

## Solutions & Solubility

### What is a solution?

A solution is a homogeneous mixture of two or more pure substances, which may be solids, liquids, gases or a combination of these and composed of only one phase. A homogeneous mixture is a physical combination in which particles of one or more substances (solute) are distributed uniformly throughout another substance (solvent) at the molecular or ionic level. Generally, in a solution the percentage of solvent is more than 50 percent.

### Types of solution

(A) Depending on the three physical states- gas, liquid and solid; (nine types)

1. Gas in gas; Example- air
2. Gas in liquid; Example- soda water
3. Gas in solid; Example-  $H_2$  gas absorbed by heated palladium
4. Liquid in gas; Example- water vapor in air
5. Liquid in liquid; Example- alcohol in water
6. Liquid in solid; Example- mercury in gold (mercury amalgam)
7. Solid in gas; Example- camphor ( $C_{10}H_{16}O$ , white crystalline) in air
8. Solid in liquid; Example- sugar solution
9. Solid in solid; Example- Ni-Cu alloy (monel metal)

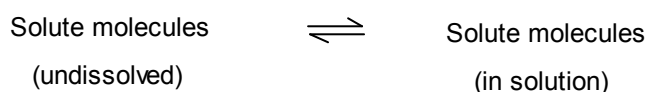
(B) Depending on the temperature; (two types)

1. *Exothermic solution*: The process of dissolution of a solute in solvent involving evolution of heat energy due to breaking and formation of bonds. Examples: CaO or NaOH or strong acids in  $H_2O$  etc.
2. *Endothermic solution*: The process of dissolution of a solute in solvent involving absorption of heat energy due to breaking and formation of bonds. Examples:  $NH_4NO_3$  or glucose in  $H_2O$ , evaporation of  $H_2O$  etc.

(C) Depending on the equilibrium; (three types)

1. A **saturated solution** is a solution containing the maximum concentration of a solute under certain temperature and pressure. Additional solute will not dissolve in a saturated solution and simply settle down as undissolved solids.

A solution in which dissolved solute and undissolved solute are in equilibrium. There exists a dynamic equilibrium between the undissolved solute molecules and the solute molecules in saturated solution.



2. A **supersaturated solution** is a solution containing more solute than a saturated solution. The solubility of a solution increases as the temperature or pressure is increased. This means that as the temperature rises, more solute can be dissolved. Increased pressure also increases maximum possible saturation and allows for a supersaturated solution.

3. An **unsaturated solution** is a solution containing less solute than a saturated solution. An unsaturated solution has room for additional solute to be added and fully dissolved, without settling and sedimentation occurring.

## Properties Solvents

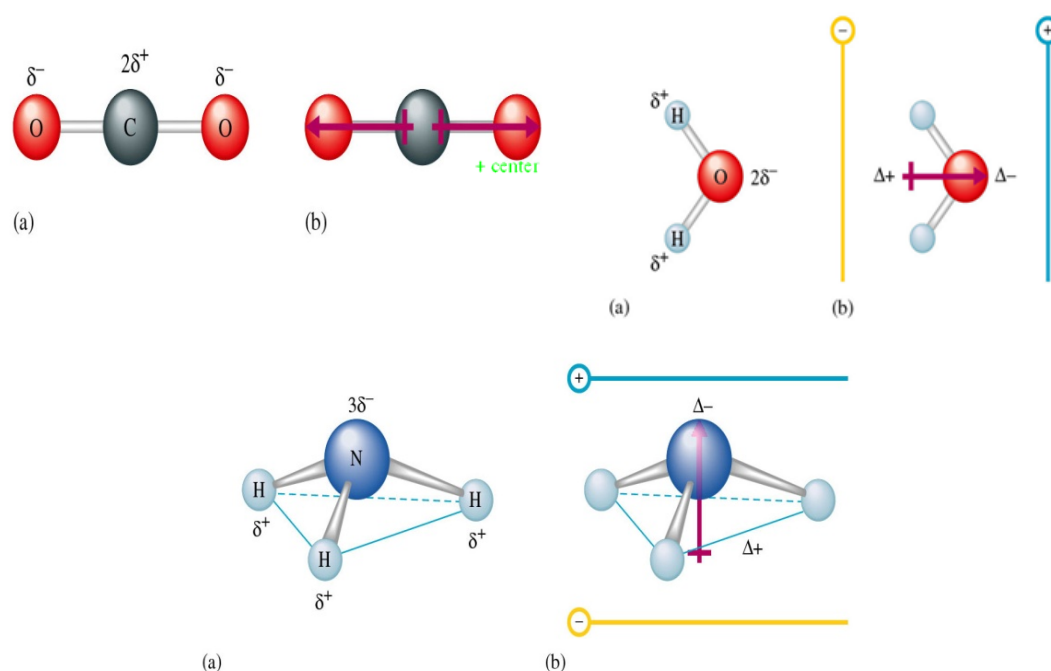
### What is Solvents?

The vast majority of chemical reactions are performed in solution. The solvent fulfills several functions during a chemical reaction. It solvates the reactants and reagents so that they dissolve. Generally a good solvent should meet the following criteria.

- It should be inert to the reaction conditions.
- It should dissolve the reactants and reagents.
- It should have an appropriate boiling point.
- It should be easily removed at the end of the reaction.

Non-polar reactants will dissolve in non-polar solvents. Polar reactants will dissolve in polar solvents. For our purposes there are three measures of the polarity of a solvent: (a) Dipole moment, (b) Dielectric constant, (c) Miscibility with water.

- (a) **Dipole moment:** It occurs due to equal amount of positive and negative charge separated by a distance within a molecule. Mathematically,  $\mu = q \times r$ ; where  $\mu$  = dipole moment (unit is Debye, D),  $q$  = charge of atom in coulomb and  $r$  = distance between charges in Å. Knowledge of dipole moment is useful to know the extent of polar character and geometrical shape of a molecule.



**Figure:** Dipole moment of (a) H<sub>2</sub>O, (b) CO<sub>2</sub> and (c) NH<sub>3</sub>

- (b) **Dielectric constant:** The dielectric constant of a solvent may be defined as its capacity to weaken the force of attraction between the electrical charges in that solvent. It is a

measure of the polarity of the solvent. Mathematically,  $F = \frac{e^2}{rD}$ ; where  $D$  = dielectric constant,  $e$  = charge,  $F$  = force of attraction and  $r$  = distance between charges.

Molecules with *large dipole moments* and *high dielectric constants* are considered **polar**. Those with *low dipole moments* and *small dielectric constants* are classified as **non-polar**. On an operational basis, solvents that are miscible with water are polar, while those that are not are non-polar.

## Solubility

The amount of a substance that dissolves in a given quantity of solvent at a given temperature to form a saturated solution is called its *solubility*.

### Factors Affecting Solubility

#### (a) Nature of the solute and solvent

- (i) Ionic and polar substances dissolve in polar solvent, e.g. NaCl in H<sub>2</sub>O
  - (ii) Nonpolar substances are dissolved in nonpolar solvents, e.g. Napthalene, oil etc. in C<sub>6</sub>H<sub>6</sub>, CCl<sub>4</sub>.
- ‘Like dissolves like’ - that means substances dissolve in chemically similar solvents.

#### (b) Effect of temperature

A higher temperature increases both the rate of dissolution and also the solubility of the solute.

#### (c) Rate of solution

- (i) At a low temperature the rate of solution is quite low. At higher temperature dissolution of more solute causes.
- (ii) The rate of dissolution may be increased by shaking or stirring of the solvent-solute mixture.
- (iii) **Particle size factor:** The process of solution being a surface phenomenon, the greater the surface of contact between the solvent and the solute, the higher will be rate of solution.

### Mechanism of dissolution: How do the evolution and the absorption of heat arises?

To explain this, we have to analyze the process of dissolution of a solute in a solvent. For example, the dissolution of common salt, NaCl in H<sub>2</sub>O.

The process involves the following sequences:

- (a) H<sub>2</sub>O molecules attack the Na<sup>+</sup> particles and detach these from crystal lattice against the attractive force of the adjoining particles i.e. the Cl<sup>-</sup> ions.
- (b) The solvent particles may require to be pulled apart to make room for Na<sup>+</sup> particles.
- (c) The Na<sup>+</sup> particles are solvated (the interaction of ions of a solute with molecules of solvent) by the solvent molecules.

Energy is required for operations (a) and (b) while as a result of operation (c) energy is liberated.

When the energy requirement for the operations (a) and (b) is greater than that released from operation (c), the temperature of the system goes down i.e. **heat is absorbed** during the

dissolution of NaCl molecule. The amount of heat absorbed is called **positive heat** of solution (**endothermic system**).

When the energy requirement for the operations (a) and (b) is less than that released from operation (c), the temperature of the system goes up i.e. **heat is evolved** during the dissolution of NaCl molecule. The amount of heat evolved is called **negative heat** of solution (**exothermic system**).

**Problem-1:** Calculation of normality of strong acids,

- (a) 36% (w/w) HCl, specific gravity 1.18 and
- (b) 96% (w/w) H<sub>2</sub>SO<sub>4</sub>, specific gravity 1.84

## Gas Laws

The gas laws are a set of laws that describe the relationship between temperature ( $T$ ), pressure ( $P$ ) and volume ( $V$ ) of gases.

**Boyle's law** (1662, Relation between volume and pressure of gas):

*Boyle's Law states that the product of the volume and pressure of a fixed quantity of an ideal gas is constant, given constant temperature.* Expressed mathematically, the formula for Boyle's law is:

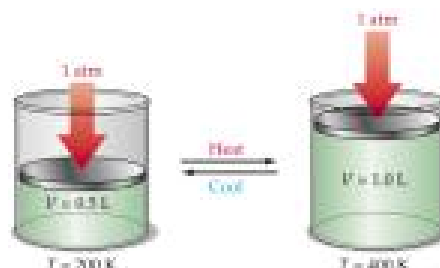
$$PV = k$$

where:

$V$  is volume of the gas.

$P$  is the pressure of the gas.

$k$  is a constant



**Charles law** (1787, relating volume and temperature):

*Charles's law states that at constant pressure, the volume of a given mass of a gas increases or decreases by the same factor as its temperature (in Kelvin's) increases or decreases.*

The formula for the law is:

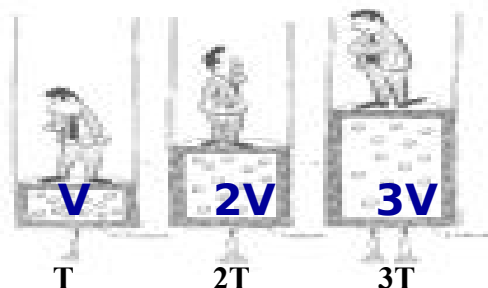
$$\frac{V}{T} = k$$

where:

$V$  is the volume.

$T$  is the temperature (measured in Kelvin's).

$k$  is a constant.



**Gay-Lussac's law** (1809, relating pressure and temperature):

*The pressure of a fixed amount of gas at fixed volume is directly proportional to its temperature in kelvins. i.e.  $P/T = K$*

These three laws were combined to form the combined gas law

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$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$


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## Ideal Gas Law

With the addition of Avogadro's law, this gave way to the ideal gas law-

$$PV = nRT$$

*i.e. "The state of an amount of gas is determined by its pressure, volume, and temperature"*

where,  $P$  is the pressure (SI unit: Pascal)

$V$  is the volume (SI unit: cubic meter)

$n$  is the number of moles of gas

$R$  is the ideal gas constant (SI: 8.3145 J/(mol K))

$T$  is the temperature (SI unit: Kelvin).

The ideal gas law is the most accurate for monoatomic gases at high temperatures and low pressures. Because at lower pressure the molecular size becomes less important for larger volumes and intermolecular attractions diminishes with increasing temperatures.

## Ideal gases

*Ideal gas is a hypothetical gas that obeys the gas laws exactly.* An ideal gas would consist of molecules that occupy negligible space and have negligible forces between them.

## Avogadro's law (1811)

*Equal volumes of all gases contain equal numbers of molecules (Avogadro's no.,  $6.023 \times 10^{23}$ ) at the same pressure and temperature.* The law, often called Avogadro's hypothesis, is true only for ideal gases.

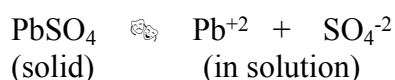
**S.T.P.** - Standard temperature and pressure (or formerly known as N.T.P. - normal temperature and pressure) are used when comparing the properties of gases. They are 273 K (or 0°C) and 101 Pa (or 760 mmHg).

## Solubility Product & pH

### What is solubility product law?

The product of concentrations of ions arising out of a sparingly (weakly) soluble salt in a saturated solution at any constant temperature is a constant is known as *solubility product law*.

For example, lead sulphate is a sparingly soluble electrolyte.



According to the solubility product law,

$$[\text{Pb}^{+2}] [\text{SO}_4^{-2}] = \text{a constant}$$

where  $[Pb^{+2}]$  = concentration of  $Pb^{+2}$  ions as gram ions per liter and  $[SO_4^{-2}]$  = concentration of  $SO_4^{-2}$  ions as gram ions per liter.

