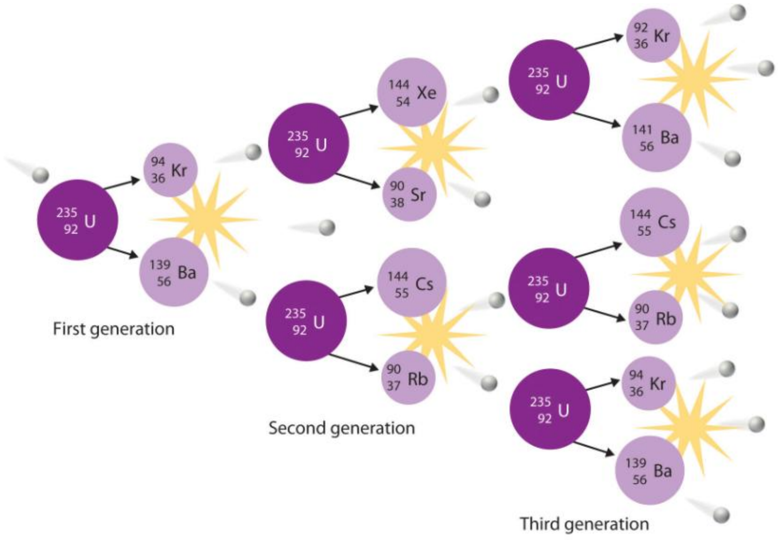
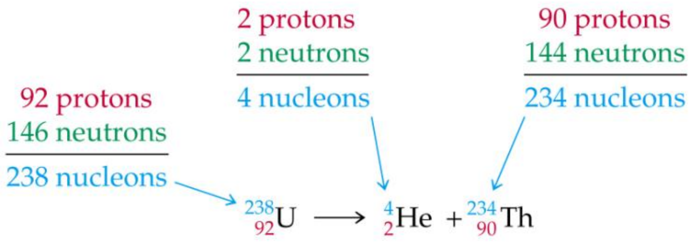
KARNATAKA STATE OPEN UNIVERSITY

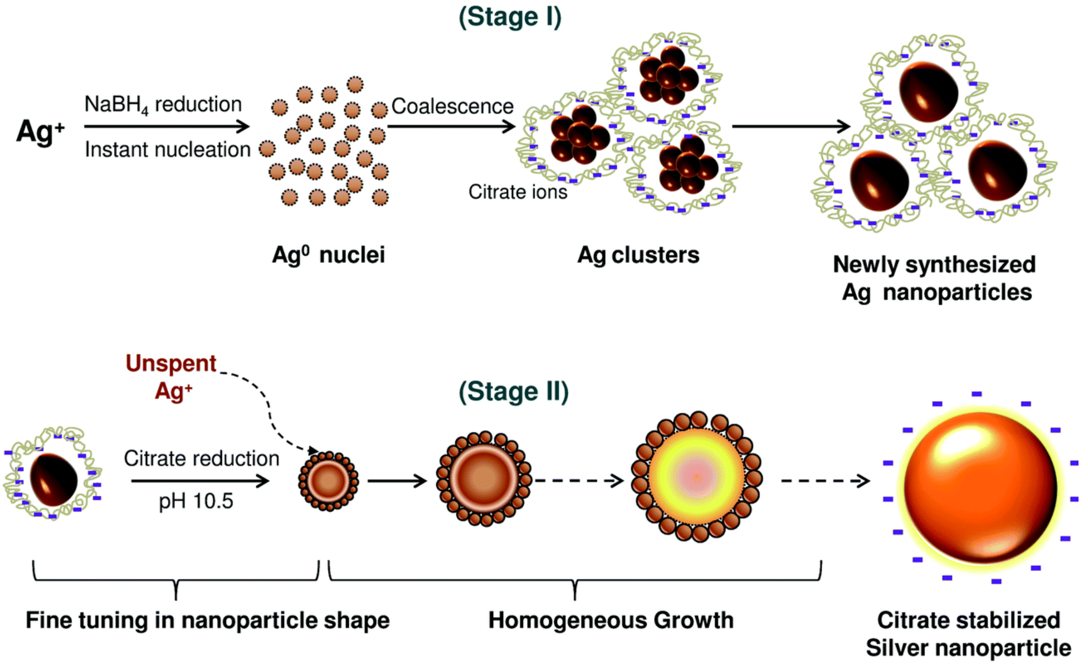
Mukthagangotri, Mysore – 570 006

M.Sc. CHEMISTRY

(FOURTH SEMESTER)







Course: MCH T 4.3 **Block 1, 2,3 and 4**

PHYSICAL CHEMISTRY- IV

M.Sc. CHEMISTRY

FOURTH SEMESTER

COURSE: MCHT 4.3

PHYSICAL CHEMISTRY-IV

Course Design Committee

Prof. Shivalingaiah. D	**Prof. Devegowda .T. D**
Vice-Chancellor & Chairperson	Dean (Academic) & Convener
Karnataka State Open University	Karnataka State Open University
Mukthagangothri, Mysore - 570 006	Mukthagangothri, Mysore - 570 006

COURSE WRITER

Prof. Rangaswamy. S. Y **Block 4.3.1 and 4.3.2**
Professor (Rtd)
Department of Studies in Chemisty
University of Mysore, Manasagangothri
Mysuru.

Prof. Ananda. S **Block 4.3.3 and 4.3.4**
Professor
Department of Studies in Chemisty
University of Mysore, Manasagangothri
Mysuru.

Course Coordinator and Course editor

Dr. M. Umashankara
Assistant Professor and Chairman
Department of Studies in Chemistry
Karnataka State Open University
Mukthagangothri, Mysore - 570 006

PUBLISHER

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COURSE INTRODUCTION

In the most general sense thermodynamics is the study of energy, its transformations and its relationship to the properties of matter. In its engineering applications thermodynamics has two major objectives. One of these is to describe the properties of matter when it exists in what is called an equilibrium state, a condition in which its properties show no tendency to change. The other objective is to describe processes in which the properties of matter undergo changes and to relate these changes to the energy transfers in the form of heat and work which accompany them. These objectives are closely related. The state of a system is an important concept in thermodynamics and is defined as the complete set of all its properties which can change during various specified processes. The properties which comprise this set depend on the kinds of interactions which can take place both within the system and between the system and its surroundings. Statistical thermodynamics link between microscopic properties of matter and its bulk properties. Two key ideas: Boltzmann distribution predicts populations of states in systems at thermal equilibrium. Its derivation in terms of the distribution of particles over available states. The derivation leads naturally to the introduction of partition function. How to interpret partition function and calculate it in simple cases. How to extract thermodynamic information from the partition function. Generalize to include systems that are composed of assemblies of interacting particles. Very similar equations but much more widely applicable. This you will studied in first block

In the second block you will learn more abou nuclear chemistry. Nuclear chemistry is the subdiscipline of chemistry that is concerned with changes in the nucleus of elements. These changes are the source of radioactivity. nuclide, nucleon, radioactivity, $\alpha-$ $\beta-$ $\gamma-$radiation, nuclear reaction equation, daughter nucleus, electron capture, positron, fission, fusion, rate of decay, decay constant, half-life, carbon-14 dating, nuclear binding energy. Nucleons two subatomic particles that reside in the nucleus known as protons and neutrons. Isotopes Differ in number of neutrons only. They are distinguished by their mass numbers.

${}^{233}_{92}U$ is Uranium with an atomic mass of 233 and atomic number of 92. The number of neutrons is found by subtraction of the two numbers nuclide applies to a nucleus with a specified number of protons and neutrons. Nuclei that are radioactive are radionuclides and the atoms containing these nuclei are radioisotopes.

In the third block you will going introduce about polymer chemistry. We all aware about polymer material. In this course you will going to study bout different types of polymers their properties, their synthesis and the kinetics of polymer reaction. Moreover you will study the different methods of determination molecular mass of the polymers.

In forth block of this course, you are going to introduced a new subject called Nanotechnology. Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1 to 100 nanometers. The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled “There’s Plenty of Room at the Bottom” by physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology (CalTech) on December 29, 1959, long before the term nanotechnology was used. In his talk, Feynman described a process in which scientists would be able to manipulate and control individual atoms and molecules. Over a decade later, in his explorations of ultraprecision machining, Professor Norio Taniguchi coined the term nanotechnology. It wasn't until 1981, with the development of the scanning tunneling microscope that could "see" individual atoms, that modern nanotechnology began.

It’s hard to imagine just how small nanotechnology is. One nanometer is a billionth of a meter, or 10-9 of a meter. Here are a few illustrative examples:

There are 25,400,000 nanometers in an inch

A sheet of newspaper is about 100,000 nanometers thick

On a comparative scale, if a marble were a nanometer, then one meter would be the size of the Earth. Nanoscience and nanotechnology involve the ability to see and to control individual atoms and molecules. Everything on Earth is made up of atom, the food we eat, the clothes we wear, the buildings and houses we live in, and our own bodies. But something as small as an atom is impossible to see with the naked eye. In fact, it’s impossible to see with the microscopes typically used in a high school science classes.

UNIT-1

Structure

1.0 Objectives of the unit

After studying this unit you are able to

- Explain the basic concepts of distribution
- Recognize the relationship between thermodynamic probability and entropy
- Explain the Stirling approximation
- Identify the types of Ensembles
- Explain the Micro cannonical ensemble
- Explain the Canonical ensemble
- Explain the Grand canonical ensemble
- Derive the equation for Maxwell-Boltzmann distribution law
- Derive the equation for Maxwell's distribution of molecular velocities
- Derive the equation for Most probable velocity (U_x)
- Derive the equation for Average velocity <Ux>
- Derive the equation for Root mean square velocity ($\overline{U_x}$)
- Identify the relationship between U_x,< U_x> $\overline{U_x}$

1.1 Introduction

Statistical thermodynamics provides a link between classical thermodynamics and quantum mechanics or wave mechanics. Macroscopic systems are considered in classical thermodynamics. Thermodynamics defines the equilibrium properties of these systems in terms of variables upon which the system depends. So, the energy of a gaseous system depends on the temperature, volume and the number of moles of gas present in the system. For fixed values of these variables, the properties of the system will have definite values and they change only when the variables are changed. However, a macroscopic system is composed of a large number of microscopic constituents such as atoms, molecules etc. it is very strange that at no time does chemical thermodynamics exhibit any curiosity about the nature, structure and the energy states of the microscopic constituents nor about the manner in which these microscopic factors combine to give the properties of the macroscopic systems.

It is obvious that the thermodynamic properties of a system cannot be independent of the nature of the microscopic constituents present in it. A new approach namely, that of statistical thermodynamics has since been made to calculate the properties of the microscopic systems. In this procedure, matter is pictured as composed of innumerable particles in motion. The motion of these particles is governed by the laws of dynamics in fact subject to quantum mechanical principles. Even in the smallest system taken, the number of particles is so large that it is impossible to follow the behavior of every individual particle. So statistical methods are utilized to find the properties of the system particularly to ascertain what fraction of the molecules has a given energy. So in classical thermodynamics, we consider the macroscopic systems while in statistical thermodynamics microscopic systems are considered.

The statistical methods are applicable to both systems in equilibrium and time dependent systems. The properties in a large assembly of particles can be predicted using the laws of probability. The word probability is commonly used to indicate the likelihood of an event taking place. The probability of a certain distribution of molecules among the energy levels can be defined as the ratio of number of ways of realizing the given distribution and the total number of possible arrangements

"Statistical thermodynamics is the science that deals with the application of the postulates, theorems and methods of statistical classical mechanics and statistical quantum mechanics to the description, understanding and solutions of thermodynamic problems"

In principle, statistical thermodynamics does not have the rigor and exactness of thermodynamics because there is no method of proving the validity of the postulates of statistical mechanics. Despite this lack of rigor, we find the study of statistical thermodynamics gives us a good understanding of the laws of thermodynamics in terms of the properties of individual molecules. It enables us to calculate the exact values of specific heats, entropies, free energies, equilibrium constants etc.

Statistical thermodynamics has certain limitations. There are some discrepancies in the case of large and complicated molecules, gases at high pressure etc.

1.2 Concepts of distribution

We are familiar with the Maxwell distribution law for kinetic energy of molecules and Planck's distribution for energies of harmonic oscillator. The statistical treatment is based on an important principle ie, *most probable distribution*. In a system containing very large number of particles, deviations from the most probable distribution need not be considered in defining the equilibrium conditions.

1.3 Thermodynamic probability (W)

Planck introduced the concept of thermodynamic probability or statistical probability (W)

Let us consider a system of volume (v) containing the total number of molecules (N) which are identical and distinguishable. Let the total energy of all the molecules present in the system is E at any temperature. It is obvious that all the molecules will not have the same energy.

Let us suppose that n_o molecules will have energy t_o, n_1 molecules will have energy t_1, etc.… Then the total number of molecules in the system (N) is given by

$N = n_0t_0 + n_1t_1 + n_2t_2 + \ldots + n_it_i = \sum_{i=0}^{i=i} n_i - - - - - (1)$

And the total energy of all the molecules in the system (E) is given by

$$E = n_0t_0 + n_1t_1 + \cdots \ldots\ldots + n_it_i = \sum n_it_i - - - - - (2)$$

There are many number of ways in which the molecules will distribute themselves among various energy levels. Obviously it will be interesting to calculate the total number of ways of distribution of molecules among distribution of molecules among different energy levels. The mathematical answer to this problem can be obtained from the following example:

Consider two houses X and Y in which four persons a, b, c and d are to be accommodated. These four persons can be distributed as follows (Fig 1)

Houses	Number of Persons				
X	4	3	2	1	0
Y	o	1	2	3	4

Fig.1 distribution of four persons

There are five possible combinations often called macrostates. Corresponding to anyone of these five macrostates, there may arises a number of complexions or microstates. Thus, for the macrostate (X = 1 and Y = 3) there are four possibilities as described in figure 2

X=1 and Y=3

Houses	Persons			
X	a	b	c	d
Y	bed	acd	abd	abe

Fig.2 distribution of a,b,c and d for the microstate X=1 and Y=3

The number of microstates in a given macrostate can be obtained from the permutations of the individuals in the macro state. In this case the total permutation of a,b,c and d is 4! = 4×3×2×1=24. But this number also includes the permutations of the there members of house Y which is 3!

$= 3 \times 2 \times 1 = 6$

Hence, the real number of microstates or complexions would be

$$\frac{4!}{3!} = \frac{4 \times 3 \times 2 \times 1}{3 \times 2 \times 1} = 4$$

In general, if the total number of molecules in the system is N and if they are to be accommodated in several energy levels so as to satisfy equations (1) and (2), then mathematically the number of microstates for a given macrostate is given by the relation

$$w = \frac{N!}{n_0!\,n_1!\,n_2!\ldots\ldots n_i!} --- (3)$$

$$w = \frac{N!}{\pi n_i!} ----(4)$$

where the symbol π denotes the product of the terms.

Planck called this term W as the thermodynamic probability or statistical probability. It represents the maximum number of different ways in which a system in a given state may be realized or it is the total number of possible microstates for any given macrostate.

1.4 Problems

1. Calculate the number of ways of distributing distinguishable molecules a, b and c between three energy levels so as to obtain $n_o=1$, $n_1=1$ and $n_2=1$

We know that $w = \frac{N!}{n_0!n_1!n_{2!}}$

Given N=3,$n_0 = 1, n_1 = 1, n_2 = 1$

$$\therefore w = \frac{3!}{1!\,1!\,1!} = \frac{3 \times 2 \times 1}{1 \times 1 \times 1} = 6$$

There are six possible ways of distributing there molecules a, b and c

2. Calculate the number of ways of distributing four molecules in four energy levels so that there are two molecules in the level 0, 1 molecule in level 1, 1 molecule in level 2 and zero in level 3

$$w = \frac{N!}{n_0!\,n_1!\,n_2!\,n_3!}$$

Given : $N=4, n_0=2, n_1=2, n_1=1, n_2=1$ *and* $n_3=0$

$$\therefore w = \frac{4!}{2!\,1!\,1!\,0!}$$

$$\frac{4X3X2X1}{2X1X1X1}$$

= 12

1.5 Relationship between thermodynamic probability and entropy (Boltzmann – Planck equation)

Let us consider two vessels being connected by a stopcock. Let us imagine that one vessel contains gas at a high pressure and the other is evacuated (Figure. 3). On opening the stopcock, there is a strong probability that the gas distributes itself between two vessels. The flow of gas occurs spontaneously.

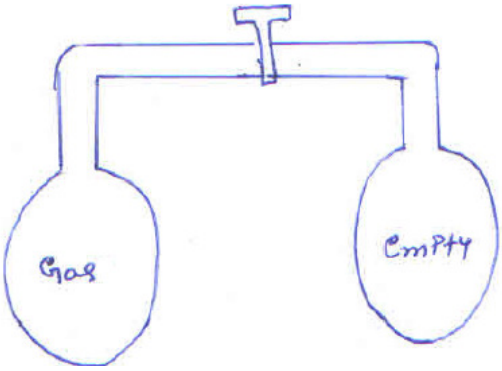


Figure 3

So, a spontaneous process may be regarded as a change from a less probable state to a more probable state. But we are aware of the fact that during a spontaneous process, the entropy increases. Hence, during the spontaneous process, both entropy and probability increases. So, there must be a definite relation between the two. If S be the entropy of the system and W, the thermodynamic probability, the relation between the two quantities is

$$S=f(w)----(5)$$

The nature of the function f (W) can be ascertained by considering two systems having entropies S_1 and S_2 and probabilities W_1 and W_2 respectively. Since the entropy is an extensive property, the entropy (S_{12}) of the combined system is

$$S_{12}=S_1+S_2----(6)$$

And the probability of the combined system (W_{12}) is given by

$$W_{12}=W_1.W_2----(7)$$

$$S_{12}=f(W_{12})$$

$$S_{12} = S_1+S_2 = f(W_1.W_2)$$

For two individual systems

$$S_1= f(W_1) \text{ and } S_2= f(W_2)----(8)$$

It follows that

$$f(W_1,W_2)= f(W_1) + f(W_2)----(9)$$

This will be true only if the function is logarithmic. Hence, the above equation can be written as

$$S \propto \ln w$$

Or $$S = K\ln w ----(10)$$

The magnitude of proportionality constant K is found to be the same as that of the Boltzmann constant. Equation (10) is called the Boltzmann-Planck equation.

1.6 Stirling approximation

For distribution of N particles, we have to evaluate a function N! or lnN!. For small values of N, the function can be easily computed. However, for very large values of N, simple computation is difficult. Therefore, a simple method is required for the evaluation of N! or lnN!. Stirling introduced the approximation for the systems containing a very large number of particles or molecules

$$\ln N! = NlnN - N ----(11)$$

$$and\ N! = N^N.e^{-N} --- (12)$$

Stirling approximation is unreliable for small values of N but is a good approximation for large values of N (Table.1)

Table. 1

Values of ln N!

N	ln N!	
	Direct	From equation (11)
5	4.7875	3.0447
10	15.1044	13.026
20	42.3456	39.9146
1000	--------	5907.76
10^5	--------	10.515×10^5

Problem: calculate the value of ln 6! With and without stirling approximation

The value of $6! = 6 \times 5 \times 4 \times 3 \times 2 \times 1 = 720$

$$\therefore \ln 720 = 2.303 \log 720$$

$$= 6.579$$

By String approximation

$$\text{Ln } 6! = 6\ln 6 - 6$$

$$= 6\times 2.33 \log 6 - 6$$

$$= 4.750$$

1.7 Ensemble

An ensemble is simply a very large collection of identical microsystems which are allowed to interact. It can be emphasized that

a) There is no restriction on the nature of the contents of each system ie each system may be multiphase and contain dependent (interacting) particles and

b) The number of systems in an ensemble is very large so that statistical approximation can be applied without any serious error.

1.8 Ensemble average

It is the average value of any property M of the system taken over all the systems that are members of the ensemble

$$\bar{M} = \sum M_j/\in$$

The two basic postulates to relate the concept of an ensemble for calculating average values are

i) The average of any mechanical variable M over certain time t is equal to the ensemble average $\bar{M}$ provided the system of the ensemble replicates the thermodynamic state and surroundings of actual system.

ii) In microcannonical ensemble the members are distributed in equal probability over possible quantum states consistent with the values of N, V and E

1.9 Types of Ensembles

Different ensembles are distinguished by the condition governing the interaction of one system with the other. There are three most important thermodynamic environment conditions which can represent the interaction of one system with another. The three types of ensembles are

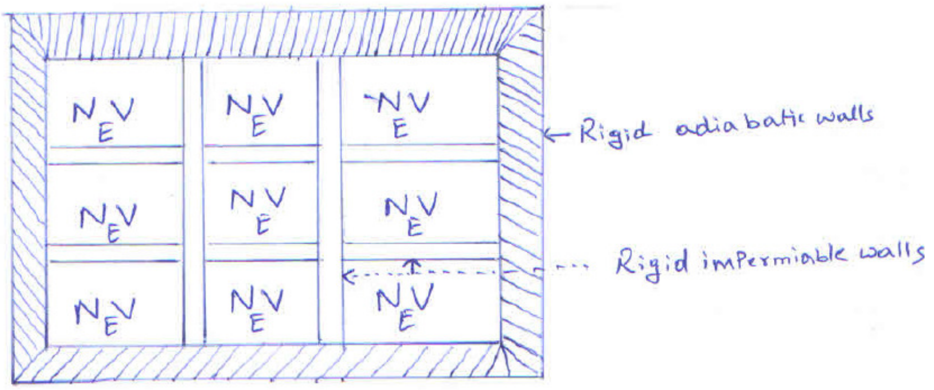
i) Micro cannonical ensemble

ii) Canonical ensemble

iii)Grand canonical ensemble

1.10 Micro cannonical ensemble

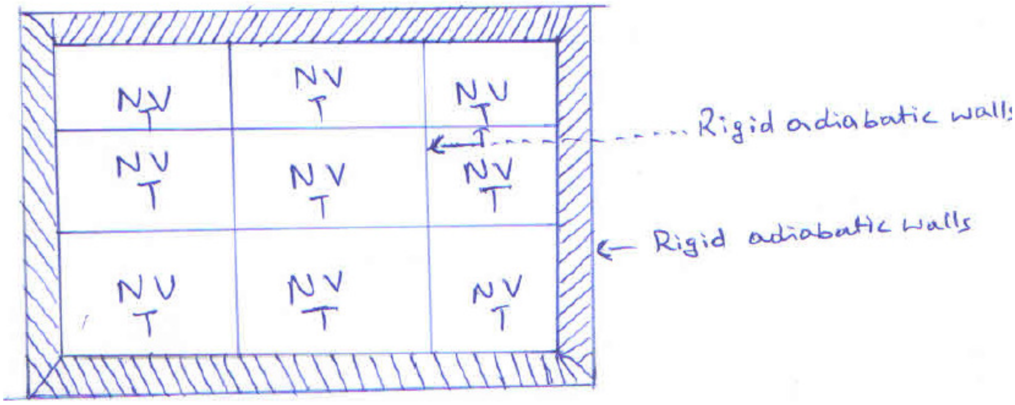
Each system is assumed to be concurred with the isolated assembly of independent particles



It is a system of constant volume (V), energy (E) and the number of molecules (N) and is separated from its neighbors with rigid impermeable walls (Fig. 4). It can neither exchange energy nor material with its neighbors. This is characterized by N, V and E and is called micro cannonical ensemble.

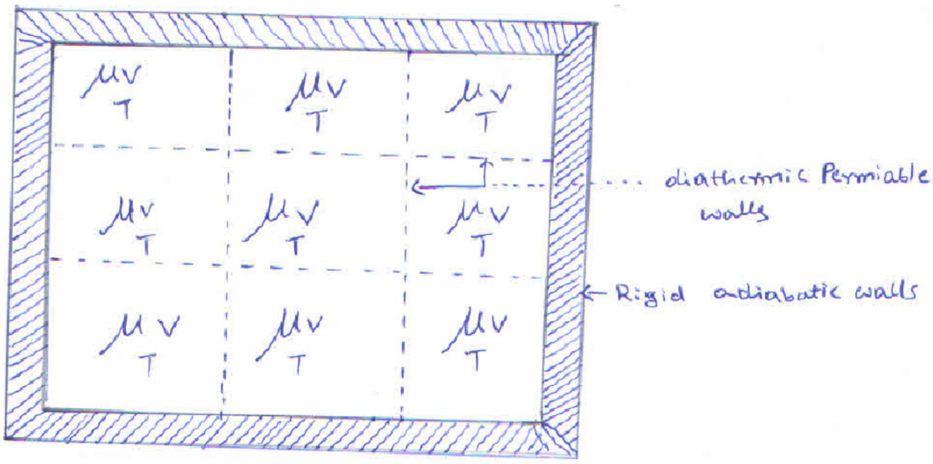
1.11 Canonical ensemble

Each system is associated to be closed and fixed volume (V), number of molecules (N) and temperature (T) but separated from its neighbors by diathermic walls so that all systems are in thermal equilibrium (Fig. 5) ie the system is characterized by constant N, V and T. This is a closed isothermal system and is called canonical ensemble.



1.12 Grand canonical ensemble

Each system is considered to be of constant volume (V) chemical potential (M) and temperature (T) but open and separated from its neighbors by diathermic permeable walls (Fig. 6). This is an open isothermal system and is characterized by constant M, V and T. Such a system is called grand canonical ensemble.



1.13 Maxwell-Boltzmann distribution law Or Most probable distribution

Consider a system containing N molecules having a total energy E. it is obvious that all the molecules will not be in the same energy level. In a given distribution, let there be no molecules in energy level E_o, n_1 molecules in energy level E_1 etc. Then the expression for the total number of molecules present in the system is given by

$N = n_0 + n_1 + n_2 + \ldots\ldots + n_i = \sum n_i -----(13)$

The total energy of all the molecules is given by

$E = n_0E_0+n_1E_1+n_2E_2+\ldots\ldots+ n_iE_i = \sum n_i ---(14)$

In deriving the man well-Boltzmann equation, a number of assumptions are made

i) The molecules present in the system are identical and distinguishable

ii) The molecules present in the system are supported to be ideal

iii)Sterling approximation.

Suppose n_i of the number of molecules occupying the energy level E_i, then the Maxwell-Boltzmann distribution equation or the most probable distribution of n_i molecules is given by

$$n_i = \frac{Ng_i e^{-E_i/kt}}{\sum g_i e^{-E_i/kt}} ----(15)$$

$$\text{Or } n_i = \frac{Ng_i e^{-E_i/kt}}{Q} ----(16)$$

Where N is the total number of molecules present in the system, g_i is the degeneracy factor or statistical weight factor for the i^{th} energy level, K is the Boltzmann constant and T is the temperature

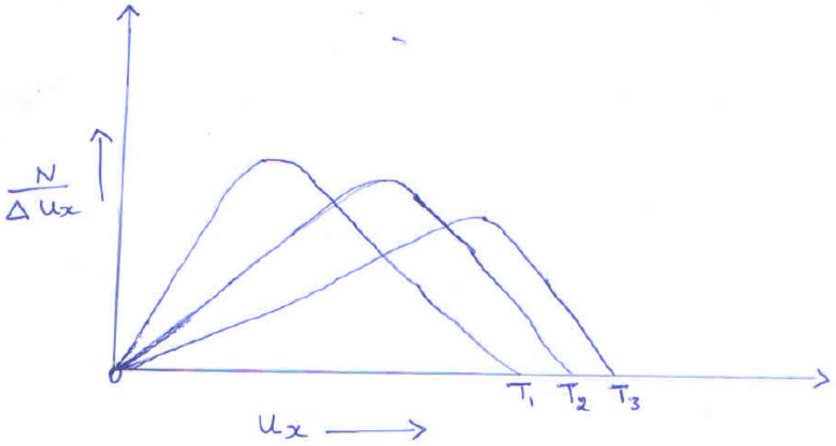
where $Q = \sum g_i e^{-t_i/kt} ----(17)$

Q is the partition function. The derivation of equations (15) and (16) is given under maxwell-Boltzmann statistics.

1.14 Maxwell's distribution of molecular velocities

In a gas, molecules move in a zigzag way in all directions with different velocities. All molecules do not possess the same velocity because of redistribution of both energy and velocity as a result of collisions.

Consider a gas containing N molecules having velocities in the X-direction is Ux. The ΔU_xspan of velocities into equal intervals and N is the number of molecules whose U_x values fall in different intervals. Plot a graph of a fraction of molecules in a certain velocity range divided by the width of the velocity range ($N/\Delta U_x$) against average velocity (U_x)



Maxwell utilized probability considerations to show that the actual distribution of molecular velocities in a gas depends on the temperature (T) and molecular weight of gas (M) and is given by

$$\frac{N}{\Delta U_x} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}. e^{-MU_x^2/2RT}. U_x^2 - - - - - (18)$$

Equation (18) is known as Maxwell's law of distribution of molecular velocities. The significance of the law may be seen from the plots of $N/\Delta U_x$ against U_x at constant temperatures ($T_3 > T_2 > T_1$)

The area under the whole curve indicates the total number of molecules. The fractions of molecules having smaller and larger velocities are small. Majority of molecules have velocities lying within this limited range with increase of temperature the fraction of molecules having lower speeds decreases where as those having large speeds increases. Both low and very high speeds are improbable and most of the molecules in a gas have velocities grouped about the most probable velocity corresponding to the peak of the curve at each temperature. By changing the temperatures the shape of the curve remains same but increase of temperature results in a flattening of the maximum. The remarkable effect of temperature in increasing the proportion of molecules possessing high velocities is due to the presence of the exponential factor in equation (18)

1.15 Most probable velocity (U_x)

We know that

$$\frac{N}{\Delta U_x} = 4\pi(\frac{M}{2\pi RT})^{3/2}. e^{-MU_x^2/2RT} U_x^2 - - - (18)$$

Differentiating equation (18) with respect to U_x and equated to zero.

$$\left(1 - \frac{MU_x^2}{2RT}\right) U_x. e^{-MU_x^2/2RT} = 0$$

Taking $\left(1-\frac{MU_x^2}{2RT}\right)=0$, then a solution of above equation $\frac{-MU_x^2}{2RT}=1$

$$U_x^2=\frac{2RT}{M}$$

$$or\ U_x=\left(\frac{2RT}{M}\right)^{1/2} ---(19)$$

This gives the condition for maximum and the corresponding value of Ux is called the most probable velocity which is defined as the velocity of gas possessed by maximum number of molecules at a given temperature.

1.16 Average velocity <Ux>

The fraction of molecules with velocities Ux in the range $U_x\ and\ U_x+dU_x\ is\ given\ by$

$$f(U_x).dU_x=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-MU_x^2/2RT} ----(20)$$

Average velocity $<U_x>$ is obtained by taking the sum of all the velocities and dividing by the total number of molecules N

$$<U_x>=\frac{U_1+U_2+U_3...+U_N}{N} \text{ or } <U_x>=\frac{\sum U_N}{N} \text{ ------(21)}$$

Average velocity is the summation of each possible velocity times the probability P(U_x) of that velocity and is given by

$$<U_x>=\sum U_xP(U_x) ----(22).$$

The probability that a molecule has a velocity between Ux and U_x+dU_x is represented by f$(U_x)dU_x$

$$<U_x>=\int_0^\infty U_xf(U_x)dU_x ----(23)$$

From Maxwell distribution, we have

$$<U_x>=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-MU_x^2/2RT}.U_x^3dU_x -----(24)$$

Substituting $x^2=\frac{MU_x^2}{2RT}$ and $dU_x=2RTxdx/MU_x$ and using $\int_0^\infty x^3e^{-x^2}dx=\frac{1}{2}----(25)$

$$\text{we get} <U_x>=\left(\frac{8RT}{\pi M}\right)^{1/2} -----(26)$$

where < U_x> is the average velocity which is defined as the average of the various velocities possessed by the molecules.

1.17 Root mean square velocity ($\overline{U_x}$)

The root mean square velocity ($\overline{Ux}$) is defined as

$$< \overline{U_x} >= \sqrt{\frac{n_1U_1^2 + n_2U_2^2 + ----}{N}} ----(27)$$

Where $n_1$are the number of molecules having velocity U_1, n_2 are the number of molecules having velocity U_2 etc and N is the total number of molecules present in the system.

This can also be written as

$$\overline{U_x} = \left(\frac{1}{N}\sum u_{X_i}^2\right)^{1/2} ------ (28)$$

The values of $\overline{U_x}$is obtained by multiplying each velocity squared by the probability of the velocity

$$\overline{U_x} = \int_0^\infty U_X^2 F(U_x).dU_x ----(29)$$

Substituting the Maxwell distribution and using the relation

$$\overline{U_x} = \int_0^\infty x^4\, e^{-x^2}.dx = \frac{3}{8}\sqrt{\pi} ----(30)$$

we get $\overline{U_x} = \left(\frac{3RT}{M}\right)^{1/2} --- (31)$

1.18 Relationship between U_x,< U_x> $\overline{U_x}$

The relationship between the most probable velocity (U_x), average velocity (<U_x>) and the root mean square velocity ($\overline{U_x}$) are

$$U_x = \left(\frac{2RT}{M}\right)^{1/2} ----(19)$$

$$< U_x > = \left(\frac{8RT}{\pi M}\right)^{1/2} ----(26)$$

$$\text{and } \overline{U_x} = \left(\frac{3RT}{M}\right)^{1/2} -------(31)$$

$$Ux: <U_x> :\overline{U_x} = \left(\frac{2RT}{M}\right)^{1/2} : \left(\frac{8RT}{\pi M}\right)^{1/2} : \left(\frac{3RT}{M}\right)^{1/2} --- (32)$$

1.19 Summary of the unit

Statistical Mechanics is the study of macroscopic phenomena from a microscopic point of view. Statistical Mechanics helps us to understand, explain and predict macroscopic behavior of a collection of entities (e.g. molecules) given the microscopic behavior (e.g. inter-molecular interactions). The branch of statistical mechanics that deals with equilibrium thermodynamics behavior (e.g. pressure, entropy, free energy) is called Statistical Thermodynamics. Only certain problems in statistical thermodynamics are exactly solvable (e.g. ideal gas, Einstein crystal, Ising model in one and two dimensions, etc.).

The state of a macroscopic system can be specified by few properties. For example, a pure liquid can be described completely by it mass, pressure and temperature. However, for each macroscopic state, there exist a large number of microscopic states corresponding to it. For quantum systems, each microscopic state is described by the eigenfunction obtained by solving the Schrodinger wave equation. For classical systems, the positions and momenta of all its constituent molecules describe each microscopic state. An ensemble of systems is a collection of various microscopic states of the system that correspond to the single macroscopic state of the system whose properties we are investigating. Depending upon the thermodynamic environment of the system, we can create various representative ensembles.

In the macroscopic limit, the grand canonical ensemble is always the easiest to work with. However, when working with only a few particles, there are differences between the restriction that only those states with exactly N particles are considered, as opposed to the restriction that the average number is N. This difference can matter when the fluctuation of the number, which usually goes as √N, is not much less than N itself.

1.20 Key words

Concepts of distribution; Thermodynamic probability (W); Boltzmann – Planck equation; Stirling approximation; Ensemble; Micro cannonical ensemble; Grand canonical ensemble; Maxwell-Boltzmann distribution law; Maxwell's distribution of molecular velocities; Most probable velocity (U_x); Average velocity <Ux>; Root mean square velocity ($\overline{U_x}$);

1.21 References for further study

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1.22 Questions for self understanding

1) Discuss the concepts of distribution.

2) Explain the term thermodynamic probability (W) with suitable example.

3) What is the relationship between thermodynamic probability and entropy (Boltzmann – Planck Equation)?

4) Discuss the Stirling approximation.

5) What is ensemble?

6) Explain the ensemble average

7) Explain the following types of ensembles

  a) Micro cannonical ensemble

  b) Canonical ensemble

  c) Grand canonical ensemble

9) Discuss the Maxwell-Boltzmann distribution law Or Most probable distribution

10) Explain the Maxwell's distribution of molecular velocities

11) Derive the equation for most probable velocity (U_x)

12) Derive the equation for average velocity <Ux>

13) Derive the equation for root mean square velocity $(\overline{U_x})$

14) Discuss the relationship between U_x,< U_x> $\overline{U_x}$

UNIT-2

Structure

2.0 Objectives of the unit

After studying this unit you are able to

- Derive the equation for Maxwell - Boltzmann statistics
- Derive the equation for evaluation of molar entropies
- Write the assumption of quantum statistics
- Derive the equation for Bose – Einstein Statistics
- Derive the equation for Fermi-Dirac Statistics
- Compare the Maxwell–Boltzmann (M-B),Bose–Einstein(B-E) and Fermi-Dirac (F-D) Statistics

2.1 Introduction

The goal of statistical mechanics is to understand how the macroscopic properties of materials arise from the microscopic behavior of their constituent particles.

Examples include,

- Specific heat capacity and its variation with temperature;
- The entropy of a sample of material, and its relationship with temperature and internal energy;
- The magnetic properties of materials.

A key concept of statistical mechanics is that many different microstates can correspond to a single macrostate. However, specifying the macrostate imposes constraints on the possible microstates. Statistical mechanics explores the relationship between microstates and macrostates.

Boltzmann distribution tells us how particles in a system in thermal equilibrium are distributed between the energy levels in the system. In a classical system, there is a continuous range of energies available to the particles; but in a quantum system, the available energies take discrete values.

The Boltzmann distribution turns out to be the basis of many important properties of materials. It also helps us to understand the physical significance of concepts arising in thermodynamics, including temperature and entropy. The Boltzmann distribution relies on a number of assumptions and approximations. We shall consider these in some detail.

2.2 Maxwell - Boltzmann statistics

Consider a system containing N molecules having a total energy E. it is obvious that all the molecules will not be in the same energy level. In a given distribution let there be no molecules in energy level E_o, n_1 in energy level E_1 etc. then the expressions for the total number of molecules (N) and the total energy of all the molecules present in the system (E) are given by

N= $n_0 + n_1 + n_2 + \ldots + n_i = \sum n_i ----(33)$

E = $n_0t_0 + n_1t_1 + n_2t_2 + \ldots + n_it_i = \sum n_i t_i ----(34)$

The thermodynamics probability of this distribution (W) is

W =$\frac{N!}{n_0!n_1!\ldots\ldots\ldots} = \frac{N!}{\pi n_i!} --- (35)$

Where $\pi\ is\ the\ product\ of\ all\ the\ terms$

Taking logarithms of equation (35)

$$\ln W = \ln N! - \sum n_i! ----(36)$$

According to striving approximation

$$\ln N! = N \ln N - N$$

Substituting in equation (36)

We get $\ln w = N \ln N - N - \sum n_i \ln n_i + \sum n_i$

=N/n N-$\sum n_i \ln n_i since\ \sum n_i = N$

$$\therefore \ln w = N \ln N - \sum n_i \ln n_i ----(37)$$

Now, we can attempt to find me most probable distribution of the molecules among different energy levels. The most probable distribution will be achieved when the system attains equilibrium. Hence, at equilibrium distribution, the magnitude of W is maximum, and therefore lnW is maximum.

Hence, at equilibrium

dln $w = 0 ----(38)$

Differentiating equation (37)

dln $W = d(N \ln N) - d(\sum n_i \ln n_i) = 0$

$$\therefore d(\sum n_i \ln n_i) = 0$$

$$\sum \ln n_i \, dn_i + \sum dn_i = 0 ----(39)$$

$$As \sum n_i = N ; \sum dn_i = dN = 0$$

Equation (39) becomes

$$\sum \ln n_i \, dn_i = 0\text{--------- (40)}$$

We must remember that for a given system, the total number of molecules (N) and the total energy (E) remain constant.

$$\sum n_i = N; dN = \sum dn_i = 0 - - - (41)$$

$$\sum n_i E_i = E; dE = \sum E_i dn_i = 0 - - - - (42)$$

Multiplying equations (41) and (42) by LaGrange method of undetermined arbitrary multipliers α and β and adding equation (40)

We get

$$\sum \ln n_i dn_i + \alpha \sum dn_i + \beta \sum E_i dn_i = 0$$

$$\left(\sum \ln n_i + \alpha + \beta \sum E_i\right) dn_i = 0$$

$$\sum \ln n_i + \alpha + \beta \sum E_i = 0 - - - (43)$$

Since α and β are independent, the restraining condition may be removed such that equation (43) becomes

$$\ln n_i + \alpha + \beta E_i = 0$$

$$\mathrm{Ln}\, n_i = -\alpha - \beta E_i$$

$$\text{or } n_i = e^{-\alpha}. e^{-\beta E_i} - - - (44)$$

To determine the value of α, the following method is adopted.

Equation (44) can be written as

$$\sum n_i = e^{-\alpha}. \sum e^{-\beta E_i}$$

$$N = e^{-\alpha}. \sum e^{-\beta E_i} \qquad since \sum n_i = N$$

$$\therefore e^{-\alpha} = \frac{N}{\sum e^{-\beta E_i}} - - - (45)$$

$$e^{\alpha} = \frac{Q}{N} - - - - (47)$$

Substituting equation (45) in equation (44)

We get $n_i = \dfrac{Ne^{-\beta E}}{\sum e^{-\beta E_i}} - - - - - - (48)$

Equation (48) is sometimes known as the Boltzmann distribution equation

The fraction of the total number of molecules is given by

$$\frac{n_i}{N} = \frac{e^{-\beta E_i}}{\sum e^{-\beta E_i}} - - - - - - (49)$$

It should be noted that in deriving the above equation no restriction was imposed with regard to the nature of energy ie, whether the energy is rotational or vibrational etc. Hence, this equation must be regarded as applicable to the distribution of total energy or any form of energy which has a constant value for the given system. However, in deriving this equation, a number of assumption were made

i) Molecules are assumed to be identical and distinguishable

ii) Stirling approximation

iii)The molecules of the gas are supposed to be ideal.

In a given energy level i, all the molecules may have the same energy E_i, but the energy may be arranged in different ways for different molecules. When there is a possibility of different ways of arrangement in a state, the state is said to be degenerate. If there are g_i numbers of possible distribution of energy in a given energy level i, then the state is called the *degeneracy factor or statistical weight factor*

2.3 Illustration

Let us consider a system containing 100 molecules having their velocity C = $\sqrt{51}$ or $C^2 = 51$ But the velocity components of different molecules may be different as follows.

If C_x, C_y and C_z are the velocity components in three directions x, y and z

Then $C^2 = C_x^2 + C_y^2 + C_z^2$

Number of molecules	C_x	C_y	C_z	C^2
10 may have	7	1	1	51
15 may have	1	1	7	51
20 may have	1	7	1	51
15 may have	5	5	1	51
20 may have	5	1	5	51
20 may have	1	5	5	51

ie, six complexions are possible for the distribution of velocities among different components. Then the system is said to be six fold degenerate or statistical weight factor (gi) is 6.

Equation (49) can be written as

$$\frac{n_i}{N} = \frac{g_i e^{-\beta E_i}}{\sum g_i e^{-\beta E_i}} - - - - - (50)$$

Now, let us calculate the value of β as follows

The denominator $\sum g_i e^{-\beta E_i}$in expression (49) is a sum of the factor $e^{-\beta E_i}$ over all the energy levels. It is called the partition function (Q).

Equation (48) can be written as

$$n_i = \frac{Ne^{-\beta E_i}}{\sum e^{-\beta E_i}} = \frac{Ne^{-\beta E_i}}{Q} ------(51)$$

Taking logarithms

$$\ln n_i = \ln N - \ln Q - \beta E_i ----(52)$$

According to Boltzmann – planck equation

$$S = kln\, w \; or \frac{S}{k} = \ln w --- (53)$$

From equation (37), we have

$$\ln w = N \ln N - \sum n_i lnn_i --- (37)$$

Comparing equations (37) and (53)

$$\frac{S}{k} = N \ln N - \sum n_i \ln n_i ----(54)$$

Substituting equation (52) in equation (54)

$$we\ get \frac{S}{k} = Nln\, N - \sum n_i\, [\ln N - \ln Q - \ \beta E_i]$$

$$= NlnN - NlnN + Nln\, Q + \beta \sum n_i E_i$$

$$= N \ln Q + \beta E \; since \; \sum n_i\, E_i = E$$

$$\therefore S = kn \ln Q + k\beta E ------ (55)$$

Differentiating equation (55) with respect to energy at constant volume

$$\left(\frac{dS}{dE}\right)_v = kn \left(\frac{d \ln Q}{dE}\right)_v + k\beta + kE \left(\frac{d\beta}{dE}\right)_v$$

$$= \frac{kN}{Q} \left(\frac{dQ}{dE}\right)_v + k\beta + kE \left(\frac{d\beta}{dE}\right)_v$$

$$= \frac{rN}{Q} \left(\frac{dQ}{d\beta}\right)_v \left(\frac{d\beta}{dE}\right)_v + k\beta + kE \left(\frac{d\beta}{dE}\right)_v --- (56)$$

But Q=$\sum e^{-\beta E_i} ----(57)$

Differentiating (57) with respect to β at constant volume

We get $\left(\frac{dQ}{d\beta}\right)_v = -\sum E_i e^{-\beta E_i} ----(58)$

But E = $\sum n_i E_i$ or $\sum E_i = \frac{E}{N}$------------ (59) since $\sum n_i = N$

Substituting equation (59) in equation (58)

We get $\left(\frac{dQ}{d\beta}\right)_v = -\frac{E}{N} \sum e^{-\beta E_i} = -\frac{E}{N} Q ----(60)$

Substituting the value of $\left(\frac{dQ}{d\beta}\right)_V$ $in\ equation\ (56)$

$$\left(\frac{dS}{dE}\right)_V = \frac{kN}{Q}\left(-\frac{E}{N}Q\right)\left(\frac{d\beta}{dE}\right)_v + k\beta + kE\left(\frac{d\beta}{dE}\right)_v$$

$$= k\beta --- (61)$$

From 1st law of thermodynamics

We have Dq= dE+ pdV----(62)

But dS = $\frac{Dq}{T}$ $or\ Dq = TdS ----(63)$

Comparing equations (62) and (63)

Tds=dE+Pdv---(64)

At constant volume

Tds=dE

Or $\left(\frac{dS}{dE}\right)_V = \frac{1}{T} --- (65)$

Comparing equations (65) and (61)

We get k$\beta = \frac{1}{T}$ $or\ \beta = \frac{1}{kT} ----(66)$

Hence, the Maxwell-Boltzmann equation becomes

$$n_i = \frac{Ne^{-E_i/kt}}{\sum e^{-E_i/kt}} --- (67)$$

$$\text{Or } n_i = \frac{Ng_i e^{\frac{-E_i}{kT}}}{\sum g_i e^{\frac{-E_i}{kT}}} \text{ --------------- (68)}$$

$$\text{Or } n_i = \frac{Ng_i e^{\frac{-E_i}{kT}}}{\beta e^{\frac{-E_i}{kT}}} \text{ ----------------- (69)}$$

$$\text{or } n_i = \frac{g_i}{\beta e^{\frac{E_i}{kt}}} \text{ ----------- (70)} \quad since\ \beta = \frac{Q}{N}$$

Equations (69) to (70) are the various forms of Maxwell – Boltzmann distribution law

2.4 Evaluation of molar entropies

Consider the distribution of N molecules into i groups such that n_0 are in groups 0, n_1 are in group 1 etc. Then the thermodynamics probability (W) is given by .

$$w = \frac{N!}{n_o!\,n_1!} --- (71)$$

The above expression has been derived from classical mechanics. But according to quantum statistics, this equation needs modification in two ways.

a) For the degeneracy of energy levels

i.e

$$w = \frac{N!\, g_0^{n_0}!\, g_1^{n_1}!\, g_2^{n_2}! \ldots.}{n_0!\, n_1!\, n_2! \ldots\ldots.} - - - - - (72)$$

b) For the indistinguishability of the molecules which is done by dividing equation (72) by N !

Then $$W = \frac{g_0^{n_0} . g_1^{n_1} . g_2^{n_2}}{n_0! n_1! n_2! \ldots.} - - - - (73)$$

Equation (73) can be regarded as an expression for the thermodynamic probability derived from quantum statistics.

Taking logarithms of equation (73)

$$\ln w = (n_0 \ln g_0 + n_1 \ln g_1 + \cdots) - (\sum \ln n_i\, !)$$

$$\sum n_i \ln g_i - \sum \ln n_i! - - - - - (74)$$

Applying sterling approximation

$$\sum \ln n_i! = \sum n_i \ln - \sum n_i$$

Substituting in equation (74)

$$\ln \mathrm{w} = \sum n_i \ln g_i - \sum n_i \ln n_i + \sum n_i$$

According to Maxwell-Boltzmann distribution law

$$n_i = \frac{N g_i e^{\frac{-E_i}{kT}}}{Q}$$

Taking logarithms

$$\ln n_i = \ln N + \ln g_i - \ln Q - \frac{E_i}{kT}$$

Multiplying the above equation by $-n_i$

$$-n_i \ln n_i = -n_i \ln N + n_i \ln Q - n_i ln g_i + \frac{n_i E_i}{kT} - - - - - (76)$$

Substituting equation (76) in equation (75)

$$\ln W = \sum n_i \ln g_i - \sum n_i \ln N + \sum n_i \ln Q - \sum n_i \ln g_i + \frac{\sum n_i E_i}{kT} + \mathrm{N}$$

$$= N\ln\frac{Q}{N} + \frac{E}{kT} + N - - - (77) since \sum n_i E_i = E$$

But $E = kT^2\left(\frac{d\ln Q}{dT}\right)$

$$\therefore \ln W = \frac{N}{n}\frac{Q}{N} + \frac{RT}{R}\left(\frac{d\ln Q}{dT}\right) + N - - - (78)$$

But $S = RN\ln\frac{Q}{N} + kT\left(\frac{d\ln Q}{dT}\right) + R - - - (79)\ since\ kN = R$

2.5 Quantum statistics

Maxwell – Boltzmann statistics is also called classical statistics in which the individual Particles are considered as distinguishable and any number of particles can occupy any energy level. Boltzmann statistics is not applicable to particles which are indistinguishable. Indistinguishable particles are classified into two groups according to quantum statistics.

i) Particles with zero or integral values of spin which require their overall wave function symmetrical ie the wave function whose sing does not change on inter changing the coordinates of any two particles. These are called Bosons and they obey Bose – Einstein statistics

Ex : photons, deuterons and nuclei of atoms of even mass number

ii) Particles with half integral value of spin 1/2 ,3/2,5/2 etc which require their overall wave unction to be anti symmetric ie the sign of the wave function changes on interchanging the coordinates of any two particles. These particles are called Fermions and they obey Fermi – Dirac statistics.

Ex : Electrons, protons, neutrons and nuclei of atoms of odd mass number.

The Boltzmann distribution equation is applicable to the distribution of particles in a system containing gases at low density. This law fails to explain the distribution of particles in a system containing gasses at high density as well as the indistinguishability of the particles. This has led to the derivation of two more distribution equations namely Bose-Einstein and Fermi – Dirac equations.

2.6 Bose – Einstein Statistics

Suppose the N indistinguishable particles that constitute the system are divided into a series of quantum groups with the number of particles n_o, n_1 …… in each group having energies E_o, E_1 ……..respectively. The total number of particles and the total energy of all the particles present in a system are constant.

Let there be g_i degenerate energy levels. Since the complete Eigen function for the Bose – Einstein statistics is to be symmetric, there is no restriction on the number of particles associated with particular function. Let us imagine a box divided by (g_i – 1) partitions into g_i sections. The n_i particles are then supposed to be distributed among these sections. The total number of permutations of n_i particles and the (g_i–1) partitions is (n_i + g_i-1)!. Since the n_i particles are indistinguishable, permutations among the particles themselves do not produce a new arrangement. The total number therefore should be divided by n_i! Further, the permutations among the (g_i-1) partitions do not alter the fact that there are still sections. Hence, division of the total number of permutations by (g_i-1)! is also necessary.

The thermodynamic probability of the distribution of particles among various energy levels in given by

$$w = \pi \frac{(n_i + g_i - 1)}{n_i!\,(g_i - 1)!} - - - - - - (80)$$

The symbol $\pi\ represents\ the\ products\ of\ a\ series\ of\ similar\ terms.$

Taking logarithms of equation (80)

$$\ln w = \sum \ln(n_i + g_i - 1)! - \sum \ln n_i! - \sum \ln(g_i - 1)!$$

Neglecting 1 and applying strling approximation

$$\ln w = \sum (n_i + g_i)\ln(n_i + g_i) - \sum n_i - \sum g_i - \sum n_i \ln n_i + \sum n_i$$
$$- \sum g_i \ln g_i + \sum g_i$$

$$\ln w = \sum (n_i + g_i)\ln(n_i + g_i) - \sum n_i \ln n_i - \sum g_i ln g_i$$

$$\ln w = \sum n_i \ln(n_i + g_i) + \sum g_i \ln(n_i + g_i) - \sum n_i \ln n_i - \sum g_i \ln g_i$$

$$= \sum n_i \ln\left(\frac{n_i + g_i}{n_i}\right) + \sum g_i \ln\left(\frac{n_i}{g_i} + 1\right) - - - - (81)$$

Differentiating equation (81) with respect to n_i, keeping g_i constant

$$d \ln w = \sum \ln\left(1 + \frac{g_i}{n_i}\right) dn_i - - - - (82)$$

At equilibrium distribution ln w = 0

$$\therefore \sum \ln\left(1 + \frac{g_i}{n_i}\right) dn_i = 0 - - - - - - (83)$$

We have $\sum dn_i = 0 - - - - (84)$

$$\sum E_i dn_i = 0 - - - - (85)$$

Multiplying equations (84) by α and (85) by β, adding them and subtracting equation (83)

$$\alpha \sum dn_i + \beta \sum E_i dn_i - \sum \ln(1 + \frac{g_i}{n_i})\, dn_i = 0$$

$$\sum\left[\alpha+\beta E_i-\ln(1+\frac{g_i}{n_i})\right]dn_i=0$$

Or $\alpha+\beta t_i-\ln(1+\frac{g_i}{n_i})=0$

$$\ln(1+\frac{g_i}{n_i})=\alpha+\beta E_i$$

$$\left(1+\frac{g_i}{n_i}\right)=e^{\alpha}+\beta E_i$$

But $e^{\alpha}=\frac{Q}{N}=\beta----(47)$

$$\therefore\left(1+\frac{g_i}{n_i}\right)=\beta e^{\beta E_i}=\beta e^{\frac{E_i}{kT}}\ since\ \beta=1/kT$$

Or $\frac{g_i}{n_i}=(\beta e^{\frac{E_i}{kT}}-1)$

Or $n_i=\frac{g_i}{(\beta e^{\frac{E_i}{kT}}-1)}$------------- (86)

The equation (86) is the mathematical representation of Bose – Einstein statistics for the most probable distribution of particles among different energy levels.

When E_i is very large, one in the denominator of equation (86) can be neglected. Then, the equation (86) reduces to Maxwell – Boltzmann statistics ie,

$n_i=\frac{g_i}{\beta e^{\frac{E_i}{kT}}}$------(70)

2.7 Fermi-Dirac Statistics

In deriving Maxwell – Boltzmann and Bose – Einstein equations, there was no restriction on the number of particles in a given energy level. But while applying Fermi – Dirac statistics for particles the distribution will have to be done keeping in mind the Pauli's exclusion principle. According to this principle, no two electrons in an atom can be in the same energy level. Hence, not more than one particle can be assigned to the particular energy state.

The thermodynamic probability for the distribution of n_i indistinguishable particles among various energy levels keeping in view the Pauli exclusion principle is given by

$$w=\pi\frac{g_i!}{n_i!\,(g_i-n_i)}-----(87)$$

Taking logarithms

$$\ln w=\sum\ln g_i!-\sum\ln n_i!-\sum\ln(g_i-n_i)!$$

Applying stirling approximation

$$\ln w = \sum g_i \ln g_i - \sum g_i - \sum n_i \ln n_i + \sum n_i$$

$$- \sum (g_i - n_i) \ln(g_i - n_i) + \sum g_i - \sum n_i$$

$$= \sum g_i \ln g_i - \sum n_i \ln n_i - \sum (g_i - n_i) \ln(g_i - n_i) - - - - (88)$$

Differentiating equation (88) with respect to n_i keeping g_i constant

$$d \ln w = \sum \ln\left(\frac{g_i - n_i}{n_i}\right) dn_i - - - - (89)$$

At equilibrium distribution, $d \ln w = 0$

Hence, $\sum \ln(\frac{g_i - n_i}{n_i})\, dn_i = 0 - - -\ (90)$

We have

$$\sum dn_i = 0 - - - - (91)$$

$$\sum E_i dn_i = 0 - - - - (92)$$

Multiplying equations (91) by $\alpha, (92) by\ \beta$ adding them and subtracting equation (90)

$$\alpha \sum dn_i + \beta \sum E_i\, dn_i - \sum \ln\left(\frac{g_i - n_i}{n_i}\right) dn_i = 0$$

$$\sum [\alpha + \beta E_i - \ln(\frac{g_i}{n_i} - 1)] dn_i = 0$$

$$\alpha + \beta E_i - \ln\left(\frac{g_i}{n_i} - 1\right) = 0$$

$$\ln\left(\frac{g_i}{n_i} - 1\right) = \alpha + \beta E_i$$

$$\left(\frac{g_i}{n_i} - 1\right) = e^{\alpha}.e^{\beta E_i} - - -\ (93)$$

But $e^{\alpha} = \frac{Q}{N} = \beta\ and\ \beta = \frac{1}{kT}$

Inserting is equation (93)

We get $\left(\frac{g_i}{n_i} - 1\right) = \beta e^{\frac{E_i}{kT}}$

$$\frac{n_i}{g_i} = \left(\beta e^{\frac{E_i}{kT}} + 1\right)$$

Or $n_i = \dfrac{g_i}{\left(\beta e^{\frac{E_i}{kT}} + 1\right)}$

The most probable distribution of n_i indistinguishable particles among various energy levels obeying Fermi – Dirac statistics is given by equation (94)

2.8 Comparison between Maxwell – Boltzmann (M-B), Bose – Einstein (B-E) and Fermi-Dirac (F-D) Statistics

M – B	B – E	F – D
1. Particles are distinguishable	Indistinguishable	Indistinguishable
2. Derived on the basis of Classical mechanies	on the basis of quantum statistics	an the basis of quantum statistics
3. No restriction on the no Of particles occupying any Energy level	No restriction of the no of particles occupying any energy level	one particle per energy level (Pauli exclusion principle)
4. Applicable to particles Which are ideal	Applicable to Bosons	Applicable to Fermions
5. No symmetry Restrictions	Wave function is symmetric	Wave function is ant symmetric
6.$n_i = \frac{g_i}{\beta e^{\frac{E_i}{kT}}}.$	$n_i = \frac{g_i}{(\beta e^{\frac{E_i}{kT}} - 1)}$	$n_i = \frac{g_i}{(\beta e^{\frac{E_i}{kT}} + 1)}$

2.9 Problems

1) Calculate the number of ways of distributing 3 distinguishing molecules between three energy levels. Each energy level is occupied by one molecule.

We know that

$$w = \frac{N!}{n_0!n_1!n_2!}$$

Given: $N=3$, $n_0=1, n_1=1, n_2=1$

$$\therefore w = \frac{3!}{1!1!1!} = \frac{3\times2\times1}{1\times1\times1} = 6$$

2) Four identical particles are to be distributed between two identical containers so that each container has two particles in it. What is the number of possible arrangements for distinguishable and Indistinguishable particles?

(i) For distinguishable particles

We know that

$w = \frac{N!}{n_0!n_1!}$. Given: $N=4, n_0=2, n_1=2$

$$\therefore w = \frac{4!}{2!\,2!} = \frac{4\times3\times2\times1}{2\times1\times2\times1} = 6$$

And (ii) for indistinguishable particles

We know that

$$w = \frac{2^2 \times 2^2}{2!\,2!} = \frac{4 \times 4}{2 \times 1 \times 2 \times 1} = 4$$

3) Distribute two particles in three levels following the rules of Bose-Einstein and Fermi-Dirac statists

i) For Bose-Einstein statisties

We have $W = \frac{(n_i + g_i - 1)}{n_i!(g_i - 1)!}$

Given $n_i=2$ and $g_i=3$

$$\therefore w = \frac{3!}{2!\,(3-2)!} = \frac{3!}{2!\,1!} = \frac{3 \times 2 \times 1}{2 \times 1 \times 1} = 3$$

4) Calculate the number of ways of distribution of 2 Fermions among 4 energy states.

For Fermi-Dirac statistics

We have $$W = \frac{g_i!}{n_i!(g_i - n_i)!}$$

Given $n_i = 2$ and $g_i = 4$

$$w = \frac{4!}{2!\,(4-2)!} = \frac{4!}{2!\,2!}$$

$$= \frac{4 \times 3 \times 2 \times 1}{2 \times 1 \times 2 \times 1} = 6$$

5) Obtain the probability distribution for a system of four particles distributed in such a way that two are in E_0, none in E_1, and one each in E_2 and E_3

We have $$W = \frac{N!}{n_0!n_1!n_2!n_3!}$$

Given N = 4, $n_0 = 2$, $n_1 = 0$, $n_2 = 1$ and $n_3 = 1$

$$w = \frac{4!}{2!\,0!\,1!\,1!} = \frac{4 \times 3 \times 2 \times 1}{2 \times 1 \times 0 \times 1 \times 1} = \frac{24}{2 \times 1 \times 1 \times 1 \times 1} \; since\ 0! = 1$$

W=12

2.10 Summary of the unit

In statistical mechanics, Maxwell–Boltzmann statistics describes the average distribution of non-interacting material particles over various energy states in thermal equilibrium, and is applicable when the temperature is high enough or the particle density is low enough to render quantum effects negligible.

The distribution function f(E) is the probability that a particle is in energy state E. The distribution function is a generalization of the ideas of discrete probability to the case where energy can be treated as a continuous variable. Three distinctly different distribution functions are found in nature. The term A in the denominator of each distribution is a normalization term which may change with temperature.

Maxwell-Boltzmann (classical)

$$f(E) = \frac{1}{Ae^{E/kT}}$$

Bose-Einstein (quantum)

$$f(E) = \frac{1}{Ae^{E/kT} - 1}$$

Fermi-Dirac (quantum)

$$f(E) = \frac{1}{Ae^{E/kT} + 1}$$

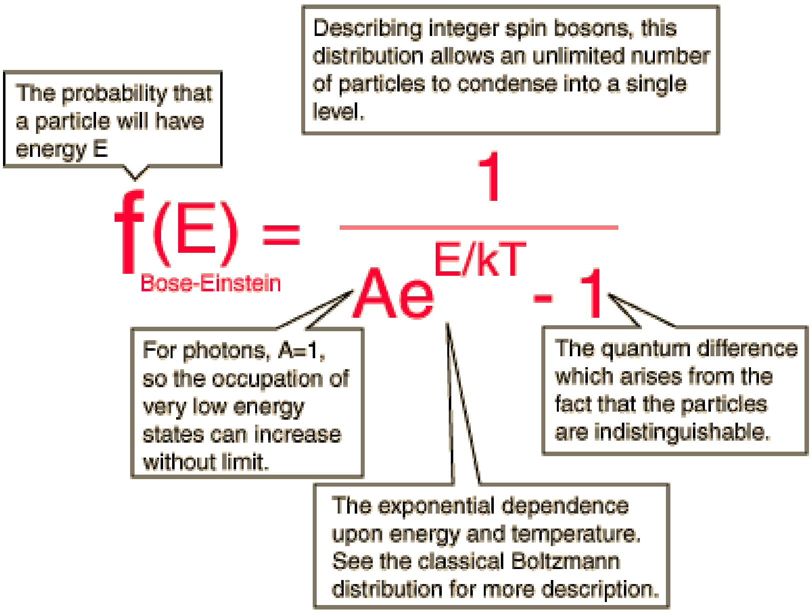
Maxwell-Boltzmann (Classical) distribution is identical but distinguishable particles, example; Molecular speed distribution. Besides the presumption of distinguishability, classical statistical physics postulates further that:

There is no restriction on the number of particles which can occupy a given state.

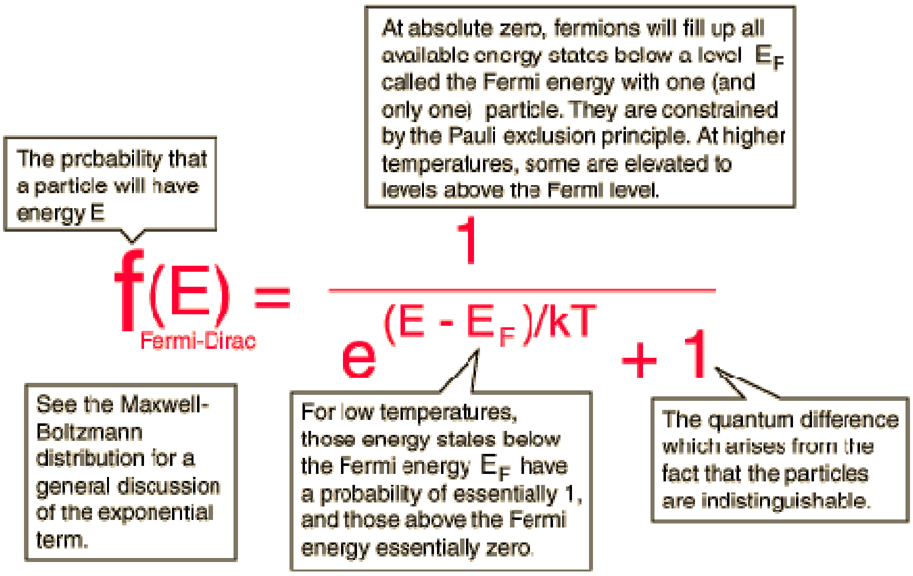
At thermal equilibrium, the distribution of particles among the available energy states will take the most probable distribution consistent with the total available energy and total number of particles.

Every specific state of the system has equal probability.

The Bose-Einstein distribution describes the statistical behavior of integer spin particles (bosons). At low temperatures, bosons can behave very differently than fermions because an unlimited number of them can collect into the same energy state, a phenomenon called "condensation". Bose-Einstein (quantum) distribution is identical indistinguishable particles with integer spin (bosons), example; thermal radiation Specific heat.



The Fermi-Dirac distribution applies to fermions, particles with half-integer spin which must obey the Pauli Exclusion Principle. Each type of distribution function has a normalization term multiplying the exponential in the denominator which may be temperature dependent. Fermi-Dirac (quantum) identical indistinguishable particles with half-integer spin (fermions), example, Electrons in a metal, Conduction in semiconductor. The significance of the Fermi energy is most clearly seem by setting T=0. At absolute zero, the probability is = 1 for energies less than the Fermi energy and zero for energies greater than the Fermi energy. We picture all the levels up to the Fermi energy as filled, but no particle has a greater energy. This is entirely consistent with the Pauli Exclusion Principle where each quantum state can have one but only one particle.



$$f(E)_{\text{Fermi-Dirac}} = \frac{1}{e^{(E - E_F)/kT} + 1}$$

At absolute zero, fermions will fill up all available energy states below a level E_F called the Fermi energy with one (and only one) particle. They are constrained by the Pauli exclusion principle. At higher temperatures, some are elevated to levels above the Fermi level.

The probability that a particle will have energy E

See the Maxwell-Boltzmann distribution for a general discussion of the exponential term.

For low temperatures, those energy states below the Fermi energy E_F have a probability of essentially 1, and those above the Fermi energy essentially zero.

The quantum difference which arises from the fact that the particles are indistinguishable.

2.11 Key words

Maxwell - Boltzmann statistics; Evaluation of molar entropies; Quantum statistics

Bose – Einstein Statistics; Fermi-Dirac Statistic

2.13References for further study

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2.13 Questions for self understanding

1) Derive the Boltzmann distribution.

2) Write the formula for the partition function.

3) Explain the relationships between number of microstates and entropy, and the distribution parameter β and thermodynamic temperature.

4) Give the relationships between energy and partition function

5) Derive the equation for Maxwell - Boltzmann statistics

6) Illustrate Maxwell - Boltzmann statistics

7) Evaluate the molar entropies

8) Discuss about quantum statistics

9) Evaluate Bose – Einstein Statistics

10) Evaluate Fermi-Dirac Statistics

11) Explain the comparison between Maxwell–Boltzmann (M-B), Bose –Einstein (B-E) and Fermi-Dirac (F-D) Statistics

UNIT-3

Structure

3.0 Objectives of the unit

3.1 Introduction

3.2 Partition functions (Q)

3.3 Molar partition function (Z)

3.4 Determination of partition function

3.5 Translational partition function (Q_{tr})

3.6 Problem

3.7 Rotational partition function (Qr)

3.8 Problem

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3.11 Total partition function (Q)

3.12 Summary of the unit

3.13 Key words

3.14 References for further study

3.15 Questions for self understanding

3.0 Objectives of the unit

After studying this unit you are able to

- Explain the significance of partition functions (Q)
- Write the equation for calculating molar partition function (Z)
- Write the equation for calculating translational partition function (Q_{tr})
- Write the equation for calculating rotational partition function (Qr)
- Write the equation for calculating vibrational partition function (Q_v)
- Write the equation for calculating electronic partition function (Q_e)
- Write the equation for calculating total partition function (Q) of a molecule or atom

3.1 Introduction

Partition functions play a central role in statistical mechanics. They are the key to calculating the thermodynamics functions. The mathematical definition is

$$q = \sum g_i e^{-\varepsilon i / kT}$$

where g_i = the degeneracy of energy level ε_i

Molecules will distribute themselves over the available energy levels according to the Boltzmann distribution. Physical interpretation of q is the measure of the number of thermally accessible energy states. Note that it is a function of the pattern of energy levels (ε_i) and temperature (T)

3.2 Partition functions (Q)

Let us consider a gas containing N molecules. As is well known, all the N molecules will not possess the same energy. If n_i molecules each having energy E_i, then according to Man well-Boltzmann distribution law, we have

$$n_i = \frac{N g_i e^{\frac{-E_i}{kT}}}{\sum g_i e^{\frac{-E_i}{kT}}} \quad \text{-------(95)}$$

If n_0 molecules each having energy E_0, then

We have

$$n_0 = \frac{N g_0 e^{\frac{-E_0}{kT}}}{\sum g_i e^{\frac{-E_i}{kT}}} \quad \text{------(96)}$$

Dividing (95) by (96)

$$\frac{n_i}{n_0} = \frac{g_0 e^{\frac{-E_i}{kT}}}{\sum g_0 e^{\frac{-E_i}{kT}}} = \frac{g_i e^{\frac{-(E_i - E_o)}{kT}}}{g_0} \text{------------- (97)}$$

It has been shown by wave mechanics that even at absolute zero of temperature, a molecule will have a definite amount of energy called the *Zero point energy*. If E_0 is the zero point energy, for computational purposes, it can be taken as equal to zero ie, this is taken as the reference state to assign energies for the molecules in other states.

Equation (97) can be written as

$$n_i = \frac{n_0 g_i e^{\frac{-E_i}{kT}}}{g_0} \qquad \text{---------------(98)}$$

But N = $n_0 + n_1 + n_3 + \ldots .. + n_i$

$$\therefore N = \frac{n_0 g_0 e^{\frac{-E_0}{kT}}}{g_0} + \frac{n_0 g_1 e^{\frac{-E_1}{kT}}}{g_0} + \frac{n_0 g_2 e^{\frac{-E_2}{kT}}}{g_0} + \cdots ..$$

$$= \frac{n_0}{g_0}\left[g_0 e^{\frac{-E_0}{kT}} + g_1 e^{\frac{-E_1}{kT}} + g_2 e^{\frac{-E_2}{kT}} + \cdots\right]$$

$$N = \frac{n_0}{g_0} \sum g_i e^{\frac{-E_i}{kT}}$$

$$\text{Or } N = \frac{n_0}{g_0} \; Q - - - -(99)$$

Where $Q = \sum g_i e^{\frac{-E_i}{kT}}$ and is called the Partition function

Partition function actually tells us how the molecules in a system are partitioned between various energy levels. It is evident from the expression that if g values are large, large values of Q are obtained. Knowing the value of partition function, one can calculate various thermodynamic quantities. However, there is only one condition that the system must consist of an ideal or virtually ideal gas. If the statistical weight factor for each energy level is unity, then $Q = \sum e^{\frac{-E_i}{kT}}$ molecular partition function. Since g_i =1.Q is a molecular partition function.

3.3 Molar partition function (Z)

Invariably one has to deal with large-scale systems in which the amounts of substances are in gm moles.

Let us consider a system which may be supposed to be constituted a large number of smaller ones each with a gm mole of the substance, ie, the individual unit is not the molecule but a mole. Let there are z systems and in each of these there any Avogadro number of molecules.

Then the average energy (E) of such a unit is given by

$$E = \frac{\sum x_i E_i}{\sum x_i}$$

If Z is the partition function

$$Z = \sum e^{\frac{-E_i}{kT}}$$

It is possible to show that

$$E = kT^2 \left(\frac{d \ln Z}{dT}\right) ------ (100)$$

Where Z is the molar partition function but we know that the energy of a gm-mole is given by the equation

$$E = NkT^2 \left(\frac{d \ln Z}{dT}\right) = kT^2 \left(\frac{d \ln Q^N}{dT}\right) ----(101)$$

$$Z = Q^N ----(102)$$

where Z is a molar partition function, Q is a molecular partition function and N is the Avogadro number.

3.4 Determination of partition function

The total energy E_i possessed by a molecule is the contribution of various types of energies such as translational (E_{tr}), rotational (E_r), vibrational (E_v), Electronic (E_e) etc. For most of the polyatomic molecules except for NO and O_2, the electronic contribution to the total energy can be ignored at ordinary temperature but at high temperature, its contribution will be quite considerable. So, it is possible to write

$$E_i = E_{tr} + E_r + E_v + E_e + \cdots$$

$$e^{\frac{-E_i}{kT}} = e^{\frac{-E_{tr}}{kT}} . e^{\frac{-E_r}{kT}} . e^{\frac{-E_e}{kT}}$$

and $Q = \sum g_i e^{\frac{-E_i}{kT}}$

And each exponential in this equation may be taken as the product of a number of terms of the same type one for each kind of energy. Also, the product of separate factors for various kinds of energy.

$$Q = \sum \left(g_{tr} e^{-E_r/kT} . g_r e^{-E_r/kT} . g_v e^{-E_v/kT} . g_e e^{-E_e/kT} \right)$$

Here $\sum g_{tr} e^{-E_{tr}/kT} = Q_{tr} = translation\ partition\ function$

$$\sum g_r e^{-E_r/kT} = Q_r = rotaional\ partition\ function$$

$$\sum g_v e^{-E_v/kT} = Q_v = vibrational\ partition\ function$$

$$\sum g_e e^{E/kT} = Q_e = eectronic\ partition\ function$$

The above equation can be written as

$$Q = Q_{tr}. Q_r. Q_v. Q_e - - - - (103)$$

This multiplicative property of the partition function for different kinds of energy makes it possible to calculate the partition function even in quite complicated cases.

$$\log Q = \log Q_{tr} + \log Q_r + \log Q_v + \log Q_e$$

$$E = kT^2 \left(\frac{d \ln Q_{tr}}{dT} \right) + kT^2 \left(\frac{d \ln Q_r}{dT} \right) + kT^2 \left(\frac{d \ln Q_v}{dT} \right) + kT^2 \left(\frac{d \ln Q_e}{dT} \right)$$

$$C_V = \frac{\delta}{\delta T} \left[kT^2 \left(\frac{d \ln Q_{tr}}{dT} \right)_v \right] + \frac{\delta}{\delta T} \left[kT^2 \left(\frac{d \ln Q_r}{dT} \right)_v \right] + \frac{\delta}{\delta T} \left[kT^2 \left(\frac{d \ln Q_v}{dT} \right)_v \right] + \frac{\delta}{\delta T} \left[RT^2 \left(\frac{d \ln Q_e}{dT} \right)_v \right]$$

Were E is the total energy and C_v s the heat capacity at constant volume

3.5 Translational partition function (Q_{tr})

All kinds of molecules – monatomic as well as polyatomic possess translational energy. The quantum mechanical expression for the translational energy per molecule $[E_{tr}]$ in one direction is given by

$$E_{tr} = \frac{n^2 h^2}{8ml^2} \text{----(104)}$$

Were n is the translational quantum number, m is a mass and *l* is the length of the container. The translational partition function of a molecule ($Q_{tr}(1)$) in one direction is given by

$$\therefore Q_{tr} = \sum g_{tr} e^{-E_{tr}(1)/kT}$$

The statistical weight factor for each translational energy level is unity. Hence, $g_{tr} = 1$

$$Q_{tr} = \sum e^{-E_r/kT} ------ (105)$$

Substituting for E_{tr} in equation (105)

$$Q_{tr}(1) = \sum e^{-E_{tr}(1)/kT} ----(106)$$

Since the translational energy levels are closely spaced ie, to say the quanta are extremely small, the summation in equation (106) may be replaced by integration

Thus $Q_{tr} = \int_0^\infty e^{-n^2h^2/8ml^2kT} ----(107)$

Put $\propto^2 = \frac{n^2h^2}{8ml^2kT} \quad \therefore n^2 = \frac{8ml^2kT}{h^2}\propto^2$

$$n = \frac{l \propto}{h}(8mkT)^{1/2}$$

$$\therefore dn = \frac{l}{h}(8mkT)^{1/2}\, d\alpha$$

Substituting the value of dn in equation (107)

We get $Q_{tr(1)} = \int_0^\infty e^{-\propto^2}\frac{l}{h}(8mkT)^{1/2} d \propto$

$Q_{tr} = \frac{l}{h}(8mkT)^{1/2}\int_0^\infty e^{-\propto^2}\ d \propto$------(108)

This is a definite integral whose value is $\frac{\sqrt{\pi}}{2}$

Substituting the value of the integral in equation (108)

We get $$Q_{tr} = \frac{l}{h}(8mkT)^{1/2}.\frac{\sqrt{\pi}}{2}$$

$$Q_{tr} = \frac{(2\pi mkT)^{1/2}}{h}.l ----(109)$$

Since the contributions for the three translational degrees of freedom are the same, the total translational partition function (Q_{tr}) for a molecule is

$$Q_{tr} = \frac{(2\pi mkT)^{3/2}}{h^3}l^3 ----(110)$$

Since l^3=V

$$Q_{tr} = \frac{(2\pi mkT)^{1/2}}{h^3}V ----(111)$$

For one mole of an ideal gas PV=RT or V= $\frac{\mathrm{RT}}{P}$

$$\therefore Q_{tr} = \frac{(2\pi mkT)^{3/2}}{h^3} . \frac{RT}{p} - - - - (112)$$

Equations (110), (111) and (112) are the expressions for translational partition function.

The translational energy (E_{tr}) is given by

$$E_{tr} = RT^2 \left(\frac{d \ln Q_{tr}}{dT}\right) - - - (113)$$

Substituting for Q_{tr} in equation (113)

$$E_{tr} = RT^2 \left[\frac{d}{dT}\left\{ln \ \frac{(2\pi mkT)^{1/2}}{h^3} V\right\}\right]$$

As $\pi, R, m, V \ and \ h \ are \ constants$

$$E_{tr} = RT^2 \left[\frac{d}{dT} \ln \frac{(2\pi mk)^{3/2}}{h^3} \ V + \frac{d}{dT} \ (\ln T)^{3/2}\right]$$

$$E_{tr} = RT^2 \left[\frac{3}{2} . \frac{1}{T}\right] = \frac{3}{2} RT - - - (114)$$

$$\therefore C_v = \left(\frac{dE_{tr}}{dT}\right)_V = \frac{d}{dT}\left(\frac{3}{2} RT\right)$$

$$C_v = \frac{3}{2} R - - (115)$$

3.6 Problem

Calculate the translational partition function for one mole of oxygen at 1 atm and 25^0 c assuming the gas to behave ideally.

