III Year

Major II- PHYSICAL CHEMISTRY- II

Manonmaniam Sundaranar University (MSU)

Directorate of distance and continuing Education

மனோன்மணியம் சுந்தரனார் பல்கலைக்கழகம்
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Tirunelveli - 627 012 , Tamil Nadu , India

III Year

Major II- PHYSICAL CHEMISTRY- II

UNIT-I CHEMICAL KINETICS

Rate of reaction- -expressing reaction rates- factors influencing rate- order and molecularity of reactions- simple differential equation for first order, second order and zero order reactions. Effect of temperature on rate constant. The activation energy. -determination of Arrhenius frequency factor and energy of activation- The theory of Absolute reaction rates.

UNIT-Il ELECTROCHEMISTRY

Metallic and electrolytic conductance —Definitions of specific, equivalent and molar

Conductance —Variation of conductance with dilution. Transport number~ - determination—Kohlrausch’s law —applications — conductometric titrations- Theory of strong electrolytes —Debye — Huckel — Onsager theory

Galvanic cells — Reversible and Irreversible cells — EMF and its measurement —standard Hydrogen electrode — calomel electrode —standard reduction potentials — electro chemical series —significance— potentiometric titrations.

Unit - III PHASEEQUILIBRIA

Phase rule - phase, component, degree of freedom

One-component system: Phase diagrams of Water and Sulphur systems.

.Two, component system:
(i) Simple eutectic: Lead-silver system and potassium iodide-water system.
(ii) Formation of compound with congruent melting point- Magnesium — zinc system

Unit -IV SPECTROSCOPY

Introduction - various types of molecular spectra.

UV-visible spectroscopy types of transitions in molecules - applications

IR spectroscopy theory - stretching and bending vibrations - important spectral regions for the characterization of functional groups – finger print region – vibrational modes of H_2O and CO_2

NMR spectroscopy: Theory of NMR, chemical shift - factors affecting chemical shift - internal standard, - NMR spectrum of ethanol.

UNIT.V GROUP THEORPY

Symmetry operations and symmetry elements - identity element - groups and their basic properties —Abelian and cyclic groups - classification of molecules into point groups - the symmetry operations of a molecule form a group - C_{2v} and C_{3v}, point groups - group multiplication tables

NANOCHEMISTRY

Definition - size dependent properties: magnetic, electrical and optical properties – quantum dots.
Synthesis of nanomaterials - bottom-up and top-down approaches - thin film deposition catalytic assisted growth - chemical vapour deposition - sol gel method - chemical reduction Fullerenes - carbon nanotubes -single walled and multi walled nano tubes — structures - carbon nanofibre - nanocomposites

UNIT I

CHEMICAL KINETICS

Unit –I

1.0 AIMS AND OBJECTIVES

After studying this unit you should be able to

- **Explain rate of the reaction**
- **Explain the order of the reaction**
- **Explain the factors affecting the rate of the chemical reaction**
- **Explain The Arrhenius equation**
- **Explain Activation energy**
- **Explain Transition state theory**

1.1 INTRODUCTION

Chemical kinetics, also known as **reaction kinetics**, is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

1.2 RATE OF REACTION

Define Rate of Reaction and also give its units.

The rate of reaction can be defined as the change in the concentration of any one of the reactants or products per unit time. The rate of the reaction depends on the molar concentrations of the reactants. The rate of the reaction means the speed with which the reaction takes place. This is expressed either in terms of decrease in the concentration of a reactant per unit time or increase in the concentration of a product per unit time. The rate of reaction varies with time.

Rate of reaction = decrease in the concentration of a reactant / Time interval = increase in the concentration of a product / Time interval

Consider the reaction:

$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

Suppose in a time interval Δt, decrease in concentration of PCl_5 is $\Delta\ [PCl_5]$ and increase in the concentration of PCl_3 and $Cl_2$are $\Delta\ [PCl_3]$ and $\Delta\ [Cl_2]$ respectively, where square brackets indicate molar concentrations in moles / litre of the substances involved. Hence,

$$\text{Rate of reaction} = -\Delta\,[PCl_5] / \Delta t = +\Delta\,[PCl_3] / \Delta t = +\Delta\,[Cl_2] / \Delta t$$

The minus sign along with the first term is used simply to show that the concentration of the reactant (PCl_5) is decreasing while plus sign along with the other two term is used simply to show that the concentration of the products (PCl_3 and Cl_2) is increasing.

Units of the Rate of Reaction:

As concentration is usually expressed in moles / litre and the time is taken in seconds or minutes, the unit of rate of reaction is moles litre^{-1} sec^{-1} or moles litre^{-1} min^{-1}

Order of reaction:

The sum of concentration terms on which the rate of a reaction actually depends as observed experimentally is called the order of the reaction i.e. the sum of the powers or exponents to which the concentration or pressure terms are raised in order to determine the rate of the reaction.

Order of a reaction is an experimental quantity. A reaction is said to be of the zero order, first order, second order, and third order if some of concentration terms is equal to 0, 1, 2 and 3 respectively. Example:

Photosynthesis of HCl:

$$H_2\,(g) + Cl_2\,(g) + h\nu \longrightarrow 2HCl$$

Experimentally, it is found that the rate of reaction is independently of the concentration of H_2 and Cl_2. Hence it is a reaction of the zero order. Hence for such reactions:

$$\text{Rate} = k$$

Dissociation of N_2O_5

$$2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$$

Experimentally, it is found that the rate of reaction is directly proportional to $[N_2O_5]$ i.e. it depends only on one concentration term. Hence the reaction is said to be of first order.

1.4 MOLECULARITY

In case of chemical reactions i.e. reactions involving a number of atoms, ions, molecules of the reactants in the balanced equation, the chances for all the atoms, ions or molecules of the reactants to come together and collide are very rare. Hence in such cases, the reactions are supposed to take place in a number of steps. The slowest step is the rate determining step.

The number of atoms, ions or molecules taking place in te slowest step i.e. the rate determining step is called the molecularity of the reaction of complex reactions.

Hence, the molecularity of the reaction must always be a whole number whereas the order of a reaction can be fractional.

Distinguish between order of a reaction and molecularity of a reaction?

The main difference between the order of a reaction and molecularity of a reaction are given below:

ORDER OF A REACTION	MOLECULARITY OF A REACTION
It is sum of the concentration terms on which the rate of reaction actually depends or it is the sum of the exponents of the concentrations in the rate law equation.	It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.
It need not be a whole number i.e. it can be fractional as well as zero.	It is always a whole number.
It can be determined experimentally only and cannot be calculated.	It can be calculated by simply adding the molecules of the slowest step.
It is for the overall reaction and no separate steps are written to obtain it.	The overall molecularity of a complex reaction has no significance. It is only slowest step whose molecularity has significance for the overall reaction.
Even the order of a simple reaction may not be equal to the number of molecules of the reactants as seen from the unbalance equation.	For simple reactions, the molecularity can usually be obtained from the Stoichiometry of the equation.

1.5 RATE CONSTANT

Define Rate constant and also discuss its characteristics

Rate constant may be defined as the rate of the reaction when the concentration of each reactant is taken as unity. That is why the rate constant is also known as specific reaction rate.

Characteristics of rate constant:

Some important characteristics of the rate constant are as follows:

1. Rate constant is a measure of the rate of reaction. Greater is the value of the rate constant, faster is the reaction.
2. Each reaction has a definite value of the rate constant at a particular temperature.
3. The value of the rate constant for the same reaction changes with temperature.
4. The value of the rate constant of a reaction does not depend upon the concentrations of the reactants.
5. The units of the rate constant depend upon the order of reaction.

2.0 ORDER OF REACTION

"The order of reaction is defined as the sum of all the exponents of the reactants involved in the rate equation."

It should be noted down that all the molecules shown in a chemical equation do not determine the value of order of reaction but only those molecules whose concentrations are changed are included in the determination the order of a reaction. In other words:

"The number of reacting molecules whose concentration alters as a result of chemical reaction is termed as the order of reaction."

For example:

$$2NO + O_2 \dashrightarrow 2NO_2$$

$dx/dt = k[NO]^2[O_2]$, the reaction is of third order as 2 + 1 = 3

For a reaction maximum order is three and the minimum is zero.

2.1 FIRST ORDER REACTIONS

The reaction in which only one molecule undergoes a chemical change is called first order reactions.

Example:

$$N_2O_5 \dashrightarrow 2NO_2 + \frac{1}{2} O_2$$

2.2SECOND ORDER REACTIONS

The reaction in which two molecules undergo a chemical change is called second order reactions. Example:

$$\mathbf{2CH_3CHO \dashrightarrow 2CH_4 + 2\,CO}$$

2.3 THIRD ORDER REACTIONS

The reaction in which only three molecules undergo a chemical change is called third order reactions. Example:

$$2NO + O_2 \dashrightarrow 2NO_2$$

2.3.1Rate and Order of Reactions

The rate **of a chemical reaction** is the amount of substance reacted or produced per unit time. The *rate law* is an expression indicating how the *rate* depends on the concentrations of the reactants and catalysts. The *power of the concentration* in the rate law expression is called the **order** with respect to the reactant or catalyst.

2.3.2First-Order Reactions

A **first-order reaction** is a reaction that proceeds at a rate that depends *linearly* on only one reactant concentration.

2.3.2.1The Differential Representation

Differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, whereas integrated rate laws are used for determining the reaction order and the value of the rate constant from experimental measurements. The differential equation describing first-order kinetics is given below:

$\text{Rate}=-d[A]/dt=k[A]^1=k[A](1)$

The "rate" is the reaction rate (in units of molar/time) and k is the reaction rate coefficient (in units of 1/time). However, the units of k vary for non-first-order reactions. These differential equations are separable, which simplifies the solutions as demonstrated below.

2.3.3Second-Order Reactions

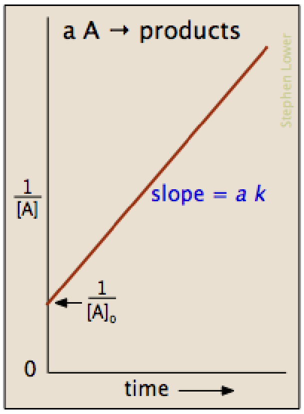
Many important biological reactions, such as the formation of double-stranded DNA from two complementary strands, can be described using second order kinetics. In a second-order reaction, the sum of the exponents in the rate law is equal to two. The two most common forms of second-order reactions will be discussed in detail in this section.

Reaction Rate

Integration of the second-order rate law

$d[A]/dt=-k[A]^2$

which is easily rearranged into a form of the equation for a straight line and yields plots similar to the one shown on the left below.



The half-life is given by

$$t_{1/2}=1/k[Ao]$$

Notice that the half-life of a second-order reaction depends on the initial concentration, in contrast to first-order reactions. For this reason, the concept of half-life for a second-order reaction is far less useful. Reaction rates are discussed in more detail here. Reaction orders are defined here. Here are explanations of zero and first order reactions.

Case 1: Identical Reactants (A + A → P)

Two of the same reactant (A) combine in a single elementary step.

$$A+A\longrightarrow P$$

$$2A\longrightarrow P$$

The reaction rate for this step can be written as

$$Rate=-1/2d[A]dt=+d[P]dt$$

and the rate of loss of reactant A

$$dA/dt=-k[A][A]=-k[A]^2$$

where k is a second order rate constant with units of M^{-1} min^{-1} or M^{-1} s^{-1}. Therefore, doubling the concentration of reactant A will quadruple the rate of the reaction. In this particular case, another reactant (B) could be present with A; however, its concentration does not affect the rate of the reaction, i.e., the reaction order with respect to B is zero, and we can express the rate law as $v=k[A]^2[B]^0$.

Case 2: Different Reactants (A + B → P)

Two different reactants (A and B) combine in a single elementary step.

$$A+B\longrightarrow P$$

The reaction rate for this step can be written as

$$Rate=-d[A]/dt=-d[B]/dt=+d[P]/dt$$

and the rate of loss of reactant A

$$d[A]/dt=-k[A][B]$$

where the reaction order with respect to each reactant is 1. This means that when the concentration of reactant A is doubled, the rate of the reaction will double, and quadrupling the concentration of reactant in a separate experiment will quadruple the rate. If we double the concentration of A and quadruple the concentration of B at the same time, then the reaction rate is increased by a factor of 8. This relationship holds true for any varying concentrations of A or B.

2.3.4 Zero-Order Reactions

In some reactions, the rate is *apparently* independent of the reactant concentration. The rates of these **zero-order reactions** do not vary with increasing nor decreasing reactants concentrations. This means that the rate of the reaction is equal to the rate constant, k, of that reaction. This property differs from both first-order reactions and second-order reactions.

Origin of Zero Order Kinetics

Zero-order kinetics is *always* an artifact of the conditions under which the reaction is carried out. For this reason, reactions that follow zero-order kinetics are often referred to as pseudo-zero-order reactions. Clearly, a zero-order process cannot continue after a reactant has been exhausted. Just before this point is reached, the reaction will revert to another rate law instead of falling directly to zero as depicted at the upper left.

There are two general conditions that can give rise to zero-order rates:

1. Only a small fraction of the reactant molecules are in a location or state in which they are able to react, and this fraction is continually replenished from the larger pool.
2. When two or more reactants are involved, the concentrations of some are much greater than those of others

This situation commonly occurs when a reaction is catalyzed by attachment to a solid surface (*heterogeneous catalysis*) or to an enzyme.

Example 1: Decomposition of Nitrous Oxide

Nitrous oxide will decompose exothermically into nitrogen and oxygen, at a temperature of approximately 575 °C

$$2N_2O-\rightarrow---> 2N_2(g)+O_2(g)$$

This reaction in the presence of a hot platinum wire (which acts as a catalyst) is zero-order, but it follows more conventional second order kinetics when carried out entirely in the gas phase.

$$2N_2O\longrightarrow 2N_2\,(g)+O_2(g)$$

In this case, the N_2O molecules that react are limited to those that have attached themselves to the surface of the solid catalyst. Once all of the sites on the limited surface of the catalyst have been occupied, additional gas-phase molecules must wait until the decomposition of one of the adsorbed molecules frees up a surface site.

Enzyme-catalyzed reactions in organisms begin with the attachment of the substrate to the active site on the enzyme, leading to the formation of an *enzyme-substrate complex*. If the number of enzyme molecules is limited in relation to substrate molecules, then the reaction may appear to be zero-order.

This is most often seen when two or more reactants are involved. Thus if the reaction

$$A+B\rightarrow \text{products} \qquad (1)$$

is first-order in both reactants so that

$$\text{rate}=k\,[A][B] \qquad (2)$$

If B is present in *great excess*, then the reaction will appear to be zero order in B (and first order overall). This commonly happens when B is also the solvent that the reaction occurs in.

Differential Form of the Zeroth Order Rate Law

$$\text{Rate} = -d[A]/dt = k[A]^0 = k = \text{constant} \qquad (3)$$

where Rate is the reaction rate and k is the reaction rate coefficient. In this example, the units of k are M/s. The units can vary with other types of reactions. For zero-order reactions, the units of the rate constants are always M/s. In higher order reactions, k will have different units.

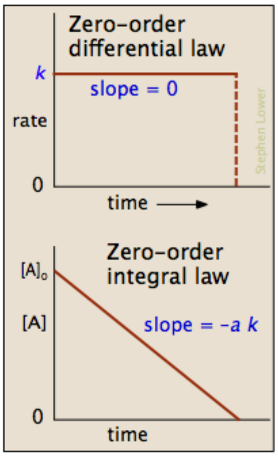


***Figure**: Rate vs. time (A) and Concentration vs. time for a zero order reaction.*

2.4 FACTORS AFFECTING RATE OF CHEMICAL REACTION

Following are the main factors that influence the rate of a chemical reaction.

Different reactants have different energies of activation. Reaction between polar or ionic molecules is very fast. Oxidation-Reduction reactions are slower than ionic reactions because they involve transfer of electrons and bond rearrangement. The physical state of reacting substances are important in determining their reactivities. The reaction in which ionic solutions are involved also take place at high speed.

2.4.1 CONCENTRATION OF REACTANTS

The concentration of reactants plays an important role in chemical kinetics. It is usually true that by increasing the amount of reactants, the rate of reaction is increased. As we know that an increase in concentration of reactants increases the number of molecules. According to collision theory, the greater the number of molecules the higher is the collision ratio, consequently faster is the rate of reaction.

2.4.2 SURFACE AREA OF REACTANTS

In heterogeneous reactions, the rate of reaction depends upon the surface area of solid reactant. Greater the surface area, higher is the rate of reaction. For example finely divided calcium carbonate (marble) reacts more quickly with hydrochloric acid than calcium carbonate chips. It is due to the fact that powered calcium carbonate offers larger surface area to the reacting acid. In other words, by increasing the surface area of reactant, rate of reaction increases due to greater contact between individual particles and also due to the fact that the surface molecules reacts more quickly.

2.4.3 TEMPERATURE

The rate of reaction increases with the rise of temperature. It can be explain by the fact that at higher temperature, a greater fraction of colliding molecules posse the necessary energy of activation.Generally an increase of every 10^oK in temperature doubles the rate.As the temperature increases the velocity of molecules also increases which results in the increase in the frequency of collision.The rise in temperature rises the kinetic energy of each molecule. It has been found that by raising the temperature by 10k, the fraction of molecule possessing threshold or activation energy becomes double. As a result the no of effective collision is also double, hence rate is doubled.

2.4.4 PRESENCE OF CATALYST

A catalyst is a substance, which controls the rate of reaction without itself undergoing a permanent chemical change. Catalysts are of two types

Positive catalyst:

A positive catalyst increases the rate of reaction by lowering the energy of activation. Thus in the presence of a positive catalyst, the greater fraction of the total molecule will posses lower energy of activation and collided successfully in a short period of time, there by increasing the rate of reaction

Negative catalyst or inhibitor:

A negative catalyst retards the rate of reaction. Negative catalyst do not lower the energy of activation rather they are combined with reactant molecule thus decreasing the number of colliding reactant molecules. This decreases the effective collisions, hence rate of reaction.

Role of positive catalyst

A positive catalyst functions by providing an alternate path to the reaction or by the formation of a transition (intermediate) compound having low energy of activation. The activation energy of this path is lower. As a result rate of reaction is increased.

Role of negative catalyst

A negative catalyst does not lower the energy of activation rather it combines with the reactant molecules, thus decreasing the number of colliding reactant molecules. This decreases the effective collisions, hence rate of reaction.

Not all reactions are affected by light or radiation but few reactions, which are usually free radicals, or photo chemical reactions are influenced by light. Light activates some of the reactant molecules producing free radicals. Since free radicals are very exited, therefore, they react immediately with other molecules to form products. The concentration of reactants does not influence the rate of such reactions, so they are zero order reaction. We know that that light consists of photon. When photons strike the reactant molecule, they provide necessary activation energy to the reactant molecules.

3.0 THE ARRHENIUS EQUATION

The actual dependence of the rate constant on temperature is given by the Arrhenius equation.

$$k = Ae^{-Ea/RT}$$

Where:

k is the rate constant

A is the Arrhenius factor (different for every reaction)

e is the natural log base

Ea is the minimum energy required for a reaction to take place (known as the activation energy)

R is the universal gas constant (8.314 J kg^{-1} $^{o}C^{-1}$)

T is the absolute temperature in Kelvin

Arrhenius' constant, A - the pre-exponential factor

It is possible for colliding particles to possess enough energy for reaction, but still not have a successful collision (one that results in reaction). This is accounted for by the Arrhenius constant 'A' , also called the pre-exponential or frequency factor.

Imagine a collision between two cars; clearly more damage is going to be caused by a head on collision than a glancing scrape.

The Arrhenius constant (pre-exponential or frequency factor) is a number between 0 and 1, that reflects the proportion of successful collisions amongst those particles with enough energy for reaction.

For example, when A is very small, only a small proportion of collisions lead to reaction, regardless of the energy, When A = 1, all collisions with sufficient energy cause reaction.

Using the Arrhenius equation

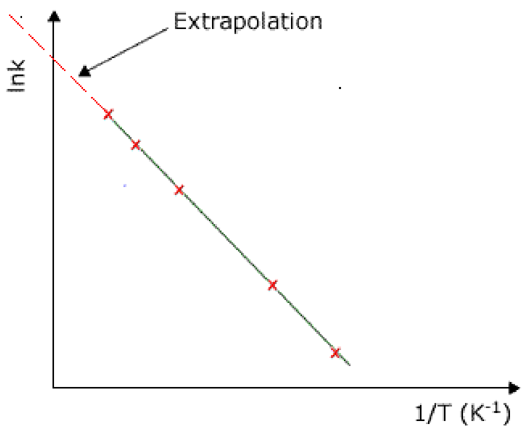
In reality, the basic form of the Arrhenius equation is not very convenient for graphing or analysing date. To analyse experiments at different temperatures we usually use the natural log form of the equation:

$$k = Ae^{-Ea/RT}$$

taking natural logs throughout this gives:

$$\ln k = \ln A - Ea/RT$$

Thus a plot of lnk against 1/RT, 1/T or any variation, will allow us to find the activation energy of a specific reaction as a function of the gradient, and the Arrhenius constant as a function of the intercept to the y axis.



A typical plot used to calculate the activation energy from the Arrhenius equation.

In this graph the gradient of the line is equal to -Ea/R

Extrapolation of the line to the y axis gives an intercept value of lnA

When the temperature is increased the term Ea/RT gets smaller. This means in turn, that the term $e^{-Ea/RT}$gets bigger.

Alternatively two results may be analysed simultaneously to obtain values for Ea, the activation energy and the Orientation factor, A. This is not particularly reliable as only two values for the rate constant are used at two different temperatures. This can introduce large errors because of too little data.

Example: Calculate the rate constant when T = 300K (A = 0.3, Ea = 50kJ mol^{-1})

$k = Ae-Ea/RT$

$Ea/RT = 50000/(8.314 \times 300) = 20.05$

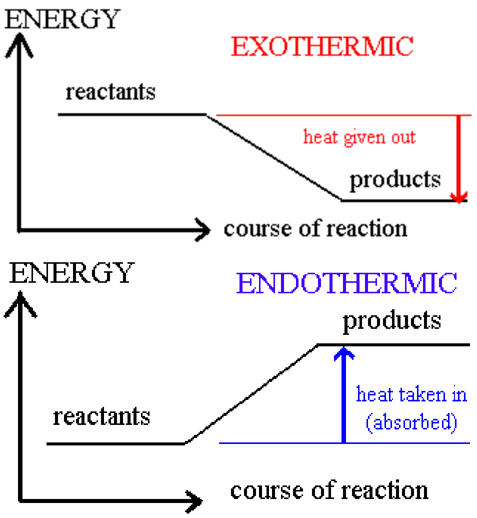
$e-Ea/RT = 1.97 \times 10-9$

$k = Ae-Ea/RT$

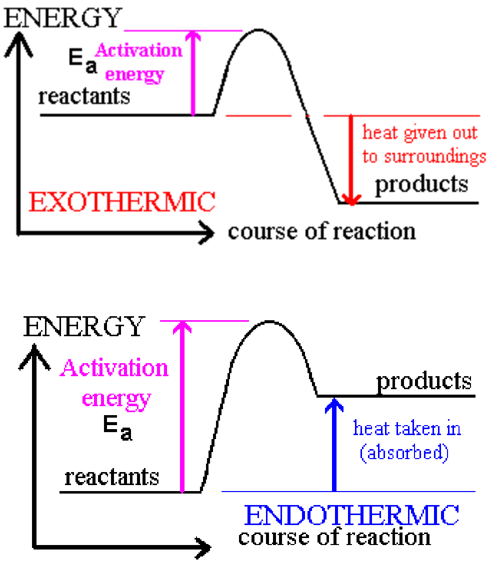
$$\boxed{\mathbf{k = 5.90 \times 10^{-10}}}$$

4.0 ENERGY OF ACTIVATION

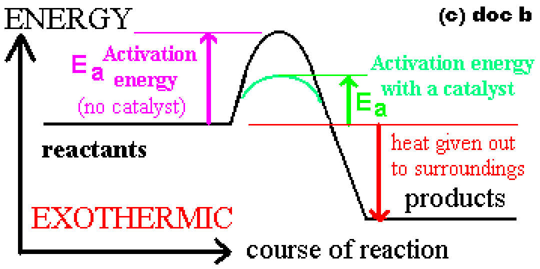
When gases or liquids are heated the particles gain kinetic energy and move faster increasing the chance of collision between reactant molecules and therefore the increased chance of a fruitful collision (i.e. one resulting in product formation).However! this is NOT the main reason for the increased reaction speed on increasing the temperature of reactant molecules because most molecular collisions do not result in chemical change. Before any change takes place on collision, the colliding molecules must have a minimum kinetic energy called the activation energy (denoted by E_a)..Its a sort of 'threshold' energy required before any bonds can be broken i.e. before a reaction can take place.Do not confuse activation energy with the overall energy change also shown in the energy profile diagrams below, that is the overall energy absorbed-taken in by the system (endothermic) or given out to the surroundings (exothermic).It does not matter whether the reaction is an exothermic or an endothermic energy change (see the pair of reaction profile diagrams below).Higher temperature molecules in gases and liquids have a greater average kinetic energy and so a greater proportion of them will then have the required activation energy to react on collision. The increased chance of higher energy collisions greatly increases the speed of the reaction because it greatly increases the chance of a fruitful collision forming the reaction products by bonds being broken in the reactants and new bonds formed in the reaction products. The activation energy 'hump' can be related to the process of bond breaking and making .Up the hump is endothermic, representing breaking bonds (energy absorbed, needed to pull atoms apart),down the other side of the hump is exothermic, representing bond formation (energy released, as atoms become electronically more stable).The 'reaction profile' diagrams below illustrate the course or progress of a reaction in terms of the energy changes taking place. Reaction profiles can be used to show the relative energies of reactants and products, the activation energy and the overall energy change of a reaction. Examples of an exothermic reaction profile and an endothermic reaction profile are shown below, with and without the activation energy - which must be reached on collision, before a reaction can occur.

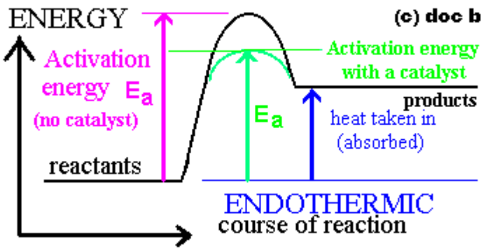


ENERGY PROFILES for chemical reactions Simple energy level diagrams for exothermic and endothermic reactions NOT showing the activation energy



ENERGY PROFILES for chemical reactions Energy level diagrams for exothermic and endothermic reactions showing the activation energy (E_a) 'hump' which must be overcome before a chemical reaction can take place



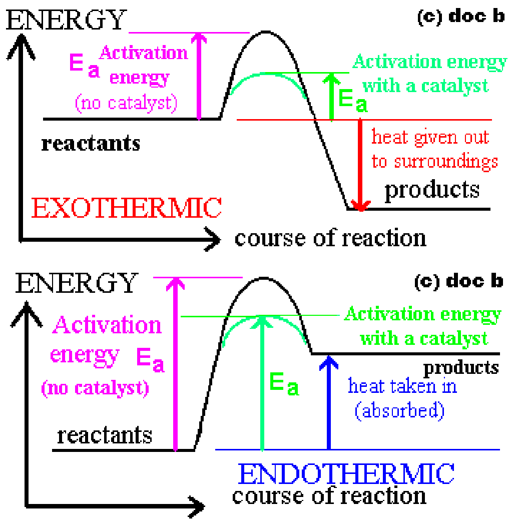


Note that the effect of a catalyst is to lower the activation energy E_a, enabling the reaction to go faster BUT it does NOT affect the overall energy change of the reaction. The catalyst provides a different pathway for the reaction that needs less energy to initiate it but it does NOT change the energy transfer value irrespective of whether it is an exothermic or an endothermic reaction.

4.0.1 Catalysts and activation energy

- Catalysts increase the rate of a reaction by helping break chemical bonds in reactant molecules.

  This effectively means the activation energy is reduced (see diagram 'humps' below).Therefore at the same temperature, more reactant molecules have enough kinetic energy to react compared to the uncatalysed situation and so the reaction speeds up with the greater chance of a 'fruitful' collision. Note that a catalyst does NOT change the energy of the molecules, it reduces the threshold kinetic energy needed for a molecules to react. The overall energy change for a catalysed reaction is identical to the energy change for the same uncatalysed reaction.
- Although a true catalyst does take part in the reaction, it does not get used up and can be reused with more reactants, it may change chemically on a temporary basis but would be reformed as the reaction products also form.
- However a solid catalyst might change physically permanently by becoming more finely divided, especially if the reaction is exothermic.
- Also note from the diagram that although the activation energy is reduced, the overall exothermic or endothermic energy change is the same for both the catalysed or uncatalysed reaction. The catalyst might help break the bonds BUT it cannot change the actual bond energies.



ENERGY PROFILES for chemical reactions

4.1 TRANSITION STATE THEORY (TST) OR ABSOLUTE REACTION RATE THEORY (ARRT) OR ACTIVATED COMPLEX THEORY (ACT):

This theory was developed by H. Eyring, Polanyi and Evans in 1935.

Postulates:

i) The reactant molecules first excited to form an activated complex. This activated complex is in equilibrium with the reactants.

Reactants [Activated complex]

ii) Activated complex is having four translational degree of freedom along the reaction coordinate and one vibrational degree of freedom less than that of the normal molecule. The extra translational degree of freedom is formed from one viberational degree.

iii) The rate of the reaction is given by the rate of decomposition of products.

[Activate complex] Products

Derivation:

Let us consider a bimolecular reaction,

A+B Products

Rate = k[A][B]

According to ARRT the mechanism is

A+B-----------→ [AB] Products

Reactants Activated complex

Where K is the equilibrium constant between the reactants and activated complex. The rate of the reaction will depend upon two factors.

i) The concentration of [AB] (calculated by using statistical mechanics).

ii) The rate at which [AB] breaks upto yield products.

A+B [AB]

On applying the law of mass action,

$$K = \frac{[(AB)^{\neq}]}{[A][B]}$$

Where K is the equilibrium constant between the reactants and activated complex.

From classical mechanics,

$$\text{Energy of vibration} = \frac{RT}{N_A} = k_BT$$

Where k_B is Boltzmann constant, R/N

From quantum mechanics,

Energy of vibration = hv

Where h is Planck's constant and v-frequency of the vibration Comparing eqns (3) and (4), we get.

$$hv = \frac{RT}{N_A}$$

$$v = \frac{RT}{hN_A}$$

$$\text{(or) } v = \frac{k_BT}{h}$$

The vibrational frequency v is the rate at which the activated complex molecules move across the enery barrier. The rate constant 'k' can be identified with v.

rate = v[(AB)]

Substituting the value of [(AB)] from eqn (2), we get

rate = v [A] [B] K

Comparing eqns (1) and (7) we get

$$k[A][B] = v\,[A]\,[B]\,K$$

$$k = vK$$

Substituting the value of v from eqn (5) and (5a) we get

$$k=\frac{k_BT}{h}\,K \text{ (or) } \frac{RT}{hN_A}K$$

The equilibrium constant K can be expressed in terms of the standard Gibbs free energy for the activation process.

$$(\Delta G^0)^{\neq} = -RT\ell nK^{\neq}$$

$$\text{and} \quad (\Delta G^0)^{\neq} = (\Delta H^0)^{\neq} - T(\Delta S^0)^{\neq}$$

From eqn (10) we get,

$$\frac{(\Delta G0)^{\neq}}{RT} = \ell nK^{\neq}$$

$$K^{\neq} = e^{(\Delta G^0)^{\neq}/RT}$$

Substituting the value of (G)from eqn (11) we get

$$K^{\neq} = e^{(\Delta G^0)^{\neq}/RT} .\, e^{(\Delta S^0)^{\neq}/R}$$

Eqn (9) becomes

$$k = \frac{k_BT}{h}\, e^{(\Delta G^0)^{\neq}/RT} .\, e^{(\Delta S^0)^{\neq}/R}$$

Equation (14) is known as Eyring equation

When $(\Delta G^0)^{\neq}$ is standard entropy of activation,

$(\Delta G^0)^{\neq}$ is standard free energy of activation, and

$(\Delta G^0)^{\neq}$ is standard enthalpy of activation,

Significance of the equation of APRT:

We know that,

$$k = \frac{k_BT}{h}\, e^{(\Delta G^0)^{\neq}/RT}$$

The equation (1) involves two factors,

$$\text{ie } k = \frac{k_BT}{h}\, e^{(\Delta G^0)^{\neq}/RT}$$

i) The first factor $\frac{k_BT}{h}$ is constant at constant temperature.

ii) The second factor $e^{(\Delta G^0)^{\neq}/RT}$ contains a negative sign. Hence the rate of the reaction depends on the free energy of activation. i.e. At particular temperature, greater the value of the $e^{(\Delta G^0)^{\neq}}$ the slower will be the reaction.

Comparison with Arrhenius equation:

We know that according to ARRT

$$k = k = \frac{k_BT}{h}\, e^{(\Delta G^0)^{\neq}/RT} .\, e^{(\Delta S^0)^{\neq}/R}$$

But according to Arrhenius equation

$$k = A.e^{-Ea/RT}$$

Taking ℓn on both sides of eqn (1), we get

$$\ell nk = \ell n\left[\frac{k_BT}{h}\, e^{(\Delta H^0)^{\neq}/RT} .\, e^{(\Delta S^0)^{\neq}/R}\right]$$

$$= \ell n\,\frac{k_BT}{h} + \ell n\, e^{(\Delta H^0)^{\neq}/RT} + \ell n\, e^{(\Delta S^0)^{\neq}/R}$$

$$\ell nk = \ell n\,\frac{k_BT}{h} + \ell nT - \frac{(\Delta H^0)^{\neq}}{RT} + \frac{(\Delta S^0)^{\neq}}{R}$$

Differentiating both sides w.r.t T.

$$- \frac{d}{dt} (\ell nk) = \frac{1}{T} + \frac{(\Delta H^0)^{\neq}}{RT^2}$$

$$\frac{d}{dt} (\ell nk) = \frac{RT + (\Delta H^0)^{\neq}}{RT^2}$$

Both ℓn on both sides of eqn (2) we get,

$\ell nk = \ell n (A. e^{-E_a/RT}$

$$\ell nk = \ell n A - \frac{E_a}{RT}$$

Differentiating both sides w.r.t.T

$$\frac{d}{dt} (\ell nk) = \frac{E_a}{RT}$$

$$E_a = RT + (\Delta H^0)^{\neq}$$

or $(\Delta H^0)^{\neq} = E_a - RT$

Comparison with the collision theory

According to ARRT, $k = \frac{k_B T}{h} e^{(\Delta G^0)^{\neq} / RT} . e^{(\Delta S^0)^{\neq} / R}$

But according to collision theory,

$k = p.Z . e^{-E_a/RT}$

Assume $e^{(\Delta H^0)^{\neq}} = E_a$ in equation (1)

Comparing eqn (1) and eqn (2), we get

$$\frac{k_B T}{h} e^{-E_a/RT} . e^{(\Delta S^0)^{\neq} / R} = p.Z . e^{-E_a/RT}$$

$$pZ = \frac{k_B T}{h} . e^{(\Delta S^0)^{\neq} / R}$$

Advantages of transition state theory ARRT over collision theory:

i) Collision theory is based on less accurate classical mechanics and kinetic theory. While ARRT is based on more accurate statistical mechanics and thermodynamics.
ii) Collision theory considers effective collision, but ARRT considers the formation and decomposition of activated molecule $[AB]^{\neq}$.
iii) Collision theory considers only translational energy whereas ARRT considers all degrees of freedom.
iv) The steric factor ‘p’ is introduced arbitrarily in collision theory. While $\Delta S^{\neq}$ is included in ARRT.

Check your progress

- Explain how concentration affects the rate of a reaction.
- Explain how temperature affects the rate of a reaction.
- Explain how amount of surface area affects the rate of a reaction.
- Explain how a catalyst affects the rate of a reaction.
- Explain why a match has little effect on lighting a lump of coal, yet a spark can cause coal dust to ignite with explosive force.
- Which of the factors that affect the rate of a reaction affect the collision frequency (number of collisions per second)?

References

1. Laidler, K.J. *Chemical Kinetics* (3rd ed., Harper and Row 1987) p.359-360 ISBN 0-06-043862-2
2. Espenson, J.H. *Chemical Kinetics and Reaction Mechanisms* (2nd ed., McGraw-Hill 2002), p.264-6 ISBN 0-07-288362-6

UNIT II

ELECTRO CHEMISTRY - I

CONTENTS

ELECTRO CHEMISTRY - I

2.0 AIMS AND OBJECTIVES

After studying the unit you should be able to

- Explain specific conductance, Equivalent conductance
- Explain Debye-Huckel Theory of Strong Electrolytes
- Describe Kohlrausch’s law (law of independent migration of ions)
- Describe conductometric titration

2.1 INTRODUCTION

Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity, which can be generated by movements of electrons from one element to another in a reaction known as an oxidation-reduction ("redox") reaction. When a chemical reaction is caused by an externally supplied current, as in electrolysis, or if an electric current is produced by a spontaneous chemical reaction as in a battery, it is called an *electrochemical* reaction. Chemical reactions where electrons are transferred directly between molecules and/or atoms are called oxidation-reduction or (redox) reactions. In general, electrochemistry describes the overall reactions when individual redox reactions are separate but connected by an external electric circuit and an intervening electrolyte

2.2 BASIC CONCEPTS

2.2.1 a) Specific conductance:

The resistance of any conductor varies directly as its length ‘l’ and inversely proportional to its cross-sectional area. (a).

i.e., $R \alpha \frac{l}{a} \Rightarrow \qquad R = \rho \frac{l}{a}$

where ρ is the specific resistance of the material depending upon the nature of the material and it is defined as the resistance of a specimen 1cm in length and 1cm^2 cross-section. i.e resistance of one cc of the material.

Specific conductance is also defined as the reciprocal of specific resistance.

K (kappa) = $\frac{1}{\rho} = \frac{1}{R} . \frac{l}{a} = G. \frac{l}{a}$ (when G is conductance)

[Unit of K is mho cm^{-1} (or) Sm^{-1}]

i.e. conductance of one cc of the material.

2.2.2 b) Equivalent conductance ‘ Λ ’

It is defined as the conducting power of all the ions produced by one equivalent of an electrolyte in a given solution.

Unit of Λ = mho cm^2

Relation between K and Λ :

For 1cc of the solution, Λ = K

for 1000 cc of the solution, Λ = 1000 K

2.2.3 c) Molar conductance Λ_m :

It is defined as the conducting power of all the ions produced by one mole of an electrolyte in a given solution.

$\Lambda_m = \frac{K}{C}$ Unit = Sm^2 mol^{-1} (or) mho cm^2 mol^{-1}

where C is the concentration of the solution in moles per cc. In this chapter, Λ is used instead of A_m.

2.2.4 d) Strongelectrolyte :

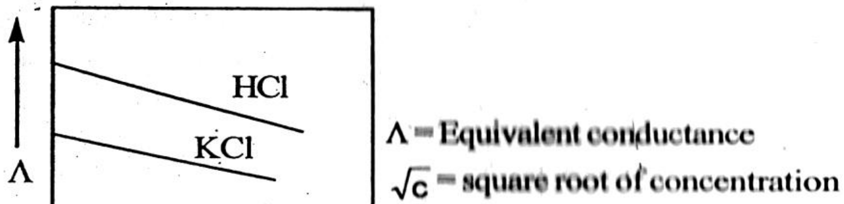
Substances which largely dissociated when dissolved in water are known as strong electrolytes.

