodePotential:** The tendency of an electrode to lose electrons is called oxidation potential and the tendency of an electrode to gain electrons is called the reduction potential.

Electrochemical cell

- An electrochemical cell is a device that produces an electric current from energy released by a spontaneous redox reaction.
- This kind of cell includes the Galvanic cell or Voltaic cell.
- Electrochemical cells have two conductive electrodes (the anode and the cathode).
- The anode is defined as the electrode where oxidation occurs and the cathode is the electrode where the reduction takes place.
- Electrodes can be made from any sufficiently conductive materials, such as metals, semiconductors, graphite, and even conductive polymers.
- In between these electrodes is the electrolyte, which contains ions that can freely move.

- The study of the exchange of chemical and electrical energy.
- Oxidation-Reduction reactions take place in <u>electrochemical cells.</u>
- Each electrochemical cell consists of two solid conductors called electrodes.

There are 2 types of cells:
- Galvanic/ VoltaicCell
- Electrolytic Cell

Galvanic / Voltaic Cell
- The galvanic cell uses two different metal electrodes, each in an electrolyte where the positively charge dions are the oxidized form of the electrode metal.
- One electrode will undergo oxidation (the anode) and the other will undergo reduction (the cathode).
- The metal of the anode will oxidize, going from an oxidation state of 0(in the solid form) to a positive oxidation state and become anion.
- At the cathode, the metal ion in solution will accept one or more electrons from the anode and the ion's oxidation state is reduced to 0. This forms a solid metal that electrodeposits on the cathode.
- The two electrodes must be electrically connected to each other, allowing for a flow of electrons that leave the metal of the anode and flow through this connection to the ions at the surface of the cathode.
- This flow of electrons is an electrical current that can be used to do work, such as turn a motor or power a light.
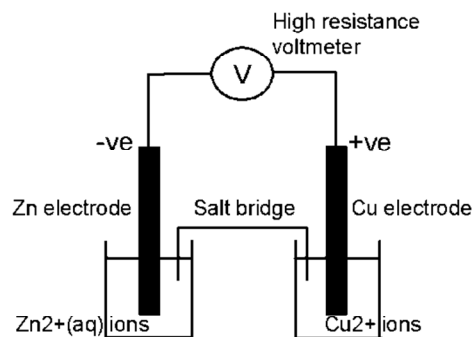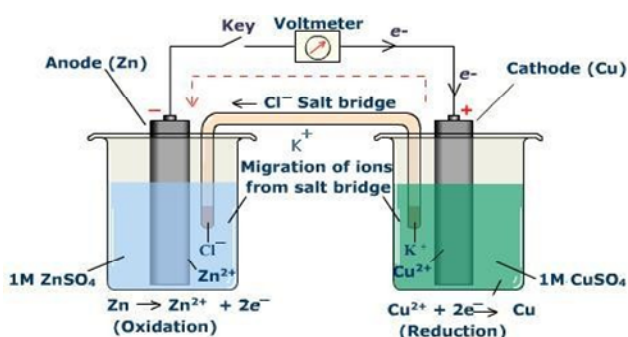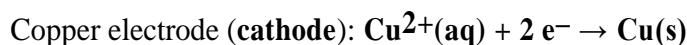

- In this example, the anode is zinc metal which oxidizes (loses electrons) to form zinc ions in solution, and copper ions accept electrons from the copper metal electrode and the ions deposited the copper cathode as an electro deposit.
- This cell forms a simple battery as it will spontaneously generate a flow of electrical current from the anode to the cathode through the external connection.
- This reaction can be driven in reverse by applying a voltage, resulting in the deposition of zinc metal at the anode and formation of copper ions at the cathode.
- To provide a complete electric circuit, there must also be anionic conduction path between the anode and cathode electrolytes in addition to the electron conduction
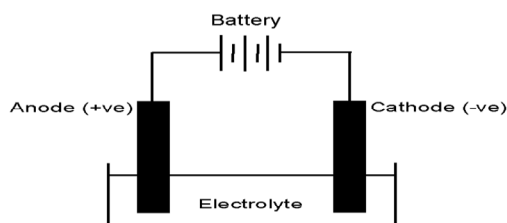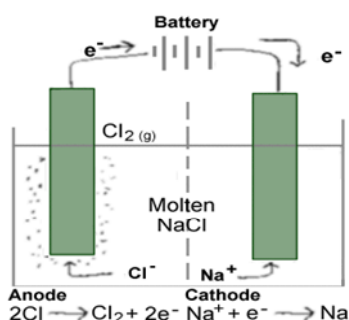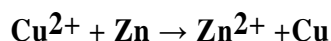
path.

- The simplest ionic conduction path is to provide a liquid junction.
- To avoid mixing between the two electrolytes, the liquid junction can be provided through a porous plug that allows ion flow while reducing electrolyte mixing.
- To further minimize mixing of the electrolytes, as a bridge can be used which consists of an electrolyte saturated gel in an inverted U-tube.

- As the negatively charged electrons flow in one direction around this circuit, the positively charged metal ions flow in the opposite direction in the electrolyte.
- A galvanic cell whose electrodes are zinc and copper submerged in zinc sulfate and copper sulfate, respectively, is known as a Daniell cell.
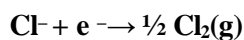 Half reactions for a Daniell cell are these:

  Zincelectrode(**anode**): $\mathbf{Zn(s)\text{-}2e^-\!\rightarrow\! Zn^{2+}(aq)}$
  Copper electrode (**cathode**): $\mathbf{Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)}$

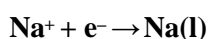 Cellreaction: $\mathbf{Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu}$

Electrolytic Cells

- Electrolysis is the process of decomposition of an electrolyte by the passage of electricity through its aqueous solution or molten state.
- Electrolysis is refers to the decomposition of a substance by an electric current.
- Similarly, chloride ions migrate to the anode and are oxidized to form chlorine gas.
- This type of cell is used to produce sodium metal and chlorine gas out of sodium chloride salt.
- Electrolysis of molten alkali halides is the usual industrial method of preparing the alkali metals:

  anode:
  $Cl^- + e^- \rightarrow \frac{1}{2}\,Cl_2(g)$
  cathode:
  $Na^+ + e^- \rightarrow Na(l)$

  Net: $Na^+ + Cl^- \rightarrow Na(l) + \frac{1}{2}Cl_2(g)$

- The redox reaction in an electrolytic cell is non spontaneous.