We have $Q_{tr} = \frac{(2\pi mkT)^{3/2}}{h^3} \frac{RT}{P}$

$$m = \frac{32}{6.023 \times 10^{23}} = 5.313 \times 10^{-23} g$$

P= 1 atom, T=273+25=298K

R=82.06 cc atm

k=1.38×10^{-6} erg

$$Q_{tr} = \frac{(2 \times 3.14 \times 5.313 \times 10^{-16} \times 298)}{(6.624 \times 10^{-27})^3}$$

$$Q_{tr} = 4.28 \times 10^{30}$$

To work

Calculate the translational partition function for one mole of N_2 at 1 atm and 25^0c assuming the gas to behave ideally.

3.7 Rotational partition function (Qr)

The rotational energy of a molecule E_r depends on the rotational quantum number J. the statistical weight factor for each rotational energy level is given by

$$g_r = (2J + 1)$$

The rotational partition function is given by

$$Q_r = \sum g_r e^{-\frac{E_r}{kT}}$$

$$\sum(2J + 1)g_r e^{-\frac{E_r}{kT}} \text{-------------- (116)}$$

Assuming the diatomic molecule to be a region rotator, the rotational energy is given by

$$E_r = \frac{h^2}{8\pi^2 I}J(J + 1)$$

Where I is the moment of inertia whose value is given by $I = \mu r^2$ where μ is the reduced mass and r is the inter nuclear distance

But $\mu = \frac{m_1+m_2}{m_1 m_2}$

where m_1 and m_2 are the masses of atoms in a diatomic molecule.

Substituting the value of E_r in equation (116)

We get $Q_r = \sum(2J + 1)\, e^{-\frac{h^2}{8\pi^2 I}\frac{J(J+1)}{kT}}$ ------- (117)

Put $\alpha = \frac{h^2}{8\pi^2 IkT}$ and $\beta = J(J + 1)$

Therefore $Q_r = \sum(2J + 1)\, e^{-\alpha\beta}$----------- (118)

Assuming that the rotational energy levels are very closely spaced, the summation in (118) may be replaced by integration

$Q_r = \int_0^\infty (2J + 1)e^{-\alpha\beta} dJ$----------- (119)

$$\beta = J(J + 1) = J^2 + J$$

$$d\beta = 2JdJ + dJ = dJ(2J + 1)$$

Or $dJ = \frac{d\beta}{(2J+1)}$

Inserting the value of d*J* in equation (119)

$$Q_r = \int_0^\infty (2J + 1)e^{-\alpha\beta}\frac{d\beta}{(2J + 1)}$$

$$Q_r = \int_0^\infty e^{-\alpha\beta} d\beta \text{------- (120)}$$

This is definite integral whose value is $\frac{1}{\alpha}$

Therefore $$\frac{1}{\alpha} = \frac{8\pi^2 IkT}{h^2}$$

Or $$Q_r = \frac{8\pi^2 IkT}{h^2} \text{ ------------- (121)}$$

Equation (121) is applicable to heteronuclear diatomic molecules such as HCl, CO, NO etc. but for hononuclear diatomic molecules, the equation (121) can be modified as

$$Q_r = \frac{8\pi^2 IkT}{\sigma h^2}$$

Were σ is called symmetry factor and its value depends on the nature of the molecule.

Example σ = 2 for O_2, N_2, H_2, etc.…

σ = 1 for CO, HCl, NO etc.….

the rotational energy (E_r) is given by

$$E_r = RT^2\left(\frac{dlnQ_r}{dT}\right)$$

$$= RT^2\left[\frac{d}{dT}ln\left(\frac{8\pi^2 IkT}{h^2}\right)\right]$$

$$E_r = RT^2.\frac{1}{T}$$

$$E_r = RT \text{ ------------- (123)}$$

$$C_v = \left(\frac{dE_r}{dT}\right)_v = \frac{d(RT)}{dT}$$

$$C_v = R \text{------- (124)}$$

3.8 Problem

Calculate the rotational partition function for N_2 molecule at 25^0c

Given $\sigma_{N_2} = 2, I_{N_2} = 13.9\ X10^{-40} gcm^2$

$$Q_r = \frac{8\pi^2 IkT}{\sigma h^2}$$

k = $1.38X10^{-16}$ erg

h = $6.624 \text{ X } 10^{-27}$ erg

T = 273 + 25 = 298K

$$= \frac{8\ X\ (3.14)^2 X\ 13.9\ X10^{-40} X\ 1.38\ X\ 10^{-16} X\ 298}{2\ X\ (6.624\ X10^{-27})^2}$$

= 51.38

To work Calculate the rotational partition function for CO molecule at 25^0c

Given $\sigma = 1, I_{CO} = 14.5\,X10^{-40} gcm^2$

3.9 Vibrational partition function (Q_v)

The vibrational energy of a linear harmonic oscillator is given by the expression

$$E_v = \left(V + \frac{1}{2}\right) h\vartheta$$

Where V is the vibrational quantum number which can have values 0,1,2….. and ϑ is the frequency of vibration.

In the ground state, V = 0

$$E_v = \left(\frac{1}{2}\right) h\vartheta$$

So the vibrational energy of a molecule in excess of the zero point energy is given by

$$E_v = \left(V + \tfrac{1}{2}\right) h\vartheta - \tfrac{1}{2} h\vartheta \qquad \text{(Zero point energy)}$$

$$E_v = Vh\vartheta \text{---------- (125)}$$

The vibrational partition function is given by

$$Q_v = \sum g_v e^{-\frac{E_v}{kT}} \text{-------------- (126)}$$

The statistical weight factor of each vibrational energy level is unity ie,$g_v = 1$

Equation (129) becomes

$$Q_v = \sum e^{-\frac{E_v}{kT}} = \sum e^{-\frac{Vh\vartheta}{kT}} \text{------- (127)}$$

Put $\frac{h\vartheta}{kT} = x$ and V= 0,1, 2…..etc

$$Q_v = 1 + e^{-x} + e^{-2x} + e^{-3x} + ------$$

$$= (1 - e^{-x})^{-1}$$

$$Q_v = \frac{1}{(1-e^{-x})} = \frac{1}{\left(1-e^{-\frac{h\vartheta}{kT}}\right)} \text{----------- (128)}$$

But $\vartheta = C\omega_e$ where C is the velocity of light and ω_e is the fundamental vibrational partition function.

The vibrational energy is given by

$$E_v = RT^2 \left(\frac{dlnQ_v}{dT}\right)$$

$$= RT^2 \left[\frac{d}{dT} ln \frac{1}{\left(1 - e^{-\frac{h\vartheta}{kT}}\right)} \right]$$

After simplification, we get

$$E_v = \frac{RT\left(\frac{h\vartheta}{kT}\right)}{\left(e^{\frac{h\vartheta}{kT}} - 1\right)} \text{-------- (130)}$$

$$C_v = \left(\frac{dE_v}{dT}\right)_v = \frac{d}{dT}\left[\frac{RT\left(\frac{h\vartheta}{kT}\right)}{\left(e^{\frac{h\vartheta}{kT}} - 1\right)}\right]$$

$$C_v = R\left(\frac{h\vartheta}{kT}\right)^2 \frac{e^{\frac{h\vartheta}{kT}}}{\left(e^{\frac{h\vartheta}{kT}} - 1\right)^2} \text{------------- (131)}$$

Equation (131) is the expression for C_v for one linear vibration

For vibrations of atoms in three directions we have

$$C_v = 3R\left(\frac{h\vartheta}{kT}\right)^2 \frac{e^{\frac{h\vartheta}{kT}}}{\left(e^{\frac{h\vartheta}{kT}} - 1\right)^2} \text{------------- (132)}$$

3.10 Electronic partition function (Q_e)

The statistical weight factor for each electronic energy level $g_e = (2J + 1)$ where J is the electronic quantum number,

The electronic partition function is given by

$$Q_e = \sum g_e e^{-\frac{E_e}{kT}}$$

$$Q_e = \sum(2J + 1)e^{-\frac{E_e}{kT}} \text{--------- (133)}$$

At moderate temperature, most of the atoms and molecules remain in the ground state as electronic energy separation is very large.

Hence $E_e = 0$

Therefore $Q_e = 1$

3.11 Total partition function (Q)

The total partition function is given by

$$Q = Q_{tr}\ X\ Q_r\ X\ Q_v\ X\ Q_e$$

$$Q = \frac{(2\pi kT)^{\frac{3}{2}}}{h^3} V \, X \, \frac{8\pi^2 IkT}{\sigma h^2} \, X \, \frac{1}{\left(1-e^{-\frac{h\vartheta}{kT}}\right)} \, X \, 1 \text{------- (134)}$$

3.12 Summary of the unit

The partition function comes from a way of counting the particles of a system when the particles are distributed over the available energy levels in accord with the Boltzmann distribution.

The way to count the particles Count the particles like this. First, represent the total number of particles by N. Then represent the number in the lowest energy level, or ground state, by n_0, represent the number in the first excited state by n_1, the number in the second excited state by n_2, and so on. Then represent the total number of particles, N, as the sum of the numbers in each energy level:

$$N = n_0 + n_1 + n_2 + n_3 + n_4 \,.....$$

In the Boltzmann distribution the number of particles in the first excited state is a fraction of the number of particles in the ground state, and that fraction is $\frac{1}{e^{\varepsilon_1/kT}}$, where ε_1 is the energy of the first excited state, relative to the ground state, k is Boltzmann's constant, and T is the absolute temperature. Represent the number of particles in the first excited state as n_0 times this fraction: $n_0 \frac{1}{e^{\varepsilon_1/kT}}$

The number of particles in the second excited state is also a fraction of the number of particles in the ground state, and this second fraction is $\frac{1}{e^{\varepsilon_2/kT}}$. This second fraction, however, is smaller than the first fraction because ε_2 is greater than ε_1. Represent the number of particles in the second excited state as n_0 times this second fraction: $n_0 \frac{1}{e^{\varepsilon_2/kT}}$.

The partition function is the ratio of the total number of particles to the number of particles in the ground state. The partition function is the number of times larger the total number of particles is than the number of particles in the ground state. The partition function is a measure of the degree to which the particles are spread out over, or partitioned among, the energy levels. The partition function can also be seen to be the total number of particles expressed as the sum of the numbers of particles of each energy, with the population of the ground state being the unit of measure of population The population of the ground state (the most highly populated state) is taken to be 1, and the populations of the other energy states are expressed as fractions of the population of the ground state. Considered in this way the partition function can be seen as a sum of the relative occupancies of states. It is for this reason that the partition function is also called the sum-overstates, or Zustandsumme.

3.13 Key words

Partition functions (Q); Molar partition function (Z); Translational partition function (Q_{tr}); Rotational partition function (Qr); Vibrational partition function (Q_v); Electronic partition function (Q_e); Total partition function (Q)

3.15 References for further study

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3.15 Questions for self understanding

1) Explain partition functions (Q) and its significance

2) Write a note on molar partition function (Z)

3) Write a note on determination of partition function

4) Derive the expression of calculating the translational partition function (Q_{tr})

5) Derive the expression of calculating the Rotational partition function (Qr)

6) Derive the expression of calculating the Vibrational partition function (Q_v)

7) Derive the expression of calculating the Electronic partition function (Q_e)

8) Write the equation of total partition function (Q)

UNIT-4

Structure

4.0 Objectives of the unit

After studying this unit you are able to

- Evaluate the thermodynamic functions in terms of partition functions
- Evaluate the equilibrium constant from partition functions
- Evaluate the entropy of a monatomic gas (Sacker – Tetrad equation)
- Compare the third law of thermodynamics and statistical entropies
- Compare the heat capacity behavior of solids (classical Approach)
- Explain the quantum theory of heat capacities
- Write the Einstein equation
- Write the Debye equation
- Explain the Debye characteristic temperature (θ)

4.1 Introduction

In this unit we will apply the concepts of statistical thermodynamics to the calculation of chemically significant quantities. First, we establish the relations between thermodynamic functions and partition functions. Next, we show that the molecular partition function can be factorized into contributions from each mode of motion and establish the formulas for the partition functions for translational, rotational, and vibrational modes of motion and the contribution of electronic excitation. These contributions can be calculated from spectroscopic data. Finally, we turn to specific applications, which include the mean energies of modes of motion, the heat capacities of substances, and residual entropies. In the final section, we see how to calculate the equilibrium constant of a reaction and through that calculation understand some of the molecular features that determine the magnitudes of equilibrium constants and their variation with temperature.

A partition function is the bridge between thermodynamics, spectroscopy, and quantum mechanics. Once it is known, a partition function can be used to calculate thermodynamic functions, heat capacities, entropies, and equilibrium constants. It also sheds light on the significance of these properties.

4.2 Evaluation of thermodynamic functions in terms of partition functions

It is possible to utilize the partition function and the Maxwell-Boltzmann distribution equation to evaluate various thermodynamic parameters.

7. Internal energy (E)

The internal energy of a system containing N molecules is given by

$$E = \sum n_i E_i$$

According to Maxwell - Boltzmann distribution law

$$n_i = \frac{Ne^{-\frac{E_i}{kT}}}{Q}$$

Therefore $E = \sum E_i \frac{N}{Q} e^{-\frac{E_i}{kT}} = \frac{N}{Q} \sum E_i e^{-\frac{E_i}{kT}}$------------ (135)

But $Q = \sum e^{-\frac{E_i}{kT}}$

Differentiating the above equation with respect to T

$$\left(\frac{dQ}{dT}\right) = \frac{1}{kT^2} \sum E_i e^{-\frac{E_i}{kT}}$$

Therefore $\sum E_i e^{-\frac{E_i}{kT}} = kT^2 \left(\frac{dQ}{dT}\right)$------------ (136)

Substituting equation (136) in equation (135) we get

$$E = \frac{N}{Q} kT^2 \left(\frac{dQ}{dT}\right)$$

$$= NkT^2 \left(\frac{dlnQ}{dT}\right)$$

$$E = RT^2 \left(\frac{dlnQ}{dT}\right) \text{------------------(137)}$$

8. Entropy (S)

We have from equation (55)

$$S = kNlnQ + k\beta E$$

But $\beta = \frac{1}{kT}$

Therefore $S = kNlnQ + \frac{E}{T}$

Substituting for E from equation (137) we get

$$S = kNlnQ + RT \left(\frac{dlnQ}{dT}\right)$$

$$S = RlnQ + RT \left(\frac{dlnQ}{dT}\right) \text{-------------- (138)}$$

3. Helmholtz free energy (A)

We know that $A = E - TS$

$$= E - T \left(kNlnQ + \frac{E}{T}\right)$$

$$= E - kNTlnQ + E$$

$$A = -RTlnQ$$---------- (139)

4. Pressure (P)

We know that

$$A\ =\ E - TS$$

$$dA = dE - TdS - SdT$$

But $$Dq = dE + PdV\ or\ dE = Dq - PdV$$

Therefore $$dA = Dq - PdV - TdS - SdT$$

$$dA = -PdV - SdT \quad \text{since } Dq = TdS$$

At constant temperature

$$\left(\frac{dA}{dV}\right)_T = -P$$

Or $$P\ =\ -\left(\frac{dA}{dT}\right)_T$$

$$= -\left(\frac{dA}{dQ}\right)_T\left(\frac{dQ}{dV}\right)_T$$---------------- (140)

But $$A\ =\ -RTlnQ$$

Or $$\left(\frac{dA}{dQ}\right)_T = -\frac{RT}{Q}$$

Substituting in equation (140)

$$P\ =\ \frac{RT}{Q}\left(\frac{dQ}{dV}\right)_T = RT\left(\frac{dlnQ}{dT}\right)_T$$-------------- (141)

5. Gibbs free energy (G)

We know that

$$G = A + PV$$

Substituting for A and P

$$G = -RTlnQ + RT\left(\frac{dlnQ}{dV}\right)_T . V$$

$$= -RTlnQ + RT\left(\frac{dlnQ}{dlnV}\right)_T$$

Or $$G = -RT\left[lnQ + \left(\frac{dlnQ}{dlnV}\right)_T\right]$$---------------- (142)

6. **Enthalpy or Heat content (H)**

$$H = E + PV$$

Inserting for E and P

$$H\ =\ RT^2\left(\frac{dlnQ}{dT}\right) + RT\left(\frac{dlnQ}{dV}\right)_T . V$$

$$= RT^2\left(\frac{dlnQ}{dT}\right) + RT\left(\frac{dlnQ}{dlnV}\right)_T$$

$$= RT\left(\frac{dlnQ}{dlnT}\right) + RT\left(\frac{dlnQ}{dlnV}\right)_T$$

$$H = RT\left[\left(\frac{dlnQ}{dlnT}\right) + \left(\frac{dlnQ}{dlnV}\right)_T\right] \text{------------- (143)}$$

7. Heat capacity (Cv)

$$C_V = \left(\frac{dE}{dT}\right)_V$$

But $E = RT^2\left(\frac{dlnQ}{dT}\right)$

$$\therefore\ C_V = \frac{d}{dT}\left[RT^2\left(\frac{dlnQ}{dT}\right)\right] \text{---------------- (144)}$$

4.3 Evaluation of Equilibrium constant from partition functions

We know that

$$E = E^0 + RT^2\left(\frac{dlnQ}{dT}\right) \text{------------- (145)}$$

$$S = Rln\frac{Q}{N} + RT\left(\frac{dlnQ}{dT}\right)_V + R \text{ ------------------ (146)}$$

$$G = H - TS = E + PV - TS$$

Or $G = E + R - TS$-------- (147) since $PV = RT$

Substituting the values for E and S in (147)

$$G = E^0 + RT^2\left(\frac{dlnQ}{dT}\right) + RT - T\left[Rln\frac{Q}{N} + RT\left(\frac{dlnQ}{dT}\right) + R\right]$$

$$G = E^0 + RT^2\left(\frac{dlnQ}{dT}\right) + RT - RTln\frac{Q}{N} - RT^2\left(\frac{dlnQ}{dT}\right) - RT$$

$$G = E^0 - RTln\frac{Q}{N} \text{---------- (148)}$$

We know that $H = E + PV = E + RT$

At 0K, $H^0 = E^0$

$$G^0 = H^0 - RTln\frac{Q}{N} \text{----------- (149)}$$

Consider a homogeneous gaseous reaction.

$$aA + bB \leftrightarrow cC + dD$$

where a, b, c and d are the number of moles of the substances A, B, C and D respectively.

$$\Delta G^0 = d(G^0)_D + c(G^0)_C - a(G^0)_A - b(G^0)_B$$

Inserting the values of G^0in the above equation

$$\Delta G^0 = d\left\{H_D^0 - RTln\left(\frac{Q_0}{N}\right)_D\right\} + c\left\{H_C^0 - RTln\left(\frac{Q_0}{N}\right)_D\right\} - a\left\{H_A^0 - RTln\left(\frac{Q_0}{N}\right)_A\right\}$$
$$- b\left\{H_B^0 - RTln\left(\frac{Q_0}{N}\right)_B\right\}$$

$$\Delta G^0 = \Delta H^0 - RTln\frac{\left(\frac{Q_0}{N}\right)_D^d\left(\frac{Q_0}{N}\right)_C^c}{\left(\frac{Q_0}{N}\right)_B^b\left(\frac{Q_0}{N}\right)_A^a} \text{------------ (150)}$$

We know that $\Delta G_0 = -RTlnK_P$

where K_p is the equilibrium constant

$$-RTlnK_P = \Delta H^0 - RTln\left[J_{\left(\frac{Q_0}{N}\right)}\right]$$

$$K_p = \left[J_{\left(\frac{Q_0}{N}\right)}\right] e^{-\frac{\Delta H^0}{RT}}$$

Or $$K_p = \frac{\left(\frac{Q_0}{N}\right)_D^d\left(\frac{Q_0}{N}\right)_C^c}{\left(\frac{Q_0}{N}\right)_B^b\left(\frac{Q_0}{N}\right)_A^a}\ e^{-\frac{\Delta H^0}{RT}} \text{---------- (151)}$$

The equilibrium constant for the reaction at any temperature can be calculated using equation (151)

4.4 Entropy of a monatomic gas (Sacker – Tetrad equation)

A monatomic gas will have only translational energy (and electronic energy it is considerable)

$$Q = Q_{tr}.Q_e$$

But $$Q_{tr} = \frac{(2\pi kT)^{\frac{3}{2}}}{h^3}.V$$

$$\therefore Q = \frac{(2\pi kT)^{\frac{3}{2}}}{h^3}.V.Q_e$$

$$lnQ_{tr} = ln\frac{(2\pi kT)^{\frac{3}{2}}}{h^3}.V$$

$$ln\frac{(2\pi k)^{\frac{3}{2}}}{h^3}.V + \frac{3}{2}lnT$$

$$\left(\frac{dlnQ_{tr}}{dT}\right) = \frac{3}{2}\frac{1}{T} \text{------------ (152)}$$

Multiplying equation (152) by RT we get

$$RT\left(\frac{dlnQ_{tr}}{dT}\right) = \frac{3}{2}R$$

Assuming Q_e to be independent of temperature the molar entropy is given by

$$S = Rln\frac{Q}{N} + RT\left(\frac{dlnQ}{dT}\right) + R\text{---------} \ (79)$$

$$= Rln\left[Q_e\frac{(2\pi kT)^{\frac{3}{2}}}{Nh^3}.V\right] + \frac{3}{2}R + R$$

$$= Rln\left[Q_e\frac{(2\pi kT)^{\frac{3}{2}}}{Nh^3}.\frac{RT}{P}\right] + \frac{5}{2}R\text{----------} \ (153)$$

Since $V = \frac{RT}{P}$

Equation (153) is called the sacker - Tetrad equation.

Equation (153) can be further simplified as

$$S = R\left[\frac{3}{2}lnm + \frac{5}{2}lnT - lnP + lnQ_e + ln\frac{R}{N}\left(\frac{2\pi k}{h^2}\right)^{\frac{3}{2}} + \frac{5}{2}\right]$$

Inserting the values of constants and on simplification

We get

$$S = 2.303R\left[\frac{3}{2}logM + \frac{5}{2}logT - logP + lnQ_e + logQ_e - 0.5033\right]$$

where M is the molecular weight of the substance. At P = 1 atm, we have the molar entropy of the substance behaving as an ideal gas.

Standard entropy

$$S^0 = 4.576\left[\frac{3}{2}logM + \frac{5}{2}logT + lnQ_e + logQ_e - 0.5033\right]\text{------------} \ (154)$$

where R = 1.987 cal/deg/mol

4.5 Problem

Calculate the standard entropy of atomic chlorine at 25^0C. given Qe = 4.03

We Have $S^0 = 4.576\left[\frac{3}{2}logM + \frac{5}{2}logT + logQ_e - 0.5033\right]$

Given M = 35.5, T = 273+25 = 298K, $Q_e = 4.03$

$$S^0 = 44.576\left[\frac{3}{2}\log 35.5 + \frac{5}{4}log298 + log4.03 - 0.5033\right]$$

$$S^0 = 39.4 \text{ cal/deg/mol}$$

4.6 Comparison of third law and statistical entropies

Entropies of substances calculated using the third law of thermodynamics are called third law entropies or thermal entropies while the entropies calculated using Boltzmann – Planck equation ($S = klnW$) are called statistical entropies. However, the statistical entropies are more rigorous. It is found that the thermal entropies are lower than the statistical entropies, the deviation ranging from 3.1 to 4.8 $JK^{-1}mol^{-1}$. One can conclude that the entropies of substances such as H_2, D_2, CO, NO, N_2O, H_2O etc are not zero at 0K as the third law predicts but are finite. *These entropies are called residual entropies*. The existence of residual entropy in a crystal at 0K is probably due to the alternative arrangements of molecules in the solid. Such arrangements in the case of CO and N_2O are shown below :

Alternative molecular arrangements

CO COCOCO	CO COOC OC
CO COCOCO	CO OC OCCO
NNO NNONNONNO	NNONNO ONN ONN
NNO NNONNONNO	NNO ONN ONN NNO
Perfect crystal	Actual crystal

Thus, close to 0K each molecule can assume two states, so the entropy of a crystal containing N molecules is given by

$S = k$lnW with $W = 2^N (Where\ N\ is\ the\ Avogardo\ number)$

$$S = NklnW = since\ Nk = R$$

$$= 8.314\ X2.303\ lof2$$

$$= 5.76 JK^{-1}mol^{-1}$$

Since the residual entropies are found to be less experimentally than this value, it is evident that the two alternative orientations of the CO and N_2O molecules in the solid state at 0K are not completely random.

The thermal entropies of H_2 and D_2 are also less than the corresponding statistical entropies. The calculation of statistical entropy assumes that there exists an equilibrium between ortho H_2 and para H_2 at all temperature. The entropy of mixing of ortho H_2 and para H_2 is found to be 18.37 $JK^{-1}mol^{-1}$ in the vicinity of 0K. When this value is added to the thermal entropy the agreement with the statistical entropy is very good.

The occurrence of residual entropy in ice is also attributed to the molecular disorder at 0K. In ice crystals, each water molecule is tetrahedral coordinated to four other water molecules by hydrogen bonds. The hydrogen atoms of each hydrogen bond can exist in either of the two potential energy minima. This enables the crystal to exist in many configurations at 0K. On this basis the residual entropy can be calculated to be 3.4 $JK^{-1}mol^{-1}$ which is in close agreement with the observed value.

4.7 Heat capacity behavior of solids (classical Approach)

An ideal solid may be assumed to consist of a space lattice of independent atomic units and the constituent particles take up equilibrium positions of minimum potential energy, where the forces of attraction and repulsion exacts balance each other.

The atoms or ions are not at rest but vibrate about their equilibrium positions even at absolute zero and as the temperature is raised, the amplitude of vibration increases and hence so also the potential and kinetic energies. It is the rate of increase of vibrational energy with temperature that determines the heat capacity of the solid. Before understanding the subject from theoretical stand point, let us first examine some experimental facts.

Dulong and Petit found that the product of the atomic weight and specific heat of solid elements was constant ie, *all solid elements have the same heat capacity per gram atom or the atoms of all elements have the same heat capacity. Any of these statements may be taken as the statement of the law of Dulong and petit.*

This law is not exact but the data given below

Element	**Atomic weight**	**Heat capacity (cal)** (Cv)
Li	7	6.4
Al	27	5.7
Ca	40	6.0
Fe	56	`6.2
Au	75	6.2
Ag	108	6.2
I	127	6.6
Ta	181	5.9
Hg	200	6.6
U	238	6.4

We know that

$$PV = \frac{1}{3}Nm\overline{C^2}$$

Where N is the number of molecules of mass m and $\overline{C^2}$ is the mean square velocity. In a gram atom, there are N atoms. Vibrations may occur in three directions. Each direction will have two degrees of freedom and each degree of freedom will have energy $\frac{1}{2}kT$

$$E = NX\ 3\ X\ 2\ X\ \frac{1}{2}kT = 3RT$$

$$PV = \frac{1}{3} Nm\overline{C^2} = RT$$

$$= \frac{2}{3} X \frac{1}{2} Nm\overline{C^2} = RT$$

$$Nm\overline{C^2} = 3RT$$

$$C_V = \left(\frac{dE}{dT}\right)_V$$

$$\left[\frac{d(3RT)}{dT}\right]_V$$

$C_V = 3R = 3X1.987 \sim 6$ Cals/deg/mol

since R = 1.987 Cal/deg/mol

The heat capacities are almost about 6.2 ± 0.4 cals /deg/ mol in a range of atomic weight from 7 to 238. However, certain elements namely Be, B, C and Si showed exceptionally low heat capacities, the values being 3.5, 2.5. 1.35 (diamond) and 4.7 cal/deg respectively. The heat capacities of these elements increased rapidly with rise in temperature.

Ex : For diamond

Temp (^{0}C):	-50	10.7	35.5	206	615	808
Heat capacity (Cv in cal / deg)	0.76	1.185	2.11	3.28	5.33	5.44

It was thought possible that the Dulong and Petit law would apply to all substances at elevated temperature. This view was incorrect however for the heat capacities of those elements which appear to obey the law at ordinary temperature increase to some extent with increasing temperature and for several elements, values as high as 9 cal are attained at melting temperature. Dulong and petite’s observation of atomic heat capacity of 6 cal / dag has shown to be of theoretical significance.

4.8 Quantum theory of heat capacities

The classical theory given above not only requires the atomic heat capacity to be 3R per gram atom but it should be independent of temperature; all specific heats increase with temperature and the effect is more marked for the light elements whose heat capacity is exceptionally low. And the atomic heats of those elements having values of about 6cal/deg at normal temperature diminish at low temperature. There are two theories of heat capacities namely Einstein theory and Debye theory.

4.9 The Einstein equation

An important step was taken by Einstein when he applied the quantum theory to the problem of the heat capacity of solids. According to Planck the average energy of vibration ($\bar{E}$) of a linear oscillator ie oscillating in one direction in space in exec as of the geropoint energy is given by

$$\bar{E} = \frac{h\vartheta}{\left(e^{\frac{h\vartheta}{kT}}-1\right)} \text{ ---------- (155)}$$

One gram atom of an element can however be regarded as a system of 3N linear oscillators, N being the Avogadro number. The energy per gram atom is given by

$$E = 3N\frac{h\vartheta}{\left(e^{\frac{h\vartheta}{kT}}-1\right)} \text{ ---------- (156)}$$

The Einsein equation for the heat capacity at constant Volume is

$$C_V = \left(\frac{dE}{dT}\right)_V = \frac{d}{dT}\left[3N\frac{h\vartheta}{\left(e^{\frac{h\vartheta}{kT}}-1\right)}\right]$$

$$C_V = 3R\left(\frac{dE}{dT}\right)^2 = \frac{h\vartheta}{\left(e^{\frac{h\vartheta}{kT}}-1\right)^2} \text{----------- (157)}$$

According to this relationship, Cv should approach zero at very low temperature, whereas at high temperature when $\frac{h\vartheta}{kT}$ is small in comparison with unity. The value becomes 3R in agreement with the classical treatment and Dulong and Petit law. Under the latter conditions an appreciable number of vibrational levels are occupied and the atom behaves as if it were a classical oscillator. For most of the elements $\frac{h\vartheta}{kT}$ is sufficiently small at ordinary temperature for the atomic heat capacity to be about 6 cal/der but it ϑ is large ie when the atoms are very firmly bound as in diamond, a much higher temperature is necessary before the classical heat capacity is attained.

In general, those elements which constitute exceptions to the Dulong and Petit law have high value of ϑ, the characteristic frequency of atomic oscillators.

Limitation

Einstein's theory fails in predicting the Cv values in the lower and intermediate temperature ranges. The values predicted by it are lower than those actually observed.

4.10 The Debye equation

Debye developed a modified equation which gave a very satisfactory agreement with experiment over the entire range of temperature.

Debye suggested that

a) A solid is assumed to be an elastic body and vibrations of the whole should be considered and

b) The 3 N modes of vibrations are not all identical but are distributed among a spectrum of frequencies. The frequencies range from o ($\vartheta = 0$) to a maximum frequency ϑ_m ($\vartheta = \vartheta_m$) which is characteristic of the solid.

The total number of ways, Z in which an elastic medium of volume V can vibrate with a frequency, ϑ then $d\vartheta$ between the frequency range ϑ and $\vartheta + d\vartheta$ will be given by

$$dZ = \frac{4\pi V}{C^3}\vartheta^2 d\vartheta \text{------ (158)}$$

A gram atom contains N atoms, the total number of possible vibrations will be 3N

$$\therefore \int dZ = \int_0^{\vartheta_m} \frac{4\pi V}{C^3}\vartheta^2 d\vartheta$$

$$= \frac{4\pi\vartheta_m^3}{3C^3}V = 3N \text{--------- (159)}$$

$$\therefore V = \frac{9NC^3}{4\pi\vartheta_m^3} \text{------------ (160)}$$

Substituting the value of V in equation (158) we get

$$dZ = \frac{4\pi}{C^3}\cdot\frac{9NC^3}{4\pi\vartheta_m^3}\vartheta^2 d\vartheta$$

$$\therefore dZ = \frac{9N}{\vartheta_m^3}\vartheta^2 d\vartheta \text{------------- (161)}$$

We know that

$$\bar{E} = \frac{h\vartheta}{\left(e^{\frac{h\vartheta}{kT}}-1\right)} \text{ ---------- (155)}$$

The total energy of a gram atoms of solid will be

$$E = \int_0^{\vartheta_m} \bar{E}\, dZ = \int_0^{\vartheta_m} \frac{h\vartheta}{\left(e^{\frac{h\vartheta}{kT}}-1\right)}\frac{9N}{\vartheta_m^3}\vartheta^2 d\vartheta$$

$$E = \frac{9Nh}{\vartheta_m^3}\int_0^{\vartheta_m} \frac{\vartheta^3}{\left(e^{\frac{h\vartheta}{kT}}-1\right)} d\vartheta \text{-------------- (162)}$$

Put $x = \frac{h\vartheta}{kT}$ or $\vartheta = \frac{kT}{h}x$

$$\therefore\ \vartheta^3 d\vartheta = \left(\frac{kT}{h}\right)^4 x^3 dx$$

Therefore equation (162) can be written as

$$E = \frac{9N(kT)^4}{(h\vartheta_m)^3}\int_0^{x_m}\frac{x^3}{(e^x-1)}dx \text{------------ (163)}$$

Now let us consider the heat capacity separately for high and low temperatures

(i) When temperature is high, x is small and

$$\therefore \int_0^{x_m}\frac{x^3}{(e^x-1)}dx = \frac{1}{3}x_m^3$$

Hence $$E = \frac{9N(kT)^4}{(h\vartheta_m)^3}.\frac{1}{3}x_m^3 = 3Nkt = 3RT \text{--------- (164)}$$

Therefore heat capacity $C_V = \left(\frac{dE}{dT}\right)_V = \frac{d(3RT)}{dT} = 3R$------- (165)

(ii) When temperature is low, x is large. The value of the integral is

$$\int_0^{x_m}\frac{x^3}{(e^x-1)}dx = \frac{\pi^4}{15}$$

Hence $$E = \frac{9N(kT)^4}{(h\vartheta_m)^3}\frac{\pi^4}{15}$$

$$E = \frac{3N}{5}\frac{(\pi kT)^4}{(h\vartheta_m)^3} \text{---------------(166)}$$

$\therefore$ Heat capacity $C_V = \left(\frac{dE}{dT}\right)_V$

$$C_V = \frac{d}{dT}\left[\frac{3N}{5}\frac{(\pi kT)^4}{(h\vartheta_m)^3}\right]$$

$$C_V = \frac{12\pi^4}{5}Nk\left[\left(\frac{kT}{h\vartheta_m}\right)^3\right]$$

Put $\theta = \frac{h\vartheta_m}{k}$ where θ is the Debye characteristic temperature

$$C_V = \frac{12\pi^4}{5}R\left[\left(\frac{T}{\theta}\right)^3\right] \text{---------- (167)}$$

Substituting the values of π and R and on simplification, we get

$$C_V = 464.4\left[\left(\frac{T}{\theta}\right)^3\right] \text{--------- (168)}$$

Equation (168) is known as Debye T^3 law and is applicable at low temperatures bellow 20K

For a given substance, at very low temperature

$$C_V = \frac{464.4}{\theta^3}T^3 = \alpha T^3 \text{---------} (169)$$

From equation (168), the value of θ and therefore ϑ_m of a substance at low temperature can be calculated from an experimental value of C_V.

The Debye equation predicates that the heat capacity of a solid is a function of temperature and depends upon only the characteristic maximum frequency (ϑ_m). If the heat capacities of different solids are plotted against $\frac{T}{\theta} = \frac{kT}{h\vartheta_m}$, they should all fall on the same line (Fig.8)

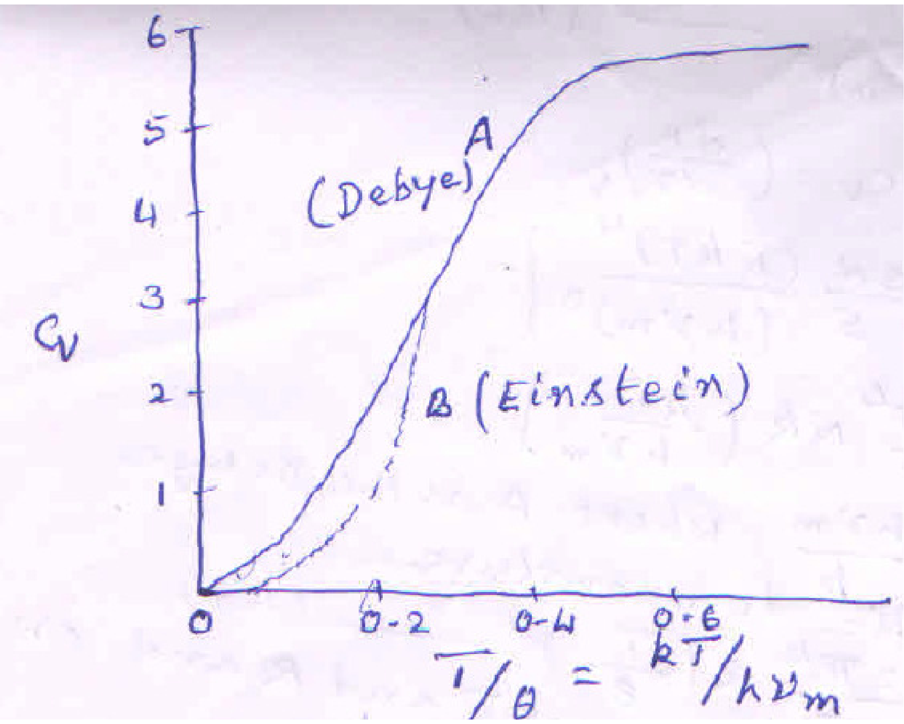

Figure 8

The values of θ of a few solids are given below

Debye characteristic temperature ($\boldsymbol{\theta}$)

Solid	θ	Solid	θ	Solid	θ
Na	159	Au	180	C	1910
K	100	ZN	235	**	1000
		Pb	88	Fe	433
Cu	313	MG	290	Ni	375
AG	215	Ca	230	Al	389

4.11 Debye characteristic temperature (θ)

The only quantity in the Debye treatment that is dependent on the nature of the metal is the characteristic temperature which is related to the characteristic maximum frequency (ϑ_m)

$$\text{ie, } \theta = \frac{h\vartheta_m}{k}$$

The values of θ can be determined from the measurement of neat capacity values.

4.12 Summary of the unit

A partition function is the essential link between the coordinates of microscopic systems and the thermodynamic properties. Once it has been evaluated, all the physical properties, such as U, S, Cp, Cv etc. can be estimated.

Energy may be stored in a molecule in various modes. The total energy of a molecule is

$$\varepsilon = \varepsilon_{tran} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{elect} + \varepsilon_{nucl} + \varepsilon_{chem}$$

The degeneracies of an energy level are multiplicative:

$$g = g_{tran} \cdot g_{rot} \cdot g_{vib} \cdot g_{elect} \cdot g_{nucl} \cdot g_{chem}$$

4.13 Keywords

Internal energy (E); Entropy (S); Helmholtz free energy (A); Pressure (P); Gibbs free energy (G) ; Enthalpy or Heat content (H); Sacker – Tetrad equation; Statistical entropies; Einstein equation ; Debye equation

Debye characteristic temperature (θ)

4.15 References for further study

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4.15 Question for self understanding

1) Evaluate the following thermodynamic functions in terms of partition functions.

a) Internal energy (E).

b) Entropy (S).

c) Helmholtz free energy (A).

d) Pressure (P).

e) Gibbs free energy (G).

f) Enthalpy or Heat content (H).

2) Evaluate the equilibrium constant from partition functions.

3) Derive the equation for entropy of a monatomic gas (Sacker – Tetrad equation).

4) Compare the third law of thermodynamics and statistical entropies.

5) Write a note on heat capacity behavior of solids (classical Approach).

6) Explain the quantum theory of heat capacities.

7) Discuss the Einstein equation quantum theory of heat capacity and states its limitations.

8) Derive the Debye equation for quantum theory of heat capacities.

9) What is Debye characteristic temperature (θ)?

Question Bank

1. What is the minimum condition for suitability of Sterling approximation?
2. Define the term Ensemble. Discuss briefly various types of Ensembles
3. Derive the expressions for most probable velocity, average velocity and root mean square velocity.
4. Deduce Maxwell-Boltzmann distribution equation.
5. Derive the relation between thermodynamic probability and Entropy. (Boltzmann-Planck equation)
6. Derive the expression for Bose – Einstein statistics.
7. Derive the expression for Fermi-Dirac statistics.
8. Compare the important features of Maxwell-Boltzmann, Bose-Einstein and Firm-Dirac distribution equations
9. Distinguish between Bosons and Fermions.
10. Define the term partition function. Write the significance of partition function and give the relation between molecular partition function and molar partition function.
11. Drive the expression for translational partition function
12. Deduce the expression for rotational partition function
13. Evaluate the following thermodynamic Parameters in terms of partition functions
    a) Internal energy
    b) Entropy
    c) Enthalpy
    d) Gibbs free energy and
    e) Equilibrium constant
14. Deduce the expression for molar entropy in terms of partition function
15. Derive Sacker - Tetrode equation for a monatomic gas.
16. Give the comparison between third law and statistical entropies.
17. Mention the limitations of Einstein heat capacity equation
18. Derive Einstein heat capacity equation
19. Deduce Debye heat capacity equation
20. Define the term Debye characteristic temperature.
21. Write the assumptions made by Delong and Petit, Einstein and Debye, for explaining heat capacity of solids.
22. Calculate the vibrational partition function for H_2 at 300K. The vibrational frequency is 4654 cm^{-1}

23. Calculate the translational partition function for O_2 at 1atm and 298 K in a vessel of volume 24.4 cm^3
24. Calculate the heat capacity at constant volume (C_V) of diamond at 1080 K. (Given θ = 1860 K)
25. The equilibrium internuclear distance of $^{127}I_2$ is 2.66 X 10^{-10} m. Calculate its moment of inertia and rotational partition function at 300 K (Given $k = 1.38X10^{-23} JK^{-1}$ and $\sigma = 2$)

UNIT-5

Structure

5.0 Objectives of the unit

After studying this unit you are able to

- Classify the nuclides based on their stability
- Explain the reason for radioactive decay
- List out the different types of radioactive decay
- Write the radioactive decay schemes for given radioactive element
- List the general characteristics of radioactive decay
- Explain the decay kinetics
- Explain the Half-life and the mean life period
- Explain the Parent-Daughter decay growth relationships

5.1 Introduction

We know that the atomic nucleus consists of three particles namely protons, neutrons and electrons. Neutrons and protons are present in the nucleus and electrons are present in the extra nuclear region of the atom. Transformations which involve changes in the atomic nucleus were observed and these transformations are called nuclear reactions. The study of nuclear reactions led to the development of new branch of chemistry called *nuclear chemistry*. It may be defined as the branch of chemistry whish deals with the study of atomic nucleus and nuclear charges. It also deals with the study of effects of ionizing radiation on matter.

5.2 Classification of nuclides

An atomic nucleus in general is represented as

$$ {}^{A}_{Z}X $$

Where X is an element or the atom of the nucleus, Z is the atomic number or the number of protons and A is the atomic weight or the mass number. The number of neutrons (N) is given by (A-Z).

Since atom is very small, the mass of the atom is expressed as atomic mass unit(amu). Atomic mass unit is defined as 1/12 of mass of 1 atom of ${}^{12}_{-2}C$

1amu = ½ $(1.99 * 10^{-26}$ Kg)

Or 1 amu = $1.6605 \text{ X } 10^{-27}$ Kg

According to Einstein

$E = mc^2 = (1.6605 \times 10^{-27})(3 \times 10^8)^2$

$= 14.919 \times 10^{-11}$J

= 9.313×10^8J

Hence, the energy equivalent of 1amu = 931 Mev

Nuclides can be grouped together as follows

i) Isotopes

The nuclei of the same chemical elements having the same number of protons(Z) or the same atomic number but different mass number(A) or different number of neutrons (N) are called isotopes.

Example: a) Hydrogen nucleus has three isotopes

$$^{1}_{1}H, ^{2}_{1}H \text{ and } ^{3}_{1}H$$

b) Chlorine nucleus has five isotopes

$$^{34}_{17}Cl, ^{35}_{17}Cl, ^{37}_{17}Cl, ^{37}_{17}Cl \text{ and } ^{38}_{17}Cl$$

i) Isobars

The nuclei of different neighboring chemical elements having the same mass number (A) but different atomic number (Z) are called isobars. In this case number of neutrons will also be different the subscript on the right of the nucleus shows the values of N.

Example a) $^{3}_{1}H_2\,^{3}_{2}He_1$

b) $^{14}_{6}C_8\,^{14}_{7}N_7$

ii) Mirror nuclei

Pair of isobars in which Z and N values differ by one unit and interchanges are called mirror nuclei

Example a)$^{3}_{1}H - ^{3}_{2}He$

b)$^{15}_{7}N_8 - ^{15}_{8}O_7$

iii)Isomers

Two nuclides having the same values of Z, N and hence A, but differing in energy states constitute nuclear isomers.

Ex: a) ^{60m}Co and ^{60}Co

b) ^{80m}Br and ^{80}Br (here m stands for meta stable state

v) Isotones

There are nuclei having the same number of neutrons but different values of Z and A.

Example

a) $^{3}_{1}H_2 - ^{4}_{2}He_2$

b) ${}^{13}_{6}C_7 \; - {}^{14}_{7}N_7$

5.3 Stable and radioactive nuclides

The nuclides can be classified into two type namely stable and radioactive or unstable nuclides. The nuclides in which number of protons or neutrons remains unchanged are called stable nuclide.

Ex: ^{16}O, ^{23}Na, ^{35}Cl, ^{19}F, etc….

The nuclides undergo spontaneous change with time forming new nuclides in one or the other way are called radioactive nuclides.

Ex: ^{3}H, ^{14}C, ^{15}S, ^{32}P etc….

5.4 Radioactive decay

Henri Becquerel placed a crystal of potassiuranylsulphate $K_2UO_2(SO_4).2H_2O$ near a photographic plate which was wrapped in a black paper. He found that fogging on the photographic plate. From this he concluded that certain type of penetrating rays were emitted by uranium salt which could pass through the black paper and affect photographic plate. Further investigations revealed that the radiations emitted consists of α particles, β particle and γ rays.

It was found that the nuclei of all elements with atomic number (Z) > 83 are unstable and hence decay spontaneously with the emission of α-particles, β-particles and γ-rays. This phenomenon of emission of radiations by certain substances like uranium is called radioactivity while such substances are said to be radioactive. If the decay occurs spontaneously it is called natural radioactivity. If the nuclear breakdown is caused by exposure to radioactive particles, then the phenomenon is called artificial or induced radioactivity.

5.5 Types of Radioactive decay

Important modes of nuclear decay are presented in Table.1.

Table 1

Type of Decay	General nuclear reactions	examples
α-	${}^{A}_{Z}X \dashrightarrow {}^{A-4}_{Z-2}Y + \propto ({}^{4}_{2}He)$	${}^{226}_{88}Ra \dashrightarrow {}^{222}_{86}Rn + {}^{4}_{2}He(\propto)$
β$^-$ (negatren decay)	${}^{A}_{Z}X \dashrightarrow {}_{Z+1}{}^{A}Y + \beta^- + \bar{\gamma}$ ${}^{1}_{0}n \dashrightarrow {}^{1}_{1}P + \beta^- + \bar{\gamma}$	${}^{32}_{15}P \rightarrow {}^{32}_{16}S + \beta^- + \bar{\gamma}$
β$^+$ Electron decay	${}^{A}_{Z}X \dashrightarrow {}_{Z-1}{}^{A}Y + \beta^+ + \gamma$ ${}^{1}_{1}P \dashrightarrow {}^{1}_{0}n + \beta^+ + \gamma$	${}^{22}_{22}Na \dashrightarrow {}^{22}_{10}Ne + \beta^+ + \gamma$

Electroncapture (EC)	$^{A}_{Z}X + e --\rightarrow {}_{Z-1}^{A}Y + \gamma$ $^{1}_{1}P + e --\rightarrow {}^{1}_{0}n + \gamma$	$^{55}_{26}Fe + e --\rightarrow {}^{55}_{25}Mn + \gamma$
Isomeric transition (IT)	$^{Am}_{Z}X + e \longrightarrow {}^{A}_{Z}X + \gamma$	$^{60m}_{27}Co --\rightarrow {}^{60}_{27}Co + \gamma$

In the above table, Z is the atomic number, A is the mass number, n is the neutron, P is the proton, γ is the neutrino, $\bar{\gamma}$ is the antineutrino and m signifies that the nucleus is in a meta stable excited state prior to its decay.

5.6 Decay Schemes

Emission of an ∝-particle(helium nucleus) by a radioactive nuclide results in the formation of a new element which has a mass number less by 4 units and atomic number less by 2 units. Thus emission of α-particles causes a decrease of two units in its atomic number and four units in mass number.

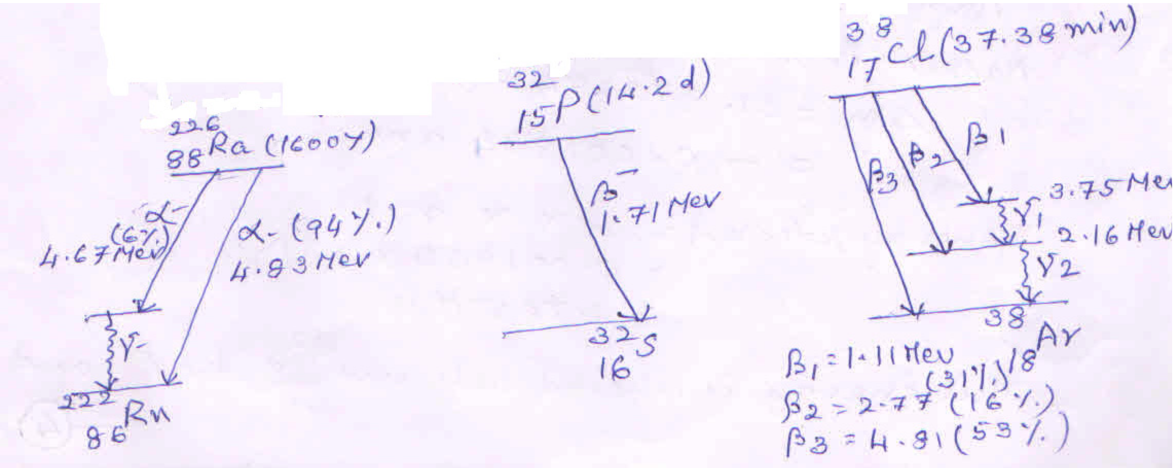
EX:-$^{238}_{92}U --\rightarrow {}^{234}_{90}Th + {}^{4}_{2}He(\propto -particle)$

When a radioactive nuclide loses a β particle, the atomic number of the nucleus formed increase by one unit and the mass number remains unchanged

Ex:-$^{234}_{90}Th --\rightarrow {}^{234}_{91}Pa + \beta^{-}({}^{0}_{-}e)$

Thus the emission of ∝ partcles, β-particle and γ- particle lead to the formation of new elements which occupy two places to the left (β^-decay), one place to the right (γ^-decay) and one place to the left (β^+ decay). The decay scheme presents a graphical representation of the nuclear transformation. Isomeric transition (IT) signifies the emission of γ-radiation by a daughter nucleus in returning from the excited state to the ground state.

Some typical decay schemes are given below (Fig 1)



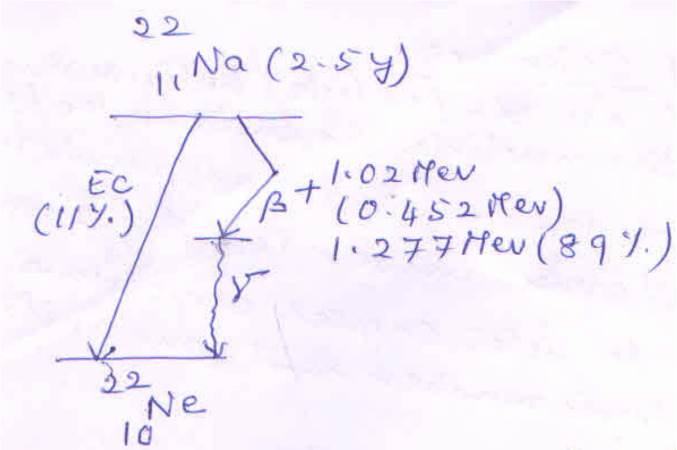


Figure 1: Typical decay schemes

5.7 General characteristics of radioactive decay

General characteristics common to all forms of radioactive decay are presented below.

a) Mass loss and energy release

The sum of the masses of the products of the radioactive decay is always less than of the parent nuclei. In other words, *nuclear decay is always accompanied by a net loss of mass which is responsible for the process to be spontaneous and irreversible.* The equivalent of the mass loss appears as the recoil energy of the daughter nucleus and the kinetic energy of the particle and the energy of the photon emitted if any.

Ex: $^{32}_{15}P \; --\rightarrow \; ^{32}_{16}S + \beta^- + \bar{\gamma}$

Mass of ^{32}P = 31.973908 amu

Mass of ^{32}S = 31.972074 amu

Mass loss or mass defects (Δm) is given by

$$\Delta m = 31.972074 - 31.973908$$

$$= -0.001834 \text{ amu}$$

$$\text{Energy released} = \Delta m \times 931$$

$$= 0.001834 \times 931$$

$$= 1.705 \text{Mev}$$

This energy is shared between ^{32}S, the β^- and $\bar{\gamma}$.

b) Nuclear Radiations

Either helium (α-decay) or electrons (β^-decay) or positrons (β^+decay) are emitted during the decay of radioactive nucleus. In many cases these particles are accompanied by γ-photons.

$\beta^{\mp}$Particles are accompanied invariably by neutrino γ (with β^+) and antinentrino $\bar{\gamma}$(with β^-). These radiations are of high energy (10^3 -10^6) and have high penetrating power through matter. The ranges of penetration through air of a given energy in the order

$$R_\gamma \gg R_\beta > R_\propto$$

They ionize the atoms of the matter they pass through and the ionization power is of the order

$$I_\alpha > I_\beta \gg I_\gamma$$

Because of their higher energy, the *nuclear radiations affect characteristic physical and chemical reactions in the matter they pass through are referred to as radiation damage*. The energy spectra of the radiations are characteristic. The α and γ^- spectra consists of a few sharp monoenergic lines while the β^-spectrum is a continuum from nearly zero to a definite maximum.

Example

The alphas from ^{244}Cm consist of fair lines 5.508, 5.568, 5.763 and 5.805 Mev and the gammas are 0.293, 0.142 and 0.043 Mev while the β^- spectrum from ^{210}Bi is a continuum from 0 to 1.17 Mev with a broad peak around 0.1 to 0.3 Mev.

5.8 Decay Kinetics

All radioactive decays are spontaneous. They obey the same kinetic laws. The mechanisms may be different.

The rate of radioactive decay at any instant is directly proportional to the number of its atoms present at that instant. The radioactive decay follows first order rate law namely

$$\frac{-dN}{dt} \propto N$$

$$-\frac{dN}{dt} = \lambda N - - - (1)$$

Where $\frac{dN}{dt}$ represents the rate of decay, negative sign represents the decrease in the number of atoms as the increase in time, N is the number of atoms at that time and λ is the proportionality constant called the decay constant or disintegration constant.

Rearranging equation (1)

$$-\frac{dN}{N} = \lambda dt$$

on integration

$$-\ln N = \lambda t + C - - - (2)$$

where C is integration constant. To evaluate C, when t = 0, N = N_0 where N_0 is the initial number of atoms at t = 0 C = -ln N_0----(3)

Substituting in equation (3), we get

$$-\ln N = \lambda t - \ln N_0$$

$$\ln N_0 - \ln N = \lambda t$$

$$\ln N - \ln N_0 = -\lambda t$$

$$\frac{N}{N_0} = e^{-\lambda t}$$

$$N = N_0 e^{-\lambda t} - - - (4)$$

$$\log N = \log N_0 - \frac{\lambda t}{2.303} \quad \text{---(5)}$$

In radioactive measurements, one would determine the activity of the radio nuclide (A). The equation (4) can be written in terms of activity as

$$A = A_0 e^{-\lambda t} - - - - (6)$$

The plots N against t and log N against t are given in the Figure 2.

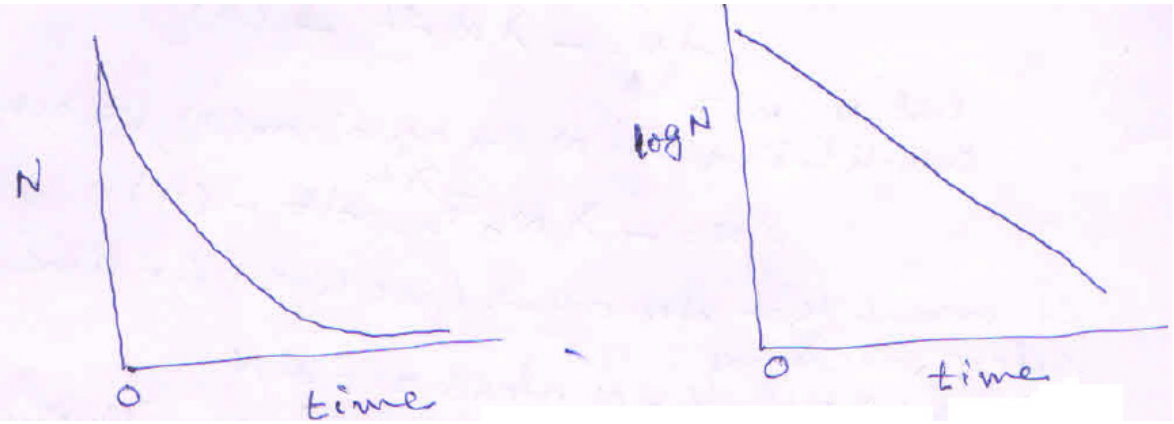


Figure 2: plots of N vs T

The slope of the line of log N vs t and $\log N$ vs t gives $\frac{\lambda}{2.303}$ from which the decay constant (λ) can be evaluated.

5.9 The Half-life and the mean life period

The half-life period ($t_{1/2}$) is defined as the time required for a given amount of the radionuclide to decay exactly to half its original value.

We know that

$$N = N_o e^{-\lambda t} \text{--------(4)}$$

$$\text{Log N} = \log N_o - \frac{\lambda t}{2.3.3} \quad \text{----- (5)}$$

At half life period i.e when t = $t_{\frac{1}{2}}$, N = $\left(\frac{N_0}{2}\right)$

Substituting in equation (5), we get

$$log\frac{N_0}{2} = logN_0 - \frac{\lambda t_{1/2}}{2.303}$$

$$\frac{\lambda t_{1/2}}{2.303} = logN_0 - log\frac{N_0}{2}$$

$$\frac{\lambda t_{1/2}}{2.303} = log\frac{N_0}{N_0}X2 = log2$$

$$\lambda t_{1/2} = 2.303Xlog2 = 2.303X0.3010$$

$$\lambda = \frac{0.693}{t_{1/2}}$$

$$\text{Or } t_{1/2} = \frac{0.693}{\lambda} \text{------------(7)}$$

It is possible to determine the average or mean life expectancy of the radioactive atoms.

We Know that

$$-\frac{dN}{dt} = \lambda N \text{----(8)}$$

But $N = N_0 e^{-(\lambda t)}$

Substituting for N in equation (8), we get

$$dN = \lambda N_0 e^{-\lambda t} dt \text{------(9)}$$

It means that dN atoms have lived for time t before decaying

Total life of N atoms = tdN

Total life of all the atoms in the radioactive nuclide is given by

$T_{total} = \int_0^\infty t\, dN$------------(10)

Substituting for dN in equation (10), we get

$$T_{total} = \int_0^\infty t\, \lambda N_0 e^{-\lambda t} dt$$

$$\lambda N_0 \int_0^\infty t\, e^{-\lambda t} dt \qquad ----(11)$$

$$= \lambda N_0 \left[\left\{ \frac{te^{-\lambda t}}{-\lambda} \right\}_0^\infty - \int_0^\infty \frac{e^{-\lambda t}}{-\lambda} dt \right]$$

$$= \lambda N_0 \left[0 + \frac{1}{\lambda} . \frac{e^{-\lambda t}}{-\lambda} \right]_0^\infty$$

$$T_{total} = \frac{\lambda N_0}{\lambda^2} \left[e^{-\lambda t} \right] \text{------------ (12)}$$

We know that $e^0 = 1 \; and \; e^{-\infty} = 0$

$$\therefore T_{total} = -\frac{N_0}{\lambda} [e^{-\infty} - e^{-0}] = \frac{N_0}{\lambda} ----(13)$$

The mean or average life is given by

$$Mean\ life(T) = \frac{Sum\ of\ lives\ of\ all\ atoms}{Total\ number\ of\ atoms} = \frac{T_{total}}{N_0} ----- (14)$$

$$\therefore T = \frac{T_{total}}{N_0} = \frac{n_0}{\lambda N_0} = \frac{1}{\lambda} ----(15)$$

We know that $\lambda = \frac{0.693}{t_{1/2}}$

Substituting the value $\lambda\ in\ , we\ get$

$$\tau = \frac{t_{1/2}}{0.693} = 1.44 t_{1/2}$$

i.e $\tau = 1.44\ e_{1/2} ----- (16)$

In this way the half life and mean life of a radioactive nuclide are related.

5.10 Units of radioactivity

Curie is the unit of radioactivity. It is defined as the rate of disintegration of 1gm of radium (^{226}Ra)

1 g of ^{226} Ra has $6.023 \times \frac{10^{23}}{226} = 2.27 \times 10^{21}$ atoms

The half life of Ra is 1600y

$$\therefore \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{1600 \times 365 \times 24 \times 60 \times 60} = 1.38 \times 10^{-11} S^{-1}$$

$$\therefore 1\ curie(ci) = \lambda N = 1.38 \times 10^{-11} \times 2.27 \times 10^{21}$$

$= 3.7\times10^{10}$ disintegrations/S

Fractions of the unit mci, µci and multiples of $R_{ci}$and M_{ci} are also used.

The SI unit of radioactivity is the Becquerel(Bq). If is defined as the activity due to one disintegration per second.

1 Bq= 1 dps

The curie and Becquerel are related as

1 ci=3.7 ×10 dps

1 Bq= 1 dps

1 ci $=3.7\times 10^{10}$ Bq

Rutherford (Rd) has also been suggested as a unit of radioactivity

1 Rd= 10^6 dps

Or 1 Rd = 10^6 Bq

Radioactive nuclides are priced on the basis of their activity.

5.11 Parent-Daughter decay growth relationships

When a parent (radionuclide) decays the resulting atom (daughter) may be radioactive with a half-life greater than or equal to or less than the parent or stable. These cases are discussed separately.

The daughter nucleus is stable

The radioactive parent decays continuously and completely the amount of daughter grows at the same rate to reach a constant maximum equal to the initial amount of parent. Both the decay of parent and growth of daughter follow the same rate law

$$-\frac{dN_1}{dt} = \frac{dN_2}{dt} = \lambda_1 N_1 \text{-------(17)}$$

Since there is no equilibrium between the parent and the daughter at any time, the number of atoms of parent (N_1) and that of the daughter (N_2) at time t are given by

$N_1= N_0\, e^{-\lambda_1 t}$

$N_2= N_0-N_1 = N_0-N_0e^{-\lambda_1 t}$

$N_2= N_0\,(1- e^{-\lambda_1 t})$--------(18)

Each parent atom decays producing one daughter atom.

Parent atoms: At zero time ie, t = 0, the number of parent atoms are N_0

At time t

$$N = N_0 e^{-\lambda_1 t}$$

Or $N_0 = N\, e^{\lambda_1 t}$-----------(19)

Daughter atoms: At zero time ie, t = 0, the number of daughter atoms is zero. At time t, N^1 is the number of daughter atoms or parent atoms decayed.

$N^1 = (N_0 - N) = (Ne^{\lambda t} - N)$

$N^1 = N(e^{\lambda t} -1\,)$---------(20)

Expanding $(e^{\lambda t} - 1)$ and taking only the first term i.e $(e^{\lambda t} - 1) \sim \lambda t$

$$N^1 = N\,\lambda t$$

$$N^1/N = \lambda t \text{-------}(21)$$

The ratio of the amounts of the daughter to the parent at any time is simply λt.

5.12 Chains of disintegration

A parent nucleus gives rise to a radioactive daughter, the latter further decay in one more steps until a stable end product is reached. This type of disintegration is called a decay chain.

Ex: $^{238}U \xrightarrow{\alpha} \xrightarrow{\alpha} {}^{230}Th \xrightarrow{\alpha} {}^{226}Ra \xrightarrow{\alpha} {}^{222}Rn \xrightarrow{\alpha} {}^{218}Po \xrightarrow{\alpha}$

$^{214}Pb \xrightarrow{\beta-} {}^{214}Bi \xrightarrow{\beta-} {}^{206}Pb$(stable)

The above is the example for disintegration of natural radioactivity.

$^{90}Sr \xrightarrow{\beta-} Y \xrightarrow{\beta-} {}^{90}Zr$ (stable)

Since the half-lives of radio elements differ widely, the growth and decay curves of the intermediate nuclides are complex and differ from system to system. We shall derive a general expression for the number of daughter atoms as a function of time.

5.13 General expression for the activity of a daughter nuclide

Consider a radionuclide parent (X) which decays to form daughter (Y). Y is also radioactive and it decays to form Z. This can be represented as

$$X \overset{\lambda_1}{\rightarrow} Y \overset{\lambda_2}{\rightarrow} Z$$

The rate of decay of parent(X) is given by

$$-\frac{d_{N_1}}{dt} = \lambda_1 N_1$$

We know that $N_1 = N_1^0 e^{-\lambda_1 t}$

$$\therefore -\frac{dN_1}{dt} = \lambda_1 N_1^0 e^{-\lambda_1 t}\text{-------(22)}$$

Where N_1^0 are the parent atoms at t = 0

As the daughter is formed at the same rate at which the parent decays. Then the rate of formation of daughter is given by

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2\text{------(23)}$$

$$= \lambda_1 N_1^0 e^{-\lambda_1 t} - \lambda_2 N_2$$

$$\frac{dN_2}{dt} + \lambda_2 N_2 = \lambda_1 N_1^0 e^{-\lambda_1 t}\text{------(24)}$$

Multiplying equation (24) by $e^{\lambda_2 t}$

$$e^{\lambda_2 t}\frac{dN_2}{dt} + \lambda_2 N_2 e^{\lambda_2 t} = \lambda_1 N_1^0 e^{(\lambda_2 - \lambda_1)t}\text{---------(25)}$$

Writing the left hand side of equation (25) as a differential, we have

$$\frac{d(N_2 e^{\lambda_2 t})}{dt} = \lambda_1 N_1^0 e^{(\lambda_2 - \lambda_1)t}\text{-------(26)}$$

On integration of equation (26), we get

$$N_2 e^{\lambda_2 t} = \frac{\lambda_1}{\lambda_1 - \lambda_2} N_1^0 e^{(\lambda_2 - \lambda_1)t} + C\text{---(27)}$$

where C is an integration constant

Dividing equation (27) by $e^{\lambda_2 t}$, we get

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 e^{-\lambda_1 t} + Ce^{-\lambda_2 t}\text{-----(28)}$$

C may be evaluated by putting $N_2 = N_2^0$ when t = 0

$$N_2^0 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 + C$$

$$\therefore C = N_2^0 - \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0\text{-------(29)}$$

Substituting the value of C in equation (28), we get

$$N_2 = \left(\frac{\lambda_1}{\lambda_2 - \lambda_1}\right) N_1^0 e^{-\lambda_1 t} - \left(\frac{\lambda_1}{\lambda_2 - \lambda_1}\right) N_1^0 e^{-\lambda_2 t} + N_2^0 e^{-\lambda_2 t}$$

Or

$$N_2 = \left(\frac{\lambda_1}{\lambda_2 - \lambda_1}\right) N_1^0\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) + N_2^0 e^{-\lambda_{2t}} - - - - - - - -(30)$$

The first term on the right hand side of equation (30) denotes the growth of daughter from parent and the decay of daughter atoms and the last term denotes the contribution of daughter atoms at any time when they present initially. In this case N_2^0= 0

Equation (30) reduces to

N$_2$= $\left(\frac{\lambda_1}{\lambda_2-\lambda_1}\right) N_1^0\left(e^{-\lambda_1 t}-e^{-\lambda_2 t}\right)-----------(31)$

This treatment can be extended to a chain of any number of radioactive products.

5.14 Radioactive equilibrium

Radioactive decay occurs in stages and the Products of decay are radioactive themselves in each stage, the radioactive pairs (parent and daughter) are said to be in a radioactive equilibrium. Since the radioactive decays are irreversible, the term steady state is more appropriate than the equilibrium state.(The radioactive equilibrium here implies only a constant ratio of the product and parent amounts both decreasing with time at a constant rate equal to that of the parent.)

In the steady state the radioactive pairs will not have the same half-lives. Depending on which of the two radioactive species has the longer half-life, two general cases arise. *If the Parents half-life is greater than that of the daughter, a steady state called the Transient equilibrium is reached. When a very long lived parent decays giving a short lived daughter element provided that no daughter substance removed or allowed to escape for long time , a state of equilibrium called secular equilibrium is attained.* Secular equilibrium is limiting case of transient equilibrium, the difference is only in degree.

5.15 Transient equilibrium

If the parent's half-life is greater than that of the daughter, a Transient equilibrium is attained. However, the half-lives of parent and daughter nuclides differ by a small factor about 10.

We have

$$N_2 = \left(\frac{\lambda_1}{\lambda_2-\lambda_1}\right) N_1^0\left(e^{-\lambda_1 t}-e^{-\lambda_2 t}\right)\text{-----------------------}(31)$$

It follows that the decay constant of the parent (λ_1) is less than that of the daughter (λ_2).

i.e $\lambda_1 < \lambda_2$. Since the equation (31) is a function of time, after becomes very large, $e^{-\lambda_2 t}$ becomes negligible as compared to $e^{-\lambda_1 t}$

$$N_2= \left(\frac{\lambda_1}{\lambda_2-\lambda_1}\right) N_1^0 e^{-\lambda_1 t} = \left(\frac{\lambda_1}{\lambda_2-\lambda_1}\right) N_1 \quad \text{since } N_1 = N_1^0 e^{-\lambda_1 t}$$

$$\therefore \frac{N_1}{N_2} = \left(\frac{\lambda_2-\lambda_1}{\lambda_1}\right)\text{-------}(32)$$

Expressing the number of atoms in terms of measured activities.

$$\frac{A_1}{A_2} = \frac{\lambda_1 N_1}{\lambda_2 N_2} \text{---(33)}$$

Substituting the value N_1/N_2 in equation (33)

$$\frac{A_1}{A_2} = \frac{\lambda_1}{\lambda_2}\left(\frac{\lambda_2 - \lambda_1}{\lambda_1}\right) = \frac{\lambda_2 - \lambda_1}{\lambda_2}$$

$$\frac{A_1}{A_2} = \left(1 - \frac{\lambda_1}{\lambda_2}\right) \text{---(34)}$$

Thus the ratio of activities ($\frac{A_1}{A_2}$) may have any value between 0 and 1 which depends on the ratio of decay constant.

Ex:- $^{140}\mathbf{Ba} \xrightarrow{\beta-} {}^{140}\mathbf{La} \xrightarrow{\beta-} {}^{140}\mathrm{Ce}$ (Stable)

$(t_{1/2} = 12.8d)$ $(t_{1/2} = 1.67d)$

$^{222}\mathrm{Ra} \xrightarrow{\alpha} {}^{218}\mathrm{Po} \xrightarrow{\alpha} decay\ series$

$(t_{1/2} = 38.2d)$ $(t_{1/2} = 3.05min)$

The transient equilibrium is given in the

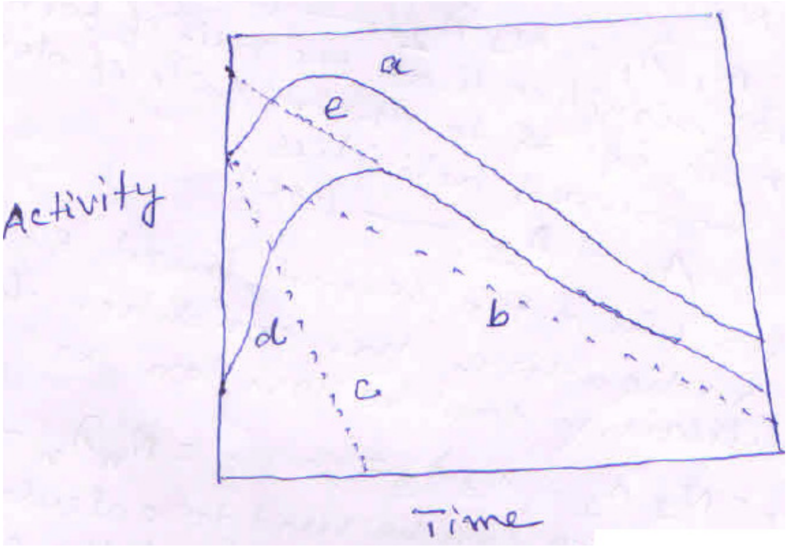


Figure 3: Transient equilibrium

where a) Total activity of an initially pure fraction

b) Activity due to parent

c) Decay of freshly reported daughter fraction

d) Daughter activity growing in freshly

e) Total daughter activity in parent and daughter fractions.

5.16 Secular Equilibrium

In this type equilibrium the half life of Parent is many times greater than that of daughter. Normally the difference in half-lives is of the order of 10^4 or more. The activity of a parent exhibits no appreciable charge during many half life periods of daughter. The examples of this type are

$$^{140}\mathbf{Ra} \xrightarrow{\alpha} {}^{140}\mathbf{Rn} \xrightarrow{\alpha} \text{decay series}$$

$$(t_{1/2} = 1600y) \qquad (t_{1/2} = 3.82d) \qquad \text{(stable)}$$

$$^{238}\mathbf{U} \xrightarrow{\alpha} {}^{234}\mathrm{Th} \xrightarrow{\beta} decay\ serie$$

$$(t_{1/2} = 4.5 \times 10^9 y) \qquad (t_{1/2} = 24.1d)$$

We have

$$\therefore N_2 = \left(\frac{\lambda_1}{\lambda_2 - \lambda_1}\right) N_1^0 \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) \text{------(31)}$$

Under the above conditions, $(\lambda_2 - \lambda_1) \approx \lambda_2$

$$\therefore \quad N_2 = \frac{\lambda_1}{\lambda_2} N_1^0 e^{-\lambda_1 t} = \frac{\lambda_1}{\lambda_1} N_1$$

$$\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1}$$

Or $$N_1\lambda_1 = N_2\lambda_2 \text{-------(35)}$$

Equation (35) signifies that the rate of formation of daughter is equal to their rate of decay, In terms of the measured activities,

$$A_1 = A_2 \text{ -------------(36)}$$

In cases where the second, third etc… daughter nuclides are radioactive, the condition for secular equilibrium can be written as

$$N_1\lambda_1 = N_2\lambda_2 = N_3\lambda_3 = \cdots \ldots \ldots \ldots = N_n\lambda_n \text{--------------------(37)}$$

This relationship can be used to calculate the half-life of any one nuclide provided the other is known and relative amounts of the two members in equilibrium are known. The secular equilibrium is given in the Figure 4.

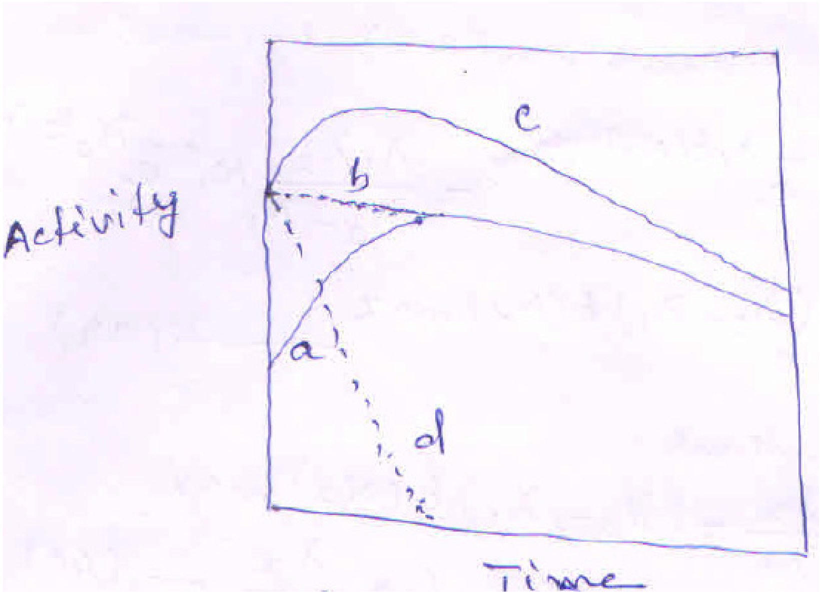


Figure 4: Secular equilibrium

where a) Daughter activity growing in freshly purified parent fraction

b) Activity of parent

c) Total activity of an initially pure parent fraction and

d) Decay of freshly separated daughter fraction.

5.17 The case of no equilibrium

When the half life of the parent $(t_{1/2})_p$ is less than that of the daughter $(t_{1/2})_d$ ie, $(t_{1/2})_p < (t_{1/2})_d$, this type of equilibrium is established. As the parent decays, the rate of formation of daughter is faster than its own decay, the daughter grows to a maximum and finally decays.

We have

$$N_2 = \left(\frac{\lambda_1}{\lambda_2-\lambda_1}\right) N_1^0\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right)\text{-----------(31)}$$

Differentiating with respect to time, we get

$$\frac{dN_2}{dt} = -\left(\frac{\lambda_1^2}{\lambda_1-\lambda_1}\right) N_1^0 e^{-\lambda_1 t} + \frac{\lambda_1\lambda_2}{\lambda_2-\lambda_1} N_1^0 e^{-\lambda_2 t}\text{-------------(38)}$$

If $t = t(N_2)_{max}$ ie, the time required for the daughter activity growing to a maximum , then $\frac{dN_2}{dt} = 0$ equation (38) become

$$\frac{\lambda_1^2}{\lambda_2-\lambda_1} N_1^0 e^{-\lambda_1 t(N_2)max} = \frac{\lambda_1\lambda_2}{\lambda_2-\lambda_1} N_1^0 e^{-\lambda_2 t(N_2)max}$$

$$\frac{\lambda_2}{\lambda_1} = e^{(\lambda_2-\lambda_1)t(N_2)max} \text{-------------(39)}$$

Taking logarithms

$$2.303\log\frac{\lambda_2}{\lambda_1} = (\lambda_2 - \lambda_1)t(N_2)max$$

$$\therefore t(N_2)_{max} = \frac{2.303}{\lambda_2-\lambda_1}\log\frac{\lambda_2}{\lambda_1} \text{-------(40)}$$

Examples for the case of no equilibrium are

$^{92}Sr \xrightarrow{\beta-} Y \xrightarrow{\beta-} {}^{92}Zr$

($t_{1/2}$=2.7h) ($t_{1/2}$=3.6h) (Stable)

$^{143}Ce \xrightarrow{\beta-} Pr \xrightarrow{\beta-} {}^{143}Nd$

($t_{1/2}$=33h) ($t_{1/2}$=13.7d) (stable)

Figure 5, shows the case of no equilibrium

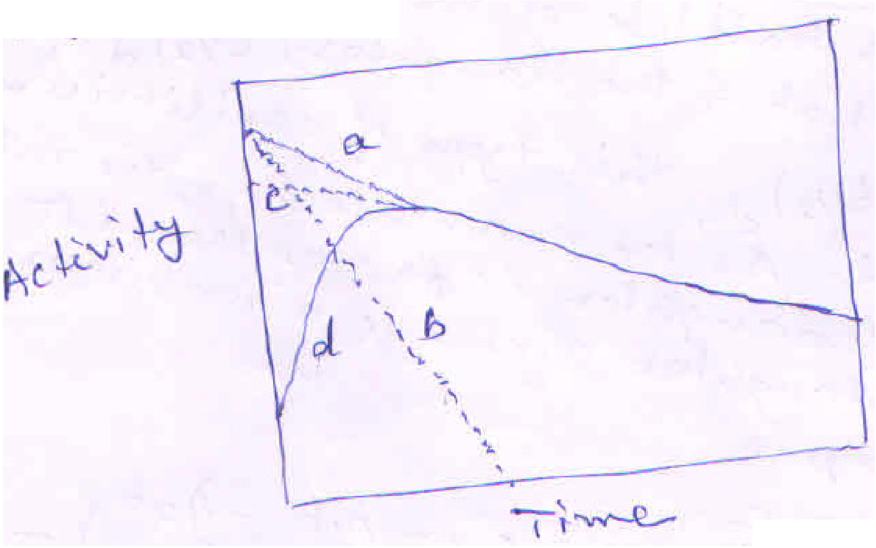


Figure 5: The case of no equilibrium

where a) Total activity

b) Activity due to parent

c) Extrapolation of final decay curve to zero time and

d) Daughter activity in initially pure parent.