### Example-1:

The solubility of  $PbSO_4$  in  $H_2O$  at  $25^\circ C$  is found to be 0.0037 gm/100gm  $H_2O$ . Find its solubility product ( $K_{sp}$ ) at that temperature. (Mol.wt. of  $PbSO_4$  is 303.37)

**Solution:** The molecular weight of  $PbSO_4 = 303.37$

$$\begin{aligned} \square \quad \text{The solubility of } PbSO_4 &= 0.0037\text{g}/100\text{g } H_2O = 0.0037\text{g}/100\text{ml } H_2O \\ &= 0.037\text{g}/1000\text{ml } H_2O = 0.037 \text{ gm/liter } H_2O \\ &= \frac{0.037}{303.37} \text{ mole/liter } H_2O \\ &= 1.2 \times 10^{-4} \text{ mole/liter } H_2O \end{aligned}$$

Since  $PbSO_4$  dissociates completely in  $H_2O$ , each molecule of it on dissociation produces,

$$\begin{aligned} 1.2 \times 10^{-4} \text{ moles } Pb^{+2} \text{ ions/liter} \\ 1.2 \times 10^{-4} \text{ moles } SO_4^{-2} \text{ ions/liter} \end{aligned}$$

$$\square \quad K_{sp} = [Pb^{+2}] [SO_4^{-2}] = (1.2 \times 10^{-4})(1.2 \times 10^{-4}) = 1.44 \times 10^{-8} \quad \underline{\text{Ans.}}$$

**Problem-2.** The solubility product of  $CuCl_2$  is  $3.2 \times 10^{-7}$  at  $25^\circ C$ . Calculate the solubility of  $CuCl_2$  in. (Answer:  $4.3 \times 10^{-3}$  mole litre<sup>-1</sup>)

**Problem-3.**  $K_{sp}$  of  $CaF_2$  is  $1.7 \times 10^{-10}$  and its mol. wt. is 78 g mole<sup>-1</sup>. What volume of the saturated solution will contain 0.078 g of  $CaF_2$ ? (Answer: 2.9 litre)

### SOLUBILITY PRODUCT VS IONIC PRODUCT:

The *solubility product* of an insoluble substance is the product of the concentrations of its ions at equilibrium.

The *ionic product* is the product of actual concentrations of ions that may or may not be in equilibrium with the solid.

### SOLUBILITY PRODUCT PRINCIPLE:

- o When the ionic product is equal to the solubility product, the solution is saturated.
- o When the ionic product exceeds the solubility product, the solution is supersaturated and precipitation will occur.
- o When the ionic product is less than the solubility product, the solution will be unsaturated.

**Common-ion effect:** The reduction of the degree of dissociation of a salt by the addition of a common-ion is called the common-ion effect. For example- NaCl in AgCl solution.



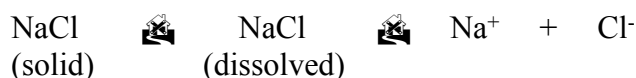
Addition of NaCl shift equilibrium to left due to excess  $\text{Cl}^-$  ions and decrease solubility of AgCl.

## APPLICATION OF SOLUBILITY PRODUCT PRINCIPLE:

The concept of solubility product mentioned above finds a number of applications:

### (1) Purification of common salt.

A saturated solution of common salt freed from suspended impurities is taken and HCl gas passed through it. The equilibrium



On passing HCl gas, the concentration of  $\text{Cl}^-$  ions is increased because HCl is highly ionized. The ionic product  $[\text{Na}^+][\text{Cl}^-]$  thus considerably increases so much so that it exceeds the solubility product of sodium chloride at the given temperature. The result is a supersaturated solution of NaCl from which solid NaCl precipitates out in order to restore the equilibrium.

### (2) Salting out of soap.

Ordinary soap is a mixture of the sodium salts of higher fatty acids and is obtained in the form of a concentrated solution as a result of saponification. From the solution, soap precipitates out on the addition of a saturated common salt solution because the concentration of  $[\text{Na}^+]$  ions increases and the ionic product  $[\text{Na}^+][\text{C}_n\text{H}_{2n+1}\text{COO}^-]$  exceeds the solubility product of soap at that temperature.

**Problem-4.** Calculate the solubility of AgCl ( $K_{sp} = 1.7 \times 10^{-10}$ ) in 0.01 M NaCl solution.

**Problem-5.**  $K_{sp}$  of  $\text{Mg}(\text{OH})_2$  is  $1.8 \times 10^{-11}$  at  $25^\circ\text{C}$ . Calculate the solubility of  $\text{Mg}(\text{OH})_2$  in 0.1 M aqueous NaOH solution.

## IONIC PRODUCT OF WATER: IONIZATION OF WATER

Water is known to be slightly ionized,



But  $\text{H}^+$  ions get hydrated to  $\text{H}_3\text{O}^+$  ions by water, acting as a base. Water act as an acid by losing  $\text{H}^+$  ion. Thus



Applying law of chemical equilibrium,

$$K = \frac{[H^+][OH^-]}{[H_2O]},$$

In case of dilute solution,

$$K [H_2O] = [H^+] [OH^-],$$

Since the ionic concentrations are very small, the concentration of unionized water may be taken as constant, thus

$$K [H_2O] = K_w,$$

$$\therefore K_w = [H^+] [OH^-] = [H_3O^+] [OH^-]$$

$K_w$  is known as ionic product of water and may be defined as the product of concentration of  $H^+$  ions and  $OH^-$  ions in pure water. It is constant at constant temperature.

$$\text{At } 25^\circ\text{C, the value of } K_w \text{ is } 1 \times 10^{-14}.$$

In case of pure water and also in the case of neutral solutions, the molar concentration of  $H^+$  ions and  $OH^-$  ions are equal.

$$[H^+] = [OH^-] = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7} \text{ moles/litre}$$

For neutral solution  $[H^+] = [OH^-] = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7} \text{ moles/litre}$ .

For acidic solution  $[H^+] \gg 1 \times 10^{-7} > [OH^-] \text{ moles/litre}$ .

For basic solution  $[OH^-] \gg 1 \times 10^{-7} > [H^+] \text{ moles/litre}$ .

Now hydrogen ion concentration and hydroxide ion concentration can be expressed in terms of ionic product of water by the following way--

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{[OH^-]} \quad \text{and} \quad [OH^-] = \frac{K_w}{[H^+]} = \frac{1 \times 10^{-14}}{[H^+]}$$

**pH value:** The acidity or the basicity of a solution can be expressed in terms of hydrogen ion concentration. pH of a solution is the negative logarithm of hydrogen ion concentration (called pH scale, Sorensen in 1909).

$$\text{pH} = -\log_{10} [H^+] = \log_{10} \frac{1}{[H^+]}$$

$$\text{pOH} = -\log_{10} [OH^-] = \log_{10} \frac{1}{[OH^-]}$$

For pure water,  $[H^+] = [OH^-] = 1 \times 10^{-7} \text{ moles/litre}$

$$\therefore \text{pH} = -\log_{10} [1 \times 10^{-7}] = -(-7) = 7$$

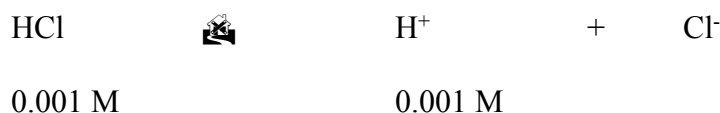


$$\therefore \text{pOH} = -\log_{10} [1 \times 10^{-7}] = 7$$

$$\therefore \text{pH} + \text{pOH} = 7 + 7 = 14$$

**Example-2:** Calculate the pH of 0.001 M HCl.

**Solution:** HCl is a strong acid and it is completely dissociated in aqueous solution.



For every molecule of HCl, there is one  $\text{H}^+$ , therefore

$$[\text{H}^+] = [\text{HCl}]$$

or  $[\text{H}^+] = 0.001 \text{ M}$

$$\begin{aligned} \therefore \text{pH} &= -\log(0.001) \\ &= -\log(1 \times 10^{-3}) \\ &= -\log 1 + 3 \log 10 \\ &= 3 \end{aligned}$$

Therefore the pH of 0.001 M HCl is 3. Ans.

**Problem 6.** Calculate pH and pOH of 0.02 M  $\text{H}_2\text{SO}_4$  solution.  $K_w = 1 \times 10^{-14}$  at  $25^\circ\text{C}$ .

**Problem-7.** pH of an aqueous solution of HCl is 2.699 at  $25^\circ\text{C}$ . Calculate the molarity of the solution.

**Importance of pH in our daily Life:**

- ☞ **All living organisms are pH sensitive and can survive only in a narrow range of pH.**
- ☞ **Most foods are slightly acidic; our "bodily fluids" are slightly alkaline,** as is seawater— not surprising, since early animal life began in the oceans. The pH of freshly-distilled water will go downward as it takes up carbon dioxide from the air. "Acid" rain is by definition more acidic than pure water in equilibrium with atmospheric  $\text{CO}_2$ , owing mainly to sulfuric and nitric acids that originate from fossil-fuel emissions of nitrogen oxides and  $\text{SO}_2$ .
- ☞ **Plants and animals are pH sensitive:** Our body works within the pH range of 7.0 to 7.8. When pH of rain water is less than 5.6, it is called acid rain. When acid rain flows into the rivers, it lowers the pH of the river water. The survival of aquatic life in such rivers becomes difficult.
- ☞ **pH of the soil:** Plants require a specific pH range for their healthy growth.

- ✚ **pH in our digestive system:** It is very interesting to note that our stomach produces hydrochloric acid. It helps in the digestion of food without harming the stomach. During indigestion the stomach produces too much acid and this causes pain and irritation. To get rid of this pain, people use bases called antacids. These antacids neutralise the excess acid.
- ✚ **pH change as the cause of tooth decay:** Tooth decay starts when the pH of the mouth is lower than 5.5. Tooth enamel, made up of calcium phosphate is the hardest substance in the body. It does not dissolve in water, but is corroded when the pH in the mouth is below 5.5. Bacteria present in the mouth produce acids by degradation of sugar and food particles remaining in the mouth after eating. The best way to prevent this is to clean the mouth after eating food. Using toothpastes, which are generally basic, for cleaning the teeth can neutralise the excess acid and prevent tooth decay.
- ✚ **Self defence by animals and plants through chemical warfare:** Wasps (insect) and jellyfish have an alkaline sting and bees have an acidic sting. So with wasps stung area can be treated with vinegar, and bees with soap or baking soda. Stinging hair of nettle (plant) leaves inject methanoic acid causing burning pain.
- ✚ The balance of pH in our body also helps to regulate our breathing rate (carbonic acid in our blood), controls microorganisms on skin, and activates enzymes. Blood has a pH which needs to be maintained between 7.35 and 7.45, or else serious illness and death may occur.

## ELECTROCHEMISTRY

Electrochemistry is a branch of chemistry that studies chemical reactions which take place in a solution at the interface of an electron conductor (a metal or a semiconductor) and an ionic conductor (the electrolyte), and which involve electron transfer between the electrode and the electrolyte or species in solution.

If a chemical reaction is driven by an external 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.

### Electrolytes:

Electrolytes are electrovalent substances that form ions in solution which conduct an electric current.

### Electrolysis:

*The phenomenon of decomposition of an electrolyte by passing electric current through its solution is termed electrolysis.* In chemistry and manufacturing, **electrolysis** is a method of using a direct electric current (DC) to drive an otherwise non-spontaneous chemical reaction. Electrolysis is commercially important in the separation and purification of elements from

naturally occurring sources such as ores using an electrolytic cell. It is also used for the protection and beautification of metallic materials which popularly known as electroplating.

### Electrical Units:

Coulomb- a unit quantity of electricity

Ampere- a unit rate of flow of electricity

Ohm- a unit of electrical resistance

Volt- a unit of electromotive force

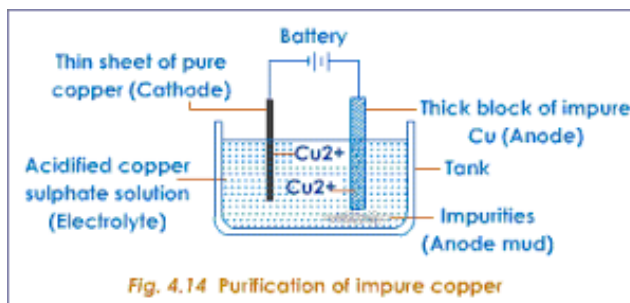


Fig: Mechanism of Electrolysis

### Conductance of electrolytes:

The power of electrolytes to conduct electrical currents is termed conductivity or conductance of electrolytes. It is reciprocal of the resistance (R) and denoted by C. So,  $C=R^{-1}$ . The unit of conductance is  $\text{ohm}^{-1}$  or mho or Siemens (S).

