

2ND SEM COMPLEMENTARY CHEMISTRY  
CALICUT UNIVERSITY

PHYSICAL CHEMISTRY  
2019 ADMISSION ONWARDS



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**SEMESTER II**  
**Course Code: CHE2C02**  
**Complementary Course II: PHYSICAL CHEMISTRY**

**Objective(s) :** To provide the students a thorough knowledge about different terminologies in thermodynamics and the continuity between different states of matter. It will also impart an idea behind basic principles of electrochemistry.

**Module I: Thermodynamics (6 hrs)**

Definition of thermodynamic terms - System – Surroundings - Types of systems.

First law of Thermodynamics - Internal energy - Significance of internal energy change – Enthalpy. Second law of Thermodynamics - Entropy and spontaneity - Statement of second law based on entropy. Entropy change in phase transitions (derivation not required) – Entropy of fusion, vaporization and sublimation. The concept of Gibbs free energy – Physical significance of free energy - Conditions for equilibrium and spontaneity based on  $\Delta G$  values - Effect of temperature on spontaneity of reaction. Third law of Thermodynamics.

**References**

1. B. R. Puri, L. R. Sharma, M. S. Pathania, *Principles of Physical Chemistry*, 46th Edn., Vishal Publishing Company, New Delhi, 2013.
2. J. Rajaram, J. C. Kuriacose, *Chemical Thermodynamics*, Pearson Education, New Delhi, 2013.

**Module II: Gaseous and Solid States (10 hrs)**

*Gaseous State:* Introduction - Kinetic molecular model of gases – Maxwell distribution of velocities and its use in calculating molecular velocities – Average velocity, RMS velocity and most probable velocity (derivations not required) – Boyle's law – Charles's law – Ideal gas equation – Behaviour of real gases – Deviation from ideal behavior - Van der Waals equation (derivation not required).

*Solid State:* Introduction - Isotropy and anisotropy - Symmetry elements in crystals – The seven crystal systems – Miller indices - Bravais lattices – Bragg's equation (derivation required) and its applications (mention only). Defects in crystals: Non-stoichiometric and stoichiometric defects - Extrinsic and intrinsic defects.

**References**

1. K. L. Kapoor, *A Textbook of Physical chemistry*, Volumes 1, Macmillan India Ltd.
2. B. R. Puri, L. R. Sharma, M. S. Pathania, *Elements of Physical chemistry*, Vishal Pub. Co

**Module III: Liquid State and Solutions (6 hrs)**

*Liquid State:* Introduction - Vapour pressure, surface tension and viscosity – Explanation of these properties on the basis of intermolecular attraction.

*Solutions:* Kinds of solutions - Solubility of gases in liquids – Henry's law and its applications- Colligative properties - Osmotic pressure - Laws of osmotic pressure - Reverse osmosis and its applications - Determination of molecular mass using colligative properties.

**References**

1. K. L. Kapoor, *A Textbook of Physical chemistry*, Volumes 1, Macmillan India Ltd.
2. B. R. Puri, L. R. Sharma, M. S. Pathania, *Elements of Physical chemistry*, Vishal Pub. Co.

#### Module IV: Electrochemistry (10 hrs)

Specific conductance, equivalent conductance and molar conductance - Variation of conductance with dilution - Kohlrausch's law - Degree of ionization of weak electrolytes - Application of conductance measurements – Conductometric titrations. Galvanic cells - Cell and electrode potentials - IUPAC sign convention – Reference electrodes– Standard Hydrogen electrode–Calomel electrode- Standard electrode potential – Nernst equation - H<sub>2</sub>-O<sub>2</sub> fuel cell. Ostwald's dilution law – Buffer solutions –Buffer action [acetic acid/sodium acetate & NH<sub>4</sub>OH/NH<sub>4</sub>Cl], applications of buffers.

#### References

1. P. Atkins. J. Paula, Atkins, *Physical Chemistry*. 8th Edn. Oxford University Press, 2006.
3. K. K. Sharma, L. K. Sharma, *A Textbook of Physical Chemistry*, 5th Edn., Vikas Publishing House, New Delhi, 2012.
4. Gordon M. Barrow, *Physical Chemistry*, 5th Edn., Tata McGraw Hill Education, New Delhi, 2006.
5. F. Daniels, R. A. Alberty, *Physical Chemistry*, 5th Edn., John Wiley and Sons, Canada, 1980.



## MODULE-I: THERMODYNAMICS

### Basic terminology of Thermodynamics

- **System:** Part of universe in which observations are made
  - a) *Homogeneous system:* contains only one phase; it will be uniform throughout
  - b) *Heterogeneous system:* contains two or more phases; it will not be uniform throughout
- **Surroundings:** part of universe excluding system
- **Universe:** System + Surroundings

### Types of systems

- **Open system:** There is exchange of energy and matter between system and surrounding  
(Example: Boiling water in an open beaker)
- **Closed systems:** There is no exchange of matter, but exchange of energy is possible between system and surroundings.  
(Example: Hot tea enclosed in a vessel with conducting walls)
- **Isolated system:** There is no exchange of energy or matter between the system and surroundings  
(Example: Hot tea in a thermo flask)

### Macroscopic properties

- Thermodynamic property associated with the collective behavior of the particles in a macroscopic system  
(Examples: pressure, volume, temperature, density, surface tension etc.)
- **Intensive property:** Properties which are independent of amount and size of matter present in the system.  
(Examples: Temperature, Pressure, Viscosity, Density etc.)
- **Extensive property:** Properties which depends upon amount of substance and size of matter present in the system.  
(Examples: Mass, Volume, Surface area etc.)

## The state of a system

- The state of a system can be described by properties such as its pressure ( $p$ ), temperature ( $T$ ), volume ( $V$ ), composition of the system, etc.
- Variable such as  $p$ ,  $V$ ,  $T$  are called state variables or state functions
- Whenever there occurs a change in one of the macroscopic properties of a system, it is said to undergo a change in state.

## State function and path function

- **State function:** property of a system whose values depends only upon the state of the system and not on the path followed by the system  
(Examples: Pressure, Volume, Entropy, Enthalpy etc.)
- **Path function:** properties which depends upon both the state and path followed by the system  
(Examples: Heat, Work etc.)

## Process

- Operation by which a system changes from one state to another
- A process involves change in one or more state variables
- Finite changes in variables ( $P$ ,  $V$ ,  $T$ ,  $U$ ) are represented by  $\Delta$  ( $\Delta P$   $\Delta V$   $\Delta T$  etc)
- Infinitesimally small changes are represented as  $dP$ ,  $dT$ ,  $dV$  etc.

## Types of process

- Isothermal – Process in which  $T$  of system remains constant ( $\Delta T=0$ )
- Adiabatic – no heat enters or leaves the system
- Isochoric – process in which  $V$  remains constant ( $\Delta V=0$ )
- Isobaric - process in which  $P$  remains constant ( $\Delta P=0$ )
- Cyclic – If a system returns to its initial state after a series of different processes, the overall reaction process is called as a cyclic process.
- Endothermic – Process in which energy is absorbed as heat.

- Exothermic – process in which energy is liberated as heat.

## Thermodynamic Equilibrium

- Equilibrium state represents that there is no change in macroscopic properties of a system with time
1. Thermal equilibrium
  2. Mechanical equilibrium
  3. Chemical equilibrium

## Energy Work and Heat

### a) Energy

- Capacity to do work
- Work done by the system – energy is reduced.
- Work done on the system – energy is increased.
- Energy of an object can be either potential energy or kinetic energy.
- Energy is state function

### b) Work

- Exertion of force (f) in moving an object through distance (d)
- $$w = f \cdot d$$
- Work is defined as the energy transfer between the system and surroundings due to the existence of unbalanced force between the two.

### Pressure-volume work or expansion work

- A system alters its volume against an opposing force.
- E.g.: expansion or contraction of gas confined in a cylinder by a piston against constant external pressure  $P_{\text{ext}}$
- If  $\Delta V$  is the change in volume then the work done is given by

$$W = - P_{\text{ext}} \Delta V$$

- By SI convention work done on the system is positive and work done by the system is negative
- Work is a path function.

### c) Heat

- When a system changes from one state to another the gain or loss of energy may occur in the form of heat.
- Heat is the exchange of energy that happens between the system and the surroundings through thermal motion when there exists a temperature difference between them,
- The heat energy transfer from hot body to cold body and at last attain a thermal equilibrium.
- For exothermic process  $q$  is negative
- For endothermic process  $q$  is positive
- Heat is a path function

### First law of thermodynamics

- Total energy of the system

$$E_{\text{total}} = V + K + U$$

$V$  = potential energy

$K$  = kinetic energy

$U$  = internal energy

### Internal energy

- Sum of total of kinetic energies associated with translation rotational, vibrational, electronic and nuclear motions at molecular level
- The change in internal energy

$$\Delta U = U_2 - U_1$$

### Mathematical form of First law of thermodynamics

- Energy can neither be created nor be destroyed. Although it may converted from one form to another

$$\Delta U = q + w$$

$W$  = work done on the system

$Q$  = heat

$W = +ve$  when work done on the system

$W = -ve$  when work done by the system

$q = +ve$  when heat is added to the system

$q = -ve$  when heat is lost by the system

## Significance of internal energy change

$$\Delta U = q_v$$

Internal energy change = Heat absorbed or evolved at constant volume

## Enthalpy

- Sum of internal energy and pressure volume energy

$$H = U + PV$$

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

$$q_p = q_v + P\Delta V$$

## Enthalpy change in a reaction

$$\Delta_r H = \Delta_r U + \Delta n_g RT$$

$$q_p = q_v + \Delta n_g RT$$

## Limitations of first law

1. it fails to explain the extent to which one form of energy can be transformed to another,
2. It does not tell us anything about the direction of a process
3. It cannot predict feasibility of a process
4. It does not rule out the existence of a 100% efficient heat engine which is, in fact impossible.

## Second law of Thermodynamics

### Spontaneous and Non spontaneous process

- Spontaneous process**

A process that has natural urge to take place by itself

- Non Spontaneous process**



Process that has no natural urge to take place by itself and can be occur by an extra work supplied to the system.

## Entropy

- Measure of disorderness of the system.

$$\Delta S = dq_{\text{rev}}/T$$

## Entropy criteria for reversible and irreversible process

- **Reversible process**

In a reversible process entropy of universe remains unaltered

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

- **Irreversible process**

In an irreversible process entropy of universe increases

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

## Second Law of thermodynamics

- Entropy of universe remains constant during a reversible process and it increases for an irreversible process.

**For reversible process,**

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

**For Irreversible process**

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

## Other statements

- In the course of every spontaneous process, enthalpy of universe increases
- The entropy of universe increases continuously

## Entropy criterion for equilibrium

At equilibrium

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

## Phase changes

### 1. Entropy of fusion ( $\Delta_{\text{fus}}S$ )

- Entropy change accompanying in the conversion of 1 mole of the solid substance into its liquid form at its melting point

$$\Delta_{\text{fus}}S = \Delta_{\text{fus}}H/T_f$$

### 2. Entropy of vaporization ( $\Delta_{\text{vap}}S$ )

- Entropy change accompanying in the conversion of 1 mole of liquid substance into vapor at its boiling point.

$$\Delta_{\text{vap}}S = \Delta_{\text{vap}}H/T$$

### 3. Entropy of sublimation ( $\Delta_{\text{sub}}S$ )

- Entropy change accompanying the conversion of 1 mole of solid substance into its vapor form at its sublimation.

$$\Delta_{\text{sub}}S = \Delta_{\text{sub}}H/T$$

## Gibbs free energy

$$\Delta G = \Delta H - T\Delta S \rightarrow \text{Gibb's Helmholtz equation}$$

- Free energy of a system is the maximum amount of energy available with it that can be converted to useful work.
- For reversible process,

$$(\Delta G)_{T,P} = 0$$

- For irreversible process,

$$(\Delta G)_{TIP} < 0$$

### Condition for spontaneous process

Sl no	$\Delta H$	$\Delta S$	$\Delta G = \Delta H - T\Delta S$	Whether process is spontaneous or not
1	-	+	-ve at all T	Spontaneous at all T
2	-	-	-ve only at sufficiently low T such that $\Delta H > T\Delta S$	Spontaneous only at Low T such that $\Delta H > T\Delta S$
3	+ve	+ve	Negative only at T Sufficiently high such that $\Delta H < T\Delta S$	Spontaneous only at high T such that $\Delta H < T\Delta S$
4	+	-ve	Positive at all T	Non-spontaneous at all T

### Standard Gibb's free energy change

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

### Third law of thermodynamics

- At absolute Zero, the entropy of a perfectly crystalline solid is Zero.

