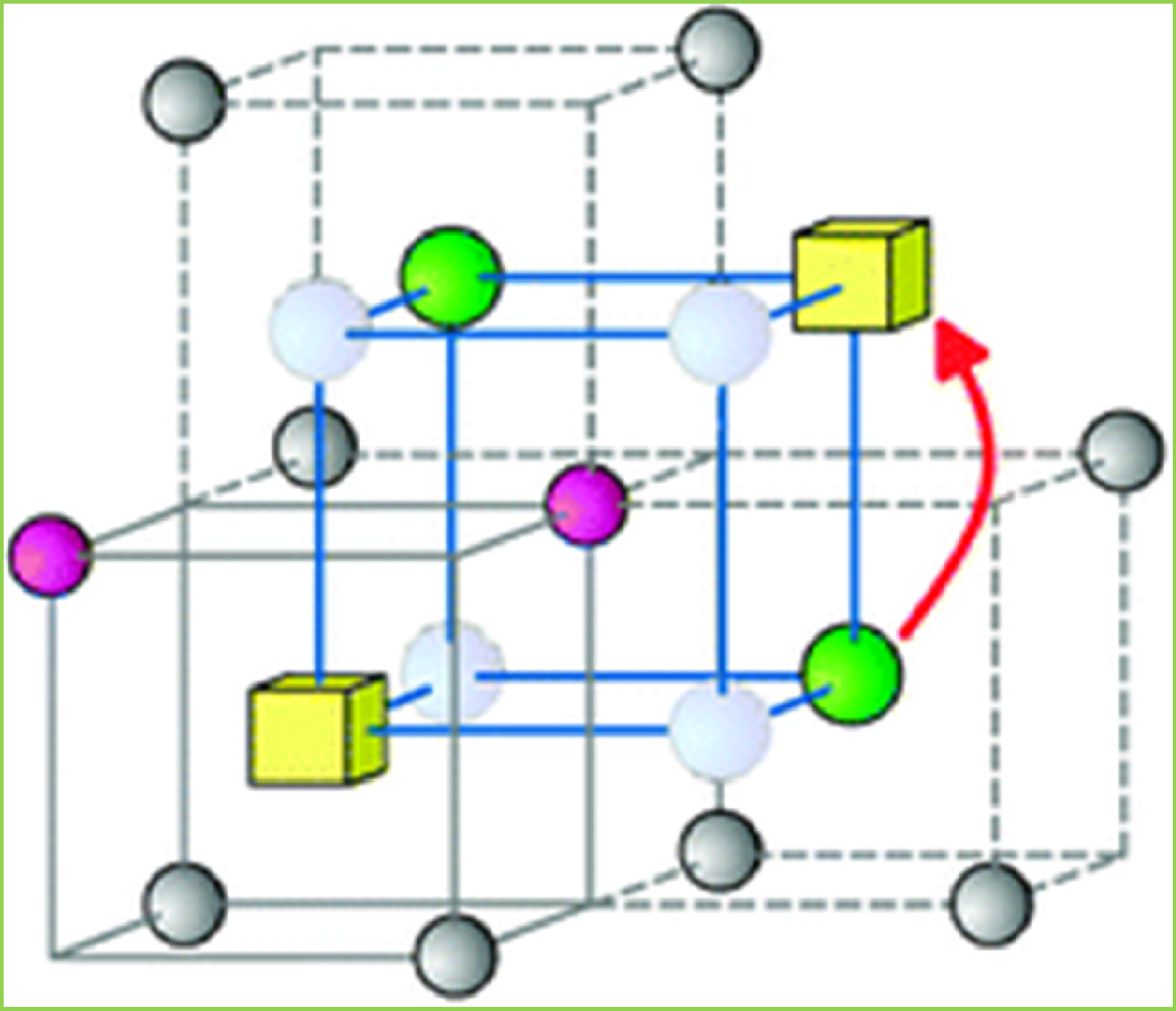
BSCCH- 103

B. Sc. I YEAR

PHYSICAL CHEMISTRY-I



SCHOOL OF SCIENCES

DEPARTMENT OF CHEMISTRY

UTTARAKHAND OPEN UNIVERSITY

BSCCH-103

PHYSICAL CHEMISTRY-I

SCHOOL OF SCIENCES
DEPARTMENT OF CHEMISTRY
UTTARAKHAND OPEN UNIVERSITY

Phone No. 05946-261122, 261123
Toll free No. 18001804025
Fax No. 05946-264232, E. mail info@uou.ac.in
htpp://uou.ac.in

Board of Studies

Prof. Govind Singh
Director, School of Sciences
Uttarakhand Open University

Prof S.P. S. Mehta
Professor Chemistry
Department of Chemistry
DSB Campus, Kumaun University
Nainital

Dr. Charu C. Pant
Programme Coordinator
Department of Chemistry
School of Sciences,
Uttarakhand Open University
Haldwani, Nainital

Prof. B. S. Saraswat
Professor Chemistry
Department of Chemistry
School of Sciences, IGNOU New Delhi

Prof. D. S. Rawat
Professor Chemistry
Department of Chemistry
Delhi University, Delhi

Programme Coordinator

Dr. Charu C. Pant
Department of Chemistry
School of Sciences,
Uttarakhand Open University
Haldwani, Nainital

Dr. Shalini Singh
Department of Chemistry
School of Sciences,
Uttarakhand Open University
Haldwani, Nainital

Unit Written By:	**Unit No.**
1. **Dr. K. B. Melkani** (Retd. Professor.) Department of Chemistry DSB Campus Kumaun University, Nainital	**02, 03, 04, 05, 06, 07, 08, 09, 10, 11& 12**
4. **Dr. Charu C. Pant** Department of Chemistry School of Sciences, Uttarakhand Open University, Haldwani.	**01**

Course Editor

Dr. R .D. Kaushik
Professor & Dean
Department of Chemistry
Faculty of Science
Gurukul Kangri Mahavidyalaya , Haridwar

Title : Physical Chemistry-I
ISBN No. : 978-93-85740-55-8

Edition : 2017
Published by : Uttarakhand Open University, Haldwani, Nainital- 263139

CONTENTS

BLOCK 1: MATHEMATICAL AND COMPUTERS FUNDAMENTALS

BLOCK 2: STATES OF MATTER

BLOCK 3: DYNAMICS AND MACROMOLECULES

BLOCK 4: THERMODYNAMICS-I

UNIT 1: UNITES AND DIMENSIONS

CONTENTS:

1.1 OBJECTIVES

- Use the SI system.
- Know the SI base units.
- State rough equivalents for the SI base units in the English system.
- Read and write the symbols for SI units.
- Recognize unit prefixes and their abbreviations.
- Build derived units from the basic units for mass, length, temperature, and time.
- Convert measurements from SI units to English and from one prefixed unit to another.
- Use derived units like density and speed as conversion factors.
- Use percentages, parts per thousand, and parts per million as conversion factors.
- Use and report measurements carefully.
- Consider the reliability of a measurement in decisions based on measurements.
- Clearly distinguish between precision and accuracy
- Exact numbers and measurements
- systematic error and random error

1.2 INTRODUCTION

All the physical quantities are given by a few fundamental quantities or their combinations. The units of such fundamental quantities are called base units, combinations of them being called derived units. The system in which length, mass, velocity, density and time are adopted as the basic quantities, and from which the units of other quantities are derived, is called the absolute system of units.

1.3 BASIC UNITS, DERIVED UNIT AND SI PREFIXES

A unit is a particular way of attaching a number to the quantitative dimension. Measured physical properties have a basic dimension in which they are measured. There may be many units that are used to measure this dimension. This is best shown by example. The thickness of an object has the dimension of length. Length can be measured in a wide range of units including inches, feet, yards, meters, kilometers, micrometers, Angstrom units, furlongs, fathoms, light-years and many more. The thickness of an object cannot be measured in kilograms, however. That is because the kilogram is a unit used to measure quantities that have the fundamental dimension of mass.