### Specific Conductance ( $\kappa$ , kappa):

The conductance of one centimeter cube of a solution of an electrolyte is called ‘specific conductance’.

$$\text{Unit: } \kappa = \frac{1}{l} \times \frac{1}{R} \times \frac{l}{A} \times \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} = \text{ohm}^{-1} \text{cm}^{-1} \left[ \text{or } R \propto \frac{l}{A}, \text{ or } R \propto l \times \frac{1}{A} \right]$$

### Equivalent Conductance ( $\lambda$ , lambda):

The conductance of an electrolyte obtained by dissolving one gram-equivalent of it in V cc of water is known as ‘equivalent conductance’.

$$\text{Mathematically, } \lambda = \kappa \times V$$

$$\text{Unit: } \lambda = \kappa \times V = \frac{1}{R} \times \frac{l}{A} \times V \times \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} \times \frac{\text{cm}^3}{\text{eqvt.}} \\ = \text{ohm}^{-1} \text{cm}^2 \text{eqvt.}^{-1}$$

### Kohlrausch’s Law (1875):

“ The equivalent conductance of an electrolyte at infinite dilution\* ( $\lambda_{\infty}$ ) is equal to the sum of the equivalent conductances of the component ions”.

\* when the mobility of the ions in solution is almost zero.

Mathematically, we can write-

$$\lambda_{\infty} = \lambda_a + \lambda_c$$

where  $\lambda_a$  is the equivalent conductance of the anion and  $\lambda_c$  is that of cation.

For Example, the equivalent conductance of NaCl at infinite dilution at 25°C is 126.45. The equivalent conductances of  $\text{Na}^+$  and  $\text{Cl}^-$  ions are 50.11  $\text{ohm}^{-1}$  and 76.34  $\text{ohm}^{-1}$  respectively. Thus,

$$\lambda_{\infty}(\text{NaCl}) = \lambda_{\infty}(\text{Na}^+) + \lambda_{\infty}(\text{Cl}^-),$$

or  $126.45 = 50.11 + 76.34$

This is in good agreement with Kohlrausch's law.

**Example-1:** Calculate the equivalent conductance of  $\text{NH}_4\text{OH}$  at infinite dilution at 20°C. Given:  $\lambda_{\infty}(\text{NH}_4\text{Cl}) = 130$ ,  $\lambda_{\infty}(\text{OH}^-) = 174$  and  $\lambda_{\infty}(\text{Cl}^-) = 66$ .

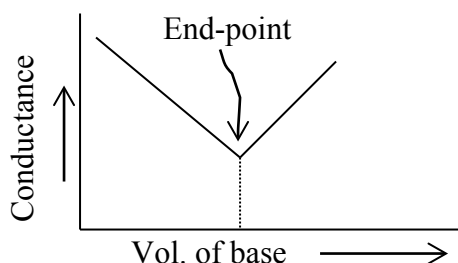
Solution: Applying the Kohlrausch's law,

$$\begin{aligned}\lambda_{\infty}(\text{NH}_4\text{OH}) &= \lambda_{\infty}(\text{NH}_4\text{Cl}) + \lambda_{\infty}(\text{OH}^-) - \lambda_{\infty}(\text{Cl}^-) \\ &= 130 + 174 - 66 = 238 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt.}^{-1} \quad \text{Ans.}\end{aligned}$$

### Conductometric Titrations:

“Titrations in which conductance measurements are made use of in determining the end-point of acid-alkali reactions, some displacement reactions or precipitation reactions are called conductometric titrations”.

(1) Titration of a **strong acid** against a **strong base**.

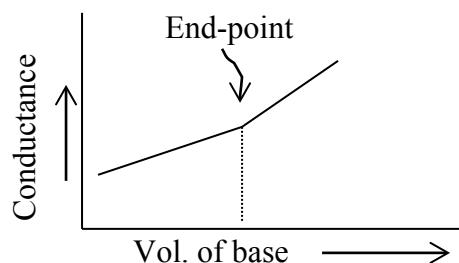
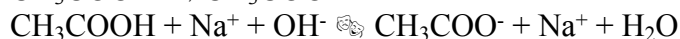


**Figure:**  
Conductometric  
titration curve for  
HCl and NaOH

- Before addition of alkali, conductance of the solution is due to presence of  $\text{H}^+$  and  $\text{Cl}^-$  ions.
- $\text{H}^+$  possesses greatest mobility of any ion, hence the conductance is greater.
- After addition of NaOH,  $\text{H}^+$  is removed by  $\text{OH}^-$  forming feebly (weakly) ionized  $\text{H}_2\text{O}$  molecules and their ( $\text{H}^+$ ) place is taken by slow moving  $\text{Na}^+$  ions.

- The conductance of the solution decreases with further addition of alkali and reach minimum (end-point).
- With further addition of NaOH solution, conductance increases since  $\text{OH}^-$  ions do not consume in the reaction in the form of  $\text{H}_2\text{O}$  molecule.

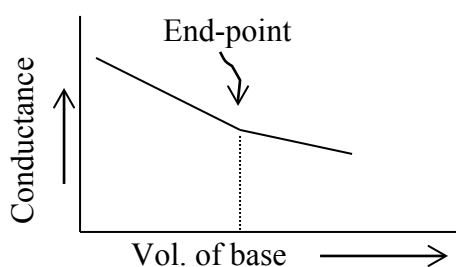
(2) Titration of a **weak acid** against a **strong base**.



**Figure:**  
Conductometric  
titration curve for  
 $\text{CH}_3\text{COOH}$  and  $\text{NaOH}$

- Initial conductance is low because of the poor dissociation of the weak acid.
- Sodium acetate formed; at first suppress the ionization due to common-ion-effect.
- Conductance begins to increase with the further addition of alkali.

(3) Titration of a **strong acid** against a **weak base**.

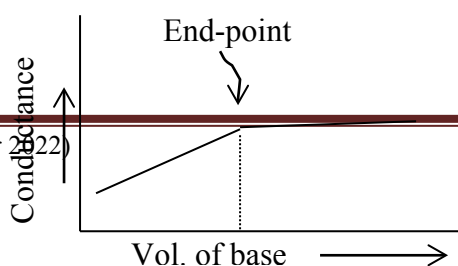


**Figure:**  
Conductometric  
titration curve for  
 $\text{HCl}$  and  $\text{NH}_4\text{OH}$

- In this case, the conductance of the solution will first decrease due to the fixing up of the fast moving  $\text{H}^+$  ions and their replacement by slow moving  $\text{NH}_4^+$ .

(4) Titration of a **weak acid** against a **weak base**.

- The initial conductance of the solution is low due to poor dissociation of the weak acid.
- It starts increasing as the salt  $\text{CH}_3\text{COONH}_4$  is formed.
- After the equivalence point, the conductivity remains almost constant because the free base  $\text{NH}_4\text{OH}$  is a weak electrolyte.



**Figure:**  
Conductometric  
titration curve for  
 $\text{CH}_3\text{COOH}$  and  
 $\text{NH}_4\text{OH}$

This conductometric method is suitable as such titration give a quite sharp end-point.

**Advantages of conductometric titrations over volumetric titrations:**

- (1) coloured solutions where no indicator is found to work satisfactorily can be successfully titrated by this method.
- (2) The method is useful for the titration of weak acids against weak bases which do not give a sharp change of colour with indicators in ordinary volumetric analysis.
- (3) More accurate results are obtained because the end-point is determined graphically.

**Precautions:**

- (a) Temperature should be kept constant throughout the experiment.
- (b) The titrant (standard solution in burette) should be 10 times stronger so that the volume change is as little as possible.

**Differences between conductometric titrations and volumetric titrations:**

<i>Conductometric titrations</i>	<i>Volumetric titrations</i>
1. Conductance measurements are done to check end-points.	1. Volume measurements are done to check end-points.
2. Titration can be carried out even with coloured solution.	2. Titration fails in coloured solution as suitable indicators are not available sometimes.
3. Accurate results are obtained.	3. Results are not so accurate.
4. End-points are determined graphically.	4. End-points are determined by change of colour of indicator.
5. Successful even in weak acids and bases.	5. Not successful in weak acids and bases.

**Electrolytic and Electronic Conductors:**

<i>Electrolytic conductors</i>	<i>Electronic conductors (or metallic conductors)</i>
(1) Electrolytic conduction takes place by actual movement of ions, positive and negative towards the opposite electrodes.	(1) Electronic conduction takes place without any transfer of material during the passage of the current.
(2) This is attended with chemical changes at the electrode.	(2) No chemical change takes place during electronic conduction.
(3) Electrolytic conductor becomes more conducting at higher temperatures.	(3) The resistance of these conductors increases at higher temperature.
(4) Fused salts of electrovalent compounds, solution of electrovalent and some covalent compounds in water and in a few other polar solvents are examples of these conductors.	(4) Metals in general and alloys are classed as electronic conductor. Carbon a non-metal and certain solid salts (cadmium sulphide, cupric sulphide etc.) are also belong to this group.

## Battery Chemistry

A battery is a device that converts chemical energy into electrical energy. This is done by means of an electro-chemical oxidation-reduction reaction of its active materials. This process involves the transfer of electrons from one material to another through an electric circuit.

## Types of Batteries

They are two types of batteries- Primary batteries and Secondary or storage batteries. Primary batteries can provide only one continuous discharge, cannot be reused and re-charged. They are used as a source of dc power for everyday items such as flashlights and transistor radios.

A secondary or storage battery is made of several chemical and elemental materials. These materials change during charging and discharging and this change is reversible. After the battery has discharged, it is brought back to a charged state, by causing the current to flow back through the battery in the opposite direction. The electrodes are thus returned to approx. their original state. The most common battery of this type is lead- (sulfuric) acid battery. Secondary batteries are used as a source of dc power when the battery is the main source of power and many discharge and charge cycles are required, such as electrical vehicles, mine locomotives, submarines, or standby power required such as telephone exchange and emergency lighting. They are often used to supply large, short time repetitive power requirements such as car and airplane batteries. They are also used for load leveling of an electric power supply network.

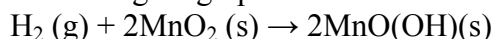
The discharge reaction can be written for a primary battery as follows:

**Anode (Oxidation):**  $\text{Zn (s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

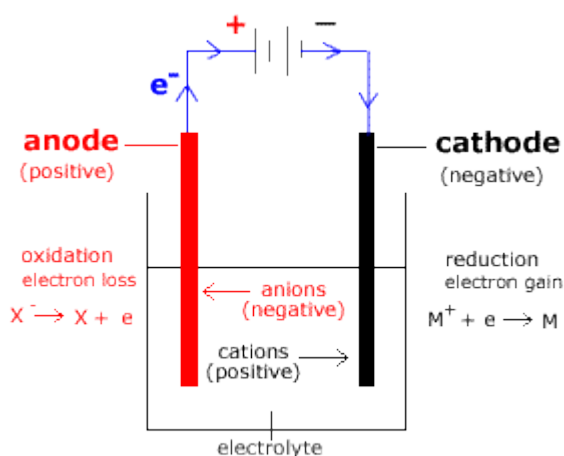
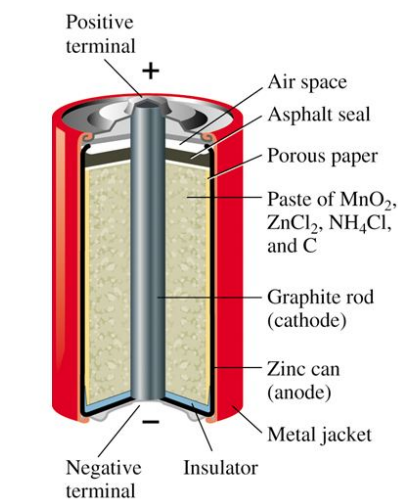
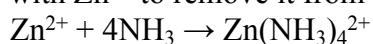
**Cathode (Reduction):**  $2\text{NH}_4^+ + 2\text{e}^- \rightarrow 2\text{NH}_3 (\text{g}) + 2\text{H}_2 (\text{g})$

**Cell Reaction:**  $\text{Zn (s)} \mid \text{Zn}^{2+} (\text{aq}) \parallel 2\text{NH}_4^+ (\text{aq}), [\text{NH}_3 (\text{aq}) + \text{H}_2 (\text{g})] \mid \text{C (gr)}; E = 1.5\text{V}$

Then  $\text{MnO}_2$  prevents  $\text{H}_2$  from collecting on graphite rod:



At the anode,  $\text{NH}_3$  combines with  $\text{Zn}^{2+}$  to remove it from the reaction:

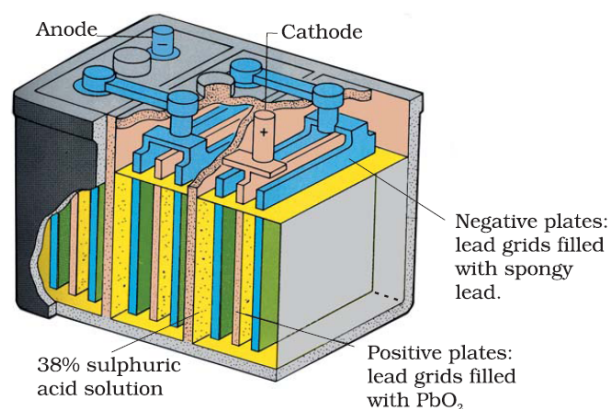
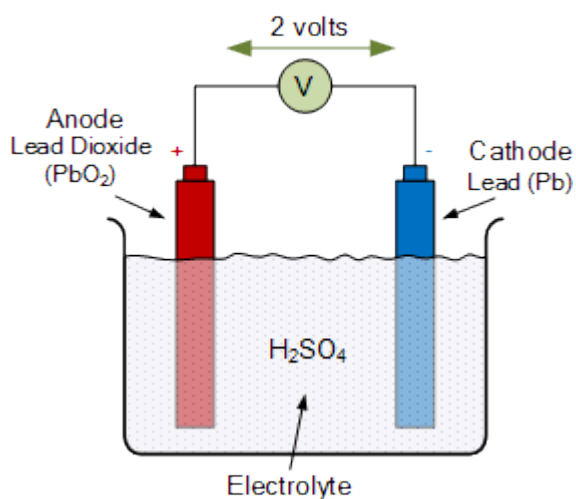


The discharge and charge reactions can be written for secondary batteries as follows:

**Anode (Oxidation):**  $\text{Pb (s)} + \text{H}_2\text{SO}_4 (\text{aq}) \rightarrow \text{PbSO}_4 (\text{s}) + 2\text{e}^- + 2\text{H}^+ (\text{aq})$

**Cathode (Reduction):**  $\text{PbO}_2 (\text{s}) + 2\text{H}^+ + \text{H}_2\text{SO}_4 (\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4 (\text{s}) + 2\text{H}_2\text{O (l)}$   
 $\rightarrow$  (discharging)

**Overall Reaction:**  $\text{PbO}_2 (\text{s}) + \text{Pb (s)} + 2\text{H}_2\text{SO}_4 (\text{aq}) = 2\text{PbSO}_4 (\text{s}) + 2\text{H}_2\text{O (l)}$   
 $\leftarrow$  (charging)

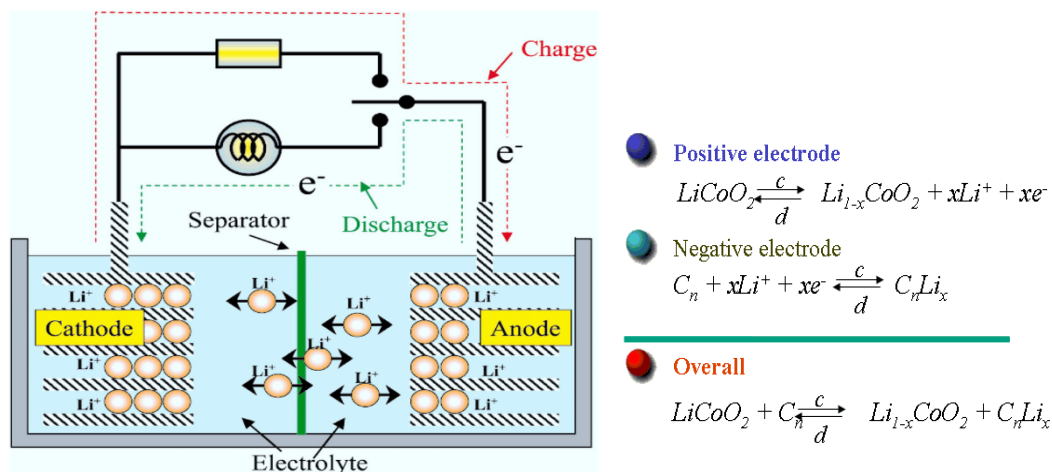


Repeated charging causes hydrolysis of  $\text{H}_2\text{O}$  into  $\text{H}_2$  and  $\text{O}_2$ , so distilled water is added sometimes to keep  $\text{H}_2\text{SO}_4$  concentration constant.



## LITHIUM ION BATTERY

A **lithium-ion battery** or **Li-ion battery** is a type of **rechargeable battery** composed of cells in which **lithium ions** move from the negative **electrode** through an **electrolyte** to the positive electrode during discharge and back when charging.



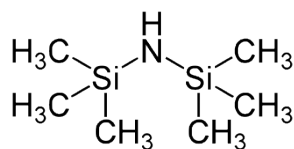
Rechargeable lithium ion cells are the key components of today's information rich mobile society. Lithium ion battery has highest volumetric and gravimetric energy density (smaller and lighter) compare to other battery technologies. **Current lithium ion technology is based on a layered LiCoO<sub>2</sub> cathode and graphite anode.**

## PHOTOLITHOGRAPHY

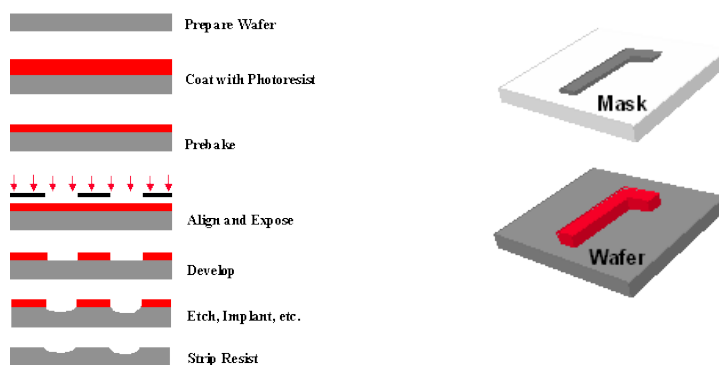
Lithography is a method of printing from a stone or a metal plate with a smooth surface originally based on the immiscibility of oil and water. It was invented in 1796 by German author and actor Alois Senefelder as a cheap method of publishing theatrical works. Lithography can be used to print text or artwork onto paper or other suitable material. In modern lithography, the image is made of a polymer coating applied to a flexible aluminum plate. The image can be printed directly from the plate, or it can be offset, by transferring the image onto a flexible sheet (rubber) for printing and publication.

The related term "photolithography" refers to when photographic images are used in lithographic printing. It plays an important role in the fabrication and mass production of integrated circuits (IC) in the microelectronics industry. The photolithography process involves light exposure through a mask to project the image of a circuit, much like a negative image in standard photography. This process hardens a photo-resistive layer on the printed circuit board (PCB) or silicon wafer (of microprocessors). The hardened areas stay behind in the form of circuit paths of PCBs. Unexposed areas are then dissolved away by a solution bath, such as an acid in wet methods or plasma-like oxygen ions in dry methods.

Silicon wafers are solid pieces of nearly-pure (99.99%) silicon. Photoresist compounds are used to create a mask on the surface of a silicon wafer. Photoresists have three major components, a solvent, resin, and sensitizer (or photoactive compound). The compound is applied to the silicon wafer in liquid form and polymerization is controlled through exposure to light. A common method to increase adhesion of photoresist on the silicon wafer surface is to treat the wafer with Hexamethyldisilazane, C<sub>6</sub>H<sub>19</sub>NSi<sub>2</sub> (HMDS).



The general sequence of processing steps for a typical photolithography process is as follows: substrate preparation, photoresist spin coat, prebake, exposure, post-exposure bake, development, and postbake. A resist strip is the final operation in the lithographic process, after the resist pattern has been transferred into the underlying layer. This sequence is shown diagrammatically in Figure 1:



**Figure 1.** Example of a typical sequence of lithographic processing steps (with no post-exposure bake in this case), illustrated for a positive resist.

## PHASE RULE AND PHASE DIAGRAM

### Phase rule

American physicist Willard Gibbs as early as 1874 gave a relationship mathematically governing all heterogeneous equilibria that is known as Phase rule or Gibb's Phase rule as following:

$$F = C - P + 2$$

Where  $F$  = degrees of freedom,  $C$  = components (number of components in a system) and  $P$  = number of phases.

### Characteristics of Phase rule

- (i) It deals with the behavior of **heterogeneous systems**.
- (ii) It is applied to predict qualitatively by means of a diagram the effect of changing pressure, temperature and concentration on a heterogeneous system in equilibrium.
- (iii) It allows us to predict the number of stable phases that may exist in equilibrium for a particular system.

**Homogeneous system:** A system consisting of one phase is called a *homogeneous system*.

**Heterogeneous system:** A system consisting of two or more phases is *heterogeneous system*.

**Phase (P)**

Definition: A phase is a form of matter that is homogeneous in chemical composition and physical state. Typical phases are solid, liquid and gas. Two immiscible liquids (or liquid mixtures with different compositions) separated by a distinct boundary are counted as two different phases, as are two immiscible solids.

**Examples-**

- (a) A system containing liquid water is 1-phase system,
- (b) A system containing liquid water and water vapor is 2-phase system,
- (c) A system containing liquid water, water vapor and solid ice is 3-phase system.

**More examples**

- (a) Pure substances (solid, liquid or gas):  $O_2$ ,  $C_6H_6$ ,  $H_2O$  etc. 1-phase systems;
- (b) Mixtures of gases:  $O_2$  and  $N_2$  1-phase systems;
- (c) Miscible liquids:  $H_2O$  and ethanol 1-phase system;
- (d) Non-miscible liquids:  $CHCl_3$  and  $H_2O$  2-phase systems;
- (e) Aqueous solution:  $NaCl$  in  $H_2O$  1-phase system;
- (f) Mixtures of solids: monoclinic and rhombic sulfur 2-phase systems; (physical properties different)

**Components (C)**

Definition: The number of components (C) is the number of chemically independent constituents of the system.

Examples

- (1)  $H_2O$  and sulfur system 1-component system;  
 $H_2O$ : three phases- solid ice, water and water vapor but one chemical individual,  $H_2O$ .  
Sulfur: four phases- rhombic, monoclinic, liquid and vapor but one chemical individual.
- (2) Mixtures of gases: (e.g.  $O_2$  and  $N_2$ ) 1-phase, two components;
- (3)  $NaCl$  solution:  $H_2O$  and  $NaCl$  1-phase, two components;

**Degree of Freedom (F)**

**Definition:** The number of degrees of freedom (F) is the number of independent intensive variables, i.e. the largest number of thermodynamic parameters such as temperature or pressure that can be varied simultaneously without affecting one another or without changing the number of phases present at equilibrium. A system is defined completely when it retains the same state of equilibrium with the specified variables.

A system  $F = 0$ , non-variant ☹️ no degree of freedom

A system  $F = 1$ , uni-variant ☹️ one degree of freedom

A system  $F = 2$ , bi-variant ☹️ two degree of freedom

### Examples

(1) For a pure gas,  $F = 2$ ;

$PV = RT$ , if factors P and T are specified V is fixed automatically.

(2) For a mixture of gases,  $F = 3$ ;

Composition, temperature and pressure are specified. Volume is fixed automatically.

(3) For Water ➡ Water vapor,  $F = 1$ ;

Temperature or pressure is specified, the other is fixed automatically.

### One-component systems: Phase diagrams

For a one-component system,  $C = 1$ ;  $\square F = C - P + 2 = 1 - P + 2 = 3 - P$

Case-1. One phase,  $F = 3 - P = 3 - 1 = 2$ ;  $\square$  The system is bi-variant

Two variables- temperature and pressure

A single phase system is represented by an '**Area**' on a P,T-graph.

Case-2. Two phases,  $F = 3 - P = 3 - 2 = 1$ ;  $\square$  The system is mono-variant

One variable- temperature or pressure

A two-phase system is depicted by a '**Line**' on a P,T-graph.

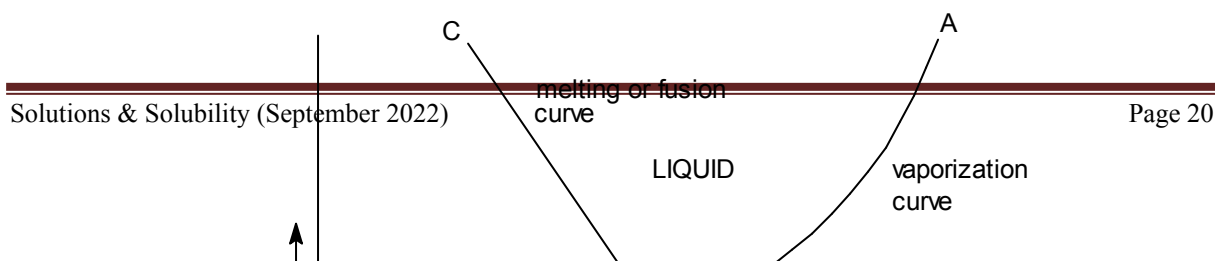
Case-3. Three phases,  $F = 3 - P = 3 - 3 = 0$ ;  $\square$  The system is in-variant

Two variables- temperature and pressure are definite

A three-phase system is represented by a '**Point**' on P,T-graph.