Examples : i) Mineral acids like HCI, HNO_3. H_2SO_4, etc.

ii) Bases like NaOH, KOH, etc.

iii) All salts (eg : KCI)

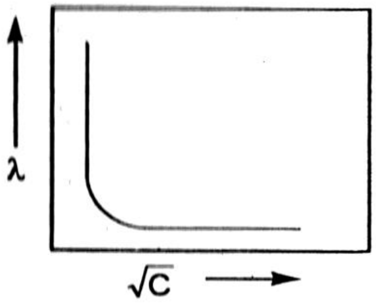
Strong electrolytes show slight increase in equivalent conductance on dilution.



2.2.5 Weak electorlytes :

Substances which dissociated only to a small extend when dissolved in water are known as weak electrolytes. Examples : Acetic acid, HCN, HBO_3, NH_3, anion etc.

Weak electrolytes shwo a very high increase in equivalent conductance on dilution.



2.2.6 g) Variation of molar conductance with dilution:

Molar conductance of an electrolyte increases with increase in dilution. The molar conductance of concentration of zero or infinite dilution is called molar conductance at zero concentration or molar conductance at infinite dilution, Λ_m^0 or Λ_0

2.3 DEBYE-HUCKEL THEORY OF STRONG ELECTROLYTES

(Inter-ionic attraction theory)

According to Arrhenius, the increase in conductance on dilution is due to the increase in ionisation. This explanation cannot be applied to strong electrolytes.

According to Debye-Huckel theory, the strong electrolytes are completely ionised (dissociated) at all concentration. But strong electrolytes show slight variation in conductance with concentration. This can be explained by Debye-Huckel and Onsager.

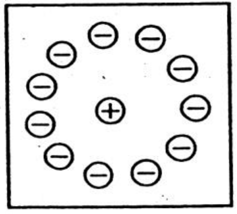
2.3.1 Debye-Huckel-Onsager theory

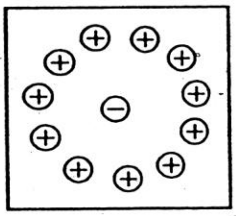
Accoridng to this theory, the decrease in equivalent conductance at higher concentration is due to the decrease in the movement of the ions. The movement of the ions decreases due to inter ionic attraction which is caused by the following two effects.

i) Asymmetric effect (Relaxation effect)

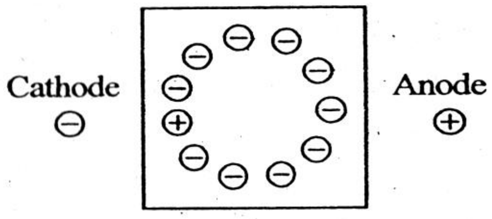
According to this effect, each ion in solution is surrounded by an atmosphere of oppositely charged ions.

Symmetrical ionic atmosphere :





ii) Asymmetric ionic atmosphere:



Thus the central ⊕ ve ion is symmetrically surrounded by the –ve ions to give symmetrical ionic atmosphere. When an electric field is applied, the central ⊕ ve ion moves towards the cathode and the –ve ionic atmosphere move towards the anode. Thus the symmetrical ionic atmosphere is destroyed.

Thus the symmetrical ionic atmosphere will breakup and a new ionic atmosphere around the moving central ion will be formed. This process of dispersing and building up of ionic atmosphere will take some time gap, which is known as relaxation time.

Totally the ion experiences a retarding force and the movement of the ion is slowed down. This effect is known as assymetric effect or relaxation effect.

iii) Electrophoretic effect

Ions are generally solvated and carry the associated solvent molecules. Due to the applied electric field, a +ve ion move towards the cathode through the solvent medium, which carries –ve ions towards the anode. This effect is known as counter current effect. Similar effect also arises in the movement of the –ve ion. The counter current effect shows down the movement of the ions. The overall effect is known as electrophoretic effect.

2.4 DEBYE-HUCKEL ONSAGER EQUATION :

A mathematical equation was derived by Debye-Huckel to account for the assymmetric and electrophoretic effect.

Later this equation was slightly modified by Onsager to account for Brownian movement. The Onsager equation for uni-univalent electrolytes (Binary strong electrolytes) such as KCI, for a given solvent and at a given temperature is

$$\Lambda_c = \Lambda_0 - [A + B\Lambda_0]\sqrt{c}$$

where A and B are constants

c is the concentration in moles/lit.

Λ_c is the equivalent conductance at a given concentration

Λ_0 is the equivalent conductance at a zero concentration

The term $B\Lambda_0$ and A are asymmetric and electropheritic effect respectively.

Verification :

This equation is verified by plotting C and concentration $(\sqrt{c})$. A straight line is obtained with negative slop (A + $B\Lambda_0$) and intercept Λ_0.

Defects (Limitations) of Debye-Huckel theory:

i) The value of slope obtained from the graph Λ_c against $\sqrt{c}$ is,

slope = - [A + $B\Lambda_0$]

This is found to be correct only for uni-univalent electrolytes like HCI, KCI, $AgNO_3$ and $NaNO_3$

Deviations are observed for bi-bivalent electolytes (Example : $BaSO_4$, $MgSO_4$, etc.,) This is due to the incomplete dissociation. The Onsager equation can be corrected as follows.

$$\Lambda_c = \Lambda_0 - [A + B\Lambda_0]\alpha\sqrt{c}$$

where α - degree of dissociation.

ii) When the solution is dilute or infinite or zero concentration, $\Lambda_m = \Lambda_m^0$, molar conductance is equal to molar conductance at infinite dilution.

iii) The values of A and B for water at 25ºC are 60.2 and 0.229 respectively. At lower concentration (upto 0.02M), the equation is correct and at higher concentration slight derivations are observed.

2.5. TRANSPORT NUMBER (HITTORF'S NUMBER)

The fraction of the total current carried by each ion is called its trasport number.

If u_+, u_- are the speed or mobility of cations and anions, then,

Transport number of cation, $t_+ = \frac{u_+}{u_+ + u_-}$

Transport number of anions, $t_- = \frac{u_-}{u_+ + u_-}$

Note : i) $t_+ + t_- = 1$, $t_+ = 1 - t_-$

ii) Transport no. for an ions is not constant. It depends upon the second ion which is present in the salt.

Hittorf's observations:

i) The no. of the ions discharged at each electrode depends upon the sum of the speeds or mobilities of the two ions.

ii) Fall in concentration around any electrolyte is proportional to the speed of the ion moving away from it.

i.e. Fall in concentration around anode α speed of the cation, u_+

Fall in concentration around cathode α speed of the cation, u_-

i.e. $\frac{\text{Mobility of the cation}}{\text{Mobility of the anion}} = \frac{\text{Fall of concentration around anode}}{\text{Fall of concentration around cathode}}$

2.5.1 Determination of transport number:

i) Hittorf's method:

The method is based on the principle that the fall in concentration around an electrode is proportional to the speed of the ion moving away from it.

i.e.

$$\frac{\text{Mobility of the cation } (u_+)}{\text{Mobility of the anion } (u_-)} = \frac{\text{Fall of concentration around anode}}{\text{Fall of concentration around cathode}}$$

Add +1 on both sides,

$$1+\frac{u_+}{u_-} = 1+\frac{\text{Fall of concentration around anode}}{\text{Fall of concentration around cathode}}$$

$$\frac{u_- u_+}{u_-} = 1+\frac{\text{Fall of concentration around anode}}{\text{Fall of concentration around cathode}}$$

$$\text{(or) } \frac{u_-}{u_+ + u_-} = \frac{\text{Fall of concentration around anode}}{\text{Fall of concentration around cathode + anode}}$$

$$\text{(or) } t_- = \frac{\text{Fall of concentration around anode}}{\text{Fall of concentration around two electrodes}}$$

$$\text{Similarly, } t_+ = \frac{\text{Fall of concentration around anode}}{\text{Fall of concentration around two electrodes}}$$

$$t_+ = \frac{\text{Number of equivalent of electrolyte lost from anode compartment}}{\text{Total number of equivalents of electrolyte lost from both compartment}}$$

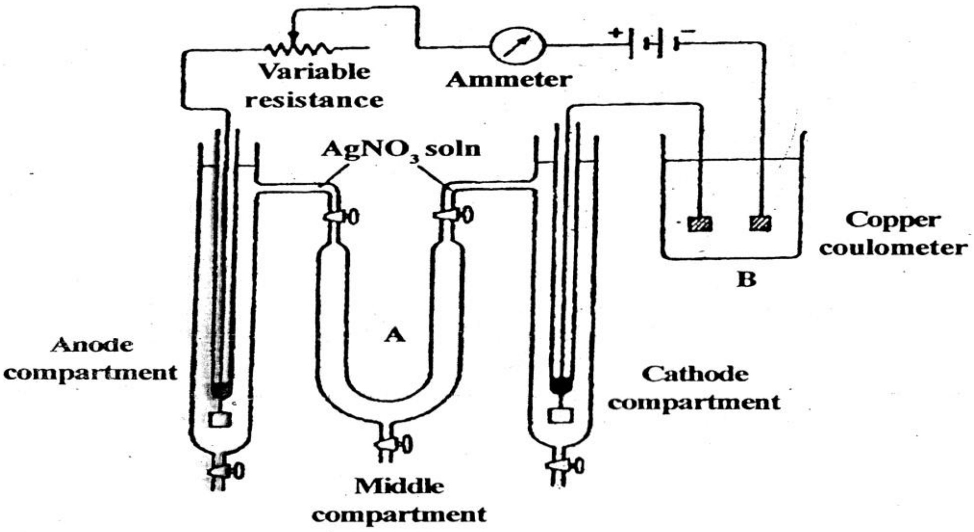
But total no. of g equivalents lost from both the compartments is equal to the no. of g equivalent deposited on each electrode.

$$\text{i.e., } t_+ = \frac{\text{No. of g equivalent lost from the anode compartment}}{\text{No. of equivalent deposited on each electrode}}$$

According to the Faraday's second law, the no. of g equivalents deposited on each electrode must be equal to no. of g equivalents of copper deposited in a copper coulometer by the same quantity of electricity.

$$t_+ = \frac{\text{No. of equivalent to electrolyte lost from the anode compartment}}{\text{No. of equivalent of Cu or Ag deposited in the coulomter}}$$

Experiment :



The apparatus consists of i) transport cell A, which consists of anode compartment, middle compartment and cathode compartment. ii) Copper coulometer, B.

The transport cell is filled with $AgNO_3$ solution. The electrolytes is carriedout using Pt-electrodes. A current of about 10 ampere is passed through the solution in the transport cell and Cu-coulometer for 2 to 3 hours. After electrolysis, the solution is drawn out from the anodic compartment and the change is concentration is determined.

Calculation :

Before electrolysis:

1g of $AgNO_3$ solution contains 'a' g of $AgNO_3$ = $\frac{a}{170}$ gram equivalent of $AgNO_3$. Let it be 'x' gram equivalents.

After electrolysis :

1g of $AgNO_3$ solution contains 'b' g of $AgNO_3$ = $\frac{b}{170}$ gram equivalent of $AgNO_3$. Let it be 'y' gram equivalents.

$\therefore$ Fall in concentration in the anode compartment = x – y gram equivalents of $AgNO_3$.

Since copper- coulometer is connected, the wt. of copper deposited in the same time is 'w' g = $\frac{w}{71.8}$ gram equivalent. Let it be 'z' gram equivalent.

$$\therefore \text{ Transport number of cation } = \frac{\text{Fall in concn. in anode compartment}}{\text{Amount of Cu deposited in the coulometer}}$$

$$t_{Ag+} = \frac{(x-y)}{z}$$

$$\therefore t_{NO_3^-} = 1 - \frac{x-y}{z}$$

where, t_{Ag+} and $t_{NO_3^-}$ are the transport number of Ag^+ and No_3^- ions respectively.

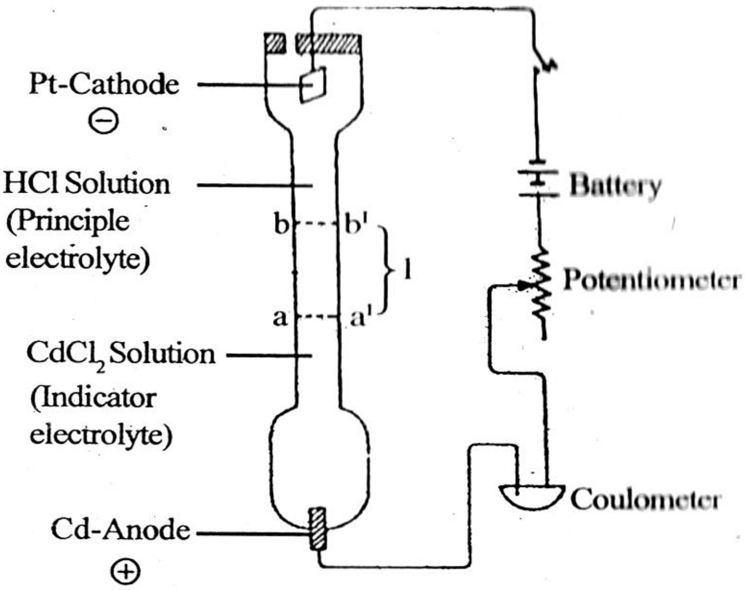
2.5.2 Determination of transport number of moving boundary method

Principle:

The principle of this method is to observe directly the mobility of the ions by passing current.

Experiment:

To determine the transport number of H^+ ion, solution of Cl (principle electrolyte) is introduced above the solution of $CdCl_2$ (indicator electrolyte) in a tube as shown in the figures.



The cathode is platinum (top) and the anode is cadmium metal (bottom). Before passing current, the mobility of Cd^{2+} ions is equal to that of H^+ ions. Thus at the junction of the two liquids, a sharp boundary is seen (aa^1)

By passing current, H^+ ions move towards the cathode. The gap formed by the upward movement of the H^+ ions is filled by the Cd^{2+} ions. Thus the boundary moves up (bb^1).

Calculation :

Let the concentration of HCI solution be C g.equi/1000

Distance through which the boundary moves = *l* cm

Area of cross section of the tube = a cm^2

$\therefore$ Volume of HCI solution moved up, V = 1.a cm^3

$\therefore$ The concentration of H^+ ions moved up $= \frac{C.V}{1000}$ g equi.

$= \frac{C.l.a}{1000}$ g equi.

Total current carried by the H^+ ions = Q Faraday
(measured by using coulometer)

$\therefore$ Transport number of H^+ ions is

$$t_{H^+} = \frac{\text{conc. of } H^+ \text{ion moved up}}{\text{Total current carried}}$$

$$t_{H^+} = \frac{C.la}{1000Q}$$

$$t_{H^+} = \frac{CV}{1000Q}$$

where C is the concentration of the soln in g equi/litre,
V is the volume of the soln moved up
Q is the current in Faraday passed

2.6. KOHLRAUSCH'S LAW (LAW OF INDEPENDENT MIGRATION OF IONS)

At infinite dilution, each ion contributes a definite amount to the total equivalent conductance of the electrolyte, irrespective of the nature of the other ion. This idea was given in the form of the law called Kohlrausch’s law. The law states that the equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the ionic conductances of the cations and anions.

$$\Lambda^0_m = \lambda^0_+ + \lambda^0_-$$

where Λ^0_m - equivalent conductance at infinite dilution

λ^0_+ - ionic conductance at infinite dilution of cations.

λ^0_- - ionic conductance at infinite dilution of anions.

2.6.1Applications of Kohlrausch’s law

i) Calculation of Λ^0_m for weak electrollytes :

For weak electrolytes, the ionisation is not complete even at very dilute solution. It is very difficult to determine its Λ^0_m value. But it can be determined indirectly using Kohlrausch’s law.

Example : Λ^0_m for acetic acid (weak electrolyte) is determined by knowing Λ^0_m of strong electrolytes HCI, NaCI and CH_3COONa.

$$\Lambda^0_{CH_3COOH} = \lambda_{CH_3COO^-} + \lambda^0_{h^+}$$

$$\Lambda^0_{CH_3COOH} = \lambda_{CH_3COONa} + \lambda^0_{HCl} - \Lambda^0_{NaCl}$$

$$= \left(\lambda^0{}_{CH_3COONa} + \lambda^0_{Na}\right) + \left(\lambda^0_{H^+} + \lambda^0_{Cl^-}\right)$$

$$\Lambda^0_{CH_3COOH} = \lambda^0{}_{CH_3COO} + \lambda^0_{H^-}$$

$$\text{Similarly } \Lambda^0_{NH_4OH} = \Lambda^0_{NH_4Cl} + \Lambda^0_{NaOH} - \Lambda^0_{NaCl}$$

$$\Lambda^0_{AgCl} = \Lambda^0_{NH_4Cl} + \Lambda^0_{AgNO_3} - \Lambda^0_{NH_4NO_3}$$

ii) Determination of transport number :

The relation between transport number of ions and their molar conductance is

$$t^0_\pm = \frac{\lambda^0_\pm}{\lambda^0_m} = \frac{\lambda^0_\pm}{\lambda^0_+ + \lambda^0_-} \qquad \text{------------------ (1)}$$

We know that

$$t^0_\pm = Fu^0_\pm \qquad \text{------------------ (2)}$$

Combining eqns (1), (2), we get

$$t^0_\pm = \frac{\lambda^0_\pm}{\lambda^0_+ + \lambda^0_-} = \frac{Fu^0_\pm}{u^0_+ + u^0_-}$$

Thus if molar conductances of ions and their mobilities at infinite dilution are known, the transport no. of ions at infinite dilution can be easily.

Problem :

The equivalent conductances at infinite dilution of HCl, NaCl and CH_3COONa are 426.16, 26.45 and 91.00 $ohm^{-1}\ cm^2$. Calculate the equivalent conductance of acetic acid at infinite dilution.

Solution :

Given $\Lambda^0_{HCl} = 426.16\ ohm^{-1}cm^2;\ \Lambda^0_{NaCl} = 26.45\ ohm^{-1}cm^2$

$$\Lambda^0_{CH_3COONa} = 91.00\ \text{ohm}^{-1}\text{cm}^2$$

$$\Lambda^0_{CH_3COOH} = \Lambda^0_{CH_3COONa} + \Lambda^0_{HCl} - \Lambda^0_{NaCl}$$

$$= 517.16 - 26.45 = 490.71\ \text{ohm}^{-1}\text{cm}^2$$

iii) Determination of degree of dissociation of weak electrolyte:

Degree of dissociation of a weak electrolyte (α) is given as

$$\alpha = \frac{\Lambda_m}{\Lambda^0_m}$$

where, Λ_m - molar conductance of an electrolyte at a given concentration and

Λ_m - molar conductance at infinite dilution

Applying Kohlrausch's law, Λ_m

$$\Lambda_m = \lambda^0_+ + \lambda^0_-$$

can be calculated.

iv) Determination of solubility of a sparingly soluble salts:

The solubility of sparingly soluble salt like AgCl can be determined using Kohlrausch's law as follows.

The molar conductance (Λ_m) of the salt is

$$\Lambda_m = \frac{1000K}{C} \qquad \text{---------- (1)}$$

where K (Kappa) – specific conductance of the salt

Since the solubility of AgCl is very low and also the concentration of the solution 'C' is nothing but the solubility 's' (ie) C = S

$$\therefore \Lambda_m = \Lambda^0_{AgCl}$$

The equation (1) becomes

$$\Lambda^0_{AgCl} = \frac{1000K}{S} \qquad \text{---------- (2)}$$

Λ^0_{AgCl} can be determined by using Kohrausch's law.

$$\Lambda^0_{AgCl} = \lambda^0_{Ag} + \lambda^0_{Cl^-}$$

Thus by knowing K, we can calculate the solubility of the salt by the following equations.

$$S = \frac{1000\,K}{\Lambda^0_{AgCl}}$$

v) Determination of ionic product of water (K_w)

The ionic product of water $K_w = [H^+][OH^-]$ at $25^o C$

The specific conductance of water (K) at 25ºC is 5.54×10^{-8} mho cm^{-1} or $5.54 \times 10^{-6} Sm^{-1}$

The equivalent conductance of water (λ_{H_2O}) at 25ºC is

$$A_{H_2O} = \frac{1000\,K}{C} \qquad \text{---------- (1)}$$

where 'C' is the concentration of water, since one mole of water contains one H^+ and one OH^- ions [$H_2O = H^+ + OH^-$]

$$\therefore C = [H^+] = [OH^-]$$

At 25ºC, the ionic conductance of H^+ and OH^- ions are

$$\lambda_{H^+} = 350,\ \lambda_{OH^-} = 200$$

Using Kohlrausch's law

$$\lambda^0{}_{H_2O} = \lambda_{H^+} + \lambda_{OH^-} = 350 + 200 = 550$$

$\therefore$ Equation (1) becomes,

$$\lambda^0{}_{H_2O} = \frac{1000K}{C}$$

$$550 = \frac{1000 \times 5.5 \times 10^{-8}}{C}$$

$$\therefore C = \frac{1000 \times 5.5 \times 10^{-8}}{550} = 1 \times 10^{-7} \text{ moles lit}^{-1}$$

$\therefore [H^+] = [OH^-] = 1 \times 10^{-7}$ moles lit.$^{-1}$

$\therefore$ Ionic product of water, $K_w = [H^+]\,[OH^-]$
$= (1 \times 10^{-7})\,(1 \times 10^{-7})$
$K_w = 1 \times 10^{-14}\ mol^2 dm^{-6}$

Mobilities of Hydrogen and hydroxyl ions

H^+ and OH^- ions have unusually high ionic mobilities it hydrolic solvents like water, alcohol etc.

In water, the H^+ ions forms hydrated H_3O^+ ion. This H_3O ions is able to transfer H^+ ion to the neighbouring hydrogen bonded water molecules by rearrangement of hydrogen bonds. Due to this, the H^+ ion have high ionic mobility. Its value is $36.25 \times 10^{-8} m^2 V^{-1} s^{-1}$ at 25ºC in water at infinite dilution. Similarly the high ionic mobility of OH^- ion in water is due to H^+ ion transfer between OH^- ion and water.

2.7. CONDUCTOMETRIC TITRATIONS

Titration in which the end point is determined by conductance measurement is known as conductometric titration. The principle involved in this titration is "conductance depends upon the number and mobility of the ions in solution". The end point of this titration can be determined graphically by plotting conductance (y-axis) against volume of the titrant added (x-axis). The point of intersection of the two curves in the end point and the concentration of the solution can be determined.

The importance conductometric titrations are,

2.7.1 Acid-base titrations :

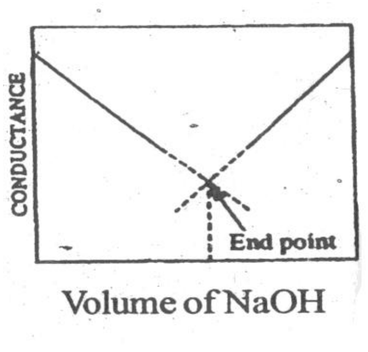
a) Strong acid against strong base (HCl × NaOH)

The acid is taken in the beaker and the NaOH in the burette. The conductance of HCl is high due to the presence of H^+ and Cl^- ions.

When alkali is added gradually, the fast moving H^+ ions are replaced by slow moving Na^+ ions. Hence conductance decreases till neutralisation.

$$(H^+ + Cl^-) + (Na^+ + OH^-) \longrightarrow (Na^+ + Cl^-)\ H_2O$$

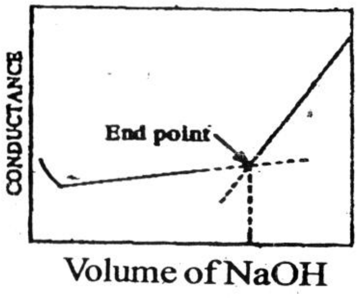
After the end point, further addition of NaOH will increase the conductance due to increase in the number of fast moving OH^- ions.



2.7.2 Weak acid against strong base (CH_3COOH × NaOH)

The acid is taken in the conductivity cell and the NaOH is taken in the burette. The conductance of the acid is low due to its poor ionisation.

When CH_3COOH is titrated against sodium hydroxide, the initial conductance will decrease due to the formation of salt sodium acetate. The salt suppress the ionisation of acetic acid by common ion effect. Then the conductance slightly increases due to the conducting power of the salt exceeds that of the acetic acid.



$CH_3COOH + (Na^+ + OH^-) \longrightarrow (CH_3COO^- + Na^+) + H_2O$

After the end point, further addition of NaOH will increase the conductance sharply due to increase in the number of fast moving OH^- ions.

2.7.3 Strong acid against weak base (HCl × NH_4OH)

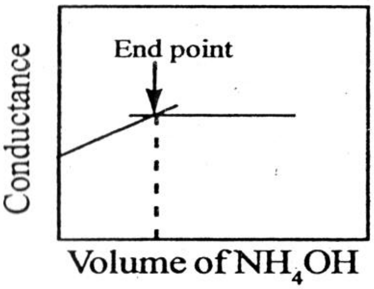
When the titrant NH_4OH is added to HCl, the conductance decreases sharply due to the replacement of fast moving H^+ ions by slow moving NH_4^+ ions.

$$\left(H^+ + Cl^-\right) + NH_4OH \longrightarrow \left(NH_4^+ + Cl^-\right) + H_2O$$

After the end point, further addition of NH_4OH will not produce any change in conductance and it remains constant.

2.7.4 Weak acid against weak base [CH_4COOH × NH_4OH]

When NH_4OH is added, to CH_3COOH, the conductance increases due to the formation of the salt, ammonium acetate.

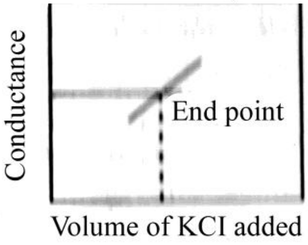


$$CH3COOH + NH_4OH \longrightarrow \underset{\text{amm.acetate}}{CH_3COONH_4} + HOH$$

After the neutralisation of the acid, further addition of NH_4OH will not produced any change in conductance due to poor ionisation.

2.7.5 Precipitation titrations [$AgNO_3$ × KCl]

$AgNO_3$ is taken in the conductivity cell and KCl is taken in the burette. The conductance of $AgNO_3$ is low due to its poor ionisation.



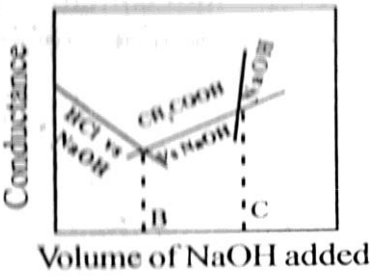
When the titrant KCl is added the Ag^+ ions are replaced by K^+ ions, AgCl is precipitated.

$$Ag^+NO_3^- + K^+ + Cl^- \longrightarrow AgCl + K^+ + NO_3^-$$

But both Ag^+ and K^+ ions have same mobility. Thus the conductance of the solution does not change. After the end point, further addition of $AgNO_3$ increases the conductance due to the excess of fast moving Ag^+ ions.

2.7.6 Titration of mixture of a strong acid and a weak acid against a strong base

Suppose a mixture of HCl (strong acid) and CH_3COOH (weak acid) is to be titrated against NOH. Since HCl is a strong acid, it will titrated first. After complete neutralisation of HCl, then CH_3COOH will titrated next. The titration curve is shown in the following figure.



Two end points B and C are obtained. The point B corresponds to neutralisation of HCl, the point 'C' corresponds to the neutralisation of CH_3COOH.

2.7.7 Advances of conductometric titration

i) Coloured solutions can be successfully titrated by this method, which cannot be determined by ordinary volumetric methods.

ii) Titration between weak acid and weak base can be determined.

iii) More accurate results can be obtained. compared to ordinary volumetric method.

iv) No special care is necessary near the end point as it is determined graphically.

2.8 QUESTIONS FOR DISCUSSION

Define Kohlrausch's law and its applications ?

Explain conductometric titrations?

SUGGESTED READINGS

1. Atkins, P. de Paula, J. Physical Chemistry for the Life Sciences. pg 209-225. 2006. Oxford Univeristy Press. New York.
2. Zumdahl, S. Zumdahl, S. Chemistry. Pg 215-220. 2007. Houghton Mifflin Company. New Jersey.
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ELECTRO CHEMISTRY – II

CONTENTS

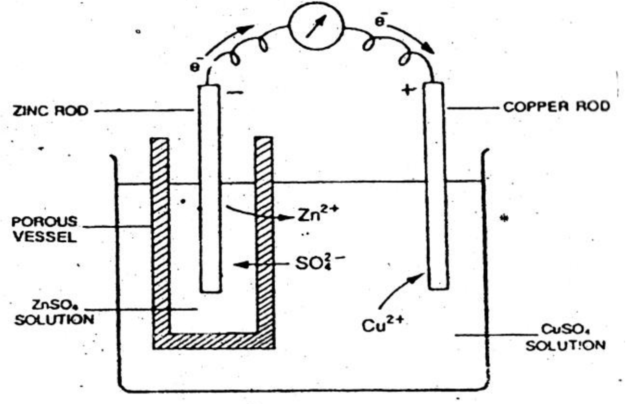
ELECTRO CHEMISTRY – II

AIMS AND OBJECTIVES

After study this unit you should able to explain, EMF and electrode potential, cell potential (or) electrochemical series, cells, potentiometric titrations, etc

2.10 EMF AND ELECTRODE POTENTIAL

The electrode potential, the electrode reaction, the cell reaction and EMF of the cell can be explained by taking Daniel cell as an example (figure)



Daniel Cell

It consists of a Zn – electrode dipped in $ZnSO_4$ solution and a Cu-electrode dipped in $CuSO_4$ solution. Both these solutions are separated by porus vessel.

When both the electrodes are connected by a wire externally, chemical reaction occurs. Oxidation reaction takes place at the Zn-electrode (i.e) Zn-rod dissolves in the solution producing Zn^{2+} ions.

$Zn \longrightarrow Zn^{2+} + 2e^-$ (oxidation half reaction)

Thus Zn-electrode is called –ve electrode and sends electrons with the outer circuit.

Reduction reaction occurs at the Cu-electrode (i.e) Cu^{2+} ion from the solution undergoes reduction by taking two electrons to form Cu-metal and deposited on the Cu-electrode.

$Cu^{2+} + 2e^- \longrightarrow Cu$ (Reduction half reaction

Metal

2.10 .1 Cell reaction:

The net chemical reaction obtained by adding the two half reactions is called the cell reaction.

$$\begin{array}{lcll} Zn & \longrightarrow & Zn^{2+} + 2e & \text{(oxidation} \\ Cu^{2+} + 2e & \longrightarrow & Cu & \text{(reduction)} \\ \hline Zn_{(s)} + Cu^{2+}_{(aq)} & \longrightarrow & Zn^{2+}_{(aq)} + Cu_{(s)} & \end{array}$$

2.10 .2 Cell representation :

The Daniel cell may be represented by writing the anode and left hand side and the cathode at right hand side.

porus vessel

Zn / Zn^{2+} // Cu^{2+} / Cu

-ve Electrode +ve Electrode

(Oxidation (reduction)

2.11 CELL POTENTIAL (OR) EMF

The electrons are flowing from Zn electrode to the Cu-electrode through the outer circuit. This causes the flow of current and it is determined by the "push" of electrons at the anode and attraction of electrons at the cathode. These two forces produced the "driving force". This driving force is called the Electromotive force (EMF) or the cell potential. It is expressed in volts.

2.11.1 Cell representation and conventions:

A cell consists of two half cells. Each half cell consists of a metal electrode in contact with the metal ions in solution.

For writing the cell representation, the following conventions are followed.

i) A single vertical line represents a phase boundary between the metal electrode and the metal ions in solution.

phase boundary

Zn / Zn^{2+} ; Cu^{2+} / Cu

Anode half cell cathode half cell

ii) A double vertical line represents the alt bridge or porous vessel to prevent the electrolytes from mixing and permits the ions to flow.

iii) The anode half cell is written on the left and the cathode half cell is on the right.

iv) In the complete cell representation, the two half cells are separated by a double vertical line (salt bridge)

Example : The Zn-Gu cell can be written as

salt bridge

Zn / Zn^{2+} // Cu^{2+} / Cu

Anode half cell cathode half cell

v) The symbol for an inert electrode, like Pt-electrode is enclosed in a brackets.

inert electrode

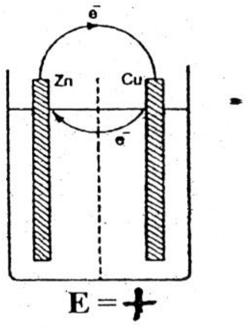
Example : M / $^{M2+}$ / H^+ / H_2 (Pt)

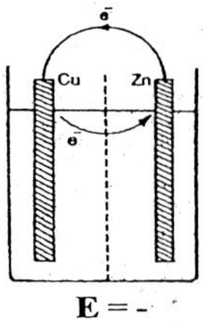
vi) The value of EMF (E) of a cell is written on the right end of the cell diagram.

Example : Zn / $ZnSO_4$ // $CuSO_4$ / Cu E = +1.1V

2.11.2 Convention regarding Sign of emf value:

The sign of emf value reflects the direction of electrons to flow externally from one electrode to another.





Examples : i) Zn/$ZnSO_4$ // $CuSO_4$ / Cu E = +1.1V
Oxidation Reduction
Here the Cu-oxidation is +ve (cathode)
ii) Cu / $CuSO_4$ // $ZnSO_4$ / Zn E = -1.1V
oxidation Reduction

2.11.3 Standard cell:

A cell which has the following characters is known as standard cell.

i) Its potential (emf) must be reproducible.
ii) Its emf remains constant for a long period.
iii) The cell should be reversible
iv) It should not be damaged by the passage of current through it.
v) Its temperature coefficient must be very low.

Example : Western Standard Cell

The commonly used standard cell is Western-Cadmium cell (or) Western cell. The cell is represented as,

Cd (Hg)x 12.5% cadmium amalgam	/ $3CdSO_4.8H_2O$ (saturated soln.)	/ $Hg_2SO_{4(s)}$	/ Hg

2.11.4 Single electrode potential

Each cell is made up of two electrons. One electrode is called –ve electrode where oxidation takes place and other electrode +ve electrode where reduction takes place.

Example : Zn / Zn^{2+} // Cu^{2+} / Cu
Half cell Half cell
(-ve electrode) (+ve electrode)

Each electrode which is contact with its own ion in solution is called half cell (or) single electrode.

The tendency of an electrode to loose or gain electrons (oxidation or reduction) when it is in contact with its own ions in solution is called single electrode potential or electrode potential.

The potential of an electrode which undergoes oxidation is called oxidation potential and the potential of an electrode which undergoes reduction is called reduction potential.

2.11.5 Standard electrode potential:

If the concentration of the ions is unity and temperature is 25ºC, the single electrode potential obtained is called standard electrode potential (E^0) and such electrode is called standard electrode.

Example : Standard Hydrogen Electrode (SHE) is,

$H_{2(g)}$ (Pt) / $H^+_{(C = 1)}$

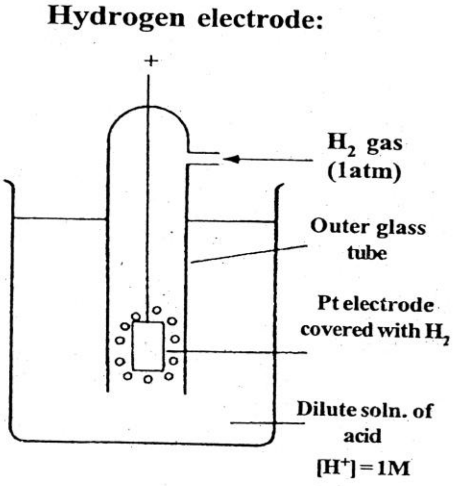
The E^0 for SHE is zero volt at 25ºC

(i.e) E^0_{SHE} = 0 volt.

2.12 REFERENCE ELECTRODES

2.12.1 Hydrogen electrode:

It is a primary standard electrode or a primary reference electrode. It consists of a Pt – wire coated with Pt-black to absorb hydrogen gas. It is surrounded by an outer glass tube containing an inlet for hydrogen gas at the top. This set up is placed in a dilute solution of an acid.



When pure hydrogen gas is passed into the glass tube at one atmospheric pressure, a part of it is covered (absorbed) by the –black. Now an equilibrium is established between the absorbed hydrogen gas on the surface of the electrode and the H^+ ion of the acid solution. The electrode reaction is

$$H^+ (aq) + e^- \rightleftharpoons \frac{1}{2} H_2(g)$$

The electrode is reversible w.r.t hydrogen ion.

The electrode is represented as

$$Pt, H_{2(g)}, / H^+$$

At 25ºC, when the pressure of H_2 gas is 1 atmosphere, the concentration of H^+ ion is 1 g.mole / lit, now it is known as Standard Hydrogen Electrode (SHE). The potential of SHE is fixed as zero volt at 25ºC.

Advantages:

i) It can be used as a wide range of pH.

ii) It exhibits no salt error

iii) It is the fundamental electrode, its potential is zero volt at 25ºC.

Disadvantages :

i) Presence of impurities in H_2 gas make poison the electrode.

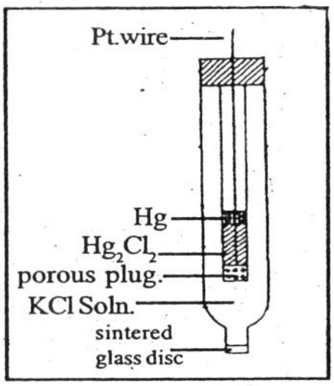
ii) To maintain the H_2 gas pressure at 1 atmosphere is difficult.

iii) It cannot be used for solution containing strong oxidising agent.

2.12.2 Calomel electrode :

Calomel electrode is a secondary standard or a secondary reference electrode.

It consists of a narrow central glass tube in which mercury and solid calomel (Hg_2Cl_2) are held by a porous plug. For electrical contact, a platinum wire dips into the mercury. The potassium chloride solution (0.1N or 1.0N or saturated) contained in the electrode makes contact with other electrode through a sintered glass disc. The disc function as a salt bride (between the two electrode solution).



This electrode is represented as

$$Hg, Hg_2Cl_{2(s)} \text{ (solution), KCl}$$

The electrode reaction is

$$Hg_2Cl^-_{2(s)} + 2e^- \rightleftharpoons 2 Hg (l) + 2Cl^- (aq)$$

Calomel electrode is reversible with represent to the Cl^- ion. The potential of the calomel electrode depends on the concentration of KCl solution.

Name of the calomel electrode	[KCl]	EMF (in volt)
Decinormal calomel electrode (DNCE)	0.14N	0.333
Normal Calomel Electrode (NCE)	1N	0.281
Saturated Calomel Electrode (SCE)	saturated	0.242

2.13 ELECTROCHEMICAL SERIES

With reference to the standard hydrogen electrode, the electrodes are arranged in the decreasing order of their standard reduction potentials at 25ºC. This is called electro chemical series.

Electrode	**E^0 volts**
Au^{3+}, Au	+ 1.50
Hg^{2+}, Hg_2^{2+}, (Pt)	+ 0.92
Ag^{+}, Ag	+ 0.80
$Fe^{3+,}$ Fe^{2+}, (Pt)	+ 0.77
Cu^{2+}, Cu	+ 0.34
$2H^{+}$, H_2, (Pt)	0.00
Pb^{2+}, Pb	- 0.13
Sn^{2+}, Sn	- 0.15
Fe^{2+}, Fe	- 0.44
Zn^{2+}, Zn	- 0.70
Na^{2+}, Na	- 2.71

Applications or Significance:

i) A high positive value of E^0 indicates that the electrode undergoes reduction (by accepting electrons). A high negative value of E^0 indicates that the electrode undergoes oxidation (by donating electrons).

ii) The emf of the cell reaction can be easily determined with the help of E^0 values.

