KARPAGAM UNIVERSITY
Karpagam Academy of Higher Education
(Deemed University Established Under Section 3 of UGC Act 1956)
COIMBATORE-21
DEPARTMENT OF CHEMISTRY

Semester-I **5H 5C**

17CHU102 PHYSICAL CHEMISTRY I:

STATES OF MATTER AND IONIC EQUILIBRIUM

Instruction Hours/week:L: 5 T:0 P:0 **Marks: Internal: 40 External: 60 Total:100**

Scope

The course presents the knowledge about the different states of matter and their behaviour. Also it deals with ionic equilibrium proving the knowledge about the electrolytes and buffer solutions.

Program Outcome

1. To understand the different types of matter and their behaviour.
2. To provide knowledge about the gaseous state and kinetic theory of gases.
3. To provide a knowledge about the behaviour of real gases and how it differs from ideal gas.
4. To provide knowledge about the liquid state and its properties like surface tension and viscosity.
5. To provide knowledge about the solid state and different types of crystals.
6. To provide a knowledge about ionisation of electrolytes and buffer solutions.

Program Learning Outcome

After the completion of the course the student knows about gaseous state, behaviour of real gases, properties like surface tension and viscosity. Also he gains the knowledge on solid state and different types of crystals, ionisation of electrolytes and buffer solutions.

UNIT I

Gaseous state: Kinetic molecular model of a gas: postulates and derivation of the kinetic gas equation; collision frequency; collision diameter; mean free path and viscosity of gases, including their temperature and pressure dependence, relation between mean free path and coefficient of viscosity, calculation of ζ from η; variation of viscosity with temperature and pressure. Maxwell distribution and its use in evaluating molecular velocities (average, root mean square and most probable) and average kinetic energy, law of equipartition of energy, degrees of freedom and molecular basis of heat capacities.

UNIT II

Behaviour of real gases: Deviations from ideal gas behaviour, compressibility factor, Z, and its variation with pressure and temperature for different gases. Causes of deviation from ideal behaviour. Van der Waals equation of state, its derivation and application in explaining real gas behaviour, calculation of Boyle temperature. Isotherms of real gases and their comparison with Van der Waals isotherms, continuity of states, critical state, relation between critical constants and Van der Waals constants, law of corresponding states.

Liquid state: Qualitative treatment of the structure of the liquid state; physical properties of liquids, vapour pressure, surface tension coefficient of viscosity, and their determination. Effect of addition of various solutes on surface tension and viscosity. Explanation of cleansing action of detergents. Temperature variation of viscosity of liquids and comparison with that of gases.

UNIT III

Solid state: Nature of the solid state, law of constancy of interfacial angles, law of rational indices, Miller indices, elementary ideas of symmetry, symmetry elements and symmetry operations, qualitative idea of point and space groups, seven crystal systems and fourteen Bravais lattices; X-ray diffraction, Bragg's law, a simple account of rotating crystal method and powder pattern method. Analysis of powder diffraction patterns of NaCl, CsCl and KCl.

UNIT IV

Ionic equilibria: Strong, moderate and weak electrolytes, degree of ionization, factors affecting degree of ionization, ionization constant and ionic product of water. Ionization of weak acids and bases, pH scale, common ion effect; Ostwald dilution law, dissociation constants of mono and diprotic acids. Salt hydrolysis-calculation of hydrolysis constant, degree of hydrolysis and pH for different salts.

UNIT V

Buffer solutions; derivation of Henderson equation and its applications. Solubility and solubility product of sparingly soluble salts – applications of solubility product principle. Qualitative treatment of acid – base titration curves (calculation of pH at various stages). Theory of acid– base indicators; selection of indicators and their limitations.

Suggested Readings:

Text Books:

1. Atkins, P. W. & Paula, J. de Atkin's. (2006). *Physical Chemistry Ed.* Oxford University Press.
2. Ball D. W. (2007). *Physical Chemistry.* India : Thomson Press.
3. Madan R.L. (201, Chemistry for Degree Students, S. Chand Pvt. Ltd, New Delhi

Reference Books:

1. Castellan, G. W. (2004). *Physical Chemistry*. 4th Ed. Narosa.
2. Mortimer, R. G. (2009). *Physical Chemistry*. 3rd Ed. NOIDA, UP : Elsevier.
3. Puri Sharma, (2013). Elements of Physical Chemistry, Vishal Publishing Co, New Delhi

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DEPARTMENT OF CHEMISTRY

Name of the Staff : **Dr. J. BALAJI**
Department : **CHEMISTRY**
Title of the Paper : **States of Matter and Ionic Equilibrium**
Paper Code : **17CHU102**
Class : **I- B.Sc Chemistry**
Year and Semester : **2017-18 and Ist Semester**
Total Lecture hours : **76 hrs**

Lecture Plan

Unit-I : Gaseous state **Hours Required : 15 hrs**

S.No	Lecture topics	Supporting materials
1.	Introduction to gaseous state	T1: 684; R1: 57-58
2.	Postulates and derivation of the kinetic gas equation	T1: 684; R1: 64-67
3.	Collision frequency; collision diameter;	T1: 707-708
4.	Mean free path and viscosity of gases	R1: 72-74
5.	Temperature and pressure dependence	T1: 703
6.	Relation between mean free path and coefficient of viscosity,	T1: 703
7.	calculation of ζ from η	R1: 72-74
8.	Variation of viscosity with temperature and pressure	R1: 76-77
9.	Maxwell distribution	T1: 691-692
10.	Evaluating molecular velocities	R1: 69-70
11.	Average, root mean square and most probable kinetic energy	T1: 693
12.	Average kinetic energy	T1: 694
13.	law of equipartition of energy	R1: 70-71
14.	degrees of freedom and molecular basis of heat capacities	T1: 698-699; R1: 80-81
15.	Recapitulation and discussion of Important questions	

Textbooks:

T1: R.L. Madan, 2015, Chemistry for Degree Students, S. Chand Pvt. Ltd, New Delhi

R1: Puri Sharma, 2013, Elements of Physical Chemistry, Vishal Publishing Co, New Delhi

Unit-II: Behaviour of real gases **Hours Required: 15 hrs**

S.No	Lecture topics	Supporting materials
1.	Behaviour of real gases	T1: 704
2.	Deviations from ideal gas behaviour	R1: 91-92
3.	Compressibility factor, Z, and its variation with pressure and temperature for different gases	T1: 705
4.	Causes of deviation from ideal behaviour.	T1: 706
5.	Van der Waals equation of state	R1: 93-94
6.	Derivation and application in explaining real gas behaviour, calculation of Boyle temperature	T1: 711 R1: 96-97
7.	Isotherms of real gases and their comparison with Van der Waals isotherms	T1: 715-717; R1: 99-102
8.	Variation of viscosity with temperature	T1: 732,733
9.	Variation of viscosity with pressure	T1: 733, 734
10.	Relation between critical constants and Van der Waals constants, law of corresponding states.	T1: 732-738; R1: 114-123
11.	Surface tension coefficient of viscosity, and their determination.	T1: 738
12.	Effect of addition of various solutes on surface tension and viscosity	R1: 121
13.	Explanation of cleansing action of detergents	T1: 738
14.	. Temperature variation of viscosity of liquids and comparison with that of gases	R1: 121
15.	Recapitulation and discussion of Important questions	

Textbooks:

T1: R.L. Madan, 2015, Chemistry for Degree Students, S. Chand Pvt. Ltd, New Delhi

R1: Puri Sharma, 2013, Elements of Physical Chemistry, Vishal Publishing Co, New Delhi

Unit-III: Solid state **Hours Required:16 hrs**

S.No	Lecture topics	Supporting materials
1.	Introduction of Nature of the solid state	T1: 773
2.	Law of constancy of interfacial angles	R1: 146
3.	Law of rational indices	T1: 777-779
4.	Law of Miller indices	R1: 154-156
5.	Elementary ideas of symmetry	T1: 706
6.	Symmetry elements and symmetry operation	R1: 93-94
7.	Seven crystal systems	T1:780-781
8.	Fourteen Bravais lattices	R1: 148-149
9.	Symmetry operations	T1: 775-780
10.	qualitative idea of point and space groups	R1: 148-149
11.	X-ray diffraction	T1: 784
12.	Bragg’s law	R1:156-157
13.	A simple account of rotating crystal method	T1: 785-786; R1: 157
14.	Powder pattern method	T1: 786-787; R1: 157-158
15.	Analysis of powder diffraction patterns of NaCl, CsCl and KCl.	T1: 789; R1: 159-160
16.	Recapitulation and discussion of Important questions	

Textbooks:

T1: R.L. Madan, 2015, Chemistry for Degree Students, S. Chand Pvt. Ltd, New Delhi

R1: Puri Sharma, 2013, Elements of Physical Chemistry, Vishal Publishing Co, New Delhi

Unit-IV: Ionic equilibria Hours Required: 15 hrs

S.No	Lecture topics	Supporting materials
1.	Strong, moderate and weak electrolytes	R1: 487
2.	Degree of ionization	T1:980; R1: 490-491
3.	Factors affecting degree of ionization	T1: 980-981
4.	Ionization constant	R1:494
5.	Ionic product of water	R1:495
6.	Ionization of weak acids	T1: 983-984
7.	Ionization of bases	T1: 984-985
8.	pH scale	R1:495-497
9.	Common ion effect	R1:497
10.	Dissociation constants of mono acids	R1:492-493
11.	Dissociation constants of diprotic acids	R1:493-494
12.	Salt hydrolysis-calculation of hydrolysis constant	T1: 1084-1085; R1: 502-504
13.	Degree of hydrolysis	R1:508
14.	pH for different salts	R1:508
15.	Recapitulation and discussion of Important questions	

Textbooks:

T1: R.L. Madan, 2015, Chemistry for Degree Students, S. Chand Pvt. Ltd, New Delhi

R1: Puri Sharma, 2013, Elements of Physical Chemistry, Vishal Publishing Co, New Delhi

Unit-V: Buffer solutions Hours Required: 15 hrs

S.No	Lecture topics	Supporting materials
1.	Buffer solutions introduction	T1 : 1076-1078
2.	Buffer solutions examples	R1: 498-499
3.	Derivation of Henderson equation	T1 : 1078-1079
4.	Application of buffer solutions	T1 : 1079-1081
5.	Solubility and solubility product of sparingly soluble salts	R1: 514-516
6.	Applications of solubility product principle	R1: 514-519
7.	Qualitative treatment of acid – base titration curves	R1: 588
8.	Calculation of pH at various stages	R1: 588 - 590
9.	Theory of Acid-Base indicators	R1: 590 - 591
10.	Theory of Acid-Base indicators	R1: 591 - 592
11.	Quinonil Theory of acid-base theory	R1: 508 - 512
12.	Solutions of Indicators	R1: 508 - 512
13.	Limitations of indicators	R1: 512
14.	Discussion of end semester question paper	
15.	Recapitulation and discussion of Important questions	

Textbooks :

T1: R.L. Madan, 2015, Chemistry for Degree Students, S. Chand Pvt. Ltd, New Delhi

R1: Puri Sharma, 2013, Elements of Physical Chemistry, Vishal Publishing Co, New Delhi

UNIT I

GASEOUS STATE - I

Kinetic molecular model of a gas: postulates and derivation of the kinetic gas equation; collision frequency; collision diameter; mean free path and viscosity of gases, including their temperature and pressure dependence, relation between mean free path and coefficient of viscosity, calculation of ζ from η; variation of viscosity with temperature and pressure. Maxwell distribution and its use in evaluating molecular velocities (average, root mean square and most probable) and average kinetic energy, law of equipartition of energy, degrees of freedom and molecular basis of heat capacities.

Introduction

Thus matter is classified mainly into three categories depending upon its physical state namely solid, liquid and gaseous states.

Distinction between three states of matter

S.No	Property	Solid	Liquid	Gas
1	Shape	Definite shape	Indefinite shape	Indefinite shape
2	Volume	Definite Volume	Definite Volume	Indefinite Volume
3	Inter particular Forces	Strong Inter particular Forces	Comparatively weaker Inter particular Forces	Inte rparticular forces are negligible
4	Inter particular Space	Negligible inter particular space	Comparatively large inter particular space	Very large Inter particular space
5	Particular Motion	Particle motion is restricted to vibratory motion.	Particle motion is very slow	Particle motion is very rapid and also random.
6	Packing of Particles	Particles are very Closely packed	Particles are loosely packed	Particles are very loosely packed
7	Compressibility	Incompressible	Compressible	Highly Compressible
8	Density	Very High Density	Low Density	Very low density

Parameters of Gases

The characteristics of gases are described in terms of following four parameters

- Mass
- Volume
- Pressure
- Temperature

1. Mass (m):

The mass of the gas is related to the number of moles as

$n = w/M$

Where n = number of moles

w = mass of gas in grams

M = molecular mass of the gas

2. Volume (V):

Since gases occupy the entire space available to them, therefore the gas volume means the volume of the container in which the gas is enclosed.

Units of Volume: Volume is generally expressed in **litre (L), cm^3** & **dm^3**

$$1m^3 = 10^3 \text{ litre} = 10^3 \text{ dm}^3 = 10^6 \text{ cm}^3.$$

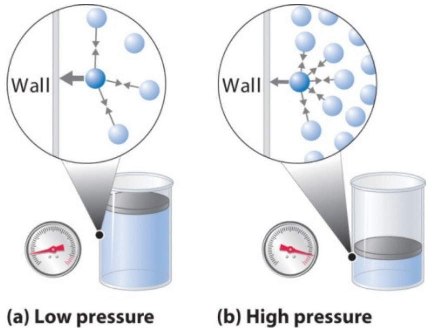
3. Pressure:

Pressure of the gas is due to its collisions with walls of its container *i.e.* the force exerted by the gas per unit area on the walls of the container is equal to its pressure.

$$P(pressure) = \frac{F(Force)}{A(Area)} = \frac{Mass \times Accelaration}{Area}$$

Pressure is exerted by a gas due to kinetic energy of its molecules.

As temperature increases, the kinetic energy of molecules increases, which results in increase in pressure of the gas. So, pressure of any gas is directly proportional to its temperature.



Units of Pressure:

The pressure of a gas is expressed in **atm, Pa, Nm–2, bar** and **lb/In2 (psi).**

760 mm = 1 atm = 10132.5 KPa = 101325 Pa = 101325 Nm^{-2}

760 mm of Hg = 1.01325 bar = 1013.25 milli bar = 14.7 lb/2n^{2} (psi)

3. Temperature (T):

Temperature is defined as the degree of hotness. The SI unit of temperature is Kelvin. ^{o}C and ^{o}F are the two other units used for measuring temperature. On the Celsius scale water freezes at 0°C and boils at 100°C where as in the Kelvin scale water freezes at 273 K and boils at 373 K.

K = ^{o}C + 273.5

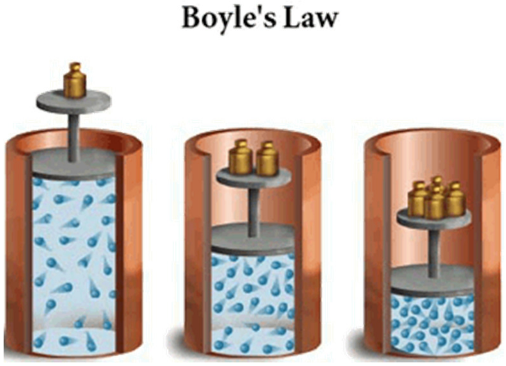
F = (9/5) ^{o}C + 32

Gas Laws:

1. Boyle's Law:-

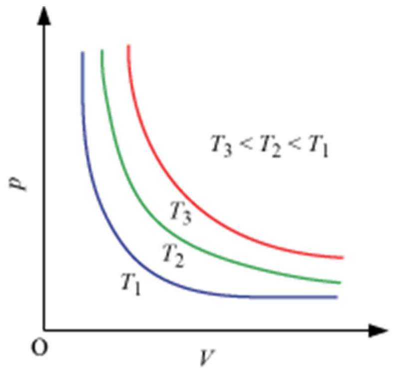
"At constant temperature, the pressure of a fixed amount (i.e., number of moles n) of gas varies inversely with its volume".

$$P_1V_1 = P_2V_2 = Constant \Rightarrow \frac{P_1}{P_2} = \frac{V_1}{V_2}$$

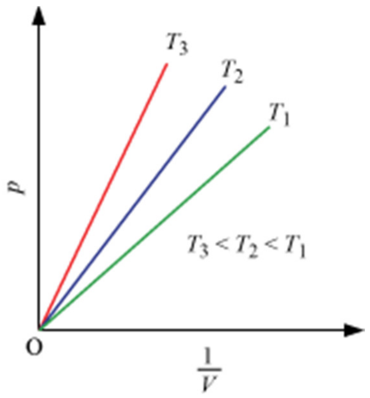


Graphical Representation of Boyle's Law :

- A plot of P versus $1/V$ at constant temperature for a fixed mass of gas would be a straight line passing through the origin.
- A plot of P versus V at constant temperature for a fixed mass of a gas would be a rectangular hyperbola.

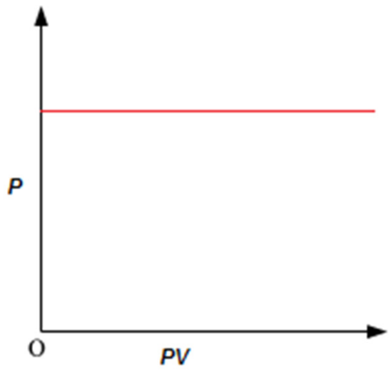


p vs V graph



p vs $\frac{1}{V}$ graph

- A plot of P (or V) versus PV at constant temperature for a fixed mass of a gas is a straight line parallel to the PV *axis.*

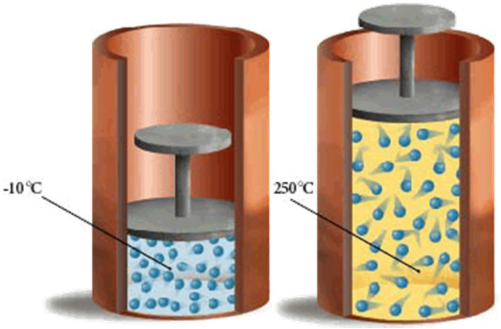


P vs PV graph

2. Charles' Law:-

"At constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature"

Charles's Law

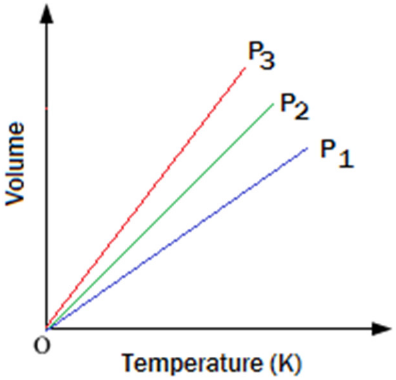


$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = constant$$

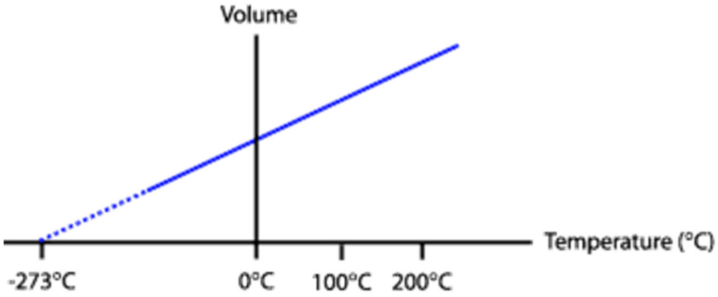
or $\log V - \log T = \text{Constant}$

Graphical Representation of Charles's Law :

1. For a definite mass of the gas a plot of *V* vs *T* (^{o}K) at constant pressure is a straight line passing through the origin.



2. A plot of *V* vs *t* (^{o}C) at constant pressure is a straight line cutting the temperature axis at -273 ^{o}C



3. Combined Gas Law:-

This law states that "*at constant volume, the pressure of a given mass of a gas is directly proportional to its absolute temperature*".

the combination of Boyle's Law and Charles' Law:

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

4. Gay Lussac's Law:

$$P \alpha T \text{ (at constant volume)}$$

$$\Rightarrow P = kT \Rightarrow \frac{P}{T} = k = constant$$

Where,

P **= Pressure of Gas**

T **= Absolute Temperature**

If the pressure and temperature of a gas changes from P_1 & T_1 to P_2 & T_2 , volume remaining constant , we have

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = constant$$

$$\text{or } \log P - \log T = \text{constant}$$

$$P_t = P_0(1 + \frac{t}{273.15})$$

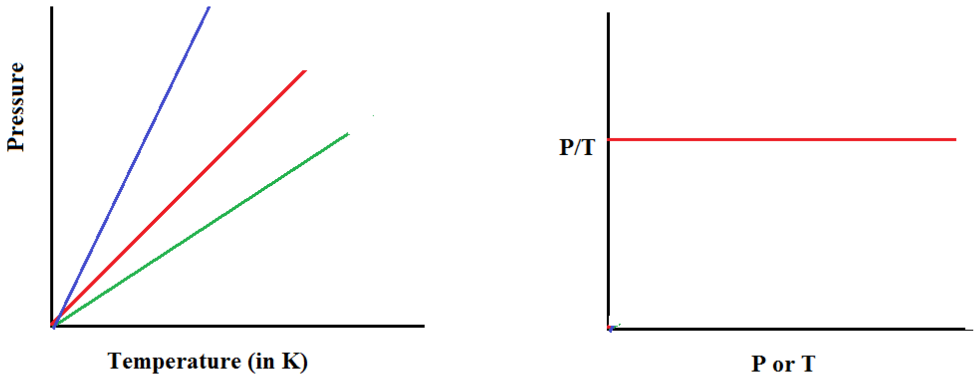
where,

P_t = Pressure of gas at t °C

Po = Pressure of gas at 0 °C

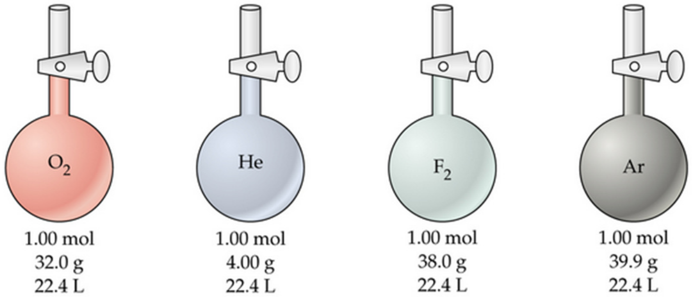
t = Temperature in °C.

Graphical Representation of Gay-Lussac's Law



5. Avogadro Law:

"Samples of different gases which contain the same number of molecules (any complexity, size, shape) occupy the same volume at the same temperature and pressure".



It follows from Avogadro's hypothesis that $V \alpha n$ (when T and P are constant).

Mathematically

$$V \alpha n \Rightarrow V = kn$$

$$\Rightarrow \frac{V}{n} = k = Constant$$

Kinetic molecular theory of gases:

- Gases are made of large number of identical particles (atoms or molecules), which are very small and perfectly hard spheres.
- The actual volume of the molecules is negligible as compare to the space between them and hence they are considered as the point masses.
- Interaction between the particles is negligible.
- Particles of a gas are always in constant and random motion and the collision between them is perfectly elastic.
- The average kinetic energy of the particles of a gas is directly proportional to the absolute temperature.
- Pressure of the gas is due to the collision between gas molecules and walls of the container.

On the basis of this model, it is possible to derive the following expression for a gas:

The Kinetic Equation

$$pV = \frac{1}{3}mnu^2$$

$$\Rightarrow u^2 = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}}$$

Collisions

Collisions are one of the most fundamental processes in chemistry, and provide the mechanism by which both chemical reactions and energy transfer occur in a gas. The rate at which collisions occur determines the timescale of these events, and is therefore an important property for us to be able to calculate. The rate of collisions is usually expressed as a *collision frequency*, defined as the number of collisions a molecule undergoes per unit time. We will use kinetic theory to calculate collision frequencies for two cases: collisions with the container walls; and intermolecular collisions.

(i) Collisions with the container walls.

We have done much of the work required to calculate the frequency of collisions with the container walls in Section 7. There we showed that for a wall of area *A*, all molecules in a volume *Av*xΔt with positive velocities will collide with the wall in the time interval Δt. We can use our probability distribution *p*(*v*x) from Equation (8.8) to determine the average value <*V*> of this volume

Collisions with other molecules.

To determine the number of collisions a molecule undergoes with other molecules per unit time, we need to introduce the concept of the collision cross section, σ. This is defined as the cross sectional area that the centres of two particles must lie within if they are to collide. In the kinetic model, the particles act like hard spheres (there are no intermolecular forces) and a collision only occurs when the centres of two particles are separated by a distance equal to the particle diameter, d. This is shown in the figure below. Imagine that we have 'frozen' the motion of all of the particles apart from the darker coloured particle on the left. We can see that this particle will only collide with particles whose centres are within the cross sectional area $\sigma = \pi d^2$.

Collision diameter:

Collision is an event in which the centres of two identical molecules come within a distance σ from one another. Sigma σ which is the distance between centres of the molecules at the point of closest approach is called the collision diameter.

Collision number:

The number of molecules with which a single molecule will collide per unit time per unit volume of the gas is called collision number.

Collision frequency**,** defined as the number of collisions a molecule undergoes per unit time.

Mean free path

The average distance a molecule travels between collisions is called the *mean free path*, usually given the symbol λ. The time between collisions is just the inverse of the collision frequency i.e. 1/*z*. If the molecule is travelling at a mean speed <*v*>, then (since distance = velocity x time) the mean free path is

$$\lambda = \frac{<v>}{z}$$

At standard pressure and temperature, the mean free path is generally of the order of a few tens of nanometres. Since z is proportional to pressure, λ is inversely proportional to pressure e.g. doubling the pressure will halve the mean free path.

Gases

Viscosity in gases arises principally from the molecular diffusion that transports momentum between layers of flow. The kinetic theory of gases allows accurate prediction of the behavior of gaseous viscosity.

Within the regime where the theory is applicable:

- Viscosity is independent of pressure and
- Viscosity increases as temperature increases.

To understand why the viscosity is independent of pressure, consider two adjacent boundary layers (A and B) moving with respect to each other. The internal friction (the viscosity) of the gas is determined by the probability a particle of layer A enters layer B with a corresponding transfer of momentum. Maxwell's calculations show that the viscosity coefficient is proportional to the density, the mean free path, and the mean velocity of the atoms. On the other hand, the *mean free path* is inversely proportional to the density. So an increase in density due to an increase in pressure doesn't result in any change in viscosity.

Relation to mean free path of diffusing particles

In relation to diffusion, the kinematic viscosity provides a better understanding of the behavior of mass transport of a dilute species. Viscosity is related to shear stress and the rate of shear in a fluid, which illustrates its dependence on the mean free path, λ, of the diffusing particles. From fluid mechanics, for a Newtonian fluid, the shear stress, τ, on a unit area moving parallel to itself, is found to be proportional to the rate of change of velocity with distance perpendicular to the unit area: for a unit area parallel to the x-z plane, moving along the x axis. We will derive this formula and show how μ is related to λ. Interpreting shear stress as the time rate of change of momentum, p, per unit area A (rate of momentum flux) of an arbitrary control surface gives where is the average velocity, along the x axis, of fluid molecules hitting the unit area, with respect to the unit area and is the rate of fluid mass hitting the surface. By making simplified assumption that the velocity of the molecules depends linearly on the distance they are coming from, the mean velocity depends linearly on the mean distance: Further manipulation will show,

Where, ρ is the density of the fluid, $\bar{u}$ is the average molecular speed ( ), μ is the dynamic viscosity. Note, that the mean free path itself typically depends (inversely) on the density.

Effect of temperature on the viscosity of a gas

Sutherland's formula can be used to derive the dynamic viscosity of an ideal gas as a function of

the temperature:

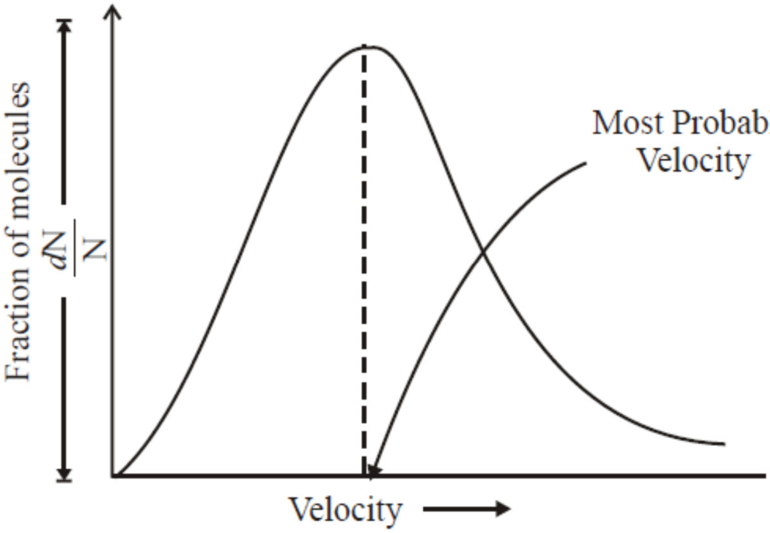
constant for the gas. in Sutherland's formula:

- μ = dynamic viscosity (Pa·s or μPa·s) at input temperature T,
- μ_0 = reference viscosity (in the same units as μ) at reference temperature T_0,
- T = input temperature (kelvin),
- T_0 = reference temperature (kelvin),
- C = Sutherland's constant for the gaseous material in question.

Valid for temperatures between $0 < T < 555$ K with an error due to pressure less than 10% below 3.45 MPa. According to Sutherland's formula, if the absolute temperature is less than C, the relative change in viscosity for a small change in temperature is greater than the relative change in the absolute temperature, but it is smaller when T is above C. The kinematic viscosity though always increases faster than the temperature (that is, d log(ν)/d log(T) is greater than 1).

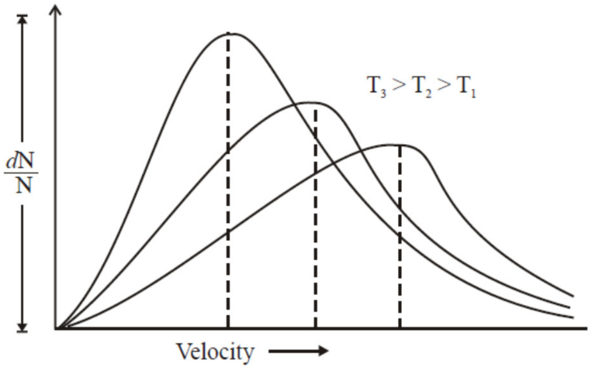
According to Maxwell in a gas all the molecules are in a state of constant rapid random motion and they collide with one another and with the walls of the vessel. During collision the resdistribution of the energy takes place. As a result their speed and the kinetic energy changes. Therefore at any instant different molecules have different speed and hence **States of matter** different kinetic energy. At the given temperature even though the speed of the individual molecule constinuously changes, the fraction of the molecules having the same speed remains constant and this is known as **Maxwell–Bolttzmann Distribution Law.**

At the given temperature this fraction is denoted by dN/N where dN is number of molecules having the same velocity and N is the total number of the molecules present in the gas. At the given temperature this fraction of the molecule is plotted against the molecular speed as shown as figure



Maxwells' distribution of velocities at constant termperature

In above Fig.the maximum in the distribution curve corresponds to the speed possessed by the highest fraction of the molecule, this is known as **most probable speed**. It may be noted that if the temperature is increased the fraction of the molecule with higher speeds increases thus the most probable speed increases with increase of temperature. The temperature dependence of the distribution of the speed is as shown



Effect of temperature on distribution of velocities.

At the given temperature the most probable speed is given by the following expression.

$$U_{mp} = \sqrt{\frac{2RT}{M}}$$

the three speeds, root mean square speed, average speed and most probable speed are related by the following expressions

$$u_{\mathrm{rms}} : u_{av} : u_{mp} :: \sqrt{3} : \sqrt{8/\pi} : \sqrt{2}$$

and also 1.224 : 1.128 : 1, so

$$u_{\mathrm{rms}} > u_{av} > u_{mp}$$

The most probable velocity *ump* increases with the use in temperature of a gas.

Root Mean Square Velocity

Root mean square velocity is the square root of the average of the squares of all the molecular velocities. Mathematically,

$$\text{RMS Velocity} = \sqrt{\left(C_1^2 + C_2^2 + \ldots + C_N^2\right)/N}$$

where C1, C2.... CN the molecular velocities.

Average Velocities

This is defined as

$$u_{av} = \frac{u_1 + u_2 + \ldots + u_N}{N}$$

and is given by the expression

$$u_{av} = \sqrt{\frac{8\,RT}{\pi M}}$$

Velocities of gas molecules

- **Average Velocity**

Average velocity =

$$\frac{u_1 + u_2 + u_3 + u_4 + u_n}{n} = \frac{n_1u_1 + n_2u_2 + n_3u_3 + . + n_nu_n}{n_1 + n_2 + n_3 + . + n_4}$$

$$U_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8pV}{\pi M}}$$

- **Root Mean Square Velocity:-**

Maxwell proposed the term U_{rms} as the square root of means of square of all such velocities.

$$U_{rms}^2 \frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + u_n^2}{n} = \frac{n_1u_1^2 + n_2u_2^2 + n_3u_3^2 + . + n_nu_n^2}{n_1 + n_2 + n_3 + . + n_4}$$

also

$$U_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3pV}{M}}$$

- **Most probable velocity:-**

It is the velocity which is possessed by maximum no. of molecules.

$$U_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2pV}{M}}$$

Furthermore

$$u_{mp} : u_{av} : u_{rms} ::: \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : 1.224$$

$$\Rightarrow u_{mp} : u_{av} : u_{rms} ::: 1 : 1.128 : 1.224$$

Kinetic Energy of Gas

As per kinetic equation

$$pV = \frac{1}{3}mnu^2$$

For 1 mole m × n = Molecular Mass (M)

$$pV = \frac{1}{3}Mu^2 = \frac{2}{3} \times \frac{1}{2}Mu^2 = \frac{2}{3} \times \frac{2}{3} \times K.E./mole = \frac{3}{2}RT$$

Also

$$\frac{K.E.}{Molecule} = \frac{3}{2}\frac{RT}{N} = \frac{3}{2}kT$$

Where k is the Boltzmann constant (k = R / N)

Degrees of Freedom

Each individual gas molecule can translate in any spatial direction. In addition, the individual atoms can rotate about any axis. Multi-atomic gas molecules may undergo rotational motions associated with the structure of the molecule. Additionally, there may be intermolecular vibrational motion between nearby gas particles, and vibrational motion arising from intramolecular forces between atoms that form the molecules. Further, there may be more contributions to the internal energy due to the internal structure of the individual atoms. Any type of motion that contributes a quadratic term in some generalized coordinate to the internal energy is called a degree of freedom. Examples include the displacement x of a particle undergoing one-dimensional simple harmonic motion position with a corresponding contribution of (1/ 2) kx^2 to the potential energy, the x -component of the velocity vx for translational motion with a corresponding contribution of (1/ 2) $mv_x{}^2$ to the kinetic energy, and z-component of angular velocity ω z for rotational motion with a corresponding contribution of (1/ 2)Iz $\omega_z{}^2$ to the rotational kinetic energy where Iz is the moment of inertia about the z-axis. A single atom can have three translational degrees of freedom and three rotational degrees of freedom, as well as internal degrees of freedom associated with its atomic structure.

Equipartition of Energy

We shall make our first assumption about how the internal energy distributes itself among N gas molecules, as follows:

Each independent degree of freedom has an equal amount of energy equal to (1/ 2) kT ,

where the constant k is called the Boltzmann constant and is equal to $k = 1.3806505\times10^{-23}$ J· K^{-1}.

The total internal energy of the ideal gas is then

$$E_{\text{internal}} = N(\text{\# of degrees of freedom})\ 1/2\ kT\ .$$

This equal division of the energy is called the equipartition of the energy. The Boltzmann constant is an arbitrary constant and fixes a choice of temperature scale. Its value is chosen such that the temperature scale. closely agrees with the temperature scales discussed. According to our classical theory of the gas, all of these modes (translational, rotational, vibrational) should be equally occupied at all temperatures but in fact they are not. This important deviation from classical physics was historically the first instance where a more detailed model of the atom was needed to correctly describe the experimental observations. Not all of the three rotational degrees of freedom contribute to the energy at all temperatures. As an example, a nitrogen molecule, N_2, has three translational degrees of freedom but only two rotational degrees of freedom at temperatures lower than the temperature at which the diatomic molecule would dissociate (the theory of quantum mechanics in necessary to understand this phenomena). Diatomic nitrogen also has an intramolecular vibrational degree of freedom that does not contribute to the internal energy at room temperatures.

Equipartition of Energy

The theorem of equipartition of energy states that molecules in thermal equilibrium have the same average energy associated with each independent degree of freedom of their motion and that the energy is

$\frac{1}{2}kT$ per molecule

$\frac{1}{2}RT$ per mole

k = Boltzmann's constant

R = gas constant

$\frac{3}{2}kT$

$\frac{3}{2}RT$

For three translational degrees of freedom, such as in an ideal monoatomic gas.

The equipartition result

$$KE_{avg} = \frac{3}{2}kT$$

serves well in the definition of kinetic temperature since that involves just the translational degrees of freedom, but it fails to predict the specific heats of polyatomic gases because the increase in internal energy associated with heating such gases adds energy to rotational and perhaps vibrational degrees of freedom. Each vibrational mode will get kT/2 for kinetic energy and kT/2 for potential energy - equality of kinetic and potential energy is addressed in the virial theorem. Equipartition of energy also has implication for electromagnetic radiation when it is in equilibrium with matter, each mode of radiation having kT of energy in the Rayleigh-Jeans law.

For the translational degrees of freedom only, equipartition can be shown to follow from the Boltzmann distribution.

$$KE_{avg} = \left[\overline{\frac{1}{2}mv^2}\right] = \frac{3}{2}kT$$

Mean free path and viscosity of gases

The intuitive development of the mean free path expression suffers from a significant flaw - it assumes that the "target" molecules are at rest when in fact they have a high average velocity. What is needed is the average relative velocity, and the calculation of that velocity from the molecular speed distribution yields the result which revises the expression for the effective volume swept out in time t

Effective volume of targets swept

$$\pi d^2 \sqrt{2}\, \bar{v} t$$

The number of collisions is $\sqrt{2}$ times the number with stationary targets.

The resulting mean free path is

$$\lambda = \frac{1}{\sqrt{2}\, \pi d^2 n_V}$$

The number of molecules per unit volume can be determined from Avogadro's number and the ideal gas law, leading to

$$n_V = \frac{nN_A}{V} = \frac{nN_A}{\frac{nRT}{P}} = \frac{N_A P}{RT}$$

Mean free path

$$\lambda = \frac{RT}{\sqrt{2}\pi d^2 N_A P}$$

It should be noted that this expression for the mean free path of molecules treats them as hard spheres, whereas real molecules are not. For noble gases, the collisions are probably close to being perfectly elastic, so the hard sphere approximation is probably a good one. But real molecules may have a dipole moment and have significant electrical interaction as they approach each other. This has been approached by using an electrical potential for the molecules to refine the calculation, and also by using the measured viscosity of the gas as a parameter to refine the estimate of the mean free path of molecules in real gases.

Heat Capacity

The *heat capacity* of a defined system is the amount of heat (usually expressed in calories, kilocalories, or joules) needed to raise the system's temperature by one degree (usually expressed in Celsius or Kelvin). It is expressed in units of thermal energy per degree temperature. To aid in the analysis of systems having certain specific dimensions, *molar heat capacity* and *specific heat capacity* can be used. To measure the heat capacity of a reaction, a calorimeter must be used.

Bomb calorimeters are used for constant volume heat capacities, although a coffee-cup calorimeter is sufficient for a constant pressure heat capacity.

Molar Heat Capacity

The amount of heat needed to increase the temperature of one mole of a substance by one degree is the molar heat capacity. It is expressed in joules per moles per degrees Celsius (or Kelvin). JoulesMoles∘C. For example, the molar heat capacity of lead is 26.65 JoulesMolesC, which means that it takes 26.65 Joules of heat to raise 1 mole of lead by °C.

Specific Heat Capacity

The amount of heat needed to increase the temperature of one gram of a substance by one degree is the specific heat capacity. It is expressed in joules per gram per degree Celsius, JoulesGrams∘C. Because the specific heat of lead is 0.128 JoulesGrams∘C, it 0.128 Joules of heat is required to raise one gram of lead by one °C.

Molar heat capacity of ideal gases:-the amount of heat required to raise the temperature of 1 mole of a gas trough 1^0C.

$C_P - C_V = R$ &

Poisson's ratio (γ) = C_P/C_V

For monatomic gas C_p = 5 cal and C_v =3 cal

$\gamma = 5/3 = 1.67$

For diatomic gas C_p = 7 cal and C_v = 5 cal

$\gamma = 7/5 = 1.4$

For polyatomic gas C_p = 8 cal and C_v= cal

$\gamma = 8/6 = 1.33$

Also $C_p = C_pm$,

Where, C_p and C_v are specific heat and m, is molecular weight.

Possible questions

Part A

1. The arithemetic mean of the velocities possessed by the different molecules of a gas at a particular temperature is

   a) **Average velocity** b) Root mean square velocity

   c) Most probable velocity d) Steady velocity

2. The square root of the mean of the squares of the different velocities

   a) Average velocity b) **Root mean square velocity**

   c) Most probable velocity d) Steady velocity,

3. Most probable velocity is equal to

   a) **0.816 u** b) 0.816 v c) 0.816 k d) 0.816 α

4. Average velocity is equal to

   a) 0.**921 u** b) 0.816 u c) 0.921 α d) 0.816 k

5. Collision number is represented as

   a) σ (sigma) b) **Z_1** c) Z_{12} d) Λ (lambda)

6. Collision frequency is represented as

   a) σ (sigma) b) Z_1 c) **Z_{12}** d) Λ (lambda)

7. Mean free path is represented as,

   a) σ (sigma) b) Z_1 c) Z_{12} d) **Λ (lambda)**

8. The distance between centers of the molecules at the point of closest approach is

   a) **Collision diameter** b) Collision frequency

   c) Collision number d) Mean free path

9. Cooling and compression of it brings about its liquification

   a) Soild b) liquid c) **gas** d) plasma

10. They exhibit the property diffusion,

    a) liquid b) solid c) **gas** d) plasma

11. At ordinary conditions of temperatures and pressure their densities are low

    a) Plasma b) liquid c) **gas** d) Solid

12. At a particular temperature the fraction of molecules possessing particular velocities remain almost constant. Such state is called

    a) Tranisition state b) Intermediate c) **Steady state** d) Equilibrium state

13. Collision number is represented as

    a) σ (sigma) b) **Z**, c) Z_{12} d) Λ (lambda)

14. Collision frequency is represented as

    a) Λ (lambda) b) Z_1 c) **Z_{12}** d) σ (sigma)

15. Mean free path is represented as,

    a) Z_1 b) σ (sigma) c) Z_{12} d) **Λ (lambda)**

16. The distance between centres of the molecules at the point of closest approach is

    a) Collision diameter **b)** Collision frequency c) Collision number d) Mean free path

17. The arithemetic mean of the velocities possessed by the different molecules of a gas at a particular temperature is

    a) Average velocity b) Root mean square velocity

    c) Most probable velocity d) Steady velocity

18. The square root of the mean of the squares of the different velocities

    a) Most probable velocity b) **Root mean square velocity**

    c) Average velocity d) Steady velocity

19. Most probable velocity is equal to

    a) 0.816 u b) 0.816 v c) 0.816 k d) 0.816 α

20. Average velocity is equal to

    a) 0.921 u b) 0.816 u c) 0.921 α d) 0.816 k

Part B

1. What is meant by collision diameter
2. What is meant by collision frequency
3. What is meant by mean free path
4. What is meant by viscosity of a substance

5. What is meant by surface tension
6. What is meant by most probable velocity of a gas
7. Explain average velocity of a gas
8. What is meant by root mean square velocity
9. State equipartition energy theorem
10. What do you understood by the term"degree of freedom"
11. Define specific heat capacity of a substance
12. Define molar heat capacity of a substance

Part C

1. What are the assumptions made by Maxwell and Boltzmann to explain the behavior of gases.
2. Explain Maxwell distribution of velocities. Explain most probable velocity, average velocity and root mean square velocity of gases.
3. Derive the equation $PV = 1/3\ mnc^2$ which is called kinetic gas equation.
4. Explain in detail about the Degrees of freedom of a gaseous molecule.

Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answer
Unit 1					
The number of coordinates required to specify the position of all the atoms in a molecule is called	Degrees of freedom	equipartition of energy	most probable velocity	collision frequency	Degrees of freedom
The number of degrees of freedom with respect to the translational motion of a molecule is	One	two	three	four	three
The number of degrees of freedom with respect to the rotational motion of a linear molecule is	One	two	three	four	two
The number of degrees of freedom with respect to the rotational motion of a Non- linear molecule is	One	two	three	four	three
The number of degrees of freedom with respect to the vibrational motion of a Non- linear molecule is	3N-5	three	3N-6	four	3N-6
The number of degrees of freedom with respect to the vibrational motion of a linear molecule is	3N-5	three	3N-6	four	3N-5
The total number of vibrational degrees of freedom of a diatomic molecule hydrogen is	One	two	three	four	One
The total number of vibrational degrees of freedom of a linear polyatomic molecule acetylene is	Six	two	three	Seven	Seven
The total number of vibrational degrees of freedom of a non-linear polyatomic molecule HCHO is	Six	two	three	Seven	Six
The total degrees of freedom for a molecule is	2N	4N	9N	3N	3N
Energy contributed by each translational degrees of freedom	½ KT	3/2 KT	3/4 KT	5/8 KT	½ KT
Energy contributed by each rotational degrees of freedom	½ KT	3/2 KT	3/4 KT	5/8 KT	½ KT
Energy contributed by each vibrational degrees of freedom	½ KT	KT	3/4 KT	5/8 KT	KT
Collision diameter is represented as	σ (sigma)	Z_1	Z_{12}	Λ (lambda)	σ (sigma)
Collision number is represented as	σ (sigma)	Z_1	Z_{12}	Λ (lambda)	Z_1
Collision frequency is represented as	σ (sigma)	Z_1	Z_{12}	Λ (lambda)	Z_{12}
Mean free path is represented as	σ (sigma)	Z_1	Z_{12}	Λ (lambda)	Λ (lambda)
The distance between centres of the molecules at the point of closest approach is	Collision diameter	Collision frequency	Collision number	Mean free path	Collision diameter
The number of molecules with which a single molecule will collide per unit time per unit volume is	Collision diameter	Collision frequency	Collision number	Mean free path	Collision number
Mean distance tracelled by a gas molecule between two successive collisions	Collision diameter	Collision frequency	Collision number	Mean free path	Mean free path
Number of molecular collisions occurring per unit time per unit volume of the gas is	Collision diameter	Collision frequency	Collision number	Mean free path	Collision frequency
Collision diameter is	The distance between centres of the molecules at the point of closest approach	The number of molecules with which a single molecule will collide per unit time per unit volume	Mean distance travelled by a gas molecule between two successive collisions	Number of molecular collisions occurring per unit time per unit volume of the gas	The distance between centres of the molecules at the point of closest approach
Collision Number is	The distance between centres of the molecules at the point of closest approach	The number of molecules with which a single molecule will collide per unit time per unit volume	Mean distance travelled by a gas molecule between two successive collisions	Number of molecular collisions occurring per unit time per unit volume of the gas	The number of molecules with which a single molecule will collide per unit time per unit volume
Collision frequency is	The distance between centres of the molecules at the point of closest approach	The number of molecules with which a single molecule will collide per unit time per unit volume	Mean distance travelled by a gas molecule between two successive collisions	Number of molecular collisions occurring per unit time per unit volume of the gas	Number of molecular collisions occurring per unit time per unit volume of the gas

Mean free path is	The distance between centres of the molecules at the point of closest approach	The number of molecules with which a single molecule will collide per unit time per unit volume	Mean distance travelled by a gas molecule between two successive collisions	Number of molecular collisions occurring per unit time per unit volume of the gas	Mean distance travelled by a gas molecule between two successive collisions
They fill up the whole vessel in which they are placed	Soild	liquid	gas	plasma	gas
They exert pressure on the walls of the vessel in which they are taken	Soild	liquid	gas	plasma	gas
They can be compressed by applying pressure	Soild	liquid	gas	plasma	gas
Cooling and compression of it brings about its liquification	Soild	liquid	gas	plasma	gas
They exhibit the property diffusion	Soild	liquid	gas	plasma	gas
At ordinary conditions of temperatures and pressure, their densities are low	Soild	liquid	gas	plasma	gas
At a particular temperature, the fraction of molecules possessing particular velocities remain almost constant. Such state is called	Tranisition state	Intermediate	Steady state	Equilibrium state	Steady state
From the Maxwells distribution of velocities, it may be noted that the fraction of molecules having zero velocity is	Zero	Unity	Maximum	Inbetween zero and unity	Zero
From the Maxwells distribution of velocities, it may be noted that the molecules which are motionless are	Zero	Unity	Maximum	Inbetween zero and unity	Zero
The velocity possessed by the maximum fraction of the molecules of the gas at a particular temperature is	Average velocity	Root mean square velocity	Most probable velocity	Steady velocity	Most probable velocity
The arithemetic mean of the velocities possessed by the different molecules of a gas at a particular temperature is	Average velocity	Root mean square velocity	Most probable velocity	Steady velocity	Average velocity
The square root of the mean of the squares of the different velocities	Average velocity	Root mean square velocity	Most probable velocity	Steady velocity	Root mean square
Most probable velocity is equal to	0.816 u	0.816 v	0.816 k	0.816 α	0.816 u
Average velocity is equal to	0.921 u	0.816 u	0.921 α	0.816 k	0.921 u
From kinetic theory of gases the total translational kinetic energy of a molecule is	3/2 KT	½ KT	3KT	4KT	3/2 KT
Energy contributed by each translational degree of freedom is	3/2 KT	½ KT	3KT	4KT	½ KT
Energy contributed by each rotational degree of freedom is	3/2 KT	½ KT	3KT	4KT	½ KT
Energy contributed by each vibrational degree of freedom is	KT	½ KT	3KT	4KT	KT
The mean free path varies	Directly as temperature	Indirectly as temperature	Directly as Pressure	Directly as volume	Directly as temperature
Collision frequency varies	Directly as temperature	Indirectly as temperature	Directly as Pressure	Directly as square root of absolute temperature	Directly as square root of absolute temperature
According to kinetic theory of gases	All the molecules of a particular gas are identical in mass and size	All the molecules of a particular gas are identical in mass and not in size	All the molecules of a particular gas are identical in size but different mass	All the molecules of a particular gas are different in mass and size	All the molecules of a particular gas are identical in mass and size
One of the postulate of kinetic theory of gases is	The actual volume of the molecules of a gas is negligible as compared to the total volume of the gas	The actual area of the molecules of a gas is negligible as compared to the total volume of the gas	The actual volume of the molecules of a gas is negligible as compared to the total area of the gas	The actual size of the molecules of a gas is negligible as compared to the total volume of the gas	The actual volume of the molecules of a gas is negligible as compared to the total volume of the gas
According to kinetic theory of gases	The molecules are moving continuously in one directions with different velocities	The molecules are moving continuously in different directions with same velocities	The molecules are moving continuously in same direction with same velocities	The molecules are moving continuously in different directions with different velocities	The molecules are moving continuously in different directions with different velocities
As per Maxwell and Boltzmann theory of gases	The forces of attraction is appreciable and repulsion between them are negligible	The forces of attraction is negligible but or repulsion between them is appreciable	The forces of attraction or repulsion between them are very high	The forces of attraction or repulsion between them are negligible	The forces of attraction or repulsion between them are negligible

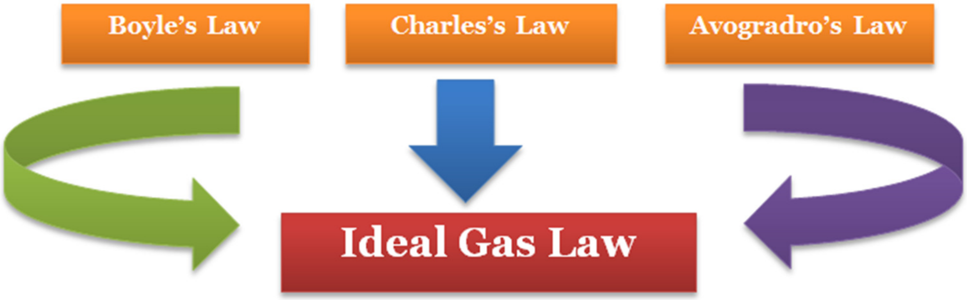
As per Maxwell and Boltzmann theory of gases	Molecules possess different kinetic energies	Molecules possess same kinetic energies in different directions	Molecules possess same kinetic energies in same directions	Molecules possess different potential energies	Molecules possess different kinetic energies
Characteristic property of a gas is	They fill up half of the whole vessel in which they are placed	They fill up the whole vessel in which they are placed	They fill up only in the bottom of the vessel in which they are placed	They fill up only in the top of the vessel in which they are placed	They fill up the whole vessel in which they are placed
Momentum of a molecule is	mv	2mv	½ mv	$M(V_1+ V_2)$	mv
As per Newtons law the change of momentum in one second is	Pressure	Force	torque	Root mean square velocity	Force
Pressure is defined as	work done during expansion	Work per second	Force per unit area	Work done during compression	Force per unit area
With respect to Gases	They fill up the whole vessel in which they are placed	They cannot be compressed by applying pressure	At ordinary conditions of T and P, their densities are high	They cannot be liquified	They fill up the whole vessel in which they are placed
The property of gases is	They fill up only half of the whole vessel in which they are placed	They can be compressed by applying pressure	At ordinary conditions of T and P, their densities are high	They cannot be liquified	They can be compressed by applying pressure
It is applicable for gases	They fill up only half of the whole vessel in which they are placed	They cannot be compressed by applying pressure	At ordinary conditions of T and P, their densities are low	They cannot be liquified	At ordinary conditions of T and P, their densities are low
3N-6 number of vibrational degrees of freedom is possible for	Linear molecule	Non linear molecule	Octahedral molecule	Tetrahedral molecule	Non linear molecule
3N-5 number of vibrational degrees of freedom is possible for	Linear molecule	Non linear molecule	Octahedral molecule	Tetrahedral molecule	linear molecule
The root mean square velocity of nitrogen at NTP is	49200 cm per second	99200 cm per second	4.9 cm per second	9,200 cm per second	49200 cm per second

UNIT II
GASEOUS STATE - II

Behaviour of real gases: Deviations from ideal gas behaviour, compressibility factor, Z, and its variation with pressure and temperature for different gases. Causes of deviation from ideal behaviour. Van der Waals equation of state, its derivation and application in explaining real gas behaviour, calculation of Boyle temperature. Isotherms of real gases and their comparison with van der Waals isotherms, continuity of states, critical state, relation between critical constants and van der Waals constants, law of corresponding states.

Ideal Gas Equation:

Ideal gas obey all the three laws i.e. Boyle's, Charles's, and Avogadro's law strictly.



pv = nRT

Where,

where R is the constant of proportionality or universal gas constant

The value of R was found out to be

$R = 8.314\ J\ mol^{-1}\ K^{-1}$

$R = 0.0821$ litre atm $K^{-1}\ mol^{-1}$

$R = 2$ cal $K^{-1}\ mol^{-1}$

Ideal gas equation is also known as equation ofstate.

Deviation from ideal gas behavior:

For ideal gas,

Compressibility factor i.e. $Z = PV/nRT = 1$

For non-Ideal gas, $Z \neq 1$

Thus for non-ideal gas,Z can be < 1 or > 1

When $Z < 1$, it is a negative deviation. It shows that the gas is more compressible than expected from ideal behaviour.

When $Z > 1$, it is a positive deviation. It shows that the gas is less compressible than expected from ideal behaviour.

1. Causes of deviation from ideal behaviour:

The volume occupied by gas molecules is negligibly small as compared to the volume occupied by the gas.

The forces of attraction between gas molecules are negligible.

2. Van der waals Equation:

$$(P + \frac{an^2}{V^2})(V - nb) = nRT$$

Where,

a and b are van der waals constants.

At low pressures:

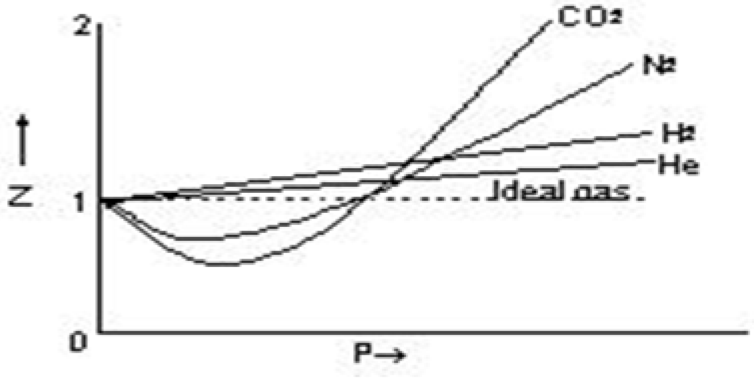
$PV = RT - a/V$

or

$PV < RT$

This accounts for the dip in PV vs P isotherm at low pressure

At fairly high pressures



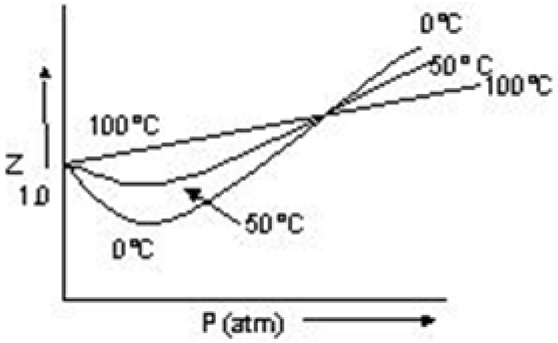
a/V^2 may be neglected in comparison with P. The Vander Waals equation becomes

$PV = RT + Pb$

or

$PV > RT$

This accounts for the rising parts of the PV vs P isotherm at high pressures



Boyle's Temperature (T_b) :-temperature at which real gas obeys the gas laws over a wide range of pressure.

$T_b = a / Rb = 1/2\ T_1$

Deviation from ideal gases

The gas laws mentioned above are strictly valid for an ideal gas under all conditions of temperature and pressure. Reas gases show deviations from these laws at low temperature and high pressure. These deviations can be shown clearly by plotting PV/nRT as a function of pressure at constant temperature,

$$\frac{pV}{nRT} = \frac{V_{\text{observed}}}{V_{\text{ideal}}} = Z\ (\text{compressibility factor})$$

Gases deviate from ideal behaviour due to the following faulty assumptions of kinetic theory :

1. Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.
2. There is no force of attraction between the molecules of a gas.

Contrary to assumption(1), the volume occupied by the molecules of a gas becomes significant at high pressures. If *nb* is the volume occupied by the molecules, the actual volume of the gas is (*V* – *nb*). Assumption (2) too doesn't hold good as at high pressures molecular interactions start operating. Molecules are dragged back by other molecules which affects the pressure exerted by them on the walls of the container.

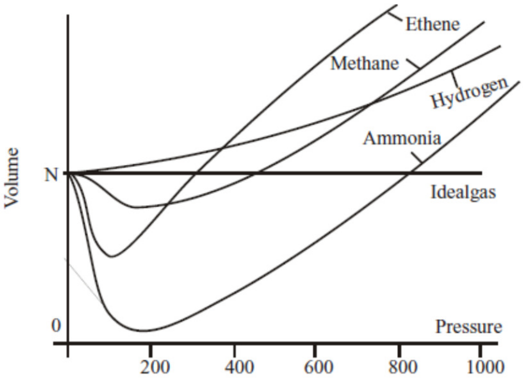
$$P_{ideal} = P_{real} + \frac{an^2}{V^2}$$

(Preal is observed pressure and An^2/V^2 is correction term)

In view of the corrections for pressure and volume, ideal gas equation can be rewritten as

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

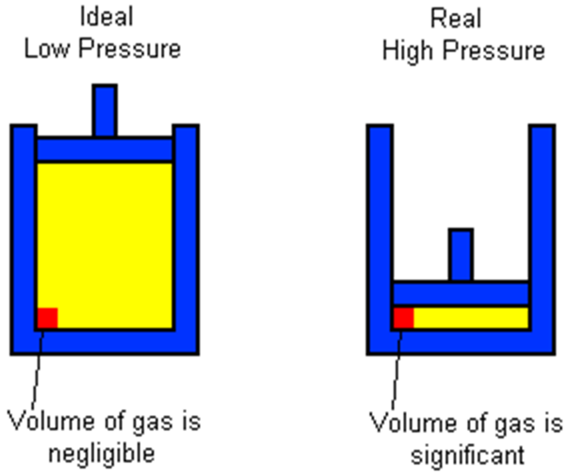
This is known as van der Waals equation



The plot volume versus P for real gases

Deviation from Ideal Gas Behavior

A gas which obeys the gas laws and the gas equation PV = nRT strictly at all temperatures and pressures is said to be an ideal gas.The molecules of ideal gases are assumed to be volume less points with no attractive forces between one another. But no real gas strictly obeys the gas equation at all temperatures and pressures. Deviations from ideal behaviour are observed particularly at high pressures or low temperatures.



The deviation from ideal behaviour is expressed by introducing a factor Z known as compressibility factor in the ideal gas equation. Z may be expressed as Z = PV / nRT

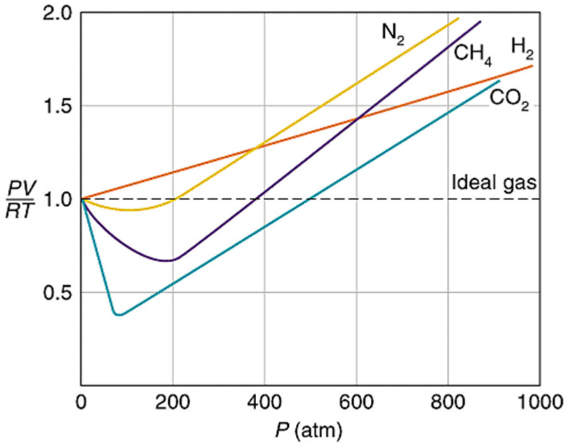
In case of ideal gas, PV= NRT Z=1

In case of ideal gas, PV= NRt $Z \neq 1$

Thus in case of real gases Z can be < 1 or > 1

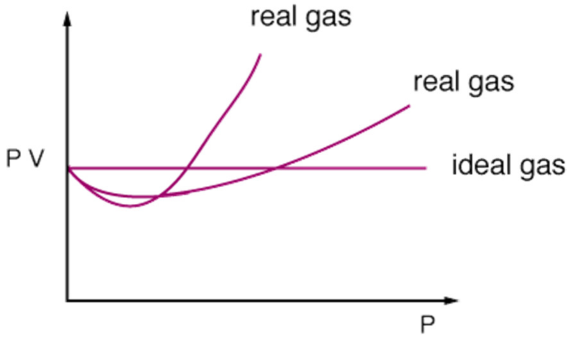
When Z < 1, it is a negative deviation. It shows that the gas is more compressible than expected from ideal behaviour.

When Z > 1, it is a positive deviation. It shows that the gas is less compressible than expected from ideal behaviour.



Causes of deviation from ideal behaviour

The causes of deviations from ideal behaviour may be due to the following two assumptions of kinetic theory of gases. The volume occupied by gas molecules is negligibly small as compared to the volume occupied by the gas. The forces of attraction between gas molecules are egligible. The first assumption is valid only at low pressures and high temperature, when the volume occupied by the gas molecules is negligible as compared to the total volume of the gas. But at low temperature or at high pressure, the molecules being in compressible the volumes of molecules are no more negligible as compared to the total volume of the gas.

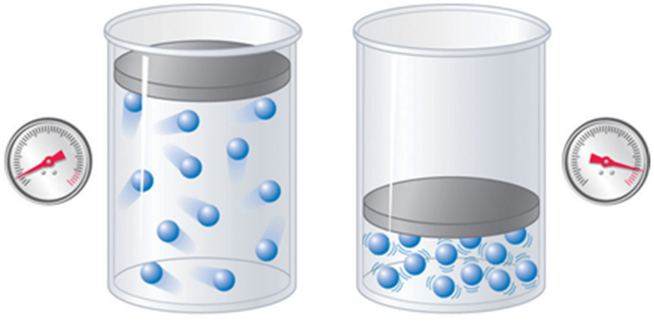


The second assumption is not valid when the pressure is high and temperature is low. But at high pressure or low temperature when the total volume of gas is small, the forces of attraction become appreciable and cannot be ignored.

Van der Waals' Equation of State for a Real Gas

This equation can be derived by considering a real gas and 'converting ' it to an ideal gas.

Volume correction:



(a) Low pressure (b) High pressure

We know that for an ideal gas P´V = nRT. Now in a real gas the molecular volume cannot be ignored and therefore let us assume that 'b' is the volume excluded (out of the volume of container) for the moving gas molecules per mole of a gas. Therefore due to n moles of a gas the volume excluded would be nb. \ a real gas in a container of volume V has only available volume of (V - nb) and this can be thought of as an ideal gas in container of volume (V - nb).

Hence, Ideal volume

$V_i = V - nb$ ………...(i)

n = Number of moles of real gas

V = Volume of the gas

b = A constant whose value depends upon the nature of the gas

b = 4 × volume of a single molecule $= 4 \times 6.023 \times 1023 \times (4/3)\pi r3$, where r is the radius of a molecule.

Pressure correction:

Let us assume that the real gas exerts a pressure P. The molecules that exert the force on the container will get attracted by molecules of the immediate layer which are assumed not to be exerting pressure. It can be seen that the pressure the real gas exerts would be less than the pressure an ideal gas would have exerted. The real gas experiences attractions by its molecules in the reverse direction. Therefore if a real gas exerts a pressure P, then an ideal gas would exert a pressure equal to P + p (p is the pressure lost by the gas molecules due to attractions). This small pressure p would be directly proportional to the extent of attraction between the molecules which are hitting the container wall and the molecules which are attracting these.

Therefore $p \propto n/v$ (concentration of molecules which are hitting the container's wall)

$P \propto n/v$ (concentration of molecules which are attracting these molecules) $\Rightarrow$ $p \propto n2/v2$

$P = an2/v2$ where a is the constant of proportionality which depends on the nature of gas.

A higher value of 'a' reflects the increased attraction between gas molecules.

Hence ideal pressure

$P_i = (P + an2 / V2)$ …….......(ii)

Here,

n = Number of moles of real gas

V = Volume of the gas

a = A constant whose value depends upon the nature of the gas

Substituting the values of ideal volume and ideal pressure in ideal gas equation i.e. pV=nRT, the modified equation is obtained as

‘V’ is large and ‘b’ is negligible in comparison with V.

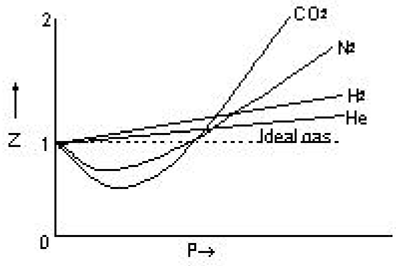
The Vander Waals equation reduces to:

$(P + a / V^2) V = RT$;

$PV + a/ V = RT$

$PV = RT – a/V$ or $PV < RT$

This accounts for the dip in PV vs P isotherm at low pressures.



- **At fairly high pressures**

a/V^2 may be neglected in comparison with P.

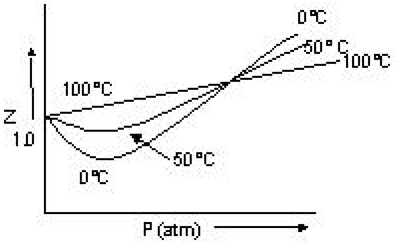
The Vander Waals equation becomes

$P (V – b) = RT$

$PV – Pb = RT$

$PV = RT + Pb$ or $PV > RT$

This accounts for the rising parts of the PV vs P isotherm at high pressures.



- **At very low pressures:**

V becomes so large that both b and a/V^2 become negligible and the Vander Waals equation reduces to $PV = RT$. This shows why gases approach ideal behaviour at very low pressures.

- **Hydrogen and Helium:**

These are two lightest gases known. Their molecules have very small masses. The attractive forces between such molecules will be extensively small. So a/V^2 is negligible even at ordinary temperatures.

Thus PV > RT. Thus Vander Waals equation explains quantitatively the observed behaviour of real gases and so is an improvement over the ideal gas equation. Vander Waals equation accounts for the behaviour of real gases.

At low pressures, the gas equation can be written as,

$(P + a/v^2{}_m) (V_m) = RT$

or

$Z = V_m / RT = 1 – a/V_mRT$

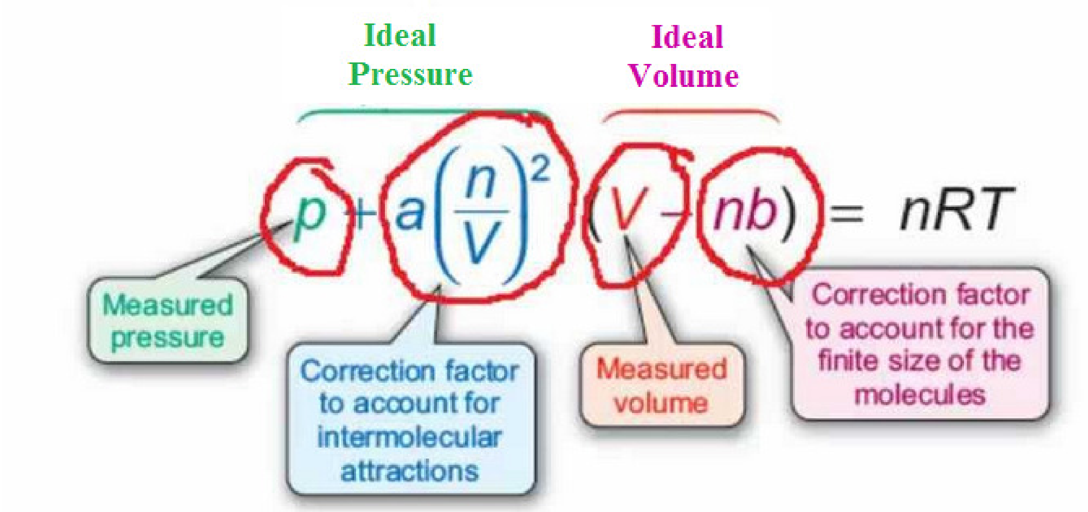
Where Z is known as compressibility factor. Its value at low pressure is less than 1 and it decreases with increase of P. For a given value of V_m, Z has more value at higher temperature.

At high pressures, the gas equation can be written as

$P (V_m – b) = RT$

$Z = PV_m / RT = 1 + Pb / RT$

Here, the compressibility factor increases with increase of pressure at constant temperature and it decreases with increase of temperature at constant pressure. For the gases H_2 and He, the above behaviour is observed even at low pressures, since for these gases, the value of ‘a’ is extremely small.



Some other important definitions

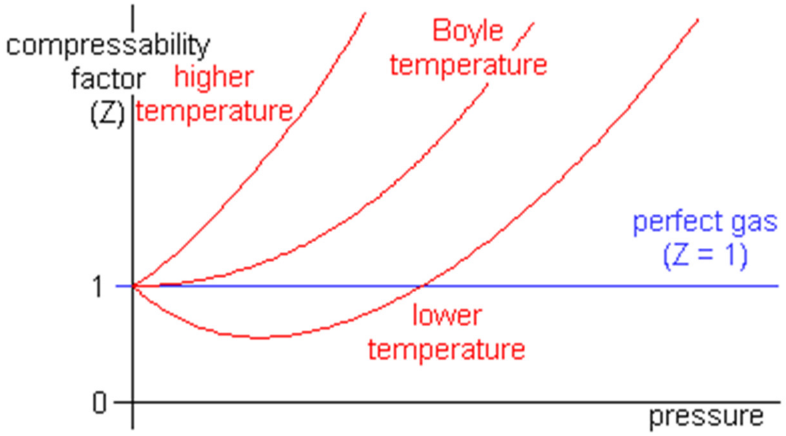
- **Relative Humidity (RH)**

At a given temperature it is given by equation

RH = (partial pressure of water in air) / (vapour pressure of water)

- **Boyle's Temperature (T_b)**

Temperature at which real gas obeys the gas laws over a wide range of pressure is called Boyle's Temperature. Gases which are easily liquefied have a high Boyle's temperature [$T_b(O_2)$] = 46 K] whereas the gases which are difficult to liquefy have a low Boyle's temperature [T_b(He) = 26K].



Boyle's temperature(T_b) = a / Rb = 1/2 T_1

where T_i is called Inversion Temperature and a, b are called van der Waals constant.

- **Critical Temperature (T_c):**

It (T_c) is the maximum temperature at which a gas can be liquefied i.e. the temperature above which a gas can't exist as liquid.

T = 8a / 27Rb

- **Critical Pressure (P_c):**

It is the minimum pressure required to cause liquefaction at T_c

$P_c = a/27b^2$

- **Critical Volume:**

It is the volume occupied by one mol of a gas at T_c and P_c

$V_c = 3b$

Molar heat capacity of ideal gases:

Specific heat c, of a substance is defined as the amount of heat required to raise the temperature of is defined as the amount of heat required to raise the temperature of 1 g of substance through 1^0C, the unit of specific heat is calorie g^{-1} K^{-1}. (1 cal is defined as the amount of heat required to raise the temperature of 1 g of water through 1^0C)

Molar heat capacity C, is defined as the amount of heat required to raise the temperature of 1 mole of a gas through 1^0C. Thus,

Molar heat capacity = Sp. Heat molecular wt. Of the gas

For gases there are two values of molar heats, i.e., molar heat at constant pressure and molar heat at constant molar heat at constant volume respectively denoted by C_p and C_v. C_p is greater than C_v and C_p-R = 2 cal mol^{-1} K^{-1}

From the ratio of C_p and C_v, we get the idea of atomicity of gas.

For monatomic gas C_p = 5 cal and C_v =3 cal
∴ ($\gamma = 5/3 = 1.67$ (γ is poisson's ratio = C_p / C_v)

For diatomic gas C_p = 7 cal and C_v = 5 cal

$\gamma = 7/5 = 1.40$

For polyatomic gas C_p = 8 cal and C_v= cal

$\gamma = 8/6 = 1.33$

also $C_p = C_p m$,
where, C_p and C_v are specific heat and m, is molecular weight

The **compressibility factor** (**Z**), also known as the **compression factor**, is the ratio of the molar volume of a gas to the molar volume of an ideal gas at the same temperature and pressure. It is a useful thermodynamic property for modifying the ideal gas law to account for thereal gas behavior.[1] In general, deviation from ideal behavior becomes more significant the closer a gas is to a phase change, the lower the temperature or the larger the pressure.

Physical reason for temperature and pressure dependence

Deviations of the compressibility factor, *Z*, from unity are due to attractive and repulsive Intermolecular forces. At a given temperature and pressure, repulsive forces tend to make the volume larger than for an ideal gas; when these forces dominate *Z* is greater than unity.

When attractive forces dominate, Z is less than unity. The relative importance of attractive forces decreases as temperature increases (see effect on gases).

As seen above, the behavior of Z is qualitatively similar for all gases. Molecular nitrogen, N_2, is used here to further describe and understand that behavior. All data used in this section were obtained from the NIST Chemistry WebBook. It is useful to note that for N_2 the normal boiling point of the liquid is 77.4 K and the critical point is at 126.2 K and 34.0 bar.

The figure on the right shows an overview covering a wide temperature range. At low temperature (100 K), the curve has a characteristic check-mark shape, the rising portion of the curve is very nearly directly proportional to pressure. At intermediate temperature (160 K), there is a smooth curve with a broad minimum; although the high pressure portion is again nearly linear, it is no longer directly proportional to pressure. Finally, at high temperature (400 K), Z is above unity at all pressures. For all curves, Z approaches the ideal gas value of unity at low pressure and exceeds that value at very high pressure.

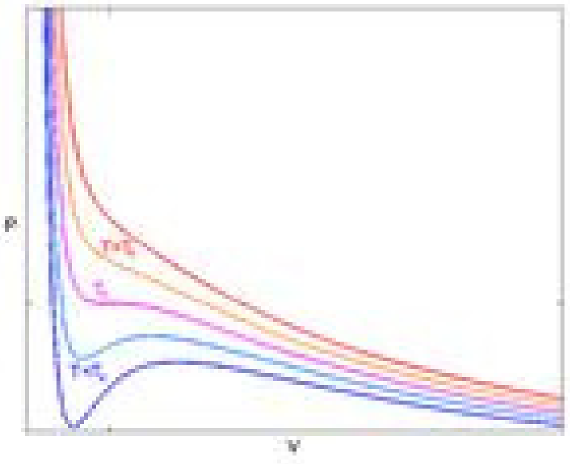
To better understand these curves, a closer look at the behavior for low temperature and pressure is given in the second figure. All of the curves start out with Z equal to unity at zero pressure and Z initially decreases as pressure increases. N_2 is a gas under these conditions, so the distance between molecules is large, but becomes smaller as pressure increases. This increases the attractive interactions between molecules, pulling the molecules closer together and causing the volume to be less than for an ideal gas at the same temperature and pressure. Higher temperature reduces the effect of the attractive interactions and the gas behaves in a more nearly ideal manner.

As the pressure increases, the gas eventually reaches the gas-liquid coexistence curve, shown by the dashed line in the figure. When that happens, the attractive interactions have become strong enough to overcome the tendency of thermal motion to cause the molecules to spread out; so the gas condenses to form a liquid. Points on the vertical portions of the curves correspond to N_2 being partly gas and partly liquid. On the coexistence curve, there are then two possible values for Z, a larger one corresponding to the gas and a smaller value corresponding to the liquid. Once all the gas has been converted to liquid, the volume decreases only slightly with further increases in pressure; then Z is very nearly proportional to pressure.

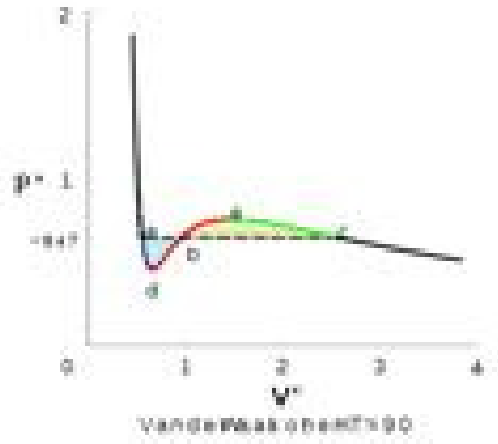
As temperature and pressure increase along the coexistence curve, the gas becomes more like a liquid and the liquid becomes more like a gas. At the critical point, the two are the same. So for temperatures above the critical temperature (126.2 K), there is no phase transition; as pressure increases the gas gradually transforms into something more like a liquid. Just above the critical point there is a range of pressure for which Z drops quite rapidly (see the 130 K curve), but at higher temperatures the process is entirely gradual. The final figures shows the behavior at temperatures well above the critical temperatures. The repulsive interactions are essentially unaffected by temperature, but the attractive interaction have less and less influence. Thus, at sufficiently high temperature, the repulsive interactions dominate at all pressures.

This can be seen in the graph showing the high temperature behavior. As temperature increases, the initial slope becomes less negative, the pressure at which *Z* is a minimum gets smaller, and the pressure at which repulsive interactions start to dominate, i.e. where *Z* goes from less than unity to greater than unity, gets smaller. At the Boyle temperature (327 K for N_2), the attractive and repulsive effects cancel each other at low pressure. Then *Z* remains at the ideal gas value of unity up to pressures of several tens of bar. Above the Boyle temperature, the compressibility factor is always greater than unity and increases slowly but steadily as pressure increases.

Isotherms for Real Gases



The above figure shows an isothermal plot for a real gas. For large T, the isotherms look like those of an ideal gas. But as T falls, especially below a critical temperature T_C, we see that the behavior is no longer ideal. The curves below Tc pass through a phase change of liquid to vapor. The critical temperature T_C has a inflection or critical point CP, where the pressure is transitioning from decreasing to increasing. As we go along an isotherm along or below T_C, the pressure decreases, and begins increasing till we reach a maximum. Then the pressure begins falling again and becomes more or less constant. Because the pressure no longer increases as the volume becomes less, these regions are unstable.



The above figure shows an isotherm below T_C that is labelled for clarification purposes. Starting at the right side of the diagram, the area after point c is where the pressure eventually becomes basically constant and the volume is small. Point c is where condensation occurs as the gas begins liquefying as we continue along the left of the plot. Between c and b is a phase where the liquid and vapor are in equilibrium. Point e is a maximum, and point d is a minimum. Ed is unstable and has not been observed in a lab. Pure supersaturated vapors have been measured along ec, and super cooled liquids have been measured along ad. Remember, supersaturated liquids have dissolved solute beyond the solubility limit, and super cooled liquids are those that are cooled to temperatures below that of their ordinary freezing points. At point a, the substance is now wholly a liquid. The pressure begins rising rapidly because it takes a great deal of it to compress a liquid.

Van der Waals Equation

The behavior of real gases usually agrees with the predictions of the ideal gas equation to within ± 5% at normal temperatures and pressures. At low temperatures or high pressures, real gases deviate significantly from ideal gas behavior. In 1873, while searching for a way to link the behavior of liquids and gases, the Dutch physicist Johannes van der Waals developed an explanation for these deviations and an equation that was able to fit the behavior of real gases over a much wider range of pressures. Van der Waals realized that two of the assumptions of the kinetic molecular theory were questionable. The kinetic theory assumes that gas particles occupy a negligible fraction of the total volume of the gas. It also assumes that the force of attraction between gas molecules is zero.

The first assumption works at pressures close to 1 atm. But something happens to the validity of this assumption as the gas is compressed. Imagine for the moment that the atoms or molecules in a gas were all clustered in one corner of a cylinder, as shown in the figure below. At normal pressures, the volume occupied by these particles is a negligibly small fraction of the total volume of the gas. But at high pressures, this is no longer true. As a result, real gases are not as compressible at high pressures as an ideal gas. The volume of a real gas is therefore larger than expected from the ideal gas equation at high pressures.

Van der Waals proposed that we correct for the fact that the volume of a real gas is too large at high pressures by *subtracting* a term from the volume of the real gas before we substitute it into the ideal gas equation. He therefore introduced a constant

constant (b) into the ideal gas equation that was equal to the volume actually occupied by a mole of gas particles. Because the volume of the gas particles depends on the number of moles of gas in the container, the term that is subtracted from the real volume of the gas is equal to the number of moles of gas times b.

$$P(V - nb) = nRT$$

When the pressure is relatively small, and the volume is reasonably large, the *nb* term is too small to make any difference in the calculation. But at high pressures, when the volume of the gas is small, the *nb*term corrects for the fact that the volume of a real gas is larger than expected from the ideal gas equation.

The assumption that there is no force of attraction between gas particles cannot be true. If it was, gases would never condense to form liquids. In reality, there is a small force of attraction between gas molecules that tends to hold the molecules together. This force of attraction has two consequences: (1) gases condense to form liquids at low temperatures and (2) the pressure of a real gas is sometimes smaller than expected for an ideal gas.

To correct for the fact that the pressure of a real gas is smaller than expected from the ideal gas equation, van der Waals *added* a term to the pressure in this equation. This term contained a second constant (*a*) and has the form: an^2/V^2. The complete **van der Waals equation** is therefore written as follows.

$$[P + \frac{an^2}{V^2}](V - nb) = nRT$$

This equation is something of a mixed blessing. It provides a much better fit with the behavior of a real gas than the ideal gas equation. But it does this at the cost of a loss in generality. The ideal gas equation is equally valid for any gas, whereas the van der Waals equation contains a pair of constants (*a* and *b*) that change from gas to gas.

The ideal gas equation predicts that a plot of *PV* versus *P* for a gas would be a horizontal line because *PV* should be a constant. Experimental data for *PV* versus *P* for H_2 and N_2 gas at 0°C and CO_2 at 40C are given in the figure below. Values of the van der Waals constants for these and other gases are given in the table below.

The magnitude of the deviations from ideal gas behavior can be illustrated by comparing the results of calculations using the ideal gas equation and the van der Waals equation for 1.00 mole of CO_2 at 0^oC in containers of different volumes. Let's start with a 22.4 L container.

According to the ideal gas equation, the pressure of this gas should be 1.00 atm.

$$P = \frac{nRT}{V} = \frac{(1.00\ mol)(0.08206\ \frac{L\ atm}{mol\ K})(273\ K)}{(22.4\ L)} = 1.00\ atm$$

Substituting what we know about CO_2 into the van der Waals equation gives a much more complex equation.

$$[P + \frac{an^2}{V^2}](V - nb) = nRT$$

$$[P + \frac{(3.592\ \frac{L^2\ atm}{mol^2})(1.00\ mol)^2}{(22.4\ L)^2}][22.4\ L - (1.00\ mol)(0.04267\ \frac{L}{mol})] =$$

$$(1.00\ mol)(0.08206\ \frac{L\ atm}{mol\ K})(273\ K)$$

This equation can be solved, however, for the pressure of the gas.

$$P = 0.995 \text{ atm}$$

At normal temperatures and pressures, the ideal gas and van der Waals equations give essentially the same results.

Let's now repeat this calculation, assuming that the gas is compressed so that it fills a container that has a volume of only 0.200 liters. According to the ideal gas equation, the pressure would have to be increased to 112 atm to compress 1.00 mol of CO_2 at 0C to a volume of 0.200 L.

$$P = \frac{nRT}{V} = \frac{(1.00\ mol)(0.08206\ \frac{L\ atm}{mol\ K})(273\ K)}{(0.200\ L)} = 112\ atm$$

The van der Waals equation, however, predicts that the pressure will only have to increase to 52.6 atm to achieve the same results.

$$[P + \frac{(3.592\ \frac{L^2\ atm}{mol^2})(1.00\ mol)^2}{(0.200\ L)^2}][0.200\ L - (1.00\ mol)(0.04267\ \frac{L}{mol})] =$$

$$(1.00\ mol)(0.08206\ \frac{L\ atm}{mol\ K})(273\ K)$$

$P = 52.6$ atm

The van der Waals equation was proposed in the year 1873. It was a first step towards taking into account interaction forces which are acting between real gases molecules.

The equation of state of the perfect gas refers to a gas consisting of point like items which do not interact with one another.

Instead of this van der Waals proposed an equation

(1)

$$(v-b)\left(p+\frac{a}{v^2}\right)=RT,$$

where a and b are the so-called van der Waals constants and which have different values for each gas.

The b correction takes into account the fact that, according to van der Waals. the real gas molecules can move not in the total volume occupied by the gas, but only in a part of this volume which is defined by subtracting what he called the molecules own volume. The correction a/v^2 — proportional to the square of density-takes into account the attraction forces existing between gas molecules. According to the van der Waals assumption, these forces decrease the pressure against the vessel walls, because the molecules which are close to the wall are subjected to attraction of other molecules.

The a and b constants are to be considered as empirical; they have to be derived from experimental data on the density, temperature and pressure interdependence. For a number of technically important gases the van der Waals constants are tabulated.