- Electrical energy is required to induce the electrolysis reaction.
- An example of an electrolytic cell is shown below, in which molten NaCl is electrolyzed to form liquid sodium and chlorine gas.
- The sodium ions migrate toward the cathode, where they are reduced to sodium metal.

☐ **Anionsareattractedtowardstheanodewheretheyundergooxidation.**
☐ **Electronsflowfromtheanodetothecathodewherecationsundergo reduction.**

Types of Electrodes

- In an electrochemical cell, there are two electrodes, positive and negative.
- Each electrode constitutes a half cell or a single electrode.
- Although a number of electrodes are possible but the more important of these electrodes are grouped into the following types:

1. Metal-metal ion electrodes (electrode reversible w. r. t cations)
2. Non-metal ion electrode(electrode reversible w. r. t anions)
3. Metal-metal insoluble salt an ion electrode
4. Oxidation-reduction or redox electrodes.
5. Metal-amalgam electrodes

1. Metal-metal ionelectrodes:

When a metal is in contact with its own ions containing solution, then metal-metal ion electrode is formed.

Generally these types of electrodes are reversible w. r. t. cations. Eg.:

$$Zn_{(s)}/Zn^{2+}_{(aq)}$$
$$Cu_{(s)}/Cu^{2+}_{(aq)}$$
$$Ni_{(s)}/Ni^{2+}_{(aq)}$$
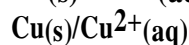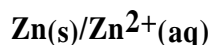
These electrodes are working reversibly

eg.: $Zn_{(s)}/Zn^{2+}_{(aq)}$

Oxidation reaction: $Zn_{(s)} - 2e^- \rightarrow Zn^{2+}_{(aq)}$

Reduction reaction: $Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$

If the potential of the electrode is measured under standard condition the potential is known as standard potential.

2. Non-metal ion electrode:

- When the hydrogen gas is passed over platinum wire, which is dipped in a solution containing ($1MH_3O^+$) then non-metal ion electrode is formed.
- If this electrode is working in a standard condition then electrode is known as standard hydrogen electrode (SHE).

$$Pt/H_2{(g)}/H^+{(aq)}$$
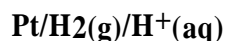
These electrodes are reversible with respect to anions.

Reaction occurring on **$Pt/Br_2{(g)}/Br^-{(aq)}$**

Oxidation reaction: $2Br^-(aq) - 2e^- \rightarrow Br_2(g)$

Reduction reaction: $Br_2(g) + 2e^- \rightarrow 2Br^-(aq)$

3. Metal -metal insoluble salt anion electrode:

• When a metal electrode is coated with a thin layer of its sparingly soluble salt and keeping this electrode in the solution containing common anion this electrode is formed.
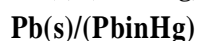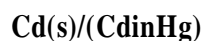
Eg:

$$Ag/AgCl/Cl^-(aq)$$
$$Pb/PbSO_4/SO_4^{2-}aq)$$
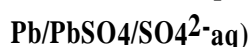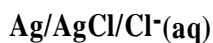
4. Metal - amalgum electrode:

• When a metal is dissolved in mercury, the solution is known as amalgum.
• Keeping a metal rod in amalgum, metal amalgam electrode is formed.
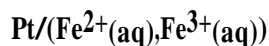
Eg: $Cd(s)/(CdinHg)$
$Pb(s)/(PbinHg)$

• The advantage of this type of electrode is highly reactive metal are not used directly as an electrode but they are used in a form of amalgum.

5. Oxidation-reduction(redox)electrodes:

• These are electrodes in which the emf arises from the presence of ions of a substance in two different oxidation states.
• These electrodes are setup by dipping an inert metal like gold or platinum in to a solution containing ions in two different oxidation states of the substance.
• Eg. A platinum wire immersed in a solution of ferrous and ferric ions or stannous and stannic ions constitutes a redox electrode.
• These electrodes are represented as

$$Pt/(Fe^{2+}(aq), Fe^{3+}(aq))$$

Oxidation reaction: $Fe^{2+} - e^- \rightarrow Fe^{3+}(aq)$

Reduction reaction: $Fe^{3+} + e^- \rightarrow Fe^{2+}(aq)$

Standard cell (Weston cell)

- Weston cell is known as standard cell because its potential does not change for alonger time and its temperature coefficient is too low.
- To construct Weston cell, one H-shape glass tube is used.
- One end of the glass tube is filled with cadmium amalgam and crystals of solid $CdSO_4$ kept on cadmium amalgam.
- Other end of the tube is filled with pure mercury and there is a layer of mercurous sulphate(Hg_2SO_4)on mercury and crystal of solid CdSO4is kept on the mercury paste.
- The whole tube is filled with saturated solution of Cadmium sulphate at 4^0C then the glass tube is sealed. The cell is represented as:

Cd/Cd in Hg/solid CdSO4 .8 H2O/sat.soln of CdSO4/solid CdSO4 . 8 H2O/HgSO4/Hg
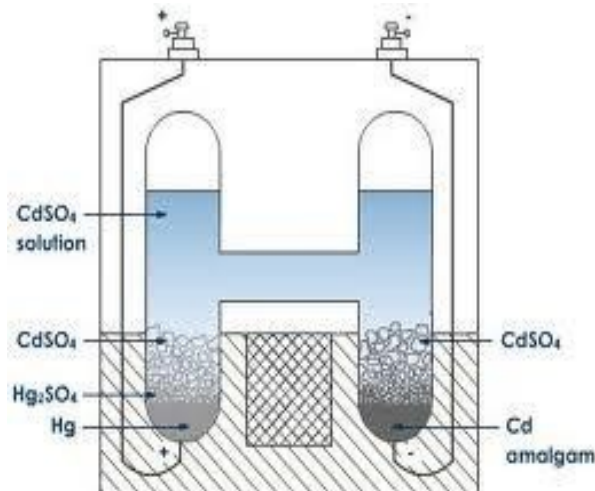
- The **Weston cell**, is a wet-chemical cell that produces a highly stable voltage suitable as a laboratory standard for calibration of voltmeters.
- The anode is an amalgam of cadmium with mercury with a cathode of pure mercury over which a paste of mercurous sulphate and mercury is placed. The electrolyte is a saturated solution of cadmium sulfate octahydrate, and the depolarizer is a paste of mercurous sulfate.
- As shown in the illustration, the cell is setup in an H-shaped glass vessel with the cadmium amalgam in one leg and the pure mercury in the other. Electrical connections to the cadmium amalgam and the mercury are made by platinum wires fused through the lower ends of the legs.