Example : In the Daniel cell

$Zn / Zn^2 // Cu^{2+} / Cu$

$Zn \longrightarrow Zn^2$ $2e^-$ (oxidation) $E^0 = -0.75v$

$Cu^{2+} + 2e^- \longrightarrow Cu$ (reduction) $E^0 = 0.34v$

$Zn_{(s)} + Cu^{2+}_{(aq)}$ ca$Zn^{2+}_{(aq)} + Cu_{(s)}$ (cell reaction

E_{cell} Redn.potential of RHS – Redn. potential of LHS
electrode electrode

$E^0_R – E^0_1$ 0.34 – (-0.76) = 1.10V

iii) The feasibility of the cell reaction can also be predicted with the help of E^0 values. From E^0 values, emf of the cell is calculated.

$E_{cell} – E^0_R – E^0_1$

If, E_{cell} is –ve, the reaction will be feasible

If, E_{cell} –ve, the reaction will not be feasible

Example : Predict the following reaction is feasible (or) not.

$2Ag + Zn^2 \longrightarrow 2Ag + Zn$

The half cell reactions are

Anode (oxidation) $2Ag \longrightarrow 2Ag^+ + 2e^-; E^0 = 0.80V$

Cathode (Reduction) $2Ag \longrightarrow 2Ag^+ + 2e^-; E^0 = 0.80V$

Cell reaction $2Ag + Zn^2 s2Ag + Zn$

E_{cell} $E^0_R - E^0_L = -0.76 - 0.80 \ - 1.56$

Since, the value of E_{cell} is –ve. Thus the reaction is not feasible.

vi) The metal will displace another metal from its salt solution or not can be predicted by electrochemical series. Generally a metal lower down the electrochemical series can precipitate the one higher up the series.

v) The metal will displace hydrogen from a dilute acid or not can be predicted by electrochemical series.

(i.e.) Any metal above the hydrogen in the series is a weaker reducing agent and cannot reduce H^- and H_2 gas. Any metal lying below the hydrogen in the series is a stronger reducing agent and can reduce H^+ to H_2 gas.

Example: Zn can liberate H_2 gas from dil.H_2SO_4. But Cu can not. The reason is Zn is lying below and Cu is above the hydrogen in the electro chemical series.

$$Zn + 2H^+ \xrightarrow[\text{(dil.}H_2SO_4\text{)}]{} Zn^{2-} + H_2\uparrow$$

$$Cu + 2H^+ \cancel{\xrightarrow[\text{(dil.}H_2SO_4\text{)}]{}} Cu^2 + H_2\uparrow$$

2.14 CELLS

2.14,1 REVERSIBLE CELL:

A cell which has the following conditions is known as reversible cell.

i) The external emf equal to that of the cell emf is applied in opposite direction, no reaction should occur on either of the electrodes.

ii) The external emf is infinitesimally increased, the current will start to flow into the cell and the cell reaction gets reversed.

Eg : Daniel cell

The normal equation is,

$$Zn + Cu^{2-} \longrightarrow Zn^{2+} + Cu$$

If an external emf is increased infinitesimally, the cell reaction is reversed.

$$Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn$$

Thus the Daniel cell is a reversible cell.

2.14.2 IRREVERSIBLE CELL

A cell which does not satisfy the condition of reversibility is known as irreversible cell (i.e.) its chemical reaction can not be reversed by the application of external emf.

Example : A cell composed of Zn and Cu electrodes dipped in a solution H_2SO_4

$$Zn / H_2SO_4 / Cu$$

When these two electrodes are connected, zinc dissolves into the solution and hydrogen is liberated at the cathode (Cu^- electrode)

$$Zn + 2H^{\oplus} \longrightarrow Zn^{2+} + H_2\uparrow$$

When the cell is connected, zinc dissolves into the solution and hydrogen is liberated at the cathode (Cu^- electrode)

$$Cu + 2H^{\oplus} \longrightarrow Cu^{2+} + H_2\uparrow$$

The original state is note reproduced. The cell reaction is also not reversed. Thus it is an irreversible cell.

2.15 POTENTIOMETRIC TITRATIONS

Titrations in which the end point is determined by measurement of electrode potential are known as potentiometric titrations. Three types of potentiometric titration are possible.

a) Acid-base titrations
b) Oxidation-reduction (Redox) titrations
c) Precipitation titrations.

2.15 .1 Acid-base titrations

The acid-base titration involve changes in the concentration of H^+ ions or changes in the pH of the solution.

Hydrogen electrode (or) glass electrode is immersed in the known volume of the acid solution whose strength is to be determined. The indicator electrode is connected to a standard calomel electrode (reference) to form a galvanic cell.

It may be represented as

Pt_2H_2 (1 atm), H^+ (unkonwn) || KCl (sat soln), Hg_2Cl_2 (s), Hg

Hydrogen electrode || SCE

The EMF of the cell is measured potentiometrically. It is given by

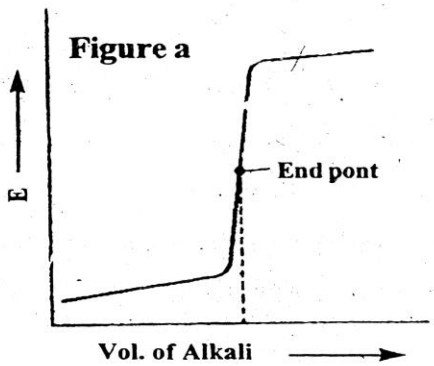
$E = E_R - E_L = E_{calomel} - E_{hydrogen}$

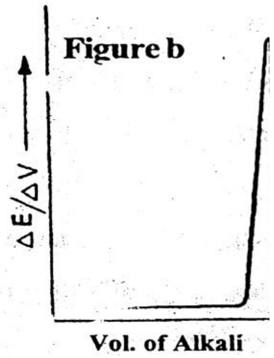
$= 0.2422 + 0.0591$ pH

Example : HCl × NaOH

When NaOH is added, the H^+ ion concentration goes on decreasing ie pH of the solution goes on increasing. Hence the emf of the cell (E) rises gradually. Near the end point the emf rises sharply. After the end point, the emf changes slightly on the addition of excess of alkali.

The emf of the cell (E) is plotted against the volume of alkali added. The type of curve obtained for the titration of strong acid against strong base (HCl vs NaOH) is shown in the Figure a. The steepest portion of the curve indicates the end point. For every dilute solutions, or weak acids or weak bases, the end point detection is very difficult. It such cases, $\frac{\Delta E}{\Delta V}$ is ploted against volume of the alkali added (Figure b). The maximum of the curve indicates the end point.

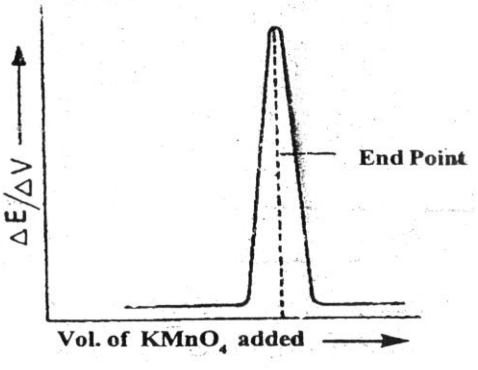




2.15 .2 Oxidation – reduction titrations (Redox – titrations)

Consider the titration of $FeSO_4$ against $KMnO_4$ (or $K_2Cr_2O_7$). The platinum electrode (indicator electrode) is connected to a calomel electrode (reference electrode) and is immersed in the known volume of $FeSO_4$ solution. The complete cell thus formed is

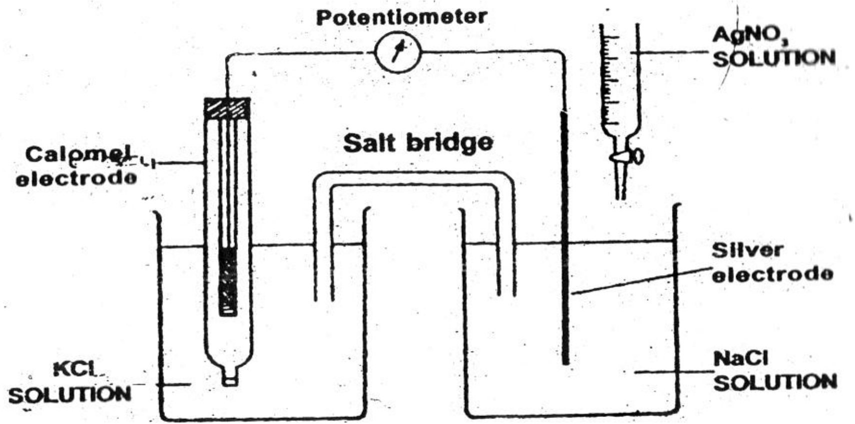
$Pt / Fe^{2+}, Fe^{3+}$ || SCE



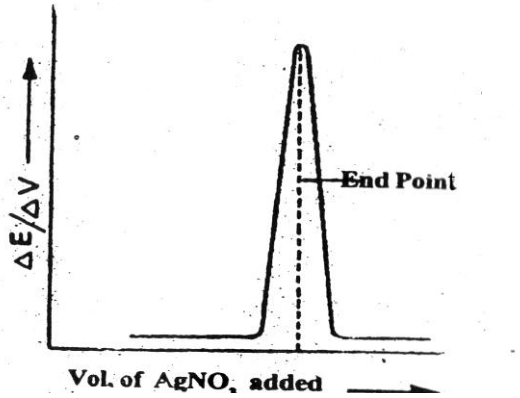
When $KMnO_4$ is added from the burette, the emf rises. Near the end point the emf rises sharply. The end point of this titration is determined by plotting $\frac{\Delta E}{\Delta V}$ against volume of $KMnO_4$ added.

2.15 .3 Precipitation titration

Consider the titration $AgNO_3$ with NaCl solution. A silver electrode (indicator electrode) is dipped in the unknown sodium chloride. It is connected to a calomel electrode (reference electrode) through a salt bridge as shown in the figure. The emf (E) of the cell depends upon upon the concentration of Ag^+ ions around the silver electrode.



Initially the concentration of Ag^+ ions will be zero. When the $AgNO_3$ solution is added from the burette, AgCl is precipitated. Now a reversible silver – silver chloride electrode is setup. As a result, the solution contains a small concentration of Ag^+ ions and the emf (E) will rises gradually. The emf point of this titration is determiend by plotting $\Delta E / \Delta V$ against volume of the $AgNO_3$ added.



2.15 .4 Advantages of potentiometric titrations:

i) Used to findout the end point of coloured solutions where no indicator is effective.

ii) In oxidation – reduction titrations, the use of external, indicator is eliminated.

iii) Used in acid – base titrations where no suitable indicator is found to work, Example : weak acid Vs weak base.

2.16 QUESTIONS FOR DISCUSSION

Define cell reaction?

Discuss conductometric titrations?

2.17 SUGGESTED READINGS

1. Basic Physical Chemistry, by Wolfgang Schärtl - Bookboon , 2014 (ONLINE)
2. Atkins, P. de Paula, J. Physical Chemistry for the Life Sciences. pg 209-225. 2006. Oxford Univeristy Press. New York.
3. Zumdahl, S. Zumdahl, S. Chemistry. Pg 215-220. 2007. Houghton Mifflin Company. New Jersey.
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UNIT III
PHASE RULE

CONTENTS

3.0 AIMS AND OBJECTIVES

After study this unit you should able to,

- Explain Phase, Phase rule
- Draw and explain Phase diagram.
- Elucidate one component system ,two component systems two component alloy system (or) multi component equilibria,Reduced phase rule (or) condensed system

3.1 INTRODUCTION

For a system at equilibrium the phase rule relates:

P = number of phases that can coexist, to
C = number of components making up the phases, and
F = degrees of freedom.
Where these three variables are related in the equation
P + F = C + 2

The degrees of freedom represent the environmental conditions which can be independantly varied without changing the number of phases in the system. Conditions include:

Temperature,
Pressure,
Chemical Composition, Oxygen Fugacity ,etc .

3.2 DEFINITIONS

3.2.1 System: An assemblage of materials that is isolated in some manner from rest of the universe.

- ***isolated system:***one that does not exchange matter or energy with its surroundings.
- ***closed system:*** one that exchanges only energy with its surroundings.
- ***open system:*** one that exchanges both matter and energy with its surroundings.
- ***adiabatic system:*** a system with changes in energy caused only by a change in volume as pressure changes.

3.2.2 Equilibrium: The lowest energy state of a system in which there is no tendency for a spontaneous change.

3.2.3 Metastable Equilibrium: state of a system which is not in its lowest energy state at the imposed conditions, but cannot spontaneously change due to high activation energy for change.

All chemical reactions are broadly classified into 2 types:

1) Irreversible Reactions : $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$
2) Reversible reactions:
   (a) Homogeneous reversible reactions
   Eg: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   (b) Heterogeneous reversible reactions
   Eg: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

The reversible reactions are represented by 2 arrows in the opposite directions. The homogeneous reversible reactions can be studied by the law of mass action and the heterogeneous reversible reactions using the phase rule, given by Willard Gibbs (1874) which is defined as,

3.3 PHASE RULE:

If the equilibrium between any numbers of phases is not influenced by gravitational/electrical/ magnetic forces but is influenced by pressure, temperature and concentration, then the number of degrees of freedom (F) is related to the number of components (C) and the number of phases (P) as: $F = C - P + 2$

Explanation of terms with examples

3.3.1 PHASE (P):

PHASE is defined as, “any homogeneous physically distinct and mechanically separable portions of a system which is separated from other parts of the system by definite boundaries”.

a) Gaseous phase (g):

All gases are completely miscible and have no boundaries between them. Hence all gases constitute a single phase.

Eg: Air, a mixture of O_2, H_2, N_2, CO_2 and water vapor, etc., constitutes a single phase.

(b) Liquid Phase (l):

The number of liquid phases depends on the number of liquids present and their miscibility‟s.

(i) If two liquids are immiscible, they will form two separate liquid phases. (e.g.) Benzene – Water system.

(ii) If two liquids are completely miscible, they will form only one liquid phase. (e.g.) Alcohol - Water system.

(c) Solid Phase (s):

Every solid constitutes a separate single phase. (e.g.) *Decomposition of $CaCO_3$*

$$\mathbf{CaCO_3(s) \rightleftharpoons CaO\,(s) + CO_2(g)}$$

It involves 3 phases namely solid $CaCO_3$, solid CaO and gaseous CO_2

Other examples:

1) A water system has 3 phases namely one solid, one liquid and one gaseous phase.

$$\mathbf{Ice(s) \rightleftharpoons Water(l) \rightleftharpoons Vapour(g)}$$

2) A solution of a substance in a solvent constitutes only one phase. *(e.g.)* Sugar solution in water.

3) An emulsion of oil in water forms two phases

4) $\mathbf{MgCO_3\,(s) \rightleftharpoons MgO\,(s) + CO_2\,(g)}$

It involves 3 phases, solid $MgCO_3$, solid MgO and gaseous CO_2.

5) Rhombic sulphur (s) ––––> Monoclinic sulphur (s). It forms 2 phases.

6) Consider the following heterogeneous system.

$$\mathbf{CuSO_4(s) + 5H_2O\,(l) \rightleftharpoons CuSO_4 \, . \, 5H_2O\,(s)}$$

It involves 3 phases namely, 2 solids and 1 liquid phase.

3.3.2 COMPONENT (C):

Component is defined as, “the minimum number of independent variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation”.

Examples:

(a) Consider a water system consisting of three phases.

$$\mathbf{Ice(s) \rightleftharpoons Water(l) \rightleftharpoons Vapour(g)}$$

The chemical composition of all the three phases is H2O. Hence the number of component is one.

(b) Sulphur exists in 4 phases namely rhombic, monoclinic, liquid and vapour, but the chemical composition is only sulphur. Hence it is a one component system.

(c) Thermal decomposition of $CaCO_3$

$$\mathbf{CaCO_3s) \rightleftharpoons CaO\,(s) + CO_2(g)}$$

The system has 3 phases namely, solid $CaCO_3$, solid CaO and gaseous $CO_2$and 2 components, as the composition of each of the above phases can be expressed as equations considering any two of the three components present. When $CaCO_3$and CaO are considered as components, the chemical equations are:

Phase	Components
$CaCO_3$	$CaCO_3 + 0CaO$
CaO	$0CaCO_3 + CaO$
CO_2	$CaCO_3 - CaO$

(d) **$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$**

This system has 3 phases and 2 components namely, PCl_3 and Cl_2.

(e) An aqueous solution of NaCl is a two component system. The constituents are NaCl and H_2O.

(f) **$CuSO_4.\ 5H_2O(s) \rightleftharpoons CuSO_4\ .\ 3H_2O(s) + 2H_2O(g)$**

It is also a two component system as components are $CuSO_4.3H_2O$ and H_2O.

(g) In the dissociation of NH_4Cl , the following equilibrium occurs.

$$NH_4Cl\ (s) \rightleftharpoons NH_3\ (g) + HCl\ (g)$$

The system consists of 2 phases namely solid NH_4Cl and the gaseous mixture containing NH_3 + HCl. When $NH_3$and HCl are present in equivalent quantities the composition of both the phases can be represented by NH_4Cl and hence the system will be a one component system.

3.3.3. DEGREE OF FREEDOM (F)

Degree of freedom is defined as, "the minimum number of independent variable factors like temperature, pressure and concentration, which must be fixed in order to define the system completely".

A system having 1, 2, 3 or 0 degrees of freedom are called as univariant, bivariant, trivariant and non-variant systems respectively.

Examples:

(a) Consider the following equilibrium

$$\text{Ice(s)} \rightleftharpoons \text{Water(l)} \rightleftharpoons \text{Vapour(g)}$$

These 3 phases will be in equilibrium only at a particular temperature and pressure. Hence, this system does not have any degree of freedom, so it is non-variant (or) zero-variant (or) in-variant system.

(b) Consider the following equilibrium

$$\text{Liquid Water(l)} \rightleftharpoons \text{Water- vapour(g)}$$

Here liquid water is in equilibrium with water vapour. Hence any one of the degrees of freedom such as temperature (or) pressure has to be fixed to define the system. Therefore the degree of freedom is one.

(c) For a gaseous mixture of N_2 and H_2, both the pressure and temperature must be fixed to define the system. Hence, the system is bivariant.

3.4 PHASE DIAGRAM

Phase diagram is a graph obtained by plotting one degree of freedom against theother.

Types of Phase Diagrams

(i) P-T Diagram

If the phase diagram is plotted between temperature and pressure, the diagram is called P -T diagram. P -T diagram is used for one component system.

(ii) T-C Diagram

If the phase diagram is plotted between temperature and composition, the diagram is called T-C diagram.T- C diagram is used for two component system

Uses of Phase Diagram:

It helps in

(i) Predicting whether an eutectic alloy (or) a solid solution is formed on cooling a homogeneous liquid containing mixture of two metals.

1.12. Understanding the properties of materials in the heterogeneous equilibrium system.

1.13. Studying of low melting eutectic alloys, used in soldering.

3.5 ONE COMPONENT SYSTEM

APPLICATIONS OF PHASE RULE - TO ONE COMPONENT SYSTEM

3.5.1 The Water System

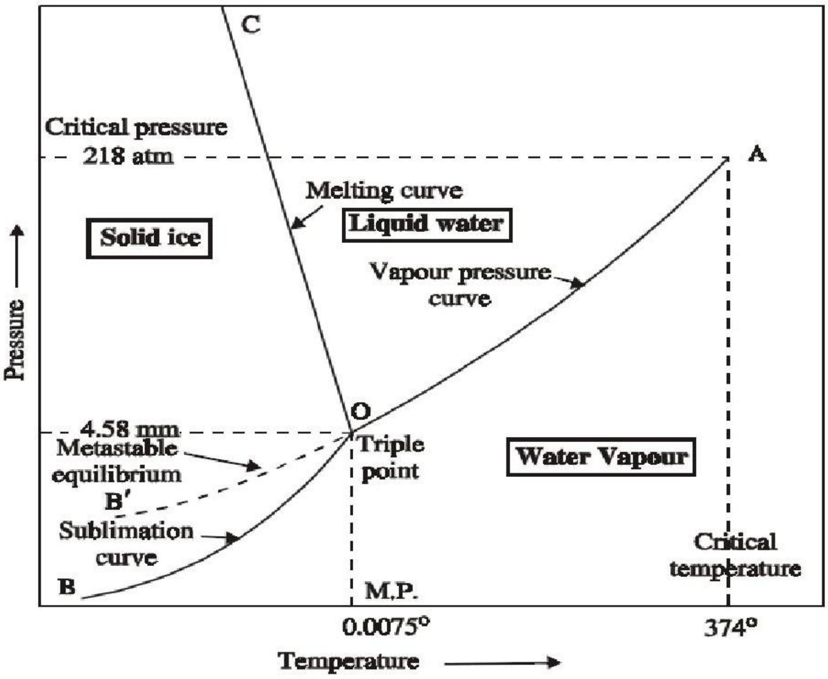
Water exists in 3 possible phases, namely solid ice, liquid water and water-vapour. Hence, there can be three forms of equilibria, each involving two phases such as.

Solid Ice $\rightleftharpoons$ **Liquid Water**

Liquid Water $\rightleftharpoons$ **Water- vapour**

Solid Ice $\rightleftharpoons$ **Water- vapour**

The phase diagram for the water system is as follows and it contains curves, areas, and triple point.



Curve OA

The curve OA is called vapourisation curve, it represents the equilibrium between water and vapour.

At any point on the curve the following equilibrium will exist.

Liquid Water $\rightleftharpoons$ **Water- vapour**

This equilibrium (i.e. line OA) will extend upto the critical temperature (374°C).

Beyond the critical temperature the equilibrium will disappear and only water vapour will exist

Curve OB

The curve OB is called sublimation curve of ice, it represents the equilibrium between solid ice and water-vapour.

At any point on the curve the following equilibrium will exist.

$$\textbf{Solid Ice} \rightleftharpoons \textbf{Water- vapour}$$

This equilibrium (i.e.line OB) will extend up to the absolute zero (− 273°C)

Beyond absolute zero only solid ice will exist and no water-vapour.

Curve OC

The curve OC is called melting point curve of ice, it represents the equilibrium between ice and water.

At any point on the curve the following equilibrium will exist.

$$\textbf{Solid Ice} \rightleftharpoons \textbf{Liquid Water}$$

The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure.

Curve OB′(Metastable Equilibrium)

The curve OB′ is called vapour pressure curve of the super-cooled water (or) metastable equilibrium where the following equilibrium will exist.

$$\textbf{Super- cooled water} \rightleftharpoons \textbf{Water- vapour}$$

Sometimes water can be cooled below it"s freezing point (0°C) without the formation of ice, this water is called super-cooled water.

Super cooled water is unstable and it can be converted into solid ice by “seeding” (or) by slight disturbance.

Along the curves OA,OB,OC and OB′

The no. of phases(P) is 2 ,component(C) is 1 and the degree of freedom of the system is one i.e., univariant. This is predicted by the phase rule:

$$\mathbf{F = C - P + 2;\ F = 1 - 2 + 2;\ F = 1}$$

Therefore, either temperature (or) pressure must be fixed to define the system.

Point ‘O’ (Triple point)

The three curves OA, OB and OC meet at a point „O", where three phases namely solid ice, liquid water and water-vapour are simultaneously at equilibrium.

This point is called triple point, at this point the following equilibrium will exist

$$\textbf{Ice(s)} \rightleftharpoons \textbf{Water(l)} \rightleftharpoons \textbf{Vapour(g)}$$

At this point the no. of phases(P) is 3, component(C) is 1 and the degree of freedom of the system is zero i.e., nonvariant. This is predicted by the phase rule:

$$\mathbf{F = C - P + 2;\ F = 1 - 3 + 2;\ F = 0}$$

This takes place only at a constant temperature (0.0075°C) and pressure (4.58 mm of Hg).

Areas

Areas AOC, BOC, AOB represents liquid water, solid ice and water-vapour respectively where the no. of phases(P) and component(C) are one. Hence the degree of freedom of the system is two i.e., bivariant. This is predicted by the phase rule:

$$\mathbf{F = C - P + 2;\ F = 1 - 1 + 2;\ F = 2}$$

Therefore, both temperature and pressure must be fixed to define the system at any point in the areas.

3.5.2 THE SULPHUR SYSTEM

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

(*a*) Two solid polymorphic forms :

- (*i*) Rhombic Sulphur (S_R)
- (*ii*) Monoclinic Sulphur (S_M)

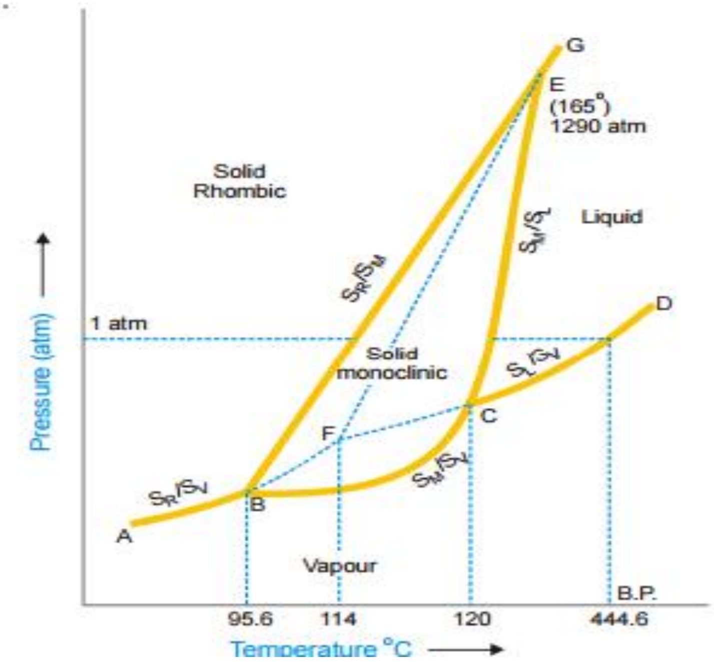
(*b*) Sulphur Liquid (S_L)

(*c*) Sulphur Vapour (S_V)

All the four phase can be represented by the only chemical individual ‘sulphur’ itself and hence one component of the system.

The two crystalline forms of sulphur S_R and S_M exhibit enantiotropy with a transition point at 95.6°C. Below this temperature $S_R$is stable, while above it $S_M$is the stable variety. At 95.6°C eachform can be gradually transformed to the other and the two are in equilibrium. At 120°C, S_M melts. Thus,

$$S_R \overset{95.61^\circ}{\rightleftharpoons} S_M \overset{120^\circ}{\rightleftharpoons} S_L$$



The phase diagram for the sulphur system is shown in Fig. 19.4. The **salient features of thephase diagram** are described below.

(*i*) The six curves *AB, BC, CD, BE, CE, EG*

(ii) The three Triple points *B, C, E*

(iii) (*iii*) The four areas :

ABG marked ‘solid Rhombic’
BEC marked ‘solid Monoclinic’
GECD marked ‘liquid Sulphur’
ABCD marked ‘Sulphur vapour’

Let us now proceed to discuss the significance of these features :

1. The curves *AB, BC, CD, BE, CE, EG*

These *six curves* divide the diagram into *four* areas.

Curve *AB*, the Vapour Pressure curve of S_R. It shows the vapour pressure of solid rhombicsulphur (S_R) at different temperatures. Along this curve the two phases S_R and sulphur vapour (S_V) are in equilibrium. The system S_R/S_V has one degree of freedom,

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

i.e., it is *monovariant.*

Curve *BC*, the Vapour Pressure curve of S_M. It shows variation of the vapour pressure of monoclinic sulphur (S_M) with temperature. S_M and S_V coexist in equilibrium along this curve. The system S_M/S_V is *monovariant*.

Curve *CD*, the Vapour Pressure curve of S_L. It depicts the variation of the vapour pressure of liquid sulphur (S_L) with temperature. S_L and S_V are in equilibrium along *CD*. The two phase system S_L/S_V is monovariant. One atmosphere line meets this curve at a temperature (444.6ºC) which is the boiling point of sulphur.

Curve *BE*, the Transition curve. It shows the effect of pressure on the transition temperature for S_R and S_M. As two solid phases are in equilibrium along the curve, the system S_R/S_M is *monovariant.* The transformation of S_R and S_M is accompanied by increase of volume (density of $S_R = 2.04$; $S_M = 1.9$) and absorption of heat *i.e.*,

$$S_R + Q \text{ (heat energy)} \rightleftharpoons S_M$$

Thus the increase of pressure will shift the equilibrium to the left (*Le Chatelier's Principle*) and the transition temperature will, therefore, be raised. This is why the line *BE* slopes away from the pressure axis showing thereby that the transition temperature is raised with increase of pressure.

Curve *CE*, the Fusion curve of S_M. It represents the effect of pressure on the melting point of S_M. The two phases in equilibrium along this curve are S_M and S_L. The system S_M/S_L is *monovariant.* As the melting or fusion of S_M is accompanied by a slight increase of volume, the melting point will rise by increase of pressure (*Le Chatelier's principle*). Thus the curve *CE* slopes slightly away from the pressure axis. The curve ends at *E* because S_M ceases to exist beyond this point.

Curve *EG*, the Fusion curve for S_R. Here the two phases in equilibrium are S_R and S_L. The number of phases being two, the system S_R/S_L is *monovariant.*

2 The Triple points *B, C, E*

Triple point B. This is the meeting point of the three curves *AB*, *BC* and *BE*. Three phases, solid

S_R, solid S_M and S_V are in equilibrium at the point B. There being three phases and one component, the system $S_R/S_M/S_L$ is *nonvariant.*

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

At *B*, S_R is changed to S_M and the process is reversible. Thus the temperature corresponding to

B is the *transition temperature* (95.6ºC).

Triple point *C*. The curves *BC*, CD, CE meet at this point. The three phases in equilibrium are S_M, S_L and S_V. There being three phases and one component, the system $S_M/S_L/S_V$ is *nonvariant.* The temperature corresponding to *C* as indicated on the phase diagram is 120ºC. This is the melting point of S_M.

Triple point *E*. The two lines *CE* and *BE*, having different inclinations away from the pressure axis, meet at E where a third line *EG* also joins. The three phases S_R, S_M and S_L are in equilibrium and the system at the point *E* is *nonvariant*. This point gives the conditions of existence of the system $S_R/S_M/S_L$ at 155ºC and 1290 atmospheres pressure.

(3) The Areas

The phase diagram of the sulphur system has **four areas** or **regions.** These are labelled as rhombic sulphur, monoclinic sulphur, liquid sulphur and vapour. These represent single phase systems which have two degrees of freedom,

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

That is, each of the systems S_R, S_M, S_L, and S_V are *bivariant.*

(4) Metastable Equilibria

The change of S_R to S_M takes place very slowly. If enough time for the change is not allowed and S_R is heated rapidly, it is possible to pass well above the transition point without getting S_M. In that case, there being three phases (S_R, S_L, S_V) only and one component, the phase diagram, like that of water system, will consist of three curves, one triple point and three areas.

The dashed curve *BF*, the Vapour Pressure curve of metastable S_R. This is a continuation ofthe vapour pressure curve *AB* of stable S_R. The metastable phases S_R and S_V are in equilibrium along this curve. It is a *monovariant system*.

The dashed curve CF, the Vapour Pressure curve of supercooled S_L. On supercooling liquidsulphur, the dashed curve *CF* is obtained. It is, in fact, the back prolongation of *DC*. The curve *CF* represents the metastable equilibrium between supercooled S_L and S_V. Thus it may be designated as the vapour pressure curve of supercooled S_L. It meets the dashed curve *BF* at *F*.

The dashed curve *FE*, the Fusion curve of metastable S_R. The two metastable phases $S_R$and $S_L$are in equilibrium along this curve and the system is *monovariant.* This shows that the melting point of metastable S_R is increased with pressure. Beyond *E*, this curve depicts the conditions for the stable equilibrium S_R/S_L as the metastable S_R disappears.

The metastable Triple point *F*. At this point, three metastable phases S_R, $S_L$and $S_V$are inequilibrium. The system is a metastable triple point with no degree of freedom. The corresponding temperature is the melting point of metastable S_R (114°C).

3.6 TWOCOMPONENT ALLOY SYSTEM (or) MULTI COMPONENTEQUILIBRIA

Reduced Phase Rule (or) Condensed System

The maximum number of degree of freedom for a two component system will be three, when the system exists as a single phase.

$$\mathbf{F = C - P + 2;\ F = 2 - 1 + 2;\ F = 3}$$

In order to represent the conditions of equilibrium graphically, it requires three co-ordinates, namely P, T and C. This requires three dimensional graph, which cannot be conveniently represented on paper. Therefore, any two of the three variables must be chosen for graphical representation.

A Solid-liquid equilibrium of an alloy has practically no gaseous phase and the effect of pressure is negligible. Therefore, experiments are conducted under atmospheric pressure.

Thus, the system in which only the solid and liquid phases are considered and the gas phase is ignored is called a condensed system.

Since the pressure is kept constant, the phase rule becomes

$$\mathbf{F' = C - P + 1}$$

This equation is called reduced phase rule (or) condensed phase rule.

3.6.1 Classification of Two Component System

Based on the solubility and reactive ability, the two component systems are classified into three types.

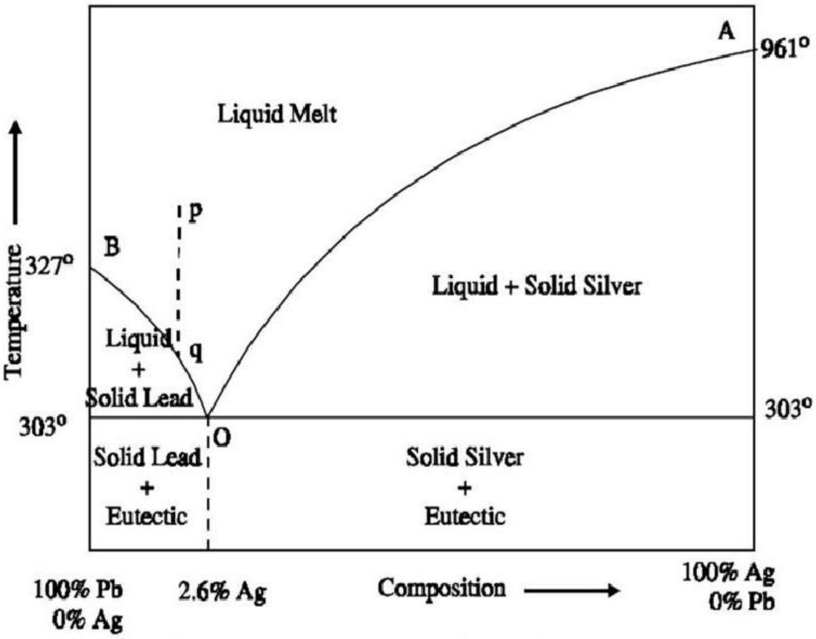
(i) Simple eutectic formation.
(ii) (a) Formation of compound with congruent melting point.
(b) Formation of compound with incongruent melting point.

(i) Simple Eutectic Formation

A binary system having two substances, which are completely miscible in the liquid state, but completely immiscible in the solid state, is known as eutectic (easy melt) system. They do not react chemically. Of the different mixtures of two substances, a mixture having the lowest melting point is known as the eutectic mixture

(ii) Formation of compound with congruent melting point
The binary alloy systems with two substances form one or more compounds with definite proportions. Of the compounds, a compound is said to have congruent melting point, if it melts exactly at a constant temperature into liquid, having the same composition as that of the solid.

(ii) Formation of compound with incongruent melting point
Of the above compounds, a compound is said to have incongruent melting point, if it decomposes completely at a temperature below its melting point forming a new solid phase with a different composition from that of the original.
(iii) Formation of solid solution
A binary system in which two substances, especially metals, are completely miscible in both solid and liquid states form solid solutions and their mixing takes place in the atomic levels. This happens only when the atomic radius of the two metals not differ by more than 15%.



Phase diagram of Lead - Silver system

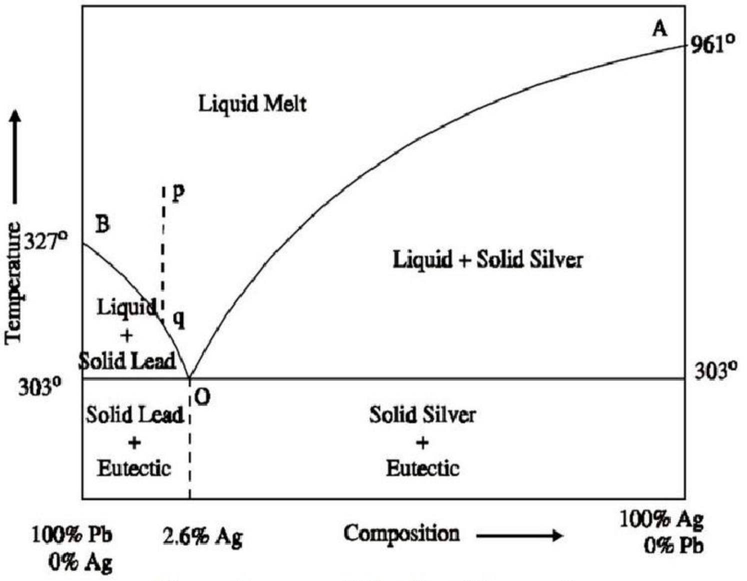
3.6.2 BINARY ALLOY SYSTEM (OR) THE SIMPLE EUTECTIC SYSTEM

The Lead-Silver System

The Lead-Silver system is studied at constant pressure and the vapour phase is ignored. Hence the condensed phase rule is used:

$$\mathbf{F' = C - P + 1}$$

The phase diagram of lead-silver system is shown as follows. It contains curves, areas and eutectic point.



Phase diagram of Lead - Silver system

(i) Curve AO

The curve AO is known as freezing point curve of silver. Point A is the melting point of pure Ag (961°C). The curve AO shows the melting point depression of Ag by the successive addition of Pb. Along this curve AO, solid Ag and the melt are in equilibrium.

$$\textbf{Solid Ag} \rightleftharpoons \textbf{Liquid Melt}$$

(ii) Curve BO

The curve BO is known as freezing point curve of lead. Point B is the melting point of pure lead (327°C). The curve BO shows the melting point depression of Pb by the successive addition of Ag. Along this curve BO, solid Pb and the melt are in equilibrium.

$$\textbf{Solid Pb} \rightleftharpoons \textbf{Liquid Melt}$$

Along the curves AO and BO

The degree of freedom according to reduced phase rule is as follows:

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

The system is univariant which means either temperature (or) composition must be fixed to define the system.

(iii) Point 'O' (Eutectic point)

The curves AO and BO meet at point „O‟ at a temperature of 303°C, where three phases (solid Ag, solid Pb and their liquid melt) are in equilibrium.

$$\textbf{Solid Ag + Solid Pb} \rightleftharpoons \textbf{Liquid Melt}$$

According to reduced phase rule equation.

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

The system is non-variant.

The point „O‟ is called eutectic point or eutectic temperature and its corresponding composition, 97.4%Pb + 2.6%Ag, is called eutectic composition.

Below this point the eutectic compound and the metal solidify.

(iv) Area

The area above the line AOB has a single phase (molten Pb+Ag) or liquid melt. According to reduced phase rule the degree of freedom.

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

The system is bivariant which means both the temperature and composition have to be fixed to define the system completely.

The area below the line AO (solid Ag + liquid melt), below the line BO (solid Pb +

liquid melt) and below the point „O‟ (Eutectic compound + solid Ag or solid Pb) have two phases and hence the system is univariant

$$\mathbf{F' = C - P + 1;\ F' = 2 - 2 + 1;\ F' = 1.}$$

Application of Pattinson's process for the desilverisation of Argentiferous lead

The argentiferous lead, having a very small amount of silver (say 0.1%), is heated to a temperature above its melting point, so that the system has only the liquid phase represented by the point "**p**‟ in the phase diagram .

It is then allowed to cool where the temperature decreases along the line "**pq**‟. As soon as the point "**q**‟ is reached, Pb is crystallised out and the solution will contain relatively increasing amounts of "Ag‟. On further cooling, more and more of "Pb‟ is separated along the line "BO‟. The melt continues to be richer and richer in Ag until the point „O‟ is reached, where the percentage of Ag rises to 2.6%.