5.18 Parent and Daughter having nearly the same half-life

This case of perfect equality of decay rates of parent and daughter is almost nonexistent. However, there are some cases where the two decay rates are close to each other. Now, we shall consider a limiting case of equal decay rates.

$$X \xrightarrow{\lambda_1} Y \xrightarrow{\lambda_2} Z$$

In this case $(t_{1/2})_X \approx (t_{1/2})_Y$ and hence $\lambda_1 = \lambda_2 = \lambda$

The rate of formation of daughter is

$$\left(\frac{dN_2}{dt}\right) = \lambda_1 N_1 - \lambda_2 N_2 = \lambda N_1^0 e^{-\lambda t} - \lambda N_2$$

$$= A_1 e^{-\lambda t} - \lambda N_2 \text{--------(41)}$$

where $A_1 = \lambda N_1^0$

Integrating equation (41) and assuming that there is no daughter element at t = 0

We have

$$N_2 = A_1 t e^{-\lambda t} = \lambda N_1^0 t e^{-\lambda t}$$

We know that

$$A_2 = N_2 \lambda_2 = \lambda^2 N_1^0 t e^{-\lambda t}$$

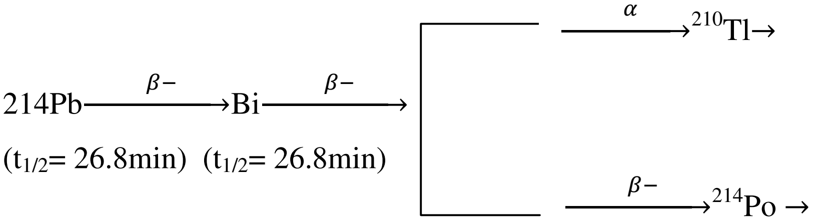
$$= \lambda A_1 t$$

$$= \lambda A_1 t = \frac{0.693 A_1 t}{t_{1/2}} \text{ ------------ (42)}$$

Ex:

$$^{131}Ba \xrightarrow{\beta-} Cs \xrightarrow{\beta-} {}^{131}Xe \text{ (stable)}$$

$(t_{1/2} = 11.5d)$ $(t_{1/2} = 9.7d)$



5.19 Branching decay

Some nuclides decay by two or more alternative modes giving rise to two or more products with different properties. This kind of decay is known as branching decay. It happens whenever the daughter nucleus resulting by alternative paths have each a mass less than that of the parent. For each branch of decay there is a characteristic partial decay constant (λ_1, λ_2, λ_3…..) and the total decay constant is given by

$$\lambda_{total} = \lambda_1 + \lambda_2 + \lambda_3 + \ldots \quad (43)$$

The corresponding partial half lives are given by

$(t_{½})_1 = 0.693/\lambda_1$; $(t_{½})_2 = 0.693/\lambda_2$; etc

And the total half life period is given by

$$(t_{½})_t = (t_{½})_1 + (t_{½})_2 + \text{----------}(44)$$

$(t_{½})_t = 0.693/\lambda_1 + 0.693/\lambda_2$ ------------------------------(45)

The subscript t stands for total. The fraction of the parent (fi) decaying by ith mode is donoted by

Fi= Yi/ Yt------------(46)

Ex:

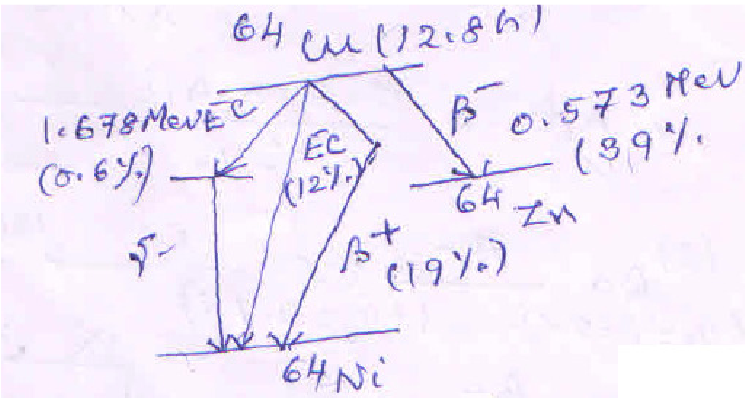


Figure 6: Branching decay of ^{64}Cu

In the above example ^{64}Cu decays by three different paths namely β^-, β^+ and EC giving ^{64}Zn and ^{64}Ni

5.20 Determination of half-lives

The decay constant λ can be experimentally determined with the help of equation

$$\text{Log N} = \text{Log}N_0 - \frac{\lambda t}{2.303}$$

Since the number of atoms N is proportional to the measured activity A, the above equation can be written as

$$\text{Log A} = \text{Log A}_0 - 0.4343\lambda t$$

A plot of logA against time is drawn in figure 7. A straight line graph is obtained with a negative slope. Measure the slope

$$\text{Slope} = \frac{\lambda}{2.303}$$

$$\lambda = 2.303 \times slope$$

The decay constant obtained from the slope of the line is related to the half-life of the radionuclide as

$$\therefore = \frac{0.693}{t_{1/2}} or\ t_{1/2} = \frac{0.693}{\lambda}$$

In this way, the half life of the radio nuclide can be determined

Figure 7: Graphical method of determining the half life

Half lives in the range from several seconds to several years are determined in this way. The counting of the particles emitted is done by an appropriate detection instrument.

However, the above procedure is not satisfactory for complicated growth and decay curves. We shall discuss few suitable procedures for different decaycurves.

(a) For half-lives neither too short nor too long:

The above method can be used for the determination of half lives ranging from the order of a fraction a second to several months.

(b) For a mixture of independent half lives:

Suppose there is a mixture containing two or more radio elements, each will exhibit its owndecay independently and the curve describing the decay would then show and inflection or change in slope. Figure 8 describes such a mixture of two radioisotopes. The half lives of the two isotopes can be determined by the extrapolation of the longer lived isotope back to zero time and subtracting this extrapolated curve from the total curve. The half life of the longer lived component can be obtained from the extrapolated curve and that of the shorter lived isotope from the subtracted curve.

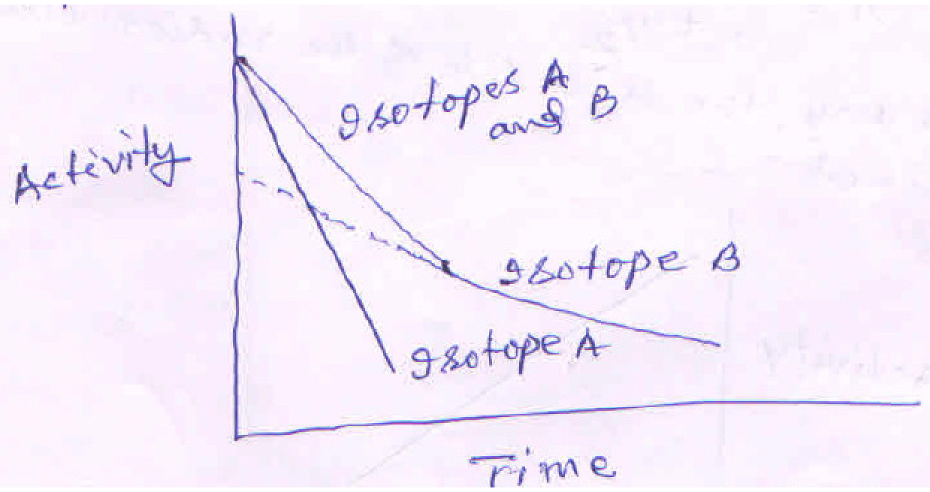


Figure 8: Decay of two independently decaying isotopes present in a mixture.

Sometimes difficulties may arise in the analysis of the decay curve of a mixture. In such cases it is convenient to measure decay curves separately. This can be done by using several different thickness of absorbing material to obtain curves or by using selective detection instrument. Absorbing materials are used to suppress radiations coming from some components.

(c) For moderately long half life:

In this method, measure the total number of particles emitted in a given time from the known weight of the radioactive sample

We know that

$$-\frac{dN}{dt} = \lambda N$$

$$or\ \lambda = -\frac{dN/dt}{N}$$

N can be calculated by

$$\mathrm{N} = \frac{weight\ of\ the\ sample \times Avogadro\ number}{atomic\ weight\ of\ the\ radio\ element}$$

and $\frac{dN}{dt}$ is obtained from the measured number of particles in a definite time interval. This method is more accurate for radio isotopes emitting particles.

(c) For a very short half life

Variable decay coincidence method can be used for the determination of a very short half life of a radionuclide. In this methods, the electric pulse produced by the radiation from the parent is electricity delayed by a time 't' and then recorded in coincidence with the radiation from the daughter which produced a pulse in the detector at that time. This follows that the coincidence counting rate varies as time varies.

A plot of log of coincidence rates against time gives the decay curve from which the half life of the nuclide is determined. G.M counters and scintillation counters have been used to measure the coincidence rates.

5.21 Nuclear Stability

We know that some nuclides are stable while others are unstable or radioactive. Since radioactivity is a nuclear phenomenon it must have some connection with the instability of the nucleus. A study of the characteristics of a large number of stable and radioactive nuclides shows that the following are the important factors involved.

(a) Even- odd nature of the number of protons and neutrons

We know that the nucleus consists of protons(Z) and neutrons (N). The frequency distribution of stable nuclides in terms of evenness or oddness of number of protons and neutrons present in the nucleus is presented in the Table 2.

Table 2 Frequency Distribution of stable nuclides

Z	N	A=(Z+N)	Number of stable nuclides	Examples
Even	Even	Even	165	${}^{4}_{2}He, {}^{24}_{12}Mg, {}^{208}_{128}Pb$
Even	Odd	Odd	55	${}^{17}_{8}O, {}^{25}_{12}Mg, {}^{157}_{26}Fe$
Odd	Even	Odd	50	${}^{7}_{3}Li, {}^{19}_{9}F, {}^{63}_{29}Cu$
Odd	Odd	even	4	${}^{2}_{1}H, {}^{6}_{3}Li, {}^{10}_{5}B, {}^{14}_{7}N$

One can come to the following conclusions from the table 2

i) There are maximum numbers of stable nuclides when Z and N are both even suggesting that there is a tendency to form p-p and n-n pairs as conducive to stability.

j) The number of stable nuclides in which either Z or N is odd is about 1/3 of those where both Z and N are even. The number of stable nuclides of odd A is almost the same when Z is odd or N is odd suggest that the possibility of neutrons and protons behaving similarly.

(b) <u>The neutron proton ratio (N/Z)</u>

The stability of nucleus is mainly influence by the relative number of protons and neutrons. The lighter nuclides (Z = 20) have equal number of protons and neutrons (Table 3)

Table 3 N/Z ratio in some table nuclides

nuclides	^{2}H	^{20}Ne	^{40}Ca	^{64}Zn	^{90}Zr	^{120}Sn	^{150}Nd	^{202}Hg
Z	1	10	20	30	40	50	60	80
N	1	10	20	34	50	70	90	122
N/Z	1.00	1.00	1.00	1.13	1.25	1.50	1.50	1.53

The N/Z ratio is one for all light nuclides up to ^{40}Ca and thereafter the ratio is greater than one for heavy nuclie.

The variation of N against Z is given in Figure 9. Fig 9 is known as the Segre Chart

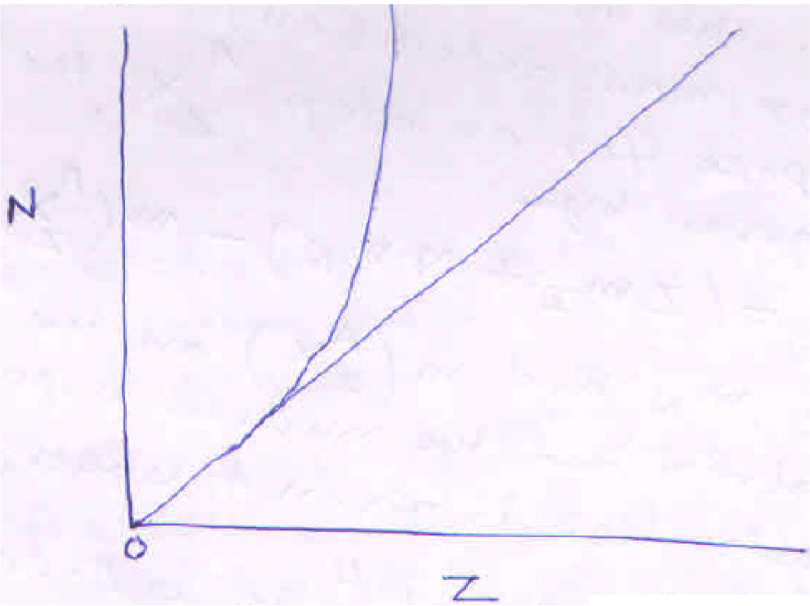


Figure 9: A Plot of N against Z

The $\frac{N}{Z}$ ratio lies in the range of 1.0 to 1.6 (Table 3) indicates a stable nucei. The elements lying within the range of 1.0 to 1.6 constitute the stability zone or stability belt. Elements which do not fall within the stability zone are unstable. The nuclie whose $\frac{N}{Z}$ is either <1 or >1.6 disintegrate giving out α,β or a γ ray in their attempt to attain stability. Emission of α - particles increases the N/Z while an emission of β-decreases the $\frac{N}{Z}$. The decay process continues till the N/Z falls within the stability zone.

Thus, $\frac{N}{Z}$ ratio appears to be another factor responsible for nuclear stability.

5.22 Mass Defect or Mass loss (Δm)

We know that the atomic nuclei are made up of Protons and neutrons. The mass of protons and that of a neutron are not whole numbers which is revealed from mass spectrograph. One would expect the mass of the nuclide to be sum of the masses of protons and neutrons in reality, but the actual mass of every nucleus is not equal to the sum of the masses of protons and neutrons consisting the nucleus. Thus the actual mass of the nucleus is always less than the sum of the masses of the nucleus (nucleon means protons and neutrons). This mass difference is called the mass loss or mass defect (Δm).

Suppose for an atom ${}^{A}_{Z}X$, the mass

$\Delta m = (Zm_z + Nm_N) - m({}^{A}_{Z}X)$----(47)

Where m_z, m_N and m(${}^{A}_{Z}X$) are the masses of Proton,neutron and the nucleus respectively.

An illustration is given to understand mass defect.

The actual mass of He is 4.0026 amu

Mass of proton = 1.0078 amu

Mass of a neutron =1.0087 amu

The number of protons and neutrons present in the helium nucleus are 2.

Substituting these values in equation and solving for , we get

-$\Delta m = 0.0304 amu$-----

c) *Packing fraction (f)*

It is possible to measure the exact isotopic masses using sensitive mass spectrometers. Although the atomic masses are nearly whole numbers, yet they differ from whole number. The deviation of nucleus mass from whole number is expressed in terms of packing fraction (f). *It is defined as the difference between the actual nuclear mass and mass number divided by the mass number and is denoted by*

$$f = \frac{Aactual\ nuclear\ mass - Mass\ number}{Massnumber} X10^4$$

Science the packing fraction is a very small quantity it is generally multiplied by 10^4.

To illustrate,

The actual mass of ^{35}Cl nucleus is 34.98 amu

$$f = \left(\frac{34.98-35}{35}\right) \times 10^4$$

$$= -0.00057 \times 10^4$$

= -5.7

Packing fraction is a measure of stability of the nucleus. It can have both positive and negative values. If the value of packing fraction is negative, then the nucleus is stable while if f is positive, then the nucleus is unstable. A plot of f x 10^4 against mass number of various nucleides are given in Figure 10

Figure 10: Aplot of f against A

The nuclides having negative values of f are more stable while nuclides having positive values of f are unstable.

d) Binding Energy (B)

The binding energy of the nucleus is defined as the energy released in the formation of a given nucleus from protons and neutrons. The binding energy is given by the relation

$$B = \text{mass defect} \times 931 \text{ MeV}$$

$$= \Delta m \times 931 \text{ Mev} \quad \text{-------------(48)}$$

Binding energy per nucleon ($\bar{B}$) is given by

$$\bar{B} = \frac{B}{number\ of\ nucleons} \text{--Mev---(49)}$$

To illustrate, let us consider two examples.

a) $^{2}_{1}H$ And b) $^{56}_{26}Fe$

a) $^{2}_{1}H$; mass of $^{2}_{1}H$=2.014102 amu

$^{2}_{1}H$ contains 1 proton and 1 neutron

$$^{Z}m_{z} = (1\times1.0078725)\text{amu}$$

$$^{N}m_{N} = (1\times1.002388)\text{amu}$$

$$\Delta m = (Zm_z + Nm_N) - m({}_{1}^{2}H)$$

$$= (1.007825 + 1.008665) - 2.014102$$

$$= 0.002388\text{amu}$$

$$B = \Delta m \times 931$$

$$= 0.002388 \times 931 = 2.223 \text{ Mev}$$

$$\bar{B} = \frac{B}{2} = \frac{2.223}{2} = 1.1116Mev$$

c) ${}_{26}^{56}Fe$

Mass of ${}_{26}^{56}Fe$ = 55.934932amu

${}_{26}^{56}Fe$ Contains 26 protons and 30 neutrons

$$^{Z}m_z = (26 \times 1.0078725)\text{amu}$$

$$^{N}m_N = (30 \times 1.002388)\text{amu}$$

$$\Delta m = (261.007825 + 30 \times 1.008665) - 55.934932$$

$$\Delta m = 0.528468\ amu$$

$$B = 0.528468 \times 931$$

$$= 492.000371 \text{ Mev}$$

$$\bar{B} = \frac{B}{56} = \frac{492.000371}{56} = 8.7858 \text{ Mev}$$

The finding energy per nucleon($\bar{B}$) have been calculated in the same manner and a plot of $\bar{B}$ against the mass number (A) is given in figure 11.

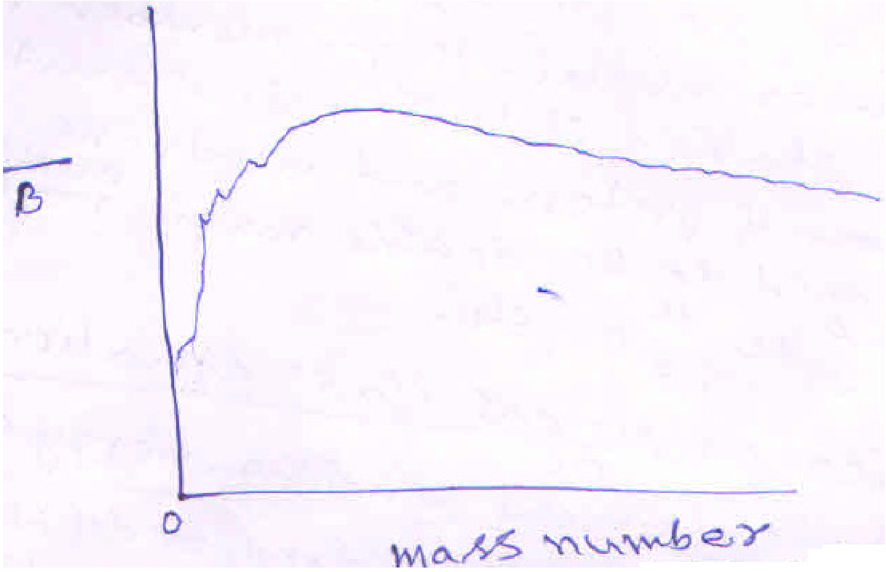


Figure 11: A plot of against A

The binding energy is positive for all nuclides because protons and neutrons attract one another when brought them to within a nuclear distance. An inspection of Fig.11 reveals the following:

i) Light nuclides (A < 30)

Among the lighter nuclides, the $\bar{B}$ for a nucleus of even A is lighter than that for the neighboring odd nuclei. The larger the mass defect, larger will be the binding energy and more stable will be the nucleus. The higher binding energy of ^{4}He ,^{12}C, ^{16}O etc shows that the nuclei are more stable.

ii) Medium nuclides(30 < A <90)

The $\bar{B}$ value rises sharply from 8Mev for A=16 to about 8.3 Mev for A between 28-32. The broad maximum being around A=60 or the region iron, cobalt and nickel.

iii) Heavy nucleus(A > 90)

The $\bar{B}$ value decreases from 8.7 to 7.7 Mev A = 210. $^{209}_{83}Bi$ is the heaviest stable nuclide. Beyond this the nuclides are unstable and radioactive.

5.23 Magic numbers

The nuclei which have either the number of Protons (Z) or the number of neutrons (N) is equal to 2, 8, 20, 50, 82 or 126 are called magic number nuclei. Magic number nuclei are highly stable. *If the nucleus contains magic number of protons and neutrons such nucleus is said to be double magic number nucleus.*

For example: $^{4}_{2}He$, $^{16}_{8}O$ Etc…..

5.24 The Semiempirical Mass equation (The Semiempirical finding energy equation)

On the basic of liquid drop model weizsacker proposed the semiempirical mass equation. This equation contains five terms.

Binding energy(B) = $B_v + B_s + B_s + B_c + B_a + B_p$------(50)

Where B_v is the Volume energy

$$B_V = a_v A, where\ a_v = 14.1\ Mev$$

B_s is the surface energy

$$B_s = -a_s A^{2/3}, where\ a_s = 13.0\ Mev$$

$B_c$is the coulomb energy

$$B_c = -a_c Z(Z-1)A^{-\frac{1}{3}} where\ a_c = 0.595\ Mev$$

B_a is the asymmetry energy

$$B_a = -a_a(A-2Z)^2\, A^{-\frac{1}{3}}\ where\ a_c = 19\ Mev$$

And Bp is the pairing energy

$$B_p = \pm a_p A^{-1}; where\ a_p = 135$$

+ for even Z and even N, - for odd Z and odd N and 0 for odd A

Inserting the above terms in equation (5)

We get

B = $14.1\,A - 13A^{\frac{2}{3}} - 0.595Z(Z-1)A^{-\frac{1}{3}} - 19(A-2Z)^2A^{-1} \pm 135A^{-1}$----------------(51)

Equation (51) can be used to calculater the finding energy of the nucleus.

5.25 Problems

1. A radio nuclide decays after 68 min only ¼ of its original amount remains. Calculate the decay constant and halflife period.

$\lambda = \frac{2.303}{t}\log\frac{N_0}{N}$where t=68min , $N_0 = 1\ and\ N = \frac{1}{4}$

$$\therefore \lambda = \frac{\frac{2.303}{68}\log N_0}{N}$$

When t = 68 min, N_0 = 1 and N = $\frac{1}{4}$

$$\therefore \lambda = \frac{2.303}{68}\log\left(\frac{1}{\frac{1}{4}}\right) = \frac{2.303}{68}\log 4$$

=0.0204min

$$t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{0.0204} = 34\ min$$

2. In an experiment it was found that randon lost half of its activity in 3 days and 30 hrs. Calculate 1) λ and 2) average life period(τ)

$$t_{\frac{1}{2}} = 3\ days\ and\ 30\ hrs$$

=102hrs×60 min = 6120 min

$$t_{\frac{1}{2}} = \frac{0.693}{\lambda}\ or\ \lambda = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{6120} = 1.13 \times 10^{-4} min$$

$$\tau = \frac{1}{\lambda} = \frac{1}{1.13\times10^{-4}} = 8.85 \times 10^3 min$$

5.26 Summary of the unit

The fundamental law of radioactive decay is based on the fact that the decay, i.e. the transition of a parent nucleus to a daughter nucleus is a purely statistical process. The disintegration (decay) probability is a fundamental property of an atomic nucleus and remains equal in time. Mathematically this law is expressed as

$$dN = \lambda N dt$$

The process of radioactive decay is governed by statistical chance. This chance of decay is equivalent to the degree of instability of the parent nucleus. Each radioactive nuclide has its specific degree of instability which, as we will see, is going to be expressed by the half-life assigned to this nuclide.

The radioactivity of a sample is more complicated if it consists of two or more components, such as i) in the case of a mixture of independent activities, ii) if one specific type of nuclide shows two modes of decay, so-called branching decay, and iii) if we are dealing with a nuclear decay series in which also the daughter nuclides are radioactive.

It is a common practice to use the half-life ($T_{1/2}$) instead of the decay constant (λ) for indicating the degree of instability or the decay rate of a radioactive nuclide. This is defined as the period of time in which half of the radioactivity has disappeared (half of the nuclei have disintegrated).

The mean life of a nuclide is the sum of the life times of a certain number of nuclei (before they have all disintegrated) divided by the number of nuclei. During the time interval dt a number of dN nuclei disintegrate. These "lived" during a period t, which amounts to a total life time for dN nuclei

5.27 Key words

Classification of nuclides; Stable and radioactive nuclides; Radioactive decay; Types of Radioactive decay; Decay Schemes; General characteristics of radioactive decay; Decay Kinetics; The Half-life and the mean life period; Units of radioactivity; Parent-Daughter decay growth relationships; Chains of disintegration; General expression for the activity of a daughter nuclide; Radioactive equilibrium; Transient equilibrium; Secular Equilibrium; The case of no equilibrium; Parent and Daughter having nearly the same half-life; Branching decay; Determination of half-lives; Nuclear Stability; Mass Defect or Mass loss (Δm); Magic numbers

5.28 References for further study

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5.29 Questions for self understanding

1) What are stable and radioactive nuclides? Give one example for each.

2) Discuss about radioactive decay.

3) Explain the different types of Radioactive decay with suitable example.

4) Write a decay schemes for radioactive nucleus of your choice.

5) List out the general characteristics of radioactive decay.

6) Write Decay kinetics for radioactive element.

7) What are Half-life and Mean life period.

8) Discuss about units of radioactivity.

9) Explain the Parent-Daughter decay growth relationships.

10) Discuss about chains of disintegration.

11) Write the general expression for the activity of a daughter nuclide.

12) Write short notes on

    1) Radioactive equilibrium
    2) Transient equilibrium
    3) Secular Equilibrium
    4) Branching decay

13) Discuss equilibrium in the following case

    i) Parent and Daughter having nearly the same half-life

14) How do you determine the half-lives of radioactive element?

15) Discuss about nuclear Stability.

16) Write a note on Mass Defect or Mass loss (Δm)

17) What is Magic numbers? Explain its significance.

UNIT-6

Structure

6.0 Objectives of the unit

After studying this unit you are able to

- Explain the Geiger-Nuttal rule
- Explain the theory of α-decay
- Explain the tunnel effect
- Explain the beta decay (β-decay)
- Explain the Fermi's theory of β-decay
- Explain the γ-emission (Nuclear deexicitation)
- List the types of nuclear reactions
- Calculate the energies of nuclear reactions
- Convert one curie into weight of radioactive nuclide
- Explain the Szilard-Chalmers process (Hot atom chemistry)
- Explain the Geiger-Muller Counter (G-M Counter)

6.1 Introduction

The late 1800s and early 1900s were a period of intense research into the new "nuclear" realm of chemistry. In 1896 Henri Becquerel found that a sample of uranium he was doing experiments with had a special property. After he was done with a series of experiments using the uranium, he put it into a drawer with a photographic plate. A photographic plate is a piece of glass covered in chemicals. It was used as the "film" in old style cameras. Becquerel was surprised to find out later that the uranium had caused the plate to be fogged up, as if it had been exposed to light. He correctly assumed that the uranium was emitting radiation similar to visible light. He was even able to show that a magnetic field seemed to change the direction that this invisible radiation traveled. Shortly after this, Marie and Pierre Curie isolated two other radioactive elements, polonium and radium. No matter what physical or chemical stresses they placed on these elements, they continued to emit radiation just like the uranium that Becquerel had used. Since nothing they did could stop the radioactivity, they believed that the radioactivity must come from deep within the atom, in what we would today call the nucleus.

We now know that radioactivity actually results from the decay (disintegration) of an unstable nucleus. This process fundamentally changes the nucleus of the element itself. The radiation that we measure is evidence of events happening inside the nucleus. In many cases this will actually result in the element changing to a different element, a process called transmutation. The reason these decays happen is because they result in more stable nuclei.

6.2 A review of α, β and γ decays

The following modes of decay will be discussed.

Alpha decay (α-decay)

Consider a nuclear reaction undergoing α decay

$^{226}_{88}\text{RA} \rightarrow {}^{222}_{86}\text{Rn} + \alpha({}^{4}_{2}\text{He})$

When the parent nucleus emits an α particle giving a daughter nucleus which has four units of mass loss and two units of charge loss ie, shifting two places to the left in the periodic table. All nuclides of $Z > 83$ tend to undergo α decay.

6.4 The range and ionizing power of α particles

α-particles have a range of few cm in air and 0.004 cm in aluminum. The term "range" in air refers to the distance in air from the source up to which practically all the emitted α- particles traverse. The range (R) is related to the energy of the particle (E) by the expression

$$R = 0.318E^{3/2} ----(52)$$

Using this relation, the energy of particles can be calculated provided the value of R is known. When an α-particle passes through any matter, it loses energy. The stopping power (S) of a medium is defined as

$$S = -\frac{dE}{sx}$$

S is expressed as

$$S \approx \frac{R_{air}}{R_{medium}} ----(53)$$

The stopping power of the medium is obtained from the ratio of mean ranges in air to that of the medium.

6.4 Energy spectrum of α-particles

The α particle energy spectrum consists of a monoergic corresponding to the decay of parent nucleus. The maximum energy of decay is given by

$$E = \left[m_p - (m_r - m_\alpha)\right] ----\rightarrow(54)$$

Where m_p is the mass of the protons and m_r is the mass of the recoil nucleus.

6.5 Geiger-Nuttal rule

The relationship between the energy of the α particle emitted from different nuclides and the halflives of the emitters is given by Geiger and Nuttal in the form of an empirical relation and is known as Geiger-Nuttal rule.

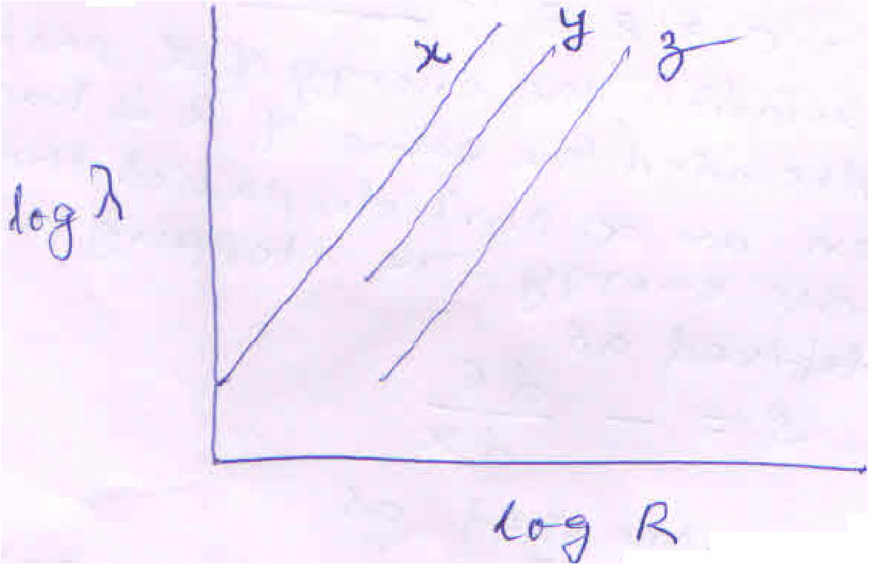

Figure 12: A plot of logλ against log R for different α-emitters

where x represents (4n + 2) uranium radioactive series

y represents (4n + 0) thorium radioactive series and

z represents (4n + 3) actinium series.

Mathematically it is represented as

$$\log \lambda = A \log R + B - - - (55)$$

Where A and B are constants. When there is a decrease in their halflives the energy of α-particles increases. A plot of logλ against log R (R = 0.318 $E^{3/2}$) for different α emitting nuclides is drawn α-emitters of a given radioactive series fall on the same line. x, y and z are for the naturally occurring series (4n+2) ,(4n+0) and (4n+3) and the lines are almost parallel.

6.6 Theory of α-decay

It was a problem in classical mechanics that it was not clear how α particles of energy between 4 and 9 Mev able to escape from the nuclei against a coulomb barrier of the order of ~30 Mev. Now the question arises whether the α particles with the same amount of energy from the outside can enter the nucleus. But actually it does not happen because electrostatic repulsion prevents the α particles entering the nucleus from the outside which was proved from the experiments of Rutherford.

6.7 A Wave mechanical solution: The Tunnel effect

The problem of α decay is similar to that of the particle in a box in wave mechanisms. Classical laws expect a node ie zero amplitude for the particle at the wall of the Colombo barrier (V > E), while in wave mechanics, a small finite amplitude is possible at the boundary provided the potential barrier is not infinitely high or infinitely wide (Figure 13 A and 13 B)

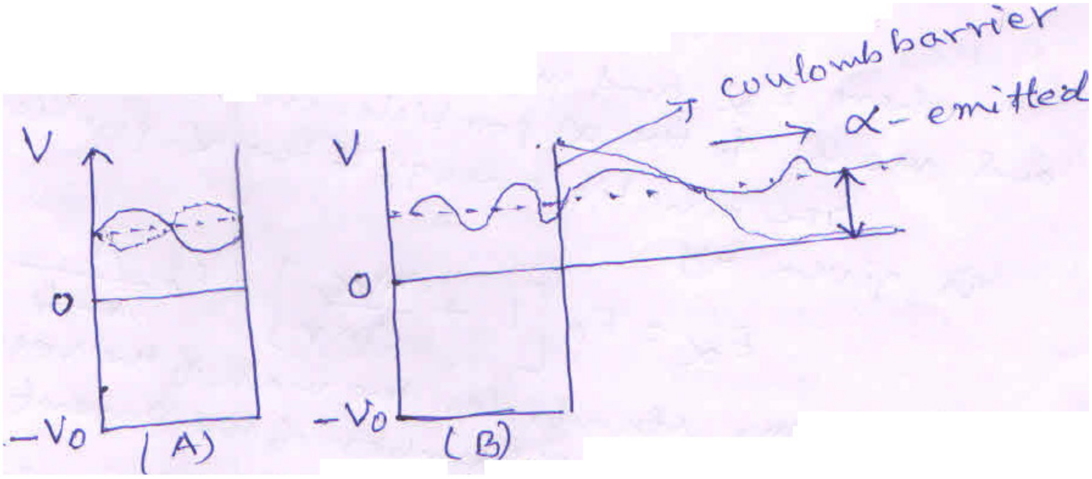

Figure 13: the problem of α-decay where A) is the classical model and B) is the tunnel effect

As a result, the particle is able to traverse the barrier once in a way as if it had found tunnel in the barrier. A solution to the Schrodinger equation for the α-particle shows that there is a finite probability for the escape of α-particle.

The wave mechanical theory of α-decay was developed by Gamow and Condon and Gurney. This theory assumes preformation of α-particles in the nucleus before its emission. The probability of preformation varies between 0.1 and 1.0 the value approaching unity for even Z, even N nuclei. The decay constant for α-emission on this theory is given by

$$\lambda = \theta\lambda_o P - - -\text{----}(56)$$

where θ is the preformatuion factor, $\lambda_0$is the frequency factor denoting the number of times an α-particle arrives at the nuclear border and p is the probability of escape.

The frequency factor (λ_0) is given by

$$V_\alpha = \frac{v_\alpha}{2R} - - - - - - - - - - \text{-}(57)$$

Where V_α is the velocity of particle and R is the effective radius (2R is the effective diameter)

$v_\alpha$is given by

$$v_\alpha = \sqrt{\frac{2E_\alpha}{m_\alpha}}\text{---------(58)}$$

where E_α and m_α are kinetic energy and mass of the α-particle inside the nucleus.

The kinetic energy of the α-particle is given by

$$E_\alpha = E_0\left[1 + \frac{m_\alpha}{m_\gamma}\right] = E_0\,\frac{A}{A-4}\text{----(59)}$$

where m_r stands for the mass of the recoil nucleus and A is the mass number of the parent. The frequency factor gives the information about the α particle reaching the effective border of the nucleus.

The escape of α-particle is given by the probability factor and is given by

$$\mathrm{P} = e^{-[\frac{4z_\alpha\, z_\gamma e^2}{\hbar v\alpha}(b - Sinb\; Cosb)]}\text{-----(60)}$$

$$\text{where b} = Cos^{-1}\left[\frac{m_\alpha v_\alpha^2 R}{4e^2(Z-2)}\right]^{\frac{1}{2}}$$

The probability factor is also referred to as the permeability or transparency or transparency of potential barrier.

The values of p and λ_0 are substituted in equation (56) and on simplification, we get

$$\log\lambda \approx (a-b)\frac{(Z-2)}{V_\alpha}\text{-----(61)}$$

where a and b are constants. The wave mechanical theory of α decay is applicable to even Z even N α–emitting nucliides which have no resultant spin. When Z or N or both are odd, this theory is less satisifactory.

6.8 Beta decay (β-decay)

There are three types of β-decay namely negatron decay(β-), positron decay (β-) and electron capture (EC).

In the case of negatron decay, one of the neutrons of the parent nucleus transforms into a proton and an anti neutrino is emitted along with proton.

$${}^{1}_{0}\mathrm{n} \rightarrow {}^{1}_{1}\mathrm{P} + \beta^{-} + \bar{\gamma}\text{ (antineutrino)}$$

$${}^{24}_{11}\mathrm{Na} \rightarrow {}^{24}_{12}\mathrm{Mg} + \beta^{-} + \bar{\gamma}$$

In the case of positron decay, one of the protons of the parent nucleus transforms into a neutron and a neutrino is emitted along with positron and neutron

$${}^{1}_{1}\mathrm{P} \rightarrow {}^{1}_{0}\mathrm{n} + \beta^{+} + \gamma\text{ (neutrino)}$$

$${}^{22}_{11}\mathrm{Na} \rightarrow {}^{22}_{10}\mathrm{Ne} + \beta^{+} + \gamma$$

The process of electron capture (EC) is similar to that of positron decay.

$^{1}_{1}P$+e(from outer shell) → $^{1}_{0}n + \gamma$

$^{55}_{26}Fe \xrightarrow{EC} {}^{55}_{25}Mn + \gamma$

6.9 Range and absorption of β-particle

β-particles are more penetrating and less ionizing than α-particles.

(a) β-particle energy

When the number of β-particles pass through matter, the number decreases exponentially with the thickness of the absorbing medium.

Thus

$$N_x = N_0 e^{-\mu x} \text{-------(62)}$$

where N_x and N_0 are numbers of β-particles after passing through the thickness x and zero thickness of the absorber and μ is the linear absorption coefficient.

The range of β-particle depends on the number of collisions the beta particales make with the atomic electrons electrons of the absorbing medium. ie on the number of electrons per unit mas or its Z/A ratio. β-particle energy spectrum is continuum because the energy of B-particles are not monoenergetic.

The empirical range energy relations are

$$R=412\, E_0(1.265 - 0.0954 \ln E_0) \text{------------(63)}$$

$$\text{and } R=530E_0 - 106 \text{-----------(64)}$$

when $E_0 > 2.5$ Mev

where E_0 is the end point energy in Mev and R is the range in mg/cm^2.

The mass of the parent atom must be greater than that of the daughter atom.

$\Delta m = (m_{parent} - m_{daughter}) > 0$in all cases of β decay.

6.10 Fermi's theory of β-decay

During n ↔ P inter conversion, the electrons positrons and the neutrinos are formed.

6.11 Sargent Curve

The empirical relationship between the decay constant and the end point energy was proposed by Sargent. Greater the end point energy E_{max}, larger the decay constant. Sargent showed that if logλ is plotted against log E for different naturally occurring β-emitters, the points fall on two straight lines (Figure 14)

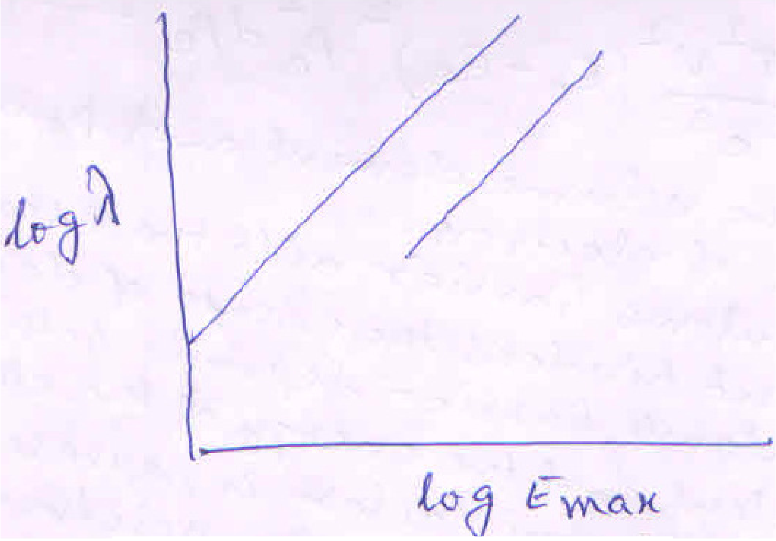

Figure 14: Sargent curves for β-emitters

For a given value of E_{max} the λ for the upper series is very larger than λ for the lower series which has been interpreted by referring to the β-decays of the upper series as allowed transitions and of the lower series as relatively forbidden transitions.

Fermi introduced a new natural force governing the interconversion of n↔P which is referred to as beta-neutrino field theory.

The Fermi force constant is found and the value is

$$G=10^{-60}Jm^3\text{-------(65)}$$

The matrix element $|M_{if}|^2$ governs the relationship between the properties of the parent (initial) and the daughter (final) wave functions of the initial(i) and final (f) nuclear states, spins, parties and arrangements of nucleus are involved in the matrix element. If the initial and final states donot differ very much, then $|M_{if}|^2$ will have a large magnitude and the transition, Parent ↔ daughter will be easy.

The number of ways of distribution ($\frac{dN}{dE_0}$) of total energy (E_0) between E_e and E_v is given by

$$\frac{dN}{dE_0} = \frac{16\pi^2 v^2}{h^6 c^3}(E_0 - E_e)^2 P_e^2 dP_e\text{----(66)}$$

where V is the volume element and P is the momentum of electrons. The effect of coulomb barrier depend both on Z of the product nucleus and the energy of the electron or positron. This Fermi factor is represented by F(Z, Ee) with Z positive for positrons and negative for electrons.

The probability of emission of an electron of momentum P(p_e) is given by

$$P_{(pe)} = \frac{4\pi^2}{hv^2}\left|M_{if}\right|^2 G^2F(z,E_e)\frac{dN}{dE_0}\text{------(67)}$$

Substituting for ($\frac{dN}{dE_0}$) in equation (67), we get

$$P_{(pe)} = \frac{64\pi^4}{h^7c^3}\left|M_{if}\right|^2 G^2F(Z,E_e)(E_o-E_e)^2\,P_e^2 dp_e - - - - - - - - \text{(68)}$$

For a given parent-daughter transition, taking$\left|M_{if}\right|^2$ constant, equation (68) reduces to

$$P_{(pe)} = constantF(Z,E_e)(E_0-E_e)^2P_e^2dp_e\text{------------(69)}$$

$$\left[\frac{P_{(pe)}}{F(Z,E_e)P_e^2}\right]^{\frac{1}{2}}\text{= conNstant } (E_0\text{-}E_e)dp_e\text{----------(70)}$$

The decay constant (λ) is given by

$$\lambda\text{= -}\int_0^{Pe(max)} P_{Pe} - - - - - -\text{--(71)}$$

Substituting equation (68) in equation (71) we get

$$\lambda\text{=}\frac{64\pi^4}{h^7c^3}c^2\left|M_{if}\right|^2\int_0^{Pe(\max)} F(Z,E_e)(E_0-E_e)^2P_e^2dP_e\text{------(72)}$$

Replacing the integral by f and putting c = $\frac{64\pi^4}{h^7c^3}$ in equation (72),we get

$$\lambda = cfC^2\left|M_{if}\right|^2\text{---(73)}$$

Taking cC^2 as C^1

$$\lambda = c^1f\left|M_{if}\right|^2\text{or f}\frac{\lambda}{c^1\left|M_{if}\right|^2}\text{== --------(74)}$$

$$\text{But } \lambda = \frac{0.693}{c^1t_{\frac{1}{2}}\left|M_{if}\right|^2}\text{ or } ft_{\frac{1}{2}} = constant\ \left|M_{if}\right|^2\text{------------(75)}$$

where constant = $\frac{0.693}{C^1}$ where $ft_{1/2}$ is the comparative half life period

The $ft_{½}$ is constant for all β-decays having the same matrix element. The value of $ft_{½}$ gives an insight into the role of the matrix element. Log $ft_{½}$ vary from 3 for the super allowed transitions corresponding to high matrix element to above 10 for highly forbidden transitions.

Two sets of selection rules have been suggested by Gamow-Teller and Fermi. The difference lies with regard to the relative spin orientation of the β-and neutrino. If the spins of the two particles are parallel, the Gamow-Teller rules hold good and of the spins are antiparallel, the Fermi rules are valid.

A plot of $[\frac{P(pe)}{F(Z,E_e)Pe^2}]^{1/2}$aginst E should be linear. Such a plot is referred to as Fermi-Kurie plot(Figure 15).

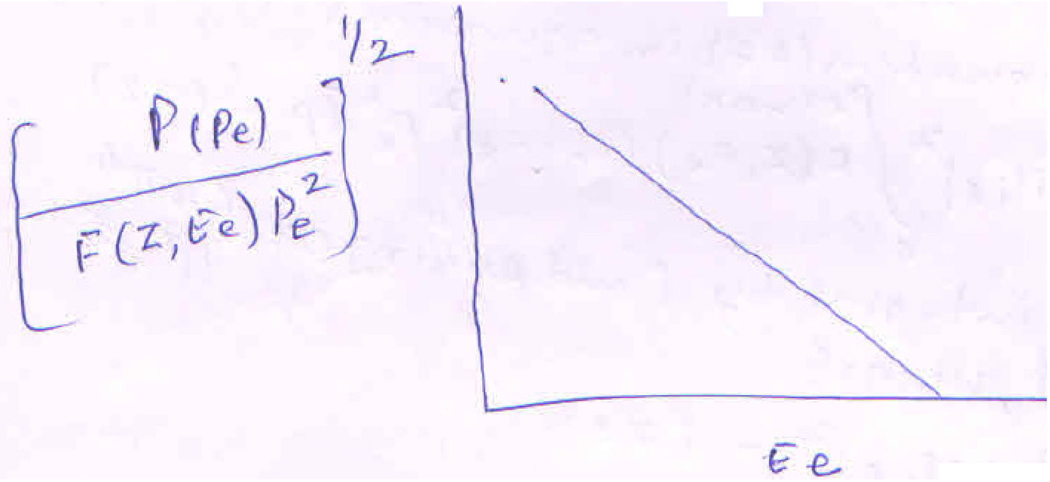

Figure 15: Fermi-Kurie plot

6.12 γ-emission (Nuclear deexicitation)

In any radioactive process the resulting daughter nucleus will be in excited state and its deexitation to the ground state will occur by γ-emission. It becomes necessary to indicate the spin and parity of the parent and daughter nuclides in γ-transition. The penetration power of γ will be very much higher and ionization power of γ will be very much lower than β-and α-particles.

A γ photos has an energy hν and angular momentum = L. h/2 with L=1,2,3 ..but not zero). The probability of γ-emission is governed by reduced transition probability whose value depends of the difference in wave functions of the initial (ψ_i) and the final states (ψ_f) and on the changes in spin (I), Party (π) and energy (E).

A distinction is made between those with $t_{1/2} < 10^{-7}$s and those with $t_{1/2} > 10^{-7}$s on the basis of half life. The half lives of those with $t_{½} < 10^{-7}$s, the transitions are virtually instantaneous and those with t ½ > 10 are termed isomeric transitions (IT). The absorption or emission of radiation is due to

a) a to and fro motion of charges giving rise to electric multipole radiation(EL) or
b) a fluctuation in the electric current flowing in closed loops giving rise to magnetic multipole radiation (ML). L stands for $|I_i - I_f|$ and L is also multiple order 2^L.

Thus L= 1, diploe, L = 2 quadrapole, L = 3, octopole whether the radiation is of the electric or magnetic multipole origin is determined by $\pi_i + \pi_f + L$. If the sum is even , the emission is EL type, if odd , it is of the ML type. Even parity is taken as +1 and odd parity as -1.

The change in energy, $\Delta E = E_i - E_f = h\nu$-----(76)

The change in spin, $\Delta I = |I_i - I_f|$=L------(77)

$$|I_i + I_f| \geq L \geq |I_i - I_f|\text{-------------(78)}$$

A is even if I and I are both integers, both are semiintegers for A is odd and A does not change in a –transition

$L = |I_i - I_f| > 0$------(79)

When $I_i = I_f$, no emission of proton takes place. The parity in the transition process is conserved. The parity of the photon emitted depends of EL or ML radiation.

Some examples for nuclear deexitation by γ-emission are given in Figure 16.

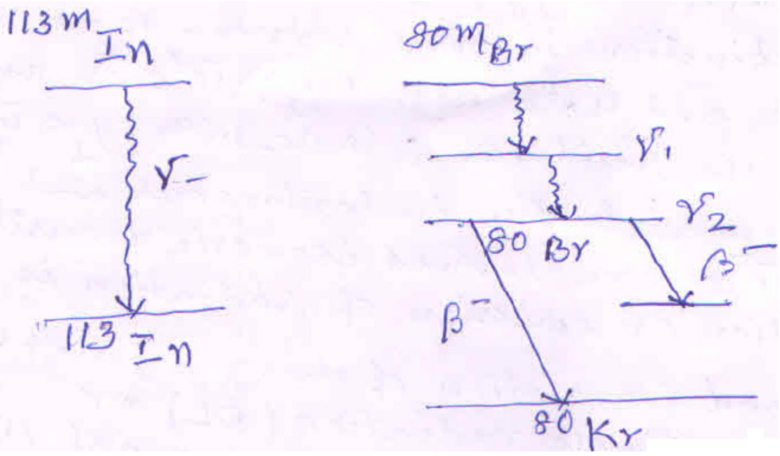

Figure 16: Nuclear deexcitation by γ-emission

6.13 Target Chemistry

When an atomic nucleus is bombarded with projectiles of light nuclei or nucleons or photons of adequate energy, a nuclear transformation of a stable nucleus takes place. This transformation is known as nuclear reaction. A nuclear reaction is generally represented as

$$ {}^{A_1}_{Z_1}X + {}^{A_2}_{Z_2}a \rightarrow {}^{A_3}_{Z_3}b + {}^{A_4}_{Z_4}Y $$

where X is a target nucleus, a is the projectile effecting the reaction, b is the ejectile and Y is the product nucleus or recoil nucleus Z_1, Z_2, Z_3 and Z_4 are the atomic numbers or numbers of protons of X ,a,b and Y respectively and A_1, A_2, A_3 and A_4 are their mass numbers. *Since the stable nucleus is used as the target and transforming it to the radio isotope by bombarding the target with a suitable projectile, the chemistry dealing with nuclear reactions is called Target Chemistry.* Normally in a nuclear reaction, the atomic numbers of all the reactants and products and atomic masses for the projectile and ejectile are omitted. A shorter form of representing a nuclear reaction is

$$^{A1}X(a,b)^{A4}Y$$

Here, the target is written first and the product is last. With the projectile and erectile inside the paranthesis in the same order but separated by a comma. *The shorter version of representing a nuclear reaction is called the Bethe notation*

Ex: $^{35}Cl(n,p)^{25}S$; $^{24}Mg(\alpha,\alpha)^{22}Na$;

$^{23}Na(n,\gamma)^{24}Na$, $^{63}Cu(p,p3n9\alpha)^{24}Na$

In the above examples, n is the neutron ($^{1}{}_{0}n$), p is the proton($^{1}{}_{1}H$), d is the deuteron($^{2}{}_{1}H$) in and γ is gama particle.

6.14 Types of nuclear reactions

One way of naming nuclear reaction is simply by naming (a,b) on the target nucleus. The nuclear reactions are distinguished based on the nature of a and b.

a) Elastic scattering

In this case, a = b, and X = Y

Ex:$^{9}B_{E}(n,n)\ ^{9}B_{e}$

The projectile strikes the target nucleus, loses a fraction of kinetic energy. There is no change in potential energy and the kinetic energy is conserved. Such a process is known as elastic scattering. The slowing down of fast neutrons by a moderator in a nuclear reactor is mainly by elastic scattering.

b) Inelastic scattering

If some of the Kinetic energy of the particle is used up in raising the potential energy of the target, then it is considered as inelastic scattering. Here the kinetic energy is not conserved.

Ex:- $^{107}Ag(n,n^{1})^{107}Ag^{*}$-------IT(44.3s)---------→ ^{107}Ag (where IT is isomeric transition)

The incoming neutron of high energy excited the target nucleus to an excited state and has a long life of 44.35 .The scattered neutron has less kinetic energy and is shown by putting the prime as superscript on the ejected neutron.

c) Photonuclear reactions

Nuclear reactions induced by high energy photons are referred to as photonuclear reactions.

Here a = γ and b = n or p

With high energy photons b may be d, t or α or even a mixture of particles. t stands for triton

Ex:-$^{2}H(\gamma, n)^{1}H$; $^{27}Al(\gamma, n2P)^{24}Na$

d) Radioactive capture

Particle on capture leads to the emission of radiation in the form of one or more γ-photons ie, b = γ. (n, γ) reactions are most common. In this an isotope of the target nucleus is obtained

Ex:-$^{23}Na(n,\gamma)^{24}Na$; $^{31}p(n,\gamma)^{32}p$

There are also (p,y) reactions

Ex: $^{19}F(p,r)^{20}Ne$; $^{27}Al(p,\gamma)^{28}Si$

e) Oppenheimer-Phillips process OR Stripping reaction

Oppenheimer and Phillips used deuterons as projectiles. Deuteron consists of a proton and a neutron. The deuteron–target interaction involves two stages

a) The splitting of the deuteron into a proton and a neutron followed by
b) The capture of the latter by the target nucleus and becomes similar to a neutron-nucleus interaction in which the excess energy is emitted as γ-radiation.

Thus *the stripping mechanism involving the (d,p) reactions at low energy with no compound nucleus formation is known as Oppenheimer-Phillips process (o-P process)*

Ex: $^{7}Li(d, p)^{8}Li$; $^{9}Be(d, p)^{10}Be$

The product is an isotope of the target. At higher energies of deuterons, the (d,n) reactions results.

Ex: $^{6}Li(d, n)^{7}Be$; $^{57}Fe(d, n)^{58}{}_{Co}$

At lower energies, deuterons are completely captured by the target. The (d, γ) reaction is taking place

Ex:$^{12}C(d, \gamma)^{14}N$; $^{138}Ba(d, \gamma)^{140}La$

Moderately high energy deuterons interact with medium mass nuclei giving rise to (d, α) reactions

Ex:$^{6}Li(d, \alpha)^{4}He$; $^{60}Ni(d, \alpha)^{58}Co$

f) Spalltion reactions

When a projectile with high energy of the order of 100 Mev interacts with the target, the target absorbs it and is excited to a state with energies far greater than the binging energies of individual nucleons. Nucleons or group of nucleons are expelled from the excited nucleus until the residual nucleus is left in a relatively stable state. These reactions are referred to as spallation reactions.

Ex:$^{63}Cu(p, p3nq\alpha)^{24}Na$

$^{79}Br(p, p7n7\alpha)^{44}Sc$

6.15 Energies of nuclear reactions

Let us consider a general reaction

X + a → b + Y

We have $(m_x + m_a)931 + E_a = (m_b + m_y)931 + E_b + E_y - - - - - (80)$

where m denotes the mass and E stands for kinetic energies.

Rearranging equation

$$(m_x + m_a - m_b - m_y)931 = (E_b + E_y - E_a) = Q$$

Or $Q = \Delta m \times 931 Mev - - - - - (81)$

where $\Delta m = (m_x + m_a - m_b - m_y$ and Q denotes the energy of the reaction in Mev . Positive Q value signifies that the reaction is exoergic while negative Q value implies for an endoergic reaction. Q is +ve when $(m_x+m_a) > (m_b+m_y)$.

Sometimes, the term Q is included in the nuclear reaction as

X + a → b + Y ±Q

Positive sign indicates the exoergic reaction and negative sign indicates the endoergic reaction.

6.16 Definition of Curie

The activity of radioactive nuclide is expressed in terms of curie(ci). It is defined s the amount of any radionuclide in which the number of disintegrations per second (dps) is 3.7×10^{10}. Mill curie(mci) decays at (3.7×10^{7}dps) and a microcurie (μci) decays at (3.7×10^{4} dps). In reactor technology killocurie(Kci) and megacurie (Mci) are used.

6.17 Conversion of one curie into weight of radioactive nuclide

Let W be the weight of radioactive nuclide. We know that the rate of decay is

$-\frac{dN}{dt} = \lambda N$-------(82)

But $N = \frac{W}{Atomicweight(A)} X Avogadro\ number\ (N_0)$

$$\therefore N = \frac{W}{A} \times N_0$$

And $\lambda = \frac{0.693}{t_{1/2}}$

Substituting the value of N and Y in equation (82) we get

$$-\frac{dN}{dt}=\frac{0.693}{t_{\frac{1}{2}}}\times\frac{wN_0}{A}$$

For 1curi, $-\frac{dN}{dt}=3.7\times10^{10}dps$

$$\therefore 3.7\times10^{10}=\frac{0.693wN_0}{t_{\frac{1}{2}}A}$$

Or $w=\frac{3.7\times10^{10}\times t_{1/2}\times A}{0.693\times N_0}for\ 1\ curie-----(83)$

For 1mci

$$w=\frac{3.7\times10^{7}\times A\times t_{\frac{1}{2}}}{0.693\times N_0}------(84)$$

$$for\ 1\mu_{Ci}w=\frac{3.7\times10^{7}\times A\times t_{\frac{1}{2}}}{0.693\times N_0}-----(85)$$

The curie represents the absolute number of atoms of the radionuclide decaying per second (dps). While the activity is measured by a counter, the actual counts per second(cps) will be a fraction of the disintegrations depending on the counter efficiency and the geometry employed. dps and cps are related by the equation

(cps) = ε(dps)--------→(86)

where ε is the efficiency of the detector, normally less than one.

6.17 Problems

1. Calculate the weight in grms (w) of 1 curie of ^{214}Pb from its halflife of 26.8 min

We know that 1 curie=3.7×10^{10}dps

For 1 curie

$w=\frac{3.7\times10^{10}\times At_{1/2}}{0.693\times N_0}$----

$$\frac{(3.7\times10^{10}\times214\times26.8\times60)}{0.693\times6.023\times10^{23}}$$

$$w=3.1\times10^{-8}g$$

2. Caluculate the weight in grams of 1 curie of ^{238}U whose half life is 4.5×10^{9}y

We know that 1 curie=3.7×10^{10}dps

For 1 curie,

$$w = \frac{3.7 \times 10^{10} \times A \times t_{\frac{1}{2}}}{0.693 \times N_0}$$

$$= \frac{3.7 \times 10^{10} \times 238 \times 4.5 \times 10^{10} \times 365 \times 24 \times 60 \times 60}{0.693 \times 6.023 \times 10^{23}}$$

$W=3.2\times10^6 g$

From the above one could notice that if the half life of the radio nuclide is less, the weight corresponding to it is small.

6.18 Szilard-Chalmers process (Hot atom chemistry)

The reaction product obtained during the Szilard-Chalmers process is radioactive and possess high energy. The atoms possessing high energy and are radioactive are called hot atoms and the chemistry which deals with these atoms are called hot atom chemistry.

Majority of thermal or slow neutron reactions are of (n, γ) type. When the target containing ^{127}I is bombarded with a slow neutron, ^{127}I is transformed into $^{128}I^*$

$$^{127}I + n^1 \rightarrow {}^{128}I^*$$

The asterisk denotes that ^{128}I is in excited state. When it returns to the ground state, the extinction energy is emitted in the form of photons.

$$^{128}I^* \rightarrow {}^{128}I + \gamma$$

According to conservation of momentum, the momentum (mv) of the recoil atom ^{128}I be equal but opposite in sign to that of the photon released which is $\frac{Ev}{C}$ where is true energy of photon and C is the velocity of light. The recoil energy (Er) can be calculated knowing energy of photon and mass of the recoil atom.

$$mv = \frac{E\gamma}{C} ------------- (87)$$

Recoil energy, $E_r = \frac{m^2v^2}{2m} = \frac{Er^2}{2mc^2}$ = ----(88)

Substituting the value of C and expressing the value of Eγ in Mev and of m in amu, the recoil energy in ev comes out to be

$$E_R = \frac{536E_r^2}{A}.ev ----(89)$$

where A is the mass number

Normally the bond energy is about 5ev. The photon energy in most of the cases is of the order of 1-5 Mev and for medium mass nuclei of A is about 50-100, the recoil energy is in the range of 5-250 ev. This value is much greater than the bond energy which is the basis of Szilard-Chalmers reaction. Table 4 gives the maximum energies of photons accompanying (n,γ) reactions with halogen atoms together with the resulting recoil energies.

Table 4

Halogen atom	E_v(Mev)	E_r(ev)
Cl	6.2	543
Br	5.1	174
I	4.8	96

Szilard and Chalmers bombarded C_2H_5I by slow neutrons in presence of water. ^{128}I atoms formed following the bond ruptures pass into aqueous phase as $^{128}I^-$, thus separated the radioisotope ^{128}I freed from the inactive ^{127}I which remains in the organic phase. The yield can be increased if iodide ions are added as carrier. Thus, a large fraction of ^{128}I formed is separated into water layer with high specific activity. This reaction is referred to as Szilard-Chalmers reaction. Organic chloro, bromo and iodo compounds, complex ions, some oxy anions and some organo metallic compounds, ferrocynaides, cobalt and platinum amino complexes etc are suitable for this mode of radioactive reparation.

6.19 Geiger-Muller Counter (G-M Counter)

The procedure for detection and measurement of α, β and γ particles are based on the fact that gases become conductors as a result of exposure to radiations from radioactive nuclides. The radiations are called ionizing radiations because they cause ionization. The rapidly moving α and β particles interact with the gas forming ion pairs. Instruments have been developed wherein the positive ions and electrons produced by ionizing radiations move towards the respective electrodes under the influence of applied potential.

Geiger and Muller have developed a device for counting the ioniozing radiations called the Geiger-Muller counter (G-M counter) which is also called Geiger –Muller tube (G-M tube).

G-M counter consists of two parts namely the G-M tube (detecting unit) and the scalar (counting unit). G-M counter is based on the multiplicative ion collection in other based on the multiplicative ion collection, in other words the G-M counter is used for counting secondary ion pairs but not the primary ions. Since the operating voltage of the G-M counter is in the range of

1000-1300 V, all the primary ions are converted into secondary ions, and in this voltage range, an avalanche of ions are produced. This was discovered by Townsend and it is referred to as Townsend Avalanche.

There are various types of G-M tubes. A very widely used G-M tube is the cylindrical end window type shown in figure 17.

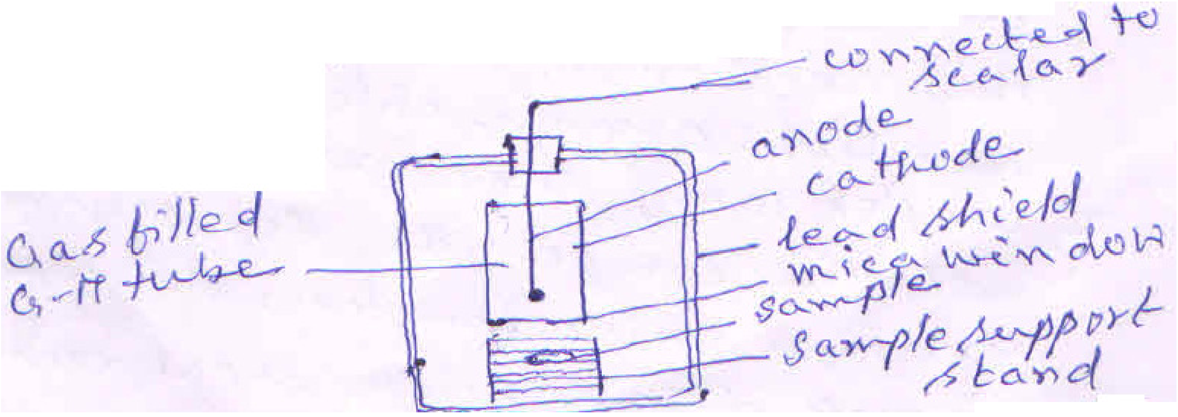

Figure 17: G-M tube

A cylindrical tube is made up of either copper or brass, closed at one end with a thin mica window and the tube itself serves as cathode. A tungsten wire at the center of the tube acts as anode. Cylinder is filled with a suitable gas (normally 90% argon and 10% methane). The radioactive sample is placed in a sample support stand. When the radiations coming from the source enters the tube, gas molecules are ionized. Ion pairs are produced (1 ion pair = 1 positive ion and 1 electron). The flows of electrons are amplified. The pulses produced (counting rate = number of counts per second) are studied as a function of applied voltage. A plot of counting rate against applied voltage is drawn (Figure 18) to find the working region (G-M plateau) of the counter.

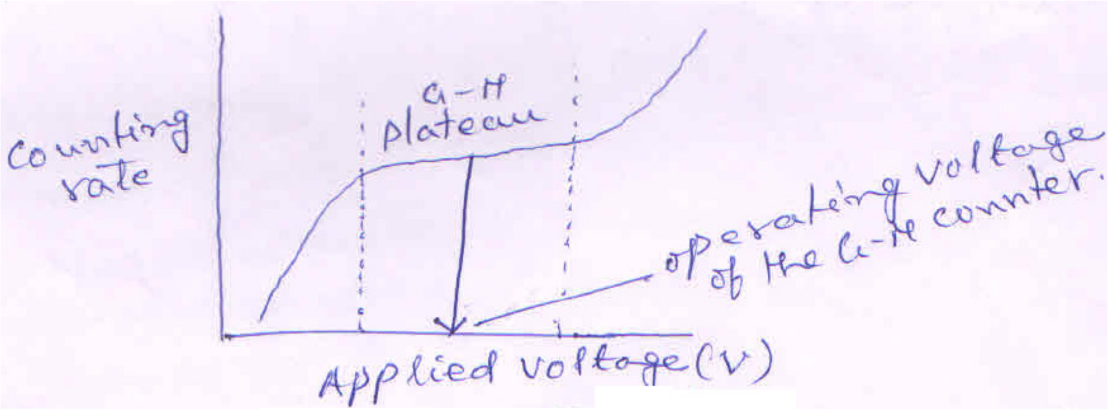

Figure 18: G-M Plateau

In G-M region, electrons moving at high speed reach the anode in 0.2μs, ionize further producing secondary electrons. The secondary electrons so produced cause further ionization and so on. In this way the multiplicative ion collection occurs and this is called Townsend Avalanche. Positive ions move towards cathode slowly because of its heaviness. A sheath of positive ions is formed. It reaches the cathode in about 200 μs. *The time taken by the positive ion sheath to reach the cathode is called the dead time. Dead time is the time during which the counter becomes insensitive to any radiation.* When positive ion sheath reaches the cathode, secondary electrons are emitted. The emitted secondary electrons move towards the anode and renew the discharge. But this discharge should be quenched. To avoid this discharge, poly atomic gases are used along with the usual filling gas. Polyatomic gases such as C_2H_5OH are used for quenching the discharge. Sometimes halogen gases such as Cl_2 or Br_2 are employed as quenching gas.

G-M counters are mainly used for detection and counting of particles. A major disadvantage of G-M counter is the dead time.

6.20 Summary of the unit

The reason the alpha radiation has such a hard time even passing through a piece of paper is because it is not a form of EMR like we might expect. It is actually the nuclei of a helium atom ${}_{4}^{2}He$. During an alpha decay, a nucleus is able to reach a more stable state be allowing 2 protons and 2 neutrons to leave the nucleus. This will result in a smaller nucleus, which is often the more stable arrangement. Because 2 protons and 2 neutrons are really just helium-4, the particle that is emitted is really helium. Because this helium is not just regular helium floating around in the air, but is “born” from a nuclear decay, we usually don't call it a helium atom. Instead we call it an alpha particle. Alpha particles come out of the nucleus as just nucleons without any electrons. So, each alpha particle has a charge of +2e. The atom that originally went through the alpha decay has just lost some of its nucleons. That must change the element somehow. It's actually pretty easy to figure out what will happen as long as we apply the conservation of nucleons.

Beta negative decay (β^-) happens during a process that at first seems crazy. A neutron falls apart and becomes a proton and an electron. In the beta negative decay, the neutron becomes a proton (which stays in the nucleus) and an electron that goes flying out (the beta particle we will use the symbol ${}_{0}^{-1}\beta$). Notice its A value is zero since it is not a nucleon, and its Z value -1 since it is the opposite charge of a proton.

The other type of beta decay is called beta positive. Beta positive is different from beta negative because the particles emitted are the exact opposite. For example, the beta positive decay emits a positive positron. A positron is sometimes called an antielectron, since it is the antimatter version of an electron. Positrons have the same mass as an electron, but their charge is +1e. We use the symbol $^{0}{}_{1}\beta$.

Gamma radiation can only be stopped by stuff like a few inches of lead. This is because unlike the other two forms of decay, gamma decays emit a form of EMR, not a particle, remember that gamma radiation is quite high up in the frequencies of the EM spectrum. This allows it to pass through anything but the densest of matter. Gamma decays happen most often after a alpha or beta decay. This happens because the nucleus has just been through a lot spitting out other subatomic particles, changing to a different element, and all that. The nucleus is basically all jiggled up and needs to release some energy somehow. An easy way to do this is to let off a gamma burst. Because we are releasing energy (not particles), the A and Z values stay the same

6.21Key words

A review of α, β and γ decays; Ionizing power of α particles; Energy spectrum of α-particles; Geiger-Nuttal rule; Theory of α-decay; The Tunnel effect; Beta decay (β-decay); Range and Absorption of β-particle; Fermi's theory of β-decay; Sargent Curve; γ-emission (Nuclear deexicitation); Target Chemistry; Types of nuclear reactions; Energies of nuclear reactions; Definition of Curie; Szilard-Chalmers process (Hot atom chemistry); Geiger-Muller Counter (G-M Counter)

6.24**References for further studies**

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6.23 Questions for self understanding

1) Write a review of α, β and γ decays

2) Discuss the range and ionizing power of α particles

3) Explain the Energy spectrum of α-particles

4) Write the Geiger-Nuttal rule

5) Discuss the theory of α-decay

6) What is Tunnel effect?

8) Write a note on beta decay (β-decay)

9) Discuss about range and absorption of β-particle

10) Discuss the Fermi's theory of β-decay

11) Write a note on Sargent Curve

12) Explain the γ-emission (Nuclear deexicitation)

13) Discuss the types of nuclear reactions

14) Discuss about energies of nuclear reactions

15) Write the definition of Curie

16) How do you convert one curie into weight of radioactive nuclide

17) Discuss the Szilard-Chalmers process (Hot atom chemistry)

18) Explain the procedure of Geiger-Muller Counter (G-M Counter) of ioniozing radiations

UNIT-7

Structure

7.0 Objectives of the unit

After studying this unit you are able to

- Explain the radiation chemistry
- Explain the interaction of electromagnetic radiation with matter
- Explain the photo electric effect
- Explain the Compton Effect
- Explain the pair Production
- Explain the photonuclear reactions
- Write the units of radiation energy
- Explain the significance of G-Value
- Explain the radiation dosimetry
- Explain the fricke dosimeter

7.1 Introduction

Alpha particles, beta particles, and gamma photons are often called ionizing radiation, because as they travel through a substance, they strip electrons from its atoms, leaving a trail of ions in their wake. Let’s explore why this happens and take a look at the effects that ionizing radiation has on our bodies.

Picture an alpha particle moving through living tissue at up to 10% the speed of light. Remember that alpha particles are helium nuclei, so they each have a +2 charge. As such a particle moves past, say, an uncharged water molecule (a large percentage of our body is water), it attracts the molecule’s electrons. One of the electrons might be pulled toward the passing alpha particle enough to escape from the water molecule, but it might not be able to catch up to the fast-moving alpha particle. Instead, the electron is quickly incorporated into another atom or molecule, forming an anion, while the water molecule that lost the electron becomes positively charged. The alpha particle continues on its way, creating many ions before slowing down enough for electrons to catch up with it and neutralize its charge. When a neutral water molecule, which has all of its electrons paired, loses one electron, the cation that is formed has an unpaired electron. Particles with unpaired electrons are called free radicals.

7.2 Radiation Chemistry

Radiation chemistry deals with the study of chemical transformation produced in a substance when it is exposed to nuclear radiation. These radiations include high energy electromagnetic radiation such as X-rays and γ –rays, high energy charged particles such as α, β….etc, accelerated heavy ions, fission products and neutrons.

7.3 Interaction of electromagnetic radiation with matter

Gama rays are electromagnetic radiations similar to X-rays but of shorter wavelength rays interact with matter in several ways. The four principle modes of interaction of γ-radiation with matter are

(i) Photo electric effect
(ii) Compton effect
(iii) Pair production
(iv) Photonuclear reactions

Now we shall discuss one by one

(v) Photo electric effect

This mode of interaction is more significant for low energy photons (10-100kev) photon of energy E_γ is absorbed by single electron of the atom and this electron is ejected with energy E_e.

$$E_e = E_\gamma - E_b \text{----------------}(90)$$

where E_b is the binding energy of the electron.

If $E\gamma > E_b$, the photoelectric emission is possible. It implies that the concept of a threshold frequencyγ_0 such that $h\gamma_0 = E_b$. Hence $E_\gamma > E_b$

$$E_e = h(\gamma - \gamma_0) - - - - - - - - - (91)$$

where γ is the frequency of photon

Equation 91 provides a method of determining the Plank's constant.

If E_γ is very high to release electron from K shell about 80% of the electrons from K shell and the rest from L shell. The hole created from K shell or L shell will be filled by successive jumps of outer electrons. Absorption of photon decreases due to photoelectric effect with increase of photon energy but increases with atomic number of the absorption material. The photoelectric absorption falls with increasing photon energy but again with a sharp rise as the energy reaches the binding energy of electron of K or L shell.

(vi) The Compton effect Or Compton scattering

For intermediate energy photons (0.1 to 10 Mev) the dominant interaction is by Compton scattering. A photon interacts with a loosely bound or free electron, transfer a part of its energy to it and itself gets scattered as a photon of reduced energy. The energy and momentum of the incident photon are shared between the scattered photon and Compton electron or recoil (Figure 19)

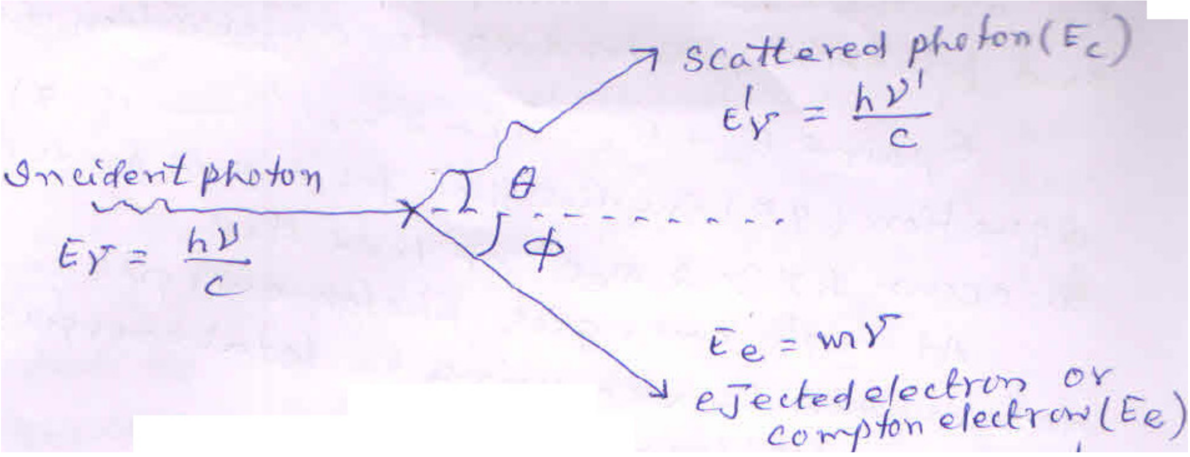

Figure 19: Compton effect

$$Energy\left(E_\gamma\right) = E^1_\gamma - E_e ------(92)$$

Momentum$\left(\frac{h\gamma}{C}\right) = \frac{h\gamma^1}{c} cos\theta + m\gamma \cos \emptyset ----- (93)$

where θ *and* φ *are* the angles of scattered photon and ejected electron.

$$\Delta\lambda = \lambda^1 - \lambda = \frac{h}{m_e c}(1 - cos\theta) ----(94)$$

where $\Delta\lambda$ is called the Compton shift

But $\theta = \frac{\pi}{2}$

$\therefore \Delta\lambda = \frac{h}{m_e C} = 2.42 \times 10^{-12} m$------(95)

which is known as the Compton wavelength.

Equation (94) can be written in terms of energy as

$$\frac{E_\gamma - E^l_\gamma}{E^l_\gamma} = \frac{E_\gamma}{m_e C^2}(1 - Cos\theta) ----(96)$$

If the energies are expressed in terms of Mev and for $\theta = \frac{\pi}{2}$, equation (96) becomes

$$\frac{E_\gamma - E^l_\gamma}{E^l_\gamma} = \frac{E_\gamma}{0.51} --- (97)$$

(vii) Pair Production

Photons of energy greater than 10 Mev, Photon absorption leads to the creation of an electron and a positron pair through the minimum energy required for pair production is $2m_e C^2 = 1.02$ MeV.

If E_- and E_+ are the kinetic energies of the emitted electrons and positrons, according to conservation of energy.

$$E_{pair} = E_- + E_+ = h\gamma - 2m_ec^2\text{-------------(98)}$$

Equation (98) implies that for a pair production to occur $h\gamma > 2m_ec^2$ or 1.02MeV

At high energies, photon energies can be determined by measuring the total energies of electron-positron pair.

(viii) Photonuclear reactions

This was discussed under types of nuclear reactions.

7.4 Units of radiation energy

(a) The rad: defined as

1 rad (γ) = absorption of 100 ergs per gram of the substance

$=10^{-5}$ J/g = $6.24\times 10^{13}\ ^{eV}/_{g}$ ($\therefore 1eV = 1.602 \times 10^{-19}J$

(b) The Gray: SI unit of dose defined as

1 gray (Gy) = 1 J/Kg =100 rads

The dose rate is expressed as rads/ Gys

(c) The Rontgen(R): physicists unit of exposure dose

1R = 0.87rad = 8.7 MGy

(d) The RBE (relative biological effectiveness)

RBE=1 for X-rays, γ-photons and β-particles

RBE = 2.5 for thermal neutrons

RBE=10 for α-particles, protons and fast neutrons.