Anode reaction: $Cd(s) -2e^- \rightarrow Cd^{2+}(aq)$

Cathode reaction: $Hg^{2+}SO_4^{2-}(s)+2e^- \rightarrow 2Hg(l)+SO_4^{2-}(aq)$

Reference cells must be applied in such a way that no current is drawn from them.

Electrodes Used in Electrolytes

Reference Electrode: The electrode whose potential is arbitrarily fixed to a certain value(zero volt) or is exactly known is called a reference electrode.

Reference electrodes:

- The electrode potential is determined by coupling the electrode with another reference electrode, the potential of which is fixed as zero.
- The best reference used is the standard hydrogen electrode.
- The standard electrode potential of the standard hydrogen electrode at all temperatures is taken as zero.
- It is very difficult to set up a hydrogen electrode.
- Hence, other referenc eelectrodes like calomel electrodes are also used.

Commonly used reference electrodes are:

1. Standard Hydrogen Electrode (**SHE**)-Primary reference electrode.
2. Standard Calomel Electrode(**SCE**)-Secondary reference electrode.
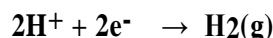
Standard Hydrogen Electrode (SHE)

- The hydrogen electrode consists of a rectangular platinum foil that is connected to a platinum wire and sealed in a glass tube.
- A jacket which is enclosed at the top and opens at the bottom surrounds this glass tube.
- Hydrogen gas is admitted through a side tube attached to the jacket.
- Hydrogen gas at 1atm. Pressure is passed into 1molHCl. In which the foil of platinized platinum (platinum black) remains immersed.
- In a cell, when this electrode acts as the anode, the reaction taking place can be represented as

$$H_2 - 2e^- \rightarrow 2H^+$$
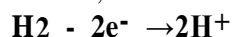
- Thus a part of hydrogen gas changes in to ions which go into the solution.
- When this electrode acts as the cathode, the electrode reaction can be represented as

$$2H^+ + 2e^- \rightarrow H_2(g)$$

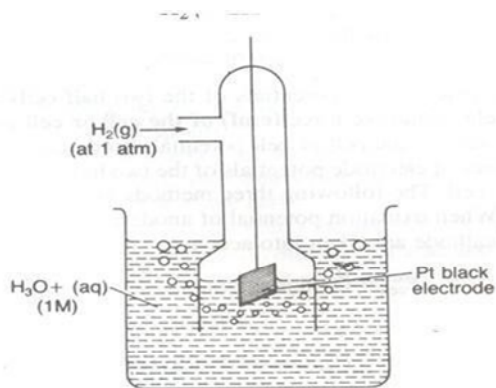Some H^+ ions form solution change into H_2 gas.

Fig. 12.10 Hydrogen electrode
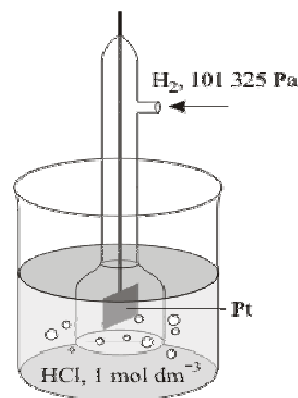
OR

- The SHE is a type of gas electrode and was widely used in early studies as a reference electrode, and as an indicator electrode for the determination of pH values.
- Hydrogen gas, at a pressure of 1atmosphere, is bubbled around the platinum electrode.
- The platinum black serves as a large surface area for the reaction to take place, and the stream of hydrogen keeps the solution saturated at the electrode site with respect to the gas.
- It is interesting to note that even though the SHE is the universal reference standard, it exists only as a theoretical electrode which scientists use as the definition of an arbitrary reference electrode with a half-cell potential of 0.00 volts.
- There as on this electrode cannot be manufactured is due to the fact that no solution can be prepared that yields a hydrogen ion activity of 1.00M.

Choice of platinum

The choice of platinum for the hydrogen electrode is due to several factors:

- Inertness of platinum(it does not corrode).
- The capability of platinum to catalyze the reaction of proton reduction.
- Excellent reproducibility of the potential.
- The surface of platinum is platinized (i.e., covered with platinum black to: increase total surface area). This improves reaction kinetics and maximum possible current.
- Use of a surface material that adsorbs hydrogen well at its interface. This also improves reaction kinetics.
- Other metals can be used for building electrodes with a similar function such as the palladium-hydrogen electrode.

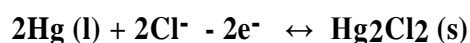### Advantages of Standard Hydrogen Electrode (SHE):

1. Very small potential is developed on the hydrogen electrode; hence it can be taken as zero.
2. In determining the single electrode potential, using S.H.E. as a reference, the potential of the unknown potential will be equal to the e.m.f. of the cell.

Disadvantages of Standard Hydrogen Electrode (SHE):

1. It is not convenient to assemble the apparatus.
2. It is difficult to get pure, dry hydrogen gas and prepare ideal platinized platinum plate.
3. The impurities present in H_2 and HCl poison the Pt, and affect the equilibrium at the electrode.
4. Platinum foil gets easily poisoned by the impurities present in the gas and HCl.
5. It is rather difficult to regulate the pressure of the H_2 gas to be at exactly 1 atm throughout the experiment.
6. Excess of H_2 bubbling out carries little HCl with it and hence the H^+ concentration decreases.
7. In such a system, it is difficult to maintain the concentration of HCl at 1M.
8. It cannot be used in the presence of oxidizing agents.