According to the method of allowing for deviation of a real gas from a perfect gas, the van der Waals equation supposedly would be valid only for small deviations, i.e., for moderate pressures. But it turned out that this equation qualitatively satisfactorily describes the real gases behavior in a wide range of parameters including the critical region.

The van der Waals equation is a cubic one with respect to the specific volume. This means that in general at a given temperature, each pressure value corresponds to three specific volume values—ν_1, ν, ν_2. The values ν_1 and $\nu_2$correspond to physically existing states of liquid and vapor. The value ν, where $(\partial p/\partial v)_T > 0$, corresponds to an unstable state and does not exist physically. As the temperature increases, the values ν_1 and ν_2 get closer and finally at the critical point all three roots coincide at the critical volume ν_c. At higher temperatures only one root of the van der Waals equation remains real, the two other being imaginary. These supercritical isotherms reveal inflexions at $\nu = \nu_c$which is close to the behavior of real substances.

The Relationship between the van der Waals Parameters and the Critical Constants

If

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

then

$$p = \frac{RT}{V - b} - \frac{a}{V^2}$$

At the critical point,

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$$

So, differentiating our expression for pressure with respect to volume at constant temperature

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0$$

so that

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3}$$

Differentiating again gives

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = +\frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0$$

so that

$$\frac{2RT_c}{(V_c - b)^3} = \frac{6a}{V_c^4}$$

Dividing these two expressions gives

$$\frac{(V_c - b)}{2} = \frac{V_c}{3}$$

and so

$$V_c = 3b$$

Substitution of this result into the expression that we obtained by differentiating once

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3}$$

gives

$$\frac{RT_c}{(3b-b)^2} = \frac{2a}{(3b)^3}$$

which, when rearranged, gives

$$T_c = \frac{8a}{27bR}$$

Substitution of the expressions for the critical volume V_c and critical temperature T_c into the van der Waals equation gives

$$\begin{aligned} p_c &= \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} \\ &= R\frac{1}{(3b-b)}\frac{8a}{27bR} - \frac{a}{9b^2} \\ &= \frac{8a}{54b^2} - \frac{a}{9b^2} \\ &= \frac{8a}{54b^2} - \frac{6a}{54b^2} \end{aligned}$$

and so

$$p_c = \frac{a}{27b^2}$$

Given these expressions for the values of the critical constants

$$\frac{T_c}{p_c} = \frac{8a}{27bR}\frac{27b^2}{a} = \frac{8b}{R}$$

so that

$$b = \frac{RT_c}{8p_c}$$

Similarly

$$T_c^2 = \frac{64a^2}{729b^2R^2}$$

$$\frac{T_c^2}{p_c} = \frac{64a^2}{729b^2R^2}\frac{27b^2}{a} = \frac{64a}{27R^2}$$

Hence

$$a = \frac{27R^2T_c^2}{64p_c}$$

Law of corresponding states

The **law of corresponding states** is an empirical law which encapsulates the finding that the equations of state for many real gases are remarkably similar when they are expressed in terms of reduced temperatures ($T_r = T/T_c$), pressures, ($p_r = p/p_c$) and volumes ($V_r = V/V_c$), where the subscript c represents the value of the property at the critical point

If two substances have the same reduced pressure and the same reduced temperature, they must have the same reduced volume.

Continuity of state

If the ends of the horizontal portions of the different Andrews isotherms are joined together, a parabolalic curve is obtained. The peak of this parabola represents the critical point. Within the parabola, the liquid and the vapour exist together in equilibrium. Outside the parabola, the substance exists only as gaseous under the conditions represented on the right side and only as liquid under the conditions represented on the left side. A careful thinking reveals that below the critical temperature it is possible to change a substance from gaseous state to liquid state without having both the phases present together at any stage.

Suppose the substance under consideration is carbon di oxide. At 13.1^{0}C, if the pressure and volume correspond to the point ‘a’ the substance is gaseous. Keeping the volume constant, if the gaseous carbondioxide is heated till it has pressure corresponding to the point ‘b’ the path ab is followed. Now keeping the pressure constant, suppose the gaseous carbondioxide is cooled the volume decreases along the path bc. At ‘c’ carbondioxide will exist as liquid. Thus nowhere along the path abc there has been more than one phase present. This is expressed by saying that the change of state from gaseous to liquid is continuous or it is referred to as the continuity of state.

Liquid state: Qualitative treatment of the structure of the liquid state; physical properties of liquids; vapour pressure, surface tension and coefficient of viscosity, and their determination. Effect of addition of various solutes on surface tension and viscosity. Explanation of cleansing action of detergents. Temperature variation of viscosity of liquids and comparison with that of gases.

Vapor Pressure of Liquids

The vapor pressure of a liquid is measure of its “volatility” n Vapor pressure is defined as the pressure exerted by the gas-phase molecules over a liquid n Vapor pressure is a strong function of temperature-the higher the temperature, the higher the vapor pressure.

Vapor Pressure and Boiling Point n The boiling point of a liquid is defined as the temperature at which the vapor pressure of the liquid is equal to the total pressure of gas over the liquid n The normal boiling point is defined as the temperature at which the vapor pressure of the liquid is equal to 1 atm , For H_2O, the normal boiling point is 100.0 ^oC, For CH_3OH, the normal boiling point is 64.6 ^oC, For C_2H_5OH, the normal boiling point is 78.3 ^oC.

Surface tension is the elastic tendency of a fluid surface which makes it acquire the least surface area possible. Surface tension allows insects (e.g. water striders), usually denser than water, to float and stride on a water surface.

At liquid-air interfaces, surface tension results from the greater attraction of liquid molecules to each other (due to cohesion) than to the molecules in the air (due to adhesion). The net effect is an inward force at its surface that causes the liquid to behave as if its surface were covered with a stretched elastic membrane. Thus, the surface becomes under tension from the imbalanced forces, which is probably where the term "surface tension" came from.[1] Because of the relatively high attraction of water molecules for each other, water has a higher surface tension (72.8 millinewtons per meter at 20 °C) compared to that of most other liquids. Surface tension is an important factor in the phenomenon of capillarity.

Causes

The cohesive forces among liquid molecules are responsible for the phenomenon of surface tension. In the bulk of the liquid, each molecule is pulled equally in every direction by neighboring liquid molecules, resulting in a net force of zero. The molecules at the surface do not have the*same* molecules on all sides of them and therefore are pulled inwards. This creates some internal pressure and forces liquid surfaces to contract to the minimal area.

Surface tension is responsible for the shape of liquid droplets. Although easily deformed, droplets of water tend to be pulled into a spherical shape by the imbalance in cohesive forces of the surface layer. In the absence of other forces, including gravity, drops of virtually all liquids would be approximately spherical. The spherical shape minimizes the necessary "wall tension" of the surface layer according to Laplace's law.

Surface tension preventing a paper clip from submerging.

Another way to view surface tension is in terms of energy. A molecule in contact with a neighbor is in a lower state of energy than if it were alone (not in contact with a neighbor). The interior molecules have as many neighbors as they can possibly have, but the boundary molecules are missing neighbors (compared to interior molecules) and therefore have a higher energy. For the liquid to minimize its energy state, the number of higher energy boundary molecules must be minimized. The minimized quantity of boundary molecules results in a minimal surface area.[2] As a result of surface area minimization, a surface will assume the smoothest shape it can (mathematical proof that "smooth" shapes minimize surface area relies on use of the Euler-Lagrange equation). Since any curvature in the surface shape results in greater area, a higher energy will also result. Consequently, the surface will push back against any curvature in much the same way as a ball pushed uphill will push back to minimize its gravitational potential energy.

Several effects of surface tension can be seen with ordinary water:

1. Beading of rain water on a waxy surface, such as a leaf. Water adheres weakly to wax and strongly to itself, so water clusters into drops. Surface tension gives them their near-spherical shape, because a sphere has the smallest possible surface area to volume ratio.

2. Separation of oil and water (in this case, water and liquid wax) is caused by a tension in the surface between dissimilar liquids. This type of surface tension is called "interface tension", but its chemistry is the same.

Surfactants

Surface tension is visible in other common phenomena, especially when surfactants are used to decrease it:

- Soap bubbles have very large surface areas with very little mass. Bubbles in pure water are unstable. The addition of surfactants, however, can have a stabilizing effect on the bubbles (see Marangoni effect). Note that surfactants actually reduce the surface tension of water by a factor of three or more.
- Emulsions are a type of solution in which surface tension plays a role. Tiny fragments of oil suspended in pure water will spontaneously assemble themselves into much larger masses. But the presence of a surfactant provides a decrease in surface tension, which permits stability of minute droplets of oil in the bulk of water (or vice versa).

- The interplay of the forces of cohesion and adhesion explains the phenomenon of capillarity. When a liquid is in contact with a solid, if the forces of adhesion between the molecules of the liquid and the solid are greater than the forces of cohesion among the liquid molecules themselves, the liquid molecules crowd towards the solid surface. The area of contact between the liquid and solid increases and the liquid thus wets the solid surface.
- The reverse phenomenon takes place when the force of cohesion is greater than the force of adhesion. These adhesion and cohesion properties result in the phenomenon of capillarity by which a liquid either rises or falls in a tube dipped into the liquid depending upon whether the force of adhesion is more than that of cohesion or not .
- The angle θ as shown in Fig. 2.4, is the area wetting contact angle made by the interface with the solid surface.

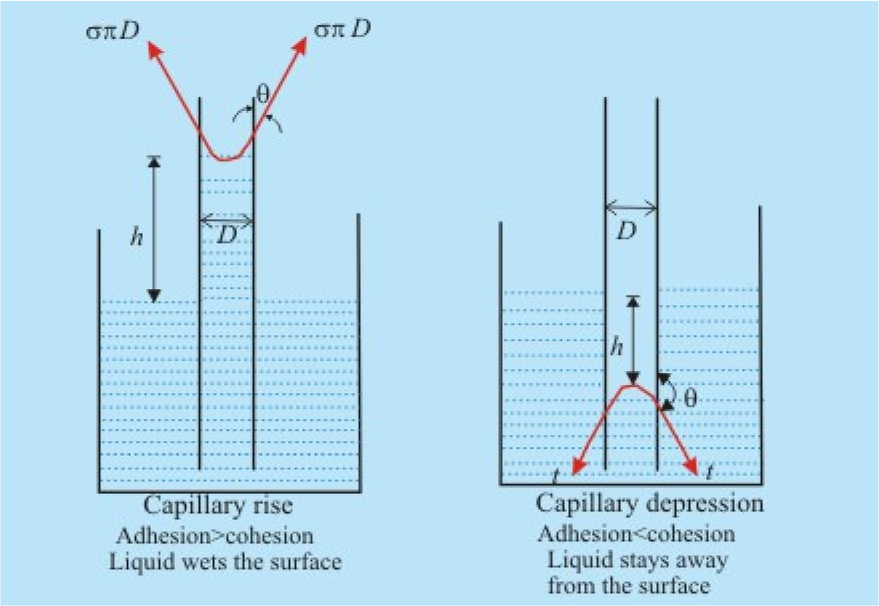


Fig 2.4 Phenomenon of Capillarity

- For pure water in contact with air in a clean glass tube, the capillary rise takes place with $\theta = 0$. Mercury causes capillary depression with an angle of contact of about 130^0 in a clean glass in contact with air. Since h varies inversely with D as found from Eq. ($h = \frac{4\sigma\cos\theta}{\rho g D}$), an appreciable capillary rise or depression is observed in tubes of small diameter only.

Viscosity

The **viscosity** of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress. For liquids, it corresponds to the informal concept of "thickness"; for example, honey has a much higher viscosity than water.

Viscosity is a property arising from collisions between neighboring particles in a fluid that are moving at different velocities. When the fluid is forced through a tube, the particles which compose the fluid generally move more quickly near the tube's axis and more slowly near its walls; therefore some stress (such as a pressure difference between the two ends of the tube) is needed to overcome the friction between particle layers to keep the fluid moving. For a given velocity pattern, the stress required is proportional to the fluid's viscosity.

For most circumstances near the conditions we live in, pressure doesn't have much effect on viscosity.

For ideal gases, viscosity depends only on temperature. For real gases, that's still a very good approximation. At this link, Viscosity, you will find Sutherland's law for viscosity of gases and you will see that the input to the equation is temperature. There is no dependence on pressure. Although it's called a *law*, it is actually just a very good fit to the data.

For liquids, changing the pressure does very little unless you increase the pressure A LOT.

This page, Factors affecting viscosity, has the following statement:

"In most cases, a fluid's viscosity increases with increasing pressure. Compared to the temperature influence, liquids are influenced very little by the applied pressure. The reason is that liquids (other than gases) are almost non-compressible at low or medium pressures. For most liquids, a considerable change in pressure from 0.1 to 30 MPa causes about the same change in viscosity as a temperature change of about 1 K (1°C)."

I wish they had written the first two sentences in the reverse order. If you read the rest of the paragraph carefully, you conclude that pressure has very little effect on viscosity. You need to increase the pressure by 300 atmospheres to get the same change in viscosity as changing the temperature by one degree C. Temperature is by far the dominant factor in viscosity. Pressure has almost no effect.

How do you define viscosity?

Viscosity is the property of a fluid by virtue of which an internal resistance comes into play when the liquid is in motion, and opposes the relative motion between its different layers. Thus, it is the resistance of a fluid to flow.

When liquid flows over flat surface, a backward viscous force acts tangentially to every layer. This force depends upon the area of the layer, velocity of the layer, and the distance of the layer from the surface.

$$F \alpha A \frac{\mathrm{d}v}{\mathrm{d}x}$$

$$F = \eta A \frac{\mathrm{d}v}{\mathrm{d}x}$$

Where η is the ***coefficient of viscosity*** of the liquid.

Stoke's Law

Stoke's law was established by an English scientist Sir George G Stokes (1819-1903).

When a spherical body moves down through an infinite column of highly viscous liquid, it drags the layer of the liquid in contact with it. As a result, the body experiences a retarding force.

Then according to Stokes law, the viscous drag force,

$$F = 6\pi\eta r v \text{ ,}$$

where, r - Radius of the spherical body

v - Velocity of the spherical body

It gives the relationship between retarding force and velocity. When viscous force plus buoyant force becomes equal to force due to gravity, the net force becomes zero. The sphere then descends with a constant terminal velocity (v_t).

Now,

$$6\pi\eta r v = \frac{4}{3}\pi r^3(\rho - \sigma)g$$

where, ρ - Density of the liquid

σ - Density of the spherical body

The force of friction which one part of the liquid offers to another part of the liquid is called viscosity. For measuring the viscosity coefficient, Ostwald viscometer method is used which is based on Poiseuille's law. According to this law, the rate of flow , can be expressed as$\eta$of liquid through a capillary tube having viscosity coefficient,

$$\eta = \pi r^4 tp/8vl$$

where, v= vol. of liquid (in ml) t= flow time (in sec.) through capillary r= radius of the capillary (in cm) l= length of the capillary (in cm) P= hydrostatic pressure (in dyne/sq.cm) = viscosity coefficient (in poise).η

Temperature Dependence of Viscosity

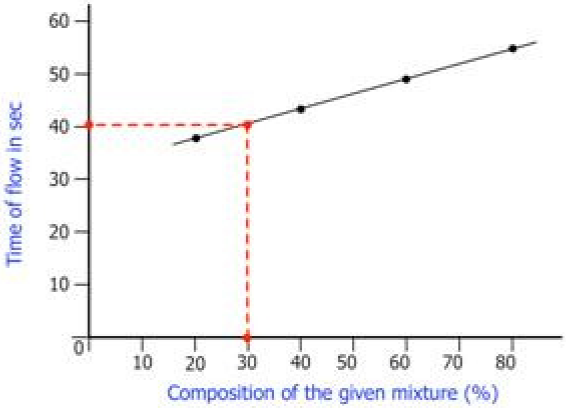
In 1889 Arrhenius expressed an equation for temperature dependent chemical reaction rates. Since then, many temperature dependent chemical and physical processes have been found to behave in accordance with Arrhenius-like equations. For the viscosity of many liquids, the viscosity decreases as the temperature increases in accordance with the following equation:

$$\eta = Ae^{\left(E_\eta / RT\right)} \quad \text{-------(6)}$$

Where *A* is a constant known as the Arrhenius constant, E_η is the activation energy for flow, *R* is the ideal gas constant, and *T* is the temperature of the liquid using an absolute scale (almost always K - the units of E_η and *R* and *T* should be chosen so that the ratio is dimensionless, *A* will have the same dimensions as η, in our case cP). A plot of η vs. $1/T$ should be linear and have a slope equal to E_η /Rif the liquid's viscosity exhibits Arrhenius-like behaviour.

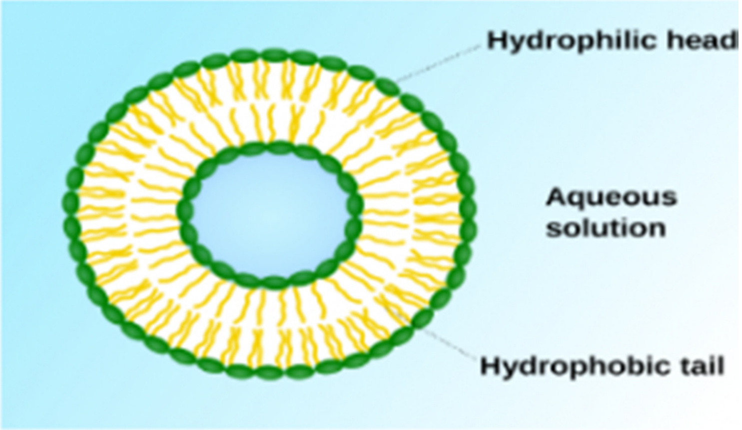
Determination of unknown composition

Using an Ostwald viscometer, we can also calculate the unknown composition of a mixture. The viscosities of mixtures of different known compositions are measured and a graph is plotted with viscosity against the compositions of the different mixtures. From the graph, the composition of the unknown mixture corresponding to the viscosity can be determined.



Cleansing action of Soaps and detergents: Most of the dirt is oily in nature and oil does not dissolve in water. The molecule of soap constitutes sodium or potassium salts of long chain carboxylic acids. In the case of soaps the carbon chain dissolves in oil and the ionic end dissolves in water. Thus the soap molecules form structures called **micelles** .In micelles one end is towards the oil droplet and the other end which is the ionic faces outside. Therefore, it forms emulsion in water and helps in dissolving the dirt r when we wash our clothes.

The soap is a kind of molecule in which both the ends have different properties. The first one is the hydrophilic end which dissolves water and is attracted towards it whereas the second one is the hydrophobic end that is dissolved in hydrocarbons and is water repulsive in nature. If on the surface of water, soap is present then the hydrophobic tail which is not soluble in water will align along the water surface.



Micelles

In water the soap molecule is uniquely oriented which helps to keep the hydrocarbon part outside the water. When the clusters of molecules are formed then hydrophobic tail comes at the interior of the cluster and the ionic end comes at the surface of the cluster and this formation is called micelle. When the soap is in the form of micelles then it has the ability to clean the oily dirt which gets accumulated at the centre. These micelles remain as a colloid in the solution. Therefore the dirt from the cloth is easily washed away .The soap solution appears cloudy as it forms a colloidal solution which scatters light.

Possible questions

PART A

1. The volume occupied by one mole of the gas at the critical temperature and pressure is
   a) Excluded volume b) Co volume c) **Critical volume** d) Pseudo volume
2. The critical temperature, critical pressure and critical volume of a gas are collectively called as
   a) Van der waals constants b) **Critical constants**
   c) Critical density d) Gas constants
3. At extremely low pressure the gases
   a) **Obey the ideal gas equation** b) Deviate more from the ideal gas equation
   c) Behave as real gases d) Behave as inert gases,
4. Gases obey the ideal gas equation at
   a) **Extremely low pressures** b) Extremely high pressures
5. In the Van der waals equation 'b' is called
   a) Excluded volume b) **Effective volume** c) Critical temperature d) Critical pressure
6. In the Van der waals equation 'b' is called
   a) **Co- volume** b) Effective volume c) Critical temperature d) Critical pressure
7. The significance of the Vander Waals constant 'a' is
   a) Measure of compressibility b) Measure of inertness
   c) Excluded volume d) **Measure of the intermolecular forces of attraction in a gas**
8. The significance of the Vander Waals constant 'b' is
   a) Measure of compressibility b) Measure of inertness c) Measure of diffussibility
   d) Measure of the intermolecular forces of attraction in a gas
9. Isotherm is
   a) A plot of 'P' and 'T' at constant V is called b) A plot of 'V' and 'T' at constant P is called c) **A plot of 'P' and 'V' at constant T is called** d) A plot of 'PV' and 'T' at constant V is called
10. Isotherms of all gases are similar except
    a) The breadth of the horizontal portion b) **Lengths of the horizontal portion**
    c) Length of the vertical portion d) Breadth of the vertical portion
11. Isotherms of all gases are similar except
    a) The breadth of the horizontal portion b) **peak of the dotted parabola are different**
    c) Length of the vertical portion d) Breadth of the vertical portion
12. In the Andrews experiments on critical phenomenon
    a) Within the parabola b) **The liquid and vapour exist together in equilibrium**

c) Solid and liquid exist in equilibrium d) Only liquid exists, Only vapour exists

13. The volume occupied by one mole of the gas at the critical temperature and pressure is
    a) Excluded volume b) Co volume c) **Critical volume** d) Pseudo volume
14. The critical temperature, critical pressure and critical volume of a gas are collectively called as
    a) Van der waals constants b) **Critical constants** c) Critical density d) Gas constants
15. At extremely low pressure the gases
    a) Obey the ideal gas equation b) Deviate more from the ideal gas equation
    c) Behave as real gases d) Behave as inert gases,
16. Gases obey the ideal gas equation at
    a) Extremely low pressures b) Extremely high pressures
    c) At low temperatures d) at low temperature and high pressure
17. In the Van der waals equation ‘b’ is called
    a) Excluded volume b) **Effective volume** c) Critical temperature d) Critical pressure
18. In the Van der waals equation ‘a’ is called
    a) Cohesive force b) Effective volume c) Critical temperature d) Critical pressure
19. The significance of the Vander Waals constant ‘a’ is
    a) Measure of compressibility b) Measure of inertness c) Excluded volume
    d) **Measure of the intermolecular forces of attraction in a gas**
20. The significance of the Vander Waals constant ‘b’ is
    a) Measure of compressibility b) Measure of inertness
    c) Measure of diffussibility d) measure of collision

Part B

1. Define compressibility factor
2. What is meant by Boyle temperature
3. What are the causes of deviation of real gases from ideal gas behavious
4. What is meant by isotherm
5. Explain critical state of a gas
6. What is meant by critical temperature of a gas
7. What is meant by critical pressure of a gas
8. What is meant by critical volume of a gas

9. What is meant by inversion temperature
10. What is meant by Joule Thomson effect
11. What is meant by law of corresponding states

Part C

1. Discuss in detail the causes of deviation of real gas from ideal behavior
2. Derive an expression for critical constants in terms of van der Waals constants
3. What is meant by viscosity? How viscosity is determined experimentally
4. What is meant by surface tension and how to determine it experimentally?
5. Explain the effects of addition of various solutes on surface tension and viscosity

Questions	**Opt-1**	**Opt-2**	**Opt-3**	**Opt-4**	**Answer**
UNIT 2					
A gas which obeys the gas equation (PV=nRT) under all conditions of temperature and pressure is called	Ideal gas	Real gas	Inert gas	Super critical gas	Ideal gas
A gas which obeys Boyles, Charles law and other gas laws under all conditions of temperature and pressure is known as	Ideal gas	Real gas	Inert gas	Super critical gas	Ideal gas
A gas which do not obey gas equation PV=nRT is called	Ideal gas	Real gas	Inert gas	Super critical gas	Real gas
A gas which obeys the gas laws fairly well under low pressure or high temperature	Ideal gas	Real gas	Inert gas	Super critical gas	Real gas
The compressibility factor ‘z’ is equal to one for	Ideal gas	Real gas	Inert gas	Super critical gas	Ideal gas
The compressibility factor ‘z’ is equal to less than one to greater than 1 for	Ideal gas	Real gas	Inert gas	Super critical gas	Real gas
The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called	Critical temperature	Boyle temperature	Charles temperature	Threshold temperature	Boyle temperature
The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called	Critical temperature	Boyle point	Charles temperature	Threshold temperature	Boyle temperature
Above Boyle temperature, a gas shows	Negative deviations only	Both positive and negative deviations	Positive deviations only	Ideal behaviour	Positive deviations only
In the Van der waals equation ‘b’ is called	Excluded volume	Effective volume	Critical temperature	Critical pressure	Excluded volume
In the Van der waals equation ‘b’ is called	Co- volume	Effective volume	Critical temperature	Critical pressure	Co- volume
The significance of the Vander Waals constant ‘a’ is	Measure of compressibility	Measure of inertness	Excluded volume	Measure of the intermolecular forces of attraction in a gas	Measure of the intermolecular forces of attraction in a gas
The significance of the Vander Waals constant ‘b’ is	Measure of compressibility	Measure of inertness	Measure of diffussibility	Measure of the intermolecular forces of attraction in a gas	Measure of compressibility
Deviation from ideal behavior of a gas is more prominent at	High pressure and low temperature	High pressure and High pressure	Low pressure and low temperature	Low pressure and High temperature	High pressure and low temperature
In the plot of ‘PV’ Vs ‘P’ for different gases at 273 K, the product PV continuously increases with increase of pressure for	Hydrogen	Carbon monoxide	Methane	Carbon tetra chloride	Hydrogen
In the plot of ‘PV’ Vs ‘P’ for different gases at 273 K, the product PV continuously increases with increase of pressure for	Carbon monoxide	helium	Methane	Carbon tetra chloride	Helium
In the plot of ‘PV’ Vs ‘P’ for different gases at 273 K, the product PV reaches a minimum and then begins to increase with increase of pressure for	Carbon monoxide	helium	Hydrogen	Carbon tetra chloride	Carbon monoxide
The temperature above which the gas cannot be liquefied, whatever high pressure we may apply on the gas	Critical temperature	Boyle temperature	Charles temperature	Threshold temperature	Critical temperature
The minimum pressure required to liquefy the gas at the critical temperature is	Cohesion pressure	Threshold pressure	Critical pressure	Boyles pressure	Critical pressure
The volume occupied by one mole of the gas at the critical temperature and pressure is	Excluded volume	Co volume	Critical volume	Pseudo volume	Critical volume
The critical temperature, critical pressure and critical volume of a gas are collectively called as	Van der waals constants	Critical constants	Critical density	Gas constants	Critical constants
At extremely low pressure the gases	Obey the ideal gas equation	Deviate more from the ideal gas equation	Behave as real gases	Behave as inert gases	Obey the ideal gas equation
Gases obey the ideal gas equation at	Extremely low pressures	Extremely high pressures	At low temperatures	At low temperature and high pressure	Extremely low pressures
Gases obey the ideal gas equation at	At High Temperatures	Extremely high pressures	At low temperatures	At low temperature and high pressure	At High Temperatures
At high temperatures gases	Obey the ideal gas equation	Deviate more from the ideal gas equation	Behave as real gases	Behave as inert gases	Obey the ideal gas equation
A plot of ‘P’ and ‘V’ at constant T is called	Critical temperature curve	Critical pressure curve	Critical volume curve	Isotherm	Isotherm

Isotherm is	A plot of ‘P’ and ‘T’ at constant V is called	A plot of ‘V’ and ‘T’ at constant P is called	A plot of ‘P’ and ‘V’ at constant T is called	A plot of ‘PV’ and ‘T’ at constant V is called	A plot of ‘P’ and ‘V’ at constant T is called
Isotherms of all gases are similar except	The breadth of the horizontal portion	Lengths of the horizontal portion	Length of the vertical portion	Breadth of the vertical portion	Lengths of the horizontal portion
Isotherms of all gases are similar except	The breadth of the horizontal portion	peak of the dotted parabola are different	Length of the vertical portion	Breadth of the vertical portion	peak of the dotted parabola are different
In the Andrews experiments on critical phenomenon, within the parabola	The liquid and vapour exist together in equilibrium	Solid and liquid exist in equilibrium	Only liquid exists	Only vapour exists	The liquid and vapour exist together in equilibrium
The change of state from gaseous to liquid is continuous or it is referred to as	Critical state	Inversion state	Continuity of state	Discontinuity of state	Continuity of state
The value of critical constant volume(V_c) is	3b	2b	8b	10b	3b
The value of critical constant Pressure(P_c) is	a/27b	27b/a	$a/27b^2$	37/a	$a/27b^2$
The value of the critical constant T_c	8a/27Rb	a/27Rb	27b/a	$a/27b^2$	8a/27Rb
The equation which relates the reduced pressure, volume and temperature is called	Van der Waals equation of state	Critical state	Reduced equation of state	Joule Thomson state	Reduced equation of state
If two substances have the same reduced pressure and same reduced temperature, they must have the same reduced volume. This is	Reduced equation of state	Law of corresponding states	Critical state	Liquification state	Law of corresponding states
The temperature to which a gas should be cooled to give normal Joule-Thomson effect is called	Critical temperature	Reduced temperature	Inversion temperature	Threshold temperature	Inversion temperature
The inversion temperature of hydrogen is	-240^0C	240^0C	-80^0C	80^0C	-80^0C
The inversion temperature of helium is	-240^0C	240^0C	-80^0C	80^0C	-240^0C
Critical pressure of carbon di oxide is	72.9 atmosphere	758 atmospheres	1 atmosphere	1000 atmospheres	72.9 atmosphere
When a gas under high pressure is allowed to expand adiabatically through a fine orfice into a region of low pressure, it is accompanied by cooling. This is	Pelties effect	Joule Thomson effect	Vanderwaals effect	Maxwell Boltzmann effect	Joule Thomson effect
Critical temperature of car bondioxide is	304.2 K	298 K	273K	383 K	304.2 K
The inward pull on the gas molecules lying near the wall depends upon	Number of molecules surrounding a molecule	Compressibility factor	Van der waals constant	Inversion temperature	Number of molecules surrounding a molecule
The inward pull on the gas molecules lying near the wall depends upon	Total Number of molecules	Compressibility factor	Van der waals constant	Inversion temperature	Total Number of molecules
The inward pull on the gas molecules lying near the wall depends upon	density	Compressibility factor	Van der waals constant	Inversion temperature	Density
As per Van der Waals the space available for the movement of the gas molecules is	(V-b)	(V+b)	PV-RT	PV+RT	(V-b)
The net force of attraction of a gas molecule lying in the centre of the container is	Zero	Unity	Negative value	Positive value	Zero
For a real gas at moderate pressure the value of PV will be less than	RT	Gas constant	V-b	V+b	RT
For a real gas at high pressure the value of PV will be greater than	RT	Gas constant	V-b	V+b	RT
Which set of conditions represent easiest way to liquefy gas	Low temperature and high pressure	Low temperature and Low pressure	High temperature and High pressure	High temperature and Low pressure	Low temperature and high pressure
An ideal gas, obeying kinetic theory of gases, can be liquified	It cannot be liquefied at any P and T	Its pressure is more than P at a temperature less than T	Its temperature is more than critical temperature	Its pressure is more than critical pressure	It cannot be liquefied at any P and T
The Van der Waals equation explains the behaviour of	Ideal gases	Real gases	vapours	Non-real gases	Real gases
Critical temperature means above this temperature at any pressure, any gas can be	liquified	Not liquified	solidified	melted	
Expansion of a gas above inversion temperature creates	cooling	heating	Constant temperature	Constant pressure	
According to the van der Waals correction to get the pressure of ideal gas in observed pressure a definite fraction for correction is	Subtracted	Added	Divided	Unchanged	
According to the van der Waals correction to get the pressure of ideal gas in observed pressure a definite fraction for correction is	Subtracted	Added	Divided	Unchanged	

Real gas will approach the behavious of ideal gas at	Low temperature and Low pressure	Low temperature and high pressure	High temperature and High pressure	High temperature and Low pressure	
An ideal gas cannot be liquefied because	Its critical temperature is always above zero	Its molecules are relatively smaller in size	It solidifies before becoming a liquid	Forces operative between its molecules are negligible	
Which is not true in case of an ideal gas	It cannot be converted into a liquid	There is no interaction between the molecules	All molecules of the gas move with same speed	At a given temperature PV is proportional to the amount of the gas	
One of the conditions represent easiest way to liquefy a gas	Low temperature	High temperature	Low pressure	Atmospheric pressure	

UNIT III

SOLID STATE

Solid state: Nature of the solid state, law of constancy of interfacial angles, law of rational indices, Miller indices, elementary ideas of symmetry, symmetry elements and symmetry operations, qualitative idea of point and space groups, seven crystal systems and fourteen Bravais lattices; X-ray diffraction, Bragg's law, a simple account of rotating crystal method and powder pattern method. Analysis of powder diffraction patterns of NaCl, CsCl and KCl.

The optical transform experiment that we performed with the lasers and the 35-mm slides was a simulation of single crystal X-ray diffraction. To study the structure of a molecule or an extended solid, we would substitute a single crystal of the material for the 35-mm slide and use X-rays instead of visible light. The resulting diffraction patterns, captured as spots on photographic film or counts on an electronic detector, would provide information about the size and symmetry of the molecular unit cell.

Single crystal X-ray diffraction is a powerful technique that is commonly used to determine the structures of new materials. However, the technique is limited by the ability to grow nearly perfect crystals that are suitable for diffraction. Due to this limitation and the time and cost-intensive nature of the technique, single crystal diffraction is not used for routine structural characterization of known materials.

For routine structural characterization of materials, ***X-ray powder diffraction*** is far more common. The samples for powder diffraction may be large crystals, or they may be in the form of a powder composed of micro crystals that are too small to be seen by the human eye. The underlying principles of the experiment are the same in both powder diffraction and single crystal diffraction, although the data analysis is much simpler in powder diffraction.

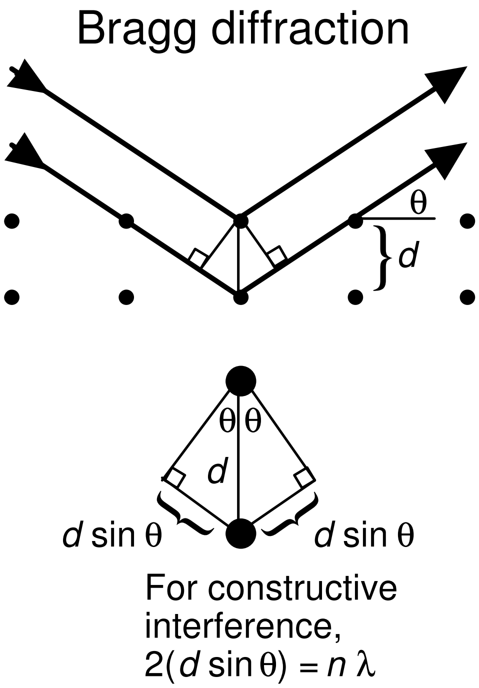
II. Unit Cells, Miller Planes, and Diffraction Data

Recall from Experiment 1 that the conditions for diffraction are governed by the conditions for constructive interference. An expanded view of the diffraction of X-rays from the repeating planes of atoms in a crystalline structure is shown in Figure 2.1. Powder diffraction patterns are typically plotted as the intensity of the diffracted X-rays vs. the angle 2θ. Peaks will appear in the diffraction pattern at $2\lambda\theta$ values when constructive interference is at a maximum, that is, when Bragg's Law (eq. 1) is satisfied.

$$n\lambda = 2d\sin\theta \qquad (1)$$

In this experiment, we will be observing first order ($n = 1$) diffraction of X-rays with a wavelength of 1.54056 Å. By measuring the 2θ values for each diffraction peak, we can calculate the d-spacing (the distance between the diffracting planes) for each diffraction peak.

Fortunately, the data analysis software has a program for *automatically* calculating the *d*-spacings for all of the peaks in the diffraction pattern.



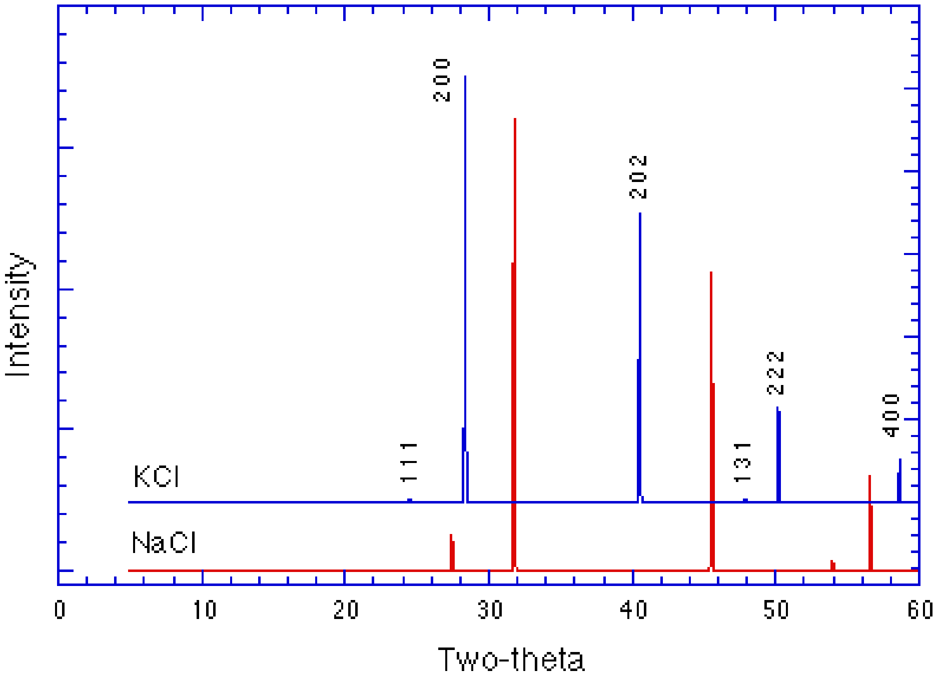


Figure 2.2. A comparison of the X-ray powder diffraction patterns of NaCl (bottom) and KCl (top). Peaks in the KCl diffraction pattern are labeled with Miller indices, *h k l*, indicating the set of lattice planes responsible for that diffraction peak. The KCl peaks are shifted to lower angles relative to the NaCl pattern due to the larger cubic unit cell of KCl.

Each crystalline substance has a unique X-ray diffraction pattern. The number of observed peaks is related to the symmetry of the unit cell (higher symmetry generally means fewer peaks). The *d*-spacings of the observed peaks are related to the repeating distances between planes of atoms in the structure. And finally, the intensities of the peaks are related to what kinds of atoms are in the repeating planes. The scattering intensities for X-rays are directly related to the number of electrons in the atom. Hence, light atoms scatter X-rays weakly, while heavy atoms scatter X-rays more effectively. These three features of a diffraction pattern: the number of peaks, the positions of the peaks, and the intensities of the peaks, define a unique, fingerprint X-ray powder pattern for every crystalline material. For example, the X-ray diffraction patterns of the iso structural compounds NaCl and KCl can be compared in Figure 2.2. Notice that the two patterns are fairly similar. The relative intensities of the peaks differ, but the primary difference is that the diffraction peaks for KCl appear at lower angles, higher *d*-spacings, than those for NaCl due to the larger unit cell of KCl.

X-ray powder diffraction is a powerful tool for characterizing the products of a solid state synthesis reaction. At the simplest level, diffraction patterns can be analyzed for phase identification that is, determining what crystalline substances are present in a given sample. More quantitatively, the peak positions can be used to refine the *lattice parameters* for a given unit cell. Unit cells in three-dimensional repeating structures have different shapes based upon the symmetry of the structure. In all cases, the unit cells are parallelepipeds, but the different shapes arise depending on restrictions placed on the lengths of the three edges (a, b, and c) and the values of the three angles (α, β, and γ). The seven different unit cell shapes or the so-called seven crystal systems that result from these restrictions are listed below in Table 2.1.

Table 2.1. The seven crystal systems and the restrictions placed on the lattice parameters of the unit cell.

Crystal System	**Lattice Parameter Restrictions**
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Monoclinic	$a \neq b \neq c$ $\alpha = \beta = 90^\circ;\ \gamma \neq 90^\circ$

Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ;\ \gamma = 120^\circ$
Trigonal*	$a = b \neq c$ $\alpha = \beta = 90^\circ;\ \gamma = 120^\circ$

*The difference between trigonal and hexagonal systems is the symmetry. A hexagonal unit cell has C_6 symmetry, whereas a trigonal unit cell only has C_3 symmetry. The restrictions shown above are for the so-called hexagonal setting of a trigonal setting. There is an alternative way to define the unit cell for trigonal systems, known as the rhombohedral setting.

Crystal Grouped by Lattices (Shape)

There are seven crystal lattice systems.

1. Cubic: not always cube shaped! You'll also find octahedrons (eight faces) and dodecahedrons (10 faces).

2. **Tetragonal** - similar to cubic crystals, but longer along one axis than the other, forming double pyramids and prisms.

3. **Orthorhombic** - like tetragonal crystals except not square in cross section (when viewing the crystal on end), forming rhombic prisms or dipyramids (two pyramids stuck together).

4. **Hexagonal** - six-sided prisms. When you look at the crystal on-end, the cross section is a hexagon.

5. **Trigonal** - possess a single 3-fold axis of rotation instead of the 6-fold axis of the hexagonal division.

6. **Triclinic** - usually not symmetrical from one side to the other, which can lead to some fairly strange shapes.
7. **Monoclinic** - like skewed tetragonal crystals, often forming prisms and double pyramids.

This is a very simplified view of crystal structures. In addition, the lattices can be primitive (only one lattice point per unit cell) or non-primitive (more than one lattice point per unit cell). Combining the 7 crystal systems with the 2 lattice types yields the 14 Bravais Lattices (named after Auguste Bravais, who worked out lattice structures in 1850).

Crystals Grouped by Properties

There are four main categories of crystals, as grouped by their chemical and physical properties:

1. **Covalent Crystals**

   A covalent crystals has true covalent bonds between all of the atoms in the crystal. You can think of a covalent crystal as one big molecule. Many covalent crystals have extremely high melting points. Examples of covalent crystals include diamond and zinc sulfide crystals.

2. **Metallic Crystals**

   Individual metal atoms of metallic crystals sit on lattice sites. This leaves the outer electrons of these atoms free to float around the lattice. Metallic crystals tend to be very dense and have high melting points.
3. **Ionic Crystals**

   The atoms of ionic crystals are held together by electrostatic forces (ionic bonds). Ionic crystals are hard and have relatively high melting points. Table salt (NaCl) is an example of this type of crystal.

4. **Molecular Crystals**

These crystals contain recognizable molecules within their structures. A molecular crystal is held together by non-covalent interactions, like van der Waals forces orhydrogen bonding. Molecular crystals tend to be soft with relatively low melting points. Rock candy, the crystalline form of table sugar or sucrose, is an example of a molecular crystal.

1. Introduction

You will already be familiar with the concept of symmetry in an everyday sense. If we say something is 'symmetrical', we usually mean it has mirror symmetry, or 'left-right' symmetry, and would look the same if viewed in a mirror. Symmetry is also very important in chemistry. Some molecules are clearly 'more symmetrical' than others, but what consequences does this have, if any? The aim of this course is to provide a systematic treatment of symmetry in chemical systems within the mathematical framework known as group theory (the reason for the name will become apparent later on). Once we have classified the symmetry of a molecule, group theory provides a powerful set of tools that provide us with considerable insight into many of its chemical and physical properties. Some applications of group theory that will be covered in this course include:

i) Predicting whether a given molecule will be chiral, or polar.

ii) Examining chemical bonding and visualising molecular orbitals.

iii) Predicting whether a molecule may absorb light of a given polarisation, and which spectroscopic transitions may be excited if it does.

iv) Investigating the vibrational motions of the molecule.