(e) The Rem (Rontgen equivalent mammal or man)

Rem = RBE X rads

(f) The Sievert : SI unit of rem

1 sievert(SV)=RBE X grays = 100 rem

7.5 G-Value

The yields of the radiation induced reactions are expressed in terms of G value of the product in radiation chemistry. It is defined as the number of molecules of the product formed per 100 eV of energy absorbed. The symbol G is followed by the formula of the compound of interest placed in parenthesis.

Ex: The decomposition of water is denoted as

G$(-H_2O)$

G is related to absorbed dose as

$$G = \frac{N}{D} \times 100 ------------ (99)$$

Where N is the number of molecules produced (decomposed) in 1 cm^3 of the substance and D is the absorbed dose in eV/cm^3. G is expressed in molecules per 100eV

7.6 Radiation dosimetry

When the radiation interacts with matter it loses energy, which can be quantitatively measured. The energy loss is expressed as the quantity of radiation energy absorbed. Radiation dosimetry is used to determine the quantity of radiation energy absorbed.

7.7 Chemical dosimetry

It is used to determine the radiation dose from the chemical change induced by radiation on a suitable substance. Chemical dosimeters are called secondary dosimeters which are widely used because of their greater convenience.

Chemical dosimeter should satisfy the following conditions

(a) The magnitude of chemical change should proportional to the radiation dose over a wide range of dose.
(b) It should be independent of temperature, energy and intensity of radiation.
(c) It should be insensitive to the presence of impurities.
(d) It should be stable under normal conditions and
(e) Analytical method should be available to measure the chemical change.

7.8 Fricke dosimeter

Fricke dosimeter (ferroussulphate) dosimeter fulfills all the above requirement. Ferroussulphate gets oxidized to ferric salt in the presence of O_2 and under the influence of radiation and the extent of oxidation is measured.

The Fricke dosimeter solution is prepared by dissolving 0.4g of ferrous ammonium sulphate [$FeSO_4(NH_4)_2SO_4.6H_2O$], 0.06 g of sodium chloride (which is used to inhibit oxidation by organic impurities) and 22ml of 95-98% H_2SO_4 and making the solution up to 1000 ml with distilled water.

To determine the absorbed dose, a sample of the Fricke solution in a thick enough container is exposed to radiation at the desired spot for a known period of time and the amount of Fe^{3+}

produced is measured spectrphotometrically at the wavelength of 304nm.The molar absorptivity coefficient may be taken as 2174 lit/mol cm or the resulting concentration of Fe^{3+} may be determined from the concentration graph of absorbance against concentration of Fe^{3+}. Taking the standard yield of Fe^{3+}, 15.5 ions per 100eV energy absorbed, the unknown dose is calculated from the measured yield of Fe^{3+}. This method gives reproducible values over a wide range of dose.

The radiation chemistry of the oxidation of Fe^{2+} to Fe^{3+} is discussed below. The mechanism for the conversion of Fe^{2+} to Fe^{3+} on radiolysis is given below

$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^-$ --------- (a)

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^-$ ---------- (b)

$Fe^{2+} + {}^{\cdot}H_2O \rightarrow Fe^{3+} + HO_2^-$ ------------- (c)

$HO_2^- + H^+ \rightarrow H_2O_2$ ---------------- (d)

Here ${}^{\cdot}HO_2$ is obtained from

${}^{\cdot}H + O_2 \rightarrow {}^{\cdot}HO_2$ ------ (e)

The yield of Fe^{3+} is given by

$G(Fe^{3+})_{air} = 2G_{H_2O_2} + 3G_H + G_{OH} ------(100)$

The G values are $G_{H_2O_2} = 0.8, G_H = 3.7$and $G_{oH} = 2.9$

$$\therefore G(Fe^{3+})_{air} = (2 \times 0.8) + (3 \times 3.7) + (1 \times 2.9)$$
$$= 15.6$$

The accepted value of $G(Fe^{3+})$ is 15.5

The average absorbed dose for the volume occupied by the dosimeter solution is determined as follows:

$$G(product) = Number\ of\ molecules\ of\ product\ formed\ per\ 100Ev\ of\ enegy\ absorbed$$

Energy absorbed

$$= \frac{100\ X\ number\ of\ molecules\ of\ product\ formed/g}{G(product)} \frac{(eV)}{g}\ X\ 1.602\ X\ 10^{-12} \frac{(erg)}{eV}\ X \frac{1}{100} \frac{(g.rad)}{(erg)} \text{----- (101)}$$

$$= \frac{1.602 \times 10^{-12} \times number\ of\ molecules\ of\ produt\ formed/g}{G_{(product)}}$$

In case of Fricke dosimeter, the yield of Fe^{3+} is

$Fe^{+3} formed \left(\frac{mol}{l}\right) = \frac{(A_i - A_b)}{\varepsilon l}$-------------- (102)

Where A_i and A_b are the absorbances of irradiated and unirradiated dosimeter solution, ε is the molar absorptivity coefficient and l is the path length.

Thus Fe^{3+} formed $= \frac{(A_i - A_b)}{\varepsilon l} \times \frac{1}{1000\rho} \times 6.023 \times 10^{23}$-------(103)

Substituting equation (103) in equation (101)

We get

Energy absorbed $= \frac{1.602 \times 10^{-12} (A_i - A_b) 6.023 \times 10^{23}}{\varepsilon l G(Fe^{3+}) 1000\rho}$

Energy absorbed $= \frac{9.649 \times 10^{-12} (A_i - A_b)}{\varepsilon l \rho \; G(Fe^{3+})} ------(104)$

Equation (104) gives the absorbed dose in rads.

7.9 Cericsulphate dosimeter

1-10 mM solution of acidified cericsulphate solution is exposed to radiation. Ce^{4+} is reduced to Ce^{3+} and the decrease in concentration is determined spectrotemetrically at the wavelength of 320nm. The accepted value of $G(Ce^{3+})$ is 2.44. The molar absorptivity coefficient (ε) is 5565 M^{-1} cm^{-1}. This dosimeter is useful for measuring high doses of the order of 10^6rads.

7.10 Radiolysis of cysteine

Radiolysis of aqueous solution of amino acids brings about deamination and decorboxylation forming aldehydes. Crysteine ($HS\text{-}CH_2\text{-}CH(NH_2)\text{-}COOH$) contains thiol group (-SH group) which acts as a self protective agent and reduces the deamination process. Crysteine (RSH) is deaerated solution is not deaminted but gives off H_2S and is oxidized to cysteine ($HOOC\text{-}CH(NH_2)\text{-}CH2\text{-}S\text{-}S\text{-}CH_2\text{-}CH(NH_2)\text{-}COOH$) or (RS-SR)

The reactions are

$^{\cdot}H + RSH \rightarrow RS^{\cdot} + H_2$

$^{\cdot}OH + RSH \rightarrow RS^{\cdot} + H_2O$

$2RS^{\cdot} \rightarrow RS\text{-}SR$

The yield of H_2S is maximum at Ph 6. G(cystine) ≈9 . In presence of oxygen, the reactions occurring are probably

$^{\cdot}H + O_2 \rightarrow HO_2^{\cdot}$

$HO_2^{\cdot} + RSH \rightarrow RS^{\cdot} + H_2O_2$

$RS^{\cdot} + O_2 \rightarrow RSO_2^{\cdot}$

$RSO_2^{\cdot} + RSH \rightarrow RS\text{-}SR + HO_2^{\cdot}$

If the irradiation is too long, the yield of crystine falls and itself oxidizes to sulphonic acid and SO_2. The irradiated crystine is deaminted but H_2S is not given off. The study of radiolysiss of compounds is of interest in radiobiology due to their remarkable protective effect on different biochemical products in vivo.

7.11 Radiolysis of biphenyl

Aromatic compounds are much more stable towards radiation than corresponding aliphatic compounds.

Ex:- Benzene is more stable towards radiation than cyclo hexane.

This is due to the resonance stabilization of the benzene ring.

Polyphenyls (biphenyl, terphenyl etc) and polynuclear aromatic compounds (naphthalene, anthracene etc) are the most radiation resistant compounds. On irradiation, these compounds give rise to small yields of a gaseous product, mainly hydrogen and a polymetric mixture containing mixtures of higher molecules weights.

The radiolysis reactions of biphenyl are

$C_{12}H_{10} \rightarrow {}^{\cdot}C_{12}H_9 + H^{\cdot}$

${}^{\cdot}C_{12}H_9 + C_{12}H_{10} \rightarrow$ polymer

$H^{\cdot} + C_{12}H_{10} \rightarrow {}^{\cdot}C_{12}H_{11} \rightarrow$ polymer

The yield of hydrogen takes place from a unimolecular process (non radical reaction)

$C_{12}H_{10} \rightarrow C_{12}H_{10}^{\cdot} \rightarrow C_{12}H_8 + H_2$

and a bimolecular process

$$\left.\begin{array}{l} C_{12}H_{10} \rightarrow C_{12}H_{10}^{\cdot} \\ C_{12}H_{10} \rightarrow C_{12}H_{10}^{\cdot} \end{array}\right\} \rightarrow C_{24}H_{18} + H_2$$

However, the yield of hydrogen and other products depend on the temperature of radiation and the total dose absorbed.

7.12 Summary of the unit

Radiation chemistry deals with the study of chemical transformation produced in a substance when it is exposed to nuclear radiation. These radiations include high energy electromagnetic radiation such as X-rays and γ –rays, high energy charged particles such as α, β….etc, accelerated heavy ions, fission products and neutrons.

Some radioactive nuclides are especially damaging because they tend to concentrate in particular parts of the body. For example, because both strontium and calcium are alkaline earth metals in group 2 on the periodic table, they combine with other elements in similar ways. Therefore, if radioactive strontium-90 is ingested, it concentrates in the bones in substances that would normally contain calcium. This can lead to bone cancer or leukemia. For similar reasons, radioactive cesium-137 can enter the cells of the body in place of its fellow alkali metal potassium, leading to tissue damage. Non-radioactive iodine and radioactive iodine-131 are both absorbed by thyroid glands. Because iodine-131 is one of the radioactive nuclides produced in nuclear power plants, the Chernobyl accident released large quantities of it. To reduce the likelihood of thyroid damage, people were directed to take large quantities of salt containing non-radioactive iodine-127. This flooding of the thyroid glands with the non-damaging form of iodine made it less likely that the iodine-131 would be absorbed

7.13 Key words

Radiation Chemistry; Interaction of electromagnetic radiation with matter; Photo electric effect; The Compton effect Or Compton scattering; Pair Production; Photonuclear reactions; Units of radiation energy; G-Value; Radiation dosimetry; Fricke dosimeter; Cericsulphate dosimeter Radiolysis of cysteine; Radiolysis of biphenyl

7.13 References for further studies

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7.15 Questions for self understanding

1) Discuss the different radiation chemistry.

2) Explain the following phenomenon of interaction of electromagnetic radiation with matter

    1) Photo electric effect
    2) The Compton effect Or Compton scattering
    3) Pair Production

4) Photonuclear reactions

3) Write a note on units of radiation energy.

4) What is meant by G-Value? Explain its significance.

5) Discuss the radiation dosimetry.

6) Discuss the Fricke dosimeter.

7) Discuss the Cericsulphate dosimeter.

8) Discuss the Radiolysis of cysteine.

9) Discuss the Radiolysis of biphenyl.

UNIT-8

Structure

8.0 Objectives of the unit

8.1 Introduction

8.2 Radio isotopes as tracers

a) Chemical investigations

8.3 Thiosulphate ion $(S_2O_3)^{2-}$

(i) Reaction mechanism

8.5 Mechanism of Friedel-Craft's reaction

8.6 Hazards in radiochemical work and Radiation protection

8.7 Radiation protection

8.8 Summary of the unit

8.9 Key words

8.10Reference for further Study

8.11 Question for self understanding

8.0 Objectives of the unit

After studying this unit you are able to

- Explain the use of radio isotopes as tracers
- Explain the method of solving the structure of thiosulphate ion $(S_2O_3)^{2-}$ using radioactive tracer
- Write method of solving the mechanism of Friedel-Craft's reaction using radioactive tracer
- List the hazards in radiochemical work and Radiation protection
- Explain the necessary of radiation protections

8.1 Introduction

Radioactive tracers are substances that contain a radioactive atom to allow easier detection and measurement. (Radioactivity is the property possessed by some elements of spontaneously emitting energy in the form of particles or waves by disintegration of their atomic nuclei.) For example, it is possible to make a molecule of water in which one of the two hydrogen atoms is a radioactive tritium (hydrogen-3) atom. This molecule behaves in almost the same way as a normal molecule of water. The main difference between the tracer molecule containing tritium and the normal molecule is that the tracer molecule continually gives off radiation that can be detected with a Geiger counter or some other type of radiation detection instrument.

One application for the tracer molecule described above would be to monitor plant growth by watering plants with it. The plants would take up the water and use it in leaves, roots, stems, flowers, and other parts in the same way it does with normal water. In this case, however, it would be possible to find out how fast the water moves into any one part of the plant. One would simply pass a Geiger counter over the plant at regular intervals and see where the water has gone.

8.2 Radio isotopes as tracers

Radio isotopes are used directly due to certain properties of the radiations emitter by them. Important use of radioactivity depends on the penetration power of emitted radiation. The indirect use of radioisotopes arises from their chemical properties. The emitted radiation acts as a means of characterizing and identifying the radiating atom. The physical and chemical properties of a radionuclide are almost identical with those of inactive atoms. This property of radioisotope helps to identify isotpes when the former is added to ordinary chemical elements consisting of a mixture of inactive isotopes. The added radioisotope is called the isotopic tracer or radioactive indicator. The use of tracer in chemistry forms a special type of methods called the tracer technique. The tracer technique depends on the following

i) The chemical properties of radioaisotopes of corresponding inactive isotope.
ii) The activity of radioisotope is capable of tracing, identifying and determining the position of the corresponding atom and
iii) This technique helps to detect very small quantities.

It is necessary to chose isotopes with half lives which are neither too short nor too long. Radiations emitted from radiosiotopes should be quantitatively measured with radiation detection instrument and the choice of the instrument depends on the type and energy of radiation. A minimum amount of radioisotope which is just sufficient should be used. Otherwise radiation hazards are involved in their use in a large scale.

Now, we shall briefly discuss some of the more important applications of isotopic tracers. The applications are grouped under the following

a) Chemical investigations
b) Physico-chemical problems
c) Analytical applications
d) Age determination
e) Medical applications
f) Agricultural applications
g) Industrial applications.

b) Chemical investigations

Isotopes are used in the elucidation of structure determination and reaction mechanism.

(ii) Structure determination

When two or more atoms of the same elements are present in a molecule, the question of their structural equivalence arise which can be solved by labeling technique. This can be illustrated by considering two examples PCl_5 and $[S_2O_3]^{2-}$.

Phosphorous penetachloride (PCl_5)

PCl_5 contains five chlorine atoms. To know whether all the five chlorine atoms in PCl occupy structurally equivalent positions, the tracer method is used.

The synthesis of PCl_5 from PCl_3 and ^{36}Cl label chlorine (Cl_2)

Labeled chlorine (Cl_2)

$$PCl_3 + {}^*Cl_2 \rightarrow P^*Cl_5$$

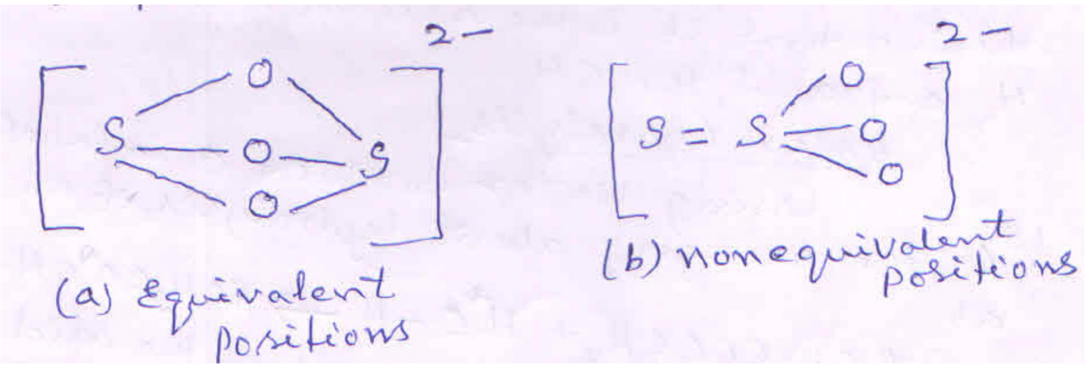
The product P^*Cl_5 on hydrolysis with water gives phosphorousoxychloride and HCl.

$$P^*Cl_5 \rightarrow POCl_3 + H^*Cl$$

It has been found experimentally that the entire radioactivity remained with HCl and not with $POCl_3$. It is obvious that two Cl atoms in PCl_5 occupy positions different from the rest of the three chloride toms. This is in agreement with the trigonalbipyramidal structure accepted for PCl_5 with three Cl atoms in the equatorial plane and two chlorine atoms along the vertices.

8.3 Thiosulphate ion $(S_2O_3)^{2-}$

One can envisage two structures for the thiosulphate ion



To know the correct structure for $(S_2O_3)^{2-}$, the following procedure is adopted.

Synthesize sodium thisulphate by boiling a solution of sodium sulphate with sulphur labeled with ^{35}S

$$Na_2SO_3 + {}^*S \rightarrow Na_2{}^*S_2O_3$$

The product is decomposed by adding to it a solution of $AgNO_3$ in presence of HNO_3.

$$Na_2{}^*S_2O_3 + AgNO_3 + HNO_3 \rightarrow Ag_2{}^*S + Na_2SO_4 + \text{other products}$$

The final products, silver sulphide and sodiumsulphate are examined which show that the activity is with silver sulphide completely. This point to a non equivalent structure for the two sulphur atoms in $(S_2O_3)^{2-}$ (structure b)

(iii)Reaction mechanism

Esterification

Using isotope traces it is possible to demonstrate that water molecule eliminated in the esterification reaction is formed from the OH of the alcohol and H of the acid or it is the other as in

$$R\text{-}CH_2\text{-}COOH + H^*OCH_3 \rightarrow R\text{-}CH_2\text{-}CO^*OCH_3 + H_2O$$

It was found that ^{18}O goes into the ester showing that it is the alcohol which contributes H and acid, the OH.

Ester hydrolysis

Using water in which O is labeled with ^{18}O for bringing about hydrolysis of an ester as

$$R\text{-}CH_2\text{-}COOH + H^*OH \rightarrow R\text{-}CH_2\text{-}CO^*OH + CH_3\text{-}HO$$

Labeled oxygen is found in the acid confirming the previous mechanism of bond rupture.

8.5 Mechanism of Friedel-Craft's reaction

A large number of reactions take place in presence of anhydrous aluminum chloride as a catalyst which are known as Friedel-Crafts reaction

$$\text{Ex:-}\ \ C_6H_6 + ClCOCH_3 \xrightarrow{AlCl_3} C_6H_5COCH_3 + HCl$$

The mechanism of reaction was confirmed by using $AlCl_3$ in which chlorine is labeled with ^{36}Cl. The following steps are involved in the mechanism.

$$\left.\begin{array}{c} CH_3COCl \rightarrow CH_3CO^+ + Cl^- \\ C_6H_6 \rightarrow C_6H_5^- + H^+ \end{array}\right\} \text{dissociation}$$

$$Al^*Cl_3 + Cl^- \rightarrow Al^*Cl_4^- \quad \text{(Catalyst –ion combination)}$$

$$C_6H_5^- + CH_3CO+ \rightarrow C_6H_5COCH_3$$

$$Al^*Cl_4^- + H^+ \rightarrow Al^*Cl_3 + H^*Cl \quad \text{(ion-ion interaction)}$$

This indicates that the product H^*Cl carries ¼ of the total activity and the catalyst, the rest. The ratio of activity of H^*Cl to that of the residual catalyst should be 1/3 which is noticed experimentally.

c) *Physico-chemical problems*

The solubility of a sparingly soluble substance

The principle of determination of the solubility is based on the fact that the radioisotope when added to the same stable isotope maintains a definite ratio.

Illustration

Prepare a stock solution of potassium iodide labeled with ^{131}I. The stock solution is diluted such that it gives about 10000 to 50000 cpm/ml. Add excess of lead acetate solution to this stock solution. Pb^*I_2 is precipitated and settles down. Remove the decantate through centrifugation. The precipitate is washed several times with water and recentrifuged to remove excess of KI completely. Finally, the precipitate is dried under the heat lamp and the specific activity (defined as the activity of the radioisotope per unit mass of the substance) of the Pb^*I_2 sample is determined. Let it be S_1 cpm/mg.

Prepare a saturated solution of a known weight of Pb^*I_2 with water at about 50^0C and then cooled to laboratory temperature. Remove 0.1 ml of the saturated solution on to plachette and the contents are dried carefully under a heat lamp. Determine the specific activity. Let it be S_2 cpm/mg

The solution of lead iodide can be calculated using the equation.

$$\frac{S_2}{S_1} \times 10^4 \text{ mg PbI}_2 \text{ per liter or}$$

$$\frac{S_2}{S_1} \times \frac{10}{M} \text{ Moles of PbI}_2 \text{ per liter}$$

where M is the molecular weight of PbI_2 (M = 461)

d) Age Detrmination^{14}C dating (carbon-14 dating)

Dating of historic and archaeological organic samples by ^{14}C dating was developed by Libby. According to him by measuring the activity of ^{14}C content it is possible to determine the age at which a plant or an animal died. Living plants provide food for themselves by photosynthesis of sugars from water and CO_2 of the atmosphere. The mass ratio $^{14}CO_2/^{12}CO_2$ of the atmosphere appears to remain constant over the ages of all living beings, plants and animals. If analyzed would give a constant value for ^{14}C which an average is taken as 15.8 dpm/g of total carbon. When a plant dies, it cannot photosynthesize anymore which results in continuous decay of ^{14}C it possessed at the time of death. The half life of ^{14}C is 5730 years.

A determination of the activity due ^{14}C of a given sample once living but now dead would permit a computation of the age of the sample i.e, the period that has remained dead. ^{14}C is a soft β-emitter. The maximum energy of β-particle is 0.155Mev ($E_\beta = 0.155 MeV$).

The age of a sample is calculated as follows

The decay constant (λ) is calculated from the half life of ^{14}C

$$\lambda = \frac{0.693}{5730} yr^{-1}$$

The decay equation is

$$N = N_0 e^{-\lambda t}$$

where t is the age of a dead sample and

$$N_0 = 15.8\ dmp/g$$

Knowing N, N_0 and λ, the age of a sample can be determined.

The more general expression applicable to residual activity of any radionuclide is

$$N = N_0(0.5)^n$$

where N is the activity of the sample after n halflives. Inserting the measured N value and N_0 can be calculated. The age of the sample under study is n × 5730 years.

e) Medical applications

The innumerable uses of radionuclides as tracers in medicine and biochemistry are known. We will discuss some typical applications of tracers in medicine. The applications can be broadly classified as

i) The use of tracers in microcurie doses for diagnostic methods for monitoring certain process.

ii) Larger doses for therapeutic purposes in the treatment of certain abnormal conditions

^{32}P: used for locating bone fractures. It can be used to study the relationship between metabolism in the brain and the level of its functional development. It has also been used to measure the number of red cells.

^{24}Na: Used for examining circulation of blood and also to assess the volume of blood in a patient.

^{59}Fe: used to examine the disorders associated with pregnancy used to improve methods for storing blood.

^{131}I: helpful in the detection of disorders of thyroid gland and may cure some of such disorders.

Large numbers of isotopes are finding the increasing uses in medicine and some of which are given the Table given below:

Purpose of study	Isotope used
Bone imaging	^{18}F,^{85}S$_r$
Cerebrospinal fluid	^{III}In
Kidney disorder	^{131}I
Liver/spleen	^{131}I,^{198}Au
Lung ventilation	^{67}Ga,^{13}1I
metabolism	^{24}Na,^{42}K

The isotope group of Bhabha atomic research center (BARC) provides ready to use radio immune assay kits for the assay of insulin human placentol lactogen and thyroid hormones

8.6 Hazards in radiochemical work and Radiation protection

The radioactive isotope when used as tracers or used as reactor fuel cause deleterious biological effects on tissues and living cells of human beings if they are not handled carefully. These harmful effects are known as radio lesions. All radioactive nuclides cause a possible radiation hazard. Radiations such as α, β, γ high energy protons, electrons produced by accelerators and neutrons from nuclear reactors are known to cause destructive biological effects.

The products formed from the action of radiation inactivate enzymes and also affect the nucleic acids leading to destructive biological effects. The action of radiation gives rise to certain macroscopic phenomenon.

Ex: cellular damage which includes breaking of chromosomes which carry the body's hereditary factors (genes), swelling of the nucleus, increase in viscosity of the cell fluid (cytoplasm) and destruction of cells.

The nature and extent of developed harmful effects on living organisms depend upon the type of radiation, on the depth to which the radiation has penetrated, on the extent of the body exposed, on the amount of radiation absorbed and finally on the period and nature of exposure namely chronic (ie prolonged or repeated) or acute. However, the minimum dose required to cause different change varies between 10 and 10^6rads but in some cases very small doses.

It should be noted that radiation when used in a carefully controlled manner is of great importance for the treatment of malignancies. A judicious use of radiation can often stop a cancerous growth but excessive exposure may result in the formation of tumors.

Radiation produced two changes in the body namely somatic effect and genetic effects.

Somatic effects (in Greek soma means body) are experienced directly by the individual exposed to radiation and ***genetic effects*** (in Greek genos means offspring) are not seen in the individual exposed but became known in subsequent generations.

The symptoms of the somatic effects are prostration, loss of weight, fever, loss of appetite, rapid heart action, severe diarrhea, bleeding of the gums and loss of air. The chronic radiation exposure causes reddening of the skin followed by blistering and formation of lesions.

Both chromosome and gene mutations can occur in the somatic cells resulting in somatic mutations, these may produce some effect that is apparent in the individual but is not passed on to the future generations. If is not passed on to the future generations. If the mutation takes place in a germ cell it is called a genetic mutation and will appear in future generation.

8.7 Radiation protection

The nature of protection depends largely on the radioactive material being handled. Precautions are to be taken to reduce exposure of personnel.

1. All radio chemical investigations should be carried out under a hood with a stainless steel interior which can be cleaned with acid for removal of contamination.
2. The special requirement is a place for storing and handling the main stock of the isotope.
3. Protective clothing should be used.
4. Rubber gloves should be used to prevent radioactive material of any kind from contact with the skin.
5. To avoid the effect of radiation is to increase the distance between the personnel and the radioactive source. Long handed tongs should be used.
6. Protective shielding should be used
7. Laboratory where the radiation work is carried out should be well ventilated.
8. Food should not be taken inside the radiation laboratory.
9. Smoking should be avoided
10. Hands, shoes and work place should be monitor for activity after the work is finished.
11. Hands should be washed well
12. Lead shielding is very essential
13. Concrete has been widely used for reactor shielding.
14. Glass utensils should be thoroughly cleaned and baked
15. Disposal of radioactive waste is very important without endangering the public. Radioactive waste may be a solid or a liquid or a gas. The gaseous waste can be discharged with the atmosphere through ventilation. The liquid waste's may be diluted with large amount of water and are disposed off by letting into drain. Solid wastes are disposed off by burial.

8.8 Summary of the unit

Radioactive tracers have applications in medicine, industry, agriculture, research, and many other fields of science and technology. For example, a number of different oil companies may take turns using the same pipeline to ship their products from the oil fields to their refineries. How do companies A, B, and C all know when their oil is passing through the pipeline? One way to solve that problem is to add a radioactive tracer to the oil. Each company would be assigned a different tracer. A technician at the receiving end of the pipeline can use a Geiger counter to make note of changes in radiation observed in the incoming oil. Such a change would indicate that oil for a different company was being received.

Another application of tracers might be in scientific research on plant nutrition. Suppose that a scientist wants to find out how plants use some nutrient such as phosphorus. The scientist could feed a group of plants fertilizer that contains radioactive phosphorus. As the plant grows, the location of the phosphorus could be detected by use of a Geiger counter. Another way to trace the movement of the phosphorus would be to place a piece of photographic film against the plant. Radiation from the phosphorus tracer would expose the film, in effect taking its own picture of its role in plant growth.

Some of the most interesting and valuable applications of radioactive tracers have been in the field of medicine. For example, when a person ingests (takes into the body) the element iodine, that element goes largely to the thyroid gland located at the base of the throat. There the iodine is used in the production of various hormones (chemical messengers) that control essential body functions such as the rate of metabolism (energy production and use).

Suppose that a physician suspects that a person's thyroid gland is not functioning properly. To investigate that possibility, the patient can be given a glass of water containing sodium iodide (similar to sodium chloride, or table salt). The iodine in the sodium iodide is radioactive. As the patient's body takes up the sodium iodide, the path of the compound through the body can be traced by means of a Geiger counter or some other detection device. The physician can determine whether the rate and location of uptake is normal or abnormal and, from that information, can diagnose any problems with the patient's thyroid gland.

8.9 Key words

Radio isotopes as tracers; Chemical investigations; Hazards in radiochemical work; Radiation protection; Radiation protection

8.10 Reference for further Study

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8.11 Question for self understanding

1) Write a note on radio isotopes as tracers

2) With example explain the use of radio isotopes chemical investigations

3) How structure of thiosulphate ion $(S_2O_3)^{2-}$ is solved using radio isotopes

4) How mechanism of Friedel-Craft's reaction is solved using radio isotopes

5) Discuss the hazards in radiochemical work

6) Explain the radiation protection used at radiochemical work

Question Bank

1. Define the term with examples

a) Isotopes b) isobars c) isofones d) isomers and e) Mirror nuclie

2. Derive the radioactive decay equation

3. Derive the general expression for the growth of a daughter from the parent

$$A \xrightarrow{\lambda_1} B \xrightarrow{\lambda_2} C$$

4. Describe various methods of determining the halflife period of a radio nuclide.

5. Mention the difference between a nuclei, a nucleus and a nucleon.

6. Discuss the stability a) binding energy b) neutron-proton ratio and c) neutron-proton ratio and d) magic number

7. Calculate the binding energy per nucleon for

$^{31}_{15}P$, $^{60}_{28}Ni$, $^{108}_{46}Pd$ and $^{295}_{78}Pt$

Given: Mass of proton: 1.000783 amd Mass of neutron: 1.00867amu

8. Calculate the atomic masses of $^{9}_{4}Be$, $^{27}_{13}Al$ and $^{63}_{29}Cu$ from the semi empirical binding energy equation

9. Define the terms and give the relationship between them

a) Half life period b) disintegration constant and c) average secular and transient

10. Explain briefly secular and transient equilibrium in the decay process.

11. Calculate the mass and numbers of atoms in one milicurie of $^{226}Ra(t_{1/2}=1600y)$

12. If one curie of ^{32}P $(t_{1/2}=14.3d)$ is stored for 24h. What weight of ^{32}S would be obtained at the end of that period?

13. A 0.1 mg sample of $^{239}_{94}Pu$ emitting α-particle undergoes 1.4 X 10^7dpm. Calculate the halflife of this sample.

14. Distinguish between α and β decays

15. Write nuclear reactions for the following

a) α-decay of $^{231}_{91}Pa$, b) β-decay of $^{227}_{90}{}^{Th}$, c) decay of $^{219}_{85}At$ to $^{215}_{85}Bi$

16, Write notes on: a) photo nuclear reactions b) oppenheimer-phillips process

17. Explain the difference between the elastic scattering and inelastic scattering

18. Discus briefly the principle and working of a GM counter.

19. Represents the following reaction in the form of Bethe's notation.

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}H$$

20. Write notes on a) Photo electric effect b) Pair production and c) Comptoneffect.
21. Define G value.
22. What is dosimetry? Describe the function of a Fricke dosimeter.
23. Explain the radiolysis of cysteine and biphenyl.
24. What is meant by tracer element? Discuss their uses.
25. Discuss briefly the applications of radioisotopes as tracers.
26. Find the recoil energy of ^{128}I following the emission of a 4.8 Mev photon.
27. Determine the recoil energy of ^{65}Zn following (n,γ) reaction in which a photon of 2.2 Mev is emitted
28. How do you determine the age of a specimen by using ^{14}C dating.
29. Discuss the nature of hazards expected in a radiochemical work.
30. Give a brief account of precautions to be taken to protect from radiation hazards.

UNIT-9

Structure

9.0 Objectives of the unit

After studying this unit you are able to

- Differentiate between Macromolecules and Polymers
- Identify the Monomer units in different polymers
- Write the structure of repeating units in given olymers
- Explain the differences between Polymers and Co-polymers
- Calculate the Degree of polymerization in given polymers
- Calculate the Number average molecular weight (M_n) of polymers
- Calculate the Molecular Average Molecular weight $\overline{M_m}$ of polymers
- Calculate the Higher average molecular weights: Mz, Mz+1 of polymers
- Explain the significance of Glass transition temperature (Tg)
- Explain the Chemical bonding and molecules forces in polymer

9.1 Introduction

Polymers form a very important class of materials without which the life seems very difficult. They are all around us in everyday use; in rubber, in plastic, in resins, and in adhesives and adhesives tapes. The word polymer is derived from greek words, *poly* = many and *mers* = parts or units of high molecular mass each molecule of which consist of a very large number of single structural units joined together in a regular manner. In other words polymers are giant molecules of high molecular weight, called macromolecules, which are build up by linking together of a large number of small molecules, called monomers. The reaction by which the monomers combine to form polymer is known as polymerization. The polymerization is a chemical reaction in which two or more substances combine together with or without evolution of anything like water, heat or any other solvents to form a molecule of high molecular weight. The product is called polymer and the starting material is called monomer.

Polymers are substances made up of recurring structural units, each of which can be regarded as derived from a specific compound called a moanomer. The number of monomeric units usually is large and variable, each sample of a given polymer being characteristically a mixture of molecules with different molecular weights. The range of molecular weights is sometimes quite narrow, but is more often very broad. The concept of polymers being mixtures of molecules with long chains of atoms connected to one another seems simple and logical, but was not accepted until the 1930's when the results of the extensive work of H. Staudinger, who received the Nobel Prize in Chemistry in 1953, finally became appreciated. Prior to Staudinger's work, polymers were believed to be colloidal aggregates of small molecules with quite nonspecific chemical structures.

The adoption of definite chemical structures for polymers has had far-reaching practical applications, because it has led to an understanding of how and why the physical and chemical properties of polymers change with the nature of the monomers from which they are synthesized. This means that to a very considerable degree the properties of a polymer can be tailored to particular practical applications. Much of the emphasis in this chapter will be on how the properties of polymers can be related to their structures.

9.2 Polymers

Polymers are materials of very high molecular mass usually greater than 5000. They occur in nature or can be chemically synthesized. The molecules of polymers are usually referred as macromolecules and they contain several thousands of atoms bound together in a systematic manner.

Cellulose, starch, proteins are examples of naturally occurring polymers. Polyethyelene, Polystryrene, polyamides, polyester and formaldehyde resin, urea formaldehyde resin are synthetic polymers which plays an very important role in modern technology as plastics, fibers resins ,rubber etc. [today it is possible to produce “macromolecules” as Tailor made” for specific purpose].

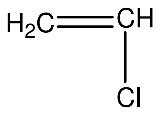
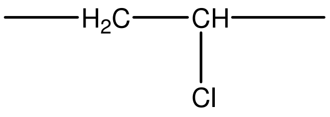
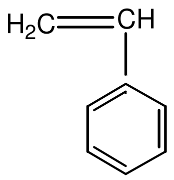
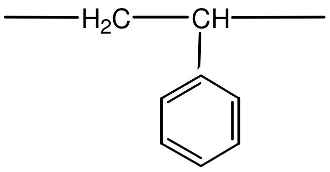
9.3 Monomers

Macromolecules consist of several structural units bound together by covalent bonds. These structural units are usually referred as the monomers. Thus *a monomer is a low molecular weight compound from which the polymer is obtained through the synthesis reaction.* These units may or may not exist in a regular manner. The individual structural unit may be single atom just like in polysulphur. $(\text{-S-})_n$ i.e –S-S-S-S-S--------S-S-S-S or may be molecules in nature as in the case of polyethylene in which the structural unit will be $(\text{-}CH_2\text{-}CH_2\text{-})$. These are also called “Repeat units”.

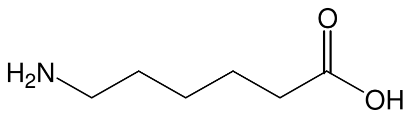
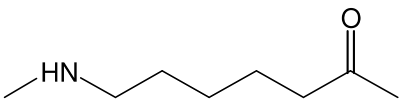
9.4 repeating units

The term “repeating unit” denotes an elementary unit which periodically repeats itself along the polymeric chain. It is defined also as monomer or monomeric unit, but not always in the correct way. *Thus repeating units are a simplified method of drawing a polymer, whose chain may extend for a long time.* A monomeric unit is a molecular structure, defined by the monomer, constituting part of the repeating unit.

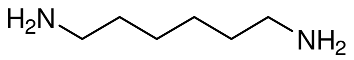
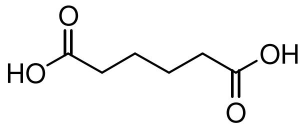
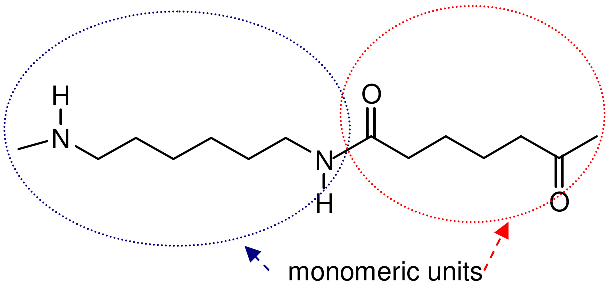
Frequently repeating unit, monomer and monomeric unit are coincident, as in the following examples.

monomer	***repeating unit/ monomeric unit***	***polymer***
$H_2C{=}CH_2$ ethylene	$—H_2C—CH_2—$	polyethylene
 $H_2C{=}CH(Cl)$ vinyl chloride	 $—H_2C—CH(Cl)—$	poly(vinyl chloride)
 styrene		polystyrene

In other cases repeating and monomer units differ from the monomer by a limited number of atoms in the chemical formula, as in the following example

monomer	***repeating unit/ monomeric unit***	***polymer***
 ε-amino-capronic acid		polyamide 6 *(nylon 6)*

In some polymers the synthesis reaction requires the alternate combination of two different monomers, the repeating unit is formed by two monomeric units. example:

monomer	***repeating unit***	***polymer***
 hexamethylendiamine  adipic acid		polyamide 6,6 *(nylon 6,6)*

More Examples of the simple macromolecules with their repeat units and monomers from which they are prepared are given below

Polymers	Repeat units	Monomers
Polyvinylacetate	$-(CH_2\text{-}CHO\text{-}CO\text{-}CH_3\text{-})_n-$	$CH_2{=}CH\text{-}O\text{-}CO\text{-}CH_3$
Cellulose	$-(C_6H_{10}O_5)_n-$	$C_6H_{12}O_6$
Polyisoprene (Natural rubber)	$-(CH_2\text{-}CH{=}C(CH_3)\text{-}CH_2)_n-$	$CH_2{=}CH\text{-}C(CH_3){=}CH_2$
Polyisobutylene	$-(CH_2\text{-}C(CH_3)_2)_n-$	$CH_2{=}C(CH_3)_2$
Polycaprolactum (Nylon)	$-(NH\text{-}(CH_2)_5\text{-}CO)_n-$	$H_2N\text{-}(CH_2)_5\text{-}COOH$

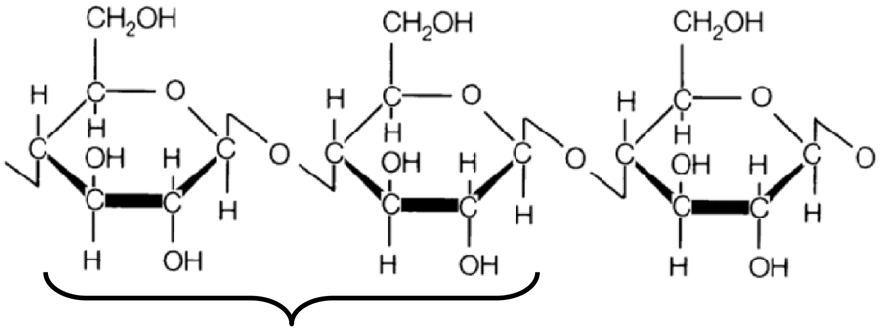
If the repetition of monomeric units in a macromolecules is similar to that of links in a chain the polymers is said to be linear or chain polymer.

ex: polyethylene, polystyrene etc.

$$n(CH_2{=}CH_2) \rightarrow -(CH_2\text{-}CH_2)_n-$$

In some cases monomeric units of macromolecules having same chemical composition but differ in spatial configuration.

Ex. Cellulose (the pyranose ring)

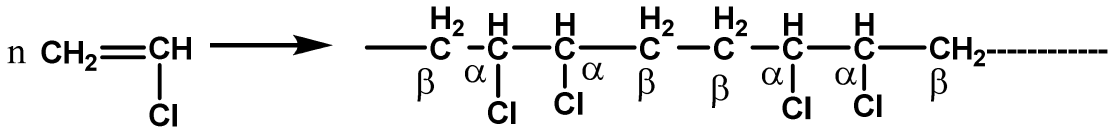


Repeat distance

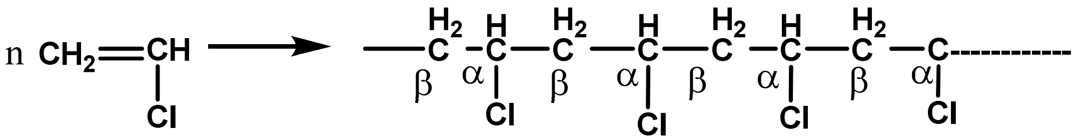
In this case the repeat unit consists of two monomeric units and their distance between the beginning repeat units to the next one is called repeat distance or Indentity period.

During the formation of the macromolecules from the monomers, particularly in case of vinyl polymers the monomers combine to form α-α, β-β or α-β arrangement.

Example: polyvinyl chloride



or



9.5 Co-polymers

Many macromolecules consists of manomeric units of different chemical composition such molecules are called Copolymers. These are different types of copolymers.

a. Alternate copolymer
b. Random copolymer
c. Block Type of copolymer
d. Graft type polymer

RANDOM

—A—A—B—A—B—A—B—B—A—B—A—A—A—B—A—B—

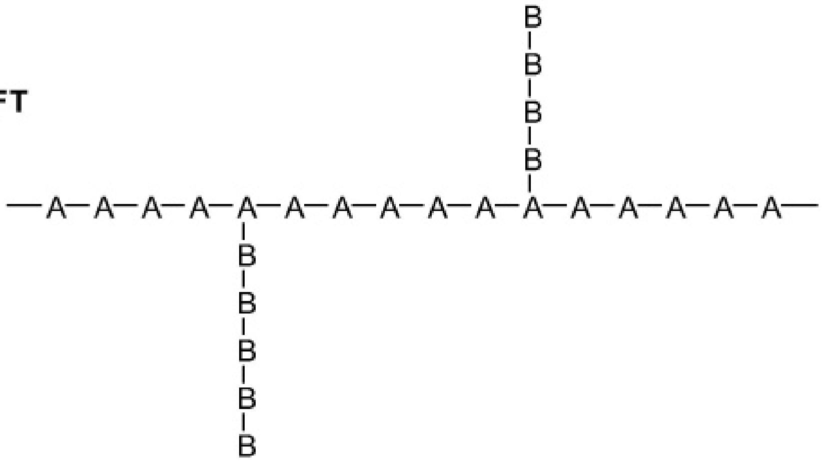
ALTERNATING

—B—A—B—A—B—A—B—A—B—A—B—A—B—A—B—A—

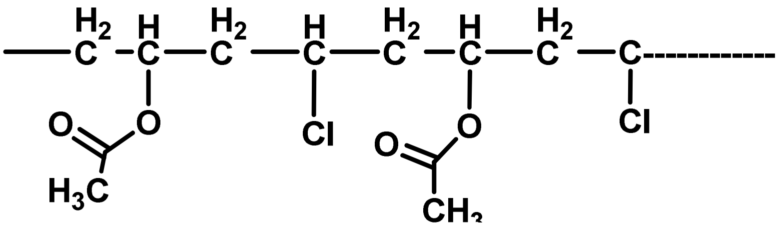
ABA-TRIBLOCK

—A—A—A—A—B—B—B—B—B—B—B—B—A—A—A—A—

GRAFT



Example for copolymer: Polymer of vinyl acetate and vinyl chloride



In many cases the polymer chain may also be branched example, Ethylene may polymerized giving branched chain polymer. The separate linear or branched polymers chains joined together along the chain giving the cross linked polymer, Extensive cross linking may lead to the formation of three dimensional net work polymers

Ex. Urea formaldehyde resin, phenol formaldehyde resin, etc….

The three dimensional cross linking occurs extensively in the final stage of the manufacture of polymers and they confirmed considerable hardness and rigidity. If the final stages are involved in heat treatment, the process is called "Thermohardening or Thermosetting", while if the three dimensional cross linking occurs in cold condition then it is called "cold setting".

The establishment of three dimensional cross linked structures is termed as "Curing" of the polymers.

Many linear polymers which are not extensively cross linked can be softened and moulded on heating these materials are said to be "Thermoplastics"

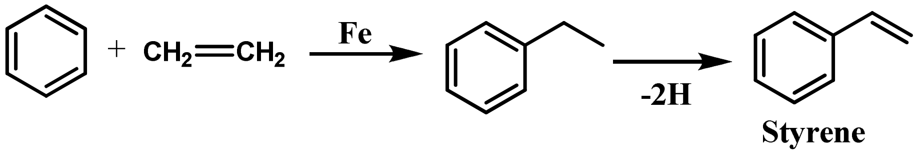
9.6 Degree of polymerization

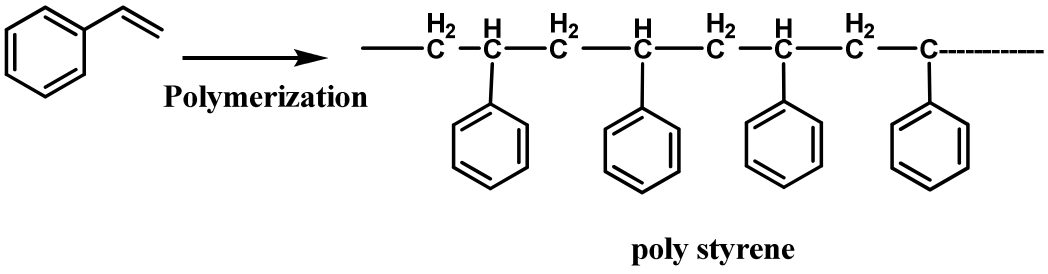
Dp = degree of polymerization merely indicates the number of repeat units in a polymers chain. Molecular weight of Polymer = D.P X Mol.wt of monomers.

9.7 Preparation of Some common synthetic polymers

a) Polystyrene

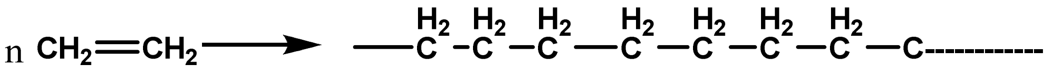
The monomer styrene is obtained by boiling ethylene through benzene in the presence of Friedal Craft catalysis and dehydrogenating the resulting ethyl benzene





b) Polyethylene

Polyethylene is obtained by polymerizing the ethylene at high temperature and pressure

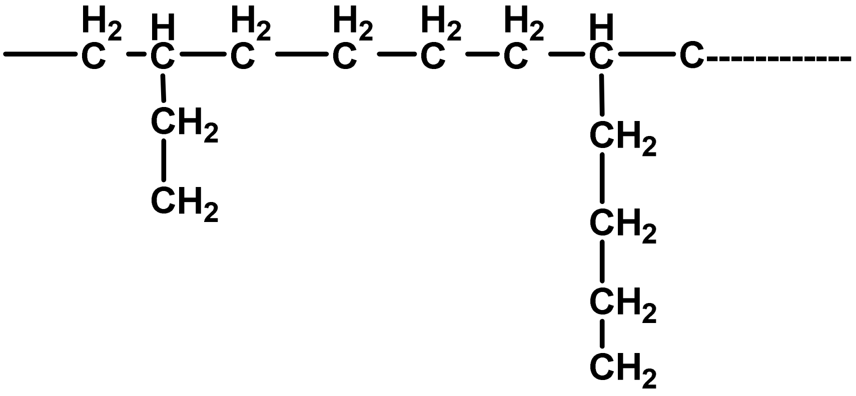


$$n\ CH_2{=}CH_2 \longrightarrow -\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-C\text{-----------}$$

Commercial polyethylene is obtained in two forms

a) Low density polyethylene (LDPE) b) High density polyethylene (HDPE)

The molecular structure of LDPE of the types



The presence of several short and long branches in LDPE prevents the close packing of the polymer chains in the solid state, as would be possible in the absence branch. This is the reason for the low density of the sample.

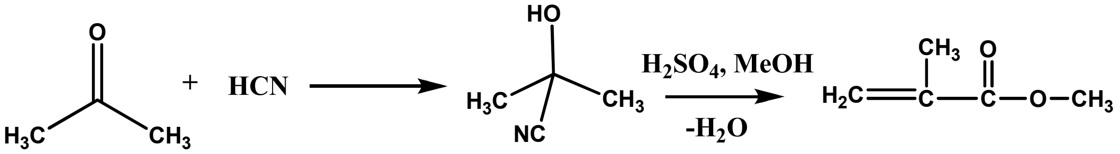
HDPE will have linear unbranched chains which are closely packed in the solid state. The difference in the molecular structure will leads to difference in their properties. Both type of polyethylenes are tougher than polystyrenes and are much more resistance to chemical attacks.

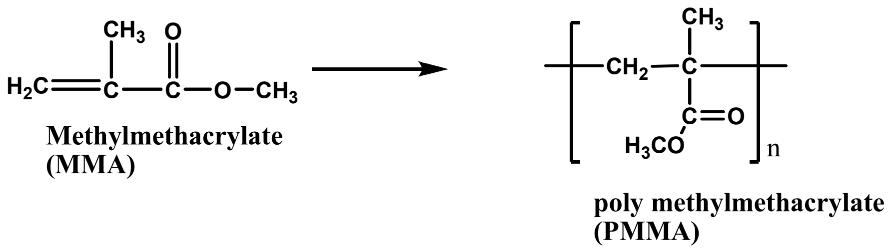
LDPE is used in toys, wires, cable, insulators, pipes, containers, the squeeze bottle etc…

HDPE is more expensive has higher strength and more inert than LDPE. It is used primarily in making industrial equipments and expensive toys.

c) Polymethyl methacrylate (PMMA)

By Cyanohydrin process

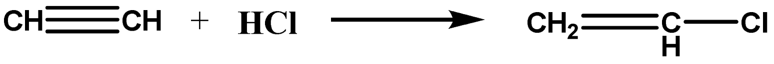




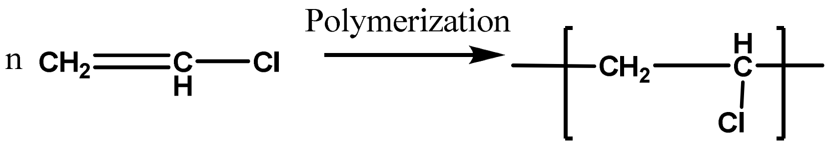
It is a transparent plastic with better toughness than polystyrene. It is used in making lenses, window pans, automatic rolls which requires light transmissions and also used in paints.

d) Polyvinyl chloride (PVC)

The monomer vinylchloride is synthesized by catalytic addition of HCl to acetylene



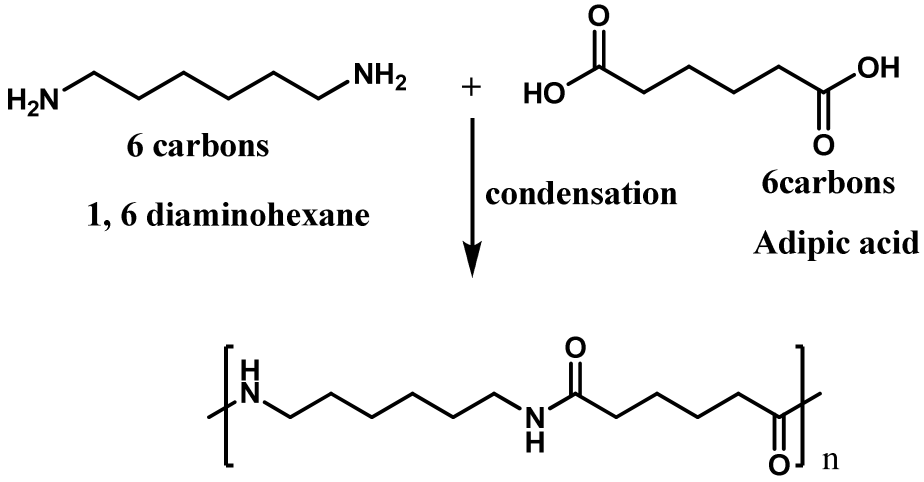
$$CH \equiv CH + HCl \longrightarrow CH_2{=}\underset{H}{C}{-}Cl$$



PVC is not very stable to heat and HCl is readily evolved, to suppress this, stabilizer like fatty acids of Sn, Be Pb is added. In the absence of solvents PVC is very tough and rigid material. It is used for making Gramphone record, extensively used for electrical insulator (PVC pipes), Floor tiles, Rain coats, Hand bags, Curtains etc.

e) Nylan-66

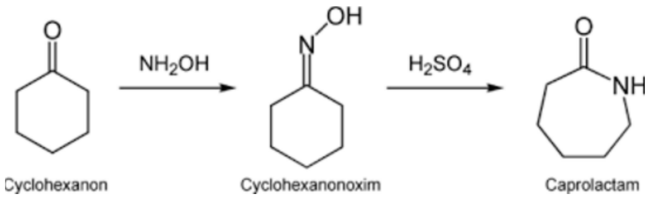
Nylon-66 is obtained from condensation 1,6 diaminohexane and adipicacid

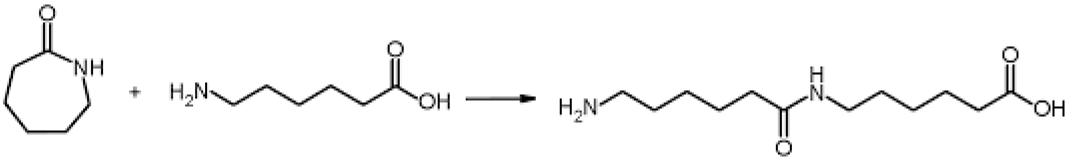


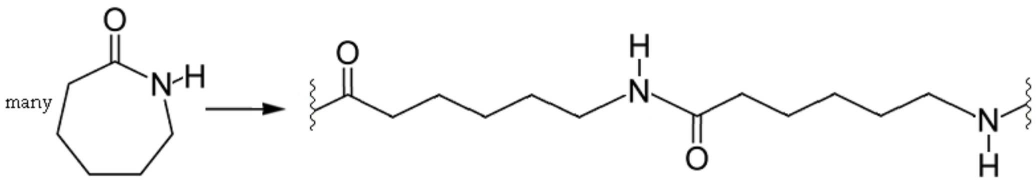
Nylon-66

f) Nylan-6

Nylon-6 is obtained from polymerizing the caprolactum, which is synthesized by Beckmann rearrangement reaction of N-hydroxy cyclohexanone oxime





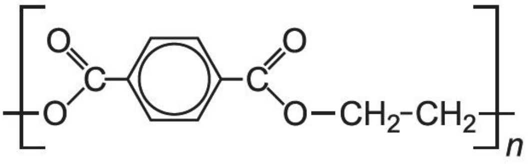


It used in the preparation of fibers, ropes substitutes for metal in bearings gears etc. It has good tensile strength and resistance.

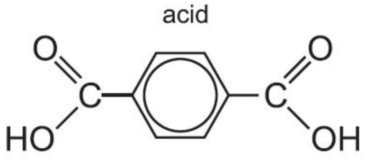
g) Poly esters

Polyesters are polymer in which the individual units are held together by ester linkages**.** thus polyesters are polymers formed from a dicarboxylic acid and a diol. They have many uses, depending on how they have been produced and the resulting orientation of the polymer chains.

Polyesters are extremely important polymers. Their most familiar applications are in clothing, food packaging and plastic water and carbonated soft drinks bottles. The most used of the polyesters has the formula



Being an ester, it is made from an acid, benzene-1,4-dicarboxylic acid (terephthalic acid), and an alcohol, ethane-1,2-diol



benzene-1,4-dicarboxylic acid
(terephthalic acid)

alcohol

$$HO-CH_2-CH_2-OH$$

ethane-1,2-diol
(ethylene glycol)

It is often known by its trivial name, polyethylene terephthalate (PET). Another useful polyester is produced from benzene-1,4-dicarboxylic acid and propane-1,3-diol (which replaces ethane-1,2-diol). It is known by its trivial name, polytrimethylene terephthalate.

9.8 Mechanism of polymerization

The linking together of a large number of small molecules termed as monomers with each other to form a macromolecule or polymer molecule through chemical reactions is termed as polymerization. It can also be defined as the fundamental process by which low molecular weight compounds are converted into high molecular weight compounds. In addition to the structural and compositional differences between polymers Flory stressed the very significant difference in the mechanism by which polymer molecules are building up. Although Flory continued to use the terms “addition polymerization” (polymerization by repeated addition processes) and “condensation polymerization” (polymerization by repeated condensation processes, i.e, with the elimination of small molecules) in his discussion of polymerization mechanism. The current terminology classifies polymerization into step growth polymerization and chain growth polymerization.

The degree of polymerization is related to the molecular mass (M) of the polymer and is given by the equation Dp = M/m

Where, m is the mass of the monomeric unit and M is the molecular weight of polymer

Thus *the degree of polymerization, or* D_P, *is usually defined as the number of monomeric units in a macromolecule or polymer or oligomer molecule.*

9.9 Molecular weight and its distribution

The molecular weight of a polymer is of prime importance in the polymer’s synthesis and application. It is important because it determines many physical properties. Molecular weight (MW) and its distribution (MWD) have a considerable effect on macroscopic properties of polymer such as toughness, tensile strength, adherence and environmental resistance, etc.

A simple chemical has fixed molecular weight but when we discuss about the molecular weight of polymer, we mean something different from that which applies to small sized compounds. Since polymers are mixture of molecules of different molecular weight, the molecular weight is expressed in the term of “average” value. This average molecular weight is basically based on either average number of repeating units, known as number *average molecular weight*, or average weight, known as *weight average molecular weight.*

9.10 Number average molecular weight (M_n)

The number average molecular weight is the statistical average molecular weight of all the polymer chains in the sample, and is defined by:

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

where M_i is the molecular weight of a chain and N_i is the number of chains of that molecular weight. M_n can be predicted by polymerization mechanisms and is measured by methods that determine the number of molecules in a sample of a given weight, for example, colligative methods such as end-group assay.

If M_n is quoted for a molecular weight distribution, there are equal numbers of molecules on either side of M_n in the distribution.

Let us consider a system containing g_1 grams of molecules each of molecular weight M_1 and g_2 grams of molecular each of molecular weight M_2

Then $\overline{\mu}_w = \dfrac{g_1M_1 + g_2M_2 + -------+g_iM_i}{g_1 + g_2 + g_3 + ---- g_i}$

$$\overline{\mu}_w = \frac{\sum_{i=1}^{i=\infty} g_iM_i}{\sum_{c=1}^{i=\infty} g_i} = w_1M_1 + w_2M_2 -----+w_iM_i$$

$$\overline{M_w} = \sum_{i=1}^{i=\infty} W_iM_i$$

$$g_1 = N_1M_1, g_2 = N_2M_2 ------- g_i = N_iM_i$$

$$\overline{M}_w = \frac{N_1M_1^2 + N_2M_2^2 + --------- N_1M_i^2}{N_1M_1 + N_2M_2 + ------ N_iM_i}$$

$$\overline{M}_w = \frac{\sum_{c=1}^{\infty} N_iM_i^2}{\sum_{i=1}^{\infty} N_iM_i}$$

$$\overline{M}_w = \frac{100\times10^6 + 200\times10^8 + 200\times10^{10}}{(100\times10^3) + (200\times10^4) + (200\times10^5)}$$

$$\overline{M}_w = 91{,}000$$

9.11 Molecular Average Molecular weight $\overline{M_m}$

The weight average molecular weight $\overline{M_W}$ is obtained in a similar manner from mass m_i of each degree of polymerization P_i according to the following equation,

$$\overline{M_W} = \frac{\sum_{i=1}^{\infty} m_i p_i}{M_0}$$

Let us consider a sample containing N_1 molecules of M_1, N_2 molecules of M_2 etc…. N_i molecules M_i , then $\overline{M_m}$ is given by the total weight of sample divided by number of molecules. Thus

$$\overline{M_n} = \frac{N_1M_1 + N_2M_2 + ------- + N_iM_i}{N_1 + N_2 + -------- N_i}$$

$$\overline{M_n} = \frac{\sum\limits_{i=1} N_iM_i}{\sum\limits_{i=1}^{\infty} N_i} ----------(1)$$

$$Ex100 --- > 10^3 \quad 200 --- > 10^4 \; 200 --- > 10^5$$

$$\overline{M_n} = \frac{100X10^3 + 200X10^4 + 200X10^5}{500} = 44{,}000$$

1 can be written as

$$\overline{M_n} = \left(\frac{N_1}{N_1 + N_2 + ---}\right)M_1 + \left(\frac{N_2}{N_1 + N_2 + ---}\right)M_2 + \left(\frac{N_i}{N_1 + N_2 + ----- N_i}\right)M_i$$

$$\overline{M_n} = X_1M_1 + X_2M_2 + -------- + X_iM_i$$

$$\overline{M_n} = \sum_{i=1}^{i=i} X_iM_i ----------------(2)$$

X = mole fraction of different type of species present in the system.

If we are dealing with pure polymer sample where the molecules differ in the degree of polymerization, then the molecular weight X mers will be equal to $x.M_0 \; i.e M_x = x.M_0$

$$\overline{M_m} = \sum_{x=1}^{x=x} X_x.M_x$$

$$\sum_{x=1}^{x=x} X_x xM_0$$

$$\overline{M}_n = M_0 \sum_{x=1}^{x} x.x_x$$

Similarly the number average degree of polymerization is defined as

$$\overline{X}_n = \frac{\sum\limits_{x=1}^{w} X.N_x}{\sum\limits_{x=1}^{w} N_x}$$

$$\overline{X}_n = \sum_{x=1}^{\infty} x.X_x$$

9.12 Higher average molecular weights: Mz, Mz+1

Thus it is evident that for polydispersed polymer system the $\overline{M}_w$ is greater than $\overline{M}_n$ (because heavier molecules contribute more to $\overline{M}_w$) and the ratio $\frac{\overline{M}_w}{\overline{M}_n}$ is measure of the polydispersity of the system. For a monodispersed system $\overline{M}_w = \overline{M}_n$. It should be noted that $\overline{M}_w$ is very sensitive to the molecules of hight molecular weight species, but $\overline{M}_n$ is sensitive for for low molecular weight species. In synthetic polymer $\frac{\overline{M}_w}{\overline{M}_n} = 2$ larger the value of ratio indicates a wide spreads in the molecular weight. In addition to the $\overline{M}_w$ and $\overline{M}_n$ frequently we evaluated average of type $\overline{M}_z$ and $\overline{M}_{z+1}$ (called Z average molecular weight and Z+1 average molecular weight)

$$\overline{M}_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} \quad \overline{M}_{z+1} = \frac{\sum N_i M_i^w}{\sum N_i M_i^3}$$

In general, a series of average molecular weights can be defined by the equation:

$$M = \frac{\sum N_i M^{n+1}}{\sum N_i M_i^n}$$

where: n = 1 gives M = M_w

n = 2 gives M = Mz

n = 3 gives M = Mz+1

The higher averages are increasingly more sensitive to high molecular weight polymers and accordingly are increasingly more difficult to measure with precision. They tend to be associated with methods that measure the motion of polymer molecules, such as diffusion or sedimentation techniques. For all synthetic polydisperse polymers Mn < Mw < Mz < Mz+1

9.13 Polydispersity of polymer

The polydispersity index (PDI) is used as a measure of the broadness of a molecular weight When the molecular weight distribution is very narrow, the number average and weight average molecular weights are essentially equal. When the distribution is broad, the weight average molecular weight is considerably greater than the number average molecular weight and broader the distribution, the greater the difference between then as shown in below figure. From these molecular averages the molecular weight distribution is represented by the ration $\frac{\overline{M_W}}{M_n}$. Thus PDI is described as $\frac{\overline{M_W}}{M_n}$ M_w can only be larger or equal to M_n, so it is always equal to or greater than 1

The larger the polydispersity index, the broader the molecular weight. A monodisperse polymer where all the chain lengths are equal (such as a protein) has an $M_w/M_n = 1$.

The best controlled synthetic polymers (narrow polymers used for calibrations) have M_w/M_n of 1.02 to 1.10. Step polymerization reactions typically yield values of M_w/M_n of around 2.0, whereas chain reactions yield M_w/M_n values between 1.5 and 20.

Tensile and impact strength increases with molecular weight. The melt viscosity of the polymer however shows different trends. At very high molecular weights, the melt viscosity rises more steeply than at low molecular weights. Molecular weight distribution also affects properties of polymers. Thus to know of a polymer properly, one must have a good knowledge of both the average molecular weight as well as its dispersion patterns.

9.14 Glass transition temperature (Tg)

In the study of polymers and their applications, it is important to understand the concept of the glass transition temperature Tg. The glass transition is a phenomenon observed in linear amorphous polymer. It occurs at fairly well defined temperature when the bulk material ceases to be brittle and glassy in character and become less rigid and more rubbery. The knowledge of Tg is essential in the selection of materials for various applications.

Many Physical properties change profoundly at the glass transition temperature, including mechanical properties and electrical properties. All of these are dependent on the relative degree of freedom for molecular motion within a given polymeric material and each can be used to monitor the point at which the glass transition occurs.

9.15 Mechanical properties of polymers

Polymers can exhibit the features of glassy, brittle solid or an elastic rubber, or that of a viscous liquid, depending on the temperature and time scale of measurement. The studies on mechanical properties of polymer can, therefore, be carried out by subjecting them to some form of mechanical stress either continuous or in a periodic manner at different rate. Some of the important properties of polymers with regard to their use as engineering material are tensile strength, compressive and flexural strength, hardness, creep, fatigue resistance and impact resistance.

Toughness of a polymer is the ability to absorb mechanical energy without fracturing. The property such as tensile strength is the maximum amount of tensile load per unit area a material can withstand, while the tensile elongation gives the measure of increase in length in response to a tensile load expressed as a percent of the original length. Elongation at break is the maximum elongation the plastic can undergo.

Strength is a measure of toughness or resistance to breakage under high velocity ompact conditions. From this point of view, polymeric maerials under normal conditions of use are thought to be brittle or tough. For example, polystyrene, poly(methylmethacrylate) and unmodified, non plasticized PVC are usually rated as brittle, breaking with a sharp fracture, plasticized PVCs are considered to be tough. In general polymeric materials are either brittle or though, depending on the temperature and rate of impact, ie, rate of deformation. Immpact strength of polymers and derived plastics depends on the position of the glass transition temperature (Tg) with respect to room temperature and ease of crystallization. Far below the glass-transition, amorphous polymers break with a brittle fracture, but they become tougher.

9.16 Chemical bonding and molecules forces in polymer

The nature of the bonds which holds atoms together in molecules is explained by quantum mechanics in terms of an "Atom consisting of a small nucleus concentrating the mass and positive charge surrounded by clouds or shells of electron relatively far away (from each other).

Chemical reactions and primary bond formation takes place among their outermost loosely bonded valence electrons. A chemical bond is polar or non polar. Extreme polar bond is the ionic bond ex. Na^+Cl^- and extreme non polar bonds in the covalent bond ex. H_2 Cl_2 etc. (which is formed in case of identical atoms). Both have electron cloud become perfectly symmetric relative to the nuclei of both the atoms. And all other bonds are intermediate between these two bonds. Thus the bond formed by dissimilar atoms Ex. HCl, HF etc is polar because the probability of the bounding electron existing in the field of the nuclei of the different atoms is unequal since the atoms differ in electron affinity. Example, in HCl electron affinity of Cl is more than that of H atom and so the average density of the electron cloud around the Cl atom is more than around the hydrogen atom. Hence, as a result of this, the molecules acquiring dipole moment (μ). But symmetrical molecules like H_2, Cl_2 CH_4 etc have zero dipole moment (Non-polar molecules) H_2O molecules is asymmetrically and hence polar (i.e dipole).

In the bonds C-OH, C-COOH, C-NH_2, C-Cl, C-F etc. the electron density is distributed unsymmetrically and so these are called "Polar bonds". Introduction of such polar bonds into nonpoalr molecules impart (gives) dipole moments to the compound.

Let us apply this consideration to polymer molecules.

1. Polymeric hydrocarbons such as ex. Polyethylene, Polyisopropene, Polypropylene, Polybutadiene, polybutadiene etc… are non polar.
2. Vinyl polymers (polyvinyl alcohol), cellulose starch, which contain large no of polar -OH groups, hence they are highly polar.

3. Polyacrylnitrile which contain many number of –CN groups, polyacrylicacid containing -COOH groups, Polyvinyl chloride containing C-Cl bonds and cellulose acetate cellulose nitrate have intermediate polarity.
4. Polyesters like polyacrylates, polymethyl metharylate are still less polar.

Thus the polarity of a polymer can be judged from the polarity of its constituent groups with allowance for

1. The symmetry of the spatial arrangement.
2. Symmetry of these groups and
3. Frequency of their occurrence along the chain.

(Usually the bound angle between successive single bonds in polymers range between 105^o to 113^0 not far from the tetrahedral angle of 109^0 28^1

Apart from these polar and non polar bonds, there is yet another type of bonds i.e, hydrogen bond which is particularly important in many polymers including proteins. Classical concept allows H atom to form only one covalent bond (associated with one atom) but in Hydrogen bond it is associated with two atoms. H bond may be considered as ionic in character but some time shows covalent in character. “The H- bonds occurs between two functional groups in the same or different molecules” and H atom is usually attached to an acidic group (a proton donor) like carbaxylic acid, Hydroxyl group, Amide group with

1. Carbonyl group.
2. Other oxygen groups like ester etc and occasionally with halogens

	Bond length
C-H……N	2.6 Å
O-H……N	2.8Å
O-H-------O	2.6 to 2.8Å
F-H-------F	2.4 Å
N-H------N	3.1 Å

The association of polar liquids like H_2O, alcohols, HF and the formation of dimmers of simple organic acid and important structural effects in polymer molecules such as nylon cellulose and proteins are due to hydrogen bonding.

9.17 Molecular Forces

There are two types of forces operating between molecules in a system.

1. Primary valence forces. Which resulting in the formation of different kinds of bonds

2. Secondary valence forces. These are inter molecular forces frequently refer it as the Vander walls forces and these forces include dipole forces induction forces dispersion forces etc.

Secondary valence forces are of great important in the formation of stable chemical compounds and those forces lead to the aggregation of molecules into solid or liquid phases. Many of the physical properties such as volatility, viscosity surface tension, frictional properties, miscibility and solubility are largely determined by these intermolecular forces.

If the intermolecular force are small, then the cohesive energy (total energy necessary to remove a molecules form a liquid or solid to a position far from its neighbor) is low and the molecules have relatively flexible chains and have properties flexible chains and have properties usually associated with “elastomers

Ex- Polyestylene ----62 (CE cals/cc)
Polyethyrene ----79
Polyvinyl --91

If intramolecular forces are high, written C.E giving stable chains (the presence solid groups) which possesses characteristic of typical plastics.

Ex. Poly hexamethylene adipamide 185
Polyacrylnitrile 237

If the C.E is still higher, the material exhibits high resistance to stress and good mechanical properties typical of fibers.

9.18 Swelling of Polymer

During the interaction of polymer with a solvent, it is often observed that the polymer swells before dissolving i.e, it increases in its mass and volume after it absorbed the lower molecular mass liquid.

If a polymer sample is cut into small pieces and put into a solvent each pieces swells separately first but afterwards they will all merge to form uniform liquid larger consisting of the polymer and liquid it has observed. At this point the system will be a true solution of the liquid in the polymer.

Swelling of polymer involves the charge in the polymer structure which sharply increases the volume of the sample. Also swelling may be limited or unlimited

Unlimited swelling result in spontaneous dissociation, it is analogous to complete miscibility of liquids like water and ethanol. *This type of swelling is also called inter structural or inter bundle swelling*. When low molecular solvents brought into contact with the polymer, first it passed into the space between the polymer chains in the bundle causing the swelling. The swollen polymer consists for some time with the layer of low molecular mass liquid and ultimately diffusion into solution having a single phase homogeneous system.

During limited swelling, the swollen polymer will not go into solution. Two coexisting phases will be formed. One of them being a solution of the low molecular mass liquid in polymer and other is the pure solvent.

And these phases will be separated by clearly visible interface and will be equilibrium with each other.

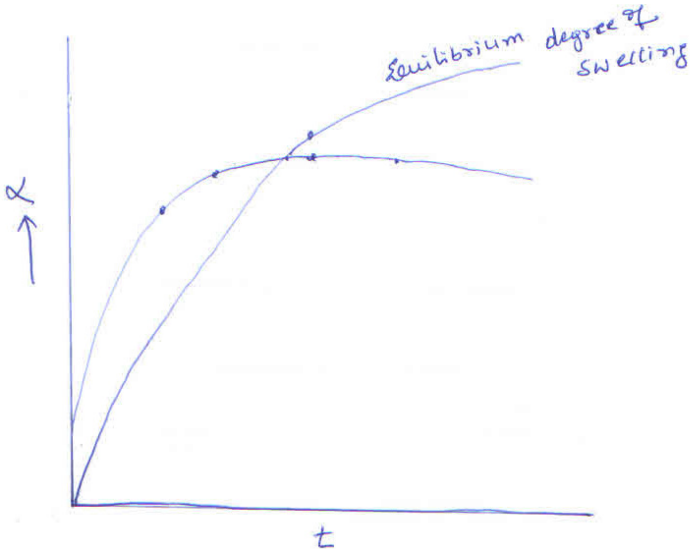
In linear polymer limited swelling is due to the fact that because of energy of interaction of polymers chain is higher than between the polymer and solvent molecules, and hence the chains do not get separated and no dissolution on will occur cross. Cross linked polymers which swell in this way forming gels.

During swelling only inter molecular bonds are distracted or ruptured. The chemical bonds in the polymer will not be ruptured. However in a few cases the high pressure developed in the swollen gels rupture the bonds thus degrade the polymers.

The capacity of the cross linked polymer to swell in different liquids is assessed by the degree of swelling, which is expressed as the amount of liquid or vapour absorbed by unit mass or unit volume of the polymer. i.e,

$$\alpha = \frac{m - m_o}{m_o} = \frac{v - v_o}{v_0}$$

Plot of α vs t will look like as shown in the below figure



Thus α become constant after some time. The volume of α corresponding to the beginning of horizontal line represents the equilibrium degree of swelling.

9.19 Factor affecting the solubility of polymers

1. During the interaction of polymer with the solvent the first step will be the formation of swollen gel and if it is highly crystalline in nature only swelling occurs.
2. The solubility relationships in polymer systems are more complex than those among the low molecular compounds due to the large size of the molecule, the viscosity of the solution and the possible presence of crystalline phase.
3. Thermodynamic properties of polymer solution are highly dependent on the molecular mass of the polymer and deviation from the ideality are much greater than in simple systems (However theories have been developed which accounts at least semiquantitatively for such deviations and predict the conditions under which a given polymer may be swollen or dissolved in particular liquid.

There are some factors which affecting the ability of polymer to form homogenous stability with solvent.

a) Nature of polymer and solvent

The swelling solution of polymers depends on the “Chemical structure of the solvent molecules i.e depends primarily on the polarity of the solvent. If the chain units are close in polarity to the solvent molecules) the energy of interaction between like and unlike molecules will be approximately same and the swelling occurs. If the polymer and solvent molecules differ greatly in polarity, neither swelling nor solution will occur.

Non polar polymer like polyethelene, polybutadiene, polyisobutelene are miscible with saturated hydrocarbons alkanes (non-polar), but do not interact with polar solvent like H_2O alcohols etc (swelling does not occurs)

Polar polymers like polyvinyl alcohol, cellulose do not interact with hydrocarbons but swells readily in water.

Very highly polar polymer swells only to a limited extent in polar liquids due to the great rigidity of their chains. Medium polarity polymer dissolves only in liquids of medium polarity

Ex. Polystyrene not dissolves in saturated hydrocarbons but dissolves in aromatic hydrocarbons, benzene, Toluene etc.

Thus we can summaries that chemical and structural similarity between polymers and solvent favors the solubility. Solution occurs when the attractive forces between polymer and solvent out ways pairs of polymer molecular or pairs of polymer chains. If the solute-solvent interactions will be greater, then the two molecules have similar polarity.

b) *Flexibility of the polymer chain*

The mechanism of dissociation of polymer may result due to separation of the chains form one another and their diffusion into the solvent. Both these process depends on the flexibility of the chains. If the chains are flexible there is no need to spend energy to separate the chain form one another and hence they easily go into solution. Thus greater the flexibility, more will be solubility of polymer in given good solvent"

c) *Molecular mass of polymer*

The higher the molecular mass of polymer i.e the greater chain lenght of degree polymerization, the higher will be the energy or the interaction between the chains. Hence the separation of long chain form each other required more energy than separating short once. Hence with increasing molecular mass of polymer (in a polymer homogeneous series) the solubility in the same solvent decrease. This is the basis of fractionation of polymers according to molecular weight.

d) *Crystalline structure of polymers*

Crystalline polymers are much less soluble than amorphous one due to the high intermolecular interaction. Therefore in this case to separate the chains away from one another, it is necessary to break a large number of bonds simultaneously, which requires considerable amount of energy hence at room temperature crystalline polymers are insoluble even in liquids of similar polymers.

Ex. At 20^0C polymers swells to a limited extent in normal hexane but dissolves in it only when heated. Poly tetraflouroethylene is insoluble in all known solvents at all temperature. Therefore in short it can be said that, the crystalline polymer, the solubility decreases with increase in the melting point and they dissolves only the temperature slightly below their melting points.

9.20 Summary of the unit

The word, polymer, implies that polymers are constructed from pieces that can be easily connected into long chains. A polymer is a macromolecule but a macromolecule may not be a polymer. Polymer contains repeating units.,examples are DNA, proteins, etc where as Macromolecules contain no repeating units. The repeating structural units are derived from some simple and reactive molecules known as monomers and are linked to each other by covalent bonds. This process of formation of polymers from respective monomers is called polymerization. The transformation of ethene to polythene and interaction of hexamethylene diamine and adipic acid leading to the formation of Nylon 6,6 are examples of two different types of polymerisation reactions. The functionality of a monomer is the number of sites it has for bonding to other monomers under the given conditions of the polymerization reaction. Thus, a bifunctional monomer, i.e., monomer with functionality two, can link to two other molecules under suitable conditions. A polyfunctional monomer is one that can react with more than two molecules under the conditions of the polymerization reactions. The number of repeating units (n) in the chain so formed is called the 'degree of polymerization' (DP = n). Polymers with a high degree of polymerization are called 'high polymers' and those with low degree of polymerization are called oligopolymers (short chain polymers or oligomers). Polymers do not exhibit strength for $n < 30$ and that the optimum strength of most of the polymers is obtained at n around 600. The useful range of n is from 200 to 2000.

9.21 Key words

Polymers; Monomers; Rrepeating units; Co-polymers; Degree of polymerization; Number average molecular weight (M_n); Molecular Average Molecular weight $\overline{M_m}$; Higher average molecular weights: Mz, Mz+1; Polydispersity of polymer; Glass transition temperature (Tg); Mechanical properties of polymers; Swelling of Polymers.