Standard Calomel electrode (SCE)

- The calomel electrode is most commonly used reference electrode.
- It consists of mercury, solid mercurous chloride (calomel) and a solution of KCl.
- Pure mercury is put at the bottom of the tube and is covered with a paste of mercurous chloride.
- A solution of KCl is introduced above the paste through the side tube shown on the right.
- The KCl solution also fills the side tube ending in a jet on the left.
- A platinum wire seal into a glass tube serves to make electrical contact of the electrode with the circuit.
- The half-cell whose electrode potential is to be determined is coupled with the calomel electrode through a salt bridge and the emf of the cell is measured.
- If the electrode acts as the anode the reaction is

$$2Hg \ (l) + 2Cl^- - 2e^- \leftrightarrow Hg_2Cl_2 \ (s)$$

- If it reacts as the cathode the reaction is

$$Hg_2Cl_2(s) + 2e^- \leftrightarrow 2Hg(l) + 2Cl^-$$
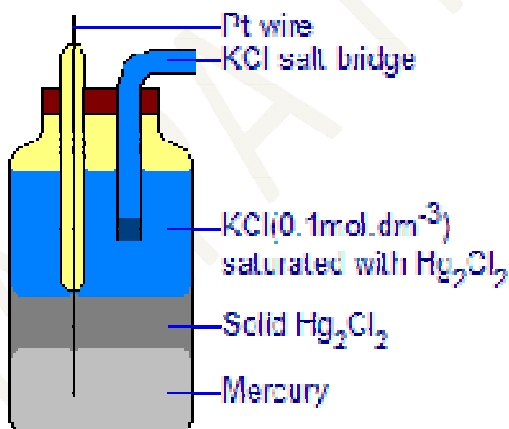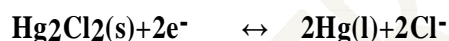
The half-cell reactionis:

$$Hg_2Cl_2(s) + 2e^- \leftrightarrow 2Hg(l) + 2Cl^-(aq)$$
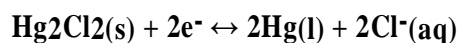
Advantages of Standard Calomel Electrode:

1. It is very handy, compact and easy to transport.
2. Its potential can remain constant and it can easily be reproduced.
3. It is easy to construct and maintain.

Quinhydrone Electrode

- The **Quinhydrone electrode** is a type of redox electrode which can be used to measure the hydrogen ion concentration (pH) of a solution in a chemical experiment. It provides an alternative to the commonly used glass electrode in a pH meter.
- An electrode consisting of a platinum wire in a solution containing Quinhydrone used to determine hydrogen-ion concentration.
- Quinhydrone is an organic compound which is equimolar mixture of quinone and hydroxyquinone.
- The electrode consists of an inert metal electrode (usually a platinum wire) in contact with Quinhydrone crystals and a water-based solution.
- It is more convenient than the hydrogen electrode in ordinary solutions because special apparatus for the preparation and control of hydrogen is not necessary.
- Quinhydrone is slightly soluble in water, dissolving to form a mixture of two substances, quinone and hydroquinone, with the two substances present at equal concentration.
- Each one of the two substances can easily be oxidized or reduced to the other.
- The potential at the inert electrode depends on the ratio of the activity of two substances (quinone-hydroquinone), and also the hydrogen ion concentration.
-
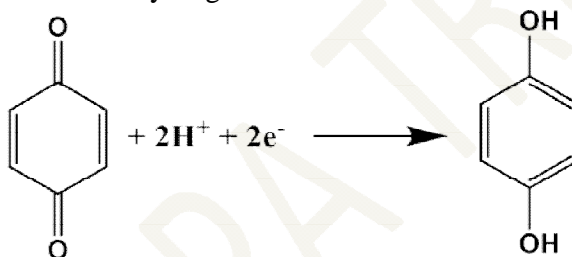
The electrode half-reaction is:

$$\text{Quinone} + 2H^+ + 2e^- \leftrightarrow \text{Hydroquinone}$$
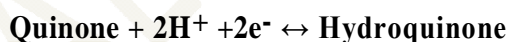
- To find out the pH of the solution, Quinhydrone electrode is combined with saturated calomel electrode & a cell is constructed as under:

Hg/Hg &HgCl$_2$ paste/Satd. Son. Of KCl//quinhydron containing solution/Pt

Ecell = E calomel oxidation + E quinhydrone reduction

$$E_{cell} = -0.242 + E°Q - \frac{0.0592}{n} \log \frac{[QH_2]}{[Q][H^+]^2}$$

Now, $[Q]/[QH_2] = 1$

$$E_{cell} = -0.242 + 0.699 - \frac{0.0592}{2} \log \frac{1}{[H^+]^2}$$

$$E_{cell} = 0.457 + 0.0592 \times \log[H^+]$$

$$-0.0592 \times \log[H^+] = 0.0457 - E_{cell}$$

Therefore,

$$pH = \frac{0.457 - Ecell}{0.0592}$$

Advantges of the quinhydrone electrode:

1. It is highly accurate in measurement.
2. It is generally used for a determination of pH of a solution.
3. It can be prepared very easily.
4. It rapidly attains the equilibrium.

Disadvantages of the Quinhydrone electrode:

1. The electrode doesn't give proper result when pH of the solution is higher than 8.
2. It doesn't give correct results when the solution consists of oxidizing impurities.
3. It is not stable for a longer period of time particularly above30°C.

NERNST EQUATION

- Electrochemistry deals with cell potential as well as energy of chemical reactions.
- The energy of a chemical system drives the charges to move, and the driving force give rise to the cell potential of a system called a galvanic cell.
- The energy aspect is also related to the chemical equilibrium.
- All these relationships are tied together in the concept of Nernst equation.
- We know that potential of the cell depends on activity of the ions, temperature and pressure as well as nature of the electrode.
- The general Nernst equation correlates the Gibb's Free Energy ΔG and the EMF of a chemical system known as the galvanic cell.