## MODULE 2- GASEOUS AND SOLID STATE

### GASEOUS STATE

- Gases are best described by 4 macroscopic physical characteristics / properties. They are
  1. pressure (P)
  2. Volume (V)
  3. Temperature (T)
  4. No of moles (n)
- All gases shows the same quantitative relationship between these properties under similar Conditions. There relationships are known as **Gas laws**.
- Gas laws are based on kinetic theory of gases.

### Kinetic theory of Gases

- This theory makes the following assumptions (postulates)
  1. A gas is made up of very minute particles called molecules.
  2. Molecules are so small. So that the actual Volume of molecules is negligible when compared to total volume of gas. Thus,most volume of gas is empty space(We can Compress gas easily)
  3. The molecules are in Constant rapid random motion. The molecules Collide with one another and also with the walls of the Container.
  4. The pressure of the gas is due to collision of molecules on the walls of the container.
  5. The Collisions are elastic. i.e, there is no net loss of energy during Collision.
  6. Molecules are considered to be perfectly spherical in shape & and elastic in nature.
  7. There is no force of attraction between molecules.
  8. Average kinetic energy of molecules is proportional to the absolute temperature. So all gases at same temperature have the same K.E.
  9. The movement of molecules is not affected by gravity.
  10. Since there is no force of attraction, molecules moves in a straight line.

### Explanation of Gas laws based on kinetic theory

#### Boyle's law

- When the volume of a gas is decreased the molecules come closer and closer. So the number of Collisions increases. Thus pressure of the gas increases because of the increased collision on the walls of the Container.

- Thus, *The Volume of a given mass of a gas is inversely proportional to pressure of the gas at a given temperature.* This is **Boyle's law**.

$$V \propto 1/P$$

$$V = \text{a constant} \times 1/P$$

$$PV = \text{a constant}$$

$$\text{Thus, } P_1V_1 = P_2V_2 = P_3V_3$$

### **Charle's law**

- When a gas is heated the molecules absorb energy and they move faster. So, they collide with the walls of the container with greater force.
- If the walls of the container are flexible, it will expand. Thus,

$$V \propto T$$

- Thus, *at constant pressure, the volume of given mass of gas is directly proportional to the absolute temperature.* This is charle's law

$$V/T = \text{a constant}$$

$$V_1/T_1 = V_2/T_2 = V_3/T_3$$

### **Avagadro hypothesis**

- Equal volumes of all gases under the same conditions of temperature and pressure contain equal number of moles.

$$V \propto n (T,P)$$

### **Ideal gas equation**

According to Boyle's law,  $V \propto 1/P (T,P)$

According to Charle's law,  $V \propto T (P, n)$

According to Avagadro law,  $V \propto n (T,P)$

Combining the laws, we get  $V \propto nT / P$

$$V = R nT/P$$

$$PV = nRT \quad (R \text{ is the universal gas constant for 1 mole of gas})$$

This equation is called Ideal gas equation

### **Maxwell distribution of molecular velocities**

- Molecules in a gas are in rapid, random motion
- These molecules collide with one another. So, the velocities of molecules are constantly changing.

- But the distribution of molecules remains the same, at a given temperature.
- The distribution of molecular velocities at a temperature T is given by

$$\frac{dn}{N} = 4\pi \left[ \frac{M}{2\pi RT} \right]^{3/2} e^{-Mc^2/[2RT]} c^2 dc$$

$\frac{dn}{N}$  = Fraction of molecules with velocities between  $c$  and  $c+dc$

$M$  = molecular mass

$C$  = velocity of the molecule

$N$  = total number of molecules

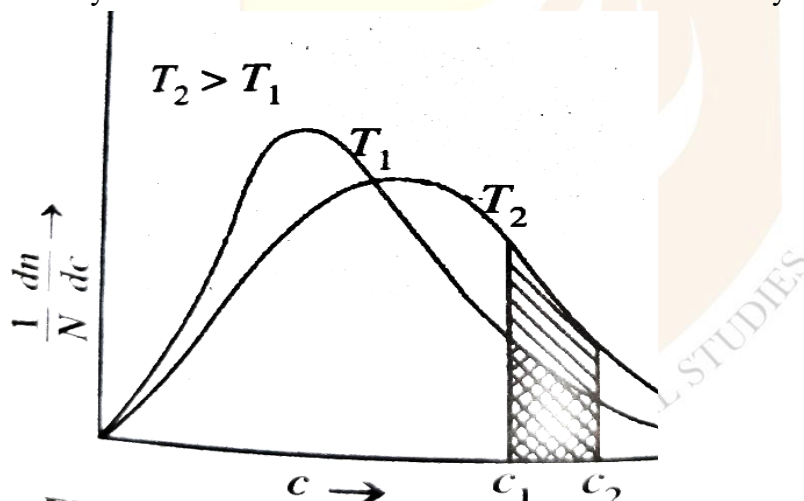
- Maxwell- Boltzmann equation can also be written as

$$\frac{dn}{N} = 4\pi \left[ \frac{m}{2\pi KT} \right]^{3/2} e^{-mc^2/[2KT]} c^2 dc$$

$m$  = mass of a single molecule

$K$  = Boltzmann constant

- Maxwell distribution of molecular velocities is generally shown as a graph plotted with velocity of molecule on x axis and fraction of molecules on y axis



The following features (points) can be noted from the graph:

1. The fraction of molecules with very low and very high velocity is very small.
2. The most probable velocity is at the peak of the curve. It is the velocity possessed by maximum molecules in a gas at given temperature.
3. With increase in temperature, there occurs a rise in the fraction of molecules having higher velocities. So the curve broadens.
4. At higher temperature  $T_2$ , the entire curve is shifted to the right. This shows velocity of the molecules increases with increase in temperature.
5. The number of molecules with high velocity increases as the temperature increases. But the fraction of molecules with most probable velocity decreases by increase in temperature. As a result the curve gets flattened downward at the top.

## Types of molecular velocities

### 1. Average velocity( $\bar{C}$ )

- The average velocity of n molecules with velocities  $C_1, C_2, C_3, \dots, C_n$  is given by

$$\bar{C} = \frac{c_1 + c_2 + c_3 + \dots + c_n}{N}$$

- To obtain average velocity of any quantity from Maxwell distribution, the quantity is multiplied by the Maxwell expression and then integrated.
- So average velocity

$$\bar{C} = \int c \times dn/N$$

$$\bar{C} = \sqrt{\frac{8RT}{\pi M}}$$

M = molecular mass of the gas

- From the above equation, it is clear that  $\bar{C}$  is proportional to square root of temperature.  
 $\bar{C} \propto \sqrt{T}$

### 2. Root mean square velocity(RMS)

- The square root of the mean of squares of the velocities possessed by all molecules at that temperature.

$$U = \sqrt{\frac{C_1^2 + C_2^2 + C_3^2 + \dots + C_n^2}{N}}$$
$$U = \sqrt{\frac{3RT}{M}}$$

- RMS velocity is proportional to square root of absolute temperature.

### 3. Most probable velocity( $\alpha$ )

- The velocity possessed by maximum number of molecules at that temperature.
- To determine this velocity Maxwell distribution equation is differentiated with respect to c.
- The resulting expression is then made equal to zero and on simplification we get most probable velocity.

$$\alpha = \sqrt{\frac{2RT}{M}}$$

**RMS velocity > Mean velocity > Most probable velocity**

- **Relation between three types of velocities**

$$\bar{C} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8}{3\pi} \times \frac{3RT}{M}} = \sqrt{\frac{8}{3\pi}} \times U = 0.9213 U$$

$$\alpha = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2}{3} \times \frac{3RT}{M}} = \sqrt{\frac{2}{3}} U = 0.816 U$$

$$\alpha: \bar{C}:U = 0.816: 0.9213:1$$

- **Relation between RMS velocity and density**

$$U = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$$



### **Ideal gases and real gases**

Ideal gases	Real Gases
Ideal gases obey all gas laws under all conditions of temperature and pressure.	Real gases obey gas laws only at low pressures and high temperature.
The volume occupied by the molecules is negligible as compared to the total volume occupied by the gas.	The volume occupied by the molecules is not negligible as compared to the total volume of the gas.
The force of attraction among the molecules are negligible.	The force of attraction are not negligible at all temperatures and pressures.
Obeys ideal gas equation $PV=nRT$	Obeys Van der Waals equation $\left( P + \frac{an^2}{V^2} \right) (V-nb) = nRT$



## **BEHAVIOUR OF REAL GASES**

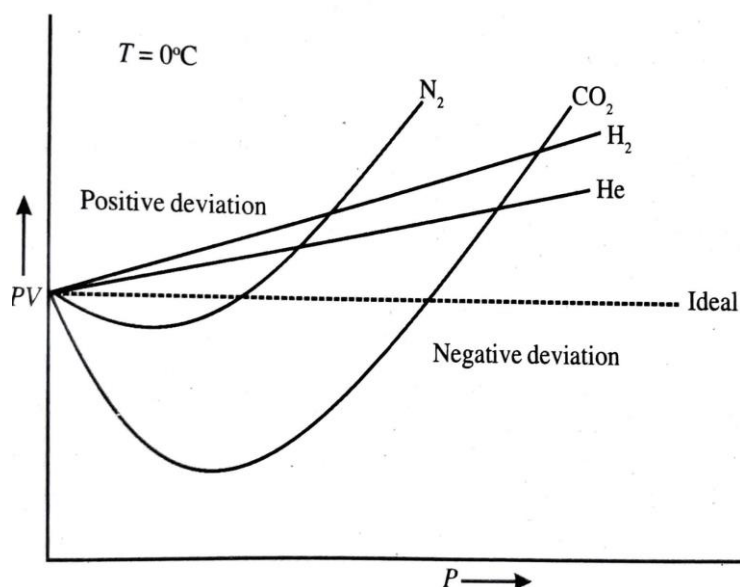


Fig. 2.6: Schematic  $PV$ - $P$  plots for real gases at constant temperature

- For ideal gases, since it obeys Boyle's law, the  $PV$ - $P$  plot at constant temperature would be a straight line parallel to pressure axis.
- For real gases, it is not straight line. Real gases show significant deviation from ideal behaviour.

### **Causes of deviation from ideal behaviour**

- Gas laws and ideal gas equation were obtained from kinetic theory of gases. Kinetic theory made 2 faulty assumptions. They are
  1. Volume of molecules can be neglected compared to total volume of gas.  
The molecule should possess an effective volume. Molecular volume can be ignored at low pressure and high temperature.
  2. There is no force of attraction between molecules.  
If there is no force of attraction between gas molecules, it is not possible to liquify a gas.