### Phase Diagrams

**Definition:** A phase diagram is a plot showing the conditions of pressure and temperature under which two or more physical states can exist together in a state of dynamic equilibrium. The diagram consists of (a) the regions or areas; (b) the lines or curves and (c) the triple point.



**(a) Regions or areas:**

The diagram is divided into three areas- solid, liquid and vapour.




Each of the three areas shows the conditions of temperature and pressure under which the respective phase can exist.

For one phase and one component,  $F = 1 - 1 + 2 = 2$  ;

Thus each area of phase diagram represents a bi-variant system.

**(b) Lines or curves:**

There are three curves/lines separating the areas, showing the condition of equilibrium between any two of the phases:

- (i) Melting or fusion curve: Solid and liquid phases are in equilibrium, Solid  Liquid; Solid and liquid line is known as melting curve.
- (ii) Vaporisation curve: Liquid and vapour phases are in equilibrium, Liquid  Vapour; Liquid and vapour line is known as vaporisation curve.
- (iii) Sublimation curve: Solid and Vapour phases are in equilibrium, Solid  Vapour; Solid and vapour line is known as sublimation curve.



For two phases and one component,  $F = 1 - 2 + 2 = 1$  ;

Thus each line of phase diagram represents a mono-variant system.

**(c) Triple point:**

The three boundary lines enclosing the three areas on the phase diagram intersect at a common point called the Triple point.

A triple point shows the conditions under which all the three phases (solid, liquid and vapour) can coexist in equilibrium.

Solid  Liquid  Vapour

For three phases and one component,  $F = 1 - 3 + 2 = 0$  ;

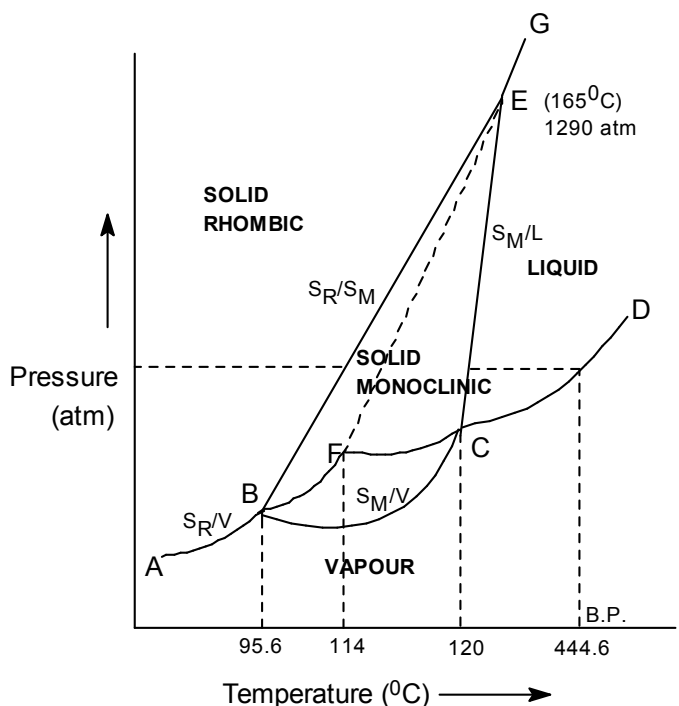
Thus at the triple point of phase diagram the system is non-variant.

## SULFUR SYSTEM

It is a one-component, four-phase system. The four phases are:

- (a) Two solid polymorphic forms:
  - (i) Rhombic Sulfur ( $S_R$ )
  - (ii) Monoclinic Sulfur ( $S_M$ )
- (b) Sulfur Liquid ( $S_L$ )
- (c) Sulfur Vapour ( $S_V$ )

The phase diagram for the sulfur system is shown in Figure.



**Fig.** The phase diagram of the system 'Sulfur'

(1) The curves AB, BC, CD, BE, CE & EG:

$F = C - P + 2 = 1 - 2 + 2 = 1$ ; one degree of freedom i.e. monovariant.

Curve AB, the vapour pressure curve of  $S_R$

Curve BC, the vapour pressure curve of  $S_M$

Curve CD, the vapour pressure curve of  $S_L$

Curve BE, the transition curve,  $S_R + Q$  (heat energy)  $\rightleftharpoons S_M$

Curve CE, the fusion curve of  $S_M$

Curve EG, the fusion curve of  $S_R$

(2) The triple points B, C & E:

$$F = C - P + 2 = 1 - 3 + 2 = 0;$$

no degree of freedom i.e. nonvariant.

(3) The Areas:

$$F = C - P + 2 = 1 - 1 + 2 = 2;$$

two degrees of freedom i.e. bivariant.

The phase diagram of the sulfur system has four areas or regions- rhombic sulfur, monoclinic sulfur, liquid sulfur and vapour.

## CHEMICAL KINETICS & CHEMICAL EQUILIBRIUM

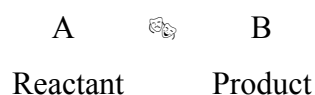
### CHEMICAL KINETICS

The branch of physical chemistry that deals with the rate of reactions is called chemical kinetics. The study of chemical kinetics includes:

- (1) The rate of a reaction and rate laws,
- (2) The factors as temperature, pressure, concentration and catalyst that influence the rate of a reaction;
- (3) The mechanism or the sequence of steps by which a reaction occurs.

#### Reaction rate

The rate of a reaction tells as to what speed the reaction occurs. For example,



The rate of a reaction is defined as the change in concentration of any of reactant or product per unit time.

$$\begin{aligned} \text{Rate of reaction} &= \text{rate of disappearance of A} \\ &= \text{rate of appearance of B} \end{aligned}$$

$$\square \quad \text{rate} = -\frac{d[A]}{dt} = +\frac{d[B]}{dt};$$

where [ ] represents the concentration in moles per litre.

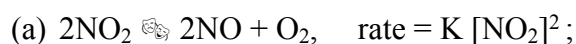
### Rate Laws

An expression, which shows how the reaction rate is related to concentrations is called the rate law or rate equation.



$$\square \quad \text{rate} = K [A]^2 [B]^3, K = \text{rate constant}$$

Example-



### Order of a Reaction

The order of a reaction is defined as the sum of the powers of concentrations in the rate law.

$$\text{rate} = K [A]^m [B]^n$$

$$\square \quad \text{order of such a reaction is } (m+n)$$

Example-

<u>Rate law</u>	<u>Reaction order</u>
rate = K [N <sub>2</sub> O <sub>5</sub> ]	1
rate = K [H <sub>2</sub> ] [I <sub>2</sub> ]	1+1=2
rate = K [H <sub>2</sub> ] [NO] <sup>2</sup>	1+2=3
rate = K [CHCl <sub>3</sub> ] [Cl <sub>2</sub> ] <sup>1/2</sup>	1+1/2=1 1/2

Reactions may be classified according to order.

If  $m + n = 1$ , it is 1<sup>st</sup> order reaction

$m + n = 2$ , it is 2<sup>nd</sup> order reaction

$m + n = 3$ , it is 3<sup>rd</sup> order reaction

## CHEMICAL EQUILIBRIUM

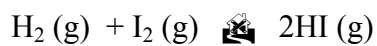
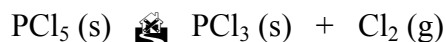
Chemical equilibrium may be defined as the state of a reversible reaction when the two opposing reactions occur at the same rate and the concentrations of reactants and products do not change with time.

Let us consider the reaction,





For example,



Characteristics of chemical equilibrium:

- (1) Constancy of concentrations,
- (2) Equilibrium can be initiated from either side,
- (3) Equilibrium can not be attained in an open vessel,
- (4) A catalyst can not change the equilibrium point,
- (5) Value of equilibrium constant does not depend upon the initial concentration of reactants,
- (6) At equilibrium change in Gibb's free energy i.e.  $\Delta G = 0$

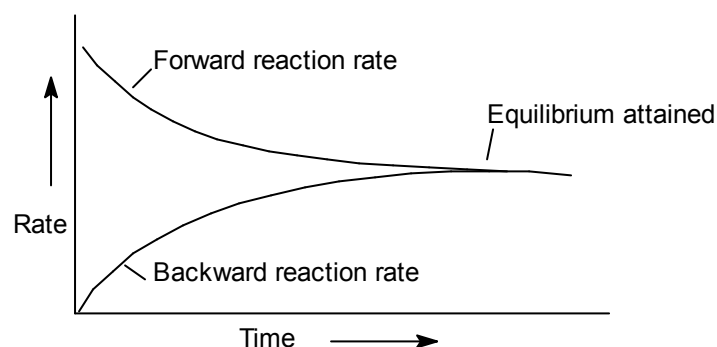


Figure: At equilibrium the forward reaction rate equals the reverse reaction rate

### Equilibrium Constant: Equilibrium Law

For a general reaction



$$\text{Rate of forward reaction} \propto [A][B] = K_1 [A][B]$$

$$\text{Rate of reverse reaction} \propto [C][D] = K_2 [C][D]$$

At equilibrium,

$$K_1 [A][B] = K_2 [C][D]$$

$$\square \quad \frac{K_1}{K_2} = \frac{[C][D]}{[A][B]}$$

The ratio  $\frac{K_1}{K_2}$  is called equilibrium constant,  $K_c$ .

$$\square \quad K_c = \frac{[C][D]}{[A][B]} = \frac{\text{Products concentrations}}{\text{Reactants concentrations}}$$

This is known as the equilibrium constant expression or equilibrium law.

## THERMOCHEMISTRY

Thermodynamics is defined as the branch of science that deals with the relationship between heat and other forms of energy, such as work. It is frequently summarized as three laws that describe restrictions on how different forms of energy can be interconverted.

### The Laws of Thermodynamics

*First law:* Energy is conserved; it can be neither created nor destroyed.

*Second law:* In an isolated system, natural processes are spontaneous when they lead to an increase in disorder, or entropy.

*Third law:* The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K).

**Thermochemistry** is the portion of thermodynamics that relates to chemical reactions. It is the study of the energy changes taking place during chemical reactions. A reaction may release or absorb energy, and a phase change may do the same, such as in melting and boiling. Thermochemistry focuses on these energy changes, particularly on the system's energy exchange with its surroundings. It is useful in predicting reactant and product quantities throughout the course of a given reaction. By calculating entropy, it is also used to predict whether a reaction is spontaneous or non-spontaneous, favorable or unfavorable.

### **Energy and Its Units**

**Energy** is the potential or capacity to move the matter. It is not a material thing but rather a property of matter. Energy exists in different forms that can be inter-converted.

In this chapter, we will be concerned with the energy of substances, or chemical energy, and its transformation during chemical reaction into heat energy. To prepare for this, we will first explore the quantitative meaning of the energy of motion (*kinetic energy*). Then we will look at the concepts of *potential energy* and of the *internal energy* of substances, which is defined in terms of the kinetic and potential energies of the particles making up the substance.

**Kinetic energy** is the energy associated with an object by virtue of its motion. An object of mass  $m$  and speed or velocity  $v$  has kinetic energy  $E_k$  equal to

$$E_k = \frac{1}{2} mv^2$$

This formula shows that the kinetic energy of an object depends on both its mass and its speed. A heavy object can move more slowly than a light object and still have the same kinetic energy. *The SI unit of energy,  $\text{kg.m}^2/\text{s}^2$ , is given the name **Joule (J)**.*

**Potential energy** is the energy an object has by virtue of its position in a field of force. For example, water at the top of a dam has potential energy (in addition to whatever kinetic energy it may possess), because the water is at a relatively high position in the gravitational force field of the earth. We can calculate this potential energy of the water from the formula:

$$E_p = mgh.$$

Here  $E_p$  is the potential energy of a quantity of water at the top of the dam,  $m$  is the mass of the water,  $g$  is the constant acceleration of gravity, and  $h$  is the height of the water measured from some standard level.

The potential energy of the water at the top of the dam is converted to kinetic energy when the water falls to a lower level. As the water falls, it moves more quickly. The potential energy decreases and the kinetic energy increases. The sum of the kinetic and potential energies of the particles making up a substance is referred to as the **internal energy**,  $U$ , of the substance. Therefore, the total energy,  $E_{\text{tot}}$ , of a quantity of water equals the sum of its kinetic and potential energies as a whole ( $E_k + E_p$ ) plus its internal energy.

$$E_{\text{tot}} = E_k + E_p + U$$

**Law of conservation of energy:** ‘Energy may be converted from one form to another, but the total quantity of energy remains constant’.

### Enthalpy and Entropy:

*Enthalpy* is a thermodynamic property of a system. Every substance contains stored chemical energy, called enthalpy, mainly by virtue of chemical bonds. Absolute enthalpy is hard to measure, but enthalpy changes ( $\Delta H$ ) during reactions are easy to measure because there will be an observable energy exchange between the chemicals and the surroundings.

$$\Delta H = \Delta E + P\Delta V$$

i.e., the change in enthalpy ( $\Delta H$ ) is the sum of the change in the internal energy ( $\Delta E$ ) and the work done ( $P\Delta V$ ).