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9.23 Questions for self understanding

1) What are Polymers? Give three examples.
2) What are Monomers? Write the structure of monomers in Nylon-66, PVC, and Natural Rubber.
3) What is meant by repeating units? How they differ from Monomers.
4) What are Co-polymers? Give two examples.
5) What is Degree of polymerization? How it can be calculated? Explain its significance.
6) Discuss the preparation of some common synthetic polymers.
7) Write a note on mechanism of polymerization
8) Discuss the molecular weight of polymers and its distribution.
9) What is meant by Number average molecular weight (M_n)? How it will be calculated?

10) What is meant by Molecular Average Molecular weight $\overline{M_m}$? How it will be calculated?

11) What is meant by higher average molecular weights Mz, Mz+1 of polymers?

12) Discuss the polydispersity of polymer.

13) What is meant by Glass transition temperature (Tg)? Explain its significance?

14) Discuss the mechanical properties of polymers.

15) Explain briefly about chemical bonding and molecules forces in polymer.

16) Explain the swelling of polymers.

17) Discuss the different factors affecting the solubility of polymers.

UNIT-10

Structure

10.0 Objectives of the unit

After studying this unit you are able to

- Write the structure of different types of polymers
- Distinguish between simple natural polymers
- Difference between condensation and addition polymers
- Explain the different techniques used for fractionation of polymers by solubility
- Explain the procedure of fractional precipitation
- Explain the procedure of Fractional Extraction (continuous fractionation)

10.1 Introduction

Thousands of different polymers have been synthesized and more will be produced in the future. Conveniently, all polymers can be assigned to one of two groups based upon their processing characteristics or the type of polymerization mechanism. A more specific classification can be made on the basis of polymer structure. Such groupings are useful because they facilitate the discussion of properties.

All polymers can be divided into two major groups based on their thermal processing behavior. In addition to classifying polymers on the basis of their processing characteristics, polymers may also be classified according to their mechanism of polymerization. In addition to classification based upon processing and polymerization characteristics, polymers may also be grouped based upon the chemical structure of their backbones. For example, polymers having all carbon atoms along their backbone are important examples of homochain polymers. Heterochain polymers that contain more than one atom type in their backbone are grouped according to the types of atoms and chemical groups (e.g., carbonyl, amide, or ester) located along the backbone. More recently, another classification scheme based on polymerization kinetics has been adopted over the more traditional addition and condensation categories. According to this scheme, all polymerization mechanisms are classified as either step growth or chain growth. Most condensation polymers are step growth, while most addition polymers are chain growth

10.2 Types of polymers

Polymers can be classified in several different ways-according to their structures, the types of reactions by which they are prepared, their physical properties, or their technological uses.

	Basis of Classification	Polymer Type
i)	Origin -	Natural, Semi synthetic, Synthetic
ii)	Thermal Response	Thermoplastic, Thermosetting

iii)	Mode of formation	Addition, Condensation
iv)	Line structure	Linear, Branched, Cross-linked
v)	Application and Physical Properties	Rubber, Plastic, Fibers
vi)	Tacticity	Isotactic, Syndiotactic, Atactic
vii)	Crystallinity	Non crystalline(amorphous), Semi-crystalline, Crystalline
viii)	Polarity	Polar, Non polar
ix)	Chain	Hetro, Homo-chain

On the basis of their occurrence in nature, polymers have been classified in three types, they are

i) ***Natural polymer:*** The polymers, which occur in nature are called natural polymer also known as biopolymers. Examples of such polymers are natural rubber, natural silk, cellulose, starch, proteins, etc..

ii) ***Semi synthetic polymer:*** They are the chemically modified natural polymers such as hydrogenated natural rubber, cellulose nitrate, methyl cellulose, etc….

iii) ***Synthetic polymer:*** The polymer which has been synthesized in the laboratory is known as synthetic polymer. These are also known as manmade polymers. Examples of such polymers are polyvinyl alcohol, polyethylene, polystyrene, polysulfone, etc..

On the basis of thermal response, polymers can be classified into two groups they are

i) ***Thermoplastic polymers:*** They can be softened or plasticized repeatedly on application of thermal energy, without much change in properties if treated with certain precautions. Example of such polymers are Polyolefins, nylons, linear polyesters and polyethers, PVC, sealing wax etc..

ii) ***Thermosetting polymers:*** Some polymers undergo certain chemical changes on heating and convert themselves into an infusible mass. The curing or setting process involves chemical reaction leading to further growth and cross linking of the polymer chain molecules and producing giant molecules. For example, Phenolic, resins, urea, epoxy resins, diene rubbers, etc.

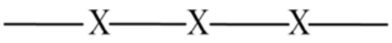
On the basis of mode of formation, polymers can be classified as

i) ***Addition polymers:*** They are formed from olefinic, diolefnic, vinyl and related monomers. They are formed from simple addition of monomer molecules to each other in a quick succession by a chain mechanism. This process is called addition polymerization. Examples of such polymers are polyethylene, polypropylene, polystyrene.

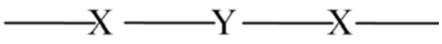
ii) ***Condensation polymers:*** They are formed from intermolecular reactions between bifuctional or polyfuctional monoer molecules having reactive functional groups such as –OH,-COOH, -NH_2, -NCO, etc….

On the basis of structure, polymers are of three types, they are

i) ***Linear polymer:*** If the monomer units are joined in a linear fashion, polymer is said to be linear polymer.

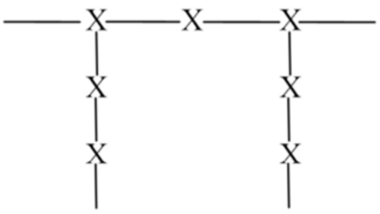


Linear Homopolymer

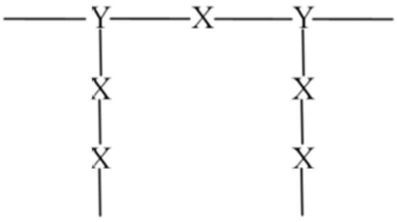


Linear Copolymer

ii) ***Branched polymer:*** When monomer units are joined in branched manner, it is called branched polymer.

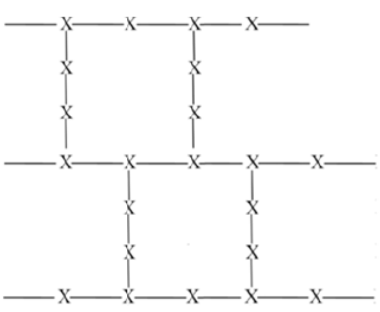


Branched Homopolymer

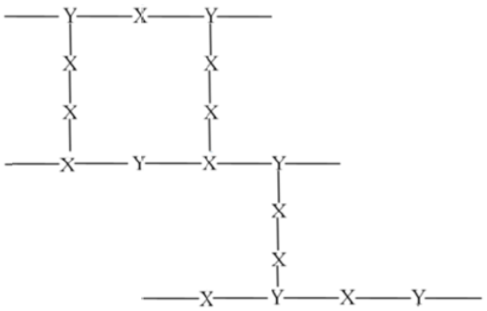


Branched Copolymer

iii) Cross linked polymer: A polymer is said to be a cross linked polymer, if the monomer units are joined in a chain fashion.



Cross linked Homopolymer



Cross linked Copolymer

Depending on its ultimate form and use a polymer can be classified as

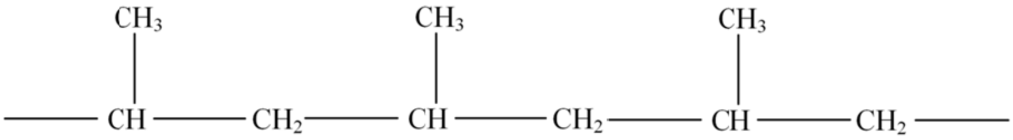
i) ***Rubber (Elastomers):*** Rubber is high molecular weight polymer with long flexible chains and weak intermolecular forces. They exhibit tensile strength in the range of 300-3000 psi and elongation at break ranging between 300-1000%. Examples are natural and synthetic rubber.

ii) ***Plastics:*** Plastics are relatively tough substances with high molecular weight that can be molded with (or without) the application of heat. These are usually much stronger than rubber. They exhibit tensile strength ranging between 4000-15000 psi and elongation at break ranging usually from 20 to 200% or even higher. The examples of plastics are, polyethylene, polypropylene, PVC, Polystyrene, etc….

iii) ***Fibers:*** Fibers are long-chain polymers characterized by highly crystalline regions resulting mainly from secondary forces. They have a much lower elasticity than plastics and elastomers. They also have high tensile strength ranging between 20,000-150,000 psi, are light weight and possess moisture absorption properties.

Tacticity may be defined as the geometric arrangement (orientation) of the characteristic group of monomer unit with respect to the main chain (backbone) of the polymers. On the basis of structure, polymer may be classified into three groups, they are

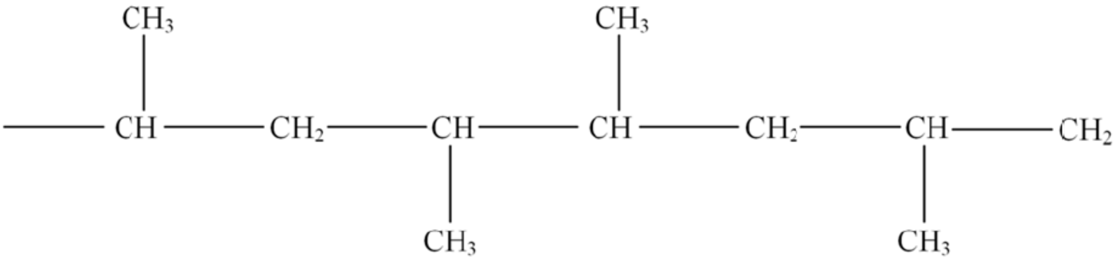
i) ***Isotactic polymer:*** It is the type of polymer in which the characteristics groups are arranged on the same side of the main chain.



$$—\overset{\overset{\displaystyle CH_3}{|}}{CH}—CH_2—\overset{\overset{\displaystyle CH_3}{|}}{CH}—CH_2—\overset{\overset{\displaystyle CH_3}{|}}{CH}—CH_2—$$

Isotactic Polypropene

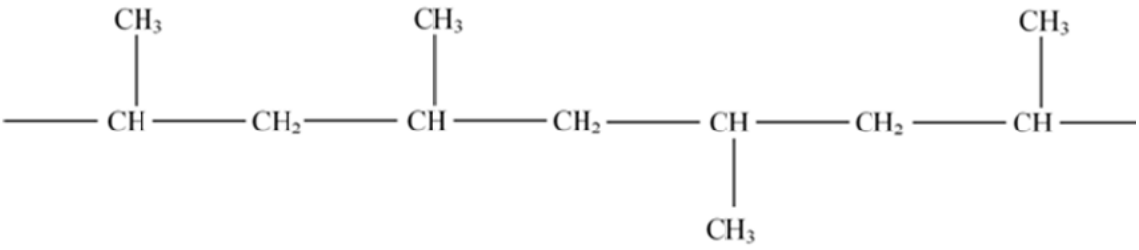
ii) ***Syndiotactic polymers:*** A polymer is said to be syndiotactic if the side groups (characteristic groups) are arranged in an alternate fashion.



$$—\overset{\overset{\displaystyle CH_3}{|}}{CH}—CH_2—\underset{\underset{\displaystyle CH_3}{|}}{CH}—\overset{\overset{\displaystyle CH_3}{|}}{CH}—CH_2—\underset{\underset{\displaystyle CH_3}{|}}{CH}—CH_2$$

Syndiotatic Polypropene

groups) are arranged in irregular fashion (randomness) around the main chain. It has proper strength and more elasticity.



$$—\overset{\overset{\displaystyle CH_3}{|}}{CH}—CH_2—\overset{\overset{\displaystyle CH_3}{|}}{CH}—CH_2—\underset{\underset{\displaystyle CH_3}{|}}{CH}—CH_2—\overset{\overset{\displaystyle CH_3}{|}}{CH}—$$

Atactic Polypropene

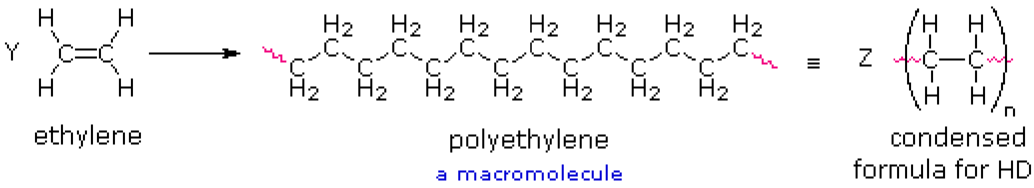
10.3 Verities of macromolecules

a) Synthetic linear organic polymers

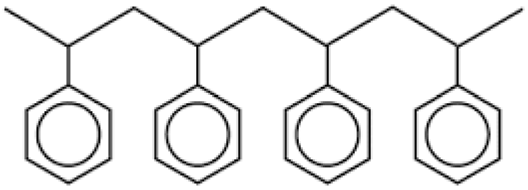
These are the simplest of all types of macromolecules which consists of long unbranched chains of small identical subunits or sometimes of two or three different kinds of subunits.

Examples,

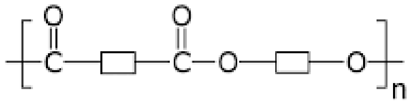
Polyethylene



Polystyrene



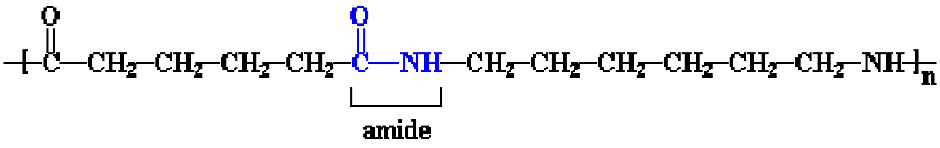
Polyesters



a polyester

Polyamides

These are prepared from the corresponding N-carboxy anhydride. Polyamides and polyesters are example of another large group known as condensation polymers. Polystyrene is an example of a large group of polymers usually known as vinyl polymers. They are addition polymers obtained by successive addition of monomers of the type $H_2C=CH-R$. Preparation of which involves the elimination of water or some other simple substance in the condensation of functional groups such as –COOH, and $-NH_3$, -OH etc.



$$\left[\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-\underbrace{\overset{O}{\overset{\|}{C}}-NH}_{\text{amide}}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH \right]_n$$

Long chain molecules of this kind are prepared so as to contain almost any number of subunits from just 10 or 20 to nearly a million. Also a given sample polymers may contain the entire spectrum of possible weights having all possible number of sub units several thousands. Molecules with different number subunits may be separated by fractionation [

A fundamental difference between synthetic polymer and ordinary " chemical" molecules is that in small molecule all the individual molecules of a given preparation have the same mass but in synthetic polymers there will be molecular of different molecular masses].

The nature of synthetic polymers indicate at once that their physical chemistry will be concerned with a vital factor which does not arise to nearly the same extent in the physical chemistry of small molecular nor in the physical chemistry of many of the naturally occurring macro molecules. This is the factor of statistics. Statistical consideration occur in classical physical chemistry, primarily when we consider the distribution of energy among an assembly of molecules but in most situations all the individual molecules are alike in size and in structure. In the case of synthetic polymers statistics pervade every facet of our investigation. Even fundamental properties like molecular weights are necessarily governed by statistical distribution and the measurement of such factor is always determined average properties.

10.4 Synthetic non-linear or branched polymers

If the monomers are bifunctional i.e, they contain two points with which polymerization occur, example, the hydroxyl groups of $HO-(CH_2)_x-OH$ or the two unsatisfied valences (or points) present as in the vinyl monomer $RHC=CH_2 \rightarrow R^{\cdot}CH-C^{\cdot}H_2$, the polymer formed will be linear.

When monomer molecules is poly functional, i.e, when it contains more than two locations (or points) susceptible to attack leading to polymerization, i.e, the resulting polymers will not be linear non-linear.

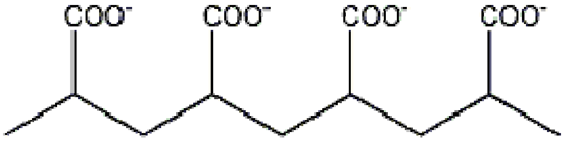
Thus the polymer obtained from the condensation of glycerol with a dicarboxylic acid will be a solid net work extending inflexibly and greatly entangled into three dimensions.

By introducing a few cross links into an essentially linear structure, like introducing a small amount of glycerol into a polymerization mixture of a glycol and a dicarboxylic acid, less highly branched polymers may be obtained. Branched polymer molecules are less easy (difficult) to characterized statistically than linear ones.

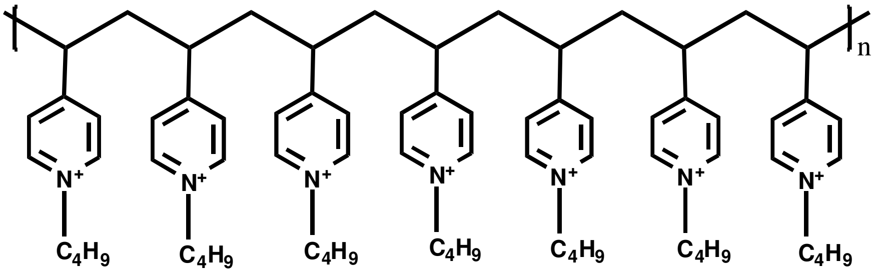
Synthetic Poly electrolytes

If the subunit of a linear polymer contains an ionic group the polymer is usually termed as the poly electrolytes.

Example, polyacrylate



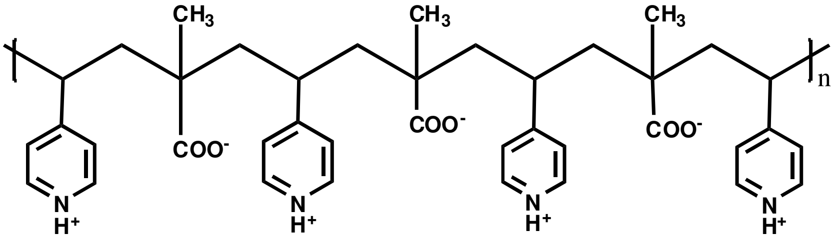
Poly N-butyl-4-vinyl-pyridiniumsalts



polyelectrolate is the anion of a weak acid and it can be converted to an unchanged polymer by titration with acid. The second is a strong electrolyte and changed at all pH values. These are soluble in polar solvents, conduct electricity and one (profoundly) firmly affected by coulombs forces between the charges possess.

Polyelectrolytes containing both +ve and –ve charges is called polyampholytes

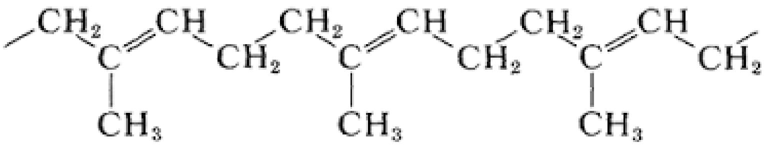
Example, copolymer of vinylpyridine and methacrylicacid.



10.5 Simple natural polymers

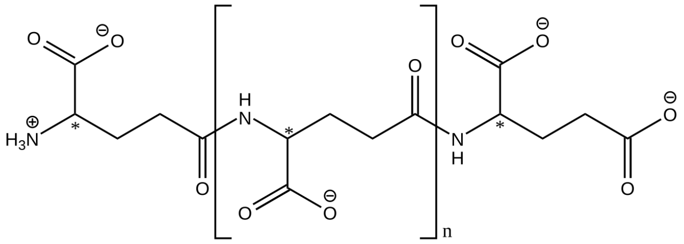
Among naturally occurring polymers there are a few which resemble the synthetic organic polymers in simplicity and in the heterogeneity of chain lengths.

Example, Natural rubber



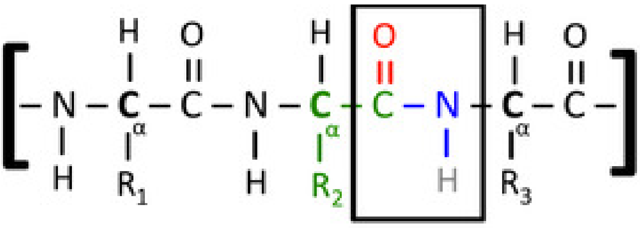
gutta-percha (*trans*-1,4-polyisoprene)

And bacterial polypeptide, poly-γ-D-glutamate



a) Proteins

Proteins are naturally occurring macromolecules each consisting of one or more polypeptides chains. These chains are built from about 20 different amino acids with the structure of the type



where $R_{1,}$ $R_{2,}$ R_3 represent the side chain of the constituent amino acids. These side chains may be non-polar (ex,-H, $-CH_3$) polar but unchanged ($-CH_2OH$) negatively charged ($-CH_2COO^-$) or positively charged ($-CH_2-CH_2-CH_2-CH_2-NH_3$). The nature of the groups decides the polarity of the macromolecule. But most proteins contain nearly all possible side chains in different proportions.

b) Nucleic acids

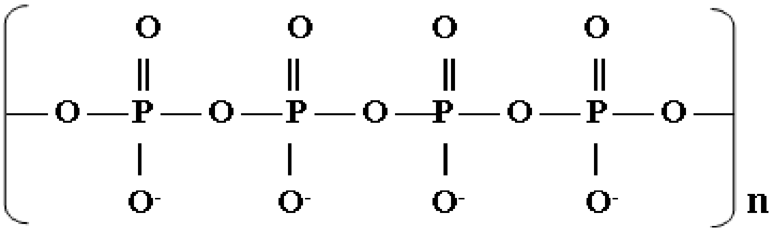
Nucleic acids occur in all forms of the living matter. They are polynucleotides. A nucleotide is a compound containing a phosphate, a pentose sugar and a pyrimidine or purine base. If the sugar is ribose the nucleic acid is called RNA, if it is deoxyestigatribose it is called DNA. The DNA samples which have been investigated originaly from variety of sources have been found to be mixture of different molecular weights average more than 4 million. RNA molecules will have molecular weight of the order one lakh

c) Neucleoproteins

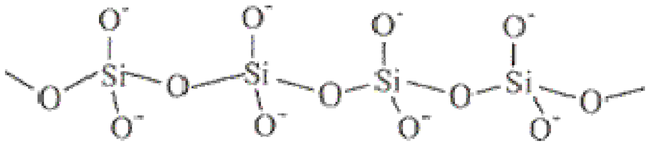
Nucleic acids generally occur in constitution with proteins. They nearly always exists definite compounds called nucleoproteins. Nucleoproteins have their molecular weight ranging from 1 million to 2 million.

10.6 Inorganic polymers

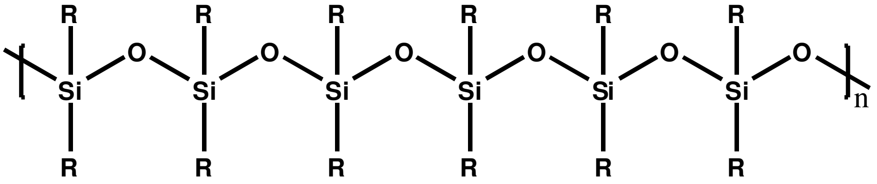
There are very few in organic substances which face logically into the macro molecular classes. Of course any crystal is said to be single or larger molecule, but the term macro molecules is generally used only if the size is maintained under verity of conditions, in solutions as well as solid state. However some inorganic substance seems to be like macro molecules, examples, ployphosphate, polysilicates which exits as polymeric ions in solutions.



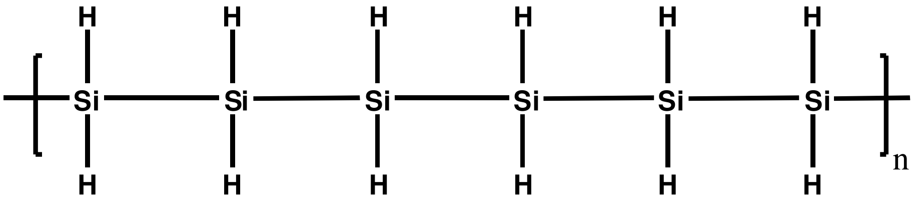
Linear structure of polyphosphate



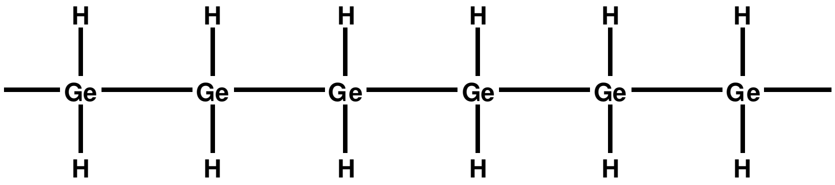
The reaction between NH_4Cl and PCl_5 yield an inorganic polymer $(PNCl_2)_x$ is formed. But the best known inorganic polymers are the silicones having the structure



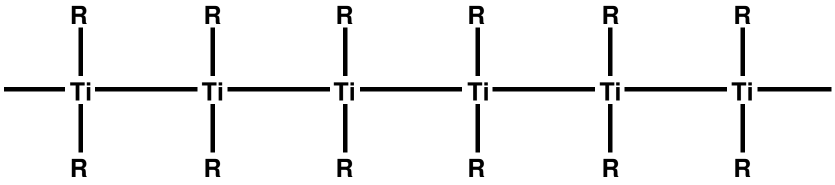
R is organic group like acetyl group. Apart from this we have the poly silicanes having structure



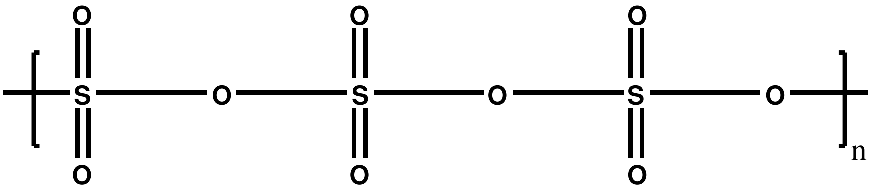
Polygermane

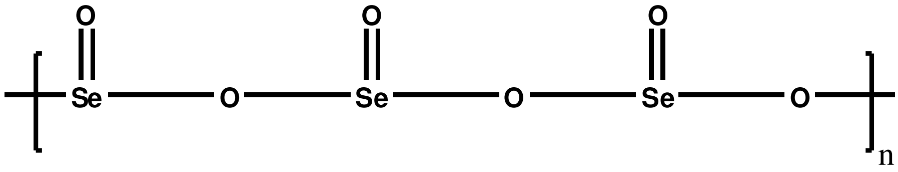


Polytitanane

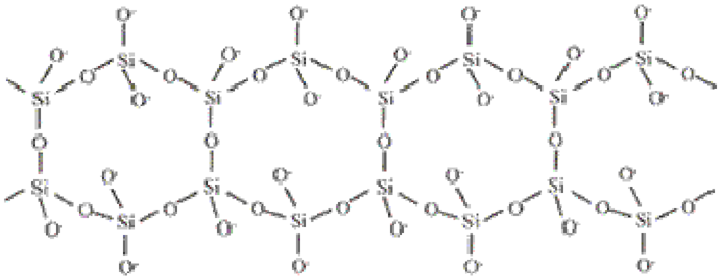


And





Amorphous silicon dioxide and poly silicic acid are inorganic polymer

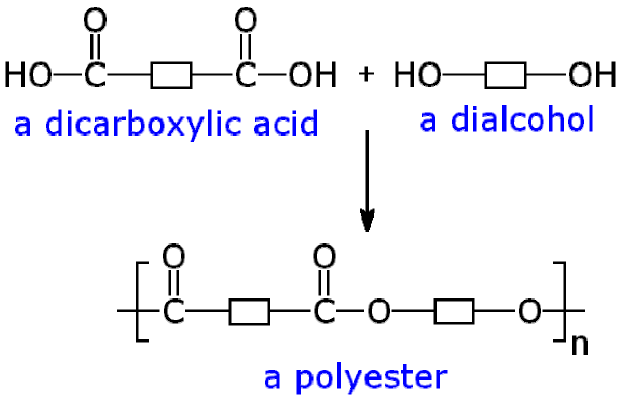


Etc……

10.7 Condensation and addition polymers

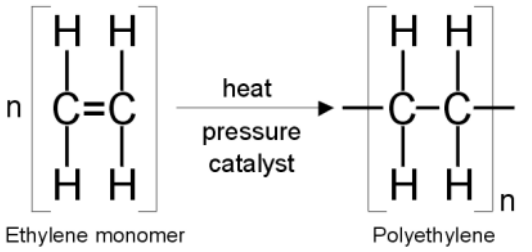
Carothers classified polymers into two groups they are condensation and addition polymers. Condensation polymers are those in which the molecular formation of the repeat unit of the polymer chain leaves certain atoms present in the monomer from which it is formed.

Example, Polyester is formed by the typical condensation reactions between bi functional monomers with the elimination of water



Addition polymers are those in which this loss of small molecules does not take place.

Example, Vinyl Polymer



The classification based on the reaction mechanism dividing polymerization into step reaction commonly producing step-reaction or condensation polymers and chain reaction commonly producing chain reaction commonly producing chain reaction or addition polymers. Condensations polymers are usually formed by the stepwise inter molecular condensation of reactive groups. Addition polymers ordinarily result from chain reactions involving some sort of active species.

10.8 Distinguishing features of chain and step polymerization mechanism

Chain or Addition Polymers	Step Polymerization
Only growth reaction adds repeating units one at a time to the chain	Any two molecules species present can react
Monomer concentration decreases steadily throughout reaction	Monomer disappears early in reaction on (at-Dp 10 less than 1% monomer remains)
High Polymer is formed at once. Polymer molecular weight changes little throughout reaction	Polymer molecular weight rises steadily throughout the reaction
Long reaction times gives high yields but affect molecular weight little	Long reaction times are essential to obtain high molecular weight
Reaction mixture contains only monomer, High Polymer and about 10^{-8} part of growing chain	At any stage all molecular species are present in any calculable distribution

Nylon-66 obtained by polymerizing the adipic-acid and hexometallene diamine $H_2N(CH_2)_6$ NH_2-$HOOC$-$(CH_2)_4$-$COOH$→ Polymers

The properties and uses all similar to Nylon-66

10.9 Fractionation of polymers by solubility

As a general rule the composition of a polymeric substance is not homogeneous. The existence of molecular weight disparity or molecular weight heterogeneity in macro molecular substance is directly responsible for the necessity of using several molecular weight averages and it also exerts a permanent influence on all the properties of the substance both in solution and in the solid state.

The fractionation of a polymeric substance means “the separation of that substance into its different molecular species using a suitable experimental technique in order to obtain homogeneous fractions”.

Most of the experimental technique developed to fractionate polymers depends with accordingly to molecular weight i.e, the method of fractionation depends on the greater solubility of the low molecular weight species in a given solvent.

Methods of fractionation polymers are divided into two classes, they are

i) Fractional precipitation and

ii) Fractional extraction

10.11 Fractional precipitation

Fractional precipitation is carried out by adding the non solvent to a solution of the polymer until a slight turbidity develops at the temperature of fractionation. Then the mixture may be warmed until it is homogeneous and allowed to cool slowly back to the required temperature (temperature of fractionation) which is well maintained carefully. The successive precipitation of polymer species form polymer solution taken place, the larger molecules precipitate first i.e, the precipitate phase contain high molecular weight of fraction and supernatant phase (solution) containing low molecular weight solution. The solution is carefully decanted and the particles of high molecular weight are separated. Again by adding the non-solvent to the supernant phase another fraction is separated by precipitation and the procedure is repeated several times to obtain different fractions of polymer.

There are two main ways of brining about precipitation

1. By the addition of precipitant (non-solvent which is responsible for precipitation is called precipitant) isothermally to a clear solution of polymer in the suitable solvent.
2. By altering the temperature, keeping the total concentration constant.

Both methods are widely used sometimes solvent volatilization is used i.e, successive precipitation of polymer solution in a solvent/non-solvent mixture by controlling evaporation of the more volatile solvent. The larger molecular precipitate first

For getting effective fractionation

i) The solvent and the precipitant (non solvent) should be chosen in such a way that precipitation occur over a relatively wide range of solvent composition i.e, precipitation should complete before a ratio of non solvent: solvent reached two high

ii) The other considerations are stability and volatility of the liquids and their ability to form highly swollen mobile gel phase.

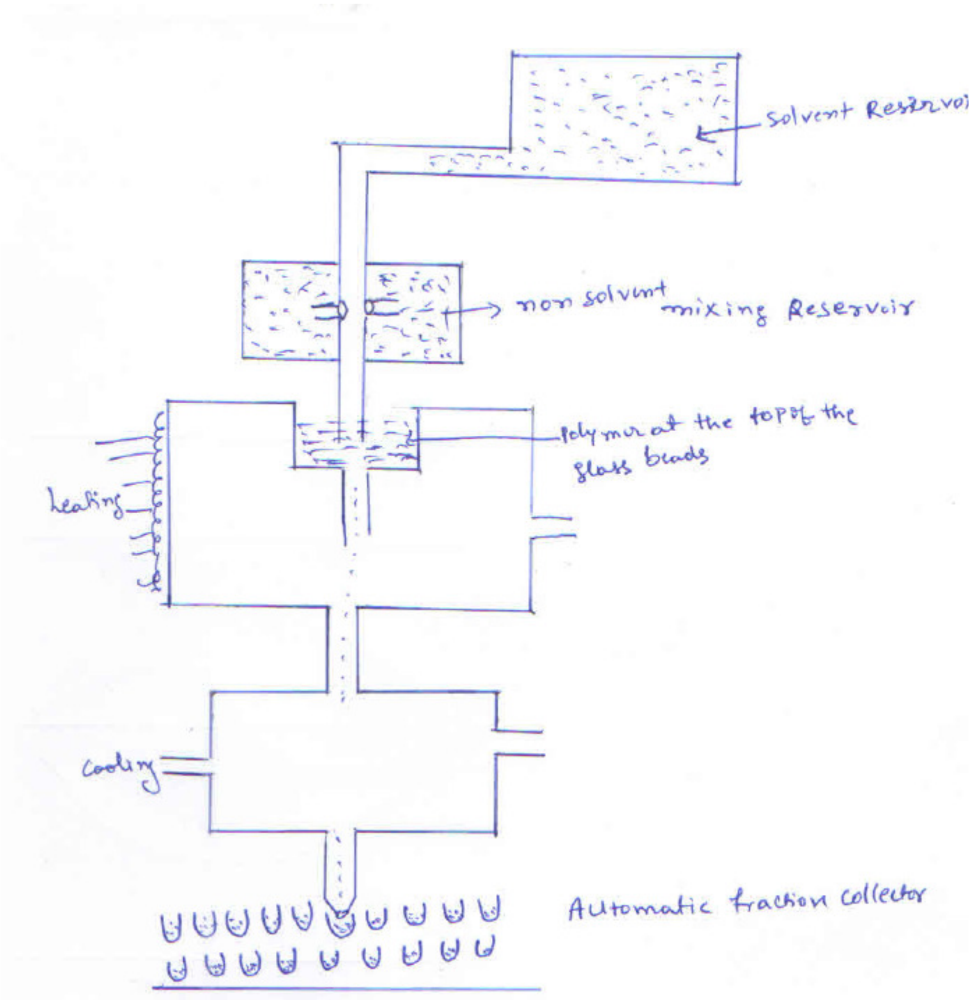
Example: Poly (1-butene), cyclohexonol: Glycol (3:1) 115^{0}C

Polyethylene, Xylene:n-propanol 90^{0}C

However this process seems to be quite tedious, so in practice continuous methods based on some principles is used)

10.12 Fractional Extraction (continuous fractionation)

Direct and successive extraction of polymer with a liquid of increasing solvent power “smaller molecules are extracted first” [in previous case larger molecules are precipitated and extracted first]



In this method the polymer is placed at the top of the column of glass beads as shown in figure the upper portion of the column is heated and the lower portion is cooled.

The polymer is saturated with the non-solvent (precipitation occurs), then the system is gradually cooling enriched with the solvent. At first only the material of lowest molecular weight will go into solution (solvent reacts with low molecular species) and this occurs at an elevated temperature. When this portion of the polymer solution reaches the colder part of the column, it will be re-precipitated and stays there till a more enriched solvent comes along. In this way the material continuously dissolved and re-precipitated as it process down the column accordingly to the molecular weight. A fractional collector at the exit of the column automatically separated the sample whose weight and molecular weight may be determined. This is one of the best methods used for separation of polymers.

Some other methods

10.13 Turbidimetric titration

Continuous precipitation of polymer species from a very dilute solution by progressive addition of non solvent i.e, in the absence of coagulation the amount of polymer precipitated can be measured by the increase in OD(optical density) of the solution (by using turbidimetry). The larger molecules precipitated first.

The method can also be reversed i.e, the polymer is precipitated first completely by non solvent and then re dissolved by progressive addition of solvent which decrease the OD (hence using O.D and amount of solvent or non solvent added, we can calculate molecular weight of species (This is analytical method).

a) Film extraction

A metal foil is created thinly with polymer, the foil is cut into strips and extracted simultaneously with solvent non solvent mixture of increasing solvent power. Smaller molecular are extracted first.

b) Fractionation by Chromatography

The adsorption of polymer species on an active support depends on the molecular weight

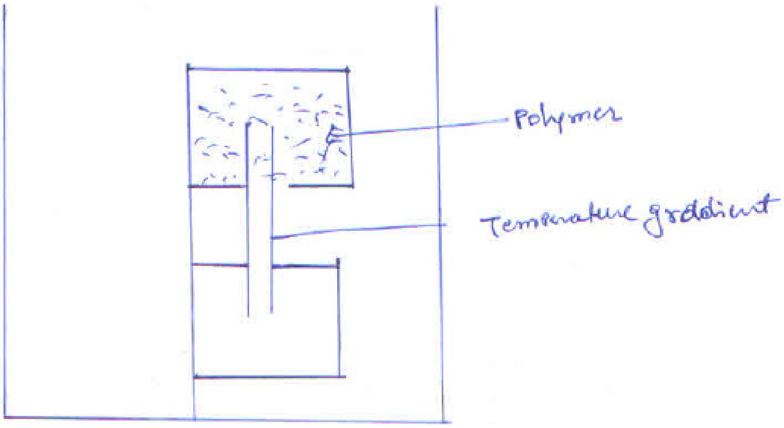
c) Fractionation by sedimentation

i) sedimentation velocity
ii) sedimentation energy

d) Fractionation by diffusion

10.16 Thermal diffusion

Polymer is place in between two reservoir or surface, introduce temperature gradient which give rise to thermal circulation of molecules. The thermal diffusion is more for the larger molecular than for smaller so that producing a separation of polymer species, migrate to forms reservoir.

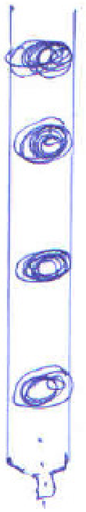


10. l7 Brownian diffusion

In this method polymer species diffuse with different rate from solution to solvent depending on molecular weight it is also an analytical method

10.18 Fractional by Zone melting

A solid solvent is packed in a column a small amount of polymer is put on top of the solid solvent and dissolved by heating a narrow zone. Polymer species move down the column at different rates depending on their molecular size during the molten stage. At the end the polymer is distributed throughout the entire column and recovered by solvent cutting the solid and subliming the solvent and non solvent. This method has no clear definite since it depends with several factors such as tap which increase the solubility hence many more as solvent or pressure increases or decreases may influence the solubility or mixing of solvent to non solvent may affect the solubility.



We can express solvent and non solvent with reference to solvent power i.e, the solubility varies with solvent power which depends inter above factors

10.19 Kinetics of Condensation Polymerization (Step wise polymerization)

Monomers contain at least two functional groups would undergo condensation polymerization. Functional groups such as –COOH, -OH, $-NH_2$ groups react each other to form a new molecule by the elimination of H_2O, or NH_3. The two reacting functional groups may be present in the same molecule just like is caproric acid $H_2N-(CH_2)_5-$ COOH or in separate molecules like HO-(CH_2)-OH ethylene glycol and adipic acid HOOC-$(CH_2)_4$-COOH. If they are in the same monomer molecule the concentration of the functional groups would remain equimolar through the reaction and schematically represented by

$$(A\text{-}R\text{-}B) \rightleftharpoons A\text{-}R\text{-}B\text{-}[A\text{-}R\text{-}B]_{n-2}\text{-}A\text{-}R\text{-}B + [W] \text{---------} (1)$$

If the functional group of the link are located on two different monomers such as A-R-A, B-R^1-B. The analysis on the general case is fairly complex. For simple case in which the two types of the monomer present in the equimolar components, the scheme may be written as

$$\frac{n}{2}(A-R-A)+\frac{n}{2}\left(B-R^1-B\right)\rightleftarrows A-R-A-\left\{B-R^1-B-A-R-A\right\}_{\frac{n}{2}}-B-R^1-B+[W]$$

----- (2)

The reaction (1) and (2) consists of several elementary reactions elementary reaction corresponding to (1) can be represented by

$$p_m + p_n \underset{k^1_{mn}}{\overset{k_{mn}}{\rightleftarrows}} p_{m+n} + W \text{ ----------- (3)}$$

where m,n = 1,2,3,4,---------∞

$$p_m = A-R-B-[A-R-B]_{m-2}-A-R-B$$
$$P_n = A-R-B-[A-R-B]_{n-2}-A-R-B$$

$\kappa_{m,n}$ *and* κ'_{mn} are rate constants of backward and forward reactions. In (3) n and m can take any value 1 to ∞ i.e polymeric species react not only with another polymeric species but also with a monomer, a dimer, trimer etc….. Reaction (3) shown in general to be reversible. In the initial stages, In the initial stages of polymerization the concentration of the product would be small and the extent of the reverse reaction would be negligible. Under such conditions the reaction represents by (3) would be considered as an irreversible reaction without much error. And also in several commercial polymerization vacuum is created around the reaction mass and the product is continuously removed from the reaction so that the equilibrium shifts completely towards the conversion of the monomers to the polymers.

The elementary reactions corresponding to the 2nd type of condensation polymerization is not simple as (1)

10.20 Equilibrium of Condensation Polymerization

As in the case of chemical reaction simple molecules, condensation polymerizations have also a state of equilibrium. In the earlier discussion, the argument were restricted to irreversible polymerization, but as one approach higher conversion, the reaction becomes reversible ultimately approaches equilibrium Thus for polymerization.

$$p_m + p_n \underset{\kappa'_{mn}}{\overset{k_{mn}}{\rightleftarrows}} p_{m+n} + w-----------(1)$$

Equilibrium consnt can be written as

$$K_{m,n} = \left|\frac{[p_{m+n}][w]}{[p_m][p_n]}\right|---------(2)=\frac{k_{m,n}}{k'_{m,n}}$$

The reaction between the parameters ΔS, ΔH and K given equation

$$\left[\frac{\delta\left(\ln \bar{x}_n\right)}{\delta\left(1/T\right)}\right] = \frac{-\Delta H}{2R} ------------------(3)$$

(ΔH is –ve indicate the evolution *of heat*)

As per the equation (3) $\bar{x}_n$ increases as T is reduced. Thus logically one could expect condensation polymerization carried out best at low temperature to yield products of very high molecular weight. But normally this is not done because at low temperature the rate of polymerization would be very small. Thus to have reasonable rates one has to work either at optimum temperature. However it is noted that for condensation polymerization $\bar{x}_n$ and the extent of reaction (pe) will increases with decreasing temperature. When heat of reaction ΔS is constant and concentration of the reaction product [Wce]*is independent of temperature.

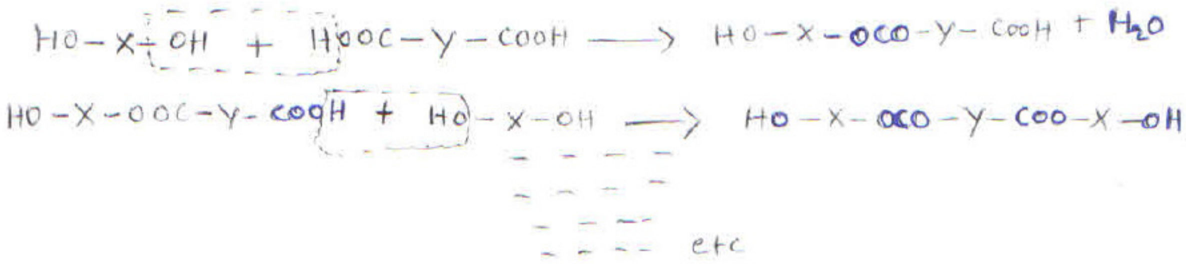
The typical example is polyester formation

$x\ HO\text{-}(CH_2)_n\text{-}COOH \rightarrow H\text{-}[O\text{-}(CH_2)_n\text{-}CO\text{-}]_x\text{-}OH + (x\text{-}1)\ H_2O$

or corresponding reaction starting with a glycol and a dicarbolicy acid

$½\ x\ HO\text{-}(CH_2)_n\text{-}OH + ½\ x\ HOOC\text{-}(CH_2)_n\text{-}COOH \rightarrow H\text{-}[O\text{-}(CH_2)_n\text{-}O\text{-}OC\text{-}(CH_2)_n\text{-}CO\text{-}O]\text{-}H + (X\text{-}1)H_2O$

The steps of the polymerization process would then be of the type

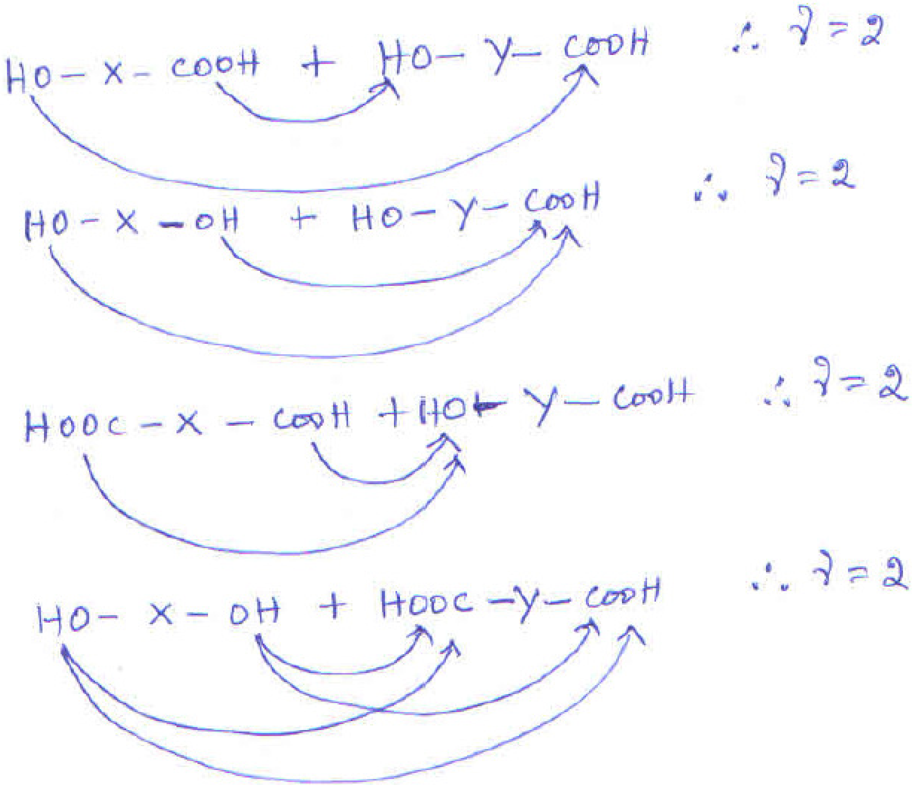


The rate of any reaction is given by

$$\frac{d}{dt}[productspecies] = \gamma k[catalyst][reactentspecies1][reactentspecies2]$$

k rate constant (between long chain molecules with a single –OH group or COOH group), γ the multiplicity factor depends on number and type of functional group

For example: HO-X-COOH+ HO-y-COOH Therefore γ = 2



If the two reactant species are identical,

Example; HO-X-OOC-Y-COOH + HO-X-COO-Y-COOH additional factor ½ is introduced. It is well known that the reaction between the glycol and dicarboxylic acid is catalysed by an acid. In the absence of added strong acid, a second molecule of the acid being esterifies acts as a catalyst. The reaction is followed by measuring the rate of disappearance of carboxylic groups. i.e

$$-\frac{d}{dt}[COOH]=k[COOH]^2[OH]\left[Catalyst=2^{nd}\ of\ COOH\right]$$

$$If\ [COOH]=[OH]=C\ then$$

$$-\frac{dc}{dt}=kc^3------(2)$$

$$-\frac{dc}{c^3}=kdt$$

$$\frac{1}{2c^2}=kt+X------(3)$$

$$Then$$

$$\frac{1}{2c^2}=kt+\frac{1}{2C_0^2}$$

$$\therefore 2kt = \frac{1}{C^2} - \frac{1}{C_0^2} ------(4)$$

Now it is convenient to introduce the extent of reaction ‘p’ to define as the fraction of the functional groups that has reacted at time t i.e

$$p = \frac{c_o - c}{c_o} = 1 - \frac{c}{c_o}$$

$$\therefore {}^{c}\!/_{c_o} = (1-p) \quad or\, C = C_o(1-p) -------(5)$$

$$substitute\, 5\, in\, 4$$

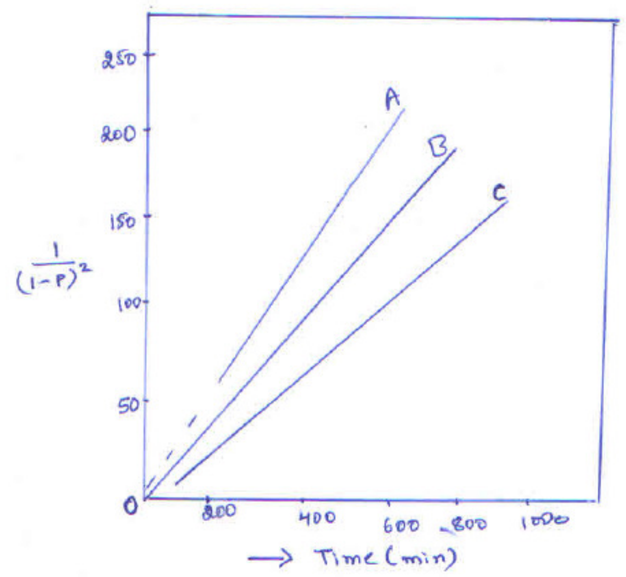
$$2kt = \frac{1}{C_0^2(1-p)^2} - \frac{1}{C_0^2} = \frac{1}{C_0^2}\left[\frac{1}{(1-p)^2} - 1\right]$$

$$\therefore 2C_0^2 kt = \frac{1}{(1-p)^2} - 1$$

$$or$$

$$\frac{1}{(1-p)^2} = 2C_0^2 kt + 1 ----------(6)$$

Therefore A plot of $\frac{1}{(1-p)^2}$ vs time gives a straight line. The slope of which gives rate constant of the reaction



(A) Condensation of diethylene glycol with adipic acid at 202^{0}C

(B) Condensation of diethylene glycol with adipic acid at 166^{0}C

(C) Condensation of diethylene glycol with caproic acid

If only bi-functional reactents are present and no side reactions occurs, then the number of unreacted COOH groups = total number independent molecular (N) in the system.

Initial Number of COOH present (C_0) = total number of structural units present

Then number of average degree of polymerization $\frac{N_0}{\overline{x}_n}$ is given by

$$\overline{x}_n = {N_0}/{N} = {C_0}/{C} = \frac{1}{(1-p)}$$

$\overline{x}_n$ is the average number of monomer molecules present in polymer chain

i.e, Total number of structural units / total number of molecules in the system unreacted (independent molecules)

Anyhow, uncatalyzed esterfications requires quite long times to reach high degree of polymerization. Greater success is achieved by adding to the system small amount of catalyst (p-toluene sulfonic acid) whose concentration is constant throughout the reaction. In this case the concentration of the catalyst also included in the rate constant.

DP = length of the polymer chain (number of repeat units in the chain).

Then

$$-\frac{d}{dt}[COOH] = \kappa[COOH][OH] -------(7)$$

$$-\frac{dc}{dt} = k'C^2 -------------------(8)$$

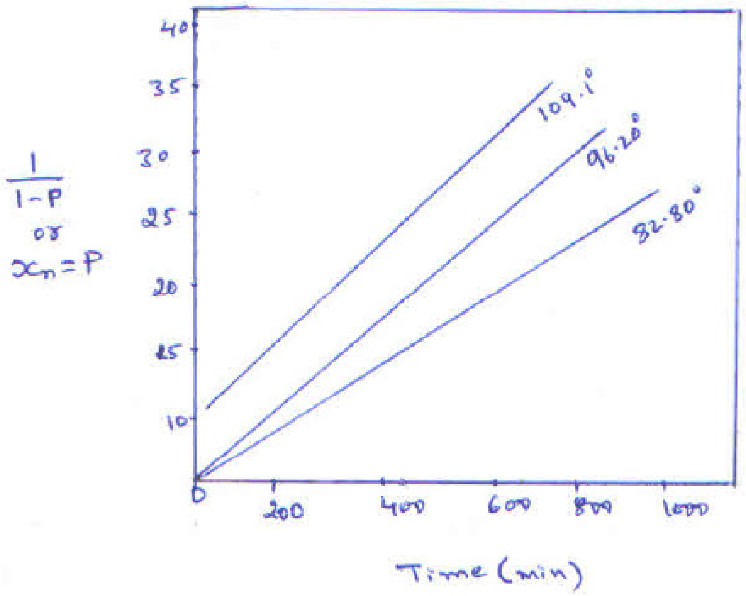
Rearranging the equation (8) integrating with t = 0, C = C_0 we get the kinetic expression

$$C_o k't = \frac{1}{(1-p)} - 1$$

$$\frac{1}{(1-p)} = C_0 k't + 1 -------(9)$$

or

$$x_n = 1 + C_0 k't$$



Therefore of $\frac{1}{(1-p)}$ vs t must be linear. The linearity observed till about 90% of the monomer are converted into the polymer. Form the slope of this line, we can evaluate rate constant of the reaction and energy of activation can be compared.

Ex. Decamethylene glycol and adipic acid with p-toluene sulfonic acid as catalyst

Ea = 11,200 cals, which is nearly equal to Ea = 10,0000observed for the esterification of diphaticacid with methanol by HCl.

10.21 Kinetic derivation of the distribution function during condensation polymerization

Let us represent the monomer, dimer trimer etc. by M_1, M_2, M_3…..etc and their concentration at any instant of time $[M_1]$, $[M_2]$, $[M_3]$ ------etc. Let C be the total concentration of all types of the species present in the system. Then

$$C=[M_1]+[M_2]+[M_3]+\dots\dots\dots\dots\dots\dots[M_x]+\dots\dots$$

$$C=\sum_{x=1}^{x=\infty}[M_x]----------------(1)$$

Let us consider the case of the condensation of monomers in the presence of a catalyst, then the rate of formation of product, i.e,

$$\frac{d}{dt}[\text{Pr}oduct]=\gamma k[Catalyst][-COOH][-OH]---------(2)$$

Ex. if we consider the polymer of the type HO-X-COOH, then the reaction of $M_1+M_1 \rightarrow M_2$ $\gamma = 2$.

Since 1) the condensation of the first molecule with the 2nd one 2) the condensation of 2nd molecule with the 1st one i.e, two molecular of M_1 disappear in that reaction.

Therefore overall rate of change of $[M_1]$ is given by

$$\frac{d}{dt}[M_1]=-2k'[M_1]\sum_{x=1}^{x=\infty}[M_x]=-2k'[M_1]C------(3)$$

$$where\,k'=k[Catalyst]$$

For any species M_x other than M_1 there will be reaction steps in which the species is formed form less polymerization ones as well as steps by which it disappears.

Ex. Formation of M_x will occur whenever a species M_j (j < x) reacts with M_{x-j}

$$\therefore The\,rate\,at\,which\,[M_x]\,formed=\kappa'\sum_{j=1}^{j=x-1}[M_i][M_{x-j}]------(4)$$

M_x may be removed by its reaction with any other species and the rate of disappearance of M_x is given by

$$2k'[M_x]\sum_{x=1}^{x=\infty}[M_x] = -2k'[M_1]C \text{------------}(5)$$

$$\therefore \textit{overall rate of } M_x \textit{i.e}$$

$$\frac{d}{dt}[M_x] = k'\sum_{j=1}^{j=x-1}\left[M_j\right]\left[M_{x-j}\right] - 2k'[M_x]C \text{------}(6)$$

If $\overline{x}_n$ is the number average degree of polymerization, then we known that $\overline{x}_n = \frac{C_0}{C}$ and for catalysed reaction

$$\frac{1}{(1-p)} = \frac{C_0}{C} = \overline{x}_n = 1 + k'C_o t$$

$$\therefore d\overline{x}_n = k'C_o dt$$

$$\therefore dt = \frac{d\overline{x}_n}{k'C_o} \text{-----------}(7)$$

Now solve the equation one by one starting form (3)

$$\frac{d}{dt}[M_1] = -2k'[M_1]C$$

$$\therefore \frac{d[M_1]k'C_0}{d\overline{x}_n} = -2k'[M_1]C$$

$$\frac{d[M_1]}{[M_1]} = -\frac{2C}{C_0}d\overline{x}_n$$

$$\frac{d[M_1]}{[M_1]} = -2.\frac{d\overline{x}_n}{\overline{x}_n} \text{--------}(8)$$

$$\textit{Integrating } (8)$$

$$\ln[M_1] = -2\ln\overline{x}_n + X \text{-----}(9)$$

$$t = 0,\ \overline{x}_n = 1 \textit{ then} [M_1] = C_0$$

$$X = \ln C_0$$

$$\ln[M_1] = \ln C_0 - 2\ln\overline{x}_n$$

$$\therefore \ln[M_1] = \ln\frac{C_0}{\overline{x}_n^2}$$

$$\therefore [M_1] = \frac{C_0}{\overline{x}_n^2} \text{------------}(10)$$

Let us solve the equation number (6) by putting x = 2, and j = 1

$$i.e\frac{d}{dt}[M_n] = k'\sum_{j=1}^{j=x-1}\left[M_j\right]\left[M_{x-j}\right] - 2k'\left[M_n\right]C$$

$$\frac{d}{dt}[M_2] = k'[M_1]^2 - 2k'[M_2]C -------(11)$$

Substituting dt

$$\frac{d[M_2]k'C_o}{d\bar{x}_n} = k'[M_1]^2 - 2k^1[M_2]C$$

$$\frac{d[M_2]}{d\bar{x}_n} = \frac{[M_1]^2}{C_0} - \frac{2[M_2]C}{C_0}$$

$$= \frac{[M_1]^2}{C_0} - \frac{2[M_2]}{\bar{x}_n}$$

$$\therefore \frac{d[M_2]}{d\bar{x}_n} = \frac{C_0^2}{[\bar{x}_n]^4 C_0} = \frac{C_0}{\bar{x}_n}$$

$$\therefore \frac{d[M_2]}{d\bar{x}_n} + \frac{2[M_2]}{\bar{x}_n} = \frac{C_0}{(\bar{x}_n)^4} ----------(12)$$

This is a linear differential equation of the first order having the general solution

$$[M_2](\bar{x}_n)^2 = \int C_0 \frac{d\bar{x}_n}{(\bar{x}_n)^2}$$

$$\therefore [M_2](\bar{x}_n)^2 = -\frac{C_0}{\bar{x}_n} + X' ----------(13)$$

$$When, t = 0, [M_2] = 0, \bar{x}_n = 1$$

$$\therefore X' = C_0$$

$$\therefore [M_2](\bar{x}_n)^2 = \frac{-C_0}{\bar{x}_n} + C_0$$

$$\therefore [M_2] = \frac{C_o\left(1 - \frac{1}{\bar{x}_n}\right)}{\bar{x}_n^{\;2}}$$

$$i.e\, M_2 = \frac{C_o}{\bar{x}_n^{\;2}}\left(1 - \frac{1}{\bar{x}_n^{\;2}}\right) ----------(14)$$

If we continuing in the same way we get differential equation of $[M_x]$ is linear i.e

$$M_3 = \frac{C_0}{\bar{x}_n^{\;2}}\left(1 - \frac{1}{\bar{x}_n}\right)^2$$

$$M_4 = \frac{C_0}{\bar{x}_n^{\,2}}\left(1-\frac{1}{\bar{x}_n}\right)^3 ----$$

$$\therefore [M_x] = \frac{C_o}{\bar{x}_n^{\,2}}\left(1-\frac{1}{\bar{x}_n}\right)^{x-1} -------(15)$$

The terns of the extent of reaction p we can write $\bar{x}_n = {}^{1}\!/_{(1-p)}$

$$[M_x] = C_o(1-p)^2\left(\frac{\bar{x}_n - 1}{\bar{x}_n}\right)^{x-1}$$

$$= C_o(1-p)^2\left(\frac{\frac{1}{1-p}-1}{\frac{1}{1-p}}\right)^{x-1}$$

$$= C_o(1-p)^2\, p^{x-1} --------------(16)$$

In terms of mole fraction of ‘x’ mer

$$X_n = \frac{[M_x]}{\sum[M_x]}$$

$$= C_o\frac{p^{x-1}(1-p)^2}{C} = \frac{p^{x-1}(1-p)^2}{(1-p)}$$

$$\therefore X_x = (1-p)\,p^{x-1} --------------(17)$$

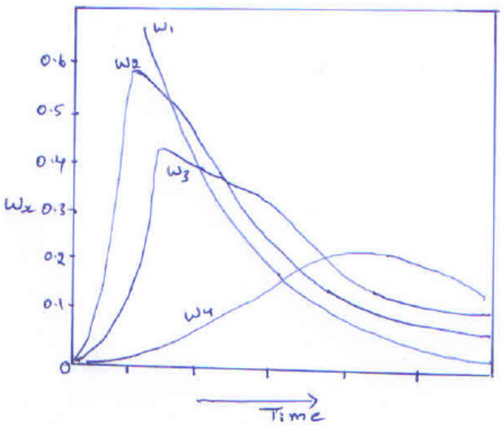
In terms of weight fraction

$$W_x = x(1-p)\,X_x$$

$$W_x = x(1-p)(1-p)\,p^{x-1}$$

$$W_x = x(1-p)^2\,P^{x-1} ------------(18)$$

P is the extent of reaction time dependent quality. Therefore since the equation 16, 17, 18 depends on p condensation polymerization proved as a function of time



It is seen that the polymerization is a progressive one. First the monomer disappears and dimmers and trimers appear instead. They in turn are replaced by higher and higher polymers. Theoretically the reaction will become end only when the entire content of the reaction mixture becomes a single molecule. However the reaction rate decreases very rapidly as C decreases.

10.22 Kinetics of addition polymerization

In this case the initiators continuously generated the growth centres in the reaction. The growth centres can either be ionic (cationic or anionic) free radicals or co-ordinated.

10.23 Kinetics of free radical polymerization

This includes three steps, they are

i) Initiation

ii) Propagation and

iii) Termination

Initiation

The initiate molecule can generate radicals by a homolytic decomposition of covalent bonds on absorption of energy (thermal, photochemical, etc…). The simplest example is benzoyl peroxide.

The production of the radical from the initiator can be given by

$$I_2 \xrightarrow{k_i} 2I \text{ ----------- } (1)$$

$$C_6H_5\text{-CO-O-O-CO-}C_6H_5 \xrightarrow{k_i} 2\ C_6H_5\text{-CO-O}^{\cdot} \rightarrow 2C6H5^{\cdot} + 2CO_2$$

Rate of production of primary radical is

$$\gamma_1^{'} = 2k_i\left[I_2\right] - - - - - (2)$$

Then the primary radical I combine with monomers according to scheme

$$I + M \xrightarrow{k_i} P_1 \text{---------- } (3)$$

Therefore the rate of secondary polymer chain radical is given by

$$\gamma_i = k_i\left[I\right]\left[M\right] - - - - - (4)$$

When there is a hostage of primary radicals are defined, the initiator efficiency ‘f’ which is the fraction of total primary radical produced by (1) which generates the polymer radical by reaction (3). Then the rate of generation of polymer radical is

$$\gamma_i = 2fk_i\left[I_2\right] - - - - - (5)$$

Propagation

Addition of the monomer molecules to the growing polymer molecules (polymer chain radical) and in general the polymer molecule p_n indicate there are n monomeric units joined together to the covalent bond in the chain radical. Then propagation reaction is written as

$$p_n + M \xrightarrow{kp_n} p_{n+1,} n = 1, 2, 3, ----500---$$

The kp_n is the rate constant of the reaction between p_n and the monomer molecule. In general this depends upon the size of the growing molecule.

Termination

In which the polymer chain radicals are destroyed, this can occur only when a polymer radical reacts with another polymer radical or with primary radical. This type of termination is called termination. Thus we have,

$P_m + P_n \xrightarrow{kmn} M_{m+n}$ (mutual termination)

$P_m + I \rightarrow M_{m+1}$ (primary termination)

M_{m+n} represent a lead polymer chain

In the case of mutual termination the inactive polymer chain formed by either combination or disproportination. In combination, the two chain radicals just combine to give an inactive chain. Whereas in disproportination one chain radical gives certain electron to the other or it involves the transfer of a H atom and forming a lead polymer chain

Kinetic equation

Let us consider a free radical polymerization brought about in the presence of initiator like Benzoyl peroxide

If the production of free radical from the initiator is 1st order one, then the rate of production of the free radical is given by

$A \xrightarrow{k_1}$ free radical

$$\gamma_i = k_1[A] ----------- (1)$$

where [A] is the concentration of the initiator

In some cases the free radicals are produced by the reaction with the monomer with the initiator. Then the rate of production of free radical is

$A + M \xrightarrow{k_1}$ free radical

$$\gamma_i = k_1[A][M] ------- (2)$$

Chain reactions may also initiate without the addition of the initiator either photo chemically or thermally. For that rate of production of initiator

$$\gamma_i = k_1 I \text{ ---------- } (3)$$

I = intensity of light used

The formation of free radicals in this event is 2nd order with respect to monomer concentration ie,

$$\gamma_i = k_1 [M]^2 \text{ ---------- } (4)$$

Chain propagation occurs by a series of successive steps. All of which may be assumed to be governed by the same rate constant k$_2$, independent of chain length. So the sequence of the propagation step can be written as

$$\left.\begin{array}{l} R^{\cdot} + M \xrightarrow{k_2} RM_1^{\cdot} \\ RM_1^{\cdot} + M \xrightarrow{k_2} RM_2^{\cdot} \\ RM_2^{\cdot} + M \xrightarrow{k_2} RM_3^{\cdot} ------ \\ ----- \\ ----- \\ ----- \\ RM_j^{\cdot} + M \xrightarrow{k_2} RM_{j+}^{\cdot} etc \end{array}\right\} ------(A)$$

These propagation steps are very much faster than any of the chain initiation reactions because of the unpaired electros. The successive propagation steps involve continuous addition of monomer.

The growth of the molecule stops only when chain termination occurs, i.e, combination between two free radicals as

$$RM_i^{\cdot} + RM_j^{\cdot} \xrightarrow{k_3} RM_{i+j}^{\cdot} ------(B)$$

To obtain the kinetic equation for addition of free radical polymerization, we make use of the fact that the successive free radicals formed are unstable. Thus after a brief initial build-up period, they disappeared as fast as they are formed, so that a steady state is reached. Then concentration for different type of free radicals $R^{\cdot}$, $RM_1^{\cdot}$, $RM_2^{\cdot}$.... etc are constant.

$$\left.\begin{aligned}
&\frac{d\left[R^{\cdot}\right]}{dt}=\gamma_i-k_2\left[R^{\cdot}\right]\left[M\right]-k_3\left[R^{\cdot}\right]\sum_{j=0}^{\infty}\left[RM_j^{\cdot}\right]=0\\
&\frac{d\left[RM_1^{\cdot}\right]}{dt}=k_2\left[R^{\cdot}\right]\left[M\right]-k_2\left[RM_1^{\cdot}\right]\left[M\right]-k_3\left[RM_1^{\cdot}\right]\sum_{j=0}^{\infty}\left[RM_j^{\cdot}\right]=0\\
&\frac{d\left[RM_2^{\cdot}\right]}{dt}=k_2\left[RM_1^{\cdot}\right]\left[M\right]-k_2\left[RM_2^{\cdot}\right]\left[M\right]-k_3\left[RM_2^{\cdot}\right]\sum_{j=0}^{\infty}\left[RM_j^{\cdot}\right]=0\\
&----------\\
&----------\\
&----------etc\\
&\frac{d\left[RM_i^{\cdot}\right]}{dt}=k_2\left[RM_{i-1}^{\cdot}\right]\left[M\right]-k_2\left[RM_i^{\cdot}\right]\left[M\right]-k_3\left[RM_i^{\cdot}\right]\sum_{j=0}^{\infty}\left[RM_j^{\cdot}\right]=0
\end{aligned}\right\}--------(5)$$

Adding all above equations we get

$$\frac{d}{dt}\left(\sum_{i=0}^{\infty}\left[RM_i^{\cdot}\right]\right)=\gamma_i-k_3\sum_{i=0}^{\infty}\left[RM_i^{\cdot}\right]\sum_{j=0}^{\infty}\left[RM_j^{\cdot}\right]=0$$

$$\gamma_i=k_3\left(\sum_{j=0}^{\infty}\left[RM_j^{\cdot}\right]\right)^2=0$$

$$or\gamma_i=k_3\left(\sum_{j=0}^{\infty}\left[RM_j^{\cdot}\right]\right)^2-------------(6)$$

This equation merely states that, when there is no change in total free radical concentration, the rate of chain initiation must equal the overall rate of chain termination.

Let us write the equation for the rate of disappearance of monomer. Since thousands of propagation steps occur for each initiation reaction, any loss of monomer which occur in the latter can be neglected. Then

$$-\frac{d[M]}{dt}=k_2[M]\sum_{j=0}^{\infty}\left[RM_j^{\cdot}\right]----------- (7)$$

Form equation (6) $\left(\frac{\gamma_i}{k_3}\right)^{\frac{1}{2}}=\sum_{j=0}^{\infty}\left[RM_j^{\cdot}\right]------------ (8)$

$$\therefore-\frac{d[M]}{dt}=k_2[M]\left(\frac{\gamma_i}{k_3}\right)^{\frac{1}{2}}---------------- (9)$$

We can also write the equation for the formation of the stable products which occurs only by the chain termination reactions, if [P] is concentration of product at any instant of time t then

$$\frac{d[P]}{dt}=\frac{1}{2}k_3\left(\sum_{i=0}^{\infty}\left[RM_i^{\cdot}\right]\right)\left(\sum_{j=0}^{\infty}\left[RM_J^{\cdot}\right]\right)\text{------}(10)$$

The factor ½ being introduced as the reaction is counted twice

From (6) we have $\frac{d[P]}{dt}=\frac{\gamma_i}{2}$ ------- (11)

Free Radical polymerization produces fully polymerized product at all stages of the reaction. The average degree of polymerization of the product which is being formed at any instant of time can be obtained by combining equations 9 and 11 as the ratio of the rate at which monomer disappears to the rate at which product molecules are formed. Their ratio will give the average value of (i + j) [equation B] in the product. If the R groups at the ends of the chain are connedect as polymer segments, the degree of polymerization is (2 + i + j). Therefore

$$\bar{x}_n=2+\frac{\frac{d[M]}{dt}}{\frac{d[p]}{dt}}=\frac{2+k_2[M]\left(\frac{v_i}{k_3}\right)^{1/2}}{\frac{v}{2}}$$

$$\bar{x}_n=2+\frac{2k_2[M]}{\left(k_3 vi\right)^{1/2}}----------------(12)$$

The exact form taken by this equation 12 depends on the nature of the initiation of the process

Case i. For thermal initiation

$V_i=k_1[M]^2$--------------------from (4)

Substitute in (9) we will get expression for rate of disappearance of monomers

$$-\frac{d}{dt}[M]=k_2\left(\frac{v_i}{k_3}\right)^{1/2}[M]-------------(9)$$

$$\therefore -\frac{d}{dt}[M]=k_2\left(\frac{k_1[M]^2}{k_3}\right)^{1/2}[M]$$

$$\therefore \frac{-d}{dt}[M]=\left(\frac{k_1}{k_3}\right)^{1/2}k_2[M]^2------------(13)$$

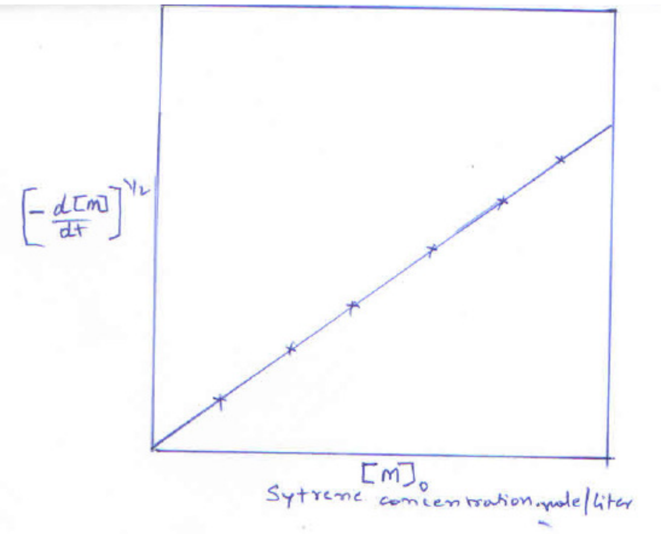
i.e, rate of reaction proportional to square of monomeric concentration indicating that 2nd order reaction

$$\overline{x}_n = 2 + \overline{x}_n = 2 + \frac{\frac{d[M]}{dt}}{\frac{d[p]}{dt}} = \frac{2 + \frac{-d}{dt}}{\frac{V_i}{2}}$$

$$\overline{x}_n = 2 + \frac{\left(\frac{k_1}{k_3}\right)^{1/2} k_2 [M]^2}{\frac{k[M]^2}{2}} = \frac{2 + 2k_2}{(k_1 k_3)^{1/2}} \text{--------}(14)$$

Thus $\overline{x}_n$ of the product is fixed by the rate constant and is independent of time t i.e, $\overline{x}_n$ is exactly the square at the beginning of the reaction and at the end, where most of the monomer is used up.

Example, thermal initiated polymerization of styrene in toluene solution.



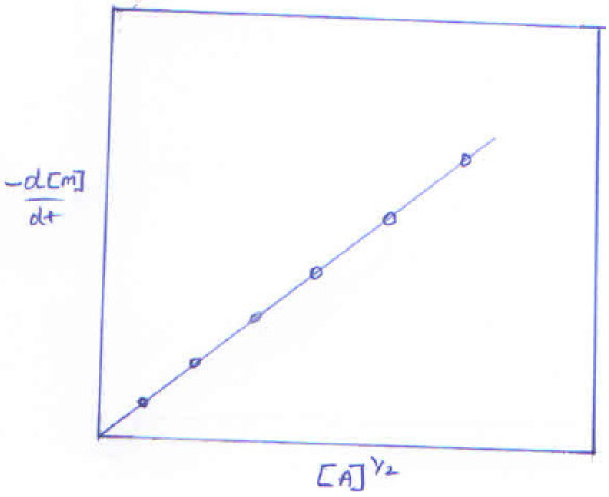
Case ii. If the initiator is used to start polymerization, then

$$V_i = k_1[A]$$

$$\frac{-d}{dt}[M] = k_2 \frac{[k_1 A]^{1/2}}{k_3}[M]$$

$$\frac{-d}{dt}[M] = k_2 \left(\frac{k_1}{k_2}\right)^{1/2} [M][A]^{1/2} \text{--------}(15)$$

$$\overline{x}_n = 2 + 2\, {}^{k_2}\!/_{(k_1 k_2)}{}^{1/2} \; \frac{[M]}{[4]^{1/2}} \text{---------}(16)$$



In this case it is possible to adjust $\overline{x_n}$ to any desired value by adjusting the relative conversations of monomers and initiator. With low initiators concentration, degree of polymerization become nearly equal to one million or more

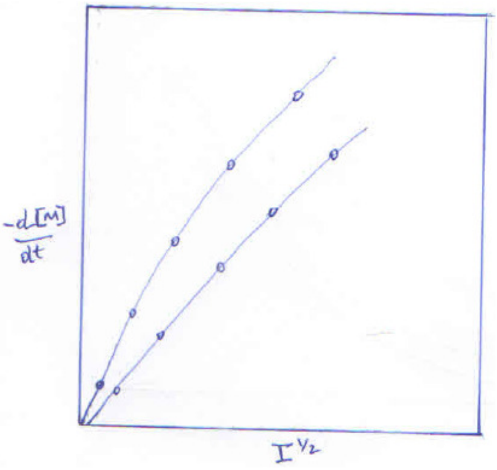
Case iii. For photochemically initiated polymerization

We have $V_i = k_1 I$ then

$$\frac{-d[M]}{dt} = k_2 \left(\frac{k_1}{k_2}\right)^{1/2} I^{1/2} [M]$$

Thus the rate depends on the square root of the light intensity

$$\bar{x}_n = k_2 \frac{(k_2/k_3)^{1/2} [M]}{k_1 I^{1/2}}$$



10.24 Distribution fraction for free radical polymerization

We had derived two equations

$$\frac{d}{dt}[RM_i] = k_2[RM_{i-1}][M] - k_2[RM_i][M] - k_3[RM_i]\sum_{j=0}^{j=\infty}[RMj]--------(1)$$

$$Vi = k_3\left(\sum_{j=0}^{\infty}\left[RM_j\right]\right)^2 ---------------(2)$$

$$[RM_i]\left\{k_2[M] + k_3\sum_{j=0}^{\infty}\left[RM_j\right]\right\} = k_2[RM_{i-1}][M]$$

$$\therefore\left[RM_j\right] = \frac{k_2[M]}{k_3\sum_{j=0}^{\infty}\left[RM_j\right] + k_2[M]}$$

$$\sum_{j=0}^{\infty}\left[RM_j\right] = \frac{k_2[M]}{k_2[M] + (k_3vi)^{1/2}}\left[RM_{j-1}\right]$$

Let us put

$$\alpha = \frac{k_2[M]}{k_2[M] + (k_3v_i)^{1/2}}---------(13)$$

$$\therefore[RM_i] = \alpha[RM_{i-1}]------------(6)$$

So it is seen that the value of α is independent of i and form equation $[RM_i]$ is related to [R] by the equation

$$\left[RM_j\right] = \alpha^i[R_1]----------------(7)$$

Because

$$\left[RM^{\cdot}_i\right] = \alpha\left[R^{\cdot}\right]\ for\, i = 1$$

$$\left[RM^{\cdot}_2\right] = \alpha\left[RM^{\cdot}_i\right] = \alpha.\alpha\left[R^{\cdot}\right] = \alpha^2\left[R^{\cdot}\right]$$

$$\left[RM^{\cdot}_3\right] = \alpha\left[RM^{\cdot}_2\right] = \alpha\alpha^2\left[R^{\cdot}\right] = \alpha^3\left[R^{\cdot}\right]$$

$$-------$$

$$-------$$

$$--------$$

$$\left[RM^{\cdot}_j\right] = \alpha^i\left[R^{\cdot}\right]$$

$$\textit{we got}$$

$$\overline{x}_n = \frac{2+2k_2\left[M\right]}{\left(k_3 v_2\right)^{1/2}} ------------(8)$$

In the above reaction, if $\overline{x}_n$ is to be larger, then the value of k_2[M] should be very larger compare to $\left(k_3 v_i\right)^{1/2}$ so that the expression

$$\alpha = \frac{k_2\left[M\right]}{k_2\left[M\right]+\left(k_3 v_i\right)^{1/2}}$$

$\left(k_3 v_i\right)^{1/2}$ is neglected so that $\alpha = \dfrac{k_2\left[M\right]}{k_2\left[M\right]}$

i.e α = 1 i.e close to unity, so that it is possible to write

$$\left[R^{\cdot}\right] \approx \left[RM^{\cdot}_{i}\right] \approx \left[RM^{\cdot}_{2}\right] \approx \left[RM^{\cdot}_{3}\right] \approx .... \approx \left[RM^{\cdot}_{i}\right]$$

$$\textit{we can write}\left(5\right) \textit{i.e } \ \alpha \ \textit{ is}$$

$$\frac{1}{\alpha} = 1 + \frac{\left(k_3 v_i\right)^{1/2}}{k_2\left[M\right]}$$

$$\therefore \frac{\left(k_3 v_i\right)}{k_2\left[M\right]} = \frac{1}{\alpha} - 1 = \left(\frac{1-\alpha}{\alpha}\right)$$

$$\left(k_3 v_i\right)^{1/2} = \left(\frac{1-\alpha}{\alpha}\right) k_2\left[M\right] --------------(9)$$

Substituting 9 in $\overline{x}_n$ we have

$$\overline{x}_n = \frac{2+2k_2\left[M\right]}{\left(k_3 v_i\right)^{1/2}}$$

$$\overline{x}_n = \frac{2+2k_2\left[M\right]}{\left(\frac{1-\alpha}{\alpha}\right) k_2\left[M\right]}$$

$$2 + \frac{2}{\frac{1-\alpha}{\alpha}} = 2 + \frac{2\alpha}{1-\alpha}$$

$$\therefore \overline{x}_n = \frac{2}{1-\alpha} ---------(10)$$

As α is independent of i, $\overline{x}_n$ should also be independent of i. The rate of formation of polymers molecules of different degree of polymerization (x) may now be computed. Independently the terminal residues as chain segments, the rate of formation of x-means is the rate of formation of all molecules of the form R-M_{x-2}-R i.e it is equal to

$$=\frac{1}{2}k_3\sum_{i=0}^{x-2}\left[RM_{i}^{\cdot}\right]\left[RM_{x-2-i}^{\cdot}\right]---------(11)$$

$$As\left[RM_{i}^{\cdot}\right]=\alpha^{i}\left[R^{\cdot}\right]\ and\left[RM_{x-2-i}^{\cdot}\right]=\alpha^{x-2-i}\left[R^{\cdot}\right]$$

$$\therefore Rate\,of\ formation\,of\ polymer$$

$$=\frac{1}{2}k_3\sum_{i=0}^{i=x-2}\alpha^{x-2-i}\alpha^{i}\left[R^{\cdot}\right]\left[R^{\cdot}\right]$$

$$=\frac{1}{2}k_3\sum_{i=0}^{i=x-2}\alpha^{x-2}\left[R^{\cdot}\right]^{2}$$

$$Rate\,of\ formation\,of\ polymer$$

$$=\frac{1}{2}k_3\left(x-1\right)\alpha^{x-2}\left[R^{\cdot}\right]^{2}$$

Now the composition of the polymerization products which is formed at any instant in the reaction will be determined by the rate at which molecules of different degree of polymerization are being formed. Then sloving for molefraction X_x

$$we\ get$$

$$X_x=\left(1-\alpha\right)^{2}\left(x-1\right)\alpha^{x-2}$$

$$wt\ fraction$$

$$W_x=\frac{xX_x}{\sum_{x=2}^{\infty}X_x}=\frac{1}{2}\left(1-\alpha\right)^{3}x\left(x-1\right)\alpha^{x-2}$$

$$Number\,of\ average\ y\,x\,are\ \ compared\ \ we\,get$$

$$\frac{\bar{X}_w}{\bar{X}_n}=\frac{\bar{M}_w}{\bar{M}_n}=\frac{2+\alpha}{2}$$

10.25 Summary of the unit

Addition polymers form when unsaturated carbon (organic) molecules react to form a long chain polymer molecule and no small molecules or atoms are eliminated during the reaction The general reaction can be represented as

nR-C=C-R → -(R-C-C-R’)n-

where R and R' can represent hydrogen atoms, halogen atoms, alkyl or other carbon-containing side chains.