### **Compressibility factor( $Z$ )**

$$PV = nRT$$

$$Z = PV/nRT$$

$$Z = PV_m/RT \quad (V_m, \text{Molar volume} = V/n)$$

- For an ideal gas,  $Z=1$
- For real gases  $Z \neq 1$
- For real gases,  $z = PV(\text{real})/nRT$
- For ideal gases,  $Z = PV(\text{ideal})/nRT$

$$V(\text{ideal}) = nRT/P$$

$$Z = V(\text{real})/V(\text{ideal})$$

- Compressibility factor is the ratio of actual molar volume to molar volume if the gas were ideal at that temperature and pressure.
- Significance of Z is that, it is the measure of deviation of a gas from ideal behaviour.

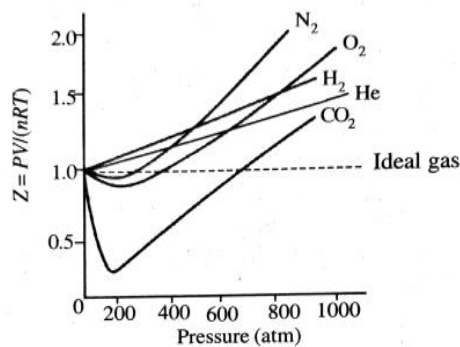


Fig. 2.7: Compressibility factor plotted as a function of pressure for various gases

- At very low pressure  $Z=1$
- At high Pressure,  $Z > 1$
- At intermediate Pressure,  $Z < 1$
- Thus, gases show ideal behaviour when volume is large and force is negligible.
- Up to what pressure will a gas behave ideally depends upon its nature and temperature.

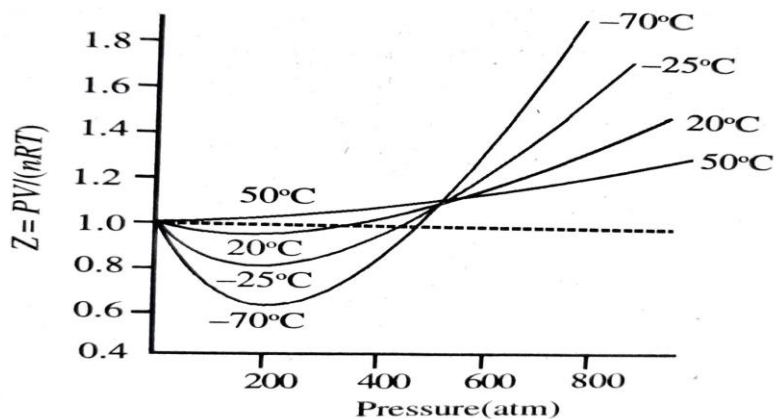


Fig. 2.8: Compressibility factor plotted against pressure for  $N_2$  at different temperatures

- The temperature at which a real gas obeys Boyle's law over an appreciable range of pressure is called **Boyle point or Boyle temperature**.
- Above Boyle point gases show,  $Z > 1$
- Below Boyle point gases show negative deviation till a minimum value.
- On increasing pressure Z keeps on increasing after the minimum.

### Van der waals equation

- Ideal gas equation is  $PV = nRT$
- To account the size of the molecule there should be a correction in  $V$  term of the equation.
- To account for the force of attraction there should be a correction in pressure term.

### Correction in volume

- The volume of gas is the space available for the free movement of the molecules. If the molecule has finite size, the volume for the free movement is  $V-b$ .  $b$  is the correction term for volume. For  $n$  moles the correction term is  $V-nb$ .

### Correction for pressure

- If there is a force of attraction, the molecules of the gas collide with the walls of the container with lesser force. To account for this reduction in pressure,  $P$  is replaced by  $(P + a/V^2)$  for 1 mol.
- For  $n$  moles, it is  $(P + n^2 a/V^2)$ .
- $a/V^2$  is the correction term for pressure.
- It accounts for the force of attraction.
- Thus, van der waals equation is written as
$$(P + n^2 a/V^2)(V - nb) = nRT \quad \text{for } n \text{ moles}$$
$$(P + a/V^2)(V - b) = RT \quad \text{for 1 mole}$$
$$a \text{ and } b \text{ are van der waals constant. } b \text{ is also called excluded volume or co-volume.}$$
- $b$  is actually 4 times the actual volume of a molecule.
$$V = 4 \times \frac{4}{3} \pi r^3$$
$$r = \text{radius of the molecule}$$
- Unit of  $a = \text{atm dm}^6 \text{ mol}^{-2}$   
or  
 $\text{atm L}^2 \text{ mol}^{-2}$
- Unit of  $b = \text{L mol}^{-1}$   
or  
 $\text{dm}^3 \text{ mol}^{-1}$

### SOLID STATE

- Solids can be crystalline solids or amorphous solids.

S.No.	Crystalline solids	Amorphous solids
1.	These have definite and regular arrangement of the constituent particles in space.	These doesn't have any regular arrangement of the constituent particles in space.
2.	These are true solids.	These are super cooled liquids or pseudo solids.
3.	These have long order in arrangement of the particles.	These have short order in arrangement of particles.
4.	These are anisotropic in nature, i.e. their physical properties are different in different directions.	These are isotropic in nature i.e. their physical properties are same in all the directions.
5.	They have sharp melting points.	They melt over a certain range of temperature.
6.	They undergo a clean cleavage when cut.	They undergo irregular cleavage when cut.
7.	They have a definite and characteristic heat of fusion.	They do not have definite heat of fusion.

### Isotropy

- If a physical property like refractive index, thermal conductivity etc. of a substance are **same** in all directions, then the substance is said to be **isotropic**.

Eg: cubic crystal and amorphous solids.

- In amorphous solids, arrangement of particles are in random and disordered. So all direction have equivalent properties.

### Anisotropy

- If the physical properties of the substance are different in different directions, the substance is said to be **anisotropic**.

Eg: crystalline compounds other than cubic

- In a crystal of AgI, the coefficient of thermal expansion is positive in one direction and negative in other direction. So, it is anisotropic.
- The particles in a crystal are arranged in a ordered manner. But, the arrangement of particles may be different in different direction. So, when a property is measured, the value may be different in different direction.

## Laws of crystallography

- Crystallography is based on three fundamental laws

### 1. The Law of constancy of interfacial angles-

- *The angle between corresponding crystal faces remains the same for a given substance, no matter how the face develops.*

### 2. The Law of symmetry-

- *All crystals of the same substance possess the same elements of symmetry.*

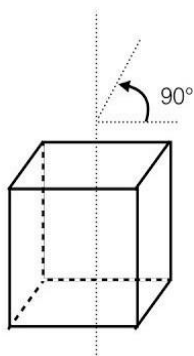
## Symmetry operation and symmetry elements

- An action which when performed on an object yield a new orientation which is indistinguishable from original- **symmetry operation**.
- A geometrical entity such as a line, plane or a point with which symmetry operation is performed- **Symmetry element**.

## Symmetry elements

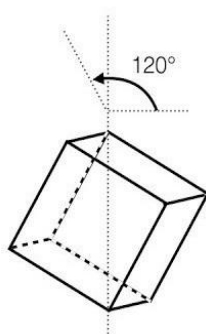
### Axis of symmetry

- It is an imaginary line passing through the centre of the crystal and if the centre is rotated about this axis, the same appearance comes more than once.
- Symbol-  $C_n$  (n is the order of rotation)



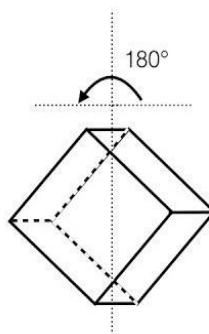
90° rotation

$$\frac{360}{90} = 4 \text{ fold axis}$$



120° rotation

$$\frac{360}{120} = 3 \text{ fold axis}$$



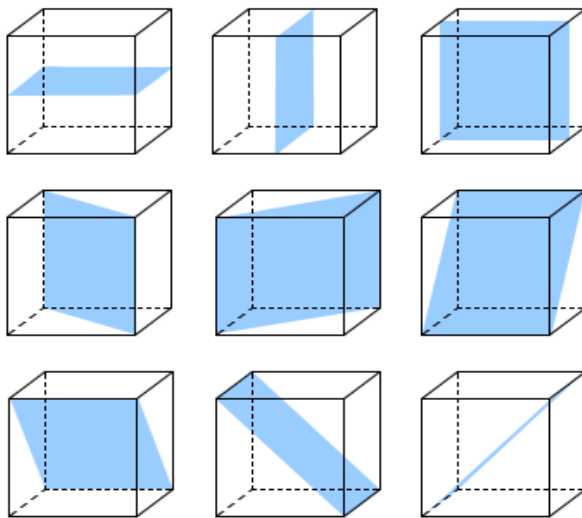
180° rotation

$$\frac{360}{180} = 2 \text{ fold axis}$$

- A cube has  
3 four fold axis( 3  $C_4$  axis)  
4 three fold axis(4  $C_3$  axis)  
6 two fold axis( 6  $C_2$  axis)

## Plane of symmetry

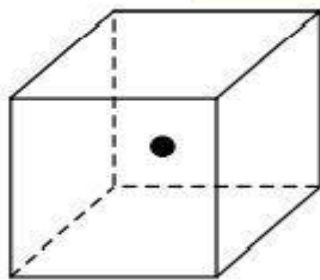
- It is an imaginary plane passing through the centre of the crystal such that the crystal can be divided into two halves, one is the mirror image of the other.



- A cube has 3 rectangular plane of symmetries and 6 diagonal plane of symmetries. In total, there are 9 plane of symmetries.

### Centre of symmetry

- It is a point at the centre of the crystal such that any line drawn through it will meet opposite faces at equal distance.



centre of symmetry

- A cube has one centre of symmetry.
- Thus, in a cubic crystal there are  $6+4+3+9+1 = 23$  symmetry elements.

### Crystallographic terms

- The geometrical form of a crystal is described by a set of three co-ordinate axes- **crystallographic axes**.
- A plane which cut all the crystallographic axes – **unit plane**
- The intercepts a,b,c that the unit plane makes on the crystallographic axes- **unit intercept**
- The ratio of the unit intercepts – **Axial ratio**

### 3.The Law of Rational indices

- The law states that the intercepts of any plane of a crystal along the crystallographic axes are either equal to unit intercepts or some simple rational number multiples of them.

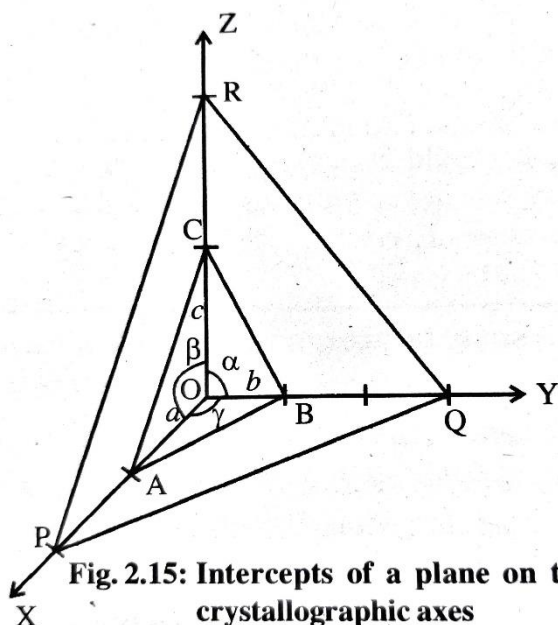


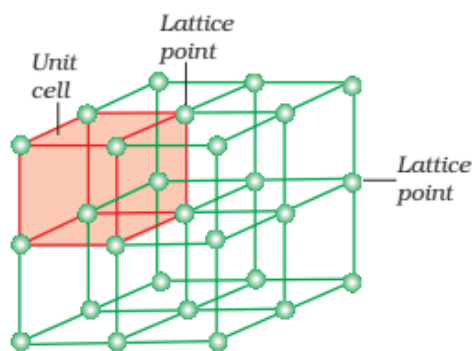
Fig. 2.15: Intercepts of a plane on the crystallographic axes

- The ratio of the intercepts of any plane on the crystallographic axes is given by  $pa: qb: rc$   
 $a, b, c$  are unit intercepts and  $p, q, r$  are rational numbers called Weiss indices.
- Weiss indices can be converted to miller indices.
  1. The reciprocals of Weiss indices are taken.
  2. Fractions are cleared by multiplying throughout with the smallest number.
- Miller indices are represented by  $(hkl)$
- The negative sign to miller indices is shown as a bar over the number.