The term units usually start by making arbitrary definitions of a unit for fundamental dimensions. Typically these fundamental dimensions are mass, length, time, electric charge and temperature. Once these units are selected for the fundamental dimensions the units for other physical quantities can be determined from the physical relations among quantities having the fundamental units. For example velocity is found as distance divided by time. Thus the dimensions of velocity must be length/time. Similarly the dimensions of acceleration, found as velocity divided by time, must be length/time^2, and the dimensions of force can be found from Newton’s second law: force equals mass times acceleration. This gives the dimensions of force as the dimensions of mass times the dimensions of acceleration or (mass) times (length) divided by (time). The symbols M, L, and T are usually used to represent dimensions of mass, length, and time, respectively.

Table 1- General Base Units:

PHYSICAL QUANTITY	SYMBOL	DIMENSION	MEASUREMENT UNIT	UNIT
Length	S	L	Meter	m
Mass	M	M	Kilogram	Kg
Time	T	T	Second	Sec
Charge	Q	Q	Coulomb	C
Temperature	T	K	kelvin	^{0}C
Area	A	L^2	Square meter	m^2
Volume	V	L^3	Cubic meter	m^3
Velocity	V	L/T	Meter per second	m/sec.
Angular velocity	W	T^{-1}	Radians per sec.	1/sec
Force	F	MLT^{-2}	Newton	Kg m/sec
Energy	E	ML2T-2	Joule	Kg m2/sec2
Heat	Q	ML2T-2	Joule	Kg m2/sec2
Density	P	ML-3	kilogram per cubic meter	Kg/m3

Pressure	P	ML-1T-2	Newton per square meter	Kg m^{-1}/sec^2

1.3.1. System of Units

(a) C.G.S (Centimeter-Grand-Second) system

(b) F.P.S. (Foot-Pound-Second) system

(c) M.K.S. (Meter-Kilogram--Second) system.

(d) M.K.S.A. (Meter-Kilogram-Second-Ampere) unit

1.3.2. The seven base units of the SI

1. Length- Meter, m: The meter is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second.

2. Mass- kilogram, kg: The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram.

3. Time- second, s: The second is the durationof 9 192 631 770 periods of the radiationcorresponding to the transition betweenthe two hyperfine levels of the ground stateof the caesium 133 atom.

4. Electric current- ampere, A: The ampere is that constant currentwhich, if maintained in two straight parallelconductors of infinite length, of negligible circular cross-section, and placed 1 metre apart in vacuum,would produce between these conductors a forceequal to 2 × 10–7newton per metre of length**.**

5. Thermodynamic temperature - Kelvin, K: the Kelvin, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.

6. Amount of substance- Mole, mol: The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12. When the mole is used, the elementary entities must be specie and may be atoms, molecules, ions, electrons, other particles, or specie groups of such particles.

7. Luminous intensity- candela, cd: The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency540 × 10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steroidal.

Table-2 The seven independent SI base units

Quantity	Unit name	Unit symbol
Length	Meter	M
Time	Second	S
Mass	Kilogram	Kg
Temperature	Kelvin	K
Electric current	Ampere	A
Amount of substance	Mole	Mol
Luminous intensity	Candela	Cd

The International System of Units

Seven physical quantities have been selected as base quantities in the 14th General Conference onWeights and Measurements, held in France in 1971. These quantities form the basis of the International System of Units, abbreviated **SI** (from its French name *Système International*) and popularly known as the *metric system*. Table 3 depicts these quantities, their unit names, and their unit symbols. (H. A. Radi and J. O. Rasmussen, *Principles of Physics*,)

Prefixes for SI units

An additional convenient way to deal with very large or very small numbers in physics is to use the prefixes listed in Table **3**. Each one of these prefixes represents a certain power of 10.