Condensation polymers form when bifunctional monomers react to form a long chain polymer molecule. Small molecules, such as water, are eliminated during the reaction.

Polyesters, polyamides, proteins and polysaccharides such as cellulose, are all examples of condensation polymers. Example, Polyesters

Polyesters form when the -OH functional group of one monomer reacts with the -COOH functional group of another monomer.

An ester link (-COO-) is formed between monomers during the reaction. H_2O is eliminated in the reaction.

A polymerization consists of several elementary steps, and a catalyst frequently influences the rates of more than one elementary steps. Detailed kinetic studies to obtain quantitative informations of elementary steps are, therefore, particularly essential to the studies on catalyses in polymerizations.

The polymerizations are divided into those with rapid initiation and those with slow initiation, according to the relative magnitude of the initiation rate with reference to the rate of propagation. When the rate of initiation is much larger than that of propagation, the sum of polymer chains produced by initiation is independent of the reaction time; that is, all the initiation reactions are completed immediately after the polymerization reaction starts. This type of polymerization is classified as one with rapid initiation. Polymerizations with rapid initiation have been observed in those initiated by ionic catalysts and in post-effect polymerizations initiated by gammaray or light irradiation.

In the polymerization with a rate of initiation much smaller than that of propagation, the initiation reactions occur continuously in the course of polymerization. This type of polymerization is classified as one with slow initiation. Polymerizations with slow initiation have been observed in those initiated with free radical initiators, gamma-ray or light irradiation and some ionic catalysts.

The kinetics of free radical polymerizations has been studied in detail and it has been established that the kinetics can be treated by a simplified analytical method based on the steady state approximation which equates the initiation and termination rates.

In case of reactivity of large molecules, it is assumed that, the reaction rate may be considered to be constant in spite of changes of molecular size of the reactants is startling. Since the rate constant of a condensation polymerization reaction is independent of molecular size, it is possible to measure the rate of reaction simply by determining the concentration of functional groups as a function of time.

10.26 Key words

Non-linear polymers; Branched polymers; Natural polymers; Condensation polymers; Addition polymers; Fractional precipitation; Fractional Extraction; Turbidimetric titration;

Thermal diffusion; Brownian diffusion; Fractional by Zone melting; Kinetics of Condensation Polymerization; Kinetics of addition polymerization; Kinetics of free radical polymerization.

10.27 References for further studies

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10.26 Questions for self understanding

1) Discuss the types of polymers presents.

2) With example explain the synthesis of non-linear or branched polymers.

3) Give three examples of simple natural polymers.

4) What are condensation and addition polymers?

5) How fractionation of polymers by solubility can be achieved?

6) Explain the fractional precipitation method of purification of polymer.

7) Discuss the fractional Extraction (continuous fractionation) method of purification of polymer.

8) Explain the turbidimetric titration method of purification of polymer.

9) Discuss the thermal diffusion method of purification of polymer.

10) Explain the Brownian diffusion method of purification of polymer.

11) Explain the fractional by Zone melting method of purification of polymer.

12) Discuss the kinetics of condensation polymerization (Step wise polymerization).

13) Deduce the equilibrium of condensation polymerization.

14) Derive the expression of kinetics of the distribution function during condensation polymerization.

15) Discuss Kinetics of addition polymerization.

16) Discuss Kinetics of free radical polymerization.

17) Explain the distribution fraction for free radical polymerization.

UNIT-11

Structure

11.0 Objectives of the unit

After studying this unit you are able to

- Explain the mechanism of cationic polymerization
- Explain the mechanism of anionic polymerization
- Explain the coordination Polymerization method
- Write the structure of Ziegler - Natta Catalysts
- Explain the Integral Heat of solution (HIS) and Dilution
- Explain the thermodynamics of polymer solution
- Explain the entropy of mixing of polymer

11.1 Introduction

Both anionic and cationic polymerization of alkenes undergoes by virtue of the flow of electrons during propagation. Anionic intiation step imvolves the formation of negatively charge carbanion group. The cationic initiation involves the formation of positively charge carbocation. Initiation of alkene polymerization by the anion-chain mechanism is formulated as involving an attack by a nucleophilic reagent $Y:^{\ominus}$ on one end of the double bond and formation of a carbanion. Attack by the carbanion on another alkene molecule would give a four-carbon carbanion, and subsequent additions to further alkene molecules would lead to a high-molecular-weight anion. The growing chain can be terminated by any reaction (such as the addition of a proton) that would destroy the carbanion on the end of the chain. Anionic polymerization of alkenes is quite difficult to achieve because few anions (or nucleophiles) are able to add readily to alkene double bonds. Anionic polymerization occurs readily only with alkenes substituted with sufficiently powerful electron-attracting groups to expedite nucleophilic attack. By this reasoning, alkynes should polymerize more readily than alkenes under anionic conditions, but there appear to be no technically important alkyne polymerization’s in operation by this or any other mechanism. Perhaps this is because the resultant polymer would be highly conjugated, and therefore highly reactive, and may not survive the experimental conditions. Polymerization of an alkene by acidic reagents can be formulated by a mechanism similar to the addition of hydrogen halides to alkene linkages. First, a proton from a suitable acid adds to an alkene to yield a carbocation. Then, in the absence of any other reasonably strong nucleophilic reagent, another alkene molecule donates an electron pair and forms a longer-chain cation. Continuation of this process can lead to a high-molecular-weight cation. Termination can occur by loss of a proton.

11.2 Ionic polymerization

There are two types of ionic polymerization reaction are widely carried out for preparation of polymers. They are

i) Cationic polymerization

Here the chain carries a carbonium ions (H_3C^+, H_2C^+R, $HC^+=0$) having an electron less than corresponding free radical.

ii) Anionic polymerization

Here chain carries an carbanion $(H_3C)^-$ negatively charged organic ion having an electron more than the corresponding free radical.

The mechanism of these polymerization reactions are less thoroughly understood than that of radical polymerization for several reasons. Reaction systems are often heterogeneouly involving inorganic catalysts and organic monomers. Unusually large effects may be produced by a third component (catalyst) present in very low concentration. Polymerization often leads to very high molecular weight polymer at an externally high rate making difficulty in obtaining kinetic data

11.3 Cationic polymerization

Cationic polymerization occurs in a similar manner to free radical polymerization, but the initiator produces cations instead of free radicals. In this case a catalyst and co catalyst are use to generate the cations which create the growth centres.

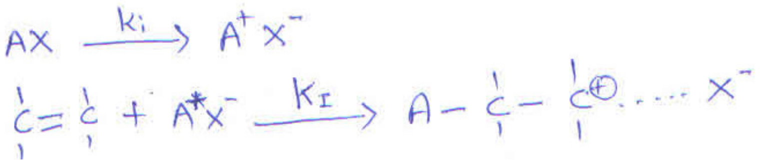
Typical catalyst for cationic polymerization are Friedal-Crafts catalyst such as $AlCl_3$, $AlBr_3$, BF_3, $SnCl_4$, H_2SO_4 and other strong Lewis acids. All these are strong electron acceptors. Most of them (Except protonic acids H_2SO_4, $HClO_4$, HCl) required a co catalyst to initiate polymerization. The co-catalyst supplies H^+ ion.

Initiation

Initiation of the ionic polymerization usually involves the transfer of an ion or an electron to or from the monomer. The monomer reacts with catalyst giving carbonium ion (anion pair). It is throught that the concentration of this pair stays close to the growing chain and throughout its life times, particularly in media of low dielectric constant.

$$\overset{|}{C}=\overset{|}{C}- \; + A^+X^- \longrightarrow A-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}^{\oplus} \cdots\cdots X^- \qquad -①$$

The true initiating species in case of cationic polymerization is A^+X^- and not the molecule AX. The neutral catalyst molecule therefore ionized in the reaction medium before the polymer ion is formed. This implies that the initiation reaction is a two step process



$$AX \xrightarrow{k_i} A^+X^-$$
$$C=C + A^+X^- \xrightarrow{k_I} A-C-C^{\oplus}\cdots X^-$$

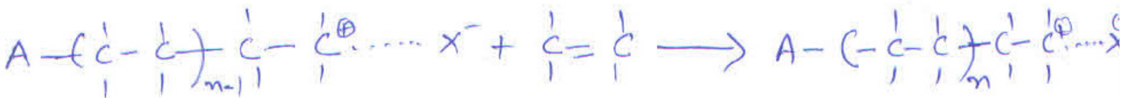
Either of these steps is the rate determining step. If the ionization is the slow step than he rate of initiation is $v_i = k_i[AX]$

However if the formation of carbonium ion is the slow step, than we have

$$V_I = k_I[M]\,[AX]$$

Propagation

The successive addition of the monomers to the carbonium ion taking place in this step



$$A-(C-C)_{n-1}-C-C^{\oplus}\cdots X^- + C=C \longrightarrow A-(C-C)_n-C-C^{\oplus}\cdots$$

Chain termination

In cationic polymerization there is no mutual termination due to the repulsion between the like charges in the two polymer ions. However the neutralization of polymer ions can by the reaction of proton from the polymer ion with the counter ion as follows

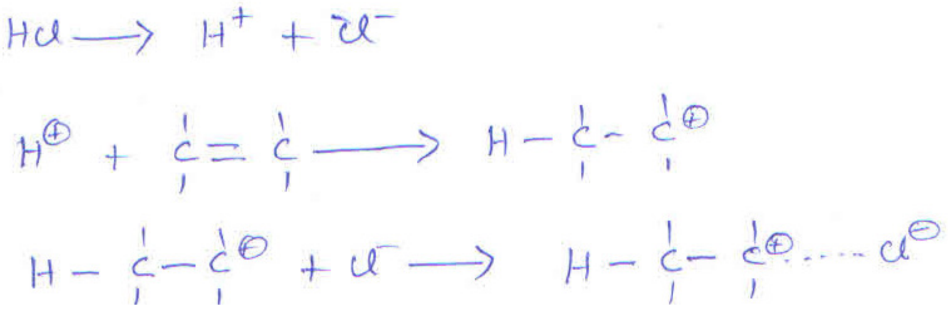
$$A(C-C)_n C-C^{\oplus}\cdots X^- \longrightarrow A(C-C)_n C=C + HX$$

Transfer reaction

The positive charge in the polymer ion is transferring to some other molecules those of impurities or other monomer molecules themselves. As in the case of radical polymerization the transfer reactions do not affect the overall rate of polymerization.

Case i

protonic acid as initiator



$$HCl \longrightarrow H^+ + Cl^-$$
$$H^{\oplus} + C=C \longrightarrow H-C-C^{\oplus}$$
$$H-C-C^{\oplus} + Cl^- \longrightarrow H-C-C^{\oplus}\cdots Cl^{\ominus}$$

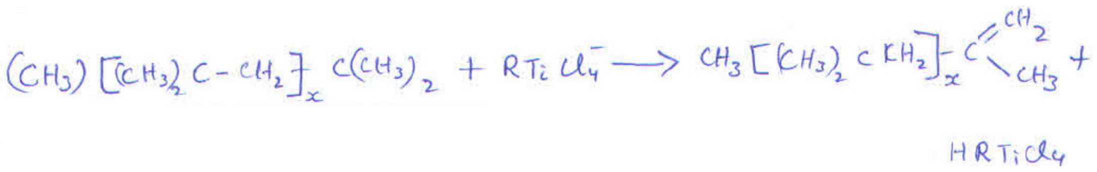
Example, polymerization of isobutylene with $TiCl_4$ catalyst,

First step is the reaction of catalyst and co-catalyst to form a complex acid

$$TiCl_4 + RH \rightarrow TiCl_4R^-H^+$$

which donates proton to an isobutylene molecule to gives a carbonium ion

Ther $H^{\oplus} + (CH_3)_2C=CH_2 \longrightarrow (CH_3)_3C^{\oplus}$ The termination reaction can take place by the rearrangement of the ion pair to yield a polymer molecule with terminal unsaturation, plus the original complex.



$$(CH_3)[(CH_3)_2C-CH_2]_x C(CH_3)_2 + RTiCl_4^- \longrightarrow CH_3[(CH_3)_2CCH_2]_x C(=CH_2)CH_3 + HRTiCl_4$$

Kinetic model

Assuming the principle of equal reactivity the kinetic model can be proposed as follows

Initiation} $A + RH \overset{k_i}{\rightleftharpoons} A-RH$ (complex acid)

$A-RH \xrightarrow{k_i} Hm^{+}\ {}^{-}AR$ (Carbonium ion)

Propagation} $HM_x^{+}\ {}^{-}AR + m \longrightarrow Hm_{x+1}^{+}\ {}^{-}AR$ $(C^{\oplus} + m \longrightarrow C^{\oplus})$ at the end

Transfer} $HM_x^{+}\ \bar{A}R + m \xrightarrow{k_{tr}} M_x + Hm^{+}\bar{A}R$ (Proton transfer counterion)

Termination} $HM_x^{+}\ {}^{-}AR \xrightarrow{k_t} M_x + A-RH$ (Proton tranfer to monomer)

Let [C] is the concentration of catalyst A, RH is the co-catalyst

The rate of initiation

$$\gamma_i = k_i[C][M] \text{------------}(1)$$

If the formation of A-RH is the rate determining step, then

$$\gamma_i = k_i^1[C] \text{ i.e, independent of [M]}$$

Since, in strong contrast to radical polymerization, termination is first order, then

Rate of termination is $\gamma_t = k_t[M_x^+]$------------ (2) where $[M_x^+]$is polymer ion concentration.

By the steady state approximation $\gamma_i = \gamma_t$

$$k_i[C][M] = k_t[M_x^+]$$

$$\therefore [M_x^+] = \frac{k_t}{k_i}[C][M] \text{--------------} (3)$$

Overall rate of polymerization is

$$\gamma_p = k_p[M_x^+][M]$$
$$= k_p\left(\frac{k_i}{k_t}\right)[C][M][M]$$
$$= \left(\frac{k_p k_i}{k_t}\right)[C][M]^2 ------------(4)$$

$\overline{x_n}$ = Rate of polymerization / rate of formation of bead polymer

$$= \frac{V_p}{V_t}$$

If the termination predominates over transfer

$$\overline{x_n} = \frac{V_p}{V_t} = \frac{k_p[Mx^+][M]}{k_t[Mx^+]} = \frac{k_p}{k_t}[M]------(5)$$

So if the termination predominates $\overline{x_n}$ is proportional to monomer concentration. i.e, depends on [M].

$$\overline{x_n} = \frac{V_p}{V_{tr}} = \frac{k_p[Mx^+][M]}{k_{tr}[Mx^+][M]} = \frac{k_p}{k_{tr}}------(6)$$

11. 4 Anionic polymerization

Anionic polymerization is caused by the compounds which give rise to anion in reaction mass. Monomers with electronegative substituents are readily susceptible to anionic polymerization. Anionic polymerization normally consists of only two elementary steps, initiation and propagation. In the absence of initiator transfer and termination does not occur.

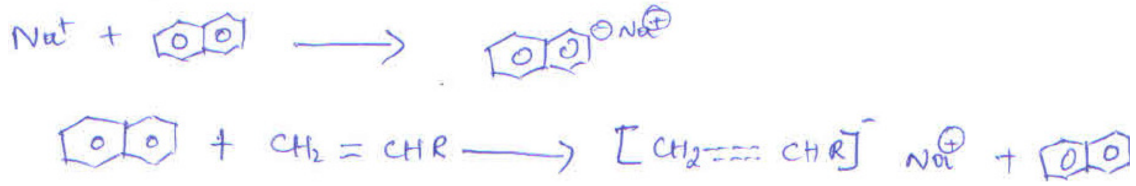
Initiation

Initiation can be brought about using different types of initiators. Typical catalysts like alkaline metals like Na, K, Li and their stable complexes with aromatic compounds, liquid NH_3, etc…..

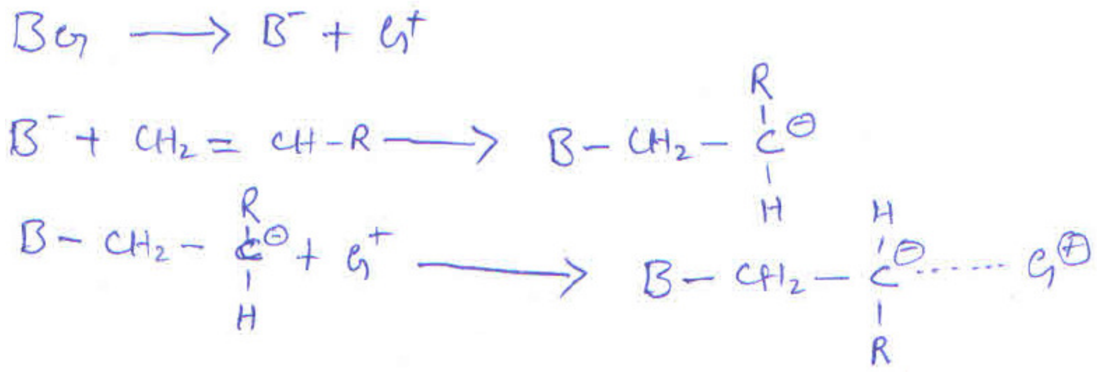
example, a) Na attacks the monomer directly

$$Na + CH_2 = CHR - [CH_2 = CHR]^{\ominus} \cdots\cdots Na^{\oplus}$$

b)

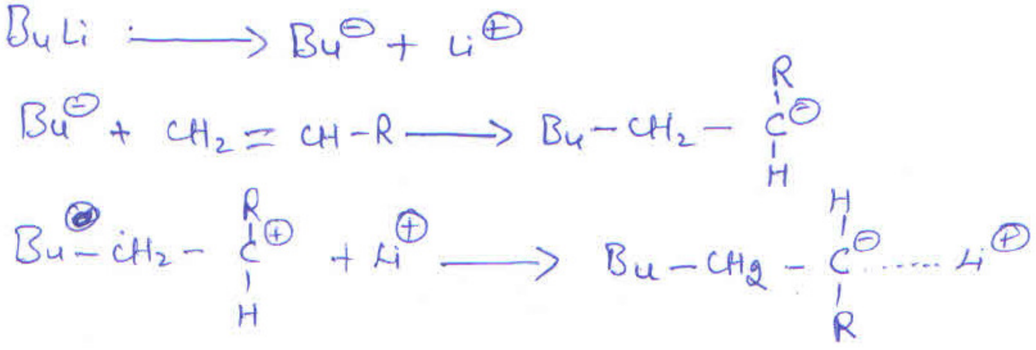


c) Lewis acid



$$BG \longrightarrow B^- + G^+$$
$$B^- + CH_2=CH-R \longrightarrow B-CH_2-\overset{R}{\underset{H}{C}}{}^{\ominus}$$
$$B-CH_2-\overset{R}{\underset{H}{C}}{}^{\ominus} + G^+ \longrightarrow B-CH_2-\overset{H}{\underset{R}{C}}{}^{\ominus}\cdots\cdots G^{\oplus}$$

d) Organometallic Compound



$$BuLi \longrightarrow Bu^{\ominus} + Li^{\oplus}$$
$$Bu^{\ominus} + CH_2=CH-R \longrightarrow Bu-CH_2-\overset{R}{\underset{H}{C}}{}^{\ominus}$$
$$Bu^{\ominus}-CH_2-\overset{R}{\underset{H}{C}}{}^{\oplus} + Li^{\oplus} \longrightarrow Bu-CH_2-\overset{H}{\underset{R}{C}}{}^{\ominus}\cdots\cdots Li^{\oplus}$$

Organomatallic compounds are the most reactive initiator

Propagation

Initiation occurs much faster than propagation, therefore propagation is rate determining step. This depends with nature of counter ion, because monomers molecules adds to the growing chain by squeezing itself between the chain and one of the counter ion, so as a result resonance, polar, steric effects plays a significance role in determining value of k_p

Termination

Unlike in cationic polymer no transfer or reaction with counter ion is taking palace. But it is considered that the small likelihood of transferring H^- when the counter ion is Na^+. Thus in anonic polymerization termination usually involves transfer and the kinetic chain is broken only if the new species is too weak to propagate. Therefore this leads to the situation that careful purification which removes all species to which transfers occurs. The termination steps in effectively eliminated and the growing chains remain active indefinitely and this is called "Living polymer".

The kinetic of anionic polymerization may be illustrated by the polymerization of styrene with potassium amide in liquid ammonia

$$\left.\begin{cases} KNH_2 \overset{k}{\rightleftarrows} K^+ + NH_2^- \\ NH_2^- + M \xrightarrow{k_i} NH_2M^- \end{cases}\right\} Initiation$$

$$\left\{ NH_2M_x^- + M \xrightarrow{k_p} NH_2M_{x+1}^- \right\} \Pr opagation$$

Termination occur when reaction of anion with molecule of NH_3

$$NH2M_x^- + NH_3 \xrightarrow{K_{tr}} MH_2M_xH + NH_2^-$$

$$\therefore v_i = k_i\left[NH_2^-\right][M] ------------ (1)$$

$$rate\,of\,ter\min ation\,v_{tr} = k_{tr}\left[NH_3\right]\left[M_x^-\right] --- (2)$$

$$At\,study\,rate\,v_i = v_{tr}$$

$$k_i\left[NH_2^-\right][M] = k_{tr}\left[NH_3\right]\left[M_x^-\right]$$

$$\left[M_x^-\right] = \frac{k_i[M]\left[NH_2^-\right]}{k_{tr}\left[NH_3\right]}$$

$$\therefore v_p = k_p\left[M_x^-\right][M]$$

$$v_p = \frac{k_pk_i\left[NH_2^-\right][M]^2}{k_{tr}\left[NH_3\right]}$$

$$\therefore \overline{x}_n = \frac{v_p}{v_{tr}} = \frac{k_p\left[M_x^-\right][M]}{k_{tr}\left[NH_3\right]\left[M_x^-\right]}$$

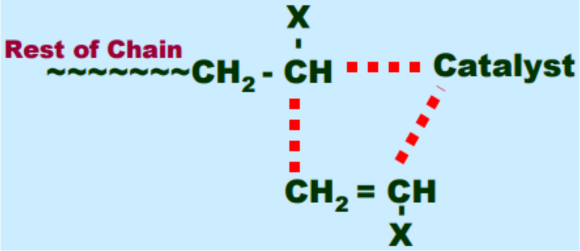
$$\overline{x}_n = \frac{k_p}{k_{tr}} \cdot \frac{[M]}{\left[NH_3\right]}$$

Hence the value of $\overline{x}_n$ is by continued the initial concentration of the monomers and the NH_3 .

Since the termination step involves transfer to some species which is not essential to the reaction, therefore anionic polymerization with carefully purified reagents may leads to systems in which termination is lowering. The resulting species called "Living" Polymer. The polymer can be killed by addition of the termination agent for example H_2O at the end of the reaction.

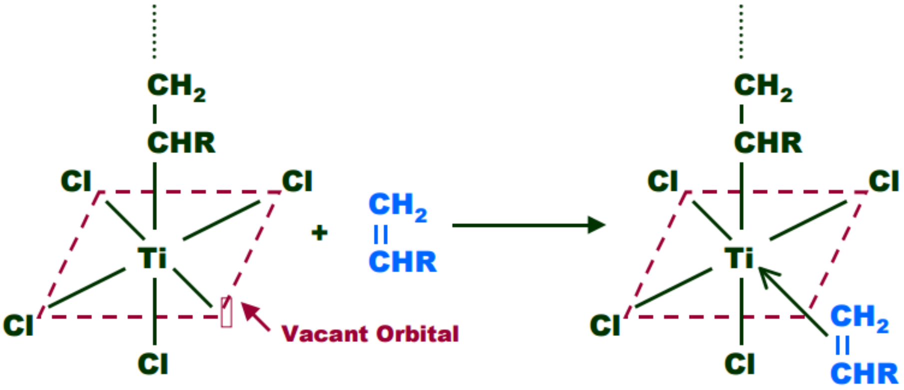
11.5 Coordination Polymerization

Some reactions are best described as coordination polymerizations, since they usually involve complexes formed between a transition metal and the 'p' electrons of the monomer (many of these reactions are similar to anionic polymerizations and could be considered under that category). These types of polymerizations usually lead to linear and stereoregular chains and often use so-called Ziegler - Natta catalysts, various metal oxides, or, more recently, metallocene catalysts.

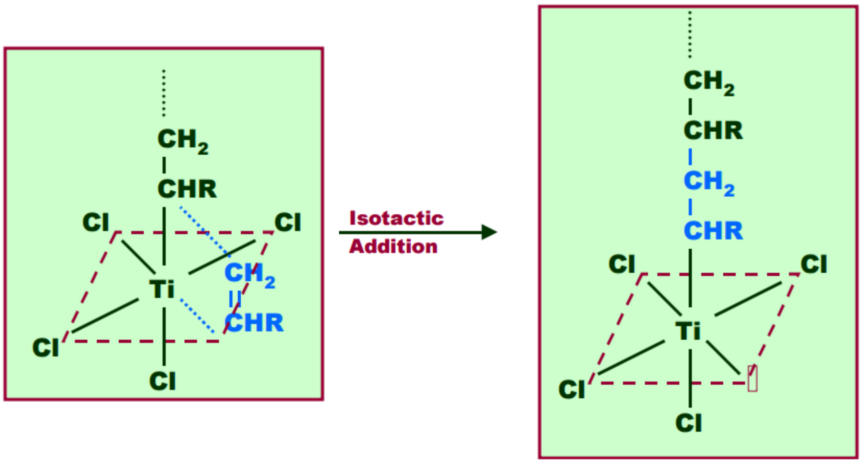


11.5.1 Ziegler - Natta Catalysts

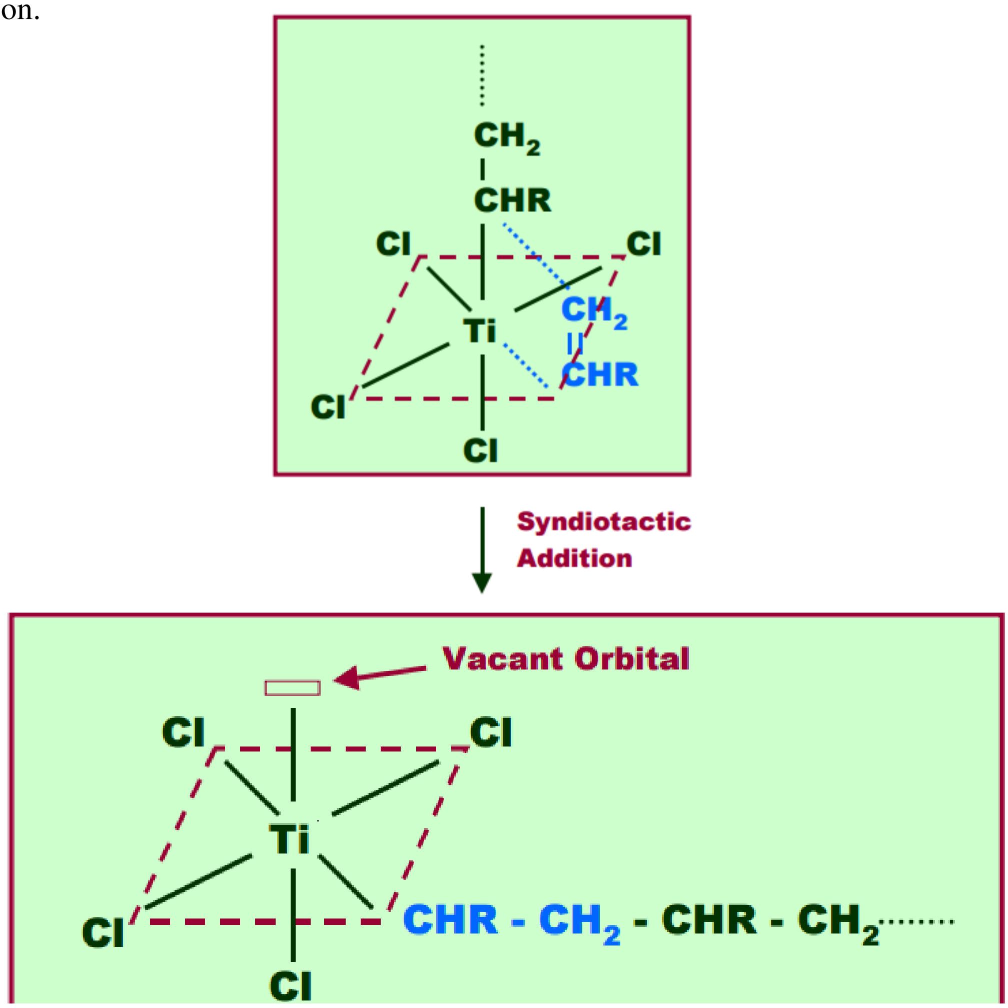
Ziegler-Natta catalysts generally consist of a metal organic compound involving a metal from groups I - III of the periodic table, such as triethyl aluminium, and a transition metal compound (from groups IV - VIII), such as titanium tetrachloride. The metal organic compound acts as a weak anionic initiator, first forming a complex whose nature is still open to debate. Polymerization proceeds by a process of insertion. The transition metal ion (Ti in this example) is connected to the end of the growing chain and simultaneously coordinates the incoming monomer at a vacant orbital site.



Two general mechanisms have been proposed and for simplicity here we simply illustrate the so -called monometallic mechanism (the other is bimetallic)



Isotactic placement can then occur if the coordinated monomer is inserted into the chain in such a way that the growing chain remains attached to the transition metal ion in the same position.



Or, if the chain becomes attached to the transition metal ion in the position of the orbital that was initially vacant, syndiotactic addition will occur. This becomes more favoured at lower temperatures, but vinyl monomers usually form isotactic chains with these catalysts. Because of the heterogeneous nature of the geometry of the catalyst surface atactic and stereoblock polymers can also be formed

Ziegler - Natta catalysts are used to polymerize a variety of aolefins (e.g. ethylene and propylene) and styrene, but many polar monomers cannot be polymerized this way as they inactivate the initiator, either through complexation or reaction with the metal components.

11.6 Integral Heat of solution (HIS) and Dilution

The heat evolved or absorbed during the formation of solution is called heat of solution or heat of mixing. If no heat absorption is observed then the process is said to be thermal.

The internal heat of solution is the heat evolved in the solvent on dissolving the known amount of solute in known amount of solvent during the preparation of solution of known concentration. It is customary refer the integral heat of solution to unit quantity of dissolved component or unit quantity by the solution formed.

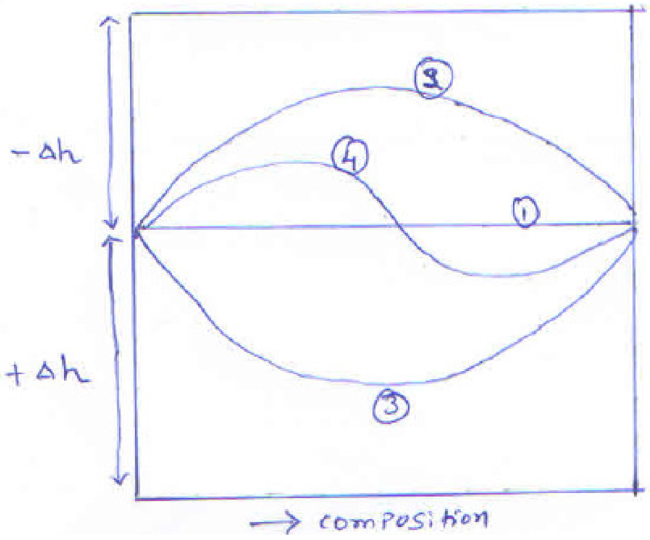
At a constant temperature and pressure the HIS merely represent the difference in the enthalpy in the solution are that of the pure components before mixing.

$$\Delta H = H_{solution} - \sum H_{components}$$

1. HIS is liquids depends on the concentration of the solution this depends is usually expressed in terms of the average entropy of mixing

   $$\Delta h = \frac{\Delta H_{total}}{n_1 + n_2}.$$

The nature of Δh mole concentration is difference or different measurable series as seen



1. Formation ofAlthernal solution at
2. Corresponding to exothermic solution
3. Endothermic solution
4. Mixing of two liquids involves evolution of heat up to certain composition and then absorption of heat at another region
5. The IHD is the heat change in diluting the solution of definite comparison with range amount of the solvent.
6. The sign of heat of mixing depends on the interaction of energies of the solvent. Suppose the bond energies of mole is substance A_2 is E_{11} and of B_2 is E_{22} and AB is E_{12}. Then when one mole of A_2 is mix with one mole of B_2, energies equivalent to E_{11} and E_{22} are spent to rupturing the bond between the molecules and energy of E_{12} is evolved during the formation of two moles AB. And hence the net heat effect will be proportional to algebraic sum of three molecules

$$-\Delta H = k\left(-E_{11} - E_{22} --+ 2E_{12}\right)$$

k is proportionality constant

Case i) In the case of Athermal mixing

$E_{11} = E_{22} = E_{12}$ then $\Delta H = 0$

Case ii) Exothermic mixing

$2E_{12} > (E_{11} + E_{22})$

Case iii) Endothermic mixing

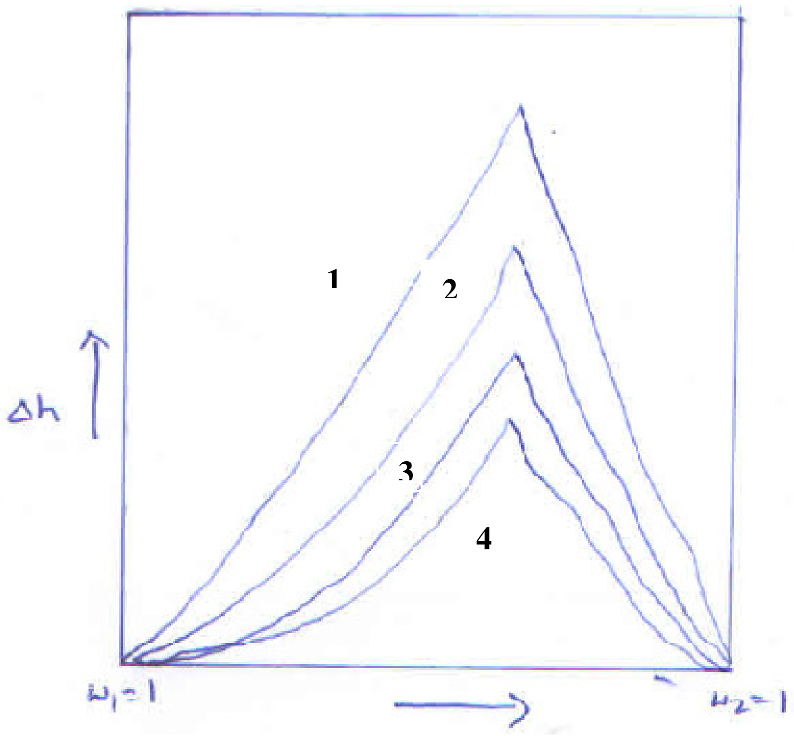
$2E_{12} < (E_{11} + E_{22})$

7. HIS of polymers can be measured calorimetrically by mixing weight portion of the polymer in a definite amount of solvent in a calorimetric vessel. On coming into contact with solvent the polymer swell and then dissolves. The pressure taking 20 to 60 mins is very small samples are used. The main difficulty in this method is the low average heat change.
8. Heat change per unit time to the mixing required greater skill. It is not possible to use large amount of polymer samples as the solution become thicker and stirring will become difficult and also time for thermal reaction become large. Hence most of the studies in HIS are made for solvent containing not more than 0.1 mole fraction of the polymer.

Table 1. Internal heats of solution of some polymers at 25^0C

Polymers	M	Solvent	ΔH Cals/gm
Polyisobutylene	30,000	n-pentane	-0.86
		n-Hexane	-0.61
		n-heptane	-0.43
Natural rubber		Benzene	+1.36
		Gesol	+0.10
		Chloroform	-3.0
Polystyrene	1,42,000	Ethyl benzene	-3.8
		Benzene	-4.0
		Toluene	-4.32
Pmm A	$3.06*10^6$	Methyl isoburate	0
		Dichloroethane	-10

It is observed from the table, solutions of polymer many be athernal exothermic or endothermic, it should be noted that integral heat of polymer solution can be obtained over the wide range of polymers. The value of average enthalpy ΔH when plotted function of weight fraction of the polymer gives curves of the type shown in below figure



1. Cellulose nirate in acetone
2. PMMA in dichloroethane
3. Cellulose triacetate in $CHCl_3$
4. Polystyrene in ethyl benzene

It can be seen from this curve that they are similar to the curves obtained for the internal heats of mixing of two low molecular mixing with the only difference that the maximum greatly shifted to high weight fraction w_2 or the higher molecular mass of the component. To obtained Δh cals/gm the integral heat of solution in the dilute solution region are determined in the usual way and the heat of solution in constant temperature solution religion are calculated the solution as follows

a. Place a unkown weight (g_2 gm) or polymer in an atmosphere of the vapour of the solvent til it absorbs a unkown weight (g_1 gm) solvent to form a concentrated solution (I)
b. Weight creation of the polymer in solution (I)

$$w_2 = \frac{g_2}{g_1 + g_2}$$

The formation this solution in which heat change which has to be determined let it be $\phi_x cals$

c. It is possible to prepare solution contacting polymer is weight farction raying form 0.5 – 1

d. To ensure uniform distribution of the components the solution is held in a sealed ampoule for 4 to 5 days

e. The ampole containing elements solution I is brollen in s calorimetric containing in a definite amount of accompanied by what change q of calories represents the IHD

f. G_2 gm of the polymer is sent dimoles in (g_1+m) gm is the represents calories and the internal heat of the is determined q

By ss low $\varphi = \varphi_x + \mu$

11.7 Thermodynamics of polymer solution

Thermodynamics of dilute solution

1. A thermodynamics of system consisting of a system characterized by the parameter like E,V,H,G, S etc
2. In the thermodynamics it is almost contemporary in complete the magnitude of the difference in their thermodynamic entities as

   $$\Delta H = H_2 - H_1 \quad \Delta S = S_2 - S_1\, etc$$

3. In the case of solutions, it is the practice to calculate the difference between the thermodynamic function for the solution and that of the components before mixing. Then entropy of mixing

   $$\Delta S_m = S_{solution} - \sum S_{componnet}$$

   Free energy mixing $\Delta G_m = G_{compoenent} - \sum G_{component}$

   Entropy of mixing $\Delta H_m = H_{solution} - \sum H_{componnet}$

4. For an ideal gas equation

   $$V_{solution} = \sum V_{amp} ; H_{solutio}$$

   $$For\, real\, solution$$

   $$V_{solution} \neq \sum V_{camp} \quad H_{solution} \neq \sum H_{comp}$$

   This has lead to the concept or view potential molar quantites

$$G_i = \mu_i = \left(\frac{\Delta \overline{G}}{\Delta n_i}\right) T, P, n_i - n_i - 1$$

5. The quantities of interact in considering solution possess the difference between the partial molar in the thermodynamic functions of compound solutions $\overline{V_i}\, \overline{S}_i \, or \, \overline{G}_i \, or \, \overline{H}_i$ and their corresponding values in the pure state $V_i^0, S_i^0 \, G_i^0 \, H^0$

   Volume change

   $$\Delta \overline{V_i} = \overline{V} - V_i$$
   $$\Delta \overline{H}_i = \overline{H}_i - H_i \text{ ------------------------(1)}$$
   $$\Delta \overline{S}_i = \overline{S}_i - S_i$$

6. All unknown the relations ar valid hr potential molar quantities as

   $$\overline{G} = H - TS$$
   $$\overline{G}_o = \overline{H}_i - \overline{T}_s$$
   $$\Delta \overline{G}_o = \Delta \mu_i = \Delta \overline{H}_i - T.\Delta \overline{S}_i$$

   For a binary solution containing N$_1$ and N$_2$ mole fraction solvent and solute respectively we can have the volume

   $$V = N_1 \overline{V_1} + N_2 \overline{V_2}$$
   $$\Delta V = N_1 \Delta \overline{V_1} + N_2 \Delta \overline{V_2}$$
   $$S = N_1 \overline{S}_1 + N_2 \overline{S}_2$$
   $$\Delta S = N_1 \Delta \overline{S}_1 + N_2 \Delta \overline{S}_2 \text{ --------- } (V)$$

7. Ideal and the molar ideal solutions, as ideal solutions are those which are packed with zero effect, i.e, $\Delta \overline{H}_i = 0$ and $\Delta H_i == 0$

8. The entropy of mixing for the ideal solution given by the relation

   $$\overline{S}_i = \Delta S_{ideal} = -R \ln N_i$$
   $$\Delta \mu_i = \Delta \overline{H}_i - T \Delta \overline{S}_i$$
   $$\Delta \overline{\mu}_i = 0 \, For \, ideal \, solution$$
   $$\Delta \mu_i = RT \ln N_i$$

   Thus the change in the chemical potential during the formation of an ideal solution depends only in the mole fraction or component in the solution however the value of $\Delta \mu_i$ is given by the solution

   $$\Delta \mu_i = RT \ln \frac{p_i}{P_i^0}$$

   P_i = potential vapour pressure or the component in the solution

P_i^0 = vapor pressure in the true state

Certain polymers can be readily dissolved in mixture of the two or more solvents where as they are not soluble in the individual solvents of mixture. This phenomenon is called co-solvency, which is great potential importance by industrial point of view

Example, cellulose nitrate contains 10-12% swell to initial solvent in ethanol and ethyl acetate, but a mixture of these taken in definite proportion dissolves cellulose nitrate unlimitedly.

11.8 Entropy of mixing of polymer

1. Entropy of mixing is the difference between the entropy of solution and that or the components in solution.

   $$\Delta\rho_{\max} = S_{Solution} - \Sigma S_{amp} ------(1)$$

2. The potential molar entropy of mixing if any component in the solution is the difference between its potential molar entropy in the solution and molar entropy

   $$\left(\Delta\bar{S}_{imix}\right) = \bar{S}_i - S_i^0 ----------------(2)$$

3. Initial solved that when two ideal gases or the substance which are almost identical in chemical contains and size thus the entropy of mixing is given by

   $$\Delta S_{mix} = -R\left(N_1 \ln N_1 + N_2 \ln N_2\right) ----------(3)$$

   The derivation in equation is based in the assumption of completely random arrangement of the molecular in the system thus for a binary solution we have

   $$\Delta S_{mix} = S_{Solu} - \left(S_1^0 + S_2^0\right)$$
   $$\Delta S_{mix} = k \ln W - \left(k \ln W_1 + k \ln w_2\right) -------(4)$$

W represent the thermodynamic properties the system, if we mix X_1 molecules of 1st component with X_2 molecules of the other complete, then the freedom for them to occupy any position they like is given by

$$w_1 = x_1! \qquad w_2 = x_2! \qquad w = \left(x_1 + x_2\right)!$$

$$\Delta S_{mix} = k \ln\left(x_1 + x_2\right)! - k\left[\ln x_1! + \ln x_2!\right]$$

$$= k\left\{\left(x_1 + x_2\right)\ln\left(x_1 + x_2\right) - \left(x_1 + x_2\right) - \left[x_1 \ln x_1 - x_1 + x_2 \ln x_2 - x_2\right]\right\}$$

$$\Delta S_{mix} = -k\left\{x_1 \ln \frac{x_1}{x_1 + x_2} + x_2 \ln \frac{x_2}{x_1 + x_2}\right\}$$

$$\Delta S_{mix} = -k\left\{x_1 \ln N_1 + x_2 \ln N_2\right\} ----------------(5)$$

N_1 and N_2 being mole fraction of components (1) and (2) respectively

Multiplying and divided by N we get

$$\Delta S_{mix} = -kN\left\{\frac{x_1}{N}\ln N_1 + \frac{x_2}{N}\ln N_2\right\}$$
$$\Delta S_{mix} = -R\{n_1 \ln N_1 + n_2 \ln N_2\}$$
$$\Delta S_{mix} = -R\{N_1 \ln N_1 + N_2 \ln N_2\} ----------(6)$$

This equation is applicable for ideal, it give what is called the ideal entropy of mixing. Ideal potential entropies can be obtained by just differentiating (6) with respect to N_1or N_2

$$\left.\begin{aligned}\Delta\overline{S}_1 &= \left[\frac{\delta(\Delta S)}{\delta n_1}\right]_{x_2} = -R\ln N_1 \\ \Delta\overline{S}_2 &= \left[\frac{\delta(\Delta S)}{\delta n_1}\right]_{n_2} = -R\ln N_2\end{aligned}\right\} \text{---------------------------------------(7)}$$

The value of ΔS can also be obtained from the heat changes free energy changes accompanied the presence of

$$\left\{\Delta S_{mix} = \frac{\Delta H - \Delta T}{T}\right\} -------------(8)$$

The value of ΔS calculated in this way for polymer solutions solution are always found to be less than the corresponding value of mixture of low molecular mass. This is mainly due to low mobility of the macromolecules and their chain segments. The restricted moment of freedom of units of polymer chain results in reducing the number of ways of arranging different molecules in polymer solution or in reducing the thermodynamic probability of the polymer solution compare to that of low molecular mass system analogue.

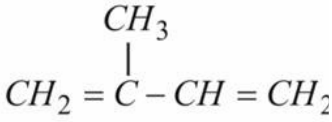
11.9 Thermoplastics

A thermoplastic is a type of plastic made from polymer resins that becomes a homogenized liquid when heated and hard when cooled. When frozen, however, a thermoplastic becomes glass-like and subject to fracture. These characteristics, which lend the material its name, are reversible. That is, it can be reheated, reshaped, and frozen repeatedly. This quality also makes thermoplastics recyclable.

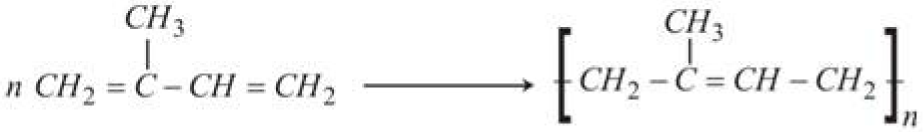
There are several kinds of thermoplastics, varying in crystalline organization and density are available. Some types are produced from polyurethane, polypropylene, polycarbonate, and acrylic. Celluloid is considered the first thermoplastic. Sometimes, thermoplastics are confused with thermosetting plastics. Although they may sound the same, they actually possess very different properties. While thermoplastics can be melted to a liquid and cooled to a solid, thermosetting plastics chemically deteriorate when subjected to heat. Ironically, however, thermosetting plastics tend to be more durable when allowed to cool than many thermoplastics.

11.10 Rubbers

Rubber is a natural polymer of Isoprene (2-Methyl -1, 3 – Butadiene). It is a linear, 1, 4 – addition polymer of Isoprene.

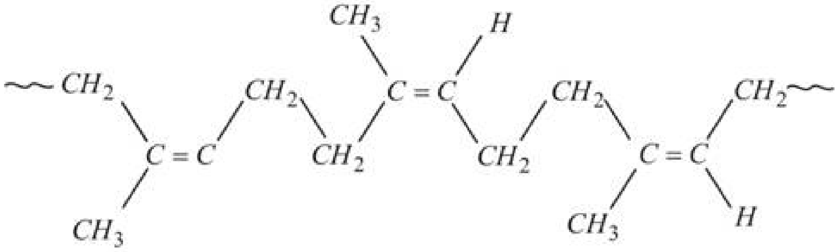


$$CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH = CH_2$$



$$n\,CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH = CH_2 \longrightarrow \left[CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH_2 \right]_n$$

Isoprene (2-Methyl -1, 3-butadiene) undergoes cis-polymerization to form natural rubber

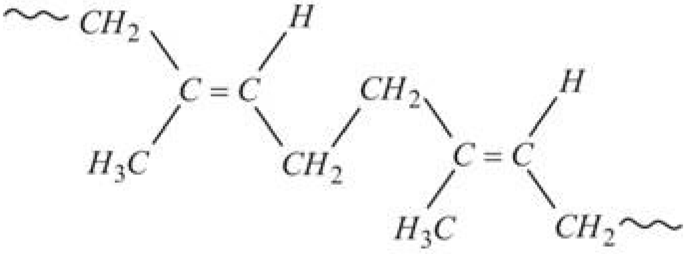


Natural rubber has elastic properties and it undergoes long range reversible extension even if relatively small force is applied to it. Therefore, it is also known as Elastomer. Natural rubber is prepared from latex which is a Colloidal Solution of Rubber in Water.

There is no polar group in the structure of Nnatural rubber. As a result the intermolecular forces of attraction (Vander waal forces of attraction) are weak. These forces of attraction are further weakened because of the cis-configuration of all the double bonds that does not permit the close interaction of polymer chains. Thus Natural Rubber (Cis Polyisoprene) does not have a straight chain but has a coiled structure. As a result of this, it gets elastic property.

11.10.1 Synthetic Rubber

Polychloroprene is called as synthetic rubber, produced from chloroprene. This undergoes trans-polymerization to produce synthetic rubber.



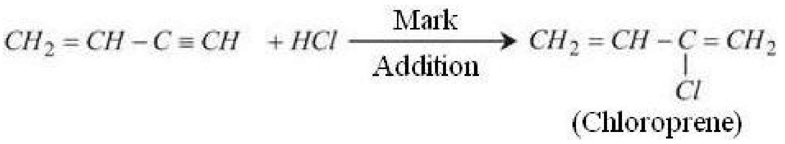
The properties of rubber so formed are determined by the nature of the substitutent groups. For example, Polychloroprene is inferior to natural rubber in some properties but superior in its resistance to oil, Organic Solvents. These differences are due to difference in nature of their monomers: Isoprene (for natural rubber) and Chloroprene (for synthetic rubber).

Synthetic Rubber (also known as Gutta-Percha) was obtained by the free radical polymerization of Isoprene. The rubber so formed has all trans- Configuration. As a result of this, synthetic rubber has a highly regular zig-zag chain which cannot be stretched .This accounts for non-elasticity of synthetic Rubber

11.10.2 Types of Synthetic Rubber

a) Neoprene

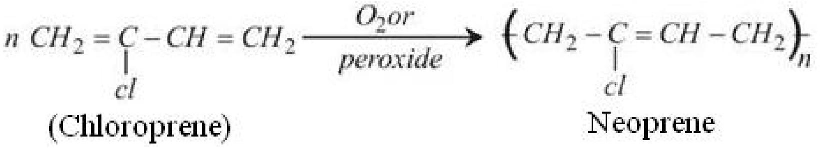
Neoprene is a polymer of chloroprene. It is also known as Polychloroprene. Chloroprene required for this process is synthesized from Vinylacetylene which performs Markonikov addition under acidic condition to produce Chloroprene



$$CH_2=CH-C\equiv CH \quad + HCl \xrightarrow[\text{Addition}]{\text{Mark}} CH_2=CH-\underset{\underset{Cl}{|}}{C}=CH_2$$

(Chloroprene)

The Chloroprene obtained undergoes Polymerization to gives Neoprene. Though no specific catalysts are needed for this process but the polymerization becomes faster in the presence of Oxygen or peroxide.



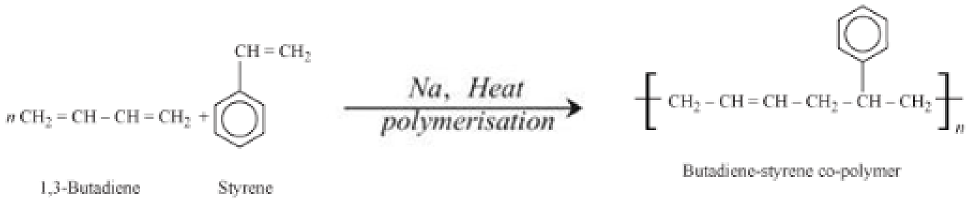
$$n\ CH_2=\underset{\underset{cl}{|}}{C}-CH=CH_2 \xrightarrow[\text{peroxide}]{O_2\text{or}} \left(CH_2-\underset{\underset{cl}{|}}{C}=CH-CH_2\right)_n$$

(Chloroprene) Neoprene

It is used in the manufacture of hoses, gaskets, shoe heels, stoppers, conveyor belts and printing rollers etc. It is also used as an insulator.

b) BUNA–S

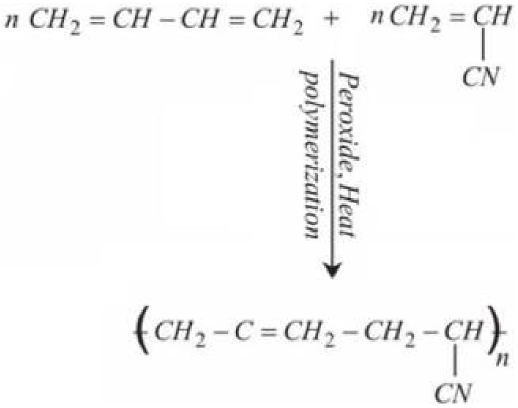
BUNA–S is a copolymer of a mixture of 1,3- Butadiene and styrene in the ratio of 3:1 in the presence of sodium (which is polymerizing agent) gives styrene – butadiene copolymer (styrene – butadiene rubber) or BUNA–S. The name BUNA–S is made up of Bu which indicates 1,3 – Butadiene, NA is for Sodium (Na) and S indicates Styrene.



Buna–S is very tough and a good substitute for natural rubber. It possesses high abrasion resistance. It has high load bearing capacity. It is used for manufacturing automobile tyres. It is used for making floor tiles, footwear components, cable insulation etc.

c) BUNA – N (Nitrile Rubber)

BUNA–N is obtained by copolymerization of 1,3 – Butadiene and acrylonitrile in presence of a peroxide catalyst. The name BUNA–N is made up of Bu which indicates 1, 3 – Butadiene, NA is for Sodium (Na) and N indicates acrylonitrile.

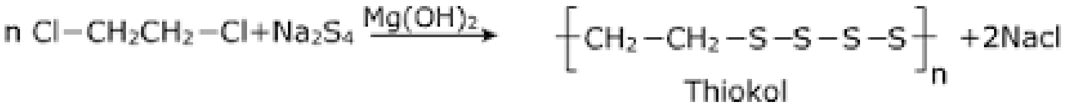


$$n\,CH_2=CH-CH=CH_2 + n\,\underset{\displaystyle CN}{\underset{|}{CH_2=CH}} \xrightarrow[\text{polymerization}]{\text{Peroxide, Heat}} \left(CH_2-C=CH_2-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}\right)_n$$

BUNA-N is resistant to the action of petrol, lubricating oils and organic solvents. It is used in making oil seals, hoses, tank linings etc.

d) Thiokol

Thiokol is prepared by copolymerization of 1, 2 – dichloroethane (ethylene dichloride) with Sodium Tetrasulphide (Na_2S_4) in presence of Magnesium hydroxide.



$$n\,Cl-CH_2CH_2-Cl+Na_2S_4 \xrightarrow{Mg(OH)_2} \underset{\text{Thiokol}}{\left[CH_2-CH_2-S-S-S-S\right]_n} + 2Nacl$$

Thiokol is also known as polysulphide rubber. It's tensile strength is slightly less than that of natural rubber. Thiokol is resistant to the action of mineral oils, solvents, oxygen & ozone.

e) Vulcanized Rubber

Natural rubber is not an important polymer for commercial purpose because of its softness and tacky (sticky) properties. Softness of natural rubber increases with the increase in temperature while brittleness increases at low temperature. Therefore, ideal temperature for using rubber is 283–335K where its elasticity is maintained. Other properties which decrease the quality of natural rubber are:

i) It has large water absorption capacity

ii) It has low tensile strength & low resistance to abrasion

iii) It is not resistant to abrasion
iv) It is easily attacked by organic reagents.

The properties of natural rubber can be improved by a process called Vulcanization. *Vulcanization is the process of introduction of Sulphur bridges between different chains by heating raw rubber with Sulphur at 373-415K.* In the absence of catalyst the process of vulcanization is slow. Some additive such as Zinc Oxide is added to accelerate the rate of Vulcanization.

11.10.3 Difference between Vulcanized rubber and Natural rubber

The new or vulcanized rubber obtained has properties that are just opposite to that of natural rubber. These properties are

a) Vulcanized rubber has excellent elasticity
b) Low water absorption tendency
c) It is resistant to the action of organic solvents
d) It is resistant to attack of oxidizing agents.

Thus vulcanized rubber is an improved form of natural rubber. In vulcanized rubber, Sulphur bridges are introduced either at their reactive allylic sites or at the site of double bond. The presence of double bond in the rubber molecule makes it's highly reactive as it provides allylic hydrogen that permits formation of Cross links between different chains. The presence of these cross links increases the toughness, strength and hardness of rubber. Due to the presence of Sulphur bridges, individual chains can no longer slip over one another but are locked together in a giant size molecule.

Note: Amount of Sulphur used for vulcanization process determines the extent of hardness or toughness of the rubber.5% Sulphur is used for making tyre rubber, 20 – 25% Sulphur is used for making Ebonite. 30% of Sulphur is for making Battery Case Rubber.

11.11 Fibers

Fiber is a natural or synthetic substance that is significantly longer than it is wide. Fibers are often used in the manufacture of other materials. The strongest engineering materials often incorporate fibers, for example carbon fiber and ultra-high-molecular-weight polyethylene.

Synthetic fibres are used for making clothes and many other useful things. They may be entirely synthetic or semisynthetic. Semisynthetic fibres, like rayons, are made by using natural polymers as the starting material. Purely synthetic fibres, on the other hand, are made from chemicals. Polyesters, nylons and acrylics are purely synthetic fibres. Synthetic fibers can often be produced very cheaply and in large amounts compared to natural fibers, but for clothing natural fibers can give some benefits, such as comfort over their synthetic counterparts

11.11.1 Types of Fibres

There are two types of fibre

i) One which are obtained from natural sources and
ii) Other which are man-made.

Fibres which are obtained from natural sources are called natural fibres. For example, cotton, silk, wool, etc. Fibres which are man-made are called man-made or synthetic fibres. For example – rayon, nylon, acrylic, etc.

11.11.2 Synthetic Fibres

Synthetic fibres are small units of chemicals joined together in the form of chain. The chain so formed is called polymer.

11.11.3 Types of Synthetic Fibres

a) Rayon

Rayon is synthesized from wood pulp. Rayon resembles silk, so it is also known as artificial silk. Rayon fibre can be dyed in different colours. Rayon is very cheap compared to silk.

Copper hydroxide is prepared by reacting copper(II) sulfate with aqueous ammonia:

$$Cu^{2+}(aq) + 2\ OH^{-} \rightarrow Cu(OH)_2\ (s)$$

The copper hydroxide reacts with additional aqueous ammonia to form tetraammoniecopper(II) hydroxide, $Cu(NH3)_4(OH)_2$. The cellulose dissolves in this complex and is regenerated upon acidification as the polymer rayon. Rayon is insoluble in aqueous solution, so it precipitates when it is squirted in the aqueous acid solution.

Rayon is used to prepare bed sheets, shirts, sarees, and many other clothes are made from rayon.

b) Nylon

Nylon was first commercially synthesized fibre. The production of nylon was started almost simultaneously in New York and London, thus it got its name (NY for New York and Lon for London) as nylon. Nylon is synthesized from coal, water and air. Fibre of nylon is very strong and it also resembles silk. Nylon is used in making of different types of clothes, ropes, socks, curtains, sleeping bags, parachutes, etc. The fibre of nylon is stronger than a steel wire of same thickness.

c) Polyester

Polyester is one of the most popular man-made fibres which are used in making clothes. It is made of repeating unit of a chemical called ester. Terylene is one of the most famous types of polyester.

Polyester is used in making different types of apparel; such as shirts, pants, jacket, bedsheets, curtains, sarees, mouse-pad, etc. Polyester is used in making ropes, fabrics for conveyor belt, cushioning and insulating material in pillow, etc.

Fabrics made from polyester fibre are almost wrinkle-free, easy to wash and have shiny appearance. It is the polyester which made the fabric cheaper in India as well as in the whole world. Terrycot is a fabric made after mixing of terylene and cotton. Polycot, polywool, etc. are other fabrics which are made by the mixing of polyester with other natural fibres.

d) Acrylic

Acrylic is another man-made fibre. Since, acrylic resembles wool so it is also known as artificial wool or synthetic wool. Acrylic is cheaper than natural wool and can be dyed in various colour. Acrylic is used in making sweaters, blanket, and other many clothes.

11.11.4 Characteristic of Synthetic Fibre

Synthetic fibres are cheaper and stronger than natural fibre. They are more durable than natural fibre. It is easy to maintain and wash the synthetic fibres. They are dried up in less time.

11.12 Summary of the unit

As in free radical polymerization, there are initiation and propagation steps in the anionic polymerization reaction. Propagation proceeds in the usual manner, but there is no termination of the type that occurs when free radicals collide. If a solvent is able to release a proton, it can react with the active site. Ammonia is an example of such a protic solvent and the reaction results in the formation of a negatively charged NH_2 ion, which can initiate the polymerization of a new chain. In other words, chain transfer to solvent. If there is nothing for the anion to react with, there is no termination. Combination with the counterion occurs in only a few instances, the ions hang around one another and their attractions are mediated by solvent. This allows the synthesis of block copolymers, because the active site stays alive. There are a lot more interesting things about anionic polymerization.

Cationic polymerizations involve an active site where there is a positive charge because, in effect, there is a deficit of one electron at the active site. Cationic polymerizations can be initiated by protonic acids or Lewis acids (the latter sometimes combined with certain halogens). Propagation then proceeds in the usual way. Unlike anionic polymerization, termination can occur by anion - cation recombination. Lots of other side reactions can occur, with trace amounts of water, chain transfer to monomer, and so on. This makes it much more difficult to make a living polymer using cationic polymerization.

11.13 Key words

Ionic polymerization; Cationic polymerization; Anionic polymerization; Coordination Polymerization; Ziegler - Natta Catalysts ; Integral Heat of solution (HIS) and Dilution; Thermodynamics of polymer solution; Entropy of mixing of polymer; Thermoplastics ; Rubbers; Fibers.

11.24References for further studies

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11.25 Questions for self understanding

1) Discuss the kinetics and mechanism of Cationic polymerization.
2) Discuss the kinetics and mechanism of Anionic polymerization.
3) Discuss the Coordination Polymerization reaction.
4) What is Ziegler - Natta Catalysts?
5) Derive the expression of Integral Heat of solution (HIS) and Dilution of polymer solution.
6) Discuss the Thermodynamics of polymer solution.
7) Derive the expression of Entropy of mixing of polymer solution.
8) What are Thermoplastics?
9) What is Rubber?
10) What is Synthetic Rubber?
11) What are the different types of synthetic Rubber?
12) Write the Difference between Vulcanized rubber and Natural rubber.
13) What are Fibers?
14) Write the different types of Fibres.
15) What are Synthetic Fibres? Give one example.

UNIT-12

Structure

12.0 Objectives of the unit

After studying this unit you are able to

- Explain the molecular weight determine of polymersby the measurements of colligative properties of solutes.
- Explain the osmotic pressure method of molecular weight determination of polymers
- Explain the Viscosity method of molecular weight determination of polymers
- Identify the relationship between the intrinsic viscosity and molecular weight
- Explain the procedure of experimental measurement of the intrinsic viscosity
- Explain the procedure of Light scattering method of molecular weight determination
- Explain the procedure of Ultra Centrifuge Method
- Explain the procedure of Sedimentation velocity method

12.1 Introduction

The molecular weight of a polymer is of prime importance in the polymer's synthesis and application. It is important because it determines many physical properties. A simple chemical has fixed molecular weight but when we discuss about the molecular weight of polymer, we mean something different from that which applies to small sized compounds. Since polymers are mixture of molecules of different molecular weight, the molecular weight is expressed in the term of "average" value.

12.2 Molecular masses of the polymer

Molecular weight distribution may treat statistically to yield several possible averages which could serve as a single overall description of the mean degree of polymerization of average molecular weight. But it is not possible to choose by convention, a certain type of average and to labelled polymer mixture consistently by this average. Because it will be found that the loss governing the dependence of a given physical properties on the molecular weight also dictates the measurement of average procedure which must be applied. Thus in considering different physical properties we are inhospitably used the different molecular wt averages

12.3 Molecular Average Molecular weight $\overline{M_m}$

Let us consider a sample containing N_1 molecules of M_1, N_2 molecules of M_2 etc…. N_i molecules M_i , then $\overline{M_m}$ is given by the total weight of sample divided by number of molecules. Thus

$$\overline{M_n} = \frac{N_1M_1 + N_2M_2 + ------ + N_iM_i}{N_1 + N_2 + ------- N_i}$$

$$\overline{M_n} = \frac{\sum\limits_{i=1} N_iM_i}{\sum\limits_{i=1}^{\infty} N_i} ----------(1)$$

$Ex100 ---> 10^3 \quad 200 ---> 10^4 \; 200 ---> 10^5$

$$\overline{M_n} = \frac{100X10^3 + 200X10^4 + 200X10^5}{500} = 44{,}000$$

1 can be written as

$$\overline{M_n} = \left(\frac{N_1}{N_1 + N_2 + ---}\right)M_1 + \left(\frac{N_2}{N_1 + N_2 + ---}\right)M_2 + \left(\frac{N_i}{N_1 + N_2 + ----- N_i}\right)M_i$$

$$\overline{M_n} = X_1M_1 + X_2M_2 + ------- + X_iM_i$$

$$\overline{M_n} = \sum_{i=1}^{i=i} X_iM_i ----------------(2)$$

X = mole fraction of different type of species present in the system.

If we are dealing with pure polymer sample where the molecules differ in the degree of polymerization, then the molecular weight X mers will be equal to $x.M_0 \; i.e\, M_x = x.M_0$

$$\overline{M_m} = \sum_{x=1}^{x=x} X_x.M_x$$

$$\sum_{x=1}^{x=x} X_x xM_0$$

$$\overline{M}_n = M_0 \sum_{x=1}^{x} x.x_x$$

Similarly the number average degree of polymerization is defined as

$$\overline{X}_n = \frac{\sum\limits_{x=1}^{w} X.N_x}{\sum\limits_{x=1}^{w} N_x}$$

$$\overline{X}_n = \sum_{x=1}^{\infty} x.X_x$$

12.4 Weight average degree is Polymerization $(\overline{M}_w)$

Let us consider a system containing g_1 grams of molecules each of molecular weight M_1 and g_2 grams of molecular each of molecular weight M_2

Then $\overline{\mu}_w = \dfrac{g_1M_1 + g_2M_2 + - - - - - - - + g_iM_i}{g_1 + g_2 + g_3 + - - - - g_i}$

$$\overline{\mu}_w = \frac{\sum_{i=1}^{i=\infty} g_iM_i}{\sum_{c=1}^{i=\infty} g_i} = w_1M_1 + w_2M_2 - - - - - + w_iM_i$$

$$\overline{M_w} = \sum_{i=1}^{i=\infty} W_iM_i$$

$$g_1 = N_1M_1, g_2 = N_2M_2 - - - - - - - g_i = N_iM_i$$

$$\overline{M}_w = \frac{N_1M_1^2 + N_2M_2^2 + - - - - - - - - - N_1M_i^2}{N_1M_1 + N_2M_2 + - - - - - - - N_iM_i}$$

$$\overline{M}_w = \frac{\sum_{c=1}^{\infty} N_iM_i^2}{\sum_{i=1}^{\infty} N_iM_i}$$

$$\overline{M}_w = \frac{100\times10^6 + 200\times10^8 + 200\times10^{10}}{(100\times10^3) + (200\times10^4) + (200\times10^5)}$$

$$\overline{M}_w = 91{,}000$$

Thus it is evident that for polydispersed polymer system the $\overline{M}_w$ is greater than $\overline{M}_n$ (because heavier molecules contribute more to $\overline{M}_w$) and the ratio $\dfrac{\overline{M}_w}{\overline{M}_n}$ is measure of the polydispersity of the system. For a monodispersed system $\overline{M}_w = \overline{M_n}$. It should be noted that $\overline{M}_w$ is very sensitive to the molecules of hight molecular weight species, but $\overline{M}_n$ is sensitive for for low molecular weight species. In synthetic polymer $\dfrac{\overline{M}_w}{\overline{M}_n} = 2$ larger the value of ratio indicates a wide spreads in the molecular weight. In addition to the $\overline{M}_w$ and $\overline{M}_n$ frequently we evaluated average of type $\overline{M}_z$ and $\overline{M}_{z+1}$ (called Z average molecular weight and Z+1 average molecular weight)

$$\overline{M}_z = \frac{\sum N_iM_i^3}{\sum N_iM_i^2} \quad \overline{M}_{z+1} = \frac{\sum N_iM_i^w}{\sum N_iM_i^3}$$

12.5 Molecular Weight determine by the measurements of colligative properties of solutes.

This method depends upon the fact that in very dilute solvents the activity of the solute is proportional to mole fraction ($a_2 \alpha X_2$). Under the condition the activity = mole fraction. Similarly the activity of solvent is proportional to its molecular weight of the solvent under such condition the activity of the solvent is equal to the mole fraction.

In very dilute solution or in the case of pure solvent activity of solvent $a_1 = 1$. As $(1-X_1) = X_2$ the measurement of the depression in the activity of solvent enables us to measures the value of X_2

$X_2 = \frac{w_2 / M_2}{w_1 / M_1}$ the molecular weight of solute M_2 can be evaluated by knowing values of W_2,W_1 and M_1.

The dispersion in the activity of the solvent can be obtained by lowering of vapor pressure of the solvent. For sufficiently dilute solutions of polymers, this lowering of vapor pressure is very small. Although this methods involves very sensitive differential monometers of dilute solution of VP is determined by relatively lowering of molecular weight, other more convenient method which are more precise or preferred. These are osmometry ebullioscopy and cryoscopic. The convincing equation for these methods of interest of polymer solution is

$$C \xrightarrow{\lim it} 0 \left(\frac{\pi}{C} \right) = \frac{RT}{M}$$

$$C \xrightarrow{\lim it} 0 \left(\frac{\Delta T_b}{C} \right) = \left(\frac{RT_0^2}{P.\Delta H_v} \right) \frac{1}{\overline{M}_n}$$

$$C \xrightarrow{\lim it} 0 \left(\frac{\Delta T_7}{C} \right) = -\left(\frac{RT_0^2}{\rho.\Delta H_f} \right) \frac{1}{\overline{M}_n}$$

ρ = density of solvent

ΔH_b and ΔH_f are the latent heat of vaporization and latent heat of fusion of the solvent, C = concentration/cc for polymer of molecular weight 20,000 and C = 0.01 gm/ml. The colligative properties and magnitude are shown in the table

Vapor ressure lowering	4×10^{-3} mm of Hg
Boling point elevation	1.3×10^{-3}
Freezing point depression	2.5×10^{-3}

Osmotic pressure 15 cm of solvent

It is evident from the figure i.e the direct measurement of vapour pressure is un recording as pressure of order 4 X 10^{-3} m of Hg cannot be easily measured. Temperature difference of 10^{-3} order can be measured considerable precession but lesser effects observed in osmotic measurement suggest this technique is most fruit full for polymer solution. The osmotic pressure of polymer solution of species 10, 00, 000 to 20,000 can be easily measured. However in the case of low molecular weight polymers diffusion is usually noticed due to osmotic membrane.

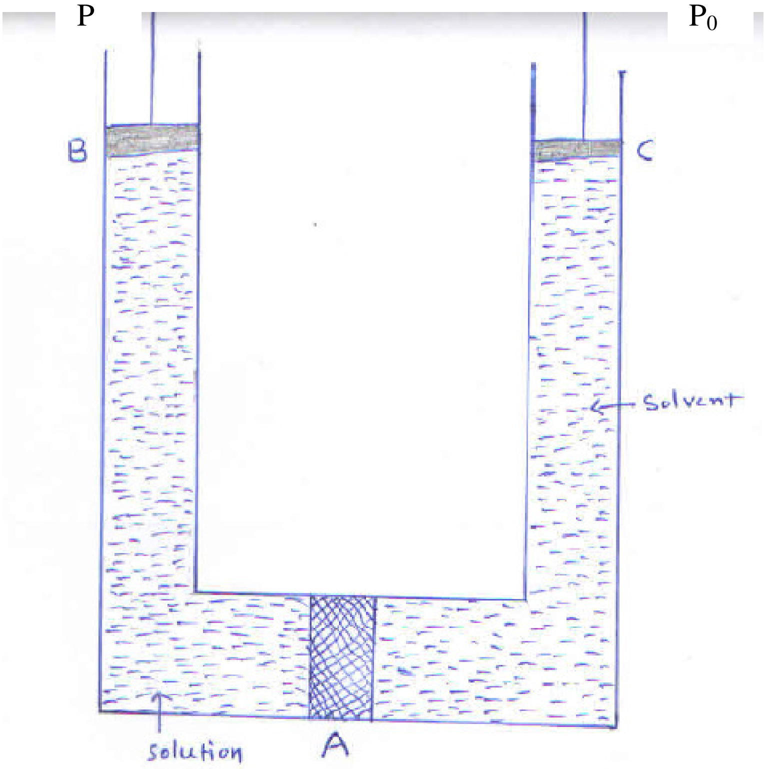
12.6 Osmotic Pressure method

Osmosis is the phenomenon of movement of solvent through a semi permeable membrane. The tendency of solvent molecules to pass spontaneously through membrane is due to in equivalency in chemical potential in solvent and solute $\mu_1 < \mu_1^0$. The osmotic pressure of a solution is the affinity between its components refer to unit volume of the solvent

$$\pi = \frac{\Delta\mu_1}{V_1}$$

This can be shown as follows

Consider a system solvent and solution being separated as shown in the figure by a semi permeable membrane.



The solvent spontaneously moves through the semi permeable membrane due to difference in the chemical potential. If sufficient pressure exerted on the pump p so as to prevent the entry of solvent to the solution, an equilibrium will be established in the system under which

$\mu_1 = \mu_1^0$

Let P_0 and p be the presence on the solvent and solution side respectively. Then the osmotic pressure is

$$\pi = P - P_0 \text{-------}(1)$$

The change in the chemical potential of the solvent side, the pressure is given by

$$\left(\frac{\delta\mu_1}{\delta p}\right)_T = V_1 ------(2)$$

Which can rearrange

$$\int_{\mu_1}^{\mu_1^0} d\,\mu_1 = V_1 \int_{p_0}^{p} dp$$

$$\therefore \mu_1^0 - \mu_1 = V_1(p - p_0)$$

$$\therefore \mu_1^0 - \mu_1 = V_1\pi$$
$$\mu_1 - \mu_1^0 = -V_1\pi$$
$$\Delta\mu = -V_1\pi --------------(3)$$

This equation holds good only in terms solution is non compressible so that V_1 is constant. Thus using the molar volume of when measuring the osmotic pressure it is possible to calculate $\Delta\mu_1$ can form equation 3. But

$$\mu_1 = \mu_1^0 + RT\ln N_1$$
$$\mu_1 - \mu_1^0 = RT\ln N_1 -----(4)$$
$$\Delta\mu_1 = -RT\ln N_1$$
$$\pi V_1 = -RT\ln N_1$$
$$\therefore \pi V_1 = -RT\ln(1 - N_2)$$
$$\therefore \pi = \frac{RT}{V_1^0}.N_2 --------(5)$$
$$\therefore \pi = \frac{RT}{V_1^0}.\frac{n_2}{n_1} = \frac{n_2RT}{V}$$

$\pi = C_2RT$ ------------- (6) Van toff equation

This equation off course is not applicable to polymer solution even it is very dilute. The concentration dependent of osmotic pressure is express by more complex equation. This results if the concentration expressed in power series as

$$\pi = RT\left(A_1C_2 + A_2C_2^2 + A_3C_2^2 + ----------\right)$$

$$\frac{\pi}{C_2} = RT\left(A_1 + A_2C_2 + A_3C_2^2 + ----------\right)---(7)$$

where C_2 is the concentration of polymer in gm/ml A_1, A_2 and A_3 are so called visual coefficient whose values can be calculated from the experimental dependence π and C_2

Howers as $C_2 \rightarrow 0$

$$C_2 \xrightarrow{\lim it} 0\left(\frac{\pi}{C_2}\right) = RTA_1 -----(8)$$

To find the value of A_1

$$\pi = C_2RT = \frac{n_2}{v}.RT$$

$$= \frac{g}{M.V}\ RT = \frac{C_2}{M}RT$$

Where Concentration = C = g/v = wt/ unit value

$$\therefore \frac{\pi}{C_2} = \frac{RT}{M}----------(9)$$

From 8 and 9

$$A_1 = \frac{1}{M}$$

$$\therefore \frac{\pi}{C_2} = RT\left(\frac{1}{M} + A_2C_2 + -----\right)$$

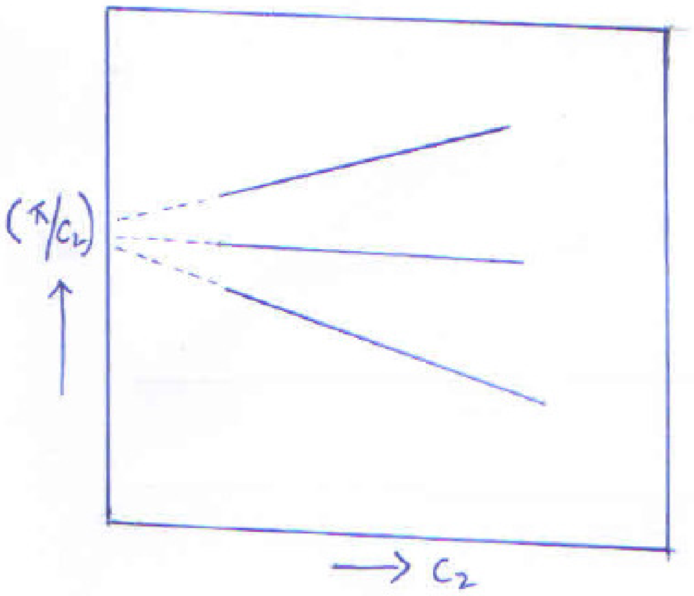
In most case value of $A_3\ (C_2)^2$ is too small. Thus equation for osmotic pressure dependence on concentration can be follows as

$$\frac{\pi}{C_2} = RT\left(\frac{1}{\overline{M}_n} + A_2C_2\right)$$

$$\frac{\pi}{C_2} = \frac{RT}{\overline{M}_n} + BC_2 ----------------(10)$$

B is called the interaction constant between the polymer and the solvent. According to equation 10 plot of $\frac{\pi}{C_2}$ vs C_2 is linear

The intercept enable us to calculate $\overline{M}_n$ and the slope gives the interaction constant B.