**Space lattice-** An array of points showing how atoms or molecules are arranged in 3-D space in a crystal.

**Unit cell-** Smallest fundamental repeating unit of a space lattice from which the entire crystal is build up by translational displacement





A portion of a three-dimensional cubic space of a crystal lattice and its unit cell.

- A unit cell can be defined by axial characteristics and angular characteristics for a particular crystal.
- Based on angular and axial characteristics, crystals can be classified into 7 systems

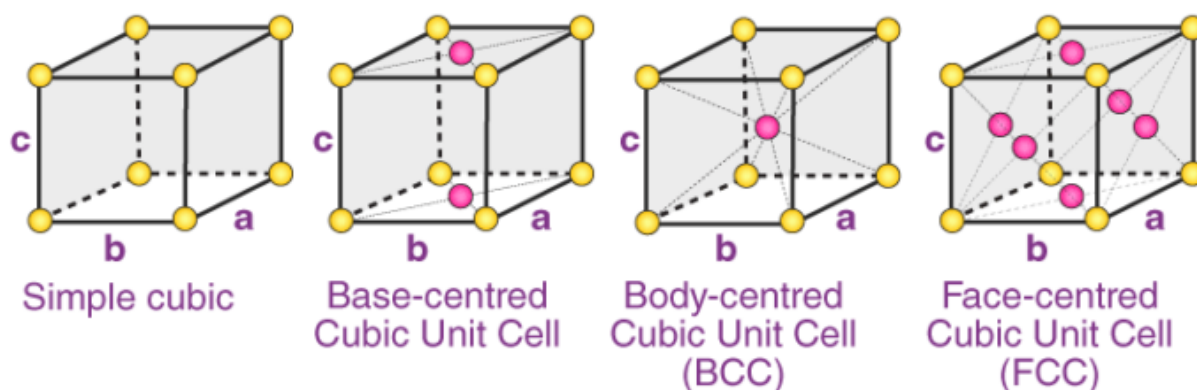
System	Unit cell characteristics	Essential symmetry	Examples
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Four three-fold axes	NaCl, KCl, $\text{CaF}_2$ , $\text{FeS}_2$ , $\text{Cu}_2\text{O}$ , ZnS, $\text{NaClO}_3$ , Pb, Au, Ag, Diamond, Alums
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	One four-fold axis	$\text{SnO}_2$ , $\text{TiO}_2$ , $\text{KH}_2\text{PO}_4$ , $\text{PbWO}_4$ , $\text{ZrSiO}_4$ , Sn
Orthorhombic (Rhombic)	$a \neq b \neq c \neq a$ $\alpha = \beta = \gamma = 90^\circ$	Three mutually perpendicular two- fold axes	$\text{KNO}_3$ , $\text{K}_2\text{SO}_4$ , $\text{PbCO}_3$ , $\text{BaSO}_4$ , $\text{Mg}_2\text{SiO}_4$ , Rhombic sulphur
Monoclinic	$a \neq b \neq c \neq a$ $\alpha = \gamma = 90^\circ \neq \beta$	One two-fold axis or mirror plane	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , Monoclinic sulphur
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$	One six-fold axis	$\text{PbI}_2$ , HgS, ZnO, CdS, Mg, Zn, Cd, Graphite
Trigonal (Rhombohedral)	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	One three-fold axis	$\text{NaNO}_3$ , ICl, As, Sb, Bi
Triclinic	$a \neq b \neq c \neq a$ $\alpha \neq \beta \neq \gamma \neq \alpha = 90^\circ$	No axes or planes	$\text{K}_2\text{Cr}_2\text{O}_7$ , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , $\text{H}_3\text{BO}_3$



## Bravais lattice

- The different possible arrangement of particles in a lattice is called Bravais lattice.
- There are 14 Bravais lattices.

Name of system	Number of Bravais lattice	Name of Bravais lattice
Cubic	3	Primitive, BCC, FCC
Tetragonal	2	Primitive, BCC
Orthorhombic	4	Primitive, BCC, FCC, End-centred
Monoclinic	2	Primitive, end-centred
Triclinic	1	Primitive
Hexagonal	1	Primitive
Rhombohedral (trigonal)	1	Primitive



- A simple cubic or primitive lattice has motifs placed at the corners, except in trigonal where two additional motifs appear along the body diagonal of the cell. There are 7 primitive unit cells.
- A Body-centred lattice has motifs at the corners and the centre. There are 3 body-centred unit cells.
- A face-centred lattice has motifs at the corners and centre of the faces. There are 2 face-centred cubic cells.
- Base-centred/ side-centred/ end-centred lattice has motifs placed at the corners and at the centres of two opposing faces. There are 2 base centred unit cells.

### Effective Number

- It is the number of particles actually belonging to a unit cell.

### Effective number of simple cube

- In a simple cube, there are particles at 8 corners. A particle at the corner is shared by 8 cubes.

So, contribution from a corner particle is  $\frac{1}{8}$ .

Total contribution from 8 corners =  $8 \times \frac{1}{8} = 1$

**Number of atoms present in a simple cubic unit cell = 1**

### Effective number of BCC

- In BCC, there are particles at 8 corners and a particle at the centre.

Contribution from 8 corners =  $8 \times \frac{1}{8} = 1$

Contribution from the centre = 1

Total contribution =  $1 + 1 = 2$

**Number of atoms present in BCC = 2**

### Effective number of FCC

- In FCC, there are particles at 8 corners and 1 particle at each face.

Contribution from 8 corners =  $\frac{1}{8} \times 8 = 1$

Contribution from a face =  $\frac{1}{2}$

Contribution from 6 faces =  $\frac{1}{2} \times 6 = 3$

Total contribution =  $3 + 1 = 4$

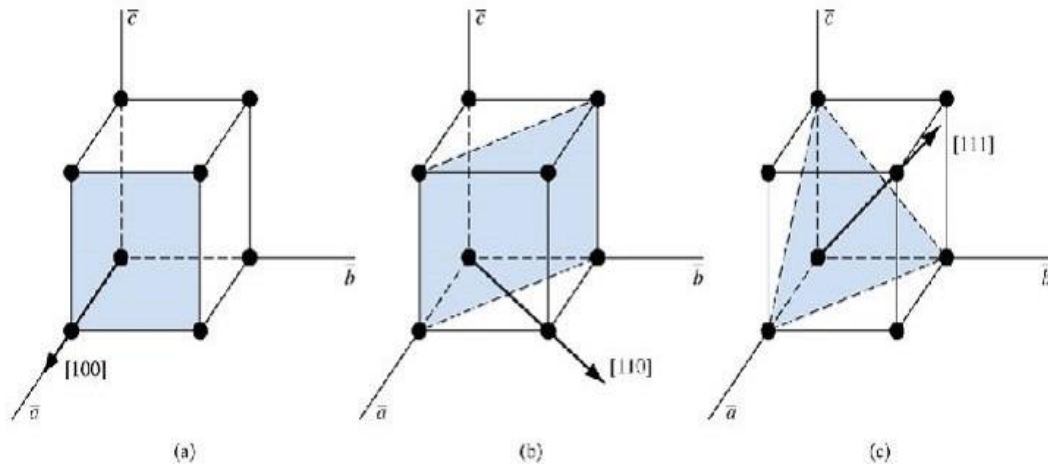
**Number of atoms present in FCC = 4**

### Lattice Planes

- The sets of parallel and equidistant planes of a crystal lattice passing through the lattice points and lying parallel to the crystal faces.

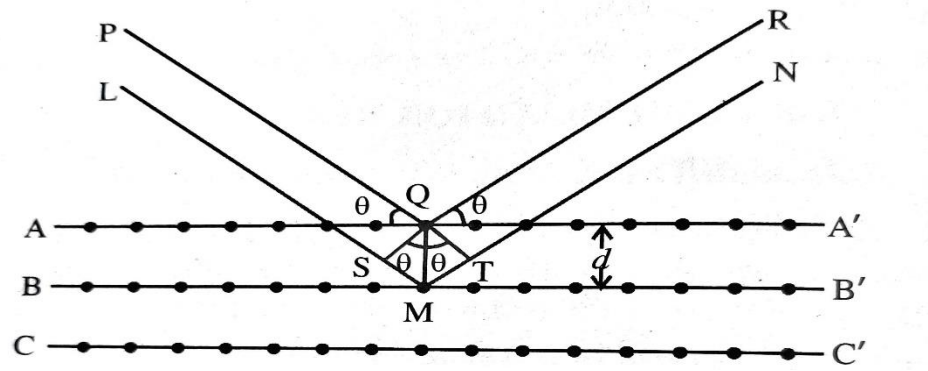
## Simple cubic lattice

- Lattice structure is completely described by (100), (110) and (111) planes.



- In BCC, there are (200), (110), (222) planes.
  - In FCC, there are (200), (220), (111) planes.
- Bragg's equation**
- X-ray diffraction is a technique used for structural determination of any crystalline substance.
  - It is based on the concept of Bragg's law
  - Bragg's law states that *x-rays reflected from different parallel planes of crystal interfere constructively when the path difference is integral multiple of wavelength of x-rays.*

### **Derivation**



Consider a number of identical parallel planes of a crystal. Let 'd' be the distance between the planes. Suppose, a beam of X-rays falls on the crystal at glancing angle  $\theta$ , some of these rays will be reflected from the upper plane at the same angle  $\theta$ .

So, here angle will be,  $\angle SQM = \angle MQT = \theta$

Also,  $PQ = LS$

$RQ = NT$

Path difference =  $SM + MT \longrightarrow (1)$

Path length is defined as an integral multiple of wavelength =  $n\lambda \longrightarrow (2)$

From (1) and (2)

$n\lambda = SM + MT \longrightarrow (3)$

In  $\triangle SQM$ ,  $\sin \theta = SM/QM$

$SM = QM \sin \theta$

$$SM = d \sin \theta \longrightarrow (4) \quad (QM = d)$$

In  $\Delta MQT$ ,  $\sin \theta = MT/QM$

$$MT = QM \sin \theta$$

$$MT = d \sin \theta \longrightarrow (5)$$

Applying, (4) and (5) in (3)

$$n\lambda = d \sin \theta + d \sin \theta$$

$$n\lambda = 2d \sin \theta$$

This equation is called Bragg's equation.  $n = 1, 2, 3, \dots$  is called the order of diffraction.

### Significance of Bragg's equation

- For a known  $\lambda$  for X-rays, the interplanar distance of a crystal can be calculated, by measuring  $\theta$  for a particular  $n$  value.
- The edge length of a cube can be calculated if  $d$  values are known.  
For a cubic lattice, edge length ( $a$ ) can be calculated using the expression

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

- The wavelength ( $\lambda$ ) of X-rays can be calculated, by measuring  $\theta$ ,  $d$  and  $n$ .
- We can calculate  $\theta$ , for a given value of  $n$ , knowing  $\lambda$  and  $d$ .