*Entropy* is another thermodynamic property, which we can consider as a measure of the disorder or randomness of a system. It is defined as

$$\Delta S = \int \frac{dQ_{\text{rev}}}{T},$$

i.e. the change in entropy ( $\Delta S$ ) of a thermodynamically reversible process equals the total heat transferred between the system and its surroundings divided by  $T$ . An ordered system has **low** entropy. A disordered system has **high** entropy. For example, in solid state molecules strongly attracted (less disorder) and in gaseous state molecules are not strongly attracted (more disorder). Due to that, entropy is greater in a gas.

Enthalpy and entropy are different quantities. Enthalpy has the units of heat, joules. Entropy has the units of heat divided by temperature, Joules per Kelvin.

### System, boundary, surrounding and universe

**System:** The portion of the physical universe, which is under thermodynamic consideration, is called a system. There are three types of system:

<i>Open system</i>	: energy & matter can transfer
<i>Closed system</i>	: energy transfers only
<i>Isolated system</i>	: no transfer

It usually consists of definite amount of a specific substance.

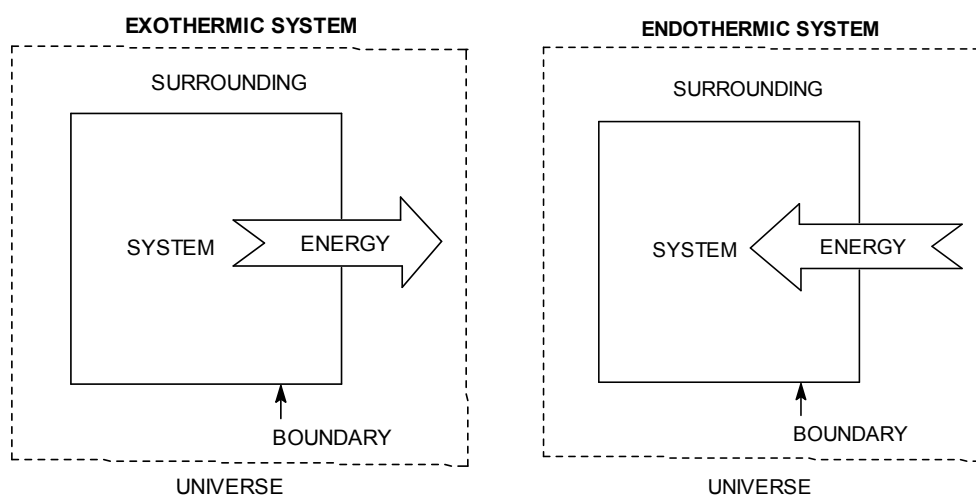
**Boundary:** The real or imaginary line that marks the limit of the system to a definite place in space is called boundary.

The boundary separates the system from the rest of the universe i.e. the surroundings.

**Surrounding:** The portion of the physical universe outside the boundary of the system is known as surrounding.

**Universe:** It consists of a system and a surrounding of that system in space.

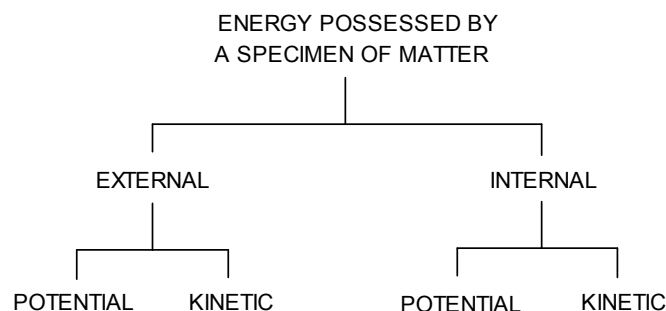
### **Exothermic and Endothermic Systems:**



**Total energy of a body:** All types of energy that a body possesses are known as total energy of a body. There are two main types of energy that a body possesses;

- (a) The external energy
- (b) The internal energy

Each of these two types can again be sub-divided into- (i) the potential energy and (ii) the kinetic energy.



**External potential energy:** Potential determined by the position of the matter relative to the earth's surface or relative to some other reference datum.

**External kinetic energy:** Kinetic determined by the speed of the movement of the matter.

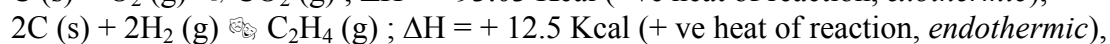
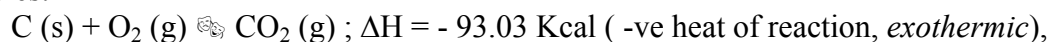
**Internal potential energy:** Potential determined by the composition, structure or relative position of the atoms including those of the subatomic particles inside the atom, and/or groups of atoms forming the molecule of the substance. The attractive & repulsive forces acting between the residents of the atoms also contribute to the potential energy of the substance.

**Internal kinetic energy:** It is due to the motion such as vibrational, rotational or spinning type motion of the molecule, atoms and sub-atomic units of the atom.

## HEAT OF REACTION

The amount of heat that is either evolved or absorbed during the course of a chemical reaction (when number of moles of reactants as represented by balanced chemical equation change completely into products) is called 'heat of reaction'.

Examples:



# Heat content of  $\text{CO}_2$  is less than the sum of heat contents of C and  $\text{O}_2$ , and hence heat is evolved.

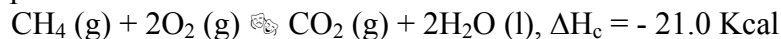
# Heat of reaction depends on the volume, the pressure, the temperature of the system, the amount and the allotropic form of the reacting substances, also on physical state and products.

### Types of heat of reaction:

(1) Heat of Combustion, (2) Heat of Formation, (3) Heat of Solution, (4) Heat of Neutralization. [Other form of heat of reactions may arise during phase change or energy changes in the case of *fusion*, *vaporization*, *sublimation* and *transition*]

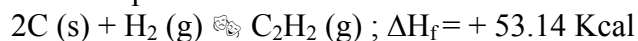
#### 1. Heat of Combustion

It is defined as the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen. Heat of combustion is always negative. Example:



#### 2. Heat of Formation

The change in enthalpy that takes place when one mole of the compound is formed from its elements. Example:



#### 3. Heat of Solution

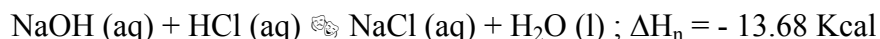
The change in enthalpy when one mole of the substance is dissolved in a specified quantity of solvent at a given temperature. Example:



#### 4. Heat of Neutralization

It is defined as the change in heat content of the system when one gram equivalent of an acid is neutralized by one gram equivalent of a base or vice versa in dilute solution.

Example:



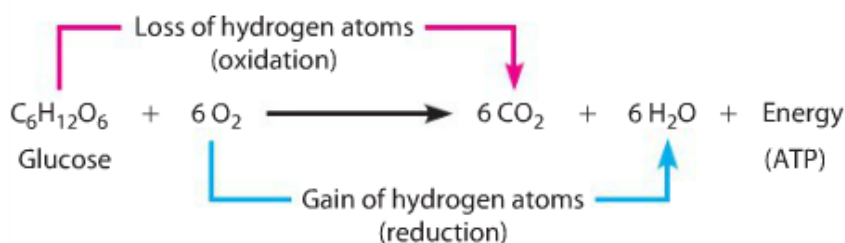
### Fuels - Foods, Commercial Fuels, and Rocket Fuels

A fuel is any substance that is burned or similarly reacted to provide heat and other forms of energy.

#### Food as Fuels

Foods fill three needs of the body: they supply substances for the growth and repair of tissue, they supply substances for the synthesis of compounds used in the regulation of body processes, and they supply energy. About 80% of the energy we need is for heat. The rest is used for muscular action, chemical processes, and other body processes.

The body generates energy from food by the same overall process as combustion, so the overall enthalpy change is the same as the heat of combustion.



#### Fossil Fuels

All of the fossil fuels in existence today were created millions of years ago when aquatic plants and animals were buried and compressed by layers of sediment at the bottoms of swamps and seas. Over time this organic matter was converted by bacterial decay and pressure to petroleum (oil), gas, and coal.

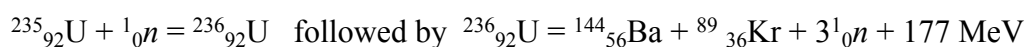
The major problem with petroleum and natural gas as fuels is their relative short supply. It has been estimated that petroleum supplies will be 80% depleted by about the year 2030. Natural-gas supplies may be depleted even sooner. Coal supplies, on the other hand, are sufficient to last several more centuries. This abundance has spurred much research into developing commercial methods for converting coal to the more easily handled liquid and gaseous fuels.

#### Rocket Fuels

Rockets are self-contained missiles propelled by the ejection of gases from an orifice. Usually these are hot gases propelled from the rocket by the reaction of a fuel with an oxidizer.

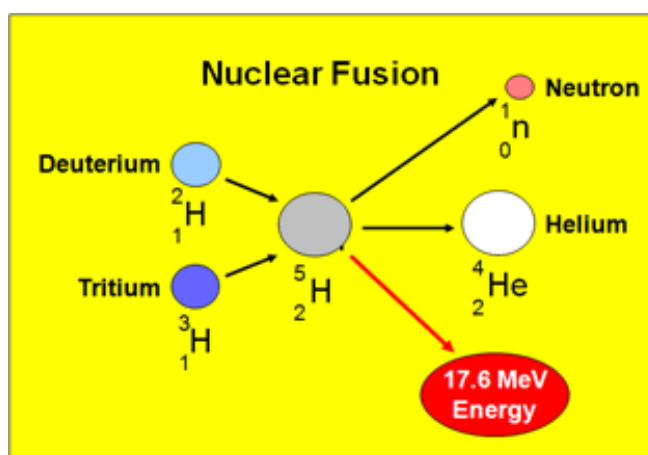
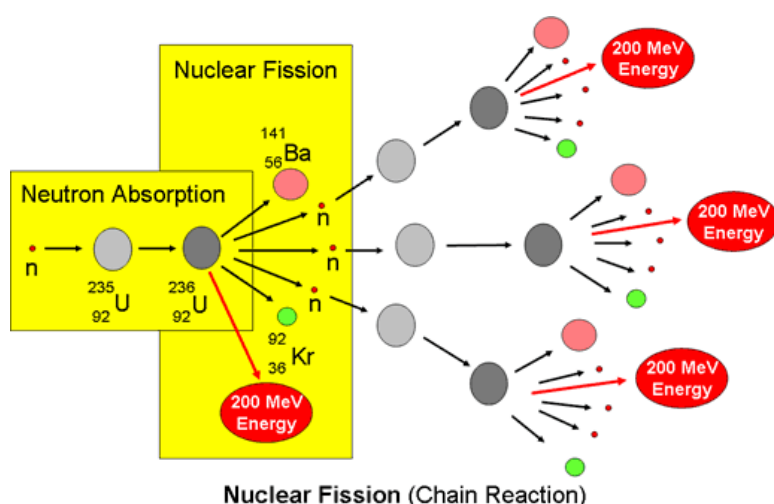
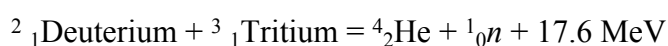
## Nuclear Fission

Large nucleus is bombarded with a neutron, huge heat is produced, can be used to generate electricity, huge nuclear waste (chain reaction).



## Nuclear Fusion

Deuterium-tritium fusion produces very high temperature, heat energy more than fission, very difficult to control, no waste.



NUCLEAR FISSION	NUCLEAR FUSION
A heavy nucleus breaks up to form two lighter nuclei.	Two light nuclei combine to form a heavy nucleus.
It involves a chain reaction.	Chain reaction is not involved.
The heavy nucleus is bombarded with neutrons.	Light nuclei are heated to an extremely high temperature.
We have proper mechanisms to control fission reaction for generating electricity.	Proper mechanisms to control fusion reaction are yet to be developed.
Disposal of nuclear waste is a great environmental problem.	Disposal of nuclear waste is not involved.

## Solid State Chemistry: Electrical Properties of Materials

Intermolecular forces and thermal energy are the two factors on which physical states of matter depend. While the intermolecular forces of attraction tend to keep the particles closer; the thermal energy tends to keep the particles apart from each other by making them move faster. When the net resultant of these two opposing forces, i.e. intermolecular forces and thermal energy, makes the particles stick together and forces them to occupy fixed positions, matters exist in solid state.