Thus, the process of raising the relative proportions of Ag in the alloy is known as Pattinson‟s process.

3.6.3 POTASSIUM IODIDE–WATER SYSTEM

It has **four phases** : (*i*) Solid KI ; (*ii*) Solution of KI in water ; (*iii*) Ice; and (*iv*) Vapour. Only two chemical constituents KI and H_2O being necessary to depict the composition of all the four phases, it is a **two-component system.**

Since the conditions for the existence of the various phases are studied at atmospheric pressure the vapour phase is ignored and the system KI-H_2O is regarded as a *condensed system.* Pressure being constant, the two variables, temperature and concentration will be considered. The *TC* diagram of the system is shown in Fig. 19.8. It consists of :

(*a*) The Curves *AO* and *OB* (*b*)

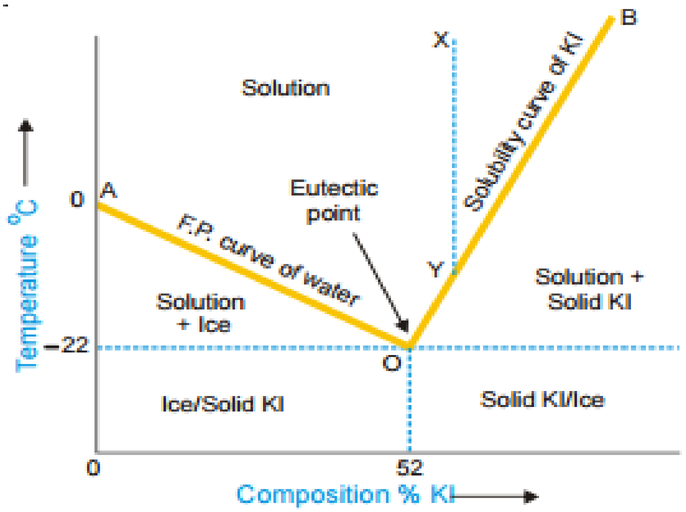
The Eutectic Point *O*

(*c*) The area above *AOB* and the areas below the curves *OA* and *BO*

The Curve *AO*; the Freezing point curve of Water. The point*A*represents the freezing point ofwater or the melting point of ice (0ºC) under normal conditions. The curve *AO* shows that the melting point of ice falls by the addition of solid KI. As more and more of KI is added, the concentration of solution and the melting temperature changes along the curve *AO*. The phases in equilibrium along the curve *AO* are ice and solution. Applying the reduced phase rule equation to the condensed system ice/solution, we have

$$F' = 2 - 2 + 1 = 1$$

Thus the system is *monovariant.*



The Eutectic point. The lowest point attainable by the addition of KI along the curve*OA*is*O*.Here the solution becomes saturated with KI and the solid KI appears as the third phase. This point is termed the *Eutectic Point* or *Cryohydric Point* as one of the components in the system is water. Applying the reduced phase rule equation to the system ice/solid KI/solution at point *O*.

$$F' = 2 - 3 + 1 = 0$$

Hence the system is *nonvariant*. That is, both the temperature (– 22ºC) and composition (52% KI + 48% ice) are fixed.

The Curve *BO*; the Solubility curve of KI. At*O*, the solution is saturated with*KI*. Thus the curve*BO* depicts the effect of temperature on the concentration of saturated solution or the solubilityof KI. The phases in equilibrium along the curve are solid KI and solution. Applying the reduced phase rule equation, we have

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

That is, the condensed system solid KI/solution is *monovariant*.

The Area above *AOB*.It represents the single phase system 'solution'. Applying the phase ruleequation,

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

Therefore the system is *bivariant*.

As labelled in the diagram, the area below *AO* shows the existence of ice and solution, while the area below *BO* depicts the presence of solid KI and solution. Below the eutectic temperature line, there can exist ice and solid KI only.

Cooling Produced by Freezing Mixtures

KI-H_2O is a typical eutectic system with a salt and water as components. Many other salts as sodium chloride, sodium nitrate, ammonium chloride and ammonium nitrate constitute eutectic systems with water and form similar phase diagrams as shown in Fig. 19.8. The facts contained in this diagram explain the **theory of freezing mixtures** which are obtained by mixing salt and ice.

When we add a salt, common salt (NaCl) to melting ice, we follow along the curve *AO*. Thus the addition of salt to the system ice/water produces a continued lowering of temperature until the eutectic point O is reached. Thus the lowest temperature attained in this way will be the eutectic temperature (– 22.0ºC). Alternatively, we may start with a concentrated solution of the salt represented by point *X* on the phase diagram. As we withdraw heat by adding ice, we travel along the dashed line *XY*. At *Y* which lies on the solubility curve *BO*, the solution becomes saturated with the salt. Onfurther withdrawing heat, we go along with the curve *BO* until the eutectic point is reached. Thus the same minimum temperature can be attained with a freezing mixture, whether we add salt to ice or ice to salt solution. The eutectic temperatures of some salt/ice systems are listed below.

System	Eutectic Temperature
NH_4Cl + ICE	– 16.0ºC
$NaCl.2H_2O$ + ICE	– 22.0ºC
KNO_2 + ICE	– 2.6ºC
$NaNO_2$ + ICE	– 18.1ºC
KCl + ICE	– 11.4ºC

Uses of Eutectic system

1. Suitable alloy composition can be predicted.

Making solders, used for joining two metal pieces together.

Differences between Melting point, Eutectic point and Triple point

1. **Melting Point:** It is the temperature at which the solid and liquid phases, having thesame composition, are in equilibrium.

Solid A $\rightleftharpoons$ Liquid A

2. **Eutectic Point:** It is the temperature at which two solids and a liquid phase are inequilibrium

Solid A + Solid B $\rightleftharpoons$ Liquid 3.

Triple Point

It is the temperature at which three phases are in equilibrium.

Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Vapour

All the eutectic points are melting points

All the melting points need not be eutectic points.

Similarly all the eutectic points are triple points, but all the triple points need not be eutectic points.

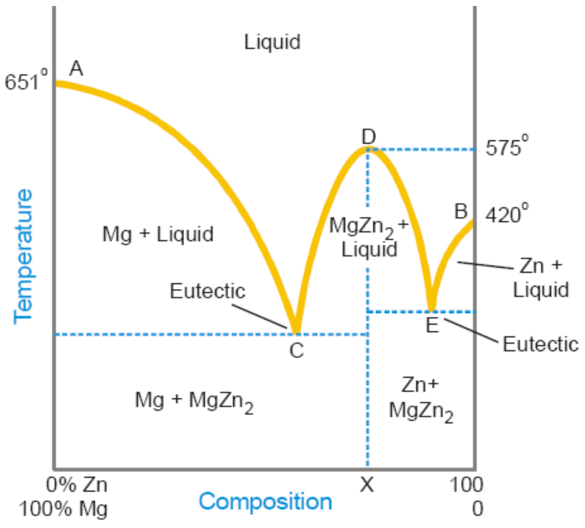
SYSTEM FORMING COMPOUNDS WITH CONGRUENT MELTING POINT:

When the components of a binary system at a particular stage form a compound which melts at a sharp temp to give a liquid of the same composition as that of solid and the temp at which the compound melt is called congruent melting point.

3.6.4 THE MAGNESIUM–ZINC SYSTEM

It is a typical 2-component system which involves the formation of an intermetallic compound $MgZn_2$. It has four phases: solid magnesium (Mg), solid zinc (Zn), solid $MgZn_2$ and the liquid solution of Mg and Zn.

The complete phase diagram of the system magnesium-zinc is shown in Fig. 19.10. It appears to be made of two simple eutectic diagrams. The one toward the left represents the eutectic system Mg-$MgZn_2$, while the one to the right the system Zn-$MgZn_2$.



The curves *AC*, *CDE* and *BE*. *AC* is the freezing point curve of magnesium; *BE* is the freezing point curve of zinc; and *CDE* is that of the compound $MgZn_2$.

The curve *AC* shows that the melting point of magnesium (651ºC) is lowered on the addition of zinc. This continues until the point *C* is reached. Here a new phase, solid $MgZn_2$ appears.

The curve *CD* shows the increase of concentration of zinc in the melt with the rise of temperature. At the maximum point *D*, the composition of the melt and the solid compound becomes the same *i.e.*, $MgZn_2$. The point D, therefore, represents the melting point of $MgZn_2$ (575ºC). The curve DE now shows the lowering of the melting point with the addition of zinc until the lowest point is attained. Here solid zinc appears.

The curve *BE* exhibits that the melting point of zinc (420ºC) falls with the addition of magnesium until the point *E* is reached.

Along the freezing point curves *AC*, *CDE* and *BE*, there are two phases in equilibrium *viz*., one solid phase (Mg, Zn, or $MgZn_2$) and the other liquid phase. Applying the reduced phase rule equation, we have

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

This shows that the system Mg/liquid, Zn/liquid and $MgZn_2$/liquid are all *monovariant.*

Eutectic points *C* and *E*. There are two eutectic points in the phase diagram. The systems at the points *C* and *E* have two components and three phases in equilibrium.

	Phases Present
C	Solid Mg, solid $MgZn_2$, Liquid
E	Solid Zn, solid $MgZn_2$, Liquid

These systems are, therefore, *nonvariant.*

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

Congruent Melting Point. As already stated, the composition of the compound $MgZn_2$ and the melt at *D* is identical. The corresponding temperature is the *congruent melting point* of the compound. Here the system has two phases *viz.*, the solid compound and the melt. Both these can be represented by one component ($MgZn_2$). Therefore the system at D is *nonvariant*,

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

The Areas. The area above the curves *AC*, *CDE* and *BE* represents the solution of magnesium and zinc (the melt). The single phase system at any point in this area is *bivariant.*

The phases present in the other regions of the phase diagram are as labelled.

3.7 USES (OR) MERITS AND DEMERITS OF PHASE RULE

1. Applicable to both physical and chemical equilibria.
2. A convenient method to classify the equilibrium systems in terms of phases, components and degree of freedom.
3. Indicates that different systems having the same degrees of freedom behave similarly.
4. Decides whether the given number of substances remains in equilibrium or not.
5. Applicable to macroscopic systems without considering their molecular structures.
6. Does not consider the nature (or) amount of substances in the system.

DEMERITS

1. Phase rule can be applied only for the heterogeneous systems in equilibrium.
2. Only three variables like P, T & C are considered, but not electrical, magnetic and gravitational forces.
3. All the phases of the system must be present under the same conditions of pressure and temperature.
4. Solid and liquid phases must not be in finely divided state, otherwise deviations occur.

3.8 QUESTIONS AND ANSWERS

- **Define Phase rule**
- **Explain the phase diagram for water molecule**

- **Explain the process of desilverisation of lead by pattinson's process**

3.9 SUGGESTED READINGS

1. Gibbs, J.W., Scientific Papers (Dover, New York, 1961)

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3. The Theory of Intermolecular Forces, A.J. Stone, Oxford University Press (Oxford), 1996.

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UNIT IV
SPECTROSCOPY

CONTENTS

4.0 AIMS AND OBJECTIVES

After studying this unit you should be able to understand and explain the various spectroscopic techniques like UV spectroscopy, IR spectroscopy and NMR spectroscopy.

4.1 UV SPECTROSCOPY

4.1.1 Introduction

The molecular spectroscopy is the study of the interaction of electromagnetic waves and matter. The scattering of sun's rays by raindrops to produce a rainbow and appearance of a colorful spectrum when a narrow beam of sunlight is passed through a triangular glass prism are the simple examples where white light is separated into the visible spectrum of primary colors. This visible light is merely a part of the whole spectrum of electromagnetic radiation, extending from the radio waves to cosmic rays. All these apparently different forms of electromagnetic radiations travel at the same velocity but characteristically differ from each other in terms of frequencies and wavelength (Table 1).

Table 1: The electromagnetic spectrum

Radiation type	Wave length		Frequency	Applications
	λ , (Ǻ)		$\nu = c / \lambda$, (Hz)	
radio	10^{14}		3×10^{4}	
Nuclear magnetic resonance	10^{12}		3×10^{6}	
Television	10^{10}		3×10^{8}	Spin orientation

Radar	10^8		3×10^{10}	
Microwave	10^7		3×10^{11}	Rotational
Far infrared	10^6		3×10^{12}	Vibrational
Near infrared	10^4		3×10^{14}	
Visible	8×10^3 -	4×10^3	3.7×10^{14} -	
			7.5×10^{14}	
Ultraviolet	3×10^3		1×10^{15}	Electronic
X-rays	1		3×10^{18}	
Gamma rays	10^{-2}		3×10^{20}	Nuclear transitions
Cosmic rays	10^{-4}		3×10^{22}	

The propagation of these radiations involves both electric and magnetic forces which give rise to their common class name electromagnetic radiation. In spectroscopy, only the effects associated with electric component of electromagnetic wave are important. Therefore, the light wave traveling through space is represented by a sinusoidal trace (figure 1). In this diagram λ is the wavelength and distance A is known as the maximum amplitude of the wave. Although a wave is frequently characterized in terms of its wavelength λ, often the terms such as wavenumber (ν), frequency (ν), cycles per second (cps) or hertz (Hz) are also used.

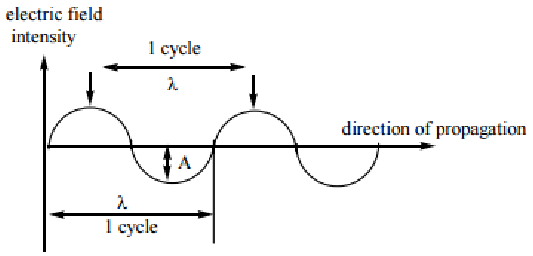


Figure 1: Wave like propagation of light (λ = wavelength , A = amplitude)

The unit commonly used to describe the wavelength is centimeters (cm), the different units are used to express the wavelengths in different parts of the electromagnetic spectrum. For example, in the ultraviolet and visible region, the units use are angstrom (Å) and nanometer (nm). In the infrared region, the commonly used unit is wavenumber (ν), which gives the number of waves per centimeter. Thus

$$1 \text{ cm} = 10^7 \text{ nm} = 10^8 \text{ Å}$$

$$1 \text{ Å} = 10^{-1} \text{ nm} = 10^{-8} \text{ cm}$$

The four quantities wavelength, wavenumber, frequency and velocity can be related to each other by following relationships

$$\text{Wavelength } (\lambda) = 1 / \bar{\nu} = c / \nu$$

$$\text{Wave-number } (\bar{\nu}) = 1 / \lambda = \nu / c$$

$$\text{Frequency } (\nu) = c / \lambda = c \bar{\nu}$$

$$\text{Velocity } (c) = \nu\lambda = \nu / \bar{\nu}$$

Absorption of Different E [illegible] Molecules

In absorption spectroscopy, though the mechanism of absorption of energy is different in the ultraviolet, infrared and nuclear magnetic resonance regions, the fundamental process is the absorption of a discrete amount of energy. The energy required for the transition from a state of lower energy (E_1) to state of higher energy (E_2) is exactly equivalent to the energy of electromagnetic radiation that causes transition.

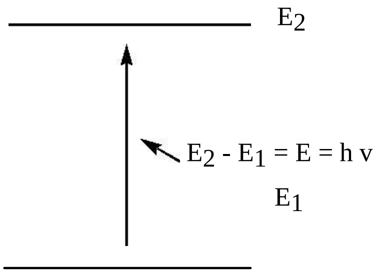


Figure 2: *Energy transition for the absorption of any electromagnetic radiation*

$$E_1 – E_2 = E = h\nu = h\,c/\lambda$$

Where E is energy of electromagnetic radiation being absorbed, h is the universal Planck's constant, 6.624×10^{-27} erg sec and ν is the frequency of incident light in cycles per second (cps or hertz, Hz), c is velocity of light 2.998×10^{10} cm s^{-1} and λ = wavelength (cm)

Therefore, higher is the frequency, higher would be the energy and longer is the wavelength, lower would be the energy. As we move from cosmic radiations to ultraviolet region to infrared region and then radio frequencies, we are gradually moving to regions of lower energies.

A molecule can only absorb a particular frequency, if there exists within the molecule an energy transition of magnitude $E = h\nu$

Although almost all parts of electromagnetic spectrum are used for understanding the matter, in organic chemistry we are mainly concerned with energy absorption from only ultraviolet and visible, infrared, microwave and radiofrequency regions.

Ultraviolet – visible spectroscopy (λ200 - 800 nm) studies the changes in electronic energylevels within the molecule arising due to transfer of electrons from π- or non-bonding orbitals. It commonly provides the knowledge about π-electron systems, conjugated unsaturations, aromatic compounds and conjugated non-bonding electron systems etc.

Infrared spectroscopy (ν400-4000 cm^{-1}) studies the changes in the vibrational and rotationmovements of the_molecules. It is commonly used to show the presence or absence of functional groups which have specific vibration frequencies viz. C=O, NH_2, OH, CH, C-O etc.

Nuclear magnetic resonance (radiofrequencyν60-600 MHz) provides the information aboutchanges in magnetic properties of certain atomic nuclei. ^{1}H and ^{13}C are the most commonly studied nuclei for their different environments and provide different signals for magnetically non-equivalent nuclei of the same atom present in the same molecule.

In the present chapter, UV-Vis and Infrared spectroscopy have been discussed.

Ultraviolet and Visible Spectroscopy

This absorption spectroscopy uses electromagnetic radiations between 190 nm to 800 nm and is divided into the ultraviolet (UV, 190-400 nm) and visible (VIS, 400-800 nm) regions. Since the absorption of ultraviolet or visible radiation by a molecule leads transition among electronic energy levels of the molecule, it is also often called as electronic spectroscopy. The information provided by this spectroscopy when combined with the information provided by NMR and IR spectral data leads to valuable structural proposals.

4.1.2 Nature of Electronic Transitions

The total energy of a molecule is the sum of its electronic, its vibrational energy and its rotational energy. Energy absorbed in the UV region produces changes in the electronic energy of the molecule. As a molecule absorbs energy, an electron is promoted from an occupied molecular orbital (usually a non-bonding n or bonding π orbital) to an unoccupied molecular orbital (an antibonding π^* or σ^* orbital) of greater potential energy (figure 3). For most molecules, the lowest-energy occupied molecular orbitals are σ orbitals, which correspond to σ bonds. The π orbitals lie at relatively higher energy levels than σ orbitals and the non-bonding orbitals that hold unshared pairs of electrons lie even at higher energies. The antibonding orbitals (π^* and σ^*) are orbitals of highest energy. The relative potential energies of these orbitals and various possible transitions have been depicted in figure 3.

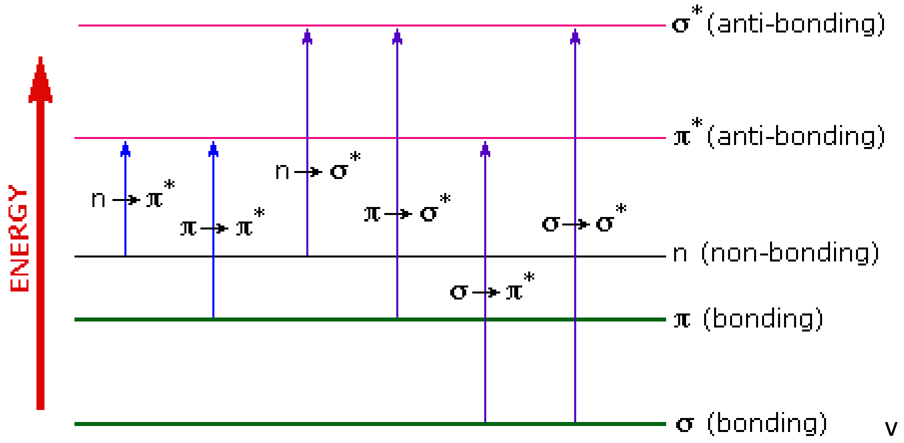


***Figure 3** : Relative energies of orbitals most commonly involved in electronic spectroscopy of organic molecules*

The saturated aliphatic hydrocarbons (alkanes) exhibit only $\sigma \rightarrow \sigma^*$ transitions but depending on the functional groups the organic molecules may undergo several possible transitions which can be placed in the increasing order of their energies viz. $n \rightarrow \pi^* < n \rightarrow \sigma^* < \pi \rightarrow \pi^* < \sigma \rightarrow \pi^* < \sigma \rightarrow \sigma^*$. Since all these transitions require fixed amount of energy (quantized), an ultraviolet or visible spectrum of a compound would consist of one or more well defined peaks, each corresponding to the transfer of an electron from one electronic level to another. If the differences between electronic energy levels of two electronic states are well defined i.e. if the nuclei of the two atoms of a diatomic molecule are held in fixed position, the peaks accordingly should be sharp. However, vibrations and rotations of nuclei occur constantly and as a result each electronic state in a molecule is associated with a largenumber of vibrational and rotational states. At room temperature, the molecules in the ground state will be in the zero vibrational level ($G\upsilon_o$). This is shown schematically in figure 4. The transition of an electron from one energy level to another is thus accompanied by simultaneous change in vibrational and rotational states and causes transitions between various vibrational and rotational levels of lower and higher energy electronic states. Therefore many radiations of closely placed frequencies are absorbed and a broad absorption band is obtained. When a molecule absorbs ultraviolet or visible light of a defined energy, an assumption is made that only one electron is excited form bonding orbital or non-bonding orbital to an anti-bonding orbital and all other electrons remain unaffected. The excited state thus produced is formed in a very short time i.e. of the order of 10^{-15} seconds. In accordance with Franck-Condon principle, during electronic excitation the atoms of the molecule do not move.

The most probable transition would appear to involve the promotion of one electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), but in many cases several transitions can be observed, giving several absorption bands in the spectrum. We can have a general view of the possible transitions prevailing in organic compounds.

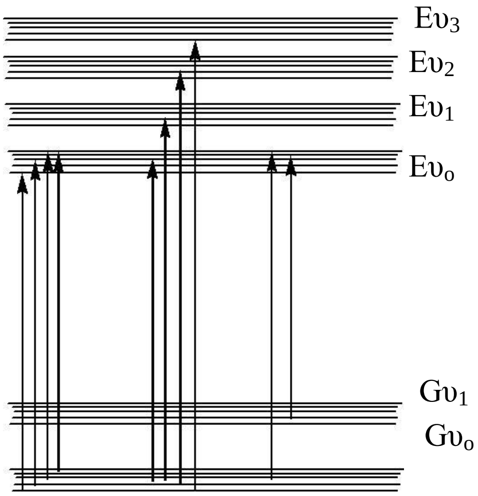


Figure 4 : *Energy level diagram showing excitation between different vibrational and rotational levels of twoelectronic states*

Alkanes can only undergo $\sigma \rightarrow \sigma^*$ transitions. These are high-energy transitions and involve very short wavelength ultraviolet light (< 150 nm). These transitions usually fall out-side the generally available measurable range of UV-visible spectrophotometers (200-1000 nm). The $\sigma \rightarrow \sigma^*$ transitions of methane and ethane are at 122 and 135 nm, respectively. In alkenes amongst the available $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions, the $\pi \rightarrow \pi^*$ transitions are of lowest energy and absorb radiations between 170-190 nm.

In saturated aliphatic ketones the lowest energy transition involves the transfer of one electron of the nonbonding electrons of oxygen to the relatively low-lying π^* anti-bonding orbital. This $n \rightarrow \pi^*$ transition is of lowest energy (~280 nm) but is of low intensity as it is symmetry forbidden. Two other available transitions are $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. The most intense band for these compounds is always due to $\pi \rightarrow \pi^*$ transition.

In conjugated dienes the $\pi \rightarrow \pi^*$ orbitals of the two alkene groups combine to form new orbitals – two bonding orbitals named as π_1 and π_2 and two antibonding orbitals named as π_3^* and π_4^*. It is apparent that a new $\pi \rightarrow \pi^*$ transition of low energy is available as a result of conjugation. Conjugated dienes as a result absorb at relatively longer wavelength than do isolated alkenes (see figure 6).

4.1.3 Principles of Absorption Spectroscopy : Beer's and Lambert's Law

The greater the number of molecules that absorb light of a given wavelength, the greater the extent of light absorption and higher the peak intensity in absorption spectrum. If there are only a few molecules that absorb radiation, the total absorption of energy is less and consequently lower intensity peak is observed. This makes the basis of Beer-Lambert Law which states that the fraction of incident radiation absorbed is proportional to the number of absorbing molecules in its path.

When the radiation passes through a solution, the amount of light absorbed or transmitted is an exponential function of the molecular concentration of the solute and also a function of length of the path of radiation through the sample. Therefore,

$$\text{Log } I_o / I = \varepsilon \, c \, l$$

Where I_o = Intensity of the incident light (or the light intensity passing through a reference cell) I = Intensity of light transmitted through the sample solution

c = concentration of the solute in mol

l^{-1} l = path length of the sample in cm

ε = molar absorptivity or the molar extinction coefficient of the substance whose light absorption is under investigation. It is a constant and is a characteristic of a given absorbing species (molecule or ion) in a particular solvent at a particular wavelength. ε is numerically equal to the absorbance of a solution of unit molar concentration (c = 1) in a cell of unit length (l = 1) and its units are liters.moles^{-1} . cm^{-1}. However, it is customary practice among organic chemists to omit the units.

The ratio I / I_o is known as transmittance T and the logarithm of the inverse ratio I_o / I is known as the absorbance A.

Therefore

$$- \text{Log } I / I_o = - \log T = \varepsilon \, c \, l$$

and $$\text{Log } I_o / I = A = \varepsilon \, c \, l$$

or $$A = \varepsilon \, c \, l$$

For presenting the absorption characteristics of a spectrum, the positions of peaks are reported as λ_{max} (in nm) values and the absorptivity is expressed in parenthesis.

4.1.4 Spectral Measurements

The UV-Vis spectra are usually measured in very dilute solutions and the most important criterion in the choice of solvent is that the solvent must be transparent within the wavelength range being examined. Table 2 lists some common solvents with their lower wavelength cut off limits. Below these limits, the solvents show excessive absorbance and should not be used to determine UV spectrum of a sample.

Table 2 : Common solvents with their cut-off limits.

S. No.	Solvent	Cut-off wavelength (nm)
1	Acetonitrile	190
2	Water	191
3	Cyclohexane	195
4	Hexane	201
5	Methanol	203
6	95% ethanol	304
7	1,4-dioxane	215
8	Ether	215
9	Dichloromethane	220
10	Chloroform	237
11	Carbon tetrachloride	257
12	Benzene	280

Of the solvents listed in table 2, water, 95% ethanol and hexane are the most commonly used solvents. Each is transparent in the region of UV-Vis spectrum. For preparing stock solutions, the sample is accurately weighed and made up to volume in volumetric flask. Aliquats are removed from this solution and appropriate dilutions are made to make solutions of desired concentration. For recording the spectrum 1 cm square quartz cell is commonly used. These require approx. 3 ml of solution. The quartz cell containing solution is placed in the path of light beam and spectrum is recorded by varying the wavelength of incident light.

4.1.5 Solvent Effects

Highly pure, non-polar solvents such as saturated hydrocarbons do not interact with solute molecules either in the ground or excited state and the absorption spectrum of a compound in these solvents is similar to the one in a pure gaseous state. However, polar solvents such as water, alcohols etc. may stabilize or destabilize the molecular orbitals of a molecule either in the ground state or in excited state and the spectrum of a compound in these solvents may significantly vary from the one recorded in a hydrocarbon solvent.

(i) π → π* Transitions

In case of π→π* transitions, the excited states are more polar than the ground state and the dipole-dipole interactions with solvent molecules lower the energy of the excited state more than that of the ground state. Therefore a polar solvent decreases the energy of π→π* transition and absorption maximum appears ~10-20 nm red shifted in going from hexane to ethanol solvent.

In case of n →π* transitions, the polar solvents form hydrogen bonds with the ground state of polar molecules more readily than with their excited states. Therefore, in polar solvents the energies of electronic transitions are increased. For example, the figure 5 shows that the absorption maximum of acetone in hexane appears at 279 nm which in water is shifted to 264 nm, with a blue shift of 15 nm.

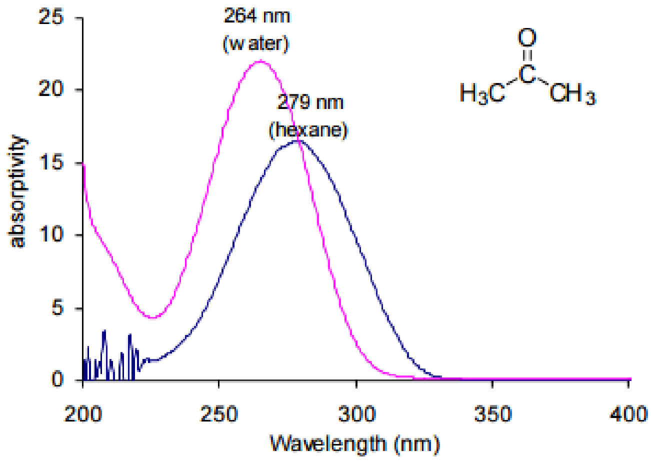


Figure 5 : UV-spectra of acetone in hexane and in water

4.1.6 Some important terms and definitions

(i) Chromophore: The energy of radiation being absorbed during excitation of electrons fromground state to excited state primarily depends on the nuclei that hold the electrons together in a bond. The group of atoms containing electrons responsible for the absorption is called chromophore. Most of the simple un-conjugated chromophores give rise to high energy transitions of little use. Some of these transitions have been listed in table 3.

Table 3: Absorption maxima of simple un-conjugated chromophores

Chromophore	Transition	ε_{max}	λ_{max}(nm)
σ – bonded electrons			
(C-C, C-H etc.)	$\sigma \rightarrow \sigma^*$		~ 150
Lone pair electrons			
-O-, -N-, -S-	$n \rightarrow \sigma^*$	100-1000	~ 190
C=O, C=N	$n \rightarrow \pi^*$	15	~300
	$\pi \rightarrow \pi^*$	500	~190
R-C≡N	$n \rightarrow \pi^*$	5	~ 170
R-COOH, $RCONH_2$, RCOOR	$n \rightarrow \pi^*$	50	~ 210
π- bonded electrons			
C=C	$\pi \rightarrow \pi^*$	14000	~ 190
C≡C	$\pi \rightarrow \pi^*$	2000	~ 195
C=O	$\pi \rightarrow \pi^*$	500	~ 180

For example, alkanes contain only single bonds with only possible $\sigma \rightarrow \sigma^*$ type electronic transitions. These transitions absorb radiations shorter than wavelengths that are experimentally accessible in usually available spectrophotometers. In saturated molecules with heteroatom bearing non-bonding pairs of electrons, $n \rightarrow \sigma^*$ transitions become available. These are also high energy transitions. In unsaturated compounds, $\pi \rightarrow \pi^*$ transitions become possible. Alkenes and alkynes absorb ~ 170 nm but the presence of substituents significantly affects their position. The carbonyl compounds and imines can also undergo $n \rightarrow \pi^*$ transitions in addition to $\pi \rightarrow \pi^*$. Amongst these, the most studied transitions are $n \rightarrow \pi^*$ as these absorb at relatively longer wavelength 280-300 nm. These are low intensity (ε 10-100) transitions.

3) **Auxochrome:** The substituents that themselves do not absorb ultraviolet radiations but

theirpresence shifts the absorption maximum to longer wavelength are called auxochromes. The substituents like methyl, hydroxyl, alkoxy, halogen, amino group etc. are some examples of auxochromes.

4) Bathochromic Shift or Red shift: A shift of an absorption maximum towards longerwavelength or lower energy.

5) Hypsochromic Shift or Blue Shift: A shift of an absorption maximum towards shorterwavelength or higher energy.

6) Hypochromic Effect: An effect that results in decreased absorption intensity.

7) Hyperchromic Effect: An effect that results in increased absorption intensity.

4.1.7 Applications of Electronic Spectroscopy in Predicting Absorption Maxima of Organic Molecules

1: Conjugated Dienes, Trienes and Polyenes

The presence of conjugate double bond decreases the energy difference between HOMO and LUMO of resulting diene. The figure 6 shows the change in energy of MO on conjugation. As a result, the radiations of longer wavelength are absorbed. The conjugation not only results in bathochromic shift (longer wavelength) but also increases the intensity of absorption. As the number of conjugated double bonds is increased, the gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is progressively lowered. Therefore, the increase in size of the conjugated system gradually shifts the absorption maximum (λ_{max}) to longer wavelength and also increases the absorption. For example, ethylene absorbs at175 nm (ε = 1000) and the conjugation in butadiene gives a strong absorption at longer wavelength at 230 nm and with higher intensity (ε = >1000).

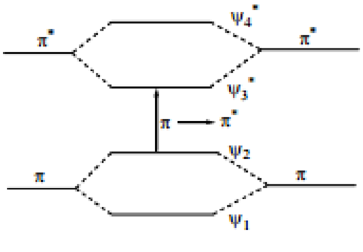


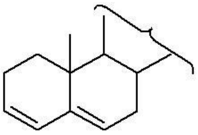
Figure 6 : Effect of conjugation on orbitals' energy and respective π-π^* transition.

The presence of alkyl substituents on double bond also produces bathochromic shift and hyperchromic effect. These effects are additive in dienes and up to some extent in trienes. The open chain dienes can achieve *s*-cis or *s*-trans conformations and similarly diene system can be homoannular or heteroannular in cyclic systems. In 1941, Woodward suggested empirical rules for predicting the absorption of open chain and six-membered ring dienes which have been later on extended to large number of dienes and trienes (Table 4).

Table 4: Empirical Rules for Diene and Triene absorptions

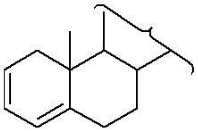
Parent open chain or heteroannular diene	214 nm
Homoannular diene	253 nm
Increments for	
(a) each alkyl substituent or ring residue	5 nm
(b) double bond extending conjugation	30 nm
(c) exocyclic double bond	5 nm
(d) lone pair conjugation	
(i) O-C(=O)-R	0 nm
(ii) O-alkyl	6 nm
(iii) S-alkyl	30 nm
(iv) –Cl, -Br	5 nm
(v) NR_2	60 nm

For example, here the absorption maxima for dienes **1** and **2** have been calculated according to Woodward rules. The comparison of calculated λ_{max} values with observed λ_{max} values highlights the importance of these rules.



1

Parent value = 214 nm
Three ring residues (3 x 5) = 15
Exocyclic double bond = 5 nm
Total = 234 nm
Observed value = 235 nm



2

Parent value = 253 nm
Three substituents = 15 nm
Ring residue = 5
Total = 273
Observed value = 275 nm

As the number of double bonds in conjugation increases, the bathochromic (towards longer wavelength) shift in lowest energy absorption maxima is observed. The increase in conjugation gradually shifts the maxima to visible region (> 400 nm) and imparts colour to the sample. Table 5 shows the λ_{max} shift in $Me(CH=CH)_n Me$ with increasing number of conjugated double bonds. β - Carotene (figure 7) responsible for red color in carrots is a typical example of polyene with 11 conjugated double bonds and exhibits λ_{max} at 445 nm.

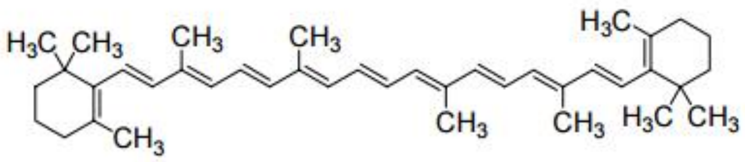
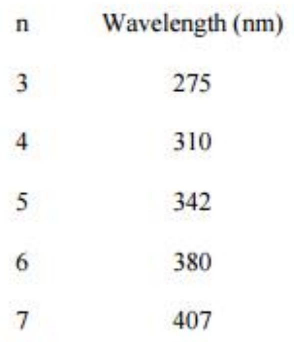


Figure 7: Structure of β-carotene

Table 5: λ_{max} values for $Me(CH=CH)_nMe$

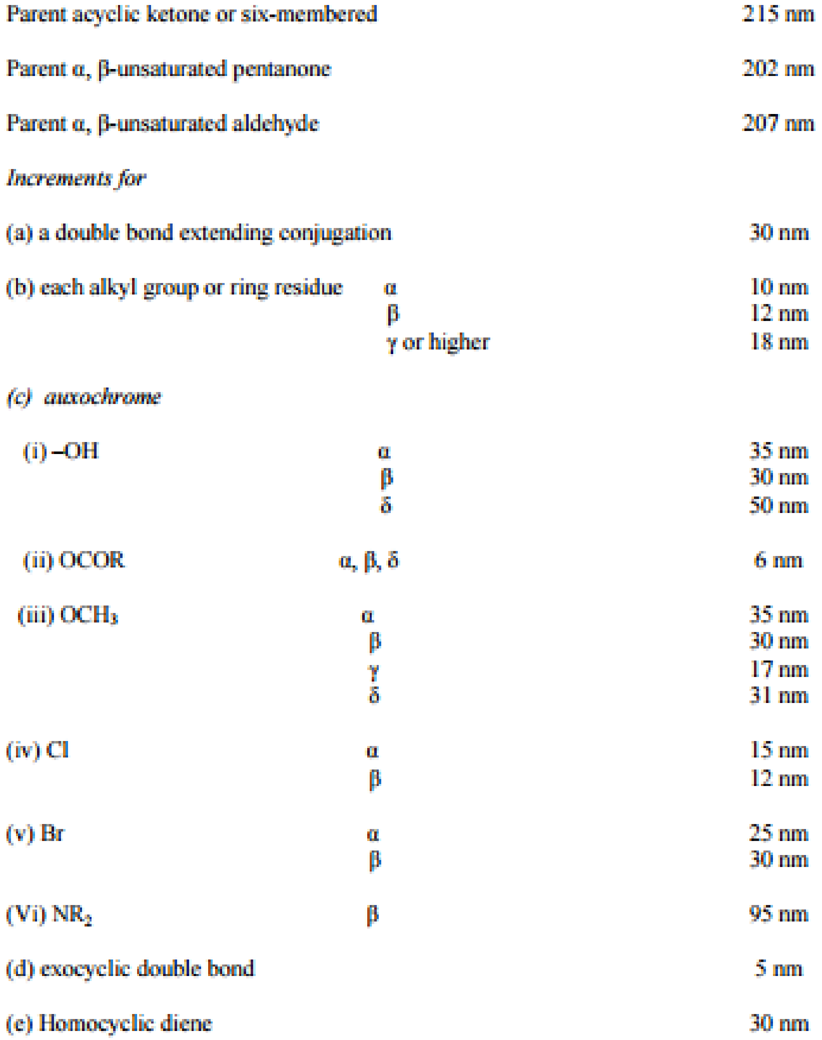


n	Wavelength (nm)
3	275
4	310
5	342
6	380
7	407

2: Carbonyl Compounds

Carbonyl compounds have two principal UV radiations, the allowed $\pi \rightarrow \pi^*$ transitions and the forbidden $n \rightarrow \pi^*$ transitions. In amides, acids, esters or acid halides, the substituents viz. NR_2, OH, OR, or –X on carbonyl group show pronounced hypsochromic effect on the $n \rightarrow \pi^*$ transitions. The hypsochromic effect is due to inductive effect of nitrogen, oxygen or halogen atoms. The heteroatom withdraws electrons from carbonyl carbon and makes carbonyl oxygen lone pair of electrons more stabilized due to its involvement in increasing C=O bond order. As a result, the $n \rightarrow \pi^*$ transition of these compounds is shifted to 200-215 nm range relative to 270 nm in aldehydes and ketones. Conjugation of the carbonyl group with double bond shifts both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions to longer wavelengths. The effect on $\pi \rightarrow \pi^*$ band is more pronounced. Woodward formulated rules to predict the position of an absorption maximum in an unknown enone. These rules have been summarized in table 6.