### Imperfections in solids (Crystal Defects)

- The deviation from the regular orderly arrangement of particles of a solid is called imperfections or crystal defects.
- The crystal defects are broadly classified into two – point defects and line defects.
- The imperfection around a point (an atom) in a crystalline substance, it is termed as point defect.
- The imperfection along a row is termed as line defect.
- **Point defects:** Point defects can be classified into three types: Stoichiometric defects, Non-stoichiometric defects and Impurity defects.

#### 1. Stoichiometric defects:

- These are point defects which do not disturb the stoichiometry of the solid. They are also called intrinsic or thermodynamic defects, because these defects can also develop when a substance is heated. They originate from interior of lattice.
- Ionic solids show two types of stoichiometric defects – Schottky defect and Frenkel defect.

#### **Schottky defect:**

- It is a vacancy defect.
- It arises due to the missing of equal number of anions and cations from the lattice site.
- It is shown by ionic crystals in which the anionic and cationic sizes are almost equal.  
Eg: NaCl, KCl, CsCl, AgBr etc.
- Due to this defect the density of the solid decreases.

#### **Frenkel defect:**

- It is a stoichiometric defect arising due to the misplacing of an ion (generally a cation) from the lattice site to the interstitial site.
- It is also called dislocation defect.

- This type of defect is shown by ionic solids in which there is a large difference in the size of the ions.
- E.g. ZnS, AgCl, AgBr, AgI etc.
- This defect does not change the density of the solid.

## **2.Non-Stoichiometric defects:**

- These are point defects which change the stoichiometry of a solid.
- These defects are of two types:

**i) Metal excess defect and ii) Metal deficiency defect**

**i) Metal excess Defect:**

Here the number of cations is greater than the number of anions. This arises in two ways:

### ***Metal excess defect due to anionic vacancies:***

- Here some of the anions are missing from the lattice site. The electrical neutrality is maintained by occupying electrons in the anionic sites. These electrons are called f-centres because they give colour to the crystal. This defect is shown by alkali metal halides.
- Eg: when NaCl is heated in an atmosphere of sodium vapour, some sodium atoms are deposited at the surface of the crystal. The Cl<sup>-</sup> ions diffuse to the surface of the crystal and combines with Na atom to form NaCl.

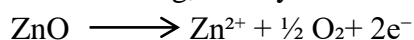


The electron so formed diffuse into the crystal and occupies the anion vacancy. These electrons absorb light energy and get excited. As a result the crystal becomes yellow in colour.

- Similarly, excess of Li makes LiCl crystals pink and excess of K makes KCl crystals violet.

### ***Metal excess defect due to extra cations at interstitial sites:***

- Here some cations occupy the interstitial sites. The electrical neutrality is maintained by occupying some electrons in adjacent interstitial sites.
- E.g. When ZnO crystals are heated, the white coloured crystals becomes yellow. This is because on heating, the crystal loses oxygen as follows:



The Zn<sup>2+</sup> ions now move to the interstitial sites and the electrons to neighbouring interstitial sites. These free electrons absorb light and undergo transition to higher level and is responsible for the yellow colour.

ii) **Metal deficiency Defect:**

Here the number of cations is smaller than the number of anions. This is mainly arises due to cation vacancies. This type of defect is commonly shown by transition metal compounds.

E.g. FeO

In FeO crystal, some of  $\text{Fe}^{2+}$  ions are lost. To maintain electrical neutrality, some other  $\text{Fe}^{2+}$  are converted to  $\text{Fe}^{3+}$ . This creates cation vacancies.

**3. Impurity Defects:**

- It is the defect arising due to the presence of foreign particles in a crystal.
- Eg: Solid solution of  $\text{CdCl}_2$  and  $\text{AgCl}$ .  
Two  $\text{Ag}^+$  ions are missing from the  $\text{AgCl}$  and one of the cation vacancy is occupied by  $\text{Cd}^{2+}$  ion. Other vacancy still remain in the lattice.
- This defect is also called substitutional impurity defects.
- This defect introduces semi-conducting properties and colour in compounds.



## MODULE 3- LIQUID STATE AND SOLUTIONS

### LIQUID STATE

- The three states of matter are solid, liquid and gases.

#### Properties of liquids

1. Significant attractive force between the molecules.
2. Molecules are relatively close together. The free space between the molecules is small- liquids are incompressible.
3. Average kinetic energy of the molecule is a function of temperature.
4. Denser than gases.
5. Rate of diffusion is slower than gases.
6. Liquids show the property of evaporation, surface tension and viscosity.

#### EVAPORATION

- Evaporation is the process by which a liquid changes into vapour. It occurs at all temperatures from freezing point to boiling point of the liquid.
- In a liquid, at any temperature, a small fraction of the molecules is moving with relatively high velocity. Such molecules have high kinetic energy. They can overcome the intermolecular attractive forces and escape through the surface of the liquid.
- Factors influencing evaporation of liquid.

1. Nature of liquid

2. Surface area.

3. Temperature.

- The extent of evaporation of a liquid is measured with the help of vapour pressure of a liquid.
- In a closed vessel, the molecules evaporating from the liquid surface are confined to a limited space. These molecules may collide among themselves or with the molecules of air. Some of them may start moving towards the surface of the liquid and enter into liquid. This is known as condensation.
- In the beginning, rate of evaporation is greater than the rate of condensation. But as more and more molecules accumulate in the space above the liquid, rate of condensation gradually increases. After some time, rate of evaporation becomes equal to the rate of condensation and an equilibrium state is reached.
- The number of molecules in the vapour above the liquid becomes constant. These molecules exert certain pressure over the surface of the liquid. This pressure is known as **equilibrium vapour pressure, saturated vapour pressure** or **vapour pressure**.
- *Vapour pressure depends on*

1. **Intermolecular forces.**

Eg: In water, ethanol and diethyl ether



Due to intermolecular hydrogen bonding, Intermolecular forces decrease in the order

Water > ethanol > diethyl ether

Vapour pressure increases in the order

Water < ethanol < diethyl ether

## 2. Temperature

- The vapour pressure of a liquid has a characteristic value at a given temperature.
- The vapour pressure of a liquid increases with increase in temperature. At higher temperature more molecules have high kinetic energy to overcome the forces of attraction and escape to form vapour.

### Boiling

- When the vapour pressure of a liquid becomes equal to atmospheric pressure, it begins to boil.
- The temperature at which boiling occurs is called the boiling point of the liquid.
- The temperature at which vapour pressure of a liquid becomes equal to 1 atm -normal boiling point.
- The temperature at which vapour pressure of a liquid becomes equal to 1 bar - standard boiling point.
- The boiling point of a liquid depends upon its nature. A more volatile liquid would boil at a lower temperature than a less volatile liquid.
- Boiling point increases with increase in atmospheric pressure and decrease with decrease in atmospheric pressure.
- The relationship between the vapour pressure P and the kelvin temperature T is given by Clapeyron- Clausius equation.

$$\ln P = - \frac{\Delta_{\text{vap}} H}{RT} + C$$

- A plot of  $\ln P$  against  $1/T$  yield a straight line with slope  $-\Delta_{\text{vap}} H/R$ . Thus, we can determine the  $\Delta_{\text{vap}} H$  from the slope.
- Integrated form

$$\log \frac{P_2}{P_1} = \frac{\Delta_{\text{vap}} H}{2.303 R} \frac{[T_2 - T_1]}{T_1 T_2}$$



## SURFACE TENSION

- Any molecule in the interior of liquid is equally attracted by neighbour molecules from all sides and it does not experience any 'net' force.
- Any molecule at the surface of a liquid is attracted by other molecules below it and at the sides.
- Due to the imbalance of forces, molecule at the surface experiences a net inward pull. As a result the surface is under tension. This phenomenon is called surface tension.
- *The **surface tension** is defined as the force acting on an imaginary line of unit length drawn on the surface of the liquid and acting perpendicular to it towards the liquid side.*
- Represented by the Greek letter *gamma*,  $\gamma$ .
- SI unit -  $\text{N m}^{-1}$ . CGS unit -  $\text{dyne cm}^{-1}$ .

## Surface energy-

- Surface molecules of a liquid experience a constant inward force. Therefore they have a higher energy than the molecules in the bulk of the liquid.
- Due to the higher energy at surface, liquids tend to have minimum number of molecules at their surface. This is achieved by *minimising the surface area*. In order to increase the *surface area*, energy is supplied or work is done.
- *The energy supplied (or work done) for increasing the surface area of a liquid by a unit amount is known as its **surface energy**.* Its units are  $\text{joule J m}^{-2}$  or  $\text{N m}^{-1}$ .

## Effect of Temperature

- On raising the temperature surface tension of a liquid decreases. It completely vanishes at the critical temperature.
- This happens due to the following two factors:
  - i) On heating, the liquids expand. This increases the intermolecular distances.
  - ii) On heating, the average kinetic energy of molecules increases.
- Due to both of these factors, the intermolecular forces become weak and the surface tension decreases.
- Ramsay- Shield equation

$$\gamma(M/\rho)^{2/3} = k (T_c - T)$$

$\rho$  = density of liquid

$T_c$  = Critical temperature

$M$  = molecular mass

$T$  = temperature in K

$\gamma$  = surface tension

### Some Effects of Surface Tension

(i) Spherical Shape of liquid drops

(ii) Capillary and meniscus formation

- The phenomenon of rise or fall of a liquid in a capillary is known as **capillary action**.
- The *capillary rise* of water in the glass capillary is due to its wetting nature as the adhesive forces are stronger than cohesive forces.
- The *capillary fall* of mercury results from the fact that cohesive forces are stronger than adhesive force.
- When a wetting liquid such as water is taken in a glass tube, the liquid tends to rise slightly along the walls of the tube for increasing its area of contact with glass. The surface of the liquid (meniscus) becomes curved. It is concave in shape.
- When a non-wetting liquid like mercury is taken in a glass tube, it tends to decrease its area of contact and depresses along the walls of the glass tube. The meniscus is convex in shape.
- The angle which the curved surface makes with the wall of the tube is called contact angle ( $\theta$ ).  $\theta < 90^\circ$  for capillary rise.  $\theta > 90^\circ$  for capillary fall.

iii) Water spreads on a glass while mercury remains as a drop

- The liquid (L) is resting on a solid (S) surface which is in equilibrium. Let  $\theta$  be the angle of contact.
- $\gamma_{GS}$ ,  $\gamma_{GL}$  and  $\gamma_{LS}$  are the surface energy of GS, GL and LS interface.
- At equilibrium

$$\gamma_{GS} = \gamma_{LS} + \gamma_{GL}\cos\theta$$

- The value of  $\theta$  depends on  $\gamma_{GS}$  and  $\gamma_{LS}$
- In case of water on glass surface, surface energy of glass- water interface is less than that of glass- air interface.
- $\gamma_{GS} > \gamma_{LS}$ ,  $\cos\theta$  is positive,  $\theta < 90^\circ$
- In case of mercury on glass surface, surface energy of glass- water interface is greater than that of glass- air interface.
- $\gamma_{GS} < \gamma_{LS}$ ,  $\cos\theta$  is negative,  $\theta > 90^\circ$

### VISCOSITY

- *Internal resistance to flow* is called **viscosity**.
- Arises due to intermolecular forces. These forces hold the layer together and oppose the movement of layers.
- When a liquid flows steadily, it flows in different layers with one layer sliding over the other. The different layers move at different rates. Such a flow is known as **laminar flow**.
- The retarding influence of slow moving layer on the adjacent fast moving layer is called viscosity
- The force of friction,  $f$  between two layers depends upon:

- i) area in contact  $A$ .
- ii) distance between the layers,  $dz$ .
- iii) difference in velocity between the layers,  $du$ .