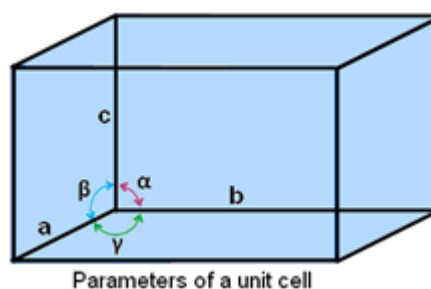
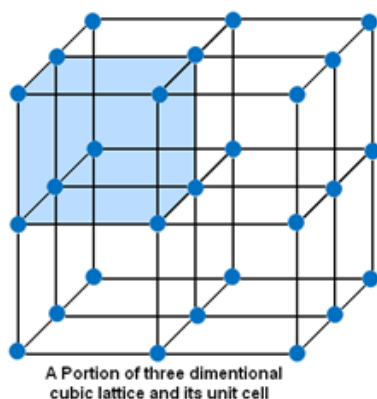
**Classification of solids** – Solids can be classified into two types on the basis of the arrangements of their constituent particles (atoms, molecules or ions). These two types are Crystalline Solid and Amorphous Solid.

**Crystalline Solid:** Solids having large number of crystals; each with definite characteristic geometrical shape; are called crystalline solids. Crystal of NaCl, Quartz, Ice, Iron, etc. are some examples of crystalline solid.

**Amorphous Solid:** Solids having irregular shapes of particles are known as Amorphous Solids. The structures of amorphous solids are similar to that of liquids. Glass, rubber, plastics, etc. are some of the examples of amorphous solids.

### Crystal Lattices and Unit Cells

The geometric arrangement of constituent particles (atoms, molecules, ions) of crystalline solids as point in space is called crystal lattice. Each constituent particle is represented by one point in a crystal lattice. These points are known as lattice point or lattice site. Lattice points in a crystal lattice are joined together by straight lines. By joining the lattice points with straight lines the geometry of the crystal lattice is formed.





**Unit Cell** – The smallest portion of a crystal lattice is called Unit Cell. By repeating in different directions unit cell generates the entire lattice.

**Parameters of a unit cell:**

- A unit cell is characterized by six parameters. These parameters are three edges ( $a$ ,  $b$  and  $c$ ) and angles between them ( $\alpha$ ,  $\beta$  and  $\gamma$ ).
- Dimensions along the edges of a unit cell is represented by  $a$ ,  $b$  and  $c$ .
- Edges of unit cell may or may not be mutually perpendicular.
- The angle between  $b$  and  $c$  is represented by  $\alpha$ , between  $a$  and  $c$  by  $\beta$  and between  $a$  and  $b$  by  $\gamma$ .

**Types of Unit Cell:** - There are two types of unit cells – Primitive and Centred Unit Cells. When particles in unit cell are present only at the corners, it is called the *primitive unit cell*. When particles are present at other positions in addition to those at corners in a unit cell, it is called a *Centred Unit Cell*. There are three types of Centred Unit Cell:

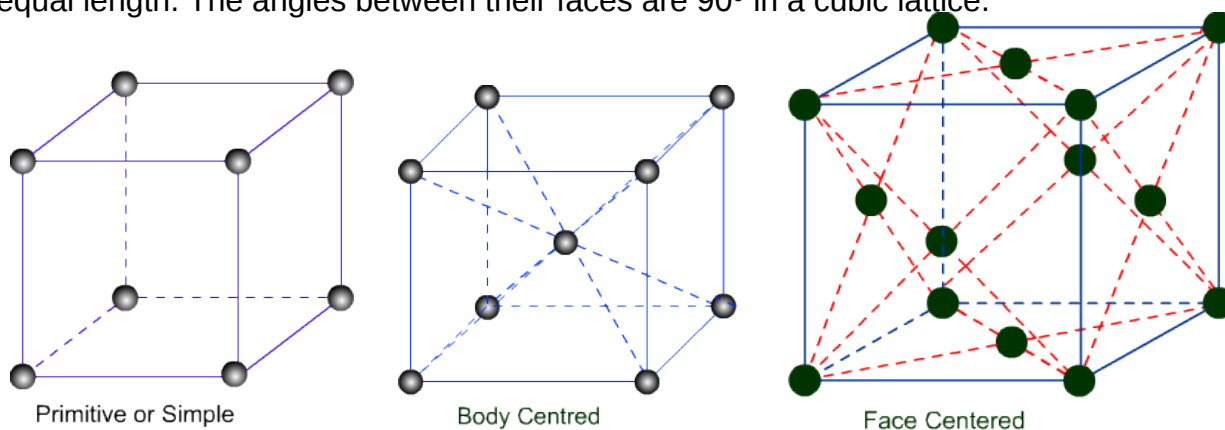
**(a) Body Centred Unit Cells:** – If one constituent particle lies at the centre of the body of a unit cell in addition to the particles lying at the corners, it is called Body-Centred Unit Cell.

**(b) Face-Centred Unit Cells:** – If one constituent particle lies at the centre of each face besides the particles lying at the corner, it is known as Face-Centred Unit Cells.

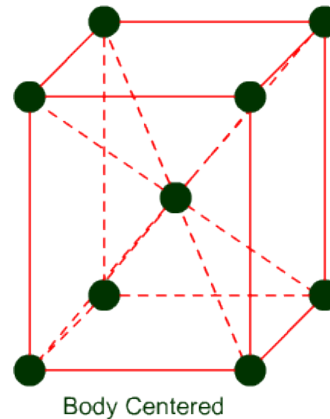
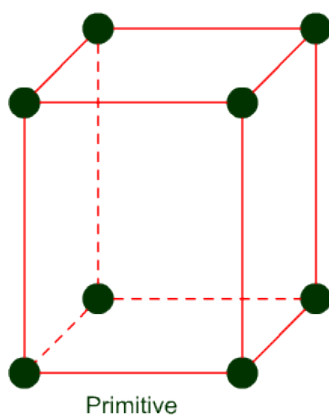
**(c) End-Centred Unit Cell:** – If one constituent particle lies at the centre of any two opposite faces besides the particles lying at the corners, it is known as End-Centred Unit Cell. It is also known as base-centred unit cell.

There are seven types of unit cell formed. These are **Cubic, Tetragonal, Orthorhombic, Monoclinic, Hexagonal, Rhombohedral or Trigonal and Triclinic**.

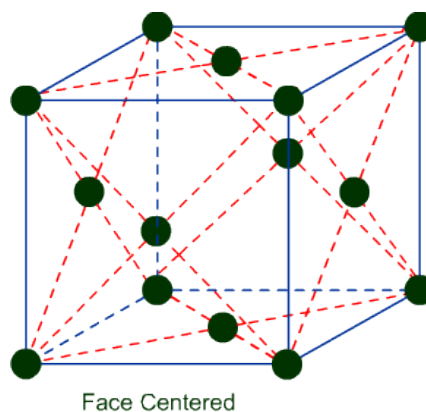
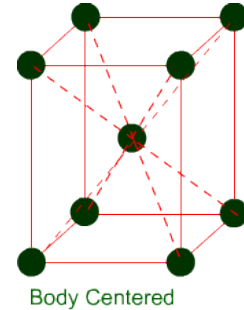
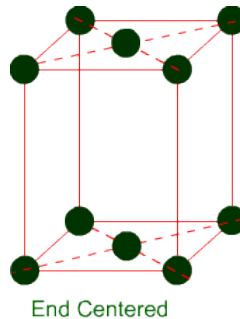
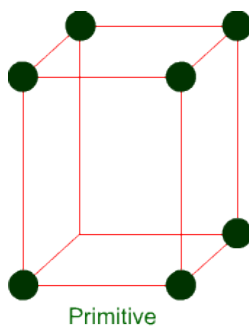
**Cubic Lattice** – There are three types of lattice possible for cubic lattice. Primitive or Simple, Body centred, Face centred lattices. In these types of lattices all sides are of equal length. The angles between their faces are  $90^\circ$  in a cubic lattice.



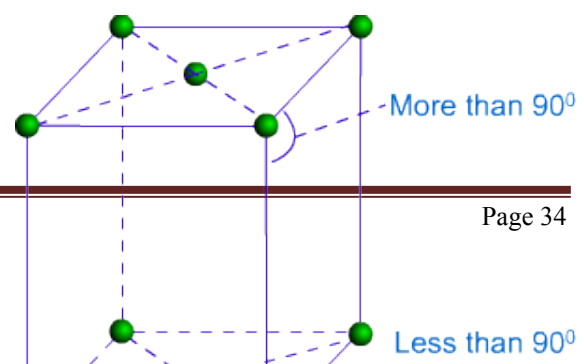
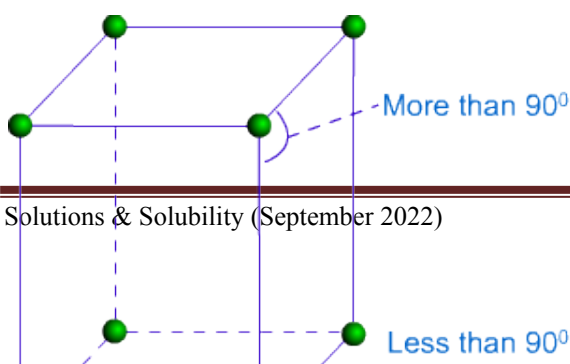
**Tetragonal Lattice** – There are two possible types of tetragonal lattices. Primitive and Body centred unit cells. In these lattices one side is different in length and angles between faces are equal to  $90^\circ$ .



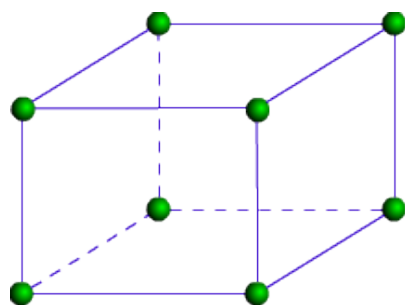
**Orthorhombic Lattice** – Four types of orthorhombic lattice are possible. They are Primitive, End-centred, Body centred and Face centred. They have unequal sides. The Angles between their faces are equal to  $90^\circ$ .



**Monoclinic Lattice** – There are two possible types of monoclinic lattice. They are Primitive and End centred. They have unequal sides and two faces have angles other than  $90^\circ$ .

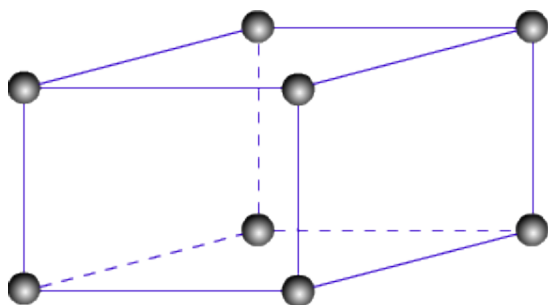


**Hexagonal lattice** – Hexagonal lattice is of one type only. It has one side is different in length to the other two and the angles on two faces are  $60^\circ$ .

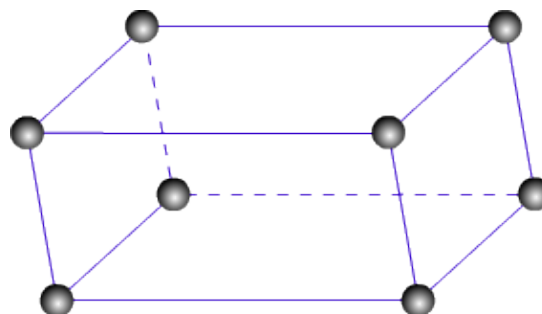


Hexagonal Lattice

**Rhombohedral Lattice** – Only one type of lattice is possible for Rhombohedral lattice. It has all sides equal and angles on two faces are less than  $90^\circ$ .



Rhombohedral Lattice



Triclinic Lattice

**Triclinic Lattice** – Triclinic lattice has only one type of lattice. It has unequal sides and none of the angles between faces are equal to  $90^\circ$ .

### Close Packed Structure

Matters exist in solid state because of close packing of their constituent particles. There are two types of close packing found in solids. These are Cubic Close Packed (ccp) and Hexagonal Close Packed (hcp) lattice.

**Cubic Close packed (ccp):**

In this type of packing, the spheres of molecules are adjacent to each other that each row of spheres in a particular dimension is a repetition of the previous row. The spheres of a particular row don't fit in the depressions between two adjacent spheres of the previous row. This type of arrangement is called AAAA type arrangement. This is also known as face centered cubic (fcc). This type of close packing of constituent particles is found in metals like copper, silver, etc.

Lattice of this cubic close packed is simple cubic and its unit cell is primitive cubic unit cell.

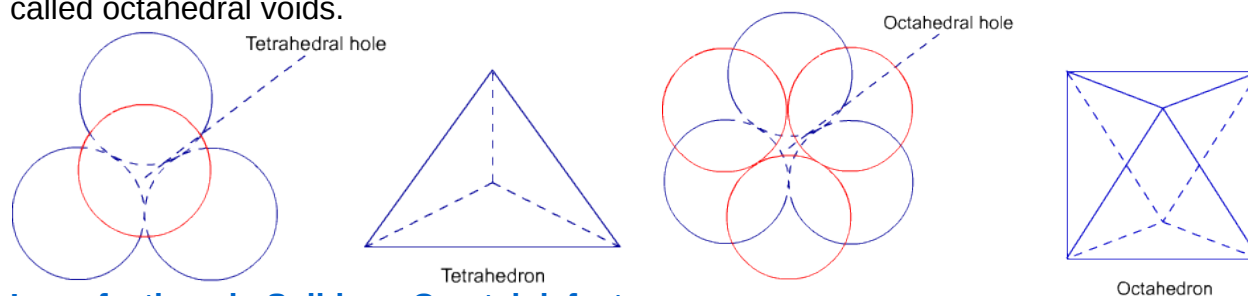
### Hexagonal Close packed (hcp):

In this type of packing, the spheres of molecules of a particular row in a particular dimension are in a position that they fit into depressions between adjacent spheres of the previous row. This type of arrangement is called ABAB type arrangement. This type of packed lattice is found in many metals such as magnesium, zinc, etc.