A symmetry operation is an action that leaves an object looking the same after it has been carried out. For example, if we take a molecule of water and rotate it by 180° about an axis passing through the central O atom (between the two H atoms) it will look the same as before. It will also look the same if we reflect it through either of two mirror planes,

Each symmetry operation has a corresponding symmetry element, which is the axis, plane, line or point with respect to which the symmetry operation is carried out. The symmetry element consists of all the points that stay in the same place when the symmetry operation is performed. In a rotation, the line of points that stay in the same place constitute a symmetry axis; in a reflection the points that remain unchanged make up a plane of symmetry. The symmetry elements that a molecule may possess are:

The symmetry elements that a molecule may possess are:

1. E - the identity. The identity operation consists of doing nothing, and the corresponding symmetry element is the entire molecule. Every molecule has at least this element.

2. Cn - an n-fold axis of rotation. Rotation by 360°/n leaves the molecule unchanged. The H2O molecule above has a C2 axis. Some molecules have more than one Cn axis, in which case the one with the highest value of n is called the principal axis. Note that by convention rotations are counterclockwise about the axis. 4

3. σ - a plane of symmetry. Reflection in the plane leaves the molecule looking the same. In a molecule that also has an axis of symmetry, a mirror plane that includes the axis is called a vertical mirror plane and is labelled σv, while one perpendicular to the axis is called a horizontal mirror plane and is labelled σh. A vertical mirror plane that bisects the angle between two C2 axes is called a dihedral mirror plane, σd.

4. i - a centre of symmetry. Inversion through the centre of symmetry leaves the molecule unchanged. Inversion consists of passing each point through the centre of inversion and out to the same distance on the other side of the molecule. An example of a molecule with a centre of inversion is shown below.

5. Sn - an n-fold improper rotation axis (also called a rotary-reflection axis). The rotary reflection operation consists of rotating through an angle 360°/n about the axis, followed by reflecting in a plane perpendicular to the axis. Note that S1 is the same as reflection and S2 is the same as inversion. The molecule shown above has two S2 axes.

6. The identity E and rotations Cn are symmetry operations that could actually be carried out on a molecule. For this reason they are called proper symmetry operations. Reflections, inversions and improper rotations can only be imagined (it is not actually possible to turn a molecule into its mirror image or to invert it without some fairly drastic

rearrangement of chemical bonds) and as such, are termed improper symmetry operations.

A note on axis definitions: Conventionally, when imposing a set of Cartesian axes on a molecule (as we will need to do later on in the course), the z axis lies along the principal axis of the molecule, the x axis lies in the plane of the molecule (or in a plane containing the largest number of atoms if the molecule is non-planar), and the y axis makes up a right handed axis system.

A crystal may possess only certain combinations of symmetry elements. Only 32 possibilities exist and these are the 32 crystal classes or crystallographic point groups. Every mineral belongs to one of these crystal classes.

CRYSTALLOGRAPHIC AXES AND SYMMETRY SYSTEMS

14 unique space-lattices produced by 3-D translation operation to can be described belonging 6 group of crystal systems when these geometrical object are grouped according to Cartesian Principle Axes, intersecting in the center of the space-lattice or crystals formed from the repetitions of them. Each two crystallographic axes define a **crystallographic plane**. They are generally taken parallel to the intersection edges of major crystal faces. They are named as **a-, b-, c-axes**, where c-axis is always vertical. In hexagonal system there are four axes **a_1, a_2, a_3** (horizontal with 120° between them), and **c** (vertical). From the origin the length of the axes are designated as (**+** or **-**), The **length** of crystallographic axes and **axial angles α, β, γ** between them may vary in different symmetry.

Symmetry Systems	Crystallographic Axes	Axial Angle
1. Cubic (Isometric)	**a: a: a**	**$\alpha=\beta=\gamma=90°$**
2. Tetragonal	**a: a: c**	**$\alpha=\beta=\gamma=90°$**
3. Hexagonal	**a: a: a: c**	**$\alpha=\beta=90°, \gamma=60-120°$**
Rhombohedral	**a: a: a: c**	**$\alpha=\beta=90°, \gamma=60-l20°$**
4. Orthorhombic	**a: b: c**	**$\alpha=\beta=\gamma=90°$**
5. Monoclinic	**a: b: c**	**$\alpha=\gamma=90°, \beta>90°$**
6. Triclinic	**a: b: c**	**$\alpha\neq\beta\neq\gamma\neq90°$**

The symmetry observed in crystals as exhibited by their crystal faces is due to the ordered internal arrangement of atoms in a crystal structure, as mentioned previously. This arrangement of atoms in crystals is called a ***lattice***.

Crystals, of course, are made up of 3-dimensional arrays of atoms. Such 3-dimensional arrays are called ***space lattices***.

There are four important points about crystal lattices that are noteworthy for our study of crystals:

1. Crystal faces develop along planes defined by the points in the lattice. In other words, all crystal faces must intersect atoms or molecules that make up the points. **A face is more commonly developed in a crystal if it intersects a larger number of lattice points.** This is known as the ***Bravais Law***.
2. **The angle between crystal faces is controlled by the spacing between lattice points.**
3. Since all crystals of the same substance will have the same spacing between lattice points (they have the same crystal structure), the **angles between corresponding faces of the same mineral will be the same**. This is known as the ***Law of constancy of interfacial angles***,

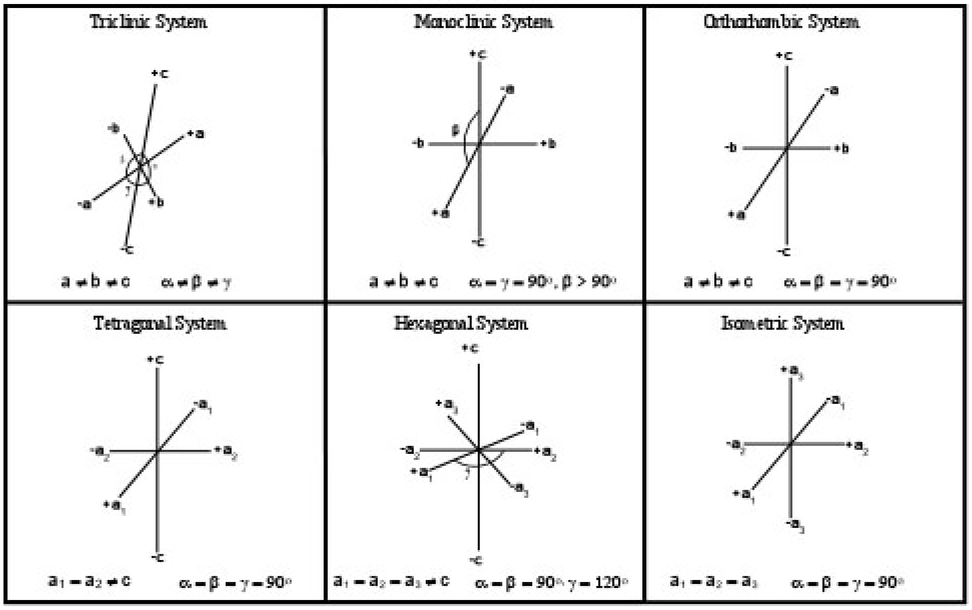
Crystallographic Axes

The crystallographic axes are imaginary lines that we can draw within the crystal lattice. These will define a coordinate system within the crystal. For 3-dimensional space lattices we need 3 or in some cases 4 crystallographic axes that define directions within the crystal lattices. Depending on the symmetry of the lattice, the directions may or may not be perpendicular to one another, and the divisions along the coordinate axes may or may not be equal along the axes. As we will see later, the lengths of the axes are in some way proportional to the lattice spacing along an axis and this is defined by the smallest group of points necessary to allow for translational symmetry to reproduce the lattice.

We here discuss the basic concepts of the crystallographic axes. As we will see, the axes are defined based on the symmetry of the lattice and the crystal. Each crystal system has different conventions that define the orientation of the axes, and the relative lengths of the axes.

4. **The symmetry of the lattice will determine the angular relationships between crystal faces.**

Crystallographic Axes



Unit Cells

The "lengths" of the various crystallographic axes are defined on the basis of the unit cell. When arrays of atoms or molecules are laid out in a space lattice we define a group of such atoms as the unit cell. This unit cell contains all the necessary points on the lattice that can be translated to repeat itself in an infinite array. In other words, the unit cell defines the basic building blocks of the crystal, and the entire crystal is made up of repeatedly translated unit cells.

Miller indices form a notation system in crystallography for planes in crystal (Bravais) lattices. In particular, a family of lattice planes is determined by three integers *h*, *k*, and *ℓ*, the *Miller indices*. They are written (hkℓ), and denote the family of planes orthogonal to where are the basis of the reciprocal lattice vectors. (Note that the plane is not always orthogonal to the linear combination of direct lattice vectors because the reciprocal lattice vectors need not be mutually orthogonal.) By convention, negative integers are written with a bar, as in 3 for −3. The integers are usually written in lowest terms, i.e. their greatest common divisor should be 1.

There are also several related notations:[1]

- the notation {hkℓ} denotes the set of all planes that are equivalent to (hkℓ) by the symmetry of the lattice.

In the context of crystal directions (not planes), the corresponding notations are:

- [hkℓ], with square instead of round brackets, denotes a direction in the basis of the *direct* lattice vectors instead of the reciprocal lattice; and
- similarly, the notation ⟨hkℓ⟩ denotes the set of all directions that are equivalent to [hkℓ] by symmetry.

☐ Miller indices are used to specify directions and planes.

☐ These directions and planes could be in lattices or in crystals.

☐ *(It should be mentioned at the outset that special care should be given to see if the indices are in a lattice or a crystal).*

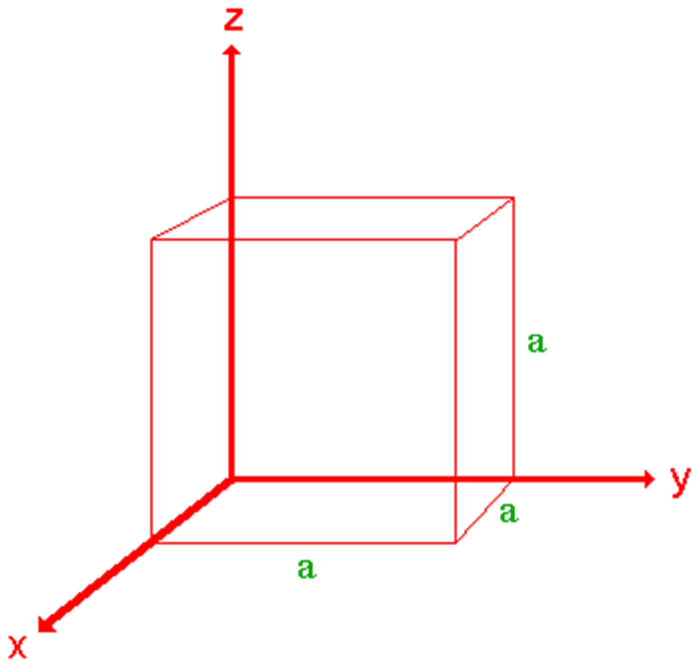
☐ The number of indices will match with the dimension of the lattice or the crystal: in 1D there will be 1 index and 2D there will be two indices etc.

☐ Some aspects of Miller indices, especially those for planes, are not intuitively understood and hence some time has to be spent to familiarize oneself with the notation.

☐ **Miller Indices (hkl)**

☐ The orientation of a surface or a crystal plane may be defined by considering how the plane (or indeed any parallel plane) intersects the main crystallographic axes of the solid. The application of a set of rules leads to the assignment of the Miller Indices , (*hkl*) ; a set of numbers which quantify the intercepts and thus may be used to uniquely identify the plane or surface.

☐ The following treatment of the procedure used to assign the Miller Indices is a simplified one (it may be best if you simply regard it as a "recipe") and only a **cubic** crystal system (one having a cubic unit cell with dimensions a x a x a) will be considered.



- ☐ **Step 1** : *Identify the intercepts on the x- , y- and z- axes.*
- ☐ In this case the intercept on the x-axis is at *x* = *a* (at the point (*a*,0,0)), but the surface is parallel to the *y*- and *z*-axes - strictly therefore there is no intercept on these two axes but we shall consider the intercept to be at infinity (∞) for the special case where the plane is parallel to an axis. The intercepts on the *x*- , *y*- and *z*-axes are thus
- ☐ Intercepts : ***a* , ∞ , ∞**
- ☐ **Step 2** : Specify the intercepts in fractional co-ordinates
- ☐ Co-ordinates are converted to fractional co-ordinates by dividing by the respective cell-dimension - for example, a point (*x*,*y*,*z*) in a unit cell of dimensions *a* x *b* x *c* has fractional co-ordinates of (*x*/*a* , *y*/*b* , *z*/*c*). In the case of a cubic unit cell each co-ordinate will simply be divided by the cubic cell constant , *a* . This gives
- ☐ Fractional Intercepts : ***a*/*a* , ∞/*a*, ∞/*a*** i.e. **1 , ∞ , ∞**
- ☐ **Step 3** : Take the reciprocals of the fractional intercepts
- ☐ This final manipulation generates the Miller Indices which (by convention) should then be specified without being separated by any commas or other symbols. The Miller Indices are also enclosed within standard brackets (….) when one is specifying a unique surface such as that being considered here.

- The reciprocals of 1 and ∞ are 1 and 0 respectively, thus yielding
- Miller Indices : **(100)**
- So the surface/plane illustrated is the (100) plane of the cubic crystal.
- (i) in some instances the Miller indices are best multiplied or divided through by a common number in order to simplify them by, for example, removing a common factor. This operation of multiplication simply generates a parallel plane which is at a different distance from the origin of the particular unit cell being considered. e.g. (200) is transformed to (100) by dividing through by 2 .
- (ii) if any of the intercepts are at negative values on the axes then the negative sign will carry through into the Miller indices; in such cases the negative sign is actually denoted by overstriking the relevant number. e.g. (00 -1) is instead denoted by $(00\bar{1})$
- (iii) in the *hcp* crystal system there are four principal axes; this leads to four Miller Indices e.g. you may see articles referring to an *hcp* (0001) surface. It is worth noting, however, that the intercepts on the first three axes are necessarily related and not completely independent; consequently the values of the first three Miller indices are also linked by a simple mathematical relationship.

X-ray crystallography is a tool used for identifying the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographercan produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information.

In a single-crystal X-ray diffraction measurement, a crystal is mounted on a goniometer. The goniometer is used to position the crystal at selected orientations. The crystal is illuminated with a finely focused monochromatic beam of X-rays, producing a diffraction pattern of regularly spaced spots known as *reflections*. The two-dimensional images taken at different orientations are converted into a three-dimensional model of the density of electrons within the crystal using the mathematical method of Fourier transforms, combined with chemical data known for the sample. Poor resolution (fuzziness) or even errors may result if the crystals are too small, or not uniform enough in their internal makeup.

Crystals are regular arrays of atoms, and X-rays can be considered waves of electromagnetic radiation. Atoms scatter X-ray waves, primarily through the atoms' electrons. Just as an ocean wave striking a lighthouse produces secondary circular waves emanating from the lighthouse, so an X-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as elastic scattering, and the electron (or lighthouse) is known as the *scatterer*. A regular array of scatterers produces a regular array of spherical waves. Although these waves cancel one another out in most directions through destructive interference, they add

constructively in a few specific directions, determined by Bragg's law:

Here *d* is the spacing between diffracting planes, is the incident angle, *n* is any integer, and λ is the wavelength of the beam. These specific directions appear as spots on the diffraction pattern called *reflections*. Thus, X-ray diffraction results from an electromagnetic wave (the X-ray) impinging on a regular array of scatterers (the repeating arrangement of atoms within the crystal).

Overview of single-crystal X-ray diffraction[edit]

Workflow for solving the structure of a molecule by X-ray crystallography.

The oldest and most precise method of X-ray crystallography is *single-crystal X-ray diffraction*, in which a beam of X-rays strikes a single crystal, producing scattered beams. When they land on a piece of film or other detector, these beams make a *diffraction pattern* of spots; the strengths and angles of these beams are recorded as the crystal is gradually rotated.[95] Each spot is called a *reflection*, since it corresponds to the reflection of the X-rays from one set of evenly spaced planes within the crystal. For single crystals of sufficient purity and regularity, X-ray diffraction data can determine the mean chemical bond lengths and angles to within a few thousandths of an angstrom and to within a few tenths of a degree, respectively. The atoms in a crystal are not static, but oscillate about their mean positions, usually by less than a few tenths of an angstrom. X-ray crystallography allows measuring the size of these oscillations.

Procedure

The technique of single-crystal X-ray crystallography has three basic steps. The first-and often most difficult-step is to obtain an adequate crystal of the material under study. The crystal should be sufficiently large (typically larger than 0.1 mm in all dimensions), pure in composition and regular in structure, with no significant internal imperfections such as cracks or twinning.

In the second step, the crystal is placed in an intense beam of X-rays, usually of a single wavelength (*monochromatic X-rays*), producing the regular pattern of reflections. As the crystal is gradually rotated, previous reflections disappear and new ones appear; the intensity of every spot is recorded at every orientation of the crystal. Multiple data sets may have to be collected, with each set covering slightly more than half a full rotation of the crystal and typically containing tens of thousands of reflections.

In the third step, these data are combined computationally with complementary chemical information to produce and refine a model of the arrangement of atoms within the crystal. The final, refined model of the atomic arrangement-now called a *crystal structure*-is usually stored in a public database.

The principle of Bragg’s Law and X-ray diffraction

The mathmetical form of Bragg's Law

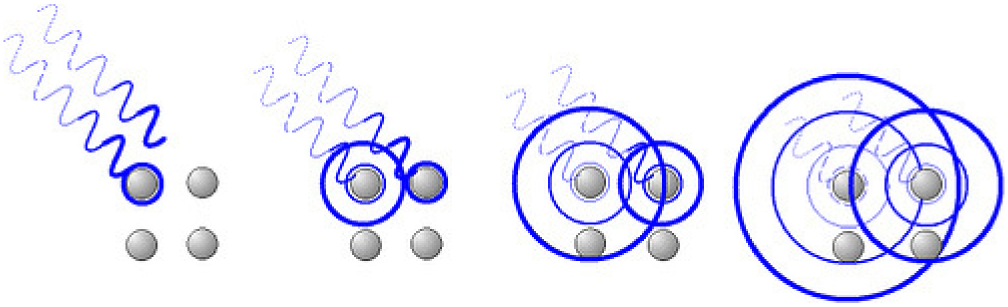
(1)

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

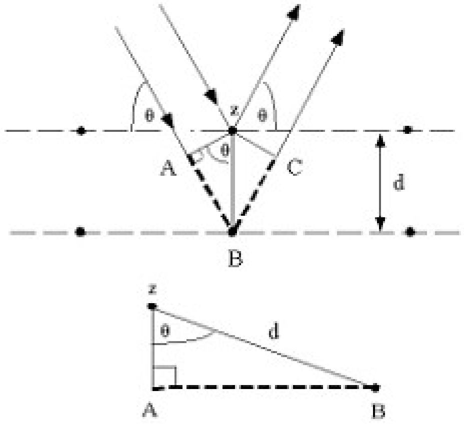
where

- n is an integer determined by the order given,
- λ is the wavelength of x-rays, and moving electrons, protons and neutrons,
- d is the spacing between the planes in the atomic lattice, and
- θ is the angle between the incident ray and the scattering planes.

1.2.2 The derivation of Bragg's Law



Bragg diffraction occurs when electromagnetic radiation or subatomic particle waves with wavelength comparable to atomic spacings, are incident upon a crystalline sample, scattered by the atoms in the system and undergo constructive interference in accordance to Bragg's law. [2]



Consider conditions necessary to make the phases of the beams coincide when the incident angle equals and reflecting angle. The rays of the incident beam are always in phase and parallel up to the point at which the top beam strikes the top layer at atom z. The second beam continues to the next layer where it is scattered by atom B. The second beam must travel the extra distance AB + BC if the two beams are to continue traveling adjacent and parallel. This extra distance must be an integral (n) multiple of the wavelength (λ) for the phases of the two beams to be the same:

\

(2)

$n\lambda = AB + BC$

Recognizing d as the hypotenuse of the right triangle Abz, we can use trigonometry to relate d and θ to the distance (AB + BC). The distance AB is opposite θ so,

(3)

$AB = d\sin\theta$

Because AB = BC eq. (2) becomes,

(4)

$n\lambda = 2AB$

Substituting eq. (3) in eq. (4) we have,

(5)

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

and Bragg's Law has been derived.

Note that if only two rows of atoms are involved, the transition from constructive to destructive interference as θ changes is gradual. However, if interference from many rows occurs, then the constructive interference peaks become very sharp with mostly destructive interference in between. This sharpening of the peaks as the number of rows increases is very similar to the sharpening of the diffraction peaks from a diffraction grating as the number of slits increases.

Powder diffraction is a scientific technique using X-ray, neutron, or electron diffraction on powder or microcrystalline samples for structural characterization of materials. An instrument dedicated to performing such powder measurements is called a**powder diffractometer**.

A diffractometer produces waves at a known frequency, which is determined by their source. The source is often x-rays, because they are the only kind of light with the correct frequency for inter-atomic-scale diffraction. However, electrons and neutrons are also common sources, with their frequency determined by their de Broglie wavelength. When these waves reach the sample, the atoms of the sample act just like a diffraction grating, producing bright spots at particular angles. By measuring the angle where these bright spots occur, the spacing of the diffraction grating can be determined by Bragg's law. Because the sample itself is the diffraction grating, this spacing is the atomic spacing.

The distinction between powder and single crystal diffraction is the degree of texturing in the sample. Single crystals have maximal texturing, and are said to be anisotropic. In contrast, in powder diffraction, every possible crystalline orientation is represented equally in a powdered sample, the isotropic case. In practice, it is sometimes necessary to rotate the sample orientation to eliminate the effects of texturing and achieve true randomness.

Mathematically, crystals can be described by a Bravais lattice with some regularity in the spacing between atoms. Because of this regularity, we can describe this structure in a different way using the reciprocal lattice, which is related to the original structure by a Fourier transform. This three-dimensional space can be described with reciprocal axes x*, y*, and z* or alternatively in spherical coordinates q, φ*, and χ*. In powder diffraction, intensity is homogeneous over φ* and χ*, and only q remains as an important measurable quantity. This is because orientational averaging causes the three-dimensional reciprocal space that is studied in single crystal diffraction to be projected onto a single dimension.

Two-dimensional powder diffraction setup with flat plate detector. When the scattered radiation is collected on a flat plate detector, the rotational averaging leads to smooth diffraction rings around the beam axis, rather than the discrete Laue spots observed in single crystal diffraction. The angle between the beam axis and the ring is called the *scattering angle* and in X-ray crystallography always denoted as 2θ (in scattering of *visible* light the convention is usually to call it θ). In accordance withBragg's law, each ring corresponds to a particular reciprocal lattice vector G in the sample crystal. This leads to the definition of the scattering vector as:

In this equation, G is the reciprocal lattice vector, q is the length of the reciprocal lattice vector, k is the momentum transfer vector, θ is half of the scattering angle, and λ is the wavelength of the radiation. Powder diffraction data are usually presented as a diffractogram in which the diffracted intensity, I, is shown as a function either of the scattering angle 2θ or as a function of the scattering vector length q. The latter variable has the advantage that the diffractogram no longer depends on the value of the wavelength λ. The advent of synchrotron sources has widened the choice of wavelength considerably. To facilitate comparability of data obtained with different wavelengths the use of q is therefore recommended and gaining acceptability.

and inorganic chemistry the **cation-anion radius ratio** is the ratio of the ionic radius of the cation to the ionic radius of the anion in a cation-anion compound. This is simply given by .

According to Pauling's rules for crystal structures, the allowed size of the cation for a given structure is determined by the critical radius ratio.[1] If the cation is too small, then it will attract the anions into each other and they will collide hence the compound will be unstable due to anion-anion repulsion; this occurs when the radius ratio drops below 0.155.

At the stability limit the cation is touching all the anions and the anions are just touching at their edges (radius ratio = 0.155). Beyond this stability limit (radius ratio < 0.155) the compound may be stable.

The table below gives the relation between radius ratio and coordination number, which may be obtained from a simple geometrical proof.[2]

Radius Ratio	Coordination number	Type of void	Example
< 0.155	2	Linear	
0.155 - 0.225	3	Triangular Planar	B_2CO_3[*citation needed*]
0.225 - 0.414	4	Tetrahedral	ZnS, CuCl
0.414 - 0.732	6	Octahedral	NaCl, MgO
0.732 - 1.000	8	Cubic	CsCl, NH_4Br

Possible questions

Part A

1. In a unit cell of NaCl lattice there are

   a) **4 NaCl units** b) 3 Na ions c) 6 sodium ions d) Six chloride ions

2. Axis of symmetry in crystals is given by the general formulae

   a) **360/n** b) N x 360 c) N x 180 d) N x 90

3. Name the equation related to X-ray diffraction by crystals is

   a) Law equation b) **Bragg's equation** c) Lewis equation d) Thomson's equation,

4. The geometric form consisting only a regular array of points in space is called

   a) Unit cell b) **lattice** c) crystal d) Amorphous solid

5. Closest packing is maximum in the crystal lattice of

   a) **Face centered cubic** b) BCC c) Simple centered cubi d) Octahedral

6. Axis of symmetry are called "Hexad"

   a) If original appearance is repeated twice

   b) **If original appearance is repeated 6 times**

   c) If original appearance is repeated after an angle of 90^0

   d) If original appearance is repeated 16 times

7. Radius ratio in NaCl is

   a) **0.524** b) 0.414 c) 0.732 d) 0.8

8. Braggs equation is

   a) $2n\lambda = d\sin\theta$ b) $n\lambda = d\sin\theta$ c) $2n/\lambda = d\sin\theta$ d) $n/\lambda = d\sin\theta$

9. If in a crystal intercepts are 1, infinity and infinity the miller indices are,

   a) **1 0 0** b) 1 0 1 c) 1 1 0 d) 0 0 0

10. How many different ways were suggested by Bravais in which similar points can be arranged in a three dimensional space.

    a) **Fourteen** b) ten c) seven d) nine

11. The line along which the adjacent faces of a crystal intersect is called

    a) **Edge** b) Form c) Zone d) Crystal habit

12. A set of similar faces of a crystal is called

    a) Edge b) **Form** c) Zone d) Crystal habit

13. If in a crystal intercepts are 1, infinity and infinity the miller indices are

    a) 1 0 0 b) 1 0 1 c) 1 1 0 d) 0 0 0

14. How many different ways were suggested by Bravais in which similar points can be arranged in a three dimensional space.

    a) Fourteen b) ten c) seven d) nine

15. The line along which the adjacent faces of a crystal intersect is called

    a) Edge b) Form c) Zone d) Crystal habit

16. A set of similar faces of a crystal is called,

    a) Edge b) **Form** c) Zone d) Crystal habit

17. If ina crystal intercepts are 1, infinity and infinity the miller indices are,

    a) 1 0 0 b) 1 0 1 c) 1 1 0 d) 0 0 0

18. How many different ways were suggested by Bravais in which similar points can be arranged in a three dimensional space.

    a) Fourteen b) ten c) seven d) nine

19. The line along which the adjacent faces of a crystal intersect is called

    a) Edge b) Form c) Zone d) Crystal habit

20. A set of similar faces of a crystal is called,

    a) Zone b) **Form** c) Edge d) Crystal habit

Part B

1. Define law of constancy of interfacial angles
2. What is meant by law of rational indicies
3. What is meant by Miller indices
4. What is meant by symmetry elements
5. Explain what is a symmetry operation
6. What are the seven crystal system
7. What are Bravis lattices
8. What is meant by plane of symmetry
9. What is meant by centre of symmetry
10. What is meant by axis of symmetry
11. States Bragg's law
12. Define a unit cell
13. What is meant by space lattice

Part C

1. Derive Bragg equation for the X-ray diffraction studies
2. Discuss the different elements of symmetry in detail.
   (i) Plane of symmetry
   (ii) Axis of symmetry
   (iii) Centre of symmetry
3. Explain detail the powder method for determination of crystal structure of a solid
4. Explain in detail the Laue photographic method for the determination of structure of solids.

5. Explain in detail the Laue photographic method for the determination of structure of solids.

Questions	**Opt-1**	**Opt-2**	**Opt-3**	**Opt-4**	**Answer**
UNIT 3					
Crystals can be classified into	7 systems	9 systems	10 systems	23 systems	7 systems
In Bragg's equation for diffraction of X-rays 'n' represents	No. of moles	Quantum number	Order of reflection	Avagadro number	Order of reflection
In a body centered cubic arrangement A ion occupies the centre while B ions occupy corners of cubic, the formulae of the solid is	AB_2	AB	A_2B	A_3B	AB
Closest packing is maximum in the crystal lattice of	Face centered cubic	BCC	Simple centered cubic	Octahedral	Face centered cubic
Axis of symmetry are called "Hexad"	If original appearance is repeated twice	If original appearance is repeated 6 times	If original appearance is repeated after an angle of 90^0	If original appearance is repeated 16 times	If original appearance is repeated 6 times
Radius ratio in NACL is	0.524	0.414	0.732	0.8	0.524
Braggs equation is	$2n\lambda = d\sin\theta$	$n\lambda = d\sin\theta$	$2n/\lambda = d\sin\theta$	$n/\lambda = d\sin\theta$	$n\lambda = d\sin\theta$
The no. of atoms per unit cell in simple cubic, face centred cubic and Body centred cubic are	1,4,2	4,1,2	2,4,1	4,8,2	1,4,2
The no. of atoms per unit cell in simple cubic	one	four	two	three	one
The no. of atoms per unit cell in face centred cubic	one	four	two	three	Four
The no. of atoms per unit cell in Body centred cubic are	one	four	two	three	two
Which one of the crystal has the highest melting point	Ionic crystal	Covalent crystal	Metallic crystal	Molecular crystal	Metallic crystal
Total number of planes, axes and centre of symmetries in a crystal is termed as	Elements of symmetry	symmetries	Symmetry operations	Symmetry operators	Elements of symmetry
In a unit cell of NaCl lattice there are	4 NaCl units	3 Na ions	6 sodium ions	Six chloride ions	4 NaCl units
Axis of symmetry in crystals is given by the general formulae	360/n	N x 360	N x 180	N x 90	360/n
Name the equation related to X-ray diffraction by crystals is	Law equation	Bragg's equation	Lewis equation	Thomson's equation	Bragg's equation
The geometric form consisting only a regular array of points in space is called	Unit cell	lattice	crystal	Amorphous solid	lattice
Coordination number for an atom in a primitive cubic unit cell is	6	8	10	12	6
Interplanar distance in crystal can be determined by the equation	$2n\lambda = d\sin\theta$	$n\lambda = d\sin\theta$	$2n/\lambda = d\sin\theta$	$n/\lambda = d\sin\theta$	$n\lambda = d\sin\theta$
Miller indices in a crystal indicate	Designation of planes in a crystal	Intercepts of plane on X-axis	Reciprocals of fractional intercepts of that plane on various axes	Structure of the crystal	Reciprocals of fractional intercepts of that plane on various axes
Reciprocals of fractional intercepts of that plane on various axes	Miller indices	Weiss indices	Mullikan indices	Unit cell	Miller indices
If a plane is parallel to an axis of crystal its Miller index will be	Zero	Infinity	one	two	Zero
If ina crystal intercepts are 1, infinity and infinity the miller indices are	1 0 0	1 0 1	1 1 0	0 0 0	1 0 0
How many different ways were suggested by Bravais in which similar points can be arranged in a three dimensional space.	Fourteen	ten	seven	nine	Fourteen
The line along which the adjacent faces of a crystal intersect is called	Edge	Form	Zone	Crystal habit	Edge
A set of similar faces of a crystal is called	Edge	Form	Zone	Crystal habit	Form
The external shape of the crystal is called	Edge	Form	Zone	Crystal habit	Crystal habit
The angle between the adjacent faces of a crystal is	Interfacial angle	Edge	Form	Zone	Interfacial angle

Edge is	The line along which the adjacent faces of a crystal intersect	A set of similar faces of a crystal	The external shape of the crystal	The angle between the adjacent faces of a crystal	The line along which the adjacent faces of a crystal intersect
A crystal Form is	The line along which the adjacent faces of a crystal intersect	A set of similar faces of a crystal	The external shape of the crystal	The angle between the adjacent faces of a crystal	A set of similar faces of a crystal
A crystal habit is	The line along which the adjacent faces of a crystal intersect	A set of similar faces of a crystal	The external shape of the crystal	The angle between the adjacent faces of a crystal	The external shape of the crystal
Interfacial angles of the crystals of a particular substance are always the same	Law of constancy of interfacial angles	Law of rationality indices	Laws of symmetry	Law of refraction	Law of constancy of interfacial angles
An imaginery point within the crystal such that any line passing through this point intersects the opposite faces of the crystal at equal distance	Centre of symmetry	Rotation of symmetry	Reflection of symmetry	Improper symmetry	Centre of symmetry
An imaginary plane passing through the crystal such that it divides the crystal into two parts in such a way that one part is the mirror image of the other	Centre of symmetry	Rotation axis of symmetry	Plane of symmetry	Improper symmetry	Plane of symmetry
An imaginary line passing through the crystal such that when the crystal is rotated about this line, exactly similar appearance occurs more than once in one complete revolution	Centre of symmetry	Rotation axis of symmetry	Plane of symmetry	Improper symmetry	Rotation axis of symmetry
Axis of symmetry are called "Tetrad"	If original appearance is repeated twice	If original appearance is repeated 4 times	If original appearance is repeated after an angle of 90^0	If original appearance is repeated 16 times	If original appearance is repeated 4 times
Axis of symmetry are called "triad"	If original appearance is repeated twice	If original appearance is repeated 3 times	If original appearance is repeated after an angle of 90^0	If original appearance is repeated 16 times	If original appearance is repeated 3 times
Axis of symmetry are called "Four fold"	If original appearance is repeated twice	If original appearance is repeated 4 times	If original appearance is repeated after an angle of 90^0	If original appearance is repeated 16 times	If original appearance is repeated 4 times
Axis of symmetry are called "three fold"	If original appearance is repeated twice	If original appearance is repeated 3 times	If original appearance is repeated after an angle of 90^0	If original appearance is repeated 16 times	If original appearance is repeated 3 times
The number of four fold axes of symmetry in a simple cube	Three	four	six	one	Three
The number of Three fold axes of symmetry in a simple cube	Three	four	six	one	Four
The number of Centre of symmetry in a simple cube	Three	four	six	one	one
When the points are present only at the corners of the unit cell	Simple cubic	Face centred cubic	End centred cubic	Body centred cubic	Simple cubic
In addition to the points at the corners, there are points at the centre of each side of the unit cell	Simple cubic	Face centred cubic	End centred cubic	Body centred cubic	Face centered cubic
In addition to the points at the corners, there are points at the centre of the end faces of the unit cell	Simple cubic	Face centred cubic	End centred cubic	Body centred cubic	End centered cell
In addition to the points at the corners, there is one point at the centre of the the unit cell	Simple cubic	Face centred cubic	End centred cubic	Body centred cubic	Body centred cubic

Simple cubic	When the points are present only at the corners of the unit cell	In addition to the points at the corners, there are points at the centre of each side of the unit cell	In addition to the points at the corners, there are points at the centre of the end faces of the unit cell	In addition to the points at the corners, there is one point at the centre of the the unit cell	When the points are present only at the corners of the unit cell
Face centred cubic	When the points are present only at the corners of the unit cell	In addition to the points at the corners, there are points at the centre of each side of the unit cell	In addition to the points at the corners, there are points at the centre of the end faces of the unit cell	In addition to the points at the corners, there is one point at the centre of the the unit cell	In addition to the points at the corners, there are points at the centre of each side of the unit cell
Body centred cubic	When the points are present only at the corners of the unit cell	In addition to the points at the corners, there are points at the centre of each side of the unit cell	In addition to the points at the corners, there are points at the centre of the end faces of the unit cell	In addition to the points at the corners, there is one point at the centre of the the unit cell	In addition to the points at the corners, there is one point at the centre of the the unit cell
End centred cubic	When the points are present only at the corners of the unit cell	In addition to the points at the corners, there are points at the centre of each side of the unit cell	In addition to the points at the corners, there are points at the centre of the end faces of the unit cell	In addition to the points at the corners, there is one point at the centre of the the unit cell	In addition to the points at the corners, there are points at the
Carbon in iron (steel) is one example of	substitutional solid solution	Interstitial solid solution	crystal defect	P-type semi conductor	Interstitial solid solution
Elements commonly used to form interstitial solid solutions include	H, Li, Na, N, C, and O	halogens	chalcogensFe, Co & Ni		Elements commonly used to form interstitial solid solutions include
For substitutional solid solutions, the Hume-Rothery rules are	The atomic diameter of the solute and solvent atoms must differ by no more than 15%	Solute atoms must be smaller than the interstitial sites in the solvent lattice	The solute and solvent should have disimilar electronegativity .	The solute and solvent should have similar ionisation energy.	The atomic diameter of the solute and solvent atoms must differ by no more than 15%
According to **Valence Bond Theory of metals** in crystalline lithium, every atom is connected with	8 or 12 lithium atoms	two lithium atoms	It is monoatomic	6 lithium atoms	8 or 12 lithium atoms
Which bonding model says 'the valence electrons are free to move through the bulk metal structure and even leave the metal, thereby producing positive ions'	Electron sea model	Valence bond model	Molecular orbital method	crystal field model	Electron sea model
Which model is called band theory	Electron sea model	Valence bond model	Molecular orbital method	crystal field model	Molecular orbital method
If the temperature of the semiconductor is increased the electrical conductivity	Decreases	Increases	do not change	first increases and then decreases	Increases
One of the useful property of a semiconductor device	passing current more easily in one direction than the other	Constant resistance for all materials	sensitive to light	sensitive to heat	passing current more easily in one direction than the other
One of the useful property of a semiconductor device	passing current equally on both the direction	showing variable resistance	sensitive to light	sensitive to heat	showing variable resistance

UNIT IV

IONIC EQUILIBRIA - I

Ionic equilibria: Strong, moderate and weak electrolytes, degree of ionization, factors affecting degree of ionization, ionization constant and ionic product of water. Ionization of weak acids and bases, pH scale, common ion effect; dissociation constants of mono and diprotic acids. Salt hydrolysis-calculation of hydrolysis constant, degree of hydrolysis and pH for different salts.

Types of Electrolytes:

The compounds which give ions either in molten state or in solution are called electrolytes. In the solid state they are bad conductors, but become good conductors either in the molten state in solution.

There are two types of electrolytes:

(1) Strong electrolytes:

These electrolytes are almost completely ionized when dissolved in a polar medium like water. In solution they are excellent conductors, e.g., HNO_3, HCl, KOH, NaOH, etc. Their degree of ionization is high and approaches unity.

(2) Weak electrolytes:

These are not completely ionized when dissolved in a polar solvent and they behave as poor conductors of electricity, e.g., CH_3COOH, H_3PO_4, H_3BO_3, NH_4OH, etc., Equlibrium between ions and unionized molecules is established in solution, e.g.,

$CH_3COOH \leftrightarrow CH_3COO^- + H^+$

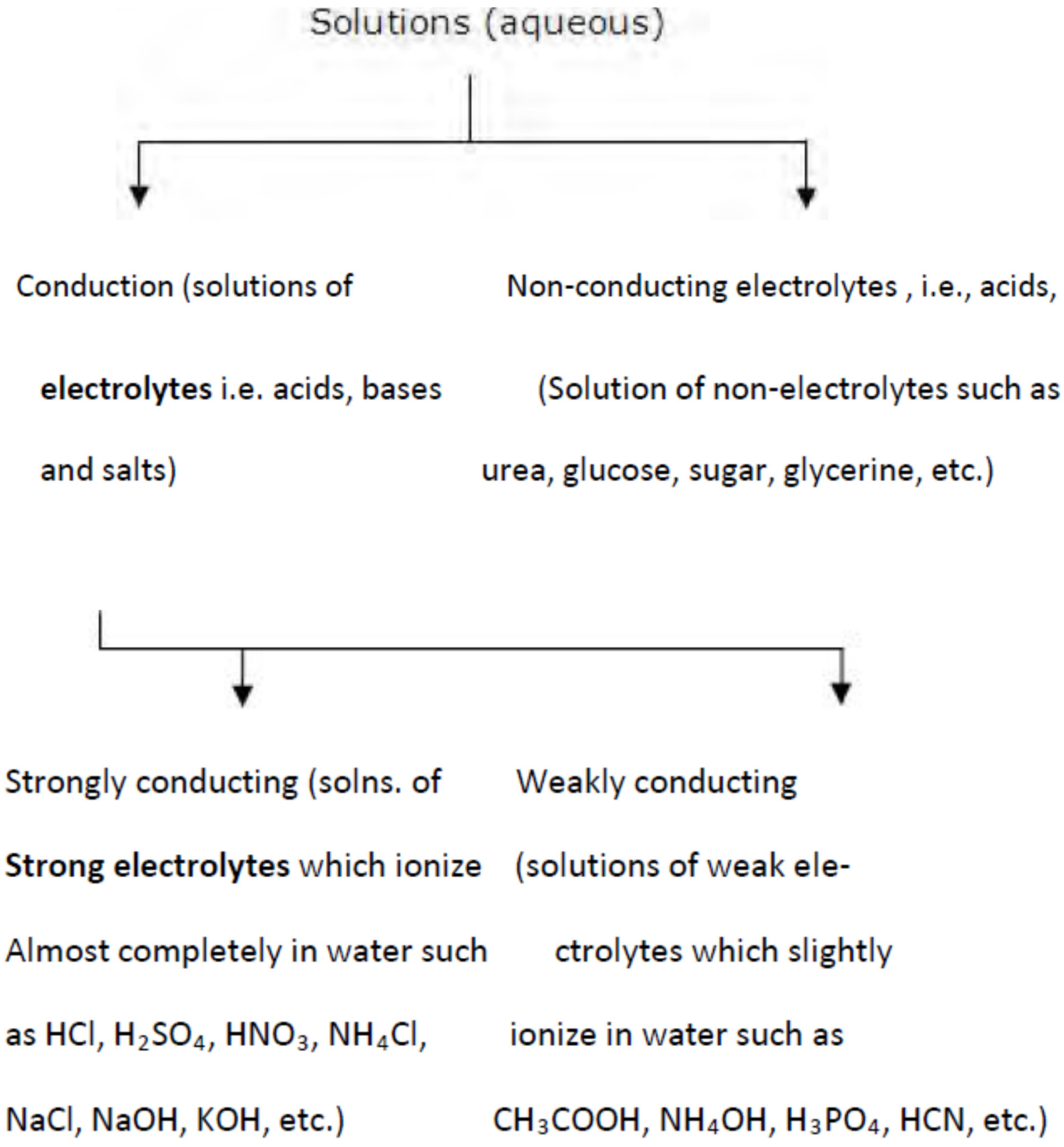
The above equilibrium is termed as ionic equilibrium. Degree of ionization of **weak electrolytes** is much less than unity.

Degree of ionization 'α' may be defined as a fraction of tital number of molecules of an **electrolyte** which dissociate into ions.

$\alpha = \%\text{ionization}/100$

= (Number of molecules dissociated as ions)/(Total number of molecules of electrolyte dissolved)

The following classification of **electrolytes** is based on their behavior in a particular solvent, i.e., water.



Solutions (aqueous)

Conduction (solutions of **electrolytes** i.e. acids, bases and salts)

Non-conducting electrolytes , i.e., acids, (Solution of non-electrolytes such as urea, glucose, sugar, glycerine, etc.)

Strongly conducting (solns. of **Strong electrolytes** which ionize Almost completely in water such as HCl, H_2SO_4, HNO_3, NH_4Cl, NaCl, NaOH, KOH, etc.)