Velocity gradient between the layers =  $du/dz$

$$f = \eta A \frac{du}{dz}$$

$\eta$  is called the coefficient of viscosity

- If  $A = 1 \text{ cm}^2$ ,  $du = 1 \text{ cm s}^{-1}$  and  $dz = 1 \text{ cm}$ , then  $f = \eta$
- Thus, coefficient of viscosity is the force of friction between two parallel layer of the liquid which have  $1 \text{ cm}^2$  area of contact, are separated by  $1 \text{ cm}$  and have a velocity difference of  $1 \text{ cm s}^{-1}$ .
- $f$  is also equal to the **external force** which is required to overcome the force of friction and maintain the steady flow between two parallel layers.

#### Unit of $\eta$

In SI system-  $\text{N m}^{-2} \text{s} = \text{Pa s}$

In CGS system-  $\text{dynes cm}^{-2} \text{s} = \text{Poise}$

- Greater the value of  $\eta$ , greater is the viscosity.- less mobile
- Fluidity,  $\phi = 1/\eta$
- Stronger the intermolecular forces, the greater is the resistance to the flow and greater is the viscosity.

#### SOLUTIONS

- Solutions are homogeneous mixtures containing two or more components.
- The component present in larger quantity is called *solvent*.
- The components present in the solution other than solvent are called *solutes*.
- Solutions containing only two components are called *binary solutions*. Each component may be in solid, liquid or gaseous state.

#### **i) Gaseous solutions**

- Gas -Gas :Mixture of  $\text{O}_2$  and  $\text{CO}_2$
- Liquid -Gas :Chloroform mixed with nitrogen gas, water-vapour in air
- Solid- Gas :Camphor in nitrogen gas, naphthalene in air

#### **ii) Liquid solutions**

- Gas- Liquid: Oxygen dissolved in water, soda water
- Liquid -Liquid : Alcohol dissolved in water, dilute acids and alkalies
- Solid -Liquid :Salt in water, glucose in water

#### **iii) Solid solutions**

- Gas - Solid : Hydrogen in Pd, Pt, Ni etc
- Liquid - Solid : Amalgam of mercury with sodium
- Solid -Solid : Brass (cu-zn)

#### Solubility of gases in liquids

- Solubility of gases in liquids is affected by nature of gas, pressure and temperature.
- *Easily liquefiable gases are more soluble in common solvents*

- If there is greater interaction between gas and liquid- solubility increases
- If there is chemical similarity between gas and liquid, solubility increases.
- As temperature increases solubility of gas decreases.
- The solubility of a gas increases with increase of pressure.

**Henry's law.** "The law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas".

Or, "the partial pressure of the gas in vapour phase ( $p$ ) is proportional to the mole fraction of the gas ( $x$ ) in the solution" and is expressed as:

$$p = K_H x$$

**$K_H$  = Henry's law constant.**

- The value of  $K_H$  depends on the nature of the gas.
- As the value of  $K_H$  increases at a given pressure, the solubility of the gas in the liquid decreases.

### Limitations of Henry's law

- Henry's law is obeyed only when
  1. The gas has low solubility in the solvent.
  2. The pressure is low.
  3. The temperature is high.
  4. The gas does not undergo a change in molecular state.

### APPLICATIONS

- To increase the solubility of  $\text{CO}_2$  in soft drinks and soda water, the bottle is sealed under high pressure.
- *Scuba divers* - At high pressure under water, the solubility of atmospheric gases in blood increases. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as *bends*.
- At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly – anoxia
- The process of expelling a dissolved gas from a solution by bubbling an unreactive gas of low solubility.

### COLLIGATIVE PROPERTIES

- The properties which depend only on the number of solute particles and not on their nature are called Colligative properties.

## Osmosis and Osmotic Pressure

- *Osmosis is the process of flow of solvent molecules from pure solvent to solution through a semipermeable membrane.*
- Or, it is the flow of solvent molecules from lower concentration side to a higher concentration side through a semi-permeable membrane (SPM).
- A membrane that allows the passage of solvent molecules only is called a semi-permeable membrane. E.g. egg membrane, all animal and plant membrane.
- Cellulose acetate is an example for artificial SPM.
- **Osmotic pressure( $\pi$ )** is defined as the excess pressure that must be applied on solution side to stop osmosis.

## Laws of osmotic pressure

### 1. **Boyle –van't Hoff law**

Temperature remaining constant, the osmotic pressure of a solution is directly proportional to its molar concentration.

$$\pi \propto C$$

$$\pi \propto 1/V$$

V = volume of solution containing 1 mole solute

### 2. **Charles- van't Hoff Law**

Concentration remaining constant, the osmotic pressure is directly proportional to the Kelvin temperature.

$$\pi \propto T$$

## Van't- Hoff osmotic pressure equation

$$\pi \propto 1/V \text{ (Boyle –van't Hoff law)}$$

$$\pi \propto T \text{ (Charles- van't Hoff Law)}$$

$$\pi \propto T/V$$

$$\pi V \propto T$$

$$\pi V = S T \quad S = \text{Solution constant}$$

$$\pi V = n S T \quad n = \text{number of moles of solute in volume } V$$

$$\pi V = n R T \quad S \approx R, R = \text{Universal gas constant}$$

## Determination of molecular mass of solute

According to van't Hoff osmotic pressure equation,

$$\pi V = n R T$$

$$n = w/M \quad w = \text{mass of non- volatile solute}$$

$$M = \text{molar mass of non- volatile solute}$$

$$\pi V = \frac{w}{M} RT$$

$$M = \frac{w RT}{\pi V}$$

By measuring the osmotic pressure of known concentration at definite temperature, the molar mass of solute can be determined using van't Hoff osmotic pressure equation

### **Determination of molar mass of polymers(proteins)**

- Osmotic pressure method is the most useful method for determination of molar mass of polymers
- Osmotic pressure are measurable for polymers and no strong membranes are needed.
- According to van' Hoff equation,

$$\pi V = \frac{w}{M} RT$$

w= mass of polymer  
M= Molar mass of polymer

$$\pi = \frac{w}{V} \frac{RT}{M}$$

(w/V =C, Concentration in g/L)

$$\pi = \frac{C}{M} RT$$

$$\frac{\pi}{C} = \frac{RT}{M}$$

- A series of osmotic pressure measurements are made and the data is extrapolated to get the actual molar mass.
- $\pi/C$  is plotted against C to get a linear plot. This when extrapolated to C=0 gives limiting value  $(\pi/C)_0$

$$(\pi/C)_0 = RT/M$$

$$\text{Molecular mass, } M = RT/(\pi/C)_0$$

### **Isotonic solutions-**

- The solutions having same osmotic pressure at the same temperature.
- When such solutions are separated by a semi-permeable membrane, *no* osmosis occurs.

### **Reverse osmosis and water purification**

- The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side.
- The pure solvent flows out of the solution through the semi permeable membrane.

- This phenomenon is called reverse osmosis and is used in desalination of sea water.
- When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane. Commonly used SPM are nylon,cellulose acetate.



## MODULE 4- ELECTROCHEMISTRY

- Branch of chemistry that deals with the inter conversion of electrical energy and chemical energy.

### Conductance of Electrolytic Solutions

- **Resistance (R):** The electrical resistance is the hindrance to the flow of electrons. Unit- ohm ( $\Omega$ ).
- The resistance of a conductor is directly proportional to the length of the conductor (l) and inversely proportional to the area of cross-section (A) of the conductor.

$$R \propto l/A$$

$R = \rho \times l/A$ , where  $\rho$  (rho) is a constant called resistivity. Its unit is ohm-metre ( $\Omega\text{m}$ ). Resistivity is defined as the resistance offered by a conductor having unit length and unit area of cross section.

- **Conductance (G):** It is the inverse of resistance.
- $G = 1/R$ . Unit is ohm<sup>-1</sup> or mho or Siemens (S)
- $G = K \times A/l$  Where, K is called conductivity.

Conductivity is the conductance of a conductor having unit length and unit area of cross-section. Unit is ohm<sup>-1</sup> m<sup>-1</sup> or mho m<sup>-1</sup> or S m<sup>-1</sup>.

- There are of two types of Conductance - electronic or metallic conductance and electrolytic or ionic conductance.

### Equivalent conductance ( $\Lambda_{eq}$ )

- The conducting power of all the ions produced from 1g equivalent of the electrolyte in solution.
- $\Lambda_{eq} = K \times V$ , V is the volume of solution in cm<sup>3</sup>. K= specific conductance.
- $\Lambda_{eq} = \frac{K \times 1000}{N}$

$$N$$

N=Normality of the solution

- Unit of  $\Lambda_{eq}$  is ohm<sup>-1</sup> cm<sup>2</sup> eq<sup>-1</sup> or S cm<sup>2</sup>eq<sup>-1</sup> or Sm<sup>2</sup>eq<sup>-1</sup>.



### Molar conductance ( $\Lambda_m$ )

- The conducting power of all the ions produced from one gram mole of electrolyte in solution.
- $\Lambda_m = K \times V'$ ,  $V'$  is the volume of solution containing 1 mole of electrolyte.
- $\Lambda_m = \frac{K \times 1000}{M}$

M

M = Molarity of the solution.

- Relation between  $\Lambda_{eq}$  and  $\Lambda_m$

$$\Lambda_{eq} = \frac{\text{Equivalent mass of the electrolyte}}{\text{Molecular mass of the electrolyte}} \times \Lambda_m$$
$$\Lambda_{eq} = \frac{\text{Molarity of the solution}}{\text{Normality of the solution}} \times \Lambda_m$$

### Cell constant

The ratio of the distance between the two electrodes in a conductivity cell to the area of cross-section of the electrode.

Cell constant,  $G^* = l/a$

Conductivity = conductance  $\times$  cell constant

### Variation of conductivity and Molar conductivity with concentration (dilution)

- Both conductivity and molar conductivity change with the concentration of the electrolyte. When a solution is diluted, its concentration decreases.

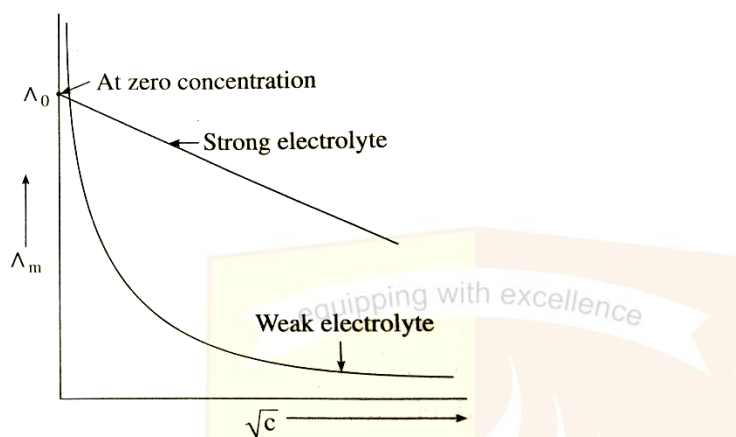
*For both strong and weak electrolytes,*

- Conductivity always decreases with dilution. Conductivity is the conductance of unit volume of electrolytic solution. As dilution increases, the number of ions per unit volume decreases and hence the conductivity decreases.
- For both strong and weak electrolytes, the molar conductivity increase with dilution (or decrease with increase in concentration).
- For strong electrolytes, as dilution increases, the force of attraction between the ions decreases and hence the ionic mobility increases. So, molar conductivity increases. When dilution reaches maximum or concentration approaches zero, the molar conductivity becomes maximum and it is called the **limiting molar conductivity ( $\lambda_m^\circ$ )**.
- For strong electrolytes, the relation between  $\lambda_m$  and concentration can be given as:

$$\lambda_m = \lambda_m^\circ - A\sqrt{c}$$

$c$  = concentration and  $A$  is a constant.