**Coordination number:** The number of adjacent particles of atoms is called coordination number.

In both ccp and hcp, each sphere is surrounded by 12 adjacent atoms, thus coordination number is equal to 12 in each case. The packing efficiency (volume of space occupied by the spheres/total volume) is 74.05 % (highest average density) for both cubic and hexagonal close packing schemes.

**Formation of voids in close packing:** Empty space left after the packing is called void. Two types of voids are formed in ccp and hcp structures. These are tetrahedral voids and octahedral voids. Tetrahedral voids are formed because of formation of tetrahedron between the layers of atoms. Thus, voids in the shape of tetrahedron are called tetrahedral voids. Octahedral voids are formed because of formation of octahedron between the layers of atoms. Thus, voids in the shape of octahedron are called octahedral voids.



### Imperfections in Solids or Crystal defects

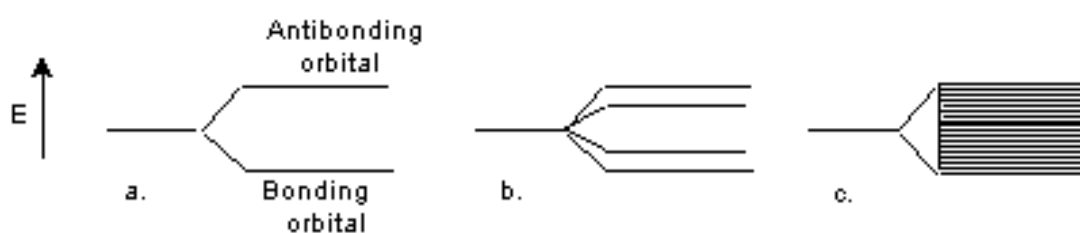
Irregularity in the arrangement of constituent particles in solids is called crystal defect or imperfection in solids. There are two types of crystal defects - **Point Defects** and **Line Defects**. Irregularities or deviation from ideal arrangement of constituent particles around the point or atom in a crystalline solid is known as *point defects*. Irregularities or deviation from ideal arrangement of constituent particles in entire row of lattice is known as *line defects*.

### Electrical Properties

Solids show amazing range of electrical conductivities. Electrical conductivity is the reciprocal of resistivity. The SI unit of resistivity is ohm meter. Whereas resistivity is the property of solids to resist flow of electricity, conductivity is the property to conduct electricity. The SI unit of conductivity ( $\sigma$ ) is  $\text{ohm}^{-1}\text{m}^{-1}$ .

## THE BAND THEORY OF CONDUCTIVITY

The band theory is the result of the application of molecular orbital theory (MOT) to metals and explains conduction in metals. According to MOT, all atomic orbitals participating in molecule formation combined to form equal number of molecular orbitals having definite energy levels. In solids, permitted electron energy levels are named as **bands**. The band containing the valence shell electrons (3s for Na) is called the **valence band**. Any band that is either vacant or partially filled is called a **conduction band**.

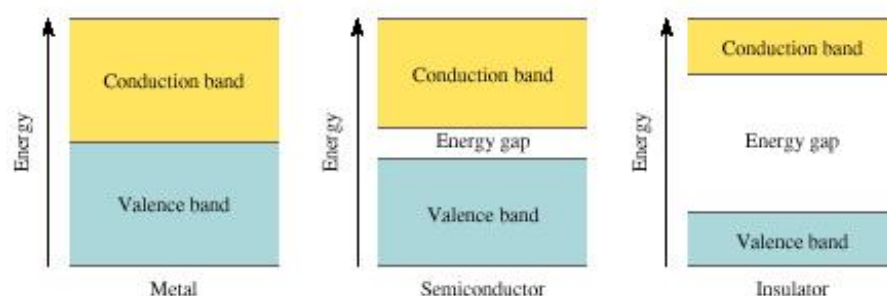


Figures above explain the formation of an energy band by the successive overlap of atomic orbitals. (a) When the two atomic orbitals of two atoms overlap, one bonding orbital and one antibonding orbital of significantly different energies are formed. (b) When four atomic orbitals of two atoms overlap, four molecular orbitals are formed. (c) With so many orbitals, the orbital energies differ very small from each other and form a virtually continuous band.

For example, conduction in Na metal: When a voltage is applied across a piece of sodium metal, conduction occurs. The current is the result of electrons in the 3s band being free to jump from atom to atom. In alkali metals the conduction band and the valence band are the same. The orbitals within the band are so similar in energy that an electron does not need to gain appreciable energy to reach the conduction band.

Metals are **conductors**. There is no band gap between their valence and conduction bands, since they overlap. There is a continuous availability of electrons in these closely spaced orbitals.

In an **insulator**, such as glass or plastic, the valence band is filled. Thus the next vacant higher-energy band becomes the conduction band. An energy gap exists between the valence band and the conduction band. This large separation prevents electrons in insulators from entering the conduction band.



**FIGURE 20.10** Comparison of the energy gaps between valence band and conduction band in a metal, a semiconductor, and an insulator. In a metal the energy gap is virtually nonexistent; in a semiconductor the energy gap is small; and in an insulator the energy gap is very large, thus making the promotion of an electron from the valence band to the conduction band difficult.

A **semiconductor**, such as Si and Ge, has a filled valence band and an empty conduction band, but in contrast to an insulator, a relatively small gap exists between these bands. A relatively small amount of thermal energy will promote an electron into the conduction band. Thus as temperature increases, the conductivity of semiconductors increases. There are two different kinds of semiconductors: **intrinsic** and **extrinsic**.

An **intrinsic semiconductor** is a semiconductor in its pure state. For every electron that jumps into the conduction band, the missing electron will generate a hole that can move freely in the valence band. The number of holes will equal the number of electrons that have jumped.

In **extrinsic semiconductors**, the band gap is controlled by purposefully adding small impurities to the material. This process is called **doping**. Doping or adding impurities to the lattice can change the electrical conductivity of the lattice and therefore vary the efficiency of the semiconductor. In extrinsic semiconductors, the number of holes will not equal the number of electrons jumped.

Silicon or germanium is doped with electron rich impurities to increase their electrical conductivity. Semiconductors so formed are called n-type semiconductors. When silicon or germanium is doped with elements, such as Boron, Aluminium or Gallium, semiconductor thus formed with electron deficient impurities; are called p-type semiconductors. Doping with electron rich or electron deficient elements creates electronic defects in semiconductors.

#### Applications of n-type and p-type semiconductors:

- Both n-type and p-type semiconductors are used in making electronic components.
- As diode which is the combination of n-type and p-type semiconductors.
- As integrated circuit (ICs).
- In photoelectric cell
- As transistors, to amplify radio and audio signal

#### Summary of band theory

- In solids, permitted electron energy levels are named as **bands**.
- The **valence band** contains electrons that can be considered to be bound to the atom. In insulators and semiconductors the valence band is full.
- The **conduction band** is a region of permitted energy levels that is empty in insulators and semiconductors, but partially filled in conductors.
- Only partially filled bands may permit conduction.
- There is a forbidden zone that forms an **energy gap** between the valence and conduction bands in insulators and semiconductors.

- That energy gap must be jumped if an electron is to move to the conduction band, and this is not normally possible in insulators because the gap is too large.
- In semiconductors, the forbidden zone is much smaller and electrons can jump the gap to the conduction zone as a result of thermal excitation.
- **Doping** of semiconductors can significantly reduce the width of the energy gap.

### Magnetic Properties:

Substance shows magnetic properties because of presence of electrons in them. Each electron in an atom behaves like a magnet because of its two types of motions - one is around their axis and other around the nucleus. Electrons in an atom because of charge over them and in motion continuously; possess small loop of current which shows the magnetic moment.

Substances are classified on the basis of magnetic properties into: (1) Paramagnetic, (2) Diamagnetic, (3) Ferromagnetic, etc.

Substances show **paramagnetism** because of presence of unpaired electrons. These unpaired electrons are attracted by magnetic field. For example  $O_2$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ , Magnesium, molybdenum, lithium, etc.

**Diamagnetic** substances are just opposite to that of paramagnetic. Substances show diamagnetic property because of presence of paired electrons and no unpaired electron. Thus, pairing of electrons cancel the magnetic property. For example;  $H_2O$ ,  $NaCl$ ,  $C_6H_6$ , etc.

Substances that are attracted strongly with magnetic field are called **ferromagnetic** substances, such as cobalt, nickel, iron, chromium oxide, etc.

Metals crystallise in one of three systems:

Hexagonal close packed (hcp). 12:12 coordination. ABAB layers.

Cubic close packed (ccp). 12:12 coordination. ABCABC layers.

Body centred cubic (bcc) 8:8 coordination. Face centred cubic (fcc) is just an alternate name for ccp.

### AMERICAN INTERNATIONAL UNIVERSITY-BANGLADESH (AIUB)

Faculty of Science & Information Technology

Department of Chemistry

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### PROBLEMS: (Acid-base, pH and Solubility)

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**Problem 1.** The solubility product of  $CuCl_2$  is  $3.2 \times 10^{-7}$  at  $25^\circ C$ . Calculate the solubility of  $CuCl_2$  in mole litre<sup>-1</sup>.

**Problem 2.** 100 ml of a saturated solution of  $Mg(OH)_2$  contains  $8.2 \times 10^{-4}$  g solute. Mol. wt. of  $Mg(OH)_2$  is 58.3 g mole<sup>-1</sup>; calculate its  $K_{sp}$ .

**Problem 3.**  $K_{sp}$  of  $CaF_2$  is  $1.7 \times 10^{-10}$  and its mol. wt. is 78 g mole<sup>-1</sup>. What volume of the saturated solution will contain 0.078 g of  $CaF_2$ ?

**Problem 4.** Will  $\text{PbCl}_2$  precipitate on mixing 1 ml of  $3 \times 10^{-3}$  M NaCl solution with 2 ml of  $1 \times 10^{-3}$  M  $\text{Pb}(\text{NO}_3)_2$  solution?

**Problem 5.** Calculate the solubility of AgCl ( $K_{\text{sp}} = 1.7 \times 10^{-10}$ ) in 0.01 M NaCl solution.

**Problem 6.**  $K_{\text{sp}}$  of  $\text{Ag}_2\text{S}$  is  $4 \times 10^{-48}$  at  $25^\circ\text{C}$ . Calculate its solubility in a pure water and 0.01 M aqueous solution of  $\text{Ag}_2\text{S}$ .

**Problem 7.**  $K_{\text{sp}}$  of  $\text{Mg}(\text{OH})_2$  is  $1.8 \times 10^{-11}$  at  $25^\circ\text{C}$ . Calculate the solubility of  $\text{Mg}(\text{OH})_2$  in 0.1 M aqueous NaOH solution.

**Problem 8.** Accepting  $K_{\text{w}} = 1 \times 10^{-14}$  at  $25^\circ\text{C}$ , calculate concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  in mole/litre in 0.1M, 0.001M and 0.0002M HCl solutions; also calculate pH and pOH of the solutions.

**Problem 9.** Calculate pH and pOH of 0.02 M  $\text{H}_2\text{SO}_4$  solution.  $K_{\text{w}} = 1 \times 10^{-14}$  at  $25^\circ\text{C}$ .

**Problem 10.** 1 litre solution at  $25^\circ\text{C}$  contains (i) 4.0 g of NaOH, (ii) 0.4 g of NaOH, (iii) 0.02 g of NaOH. Calculate the concentration of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  in each solution, also calculate pH and pOH,  $K_{\text{w}} = 1 \times 10^{-14}$ . (Mol. wt. of NaOH is 40).

**Problem 11.** pH of an aqueous solution of HCl is 2.699 at  $25^\circ\text{C}$ . Calculate the molarity of the solution.

**Problem 12.** Will  $\text{CaSO}_4$  precipitate on mixing equal volumes of 0.02 M  $\text{CaCl}_2$  and 0.04 M  $\text{Na}_2\text{SO}_4$  solution?  $K_{\text{sp}}$  of  $\text{CaSO}_4 = 2.4 \times 10^{-4}$ .

**Problem 13.** Calculation of normality of strong acids, (a) 36% HCl, sp. gr. 1.18 and (b) 96%  $\text{H}_2\text{SO}_4$ , sp. gr. 1.84

*\*only odd number*