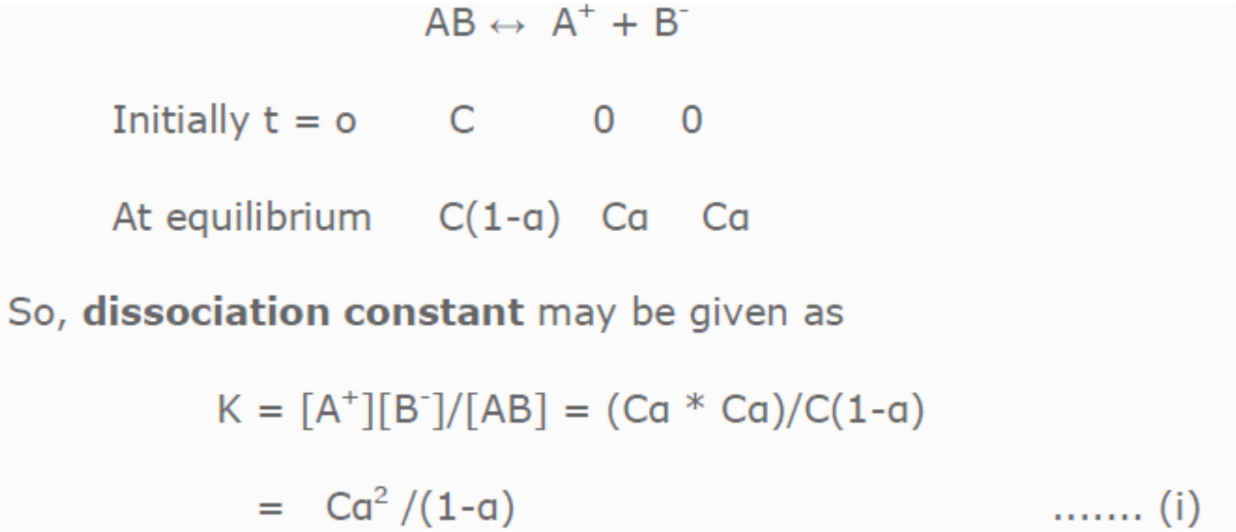
Weakly conducting (solutions of weak electrolytes which slightly ionize in water such as CH_3COOH, NH_4OH, H_3PO_4, HCN, etc.)

However, an **electrolyte** may behave as a strong one in aqueous solution, but it may behave as a weak one in another solvent. For example, sodium chloride behaves as a **strong electrolyte** and acetic acid as a **weak electrolyte** when dissolved in water but their conducting abilities are comparable in liquid ammonia solvent.

Ostwald's Dilution

According to Arrhenius theory of electrolyte dissociation, the molecules of an electrolyte in solution are constantly splitting up into ions and the ions are constantly reuniting to form unionized molecules. Therefore, a dynamic equilibrium exists between ions and unionized molecules of the electrolyte in solution. It was pointed out by **Ostwald** that like chemical equilibrium, law of mass action van be applied **to** such systems also.

Consider a binary electrolyte AB which dissociates into A^+ and B- ions and the equilibrium state is represented by the equation:



$$AB \leftrightarrow A^+ + B^-$$

Initially t = o $\quad C \quad 0 \quad 0$

At equilibrium $\quad C(1-\alpha) \quad C\alpha \quad C\alpha$

So, **dissociation constant** may be given as

$$K = [A^+][B^-]/[AB] = (C\alpha * C\alpha)/C(1-\alpha)$$

$$= C\alpha^2/(1-\alpha) \qquad \text{.......} \ (i)$$

For very weak electrolytes,

$\alpha <<< 1, (1 - \alpha) = 1$

$\therefore K = C\alpha^2$

$\alpha = \sqrt{K/C}$ .... (ii)

Concentration of any ion = $C\alpha = \sqrt{CK}$.

From equation (ii) it is a clear that degree of ionization increases on dilution.

Thus, **degree of dissociation** of a weak electrolyte is proportional to the square root of dilution.

Limitations

Limitations of Ostwald's dilution law:

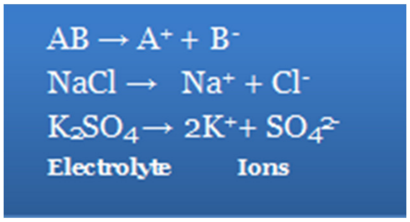
The law holds good only for weak electrolytes and fails completely in the case of strong electrolytes. The value of 'α' is determined by conductivity measurements by applying the formula Λ/Λ_∞. The value of 'α' determined at various dilutions of an electrolyte when substituted in Eq. (i) gives a constant value of K only in the case of weak electrolytes like CH_3COOH,

NH_4OH, etc. the cause of failure of **Ostwald's dilution law** in the case of strong electrolytes is due to the following factors"

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

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

- An electrolyte, when dissolved in water, breaks up into two types of charged particles, one carrying a positive charge and the other a negative charge. These charged particles are called ions. Positively charged ions are termed cations and negatively charged as anions.



$AB \rightarrow A^+ + B^-$

$NaCl \rightarrow Na^+ + Cl^-$

$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$

Electrolyte **Ions**

In its modern form, the theory assumes that solid electrolytes are composed of ions which are held together by electrostatic forces of attraction. When an electrolyte is dissolved in a solvent, these forces are weakened and the electrolyte undergoes dissociation into ions. The ions are solvated.

- The process of splitting of the molecules into ions of an electrolyte is calledionization. The fraction of the total number of molecules present in solution as ions is known as degree of ionization or degree of dissociation. It is denoted by
$$\alpha = \frac{Number\ of\ molecuiles\ dissociated\ into\ ions}{Total\ number\ of\ molecules}$$

- It has been observed that all electrolytes do not ionize to the same extent. Some are almost completely ionized while others are feebly ionized. The degree of ionization depends on a number of factors.

- Ions present in solution constantly re-unite to form neutral molecules and, thus, there is a state of dynamic equilibrium between the ionized the ionized and non-ionised molecules,
i.e., **$AB \rightleftharpoons A^+ + B^-$**
Applying the law of mass action to above equilibrium **$[A^+][B^-]/[AB] = K$**
K is known as ionization constant. The electrolytes having high value of K are termed strong electrolytes and those having low value of K as weak electrolytes.

- When an electric current is passed through the electrolytic solution, the positive ions (cations) move towards cathode and the negative ions (anions) move towards anode and get discharged, i.e., electrolysis occurs.
  The ions are discharged always in equivalent amounts, no matter what their relative speeds are.
- The electrolytic solutions is always neutral in nature as the total charge on one set of ions is always equal to the total charge on the other set of ions. However, it is not necessary that the number of two sets of ions must be equal always.
  - The properties of electrolytes in solution are the properties of ions present in solution. For example, acidic solution always contains H^+ ions while basic solution contains OH^- ions and characteristic properties of solutions are those of H^- ions and OH^- ions respectively.
  - The ions act like molecules towards depressing the freezing point, elevating the boiling point, lowering the vapour pressure and establishing the osmotic pressure.
  - The conductively of the electrolytic solution depends on the nature and number of ions as the current is carried through solution by the movement of ions.

The degree of ionization of an electrolyte in solution depends upon the following factors:

- **Nature of solute:**

When the ionisable parts of a molecule of a substance are held more by covalent bonding than by electrovalent bonding, less ions are furnished in solution. Such substances are termed weak electrolytes. H_2S, HCN, NH_4OH, CH_3COOH are examples of this class. NaCl, $Ba(NO_3)_2$, KOH, etc., are strong electrolytes, in which the transfer of electrons seems to be more or less complete, furnish ions immediately when dissolved. Strong electrolytes are almost completely ionized in solution.

- **Nature of solvent:**

The main function of the solvent is to weaken the electrostatic forces of attraction between the two ions and separate them. The force of attraction holding the ions together in any medium is expressed as

$$\mathbf{F= 1/(K)\ (q_1\ q_2)/r^2}$$

where K is the dielectric constant of medium.

Any solvent which has high value of dielectric constant has the capacity of separating ions. Water is considered to be the best solvent as it has the highest dielectric constant. The dielectric constants of some of the solvents are given below at 25^0 C.

- **Dilution:**

The extent of ionization of an electrolyte is inversely proportional to the concentration of its solution. Thus, degree of ionization increases with the increase of dilution of the solution, i.e., decreasing the concentration of the solution.

- **Temperature:**

The degree of ionization increases with the increase of temperature. This is due to the fact that at higher temperature molecular speed is increased which overcomes the forces of attraction between the ions.

(i) At normal dilution, value of α is nearly 1 for strong electrolytes, while it is very less than 1 for weak electrolytes.

(ii) Higher the dielectric constant of a solvent more is its ionising power. Water is the most powerful ionising solvent as its dielectric constant is highest.

(iii) $\alpha \propto \frac{1}{\text{Con. of solution}} \propto \frac{1}{\text{wt. of solution}}$

$\propto$ Dilution of solution $\propto$ Amount of solvent

(iv) Degree of ionisation of an electrolyte in solution increases with rise in temperature.

(v) **Presence of common ion:** The degree of ionisation of an electrolyte decreases in the presence of a strong electrolyte having a common ion.

Common ion effect

Let AB to the weak electrolyte. Considering its dissociation,

$AB \leftrightarrow A^+ + B^-$

and applying law of mass action we have

$K = [A^+][B^-]/[AB]$

The equilibrium constant, K, has a definite value at any given temperature. If now another electrolyte furnishing the A^+ and B^- ions be added to the above solution. It will increases the concentration of either A^+ ions or B^- ions (whichever has been added) and in order that K may remain constant, the concentration of AB must increases, i.e., the equilibrium will shift to the left hand side.

In other words, the degree of dissociation of an electrolyte (weak) is suppressed by the addition of another electrolyte (strong) containing a common ion. This is termed as common ion effect. Acetic acid is a weak electrolyte and its ionization is suppressed in presence of a strong acid (H^+ ion as common ion) or a strong salt like sodium acetate (acetate ion as common ion). Similarly, the addition of NH_4Cl or NaOH to NH_4OH solution will suppress the dissociation of NH_4OH due to common ion either NH^-_4 or OH^-.

As a result of common ion effect, the concentration of the ion not in common in two electrolytes, is decreased. The use of this phenomenon is made in qualitative analysis to adjust concentration of S^{2-} ions in second group and OH^- ion concentration in third group of analysis.

Ionic product of water

Pure water is a very weak electrolyte and ionises according to the equation

$H_2O \leftrightarrow H^+ + OH^-$

Applying law of mass action at equilibrium, the value of dissociation constant, K comes to

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

or $[H^+][OH^-] = K[H_20]$

Since dissociation takes place to a very small extent, the concentration of undissociated water molecules, $[H_20]$, may be regarded as constant. Thus, the product #$[H_20]$ gives another constant which is designated as K_w. So,

$[H^+][OH^-] = K_w$

The constant, K_w, is termed as ionic product of water.

The product of concentrations of H1 and OH ions in water at a particular temperature is known as ionic product of water. The value of K_w increases with the increase of temperature, i.e., the concentration of H^+ and OH^- ions increases with increase in temperature.

Temperature (°C)	Value of K_w
0	0.11×10^{-14}
10	0.31×10^{-14}
25	1.00×10^{-14}
100	7.50×10^{-14}

The value of K_w at 25°C is 1×10^{-14}. Since pure water is neutral in nature, H^+ ion concentration must be equal to OH^- ion concentration.

$[H^+] = [OH^-] = x$

or $[H^+][OH^-] = x^2 = 1 \times 10^{-14}$

or $x = 1 \times 10^{-7}\ M$

or $[H^+] = [OH^-] = 1 \times 10^{-7}\ mol\ litre^{-1}$

This shows that at 25°C, in 1 litre only 10^{-7} mole of water is in ionic form out of a total of approximately 55.5 moles.

When an acid or a base is added to water, the ionic concentration product, $[H^+][OH^-]$, remains constant, i.e., equal to K_w but concentrations of H^+ and OH^- ions do not remain equal. The addition of acid increases the hydrogen ion concentration while that of hydroxyl ion concentration decreases, i.e.,

$[H^+] > [OH^-]$; (Acidic solution)

Similarly, when a base is added, the OH^- ion concentration increases while H^+ ion concentration decreases,

i.e., $[OH^-] > [H^+]$; (Alkaline or basic solution)

In neutral solution, $[H^+] = [OH^-] = 1 \times 10^{-7}\ M$

In acidic solution, $[H^+] > [OH^-]$

or $[H^+] > 1 \times 10^{-7}\ M$

and $[OH^-] < 1 \times 10^{-7}\ M$

In alkaline solution, $[OH^-] > [H^+]$

or $[OH^-] > 1 \times 10^{-7}\ M$

and $[H^+] < 1 \times 10^{-7}\ M$

Thus, if the hydrogen ion concentration is more than 1×10^{-7} M, the solution will be acidic in nature and if less than 1×10^{-7} M, the solution will be alkaline.

$[H^+] = 10^{-0}\ 10^{-1}\ 10^{-2}\ 10^{-3}\ 10^{-4}\ 10^{-5}\ 10^{-6}$ (Acidic)

$[H^+] = 10^{-7}$ (Neutral)

$[H^+] = 10^{-14}\ 10^{-13}\ 10^{-12}\ 10^{-11}\ 10^{-10}\ 10^{-9}\ 10^{-8}$ (Alkaline)

We shall have the following table if OH^- ion concentration is taken into account.

$[OH^-] = 10^{-14}\ 10^{-13}\ 10^{-12}\ 10^{-11}\ 10^{-10}\ 10^{-9}\ 10^{-8}$ (Acidic)

$[OH^-] = 10^{-7}$ (Neutral)

$[OH^-] = 10^{-0}\ 10^{-1}\ 10^{-2}\ 10^{-3}\ 10^{-4}\ 10^{-5}\ 10^{-6}$ (Alkaline)

It is, thus, concluded that every aqueous solution, whether acidic, neutral or alkaline contains both H^+ and OH^- ions. The product of their concentrations is always constant, equal to 1×10^{-14} at 25°C. If one increases, the other decrease accordingly so that the product remains 1×10-14 at 25^o C.

If $[H^+] = 10^{-2}$ M, then $[OH^-] = 10^{-12}$ M; the product, $[H^+][OH^-] = 10^{-2} \times 10^{-12} = 10^{-14}$; the solution is acidic.

If [H+] = 10-10 M, then [OH-] = 10-4 M; the product, [H+][OH-] = 10-10 × 10-4 = 10-14; the solution is alkaline.

HYDROGENION CONCENTRATION-pH SCALE:

It is clear from the above discussion that nature of the solution (acidic, alkaline or neutral) can be represented in terms of either hydrogen ion concentration or hydroxyl ion concentration but it is convenient to express acidity or alkalinity of a solution by referring to the concentration of hydrogen ions only. Since H^+ ion concentration can vary within a wide range from 1 mol per litre to about 1.0×10^{-14} mol per litre, a logarithmic notation has been devised **by Sorensen**, in 1909, to simplify the expression of these quantities. The notation used is termed as the pH scale.

The hydrogen ion concentrations are expressed in terms of the numerical value of negative power to which 10 must be raised. This numerical value of negative power was termed as pH, *i.e.*,

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

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

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

or $pH = \log 1/[H^+]$

pH of a solution is, thus, defined as **the negative logarithm of the concentration (in mol per litre) of hydrogen ions which it contains or pH of the solution is the logarithm of the reciprocal of H^+ ion concentration.**

Just as pH indicates the hydrogen ion concentration, the pOH represents the hydroxyl ion concentration, i.e.,

pOH = -log [OH-] Considering the relationship,

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

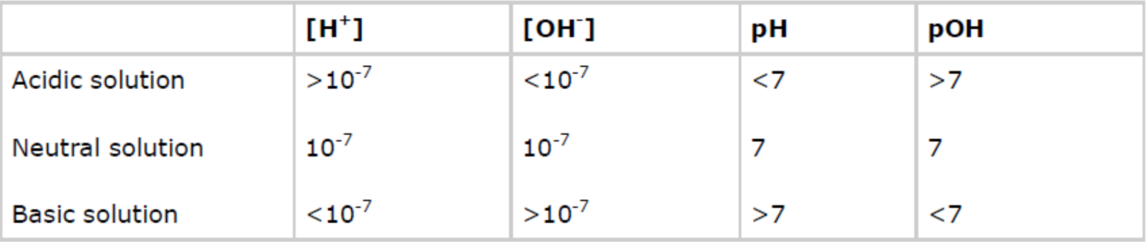
Taking log on both sides, we have

$\log [H^+] + \log [OH^-] = \log K_w = \log (1 \times 10^{-14})$

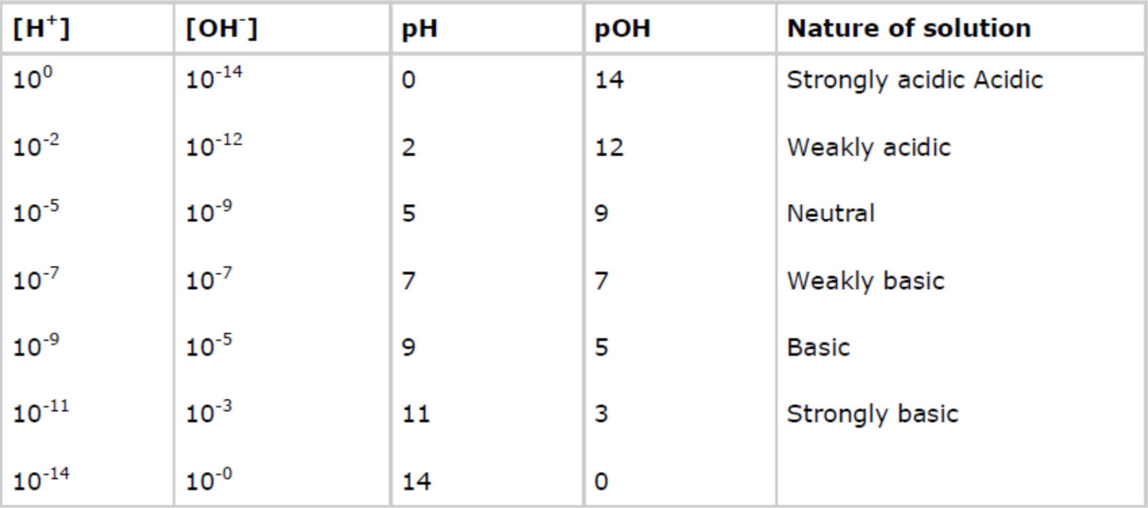
or $-\log [H^+] - \log [OH^-] = -\log K_w = -\log (1 \times 10^{-14})$

or pH + pOH = PK_w^{*} = 14

i.e., sum of pH and pOH is equal to 14 in any aqueous solution at 25°C. The above discussion can be summarised in the following manner:

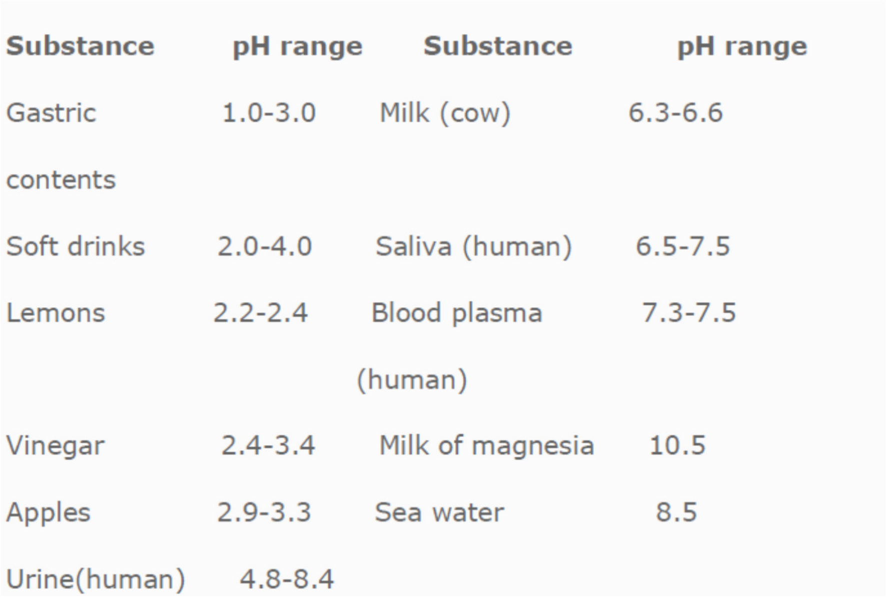


	$[H^+]$	$[OH^-]$	pH	pOH
Acidic solution	$>10^{-7}$	$<10^{-7}$	<7	>7
Neutral solution	10^{-7}	10^{-7}	7	7
Basic solution	$<10^{-7}$	$>10^{-7}$	>7	<7



$[H^+]$	$[OH^-]$	pH	pOH	Nature of solution
10^{0}	10^{-14}	0	14	Strongly acidic Acidic
10^{-2}	10^{-12}	2	12	Weakly acidic
10^{-5}	10^{-9}	5	9	Neutral
10^{-7}	10^{-7}	7	7	Weakly basic
10^{-9}	10^{-5}	9	5	Basic
10^{-11}	10^{-3}	11	3	Strongly basic
10^{-14}	10^{-0}	14	0	

The following table shows the pH range for a few common substances



Substance	pH range	Substance	pH range
Gastric contents	1.0-3.0	Milk (cow)	6.3-6.6
Soft drinks	2.0-4.0	Saliva (human)	6.5-7.5
Lemons	2.2-2.4	Blood plasma (human)	7.3-7.5
Vinegar	2.4-3.4	Milk of magnesia	10.5
Apples	2.9-3.3	Sea water	8.5
Urine(human)	4.8-8.4		

Any method which can measure the concentration of H^+ ions or OH^- ions in a solution can serve for finding pH value.

Salt Hydrolysis:

Pure water is a weak electrolyte and neutral in nature, i.e., H^+ ion concentration is exactly equal to OH" ion concentration

$[H^+] = [OH^-]$

When this condition is disturbed by decreasing the concentration of either of the two ions, the neutral nature changes into acidic or basic. When $[H^+] > [OH^-]$, the water becomes acidic and when $[H^+] < [OH^-]$, the water acquires basic nature. This is exactly the change which occurs during the phenomenon known as **salt hydrolysis.** It is defined as **a reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity.**

Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into ions. In some salts, cations are more reactive in comparison to anions and these react with water to produce H^+ ions. Thus, the solution acquires acidic nature.

$M^+ + H_2O \leftrightarrow MOH + H^+$

Weak base

In other salts, anions may be more reactive in comparison to cations and these react with water to produce OH^- ions. Thus, the solution becomes basic.

$A^- + H_2O \leftrightarrow HA + OH^-$

Weak acid

The process of **salt hydrolysis** is actually the reverse of neutralization.

Salt + Water ↔ Acid + Base

If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both the acid and the base are either strong or weak, the solution is generally neutral in nature.

As the nature of the cation or the anion of the salt determines whether its solution will be acidic or basic, it is proper to divide the salts into four categories.

(i) Salt of a strong acid and a weak base.

Examples: $FeCl_3$, $CuCl_2$, $AlCl_3$, NH_4Cl, $CuSO_4$, etc.

(ii) Salt of a strong base and a weak acid.

Examples: CH_3COONa, NaCN, $NaHCO_3$, Na_2CO_3, etc.

(iii) Salt of a weak acid and a weak base.

Examples: CH_3COONH_4, $(NH_4)_2CO_3$, NH_4HCO_3, etc.

(iv) Salt of a strong acid and a strong base.

Examples: NaCl, K_2SO_4, $NaNO_3$, NaBr, etc.

Salt of a strong acid and a weak base:

The solution of such a salt is acidic in nature. The cation of the salt which has come from **weak base** is reactive. It reacts with water to form a **weak base** and H^+ ions.

$B^+ + H_2O \leftrightarrow BOH + H^+$

Weak base

Consider, for example, NH_4Cl. It ionises in water completely into NH_4 and CF ions. ions react with water to form a **weak base** (NH_4OH) and H^+ ions.

$NH^+{}_4 + H_2O \leftrightarrow NH_4OH + H^+$

C(1-x) Cx Cx

Thus, hydrogen ion concentration increases and the solution becomes acidic.

Applying law of mass action,

$K_h = [H^x][NH_4OH]/[NH_4^+]=(Cx.Cx)/C(1-x) = (x^2C)/((1-x))$ ...... (i)

where C is the concentration of salt and x the degree of hydrolysis.

Other equilibria which exist in solution are

$NH_4OH \leftrightarrow NH^+{}_4 + OH^-$, $K_b = [NH^+{}_{4]}[OH^-]/[NH_4Oh]$ .... (ii)

$H_2O \leftrightarrow H^+ + OH^-$, $K_b = [H^+][H^-]$ ..... (iii)

From eqs. (II) and (iii)

$K_w/K_b = [H^+][NH^4OH]/[NH_4^+] = K_h$ .... (iv)

$[H^+] = [H^+][NH_4^+]/[NH_4OH] = K_w/K_b \times [NH_4^+]/[NH_4OH]$

$\log [H^+] = \log K_w - \log K_b + \log[\text{salt}]/[\text{base}]$

$-pH = -pK_w + pK_b + \log[\text{salt}]/[\text{base}]$

$pK_w - pH = pK_b + \log[\text{salt}]/[\text{base}]$

$pOH = pK_b + \log[\text{salt}]/[\text{base}]$

Relation between Hydrolysis constant and Degree of hydrolysis

The extent to which **hydrolysis** proceeds is expressed as the degree of **hydrolysis**and is defined as the fraction of one mole of the salt that is hydrolysed when the equilibrium has been attained. It is generally expressed as *h* or *x*.

h = (Amount of salt hydrolysed)/(Total salt taken)

Considering again eq. (i),

$K_h = x^2C/(1-x)$ or $K_h = h^2C/(1-h)$

When h is very small (1-h) → 1,

$H_2 = K_h \times 1/c$

or $h = \sqrt{}(K_h/C)$

$= \sqrt{}(K_w/K_b * C)$

$[H^+] = h \times C = \sqrt{}(C*K_h)/K_b$

$\log [H^+] = 1/2 \log K_w + \mathbf{1}\ 1/2 \log C - 1/2 \log K_b$

$pH = 1/2 pK_w - 1/2 \log C - 1/2\ pK_b$

$= 7 - 1/2\ pK_b - 1/2 \log C$

Salt of a Weak Acid and a Strong Base:

The solution of such a salt is basic in nature. The anion of the salt is reactive. It reacts with water to form a **weak acid** and OH^- ions.

$A^- + H_2O; \leftrightarrow HA + OH^-$

Weak acid

Consider, for example, the salt CH_3COONa. It ionises in water completely to give CH_3COO^- and Na^+ ions. CH_3COO^- ions react with water to form a **weak acid**, CH_3COOH and OH^- ions.

$CH_3COO^- + H_2O \leftrightarrow CH_3COOH + OH^-$

C(1-x) Cx Cx

Thus, OH^- ion concentration increases, the solution becomes alkaline.

Applying law of mass action,

$K_h = [CH_3COOH][OH^-]/[CH_3CO^-] = (Cx\times Cx)/C(1-x) = (Cx^2)/(1-x)$) ...... (i)

Other equations present in the solution are:

$CH_3COOH \leftrightarrow CH_3COO^- + H^+$, $K_a = [CH_3COO^-][H^+]/[CH_3COOH]$ ...... (ii)

$H_2O \leftrightarrow H^+ + OH^-$, $K_w = [H^+][OH^-]$ .... (iii)

From eqs. (ii) and (iii),

$\log [OH^-] = \log K_w - \log K_a + \log[salt]/[acid]$

$-pOH = -pK_w + pK_a + \log[salt]/[acid]$

$pK_w - pOH = pK_a + \log[salt]/[acid]$

$pH = pK_a + \log[salt]/[acid]$

Considering eq. (i) again,

$K_h = cx^2/(1-x)$ or $K_h = Ch^2/(1-h)$

When h is very small, (1-h) → 1

or $h^2 = K_h/C$

or $h = \sqrt{}K_h/C$

$[OH^-] = h \times C = \sqrt{}(CK_h) = \sqrt{}(C*K_w/K_a)$

$[H^+] = K_w/[OH^-]$

$= K_w/\sqrt{}(C*K_w/K_a) = \sqrt{}(K_a*K_w)/K_c$

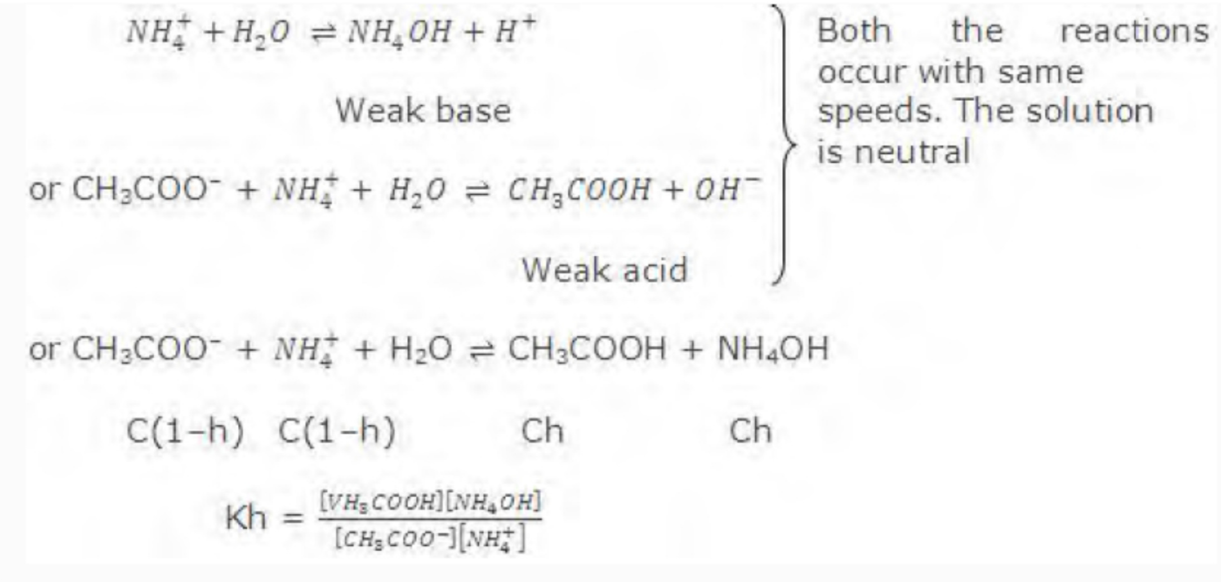
$-\log [H^+] = -1/2\log K_w - 1/2\log K_a + 1/2\log C$

$pH = 1/2pK_w + 1/2pK_a + 1/2\log C$

$= 7 + 1/2pK_a + 1/2\log C.$

Salt of a weak acid and a weak base:

Maximum **hydrolysis** occurs in the case of such a salt as both the cation and anion are reactive and react with water to produce H^+ and OFT ions. The solution is generally neutral but it can be either slightly acidic or slightly alkaline if both the reactions take place with slightly different rates. Consider, for example, the salt CH_3COONH_4. It gives CH_3COO^- and ions in solution. Both react with water.



$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

Weak base

or $CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + OH^-$

Weak acid

Both the reactions occur with same speeds. The solution is neutral

or $CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

C(1–h) C(1–h) Ch Ch

$$Kh = \frac{[VH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$$

Other equilibria which exist in solution are:

$CH_3COOH \leftrightarrow CH_3COO^- + H^+$, $K_a = [CH^3COO^-][H^+]/[CH_3COOH]$ ..... (i)

$NH_4OH \leftrightarrow NH^+_4 + OH^-$, $Kb = [NH^+_4]\ [OH^-]/[NH_4OH]$ ..... (ii)

$H_2O \leftrightarrow H^+ + OH^-$, $K_w = [H^+][OH^-]$ ..... (iii)

From Eqs. (i), (ii) and (iii),

$K_h = Kw/K_a.K_b = [CH_3COOH][NH_4OH]/[CH_3COO^-][NH^+_4]$ .... (iv)

Let C be the concentration and h be the degree of **hydrolysis**

$K_h = h^2/(1-h)^2$

When h is small, (1-h) → 1.

$K_h = h^2$

$h = \sqrt{Kh} = \sqrt{K_w}/K_{a*}K_b$

$[H^+]\ K_a \times h$

$= K_a \times \sqrt{K_w/K_{a*}K_b}$

$= \sqrt{K_{w\,*}\,K_a/K_b}$

$-\log [H^+] = -1/2\log K_a - 1/2\log K_w + 1/2\log K_b$

$pH = 1/2pK_a + 1/2pK_w - 1/2pK_b$

$= 7 + 1/2pK_a - 1/2pK_b$

When $pK_a = pK_b$, pH = 7, i.e., solution will be neutral in nature.

When $pK_a > pK_b$. The solution will be alkaline as the acid will be slightly weaker than base and pH value will be more than 7. In case $pK_a < pK_b$, the solution will be acidic as the acid is relatively stronger than base and pH will be less than 7.

Salt of a strong acid and a strong base

Such a salt, say NaCl, does not undergo **hydrolysis** as both the ions are not reactive. The solution is thus, neutral in nature.

Hydrolysis of Amphiprotic Anion:

Let us consider hydrolysis of **amphiprotic anion** only, i.e., when counter cation is not hydrolysed, example of some salts of this category are $NaHCO_3$, NaHS, Na_2HPO_4, NaH_2PO_4.

Here, $H_2PO^-_4$ and HPO^{2-}_4 are **amphiprotic anions**. pH after their **hydrolysis** can be calculated as,

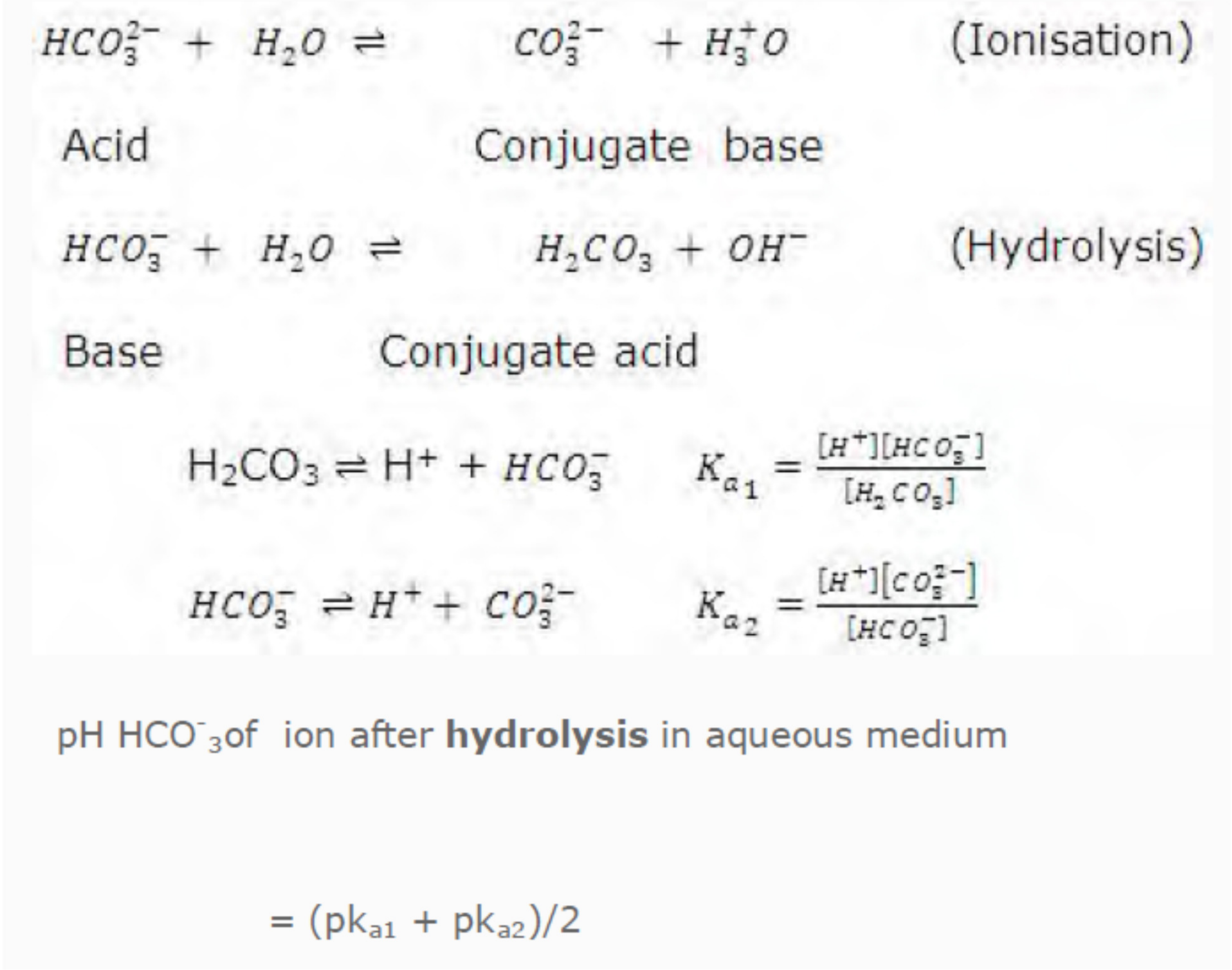
pH of $H_2PO^-_4$ in aqueous medium = $(pk_{a1} + pk_{a2})/2$

pH of $H_2PO^{2-}_4$ in aqueous medium = $(pk_{a2} + pk_{a3})/2$

Here, $H_2PO^{2-}_4$ is conjugate base of $H_2PO^-_4$ and H_3PO_4 is conjugate acid of $H_2PO^-_4$.

Similarly, $PO^{3-}_{4\,i}$s conjugate base of HPO^{-2}_4 and HPO^-_4 is conjugate acid of PO^{3-}_4.

(iv) Let us consider **amphiprotic** bicarbonate anion.



$HCO_3^{2-} + H_2O \rightleftharpoons CO_3^{2-} + H_3^+O$ (Ionisation)

Acid Conjugate base

$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$ (Hydrolysis)

Base Conjugate acid

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

pH $HCO^-_3$of ion after **hydrolysis** in aqueous medium

$= (pk_{a1} + pk_{a2})/2$

(v) Let us consider the **hydrolysis** of **amphiprotic anion** along with cation, e.g., NH_4HCO_3, NH_4HS.

In above examples both cations and anions are derived from weak base and weak acids respectively hence, both will undergo **hydrolysis** in aqueous medium.

When these salts are dissolved in water, $[H_3O^+]$ concentration can be determined as,

$[H_3O^+] = \sqrt{}k_{a1}[k_w/k_b + k_{a2}]$

pH = -log = $\sqrt{}k_{a1}[k_w/k_b + k_{a2}]$

Possible questions

PART A

1. The hydronium ion is,

   a) H^+ b) OH^- c) **H_3O^+** d) H_2O

2. Levelling point for acids can be obtained, when dissolving them in

   a) Water b) glacial acetic acid c) acidic solution d) basic solution

3. An acid, according to lewis concept

   a) accepts protons b) accepts electron c) donates electron d) donates protons

4. Lewis concept tells, every species forms

   a) ionic bond b) **covalent bond** c) metallic bond d) coordinate bond

5. Reformation of HCl in aqueous solution is very slow why?

   a) Cl^- is a weak base b) **Cl^- is a weak acid**

   c) Cl^- is a strong base d) Cl^- is a strong acid

6. In a conjugate acid-base pairs, if the acid is strong, then base is,

   a) strong b) **weak** c) neutral d) moderate

7. The extensive basic character of NaOH is due to

   a) presence of anions and cations b) **presence of OH^- ions even in solid state**

   c) presence of water of hydration d) presence of H^+ ions

8. Acetic acid is a weak acid, because

   a) it has very low tendency to donate OH^- b) **it has very low tendency to donate H^+**

   c) it has very high tendency to donate H^+ d) it has very high tendency to donate OH^-

9. In $[H_3O^+]$, the square bracket represent,

   a) concentration in moles per ml b) concentration in moles per kg

   c) **concentration in moles per litre** d) concentration in moles per mg

10. Dissociation constant varies with,

    a) Concentration b) strength c) stability d) **temperature**

11. Degree of dissociation is a measure of its capacity to furnish,

a) hydrogen atoms b) **hydrogen ions** c) chydroxyl ions d) hydronium ion

12. The dissociation constant of 0.100M acetic acid, found to be dissociated to the extent 1.33% at room temperature is

a) 1.77×10^{-6} b) **1.77×10^{-5}** c) 17.7 d) 0.177

13. A hydrogen ion indicator is a substance

a) Which changes its colour with variation in pH of the solution to which it is added

b) Which changes its colour with variation in ionic strength of the solution to which it is added c) Which changes its pH with variation in colour of the solution to which it is added d) Which changes its dielectric constant with variation in pH of the solution to which it is added

14. In the acidic solution with pH above 4.4 methyl orange gives

a) Red colour b) Blue colour c) **Yellow colour** d) Green colour

15. In a solution with pH below 3 methyl orange gives

a) Red colour b) Blue colour c) Yellow colour d) Green colour

16. The pH range over which methyl orange can be used as an indicator lies between

a) Below pH 3 b) Between 8 & 10 c) Between 6 & 8 d) **Between pH 3.0 and 4.4**

17. A hydrogen ion indicator is a substance

a) Which changes its colour with variation in pH of the solution to which it is added

b) Which changes its colour with variation in ionic strength of the solution to which it is added c) Which changes its pH with variation in colour of the solution to which it is added d) Which changes its dielectric constant with variation in pH of the solution to which it is added

18. In the acidic solution with pH above 4.4 methyl orange gives

a) Red colour b) Blue colour c) **Yellow colour** d) Green colour

19. In a solution with pH below 3 methyl orange gives

a) Red colour b) Blue colour c) Yellow colour d) Green colour

20. The pH range over which methyl orange can be used as an indicator lies between

a) Below pH 3 b) Between 8 & 10 c) Between 6 & 8 d) **Between pH 3.0 and 4.4**

Part B

1. Illustrate a strong electrolyte with suitable examples

2. What is meant by a weak electrolyte with suitable examples

3. What is the difference between a strong electgrolyte and a weak electrolyte

4. What is meant by degree of dissociation

5. What is Ostwald's dilution law

6. What is meant by PH of a solution

7. Explain PH scale

8. What is common ion effect

9. What is meant by salt hydrolysis

10. What is meant by degree of hydrolysis

Part C

1. Explain Ionic product of water
2. Discuss the degree of hydrolysis of a salt of weak acid and strong base.
3. Determine the dissociation constant of a weak acid and a base.
4. What is meant by degree of dissociation? Explain the factors affecting degree of ionization.
5. Explain common ion effect with suitable examples.