- For weak electrolytes, as dilution increases, the degree of dissociation increases. So the number of ions and hence the molar conductivity increases.
- The variation of  $\lambda_m$  for strong and weak electrolytes is shown in the following graphs:
- For strong electrolytes, the value of  $\lambda_m^\circ$  can be determined by the extrapolation of the graph.



Variation of molar conductivity with  $\sqrt{c}$

- For weak electrolytes, since the graph is not a straight line,  $\lambda_m^\circ$  values are calculated by applying Kohlrausch's law of independent migration of ions.

### Kohlrausch's law of independent migration of ions

- The law states that the limiting molar conductivity of an electrolyte can be represented as the sum of individual contributions of the anion and the cation of the electrolyte
- If an electrolyte on dissociation gives  $A^{y+}$  and  $B^{x-}$  ions, its limiting molar conductivity is given as:

$$\lambda_m^\circ = x\lambda_{+}^\circ + y\lambda_{-}^\circ$$

$$\text{For NaCl, } \lambda_m^\circ(\text{NaCl}) = \lambda^\circ(\text{Na}^+) + \lambda^\circ(\text{Cl}^-)$$

$$\text{For CaCl}_2, \lambda_m^\circ(\text{CaCl}_2) = \lambda^\circ(\text{Ca}^{2+}) + 2 \times \lambda^\circ(\text{Cl}^-)$$

### Applications of Kohlrausch's law

#### **1) Determination of $\lambda_m^\circ$ of weak electrolytes**

- By knowing the  $\lambda_m^\circ$  values of strong electrolytes, we can calculate  $\lambda_m^\circ$  of weak electrolytes.
- We can determine the  $\lambda_m^\circ$  of acetic acid ( $\text{CH}_3\text{COOH}$ ) by knowing the  $\lambda_m^\circ$  of  $\text{CH}_3\text{COONa}$ ,  $\text{NaCl}$  and  $\text{HCl}$  as follows

$$\lambda^{\circ}\text{m} (\text{CH}_3\text{COONa}) = \lambda^{\circ}\text{CH}_3\text{COO}^- + \lambda^{\circ}\text{Na}^+ \dots\dots\dots (1)$$

$$\lambda^{\circ}\text{m} (\text{HCl}) = \lambda^{\circ}\text{H}^+ + \lambda^{\circ}\text{Cl}^- \dots\dots\dots (2)$$

$$\lambda^{\circ}\text{m} (\text{NaCl}) = \lambda^{\circ}\text{Na}^+ + \lambda^{\circ}\text{Cl}^- \dots\dots\dots (3)$$

(1) + (2) - (3) gives

$$\lambda^{\circ}\text{m} (\text{CH}_3\text{COONa}) + \lambda^{\circ}\text{m} (\text{HCl}) - \lambda^{\circ}\text{m} (\text{NaCl}) = \lambda^{\circ}\text{CH}_3\text{COO}^- + \lambda^{\circ}\text{Na}^+ + \lambda^{\circ}\text{H}^+ + \lambda^{\circ}\text{Cl}^- - \lambda^{\circ}\text{Na}^+ - \lambda^{\circ}\text{Cl}^- = \lambda^{\circ}\text{CH}_3\text{COOH}$$

## 2) Determination of degree of dissociation of weak electrolytes

- By knowing the molar conductivity at a particular concentration ( $\lambda^{\circ}\text{m}$ ) and limiting molar conductivity ( $\lambda^{\circ}\text{m}$ ), we can calculate the degree of dissociation ( $\alpha$ ) as,

$$\alpha = \frac{\lambda^{\circ}\text{m}}{\lambda^{\circ}\text{m}}$$

## 3) Determination of solubility and solubility products of sparingly soluble salts

- Solubility can be determined from the equation

$$S = \frac{K_{\text{sp}}}{\lambda^{\circ}\text{m}}$$

$\lambda^{\circ}\text{m}$  can be obtained using Kohlrausch's law.

The solubility product can be obtained if solubility is known

## 4) Determination of ionic product of water

- Water is a weak electrolyte. It dissociates feebly into  $\text{H}^+$  and  $\text{OH}^-$  ions. The product of concentration of  $\text{H}^+$  and  $\text{OH}^-$  is called ionic product of water ( $K_w$ )

$$K_w = [\text{H}^+][\text{OH}^-]$$

- At 298 K,  $K_w = 1.02 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ . This value can be obtained from conductance measurement.
- By Kohlrausch's law,

$$\lambda^{\circ}\text{H}_2\text{O} = \lambda^{\circ}\text{H}^+ + \lambda^{\circ}\text{OH}^-$$

$$\lambda^{\circ}\text{H}^+ = 349.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\lambda^{\circ}\text{OH}^- = 198.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\text{Therefore, } \lambda^{\circ}\text{H}_2\text{O} = 548.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$[\text{H}^+] = \frac{\text{Specific conductance of water}}{\lambda^{\circ}\text{H}_2\text{O}} = \frac{5.54 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}}{548.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}} = 1.01 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\text{Since, } [\text{H}^+] = [\text{OH}^-] = 1.01 \times 10^{-7} \text{ mol dm}^{-3}$$

$$K_w = 1.02 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 298$$

### Conductometric titrations

- **Principle-** During the titration, one of the ions is replaced by the other and these two ions differ in the ionic conductivity. As a result, conductivity of the solution varies during titration. The equivalence point is located graphically by plotting the conductance as a function of the volume of titrant added.

- **Acid –alkali titrations**

- a) **Strong acid- strong base titrations**

- Eg: HCl X NaOH titration**

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  $\text{Na}^+$ .  $\text{H}^+$  ions react with  $\text{OH}^-$  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  $\text{OH}^-$  ions.

- b) **Weak acid- strong base titrations**

- Eg:  $\text{CH}_3\text{COOH}$  X NaOH titration**

Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of NaOH, the conductance increases as NaOH neutralizes the un-dissociated  $\text{CH}_3\text{COOH}$  to  $\text{CH}_3\text{COONa}$  which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting  $\text{OH}^-$  ions.

- c) **Strong acid- weak base titrations**

- Eg: HCl X  $\text{NH}_4\text{OH}$  titration.**

Initially the conductance is high and then it decreases due to the replacement of  $\text{H}^+$  ions by slow moving  $\text{NH}_4^+$  ions . But after the endpoint has been reached the graph becomes almost horizontal, since the excess  $\text{NH}_4\text{OH}$  is only feebly dissociated.

- d) **Weak acid- weak base titrations**

- Eg:  $\text{CH}_3\text{COOH}$  X  $\text{NH}_4\text{OH}$  titration**

Initially the conductance is low due to the feeble ionization of acetic acid. on adding  $\text{NH}_4\text{OH}$ , the conductance at first decreases due to the suppression of dissociation of  $\text{CH}_3\text{COOH}$  and  $\text{NH}_4\text{OH}$  by the common ions formed. Then conductance increases as

more salt is formed. After the equivalence point the conductance remains constant since weak bases are only feebly ionized.

### **Precipitation titrations**

- Titration which involve precipitate formation can be done conductometrically.  
Eg:  $\text{KCl} \times \text{AgNO}_3$  titration.
- $\text{KCl}$  is taken in conductivity cell and  $\text{AgNO}_3$  is added from the burette.  $\text{AgCl}$  gets precipitated.  $\text{Cl}^-$  ions are replaced by  $\text{NO}_3^-$  ions. Since, both the ions have same mobility, the conductivity remains constant. After the equivalence point, further addition of  $\text{AgNO}_3$  introduces free  $\text{Ag}^+$  and  $\text{NO}_3^-$  into the solution. Hence, conductance increases sharply.

### **GALVANIC CELLS/ ELECTROCHEMICAL CELL/VOLTAIC CELL**

- These are devices that convert chemical energy of some redox reactions to electrical energy.
- It is constructed by dipping a  $\text{Zn}$  rod in  $\text{ZnSO}_4$  solution and a  $\text{Cu}$  rod in  $\text{CuSO}_4$  solution. The two solutions are connected externally by a metallic wire through a voltmeter and a switch and internally by a salt bridge.
- A salt bridge is a U-tube containing an inert electrolyte like  $\text{KCl}$  or  $\text{NaNO}_3$  or  $\text{KNO}_3$  in a gelly like substance. The functions of a salt bridge are:
  1. To complete the electrical circuit.
  2. To maintain the electrical neutrality in the two half cells.
  3. It prevents accumulation of charges in the two electrolyte solutions.
  4. It prevents mechanical mixing of the two electrolyte solutions and avoids liquid junctions.
- The reaction taking place in a Daniel cell is
$$\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$$
This reaction is a combination of two half reactions:
  - (i)  $\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu(s)}$  (reduction half reaction)
  - (ii)  $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2 \text{e}^-$  (oxidation half reaction)
- These reactions occur in two different portions of the Daniel cell. The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called **half-cells** or **redox**

**couples.** The copper electrode may be called the reduction half-cell and the zinc electrode, the oxidation half-cell.

- In a galvanic cell, the half-cell in which *oxidation* takes place is called **anode** and it has a negative potential. The other half-cell in which *reduction* takes place is called **cathode** and it has a positive potential.
- By IUPAC convention, while representing a galvanic cell, the anode is written on the left side and the cathode on the right side. Metal and electrolyte solution are separated by putting a vertical line and a salt bridge is denoted by putting a double vertical line.
- The cell representation is  $\text{Zn(s)}/\text{Zn}^{2+}(\text{aq}, 1\text{M})//\text{Cu}^{2+}(\text{aq}, 1\text{M})/\text{Cu(s)}$

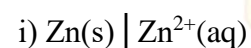
### Reversible electrodes

- The electrodes of a reversible cell are called reversible electrodes. The various types of reversible electrodes are as follows:

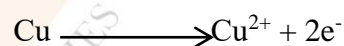
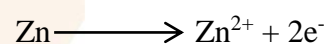
#### ***Metal-Metal ion electrode:***

- It consists of a metal rod in contact with a solution of its own ion or ions (cations), with which the electrode is reversible.
- General representation :  $\text{M(s)} \mid \text{M}^{n+}(\text{aq})$
- General electrode reaction:  $\text{M}^{n+} + n\text{e}^- \rightleftharpoons \text{M(s)}$

#### **Electrode representation**



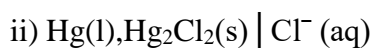
#### **Electrode reaction**



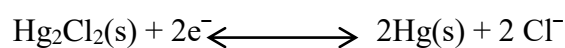
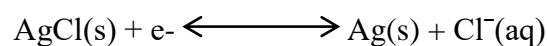
#### ***Metal –Metal sparingly salt electrode:***

- This type of electrode consists of a metal in contact with one of its insoluble salts and a solution containing a negative ion of the salt.

#### **Electrode representation**

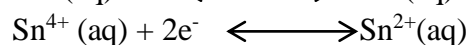
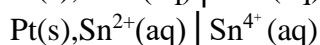
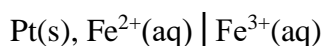


#### **Electrode reaction**



#### ***Redox electrodes:***

- This type of electrodes consists of an inert metal like platinum in contact with an aqueous solution of the salt of an element in different oxidation state.
- Eg:



## Electrode Potential

- The tendency of a metal to lose or gain electron when it is in contact with its own solution is called *electrode potential*.
- When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as **standard electrode potential**.
- According to IUPAC convention, *standard reduction potential is taken as the standard electrode potential of the cathode and anode*.
- The potential difference between the two electrodes of a galvanic cell is called the *cell potential* and is measured in volts. *The cell potential is the difference between the electrode potentials (reduction potentials) of the cathode and anode*.