For the reaction, **aA+bB=cC+dD**

Where,

A & B = reactants
C & D = products
a & b = number of moles of reactants
c & d = number of moles of product

- When 1 Faraday electricity is passed through the cell, the forward reaction becomes faster.

- According to thermodynamics, the work done in the electrochemical cell is related with decrease in the energy.

$$-\Delta G = nF\Delta E \dots\dots\dots\dots\dots\dots\dots 1$$

ΔG = Free energy change
n= the number of electrons transferred
F= Faraday constant = 96500 coulombs
ΔE= cell potential in volts

When the electrochemical cell is in a standard state,

$$- \Delta G^o = n\ F\Delta E^o \dots\dots\dots\dots\dots\dots\dots 2$$

Where,

ΔG^o = standard free energy change

ΔE^o = standard cell potential

- Whenareactionattainsequillibrium,
-

$$\Delta G^o = \Delta G$$

According to VontHoff's equation,

$$\Delta G = \Delta G^o + RT\ln K \text{------------------------------- } 3$$

Where,

R = gas constant (8.314 J mol^{-1} K^{-1})
K = equillibrium constant

But for electrochemical cell,

$$\Delta G^o = - n\ F\ \Delta\ E^o$$
&
$$\Delta G = - n\ F\ \Delta E$$

Substitute this value in equation no. 3, we get:

$$- n\ F\ \Delta\ E = - n\ F\ \Delta\ E^o + RT\ \ln K$$

Dividing above equation both the sides by –nF,

$$\Delta E = \Delta E^o - \frac{RT}{nF} \ln K \quad\text{--}4$$

This equation is known as Nernst equation.

At, 25 ^{o}C,

[273°K + 25°C = 298°K]

$$\Delta E = \Delta E^o - \frac{2.303 \times 8.31 \times 298}{n \times 96500} \log K$$

$$\Delta E = \Delta E^o - \frac{0.0592}{n} \log K \quad\text{-------------------------}5$$

- Suppose **oxidation** reaction is occurring at electrode,

$$M(s) - ne^- \rightarrow M^{n+}(aq)$$
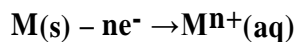
According to Nernst equation,

$$\Delta E = E^0 \frac{0.0592}{n} \log K$$

$$\Delta E = \Delta E^0 - \frac{0.0592}{n} \log \frac{[M^{n+}]}{[M_s]} \quad \text{But, } [M_{(s)}] = 1$$

$$\Delta E = \Delta E^0 - \frac{0.0592}{n} \log M^{n+} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 6$$

- Suppose **reduction** reaction is occurring at electrode,

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

According to Nernst equation,

$$\Delta E = \Delta E^0 - \frac{0.0592}{n} \log \frac{[M_{(s)}]}{[M^{n+}]} \quad \text{But, } [M_{(s)}] = 1$$

$$\Delta E = \Delta E^0 + \frac{0.0592}{n} \log [M^{n+}] \ldots\ldots\ldots\ldots\ldots 7$$

<u>Applications of Nernst Equation:</u>

- Nernst equation can be used to study the effect of electrolyte concentration on electrode potential.
- Nernst equation can also be used for the calculation of the potential of a cell under non- standard conditions.
- Determination of unknown concentration of one of the ionic species in a cell is possible with the help of Nernst equation provided E^0 cell and concentration of other ionic species is known.
- The pH of a solution can be calculated from the measurement of EMF and Nernst equation.
- Nernst equation can also be used for finding the valance of an ion or the number of electrons involved in the electrode reaction.

NEUMARICALS

1. **Calculate potential of the following half-cell at 25 $^{\circ}$C.**
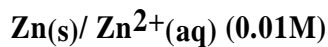
$$Zn_{(s)}/ Zn^{2+}_{(aq)} (0.01M)$$
$$E^{0} Zn^{+2}/Zn_{(s)}(reduction)= \quad - 0.76 \text{ volt}$$

$$E = E^{\circ} - \frac{0.0592}{n} \log K$$

$$= 0.76 - \frac{0.0592}{2} \log 10^{-2}$$

$$= 0.76 - \frac{0.0592}{2}(-2)$$

$$= 0.76 + 0.0592$$

$$E = 0.8192 \text{Volt}$$

2. **Calculate potential of the following half-cell at 25^{0}C.**
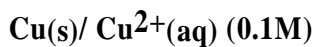
$$Cu_{(s)}/ Cu^{2+}_{(aq)} (0.1M)$$
$$E^{0} Cu^{+2}/Cu_{(s)}(reduction)= \quad - 0.34 \text{ volt}$$

$$E = E^{\circ} - \frac{0.0592}{n} \log K$$

$$= 0.34 - \frac{0.0592}{2} \log 10^{-1}$$

$$= 0.34 + \frac{0.0592}{2}$$

$$= 0.76 + 0.0296$$

$$E = 0.3696 \text{Volt}$$

3. **Calculate potential of the following half-cell at 25⁰C.**

$$Ni_{(s)}/Ni^{2+}_{(aq)} (0.01M)$$
$$E^o (reduction) = + 0.23 \text{ volt}$$
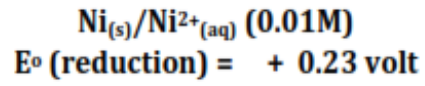
$$E = E^o - \frac{0.0592}{n} \log K$$

$$= -0.23 - \frac{0.0592}{2} \log 10^{-2}$$
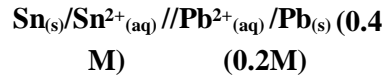
$$= -0.23 - \frac{0.0592}{2} (-2)$$

$$= -0.23 + 0.0592$$

$$E = -0.1708 \text{ Volt}$$

4. **Calculate E, $E°$, ΔG, $\Delta G°$ for the following electrochemical cell at 25°C.**

$$Sn_{(s)}/Sn^{2+}_{(aq)} //Pb^{2+}_{(aq)} /Pb_{(s)} \text{ (0.4}$$
$$\text{M)} \qquad \text{(0.2M)}$$

$$E° \text{ Sn/Sn}^{2+} = 0.140 \text{ volt } E°$$
$$Pb/Pb^{2+} = 0.126 \text{ volt}$$

Reactions:

Anode: $\qquad$ $Sn_{(s)} - 2e^- \rightarrow Sn^{2+}$ (0.4)

Cathode: $\qquad$ $Pb^{2+} + 2e^- \rightarrow Pb$

$\qquad$ (0.2 M)

-
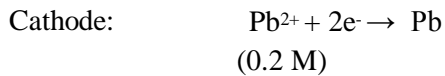
$\qquad$ **$\Delta E°$Cell** $\qquad$ $= E°_{\text{ Sn/Sn2+}} - E°_{\text{ Pb/Pb2+}}$

$\qquad\qquad\qquad\qquad\qquad$ $= 0.140 - 0.126$

$\qquad\qquad\qquad\qquad\qquad$ $= 0.014$ volt

$\qquad$ **ΔG** $\qquad\qquad$ $= - nF E°$

$\qquad\qquad\qquad\qquad\qquad$ $= - 2 \times 96500 \times 0.014$

$\qquad\qquad\qquad\qquad\qquad$ $= - 2702$ Joule

$\qquad\qquad\qquad$ 0.0592

E $= E°$ $\qquad$ --------- $\qquad$ log

$\qquad\qquad\qquad\qquad$ n

$\qquad$ $= 0.014 -$ $\dfrac{0.0592}{2}$ log $\dfrac{[Sn^{2+}]}{[Pb^{2+}]}$

$\qquad\qquad\qquad\qquad\qquad\qquad$ $\dfrac{[0.4]}{[0.2]}$

$\qquad$ $= 0.014 -$ 0.0296 log ---------

$\qquad$ $= 0.014 -$ 0.0296 log 2

$\qquad$ $= 0.014 -$ 0.0296 x 0.3010

$\qquad$ $= 0.014 -$ 0.00890

E $\quad = 5.09 \times 10^{-3}$ volt

ΔG $= - nF E$

$\qquad$ $= - 2 \times 96500 \times 5.09 \times 10^{-3}$

$\qquad$ $= - 982.33$ Joule

5. **Calculate the potential of the following electrochemical cell at 25ºC.**

$$Cr_{(s)}/Cr^{3+}_{(aq)} //Fe^{2+}_{(aq)} /Fe_{(s)} E^o$$
$$_{Cr/Cr}^{3+} = 0.74 \text{ volt}$$
$$E^o_{Fe/Fe}^{2+} = \quad 0.44 \text{ volt}$$

Reactions:

Anode: $\qquad Cr_{(s)} - 3e^- \rightarrow Cr^{3+} (0.01)$

Cathode: $\qquad Fe^{2+} + 2e^- \rightarrow Fe_{(s)}$

$\qquad$ (0.01)

For balancing the equation,

$$2Cr_{(s)} \;-\; 6e^- \quad \rightarrow \; 2Cr^{3+}$$
$$3Fe^{2+} \;+\; 6e^- \quad \rightarrow \; 3Fe$$

Net: $\qquad 2Cr_{(s)} + 3Fe^{2+} \rightarrow 2Cr^{3+} + 3Fe$
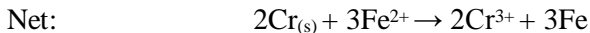
$\quad \Delta E°Cell \qquad = E°_{Cr(s)/Cr}^{3+} - E°_{Fe/Fe}^{2+}$

$\qquad\qquad\qquad = 0.74 - 0.44$

$\qquad\qquad\qquad = 0.30 \text{ volt}$

$$E = E° - \frac{0.0592}{n} \log K$$

$$= \; 0.30 - \frac{0.0592}{6} \log \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

$$= 0.30 - \frac{0.0592}{6} \log \frac{[10^{-2}]^2}{[10^{-2}]^3}$$

$$= \; 0.30 - \frac{0.0592}{6} \log \frac{10^{-4}}{10^{-6}}$$

$$= \; 0.30 - \frac{0.0592}{6} \log 10^2$$

$$= 0.30 - \frac{0.0592}{6} \times 2$$

$$= 0.30 - \frac{0.0592}{3}$$

$E \quad = 0.2802 \text{ volt}$

Conductometry

- It is the measurement of conductivity of a solution due to the mobility of cations and anions towards respective electrodes.
- **Conductance** is inversely proportional to resistance (R) i.e. C=1/R
- Unit of conductivity: mhos or ohm^{-1} or siemen
- Conductivity of a solution depends on no. of ions, charge of ions, and temperature.
- **Specific Conductance**: It is the reciprocal of specific resistance.

  i.e. $\kappa = 1 / \rho$

  ρ = resistivity of the material

  κ = Specific Conductance

  Unit of Specific conductance : ohm^{-1}cm^{-1}

- **Molar conduction:** It is the conductance of all ions present in a certain volume of solution containing one gram mole ofelectrolyte.

  i.e. $\quad$ m= $\kappa \dfrac{X1000}{M}$

  Where $\quad$ $_m$ = molarconduction

  $\quad\quad$ κ = Specific Conductance

  $\quad\quad$ M: Molarity of solution

  Unit : ohm^{-1}cm^{2} mol^{-1}

- **Equivalent conduction:** It is the conductance of all ions present in a certain volume ofsolution containing one gram equivalent ofelectrolyte.

  i.e. . $\quad$ eq= $\kappa \dfrac{X1000}{N}$

  Where $\quad$ eq =equivalentconduction

  $\quad\quad$ κ = Specific Conductance

  $\quad\quad$ N : Normality ofsolution

  Unit : ohm^{-1}cm^{2} equivalent^{-1}

Some Typical Conductometric Titration Curves are:

1. Strong Acid with a StrongBase,
E.g. HCl with NaOH: Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as H^{+} ions react with OH−ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the large conductivity of OH- ions

cm^{3} of NaOH
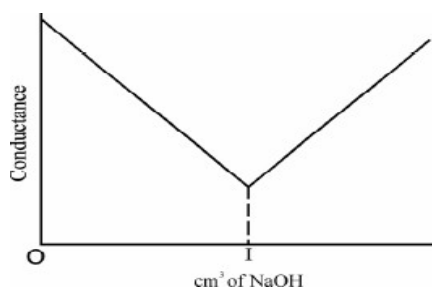
2. Weak Acid with a Strong Base, E.g. Acetic acid withNaOH:

Initially the conductance is low due to the weak ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H+ by Na+ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated CH_3COOH to CH_3COONa which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH_3COONa. Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH− ions
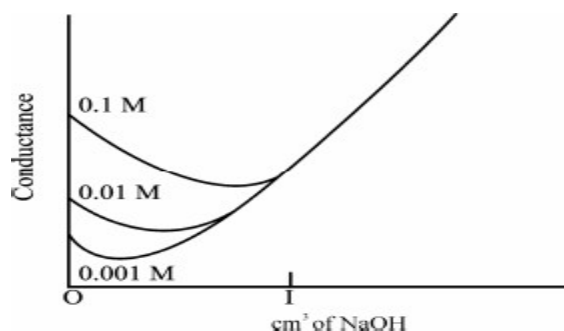
3. Strong Acid with a Weak Base, e.g. Sulphuric acid with diluteammonia:

Initially the conductance is high and then it decreases due to the replacement of H+. But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate.
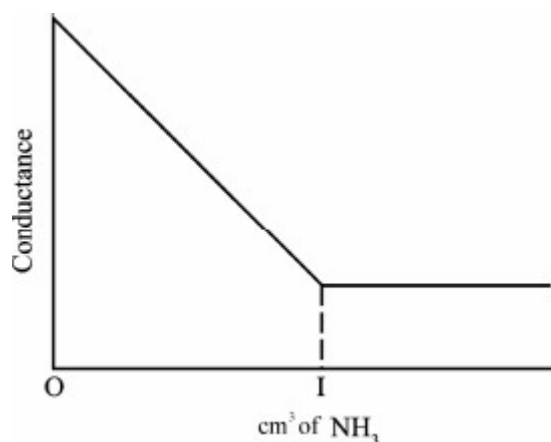
4. Weak Acid with a WeakBase:
The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base
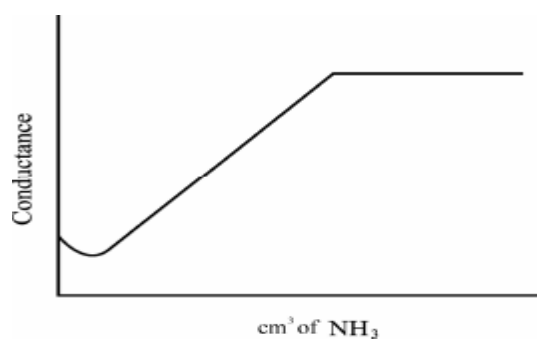
which is being added is weakly ionized and, therefore, is not much conducting.

Unit - I

Chapter -2-Green Chemistry

Introduction:

Green Chemistry or sustainable chemistry or environmentally caring chemistry is the branch of chemistry which utilizes the set of principles to reduce or eliminates the generation of hazardous substances in the design and manufacture of environmentally and economically sustainable product.

The growing attention to sustainable development includes the reduction of environmental impact and the effective utilization of renewable resources.

It can help to solve large global problems such as climate change, energy consumption of effective utilization of natural resources, especially renewable resources.

Green chemistry takes advantage for technological advancement chemical processing to achieve environmental efficiency.

Principles & Concepts of Green Chemistry United Nation:

The most important steps in the evolution of green chemistry are closely related to United States Environmental Protection Agency. In 1990, the pollution Prevention Act, approved by the American Congress in the United States, initiated to create a modus operandi for dealing with pollution in an innovative and sustainable and covered the way to green chemistry concept. Green chemistry takes advantage for technological advancement chemical processing to achieve environmental efficiency.

United States Environmental Protection Agency invented the two letter word "green chemistry" on the basis of 12 principles, they are as follows;

The 12 Principles of
GREEN CHEMISTRY

Green chemistry is an approach to chemistry that aims to maximize efficiency and minimize hazardous effects on human health and the environment. While no reaction can be perfectly 'green', the overall negative impact of chemistry research and the chemical industry can be reduced by implementing the 12 Principles of Green Chemistry wherever possible.

1. WASTE PREVENTION

Prioritize the prevention of waste, rather than cleaning up and treating waste after it has been created. Plan ahead to minimize waste at every step.

2. ATOM ECONOMY

Reduce waste at the molecular level by maximizing the number of atoms from all reagents that are incorporated into the final product. Use atom economy to evaluate reaction efficiency.

3. LESS HAZARDOUS CHEMICAL SYNTHESIS

Design chemical reactions and synthetic routes to be as safe as possible. Consider the hazards of all substances handled during the reaction, including waste.

4. DESIGNING SAFER CHEMICALS

Minimize toxicity directly by molecular design. Predict and evaluate aspects such as physical properties, toxicity, and environmental fate throughout the design process.

5. SAFER SOLVENTS & AUXILIARIES

Choose the safest solvent available for any given step. Minimize the total amount of solvents and auxiliary substances used, as these make up a large percentage of the total waste created.

6. DESIGN FOR ENERGY EFFICIENCY

Choose the least energy-intensive chemical route. Avoid heating and cooling, as well as pressurized and vacuum conditions (i.e. ambient temperature & pressure are optimal).

7. USE OF RENEWABLE FEEDSTOCKS

Use chemicals which are made from renewable (i.e. plant-based) sources, rather than other, equivalent chemicals originating from petrochemical sources.

8. REDUCE DERIVATIVES

Minimize the use of temporary derivatives such as protecting groups. Avoid derivatives to reduce reaction steps, resources required, and waste created.

9. CATALYSIS

Use catalytic instead of stoichiometric reagents in reactions. Choose catalysts to help increase selectivity, minimize waste, and reduce reaction times and energy demands.

10. DESIGN FOR DEGRADATION

Design chemicals that degrade and can be discarded easily. Ensure that both chemicals and their degradation products are not toxic, bioaccumulative, or environmentally persistent.

11. REAL-TIME POLLUTION PREVENTION

Monitor chemical reactions in real-time as they occur to prevent the formation and release of any potentially hazardous and polluting substances.