Questions	**Opt-1**	**Opt-2**	**Opt-3**	**Opt-4**	**Answer**
UNIT IV					
According to lowry- bronsted theory, an acid is	donates proton	accepts proton	donates electron	accepts proton	donates proton
How residual part acid tends to behave, when acid loses a proton	acid	base	neutral	amphoteric	base
The H^+ ions present is largely found as	H_3O^+	H^+	OH^-	H_2O	H_3O^+
which amoung the following is hydronium ion	H^+	OH^-	H_3O^+	H_2O	H_3O^+
An acid according to lowry- bronsted theory	donates proton	accepts proton	donates electron	accepts proton	donates proton
When acid loses a proton, then its residual part tends to behave like	acid	base	neutral	amphoteric	base
When acetic acid is dissolved in water, the water behaves as	solvent	acid	amphoteric	neutral	solvent
The hydronium ion is	H^+	OH^-	H_3O^+	H_2O	H_3O^+
levelling point for acids can be obtained, when dissolving them in	water	glacial acetic acid	acedic solution	basic solution	water
An acid, according to lewis concept	accepts protons	accepts electron	donates electron	donates protons	accepts electron
lewis concept tells, every species forms	ionic bond	covalent bond	metallic bond	coordinate bond	covalent bond
Reformation of HCl in aqueous solution is very slow why?	Cl^- is a weak base	Cl^- is a weak acid	Cl^- is a strong base	Cl^- is a strong acid	Cl^- is a weak base
In a conjugate acid-base pairs, if the acid is strong, then base is	strong	weak	neutral	moderate	weak
The extensive basic character of NaOH is due to	presence of anions and cations	presence of OH^- ions even in solid state	presence of water of hydration	presence of H^+ ions	presence of OH^- ions even in solid state
Acetic acid is a weak acid, because	it has very low tendency to donate OH^-	it has very low tendency to donate H^+	it has very high tendency to donate H^+	it has very high tendency to donate OH^-	it has very low tendency to donate H^+
The degree of dissociation of acids have coincidance with	strength of acid	solubility	polarity	strength of base	strength of acid
The 'levelling point' for acids can be obtained, when dissolving them in	water	glacial acetic acid	acedic solution	basic solution	water
Which one of the following is hydronium ion	H^+	OH^-	H_3O^+	H_2O	H_3O^+
The conjugate pair of ammonia in aqueous solution is	CH_3COOH^+	NH_4OH	NH_4^+	H_3O^+	NH_4^+
HCl and CH_3COOH have same acedic strength when	dissolved in water	dissolved in CH_3COOH	dissolved in HCl	dissolved in liq. Ammonia	dissolved in liq. Ammonia
Nitric acid behaves as a base when	dissolved in HF	dissolved in water	dissolved in liq.ammonia	dissolved in CH_3COOH	dissolved in HF
According to lewis concept, an acid	accepts protons	accepts electron	donates electron	donates protons	accepts electron
According to lewis concept, every species forms	ionic bond	covalent bond	metallic bond	coordinate bond	covalent bond
$HClO_4$ is more acedic than $HClO_3$, why?	$HClO_4$ has more number of oxygen atom	$HClO_4$ is soluble, where $HClO_3$ is insoluble	$HClO_4$ is covalent compound, where $HClO_3$ is ionic	$HClO_4$ has less number of oxygen atom	$HClO_4$ has more number of oxygen atom
In $[H_3O^+]$, the square bracket represent	concentration in moles per ml	concentration in moles per kg	concentration in moles per litre	concentration in moles per mg	concentration in moles per litre
Dissociation constant varies with	concentration	strength	stability	temperature	temperature
Degree of dissociation is a measure of its capacity to furnish	hydrogen atoms	hydrogen ions	hydroxyl ions	hydronium ion	hydrogen ions
The dissociation constant of 0.100M acetic acid, found to be dissociated to the extent 1.33% at room temperature is	1.77×10^{-6}	1.77×10^{-5}	17.7	0.177	1.77×10^{-5}
The dissociation constant of 0.2 M monobasic acid is 1.8×10^{-5}, then its degree of dissociation is	0.009486	9.486	0.9846	948.6	0.009486
Dissociation of phosphoric acid occurs in	three stages	two stages	one stages	ten stages	three stages
The square bracket $[H_3O^+]$ represent	concentration in moles per ml	concentration in moles per kg	concentration in moles per litre	concentration in moles per mg	concentration in moles per litre
Which of the following acid has Ka_3 value	H_2SO_4	H_3PO_4	HCLl	H_3PO_3	H_3PO_4
The dissociation constant of water is	ionic product of water	surface tension	viscosity	concentration	ionic product of water
Every aqueous solution contains	H^+	OH^-	H^+ and OH^-	H^+ or OH^-	H^+ and OH^-
The P^H value of HCl and NaOH are	1,14	1,1	14,14	3,4	1,14
Ions produced by water is	ionic product of water	surface tension	viscosity	concentration	ionic product of water
The P^H of 0.0001 M HCl is	3	4	1	14	4
The hydrogen ion concentration of a solution of P^H value 5.4 is	3.98×10^{-6}mol dm^{-3}	3.98×10^{-5}mol dm^{-3}	3.98×10^{-4}mol dm^{-3}	3.98×10^{-14}mol dm^{-3}	3.98×10^{-6}mol dm^{-3}

HCl solution of any concentration has P^H value	1	14	less than 7	3.14	less than 7
POH indicates	H$^+$ ions concentration	OH$^-$ ions concentration	H_3O^+	H_2O	OH$^-$ ions concentration
The sum of PH and POH of 0.03M aqueous solution of HCl at 25°C is	1.52	12.48	14	1	14
Addition of sodium acetate to acetic acid solution	increases the dissociation of acetic acid	decreases its acidity	suppresses the dissociation of acetic acid	increases its concentration	suppresses the dissociation of acetic acid
When Solubility product is constant	high concentration	particular room temperature	very low temperature	very high temperature	particular room temperature
What is meant byPOH	H$^+$ ions concentration	OH$^-$ ions concentration	H_3O^+	H_2O	OH$^-$ ions concentration
If the hydrogen ion concentration of a weak base decreases, then its acid-salt ratio	increases	decreases	remains unaltered	becomes zero	decreases
The hydrogen ion concentration of a solution obtained by mixing 500ml of 0.2 M acetic acid in 0.30 M sodium acetate is	1.17 x 10^{-5}mol dm^{-3}	1.17 x 10^{-6}mol dm^{-3}	1.17 x 10^{-3}mol dm^{-3}	1.17 x 10^{5}mol dm^{-3}	1.17 x 10^{-5}mol dm^{-3}
buffer mixture is a	strong acid & its salt	weak base & its salt	weak acid & its salt	strong base& its salt	weak acid & its salt
The PH of water	7	less than 7	more than 7	zero	7
Which of the following is not a buffer	sodium chloride solution	ammonium acetate solution	sodium acetate solution	potassium acetate solution	sodium chloride solution
The PH of aquous solution of ammonium acetate is	7	less than 7	more than 7	zero	7
Expression of POH	H$^+$ ions concentration	OH$^-$ ions concentration	H_3O^+	H_2O	OH$^-$ ions concentration
The capacity of a solution to resists alteration in its P^H is	buffer capacity	solubility	common ion effect	concentration	buffer capacity
The value of buffer index is always	positive	negative	zero	a constant	positive
A buffer mixture is a	strong acid & its salt	weak base & its salt	weak acid & its salt	strong base& its salt	weak acid & its salt
Henderson equation is used to calculate the P^H values for	buffer solution	buffer mixtures	acids	bases	buffer mixtures
Solubility product is constant at	high concentration	particular room temperature	very low temperature	very high temperature	particular room temperature
The solubility product of silver chloride, whose solubility in water at 25°C is 0.00179g per litre is	1.56 x 10^{10}mo^{2}l dm^{-6}	1.56 x 10^{-10}mo^{2}l dm^{-6}	1.56 x 10^{5}mo^{2}l dm^{-6}	1.56 x 10^{-15}mo^{2}l dm^{-6}	1.56 x 10^{-10}mo^{2}l dm^{-6}
Application of Henderson equation in the P^H calculation	buffer solution	buffer mixtures	acids	bases	buffer mixtures
If the ionic product of a compound exceeds the solubility product, then the compound	neutralises	precipitates	acidified	concentration becomes very high	precipitates
Which one of the following is buffer mixture	strong acid & its salt	weak base & its salt	weak acid & its salt	strong base& its salt	weak acid & its salt

UNIT V

IONIC EQUILIBRIA – II

Buffer solutions; derivation of Henderson equation and its applications. Solubility and solubility product of sparingly soluble salts – applications of solubility product principle. Qualitative treatment of acid – base titration curves (calculation of pH at various stages). Theory of acid–base indicators; selection of indicators and their limitations.

BUFFER SOLUTIONS:

For several purposes, we need solutions which should have constant pH. Many reactions, particularly the biochemical reactions, are to be carried out at a constant pH. But it is observed that solutions and even pure water (pH = 7) cannot retain the constant pH for long. If the solution comes in contact with air, it will absorb CO_2 and becomes more acidic. If the solution is stored in a glass bottle, alkaline impurities dissolve from glass and the solution becomes alkaline.

A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid (H^+ ions) or a base (OH^- ions) is called the **buffer solution.** It can also be defined as a solution of **reserve acidity** or **alkalinity** which resists change of pH upon the addition of small amount of acid or alkali.

General characteristics of a buffer solution

(i) It has a definite pH, i.e., it has reserve acidity oralkalinity.

(ii) Its pH does not change on standing for long.

(iii) Its pH does not change on dilution.

(iv) Its pH is slightly changed by the addition of small quantity of an acid or a base.

Buffer solutions can be obtained:

(i) by mixing a weak acid with its salt with a strong base,

eg;

(a) $CH_3COOH + CH_3COONa$

(b) Boric acid + Borax

(c) Phthalic acid + Potassium acid phthalate

(ii) by mixing a weak base with its salt with a strong acid,

e.g;

(a) $PNH_4OH + NH_4Cl$

(b) Glycine + Glycine hydrochloride

(iii) by a solution of ampholyte. The ampholytes or amphoteric electrolytes are the substances which show properties of both an acid and a base. Proteins and amino acids are the examples of such electrolytes.

(iv) by a mixture of an acid salt and a normal salt of a polybasic acid, e.g., $Na_2HPO_4 + Na_3PO_4$, or a salt of weak acid and a weak base, such as CH_3COONH_4.

The first and second type are also called acidic and basic buffers respectively.

Explanation of buffer action

(i) Acidic buffer:

Consider the case of the solution of acetic acid containing sodium acetate. Acetic acid is feebly ionised while sodium acetate is almost completely ionised. The mixture thus contains CH_3COOH molecules, CH_3COO^- ions, Na^+ ions, H^+ ions and OH^- ions. Thus, we have the following equilibria in solution:

$CH_3COOH \leftrightarrow H^+ + CH_3COO^-$ (Feebly ionised)

$CH_3COONa \leftrightarrow Na^+ + CH_3COC^-$ (Completely ionised)

$H_2O \leftrightarrow H^+ + OH^-$ (Very feebly ionised)

When a drop of strong acid, say HCl, is added, the H^+ ions furnished by HCl combine with CH_3COO^- ions to form feebly ionised CH_3COOH whose ionisation is further suppressed due to common ion effect. Thus, there will be a very slight effect in the overall H^+ ion concentration or pH value.

When a drop of NaOH is added, it will react with free acid to form undissociated water molecules.

$CH_3COOH + OH^- \leftrightarrow CH_3COO^- + H_2O$

Thus, OH^- ions furnished by a base are removed and pH of the solution is practically unaltered.

Buffer capacity:

The property of buffer solution to resist alteration in its pH value is known as buffer capacity. It has been found that if the ratio [Salt]/[Acid] or [Salt]/[Base] is unity, the pH of a particular buffer does not change at all. Buffer capacity is defined quantitatively as number of moles of acid or base added in one litre of solution as to change the pH by unity,

i.e..

Buffer capacity

(φ) = (No.of moles of acid or base added to 1 litre)/(Change in pH)

or $\varphi = \delta b/\delta(ph)$

where δb → number of moles of acid or base added to 1 litre solution and δ(pH) → change in pH.

Buffer capacity is maximum:

(i) When [Salt] = [Acid], i.e., $pH = pK_a$ for acid buffer

(ii) When [Salt] = [Base], i.e., $pOH = pK_b$ for base buffer under above conditions, the buffer is called efficient.

Henderson's Equation (pH of a buffer):

(i) Acidic buffer:

It consists of a mixture of weak acid and its salt (strong electrolyte). The ionisation of the weak acid, HA, can be shown by the equation

$HA \leftrightarrow H^+ + A^-$

Applying law of mass action,

$K_a = H^+A^- /[HA]$

It can be assumed that concentration of A^- ions from complete ionisation of the salt**BA** is too large to be compared with concentration of A^- ions from the acid HA.

$BA \leftrightarrow B^+ + A^-$

Thus, ***[HA]*** = Initial concentration of the acid as it is feebly ionised in presence of common ion

and $[A^-]$ = Initial concentration of the salt as it is completely ionised.

So $[H^+]$ = Ka . [Acid]/[Salt] ...... (iii)

Taking logarithm and reversing sign,

$-\log [H^+] = -\log K_a - \log[Acid]/[Salt]$

or $pH = \log[Salt]/[Acid] - \log K_a$

or $pH = pK_a + \log[Salt]/[Acid]$ ...... (iv)

This is known as Henderson's equation.

When [Salt]/[Acid] = 10 , then

$pH = 1 + pK_a$

and when [Salt]/[Acid] , then

$pH = pK_a -1$

So weak acid may be used for preparing buffer solutions having pH values lying within the ranges $pK_a + 1$ and $pK_a - 1$. The acetic acid gas a pK_a of about 4.8; it may, therefore, be used for making buffer solutions with pH values lying roughly within the ranges 3.8 to 5.8.

(ii) Basic offer:

It consists of a weak base and its salt with strong acid. Ionization of a weak base, BOH, can be represented by the equation.

$BOH \leftrightarrow B^+ + OH^-$

Applying law of mass action,

$K_b = [B^+][OH^-]/[BOH]$ .... (i)

or $[OH^-] = K_b [BOH]/[B^+]$ ...... (ii)

As the salt is completely ionized, it can be assumed that whole of B^+ ion concentration comes from the salt and contribution of weak base to B^+ ions can be ignored.

$BA \leftrightarrow B^+ + A^-$ (Completely ionised)

So $[OH^-]= K_b[Base]/[Salt]$ .... (iii)

or $pOH = \log[Salt]/[Base] \log K_b$

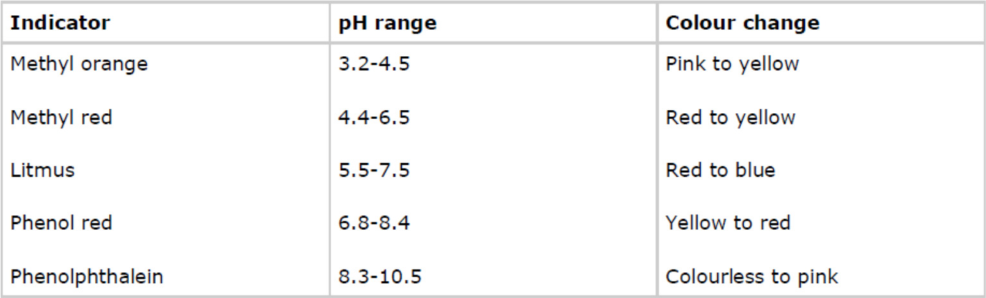
or $pOH = pKb + \log[Salt]/[Base]$ ...... (iv)

Knowing pOH, pH can be calculated by the application of the formula.

$pH + pOH = 14$

THEORY OF INDICATORS:

An **indicator** is a substance which is used to determine the end point in a titration. In acid-base **titrations**, organic substances (weak acids or weak bases) are generally used as **indicators**. They change their colour within a certain pH range. The colour change and the pH range of some common **indicators** are tabulated below:



Indicator	pH range	Colour change
Methyl orange	3.2-4.5	Pink to yellow
Methyl red	4.4-6.5	Red to yellow
Litmus	5.5-7.5	Red to blue
Phenol red	6.8-8.4	Yellow to red
Phenolphthalein	8.3-10.5	Colourless to pink

Theory of acid-base indicators: Two theories have been proposed to explain the change of colour of acid-base **indicators** with change in pH.

1. Ostwald's theory: According to this theory:

(a) The colour change is due to ionisation of the acid-base indicator. The unionised form has different colour than the ionised form.

(b) The ionisation of the **indicator** is largely affected in acids and bases as it is either a weak acid or a weak base. In case, the **indicator** is a weak acid, its ionisation is very much low in acids due to common H^+ ions while it is fairly ionised in alkalies. Similarly if the **indicator** is a weak base, its ionisation is large in acids and low in alkalies due to common OH^- ions.

Considering two important indicators **phenolphthalein** (a weak acid) and **methyl orange** (a weak base), Ostwald theory can be illustrated as follows:

Phenolphthalein: It can be represented as HPh. It ionises in solution to a small extent as:

$HPh \leftrightarrow H^+ + Ph^-$

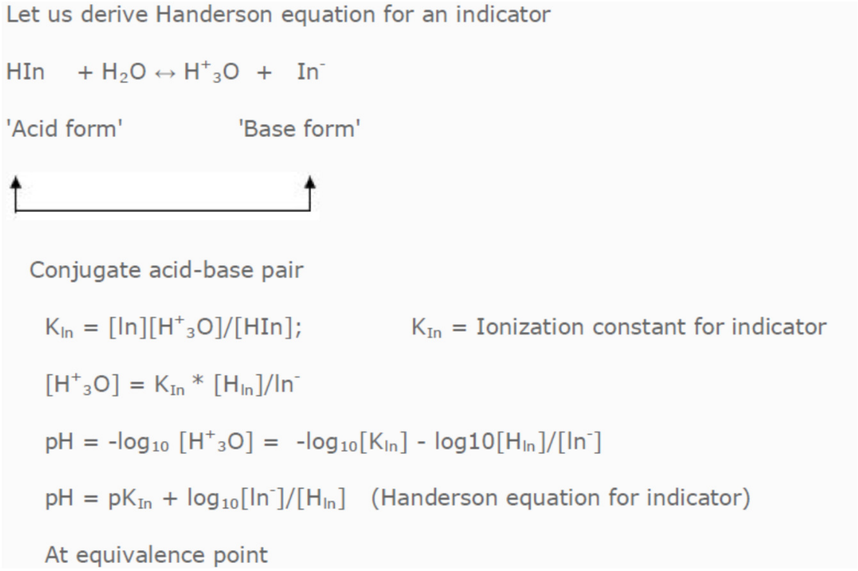
Colourless Pink

Applying law of mass action,

$K = [H^+][Ph^-]/[HpH]$

The undissociated molecules of **phenolphthalein** are colourless while Ph^- ions are pink in colour. In presence of an acid the ionisation of HPh is practically negligible as the equilibrium shifts to left hand side due to high concentration of H^+ ions. Thus, the solution would remain colourless. On addition of alkali, hydrogen ions are removed by OH^- ions in the form of water molecules and the equilibrium shifts to right hand side. Thus, the concentration of Ph^- ions increases in solution and they impart pink colour to the solution.

Let us derive Handerson equation for an indicator



Let us derive Handerson equation for an indicator

$HIn + H_2O \leftrightarrow H^+{}_3O + In^-$

'Acid form' 'Base form'

Conjugate acid-base pair

$K_{In} = [In][H^+{}_3O]/[HIn]$; K_{In} = Ionization constant for indicator

$[H^+{}_3O] = K_{In} * [H_{In}]/In^-$

$pH = -\log_{10} [H^+{}_3O] = -\log_{10}[K_{In}] - \log10[H_{In}]/[In^-]$

$pH = pK_{In} + \log_{10}[In^-]/[H_{In}]$ (Handerson equation for indicator)

At equivalence point

$[In^-] = [HIn]$ and $pH = pK_{In}$

Methyl orange: It is a very weak base and can be represented as MeOH. It is ionized in solution to give Me^+ and OH^- ions.

$MeOH \leftrightarrow Me^+ + OH^-$

Yellow Red

Applying law of mass action,

$K = [Me^+][OH^-]/[MeOH]$

In presence of an acid, OH^- ions are removed in the form of water molecules and the above equilibrium shifts to right hand side. Thus, sufficient Me^+ ions are produced which impart red colour to the solution. On addition of alkali, the concentration of OH" ions increases in the solution and the equilibrium shifts to left hand side, i.e., the ionisation of MeOH is practically negligible. Thus, the solution acquires the colour of unionised **methyl orange** molecules, i.e., yellow.

This theory also explains the reason why **phenolphthalein** is not a suitable**indicator** for **titrating** a weak base against strong acid. The OH" ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i.e., pH is not reached to 8.3. Thus, the solution does not attain pink colour. Similarly, it can be explained why **methyl orange** is not a suitable **indicator**for the **titration** of weak acid with strong base.

1. Quinonoid theory:

According to this theory:

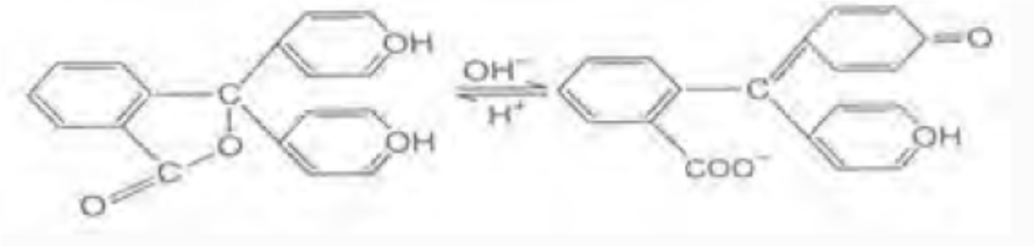
(a) The **acid-base indicators** exist in two tautomeric forms having different structures. Two forms are in equilibrium. One form is termed benzenoid form and the other quinonoid form.

(b) The two forms have different colors. The color change in due to the interconversation of one tautomeric form into other.

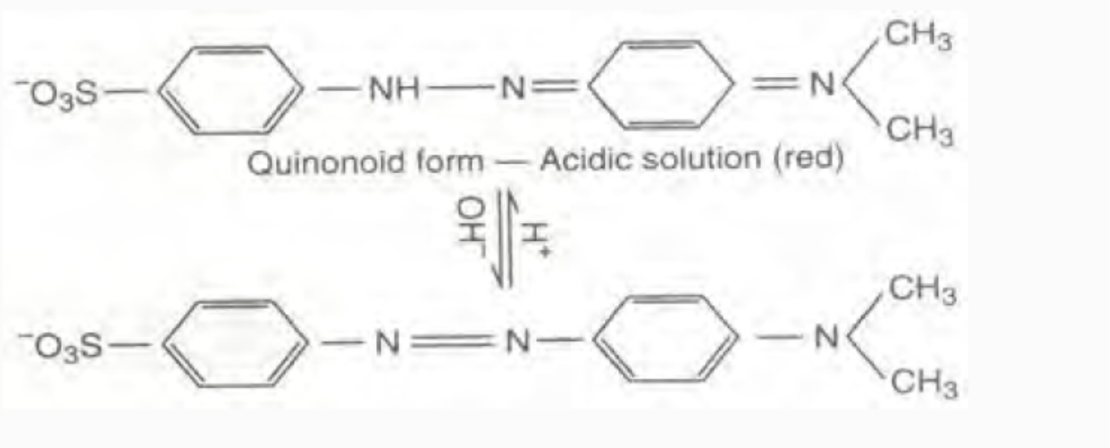
(c) One form mainly exists in acidic medium and the other in alkaline medium.

Thus, during **titration** the medium changes from acidic to alkaline or vice-versa. The change in pH converts one tautomeric form into other and thus, the colour change occurs.

Phenolphthalein has benziod form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.



Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The color of benzenoid form is yellow while that of quinoniod form is red.



Selection of suitable indicator or choice of indicator

The neutralisation reactions are of the following four types:

(i) A strong acid versus a strong base. (Fig. 10.1)

(ii) A weak acid versus a strong base. (Fig. 10.2)

(iii) A strong acid versus a weak base. (Fig. 10.3)

(iv) A weak acid versus a weak base. (Fig. 10.4)

In order to choose a suitable **indicator**, it is necessary to understand the pH changes in the above four types of **titrations**. The change in pH in the vicinity of theequivalence point is most important for this purpose. The curve obtained by plotting pH as ordinate against the volume of alkali added as abscissa is known as neutralisation or **titration curve**. The **titration curves** of the above four types of neutralisation reactions are shown in Fig. 10.1, 10.2, 10.3 and 10.4.

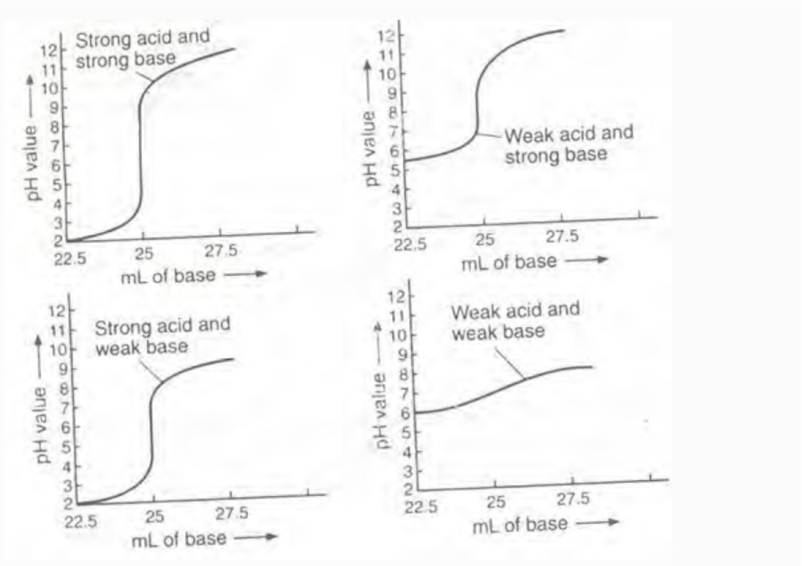
In each case 25 mL of the acid (N/10) has been **titrated** against a standard solution of a base (N/10). Each **titration curve** becomes almost vertical for somedistance (except curve 10.4) and then bends away again. This region of abrupt change in pH indicates the equivalence point. For a particular **titration**, the **indicator** should be so selected that it changes its colour within vertical distance of the curve.

(i) Strong acid vs. strong base:

pH curve of strong acid (say HCI) and strong base (say NaOH) is vertical over almost the pH range 4-10. So the indicators **phenolphthalein** (pH range 8.3 to 10.5), methyl red (pH range 4.4-6.5) and **methyl orange** (pH range 3.2-4.5) are suitable for such a **titration**.

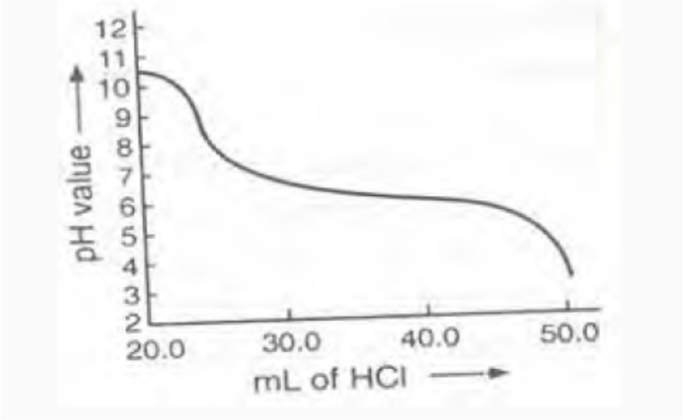
(ii) Weak acid vs. weak base:

pH curve of weak acid (say CH_3COOH of oxalic acid) and strong base (say NaOH) is vertical over the approximate pH range 7 to 11. So phenolphthalein is the suitable indicator for such a titration.



(iii) Strong acid vs. weak base:

pH curve of strong acid (say HCl or H_2SO_4 or HNO_3) with a weak base (say NH_4OH) is vertical over the pH range of 4 to 7. So the **indicators** methyl red and **methyl orange** are suitable for such a **titration**.



(iii) Weak acid vs. weak base:

pH curve of weak acid and weak base indicates that there is no vertical part and hence, no suitable **indicator** can be used for such a **titration**.

Titration of soluble carbonate with strong acid.

pH curve of sodium carbonate with HCI shows two inflection points (Fig. 10.5). First inflection point (pH 8.5) indicates conversion of carbonate into bicarbonate.

$Na_2CO_3 + HCI \rightarrow NaHCO_3 + NaCl$

As the inflection point lies in the pH range 8 to 10, phenolphthalein can be used to indicate the above conversion. The second inflection point (pH 4.3) indicates the following reaction:

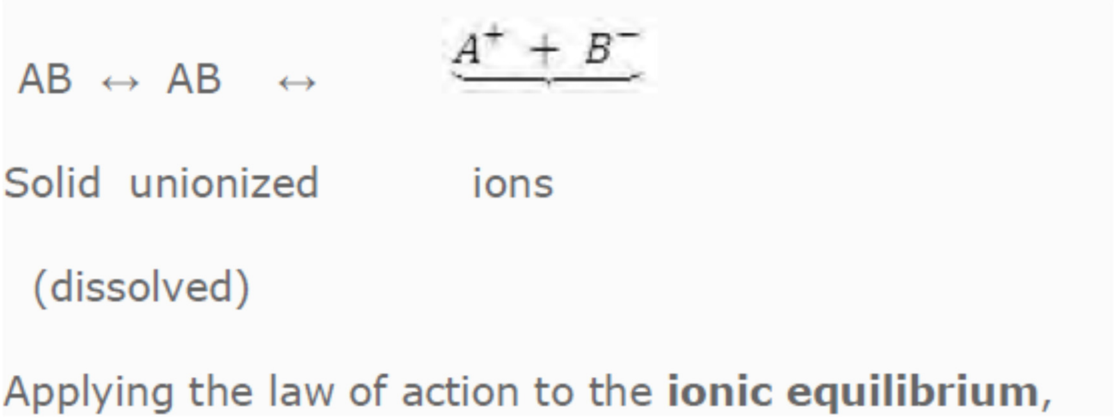
$NaHCO_3 + HCI \rightarrow NaCl + CO_2 + H_2O$

As the point lies between 3 to 5, **methyl orange** can be used.

SOLUBILITY PRODUCT:

If to a given amount of solvent at a particular temperature, a solute is added gradually in increasing amounts, a stage is reached when some of the solute remains undissolved, no matter how long we wait or how vigorously we stir. The solution is then said to be saturated. A **solution which remains in contact with undissolved solute is said to be saturated**. At saturated stage, the quantity of the solute dissolved is always constant for the given amount of a particular solvent at a definite temperature.

In case the solute is an electrolyte, its ionisation occurs in solution and degree of dissociation depends on the concentration of dissolved electrolyte at a particular temperature. Thus, in a saturated solution of an electrolyte two equilibria exist and can be represented as:



$$AB \leftrightarrow AB \leftrightarrow \underbrace{A^+ + B^-}$$

Solid unionized ions

(dissolved)

Applying the law of action to the **ionic equilibrium**,

$[A^+][B^-]/[AB]$

Since the solution is saturated, the concentration of unionised molecules of the electrolyte is constant at a particular temperature, i.e., [AB] = K'= constant.

Hence, $[A^+]\,[B^-] = K[AB] = KK = K_s$ (constant)

K_s is termed as the **solubility product**. It is defined as the product of the concentration of ions in a saturated solution of an electrolyte at a given temperature.

Consider, in general, the electrolyte of the type A_xB_y which is dissociated as:

$A_xB_y \leftrightarrow xA^{y+} + yB^{x-}$

Applying law of mass action,

$[Ay+]x[Bx-]y/[A_xB_y] = K$

When the solution is saturated,

$[A_xB_y] = K'$ (constant)

or $[A^{y+}]^x[B^{x-}]^y = K\,[A_xB_y] = KK' = K_s$ (constant)

Thus, **solubility product** is defined as the product of concentrations of the ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte at a given temperature when the solution is saturated.

Note: **Solubility product** is not the **ionic product** under all conditions but only when the solution is saturated.

Different Expressions for Solubility Products

(i) Electrolyte of the type AB:

Its ionisation is represented as:

$AB \leftrightarrow A^{+} + B^{-}$

Thus, $K_s = [A^{+}][B^{-}]$

$AgCl \leftrightarrow Ag^{+} + Cl^{-}; K_s = [Ag^{+}][Cl^{-}]$

$BaSO_4 \leftrightarrow Ba^{2+} + SO^{-2}_4; K_s = [Ba^{2+}][SO^{-2}_4]$

(ii) Electrolyte of the type AB_2:

Its ionisation is represented as:

$AB_2 \leftrightarrow A^{2+} + 2B^{-}$

Thus, $K_s = [A^{2+}][B^{-}]^2$

$PbCl_2 \leftrightarrow Pb^{2+} + 2Cl^{-}; K_s = [Pb^{2+}][Cl^{-}]^2$

$CaF_2 \leftrightarrow Ca^{2+} + 2F^{-}; K_s = [Ca^{2+}][F^{-}]^2$

(iii) Electrolyte of the type A_2B:

Its ionisation is represented as:

$A_2B \leftrightarrow 2A^{2+} + B^{2-}$

Thus, $K_s = [A^{+}]^2[B^{2-}]$

$Ag_2CrO_4 \leftrightarrow 2Ag^+ + CrO^{-2}_4$; $K_s = [Ag^+]^2[CrO^{-2}_4]$

$H_2S \leftrightarrow 2H^+ + S2^-$; $K_s = [H^+]^2[S^{2-}]$

(iv) Electrolyte of the type A_2B_3:

Its ionisation is represented as:

$A_2B_3 \leftrightarrow 2A^{3+} + 3B^{2-}$

Thus, $K_s = [A^{3+}]^2[B^{2-}]^3$

$As_2S_3 \leftrightarrow 2As^{3+} + 3S^{2-}$; $K_s = [As^{3+}]^2[S^{2-}]^3$

$Sb_2S_3 \leftrightarrow 2Sb^{3+} + 3S2^-$; $K_s = [Sb^{3+}]^2[S^{2-}]^3$

(v) Electrolyte of the type AB_3:

Its ionisation is represented as:

$AB_3 \leftrightarrow A^{3+} + 3B^-$

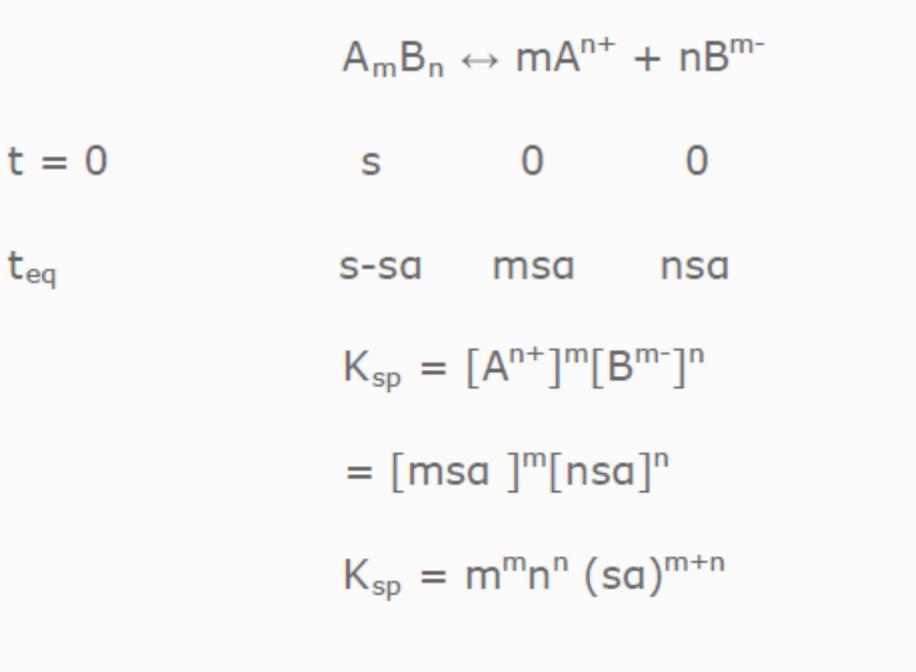
Thus, $K_s = [A^{3+}][B^{2-}]^3$

$Fe(OH)_3 \leftrightarrow Fe^{3+} + 3OH^-$; $K_s = [Fe^{3+}][OH^-]^3$

$AH_3 \leftrightarrow Al^{3+} + 3I^-$; $K_s = [Al^{3+}][I^-]^3$

Solubility product of a weak electrolyte:

Let degree of ionization of weak electrolyte A_mB_n be 'α'.



$$A_mB_n \leftrightarrow mA^{n+} + nB^{m-}$$

$t = 0$	s	0	0
t_{eq}	$s-s\alpha$	$ms\alpha$	$ns\alpha$

$$K_{sp} = [A^{n+}]^m[B^{m-}]^n$$

$$= [ms\alpha\ ]^m[ns\alpha]^n$$

$$K_{sp} = m^m n^n\ (s\alpha)^{m+n}$$

Criteria of precipitation of an electrolyte:

A very useful conclusion is derived from the **solubility product** concept. No precipitation of the electrolyte occurs if the **ionic product** is less than the**solubility product**, i.e., the solution has not reached the saturation stage.

Case I: When $K_{ip}<K_{sp}$, then solution is unsaturated in which more solute can be dissolved.

Case II: When $K_{ip} = K_{sp}$, then solution is saturated in which no more solute can be dissolved.

Case III: When $K_{ip} > K_{sp}$, then solution is supersaturated and precipitation takes place.

When the **ionic product** exceeds the **solubility product**, the equilibrium shifts towards left hand side, i.e., increasing the concentration of undissociated molecules of the electrolyte. As the solvent can hold a fixed amount of electrolyte at a definite temperature, the excess of the electrolyte is thrown out from the solution as precipitate.

Thus, for the precipitation of an electrolyte, it is necessary that the **ionic product**must exceed its **solubility product** For example, if equal volumes of 0.02 M $AgN0_3$solution and 0.02 M K_2Cr0_4 solution are mixed, the precipitation of Ag_2Cr0_4 occurs as the **ionic product** exceeds the **solubility product** of Ag_2Cr0_4 which is 2×10^{-12}

In the resulting solution,

$[Ag^+] = 0.02/2 = 0.01 = 1*10^{-2}$ M

and $[CrO^{2-}_4] = 0.02/2 = 0.01 = 1*10^{-2}$ M

Ionic product of $Ag_2CrO_4 = [Ag^+]^2 [CrO^{2-}_4]$

$= (1\times10^{-2})^2 (1\times10^{-2})$

$= 1 \times 10^{-6}$

1×10^{-6} is higher than 2×10^{-12} and thus precipitation of Ag_2CrO_4 occurs.

Applications of Solubility Product

(i) Purification of common salt

Natural common salt consists of many insoluble and soluble impurities. Saturated solution of common salt is prepared and insoluble impurities are filtered off. Hydrogen chloride gas (HCl) is circulated through the saturated solution. HCl and NaCl dissociate into their respective ions as:

$NaCl \leftrightarrow Na^+ + Cl^-$

$HCl \leftrightarrow H^+ + Cl^-$

The concentration of Cl^- ions increases considerably in solution due to ionization HCl. Hence, the ionic product $[Na^+][Cl^-]$ exceeds the solubility product of sodium chloride and, therefore, pure sodium chloride precipitates out from solution.

(ii) Salting out of soap

Soap is a sodium salt of higher acids. From the solution, soap is precipitated by the addition of concentrated solution of sodium chloride. Soap and sodium chloride are present in the form of ions.

$C_nH_{2n+1}COONa \leftrightarrow C_nH_{2n+1}COO^- + Na^+$

Soap

$NaCl \leftrightarrow Na^+ + Cl^-$

Thus, the concentration of Na+ ions increases considerably on addition of NaCl solution. Hence, the ionic product $[C_nH_{2n+1}COO^-]$ $[Na^+]$ exceeds the solubility product of soap and, therefore, soap precipitates out from the solution.

(iii) Manufacture of sodium bicarbonate (baking soda):

In Solvay's soda process. CO_2 gas is passed through ammonical brine to precipitate out $NaHCO_3$.

$NH_4OH + CO_2 \rightarrow NH_4HCO_3$

$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$

$NaHCO_3$ is precipitated first because of its lower solubility product as compared to those of NH_4Cl, NH_3HCO_3 and NaCl.

Thus, baking soda ($NaHCO_3$) can be quantifiably estimated.

(iv) Application of solubility product in quantitative analysis

1. Estimation of barium as barium sulphate:

H_2SO_4 as precipitating agent is added to the aqueous solution of $BaCl_2$.

$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$

Precipitation of $BaSO_4$ takes place when its ionic product exceeds solubility product. H_2SO_4 is added in slight excess to ensure complete precipitation. Large excess of H_2SO_4 is harmful for complex formation.

2. Estimation of silver as silver chloride:

NaCl solution is added to the silver nitrate solution, slight excess of NaCl is added to ensure complete precipitation.

$AgNO_3 + NaCl \rightarrow AgCl + NaBO_3$

Again, precipitation of AgCl takes place when ionic product of AgCl exceeds its solubility product.

3. In a similar manner. We estimate lead as lead chromate, calcium as calcium oxalate, etc.

(i) Precipitation of the sulphides of group II and IV

Hydrogen sulphide is a weak electrolyte and is used for the precipitation of various sulphides of group II and IV in quantitative analysis.

It ionizes to a small extent in water:

$H_2S \leftrightarrow 2H^+ + S^{2-}$

Applying law of mass action,

$K = ([H^+]^2 [S^{2-}])/[H_2 S]$

The concentrations of $S2^-$ ions can be decreased by increasing concentration of H^+ions and it can be increased by decreasing concentration of H^+ ions. In group II, lower concentration of sulphide ions is required as the solubility products of the sulphides of group II are low while higher concentration of sulphide ions is required in group IV as the solubility products

of the suphides of group IV are high. The values of solubility products of various sulphides are given below.

	Metal sulphide	Solubility product
Group II	Bi_2S_3	1.6×10^{-72}
	HgS	4×10^{-54}
	CuS	1×10^{-44}
	PbS	5×10^{-29}
	CdS	1.4×10^{-28}
Group IV	Cos	3×10^{-26}
	NiS	1.4×10^{-24}
	ZnS	1.0×10^{-22}
	MnS	1.4×10^{-15}

The concentration of $S2^-$ ions in group II is lowered by maintaining acidic medium. In the presence of HCl, the ionization of H_2S is suppressed due to common ion effect. The concentration is so adjusted that only ionic products of the sulphides of group II exceed their solubility products and, therefore, get precipitated. However, CdS has somewhat higher value.

For its precipitation, dilution of the solution is done which increases ionization of H_2S and thereby increasing concentration of $S2^-$ ions.

In group IV, higher concentration of $S2^-$ ions is needed. This is done by changing the medium for acidic to alkaline. Ammonium hydroxide is added, the OH^- ions furnished by NH_4OH remove H^+ ions from solution in the form of water molecules as,

$H^+ + OH^- \leftrightarrow H_2O$

More of the ionization of H_2S occurs and, thus, concentration of $S2^-$ ions increases. It becomes so high that ionic products of the sulphides of group IV exceed their solubility products add they get precipitated.

(i) Precipitation of III group hydroxides

When NH_4OH is added in presence of NH_4Cl then precipitation of II group hydroxides takes place, i.e., $Al(OH)_3$, $Fe(OH)_3$ and $Cr(OH)_3$ are precipitated. Solubility product of III group hydroxides is less than those of higher group hydroxides.

$NH_4Cl \rightarrow NH^+_4 + Cl^-$

$NH_4OH \leftrightarrow NH^+_4 + OH^-$

NH^+_4 ion furnished by NH_4Cl lowers the ionisatin of NH_4OH and hence the concentration of hydroxide ion OH^-. At low concentration of hydroxide ion only III group hydroxides precipitate.

Fractional Precipitation

It is a technique of separating two or more ions from a solution by adding a reagent that precipitates first one ion and then the second.

Let us suppose 0.1 M Ba^{2+} and 0.1 M Sr^{2+} in aqueous solution. K_2CrO_4 is added as precipitating agent. K_{sp} $BaCrO_4$ is 1.2×10^{-10} and K_{sp} $SrCrO_4$ is 3.5×10^{-5}.

$[CrO^{2-}_4]$concentration required to precipitate $BaCrO_4$

$= K_{sp}/[Ba^{2+}] = 1.2 * 10^{-10}/0.1 = 1.2 * 10^{-9}$

$BaCrO_4$ will precipitate first because it requires low concentration of CrO^{2-}_4 ions. On addition of chromate ions, $BaCrO_4$ starts precipitating when chromate ion concentration reaches 1.2×10^{-9} M. When CrO^{2-}_4 ion concentration reaches upto 3.5×10^{-4} M, then $SrCrO_4$ also starts precipitating.