Table 6: *Empirical Rules for α, β-unsaturated ketones and aldehydes absorption maxima.*



Parent acyclic ketone or six-membered		215 nm
Parent α, β-unsaturated pentanone		202 nm
Parent α, β-unsaturated aldehyde		207 nm
Increments for		
(a) a double bond extending conjugation		30 nm
(b) each alkyl group or ring residue	α	10 nm
	β	12 nm
	γ or higher	18 nm
(c) auxochrome		
(i) –OH	α	35 nm
	β	30 nm
	δ	50 nm
(ii) OCOR	α, β, δ	6 nm
(iii) OCH_3	α	35 nm
	β	30 nm
	γ	17 nm
	δ	31 nm
(iv) Cl	α	15 nm
	β	12 nm
(v) Br	α	25 nm
	β	30 nm
(Vi) NR_2	β	95 nm
(d) exocyclic double bond		5 nm
(e) Homocyclic diene		30 nm

3. Aromatic Compounds

The simplest aromatic compound is benzene. It shows two primary bands at 184 (ε = 47,000) and 202 (ε = 7400) nm and a secondary fine structure band at 255 nm (ε = 230 in cyclohexane). Substituents on the benzene ring also cause bathochromic and hypsochromic shifts of various peaks. Unlike dienes and unsaturated ketones, the effects of various substituents on the benzene ring are not predictable. However, qualitative understanding of the effects of substituents on the characteristics of UV-Vis spectrum can be considered by classifying the substituents into electron-donating and electron-withdrawing groups.

(i) Effect of Substituents with Unshared Electrons: The non-bonding electrons increase thelength of π-system through resonance and shift the primary and secondary absorption bands to longer wavelength. More is the availability of these non-bonding electrons, greater the shift will be. In addition, the presence of non-bonding electrons introduces the possibility of $n \rightarrow \pi^*$ transitions. If non-bonding electron is excited into the extended π*chromophore, the atom from which it is removed becomes electron-deficient and the π-system of aromatic ring becomes electron rich. This situation causes a separation of charge in the molecule and such excited state is called a charge-transfer or an electron-transfer excited state.

In going from benzene to t-butylphenol, the primary absorption band at 203.5 nm shifts to 220 nm and secondary absorption band at 254 nm shifts to 275 nm. Further, the increased availability of n electrons in negatively charged t-butylphenoxide ion shifts the primary band from 203.5 to 236 nm (a 32.5 nm shift) and secondary band shifts from 254 nm to 290 nm (a 36 nm shift) (Figure 8). Both bands show hyperchromic effect. On the other hand, in the case of anilinium cation, there are no n electrons for interaction and absorption properties are quite close to benzene. But in aniline, the primary band is shifted to 232 nm from 204 nm in anilinium cation and the secondary band is shifted to 285 nm from 254 nm (Figure 9).

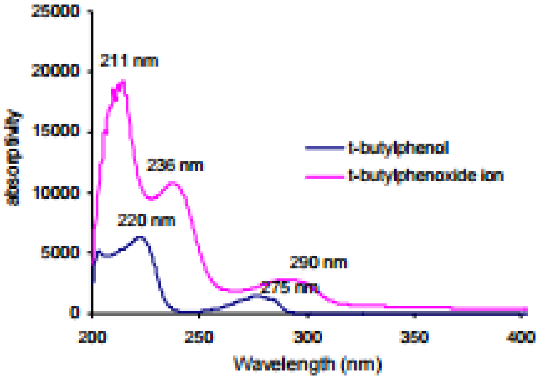


Figure 8 : UV-spectra of t-butyl phenol and t-buty phenoxide in methanol

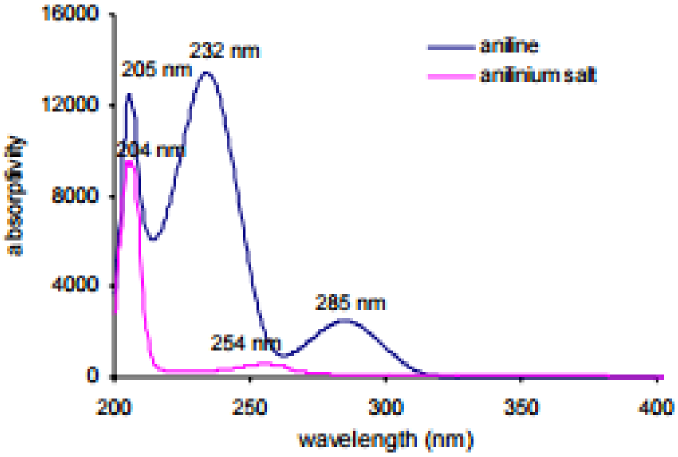


Figure 9 : UV-spectra of aniline and anilinium salt in methanol

(ii) Effect of π Conjugation: Conjugation of the benzene ring also shifts the primary band at203.5 nm more effectively to longer wavelength and secondary band at 254 nm is shifted to longer wavelength to lesser extent. In some cases, the primary band overtakes the secondary band. For example, benzoic acid shows primary band at 250 nm and secondary band at 273 nm, but cinnamic acid that has longer chromophore exhibits primary band at 273 nm and secondary band remains merged with it. Similarly, in benzaldehyde, the secondary band appears at 282 nm and primary band at 242 nm but in case of cinnamaldehyde, primary band appears at 281 nm and remains merged with secondary band (figure 10). The hyperchromic effect arising due to extended conjugation is also visible.

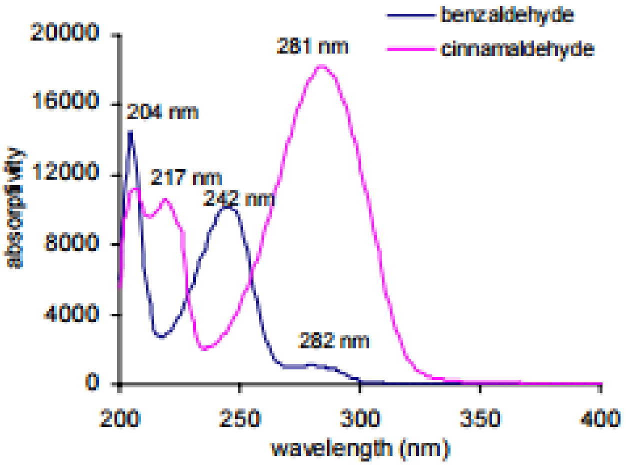


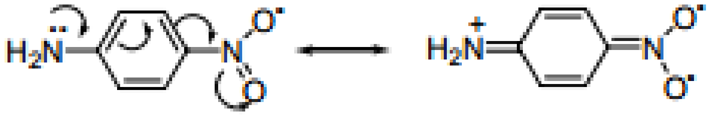
Figure 10 : UV-spectra of benzaldehyde and cinnamaldehyde in methanol

(iii) Effect of Electron-withdrawing and Electron-releasing Groups:

Electron-withdrawing substituents viz. $\overset{+}{NH_3}$, SO_2NH_2, CN, COOH, $COCH_3$, CHO and NO_2 etc. have no effect on the position of secondary absorption band of benzene ring. But their conjugation effects with π-electrons of the aromatic ring are observed. Electron-donating groups such as $-CH_3$, -Cl, -Br, - OH, $-OCH_3$, $-NH_2$ etc increase both λ_{max} and ε_{max} values of the secondary band.

In case of disubstituted benzene derivatives, it is essential to consider the effect of both the substituents.

In para-substituted benzenes, two possibilities exist. If both the groups are electron-donating then the observed spectrum is closer to monosubstituted benzene. The group with stronger effect determines the extent of shifting of primary band. If one group is electron-releasing and other is electron-withdrawing, the magnitude of red shift is grater compared to the effect of single substituent individually. This is attributed to the increased electron drift from electron-donating group to the electron-withdrawing group through π-bond of benzene ring. For example, aniline shows secondary band at 285 nm which due to presence of electron-withdrawing *p*-nitro substituent is shifted to 367 nm with a significant increase in absorptivit (figure 11).



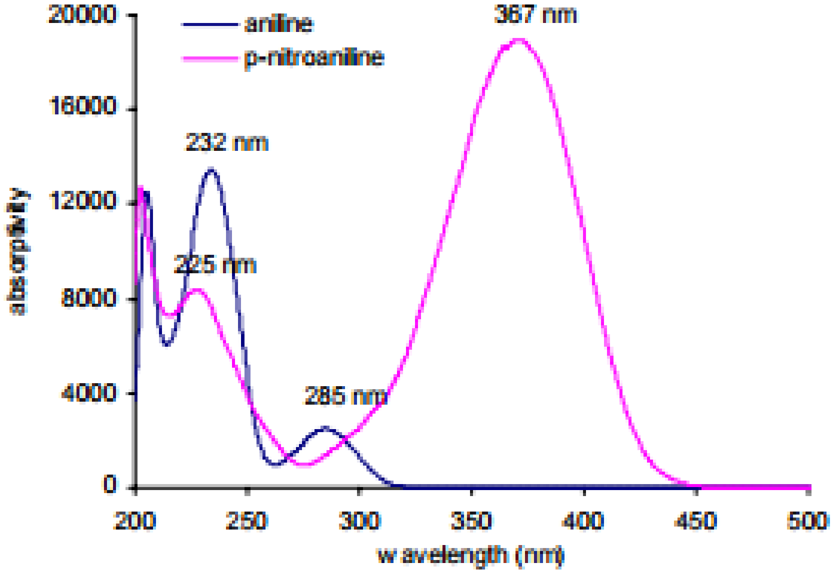


Figure 11 : UV-spectra of aniline and p-nitroaniline in methanol

If two groups of a disubstituted benzene derivative are placed ortho- or meta- to each other, the combined effect of two substiuents is observed. In case of substituted benzoyl derivatives, an empirical correction of structure with observed position of the primary absorption band has been developed. In the absence of steric hindrance to co-planarity, the calculated values are within ± 5 nm of the observed value.

(iv) Polycyclic Aromatic Compounds: In case of polycyclic aromatic hydrocarbons, due toextended conjugation, both primary and secondary bands are shifted to longer wavelength. These spectra are usually complicated but are characteristic of parent compound. The primary band at 184 nm in benzene shifts to 220 nm in case of naphthalene and 260 nm in case of anthracene.

Similarly, the structured secondary band which appears as broad band around 255 nm in benzene is shifted to 270 nm and 340 nm respectively in case of naphthalene and anthracene molecules.

4.1.8 Commercial Applications of UV and Visible Spectroscopy

The UV -Vis spectroscopy has innumerable applications in the drugs and pharmaceutical industry.

Beer-Lambert law offers a valuable and simple method for quantitative analysis. In practice, a calibration curve is constructed by plotting absorbance vs. molar concentration and the concentration of unknown with ‘X’ absorbance is determined by finding the concentration corresponding to the measured absorbance on the calibration curve. The UV spectroscopy is used extensively in determining rate constants, equilibrium constants, acid-base dissociation constants etc for chemical reactions. The use of UV spectrometry in evaluation of enzymatic assays has become very common e.g. the activity of enzyme dehydrase is assayed by measuring the formation of ergosterol at 282 nm.

4.2 INFRARED ABSORPTION SPECTROSCOPY

Contents

4.2.0 INTRODUCTION

The two atoms joined together by a chemical bond (may be single, double or triple bond), macroscopically can be composed as two balls joined by a spring. The application of a force like

(i) stretching of one or both the balls (atoms) away from each other or closer to each other (ii) bending of one of the atoms either vertically or horizontally and then release of the force results in the vibrations on the two balls (atoms). These vibrations depend on the strength of the spring and also the mode (stretching or bending) in which the force is being applied.

Similarly, at ordinary temperatures, organic molecules are in a constant state of vibrations, each bond having its characteristic stretching and bending frequencies. When infrared light radiations between 4000-400 cm^{-1} (the region most concerned to an organic chemist) are passed through a sample of an organic compound, some of these radiations are absorbed by the sample and are converted into energy of molecular vibrations. The other radiations which do not interact with the sample are transmitted through the sample without being absorbed. The plot of % transmittance against frequency is called the infrared spectrum of the sample or compound.

This study of vibrations of bonds between different atoms and varied multiplicities which depending on the elctronegativity, masses of the atom and their geometry vibrate at different but specified frequencies; is called infrared spectroscopy. The presence of such characteristic vibrational bands in an infrared spectrum indicates the presence of these bonds in the sample under investigation.

4.2.1 THEORY OF IR

IR radiation does not have enough energy to induce electronic transitions as seen with UV. Absorption of IR is restricted to compounds with small energy differences in the possible vibrational and rotational states.

For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. The alternating electrical field of the radiation (remember that electromagnetic radation consists of an oscillating electrical field and an oscillating magnetic field, perpendicular to each other) interacts with fluctuations in the dipole moment of the molecule. If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration.

Molecular vibrational frequencies lie in the IR region of the electromagnetic spectrum, and they can be measured using the IR technique. In IR, polychromatic light (light having different frequencies) is passed through a sample and the intensity of the transmitted light is measured at each frequency. When molecules absorb IR radiation, transitions occur from a ground vibrational state to an excited vibrational state (Figure 1).

For a molecule to be IR active there must be a change in dipole moment as a result of the vibration that occurs when IR radiation is absorbed. Dipole moment is a vector quantity and depends on the orientation of the molecule and the photon electric vector. The dipole moment changes as the bond expands and contracts. When all molecules are aligned as in a crystal and the photon vector points along a molecular axis such as z. Absorption occurs for the vibrations that displace the dipole along z. Vibrations that are totally x or y polarized would be absent. Dipole moment in a heteronuclear diatomic molecule can be described as uneven distribution of electron density between the atoms. One atom is more electronegative than the other and has a net negative charge.

The dipole moment can be expressed mathematically as

$$\mu=er$$

$$\mu=er$$

The relationship between IR intensity and dipole moment is given as

$$IIR\propto(d\mu/dQ)2$$

$$I_{IR}\propto(d\mu/dQ)2$$

relating this to intensity of the IR radiation, we have have the following equation below.

where $\mu\mu$ is the dipole moment and QQ is the vibrational coordinate. The *transition moment integral,* that gives information about the probability of a transition occurring, for IR can also be written as

$$\langle\psi|M^{\wedge}|\psi f\rangle$$

ii and ff represent are initial and final states. $\psi i\psi i$ is the wave function. Relating this to IR intensity we have

$$IIR\propto\langle\psi|M^{\wedge}|\psi f\rangle$$

where $M^{\wedge}M^{\wedge}$ is the dipole moment and has the Cartesian coordinates, $Mx^{\wedge}Mx^{\wedge}$,$My^{\wedge}My^{\wedge}$, $Mz^{\wedge}Mz^{\wedge}$. In order for a transition to occur by dipole selection rules , at least one of the integrals must be non zero.

4.2.2 Region of IR

The IR region of the electromagnetic spectrum ranges in wavelength from 2 -15 µm. Conventionally the IR region is subdivided into three regions, near IR, mid IR and far IR.

Most of the IR used originates from the mid IR region. The table below indicates the IR spectral regions

Region	Wavelength	Wavenumbers (V), cm^{-1}	Frequencies (v), HZ
Near	0.78 -2.5	12800 - 4000	3.8 x 10^{14} - 1.2 x 10^{14}
Middle	2.5 - 50	4000 - 200	3.8 x 10^{14} - 1.2 x 10^{14}
Far	50 -100	200 -10	3.8 x 10^{14} - 1.2 x 10^{14}
Most Used	2.5 -15	4000 -670	3.8 x 10^{14} - 1.2 x 10^{14}

IR deals with the interaction between a molecule and radiation from the electromagnetic region ranging (4000- 40 cm^{-1}). The cm^{-1} is the wave number scale and it can also be defined as 1/wavelength in cm. A linear wavenumber is often used due to its direct relationship with both frequency and energy. The frequency of the absorbed radiation causes the molecular vibrational frequency for the absorption process. The relationship is given below

$$\bar{v}(cm^{-1}) = \frac{1}{\lambda(\mu m)} \times 10^{4}\left(\frac{\mu m}{cm}\right) = \frac{v(Hz)}{c(cm/s)}$$

4.2.2.1 Near InfraRed Spectroscopy: Absorption bands in the near infrared (NIR) region (750 - 2500 nm) are weak because they arise from vibrational overtones and combination bands. Combination bands occur when two molecular vibrations are excited simultaneously. The intensity of overtone bands reduces by one order of overtone for each successive overtone. When a molecule is excited from the ground vibrational state to a higher vibrational state and the vibrational quantum number v is greater than or equal to 2 then an overtone absorption results. The first overtone results from v = 0 to v = 2. The second overtone occurs when v =0 transitions to v = 3. Transitions arising from the near ir absorption are weak, hence they are referred to as forbidden transitions but these transitions are relevant when non-destructive measurements are required such as a solid sample. Near IR spectra though have low absorption they have a high signal to noise ratio owing to intense radiation sources and NIR is able to penetrate undiluted samples and use longer path lengths; it becomes very useful for rapid measurement of more representative samples.

4.2.2.2 Far InfraRed Spectroscopy: The far IR region is particularly useful for inorganic studies due to stretching and bending vibrations of bonds between the metal atoms and ligands. The frequencies, which these vibrations are observed, are usually lower than 650 cm^{-1}. Pure rotational absorption of gases is observed in the far IR region when there is a permanent dipole moment present. Examples include H_2O, O_3, HCl.

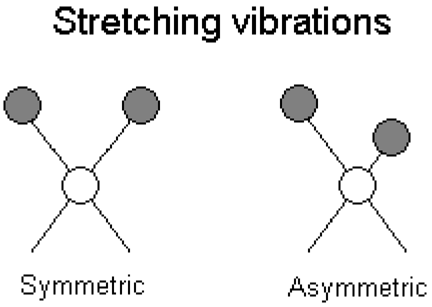
4.2.3 Molecular rotations

Rotational transitions are of little use to the spectroscopist. Rotational levels are quantized, and absorption of IR by gases yields line spectra. However, in liquids or solids, these lines broaden into a continuum due to molecular collisions and other interactions.

4.2.3 .1 Molecular vibrations

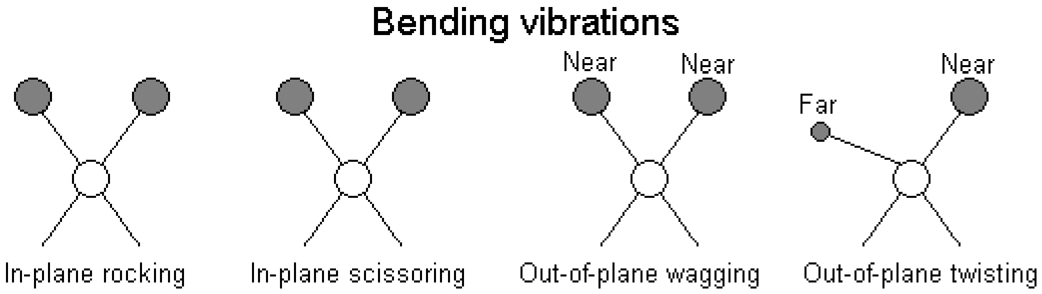
The positions of atoms in a molecules are not fixed; they are subject to a number of different vibrations. Vibrations fall into the two main catagories of *stretching* and *bending*.

4.2.3.2 Stretching: Change in inter-atomic distance along bond axis



: **4.2.3.3 Bending:** Change in angle between two bonds. There are four types of bend:

- Rocking
- Scissoring
- Wagging
- Twisting



4.2.3.4 Vibrational coupling

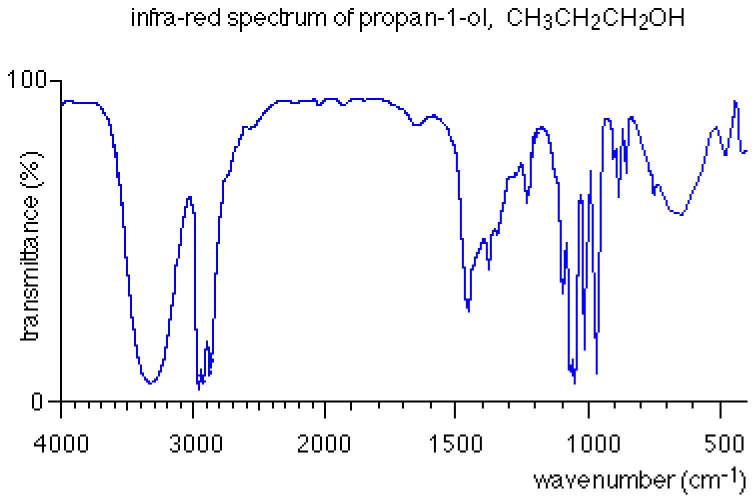
In addition to the vibrations mentioned above, interaction between vibrations can occur (*coupling*) if the vibrating bonds are joined to a single, central atom. Vibrational coupling is influenced by a number of factors;

- Strong coupling of stretching vibrations occurs when there is a common atom between the two vibrating bonds
- Coupling of bending vibrations occurs when there is a common bond between vibrating groups
- Coupling between a stretching vibration and a bending vibration occurs if the stretching bond is one side of an angle varied by bending vibration
- Coupling is greatest when the coupled groups have approximately equal energies

- No coupling is seen between groups separated by two or more bonds

4.2.3 What is the fingerprint region

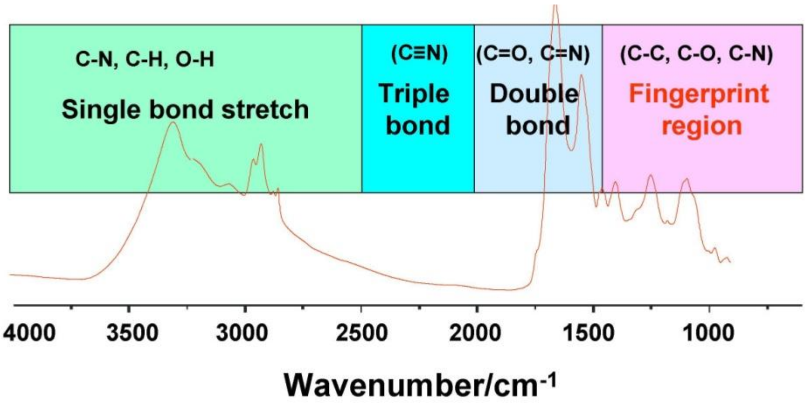
This is a typical infra-red spectrum:



Each trough is caused because energy is being absorbed from that particular frequency of infra-red radiation to excite bonds in the molecule to a higher state of vibration - either stretching or bending. Some of the troughs are easily used to identify particular bonds in a molecule. For example, the big trough at the left-hand side of the spectrum is used to identify the presence of an oxygen-hydrogen bond in an -OH group.

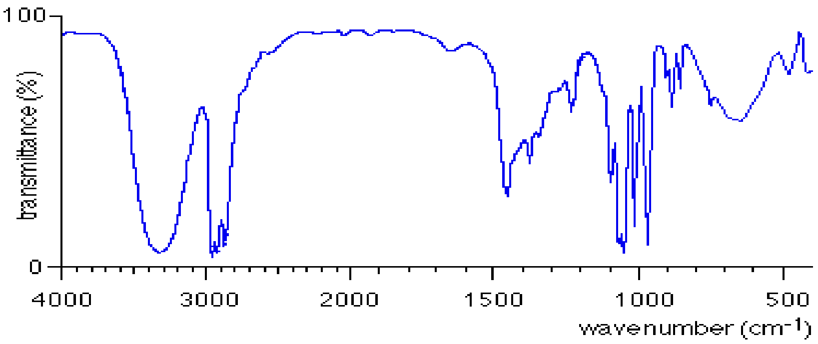
The region to the right-hand side of the diagram (from about 1500 to 500 cm-1) usually contains a very complicated series of absorptions. These are mainly due to all manner of bending vibrations within the molecule. This is called the **fingerprint region**.

It is much more difficult to pick out individual bonds in this region than it is in the "cleaner" region at higher wavenumbers. The importance of the fingerprint region is that each different compound produces a different pattern of troughs in this part of the spectrum.

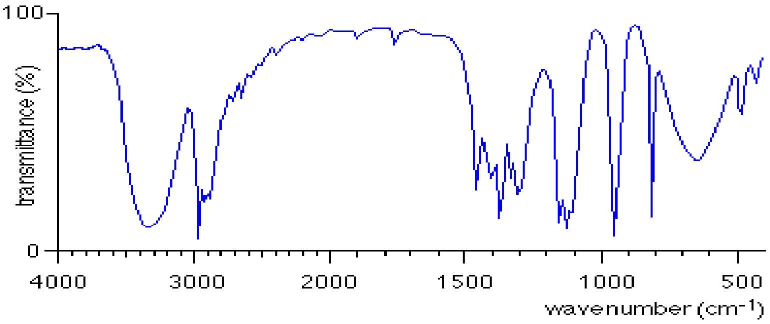


4.2.3.1 Using the fingerprint region

Compare the infra-red spectra of propan-1-ol and propan-2-ol. Both compounds contain exactly the same bonds. Both compounds have very similar troughs in the area around 3000 cm-1 - but compare them in the fingerprint region between 1500 and 500 cm-1.



infra-red spectrum of propan-1-ol, $CH_3CH_2CH_2OH$



infra-red spectrum of propan-2-ol, $CH_3CH(OH)CH_3$

The pattern in the fingerprint region is completely different and could therefore be used to identify the compound. To positively identify an unknown compound, use its infra-red spectrum to identify what sort of compound it is by looking for specific bond absorptions. That might tell you, for example, that you had an alcohol because it contained an -OH group. You would then compare the fingerprint region of its infra-red spectrum with known spectra measured under exactly the same conditions to find out which alcohol (or whatever) you had

We are familiar with resolving a translational vector into its three components along the x-, y-, and z- axes. Similarly a rotational motion can also be resolved into its components. Likewise the same is true for vibrational motion. The complex vibration that a molecule is making is really a superposition of a number of much simpler basic vibrations called “normal modes”. Therefore it is necessary to discuss the degrees of freedom.

4.2.4 Degrees of Freedom

Degree of freedom is the number of variables required to describe the motion of a particle completely. For an atom moving in 3-dimensional space, three coordinates are adequate so its degree of freedom is three. Its motion is purely translational. If we have a molecule made of N atoms (or ions), the degree of freedom becomes 3N, because each atom has 3 degrees of freedom. Furthermore, since these atoms are bonded together, all motions are not translational; some become rotational, some others vibration. For non-linear molecules, all rotational motions can be described in terms of rotations around 3 axes, the rotational degree of freedom is 3 and the remaining 3N-6 degrees of freedom constitute vibrational motion. For a linear molecule however, rotation around its own axis is no rotation because it leave the molecule unchanged. So there are only 2 rotational degrees of freedom for any linear molecule leaving 3N-5 degrees of freedom for vibration.

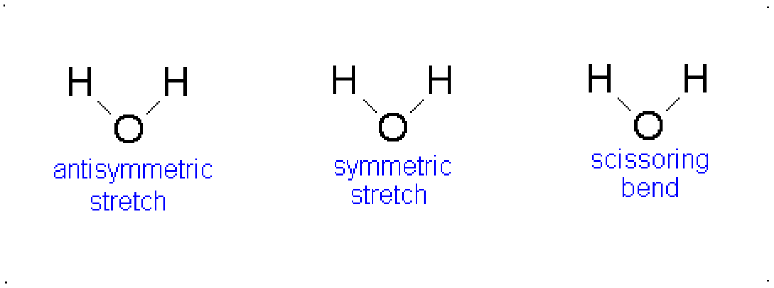
4.2.4.1Vibrational modes

1. A normal mode is a molecular vibration where some or all atoms vibrate together with the same frequency in a defined manner.
2. Normal modes are basic vibrations in terms of which any other vibration is derived by superposing suitable modes in the required proportion.
3. On the other hand, no normal mode is expressible in terms of any other normal mode. Each one is pure and has no component of any other normal mode (i.e. they are orthogonal to each other). Mathematically, the integral is
   $\int\psi A\psi BdR=0\int\psi A\psi BdR=0$ (integration is done over the entire space)

4. The required number of “normal modes” is equal to the vibrational degree of freedom available so the number of modes for a nonlinear molecule is $3N-63N-6$ and that for a linear molecule is $3N-53N-5$.
5. Each mode has a definite frequency of vibration. Sometimes 2 or 3 modes may have the same frequency but that does not change the fact that they are distinct modes; these modes are called degenerate.
6. Sometimes some modes are not IR active but they exist all the same. We shall revert back to the problem of IR activity and selection rules later.

The number of vibrational normal modes can be determined for any molecule from the formula given above. For a diatomic molecule, N = 2 so the number of modes is $3\times2-5=13\times2-5=1$. For a triatomic linear molecule (CO_2), it is $3\times3-5=43\times3-5=4$ and triatomic nonlinear molecule (H_2O), it is $3\times3-6=33\times3-6=3$ and so on.

Example 1: Water



1. The Symmetric Stretch (Example shown is an H_2O molecule at 3685 cm^{-1})
2. The Asymmetric Stretch (Example shown is an H_2O molecule at 3506 cm^{-1})
3. Bend (Example shown is an H_2O molecule at 1885 cm^{-1})

A linear molecule will have another bend in a different plane that is degenerate or has the same energy. This accounts for the extra vibrational mode.

Example 2: Carbon Dioxide

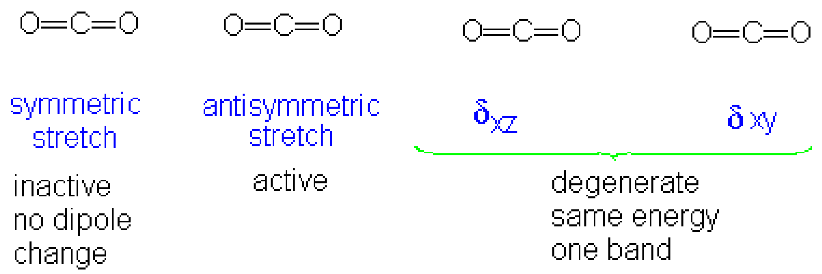


Table 8 : Important double and triple bond Stretching vibrations at a glance

	Vibration	*Frequency (cm^{-1})*	*Intensity*
Double bonds			
C=C	Alkene	1680-1600	m-w
	Aromatic	1600 and 1475	m-w
C=O	Aldehyde	1740-1720	s

Table 8 : Important double and triple bond Stretching vibrations at a glance

	Vibration	*Frequency (cm^{-1})*	*Intensity*
Double bonds			
C=C	Alkene	1680-1600	m-w
	Aromatic	1600 and 1475	m-w
C=O	Aldehyde	1740-1720	s
	ketone	1725-1705	s
	COOH	1760-1700	s
	COOR	1750-1730	s
	$CONH_2$	1680-1630	s
	Anhydride	1810 and 1760	s
	Acid chloride	1800	s
C=N	Imines	1690-1640	m-s
C=X	Allenes, ketenes, isocyanates	2270-1940	m
N=O	Nitro	1550 and 1350	s
Triple bonds			
C≡C	Alkyne	2250-2100	m-w
C≡N	Nitriles	2260-2240	m

Thus, the vibrational frequencies provide important structural information about a compound and since two same type of bonds in two different compounds would vibrate at different frequencies and so no two compounds can have exactly same infrared spectrum especially in the finger printing region. This makes IR spectroscopy a simple and versatile tool for identification of samples.

The term "infra red" covers the range of the electromagnetic spectrum between 0.78 and 1000 m. In the context of infra red spectroscopy, wavelength is measured in "wavenumbers", which have the units cm^{-1}.

wavenumber = 1 / wavelength in centimeters

It is useful to divide the infra red region into three sections; *near*, *mid* and *far* infra red;

Region	**Wavelength range** (□ m)	**Wavenumber range** (cm^{-1})
Near	0.78 - 2.5	12800 - 4000
Middle	2.5 - 50	4000 - 200
Far	50 -1000	200 - 10

The most useful I.R. region lies between 4000 - $670cm^{-1}$.

Check your progress

You should now understand how certain molecules absorb infra red radiation, and the effects that this absorption has. You should be familiar with the ways in which molecules can vibrate, and factors which influence how these vibrations interact with each other.

4.3 NMR SPECTROSCOPY

CONTENTS

4.3.1 INTRODUCTION

The interaction between the nuclei and the radiofrequency radiation is called nuclear magnetic resonance (NMR) spectroscopy. The nuclei of certain atoms or molecules are considered to be spin. In the absence of external magnetic field, the spin states of the nuclei are degenerate. (i.e) possess the equal energy levels. In the presence of external magnetic field, the degeneracy is removed and separate energy levels are possible. The nuclear transition between these energy levels can occur by the absorption of radio frequency radiation.Nuclear Magnetic Resonance spectroscopy is a powerful and theoretically complex analytical tool. On this page, we will cover the basic theory behind the technique. It is important to remember that, with NMR, we are performing experiments on the **nuclei** of atoms, not the electrons. The chemical environment of specific nuclei is deduced from information obtained about the nuclei.

4.3.2 Nuclear spin and the splitting of energy levels in a magnetic field

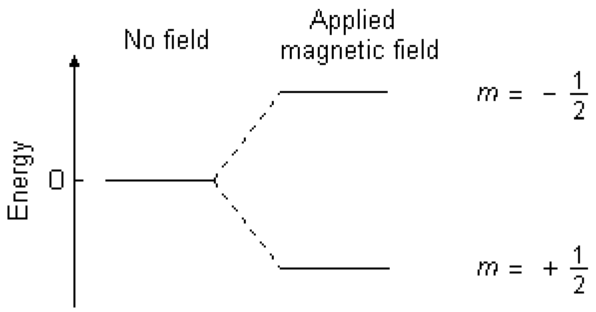
Subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axes. In many atoms (such as ^{12}C) these spins are paired against each other, such that the nucleus of the atom has no overall spin. However, in some atoms (such as ^{1}H and ^{13}C) the nucleus does possess an overall spin. The rules for determining the net spin of a nucleus are as follows;

1. If the number of neutrons **and** the number of protons are both even, then the nucleus has **NO** spin.

2. If the number of neutrons **plus** the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)
3. If the number of neutrons **and** the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

The overall spin, *I*, is important. Quantum mechanics tells us that a nucleus of spin *I* will have 2*I* + 1 possible orientations. A nucleus with spin 1/2 will have 2 possible orientations. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a *magnetic quantum number, m*.

Energy levels for a nucleus with spin quantum number 1/2



When the nucleus is in a magnetic field, the initial populations of the energy levels are determined by thermodynamics, as described by the Boltzmann distribution. This is very important, and it means that**the lower energy level will contain slightly more nuclei than the higher leve**l. It is possible to excite these nuclei into the higher level with electromagnetic radiation. The frequency of radiation needed is determined by the difference in energy between the energy levels.

4.3.3 Condition for NMR spectra:

The nuclei with a resultant nuclear spin are magnetically active and produces NMR spectra. The nuclear spin is described by the spin quantum number, I. The condition for the nuclei which exhibits NMR spectra have I > 0. The value of I for different nuclei can be predicted by the following empirical values,

i) Nuclei having even number of protons and neutrons have zero value of I. Example : ^{4}He, ^{12}C, ^{16}O and ^{32}S have I = 0. They are non magnetic and NMR inactive.

ii) Nuclei having odd number of protons and neutrons have integral value of I. Example ^{2}Hand ^{14}N have I = 1. They are magnetic and NMR active.

iii) Nuclei having odd value for the sum of protons and neutrons have half integral value of I. Example ^{1}H, ^{13}C, ^{15}N, ^{19}F and ^{31}P have I = ½. They are magnetic and NMR active.

At a time only one type of nucleus is used in NMR spectroscopy. Example : all ^{1}H or ^{13}C or ^{19}F nuclei.

The ^{1}H (proton) nucleus is most commonly studied by NMR spectroscopy because of its high natural abundance (99.98%). Also proton is invariably present in the majority of organic compounds. Hence NMR spectroscopy is also known as proton compounds. Hence

NMR spectroscopy is also known as proton magnetic resonance (PMR) or ^{1}H NMR spectroscopy.

Calculating transition energy

The nucleus has a positive charge and is spinning. This generates a small magnetic field. The nucleus therefore possesses a magnetic moment, μ, which is proportional to its spin,*I*.

$$\mu = \frac{\gamma I h}{2\pi}$$

The constant, γ, is called the *magnetogyric ratio* and is a fundamental nuclear constant which has a different value for every nucleus. *h* is Planck's constant.

The energy of a particular energy level is given by;

$$E = -\frac{\gamma h}{2\pi} m B$$

Where *B* is the strength of the magnetic field **at the nucleus**.

The difference in energy between levels (the transition energy) can be found from

$$\Delta E = \frac{\gamma h B}{2\pi}$$

This means that if the magnetic field, *B*, is increased, so is Δ*E*. It also means that if a nucleus has a relatively large magnetogyric ratio, then Δ*E* is correspondingly large.

If you had trouble understanding this section, try reading the next bit (The absorption of radiation by a nucleus in a magnetic field) and then come back.

The absorption of radiation by a nucleus in a magnetic field

In this discussion, we will be taking a "classical" view of the behaviour of the nucleus - that is, the behaviour of a charged particle in a magnetic field.

Imagine a nucleus (of spin 1/2) in a magnetic field. This nucleus is in the lower energy level (i.e. its magnetic moment does not oppose the applied field). The nucleus is spinning on its axis. In the presence of a magnetic field, this axis of rotation will *precess* around the magnetic field;**Larmor Precession**

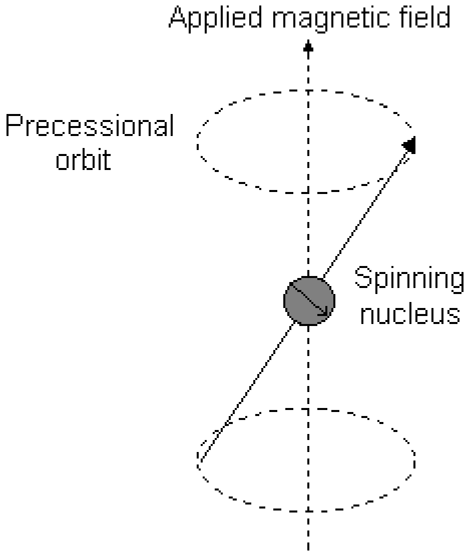
The phenomenon of nuclear magnetic resonance can also be explained by the scientist Larmor called larmor precession. When a magnetic nucleus is placed perpendicularly in an external magnetic field of strength, B_Z, it spins on its own axis. This is called Larmor precession (fig. 3). The angular frequency of the precession is known as Larmor frequency (ω) and it is directly proportional to the strength of the magnetic field B_Z.

$\omega \alpha B_Z$

$\omega = \gamma B_Z$

where γ is the gyromagnetic ration of the nucleus. It is defined as the ratio of the nuclear magnetic moment μ and the nuclear spin angular momentum. I (h/2nπ)

i.e. $\gamma = \mu/I\ (h/2\pi)\ (T^{-1}s^{-1})$



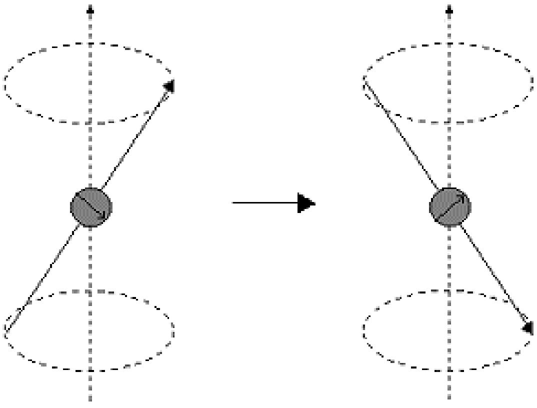
The frequency of precession is termed the *Larmor frequency*, which is identical to the transition frequency.

The potential energy of the precessing nucleus is given by;

$E = - \mu B \cos \theta$

where θ is the angle between the direction of the applied field and the axis of nuclear rotation.