12. SAFER CHEMISTRY FOR ACCIDENT PREVENTION

Choose and develop chemical procedures that are safer and inherently minimize the risk of accidents. Know the possible risks and assess them beforehand.

Importance of green synthesis:

The Green chemistry addresses many challenges such as maximize the products, minimize the waste products, designing new schemes that are environmentally and ecologically friendly.

The following are the importance of green synthesis:

1) This prevents pollution at the molecular level by atom economy
2) It gives innovative scientific solutions to real -world environment problems.
3) It provides alternative synthetic routes for feedstock and starting material.
4) Biocatalysis and bioleaching are prominent applications in green chemistry.
5) Utilization of carbon dioxide as a green solvent.
6) Biosorption is one of the important phenomena based on 12 principles of green chemistry.
   In the <u>Biosorption process</u>, number of agricultural materials such as wool, palm kernel husk, apple residue, banana husk and sawdust are being used to remove toxic metals from water.
7) Effective utilization of renewable resources as alternate energy sources such as solar energy, hydro energy.

Methods for green synthesis:

1) Alternative synthetic route for feedstock and starting materials

Example: Production of dimethyl carbonate (DMC, $CH_3OCOOCH_3$)
Dimethyl carbonate is a versatile and environmentally friendly material for chemical industry.
Due to high oxygen content and blending properties, it is used as a good component of fuel.

i) Traditional method
In this method, phosgene ($COCl_2$) and methanol (CH_3OH) are used produce DMC.

$$COCl_2 + 2CH_3OH \longrightarrow CH_3OCOOCH_3 + 2HCl$$
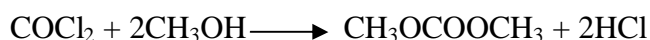
Here, phosgene (reactant) and hydrochloride acid (by product) are environmentally harmful.

ii) Greener method (Alternative method)
This method makes use of copper chloride, methanol, oxygen and carbon monoxide.

$$2CuCl + 2CH_3OH + 1/2\ O_2 \longrightarrow 2Cu(OCH_3)Cl + H_2O$$

$$2Cu(OCH_3)Cl + CO \longrightarrow 2CuCl + CH_3OCOOCH_3 \text{ (DMC)}$$
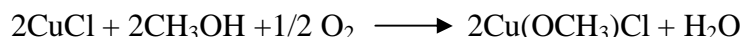
Here copper chloride further comes as a by-product, and usages of CO in this method is cheap and indirectly decrease the pollution.

2) Biocatalysis or bioleaching

Bioleaching is the exaction of specific metals from their ores by using microorganisms such as bacteria. Example: Extraction of gold

i) Traditional method
Heap leaching method is the traditional method employed for the extraction of gold using cyanide. Here, cyanide is hazardous to health and environment.

ii) Greener method (Alternative method)
In this method, *acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* bacteria are used to oxidize ferrous and sulphur. The gold will be easily separated from the ore and solution. This method is much cleaner than the traditional heap leaching method.

Application of green synthesis:

Green synthesis has wide application in many fields. Few of them are as follows:

1) Preparation of antibacterial products those are alternative for traditional chlorine or tin containing antibacterial agents such as bandages, sutures, hospital gowns, acne medication, tooth pastes, air filters, antiviral agents, etc.

2) Used for cleaning clothes such as the following:

   i) Tetraamidomacrocyclic ligand (TAML) catalyst activates hydrogen peroxide that inhibits dye transfer and is good for washing machines which use less water.

   ii) Total Impact Programme (TIP) as laundry formulation incorporates neutral pH, detergents, enzymes, surfactants, oxygen bleach and biodegradable softness.

   iii) Dry cleaning with liquid carbon dioxide, which is non-flammable, non-toxic and a renewable substance.

   iv) Use of sodium iminodisuccinate for cleaning clothes, which is a biodegradable and environmental friendly cleaning agent.

3) Used for cleaning water by using the following:

    i)   Chlorine disinfectant which is toxic to aquatic life but important for preventing diseases.

    ii)   Polymer technology for manufacture of high molecular weight, water soluble polymers in aqueous salt solution.

4)   Used for industrial cleaning by using simple green, non toxic, biodegradable surfactants, thereby replacing traditional organic solvents.

5)   Use of carbon dioxide blowing agent for polystyrene foam production, polystyrene foam is used in packing and food transportation.

6)   The conversion of waste glycerin from biodiesel production to propylene glycol.

7)   Synthesis of nanoparticles of metals. The stabilization of small particles is done by using polymers, ligands, solid matrix and surfactants. The preparation of nanoparticles in green solvent such as water and other non-toxic solvents is very popular nowadays.

Greenhouse concepts:

A greenhouse is also known as a glasshouse. In the greenhouse, plants are grown in a building or other complexes. Building of the greenhouse is made up of either glass or plastic material. In a greenhouse, the incoming UV light is absorbed consequently the temperature of air inside the greenhouse increases and retained in the building by the roof and wall, and air is warmed near the ground and flowing   within the complex.

Types of Greenhouse:
A greenhouse is divided into two types:
1) Glass greenhouse
2) Plastic greenhouse

In both types of greenhouses, the plastics used are polyethylene, polycarbonate or PMMA glass.

Uses of Glasshouse:
1) In a greenhouse, temperature, level of light and shade are maintained.
2) In a greenhouse, growth of plants is controlled by controlling temperature and lighting of house.
3) It is also used to improve the qualities of the land and also to improve food production by providing good environment.
4) It is also used for growing flowers, vegetables, fruits, and transplantation of specific plants.

5) In addition to all of these, the greenhouse is also used to produce solar fields which produce steam for solar-enhance oil.

Greenhouse effect and greenhouse gases:

In greenhouse effect, UV radiations from sun of short wavelength are absorbed through a transparent medium, but IR radiations of longer wavelength are unable to pass back from that medium. As a result, inside temperature increases, such effect is called the greenhouse effect. This effect is shown due to the absorption of excess heat by carbon dioxide present in it.

The enhanced greenhouse effects occur by human activities which release greenhouse gases into the atmospheres. The main anthropogenic of human induce greenhouse gases are carbon dioxide, nitrous oxide, hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), methane and sulphur hexafluoride.