Remaining concentration of Ba^{2+} when $SrCrO_4$ starts precipitation.

$=(K_{sp}\ BaCrO_4)/[CrO_4^{2-}] = (1.2\times10^{-10})/(3.5\times10^{-4}) = 3.4\times10^{-7}$ M

% remaining concentration = $(3.4 * 10^{-7})/0.1 * 100$

= 0.00034%

Stability Constant

Let us consider dissociation of the ion $FeBr^+$.

$FeBr^+ \leftrightarrow Fe^{2+} + Br^-$

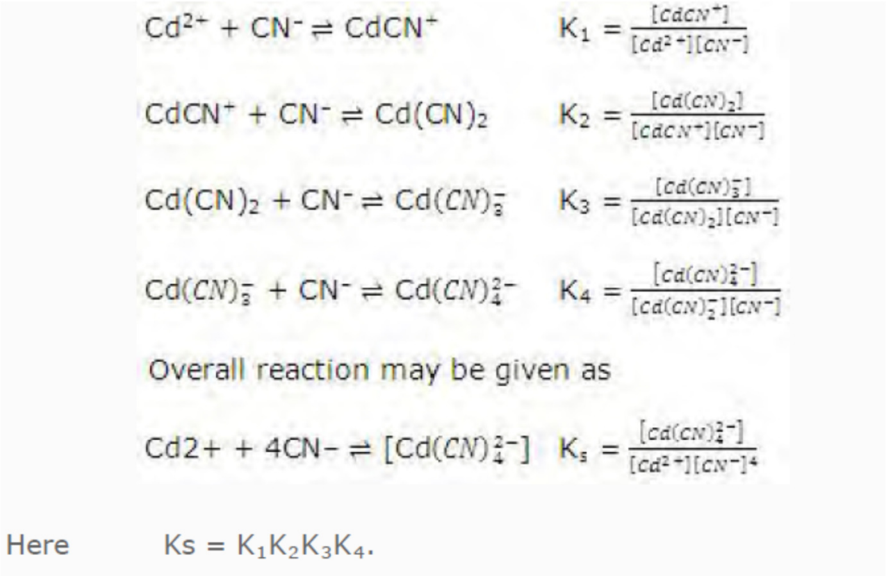
Dissociation constant for above equilibria may be given as

$K_d = [Fe^{2+}][Br^-]/[FeBr^+]$

Reciprocal of dissociation constant is called stability constant.

$K_s = [FeBr^+]/([Fe^{2+}]\ [Br^-])$

Let us consider the formation of complex $K_2Cd(CN)_4$, Complex ion is $Cd(CN_4^{2-})$ where oxidation state of central metal Cd^{2+} is (2+). Complexing process proceeds in four steps as



$Cd^{2+} + CN^- \rightleftharpoons CdCN^+ \qquad K_1 = \frac{[CdCN^+]}{[Cd^{2+}][CN^-]}$

$CdCN^+ + CN^- \rightleftharpoons Cd(CN)_2 \qquad K_2 = \frac{[Cd(CN)_2]}{[CdCN^+][CN^-]}$

$Cd(CN)_2 + CN^- \rightleftharpoons Cd(CN)_3^- \qquad K_3 = \frac{[Cd(CN)_3^-]}{[Cd(CN)_2][CN^-]}$

$Cd(CN)_3^- + CN^- \rightleftharpoons Cd(CN)_4^{2-} \qquad K_4 = \frac{[Cd(CN)_4^{2-}]}{[Cd(CN)_3^-][CN^-]}$

Overall reaction may be given as

$Cd2+ + 4CN- \rightleftharpoons [Cd(CN)_4^{2-}] \qquad K_s = \frac{[Cd(CN)_4^{2-}]}{[Cd^{2+}][CN^-]^4}$

Here $Ks = K_1K_2K_3K_4$.

Significance of stability constant:

Greater will be the value of stability constant more stable will be the complex.

Note :

(a) If on addition of a common ion in a salt solution (sparingly soluble), formation of complex ion takes place, then ionization increases, i.e., equilibrium shifts towards right hand direction to maintain the value of K_{sp} constant. It means, addition of common ion in the case of complex formation increases the solubility of the sparingly soluble salt which is against the concept of common ion effect.

(b) When we add an electrolyte to another electrolyte solution having no common ion, then ionization of the later increases.

(c) For a given electrolyte solubility product is always constant at a particular temperature.

Solubility of Metal Hydroxides in Acid Medium

H^+ ion furnished by the medium effects the solubility of metal hydroxide, say $M(OH)^2$, because of neutralization of OH^- ion by H^+ ion.

$M(OH)^2 \leftrightarrow M^{2+} + 2OH^-$

K_{sp} of $M(OH)^2 = [M2^+][OH^-]^2$

$[M^{2+}] = K_{sp}/[OH^-]^2$ $[H^+]$ $[OH^-] = K_w = 10^{-14}$

$[OH^-]^2 = 10^{-28}/[H^+]^2$

From Eqs. (i) and (ii), we have

$[M^{2+}] = K_{sp}[H^+]^2/10^{-28}$

Possible questions

Part A

1. Precipitation takes place when

   a) Ionic product of solution is equal to solubility product

   b) Ionic product of the solution is less than solubility product

   c) **Ionic product of the solution is exceeds solubility product**

   d) Square of the ionic product is equal to solubility product

2. Precipitation takes place when the product of concentration of ions

   a) is equal to solubility product b) is less than solubility product c) **exceeds solubility product** d) Square of the ionic product is equal to solubility product

3. When the ionic product of the ions in the solution exceeds solubility product then,

   a) The precipitate will dissolve b) **Precipitation takes place**

   c) The solution is saturated d) The solution is dilute

4. This is not an application of solubility product

   a) Determination of solubility of a sparingly soluble salt

   b) Predicting precipitation reactions

   c) Purification of common salt

   d) Ostwald's dilution law

5. A hydrogen ion indicator is a substance

   a) Which changes its colour with variation in pH of the solution to which it is added

   b) Which changes its colour with variation in ionic strength of the solution to which it is added c) Which changes its pH with variation in colour of the solution to which it is added d) Which changes its dielectric constant with variation in pH of the solution to which it is added

6. In the acidic solution with pH above 4.4 methyl orange gives

   a) Red colour b) Blue colour c) **Yellow colour** d) Green colour

7. In a solution with pH below 3 methyl orange gives

   a) **Red colour** b) Blue colour c) Yellow colour d) Green colour

8. The pH range over which methyl orange can be used as an indicator lies between

a) Below pH 3 b) Between 8 & 10 c) Between 6 & 8 d) **Between pH 3.0 and 4.4**

9. The precipitates of sulphides are soluble in

a) Basic solution b) Buffer solution c) **Acidic solution** d) Neutral solution

10. Cations of third group gets precipitated as hydroxides in presence of

a) **Ammonium chloride** b) Sodium chloride

c) Potassium chloride d) Magnesium sulphate

11. Silver chromate is a

a) **A sparingly soluble salt** b) Highly soluble salt

c) Used as an indicator d) used in buffer solutions,

12. Which is not a sparingly soluble salt,

a) Silver chromate b) Silver chloride c) Lead sulphide d) **Sodium chloride**

13. Precipitation takes place when

a) Ionic product of solution is equal to solubility product

b) Ionic product of the solution is less than solubility product

c) **Ionic product of the solution is exceeds solubility product**

d) Square of the ionic product is equal to solubility product

14. Precipitation takes place when the product of concentration of ions

a) is equal to solubility product b) is less than solubility product

c) **exceeds solubility product** d) Square of the ionic product is equal to solubility product

15. When the ionic product of the ions in the solution exceeds solubility product then,

a) The precipitate will dissolve b) **Precipitation takes place**

c) The solution is saturated d) the solution is dilute

16. This is not an application of solubility product

a) Determination of solubility of a sparingly soluble salt

b) Predicting precipitation reactions

c) Purification of common salt

d) **Ostwald's dilution law**

17. Precipitation takes place when

a) Ionic product of solution is equal to solubility product

b) Ionic product of the solution is less than solubility product

c) **Ionic product of the solution is exceeds solubility product**

d) Square of the ionic product is equal to solubility product

18. Precipitation takes place when the product of concentration of ions

a) is equal to solubility product b) is less than solubility product

c) **exceeds solubility product** d) Square of the ionic product is equal to solubility product

19. When the ionic product of the ions in the solution exceeds solubility product then,

a) The precipitate will dissolve b) **Precipitation takes place**

c) The solution is saturated d) the solution is dilute

20. This is not an application of solubility product

a) Determination of solubility of a sparingly soluble salt b) Predicting precipitation reactions c) Purification of common salt d) **Ostwald's dilution law**

Part B

1. What is meant by a buffer solution
2. What are the types of buffer solutions
3. What is meant by Hendersen equation
4. State solubility product principle
5. Write notes on salting out of soap
6. How pure sodium chloride is prepared
7. What is meant by an indicator
8. What is meant by the working range of an indicator
9. What is a titration curve
10. How indicators are selected based on the titration curve.

Part C

1. Explain the theory of acid-base indicators.

2. Discuss any two applications of solubility product in detail.

3. Explain in detail about the qualitative treatment of acid-base titration curves.

4. What is meant by a buffer solution? Derive Hendersen equation for a buffer solution and write its application.

5. Discuss any two applications of solubility product in detail.

Questions	**Opt-1**	**Opt-2**	**Opt-3**	**Opt-4**	**Answer**
UNIT V					
A Buffer solution is a solution whose	PH does not change much even on the addition of small amounts of acid or base.	PH does change much even on the addition of small amounts of acid or base.	Ionic concentration does not change much even on the addition of small amounts of acid or base.	Ionic concentration change much even on the addition of small amounts of acid or base.	PH does not change much even on the addition of small amounts of acid or base.
A solution of sodium chloride in water. Its PH is	4	7	10	8 to 10	7
The capacity of a solution to resist alteration in its PH, is known as	Salt hydrolysis	indicators	Buffer solutions	Buffer capacity	Buffer capacity
An acidic buffer solution is	Weak acid its salt	Weak base and its salt	Strong acid and its salt	Strong base and its salt	Weak acid its salt
An acidic buffer solution is	Acetic acid and ammonium acetate	Ammonium hydroxide & ammonium chloride	HCl and sodium chloride	NaOH and sodium acetate	Acetic acid and ammonium acetate
An basic buffer solution is	Weak acid its salt	Weak base and its salt	Strong acid and its salt	Strong base and its salt	Weak base and its salt
A basic buffer solution is	Acetic acid and ammonium acetate	Ammonium hydroxide & ammonium chloride	HCl and sodium chloride	NaOH and sodium acetate	Ammonium hydroxide & ammonium chloride
PH of a buffer solution can be calculated using	Ostwald dilution law	Commion ion effect	Henderson equation	Dissociation constant of the acid	Henderson equation
Acid-base indicator is a substance	Which changes its colour with variation in PH of the solution to which it is added.	Which changes its colour with variation in ionic strength of the solution to which it is added	Which changes its PH with variation in colour of the solution to which it is added	Which changes its dielectric constant with variation in PH of the solution to which it is added	Which changes its colour with variation in PH of the solution to which it is added
A hydrogen ion indicator is a substance	Which changes its colour with variation in PH of the solution to which it is added.	Which changes its colour with variation in ionic strength of the solution to which it is added	Which changes its PH with variation in colour of the solution to which it is added	Which changes its dielectric constant with variation in PH of the solution to which it is added	Which changes its colour with variation in PH of the solution to which it is added
In the acidic solution with PH above 4.4 methyl orange gives	Red colour	Blue colour	Yellow colour	Green colour	Yellow colour
In a solution with PH below 3 methyl orange gives	Red colour	Blue colour	Yellow colour	Green colour	Red colour
The PH range over which methyl orange can be used as an indicator lies between	Below PH 3	Between 8 & 10	Between 6 & 8	Between PH 3.0 and 4.4	Between PH 3.0 and 4.4
Below PH 8.3 Phenopthalein gives	Red colour	Blue colour	Yellow colour	Colourless solution	Colourless solution
Above PH 10 phenopthalein gives	Red colour	Blue colour	Yellow colour	Pink colour	Pink colour
Phenopthalein can be used to determine PH over the range	4 to 6	8.3 to 10	7 to 7.5	6 to 8	8.3 to 10
The working range of phenopthalein indicator is	4 to 6	8.3 to 10	7 to 7.5	6 to 8	8.3 to 10
The working range of methyl orange indicator is	Below PH 3	Between 8 & 10	Between 6 & 8	Between PH 3.0 and 4.4	Between PH 3.0 and 4.4
As per Ostwald theory an acid base indicator is a	Weak organic acid	Strong organic base	A sparingly soluble salt	Insoluble substance	Weak organic acid
As per Ostwald theory an acid base indicator is a	Weak organic base	Strong organic base	A sparingly soluble salt	Insoluble substance	Weak organic base
As per Ostwald theory an hydrogen ion indicator is a	Weak organic acid	Strong organic base	A sparingly soluble salt	Insoluble substance	Weak organic acid
As per Ostwald theory an hydrogen ion indicator is a	Weak organic base	Strong organic base	A sparingly soluble salt	Insoluble substance	Weak organic base
The product of the concentrations of the ions representating the dissociation of the electrolyte is called	Ostwalds dilution law	Common ion effect	Solubility product	Buffer capacity	Solubility product
Example for a sparingly soluble salt is	Silver chloride	Sodium chloride	Potassium chloride	Potassium nitrate	Silver chloride

Example for a sparingly soluble salt is	PbS	Sodium chloride	Potassium chloride	Potassium nitrate	PbS
Example for a sparingly soluble salt is	Sodium chloride	Barium sulphate	Potassium chloride	Potassium nitrate	Barium sulphate
The solubility of a sparingly soluble salt can be determined using	Common ion effect	Buffer capacity	Solubility product	Dissociation constant	Solubility product
One among the applications of solubility product is	Predicting precipitation reactions	Predicting Common ion effect	Predicting Buffer capacity	Predicting Dissociation constant	Predicting precipitation reactions
One among the applications of solubility product is	Determine the solubility of a sparingly soluble salt	Predicting Common ion effect	Predicting Buffer capacity	Predicting Dissociation constant	Determine the solubility of a sparingly soluble salt
Silver chloride is	A sparingly soluble salt	Highly soluble salt	Used as an indicator	Used in buffer solutions	A sparingly soluble salt
PbS is a	A sparingly soluble salt	Highly soluble salt	Used as an indicator	Used in buffer solutions	A sparingly soluble salt
Barium sulphate is a	A sparingly soluble salt	Highly soluble salt	Used as an indicator	Used in buffer solutions	A sparingly soluble salt
Precipitation takes place when	Ionic product of solution is equal to solubility product	Ionic product of the solution is less than solubility product	Ionic product of the solution is exceeds solubility product	Square of the ionic product is equal to solubility product	Ionic product is exceeds solubility product
Precipitation takes place when the product of concentration of ions	is equal to solubility product	is less than solubility product	exceeds solubility product	Square of the ionic product is equal to solubility product	exceeds solubility product
When the ionic product of the ions in the solution exceeds solubility product then	The precipitate will dissolve	Precipitation takes place	The solution is saturated	The solution is dilute	Precipitation takes place
This is not an application of solubility product	Determination of solubility of a sparingly soluble salt	Predicting precipitation reactions	Purification of common salt	Ostwald’s dilution law	Ostwald’s dilution law
Purification of common salt is the principle of	Buffer solution	Common ion effect	Asymmetric effect	Solubility product	Solubility product
Salting out of soap is the principle of	Buffer solution	Common ion effect	Asymmetric effect	Solubility product	Solubility product
Inorganic qualitative analysis is an application of	Buffer solution	Common ion effect	Solubility product	Asymmetric effect	Solubility product
Salting out of sodium chloride is called	Purification of common salt	Purification of soap	Purification of brine	Purification of soda ash	Purification of common salt
When HCl gas is passed through a saturated solution of sodium chloride	Salting out takes place	HCl is precipitated	Sodium chloride is converted into its vapour	Soap precipitates	Salting out takes place
Soap is	Sodium salt of acetic acid	Sodium salt of benzoic acid	Sodium salt of propionic acid	Sodium salt of stearic acid	Sodium salt of stearic acid
Cations of second group gets precipitated as	carbonates	hydroxides	phosphates	sulphides	sulphides
Cations of third group gets precipitated as	carbonates	hydroxides	phosphates	sulphides	hydroxides
Dissolution of precipitates of phosphates in acidic solution is an application of	Buffer solution	Common ion effect	Asymmetric effect	Solubility product	Solubility product
Dissolution of precipitates of carbonates and sulphides in acidic solution is an application of	Buffer solution	Common ion effect	Asymmetric effect	Solubility product	Solubility product
The precipitates of Phosphates are soluble in	Basic solution	Buffer solution	Acidic solution	Neutral solution	Acidic solution
The precipitates of carbonates are soluble in	Basic solution	Buffer solution	Acidic solution	Neutral solution	Acidic solution
The precipitates of sulphides are soluble in	Basic solution	Buffer solution	Acidic solution	Neutral solution	Acidic solution
Cations of third group gets precipitated as hydroxides in presence of	Ammonium chloride	Sodium chloride	Potassium chloride	Magnesium sulphate	Ammonium chloride
Silver chromate is a	A sparingly soluble salt	Highly soluble salt	Used as an indicator	Used in buffer solutions	A sparingly soluble salt

Which is not a sparingly soluble salt	Silver chromate	Silver chloride	Lead sulphide	Sodium chloride	Sodium chloride
Which is not a freely soluble salt	Sodium chloride	Potassium chloride	Sodium bromide	Silver shloride	Silver chloride
The PH range of thymol blue indicator is	1.2 to 2.8	4 to 6	6 to 8	10 to 12	1.2 to 2.8
The PH range of methyl red indicator is	1.2 to 2.8	4.2 to 6.3	6 to 8	10 to 12	4.2 to 6.3
The PH range of alizarin yellow indicator is	1.2 to 2.8	4.2 to 6.3	6 to 8	10 to 12	10 to 12
One of the indicator gives red colour in acidic solution	Methyl red	Bromophenol blue	phenopthalein	Alizarin yellow	Methyl red
One of the indicator gives yellow colour in acidic solution	Methyl red	Methyl orange	phenopthalein	Alizarin yellow	Alizarin yellow
One of the indicator gives yellow colour in basic solution	Methyl red	Phenol red	phenopthalein	Alizarin yellow	Methyl red
One of the indicator gives pink colour in basic solution	Methyl red	Phenol red	phenopthalein	Alizarin yellow	phenopthalein

Reg. No………………… [17CHU102]

KARPAGAM UNIVERSITY, COIMBATORE-21
(For the candidates admitted from 2017 batch onwards)
B.Sc CHEMISTRYDEGREE EXAMINATIONS, NOVEMBER 2017
CHEMISTRY
PHYSICAL CHEMISTRY I
(States of Matter and Ionic Equilibrium)

TIME: 2.00 Hrs **TOTAL: 50 MARKS**

PART-A
(20 x 1 = 20)

1. The arithemetie mean of the velocities possessed by the different molecules of a gas at a particular temperature is
   a) Average velocity b) Root mean square velocity
   c) Most probable velocity d) Steady velocity
2. The square root of the mean of the squares of the different velocities
   a) Average velocity b) Root mean square velocity
   c) Most probable velocity d) Steady velocity,
3. Most probable velocity is equal to
   a) 0.816 u b) 0.816 v c) 0.816 k d) 0.816 α
4. Average velocity is equal to
   a) 0.921 u b) 0.816 u c) 0.921 α d) 0.816 k
5. Collision number is represented as
   a) σ (sigma) b) Z_1 c) Z_{12} d) Λ (lambda)
6. Collision frequency is represented as
   a) σ (sigma) b) Z_1 c) Z_{12} d) Λ (lambda)
7. Mean free path is represented as,
   a) σ (sigma) b) Z_1 c) Z_{12} d) Λ (lambda)

No. of copies (111)

8. The distance between centers of the molecules at the point of closest approach is
   a) Collision diameter b) Collision frequency
   c) Collision number d) Mean free path
9. Cooling and compression of it brings about its liquification
   a) Soild b) liquid c) gas d) plasma
10. They exhibit the property diffusion,
    a) liquid b) solid c) gas d) plasma
11. At ordinary conditions of temperatures and pressure their densities are low
    a) Plasma b) liquid c) gas d) Solid
12. At a particular temperature the fraction of molecules possessing particular velocities remain almost constant. Such state is called
    a) Tranisition state b) Intermediate c) Steady state d) Equilibrium state
13. Isotherm is
    a) A plot of ‘P’ and ‘T’ at constant V is called
    a) A plot of ‘V’ and ‘T’ at constant P is called
    b) A plot of ‘P’ and ‘V’ at constant T is called
    c) A plot of ‘PV’ and ‘T’ at constant V is called
14. At ordinary conditions of temperatures and pressure, their densities are low
    a) Solid b) liquid c) gas d) plasma
15. At a particular temperature, the fraction of molecules possessing particular velocities remains almost constant. Such state is called
    a) Transition state b) Intermediate c) Steady state d) Equilibrium state
16. From the Maxwells distribution of velocities, it may be noted that the fraction of molecules having zero velocity is
    a) Zero b) Unity c) Maximum d) In between zero and unity
17. Most probable velocity is equal to
    a) 0.816 u b) 0.816 v c) 0.816 k d) 0.816 α
18. Energy contributed by each vibrational degree of freedom is
    a) KT b) ½ KT c) 3KT d) 4KT
19. As per Newtons law the change of momentum in one second is
    a) Pressure b) Force c) torque d) Root mean square velocity

20. The root mean square velocity of nitrogen at NTP is

a) 49200 cm per second	b) 99200 cm per second
c) 4.9 cm per second	d) 9,200 cm per second

PART-B (3 x 2 = 6)

ANSWER ALL THE QUESTIONS:

21. What is meant by collision diameter?
22. What is meant by collision frequency?
23. What is meant by surface tension?

PART-C (3 x 8 = 24)

ANSWER ALL THE QUESTIONS:

24. a) What are the assumptions made by Maxwell and Boltzmann to explain the behavior of gases.

OR

b) Explain Maxwell distribution of velocities.

25. a) Derive the equation PV = 1/3 mnc^2 which is called kinetic gas equation.

OR

b) Explain in detail about the Degrees of freedom of a gaseous molecule.

26. a) Explain most probable velocity, average velocity and root mean square velocity of gases.

OR

b) Derive an expression for critical constants in terms of van der Waals constants.

Reg. No……………….. **[17CHU102]**

KARPAGAM UNIVERSITY, COIMBATORE-21

(For the candidates admitted from 2017 batch onwards)

B.Sc CHEMISTRY DEGREE EXAMINATIONS, NOVEMBER 2017

CHEMISTRY

PHYSICAL CHEMISTRY I

(States of Matter and Ionic Equilibrium)

Answer Key

PART-A

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   a) **Average velocity** b) Root mean square velocity
   c) Most probable velocity d) Steady velocity
2. The square root of the mean of the squares of the different velocities
   a) Average velocity b) **Root mean square velocity**
   c) Most probable velocity d) Steady velocity,
3. Most probable velocity is equal to
   a) 0.816 u b) **0.816 v** c) 0.816 k d) 0.816 α
4. Average velocity is equal to
   a) **0.921 u** b) 0.816 u c) 0.921 α d) 0.816 k
5. Collision number is represented as
   a) σ (sigma) **b) Z_1** c) Z_{12} d) Λ (lambda)
6. Collision frequency is represented as
   a) σ (sigma) b) Z_1 **c) Z_{12}** d) Λ (lambda)
7. Mean free path is represented as,
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    a) Pressure **b) Force** c) torque d) Root mean square velocity
20. The root mean square velocity of nitrogen at NTP is
    a) 49200 cm per second b) 99200 cm per second
    c) 4.9 cm per second d) 9,200 cm per second

PART-B

21. What is meant by collision diameter?

Collision diameter:

Collision is an event in which the centres of two identical molecules come within a distance σ from one another. Sigma σ which is the distance between centres of the molecules at the point of closest approach is called the collision diameter.

22. What is meant by collision frequency?

Collision frequency:

Collision frequency defined as the number of collisions a molecule undergoes per unit time. The number of molecules with which a single molecule will collide per unit time per unit volume of the gas is called collision number.

23. What is meant by surface tension?

Surface tension is the elastic tendency of a fluid surface which makes it acquire the least surface area possible. Surface tension allows insects (e.g. water striders), usually denser than water, to float and stride on a water surface.

PART-C

24. a) What are the assumptions made by Maxwell and Boltzmann to explain the behavior of gases?

Sutherland's formula can be used to derive the dynamic viscosity of an ideal gas as a function of the temperature: formula missed

This in turn is equal to

where is a constant for the gas.

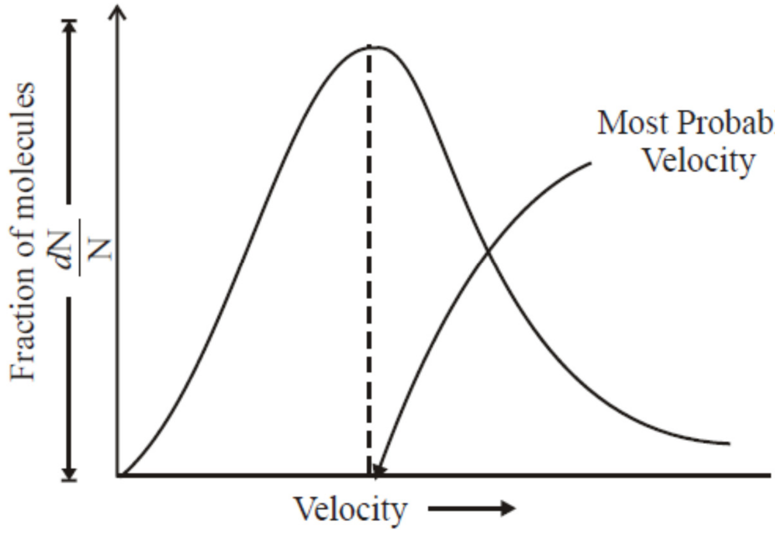
in Sutherland's formula:

- μ = dynamic viscosity (Pa·s or μPa·s) at input temperature T,
- μ_0 = reference viscosity (in the same units as μ) at reference temperature T_0,
- T = input temperature (kelvin),
- T_0 = reference temperature (kelvin),
- C = Sutherland's constant for the gaseous material in question.

Valid for temperatures between $0 < T < 555$ K with an error due to pressure less than 10% below 3.45 MPa. According to Sutherland's formula, if the absolute temperature is less than C, the relative change in viscosity for a small change in temperature is greater than the relative change in the absolute temperature, but it is smaller when T is above C. The kinematic viscosity though always increases faster than the temperature (that is, d log(ν)/d log(T) is greater than 1).

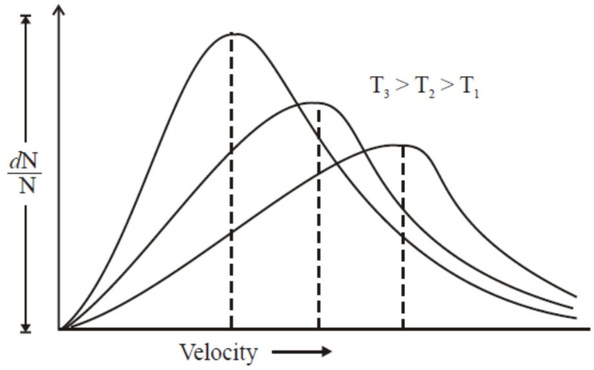
According to Maxwell in a gas all the molecules are in a state of constant rapid random motion and they collide with one another and with the walls of the vessel. During collision the resdistribution of the energy takes place. As a result their speed and the kinetic energy changes. Therefore at any instant different molecules have different speed and hence **States of matter** different kinetic energy. At the given temperature even though the speed of the individual molecule constinuously changes, the fraction of the molecules having the same speed remains constant and this is known as **Maxwell–Bolttzmann Distribution Law.**

At the given temperature this fraction is denoted by dN/N where dN is number of molecules having the same velocity and N is the total number of the molecules present in the gas. At the given temperature this fraction of the molecule is plotted against the molecular speed as shown as figure



Maxwells' distribution of velocities at constant termperature

In above Figure the maximum in the distribution curve corresponds to the speed possessed by the highest fraction of the molecule, this is known as **most probable speed**. It may be noted that if the temperature is increased the fraction of the molecule with higher speeds increases thus the most probable speed increases with increase of temperature. The temperature dependence of the distribution of the speed is as shown



Effect of temperature on distribution of velocities.

At the given temperature the most probable speed is given by the following expression.

$$U_{mp} = \sqrt{\frac{2RT}{M}}$$

the three speeds, root mean square speed, average speed and most probable speed are related by the following expressions

$$u_{\text{rms}} : u_{av} : u_{mp} :: \sqrt{3} : \sqrt{8/\pi} : \sqrt{2}$$

and also 1.224 : 1.128 : 1, so

$$u_{\text{rms}} > u_{av} > u_{mp}$$

The most probable velocity *ump* increases with the use in temperature of a gas.

Root Mean Square Velocity

Root mean square velocity is the square root of the average of the squares of all the molecular velocities. Mathematically,

$$\text{RMS Velocity} = \sqrt{\left(C_1^2 + C_2^2 + ...+ C_N^2\right)}/N$$

where C1, C2.... CN the molecular velocities.

Average Velocities

This is defined as

$$u_{av} = \frac{u_1 + u_2 + ... + u_N}{N}$$

and is given by the expression

$$u_{av} = \sqrt{\frac{8\,RT}{\pi M}}$$

Velocities of gas molecules

- **Average Velocity**

Average velocity =

$$\frac{u_1 + u_2 + u_3 + u_4 + u_n}{n} = \frac{n_1u_1 + n_2u_2 + n_3u_3 + . + n_nu_n}{n_1 + n_2 + n_3 + . + n_4}$$

$$U_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8pV}{\pi M}}$$

- **Root Mean Square Velocity:-**

Maxwell proposed the term U_{rms} as the square root of means of square of all such velocities.

$$U^2_{rms}\frac{u_1^2+u_2^2+u_3^2+u_4^2+u_n^2}{n}=\frac{n_1u_1^2+n_2u_2^2+n_3u_3^2+.+n_nu_n^2}{n_1+n_2+n_3+.+n_4}$$

also

$$U_{rms}=\sqrt{\frac{3RT}{M}}=\sqrt{\frac{3pV}{M}}$$

- **Most probable velocity:-**

It is the velocity which is possessed by maximum no. of molecules.

$$U_{mp}=\sqrt{\frac{2RT}{M}}=\sqrt{\frac{2pV}{M}}$$

Furthermore

$$u_{mp}:u_{av}:u_{rms}:::\sqrt{\frac{2RT}{M}}:\sqrt{\frac{8RT}{\pi M}}:\sqrt{\frac{3RT}{M}}=\sqrt{2}:\sqrt{\frac{8}{\pi}}:1.224$$

$$\Rightarrow u_{mp}:u_{av}:u_{rms}:::1:1.128:1.224$$

Kinetic Energy of Gas

As per kinetic equation

$$pV=\frac{1}{3}mnu^2$$

For 1 mole m × n = Molecular Mass (M)

$$pV=\frac{1}{3}Mu^2=\frac{2}{3}\times\frac{1}{2}Mu^2=\frac{2}{3}\times\frac{2}{3}\times K.E./mole=\frac{3}{2}RT$$

Also

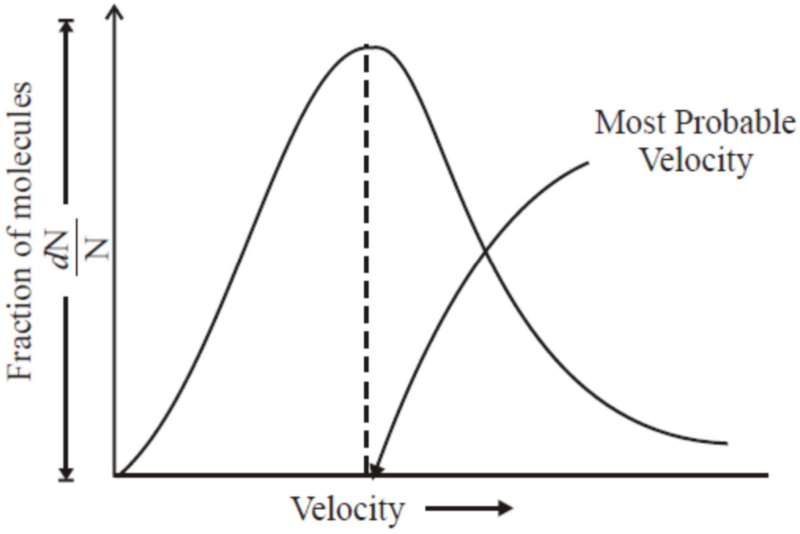
$$\frac{K.E.}{Molecule}=\frac{3}{2}\frac{RT}{N}=\frac{3}{2}kT$$

Where k is the Boltzmann constant (k = R / N)

24. b) Explain Maxwell distribution of velocities.

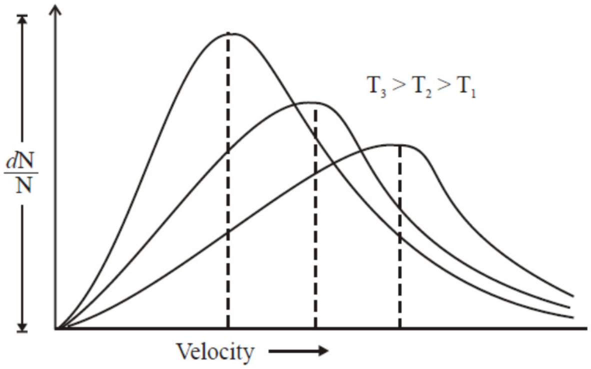
According to Maxwell in a gas all the molecules are in a state of constant rapid random motion and they collide with one another and with the walls of the vessel. During collision the resdistribution of the energy takes place. As a result their speed and the kinetic energy changes. Therefore at any instant different molecules have different speed and hence **States of matter** different kinetic energy. At the given temperature even though the speed of the individual molecule constinuously changes, the fraction of the molecules having the same speed remains constant and this is known as **Maxwell–Bolttzmann Distribution Law.**

At the given temperature this fraction is denoted by dN/N where dN is number of molecules having the same velocity and N is the total number of the molecules present in the gas. At the given temperature this fraction of the molecule is plotted against the molecular speed as shown as figure



Maxwells' distribution of velocities at constant temperature

In above Figure the maximum in the distribution curve corresponds to the speed possessed by the highest fraction of the molecule, this is known as **most probable speed**. It may be noted that if the temperature is increased the fraction of the molecule with higher speeds increases thus the most probable speed increases with increase of temperature. The temperature dependence of the distribution of the speed is as shown



Effect of temperature on distribution of velocities.

At the given temperature the most probable speed is given by the following expression.

$$U_{mp} = \sqrt{\frac{2RT}{M}}$$

the three speeds, root mean square speed, average speed and most probable speed are related by the following expressions

$$u_{\text{rms}} : u_{av} : u_{mp} :: \sqrt{3} : \sqrt{8/\pi} : \sqrt{2}$$

and also 1.224 : 1.128 : 1, so

$$u_{\text{rms}} > u_{av} > u_{mp}$$

The most probable velocity *ump* increases with the use in temperature of a gas.

Root Mean Square Velocity

Root mean square velocity is the square root of the average of the squares of all the molecular velocities. Mathematically,

$$\text{RMS Velocity} = \sqrt{\left(C_1^2 + C_2^2 + \ldots + C_N^2\right)}/N$$

where C1, C2.... CN the molecular velocities.

Average Velocities

This is defined as

$$u_{av} = \frac{u_1 + u_2 + \ldots + u_{\mathrm{N}}}{\mathrm{N}}$$

and is given by the expression

$$u_{av} = \sqrt{\frac{8\,RT}{\pi M}}$$

Velocities of gas molecules

- **Average Velocity**

Average velocity =

$$\frac{u_1 + u_2 + u_3 + u_4 + u_n}{n} = \frac{n_1u_1 + n_2u_2 + n_3u_3 + . + n_nu_n}{n_1 + n_2 + n_3 + . + n_4}$$

$$U_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8pV}{\pi M}}$$

- **Root Mean Square Velocity:-**

Maxwell proposed the term U_{rms} as the square root of means of square of all such velocities.

$$U^2_{rms}\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + u_n^2}{n} = \frac{n_1u_1^2 + n_2u_2^2 + n_3u_3^2 + . + n_nu_n^2}{n_1 + n_2 + n_3 + . + n_4}$$

also

$$U_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3pV}{M}}$$

- **Most probable velocity:-**

It is the velocity which is possessed by maximum no. of molecules.

$$U_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2pV}{M}}$$

Furthermore

$$u_{mp} : u_{av} : u_{rms} ::: \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : 1.224$$

$$\Rightarrow u_{mp} : u_{av} : u_{rms} ::: 1 : 1.128 : 1.224$$

25. a) Derive the equation PV = 1/3 mnc^2 which is called kinetic gas equation?

Kinetic Energy of Gas

As per kinetic equation

$$pV = \frac{1}{3}mnu^2$$

For 1 mole m × n = Molecular Mass (M)

$$pV = \frac{1}{3}Mu^2 = \frac{2}{3} \times \frac{1}{2}Mu^2 = \frac{2}{3} \times \frac{2}{3} \times K.E./mole = \frac{3}{2}RT$$

Also

$$\frac{K.E.}{Molecule} = \frac{3}{2}\frac{RT}{N} = \frac{3}{2}kT$$

Where k is the Boltzmann constant (k = R / N)

25. b) Explain in detail about the Degrees of freedom of a gaseous molecule ?

Degrees of Freedom

Each individual gas molecule can translate in any spatial direction. In addition, the individual atoms can rotate about any axis. Multi-atomic gas molecules may undergo rotational motions associated with the structure of the molecule. Additionally, there may be intermolecular vibrational motion between nearby gas particles, and vibrational motion arising from intramolecular forces between atoms that form the molecules. Further, there may be more contributions to the internal energy due to the internal structure of the individual atoms. Any type of motion that contributes a quadratic term in some generalized coordinate to the internal energy is called a degree of freedom. Examples include the displacement x of a particle undergoing one-dimensional simple harmonic motion position with a corresponding contribution of $(1/2)kx^2$ to the potential energy, the x -component of the velocity vx for translational motion with a corresponding contribution of $(1/2)mv_x^2$ to the kinetic energy, and z-component of angular velocity ω_z for rotational motion with a corresponding contribution of $(1/2)I_z\omega_z^2$ to the rotational kinetic energy where I_z is the moment of inertia about the z-axis. A single atom can have three translational degrees of freedom and three rotational degrees of freedom, as well as internal degrees of freedom associated with its atomic structure.

26. a) Explain most probable velocity, average velocity and root mean square velocity of gases

- **Most probable velocity:-**

It is the velocity which is possessed by maximum no. of molecules.

$$U_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2pV}{M}}$$

Furthermore

$$u_{mp} : u_{av} : u_{rms} ::: \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : 1.224$$

$$\Rightarrow u_{mp} : u_{av} : u_{rms} ::: 1 : 1.128 : 1.224$$

Root Mean Square Velocity

Root mean square velocity is the square root of the average of the squares of all the molecular velocities. Mathematically,

$$\text{RMS Velocity} = \sqrt{\left(C_1^2 + C_2^2 + ... + C_N^2\right)/N}$$

where C1, C2.... CN the molecular velocities.

Average Velocities

This is defined as

$$u_{av} = \frac{u_1 + u_2 + \ldots + u_N}{N}$$

and is given by the expression

$$u_{av} = \sqrt{\frac{8\,RT}{\pi M}}$$

Velocities of gas molecules

- **Average Velocity**

Average velocity =

$$\frac{u_1 + u_2 + u_3 + u_4 + u_n}{n} = \frac{n_1u_1 + n_2u_2 + n_3u_3 + . + n_nu_n}{n_1 + n_2 + n_3 + . + n_4}$$

$$U_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8pV}{\pi M}}$$

- **Root Mean Square Velocity:-**

Maxwell proposed the term U_{rms} as the square root of means of square of all such velocities.

$$U_{rms}^2 \frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + u_n^2}{n} = \frac{n_1u_1^2 + n_2u_2^2 + n_3u_3^2 + . + n_nu_n^2}{n_1 + n_2 + n_3 + . + n_4}$$

also

$$U_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3pV}{M}}$$

26. b) Derive an expression for critical constants in terms of van der Waals constants ?

The Relationship between the van der Waals Parameters and the Critical Constants

If

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

then

$$p = \frac{RT}{V - b} - \frac{a}{V^2}$$

At the critical point,

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$$

So, differentiating our expression for pressure with respect to volume at constant temperature

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0$$

so that

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3}$$

Differentiating again gives

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = +\frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0$$

so that

$$\frac{2RT_c}{(V_c - b)^3} = \frac{6a}{V_c^4}$$

Dividing these two expressions gives

$$\frac{(V_c - b)}{2} = \frac{V_c}{3}$$

and so

$$V_c = 3b$$

Substitution of this result into the expression that we obtained by differentiating once

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3}$$

gives

$$\frac{RT_c}{(3b - b)^2} = \frac{2a}{(3b)^3}$$

which, when rearranged, gives

$$T_c = \frac{8a}{27bR}$$

Substitution of the expressions for the critical volume V_c and critical temperature T_c into the van der Waals equation gives

$$\begin{aligned} p_c &= \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} \\ &= R\frac{1}{(3b - b)}\frac{8a}{27bR} - \frac{a}{9b^2} \\ &= \frac{8a}{54b^2} - \frac{a}{9b^2} \\ &= \frac{8a}{54b^2} - \frac{6a}{54b^2} \end{aligned}$$

and so

$$p_c = \frac{a}{27b^2}$$

Given these expressions for the values of the critical constants

$$\frac{T_c}{p_c} = \frac{8a}{27bR}\frac{27b^2}{a} = \frac{8b}{R}$$

so that

$$b = \frac{RT_c}{8p_c}$$

Similarly

$$T_c^2 = \frac{64a^2}{729b^2R^2}$$

$$\frac{T_c^2}{p_c} = \frac{64a^2}{729b^2R^2}\frac{27b^2}{a}$$
$$= \frac{64a}{27R^2}$$

Hence

$$a = \frac{27R^2T_c^2}{64p_c}$$

Rep No.................... [17CHU102]

KARPAGAM UNIVERSITY, COIMBATORE-21

(For the candidates admitted from 2017 batch onwards)

B.Sc CHEMISTRY DEGREE EXAMINATIONS, NOVEMBER 2017

PHYSICAL CHEMISTRY I

INTERNAL TEST - II

(States of Matter and Ionic Equilibrium)

TIME: 2.00 Hrs **TOTAL: 50 MARKS**

PART-A **(20 x 1 = 20)**

1. As per Van der Waals the space available for the movement of the gas molecules is

a) (V-b) b) (V+b) c) PV-RT d) PV+RT

2. The net force of attraction of a gas molecule lying in the centre of the container is

a) Zero b) Unity c) Negative value d) Positive value

3. For a real gas at moderate pressure the value of PV will be less than

a) RT b) Gas constant c) V-b d) V+b

4. Critical pressure of carbon di oxide is

a) 72.9 atmosphere b) 758 atmospheres c) 1 atmosphere d) 1000 atmospheres

5. When a gas under high pressure is allowed to expand adiabatically through a fine orifice into a region of low pressure, it is accompanied by cooling. This is

a) Pelties effect b) Joule Thomson effect

c) Vanderwaals effect d) Maxwell Boltzmann effect

6. Critical temperature of car bondioxide is

a) 304.2 K b) 298 K c) 273K d) 383 K

7. Crystals can be classified into

a) 7 systems b) 9 systems c) 10 systems d) 23 systems

8. In Bragg's equation for diffraction of X-rays 'n' represents

a) No. of moles b) Quantum number

c) Order of reflection d) Avagadro number

9. In a body centered cubic arrangement A ion occupies the centre while B ions occupy corners of cubic, the formulae of the solid is

a) AB_2 b) AB c) A_2B d) A_3B

10. Closest packing is maximum in the crystal lattice of

a) Face centered cubic b) BCC

c) Simple centered cubic d) Octahedral

11. Axis of symmetry are called "Hexad"

a) If original appearance is repeated twice

b) If original appearance is repeated 6 times

c) If original appearance is repeated after an angle of 900

d) If original appearance is repeated 16 times

12. Radius ratio in NACL is

a) 0.524 b) 0.414 c) 0.732 d) 0.8

13. In a unit cell of NaCl lattice there are

a) 4 NaCl units b) 3 Na ions c) 6 sodium ions d) Six chloride ions

14. Axis of symmetry in crystals is given by the general formulae

a) 360/n b) N x 360 c) N x 180 d) N x 90

15. Name the equation related to X-ray diffraction by crystals is

a) Law equation b) Bragg's equation c) Lewis equation d) Thomson's equation

16. The geometric form consisting only a regular array of points in space is called

a) Unit cell b) lattice c) crystal d) Amorphous solid

17. Which model is called band theory

a) Electron sea model b) Valence bond model

c) Molecular orbital method d) crystal field model

18. If the temperature of the semiconductor is increased the electrical conductivity

a) Decreases b) Increases

c) do not change d) first increases and then decreases

19. The number of fourfold axes of symmetry in a simple cube

a) Three b) four c) six d) one

20. One of the useful property of a semiconductor device

a) passing current more easily in one direction than the other

b) Constant resistance for all materials

c) sensitive to light

d) sensitive to heat

(3 x 2 = 6)

PART-B

ANSWER ALL THE QUESTIONS:

21. What is meant by law of rational indices?

22. What are Bravais lattice.

23. What is meant by Vapour pressure?

(3 x 8 = 24)

PART-C

ANSWER ALL THE QUESTIONS:

24. a) What is meant by surface tension and how to determine it experimentally?