## Measurement of Electrode Potential

- The potential of individual half-cell cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell. For this purpose, we couple the electrode with reference electrodes.
- Commonly used reference electrode is **Standard Hydrogen Electrode (SHE)** or **Normal Hydrogen Electrode (NHE)**.
- It consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution of one molar concentration and pure hydrogen gas at 1 bar pressure and 298K is bubbled through it.  
It is represented as  $\text{Pt(s), H}_2(1 \text{ bar}) \mid \text{H}^+(\text{aq}, 1\text{M})$ .
- By convention, the electrode potential of SHE is taken as zero.
- SHE can act as cathode or anode depending on other electrode.
- To determine the electrode potential of an electrode, it is connected in series with the standard hydrogen electrode and the emf of the resulting cell is determined by the equation,  
$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$
  
Since the electrode potential of SHE is zero, the value of  $E_{\text{cell}}$  is equal to the electrode potential of the given electrode.
- If on combination with SHE, reduction occurs at the electrode, measured electrode potential is given positive sign.
- If on combination with SHE, oxidation occurs at the electrode, measured electrode potential is given negative sign.



## Electrochemical series

- It is a series in which various electrodes are arranged in the decreasing order of their reduction potential.
- In this table, fluorine is at the top indicating that fluorine gas (F<sub>2</sub>) has the maximum tendency to get reduced to fluoride ions (F<sup>-</sup>). Therefore fluorine gas is the strongest oxidising agent and fluoride ion is the weakest reducing agent.
- Lithium has the lowest electrode potential indicating that lithium ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent.

## Uses

- Helps to predict the relative ease of oxidation of various elements or the relative ease of reduction of metallic cations or non-metallic elements.
- Tells us about the constitution of any cell set up by combining two standard electrodes and makes it possible to calculate the standard EMF of any such cell.
- Helps to predict the direction of displacement reactions.
- Predict whether a metal will displace hydrogen from dilute acids or not.

## Nernst Equation

- Nernst proposed an equation which relate the electrode potential of an electrode with the electrolytic concentration.
- He showed that for the electrode reaction:



The electrode potential can be given by:

$$E_{el} = E_{el}^0 - \frac{RT}{nF} \ln [M]$$

Since the concentration of any solid is taken as unity, the above equation becomes:

$$E_{el} = E_{el}^0 - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

$$E_{el} = E_{el}^0 - \frac{2.303RT}{nF} \log [M]$$



$$E_{\text{el}} = E^0_{\text{el}} + \frac{2.303RT}{nF} \log [M^{n+}]$$

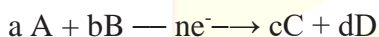
Where  $E^0_{\text{el}}$  is the standard electrode potential,  $R$  is the gas constant ( $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ),  $F$  is Faraday constant ( $96500 \text{ C mol}^{-1}$ ),  $T$  is temperature in Kelvin and  $[M^{n+}]$  is the concentration of the species,  $M^{n+}$ .

$$E_{\text{el}} = E^0_{\text{el}} + \frac{0.0591}{n} \log [M^{n+}]$$

$$E_{\text{el}} = E^0_{\text{el}} - \frac{2.303RT}{nF} \log \frac{[\text{reduced state}]}{[\text{oxidised state}]}$$

### EMF of galvanic cell

- The cell **electromotive force (emf)** of the cell is the potential difference between the two electrodes, when no current is drawn from the cell.
- $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$  Or,  $E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$ .
- $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$
- For a general electrochemical reaction of the type:



Nernst equation can be written as:

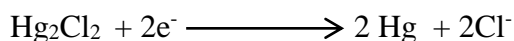
$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

### Reference electrodes

- An electrode whose potential is accurately known is known as reference electrode.
- The potential of any other electrode can be determined by coupling with reference electrode.
- Commonly used reference electrodes are standard hydrogen electrode and calomel electrode.
- Standard hydrogen electrode whose potential is fixed zero is the primary reference electrode.

### **Calomel electrode-**

- Pure mercury is placed at the bottom of a glass tube. It is covered with a paste of mercurous chloride in pure mercury. Tube is filled with KCl solution. A platinum wire is sealed into thin glass tube containing mercury at the bottom. This is to maintain electrical contact with the circuit.
- The electrode reaction is



- The cell representation is  $\text{Hg, Hg}_2\text{Cl}_2 \mid \text{KCl}$

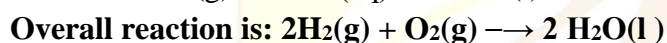
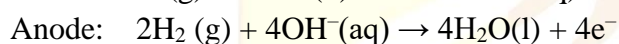
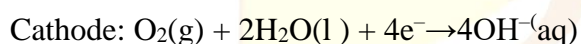
### H<sub>2</sub>-O<sub>2</sub> fuel cell

- Fuel cells are galvanic cells which convert the energy of fuel oxidation reaction (combustion of fuels like hydrogen, methane, methanol, etc) directly into electrical energy.

- Eg: H<sub>2</sub>-O<sub>2</sub> fuel cell.

Hydrogen and oxygen are bubbled through porous graphite electrodes into concentrated aqueous sodium hydroxide solution. To increase the rate of electrode reactions, catalysts like finely divided platinum metal are filled into the electrodes.

- The cell can be represented as  
 $\text{C(graphite), H}_2(\text{g}) \mid \text{NaOH(aq)} \mid \text{O}_2(\text{g}), \text{C(graphite)}$
- The cell reactions are



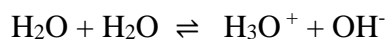
- Here, the energy of the reaction is converted to electrical energy.

#### *Advantages of Fuel cells*

- The cell works continuously as long as the reactants are supplied.
- It has higher efficiency as compared to other conventional cells.
- It is eco-friendly since water is the only product formed.
- Water obtained from H<sub>2</sub> – O<sub>2</sub> fuel cell can be used for drinking.

### The ionization constant of water (The ionic product of water)

- Water is a weak electrolyte and hence it ionizes only partially as:



$$\text{The dissociation constant, } K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{H}_2\text{O}]}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

Where K<sub>w</sub> is called ionization constant of water or ionic product of water.

- It is defined as the product of the molar concentration of hydrogen ion (hydronium ion) and hydroxyl.
- For pure water at 298K,  $[\text{H}^+] = [\text{OH}^-] = 10^{-7}\text{M}$ .
- $K_w = [\text{H}^+][\text{OH}^-] = 10^{-7} \times 10^{-7} = 10^{-14}\text{M}^2$ .

- The value of  $K_w$  is temperature dependent.
- By knowing the concentrations of  $H_3O^+$  and  $OH^-$  ions, we can predict the nature of an aqueous solution,
- If  $[H_3O^+] > [OH^-]$ , the solution is acidic  
If  $[H_3O^+] < [OH^-]$ , the solution is basic  
If  $[H_3O^+] = [OH^-]$ , the solution is neutral

### **The pH scale**

- pH is defined as the negative logarithm to the base 10 of the hydrogen ion or hydronium ion concentration in moles per litre. i.e.  $pH = -\log[H^+]$  or  $pH = -\log[H_3O^+]$
- For pure water, at 298K,  $[H^+] = 10^{-7}$ . Therefore pH of pure water is 7.
- The pH scale contains numbers from 0 to 14. If the pH is less than 7, the solution is acidic, if it is greater than 7, it is basic and if it is 7, the solution is neutral.
- Negative logarithm of hydroxyl ion concentration in mol/L is called pOH .  
i.e.  $pOH = -\log[OH^-]$

### **Relation between pH and pOH**

- We know that  $K_w = [H^+][OH^-] = 10^{-14}$  at 298K

Taking negative logarithm on both sides:

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

$$\text{Or, } pK_w = pH + pOH = 14$$

### **Ostwald's dilution law**

- Ostwald's dilution law describes the dissociation constant of the weak electrolyte with the degree of dissociation ( $\alpha$ ) and the concentration of the weak electrolyte.
- A binary electrolyte AB dissociates into  $A^+$  and  $B^-$  ions.



$$K = \frac{(c\alpha)(c\alpha)}{c - c\alpha}$$

$$K = \frac{(c\alpha)(c\alpha)}{c - c\alpha}$$

On simplifying, we get

$$K = \frac{c\alpha^2}{1 - \alpha}$$

(i) For very weak electrolytes, since  $\alpha \ll 1$ ,  $(1 - \alpha) = 1$

$$\therefore K = C\alpha^2$$

$$\alpha = \sqrt{K/C}$$

Since,  $c = 1/V$

$$\alpha = \sqrt{KV}$$

(ii) Concentration of any ion =  $C\alpha = \sqrt{CK} = \sqrt{K/V}$

- Ostwald dilution law states that, for weak electrolytes, the degree of dissociation is inversely proportional to the square root of concentration. Or it is directly proportional to the square root of the volume containing one mole of the weak electrolyte.

- Limitations of Ostwald dilution law-

Applies only to weak electrolytes. Strong electrolytes are completely ionized even at low dilutions and there is no equilibrium existing between ions and unionized molecules.

- Applications-

1) Calculation of degree of ionization of weak acids and bases.

For weak acids,  $\alpha = \sqrt{K_a/C}$

For weak bases,  $\alpha = \sqrt{K_b/C}$

2) Calculation of pH and pOH of a weak acid or base

For weak acids,  $\text{pH} = -\log C \alpha$

For weak bases,  $\text{pOH} = -\log C \alpha$

3) Calculation of ionization constants of weak acids and bases

For weak acids,  $K_a = C \alpha^2$

For weak bases,  $K_b = C \alpha^2$

### **BUFFER SOLUTIONS**

- The solution which resist any change in its pH upon addition of small amounts of acids or bases.
- There are two types of buffer solutions – acidic buffer and basic buffer.
- Acidic buffer** is a mixture of a weak acid and its salt with a strong base. E.g. a mixture of acetic acid and sodium acetate acts as an acidic buffer around pH 4.75.
- Basic buffer** is a mixture of a weak base and its salt with a strong acid. E.g. a mixture of  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$  acts as a basic buffer around pH 9.25.

### **PH of a Buffer solution – Henderson - Hasselbalch Equation**

- For an acidic buffer,  $\text{pH} = \text{pK}_a + \log[\text{Salt}]/[\text{Acid}]$
- For a basic buffer,  $\text{pOH} = \text{pK}_b + \log[\text{Salt}]/[\text{Base}]$

- $\text{pH} = 14 - \text{pOH}$

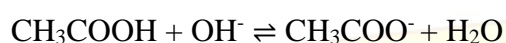
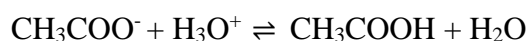
### **Mechanism of buffer action**

- The property by which a buffer solution resists any change in its pH on addition of small amount of acids or bases to it is called buffer action.

- **Acidic buffer-**

Eg: buffer action of acetic acid/ sodium acetate buffer.

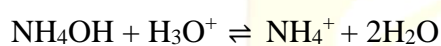
Acetic acid is weakly ionized and sodium acetate is completely ionised in solution. The addition of acid is countered by  $\text{CH}_3\text{COO}^-$  ions to form acetic acid. the addition of base is countered by  $\text{CH}_3\text{COOH}$ . Thus, pH is maintained constant.



- **Basic buffer-**

Eg: Buffer action of ammonium hydroxide/ammonium chloride buffer.

Ammonium hydroxide is weakly ionized and ammonium chloride is completely ionised in solution. The addition of acid is countered by  $\text{NH}_4\text{OH}$  and the addition of base is countered by  $\text{NH}_4^+$  ions. Thus, pH is maintained constant.



- Buffer action of the salt of weak acid and a weak base.

Eg: Ammonium acetate solution.

On adding acid, the acetate ions furnished by the salt combine with the  $\text{H}_3\text{O}^+$  to form  $\text{CH}_3\text{COOH}$ . On adding a base, ammonium ions furnished by the salt combine with  $\text{OH}^-$  to form  $\text{NH}_4\text{OH}$ .