If energy is absorbed by the nucleus, then the angle of precession, θ, will change. For a nucleus of spin 1/2, absorption of radiation "flips" the magnetic moment so that it **opposes** the applied field (the higher energy state).



It is important to realise that only a small proportion of "target" nuclei are in the lower energy state (and can absorb radiation). There is the possibility that by exciting these nuclei, the populations of the higher and lower energy levels will become equal. If this occurs, then there will be **no** further absorption of radiation. The spin system is *saturated*. The possibility of saturation means that we must be aware of the relaxation processes which return nuclei to the lower energy state.

4.3.4 Relaxation processes

How do nuclei in the higher energy state return to the lower state? Emission of radiation is insignificant because the probability of re-emission of photons varies with the cube of the frequency. At radio frequencies, re-emission is negligible. We must focus on non-radiative relaxation processes (thermodynamics!).

Ideally, the NMR spectroscopist would like relaxation rates to be fast - but not too fast. If the relaxation rate is fast, then saturation is reduced. If the relaxation rate is too fast, line-broadening in the resultant NMR spectrum is observed.

There are two major relaxation processes;

- Spin - lattice (longitudinal) relaxation
- Spin - spin (transverse) relaxation

4.3.4 .1Spin - lattice relaxation

Nuclei in an NMR experiment are in a sample. The sample in which the nuclei are held is called the *lattice*. Nuclei in the lattice are in vibrational and rotational motion, which creates a complex magnetic field. The magnetic field caused by motion of nuclei within the lattice is called the *lattice field*. This lattice field has many components. Some of these components will be equal in frequency and phase to the Larmor frequency of the nuclei of interest. These components of the lattice field can interact with nuclei in the higher energy state, and cause them to lose energy (returning to the lower state). The energy that a nucleus loses increases the amount of vibration and rotation within the lattice (resulting in a tiny rise in the temperature of the sample).

The relaxation time, T_1 (the average lifetime of nuclei in the higher energy state) is dependant on the magnetogyric ratio of the nucleus and the mobility of the lattice. As mobility increases, the vibrational and rotational frequencies increase, making it more likely for a component of the lattice field to be able to interact with excited nuclei. However, at extremely high mobilities, the probability of a component of the lattice field being able to interact with excited nuclei decreases

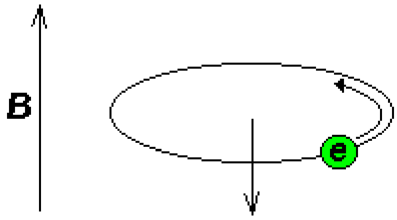
4.3.4 .2 Spin - spin relaxation

Spin - spin relaxation describes the interaction between neighbouring nuclei with identical precessional frequencies but differing magnetic quantum states. In this situation, the nuclei can exchange quantum states; a nucleus in the lower energy level will be excited, while the excited nucleus relaxes to the lower energy state. There is no **net** change in the populations of the energy states, but the average lifetime of a nucleus in the excited state will decrease. This can result in line-broadening.

4.3.5 Chemical shift

The magnetic field at the nucleus is **not** equal to the applied magnetic field; electrons around the nucleus shield it from the applied field. The difference between the applied magnetic field and the field at the nucleus is termed the *nuclear shielding*.

Consider the s-electrons in a molecule. They have spherical symmetry and circulate in the applied field, producing a magnetic field which opposes the applied field. This means that the applied field strength must be increased for the nucleus to absorb at its transition frequency. This *upfield shift* is also termed *diamagnetic shift*.



Magnetic field produced
by circulating electron

Electrons in p-orbitals have **no** spherical symmetry. They produce comparatively large magnetic fields at the nucleus, which give a *low field shift*. This "deshielding" is termed *paramagnetic shift*.

In proton (^1H) NMR, p-orbitals play no part (there aren't any!), which is why only a small range of chemical shift (10 ppm) is observed. We can easily see the effect of s-electrons on the chemical shift by looking at substituted methanes, CH_3X. As X becomes increasingly electronegative, so the electron density around the protons decreases, and they resonate at lower field strengths (increasing δ_H values).

Chemical shift is defined as *nuclear shielding / applied magnetic field*.

Chemical shift is a function of the nucleus and its environment. It is measured relative to a reference compound. For ^1H NMR, the reference is usually tetramethylsilane, Si

The difference between the magnitudes of the magnetic field at which free nuclei and molecular nuclei resonate is called chemical shift.

When an atom or molecule is placed in a magnetic field, the surrounding electron cloud induces a magnetic field at the nucleus will be slightly different from the applied field. The induced field is directly proportional to the strength of the applied field.

$B_{ind} \alpha\, B_{applied}$

$B_{ind} = \sigma B_{applied} = \sigma B_0$ .... (1)

where σ - shielding constant of screening constant.

The effective field strength experienced by the proton is

$$B_{eff} = B_{applied} - B_{ind}$$

$$= B_0 - \sigma B_0$$

$$B_{eff} = B_0 (1 - \sigma) \qquad \text{..........................} (2)$$

For two nuclei A and B,

$$B_B = B_0 (1 - \sigma_B) \qquad \text{..........................} (3)$$

$$B_A = B_0 (1 - \sigma_A) \qquad \text{..........................} (4)$$

The difference is

$$B_B – B_A = B_0 (1 - \sigma_B) – [B_0 (1 - \sigma_A)]$$

$$= B_0 – B_0\sigma_B – B_0 + B_0\sigma_A$$

$$= B_0 – (\sigma_A – \sigma_B)$$

$$B_B – B_A = B_0\delta_{AB}$$

where δ_{AB} is chemical shift of nucleus A with respect to B

$$\delta_{AB} = \frac{B_B - B_A}{B_0} \qquad \text{..........................} (6)$$

The chemical shift can also be expressed in terms of frequency.

$$\delta_{AB} = \frac{\nu_B - \nu_A}{\nu_0} \times 10^6 \text{ppm}$$

Thus, the chemical shift of a sample can be calculated as

$$\delta_{AB} = \frac{\nu_{\text{sample}} - \nu_{\text{refrence}}}{\nu_0} \times 10^6 \text{ppm} \quad \text{.........................} \ (7)$$

Generally, TMS is used as a reference and chemical shift is measured using 'δ' scale.

For TMS, $\delta = 0$ or $\tau = 10$

$\delta = 10 - \tau$

Reason for TMS used as a reference :

Tetra methyl silance (TMS) is used as reference dcompound in NMR, because,

i) It has 12 equivalent protons and gives a single sharp peak in its NMR spectrum.
ii) It has low boiling point 27ºC.
iii) It is chemically inert & non volable.
iv) It is soluble in most of the organic solvents.
v) Its signal is appeared at the extreme end of the spectrum

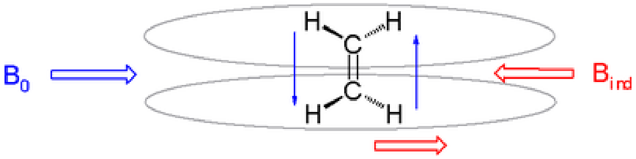
4.3.6. Factors affecting chemical shifts

Important factors influencing chemical shift are electron density, electronegativity of neighboring groups and anisotropic induced magnetic field effects.

Electron density shields a nucleus from the external field. For example, in proton NMR the electron-poor tropylium ion has its protons downfield at 9.17 ppm, those of the electron-rich cyclooctatetraenyl anion move upfield to 6.75 ppm and its dianion even more upfield to 5.56 ppm.

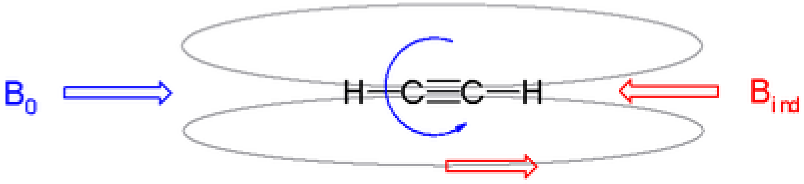
A nucleus in the vicinity of an **electronegative atom** experiences reduced electron density and the nucleus is therefore deshielded. In proton NMR of methyl halides (CH_3X) the chemical shift of the methyl protons increase in the order I < Br < Cl < F from 2.16 ppm to 4.26 ppm reflecting this trend. In carbon NMR the chemical shift of the carbon nuclei increase in the same order from around –10 ppm to 70 ppm. Also when the electronegative atom is removed further away the effect diminishes until it can be observed no longer.

Anisotropic induced magnetic field effects are the result of a local induced magnetic field experienced by a nucleus resulting from circulating electrons that can either be paramagnetic when it is parallel to the applied field or diamagnetic when it is opposed to it. It is observed in alkenes where the double bond is oriented perpendicular to the external field with pi electrons likewise circulating at right angles. The **induced magnetic field** lines are parallel to the external field at the location of the alkene protons which therefore shift downfield to a 4.5 ppm to 7.5 ppm range. The three-dimensional space where a nucleus experiences diamagnetic shift is called the shielding zone with a cone-like shape aligned with the external field.



The protons in aromatic compounds are shifted downfield even further with a signal for benzene at 7.73 ppm as a consequence of a diamagnetic ring current.

Alkyne protons by contrast resonate at high field in a 2–3 ppm range. For alkynes the most effective orientation is the external field in parallel with electrons circulation around the triple bond. In this way the acetylenic protons are located in the cone-shaped shielding zone hence the upfield shift.



Screening constant 'σ'

It is a dimensionless quantity. The value of σ depends on the electron density around the proton (Fig. 4).

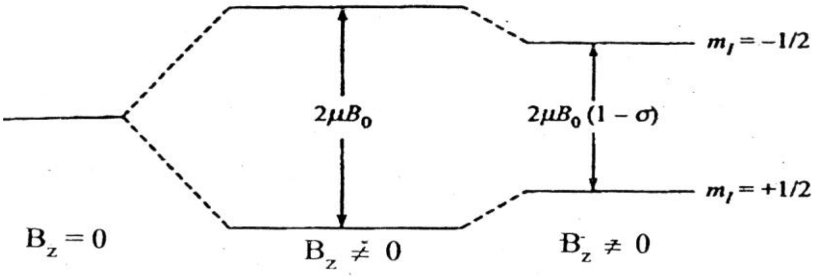


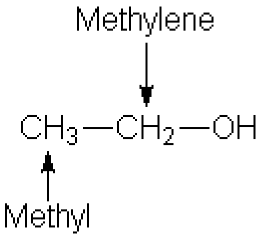
Fig 4. Bare and screened, spin ½ nucleus in B_Z

Acetaldehyde has two types of protons CHO and CH_3protons. The three protons in $CH_3$are equivalent. Since the oxygen is more electronegative the electron density around the proton in CHO is less than that around the CH_3 proton. Therefore, the screening is more for the methyl protons.

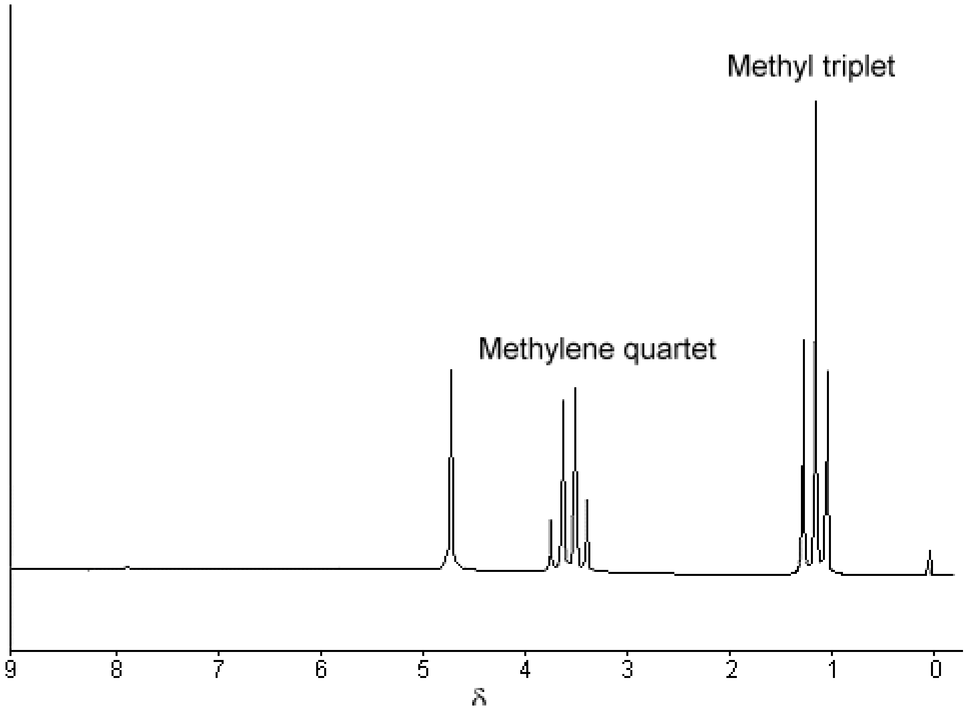
$\sigma CHO < \sigma CH_3$

4.3.7 Spin - spin coupling

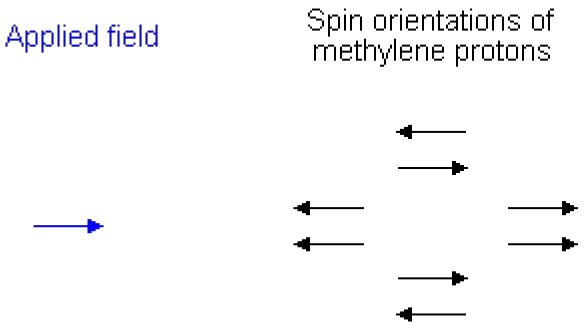
Consider the structure of ethanol;



The ^{1}H NMR spectrum of ethanol (below) shows the methyl peak has been split into three peaks (a *triplet*) and the methylene peak has been split into four peaks (a *quartet*). This occurs because there is a small interaction (*coupling*) between the two groups of protons. The spacings between the peaks of the methyl triplet are equal to the spacings between the peaks of the methylene quartet. This spacing is measured in Hertz and is called the *coupling constant, J.*

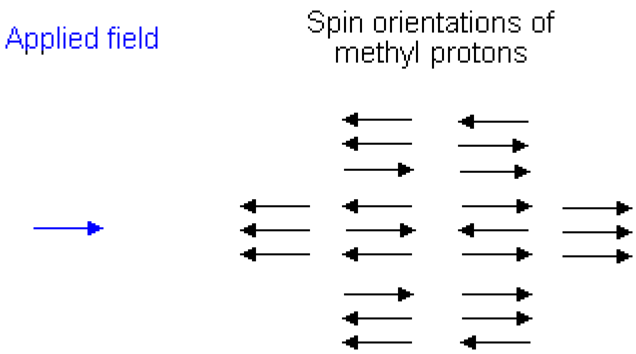


To see why the methyl peak is split into a triplet, let's look at the **methylene** protons. There are two of them, and each can have one of two possible orientations (aligned with or opposed against the applied field). This gives a total of four possible states;



In the first possible combination, spins are paired and opposed to the field. This has the effect of reducing the field experienced by the **methyl** protons; therefore a slightly higher field is needed to bring them to resonance, resulting in an upfield shift. Neither combination of spins opposed to each other has an effect on the methyl peak. The spins paired in the direction of the field produce a downfield shift. Hence, the methyl peak is split into three, with the ratio of areas 1:2:1.

Similarly, the effect of the methyl protons on the methylene protons is such that there are eight possible spin combinations for the three methyl protons;



Out of these eight groups, there are two groups of three magnetically equivalent combinations. The methylene peak is split into a quartet. The areas of the peaks in the quartet have the ration 1:3:3:1.

In a *first-order* spectrum (where the chemical shift between interacting groups is much larger than their coupling constant), interpretation of splitting patterns is quite straightforward;

- The multiplicity of a multiplet is given by the number of equivalent **protons** in **neighbouring** atoms plus one, i.e. *the n + 1 rule*
- Equivalent nuclei do not interact with each other. The three methyl protons in ethanol cause splitting of the neighbouring methylene protons; they do not cause splitting among themselves
- The coupling constant is not dependant on the applied field. Multiplets can be easily distinguished from closely spaced chemical shift peaks.

4.3.8 Theory : (Bloch and Purcell in 1946)

Atoms consists of nuclei and electrons. The nuclei have positive charges which are multiples of the protons. The nuclei have also angular momentum known as spin and characterised by the spin quantum number (I = 0, ½, 1, 1½ ....)

The angular momentum associated with a nuclear spin is given by

$$\left[(I.I+1)\right]^{1/2}.\frac{h}{2\pi}$$

Since, a nucleus possesses an electric charge, the spinning nucleus gives rise to a magnetic field whose axis coincides with the axis of spin. Thus the nucleus can be regarded as a micromagnet with the magnetic moment μ.

$$\therefore \vec{\mu}\ \alpha\ \text{spin},\ \vec{I} \qquad \text{..................}\ (1)$$

$$\vec{\mu} = g_N\, \mu_N\, \vec{I}$$

Where, g_N is called the nuclear g factor.

μ_N is the nuclear magnet on $\frac{eh}{4\mu m_p} = 5.05\times10^{-27}\,JT^{-1}(T = Tesla)$

$m_p$is the mass of the proton

e is the electronic charge

When the nucleus is placed in an external magnetic field B_Z applied in the z-direction, the energy of interaction is

$$E = -\vec{\mu}.\vec{B}_Z \qquad \text{..................}\ (2)$$

Substituting the value of $\vec{\mu}$ from eqn (1), we get

$$E = -g_N\mu_N.\vec{B}_Z\ \vec{I}$$

Since I is quantized in the presence of the magnetic field and the energy of nuclear spin is defined only by its components m_1 then,

$E_{mI} = -g_N\mu_N.\ B_Z m_I$ .... (3)

For a bare proton, I = ½, so that $m_I = \pm ½$;

i.e. $m_1 = +½;\ E_{½} = \frac{1}{2} g_N\mu_N.B_Z$ .... (4)

$m_1 = -½,\ E_{½} = +\frac{1}{2} g_N\mu_N.B_Z$ .... (5)

$m_I = -1/2,\ E_{-1/2} = +\frac{1}{2}\ g_N\mu_N\ .B_Z$

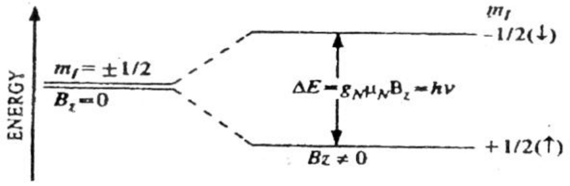


Fig. 1 Splitting of nuclear energy levels of a bare proton in a magnetic field (keeping B_Z constant and frequency is varied)

From eqns (4) and (5) the energy difference is given by

$\Delta E = g_N\mu_N.B_Z$ .... (6)

In order to flip the nucleus from the upward direction ↑ to the downward direction (↓), oscillating radio frequency perpendicular to the direction of B_Z is applied (of energy hν)

$\Delta E = g_N\mu_N.B_Z = h\nu$ .... (7)

This is called Bohr frequency condition.

Thus, the NMR frequency of a bare proton is given by

$$\nu = \frac{\Delta E}{h} = \frac{g_N\mu_N B_Z}{h} \quad \text{or } \nu \alpha\ B_Z$$

The NMR spectra can be recorded in two ways.

i) Keeping the magnetic field B_Z fixed and varying the frequency ν (fig. 1)

ii) Keeping ν fixed and varying the magnetic field B_Z (fig. 2)

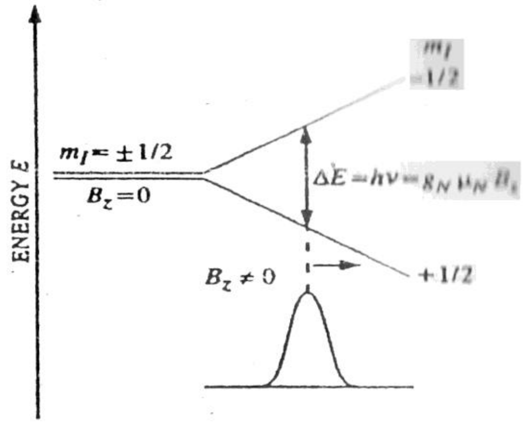
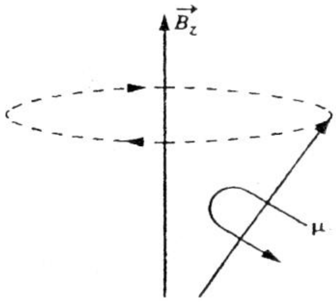


Fig. 2 Splitting of nuclear energy levels of a bare proton in a magnetic field (keeping ν constant and B_Z frequency is varied)

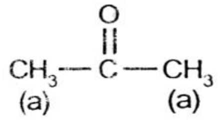
The later technique is used in modern NMR spectrometer.

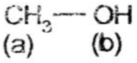
4.3.9 Signals

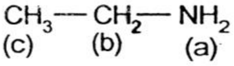
The number of signals explain the number of differently sets of equivalent protons in a molecule. Each signal corresponds to a set of equivalent protons.

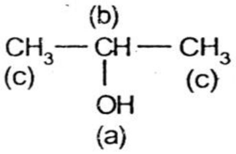


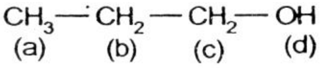
Example :

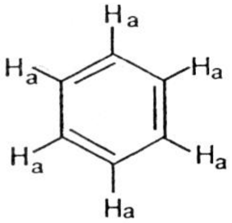
i) 
$CH_3-\overset{\overset{O}{||}}{C}-CH_3$ (a) (a) 1 nmr signal

ii) 
CH_3-OH (a) (b) 2 nmr signals

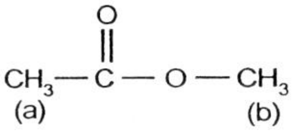
iii) 
$CH_3-CH_2-NH_2$ (c) (b) (a) 3 nmr signals

iv) 
$CH_3-CH(OH)-CH_3$ (c) (b) (a) (c) 3 nmr signals

v) 
$CH_3-CH_2-CH_2-OH$ (a) (b) (c) (d) 4 nmr signals

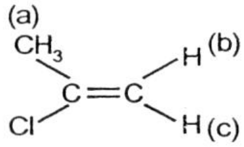
vi) 

2 nmr signals

vii) 
$CH_3-\overset{\overset{O}{||}}{C}-O-CH_3$ (a) (b) 2 nmr signals

viii) 2-chloropropane, $CH_3 - C(Cl) = CH_2$

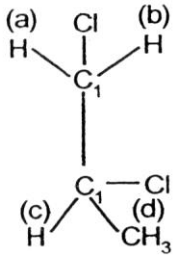
From this structure, one can two sets of equivalent protons (Two signals). But stereochemical formula shows three sets of protons in it and it gives three NMR signals.



3nmr signals

ix) 1, 2 dichloropropane, $CH_3 - CH(Cl) - CH_2Cl$.

From this structure one can expect three sets of protons (Three signals). But stereochemical formula shows four sets of protons in it and it gives four NMR signals.



4 nmr signals

7. Spin – spin coupling

When the NMR spectrum of a sample in the gaseous or the liquid states is observed under high resolution, the lines are split into the number of finer lines (multiplet). This splitting is due to the coupling of the magnetic moment of one set of equivalent protons with those of another set. This splitting is called spin-spin coupling.

The splitting pattern can usually interpreted by using two rules.

a) (n + 1) rule

b) Binomial coefficient rule $(1 + x)^n$

a) (n+1) rule

If there are ‘n’ equivalent protons that interact with the proton being studied, the lines will split into n + 1 lines, where n is the number of neighbouring protons.

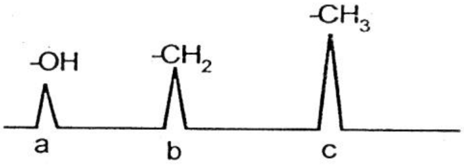
b) Binomial coefficient rule :

The intensity of the peaks in the multiplet can be obtained from the coefficients of the binomial expansion of $(1+x)^{n.}$ Thecoeffficients can be arranged in Pascal’s triangle.

No. of protons	**n + 1**	**Relative intensity**
0	1 (singlet)	1
1	2 (doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1

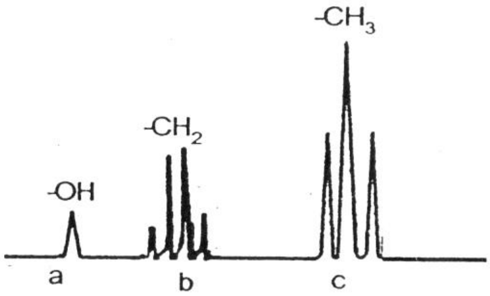
i) NMR spectrum of ethanol (Acidified ethanol/Gaseous ethanol

The low resolution NMR spectrum of ethanol $CH_3 – CH_2 – OH$ is as follows.



Low resolution NMR spectrum of ethanol

The high resolution NMR spectrum of ethanol using (n + 1) rule and the binomial coefficient rule is



High resolution NMR spectrum of ordinary sample of Ethanol

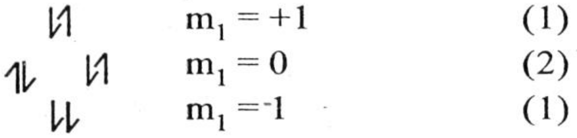
The mulplicity of the signal is due to spin-spin coupling.

a) For methyl protons :

There are two neighbouring protons (-CH_3) for CH_3 group. Hence the peak is split into three signals (triplet)

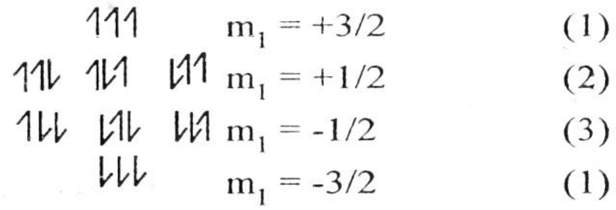
The intensity of the three signals are in the ratio of 1 : 2 : 1 (using Pascal's triangle).

Since there are two protons, the possible orientation are



b) For methylene protons:

There are three neighbouring protons (-CH_3) for – CH group. Hence the peak is split into four signals (quartet). The intensity of the four signals are in the ratio of 1:3:3:1. Since there are three protons, the possible orientation are



c) For hydroxyl proton:

The hydroxyl proton is not affected by neigbouring protons. This is due to the fast chemical exchange of protons between the –OH groups of difference molecules. So, it does not produce splitting effect. Hence only one signal is produced.

In contrast to acidified ethanol, there is not proton exchange in pure ethanol. Thus due to spin-spin splitting the CH_3 line is split into a triplet, the CH_2 line into an octet (8 lines) and the H line into a triplet.

4.3.10 Applications of NMR spectroscopy :

i) Elecidation of molecular structure :

The most important application of NMR is the elucidation of molecular structure. The points of interest in this elucidation are.

a) Number of NMR signals, which gives the number of different types of protons such as methyl proton, methylene proton, hydroxyl proton, aldehydic proton and aromatic proton.

b) Position of the signal and chemical shifts: This decides the type of proton.

c) Intensitites of signals : The intensity depends on the number of protons of a particular kind. The relative intensities of signals are measured by the areas under the different peaks obtained in the NMR spectrum.

d) Splitting of signals (under high resolution) : This gives information about the number of equivalent protons which are near neighbours to the group under study.

The above points can be illustrated with a few examples:

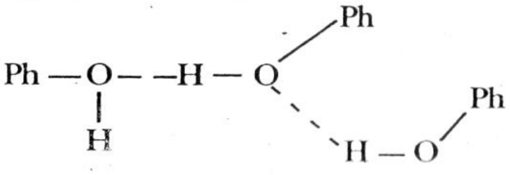
Compound	**NMR Signals**	**Splitting pattern**
$CH_3^a – CH_2^b – Cl$	2	a – triplet, b - quartet
$(CH_3^a)_2 – CH^b – Cl$	2	a – doublet, b – spetet
$CH_3^a – CO – CH_3^a$	1	a – singlet
$CH_3^a – CH^b\ O$	2	a – doublet, b – quartet
$C_6H_6^a$	1	a - signlet

ii) Hydrogen bonding

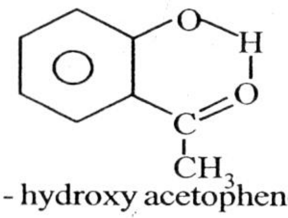
The NMR is used to study the nature of hydrogen bonding in compounds. If a proton in a compound is involved in hydrogen bonding, the resonance absorption peak occurs at a down field (higher δ - value). This is due to decreased electron density around the proton by the hydrogen bond.

Intermolecular H – bonding is affected by concentration and temperature, but intermolecular H – bonding is unaffected by these factors.

Example : At ordinary concentration, phenols have –OH proton absorption at 6.0 to 7.7 δ (down field) due to intermolecular H – bonding. At infinite dilution or at higher temperature their absorption at 4.0 to 5.0 δ (up field) due to weakening of H – bonding.



Phenol

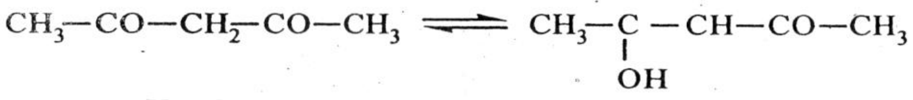


o - hydroxy acetophenone

O – hydroxy acetophenone has – OH proton absorption at 12.05δ due to intermolecular H – bonding. Its position is unaffected by dilution or temperature.

iii) Tautomerism :

NMR spectra are used in the study of keto-enol tautomerism. Example : Acetyle acetone exists the following equillibrium.



$$CH_3–CO–CH_2–CO–CH_3 \rightleftharpoons CH_3–\underset{\displaystyle OH}{\underset{|}{C}}–CH–CO–CH_3$$

Keto form Enol form

In its NMR spectrum, the areas of $–CH_2$ – (keto form) and = CH – (enol form) peaks are carefully measured and found that the acetyl acetone contains 18.6± -.6% keto form at 25ºC.

iv) Study of water of crystallisation in solids :

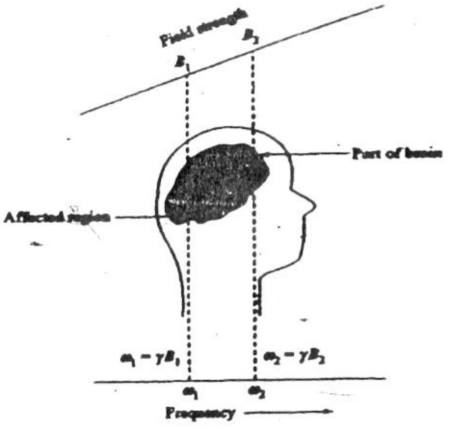
In $CuSO_4$, $2H_2O$. We would normally expect the two water molecules to be equivalent and hence only one NMR signal. Actually two signals are observed, each appearing as a doublet. This shows that the two water molecules have different orientation in space.

v) Kinetics of certain chemical reaction can be studied through NMR spectroscopy. Rates of several exchange reactions. (Example : Proton exchange between ethanol and H_3O^+, acetic acid and water) have been evaluated from line broadening measurments.

v)Nuclear Magnetic Resonance Imaging (MRI)

Nuclear magnetic resonance imaging is nothing but Magnetic Resonance Imaging (MRI). It is also known as zeugmatography or tomography. NMR imaging is based on the principle that it is possible to create two and three – dimensional "pictures" of objects, by proper adjustment of magnetic field at various depth in the sample, in the same way as a photograph or x-ray plate.

In a normal NMR experiment the samples (in the mg range) are studied in a uniform magnetic field with homogencity of none part in 10^9. But in the MRI experiment, the samples are large and inhomogeneous such as human bodies, placed in uniform magnetic fields. The applied fields are inhomogeneous so that different parts of the sample experience different fields and consequently have different resonance frequencies.



For example, when a narrow tube contains water as the sample is placed in a uniform magnetic field, the NMR spectrum displays a single sharp line. If the same simple is placed in a magnetic field a linear field gradient, the MRI spectrum displays 'n' sharp lines at a various frequencies related directly to the magnetic fields at different parts of the sample.

By taking profiles from different directions achieved by altering the directions of the magnetic fields and the linear field gradients, the images of the objects from different angles can be obtained. The profiles are then processed with the help of the image processing technique in a computer to obtain two or three dimensional images. A typical image with anotomical details is shown in the figure.

UNIT V

GROUP THEORY AND NANO CHEMISTRY

CONTENTS

5.1Aims and objectives

The aim is to motivate and enable a comprehensive knowledge on symmetry elements and symmetry operations to the students.

On successful completion of this unit you should have:

Understand the symmetry elements and symmetry operations.

5.2. INTRODUCTION

Symmetry is a very fascinating phenomenon in nature. It is found in geometrical figures such as a cube, a sphere, an equilateral triangle, a rectangle, a square, a regular pentagon, a regular hexagon etc. Its importance was recognized by eminent Greek philosophers Pythagoras and Plato.

5.2. IDENTICAL CONFIGURATION

An identical configuration is the one which is not only indistinguishable from the original one but also identical with it.

5.3. EQUIVALENT CONFIGURATION

An equivalent configuration is the one which cannot be distinguished from the original one but need not be identical with it.

5.4. SYMMETRY OPERATION

A symmetry operation is a movement of the molecule such that the resulting configuration of the molecule is indistinguishable from the original.

5.5. SYMMETRY ELEMENT

A symmetry element is a geometrical entity such as a line or a space or a point about which an operation of rotation or reflection or inversion is done.

5.6. ROTATION AXIS OF SYMMETRY (C_n)

It is also called **rotational axis**, if a rotation around an axis by 360°/n results in a molecule indistinguishable from the original. Examples are water (C_2) and ammonia (C_3). A molecule can have more than one symmetry axis and the one with the highest number of n is called the **principal axis** and takes the z-axis in a Cartesian coordinate system.

This axis of symmetry can be explained by taking the example of triangular planar boron trichloride molecule. In boron trichloride molecule an axis of symmetry is located perpendicular to the plane containing all the atoms. This is known as the C_3 axis of symmetry. In general the symbol for proper axis of symmetry is C_n where n is known as the order of the axis. The order of the axis is given by the number of rotations by θ, to get the identical configuration. *n* is alternatively given by the formula $n=\left(\frac{2\pi}{\theta}\right)$, where θ is the minimum angle of rotation to obtain the equivalent configuration. *n* has non- zero positive integral values. Boron trichloride molecule has three C_2 axes of symmetry in addition to the C_3 axis (Fig.1.1). The C_3 axis in this molecule is known as principal axis. In general, if there are C_n axes of different orders in a molecule, the axis with the highest order is referred to as the principle axis.

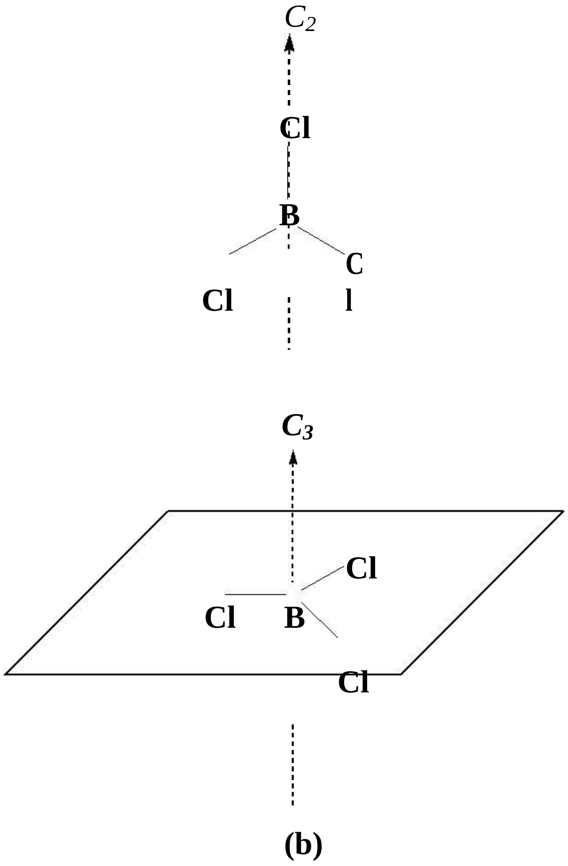


Fig.1.1. (a). The C_2 axis of symmetry in BCl_3 molecule.
(b). The C_3 principal axis in BCl_3 molecule.

5.7. PLANE OF SYMMETRY OR MIRROR PLANE (σ)

If reflection through a plane leaves an identical copy of the original molecule it has a plane of symmetry. Water has two of them: one in the plane of the molecule itself and one perpendicular to it. A symmetry plane parallel with the principal axis is dubbed vertical (σ_v) and one per perpendicular to it horizontal (σ_h). A third plane exists: if a symmetry plane bisects the angle between two n-fold axes that are perpendicular to the principal axis the plane is dihedral (δ_d). A plane can also be identified by its plane (xz),(yz) in the Cartesian coordination plane.

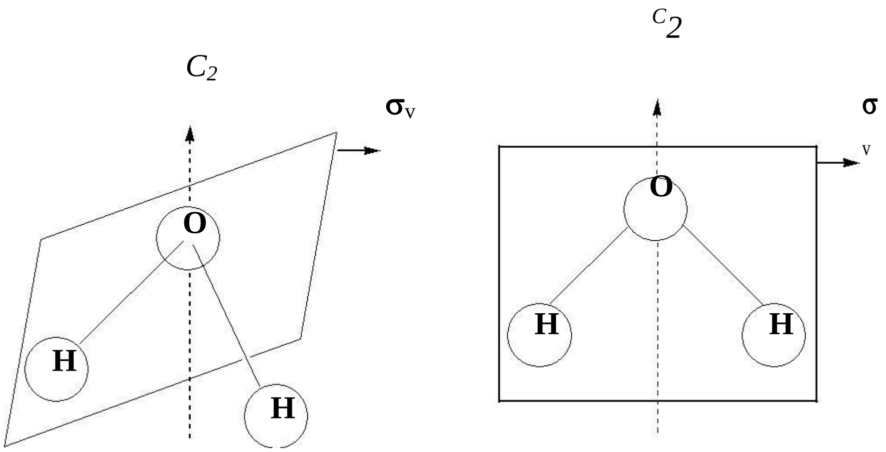


Fig. 1.2. The reflection planes in water molecule.

5.8. CENTER OF SYMMETRY OR INVERSION CENTER (i)

A molecule has a center of symmetry when for any atom in the molecule an identical atom can be found when it moves in a straight through this center an equal distance on the other side. An example is xenon tetrafluoride but not cisplatin even though both molecules are square planar.

This is a point such that any line drawn through it meets the same atom at equal distances in opposite directions. All homo-nuclear diatomic molecules possess the centre of symmetry.

Fig.1.3 lists the molecules with centre of symmetry. This element of symmetry is also called S_2 axis.

A particular symmetry element generates many symmetry operations. A C_n axis generates a set of operations $C_n^1, C_n^2, C_n^3, ...,C_n^n$. The C_n^n operation is equivalent to the identity operation.

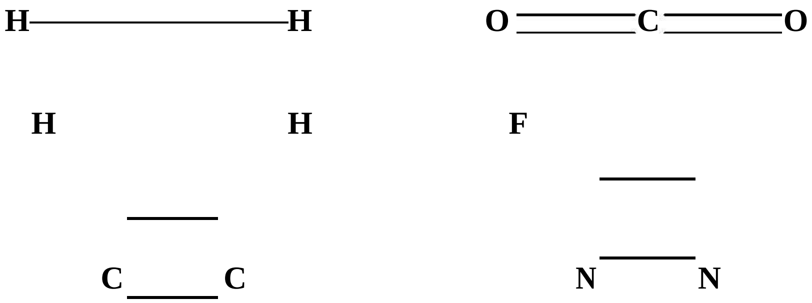


Fig.1. 3. Diagram showing molecules with centre of symmetry.