OR

b) Explain the effects of addition of various solutes on surface tension and viscosity.

25. a) Explain with suitable examples what is meant by

(i) Rotation axis of symmetry

(ii) Rotation-reflection of symmetry

(iii) Plane of symmetry

OR

b. Explain detail the powder method for determination of crystal structure of a solid

26. a) Derive Bragg equation for the X-ray diffraction studies

OR

b) Discuss the difference between crystalline and amorphous solids

Reg. No……………….. **[17CHU102]**

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b) Constant resistance for all materials

c) sensitive to light

d) sensitive to heat

PART-B

21. What is meant by law of rational indices?

The law of rational indices states that the intercepts, *OP*, *OQ*, *OR*, of the natural faces of a crystal form with the unit-cell axes **a**, **b**, **c** (see Fig. 1) are inversely proportional to prime integers, *h*, *k*, *l*. They are called the Miller indices of the face. They are usually small because the corresponding lattice planes are among the densest and have therefore a high interplanar spacing and low indices.

22. What are Bravais lattice ?.

Crystal faces develop along planes defined by the points in the lattice. In other words, all crystal faces must intersect atoms or molecules that make up the points. A face is more commonly developed in a crystal if it intersects a larger number of lattice points. This is known as the Bravais Law.

23. What is meant by Vapour pressure?

The pressure exerted by the gas in equilibrium with a solid or liquid in a closed container at a given temperature is called the vapor pressure.

PART-C

24. a) What is meant by surface tension and how to determine it experimentally?

Surface tension is the elastic tendency of a fluid surface which makes it acquire the least surface area possible. Surface tension allows insects (e.g. water striders), usually denser than water, to float and stride on a water surface.

At liquid-air interfaces, surface tension results from the greater attraction of liquid molecules to each other (due to cohesion) than to the molecules in the air (due to adhesion). The net effect is an inward force at its surface that causes the liquid to behave as if its surface were covered with a stretched elastic membrane. Thus, the surface becomes under tension from the imbalanced forces, which is probably where the term "surface tension" came from.[1] Because of the relatively high attraction of water molecules for each other, water has a higher surface tension (72.8 millinewtons per meter at 20 °C) compared to that of most other liquids. Surface tension is an important factor in the phenomenon of capillarity.

The cohesive forces among liquid molecules are responsible for the phenomenon of surface tension. In the bulk of the liquid, each molecule is pulled equally in every direction by neighboring liquid molecules, resulting in a net force of zero. The molecules at the surface do not have thesame molecules on all sides of them and therefore are pulled inwards. This creates some internal pressure and forces liquid surfaces to contract to the minimal area.

Surface tension is responsible for the shape of liquid droplets. Although easily deformed, droplets of water tend to be pulled into a spherical shape by the imbalance in cohesive forces of the surface layer. In the absence of other forces, including gravity, drops of virtually all liquids would be approximately spherical. The spherical shape minimizes the necessary "wall tension" of the surface layer according to Laplace's law.

Another way to view surface tension is in terms of energy. A molecule in contact with a neighbor is in a lower state of energy than if it were alone (not in contact with a neighbor). The interior molecules have as many neighbors as they can possibly have, but the boundary molecules are missing neighbors (compared to interior molecules) and therefore have a higher energy. For the liquid to minimize its energy state, the number of higher energy boundary molecules must be minimized. The minimized quantity of boundary molecules results in a minimal surface area.[2] As a result of surface area minimization, a surface will assume the smoothest shape it can (mathematical proof that "smooth" shapes minimize surface area relies on use of the Euler-Lagrange equation). Since any curvature in the surface shape results in greater area, a higher energy will also result. Consequently, the surface will push back against any curvature in much the same way as a ball pushed uphill will push back to minimize its gravitational potential energy.

b) **Explain the effects of addition of various solutes on surface tension and viscosity.**

Several effects of surface tension can be seen with ordinary water:

1. Beading of rain water on a waxy surface, such as a leaf. Water adheres weakly to wax and strongly to itself, so water clusters into drops. Surface tension gives them their near-spherical shape, because a sphere has the smallest possible surface area to volume ratio.

2. Separation of oil and water (in this case, water and liquid wax) is caused by a tension in the surface between dissimilar liquids. This type of surface tension is called "interface tension", but its chemistry is the same.

Surfactants

Surface tension is visible in other common phenomena, especially when surfactants are used to decrease it:

- Soap bubbles have very large surface areas with very little mass. Bubbles in pure water are unstable. The addition of surfactants, however, can have a stabilizing effect on the bubbles (see Marangoni effect). Note that surfactants actually reduce the surface tension of water by a factor of three or more.

- Emulsions are a type of solution in which surface tension plays a role. Tiny fragments of oil suspended in pure water will spontaneously assemble themselves into much larger masses. But the presence of a surfactant provides a decrease in surface tension, which permits stability of minute droplets of oil in the bulk of water (or vice versa).

Viscosity

- The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress. For liquids, it corresponds to the informal concept of "thickness"; for example, honey has a much higher viscosity than water.

- Viscosity is a property arising from collisions between neighboring particles in a fluid that are moving at different velocities. When the fluid is forced through a tube, the particles which compose the fluid generally move more quickly near the tube's axis and more slowly near its walls; therefore some stress (such as a pressure difference between the two ends of the tube) is needed to overcome the friction between particle layers to keep the fluid moving. For a given velocity pattern, the stress required is proportional to the fluid's viscosity.

- For most circumstances near the conditions we live in, pressure doesn't have much effect on viscosity.

- For ideal gases, viscosity depends only on temperature. For real gases, that's still a very good approximation. At this link, Viscosity, you will find Sutherland's law for viscosity of gases and you will see that the input to the equation is temperature. There is no dependence on pressure. Although it's called a law, it is actually just a very good fit to the data.

- For liquids, changing the pressure does very little unless you increase the pressure A LOT.

- This page, Factors affecting viscosity, has the following statement:

- "In most cases, a fluid's viscosity increases with increasing pressure. Compared to the temperature influence, liquids are influenced very little by the applied pressure. The reason is that liquids (other than gases) are almost non-compressible at low or medium pressures. For most liquids, a considerable change in pressure from 0.1 to 30 MPa causes about the same change in viscosity as a temperature change of about 1 K (1°C)."

- I wish they had written the first two sentences in the reverse order. If you read the rest of the paragraph carefully, you conclude that pressure has very little effect on viscosity. You need to increase the pressure by 300 atmospheres to get the same change in viscosity as changing the temperature by one degree C. Temperature is by far the dominant factor in viscosity. Pressure has almost no effect.

- Viscosity is the property of a fluid by virtue of which an internal resistance comes into play when the liquid is in motion, and opposes the relative motion between its different layers. Thus, it is the resistance of a fluid to flow.
- When liquid flows over flat surface, a backward viscous force acts tangentially to every layer. This force depends upon the area of the layer, velocity of the layer, and the distance of the layer from the surface.

$$F \alpha A \frac{dv}{dx}$$

$$F = \eta A \frac{dv}{dx}$$

- Where η is the ***coefficient of viscosity*** of the liquid.

25. a) Explain with suitable examples what is meant by

(i) Rotation axis of symmetry

Cn - an n-fold axis of rotation. Rotation by 360°/n leaves the molecule unchanged. The H2O molecule above has a C2 axis. Some molecules have more than one Cn axis, in which case the one with the highest value of n is called the principal axis. Note that by convention rotations are counterclockwise about the axis. 4

(ii) Rotation-reflection of symmetry

σ - a plane of symmetry. Reflection in the plane leaves the molecule looking the same. In a molecule that also has an axis of symmetry, a mirror plane that includes the axis is called a vertical mirror plane and is labelled σv, while one perpendicular to the axis is called a horizontal mirror plane and is labelled σh. A vertical mirror plane that bisects the angle between two C2 axes is called a dihedral mirror plane, σd.

Sn - an n-fold improper rotation axis (also called a rotary-reflection axis). The rotary reflection operation consists of rotating through an angle 360°/n about the axis, followed by reflecting in a plane perpendicular to the axis. Note that S1 is the same as reflection and S2 is the same as inversion. The molecule shown above has two S2 axes.

The identity E and rotations Cn are symmetry operations that could actually be carried out on a molecule. For this reason they are called proper symmetry operations. Reflections, inversions and improper rotations can only be imagined (it is not actually possible to turn a molecule into its mirror image or to invert it without some fairly drastic rearrangement of chemical bonds) and as such, are termed improper symmetry operations.

(iii) Plane of symmetry

A note on axis definitions: Conventionally, when imposing a set of Cartesian axes on a molecule (as we will need to do later on in the course), the z axis lies along the principal axis of the molecule, the x axis lies in the plane of the molecule (or in a plane containing the largest number of atoms if the molecule is non-planar), and the y axis makes up a right handed axis system.

b. Explain detail the powder method for determination of crystal structure of a solid?

Powder diffraction is a scientific technique using X-ray, neutron, or electron diffraction on powder or microcrystalline samples for structural characterization of materials. An instrument dedicated to performing such powder measurements is called apowder diffractometer.

A diffractometer produces waves at a known frequency, which is determined by their source. The source is often x-rays, because they are the only kind of light with the correct frequency for inter-atomic-scale diffraction. However, electrons and neutrons are also common sources, with their frequency determined by their de Broglie wavelength. When these waves reach the sample, the atoms of the sample act just like a diffraction grating, producing bright spots at particular angles. By measuring the angle where these bright spots occur, the spacing of the diffraction grating can be determined by Bragg's law. Because the sample itself is the diffraction grating, this spacing is the atomic spacing.

The distinction between powder and single crystal diffraction is the degree of texturing in the sample. Single crystals have maximal texturing, and are said to be anisotropic. In contrast, in powder diffraction, every possible crystalline orientation is represented equally in a powdered sample, the isotropic case. In practice, it is sometimes necessary to rotate the sample orientation to eliminate the effects of texturing and achieve true randomness.

Mathematically, crystals can be described by a Bravais lattice with some regularity in the spacing between atoms. Because of this regularity, we can describe this structure in a different way using the reciprocal lattice, which is related to the original structure by a Fourier transform. This three-dimensional space can be described with reciprocal axes x^*, y^*, and z^* or alternatively in spherical coordinates q, φ^*, and χ^*. In powder diffraction, intensity is homogeneous over φ^* and χ^*, and only q remains as an important measurable quantity. This is because orientational averaging causes the three-dimensional reciprocal space that is studied in single crystal diffraction to be projected onto a single dimension.

Two-dimensional powder diffraction setup with flat plate detector. When the scattered radiation is collected on a flat plate detector, the rotational averaging leads to smooth diffraction rings around the beam axis, rather than the discrete Laue spots observed in single crystal diffraction. The angle between the beam axis and the ring is called the scattering angle and in X-ray crystallography always denoted as 2θ (in scattering of visible light the convention is usually to call it θ). In accordance withBragg's law, each ring corresponds to a particular reciprocal lattice vector G in the sample crystal. This leads to the definition of the scattering vector as:

In this equation, G is the reciprocal lattice vector, q is the length of the reciprocal lattice vector, k is the momentum transfer vector, θ is half of the scattering angle, and λ is the wavelength of the radiation. Powder diffraction data are usually presented as a diffractogram in which the diffracted intensity, I, is shown as a function either of the scattering angle 2θ or as a function of the scattering vector length q. The latter variable has the advantage that the diffractogram no longer depends on the value of the wavelength λ. The advent of synchrotron sources has widened the choice of wavelength considerably. To facilitate comparability of data obtained with different wavelengths the use of q is therefore recommended and gaining acceptability. and inorganic chemistry the cation-anion radius ratio is the ratio of the ionic radius of the cation to the ionic radius of the anion in a cation-anion compound. This is simply given by .

According to Pauling's rules for crystal structures, the allowed size of the cation for a given structure is determined by the critical radius ratio.[1] If the cation is too small, then it will attract the anions into each other and they will collide hence the compound will be unstable due to anion-anion repulsion; this occurs when the radius ratio drops below 0.155.

At the stability limit the cation is touching all the anions and the anions are just touching at their edges (radius ratio = 0.155). Beyond this stability limit (radius ratio < 0.155) the compound may be stable.

26. a) Derive Bragg equation for the X-ray diffraction studies?

The principle of Bragg's Law and X-ray diffraction

The mathmetical form of Bragg's Law

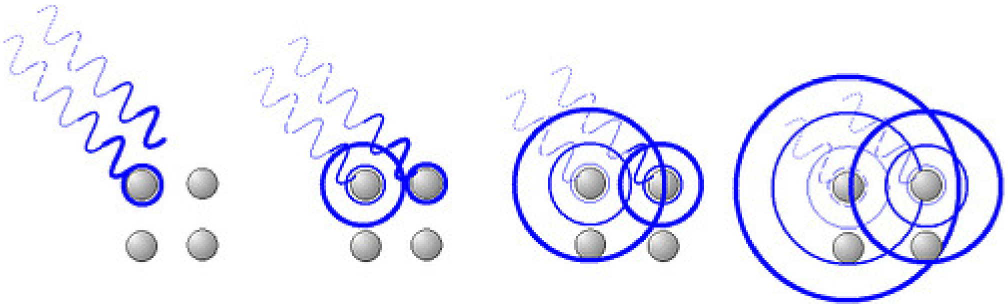
(1)

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

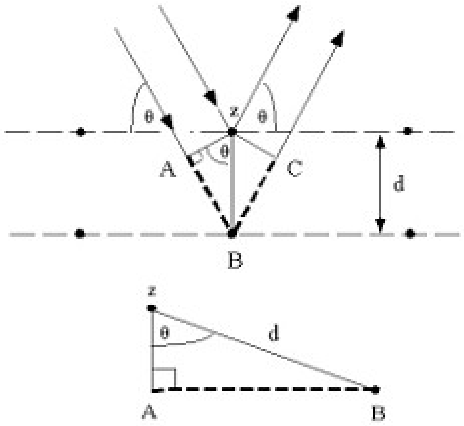
where

- n is an integer determined by the order given,
- λ is the wavelength of x-rays, and moving electrons, protons and neutrons,
- d is the spacing between the planes in the atomic lattice, and
- θ is the angle between the incident ray and the scattering planes.

The derivation of Bragg's Law



Bragg diffraction occurs when electromagnetic radiation or subatomic particle waves with wavelength comparable to atomic spacings, are incident upon a crystalline sample, scattered by the atoms in the system and undergo constructive interference in accordance to Bragg's law. [2]



Consider conditions necessary to make the phases of the beams coincide when the incident angle equals and reflecting angle. The rays of the incident beam are always in phase and parallel up to the point at which the top beam strikes the top layer at atom z. The second beam continues to the next layer where it is scattered by atom B. The second beam must travel the extra distance AB + BC if the two beams are to continue traveling adjacent and parallel. This extra distance must be an integral (n) multiple of the wavelength (λ) for the phases of the two beams to be the same:

(2)

$n\lambda=AB+BC$

Recognizing d as the hypotenuse of the right triangle Abz, we can use trigonometry to relate d and θ to the distance (AB + BC). The distance AB is opposite θ so,

(3)

$AB=d\sin\theta$

Because AB = BC eq. (2) becomes,

(4)

$n\lambda=2AB$

Substituting eq. (3) in eq. (4) we have,

(5)

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

and Bragg's Law has been derived.

Note that if only two rows of atoms are involved, the transition from constructive to destructive interference as θ changes is gradual. However, if interference from many rows occurs, then the constructive interference peaks become very sharp with mostly destructive interference in between. This sharpening of the peaks as the number of rows increases is very similar to the sharpening of the diffraction peaks from a diffraction grating as the number of slits increases.

b) Discuss the difference between crystalline and amorphous solids.

All the materials are composed of either atoms or ions or molecules. Any material is broadly classified into two broad categories, namely, solids and fluids. Fluids consist of liquids and gases. The solid materials can be classified into two types as amorphous solids and crystalline solids.

Amorphous solids

The literary meaning of amorphous is without form. The solids are neither crystalline nor polycrystalline, such as glass are called amorphous solids also called glassy, vitreous, or non crystalline. These have no periodic order, even microscopically. The difference between the crystalline solids and amorphous solids lies in the fact that during the formation of glass no heat energy is released whereas formation of crystalline arrangement would lead the release of latent of heat of fusion. Apart from glass, wood, rubber and plastics are good examples of amorphous solids.

Crystalline solids

Crystals are the unacknowledged pillars of modern technology. A crystal is a solid composed of atoms or ions or molecules arranged in an orderly repetitive array. A solid material with a regular atomic or molecular arrangement is said to be crystalline. In a crystalline arrangement, a representative unit is repeated at regular interval along any and all directions in the crystals.

Single crystals

A single crystal or mono-crystalline solid is a material in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries. The absence of the defects associated with grain boundaries can give mono-crystals unique properties, particularly mechanical, optical and electrical, which can also be anisotropic, depending on the type of crystallographic structure. These properties, in addition to making them precious in some gems, are industrially used in technological applications, especially in optics and electronics.

Reg. No……………….. [17CHU102]

KARPAGAM UNIVERSITY, COIMBATORE-21

(For the candidates admitted from 2017 batch onwards)

B.Sc CHEMISTRY DEGREE EXAMINATIONS, NOVEMBER 2017

PHYSICAL CHEMISTRY - I

INTERNAL TEST - III

(States of Matter and Ionic Equilibrium)

TIME: 2.00 Hrs **TOTAL: 50 MARKS**

PART-A **(20 x 1 = 20)**

1. An acid according to lowry- bronsted theory

   a) Donates proton b) accepts proton c) donates electron d) accepts proton

2. When acid loses a proton, then its residual part tends to behave like

   a) Acid **b) base** c) neutral d) amphoteric

3. When acetic acid is dissolved in water, the water behaves as

   a) Solvent b) acid c) amphoteric d) neutral

4. The hydronium ion is

   a) H^+ b) OH^- **c) H_3O^+** d) H_2O

5. The PH of 0.0001 M HCl is

   a) 3 **b) 4** c) 1 d) 14

6. The hydrogen ion concentration of a solution of PH value 5.4 is

   a) 3.98×10^{-6}mol dm^{-3} b) 3.98×10^{-5}mol dm^{-3}

   c) 3.98×10^{-4}mol dm^{-3} d) 3.98×10^{-14}mol dm^{-3}

7. HCl solution of any concentration has PH value

   a) 1 b) 14 **c) less than 7** d) 3.14

8. POH indicates

   a) H^+ ions concentration **b) OH^- ions concentration** c) H_3O^+ d) H_2O

9. A buffer mixture is a

   a) Strong acid & its salt b) weak base & its salt

   c) Weak acid & its salt d) strong base& its salt

10. Henderson equation is used to calculate the PH values for

    a) Buffer solution **b) buffer mixtures** c) acids d) bases

11. The capacity of a solution to resist alteration in its PH, is known as

    a) Salt hydrolysis b) indicators c) Buffer solutions **d) Buffer capacity**

12. An acidic buffer solution is

    a) Weak acid its salt b) Weak base and its salt

    c) Strong acid and its salt d) Strong base and its salt

13. A basic buffer solution is

    a) Acetic acid and ammonium acetate

    b) Ammonium hydroxide & ammonium chloride

    c) HCl and sodium chloride

    d) NaOH and sodium acetate

14. PH of a buffer solution can be calculated using

    a) Ostwald dilution law b) Commion ion effect

    c) Henderson equation d) Dissociation constant of the acid

15. The working range of phenopthalein indicator is

    a) 4 to 6 **b) 8.3 to 10** c) 7 to 7.5 d) 6 to 8

16. The working range of methyl orange indicator is

a) Below PH 3 b) Between 8 & 10 c) Between 6 & 8 **d) Between PH 3.0 and 4.4**

17. As per Ostwald theory an acid base indicator is a

a) Weak organic acid b) Strong organic base

c) A sparingly soluble salt d) Insoluble substance

18. Silver chromate is a

a) A sparingly soluble salt b) Highly soluble salt

c) Used as an indicator d) Used in buffer solutions

19. Which is not a sparingly soluble salt?

a) Silver chromate b) Silver chloride

c) Lead sulphide **d) Sodium chloride**

20. Which is not a freely soluble salt?

a) Sodium chloride b) Potassium chloride

c) Sodium bromide **d) Silver chloride**

PART-B **(3 x 2 = 6)**

ANSWER ALL THE QUESTIONS:

21. State and explain critical temperature.

22. Explain with suitable examples what is a weak electrolyte

23. What is a buffer solution? Give examples.

PART-C **(3 x 8 = 24)**

ANSWER ALL THE QUESTIONS:

24. a) Determine the dissociation constant of a weak acid and a base.

OR

b) Determine the degree of hydrolysis of salts of weak bases and strong acids.

25. a) Discuss any two applications of solubility product in detail.

OR

b) Explain in detail about the qualitative treatment of acid-base titration curves.

26. a) Explain common ion effect with suitable examples.

OR

b) What is meant by a buffer solution? Derive Hendersen equation for a buffer solution and write its application.

Reg. No……………….. **[17CHU102]**

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PHYSICAL CHEMISTRY - I

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(States of Matter and Ionic Equilibrium)

TIME: 2.00 Hrs **TOTAL: 50 MARKS**

PART-A **(20 x 1 = 20)**

1. An acid according to lowry- bronsted theory **Donates proton**
2. When acid loses a proton, then its residual part tends to behave like **base**
3. When acetic acid is dissolved in water, the water behaves as **Solvent**
4. The hydronium ion is $\mathbf{H_3O^+}$
5. The PH of 0.0001 M HCl is **4**
6. The hydrogen ion concentration of a solution of PH value 5.4 is $\mathbf{3.98 \times 10^{-6} mol\ dm^{-3}}$
7. HCl solution of any concentration has PH value **less than 7**
8. POH indicates **OH^- ions concentration**
9. A buffer mixture is a **Weak acid & its salt**
10. Henderson equation is used to calculate the PH values for **buffer mixtures**
11. The capacity of a solution to resist alteration in its PH, is known as **Buffer capacity**
12. An acidic buffer solution is **Weak acid its salt**
13. A basic buffer solution is **Ammonium hydroxide & ammonium chloride**
14. PH of a buffer solution can be calculated using **Henderson equation**
15. The working range of phenopthalein indicator is **8.3 to 10**
16. The working range of methyl orange indicator is **Between PH 3.0 and 4.4**

17. As per Ostwald theory an acid base indicator is a **Weak organic acid**

18. Silver chromate is a **A sparingly soluble salt**

19. Which is not a sparingly soluble salt? **Sodium chloride**

20. Which is not a freely soluble salt? **Silver chloride**

PART-B **(3 x 2 = 6)**

ANSWER ALL THE QUESTIONS:

21. State and explain critical temperature.

22. Explain with suitable examples what is a weak electrolyte

Weak electrolytes:

These are not completely ionized when dissolved in a polar solvent and they behave as poor conductors of electricity, e.g., CH_3COOH, H_3PO_4, H_3BO_3, NH_4OH, etc., Equlibrium between ions and unionized molecules is established in solution, e.g.,

$$CH_3COOH \leftrightarrow CH_3COO^- + H^+$$

However, an **electrolyte** may behave as a strong one in aqueous solution, but it may behave as a weak one in another solvent. For example, sodium chloride behaves as a **strong electrolyte** and acetic acid as a **weak electrolyte** when dissolved in water but their conducting abilities are comparable in liquid ammonia solvent.

23. What is a buffer solution? Give examples.

A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid (H^+ ions) or a base (OH^- ions) is called the **buffer solution.** It can also be defined as a solution of **reserve acidity** or **alkalinity** which resists change of pH upon the addition of small amount of acid or alkali.

General characteristics of a buffer solution

(i) It has a definite pH, i.e., it has reserve acidity oralkalinity.

(ii) Its pH does not change on standing for long.

(iii) Its pH does not change on dilution.

(iv) Its pH is slightly changed by the addition of small quantity of an acid or a base.

$CH_3COOH + CH_3COONa$

(b) Boric acid + Borax

(c) Phthalic acid + Potassium acid phthalate

(ii) by mixing a weak base with its salt with a strong acid,

e.g;

(a) $PNH_4OH + NH_4Cl$

(b) Glycine + Glycine hydrochloride

PART-C **(3 x 8 = 24)**

ANSWER ALL THE QUESTIONS:

24. a) Determine the dissociation constant of a weak acid and a base.

Methyl orange: It is a very weak base and can be represented as MeOH. It is ionized in solution to give Me^+ and OH^- ions.

$MeOH \leftrightarrow Me^+ + OH^-$

Yellow Red

Applying law of mass action,

$K = [Me^+][OH^-]/[MeOH]$

In presence of an acid, OH^- ions are removed in the form of water molecules and the above equilibrium shifts to right hand side. Thus, sufficient Me^+ ions are produced which impart red colour to the solution. On addition of alkali, the concentration of OH" ions increases in the solution and the equilibrium shifts to left hand side, i.e., the ionisation of MeOH is practically negligible. Thus, the solution acquires the colour of unionised **methyl orange** molecules, i.e., yellow.

This theory also explains the reason why **phenolphthalein** is not a suitable**indicator** for **titrating** a weak base against strong acid. The OH" ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i.e., pH is not reached to 8.3. Thus, the solution does not attain pink colour. Similarly, it can be explained why **methyl orange** is not a suitable **indicator**for the **titration** of weak acid with strong base.

OR

b) Determine the degree of hydrolysis of salts of weak bases and strong acids.

25. a) Discuss any two applications of solubility product in detail.

(i) Purification of common salt

Natural common salt consists of many insoluble and soluble impurities. Saturated solution of common salt is prepared and insoluble impurities are filtered off. Hydrogen chloride gas (HCl) is circulated through the saturated solution. HCl and NaCl dissociate into their respective ions as:

$NaCl \leftrightarrow Na^{+} + Cl^{-}$

$HCl \leftrightarrow H^{+} + Cl^{-}$

The concentration of Cl^{-} ions increases considerably in solution due to ionization HCl. Hence, the ionic product $[Na^{+}][Cl^{-}]$ exceeds the solubility product of sodium chloride and, therefore, pure sodium chloride precipitates out from solution.

(ii) Salting out of soap

Soap is a sodium salt of higher acids. From the solution, soap is precipitated by the addition of concentrated solution of sodium chloride. Soap and sodium chloride are present in the form of ions.

$C_nH_{2n+1}COONa \leftrightarrow C_nH_{2n+1}COO^- + Na^+$

Soap

$NaCl \leftrightarrow Na^+ + Cl^-$

Thus, the concentration of Na+ ions increases considerably on addition of NaCl solution. Hence, the ionic product $[C_nH_{2n+1}COO^-]$ $[Na^+]$ exceeds the solubility product of soap and, therefore, soap precipitates out from the solution.

(iii) Manufacture of sodium bicarbonate (baking soda):

In Solvay's soda process. CO_2 gas is passed through ammonical brine to precipitate out $NaHCO_3$.

$NH_4OH + CO_2 \rightarrow NH_4HCO_3$

$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$

$NaHCO_3$ is precipitated first because of its lower solubility product as compared to those of NH_4Cl, NH_3HCO_3 and NaCl.

Thus, baking soda ($NaHCO_3$) can be quantifiably estimated.

(iv) Application of solubility product in quantitative analysis

1. Estimation of barium as barium sulphate:

H_2SO_4 as precipitating agent is added to the aqueous solution of $BaCl_2$.

$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$

Precipitation of $BaSO_4$ takes place when its ionic product exceeds solubility product. H_2SO_4 is added in slight excess to ensure complete precipitation. Large excess of H_2SO_4 is harmful for complex formation.

2. Estimation of silver as silver chloride:

NaCl solution is added to the silver nitrate solution, slight excess of NaCl is added to ensure complete precipitation.

$AgNO_3 + NaCl \rightarrow AgCl + NaBO_3$

Again, precipitation of AgCl takes place when ionic product of AgCl exceeds its solubility product.

3. In a similar manner. We estimate lead as lead chromate, calcium as calcium oxalate, etc.

(i) Precipitation of the sulphides of group II and IV

Hydrogen sulphide is a weak electrolyte and is used for the precipitation of various sulphides of group II and IV in quantitative analysis.

It ionizes to a small extent in water:

$H_2S \leftrightarrow 2H^+ + S^{2-}$

Applying law of mass action,

$K = ([H^+]^2 [S^{2-}])/[H_2 S]$

The concentrations of $S2^-$ ions can be decreased by increasing concentration of H^+ions and it can be increased by decreasing concentration of H^+ ions. In group II, lower concentration of sulphide ions is required as the solubility products of the sulphides of group II are low while higher concentration of sulphide ions is required in group IV as the solubility products of the suphides of group IV are high. The values of solubility products of various sulphides are given below.

OR

b) Explain in detail about the qualitative treatment of acid-base titration curves.

A strong acid versus a strong base.

(ii) A weak acid versus a strong base.

(iii) A strong acid versus a weak base.

(iv) A weak acid versus a weak base.

In order to choose a suitable **indicator**, it is necessary to understand the pH changes in the above four types of **titrations**. The change in pH in the vicinity of the equivalence point is most important for this purpose. The curve obtained by plotting pH as ordinate against the volume of alkali added as abscissa is known as neutralisation or **titration curve**. The **titration curves** of the above four types of neutralisation reactions are shown in Figures.

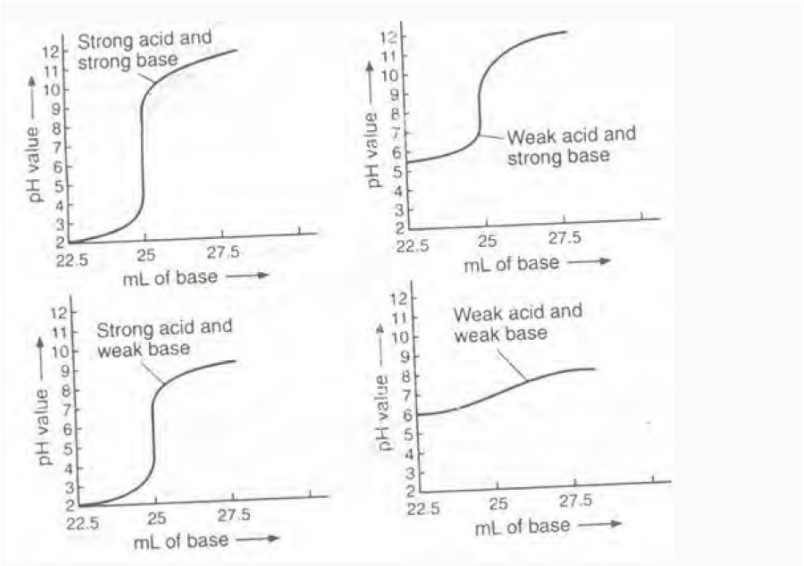
In each case 25 mL of the acid (N/10) has been **titrated** against a standard solution of a base (N/10). Each **titration curve** becomes almost vertical for some distance (except curve 10.4) and then bends away again. This region of abrupt change in pH indicates the equivalence point. For a particular **titration**, the **indicator** should be so selected that it changes its colour within vertical distance of the curve.

(i) Strong acid vs. strong base:

pH curve of strong acid (say HCI) and strong base (say NaOH) is vertical over almost the pH range 4-10. So the indicators **phenolphthalein** (pH range 8.3 to 10.5), methyl red (pH range 4.4-6.5) and **methyl orange** (pH range 3.2-4.5) are suitable for such a **titration**.

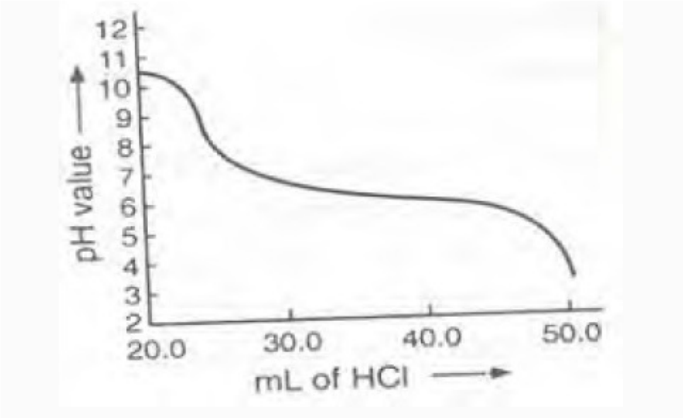
(ii) Weak acid vs. weak base:

pH curve of weak acid (say CH_3COOH of oxalic acid) and strong base (say NaOH) is vertical over the approximate pH range 7 to 11. So phenolphthalein is the suitable indicator for such a titration.



(iii) Strong acid vs. weak base:

pH curve of strong acid (say HCl or H_2SO_4 or HNO_3) with a weak base (say NH_4OH) is vertical over the pH range of 4 to 7. So the **indicators** methyl red and **methyl orange** are suitable for such a **titration**.



(iii) Weak acid vs. weak base:

pH curve of weak acid and weak base indicates that there is no vertical part and hence, no suitable **indicator** can be used for such a **titration**.

26. a) Explain common ion effect with suitable examples.

Common ion effect

Let AB to the weak electrolyte. Considering its dissociation,

$AB \leftrightarrow A^+ + B^-$

and applying law of mass action we have

$K = [A^+][B^-]/[AB]$

The equilibrium constant, K, has a definite value at any given temperature. If now another electrolyte furnishing the A^+ and B^- ions be added to the above solution. It will increases the concentration of either A^+ ions or B^- ions (whichever has been added) and in order that K may remain constant, the concentration of AB must increases, i.e., the equilibrium will shift to the left hand side.

In other words, the degree of dissociation of an electrolyte (weak) is suppressed by the addition of another electrolyte (strong) containing a common ion. This is termed as common ion effect. Acetic acid is a weak electrolyte and its ionization is suppressed in presence of a strong acid (H^+ ion as common ion) or a strong salt like sodium acetate (acetate ion as common ion). Similarly, the addition of NH_4Cl or NaOH to NH_4OH solution will suppress the dissociation of NH_4OH due to common ion either NH^-_4 or OH^-.

As a result of common ion effect, the concentration of the ion not in common in two electrolytes, is decreased. The use of this phenomenon is made in qualitative analysis to adjust concentration of S^{2-} ions in second group and OH^- ion concentration in third group of analysis.

Ionic product of water

Pure water is a very weak electrolyte and ionises according to the equation

$H_2O \leftrightarrow H^+ + OH^-$

Applying law of mass action at equilibrium, the value of dissociation constant, K comes to

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

or $[H^+][OH^-] = K[H_20]$

Since dissociation takes place to a very small extent, the concentration of undissociated water molecules, $[H_20]$, may be regarded as constant. Thus, the product #$[H_20]$ gives another constant which is designated as K_w. So,

$[H^+][OH^-] = K_w$

The constant, K_w, is termed as ionic product of water.

The product of concentrations of H1 and OH ions in water at a particular temperature is known as ionic product of water. The value of K_w increases with the increase of temperature, i.e., the concentration of H^+ and OH^- ions increases with increase in temperature.

Temperature (°C)	Value of K_w
0	0.11×10^{-14}
10	0.31×10^{-14}
25	1.00×10^{-14}
100	7.50×10^{-14}

The value of K_w at 25°C is 1×10^{-14}. Since pure water is neutral in nature, H^+ ion concentration must be equal to OH^- ion concentration.

$[H^+] = [OH^{\sim}] = x$

Or $[H^+][OH^-] = x^2 = 1 \times 10^{-14}$

Or $x = 1 \times 10^{-7} M$

or $[H^+] = [OH^-] = 1 \times 10^{-7}$ *mol litre*$^{-1}$

This shows that at 25°C, in 1 litre only 10^{-7} mole of water is in ionic form out of a total of approximately 55.5 moles.

When an acid or a base is added to water, the ionic concentration product, $[H^+][OH^-]$, remains constant, i.e., equal to K_w but concentrations of H^+ and OH^- ions do not remain equal. The addition of acid increases the hydrogen ion concentration while that of hydroxyl ion concentration decreases, i.e.,

$[H^+] > [OH^-]$; (Acidic solution)

Similarly, when a base is added, the OH^- ion concentration increases while H^+ ion concentration decreases,

i.e., $[OH^-] > [H^+]$; (Alkaline or basic solution)

In neutral solution, $[H^+] = [OH^-] = 1 \text{ x } 10^{-7}\, M$

In acidic solution, $[H^+] > [OH^-]$

or $[H^+] > 1 \text{ x } 10^{-7}\, M$

and $[OH^-] < 1 \text{ x } 10^{-7}\, M$

In alkaline solution, $[OH^-] > [H^+]$

or $[OH^-] > 1 \times 10^{-7}\, M$

and $[H^+] < 1 \text{ x } 10^{-7}\, M$

Thus, if the hydrogen ion concentration is more than $1 \text{ x } 10^{-7}$ M, the solution will be acidic in nature and if less than $1 \text{ x } 10^{-7}$ M, the solution will be alkaline.

$[H^+] = 10^{-0}\ 10^{-1}\ 10^{-2}\ 10^{-3}\ 10^{-4}\ 10^{-5}\ 10\sim^{6}$ (Acidic)

$[H^+] = 10^{-7}$ (Neutral)

$[H^+] = 10^{-14}\ 10^{-13}\ 10^{-12}\ 10^{-11}\ 10^{-10}\ 10^{-9}\ 10^{-8}$ (Alkaline)

We shall have the following table if OH^- ion concentration is taken into account.

$[OH^-] = 10^{-14}\ 10^{-13}\ 10^{-12}\ 10^{-11}\ 10^{-10}\ 10^{-9}\ 10^{-8}$ (Acidic)

$[OH^-] = 10^{-7}$ (Neutral)

$[OH^-] = 10^{-0}\ 10^{-1}\ 10^{-2}\ 10^{-3}\ 10^{-4}\ 10^{-5}\ 10^{-6}$ (Alkaline)

It is, thus, concluded that every aqueous solution, whether acidic, neutral or alkaline contains both H^+ and OH^- ions. The product of their concentrations is always constant, equal to 1×10^{-14} at 25°C. If one increases, the other decreases accordingly so that the product remains 1×10^{-14} at 25^o C.

If $[H^+] = 10^{-2}$ M, then $[OH^-] = 10^{-12}$ M; the product, $[H^+][OH^-] = 10^{-2} \times 10^{-12} = 10^{-14}$; the solution is acidic.

If [H+] = 10^{-10} M, then $[OH^-] = 10^{-4}$ M; the product, $[H^+][OH^-] = 10^{-10} \times 10^{-4} = 10^{-14}$; the solution is alkaline.

OR

b) What is meant by a buffer solution? Derive Hendersen equation for a buffer solution and write its application.

Buffer Solutions:

For several purposes, we need solutions which should have constant pH. Many reactions, particularly the biochemical reactions, are to be carried out at a constant pH. But it is observed that solutions and even pure water (pH = 7) cannot retain the constant pH for long. If the solution comes in contact with air, it will absorb CO_2 and becomes more acidic. If the solution is stored in a glass bottle, alkaline impurities dissolve from glass and the solution becomes alkaline.

A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid (H^+ ions) or a base (OH^- ions) is called the **buffer solution.** It can also be defined as a solution of **reserve acidity** or **alkalinity** which resists change of pH upon the addition of small amount of acid or alkali.

Henderson's Equation (pH of a buffer):

(i) Acidic buffer:

It consists of a mixture of weak acid and its salt (strong electrolyte). The ionisation of the weak acid, HA, can be shown by the equation

$HA \leftrightarrow H^+ + A^-$

Applying law of mass action,

$K_a = H^+A^- /[HA]$

It can be assumed that concentration of $\boldsymbol{A}^-$ ions from complete ionisation of the salt***BA*** is too large to be compared with concentration of $\boldsymbol{A}^-$ ions from the acid HA.

$BA \leftrightarrow B^+ + \boldsymbol{A}^-$

Thus, ***[HA]*** = Initial concentration of the acid as it is feebly ionised in presence of common ion

and $\boldsymbol{[A^-]}$ = Initial concentration of the salt as it is completely ionised.

So $[H^+] = Ka\ .\ [Acid]/[Salt]$ ...... (iii)

Taking logarithm and reversing sign,

$-\log\ [H^+] = -\log\ K_a - \log[Acid]/[Salt]$

or $pH = \log[Salt]/[Acid] - \log\ K_a$

or $pH = pK_a + \log[Salt]/[Acid]$ ...... (iv)

This is known as Henderson's equation.

When $[Salt]/[Acid] = 10$, then

$pH = 1 + pK_a$

and when $[Salt]/[Acid]$, then

$pH = pK_a -1$

So weak acid may be used for preparing buffer solutions having pH values lying within the ranges $pK_a + 1$ and $pK_a -1$. The acetic acid gas a pK_a of about 4.8; it may, therefore, be used for making buffer solutions with pH values lying roughly within the ranges 3.8 to 5.8.

(ii) Basic offer:

It consists of a weak base and its salt with strong acid. Ionization of a weak base, BOH, can be represented by the equation.

$BOH \leftrightarrow B^+ + OH^-$

Applying law of mass action,

$K_b = [B^+][OH^-]/[BOH]$ .... (i)

or $[OH^-] = K_b [BOH]/[B^+]$ ...... (ii)

As the salt is completely ionized, it can be assumed that whole of B^+ ion concentration comes from the salt and contribution of weak base to B^+ ions can be ignored.

$BA \leftrightarrow B^+ + A^-$ (Completely ionised)

So $[OH^-]= K_b[Base]/[Salt]$ .... (iii)

or $pOH = \log[Salt]/[Base] \log K_b$

or $pOH = pKb + \log[Salt]/[Base]$ ...... (iv)

Knowing pOH, pH can be calculated by the application of the formula.

$pH + pOH = 14$