Table -3

Factor	**Prefix**	**Symbol**	**Factor**	**Prefix**	**Symbol**
10^{24}	yotta-	Y	10−24	yocto	-y
10^{21}	zeta-	Z	10−21	zepto	-z
10^{18}	exa-	E	10−18	atto	-a
10^{15}	peta-	P	10−15	femto-	-f
10^{12}	tera-	T	10−12	pico	-p
10^{9}	giga-	G	10−9	nano	-n
10^{6}	mega	- M	10−6	micro	-μ
10^{3}	kilo	-k	10−3	milli	-m

10^2	hecta	-h	10−2	centi	-c
10^1	deca	-da	10−1	deci	-d

Common metric prefixes:

The units often have **prefixes**, indicating the power(s) of 10 by which a unit may be multiplied (for example, the prefix kilo_in kilometer indicates that the unit kilometer is 1000 times larger than the meter). They are attached to an SI unit name or symbol to form what are properly called "multiples" and "submultiples" (i.e., positive or negative powers of 10) of the SI unit. These prefixes are helpful when referring to very small or very large quantities. Instead of creating a new unit, a prefix is added. For example, when measuring short lengths such as 1/1000th of a meter, we simply write millimeter; milli denotes 1/1000th**.** The some common metric prefixes are giving below:

Table -4

Multiplication Factor	Prefix Name	Prefix Symbol
1 000 000 000 000 = 10^{12}	tera	T
1 000 000 000 = 10^{9}	giga	G
1 000 000 = 10^{6}	mega	M
1 000 = 10^{3}	kilo	k
100 = 10^{2}	hecto	h
10 = 10^{1}	deka	da
0.1 = 10^{-1}	deci	d
0.01 = 10^{-2}	centi	c
0.001 = 10^{-3}	milli	m
0.000 001 = 10^{-6}	micro	µ
0.000 000 001 = 10^{-9}	nano	n
0.000 000 000 001 = 10^{-12}	pico	p

Example 1.1

Convert the following: (a) 1 kilometre per hour to meter per second, (b) 1 mile per hour to meter per second, and (c) 1 mile per hour to kilometre per hour [to a good approximation 1mi = 1.609 km].

1.4 GRAMMATICAL RULES FOR REPRESENTING THE SI UNITES

The term SI Units is an abbreviation of the French Le System International Unites. It is the modern metric system of measurement. SI unit is now universally accepted as a standard system of measurement.

The SI units consist of

(a) Seven base units

(b) A set of prefixes

(c) Several derived units

1.4.1 Representation of SI units

Step I: The SI Base Units

The SI base units represent seven mutually independent base quantities. These quantities, their names, and the symbols that represent them are given in **Table-5.**

Quantity	**Name**	**Symbol**
Length	meter	m
Mass	Kilogram	Kg
Time	Second	s
Current	ampere	A
Temperature	Kelvin	K
Amount of mols	Mole	mol

Step II: The Prefixes

A prefix may be added to any unit to produce an integer multiple of ten of the base unit. For example, a kilogram denotes a multiple of 1000gm and a milligram denotes a multiple of a 1000 gram. **Table 6** gives the prefixes that are accepted to be used in the SI units. Prefixes are never combined. For example, mill millimeter is not written; micrometer is written instead.

Table 6:

Name	yotta	zetta	Exa	peta	tera	giga	mega	kilo	hecto	deca
Symbol	Y	Z	E	p	T	G	M	K	H	D
Factor	10^{24}	10^{21}	10^{18}	10^{15}	10^{12}	10^{9}	10^{6}	10^{3}	10^{2}	10^{1}
Nmae	deci-	cent-	milli-	micro-	nano-	pico-	femto-	atto-	zepto-	yacto-
Symbol	d	C	M	µ	n	p	f	A	z	y
Factor	10^{-1}	10^{-2}	10^{-3}	10^{-6}	10^{-9}	10^{-12}	10^{-15}	10^{-18}	10^{-21}	10^{-24}

Step III: The SI Derived Units

A system of equations involving the seven base quantities defines the derived quantities. The SI derived units follow these equations to represent the derived quantities. **Table 7** gives examples of a number of SI derived units.