5.9. ROTATION-REFLECTION AXIS N-FOLD (S_n)

It is also called **improper rotational axis**. Molecules with this symmetry element can have a 360°/n rotation around an axis followed by a reflection in a plane perpendicular to it without a net change. An example is tetrahedral silicon tetrafluoride with three S_3 axes and the staggered conformation of ethane with S_6 symmetry.

It is the line about which a rotation by a specific angle followed by reflection in a plane perpendicular to the rotation axis is performed. Fig.1.4 shows the S_6 axis in staggered from of ethane.

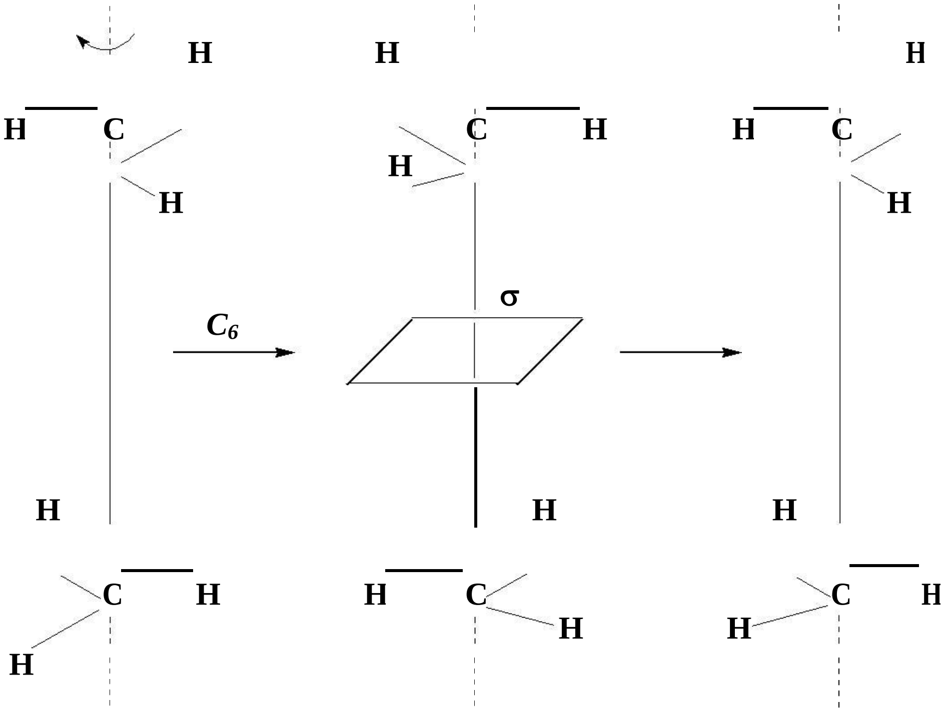


Fig.1.4. TheS_6axis in staggered form of ethane.

5.10. IDENTITY (E)

This is a default symmetry element and every molecule has one.

5.11. INVERSE OPERATIONS

Suppose for a molecule we carry out an operation P followed by Q such that Q returns all the atoms of the molecule to their original position then, Q is said to be the inverse of P. In such cases,

$QP = E = PQ$

Algebraically we can express $Q = P^{-1}$, thus we can write $P^{-1}P = E = PP^{-1}$ because an operation and its inverse always commute.

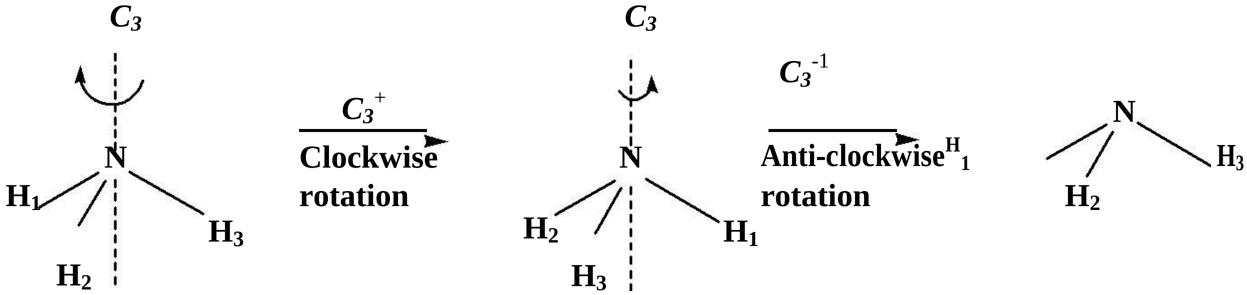
5.11.1. INVERSE OF σ And i

In the case of inversion and reflection, the carrying out of these operations in succession leads to identity E, i.e. $\sigma.\sigma=\sigma^2= E$ and $i.i= i^2= E$. Hence in these cases, these operations themselves are their own inverse that $i = i^{-1} and \sigma=\sigma^{-1}$.

5.11.2. INVERSE OF ROTATION [C_n^{-1}]

In the case of rotation, simply carrying out an operation for the second time does not give the original configuration. In C_n is the clockwise rotation by $(2\pi/n)^0$ then C_n^{-1} is an anticlockwise rotation by $(2\pi/n)^0$ about C_n. Then, $C_n^{-1}C_n= E$.

For example, in NH_3 molecule $C_3^{-1}C_3=E$.



At the same time, for NH_3, $C_3^2C_3^1=E$

The above way of carrying out the symmetry operations successively is algebraically represented as multiplication. If P and Q are two symmetry operations, PQ is a combined operation of carrying out Q first and then P. By conversion, first operation is written at right. For example, in the second case shown above for NH_3 molecule, carrying out C_2 first and then σ_v is represented as $\sigma_v C_2$.

5.11.3. INVERSE OF S_n

As with C_n^{-1}, S_n^{-1} can be defined as rotation anticlockwise by $(2\pi/n)^0$ followed by reflection with perpendicular plane. We can prove for improper axis.

$$S_n^{-1}S_n^1=(C_n^{-1}\sigma_h)(C_n^1\sigma_h)= E$$

Since $C_n^1\sigma=\sigma C_n^1$

$$S_n^{-1}S_n=(C_n^{-1}\sigma_h)\ (C_n^1\sigma_h)=(C_n^{-1}\sigma_h)\ (\sigma_h C_n^1)$$

$-1\ (\ )1\quad -1\quad -1$

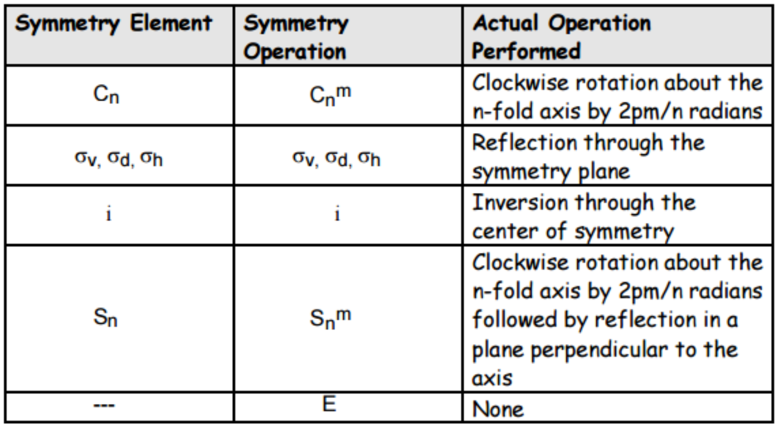
$$= C_n\sigma_h\sigma_h \quad C_n = C_n \;\; EC_n = C_n \;\; C_n = E$$

However, we can express S_n^{-1}interms of clockwise rotation about the same axis. We know that $S_n^{\,n} = E$ when n is odd. Then

$$S_n^{\,n-1} \;\; S_n^{\,1} = E \text{ (n-even) Thus,} S_n^{\,-1} = S_n^{\,n-1}$$

$$S_n^{\,2n-1} \;\; S_n^{\,1} = E \text{ (n-odd) Thus,} S_n^{\,-1} = S_n^{\,2n-1}$$

3. The symmetry operations:



Symmetry Element	**Symmetry Operation**	**Actual Operation Performed**
C_n	$C_n^{\,m}$	Clockwise rotation about the n-fold axis by 2pm/n radians
σ_v, σ_d, σ_h	σ_v, σ_d, σ_h	Reflection through the symmetry plane
i	i	Inversion through the center of symmetry
S_n	$S_n^{\,m}$	Clockwise rotation about the n-fold axis by 2pm/n radians followed by reflection in a plane perpendicular to the axis
---	E	None

5.12. LET US SUM UP

In this unit, we:
Pointed out

- Identical configuration
- Equivalent configuration
- Symmetry operation
- Symmetry element
- Rotation axis of symmetry (C_n)
- Plane of symmetry or mirror plane (σ)
- Center of symmetry or inversion center (i)
- Rotation-reflection axis n-fold (S_n)
- Identity (E)
- Inverse operations

5.13 CHECK YOUR PROGRESS

1. What is n improper axis of rotation? What are the operations generated byS_5? How many of these are the distinct operations of S_5?
2. Prove the following:

5.14. LESSON - END ACTIVITIES

1. (a) Distinguish between

(1). Symmetry element and symmetry operations.

(2). Proper and improper rotation.

(b) Show that $C_2(z)$ and $\sigma(xy)$ commute.

2. What is an inverse operation? Is this equivalent to any other combination of operations? Give an example.

5.15. SUGGESTED READINGS

1. K.V. Raman, Group Theory and its applications to Chemistry, Tata McGraw-Hill Publishing Company limited, New Delhi.

2. B.R. Puri, L.R. Sharma and M.S. Pathania, Principles of Physical Chemistry, Millennium edition, 2006- 2007.

GROUPS AND THEIR BASIC PROPERTIES

GROUPS AND THEIR BASIC PROPERTIES

The aim is to motivate and enable a comprehensive knowledge on groups and their basic properties to the students.

On successful completion of this lesson the student should have:

Understand the groups and their basic properties.

6.1. INTRODUCTION

Having defined various symmetry operations in Lesson 1 we may now ask ourselves whether it is possible to classify the molecules into ‘Groups’ on the basis of the symmetry elements they posses. Is it possible to define certain symmetry groups so that all molecules belonging to a certain group have the same type of symmetry operations? Luckily, the answer is ‘Yes’. This means that we can give an accurate description of the symmetry of any molecule by knowing to which group it belongs.

6.2. GROUP

A group is a complete set of members which are related to each other by certain rules. Each

6.2.1. BASIC PROPERTIES OF A GROUP

Certain rules have to be satisfied by the elements so that they form a group. These rules

are the following:

1. The product of any two elements and the square of any element must be elements of group (closure property).
2. There must be one element in the group which commutes with everyone of the elements and leaves it unchanged.
3. The associative law of multiplication should be valid.
4. For every element there must be a reciprocal (inverse) and this reciprocal is also an element of the group.

RULE 1

If A and B are the element of the group and if $AB = C$,C must be a member of the group. Product AB means that we perform the operation B first and then operation A i.e., the sequence of operations is from right to left. It should be noted that the other product BA need not be same as AB. BA means doing A first and then performing the operation B later. Let $BA = D$. D must be amember of the group by rule 1. Usually AB BA and so C D. However, there may be some special elements A and B each that $AB = BA$. Then A and B are said to *commute* with each other or the multiplication of A and B is *commutative.* Such a group where any two elements commute is called an *abelian* group. H_2O belongs to an abelian group. The four symmetry operations for H_2O are E, C_{2z},$\sigma_{v(xz)}$ and $\sigma'_{v(yz)}$.The inter-relationships between these operations are given in the group multiplication table (Table 2.1).

Table 2.1.

	E	$C_{2z},$	$^{\sigma}v(xz)$	$^{\sigma'}v(yz)$
E	E	$^{C}2z$	$^{\sigma}v(xz)$	$^{\sigma'}v(yz)$
$^{C}2z$	$^{C}2z$	E	$\sigma'\ v(yz)$	$\sigma v(xz)$
$^{\sigma}v(xz)$	$^{\sigma}v(xz)$	$^{\sigma'}v(yz)$	E	$^{C}2z$
$^{\sigma'}v(yz)$	$^{\sigma'}v(yz)$	$^{\sigma}v(xz)$	$^{C}2z$	E

Note that each member is its own inverse. The product of any two operations is found among the four members.

$$E^2 = C_2^2 = (\sigma_v')^2 = E$$

$$\sigma_v \sigma_v' = \sigma_v' \sigma_v = C_2; \quad C_2 \sigma_v = \sigma_v \ C_2 = \sigma_v' \ \ etc$$

RULE 2

Each group must necessarily have an element which commutes with every other element of the group and leaves it unchanged.

Let A and B be the elements of the group. Let X be the element satisfying rule 2.

i.e. $XA = AX = A$ and also $XB = BX = B$.

$BA = BX^2A; BX^2 = B = BE$, where we have set $X^2 = E$ (identity)

It is clear $BE^n = B$, n being any integer. This kind of element E which does not effect any change when multiplied with any element is a unique element and is called an identity operation

E. For water, E, the identity operation satisfies this rule. It is so for all molecules.

RULE 3

Associative law of multiplication must be valid. This means $ABCD$ is the same as $(AB)(CD)$, $(A)(BCD)$ *or* $(ABC)(D)$. ABC is the same as $A(BC)$ *or* $(AB)C$.

For example, we have for water

$C_2\sigma_v \, E\sigma_v' = (C_2\sigma_v)(E\sigma_v') = \sigma_v'\sigma_v' = E$

$C_2\sigma_v' \, E\sigma_v = C_2(\sigma_v' \, E\,)\sigma_v = C_2\sigma_v\sigma_v' = C_2$

Multiplication simply means successive application of the symmetry operations in the order right to left.

RULE 4

Inverse of an element A is denoted by A-^{1} (this does not mean 1/A). It is simply an element of the group such that $A^{-1}A=E$. In case of symmetry groups, A^{-1} is that element which undoes or annuls the effect of A. For H_2O we have, for example, C_2C_2 = E. Therefore $C_2^{-1}=C_2$ i.e., C_2 is its own inverse. This is true of all other elements for H_2O. But this is not general. For example, $C_6^2=C_3 \neq E$. Therefore C_6^{-1} is not C_6.

6.2.2. ORDER OF GROUP

The total number of elements present in a group is known as the order of the group. It is denoted by *n*.

Example:

1. Water molecule belongs to C_{2v} group of order 4 because it contains 4 elements namely E, C_{2z}, σ_v and σ'_v.
2. Ammonia belongs to C_{3v} group of order 6 as it contains 6 elements namely $E, C_3^1, C_3^2, \sigma_{v(1)}, \sigma_{v(2)}$ and $\sigma_{v(3)}$.

6.2.3. ABELIAN GROUP

A group is said to be abelian if for all pairs of elements of the group, the binary combination is commutative. That is AB = BC; BC = CB – and so on.

Example: The elements of C_{2v} point group E, C_{2z}, σ_v and σ'_v form an abelian group as all the elements of this group commute with each other.

6.2.4. NON-ABELIAN GROUP

A group is said to be non-abelian if the commutative law does not hold for the binary combinations of the elements of the group, i.e., AB BA.

Example:

The elements of C_{3v} point group $E, C_3^1, C_3^2, \sigma_{v(1)}, \sigma_{v(2)}$ and $\sigma_{v(3)}$ donot consecutive an abelian group since the elements donot follow commutative law.

6.2.5. ISOMORPHISM

Two groups are supposed to be isomorphic if they obey the following rules.

1. Both have same order and structure.
2. There is a one-to-one correspondence in all respects between the members of the two groups. If A_1, B_1, C_1, D_1 and A_2, B_2, C_2, D_2 are the members of the two isomorphic groups, A_1 corresponds to A_2, B_1 corresponds to B_2 and so on.
3. The relationship between the any two members of a group is exactly the same as the relationship between the corresponding members of the other group.

Let us take the three groups listed below:

(i) E, C_2

(ii) E, i

(iii) E, σ_h

All the three are isomorphic groups.

$E = C_2^2$; $C_2 E = C_2$

$E = i^2$; $iE = i$

$E = \sigma_h^2$; $\sigma_h E = \sigma_h$ etc.

6.3 POINT GROUPS

IT is only possible for certain combinations of symmetry elements to be present in a molecule (or any other object). As a result, we may group together molecules that possess the same symmetry elements and classify molecules according to their symmetry. These groups of symmetry elements are called point groups (due to the fact that there is at least one point in space that remains unchanged no matter which symmetry operation from the group is applied).There are two systems of notation for labeling symmetry groups, called the Schoenflies andHermann-Mauguin (or International) systems.

RULES FOR CLASSIFICATION INTO POINT GROUPS

1. If the molecule is linear, look for the highest rotational axis. This axis is infinite fold (c_∞) for a linear molecule.
    - If the molecule has a center of inversion (i) [or in other words, the two ends of the molecule are identical], then the point group is $\mathbf{D_{\infty h}}$
    - Otherwise $\mathbf{C_{\infty v}}$
2. If the molecule is non-linear and if the highest rotational axis is 3, 4 or 5 fold, look for other axes of the same order. There are 3 possibilities.
    a) Several 5-fold axes (C_5):
    The molecule belongs to $\mathbf{I_h}$ point group if it has a plane of symmetry. If not, the point group is **I**.
    b) Three 4-fold (C_4) axes:
    The molecule belongs to $\mathbf{O_h}$ point group if it has a plane of symmetry. If not, the point group is **O**.
    c) Four 3-fold axis (C_3) but no C_4 or C_5 axis:
        - If there are no mirror planes or a center of inversion, the point group is **T**
        - If there is a center of inversion, the point group is $\mathbf{T_h}$
        - If there are 6 mirror planes and three S_4 axes, the point group is $\mathbf{T_d}$

3. If only one axis has n ≥ 2 or if the axis of highest order is a C_2 axis, check for n more 2-fold axes (C_2) at right angles. If these exist and:

    - There are no mirror planes → $\mathbf{D_n}$ point group
    - Has a horizontal mirror plane → $\mathbf{D_{nh}}$ point group
    - No horizontal mirror planes, but has n vertical mirror planes → $\mathbf{D_{nd}}$ point group

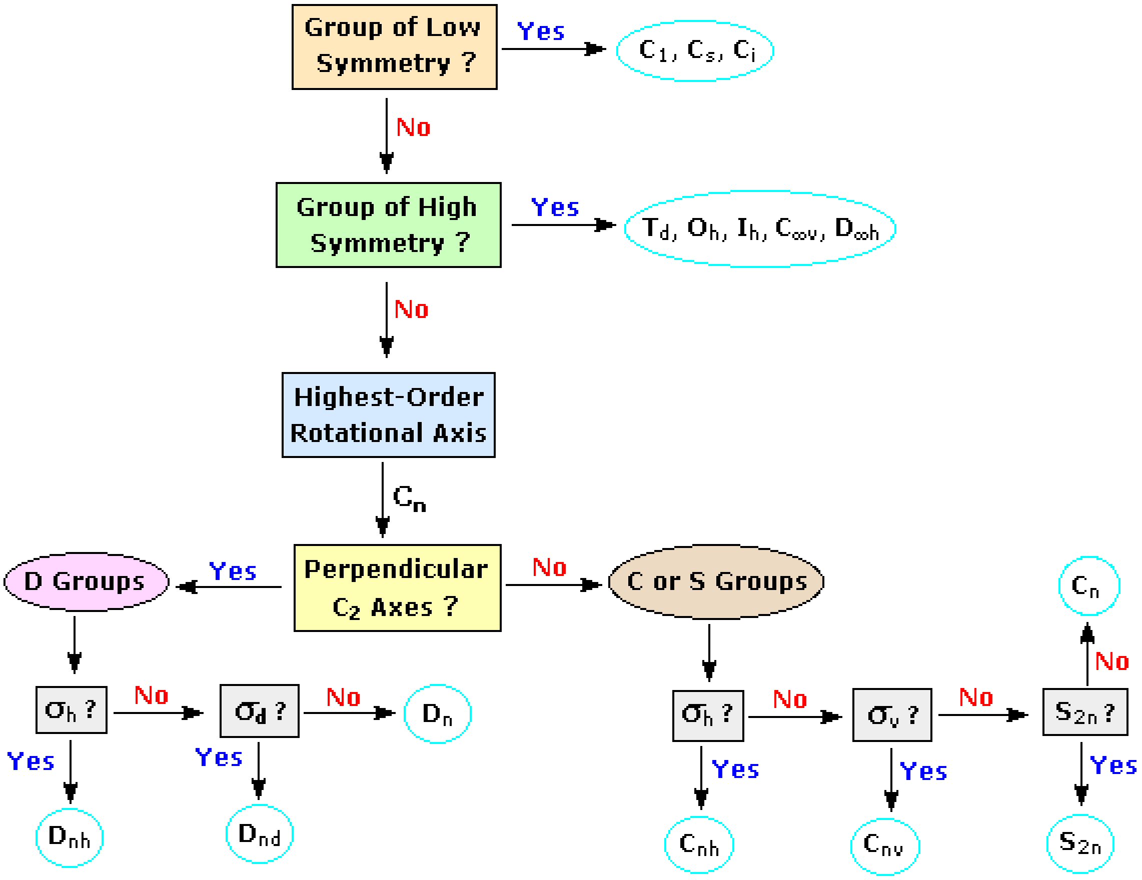
4. If only one n-fold axis exists, check for S_{2n} axis. If this exists then the point group is S_{2n}. If not, the molecule belongs to:

    - $\mathbf{C_n}$ if it has no mirror planes
    - $\mathbf{C_{nh}}$ if it has a horizontal mirror plane
    - $\mathbf{C_{nv}}$ if it has n vertical mirror planes

5. If the molecule has no symmetry axes, but has a:

    - center of inversion → point group is $\mathbf{C_i}$
    - mirror plane → point group is $\mathbf{C_s}$
    - none of the above → point group is $\mathbf{C_1}$

Point Group Decision Tree



6.4. GROUP MULTIPLICATION TABLE

Every group is characterized by a multiplication table. The relationship between the elements of the binary combinations is reflected in the multiplication table.

Consider a water molecule. It has four symmetry elements, *viz.*, E, C_2(z), σ_v(xz) and

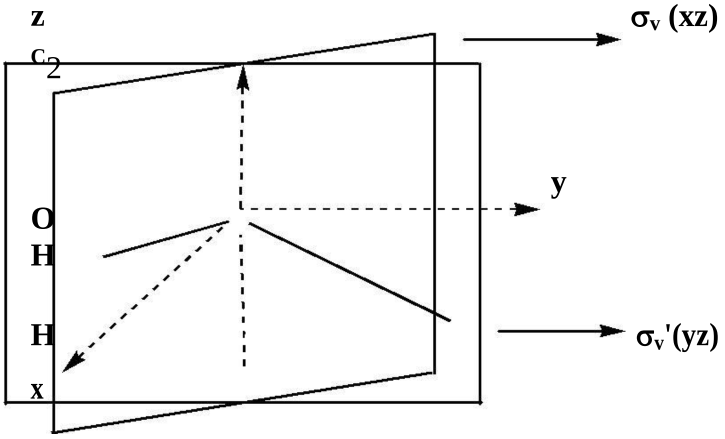


Fig. 2.2. The Four symmetry elements of H_2O molecules

We can easily show that the product of any two symmetry elements is one of the four elements of the group. Thus, for instance, $C_2(z)\sigma_v(xz) = \sigma_v'(yz)$. Proceeding this way the symmetry operations of H_2O can be listed in a group multiplication table (GMT) (Table 2.2).

	E	C_2(z)	σ_v(xz)	σ_v'(yz)
E	E	C_2(z)	σ_v(xz)	σ_v'(yz)
C_2(z)	C_2(z)	E	σ_v'(yz)	σ_v(xz)
σ_v(xz)	σ_v(xz)	σ_v'(yz)	E	C_2(z)
σ_v'(yz)	σ_v'(yz)	σ_v(xz)	C_2(z)	E

Table 2.2. Group multiplication table of the symmetry operations of H_2O molecule

TheAmmoniaMolecule

We shall introduce the concepts of symmetry and group theory by considering a concrete example–the ammonia molecule NH_3. In any symmetry operation on NH_3, the nitrogen atom remains fixed but the hydrogen atoms can be permutedin 3!=6 differentways. The axis of the molecule is called a C_3 axis, since the molecule can be rotated about it into 3 equivalent orientations, 120° apart.

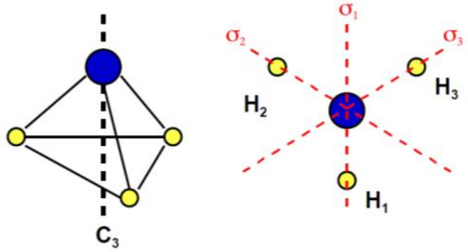
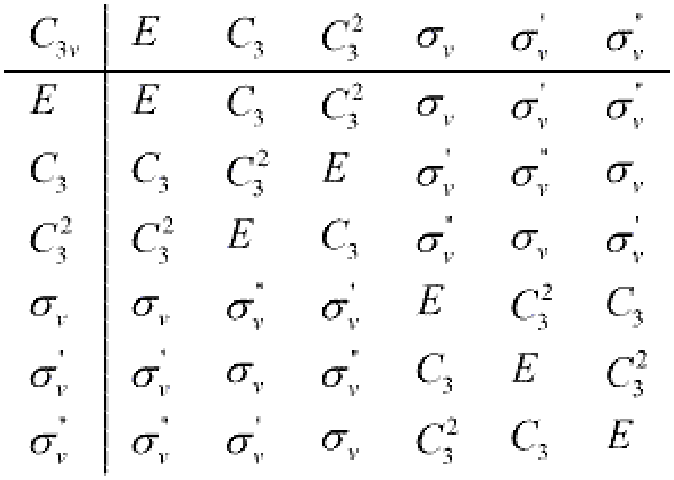


Figure 1. Two views of the ammonia molecule.

More generally, a C_n axis has n equivalent orientations, separated by $2\pi/n$ radians. The axis of highest symmetry in a molecule is called the principal axis. Three mirror planes, designated$_1$, σ2, σ3, run through the principal axis in ammonia. These are designated as σ_v or vertical planes of symmetry. Ammonia belongs to the symmetry group designated C_{3v}, characterized by a three-fold axis with three vertical planes of symmetry.

Group multiplication table of symmetry operation of NH_3 molecule



C_{3v}	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
C_3	C_3	C_3^2	E	σ_v'	σ_v''	σ_v
C_3^2	C_3^2	E	C_3	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^2	C_3
σ_v'	σ_v'	σ_v	σ_v''	C_3	E	C_3^2
σ_v''	σ_v''	σ_v'	σ_v	C_3^2	C_3	E

Notice that each operation occurs once and only once in each row and each column.

6.4.1. IMPORTANT CHARACTERISTICS OF A GROUP MULTIPLICATION TABLE

1. It consists of *h* rows and *h* columns where *h* is the order of the group.
2. Each column and row is labeled with group element.
3. The entry in the table under a given column and along given row is the product of the elements which head that column and the row (multiplication rule is strictly followed).
4. At the intersection of the column labeled by *Y* and the row labeled by *X*, we found the element which is the product *XY*.
5. The following rearrangement theorem holds good for every ‘Group Multiplication Table’.

“Each row and each column in the table lists each of the group elements once and only once. No two rows may be identical nor any two columns be identical. Thus each row and each column is a rearranged list of the group elements”.

6.5. SYMMETRY CLASSIFICATION OF MOLECULES INTO POINT GROUPS

Molecules can be classified into point groups depending on the characteristic set of symmetry elements possessed by them. A molecular group is called a point group since all the elements of symmetry present in the molecule intersect at a common point and this point remains fixed under all the symmetry operations of the molecule. The symmetry groups of the molecules

Table 2.3. Some Molecular Point Groups		
Point Group	**Symmetry Elements**	**Examples**
C_1	E	CHFClBr
C_2	E, C_2	H_2O_2
C_3	E, C_3	C_2H_6
C_s	E, σ_v	NOCl
$^{C}2v$	$E, C_2, 2\sigma_v$	H_2O, $CH_2=O$, pyridine
$^{C}3v$	$E, C_3, 3\sigma_v$	NH_3, $CHCl_3$, PH_3
$^{C}\infty v$	$E, C_\infty, \infty\sigma_v$	HCl, NO,CO
$^{C}2h$	E, C_2, σ_h, i	trans CHCl=CHCl
$^{D}2h$	$E, 3C_2, 3\sigma, i$	$CH_2=CH_2$, naphthalene
$^{D}3h$	$E, 2C_3, 3C_2 (\perp \text{ to } C_3), 3\sigma_v, \sigma_h, 2S_3$	BF_3(trigonal planar)
$^{D}4h$	$E, C_4, 4C_2 (\perp \text{ to } C_4), 2\sigma_v, 2\sigma_d, \sigma_h, C_2, S_4$(coincidence with C_4), i	$[PtCl_4]^{2-}$ (square planar)
$^{D}6h$	$E, 2C_6, 6C_2 (\perp \text{ to } C_6), 3\sigma_v, 3\sigma_d, \sigma_h, C_2, 2C_3, 2S_6, 2S_3, i$	C_6H_6
T_d	E, $4C_3, 3C_2, 3S_4$(coincidence with C_2), $6\sigma_d$	CH_4
O_h	$E, 3C_4, 4C_3, 3S_4$ and $3C_2$ (both coincident with the C4 axes), $6C_2, 4S_6, 3\sigma_h, 6\sigma_d$	SF_6

6.6. DIFFERENCE BETWEEN POINT GROUP AND SPACE GROUP

Symmetry operations do not alter the energy of the molecule. Further in all the above operations the centre of the molecule is not altered as none of the operations involve a total translational movement of the molecule. Whatever happens to the molecule, the centre (point) is not changed.

At least one point is fixed. Hence these are classified as ‘point group’ operations.

In case of crystals operations such as ‘screw rotations’ and glide plane reflections can be additionally specified. Screw rotation involves a rotation with respect to an axis and then a translation in the direction of the same axis. Glide plane reflection is a reflection in a plane followed by a translation along a line in that plane. These are particular to crystals and the classification comes under what is known as space group. Note that here even the centre changes. Thus in short, in point group, there is at least one point (centre) which is not altered after all operations while in space group it is not possible to identify such a stationary point.

6.7. LET US SUM UP

In this lesson, we:
Pointed out

- Group
- Basic properties of a group
- Order of group
- Abelian group
- Isomorphism
- Similarity transformation and classes
- Group multiplication table
- Symmetry classification of molecules into point groups
- Difference between point group and space group

6.8 CHECK YOUR PROGRESS

1. Explain why a set of numbers cannot form a group by the process of division.

2. Explain why the set of integers between 0 and $\propto$ do not form a group under the process of multiplication.

6.9. LESSON - END ACTIVITIES

1. Construct the multiplication table for the C_{3v} point group to which NH_3 molecule belongs.
2. Draw the structure of three distinct isomers of $C_2H_2Cl_2$ and determine their point groups. Which of them is polar?

6.10. REFERENCES

1. K.V. Raman, Group Theory and its applications to Chemistry, Tata McGraw-Hill Publishing Company limited, New Delhi.

UNIT V
NANO TECHNOLOGY

CONTENTS

7.1 Introduction

Nanotechnology is the science of nanotechnological devices, derived from nanomaterials. The nanomaterials are may solid materials that have special dimension in the range of the 1-100nm. Nanochemistry is a branch of nanotechnology which covers the study of nanoscale synthesis and nanometer scale materials. The prefix nano means one billionth (1×10^{-9}) and it is derived from the Latin word “nanus” (means any living thing smaller than its usual size). A nanometer (nm) is one billionth (1×10^{-9}) of a meter. For comparison, a single human hair is about 80,000nm; a red blood cell is approximately 7,000nm; a water molecule is almost 0.3nm and hydrogen atom is almost 0.04nm sizes respectively.

Nanotechnology is an extensive are which covers all the fields of science and engineering. It is sure that nanotechnology will change the nature of almost any human-made object in the next century.

7.2 Fundamental Principles:

The main principles of nanotechnology are as follows:

i) The nanotechnological devices are small in size, light weight and have unexpected physico-chemical properties that differ from the bulk material. These three characters are the basis for making new application opportunities in various fields of science and engineering.

ii) The nanomaterial shows relatively large surface area when compared with that of the same mass of material produced in the bulk from. This causes the increased chemical reactivity of the nanomaterials than the bulk from.

iii) The nanomaterial exhibits the increased quantum effect than the bulk form. The quantum effect means, when the size of the nanomaterial attains the quantum dot (1-10 nm), it has large surface area, large energy gap and higher number of electrons than the bulk materials. This quantum effect increases the optical, electrical and magnetic properties of the nanomaterials.

iv) The nanocrystallite of metals exhibit size dependent properties such as lower melting points, higher energy gaps and increased ductilities than the bulk form.

7.3 Nanoparticles and its properties

7.3 .1Definition:

Nanoparticles are ultrafine dispersive particles having size on the nanoscale between the range of 1 to 100 nm (10^{-9} - 10^{-7}m).

Nanoparticles are generally considered as the cluster or aggregate or building block of many atoms to form a solid particle in the nanocrystalline level.

7.3 .2Size relationship (size effect):

The structure of nanomaterials in three dimensional network is called nanoparticles, two dimensional network is called nanofilms and on dimensional network is called nanowire. A particle that exhibits a size of 1-10nm in one dimensional network is called quantum dot. Physical and Chemical properties of nanosized materials are influenced by the size of the particles. As the size of the nanoparticle decreases (from 100 nm to lower level), its properties will be greatly increased. The property like surface effect increases when the size of the nanoparticle decreases to lower level.

Example: A nanoparticle of 10nm diameter would have approximately 10% of atoms, whereas 1nm diameter nanoparticle would have approximately 100% of atoms on the surface.

The electronic effect like optical and fluorescence properties are greatly increased as the size nanoparticles are decreased to quantum dots (1-10nm in diameter). This effect is called quantum size effect. The property like melting point decreases as the size of the nanoparticle decreases.

Example:

A cluster (aggregation) of 10,000 sodium atoms melts at 303K. When the number of atoms is reduced to 1000, the cluster attains the nanosized sodium particle. This nanosized sodium cluster melts at 288K. When the number of sodium atoms in the cluster is still reduced, its melting point is also reduced.

7.3 .3 Nanoparticles of metals, semiconductors and oxides:

Nanoparticles are generally considered as metals, semiconductors and ceramics (oxides, carbides, sulphides and nitrides) depending on the nature of aggregation of the particles.

7.3 .4 Nanoparticles of Metal:

Most of the chemical elements are metals. When the metal atoms are combined to form a metal nanoparticle, it shows unexpected physic-chemical properties than the bulk metals.

The most common metal nanoparticle is gold nanoparticle. Gold nanoparticle is synthesized by the reduction of chloroauric acid $H[AuCl_4]$ by sodium citrate of sodium borohydride.

Example: Reduction of 50 ml solution of 0.01% $H[AuCl_4]$ by 1ml of 0.5% citrate solution gives gold nanoparticle of 16nm in diameter. Similarly the reduction of 50ml solution of 0.01% $H[AuCl_4]$ by 0.1ml of 0.5% citrate solution gives gold nanoparticle of 147 nm in diameter.

The citrate reducing agent is also used to prepare other metal nanoparticles such as Ag from $AgNO_3$, PD form $H_2[PdCl_4]$ and Pt from $H_2[PtCl_6]$. Alloyed nanoparticles (mixed nanopartilces) such as Fe-Co, Fe-Ni, Ti-Al, etc, can also be synthesized by the reduction method.

7.3 .5 Nanoparticles of Semiconductor:

The nanosized semiconductors have been synthesized due to their special optical and electrical properties. These nanosized semiconductors are used in manufacture of optoelectronic and electronic device. Generally non-oxide nanosized semiconductors like CdS, CdSe and CdTe are extensively used. These semiconductors are commonly synthesised by the pyrolysis of organometallic compounds dissolved in a dry organic solvent at a high temperature in the presence of a stabilizing (capping) agent.

Example: For the synthesis of nanosized CdSe semiconductor, dimethyl cadmium $Cd(CH_3)$ is used as the source of Cd. Trioctyphosphine selinide (TOPSe) is used as the source of Se. Tri-n-octyphosphine (TOP) and tri-n-octylphosphine oxide (TOPO) are used as solvent and capping agent respectively. The temperature range used in the pyrolysis reaction is gradually raised to 230-260^{0}C. Depending upon the temperature used, CdSe nanoparticles with a series of sizes ranging from 1.5nm to 11.5 nm in diameters are obtained.

$$Cd(CH_3)_2 + (C_8H_{17})_3 PSe \xrightarrow{\text{TOPO - TOP}} CdSe$$

7.3 .6 Nanoparticles of oxides (Nanocermics):

Nanosized oxides have been used as semiconductor and insulator in many devices. Oxides like ZnO, TiO_2, Fe_2O_3 and Cr_2O_3 are used as semiconductors whereas oxides like MgO, CaO, Al_2O_3 and SiO_2 are used as insulators.

Nanoscale metal oxides in the size of 1 to 10nm are commonly synthesized by Laser ablation (evaporation) physical method. In this method, the hot metal atoms are allowed to react with the oxygen inside the chamber to form a nanosized metal oxide. Nanosized metal oxides like, ZnO, SiO_2, TiO_2, ZrO_2, Al_2O_3 and MgO are synthesized by this method. Ultrapure nanosized metal oxides are prepared by the Sol-Gel chemical method.

7.4 Properties of Nanomaterials

Nanomaterials have the structural features in between of those of atoms and the bulk materials. While most microstructured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials. This is mainly due to the nanometer size of the materials which render them: (i) large fraction of surface atoms; (ii) high surface energy; (iii) spatial confinement; (iv) reduced imperfections, which do not exist in the corresponding bulk materials.

Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, which makes a large to be the surface or interfacial atoms, resulting in more “surface” dependent material properties. Especially when the sizes of nanomaterials are comparable to length, the entire material will be affected by the surface properties of nanomaterials. This in turn may enhance or modify the properties of the bulk materials. For example, metallic nanoparticles can be used as very active catalysts. Chemical sensors from nanoparticles and nanowires enhanced the sensitivity and sensor selectivity. The nanometer feature sizes of nanomaterials also have spatial confinement effect on the materials, which bring the quantum effects.

The energy band structure and charge carrier density in the materials can be modified quite differently from their bulk and in turn will modify the electronic and optical properties of the materials. For example, lasers and light emitting diodes (LED) from both of the quantum dots and quantum wires are very promising in the future optoelections. High density information storage using quantum dot devices is also a fast developing area. Reduced imperfections are also an important factor in determination of the properties of the nanomaterials. Nanosturctures and Nanomaterials favors of a self-purification process in that the impurities and intrinsic material defects will move to near the surface upon thermal annealing. This increased materials perfection affects the properties of nanomaterials. For example, the chemical stability for certain nanomaterials may be enhanced, the mechanical properties of nanomaterials will be better than the bulk materials. The superior mechanical properties of carbon nanotubes are well known. Due to their nanometer size, nanomaterials are already known to have many novel properties. Many novel applications of the nanomaterials rose from these novel properties have also been proposed.

7.4.1 Optical properties

One of the most fascinating and useful aspects of nanomaterials is their optical properties. Applications based on optical properties of nanomaterials include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photocatalysis, photoelectrochemistry and biomedicine.

The optical properties of nanomaterials depend on parameters such as feature size, shape, surface characteristics, and other variables including doping and interaction with the surrounding environment or other nanostructures. Likewise, shape can have dramatic influence on optical properties of metal nanostructures. Fig. () exemplifies the differencein the optical properties of metal and semiconductor nanoparticles. With the CdSe semiconductor nanoparticles, a simple change in size alters the optical properties of the nanoparticles. When metal nanoparticles are enlarged, their optical properties change only slightly as observed for the different samples of gold nanospheres in fig. (). However, when an anisotropy is added to the nanoparticle, such as growth of nanorods, the optical properties of the nanoparticles change dramatically.