Osmotic pressure of polymer solution is measured using osmometers which are devices in which the solvent and polymer solution is separated by membrane reversible to the solvent. The solvent will passed through the membrane area made usually as less as possible and the volume of the liquid to passing through membrane is small. This is represented by the difference in level between the solvent and solution on either side of the membrane. Generally capillary tubes are used to measure the difference in level. Measurements are made with osmometers

Two types of thermometers are generally used

i) Block osmometer

ii) Zimmerman osmometer

12.7 Viscosity method

This is very useful method for detecting the molecular weight of high polymers. Solution viscosity is basically a measure of the size and retention in space of polymer molecules. It is empirically related to the molecular weight or the polymers. Measure of solution viscosities are usually made by comparing efflux time ‘t’ required for the specific volume of the polymer solution to flow through a capillary tube with the corresponding efflux time ‘t_o’ for pure solvent. From the values t and t_0 and concentration of solution reveal quantities can be evaluated

Relative viscosity - $\eta_{rel} = \frac{\eta}{\eta_0} = \left(\frac{t}{t_0}\right)$ viscosity ratio

Specific viscosity $\eta_{sp} = \eta_{rel} - 1 = \left(\frac{t - t_0}{t_0}\right)$

Reduced viscosity or reduced specific viscosity $\eta_{rel} = \frac{\eta_{sp}}{c}$

Inherent viscosity $\mu_{in} = \left(\frac{\ln \eta_{red}}{e}\right)$

Intrinsic viscosity $[n] = \left(\frac{n_{sp}}{c}\right)c = 0$

It is obvious that intrinsic viscosity is independent of concentration by virtue of the fact

$\frac{n_{sp}}{c}$ is extrapolate, c = 0 but [η] is a function of the solvent used

12.8 Relationship between the intrinsic viscosity and molecular weight

Einstein's derived a relation for η of suspensions of incompressible, unchanged non interacting solid spherical particle and liquid

$$\eta = \eta_0(1 + 2.5n) - - - - - - - - -(1)$$

η_0 called viscosity of the media

n = mole fraction of the solid in the suspension.

This equation has been experimentally varyfied on suspensions of sulphur yeast at low temperature. This equation has been adopted to obtain the relation between the $[\eta]$ are molecular weight polymer in solution.

Floyg and Fox suggested that equation 1, can apply to polymer solution at low concentration considering them to be spherical in solution phase. Since the density of the polymer is different from that of the pure solvent and as polymer molecules on an average are spherical.

If n_2 number of polymer molecule in solution of volume V and V_e is effective volume of each molecule (Assuming that all molecules will have same molecular weight)

The volume fraction $V = \left(\frac{n_2}{V}\right)^{v_e} - - - - - -(2)$

If C is the concentration of polymer in grams/ deciliter

$\frac{n_2}{v} = \frac{CN_{Av}}{100M} - - - - -(5)$

M = molecular weight of polymer

The unit for C has been chosen with some purpose as in dilute solutions the volume of C approximate with very closely to the weight present of polymer in the solution.

Equation 1 can be written as

$$\eta_{rel} = \frac{n}{n_0} = 1 + 2.5V$$

$$\eta_{rel} = \frac{1 + 0.025\, N_{Av} V_e C}{M} ------(6)$$

$$\eta_{sp} = \frac{0.025\, N_{AV} v_e C}{M} ---------(7)$$

Thus it is seen that $\eta_{rel,}$ is function of concentration and increases with increasing concentration However

$$\eta_{rel} = \frac{\eta_{sp}}{C} = \frac{0.025\, N_{Av} V_o C}{M\, C}$$

$$= \frac{0.025\, N_{Av} V_e}{M}$$

which s independent of concentration

Since Einstein equations are applicable to non-interacting spherical particle, equation (6) is applicable only to polymer which are far from each other in the solution i.e under condition C→0 η_{real} of polymer solution is independent of the concentration of the polymer only under such limiting condition of C→0. But at higher concentration an equation of the type $\eta_{real} = A + B + CC^2 + ------(7)$ is formed to follow experientially

In equation 7 when C=0 $\eta_{real} = A$. The content A which in the limiting value of η_{real} at zero concentration will be the [η] = A of the system. So we will have the relation

$$[\eta] = \frac{0.025 N_{Av} V_e}{M} -----(9)$$

$$Unit\, of\, [\eta] = deciliter / gm$$

According to Flory and flux effective volume $V_e \alpha [S^2]^{\frac{3}{2}}$ (Mean square radius of gyration = S^2)

Substituting in equation 7 we get

$$[n] = \frac{\phi^1 [S^2]^{\frac{3}{2}}}{M} = \phi \left(\frac{[L^2]}{M} \right)^{3/2} \alpha_s^3\, M^{1/2} -------(10)$$

L^2= Mean sequence of the end to end distance of polymer molecules

$$\phi^1 = cons\tan t = 10^{21}$$

$$\alpha_s = \exp ansion factor\, of\ polymer$$

$$[\eta] = K.M^a -----------(11)$$

K= constant $= t\left(\frac{<L^2>}{M}\right)^{3/2}$

And ‘a’ is constant for given polymer system. Equation10 predicts the dependent upon the 3 factor

a. The stiffness of the polymer $\frac{<L^2>}{M}$ however through the terun

b. Its molecular weight through the $\frac{<L^2>}{M}$ in the terms of nature

c. Solvent polymer temperature combination through the term α_s^3

At that condition value of $\alpha_s = 1 \therefore [n]\alpha[M]^{1/2}$. This is formed to be in the case of many polymer solutions. In exactly good solvent $\alpha_s \propto M^{0.1}\, so\, that\; [\eta] \propto M^{0.8}$

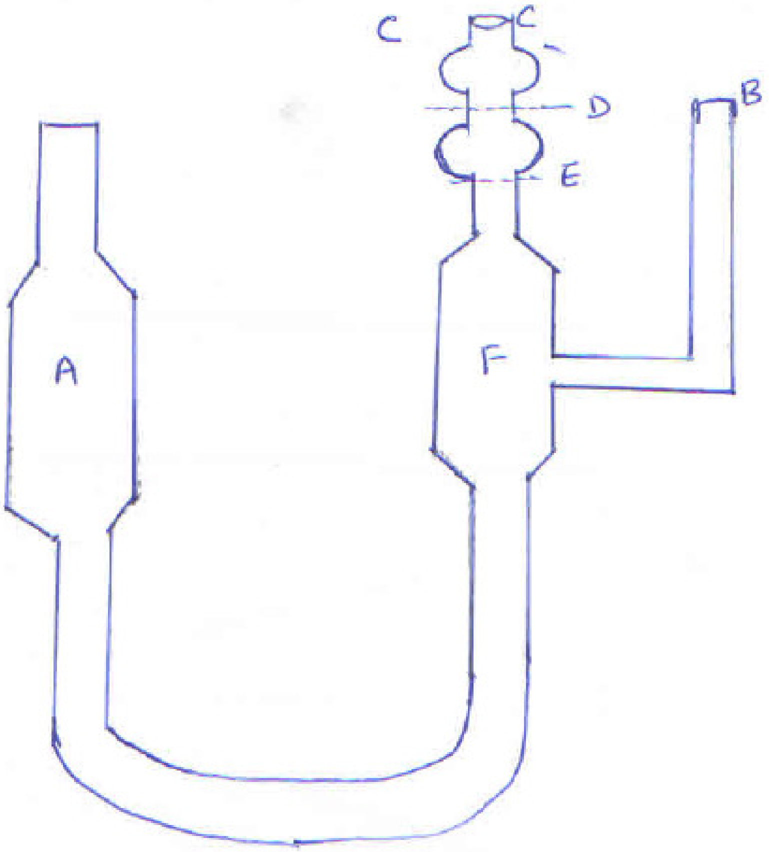
For intermediate solvent the dependence of α_s^3 on M is more difficult to predict. Hence experimentally is related to the molecular weight of the dissolved polymer in the given solvent system by the relation

$$[\eta] = KM^a$$
$$a = 0.5\, to\, 0.8$$
$$k = 10^{-4}\, to\, 10^{-5}$$

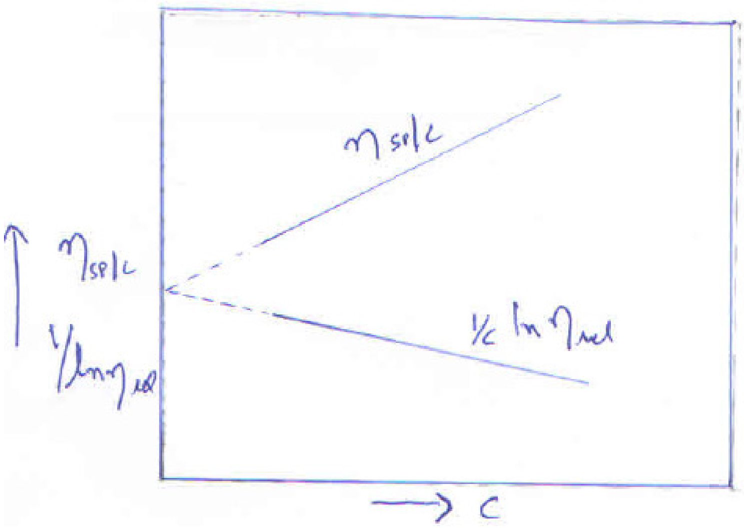
This equation refer to mark Houwime’s equation by the intrinsic viscosity of polymer

12.9 Experimental measurement of the intrinsic viscosity

To obtain the intrinsic viscosity or the polymer solution at any temperature, the viscosity at several concentrations below about 2% is determined using “Ubbelohde’s viscometer“. The polymer solution is transformed to the bulb ‘A’ (2%) after continuously cleaning the viscometer. The viscometer is immersed vertically in a thermostat. The end B is closed and the solution applied to C so that the solution becomes above the level D. The tube B is then open till the liquid in the bulb F is dried off and the pressure at this end of the capillary becomes equal to the atmospheric pressure. Thereafter the solution at end C is released at time ‘t’ taken for the solution to flow from D to E is measured. A known amount of the solvent is then added to bulb A to dilute the solution in the viscometer and the flow time is determined. The viscosity or reduced specific viscosity is calculated at several concentrations with single filling only. Viscometer having flow time 200-400 series for the solution used should be chosen so the reduced specific viscosity is plotted as concentration of curves.



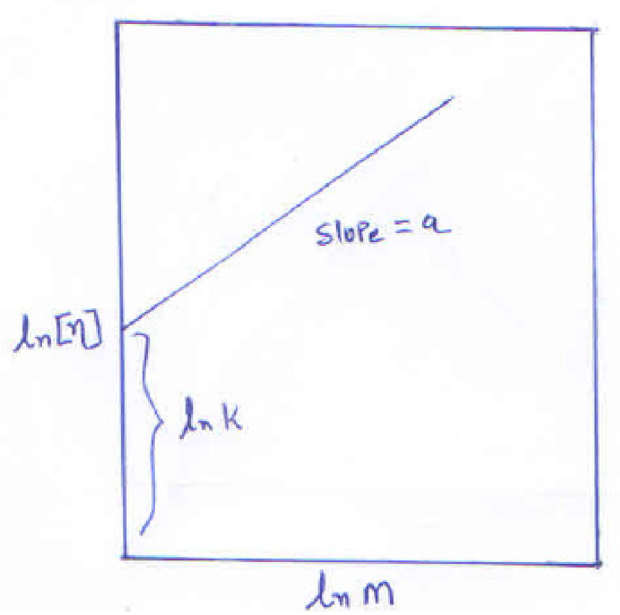
Also $\frac{1}{C}\ln\eta_{real}$ is ploted against C in the same graph as shown in the figure. Which on extrapolation to C = 0 gives the value of intrinsic viscosity by using the constant k and a. The viscosity average molecular weight can be evaluated



To get the value of constant k and a, the molecular weight of a number fraction of a synthetic polymer are determined by some absolute material like the osmotic pressure or the light reactivity method and their intrinsic viscosity measurement using the appropriate solvent

$$\ln[\eta] = \ln k + a \ln m$$

By ploting $\ln[\eta]$ vs ln [M] the value k and a can be determined.



Therefore it is generally assumed that the various fractions are effectively homogeneous so that we got

$$\overline{M}_m = \overline{M}_w = \overline{M}_v$$

If the prints are related it implies that the fraction are not homogeneous.

It is evidence that viscosity method is a secondary one in consistent with other methods of determining the molecular weight of the polymer. But here the k and a are kworn for a given polymer solvent system it becomes the one of the best and most convenient method for subsequent analysis of molecular weight

Example: during the course of polymerization process

Polymer	Solvent	T ^{0}C	10^5 K	a
Polyacrylnitrile	Dimethylformamide	20^0C	16.6	0.81
Polybutadiene	Benzene	30^0C	33.7	0.715
Polyethylene	Decaline	135^0C	67.7	0.67
	Tetraline	120^0C	23.6	0.78
Polyisoprene	Cyclohexane	27^0C	30.0	0.70
	Benzene	30^0C	18.5	0.74
Polyvinylchloride	Water	28^0C	20.0	0.70

12.10 Light scattering method of molecular weight determination

When a beam of light encounters matter, scattering of light occurs. The nuclei and electrons undergo induced vibrations in phase with the incident light wave and acts as sources of light which will be propagated in all directions.

Non- absorbing gases and liquids scattered light because of the in homogeneous structure. In pure liquids the scattering is considered due to local thermal fluctuations in density which makes the liquid optically inhomogeneous. In solutions and in mixture of liquids additional light scattering arises from irregular changes in density and refractive index due to fluctuation in composition (additional inhomogenity).

In case of polymer solution, this additional scattering though small is measured and can be related to the molecular weight of polymers.

This relationship differs somewhat according to wheather the size of the polymer molecules is smaller than or comparable to wavelength of light used.

If the polymer molecules are small in comparison to the wavelength of the monochromatic light used, the light scattering behavior is relatively simple. The size limit depends on the shape and configuration of the polymer chain.

If they are stiff and highly extended as in the case of cellulose derivatives the limit is reached at molecular weight of about 50,000. But if they are flexible and appreciably coiled the limit may not be reached until the molecular weight over 5 lakhs.

Debye gives the relationship between intensity of the scattered light, osmotic pressure and the concentration of solution by

$$\frac{HC}{\tau} = \frac{1}{\overline{M}_w} + 2A_2C - - - - - - - - - - (1)$$

where

$$H = \frac{32\pi^3 n^2}{3N\lambda^4}\left(\frac{d_n}{dc}\right)^2$$

N= Refractive index of solvent

N=Avogadro number

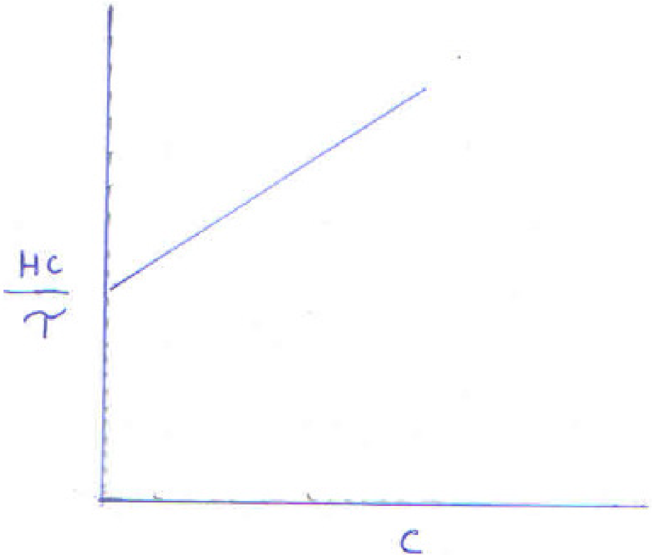
$\left(\frac{d_n}{dc}\right)$= Refractive index gradient (constant for a given solvent and temperature. Measured by interferro meter or differential refractometer)

A_2 = Second virial coefficient or interaction constant

τ = Turbidity. Which is defined as the fraction the light scattered in all direction from the incident primary beam/cm path length in the solution i.e, if the intensity of incident beam I_0 and I is the intensity when pass through the solution of length 'x' cm

$$\frac{I}{I_0} = e^{-\tau x} ------(2)$$

The plot of $\frac{HC}{\tau} vs\, C$ is linear as shown below



Slope =$2A_2$ and

Intercept $= -\frac{1}{\overline{M}_w}$

Equation (1) is for a assuming scattering particles are small compared to λ

Case ii)

Equation (1) is valid only if the light used is vertically polarized and for unpolarized light τ is multiplied by (1+ $\cos^2$ θ) where the θ is angle of observation.

Case iii)

If the dimension of polymer molecules is not small compared to λ dissymmetry of scattering exists (i.e, different intensities in difference direction. Thus the intensity of scattering light will not be the same at all angle of observation to the direction of intensity of incident beam) and turbidity of the solution is reduced by the interference between waves form different parts of the same particle. In such cases equation 1 become

$$\frac{K_\theta}{R_\theta}.C = \frac{1}{\overline{M}_w} + 2A_2C -------(3)$$

R_θ= Releigh ratio $\frac{3\pi}{16}(1+\cos^2\theta)\tau$

$$K_\theta = \frac{2\pi^2 n^2}{\lambda^4 N_A}(dn/dt)^2$$

For large size of the polymer molecules (3) become

$$\frac{K_\theta}{R_\theta}.C = \frac{1}{\overline{M}_w P(\theta)} + 2A_2C ------(4)$$

P(θ) = Scattering correction factor whose value depends on the size and shape of the molecules

$$P(\theta) = \frac{R_\theta}{R_{\theta^0}}$$

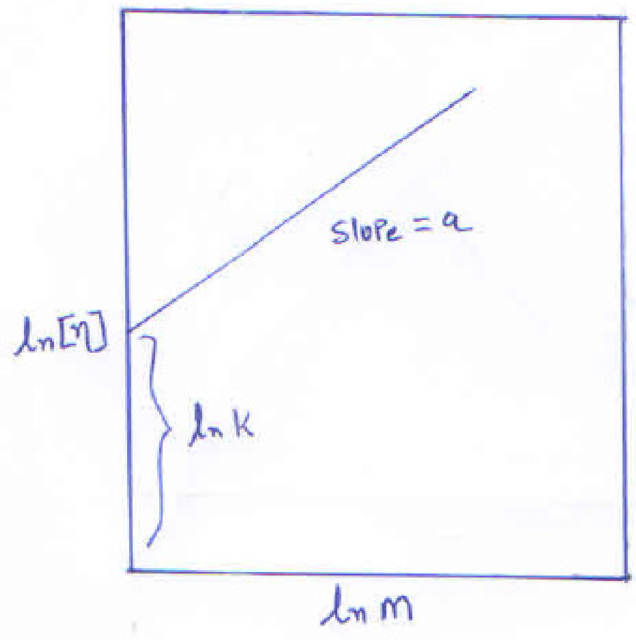
R_θ = Religh ratio for very small molecules

Commonly correction for dissymmetry is obtained by plotting "Zimm plot" in which $\frac{K_\theta C}{R_\theta}$ is plotted against $\sin^2\frac{\theta}{2} + kC$

To get the value of constants K and a the molecular weight of a number of fraction of a synthetic polymer are determined by some absolute method like the osmotic pressure or the light scattering method and their intrinsic viscosity measurement using the appropriate solvent

$$\ln[n] = \ln k + a \ln M$$

By plotting ln[n] vs ln[M] the value 'k' and 'a' can be determined .



$\overline{M}_v$ depends on 'a' as well as on the distribution of molecular species therefore 'a' is generally assumed that the various fractions are effectively homogeneous so that we got $\overline{M}_n = \overline{M}_w = \overline{M}_v$. If the points are scattered it implies that fractions are not homogeneous.

It is evident that viscosity method is secondary one in contrast with other methods of determining the molecular weight of the polymer. But when once the 'k' and 'a' are known for a given polymer solvent system, it becomes the one of the best and most convenient method for subsequent analysis of molecular weight.

12.11 Ultra Centrifuge Method

If a suspension of a solid centrifuge large particles sediment more rapidly than smaller one because centrifugal force increases with the size of the particle. This is also true for polymer molecules in dilute solutions. But it is necessary to use very strong centrifugal fields such as one given by ultracentrifuge. This is a centrifuge capable of rotation at such high speed as to give centrifugal field which are several hundreds, thousand times the acceleration due to gravity in such a field the rate of sedimentation is a function of the molecular weight of the polymer.

In an ultra centrifugal sedimentation and diffusion of polymer occurs simultaneously sedimentation leads to an upper region of almost pure solvent separated by a region solution by a boundary which is generally diffused. The diffuse boundary results from solute molecule tending to diffuse upwards into the solvent

There are two types of ultra centrifuge methods for the determination of molecular weight of polymers, they are

1. Sedimentation velocity method and
2. Sedimentation equilibrium method

12.12 Sedimentation velocity method

In sedimentation velocity method a very strong electric field is used so that the diffusion power can be neglected and the polymer molecules sediment against the opposition of the frictional forces. The rate of sedimentation is a measure of the ratio of the molecular weight to the frictional force. The frictional force is determined by the diffusion or viscosity measurements,

The centrifugal force activity on a particle of mass m at a distance 'x' from the axis of rotation will be $w^2 x(1-\bar{v}d)m ----------(1)$

Where w = angular velocity

$\bar{v}$ = partial specific volume of the particle

D=density of the solution

$\left(\frac{dx}{dt}\right)$ is the rate of sedimentation of particle, the frictional force will be $f\left(\frac{dx}{dt}\right)$

f = fractional constant

Comparing 1 and 2

$$f\left(\frac{dx}{dt}\right) = w^2 x(1-\bar{v}d)m ------(3)$$

$$\frac{1}{w^2 x}\left(\frac{dx}{dt}\right) = \frac{m(1-\bar{v})}{f} -------(4)$$

$$s = \frac{m(1-\bar{v}d)}{f} -----------(5)$$

S= swedger constant or sedimentation constant

$$S = \frac{1}{w^2 x}\left(\frac{dx}{dt}\right)$$

The value of f by Einsten equation

$D = \frac{KT}{f}$ where D = diffusion constant

$$S = \frac{m(1-\bar{v}d)}{\frac{Kt}{D}} = \frac{M(1-vd)D}{RT}$$

$$\therefore \mu = \frac{RT}{(1-\bar{v}d)} {}^{s}\!/\!_{D}$$

$$\therefore \mu = \frac{RTS}{(1-\bar{v}d)D} -----------(6)$$

Both s and D depends upon the concentration and (6) is applicable only when values at infinite dilute namely D_0 S_0 are used.

The sedimentation velocity method depends on following the movements of the boundary between the solution and solvent with time. This boundary will be fairly shown for homogeneous polymer and each compounds is in a heterogeneous polymer will be sedimentation at its own rate and own value of s, so that the boundary may vary few and value of s is difficult to obtain

12.13 Sedimentation equilibrium Expert

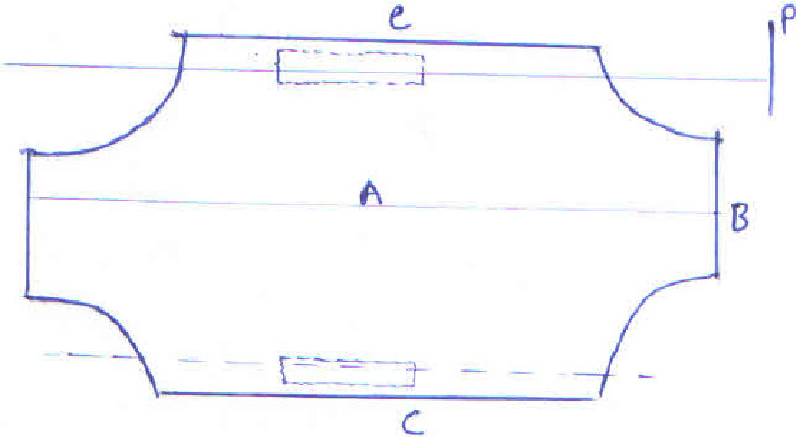
The centrifuge is operated at low speed of rotation for time up to one or two weeks under constant conditions. A thermodynamic equilibrium is reached in which the polymer is distributed in the cell mainly according to molecular weight distribution. The forces of sedimentation of each species being just balance by the tendency to diffuse back against the concentration gradient of thermal motion resulting measurement in the centrifugation field.

An equation

$$\mu = \frac{2RT \ln {}^{C_2}\!/_{C_1}}{(1-\vec{v}d)w^2\left(r_2^2 - r_1^2\right)}$$

can be derived for the distribution of polymers accordingly to the molecular masses at equilibrium

C_1 , C_2 are constant at points r_1 and r_2 form the axes of rotation. For heterogeneous polymer μ represents the weight average molecular weight. The major disadvantage of sedimentation equilibrium experiment is that days and weeks may be required to reach equilibrium and experiment remaining long and tedious



It consists of rotor (A) revolving with high speed about axe B. A cell (C) contain experimental solution through which a light it become passes then to phosphorted or photographic plate (P). By rapidly rotating the polymer solution, force approximately ½ the million times the gravity can be applied to particle. By making the measurements of two distances the molecular weight of polymer can be evaluated

{from the knowledge of rotation W can be obtained, the amount of light obsorbed proportional to the number of molecules

The successes full condition of this techniques following condition to be satisfied

1. The properties of solution remain constant, sometime in the course of several days there will be the stability as for as the components concerned
2. The polymer and the solvent must possess different density
3. The solvent must have low viscosity
4. The polymer must dissolved in solvent at room temperature

Note: The sedimentation equilibrium and osmotic pressure methods are not affected by the shape of the macro molecules since measurement are made at equilibrium. However sedimentation velocity is markedly dependent on the shape. An elongated particle offer more resistance to movement through a liquid than a spherical particle of the same mass. Hence elongated molecules will have smaller sedimentation velocity than a spherical molecule of same molecular weight. When the molecular weight obtained from sedimentation velocity and sedimentation equation measurement agrees with one another, the molecular are probably spherical. This is found to be in case of protein molecules.

12.14 Summary of the unit

A simple chemical has fixed molecular weight but when we discuss about the molecular weight of polymer, we mean something different from that which applies to small sized compounds. Since polymers are mixture of molecules of different molecular weight, the molecular weight is expressed in the term of “average” value. This average molecular weight is basically based on either average number of repeating units, known as number average molecular weight, or average weight, known as weight average molecular weight. The number average molecular weight is obtained from the number of macromolecules for each degree of polymerization, by taking for each degree of polymerization the product of the number of polymer molecules and their degree of polymerization and dividing the sum of these product by the total number of monomers. The weight average molecular weight is obtained in a similar manner from mass of each degree of polymerization according to the following equation.

$$\overline{M}_w = \frac{\sum_{i=1}^{\infty} m_i p_i}{M_o}$$

When the molecular weight distribution is very narrow, the number average and weight average molecular weights are essentially equal. When the distribution is broad, the weight average molecular weight is considerably greater than the number average molecular weight.

Some of the important methods employed for the determination of molecular weights of polymers are 1) Osmometry: which can be used for determining the masses from 104 to 106. This is one of the most accurate methods, though due to its lengthy and tedious experimental procedure it cannot be frequently used for molecular weight determination. the method involves the measurement of the osmotic pressure of solution at several concentrations. The instrument used for the determination of molecular-weights by this method is called osmometer.

12.15 Key words

Osmotic Pressure method; Viscosity method; Intrinsic viscosity; Light scattering method; Ultra Centrifuge Method; Sedimentation velocity method

12.16 References for further studies

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12.17 Questions for self understanding

1) Write a short note on molecular masses of the polymer

2) What is Molecular Average Molecular weight $\overline{M_m}$ of polymers?

3) Weight average degree is polymerization $(\overline{M}_w)$ of polymers?

4) Discuss the molecular weight determine of polymers by the measurements of colligative properties of its solutes.

5) Explain the molecular weight determine of polymers by Osmotic Pressure method

6) Explain the molecular weight determine of polymers by Viscosity method

7) Derive the expression for relation between the that intrinsic viscosity and molecular weight

8) Describe the experimental measurement of the intrinsic viscosity

9) Explain the Light scattering method of molecular weight determination

10) Explain the molecular weight determine of polymers by Ultra Centrifuge Method

11) Explain the molecular weight determine of polymers by Sedimentation velocity method

UNIT-13

Structure

13.0 Objectives of the unit

After studying this unit you are able to

- Contrast objects at the nanoscale with larger and smaller forms of matter
- Define key terms in nanotechnology
- Explain some of the ways nanomaterial properties differ from molecules and microscale particles
- Describe some of the physical and chemical characteristics that can change at the nanoscale
- Describe some of the major classes of nanomaterials produced today and their properties and potential benefits

13.1 Introduction

Nanoscience is the study of phenomenon and manipulation of materials at atomic, molecular and macro molecular scales. Nanotechnology includes the designs, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale.

Bulk materials possess continuous physical properties. The thing applies to micron-sized material. But when particles of same material are in nano-scale dimensions, the principles of classical physics are no longer capable of describing their behavior like movemet, energy etc… at this dimensions quantum mechanics principle applies. For example gold, it is yellow in colour at bulk or micron size state but it appears as red in nano-scale size. Similarly bulk siver is non-toxic whereas silver nanparticles are capable of killing viruses upon contact. Thus at nano scale dimensions, the same material can have properties (eg, optical, mechanical, electrical etc…) which are very different from the properties in the material has at the macro scale.

13.2 The nano meter scale

The prefix nano is derived from the Greek work for “dwarf”. It is hard to imagine just how small technology is. The nanometer scale is conventionally defined as 1 to 100nm. The 1 nm is equal to 1 billionth of a meter or 10^{-9} of a meter. The size range is set normally to be minimum 1nm to avoid single atoms or very small groups of atoms being designated as nano-objects. Remember that “nano” does not simply mean “very small”. There are many forms of matter much smaller than a nanometer, including electrons, atoms and most molecules. The nanoscale is in between the very small atomic regime and the larger regime of microparticles and colloids.

Therefore nanoscience and nanotechnologies deal with at least clusters of atoms of 1 nm size. The upper limit is normally 100nm but is fluid limit, often objects with greater dimensions (even 200nm) are defined as nanomaterials. One can ask the question why 100nm and why not 150nm. Or why not 1 to 1000nm. The reason is *1 to 100nm range definition itself focuses on the effect that the dimension has on a certain material ex, the insurgence of a quantum phenomenon rather than at what exact dimension this effect arises*.

Nanotechnology is the understanding, manipulation, and control of matter at dimensions of roughly 1 to100 nanometers, which is near-atomic scale, to produce new materials, devices, and structures.

The following few illustrative examples given below illustrate the how small nano meter is

- A single strand of human hair is approximately 80,000 nm wide
- A red blood cell (RBC) approximately 7000 nm wide
- A water molecule is almost 0.3nm across
- There are 25,400,000 nanometers in an inch
- A sheet of news paper is approximately 100,000 nanometer thick

The concepts and ideas behind nanoscience and nanotechnology started with the talk entitled ‘There’s plenty of room at the bottom’ by physicist Richard Feynman at an American physical society meeting at the California Institute of Technology (Cal tech) on December 1959, long before the term nanotechnology was used. In his talk, Feynman described a process in which scientists would be able to manipulate and control individual atoms and molecules.

13.3 Nano particles or nano material

There is no accepted international definition of a nanoparticle. “A particle having one or more dimensions of the order of 100nm or less is referred as Nanoparticles”. Or a nanomaterial is an object that has at least one dimension in the nanometer (approximately 1-100nm). Thus nanoparticle is a sub-classification of ultrafine particle with lengths in two or three dimensions greater than 0.001 micrometer (1 nanometer) and smaller than about 0.1 micrometer (100 nanometers) and which may or may not exhibit a size-related intensive property.

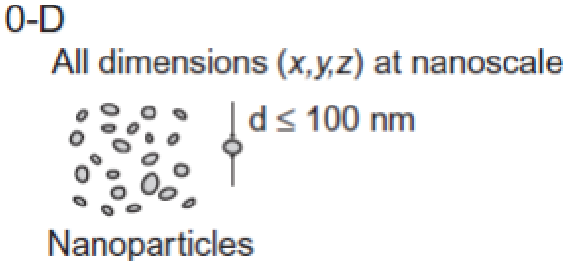
Material with one or more external dimensions, or an internal structure, on the nanoscale, which could exhibit novel characteristics compared to the same material without nanoscale features are called nanomaterials

Nanomaterials are catagorized according to their dimensions as listed below. This Classification is based on the number of dimensions, which are not confined to the nanoscale range (<100 nm).

1) Zero-dimensional (0-D),
2) One-dimensional (1-D),
3) Two-dimensional (2-D), and
4) Three-dimensional (3-D).

13.4 Zero-dimensional nanomaterials

Materials wherein all the dimensions are measured within the nanoscale (larger than 100 nm) are called Zero-dimensional nanomaterials. The most common representation of zero-dimensional nanomaterials are nanoparticles.



Nanoparticles can be

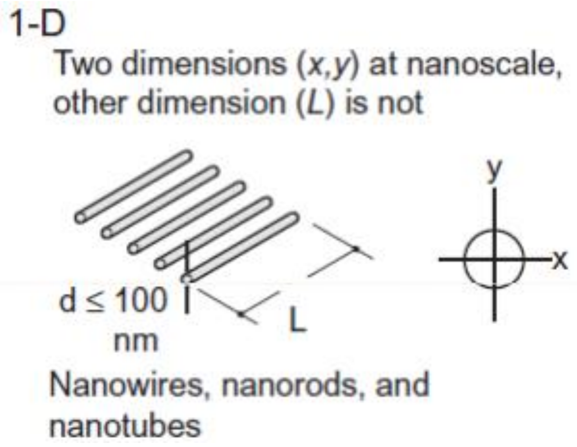
a) Amorphous or crystalline
d) Single crystalline or polycrystalline
c) Composed of single or multi-chemical elements
d) Exhibit various shapes and forms
e) Exist individually or incorporated in a matrix
f) Be metallic, ceramic, or polymeric

13.5 One-dimensional nanomaterials

Materials wherein any one dimension is outside the nano meter scale are called one-dimensional nanomaterial. This leads to needle like-shaped nanomaterials. 1-D materials include nanotubes, nanorods, and nanowires.

1-D nanomaterials can be

a) Amorphous or crystalline
b) Single crystalline or polycrystalline
c) Chemically pure or impure
d) Standalone materials or embedded in within another medium
e) Metallic, ceramic, or polymeric

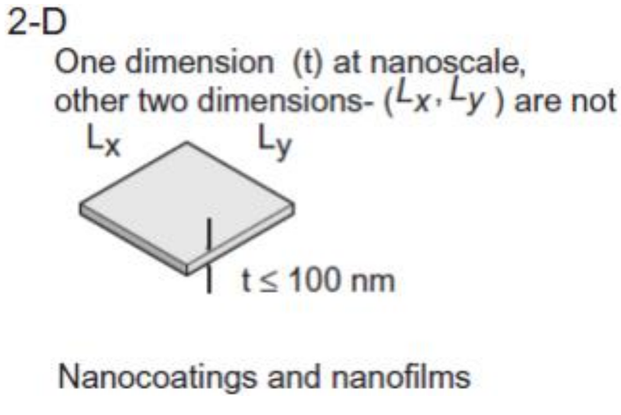


13.6 Two-dimensional nanomaterials

Materials wherein any two dimensions are not confined to the nanoscale are called 2-d nanomaterials. 2-D nanomaterials exhibit plate-like shapes. Two-dimensional nanomaterials include nanofilms, nanolayers, and nanocoatings.

2-D nanomaterials can be

a) Amorphous or crystalline
b) Made up of various chemical compositions
c) Used as a single layer or as multilayer structures
d) Deposited on a substrate
e) Integrated in a surrounding matrix material
f) Metallic, ceramic, or polymeric

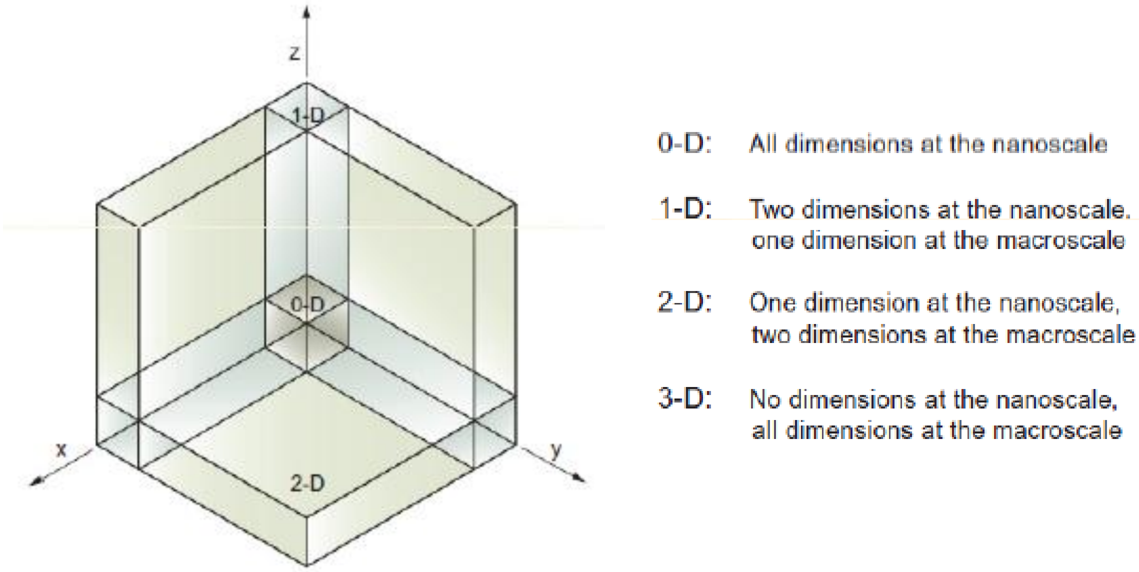


13.7 Three-dimensional nanomaterials

There dimensional nanomaterials are also called bulk nanomaterials. Bulk nanomaterials are materials that are not confined to the nanoscale in any dimension. These materials are thus characterized by having three arbitrarily dimensions above 100 nm.

Materials possess a nanocrystalline structure or involve the presence of features at the nanoscale. In terms of nanocrystalline structure, bulk nanomaterials can be composed of a multiple arrangement of nanosize crystals, most typically in different orientations.

With respect to the presence of features at the nanoscale, 3-D nanomaterials can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multinanolayers. Three-dimensional space showing the relationships among 0-D, 1-D, 2-D, and 3-D a nanomaterial is shown in below figure



13.8 Types of nanomaterials

Nano materials are of two types

a) *Non-intentionally made nanomaterials*

These refer to nano-sized pasrticles or materials that belong naturally to the environment (ex, proteins, viruses, nanoparticles produced during volcanic eruptions etc…) or that are produced by human activity without intention (such as nanoparticles produced from diesel combustion).

b) *Intentionally made nanomaterials*

These refer to nanomaterials produced deliberately through a defined fabrication process.

The properties of materials will be different at the nanoscale level because, nanomaterials have a relatively larger surface area when compared to the same mass of material produced in a larger form. These will make materials chemically more reactive and effect their strength and electrical properties. Also, quantum effects can begin to dominate the behavior of matter at the nanoscale particularly at the lower end affecting the electrical, optical and magnetic behavior of materials. Nanoscience and nanotechnology deals with the scientific study of objects with sizes in the 1-100nm range in at least 1 dimension. Materials can be produced that are nanoscale 1 dimension (For ex: thin films, layers and coatings), in 2-dimensions (for ex: nanotubes, fibres and Nanowires) or in all 3 dimensions (for ex: nanoparticles, quantum dots, nanoshells, nanorings, microcapsules).

13.9 Advantages of nanosize materials

As mention earlier nano means small, very small. The nanoscience and nanotechnogoies are very promising in maerials, engineering and related science because of following reasons.

i) At the nanometer scale, the properties of matter such as energy change. This is a direct consequence of the small size of nanomaterials physically explained as quantum effects.

ii) Properties like electrical conductivity, colour, strength and weight change when the nanoscale level is reached.

iii) The same metal can become a semiconductor or an insulator at the nanoscale level.

iv) Nanomaterials can be fabricated atom-by-atom.

v) The nanomaterials have an increase surface to volume ratio (surface area) compared to bulk materials. This has important consequences for all those process that occur at a material surface such as catalysis and detection.

13.10 Applications of nanoscience and nanotechnology

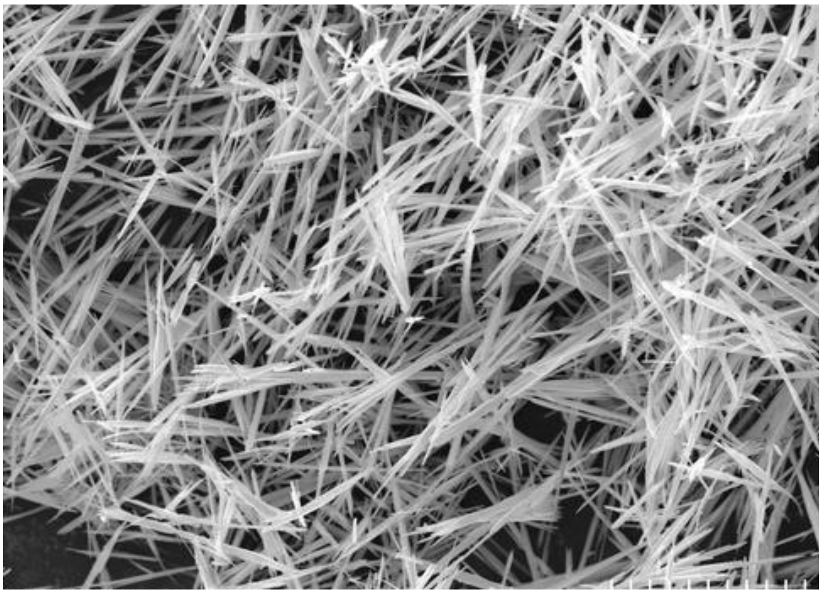
1. In sunscreens and cosmetics
2. Displays (TV screens and computer monitors)
3. Catalysts for various chemical reactions
4. Batteries (mobile phones, laptop, computers, navigation devices, remote censors)
5. Nanomedicine (medicines and tissue engineering)
6. Magnetic materials
7. Food (food processing and packaging)

13.11 The smaller size of the nanoparticles leads to

- Increases the fineness
- Increases the surface area (a large particle of size 1000nm with 6 faces, if it is reduced to 10nm particles then 600 faces, so that the surface area increases)
- one square centimeter fiber mat, if it is cut into nano scale, the foot ball ground can be covered
- Change of energy gap
- Increase of defect concentration
- Change of oxidation states (Ag^+ to Ag^O)
- Conversion of semiconductor to indirect semiconductor
- Structure and geometry of the molecule
- Change in properties like mechanical, electrical, electronic, magnetic, optical, medicinal, corrosion resistance, catalytic, photo catalytic, high temperature resistant etc,,

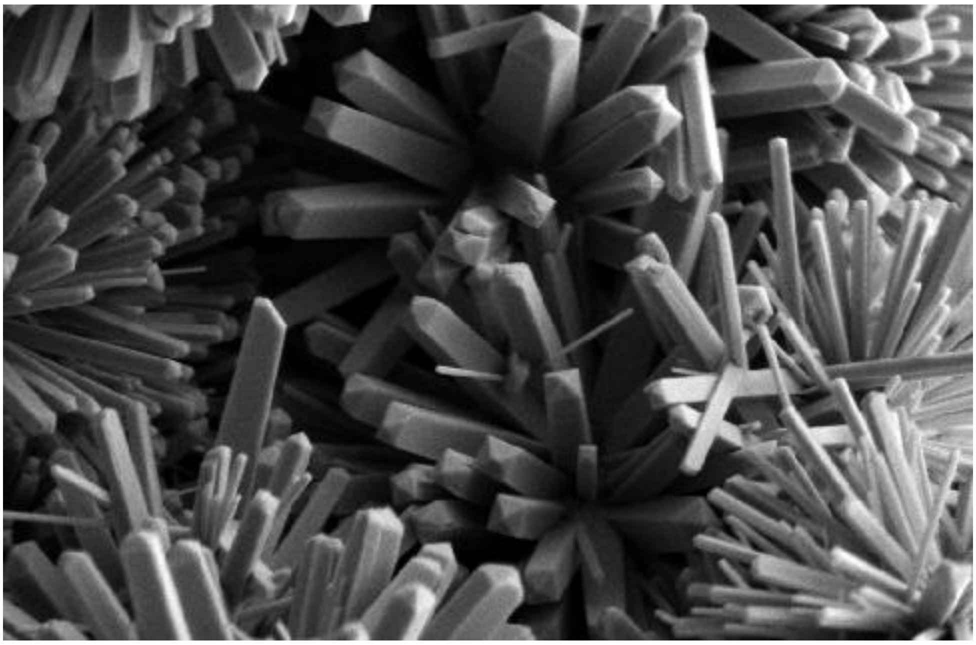
13.12 Nano wires

Nanowires are 1D nanostructures which generally have diameters of the order of tens of nanometers, with unconstrained length scales. The length to diameter ratio may be as much as 1000. The diameters of wires less than 3nm are referred as Nanowires. Nanowires also obtain by incorporation of metal ions in nanotubes are composed of nanometals such as silver, gold, iron, aluminium etc….



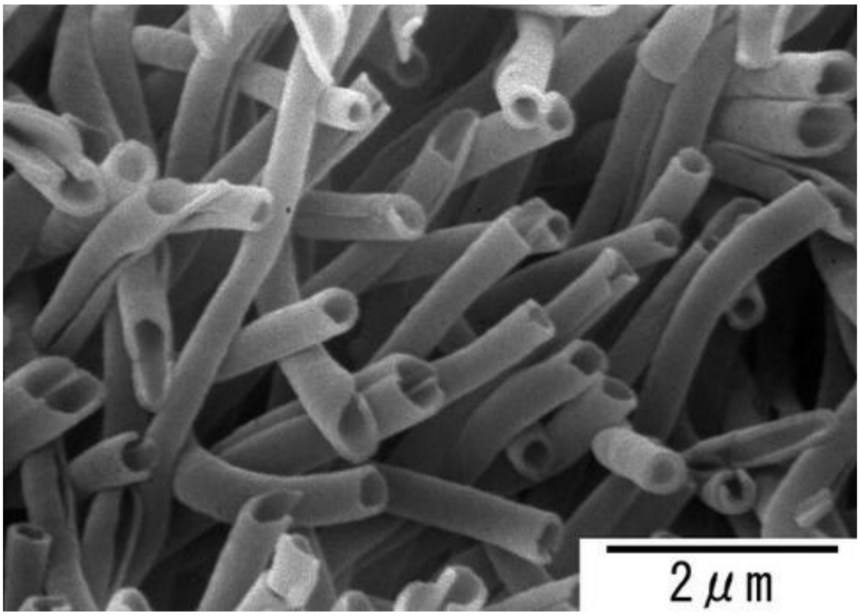
13.13 Nanorods

Nanorods are also 1D nanostructures where each of their dimensions range from 1–100 nm. *Standard aspect ratios (length divided by width) are 3-5.*



13.14 Nanotube

A nanotube is a nanometer-scale tube-like structure, which are also like nanowires, in terms of aspect ratio; but unlike wires, tubes are hollow! Nanotubes maybe single-walled or multi-walled.

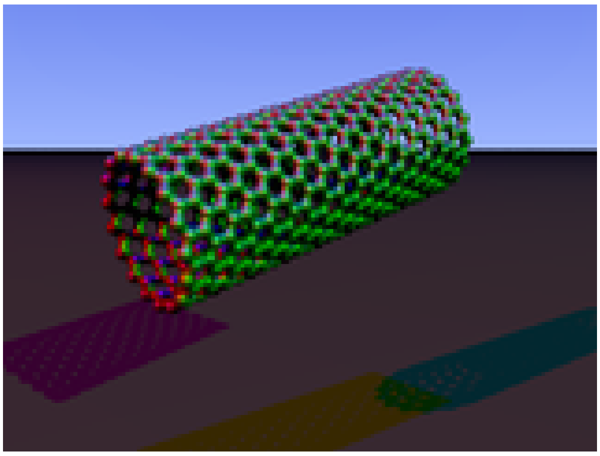


13.15 Carbon Nanotubes

The diameter of carbon tubes less than 3nm is referred as carbon nanotubes. Mainly 2 types of CNTs:

- Single wall nano tubes (SWNT)
- Multi wall nano tubes (MWNT)

Single-walled carbon nanotubes (SWNTs) are nanometer-diameter cylinders consisting of a single graphene sheet wrapped up to form a tube. Since their discovery in the early 1990s there has been intense activity exploring the electrical properties of these systems and their potential applications in electronics. These carbon nanotubes have high porosity, high surface area (2700m^2/g)- used for adsorption of gases like hydrogen



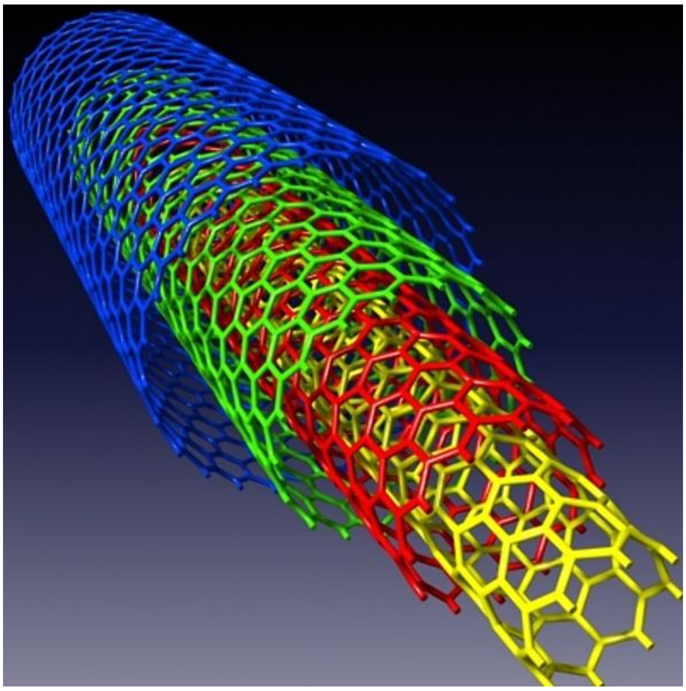
Adsorption property of Single walled nanotubes (SWNT)

SWNT	Porosity cm^3/g	Surface area m^2/g
Surface	0.049	483
Groove	0.089	22
Pore	0.062	783
Interstitial	0.119	45

Single walled nanotubes are used for adsorption of gases like H_2, O_2 and N_2, because adsorption of gases with MWNT is very high.

13.16 Multi-walled carbon nanotubes (MWNT)

Multi-walled carbon nanotubes (MWNT) consist of multiple rolled layers (concentric tubes) of graphite.



The multi-walled carbon nanotube has the outer diameter of 50-80nm and inner diameter of 5-15nm, therefore the thickness of the wall is about 45-65nm. The distance between each wall is about 0.34nm, therefore the number of layers can be calculated between 45/0.34=132 to 65/0.34=191. That is, MWCT about 132-191 layers.

Potential applications of carbon nanotubes are:

1) Additives in polymers

2) Catalysts

3) Electron field emitters for cathode ray lighting elements

4) Flat panel display

5) Gas-discharge tubes in telecom networks

6) Electromagnetic-wave absorption and shielding

7) Energy conversion

8) Lithium-battery anodes

9) Hydrogen storage

10) Nanotube composites (by filling or coating)

11) Nanoprobes for STM, AFM, and EFM tips

12) Nanolithography

13) Nanoelectrodes

14) Drug delivery

15) Sensors

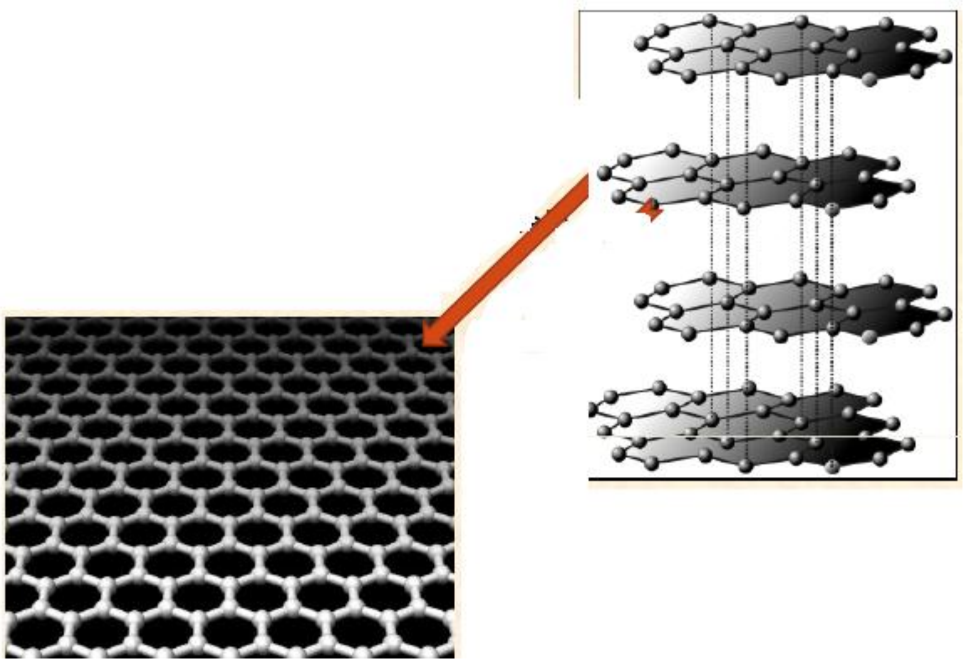
16) Reinforcements in composites

17) supercapacitor

13.17 Graphene

Graphene is an one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. It can be viewed as an atomic-scale chicken wire made of carbon atoms and their bonds.

A perfect graphene sheet, rolls into a cylinder (polyaromatic manoatomic layer of sp^2 hybridised carbon atoms). Its diameter is 2-3nm. Here the diameter of the tube is restricted, the length may be changed. If it is rolled once which is referred as SWNT. If it is rolled more than once (multi layers tube), referred as MWNT. The diameter of the carbon nanotube is 1-3nm



13.18 Synthesis of Nanocomposites

Nanoparticles may be created using several methods. Some of them may occur in nature as well. The methods of creation include attrition and pyrolysis. The two methods widely employed for nanparticle synthesis are bottoms up method and top down method

13.18.1 Attrition method

In this method macro or micro scale particles are ground in a ball mill, like a planetary ball mill, or other size reducing mechanism. The resulting particles are classified using air to recover nanoparticles. this method involves mechanical thermal cycles and yields broad size distribution (10-1000 nm) of varied particle shape or geometry impurities

13.18.2 Pyrolysis method

In pyrolysis method, a vaporous precursor (liquid or gas) is forced through a hole or opening at high pressure and burned. The resulting solid is air classified to recover oxide particles from by-product gases. Pyrolysis often results in aggregates and agglomerates rather than singleton primary particles. Instead of gas, thermal plasma can also deliver the energy necessary to cause evaporation of small micrometer size particles. The thermal plasma temperatures are in the order of 10,000 K, so that solid powder easily evaporates. Nanoparticles are formed upon cooling while exiting the plasma region.

13.18.3 Top-Down approach

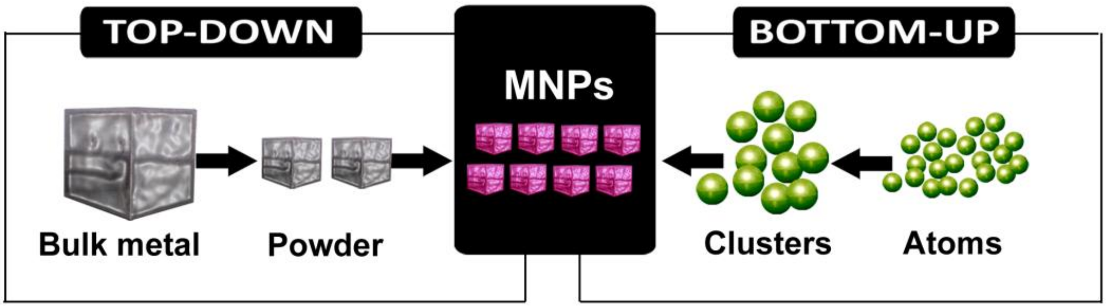
This method of nanomaterial synthesis involves conversion of millimeter-size flakes of material into nanoscale particles. The process costs some energy and does not sound very controllable, but if all goes well, it is possible to get nanoparticles that are about 5 nanometers in diameter. Thus Top down approach involves the breaking down of the bulk material into nano sized structures or particles. These techniques are an extension of those that have been used for producing micron- sized particles. An example of such a technique is high-energy wet ball milling.

13.18.4 Bottom up approach

Bottom up approach refers to the build up of a material from the bottom i.e, atom-by-atom, molecule-by-molecule, or cluster-by-cluster. This method has the potential of creating less waste and hence the more economical. Many of these techniques are still under development or are just beginning to be used for commercial production of nano powders.

13.18.5 Bottom-up vs Top-down approach of nanopartical synthesis

The “top-down” approach involves the breaking down of large pieces of material to generate the required nanostructures from them. The “bottom-up” approach implies assembling single atoms and molecules into larger nanostructures.



Getting merely a small size is not the only the requirement in nanopartical synthesis. A good characteristic of nanoparticles synthesized by any fabrication technique should posses

- ✓ Identical size of all particles (also called mono sized or with uniform size distribution.
- ✓ Identical shape or morphology.
- ✓ Identical chemical composition and crystal structure that are desired among different particles and within individual particles, such as core and composition must be the same.
- ✓ Individually dispersed or mono dispersed i.e., no agglomeration.

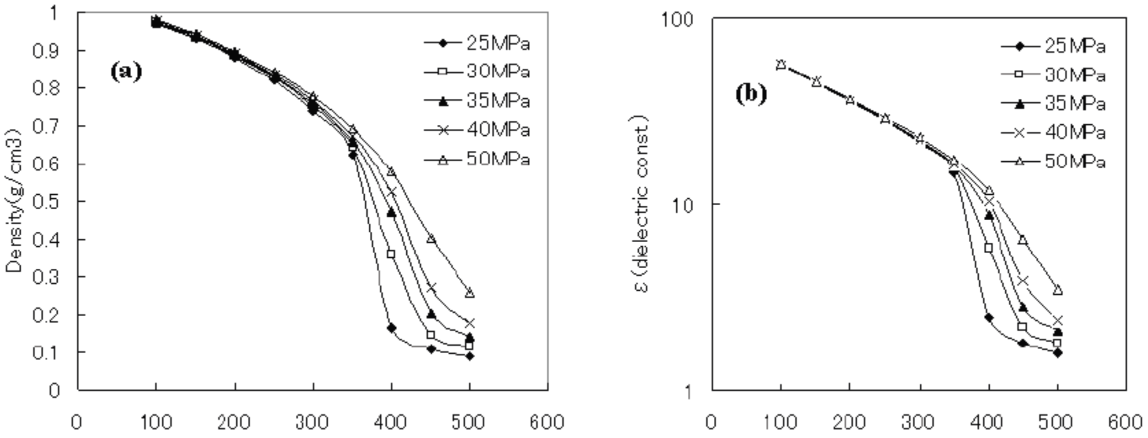
Nanomaterials are also synthesized by following methods:

- Hydrothermal method
- Sol-gel method
- Laser ablation chemical vapor transporter (CVT)
- Chemical vapor deposition (CVD)
- Electrochemical method

13.18.6 Hydrothermal method

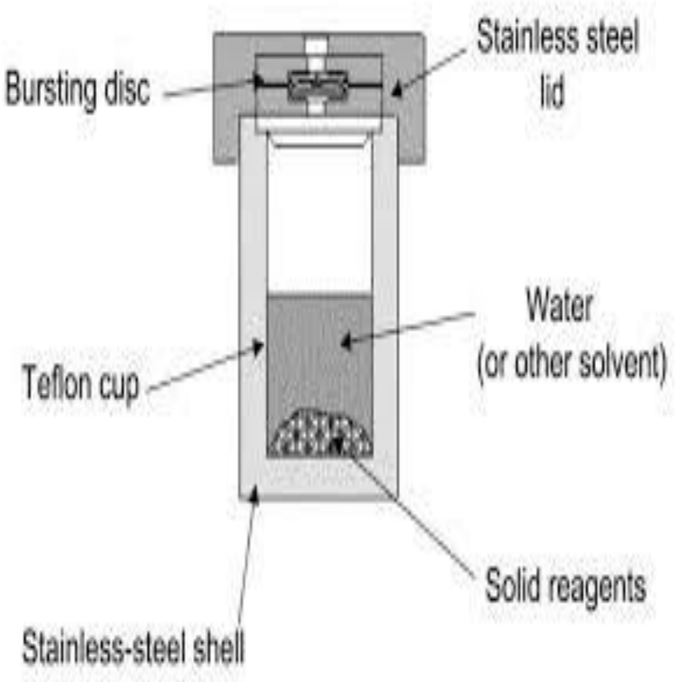
The term hydrothermal synthesis refers to any reaction in the presence of aqueous solvents or mineralizers under high pressure, high temperature (HPHT) to dissolve and recrystalize materials that are relatively insoluble under ordinary conditions.

Hydrothermal synthesis is generally defined as crystal synthesis or crystal growth under high temperature and high pressure water conditions from substances which are insoluble in ordinary temperature and pressure (<100 °C, <1 atm). Since ionic product (Kw) has a maximum value of around 250–300 °C, hydrothermal synthesis is usually carried out below 300 °C. The critical temperature and pressure of water are 374 °C and 22.1 MPa, respectively. The solvent properties for many compounds, such as dielectric constant and solubility, change dramatically under supercritical conditions. The density of water and dielectric constant are shown in below figure as a function of temperature and pressure. The dielectric constant of water is 78 at room temperature, where polar inorganic salts can be soluble in water. The dielectric constant of water decreases with increasing temperature and decreasing pressure. The dielectric constant is below 10 under supercritical conditions; the contribution of the dielectric constant to the reaction rates becomes remarkable based on the electrostatic theory. Thus, supercritical water gives a favorable reaction field for particle formation, owing to the enhancement of the reaction rate and large supersaturation based on the nucleation theory, due to lowering the solubility.



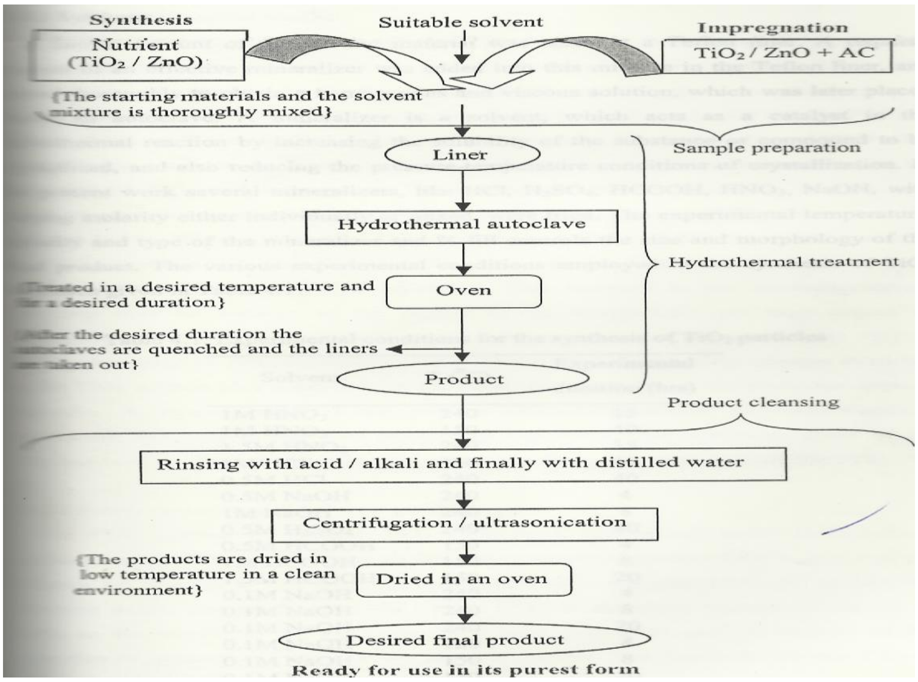
(a) Density of water as a function of temperature and pressure. (b) Dielectric constant as a function of temperature and pressure.

Nano materials prepared in a thermodynamically under closed system. Chemical reaction above room temperature and pressure takes place inside the autoclave, which includes a teflon liner. TiO_2, ZnO doped metal oxides, doped metal sulphides, ceramics etc… can be prepared by this method.



Autoclave

The flow sheet for the synthesis of nanomaterials is given below



The formation mechanism of metal oxide particles from metal nitrate solution is as follows: First, hydrated metal ions are hydrolyzed to metal hydroxide. Then, metal hydroxides proceed to precipitate as metal oxides through dehydration.

$$M(NO_3)_x + xH_2O = M(OH)_x + xHNO_3 \text{ --------------- } (1)$$

$$M(OH)_x = MO_{x/2} + x/2\ H_2O \text{ ---------------- } (2)$$

13.18.7 Sol-gel method

The sol-gel process is a wet-chemical technique (also known as chemical solution deposition) widely used recently in the fields of materials science and ceramic engineering.

Steps include in this method are

1) Formation of stable sol solution

2) Gelation via a polycondensation or polyesterification reaction

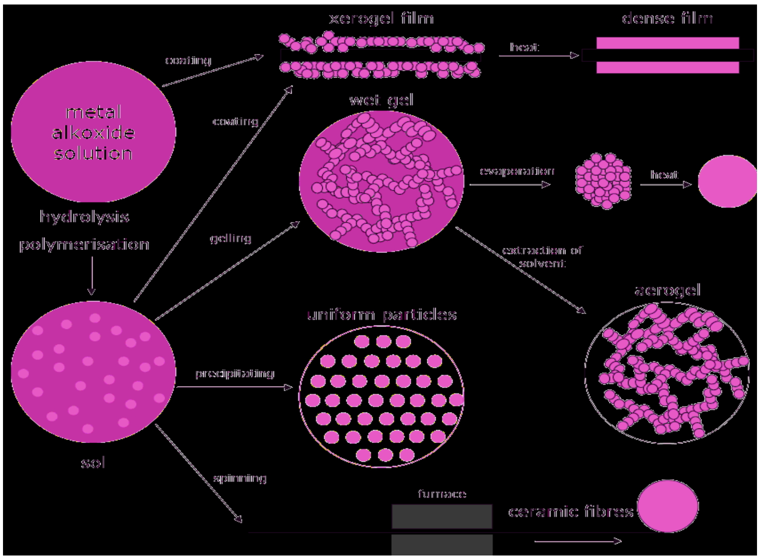
3) Gel aging into a solid mass. This causes contraction of the gel network, also phase transformations and Ostwald ripening.

4) Drying of the gel to remove liquid phases. This can lead to fundamental changes in the structure of the gel.

5) Dehydration at temperatures as high as 8000 degree C, used to remove M-OH groups for stabilizing the gel, i.e., to protect it from rehydration.

6) Densification and decomposition of the gels at high temperatures (T > 8000 degree C), i.e., to collapse the pores in the gel network and to drive out remaining organic contaminants

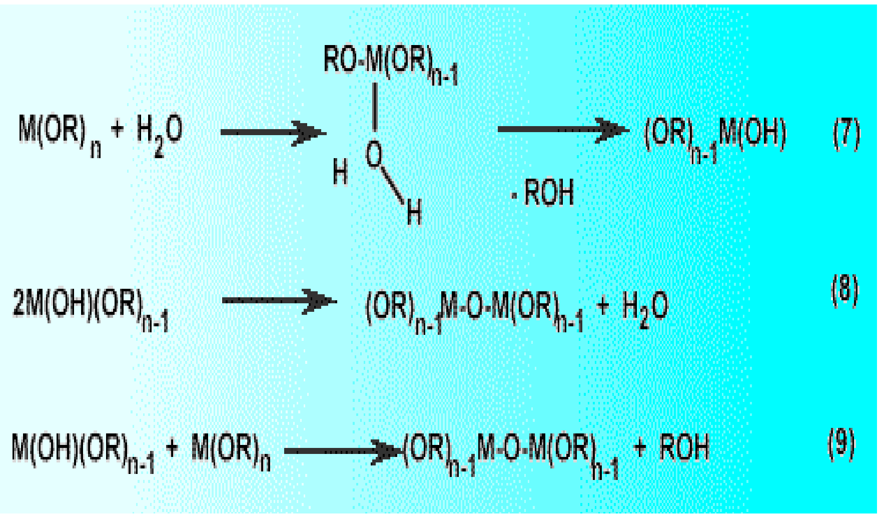
The ultimate microstructure of the final component will clearly be strongly influenced by changes implemented during this phase of processing. The precursor sol can be either deposited on a substrate to form a film (e.g. by dip-coating or spin-coating), cast into a suitable container with the desired shape (e.g. to obtain a monolithic ceramics, glasses, fibers, membranes, aerogels), or used to synthesize powders (e.g. microspheres, nanospheres).



Advantages of the sol-gel process are that it is a cheap and low-temperature technique that allows for the fine control of the product’s chemical composition. Even small quantities of dopants, such as organic dyes and rare earth metals, can be introduced in the sol and end up uniformly dispersed in the final product.

13.18.8 Metal alkoxide route

This method is based on the hydrolysis and polycondensation of the metal alkoxide which finally gives an alkoxide or oxide of metal. In this way inorganic polymeric oxide (network material) –M-O-M- is synthesized.



Addition of water causes $M(OR)_n$ to readily undergo hydrolysis (equation 7). Then it is followed by condensation step to form –M-O-M- by either dehydration (equation 8) or dealcoholation (equation 9). After obtaining metal oxide calcination to higher temperature gives pure oxides of nanomaterial

The quality of metal alkoxide depends on

1. Molar ratio of water and metal alkoxide
2. Temperature
3. pH
4. Choice of solvent

13.18.9 Multi component gel

This includes more than 1 type of metal

Eg: Ceramics, $BaTiO_3$

Let us consider 2 diff metal ions A^{2+} and B^{4+}

The stoichiometry between A/B=1

Step 1: Mixing of corresponding metal alkoxide $A(OR)_2$ and $B(OR^l)_4$ in a solvent

Step 2: Addition of water

The quality of homogeneous gel depends on 3 factors

Case 1: no reaction between $A(OR)_2$ and $B(OR^l)_4$. Here homogenity depends on rate of hydrolysis of each metal alkoxide. But in this case rate of hydrolysis is different for this 2 metal alkoxide and gives different sized clusters in sol. Hence leads to in-homogenity of gel due to differential hydrolysis.

Eg: (i) Rare earth metal and Cu oxide- adding complexing agent to make the rate of hydrolysis equal to gel homogeneous gel.

(ii) $Zn(OC_3H_7)_4$ and $Ti(OCH(OCH_3)_4)$- Acetic acid is added as complexing agent to get optically active ZnO_2 and TiO_2 gel

Case 2: Both $A(OR)_2$ and $B(OR^l)_4$ stoichiometry

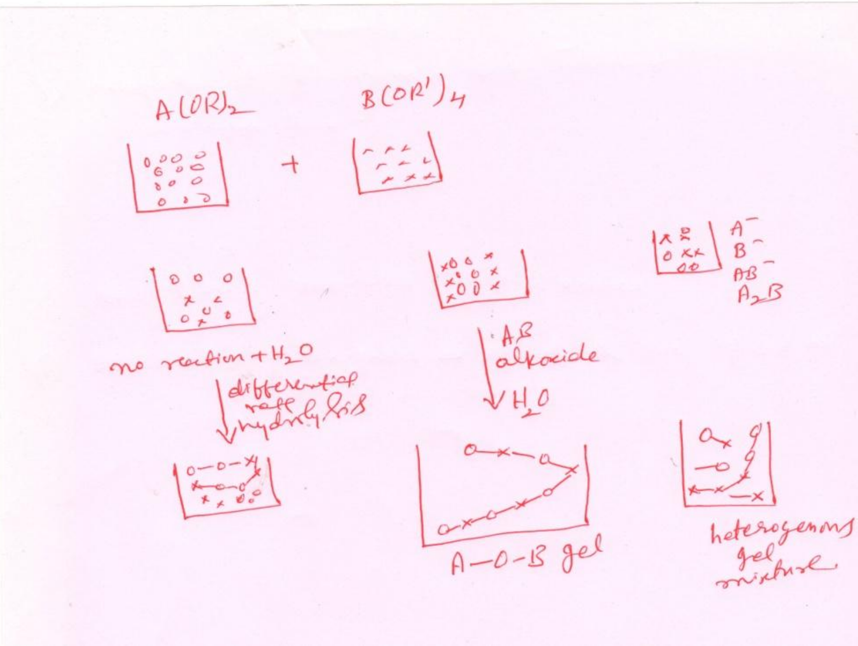
$A(OR)_2 + B(OR^l)_4 \rightarrow AB\,(OR)_2(OR^l)_4$

It acts as a single molecule. Therefore on hydrolysis and poly condensation, it gives very fine homogeneous –A-O-B- polymeric gel.

Eg: $BaTiO_3$, $LiNbO_3$

Case 3: Here mixture of diff molecular species AB^-, AB_2^-, A_2B (non- stoichiometry) are formed in precursor solution.

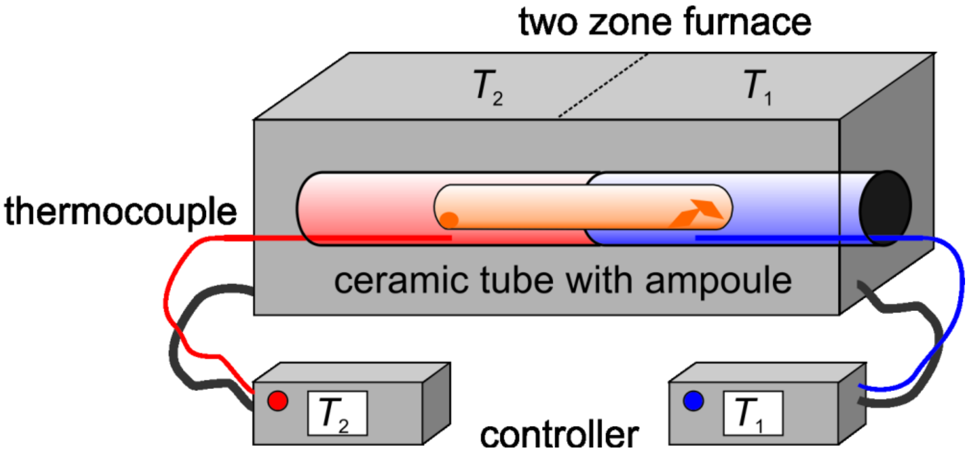
Eg: In this case resulting gel is heterogeneous



13.18.10 Chemical vapor transporter (CVT) method

This method is best suited to synthesize CNT. The graphite pellet containing catalyst (ni, Co) is placed in the middle of quartz tube filled with some inert gas This quartz tube is placed in an oven heated at 1200^0c. Then it is sublimed and deposited as ‘soot’ on conical water cold copper collector and quartz tube wall

This method mainly depends on temperature and catalyst. If the experiment is carried out without catalyst, then multi walled nano tubes are obtained. If catalyst (Ni, Co) is used with graphite pellet, then because of good absorption, composition dissolution, disassociation, diffusion of carbon species and then precipitation of solid CNT (SWNT) is enhanced. Similarly, the quality and structure of CNT is best obtained at 1200^0c



13.18.11 Electrochemical synthesis of metal oxide nanoparticles

An electrochemical synthesis is achieved by passing an electric current between two or more electrodes separated by an electrolyte. By definition, the synthesis takes place at the electrode – electrolyte interface.

Below are listed several features which distinguish electrochemical synthesis from other synthetic methods:

- Electrochemical synthesis takes place close to the electrode within the electric double layer, which has a very high potential gradient of 10^2V cm^{-1}.
- The product is deposited on the electrode in the form of a thin film or coating. Further, a solid-liquid interface facilitates the growth of conformal coatings on substrates of any shape, especially if a suitably shaped counter electrode is employed to provide uniform polarization.
- Electrochemical synthesis is a low-temperature technique limited by the boiling point of the electrolyte.
- Kinetic control can be exercised by controlling the current passed through the cell, while thermodynamic control can be exercised by choosing the applied cell potential.
- An electrochemical synthesis is an oxidation or a reduction reaction. By fine-tuning the applied cell potential, the oxidizing or reducing power can be continuously varied and suitably selected- a luxury not afforded by chemical synthesis.

- The experiments are simple to perform and the instruments are inexpensive and readily available.
- The unique features of electrosynthesis eminently qualify it to join the ranks of “chimie douce” techniques.
- The rate of electrochemical reaction is not same for all the metals, e.g., as the oxidation potential of Zn and Ru are different. The rate of dissolution for Zn (-0.716 V) is faster than Ru (+0.1 V).

13.19 Summary of the unit

Nanoparticles are the simplest form of structures with sizes in the nm range. In principle any collection of atoms bonded together with a structural radius of < 100 nm can be considered a nanoparticle. These can include, e.g., fullerens, metal clusters (agglomerates of metal atoms), large molecules, such as proteins, and even hydrogen-bonded assemblies of water molecules, which exist in water at ambient temperatures. Nanoparticles are very commonplace in nature, for instance proteins exist in almost all biological systems, metal-oxide nanoparticles are easily produced, etc. Engineered nanoparticles are intentionally designed and created with physical properties tailored to meet the needs of specific applications. They can be end products in and of themselves, as in the case of quantum dots or pharmaceutical drugs, or they can be components later incorporated into separate end products, such as carbon black in rubber products, shown in Figure 1. Either way, the particle’s physical properties are extremely important to their performance and the performance of any product into which they are ultimately incorporated.