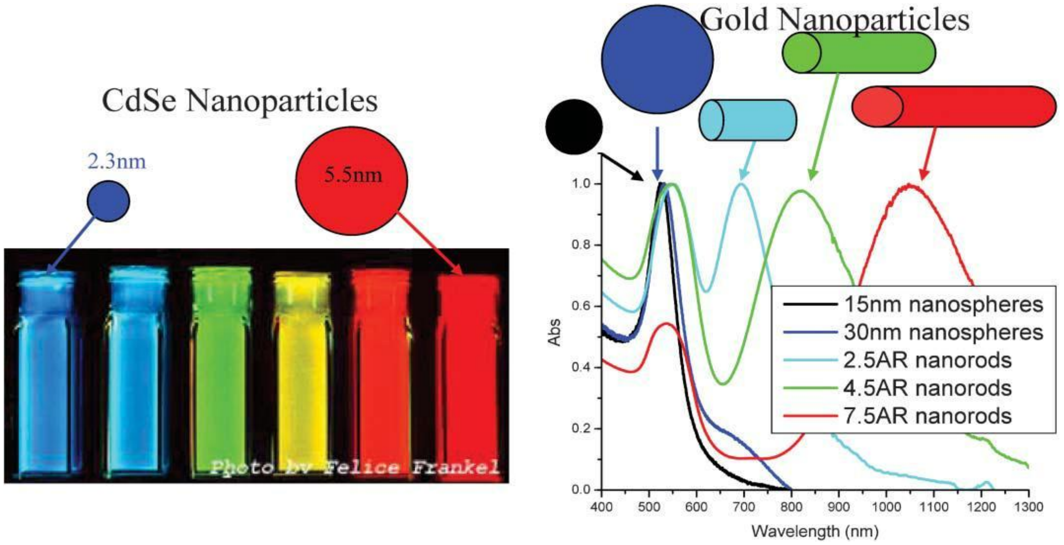


Fig.. Fluorescence emission of (CdSe) ZnS quantum dots of various sizes and absorption spectra of various sizes and shapes of gold nanoparticles (Chem. Soc. Rev., 2006, 35, 209–217).

7.4.2 Electrical properties

Electrical Properties of Nanoparticles” discuss about fundamentals of electrical conductivity in nanotubes and nanorods, carbon nanotubes, photoconductivity of nanorods, electrical conductivity of nanocomposites. One interesting method which can be used to demonstrate the steps in conductance is the mechanical thinning of a nanowire and measurement of the electrical current at a constant applied voltage. The important point here is that, with decreasing diameter of the wire, the number of electron wave modes contributing to the electrical conductivity is becoming increasingly smaller by well-defined quantized steps.

In electrically conducting carbon nanotubes, only one electron wave mode is observed which transport the electrical current. As the lengths and orientations of the carbon nanotubes are different, they touch the surface of the mercury at different times, which provides two sets of information: (i) the influence of carbon nanotube length on the resistance; and (ii) the resistances of the different nanotubes. As the nanotubes have different lengths, then with increasing protrusion of the fiber bundle an increasing number of carbon nanotubes will touch the surface of the mercury droplet and contribute to the electrical current transport.

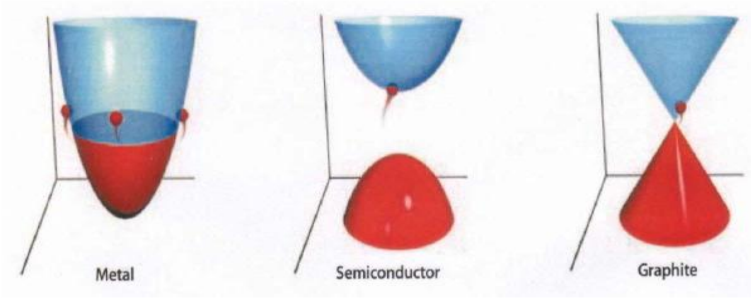


Fig.. Electrical behavior of naotubes (P. G. Collins and Ph. Avouris, *ScientificAmerican*, 62, 2000, 283).

7.4.3. Mechanical properties

“Mechanical Properties of Nanoparticles” deals with bulk metallic and ceramic materials, influence of porosity, influence of grain size, superplasticity, filled polymer composites, particle-filled polymers, polymer-based nanocomposites filled with platelets, carbon nanotube-based composites. The discussion of mechanical properties of nanomaterials is, in to some extent, only of quite basic interest, the reason being that it is problematic to produce macroscopic bodies with a high density and a grain size in the range of less than 100 nm. However, two materials, neither of which is produced by pressing and sintering, have attracted much greater interest as they will undoubtedly achieve industrial importance.

These materials are polymers which contain nanoparticles or nanotubes to improve their mechanical behaviors, and severely plastic-deformed metals, which exhibit astonishing properties. However, because of their larger grain size, the latter are generally not accepted as nanomaterials. Experimental studies on the mechanical properties of bulk nanomaterials are generally impaired by major experimental problems in producing specimens with exactly defined grain sizes and porosities. Therefore, model calculations
and molecular dynamic studies are of major importance for an understanding of the mechanical properties of these materials.

Filling polymers with nanoparticles or nanorods and nanotubes, respectively, leads to significant improvements in their mechanical properties. Such improvements depend heavily on the type of the filler and the way in which the filling is conducted. The latter point is of special importance, as any specific advantages of a nanoparticulate filler may be lost if the filler forms aggregates, thereby mimicking the large particles. Particulate-filled polymer-based nanocomposites exhibit a broad range of failure strengths and strains. This depends on the shape of the filler, particles or platelets, and on the degree of agglomeration. In this class of material, polymers filled with silicate platelets exhibit the best mechanical properties and are of the greatest economic relevance. The larger the particles of the filler or agglomerates, the poorer are the properties obtained. Although, potentially, the best composites are those filled with nanofibers or nanotubes, experience teaches that sometimes such composites have the least ductility. On the other hand, by using carbon nanotubes it is possible to produce composite fibers with extremely high strength and strain at rupture. Among the most exciting nanocomposites are the polymer-ceramic nanocomposites, where the ceramic phase is platelet-shaped. This type of composite is preferred in nature, and is found in the structure of bones, where it consists of crystallized mineral platelets of a few nanometers thickness that are bound together with collagen as the matrix. Composites consisting of a polymer matrix and defoliated phyllosilicates exhibit excellent mechanical and thermal properties.

7.4.4 Magnetic properties

Bulk gold and Pt are non-magnetic, but at the nano size they are magnetic. Surface atoms are not only different to bulk atoms, but they can also be modified by interaction with other chemical species, that is, by capping the nanoparticles. This phenomenon opens the possibility to modify the physical properties of the nanoparticles by capping them with appropriate molecules. Actually, it should be possible that non-ferromagnetic bulk materials exhibit ferromagnetic-like behavior when prepared in nano range. One can obtain magnetic nanoparticles of Pd, Pt and the surprising case of Au (that is diamagnetic in bulk) from non-magnetic bulk materials. In the case of Pt and Pd, the ferromagnetism arises from the structural changes associated with size effects.

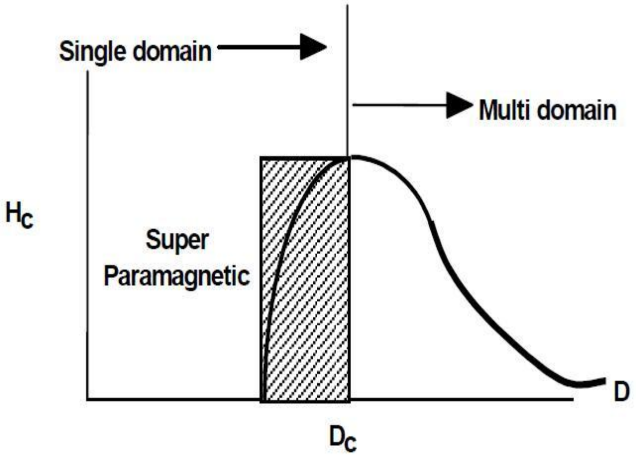


Fig.. Magnetic properties of nanostrucutred materials

However, gold nanoparticles become ferromagnetic when they are capped with appropriate molecules: the charge localized at the particle surface gives rise to ferromagnetic-like behavior.

Surface and the core of Au nanoparticles with 2 nm in diameter show ferromagnetic and paramagnetic character, respectively. The large spin-orbit coupling of these noble metals can yield to a large anisotropy and therefore exhibit high ordering temperatures. More surprisingly, permanent magnetism was observed up to room temperature for thiol-capped Au nanoparticles. For nanoparticles with sizes below 2 nm the localized carriers are in the 5d band. Bulk Au has an extremely low density of states and becomes diamagnetic, as is also the case for bare Au nanoparticles. This observation suggested that modification of the d band structure by chemical bonding can induce ferromagnetic like character in metallic clusters.

7.5 Nanomaterials' Characteristics

Category of nanomaterials	**example**
One-dimensional nanomaterials	layers, multi-layers, thin films, platelets and surface coatings. They have been developed and used for decades, particularly in the electronics industry.
Two-dimensional nanomaterials	nanowires, nanofibres made from a variety of elements other than carbon, nanotubes and, a subset of this group, carbon nanotubes.
Three-dimensional nanomaterials	are known as nanoparticles and include precipitates, colloids and quantum dots (tiny particles of semiconductor materials), and Nanocrystalline materials

7.6 Approaches of Nanotechnology (growth methods)

Bottom-up approaches seek to have smaller components built up into more complex assemblies, while top-down approaches seek to create nanoscale devices by using larger, externally controlled ones to direct their assembly.

The top-down approach often uses the traditional workshop or microfabrication methods where externally controlled tools are used to cut, mill, and shape materials into the desired shape and order.

Micropatterning techniques, such as photolithography and inkjet printing belong to this category.

Bottom-up approaches, in contrast, use the chemical properties of single molecules to cause single-molecule components to

(a) self-organize or self-assemble into some useful conformation, or

(b) rely on positional assembly.

Nanomaterial - synthesis and processing

Nanomaterials deal with very fine structures: a nanometer is a billionth of a meter. This indeed allows us to think in both the 'bottom up' or the 'top down' approaches (Fig. 5) to synthesize nanomaterials, i.e. either to assemble atoms together or to dis-assemble (break, or dissociate) bulk solids into finer pieces until they are constituted of only a few atoms. This domain is a pure example of interdisciplinary work encompassing physics, chemistry, and engineering upto medicine.

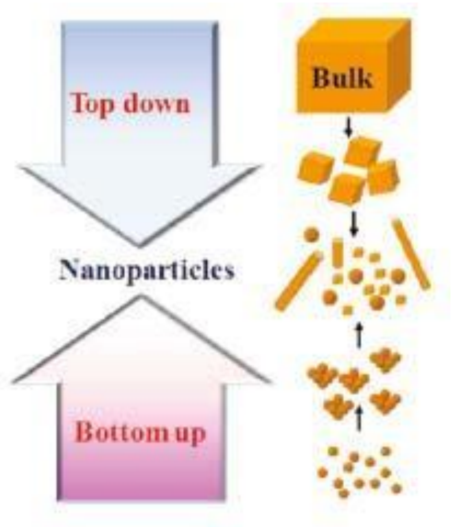


Fig. 5. Schematic illustration of the preparative methods of nanoparticles.

7.7 Synthesis of Nanosized Compounds:

Various methods have been used for the synthesis of nano materials Among these, the following these methods are important.

1) Reduction method
2) Sol-Gel method
3) Chemical Vapour Deposition (CVD) method

7.7.1 Reduction Method:

The most common method for synthesis of metal nanoparticles is the reduction of metal salts or complexes in dilute solution. A variety of reagents and methods have been developed. The various reactants, reducing agents and polymeric stabilizers (capping agents) generally used in the production of metal nanoparticles are given in the following table.

The various reactants, reducing agents and polymeric stabilizers are used in the synthesis of metal nanoparticles.

Reactants	**Reducing agents**	**Metal Nanoparticles**
Palladium chloride	Hydrogen	Pd
Hydrogen hexachloroplatinate IV	Sodium citrate	Pt
Potassium hexachloroplatinate IV	Hydroxylamine hydrochloride	Pt
Silver nitrate	Citric acid	Ag
Silver tetraozychloride	Carbon monoxide	Ag
Chloroauric acid	Sodium Citrate, Hydroxylamine hydrochloride, or Citric acid	Au
Rhodium chloride	Hydrogen peroxide	Rh

Polymeric stabilizers (Capping agents)

Poly vinylpyrrolidone, PVP; Polyvinyl alcohol, PVA: Polyethyleneimine

Reduction by Sodium citrate:

The variety of methods are now available for the synthesis of gold nanoparticles. Among these the reduction of cholorauric acid by sodium citrate is the most important method. In this method, 50ml solution of 0.01% chloroauric acid is mixed with 1ml of 0.5% sodium citrate and the mixture is kept at 100^0C till colour changes. Then add 2ml of PVP (a capping agent). The overall volume of the solution was maintained by adding water. The colloidal gold (sol) of uniform particle size of approximately 16nm in diameter is obtained.

The use of different reducing agents has marked effect on the appearance of the gold nano particles. Reduction by sodium citrate yields spherical particles, whereas faceted gold particles are formed with hydroxylamine hydrochloride [cubical with (100) facets] and a very thin layers of gold nano particles are formed with citric acid [trigonal symmetry with (111) facets].

Borohydride (BH_4) Reduction:

Borohydride reduction of metal ions can be useful for the preparation of metallic nanoparticles. For example, the sodium borohydride ($NaBH_4$) reduction Co^{2+} ions in aqueous solution in the presence of argon results in the formation of Co_2B nanoparticles.

$$2Co^{2+} + 4BH_4 + 9H_2O \longrightarrow Co_2B + 12.5H_2 + 3B(OH)_3$$

7.7.2 Sol-Gel Method:

The sol-gel process, involves the evolution of inorganic networks through the formation of a colloidal suspension (**sol**) and gelation of the sol to form a network in a continuous liquid phase (**gel**). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcination of the gel produces the oxide.

Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors such as $Si(OEt)_4$ (tetraethyl orthosilicate, or TEOS). The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides $M(OR)\mathbf{z}$ can be described as follows:

$$MOR + H_2O \rightarrow MOH + ROH \text{ (hydrolysis)}$$
$$MOH + ROM \rightarrow M\text{-}O\text{-}M + ROH \text{ (condensation)}$$

Sol-gel method of synthesizing nanomaterials is very popular amongst chemists and is widely employed to prepare oxide materials. The sol-gel process can be characterized by a series of distinct steps.

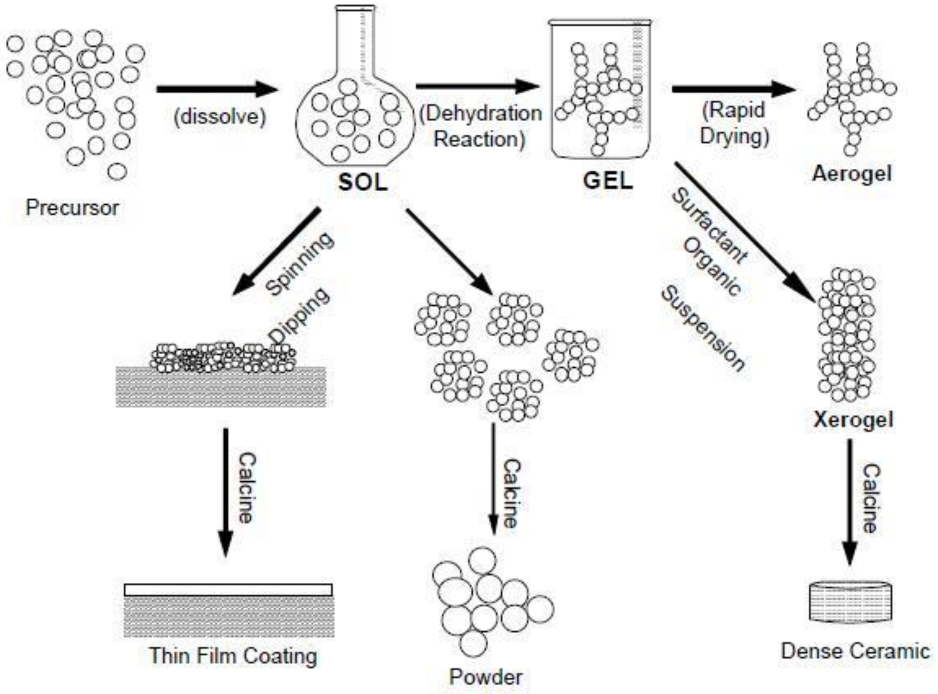


Fig. 7. Schematic representation of sol-gel process of synthesis of nanomaterials.

1. Formation of different stable solutions of the alkoxide or solvated metal precursor.
2. Gelation resulting from the formation of an oxide- or alcohol- bridged network

   (the gel) by a polycondensation reaction that results in a dramatic increase in the viscocity of the solution.
3. Aging of the gel (Syneresis), during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. Ostwald ripening (also referred to as coarsening, is the phenomenon by which smaller particles are consumed by larger particles during the growth process) and phase transformations may occur concurrently with syneresis. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.
4. Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. The drying process has itself been broken into four distinct steps: (i) the constant rate period, (ii) the critical point, (iii) the falling rate period, (iv) the second falling rate period. If isolated by thermal evaporation, the resulting monolith is termed a *xerogel*. If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an *aerogel*.
5. Dehydration, during which surface- bound M-OH groups are removed, there by

stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to 800^0C.

6. Densification and decomposition of the gels at high temperatures (T>800^0C). The pores of the gel network are collapsed, and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.

The interest in this synthesis method arises due to the possibility of synthesizing nonmetallic inorganic materials like glasses, glass ceramics or ceramic materials at very low temperatures compared to the high temperature process required by melting glass or firing ceramics.

The major difficulties to overcome in developing a successful bottom-up approach is controlling the growth of the particles and then stopping the newly formed particles from agglomerating. Other technical issues are ensuring the reactions are complete so that no unwanted reactant is left on the product and completely removing any growth aids that may have been used in the process. Also production rates of nano powders are very low by this process. The main advantage is one can get monosized nano particles by any bottom up approach.

The main advantages of this method are as follows

i) It needs low-procesing temperature

ii) It produces highly pure and more uniform nanostructured product.

iii) It can be used to synthesize any nanomaterials like ceramics, metals, alloys and composites in large quantities.

7.7.3 Chemical Vapour Deposition (CVD) Method:

CVD is the most common method to synthesise nanosized metal oxide (ceramics) carbon nanotubes (CNTs) and nanocomposite crystallites. In this method, a solid is deposited on a heated surface of the substrate using the chemical reactions occur at the vapour phase.

The chemical reaction which occurs in the vapour phase needs activation energy. This energy is provided by the any one of the following methods.

i) Thermal CVD method: In this method, the reaction is activated by a high temperature at above 900^0C.

ii) Plasma CVD method: In this method, the reaction is activated by the plasma at the temperature range of 300-700^0C.

iii) Laser CVD method: In this method, the chemical reaction is activated by the high energy laser beam.

iv) Photo Laser CVD method: In this method, the Chemical reaction is induced by the both ultraviolet radiation and laser beam.

Example: The synthesis of carbon nanotube (CNT) by this method involves two step process.

Step I : Catalyst preparation

Step II: Synthesis of CNT

Step I : Catalyst preparation

The catalyst is prepared by coating ht transition metal like Fe, Co or Ni on a substrate like SiO_2, Zeolite or metal oxide. This process of coating needs activation energy. The metal atom which is coated on the surface of the substrate acts as the catalyst.

Step II: Synthesis of CNT

The gaseous carbon sources commonly used are methane (CH_4), carbon monoxide (CO) and acetylene (C_2H_2). The activation energy is used to break the carbon source molecule into reactive atomic carbon. This atomic carbon is then allowed to diffuse through the substrate containing transition metal coating. Due to catalytic action, the atomic carbon binds on the substrate and formed as nanosized CNT.

The CNT formed in this method contains lot of impurities like amorphous carbon, metal catalyst and smaller fullerenes. Hence the CNTs are purified by various methods such as oxidation, acid treatment, annealing, ultrasonification, magnetic purification, micro filtration, cutting and chromatography.

7.8 Quantum dots

Quantum dots are tiny particles or nanocrystals of a semiconducting material with diameters in the range of 2-10 nanometers (10-50 atoms). They were first discovered in 1980.[1] Quantum dots display unique electronic properties, intermediate between those of bulk semiconductors and discrete molecules, that are partly the result of the unusually high surface-to-volume ratios for these particles.[2-4] The most apparent result of this is fluorescence, wherein the nanocrystals can produce distinctive colors determined by the size of the particles.

Due to their small size, the electrons in quantum dots are confined in a small space (quantum box), and when the radii of the semiconductor nanocrystal is smaller than the exciton Bohr radius (exciton Bohr radius is the average distance between the electron in the conduction band and the hole it leaves behind in the valence band), there is quantization of the energy levels according to Pauli's exclusion principle (**Figure 1**). The discrete, quantized energy levels of quantum dots relate them more closely to atoms than bulk materials and have resulted in quantum dots being nicknamed 'artificial atoms'. Generally, as the size of the crystal decreases, the difference in energy between the highest valence band and the lowest conduction band increases. More energy is then needed to excite the dot, and concurrently, more energy is released when the crystal returns to its ground state, resulting in a color shift from red to blue in the emitted light. As a result of this phenomenon, quantum dots can emit any color of light from the same material simply by changing the dot size. Additionally, because of the high level of control possible over the size of the nanocrystals produced, quantum dots can be tuned during manufacturing to emit any color of light.[7]

Quantum dots can be classified into different types based on their composition and structure.

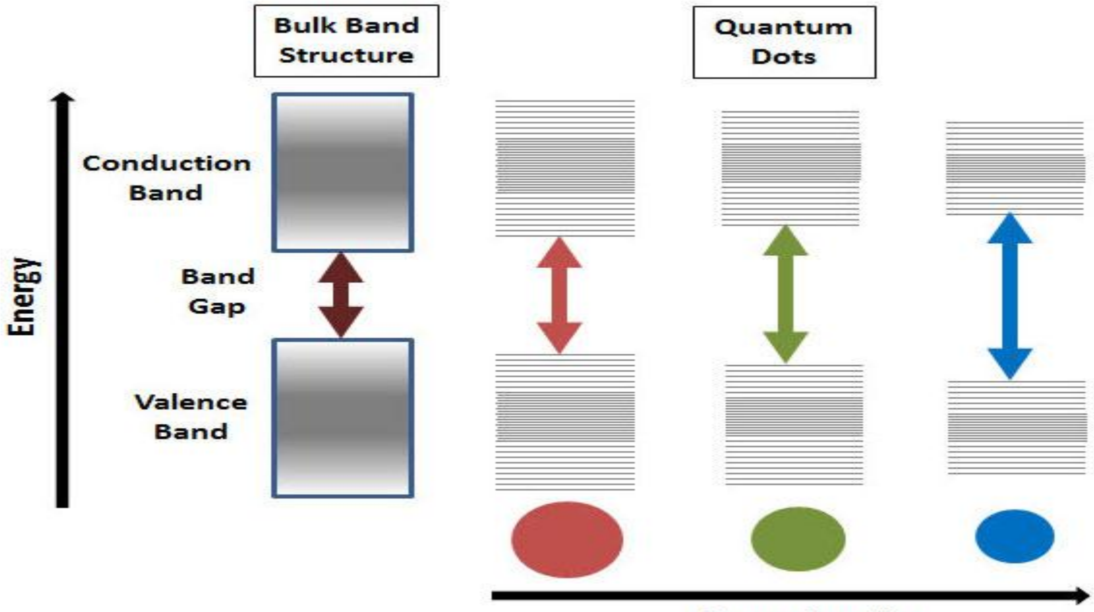


Figure 1. Splitting of energy levels in quantum dots due to the quantum confinement effect, semiconductor band gap increases with decrease in size of the nanocrystal.

Quantum Dots Applications

The unique size and composition tunable electronic property of these very small, semiconducting quantum dots make them very appealing for a variety of applications and new technologies.

Quantum dots are particularly significant for optical applications owing to their bright, pure colors along with their ability to emit rainbow of colors coupled with their high efficiencies, longer lifetimes and high extinction coefficient. Examples include LEDs and solid state lighting, displays and photovoltaics.

7.9 Nano clusters:

Clusters are the aggregate or building block of atoms or molecules whose characteristic dimensions are few nanometers. Due to their small size, the properties of the clusters are differ from the corresponding material in the bulk form.

Clusters are of four types according to the nature of chemical bonding between the aggregate atoms.

i) Van der Walls clusters:

Examples: Molecular clusters like $(N_2)N$, $(CO_2)N$ etc. In Van der walls clusters, the binding energy is less about 0.3eV per atom.

ii) Metal clusters:

Examples: Transition metal clusters of Fe, Co, Ni, etc. In metal clusters, the binding energy is moderate to strong from 0.5 to 3 eV per atom.

iii) Ionic clusters:

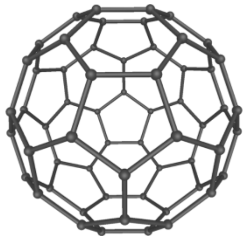
Examples: Ironic cluster like NaCl, $CsCl_2$, etc. In Ironic clusters, the binding energy is strong about 2.4 eV per atom.

iv) Network clusters:

Examples: Covalent cluster like Si, Ge, C, etc. In network clusters, the binding energy is more strong about 4 eV per atom.

7.10 Fullerenes

A **fullerene** is a molecule of carbon in the form of a hollow sphere, ellipsoid, tube, and many other shapes. Spherical fullerenes are also called Buckminsterfullerene (**buckyballs)**, and they resemble the balls used in football (soccer). Cylindrical ones are called carbon nanotubes or buckytubes. Fullerenes are similar instructure to graphite, which is composed of stacked graphene sheets of linked hexagonal rings; but they may also contain pentagonal (or sometimes heptagonal) rings.



Buckminsterfullerene is the smallest fullerene molecule containing pentagonal and hexagonal rings in which no two pentagons share an edge (which can be destabilizing, as in pentalene). It is also most common in terms of natural occurrence, as it can often be found in soot.

The structure of C_{60} is a truncated icosahedron, which resembles an association football ball of the type made of twenty hexagons and twelve pentagons, with a carbon atom at the vertices of each polygon and a bond along each polygon edge.

The van der Waals diameter of a C_{60} molecule is about 1.1 nanometers (nm).[26] The nucleus to nucleus diameter of a C_{60} molecule is about 0.71 nm.

The C_{60} molecule has two bond lengths. The 6:6 ring bonds (between two hexagons) can be considered "double bonds" and are shorter than the 6:5 bonds (between a hexagon and a pentagon). Its average bond length is 1.4 angstroms.

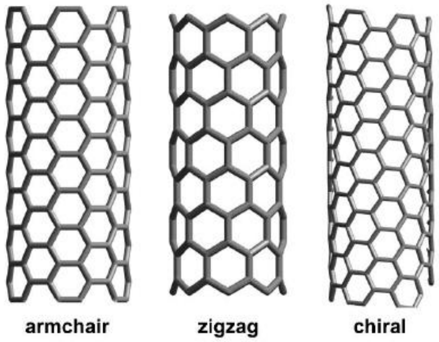
Applications

Fullerenes have been extensively used for several biomedical applications including the design of high-performance MRI contrast agents, X-Ray imaging contrast agents, photodynamic therapy and drug and gene delivery

7.11 Carbon Nano Tubes (CNTS)

Nanotubes are cylindrical fullerenes. These tubes of carbon are usually only a few nanometres wide, but they can range from less than a micrometer to several millimeters in length. They often have closed ends, but can be open-ended as well. There are also cases in which the tube reduces in diameter before closing off. Their unique molecular structure results in extraordinary macroscopic properties, including high tensile strength, high electrical conductivity, high ductility, high heat conductivity, and relative chemical inactivity (as it is cylindrical and "planar" — that is, it has no "exposed" atoms that can be easily displaced).

A Carbon Nanotube (CNT) is a ultrathin carbon fibre with nanometer size and diameter and micrometer size length. It is considered as a sheet of graphic (called grapheme) rolled up into a seamless cylinder.



Carbon nanotubes are thought to be the material of the future. There are two types of nanotubes, single-walled and multi-walled (SWCNT and MWCNT). The former are hollow cylinders consisting of graphene sheets rolled into ~ 1 nm diameter cylinders; they come in many different types as shown to the right. Multi-walled carbon nanotubes are series of concentric cylinders

Carbon nanotubes (CNTs) are an allotrope of carbon. Each nanotube is made up of mainly a hexagonal network of carbon atoms which enough pentagonalcarbons. Nanotubes generally have a length-to-diameter ratio of about 1,000. Hence, they can be considered as one dimensional structure. Such cylindrical carbon molecules have novel properties which are used in various applications in nanotechnology, electronics, optics and other fields of material science.

7.11.1 Carbon nanotubes are of two types:

i) Single-walled nanotubes (SWNTs) and

ii) Multi-walled nanotubes (MWNTs).

i) Single-walled nanotubes (SWNTs):

Most single-walled nanotubes (SWNT) can have the diameter of 1-2nm have the length of 100 μm. Now a days, single-walled nanotubes with length upto some centimeters are produced. The structure of a SWNT can be explained by a one-dimensional ultra thin layer of graphite called graphene into a seamless cylinder.

Single-wall nanotubes (SWNT) are tubes of graphite that are normally capped at the ends. They have a single cylindrical wall. The structure of a SWNT can be visualized as a layer of graphite, a single atom thick, called graphene, which is rolled into a seamless cylinder.

Most SWNT typically have a diameter of close to 1 nm. The tube length, however, can be many thousands of times longer.

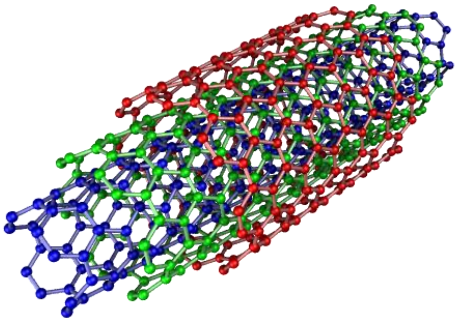
SWNT are more pliable yet harder to make than MWNT. They can be twisted, flattened, and bent into small circles or around sharp bends without breaking.

SWNT have unique electronic and mechanical properties which can be used in numerous applications, such as field-emission displays, nanocomposite materials, nanosensors, and logic elements. These materials are on the leading-edge of electronic fabrication, and are expected to play a major role in the next generation of miniaturized electronics.

ii) Multi-walled nanotubes (MWNTs):

Multi-walled nanotubes (MWNT) is composed of 2 to 30 concentric graphite layers having the diameter of 10-50nm and have the length of more than 10μm. There are two models which can be used to describe the structure of MWNT. In the Russian Doll model, sheets of graphite are arranged in concentric cylinders Figures. In the Parchment model, a single sheet of graphite is rolled in around itself, resembling a rolled up newspaper.

Multi-wall nanotubes can appear either in the form of a coaxial assembly of SWNT similar to a coaxial cable, or as a single sheet of graphite rolled into the shape of a scroll.



The diameters of MWNT are typically in the range of 5 nm to 50 nm. The interlayer distance in MWNT is close to the distance between graphene layers in graphite.

MWNT are easier to produce in high volume quantities than SWNT. However, the structure of MWNT is less well understood because of its greater complexity and variety. Regions of structural imperfection may diminish its desirable material properties.

The challenge in producing SWNT on a large scale as compared to MWNT is reflected in the prices of SWNT, which currently remain higher than MWNT.

7.11.2 Carbon nanotube – Properties:

i) Strength :

Carbon nanotubes are having high tensile strength and stiffness. The tensile strength of CNT is almost 20 times greater than that of steel. This higher tensile strengths is due to the formation of covalent sp^2 bond between the carbon atoms.

ii) Thermal conductivity:

CNTs are very good thermal conductors along the tube. The thermal conductivity of the CNT is almost 15 to 20 times greater than that of metallic conductors. For comparison, a SWNT will be able to transmit up to 6000 Watts per meter per Kelvin (W/m/K) at room temperature than a good thermal conductor of copper, which conducts only 385 W/m/K.

iii) Electrical conductivity:

CNTs are also good conductors of electricity. The electrical conductivity of CNT depends on their nanosized diameter. When the diameter of the CNT decreases. The conductivity increases. The electrical conductivity of CNT is 1,000 times greater than that of matals like copper and silver CNTs can have the property of Field Emission or Field Effect (FE) sensors, i.e. when a small amount of electric field is applied parallel to the axis of CNT, electrons are emitted at a very high speed.

7.11 .3Application of CNTs:

Some of the applications of CNTs are as follows:

i) Because of Field Effect property of CNTs, they are used for producing switches, transistors and chips which are used for making flat panel displays in televisions and computers.

ii) CNTs act as a catalyst for some chemical reactions. For example, reduction of NiO to Ni, $AlCl_3$ to Al, CdS to Cd, etc., have been carried out inside the CNTs. Here CNT acts as a carrier as well as catalyst.

iii) CNT electrodes are used in storage batteries for longer life. Because of high storage capacity of H_2, CNTs are used in Hydrogen fuel cell.

7.12. Nanofiber

Nanofibers are defined as fibers with diameters less than 100 nanometers.[2] In the textile industry, this definition is often extended to include fibers as large as 1000 nm diameter.[3] They can be produced by melt processing, interfacial polymerization, electrospinning, antisolvent-induced polymer precipitation and electrostatic spinning.Carbon nanofibers are graphitized fibers produced by catalytic synthesis.

Generally, polymeric nanofibers are produced by an electrospinning process . Electrospinning is a process that spins fibers of diameters ranging from 10nm to several hundred nanometers. This method has been known since 1934 when the first patent on electrospinning was filed. Fiber properties depend on field uniformity, polymer viscosity, electric field strength and DCD (distance between nozzle and collector). Advancements in microscopy such as scanning electron microscopy has enabled us to better understand the structure and morphology of nanofibers. At present the production rate of this process is low and measured in grams per hour

7.12 .1 **PROPERTIES OF NANOFIBERS**

Nanofibers exhibit special properties mainly due to extremely high surface to weight ratio compared to conventional nonwovens.

Low density, large surface area to mass, high pore volume, and tight pore size make the nanofiber nonwoven appropriate for a wide range of filtration applications [9].

Figure 3 shows how much smaller nanofibers are compared to a human hair, which is 50-150 µm and Figure 4 shows the size of a pollen particle compared to nanofibers. The elastic modulus of polymeric nanofibers of less than 350 nm is found to be 1.0±0.2 Gpa.

7.12 .2Applications

Nanofibers have applications in medicine, including artificial organ components, tissue engineering, implant material, drug delivery,[6]wound dressing, and medical textile materials.

Recently, researchers have found that nanofiber meshes could be used to fight against the HIV-1 virus, and be able to be used as a contraception. In wound healing nanofibers assemble at the injury site and stay put, drawing the body's own growth factors to the injury site. Protective materials include sound absorption materials, protective clothings against chemical and biological warfare agents, and sensor applications for detecting chemical agents. Nanofibers have also been used in pigments for cosmetics. Applications in the textile industry include sport apparel, sport shoes, climbing, rainwear, outerwear garments, baby diapers. Napkins with nanofibers contain antibodies against numerous biohazards and chemicals that signal by changing color

7.13.1 NANOCOMPOSITES

Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material. In the broadest sense this definition can include porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials. Size limits for these effects have been proposed <5 nm for catalytic activity, <20 nm for making a hard magnetic material soft, <50 nm for refractive index changes, and <100 nm for achievingsuperparamagnetism, mechanical strengthening or restricting matrix dislocation movement.

7.13.1 Ceramic-matrix nanocomposites

n this group of composites the main part of the volume is occupied by a ceramic, i.e. a chemical compound from the group of oxides, nitrides, borides, silicides etc.. In most cases, ceramic-matrix nanocomposites encompass a metal as the second component. Ideally both components, the metallic one and the ceramic one, are finely dispersed in each other in order to elicit the particular nanoscopic properties. Nanocomposite from these combinations were demonstrated in improving their optical, electrical and magnetic properties [6] as well as tribological, corrosion-resistance and other protective properties.

Metal-matrix nanocomposites

Metal matrix nanocomposites can also be defined as reinforced metal matrix composites. This type of composites can be classified as continuous and non-continuous reinforced materials. One of the more important nanocomposites is Carbon nanotube metal matrix composites, which is an emerging new material that is being developed to take advantage of the high tensile strength and electrical conductivity of carbon nanotube materials. Critical to the realization of CNT-MMC possessing optimal properties in these areas are the development of synthetic techniques that are (a) economically producible, (b) provide for a homogeneous dispersion of nanotubes in the metallic matrix, and (c) lead to strong interfacial adhesion between the metallic matrix and the carbon nanotubes. In addition to carbon nanotube metal matrix composites, boron nitride reinforced metal matrix composites and carbon nitride metal matrix composites are the new research areas on metal matrix nanocomposites.

7.13.2. Polymer-matrix nanocomposites

By appropriately adding nanoparticulates to a polymer matrix can enhance its performance, often dramatically, by simply capitalizing on the nature and properties of the nanoscale filler (these materials are better described by the term ***nanofilled polymer composites***). This strategy is particularly effective in yielding high performance composites, when good dispersion of the filler is achieved and the properties of the nanoscale filler are substantially different or better than those of the matrix.

Nanoparticles such as graphene, carbon nanotubes, molybdenum disulfide and tungsten disulfide are being used as reinforcing agents to fabricate mechanically strong biodegradable polymeric nanocomposites for bone tissue engineering applications. The addition of these nanoparticles in the polymer matrix at low concentrations (~0.2 weight %) cause significant improvements in the compressive and flexural mechanical properties of polymeric nanocomposites

A range of polymeric nanocomposites are used for biomedical applications such as tissue engineering, drug delivery, cellular therapies. Due to unique interactions between polymer and nanoparticles, a range of property combinations can be engineered to mimic native tissue structure and properties. A range of natural and synthetic polymers are used to design polymeric nanocomposites for biomedical applications including starch, cellulose, alginate, chitosan, collagen, gelatin, and fibrin, poly(vinyl alcohol) (PVA), poly(ethylene glycol) (PEG), poly(caprolactone) (PCL), poly(lactic-co-glycolic acid) (PLGA), and poly(glycerol sebacate) (PGS). A range of nanoparticles including ceramic, polymeric, metal oxide and carbon-based nanomaterials are incorporated within polymeric network to obtain desired property combinations.

7.14 APPLICATIONS OF NANOCHEMISTRY IN VARIOUS FIELDS:

If nanochemistry various nanosized materials like quantum dots, nanoparticles, nanoclusters, nanocrystallites, nanocomposites, carbon nanotubes are used in various fields, Same of them are given in the table.

Nanomaterial	**Application**
1) Nanocarbon tubes (CNTs)	Electronic devices, fuel cells, wear resistant rubber tyres, water proof cloth fibers, sports equipments. Etc.
2) Nanowires	Magnetic optical and electronic devices
3) Nanophosphors	High resolution monitors
4) Nanoalumina and silica	Superfine polishing technology
5) Nano iron oxide	Disk drives, audio tapes and cosmetics (lipstick)
6) Nano ZnO and TiO_2	Sunscreens
7) Quantum dot of nano Pt	Powerful catalyst
8) Aerogels	Better insulation materials
14) Nanoreactors like micelles	Adhesives and coatings
15) Nanocomposites	Medicine (drug delivery system)
11) Nanocrystalline Ni	High energy batteries with long life and less frequent charging.
12) Nano ZrO_2 and SiC	Bio-compatible, suitable for artificial heart valves due to low mass, high strength, extreme harness, wear resistance, inertness

	and corrosion resistance.
13) Semiconductor (ZnSe, ZnS, CdS, PbTe) nanoparticles	More efficient solar cells, nanoelectronical devices

SUGGESTED READINGS

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