13.20 Key words

Nano meter scale; Nano particles or nano material; Zero-dimensional nanomaterials; One-dimensional nanomaterials; Two-dimensional nanomaterials; Three-dimensional nanomaterials; Nano wires; Nanorods; Nanotube; Carbon Nanotubes; Multi-walled carbon nanotubes (MWNT) ; Graphene; Attrition method; Pyrolysis method ; Top-Down approach

Bottom up approach; Hydrothermal method; Sol-gel method; Metal alkoxide route; Multi component gel; Chemical vapor transporter (CVT) method; Electrochemical synthesis of metal oxide nanoparticles

13.21 References for further studies

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13.22 Questions for self understanding

1) With example compare the nano meter scale and micrometer scale objects?

2) What are nano particles or nano material?

3) What are zero-dimensional nanomaterials?

4) What are nne-dimensional nanomaterials?

5) What are two-dimensional nanomaterials?

6) What are three-dimensional nanomaterials?

7) Discuss the ddvantages of nanosize materials.

8) What the properties changes that smaller size of the nanoparticles associated?

9) What are nano wires?

10) What are nanorods?

11) What are nanotubes

12) Write a note on carbon nanotubes.

13) Differentiate between single- walled carbon nanotubes and multi-walled carbon nanotubes?

14) What is Graphene?

15) Explain the synthesis of nanocomposites by pttrition method.

16) Explain the synthesis of nanocomposites by pyrolysis method.

17) Explain the synthesis of nanocomposites by top-down approach.

18) Explain the synthesis of nanocomposites by bottom up approach.

19) Explain the differences in bottom-up vs top-down approach of nanopartical synthesis.

20) Explain the synthesis of nanocomposites by hydrothermal method.

21) Explain the synthesis of nanocomposites by sol-gel method.

22) Explain the synthesis of nanocomposites by metal alkoxide route.

23) Explain the synthesis of nanocomposites by multi component gel method.

24) Explain the synthesis of nanocomposites by chemical vapor transporter (CVT) method.

25) Explain the synthesis of nanocomposites by electrochemical synthesis of metal oxide nanoparticles.

UNIT-14

Structure

14.0 Objectives of the unit

After studying this unit you are able to

- Explain the sol-gel synthesis of ZrO_2 and SeO_2 nanoparticles
- Explain the synthesis of ZnO Nanoparticles by electrochemical method
- Explain the synthesis of Niobium doped ZnO Nanocomposites by electrochemical method
- Explain the synthesis with super critical water and precursor method
- Explain the advantages of hydrothermal method
- Explain the synthesis of TiO_2 nanoparticales
  Explain the synthesis of ZnO nanoparticales
- Explain the LASER ablation method

14.1 Introduction

Metal oxides play a very important role in many areas of chemistry, physics and materials science. The metal elements are able to form a large diversity of oxide compounds. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts. In the emerging field of nanotechnology, a goal is to make nanostructures or nanoarrays with special properties with respect to those of bulk or single particle species. Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites. Particle size is expected to influence three important groups of basic properties in any material. The first one comprises the structural characteristics, namely the lattice symmetry and cell parameters. Bulk oxides are usually robust and stable systems with well-defined crystallographic structures. However, the growing importance of surface free energy and stress with decreasing particle size must be considered. Changes in thermodynamic stability associate with size can induce modification of cell parameters and/or structural transformations and in extreme cases the nanoparticle can disappear due to interactions with its surrounding environment and a high surface free energy. In order to display mechanical or structural stability, a nanoparticle must have a low surface free energy. As a consequence of this requirement, phases that have a low stability in bulk materials can become very stable in nanostructures. This structural phenomenon has been detected in TiO_2, VO_x, Al_2O_3 or MoO_x oxides.

14.2 Synthesis of nanoparticulated oxides

The first requirement of any novel study of nanoparticulated oxides is the synthesis of the material. The development of systematic studies for the synthesis of oxide nanoparticles is a current challenge and, essentially, the corresponding preparation methods may be grouped in two main streams based upon the liquid-solid and gas-solid nature of the transformations. Liquid-solid transformations are possibly the most broadly used in order to control morphological characterstics with certain “chemical” versatility and usually follow a “bottom-up” approach. A number of specific methods have been developed, among which those broadly in use are

1) Co-precipitation methods

This involves dissolving a salt precursor (chloride, nitrate, etc.) in water (or other solvent) to precipitate the oxo-hydroxide form with the help of a base. Very often, control of size and chemical homogeneity in the case of mixed-metal oxides are difficult to achieve. However, the use of surfactants, sonochemical methods, and high-gravity reactive precipitation appear as novel and viable alternatives to optimize the resulting solid morphological characteristics.

2) Sol-gel processing

The method prepares metal oxides via hydrolysis of precursors, usually alcoxides in alcoholic solution, resulting in the corresponding oxo-hydroxide. Condensation of molecules by giving off water leads to the formation of a network of the metal hydroxide: Hydroxyl-species undergo polymerization by condensation and form a dense porous gel. Appropriate drying and calcinations lead to ultrafine porous oxides.

3) Microemulsion technique

Microemulsion or direct/inverse micelles represent an approach based on the formation of micro/nano-reaction vessels under a ternary mixture containing water, a surfactant and oil. Metal precursors on water will precede precipitation as oxo-hydroxides within the aqueous droplets, typically leading to monodispersed materials with size limited by the surfactant-hydroxide contact.

4) Solvothermal methods

In this case, metal complexes are decomposed thermically either by boiling in an inert atmosphere or using an autoclave with the help of pressure. A suitable surfactant agent is usually added to the reaction media to control particle size growth and limit agglomeration.

5) Template/Surface derivatized methods

Template techniques are common to some of the previous mentioned methods and use two types of tools; soft-templates (surfactants) and hard-templates (porous solids as carbon or silica). Template- and surface-mediated nanoparticles precursors have been used to synthesize self-assembly systems. Gas-solid transformation methods with broad use in the context of ultrafine oxide powder synthesis are restricted to chemical vapor deposition (CVD) and pulsed laser deposition (PLD).

6) There are a number of CVD processes used for the formation of nanoparticles among which we can highlight the classical (thermally activated/pydrolytic), metalorganic, plasma-assisted, and photo CVD methodologies.

The advantages of this methodology consist of producing uniform, pure and reproduce nanoparticles and films although requires a careful initial setting up of the experimental parameters.

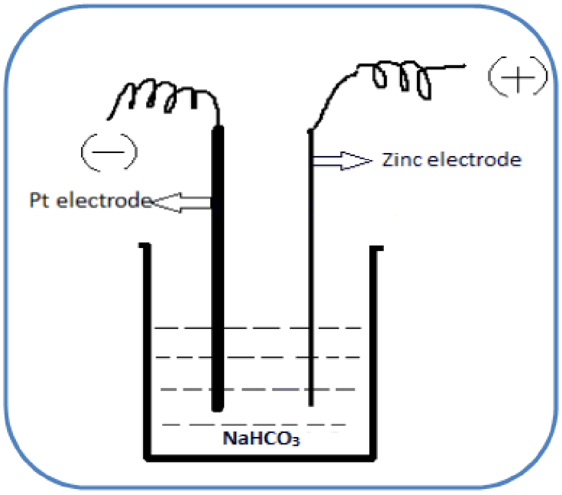
7) Multiple-pulsed laser deposition heats a target sample (4000 K) and leads to instantaneous evaporation, ionization, and decomposition, with subsequent mixing of desired atoms. The gaseous entities formed absorb radiation energy from subsequent pulses and acquire kinetic energy perpendicularly to the target to be deposited in a substrate generally heated to allow crystalline growth.

14.3 Sol-gel synthesis of ZrO_2 and SeO_2 nanoparticles

Zirconium oxide (ZrO_2) and Selenium oxide (SeO_2) nanoparticles were prepared by sol-gel method at room temperature. In this method metal chloride and solvent were used as starting materials. First required concentration of metal chloride solution was prepared by dissolving known amount of metal chloride in 25 ml of water. The solution was stirred at room temperature, and then the 3 ml of 5% ethylene glycol was added to the solution and again stirred for 3 hour at room temperature. The precursor ethylene glycol takes care for the homogeneity and pH value of the solution and helps to make a stoichiometric solution to get ZrO_2 and SeO_2 nanoparticles. Then the residue was filtered, washed with water and then dried at 353 K for an hour. The dried residue then calcined at 673 K in an electric oven to get homogeneous ZrO_2 and SeO_2 nanoparticles.

14.4 Synthesis of ZnO Nanoparticles by electrochemical method

In this method a Zinc rod is taken as anode and platinum electrode as cathode. The preparation of ZnO nanoparticles were carried in a reaction chamber containing 20ml of $NaHCO_3$ solution. A certain definite amount of current (10A- 50A) is passed through the electrochemical cell at constant potential. The experiment was run for a definite time at constant temperature. The anodic dissolution of Zn gives Zn (II) ions which are electrochemically reacted with aqueous $NaHCO_3$ to form Zn(II) oxides/hydroxide.

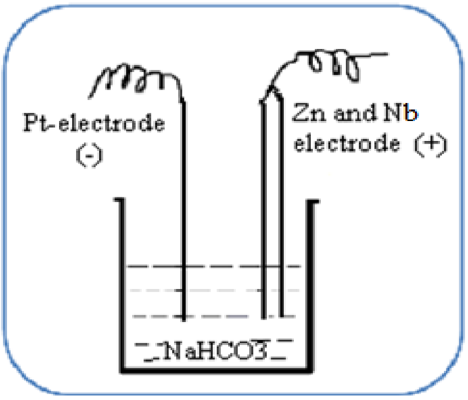


The wet powder was then dried at a temperature 750^0C-800^0C for dehydration and removal of hydroxides to get ZnO. Hence the product would be ZnO nanoparticle oxide. The electrochemical reaction takes place according to the following mechanism

$$\begin{aligned}
Zn &\rightleftharpoons Zn^{2+} + 2e^- \\
2NaHCO_3 + 2e^- &\rightleftharpoons 2CO_2 + 2Na + 2OH^- \\
Zn^{2+} + 2OH^- &\rightleftharpoons Zn(OH)_2 \\
Zn(OH)_2 &\rightleftharpoons ZnO + H_2O \\
Zn + 2NaHCO_3 &\rightleftharpoons ZnO + 2CO_2 + 2Na + H_2O
\end{aligned}$$

14.5 Synthesis of Niobium doped ZnO Nanocomposites by electrochemical method

In this method a thin film of niobium was deposited electrochemically on a platinum electrode (Pt/Nb) from niobium chloride solution (0.1M). The preparation of ZnO/Nb_2O_5 nanoparticles were carried in a reaction chamber containing 20ml of $NaHCO_3$ solution. (Pt/Nb) electrode/Zinc wire as anode and Pt electrode as cathode were used. The experiment was run until the complete dissolution of niobium from the platinum electrode surface at constant temperature. The anodic dissolution of Zn and Nb gives Zn (II) and Nb(V) ions which are electrochemically reacted with aqueous $NaHCO_3$ to form Zn(II) oxides/hydroxide with Nb(V) oxide.



The wet powder was then dried at a temperature 250^0C-400^0C for dehydration and removal of hydroxides to get ZnO/Nb_2O_5. Since the dissolution potential for Nb is more negative than Zn, it is expected that the formation of Nb_2O_5 takes place in competition with the formation of ZnO. Hence the product would be ZnO/Nb_2O_5 nanoparticle oxide. The electrochemical reaction takes place according to the following mechanism

$$Zn \rightleftharpoons Zn^{2+} + 2\bar{e}$$

$$2NaHCO_3 + 2e^- \rightleftharpoons 2CO_2 + 2Na + 2OH^-$$

$$Zn^{2+} + 2OH^- \rightleftharpoons Zn(OH)_2$$

$$Zn(OH)_2 \rightleftharpoons ZnO + H_2O$$

$$Zn + 2NaHCO_3 \rightleftharpoons ZnO + 2CO_2 + 2Na + H_2O$$

Similarly, $2Nb + 10NaHCO_3 \rightleftharpoons Nb_2O_5 + 10CO_2 + 10Na + 5H_2O$

The overall reaction is, $Zn + 2Nb \xrightarrow{NaHCO_3} ZnO/Nb_2O_5$

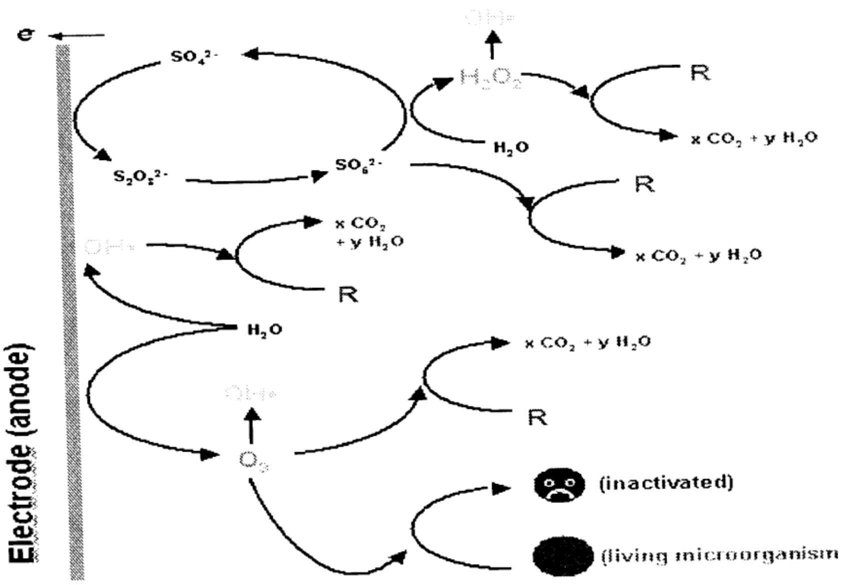
14.6 Synthesis with super critical water and precursor method

Supercritical water (SCW) and supercritical fluids (SCF) provide an excellent reaction medium for hydrothermal processing of nanoparticles, since they allow varying the reaction rate and equilibrium by shifting the dielectric constant and solvent density with respect to pressure and temperature, thus giving higher reaction rates and smaller particles. The reaction products are to be stable in SCF leading to fine particle formation.

Hydrothermal synthesis in supercritical water has advantages for synthesis of multi metal oxide compounds because the reaction rate is enhanced more than 10^3 times that under the conventional hydrothermal conditions owing to the low dielectric constant (<10) as well as products with high crystallinity. The particle size of metal oxide depends on the hydrolysis rate and solubility of the metal oxide. To achieve the control of the solvent field during nucleation and crystallization of particles, hydrothermal conditions of temperature and pressure can be varied in subcritical and supercritical water. Hydrothermal methods for preparing fine metal oxide particles in subcritical and supercritical water have been developed using batch reaction and flow reaction systems.

The temperature is maintained at 374^oC and pressure is 200 atm. This leads drastic change in density of H_2O and dielectric properties and produce strong oxidizing species which destroys organic moiety and useful to separate inorganic ions.

Generation of mixed oxidant



Efficient generation of mixed oxidant

The above reaction mechanism shows the different radicals produced acts as a very good oxidising or reducing agents for the degradation of waste water and for the synthesis of nanomaterials.

The hydrothermal technique is ideal for the processing of very fine powders having high purity, controlled stoichiometry, high quality, narrow particle size distribution, controlled morphology, uniformity, less defects, dense particles, high crystallinity, excellent reproducibility, controlled microstructure, high reactivity with ease of sintering and so on.

Further, the technique facilitates issues like energy saving, the use of larger volume equipment, better nucleation control, avoidance of pollution, higher dispersion, higher rates of reaction, better shape control, and lower temperature operations in the presence of the solvent.

Synthesis of fine metal oxide particles continuously can be achieved using supercritical water as the reacting medium. Fine metal oxide particles are formed when a variety of metal nitrates are contacted with supercritical water in a flow system. The fine particles were produced because supercritical water causes the metal hydroxides to rapidly dehydrate before significant growth takes place. The two overall reactions that lead from metal salts to metal oxides are hydrolysis and dehydration is shown below

$$M(NO_3)_x + xH_2O = M(OH)_x + xHNO_3 \text{ --------------- } (1)$$

$$M(OH)_x = MO_{x/2} + x/2\, H_2O \text{ ---------------- } (2)$$

Processing in SCW increases the rate of dehydration such that this step occurs while the particle size is small and the reaction rate is less affected by diffusion through the particle. Furthermore, the gas-like viscosity and diffusivity of water in the critical region lead to a negligible mass transfer limitation. The net effect is that the overall synthesis rate is very large. The high temperature also contributes to the high reaction rate. Several metal oxides including α-Fe_2O_3, Fe_3O_4, Co_3O_4, NiO, ZrO_2, CeO_2, $LiCoO_2$, a-$NiFe_2O_4$, Ce1xZrxO_2, etc. have been prepared through this technique.

14.7 Advantages of hydrothermal method

The hydrothermal method has many advantages e a highly homogeneous crystalline product can be obtained directly at a relatively lower reaction temperature (<150 ^{0}C); it favors a decrease in agglomeration between particles, narrow particles size distribution, phase homogeneity, and controlled particle morphology; it also offers a uniform composition, purity of the product, monodispersed particles, control over the shape and size of the particles, and so on. Hydrothermal synthesis of TiO_2 particles influenced by various parameters like temperature, experimental duration, pressure (percentage fill), solvent type, pH, and the starting charge on the resultant product.

14.8 Synthesis of TiO_2 nanoparticales

The synthesis of TiO_2 is usually carried out in small autoclaves of the Morey type, provided with Teflon liners. The conditions selected for the synthesis of TiO_2 particles are: T = < 200 ^{0}C,P < 100 bars. Such pressure temperature conditions facilitate the use of autoclaves of simple design provided with Teflon liners. The use of Teflon liners helps to obtain pure and homogeneous TiO_2 particles. Though the experimental temperature is low ~150^{0}C, TiO_2 particles with a high degree of crystallinity and desired size and shape could be achieved through a systematic understanding of the hydrothermal chemistry of the media. Several solvents like NaOH, KOH, HCl, HNO_3, HCOOH and H_2SO_4 were treated as mineralizers and it was found that HNO_3 was a better mineralizer for obtaining monodispersed nanoparticles of titania with homogeneous composition under the present experimental conditions.

14.9 Synthesis of ZnO nanoparticales

ZnO is a promising material of photonics because of its wide bandgap of 3.37 eV and high exciton binding energy of 60 meV. The wide bandgap makes ZnO a suitable material for short wavelength photonic applications while the high exciton binding energy allows efficient exciton recombination at room temperature

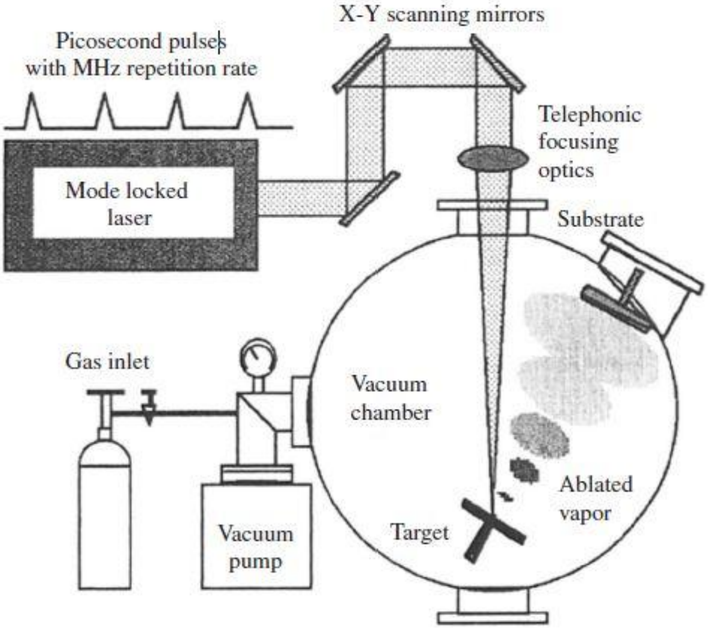
A typical hydrothermal experimental run to synthesize ZnO particles is given below.

One can use various Zn sources along with different mineralizers and additives. The experiments can be carried out within a temperature range, 100-250^{0}C. The Zn source, solvent, pH, experimental temperature and the additives control the size and shape of the particles.

A required amount of $ZnCl_2$ was taken in a Teflon liner the mineralizer solution was added to it and they were then placed inside a reactor. The reactor assembly was then placed inside the furnace and the temperature of the furnace was set to a desired temperature. After the experimental run for a particular duration (5-50 h), the reactor was quenched with an air jet and cold water and the liner was taken out. The resultant product inside the liner was separated from the solution and then rinsed with HCl (0.1 M) (when alkaline solvents are used) and NaOH (0.1 M) (when acidic solvents are used) to remove any residual alkalinity/acidity in the product and thoroughly washed with double distilled water. The product was finally dried at 35-40 ^{0}C in a dust proof environment.

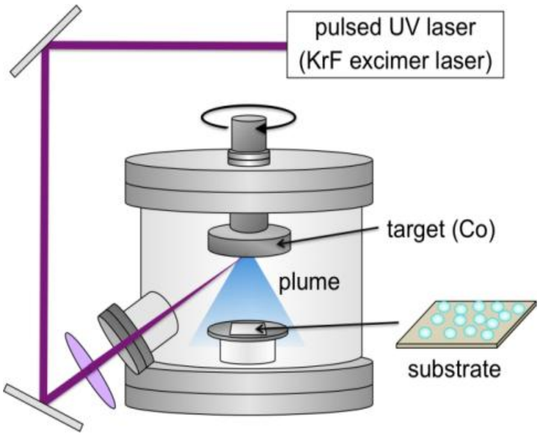
14.10 LASER ablation method

Laser ablation means the removal of material from a surface by means of laser irradiation. The term “laser ablation” is used to emphasize the nonequilibrium vapor/plasma conditions created at the surface by intense laser pulse, to distinguish from “laser evaporation,” which is heating and evaporation of material in condition of thermodynamic equilibrium. A typical schematic diagram of laser ablation is shown in the following figure.



There are two essential parts in the laser ablation device, a pulsed laser (CO_2 laser, Nd-YAG laser, ArF excimer laser, or XeCl excimer laser) and an ablation chamber. The high power of the laser beam induces large light absorption on the surface of target, which makes temperature of the absorbing material increase rapidly. As a result, the material on the surface of target vaporizes into laser plume. In some cases, the vaporized materials condensate into cluster and particle without any chemical reaction. In some other cases, the vaporized material reacts with introduced reactants to form new materials. The condensed particle will be either deposited on a substrate or collected through a filter system consisting of a glass fiber mesh. Then, the collected nanoparticle can be coated on a substrate through drop-coating or screen-printing process.

This method is best suited to synthesize CNT. The graphite pellet containing catalyst (Ni, Co) is placed in the middle of quartz tube filled with some inert gas. This quartz tube is placed in an oven heated at 1200 ^{0}C. Pulse of LASER beam interacts with graphite so that the energy of LASER beam vaporizes graphite by bombarding its surface then carbon species swept on carrier by flow of inert gas. Then it is sublimed and deposited as ‘soot’ on conical water cold copper collector and quartz tube wall. SWNT is obtained in the presence of the catalyst, otherwise if catalyst is not used MWNT is produced. The CNT can be synthesized by using different organic compounds like benzene, toluene, hexane etc and organic compounds containing plant extracts. The quality of the CNT depends upon the nature of catalyst, substrate (organic compound) and energy of the LASER.



14.11 Summary of the unit

Irrespective of the preparation method use to obtain ultrafine nano-oxides, the studies of nanoparticle preparation yielded compelling evidence concerning the fact that crystallization does not follow a traditional nucleation and growth mechanism. Although subjected to further assessment, it appears that the simple idea that a small primary size would prime nucleation as the key step of crystallization seems essentially correct and holds certain general validity, at least in solid-solid crystallization mechanisms (e.g. heating of oxo-hydroxides to form oxides). When additional liquid/gas phase crystallization steps are involved in the final formation of the nanoparticle (e.g. as in solvothermal methods), other steps like Ostwald ripening may be also of prime importance. In any case, a lot of novel insights have been recently uncover in solid-solid transformations and two main theories describe crystallization to proceed either by surface (single particle) and/or interface (two or multiple particle) nucleation. The primacy of one of them has been postulated to be a function of the oxide chemical nature and temperature, being presumably surface effects always predominant at higher temperatures. Both theories mostly received support from kinetic approaches but very recent analyses sensitive to structural order in the amorphous precursor materials have demonstrated the key role of intraparticle local order (below 1 nm) in driving the nucleation temperature onset in a broad interval of ca. 200 K, showing that the whole crystallization mechanism of oxide nanoparticles appears only compatible with some kind of intraparticle, dimensional-restricted ("surface") mechanism.

14.12 Key words

Sol-gel synthesis; ZrO_2 and SeO_2 nanoparticles; ZnO nanoparticles; Electrochemical method; Niobium doped ZnO Nanocomposites; Super critical water; TiO_2 nanoparticales; ZnO nanoparticales

LASER ablation method

14.13 References for further studies

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14.14 Questions for self understanding

1) Explain the sol-gel synthesis of ZrO_2 and SeO_2 nano particles.

2) Discuss synthesis of ZnO Nano particles by electrochemical method.

3) Discuss the synthesis of Niobium doped ZnO Nanocomposites by electrochemical method.

4) Write a note on synthesis of nano particles by super critical water method.

5) Explain the advantages of hydrothermal method.

6) Explain the synthesis of TiO_2 nano particles.

7) Explain the synthesis of ZnO nano particles.

8) Discuss the synthesis of nano particles by LASER ablation method.

UNIT-15

Structure

15.0 Objectives of the unit

After studying this unit you are able to

- Explain the role of metal oxide in nanocomposites (TiO_2 and ZnO) as photocatalysts
- Identify the criteria for a photocatalyst
- Explain the charge transfer in metal/metal ion doped semiconductor system
- Explain the photo-degradation of dye and industrial effluents by nano ZnO and TiO_2

15.1 Introduction

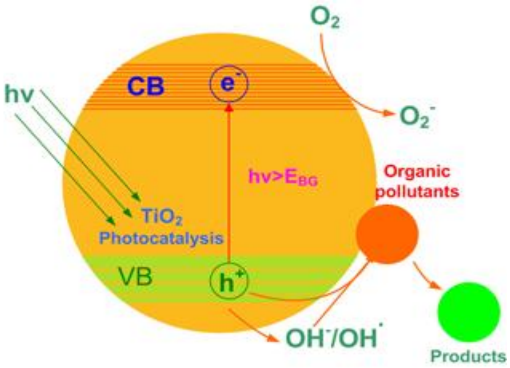
The current knowledge on oxide materials allows affirming that most of their physico-chemical properties display acute size dependence. Physico-chemical properties of special relevance in chemistry are mostly related to the industrial use of oxides as sensors, ceramics, absorbents and/or catalysts. A bunch of novel application within these fields rely on the size-dependence of the optical, (electronic and/or ionic) transport, mechanical and, obviously, surface/chemical (redox, acid/base) properties of oxide nanomaterials. We should stress that size effects in oxide chemistry have frequently two interrelated faces, structural/electronic quantum-size and size-defect or non-stoichiometry effects.

15.2 Metal oxide Nanocomposites (TiO_2 and ZnO) as photocatalysts

The processing of TiO_2 and ZnO nanoparticles occupies a unique place in hydrothermal processing of advanced materials owing to their importance as photocatalysts.

Photocatalysis is a process of decomposition of material upon exposure to radiant energy (light). Photocatalyst absorb UV radiations, which activates their electrons to higher energy level causing

a. Oxidation
b. Cleavage
c. Degradation



Metal oxide nanoparticles such as TiO_2 and ZnO are phtotocatalysts shown to degrade organic dyes to harmless, colourless end products in the presence of sun light/UV light. TiO_2 and ZnO are well studied as photocatalyts because of their high photosensitivity, stability, and large band gap and relatively low cost. Compared to TiO_2, ZnO is advantageous because it absorbs over a large region of the solar spectrum. Further both TiO_2 and ZnO are not environmental hazards and may be used for In situ degradation of organic pollutant.

The mechanism by which photodegradation occurs us a result of semiconductor nanoparticles acting as sensitizers for light-induced redox processes. Photocatalyst absorbs UV light and generates an electron/hole pair by exciting an electron from the valance band into conduction band. The excited electron and corresponding holes then promote chemical reactions that degrade the dye. This is known as an advanced oxidation process (AOP) that generates hydroxyl radicals and destroys pollutants by oxidizing dye molecules. The reaction mechanism for ZnO photocatalysis occurs as follows. Note that similar reaction mechanism also occurs for TiO_2 particlaes.

First a photon generates an electron hole pair

$MS + h\upsilon \rightarrow MS(h^+ + e^-)$ [electron-hole pair formation]

$ZnO + h\upsilon \rightarrow ZnO\ (e^-_{CB} + h^+_{VB})$

$e- + h^+ \rightarrow$ heat recombination

$e^- + M^{n+} \rightarrow M^{(n-1)}$+ reduction

If the photogenerated species does not recombine or dissipate as heat, it will react with nearby oxygen or water molecules to form oxygen and hydroxyl radicals respectively.

$e^-_{CB} + O2 \rightarrow {}^{\cdot}O^-_2$

$h^+ + H_2O_{(ads)} \rightarrow {}^{\cdot}OH + H^+$ oxidation of adsorbed (ads) water

$h^+ + 2\ {}^{\cdot}OH_{(ads)-} \rightarrow {}^{\cdot}OH + OH^-$ oxidation of hydroxide ions

The produced oxygen and hydroxyl radicals are strong oxidizers and will promote oxidation of the organic dyes on the surface, hence the term advanced oxidation process is given to the degradation process. Degradation occurs when the hydroxyl radicals react with dye molecules.

${}^{\cdot}OH + R_{(ads)} \rightarrow {}^{\cdot}R_{(ads)} + H_2O$ organic oxidation

${}^{\cdot}R_{(ads)}\ ({}^{\cdot}OH, {}^{\cdot}R_{(ads)}) \rightarrow$ products termination

where, $h\upsilon$ = light energy, h^+ = hole,

e^- = electron, Mn+ = oxidized compound,

$R^{\cdot}$ (ads) = the adsorbed organic species.

The ${}^{\bullet}OH$, h^+ and e^- which are produced during above mechanism are responsible for the oxidation and degradation of organic compounds to CO_2 and simpler inorganic salts.

The hydroxyl radical is the critical for the degradation process, final degradation of dye intermediates is crucial for environmental safety as the incomplete oxidation leads to intermediates that are often more toxic than the parent dye molecule.

15.3 Criteria for a photocatalyst

An ideal photocatalyst should be stable, inexpensive, non-toxic and, of course, highly photoactive. Another primary criteria for the degradation of organic compounds is that the redox potential of the $H_2O/^oOH$ couple E^0=-2.8V lies within the band gap of the semiconductor

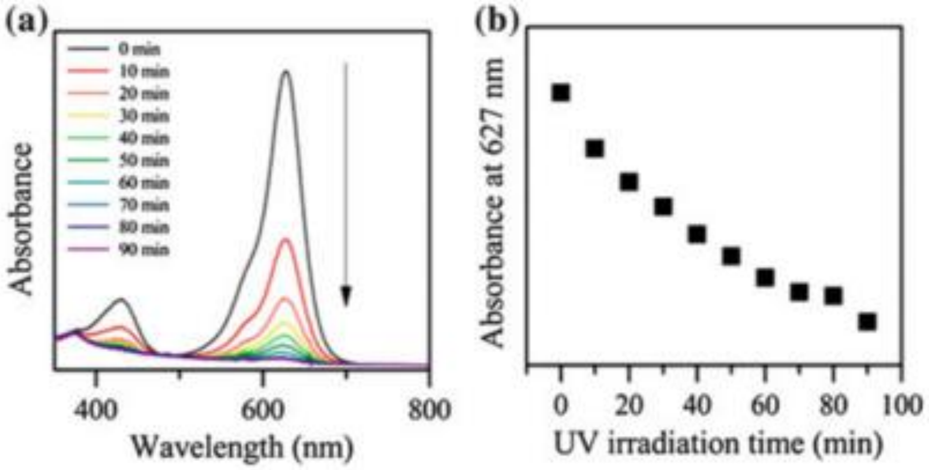
Semiconductors	Bandgap (eV)	Wavelength (nm)
TiO_2	3.0-3.2	413-388
ZnO	3.2	388
ZnS	3.6	335
CdS	2.4	516
Fe_2O_3	2.3	539
WO_3	2.8	443

TiO_2 shows maximum light scattering with virtually no absorption. It is non-toxic and chemically inert. This has been employed extensively in studies of heterogeneous photocatalysis and has been accepted as one of the best photocatalysts for the degradation of environmental contaminants. The process involves the absorption of a photon by TiO_2, leading to the promotion of an electron from the valence band to the conduction band and thus producing an electron hole. The electron in the conduction band is then removed by reaction with O_2 in the outer system; the hole in the valence band can react with ^-OH or H_2O species, which are absorbed on the surface of the TiO_2 to give the hydroxyl radical. This hydroxyl radical initiates the photocatalytic oxidation, a pollution control technology or detoxification technology, which destroys the organic chemical contaminants in air, water, and soil.

The photocatalytic activity of TiO_2 depends upon its crystal structure (anatase, or rutile), surface area, size distribution, porosity, and presence of dopants, surface hydroxyl group density, etc. These factors influence directly the production of electronehole pairs, the surface adsorption and desorption process and the redox process. TiO_2 is also used as a photoanode in photoelectrochemical solar cells.

Experimentally, observing degradation of organic dyes is quite simple. Organic dyes hav high molar absorbtivities and form brightly coloured solutions. A traditional experiment involves introducing a known amount of catalyst particles to a solution having a fixed dye concentration. The solution is then stirred under dark conditions to allow for all of the dye molecules to adsorb to the semiconductor particles surface. Then the solution is irradiated using either a UV or solar light source. At specific time points, aliquots are removed and analyzed by UV-Visible spectroscopy, which are used to determine the rate of degradation. It is important to note that solutions are stirred magnetically during the entire photodegradation process.

Below figure shows the degradation of malachite green in the presence of ZnO nanoparticles. Malachite green shows a strong absorption peak at 627nm. As the solution is exposed to UV light irradiation, the intensity of this peak decreases. The decolouration of the solution, which is easily observable by UV-Visible spectroscopy indicates degradation of malachite green in to benign products. As irradiation time increases, the degradation of dye also increases. Degradation kinetics are easily followed by plotting absorbance intensity of the dye peak is as a function of time.



a) Absorbance e spectra of malachite green oxidized in the presence of ZnO nanoparticles with respect to UV irradiation time. b) Absorbance intensity of malachite green at 627nm plotted as a function of UV irradiation time. (ZnO acts as a photocatalyst)

15.4 Charge transfer in metal/metal ion doped semiconductor system

Semiconductor-metal nanocomosites have benn widely employed in photocatalysis. The metal in contact with the semiconductor greatly enhances the overall photocatalytic efficiency. The possible role it plays in dictating the interfacial charge transfer processes has yet to been understood fully.

The principal terms involved in a photoactive semiconductor are the conduction band (CB), valance band (VB), bandgap, trap sites and Fermi level.

A semiconductor demonstrates the following processes on photoilluminstion. Light of energy greater than the band gap of the semiconductor excites the electrons from the valence band to the conduction band leaving behind a hole in the valence hand. The electrons (e) and holes (h) are available for carrying out redox activities at the semiconductor surface. Photogenerated e^-/h^+ pairs are also delocalized in the semiconductor. These locations are called trap sites (e_t and h_t). The e^-/h^+ pairs undergo recombination which results in decreasing the efficiency of the semiconductor.

Charge generation, separation, retention and transfer across a semiconductor and its surroundings are greatly affected by size quantization effect. Thus the band gap of the semiconductor will increase with decreasing particle size as evidence of quantum size effect.

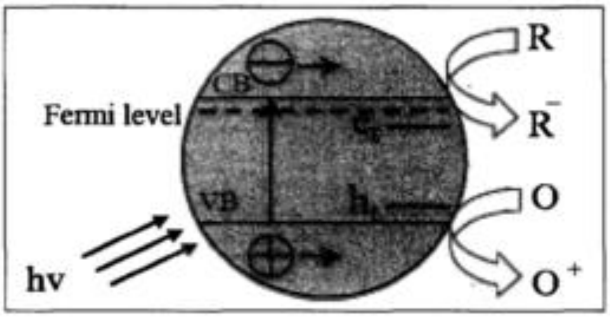
Two major drawbacks of any individual large bandgap semiconductor have been identified as

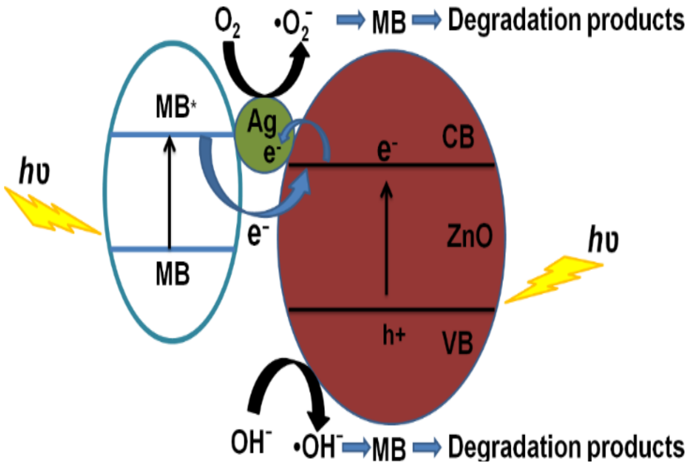
i) Recombination of photogenerated charge (electrons and holes) and

ii) Limited light harvesting ability.

These factors limit economical usage of the semiconductor. The former can be minimized by using metal on a semiconductor as the metal functions as sink for the electron and decreases recombination.

Mills and Hoffman noted that doping a catalyst with a suitable material can enhance its performance. The noble metal ions act as a sink for photoinduced charge carriers and this promotes interfacial charge-transfer processes. Mills and Hoffman further investigated the TiO_2 nanoparticles doped with metal ionby measuring photoreactivity changes ans transient charge-carrier recombination dynamics. They found that doped TiO_2 activity apperared to be a complex function of dopant concentration, dopant energy levels with the TiO_2 lattice, d-electronic configuration, dopant distribution, electron donor concentration and light intensity.





The above figure explains the effect of doping of a metal ion (Ru, Nb, Se) to ZnO or TiO_2 which gives Nanocomposites of ZnO or TiO_2. These Nanocomposites behave as indirect semiconductor. During this, recombination of h^+ and e^- is very difficult as the excited electron not directly comes back to valence band, but it has to go to intermediate energy level of dopant and then it reaches the valance level. This takes longer time for the recombination of h^+ and e^-. Therefore, the doping increases the concentration of $^{\bullet}OH$ when exposed to the radiation.

15.5 Photo-degradation of dye and industrial effluents by nano ZnO and TiO_2:

Indigo carmine dye solution/ industrial effluent (3×10^{-5} M) was prepared by dissolving in distilled water. This solution was used as a test contaminant for evaluating photocatalytic activities of the prepared ZnO and TiO_2 nanoparticles. The investigation was carried out both under sunlight and UV-light in order to check the efficiency of nanoparticles. To examine the photocatalytic activity, 20 ml of colloidal solution were transferred to centrifuge tube and centrifuged at 800 rpm to remove the dispersed catalyst and the percentage transmittance was recorded for the clear solution using colorimeter. The chemical oxygen demand was recorded both before and after degradation of the dye using dichromate oxidation method. Adsorption and the photocatalytic conversion (g %) was calculated as follows:

$$COD = \frac{8000\,(vol\ of\ FAS\ in\ blank - vol\ of\ FAS\ in\ dye\ soln)\ normality\ of\ FAS}{sample\ volume}$$

The mineralization of dye was measured by the decrease of chemical oxygen demand (COD) of the solution. COD was measured according to the standard dichromate titration method. The mineralization efficiency of dye was estimated by the following expression

$$\%\,efficiency = \frac{final\ COD - initial\ COD}{final\ COD} \times 100$$

The mechanism of photodegradation has been conjectured as seen:

$$Np + h\Upsilon \longrightarrow e^- + h^+$$

$$h^+ + H_2O \longrightarrow OH^\bullet + h^+$$

$$h^+ + OH^- \longrightarrow OH^\bullet$$

$$e^- + O_2 \longrightarrow O_2^{-\bullet}$$

$$O_2^{-\bullet} + H_2O \longrightarrow HO_2^\bullet + OH^\bullet$$

$$HO_2^\bullet + H_2O \longrightarrow OH^\bullet + H_2O$$

$$H_2O_2 \longrightarrow 2OH^\bullet$$

$$OH^\bullet + IC \longrightarrow \text{intermediate products} \longrightarrow \text{Degradation products}$$

$$O_2^{-\bullet} + IC \longrightarrow \text{intermediate products} \longrightarrow CO_2, H_2O, NH_3 \text{ and other degradation products}$$

The photodegradation depends with the concentration of the dye/affluent, pH, temperature, amount of nanomaterials, energy of the light. The optimum condition for the photodegradation can be achived by studying the kinetics of photo-degradation. These nanoparticles produce $^\bullet OH$ which are very strong oxidizing agent compared to other oxidising agents and react with almost all oranic toxic compounds which are present in the industrial affluent and waste water. This technique can be used for the treatment of waste water.

Compound	Organic or effluent treated	Initial COD (mg/l)	Final COD (mg/l)	Photodegradation efficiency (%)
ZnO:Cu	Cibacron brilliant yellow	3989.32	234.12	94.13
	Textile dyeing and printing industrial effluent	2787.12	274.36	68.62
ZnO/MgO	Eosin Yellow	2490.84	392.11	84.25
ZnO:Sn	Rhodamine-B	2987.36	284.23	67.05

ZnO/ZrO_2	Fast green FCF	4252.0	217.2	94.89
	Paper dyeing and printing press effluent	2147.31	257.21	88.02
$Ag\text{-}RuO_2$	Fast green FCF	4252.0	115.9	97.27
	Parathion pesticide	4617.67	394.34	61.14

15.6 Summary of the unit

Metal oxides play a very important role in many areas of chemistry, physics and materials science. The metal elements are able to form a large diversity of oxide compounds. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts. In the emerging field of nanotechnology, a goal is to make nanostructures or nanoarrays with special properties with respect to those of bulk or single particle species. Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites. Particle size is expected to influence three important groups of basic properties in any material. The first one comprises the structural characteristics, namely the lattice symmetry and cell parameters. Bulk oxides are usually robust and stable systems with well-defined crystallographic structures. However, the growing importance of surface free energy and stress with decreasing particle size must be considered: changes in thermodynamic stability associate with size can induce modification of cell parameters and/or structural transformations and in extreme cases the nanoparticle can disappear due to interactions with its surrounding environment and a high surface free energy. In order to display mechanical or structural stability, a nanoparticle must have a low surface free energy. As a consequence of this requirement, phases that have a low stability in bulk materials can become very stable in nanostructures. This structural phenomenon has been detected in TiO_2, VO_x, Al_2O_3 or MoO_x oxides.

15.7 Key words

Photocatalysts; Criteria for a photocatalyst; Charge transfer in metal/metal ion doped semiconductor; Photo-degradation of dye and industrial effluents by nano ZnO and TiO_2.

15.8 References for further studies

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15.9 Questions for self understanding

1) Discuss the metal oxide nanocomposites (TiO_2 and ZnO) as photocatalysts.

2) Explain the criteria for a photocatalyst.

3) Discuss the charge transfer in metal/metal ion doped semiconductor system.

4) Explain the photo-degradation of dye and industrial effluents by nano ZnO and TiO_2.

UNIT-16

Structure

16.0 Objectives of the unit

After studying this unit you are able to

- Explain the structural futures of an aerogels
- Classify the aerogels based on their structure and properties
- Explain the preparation of inorganic nanoporous aerogels
- Explain the preparation of organic nanoporous aerogels
- Explain the synthesis of carbon aerogels
- List out the advantages of aerogels
- Explain the application of nanoparticles in coloured glasses
- Explain the application of nanomaterials for renewable energy
- Explain the biosensors and chemical sensors

16.1 Introduction

Nanoporous materials have gained much attention due to their fundamental importance and potential applications in industrial processes, for example, separation and purification, catalysis, and clean fuel storage. Conventional porous solids having predominant nanoporosity are activated carbons, clay minerals, inorganic gels such as silica gel and activated alumina, and aluminosilicate zeolites.

Originally proposed by Dubinin and now officially adopted by the International Union of Pure and Applied Chemsitry (IUPAC), the pores according to their average width ware classificated into micropores ($w < 2$ nm), mesopores (2 nm $< w <$ 50nm) and macropores ($w > 50$ nm).

Porous solids with the pore width in nanometer regime are high-performance materials. In nanoporous solids, the proportion of surface atoms is great and the surface atoms exhibit different properties compared to the atoms in the bulk. Hence, it is expected that nanoporous solids give rise to unique chemical effects that form the basis for their applications. In recent years, the synthesis of nanoporous solids has received much attention, and the important methods to fabricate their pore structures have been proposed recently, such as colloidal silica imprinting, microbead patterning and presynthesized mesoporous silica scaffolding. At the very forefront of these fields, ordered mesoporous carbon, ordered microporous carbon and uniform mesoporous zeolites have been synthesized.

16.2 Aerogels

Aerogels are solids with high porosity (<100 nm) and hence possess extremely low density (~0.003 g/cm^3) and very low conductivity (~10 mW/mK). In recent years, aerogels have attracted more and more attention due to their surprising properties and their existing and potential applications in wide range of technological areas.

As per IUPAC, aerogel is defined as a gel comprised of a microporous solid in which dispersed phase is a gas. Aegerter et al. defined aerogels as gels in which the liquid has been replaced with air, with very moderate shrinkage of a solid network. Aerogel is basically a synthetic porous ultralight material derived from a gel, in which the liquid component of the gel has been replaced with a gas; for example, graphene aerogels are so light that they can rest on top of a grass leaf. The combination of high porosity and extremely small pores provides aerogels with their extreme properties: solid with extremely low density and low thermal conductivity. Aerogels are sometimes also known by different names such as frozen smoke, solid smoke, solid air, or blue smoke owing to translucent nature and the way light scatters in the material. Typical structure of an aerogel is shown in below Figure 1.

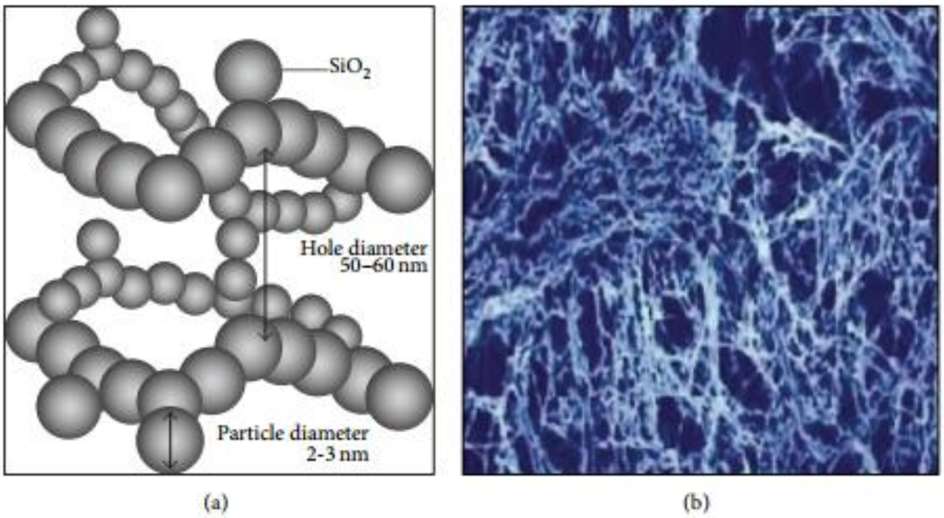


Figure 1: Nanometer scale particles and pores in an aerogel. (a) Network architecture of an aerogel. (b) Electron micrograph of a silica aerogel

16.3 Classification of Aerogels

Aerogels can be classified on the basis of the following.

a) On the basis of appearance

- i) Monolith
- ii) Powder
- iii) Film/felts

b) On the basis of preparation methods

- i) Aerogel
- ii) Xerogel
- iii) Cryogel

iv) Other aerogel-related materials

c) On the basis of different microstructures

i) Microporous aerogel (< 2 nm)

ii) Mesoporous aerogel (2-50 nm)

iii) Mixed porous aerogel

d) On the basis of chemical structure

i) Oxides

ii) Polymers

iii) Mixed

iv) Hybrid

v) Composite.

16.4 Preparation of inorganic nanoporous aerogels

Different type of aerogels can be prepared using alumina chromium, tin oxide, and carbon, but preparation of silica based aerogel is comparatively easier and reliable. Aerogels are synthesized via a sol-gel process consisting of three main steps as shown in figure 2.

1) *Gel Preparation*

Solid nanoparticles grow crosslink and finally form a three-dimensional solid network with solvent filled pores. To begin with a gel is created in solution and then the liquid is carefully removed to leave the aerogel intact; initially the creation of a colloidal suspension of solid particles known as a “sol” takes place; for example, silica gels are synthesized by hydrolyzing monomeric tetrafunctional and trifunctional silicon alkoxide precursors employing a mineral acid or a base as a catalyst. There are many ways to create silica based sol gels. One is by mixing tetraethoxysilane $Si(OC_2H5)_4$ with ethanol and water to make it polymerize and thus producing a water based silica gel as shown in below equation. A solvent, such as methanol, is used to extract and replace the water

$$Si(OCH_2C_3)_4\,(liq.) + 2H_2\,(liq.) \rightarrow SiO_2\,(solid) + CH_2CH_3OH\,(liq.)$$

2) *Aging of the Gel*

It provides strength to the structure of gel. The gel prepared earlier is aged in its mother solution. This aging process strengthens the gel, so that minimum shrinkage occurs during the drying step. After gelification, the gel is left undisturbed in the solvent to complete the reaction. After completion of reaction the aerogel product is formed. Inorganic aerogels can be prepared via sol-gel processing, a technique which requires alkoxides or metal salts in alcoholic or aqueous solutions, and subjecting to supercritical drying.

3) *Drying*

The solvent has to be removed whilst preserving the solid aerogel network. This can be done either by supercritical drying or at ambient conditions. Aerogel materials are typically prepared by removing the solvent contained in a gel matrix by extraction in a supercritical fluid medium. This can be accomplished by bringing the gel solvent system above its critical temperature and pressure and subsequently relieving pressure above the critical temperature until only vapor remains.

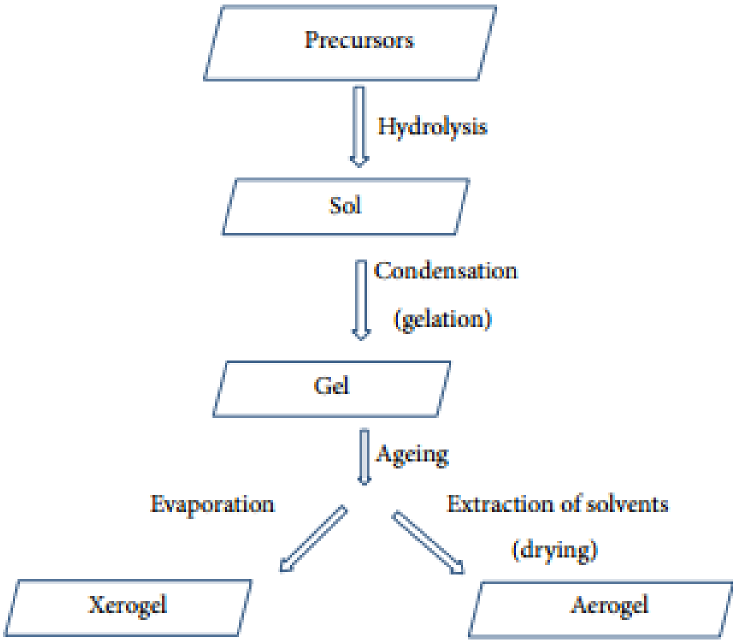


Figure 2: Distinct step of aerogel production

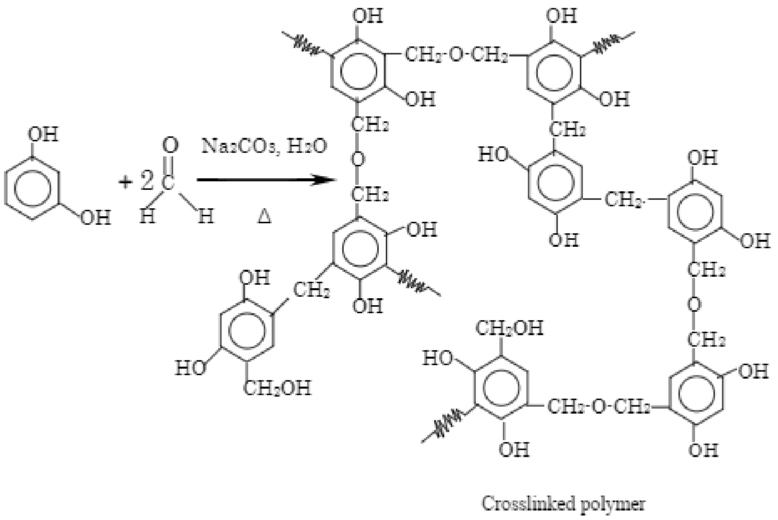
Alternatively, the gel solvent system can be extracted from the wet gel with an appropriate solvent. Liquid carbon dioxide is the most popular extraction solvent because it is inexpensive and has a relatively low critical temperature and critical pressure

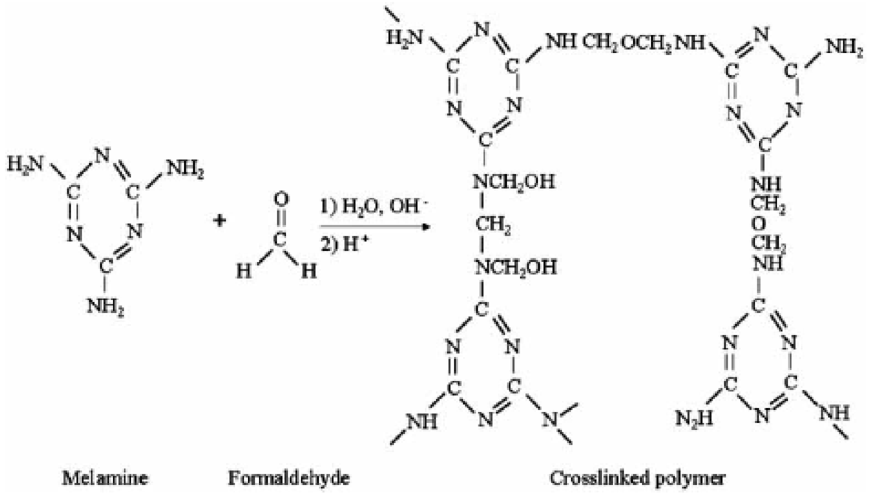
16.5 Preparation of organic nanoporous aerogels

Organic aerogels are generally prepared from a so-called sol-gel polymerization followed by supercritical drying to remove liquid from the dlicate gel structure without collapse or shrinkage. Organic aerogels have been synthesized from the systems of resorcinol–formaldehyde, melamine-formaldehyde, phenolic-furfural, polyurethane-dichloromethane, cresol-formaldehyde, phloroglucinol-formal-dehyde, epoxy-amine, diamine-aromatic dianhydride, 1,3-dimethoxybenzene or 1,3,5-trimethoxyben-zene-formaldehyde, hydroxylated benzene derivatives-alkyl or aryl aldehydes, etc…..

Figure 1 outlines the resorcinol-formaldehyde reaction and depicts the formation of a crosslinked polymer network. Variables, such as reactant ratio, pH, and temperature, influence the cross-linking chemistry and growth process that take place prior to gelation.

The size and number of resorcinol-formaldehyde clusters generated during the polymerization are controlled by the resorcinol/catalyst ratio in a formulation, thus the nanostructures can be controlled by the chemical reactions.





Resorcinol-formaldehyde aerogels was synthesized by Sol-gel polymerization of resorcinol and formaldehyde with sodium carbonate as the base catalyst was performed at 358+3 K for 7 days, the resorcinol-formaldehyde gels were washed by 0.125% trifluoroacetic acid to assist in the further condensation of hydroxymethl groups remaining in the gels to form ether bridges between resorcinol molecules. Multiple exchanges with fresh acetone were used to remove the residual water. Then all acetone was removed from the resorcinol-formaldehyde gels by CO_2 extraction. Dry resorcinolformaldehyde aerogels were lastly obtained by the supercritical drying of resorcinol-formaldehyde gels with CO_2, of which the critical temperature and pressure are 304.1 K and 7.4 MPa. Resorcinol-formaldehyde aerogels are obtained in monolithic form, which are composed of the interconnected beads of diameters smaller than 10 nm and cell sizes less than 100 nm in an open-celled structure.

The aerogel density, transparency and nanoporosity are controlled by varying the reactant concentration of the starting solution. Resorcinol–formaldehyde aerogels are easily produced in the densities of 0.035-0.100 g/cm^3. Melamine-formaldehyde aerogels have the density of 0.1-0.8g/cm^3. These aerogels are transparent. Resorcinol-formaldehyde aerogels are dark red, while melamine-formaldehyde aerogels are colorless.

16.6 Lower Cost Fabrication Pathways

Although aerogels are typically fabricated by subjecting a sol-gel precursor to critical-point-drying in order to remove background liquid without collapsing the network, supercritical drying remains difficult to apply at an industrial scale because of its expensive and potentially dangerous character. Various methods to synthesize these materials in the ways of lower cost have been recently explored. Resorcinol-formaldehyde aerogels can be made using supercritical acetone. The displacement of acetone by CO_2 is no longer necessary, so the process is shortened compared to drying with supercritical CO_2. This technique was suggested to a large scale of production for industrial purposes.

16.7 Synthesis of carbon aerogels

Pyrolyzing organic aerogels such as the resorcinol-formaldehyde aerogels in an inert atmosphere forms vitreous carbon aerogels. Carbon aerogel has a monolith form, a glittering appearance and densities of 0.04-1.3 g/cm^3. The structures and properties of carbon aerogels depend on the agglomerate structures of uniform spherical carbon particles. The individual carbon particle contains an interwoven mesh of microcrystalline platelets with the tiny micropores of ~0.6 nm. Heat treatment has an important effect in increasing the in-plane structural order of the graphene ribbons of the microstructure,

16.8 Structural features

Aerogels have an unusual combination of high porosity and small pore size, making porosity characterization by conventional techniques, such as mercury intrusion, thermoporometry, and nitrogen adsorption/desorption, very difficult. All these techniques are based on the application of capillary pressures on the aerogel network, which may cause large volumetric compressions, leading to incorrect values for pore size and volume. Aerogels are characterized with a very low permeability which can be explained in terms of pore size suitable for transport of water vapours/gases but not for water molecules. Some aerogels such as carbon aerogels can be obtained in the form of monoliths, beads, powders, or thin films and make them promising materials for application in adsorption and catalysis

An aerogel possesses the following characteristics.

1) Property characteristics

  i) Ultralow thermal conductivity

  ii) Ultralow refractive index

  iii) Ultralow dielectric constant

  iv) High surface area

  v) High refractive index

  vi) Ultralow relative density

  vii) Ultrahigh porosity

2) Structure characteristics

  i) Gel-like structure on nanoscale coherent skeletons andpores

  ii) Hierarchical and fractal microstructure

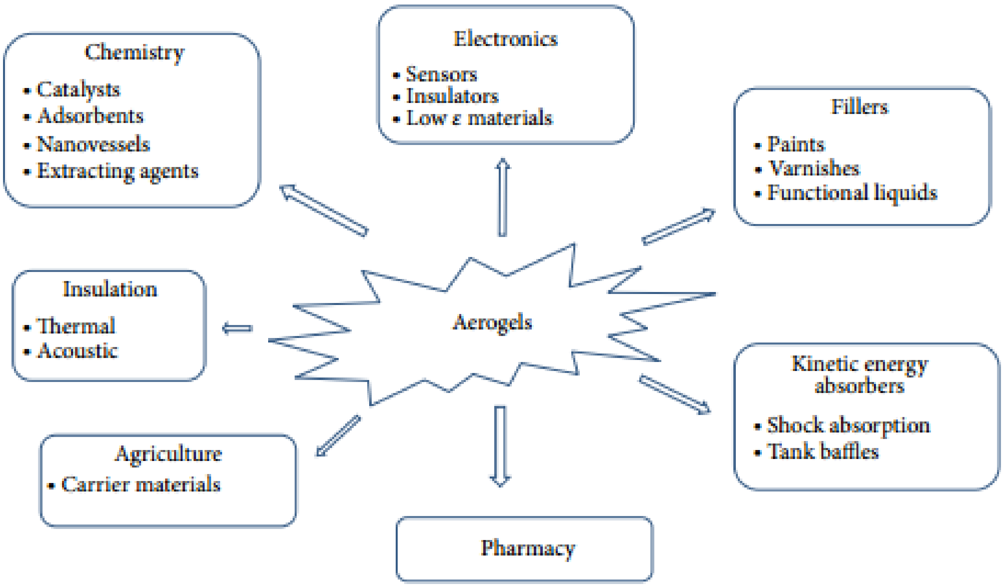
  iii) Macroscopic monolith

  iv) Randomly crosslinking network

  v) Noncrystalline matter

16.9 Advantages of aerogels

Aerogels are regarded as one of the most promising high performance thermal insulation materials for building applications today. With a low thermal conductivity (~13 mW/mK), they show remarkable characteristics compared to traditional thermal insulation materials. Also higher transmittances in the solar spectrum are of great interest for the construction sector. Another advantage of aerogels is their visible transparency for insulation applications which will allow their use in windows and skylights which give architects and engineers the opportunity of reinventing architectural solution.



For example, the low thermal conductivity, a high solar energy, and daylight transmittance in monolithic silica aerogel make it a very interesting material for use in highly energy efficient windows. For cryogenic systems, multilayered insulation (MLI) is the insulation of choice.

Our indoor environments are polluted by releasing many pollutants like chloride from tap-water, VOCs from organic solvents, formalin from furniture and paints, SOx and NOx from incomplete combustion of gasses and many hydrocarbons, and so on. Airborne contaminants are responsible for increasing some respiratory problems and allergies like asthma. The conversion of airborne contaminants into nontoxic compounds is an effective pathway for their removal and to protect our environment. Aerogels can also be used in air purification by removal of airborne contaminants and protect our environment by pollutants. The different applications of aero gels in different area are outlined in figure 3.

16.10 Application of nanoparticles in coloured glasses: Optical properties

Nanoparticles appear certain colors because they reflect (scatter) and absorb specific wavelengths of visible light. When light interacts with a nanoparticle formulation, light is either absorbed or scattered, allowing the light that continues on to reach an observers eye to appear a specific color - often referred to as the “perceived color”. When nanoparticles absorb light, the observer sees the light that is transmitted through the formulation, causing the observer to perceive light that is the opposite color than the absorbed color. For example, small gold nanoparticles absorb blue and green light and red light is transmitted through the material. To the eye of the observer the nanoparticle formulation appears red.

For a colored glass the nano metal particle is incorporated in glass. The sensitivity and kinetics of the darkening and return to normal condition depends with the size of the metal. The glass with nano particles are perfectly reversible, do not show fatigue even up to 3 lakhs cycles of coloring and decoloring.

Ex. 1: Electro-optic effect:

Electric filed interacts with optical signals to produce a change in the optical dielectric properties (due to movement of electron and photons). Acousto-optic effect: crystal is strained

Instead of electric field the refractive index is changed when the crystal is strained i,e crystal lattice has some potential. This is changed by action of strain which changes the shape and size of molecular orbital of weakly bounded electrons.

If a glass absorbs or scatters a light selectively in the visible region result in irregular transmission of light. Therefore, the glass appears colored to the human eyes, depending upon which color is transmitted.

Example

i) glasses of transition metal ion (Cr, Fe, Mn)- incomplete 3d shell

ii) Rare earth metals (La, Yb, Rb)- incomplete 4f shell

Here the color produced depending on the oxidation state, reduction state and also on the co-ordination no. of the ions.

Example

i) Co^{2+} in a silicate glass has tetrahedral co-ordination and gives deep blue color

ii) Co^{2+} in borosilicate glass has CN=6 and gives rose color

Here in many of these glasses, if there is a fine distribution of nanoparticle gives a particular coloration to the glass, in particular environment. The presence of nano particle forming a well dispersed phase in the glass responsible for coloration.

Eg: Glass containing Mn^{2+} and Fe^{3+}

$Mn^{2+} + h\surd \rightarrow Mn^{3+} + e^-$

The e^- which is ejected is arrested in the glass structure by Fe^{3+} i,e

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

Therefore, the glass looks violet color due to the presence of Mn^{3+}. This phenomenon is called photo-chromism.

The sensitivity and kinetics of darkening process of such glasses and their return to normality depends on

- Particle size
- Glass composition
- Nature of halogen ion (anions)
- Heat

Ex. 2: Gold Ruby Glass:

The ions of the metals like Au, Ag, Pt, Cu etc dissolved in the glass in presence of reducing agents like TiO_2 or antimony oxide.

Au (0.01 to 0.2% wt)

$Au \rightarrow Au^0$

$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

$Sb^{3+} \rightarrow Sb^{5+} + 2e^-$

The gold takes up these e^- and gives rise to Au^0

$Au^{3+} + 3e^- \rightarrow Au^0$

The color of gold changes by changing to nano size.

16.11 Application of nanomaterials for renewable energy

A major technological challenge for human race in 21^{st} century is the transition from fossil-fuel-based energy economy to renewable (sustainable) energy one. Collective energy demand of the planet is predicted to be doubled by the mid of 21^{st} century and to be tripled by the end of this century. There is a urgent need to develop CO_2- neutral energy sources. The sustainable energy alternatives should be cost effective.

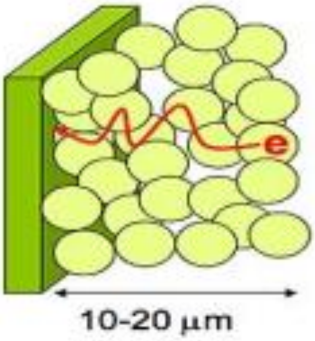
Nanotechnology provides essential improvement potentials for the development of both conventional energy sources (fossil and nuclear fuels) and Renewable energy sources like geothermal energy, sun, wind, water, tides or biomass. Breakthroughs in nanotechnology open up the possibility of moving beyond our current alternatives for energy supply by introducing technologies that are more efficient, inexpensive, and environmentally sound.

Nanotechnologies provide the potential to enhance energy efficiency across all branches of industry and to economically leverage renewable energy production through new technological solutions and optimized production technologies.

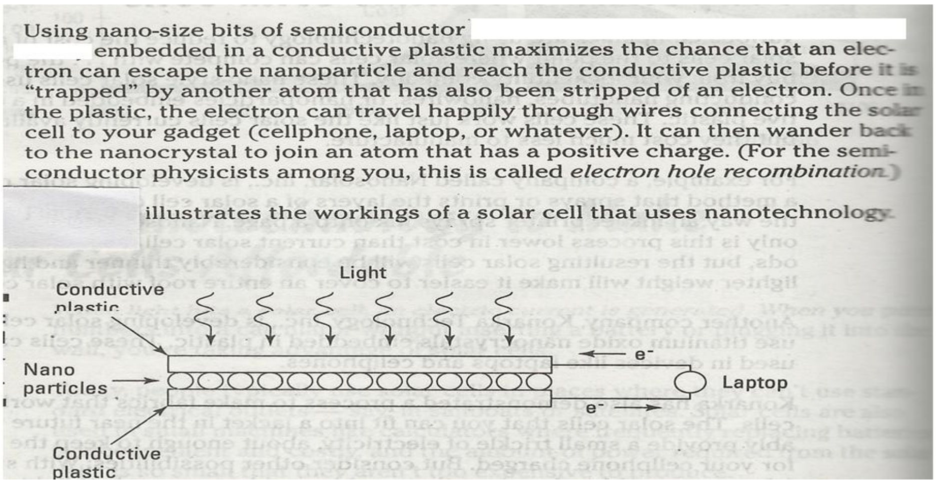
Conventional solar cells have two main drawbacks, efficiencies and their expensive manufacturing cost. The first drawback, inefficiency, is almost unavoidable with silicon cells. This is because the incoming photons, or light, must have the right energy, called the band gap energy, to knock out an electron. If the photon has less energy than the band gap energy then it will pass through. If it has more energy than the band gap, then that extra energy will be wasted as heat. These two effects alone account for the loss of around 70 percent of the radiation energy incident on the cell. Current solar cells cannot convert all the incoming light into usable energy because some of the light can escape back out of the cell into the air. Additionally, sunlight comes in a variety of colors and the cell might be more efficient at converting bluish light while being less efficient at converting reddish light.

To make the improved solar cells, the researchers began by first converting bulk silicon into discrete, nano-sized particles. Depending on their size, the nanoparticles will fluoresce in distinct colors. Nanoparticles of the desired size were then dispersed in isopropyl alcohol and dispensed onto the face of the solar cell. As the alcohol evaporated, a film of closely packed nanoparticles was left firmly fastened to the solar cell. Solar cells coated with a film of 1 nanometer, blue luminescent particles showed a power enhancement of about 60 percent in the ultraviolet range of the spectrum, but less than 3 percent in the visible range. Solar cells coated with 2.85 nanometer, red particles showed an enhancement of about 67 percent in the ultraviolet range, and about 10 percent in the visible range of the spectrum. Ultra thin films of highly mono dispersed luminescent Si nanoparticles are directly integrated on polycrystalline Si solar cells. Films of 1 nm blue luminescent or 2.85 nm red luminescent Si nanoparticles produce large voltage enhancements with improved power performance of 60% in the UV/blue range. In the visible, the enhancements are ~10% for the red and ~3% for the blue particles.

Another potential feature of these solar cells is that the nanorods could be 'tuned' to absorb various wavelengths of light. This could significantly increase the efficiency of the solar cell because more of the incident light could be utilized Single-walled carbon nanotubes to a film made of titanium-dioxide nanoparticles, doubling the efficiency of converting ultraviolet light into electrons when compared with the performance of the nanoparticles alone.



Escape route: Electrons created in a nanoparticle-based solar cell have to follow a circuitous path (red line) to reach an electrode. Many don't make it, lowering the efficiency of these cells. Researchers at Notre Dame have used carbon nanotubes to help the electrons reach the electrode, improving efficiency. Without the carbon nanotubes, electrons generated when light is absorbed by titanium-oxide particles have to jump from particle to particle to reach an electrode. Many never make it out to generate an electrical current. The carbon nanotubes "collect" the electrons and provide a more direct route to the electrode, improving the efficiency of the solar cells. The CNTs provide better electron ballistic transport property along its axis with high current density capacity on the surface of the solar cell without much loss. The alignment of the CNT with the polymer composites substrate give very high efficiency in photovoltaic conversion. The polymer composites increase contact area for better charge transfer and energy conversion. In this process, the efficiency of solar cell is about 50%



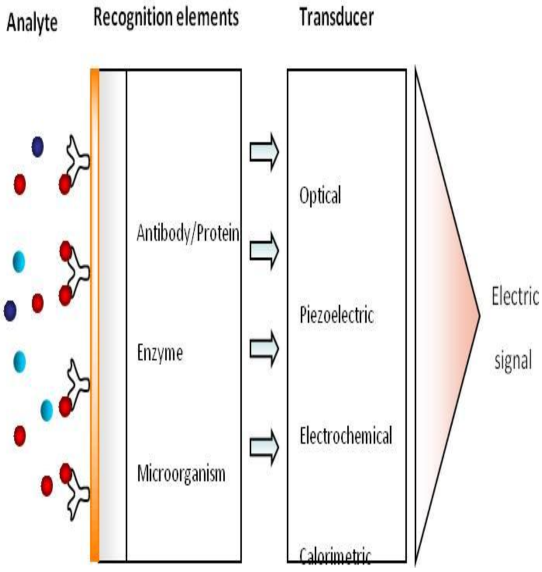
Using nano-size bits of semiconductor embedded in a conductive plastic maximizes the chance that an electron can escape the nanoparticle and reach the conductive plastic before it is "trapped" by another atom that has also been stripped of an electron. Once in the plastic, the electron can travel happily through wires connecting the solar cell to your gadget (cellphone, laptop, or whatever). It can then wander back to the nanocrystal to join an atom that has a positive charge. (For the semiconductor physicists among you, this is called *electron hole recombination*.)

illustrates the workings of a solar cell that uses nanotechnology.

16.12 Biosensors and chemical sensors

Metal nanoparticles (e.g. gold and silver nanoparticles) have long been utilized for various types of chemical and/or biological sensing applications.

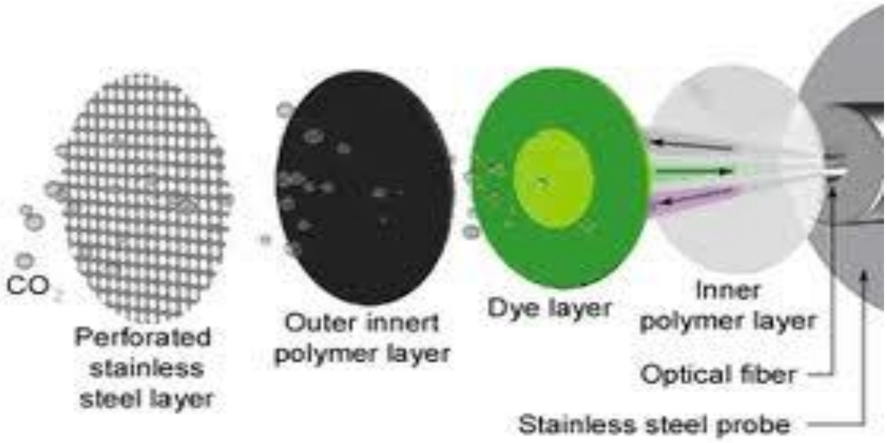
16.12.1 Biosensors



The biosensor instrument includes the self assembly of nano biomaterials (antibodies, enzymes). Due to their enhanced chemical activity, a biochemical reaction takes place due to interaction of antigen and antibody. Here the detector used should be proportional to the [antigen]. The extent of biochemical reaction takes place converted into electrical energy which is proportional to the [antigen] which is detected by the detector.

16.12.2 Chemical sensors

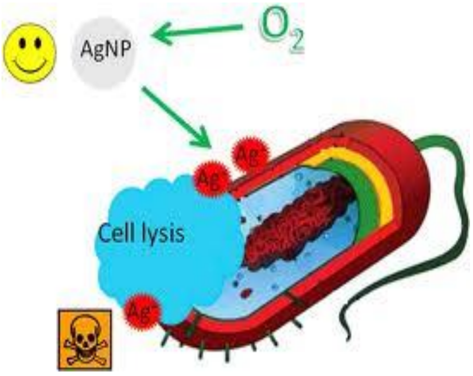
The nano Ag^+ are self assembled in Polymer and this polymer is connected to the detector. When Cl^- comes in contact with Ag^+ chemical reaction takes place and the extent of reaction is measured by the detector which gives the exact concentration of Cl^-

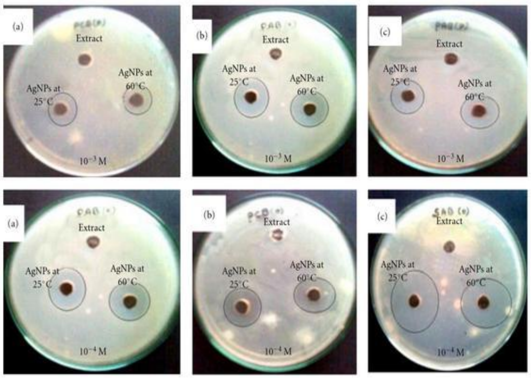


16.13 Pharmaceutical application

If the drug is nano sized (Au, Ag) the rate of dissolution and surface area is more, so the bioavailability increases.

16.14 Biological activity

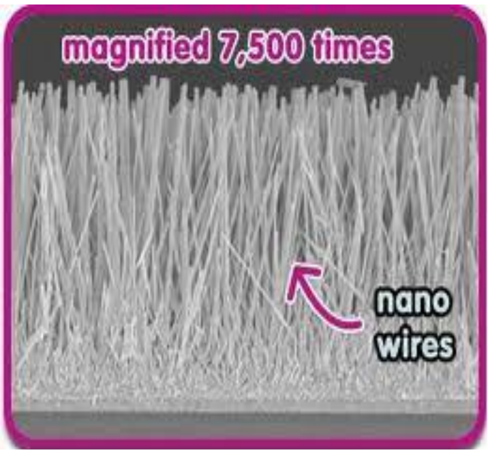


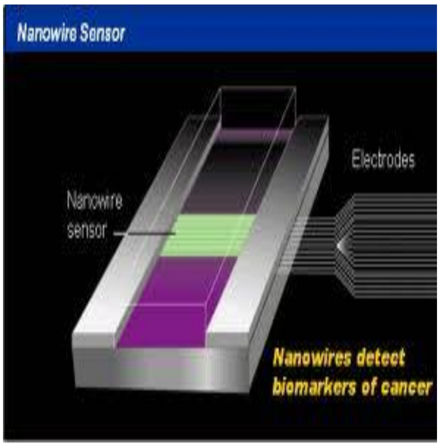


The bacterial growth will be inhibited in presence of nano particles, as the nanoparticles scavenges hydroxyl radicals (•OH).

Ex: the nanoparticles of Se-doped ZnO, Nb_2S_5/ZnS, Ru-doped ZnS show very good inhibition towards the growth of bacteria and can be used as antibacterial agent.

16.15 Application of Nanowires in electronic industries





The diameters of wires less than 3nm are referred as Nanowires. Nanowires also obtain by incorporation of metal ions in nanotubes are composed of nanometals such as silver, gold, iron, aluminium etc….

These nano wires are used

- To increase storage memory in computer
- Fabrication of new chips in computer with the use of nano wire
- A computer may contain 100-200 transistors placed layer by layer
- To improve MRAM (Magnetic Random Access memory)

16.16 Summary of the unit

The unique chemical and physical properties of nanoparticles make them extremely suitable for designing new and improved sensing devices, especially electrochemical sensors and biosensors. Many kinds of nanoparticles, such as metal, oxide and semiconductor nanoparticles have been used for constructing electrochemical sensors and biosensors, and these nanoparticles play different roles in different sensing systems. The important functions provided by nanoparticles include the immobilization of biomolecules, the catalysis of electrochemical reactions, the enhancement of electron transfer between electrode surfaces and proteins, labeling of biomolecules and even acting as reactant. A biosensor is a self-contained integrated device, which is capable of providing specific quantitative or semi-quantitative analytical information using a biological recognition element (biochemical receptor) which is retained in direct spatial contact with a transduction element.

The use of nanomaterials and structures such as semiconductors and conducting polymer nanowires, and nanoparticles (carbon nanotubes, silica nanoparticles, dendrimers, noble metals nanoparticles, gold nanoshells, superparamagnetic nanoparticles quantum dots, polymeric nanoparticles) for biosensor applications is expanding rapidly.

16.17 Key words

Aerogels; Inorganic nanoporous aerogels; Organic nanoporous aerogels; Carbon aerogels; Nanoparticles in coloured glasses; Nanomaterials for renewable energy; Biosensors and chemical sensors; Pharmaceutical application; Biological activity.

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16.19 Questions for self understanding

1) What are aerogels?

2) Discuss the classification of aerogels.

3) Explain the preparation of inorganic nanoporous aerogels.

4) Explain the preparation of organic nanoporous aerogels.

5) Explain the preparation of aerogels by lower cost fabrication pathways.

6) Explain the preparation of carbon aerogels.

7) Explain the structural features of aerogels.

8) Explain the advantages of aerogels.

9) Explain the application of nanoparticles in coloured glasses.

10) Discuss the application of nanomaterials for renewable energy.

11) Discuss the diosensors and chemical sensors application of nanomaterials.

12) Explain the application of nanowires in electronic industries.