Table 7: Examples of SI Derived Units

Derived quantity	**Name**	**Symbol**
Area	square meter	m^2
Volume	cubic meter	m^3
Wave number	reciprocal meter	m^{-1}
Mass density	kilogram per cubic meter	kg/m^3
Specific volume	cubic meter per kilogram	m^3/kg
Mass fraction	kilogram per kilogram	kg/kg = 1
Speed, velocity	meter per second	m/s
Acceleration	meter per second squared	m/s^2
Current density	ampere per square meter	A/m^2
Magnetic field strength	ampere per meter	A/m
Amt-of-substance concentration	mole per cubic meter	mol/m^3
Luminance	candela per square meter	cd/m^2

A few notable points are given below:

1. Electrical energy is often measured in kilowatt-hours (kWh) instead of mega joules.
2. "Calorie" is used as a heat unit indicating the amount of heat required to increase the temperature of 1 gm of water by 1^0C.
3. Blood pressure is measured in mmHg instead of Pa.
4. Atomic scale units used in Physics and Chemistry are angstrom, electron volt, atomic mass unit (amu), and barn.
5. Travel distance and speed of ships and aircraft are measured in nautical mile and knot (nautical mile per hour).
6. The year is not specifically included as an SI unit.
7. A metric ton is called "tone" in a few countries.
8. It is preferred to use numbers between 0.1 and 1 000 in expressing the quantity of any SI unit. Thus the quantity 15 000 m is expressed as 15 km, and 0.002 cubic centimeter is preferably written as 2 mm^3.

1.5 CONVERSION OF NON SI UNIT TO SI UNIT

1.5.1. Non SI Unit:

A number of non-SI units are commonly used, even though the SI system of units allows for complete coverage of all scientific measurements.

1.5.2. Some commonly used non-SI units

Physical quantity	Non-SI unit	Symbol	Conversion Factor
Energy	calorie	cal	1 cal = 4.184 J
Length	Ångstrom	Å	1 Å = 10^{-10} m
Mass	tonne	t	1 t = 10^3 kg
Pressure	atmosphere	atm	1 atm = 1.013 x 10^5 Pa
Temperature	degree Celsius	°C	1 °C = 1 K
Time	minute	min	1 min = 60 s
	Hour	h or hr	1 h = 3600 s
	Day	d	1 d = 86 400 s
Volume	litre	L	1 L = 1 dm^3 = 10^{-3} m^3

1.5.3. SI Unit

The International System of Units (SI) is a scientific method of expressing the magnitudes or quantities of important natural phenomena. There are seven base units in the system, from which other units are derived. This system was formerly called the meter-kilogram-second (MKS) system. See **table-2**.

1.5.4. Conversion Factors for SI and non-SI Units

To convert Column 1 into Column 2, multiply by	Column 1 SI Unit	Column 2 Non-SI Unit	To convert Column 2 into Column 1, multiply by
Length			
0.621	kilometer, km (103 m)	mile, mi	1.609
1.094	meter, m	yard, yd	0.914
3.28	meter, m	foot, ft	0.304
1.0	micrometer, m (10 6 m)	micron,	1.0
3.94x10^{2}	millimeter, mm (10 3 m)	inch, in	25.4
10	nanometer, nm (10^{9} m)	˚ Angstrom, A	0.1
Area			
2.47	hectare, ha	acre	0.405
247	square kilometer, km2 (103 m)2	acre	4.05x10^{3}
0.386	square kilometer, km2 (103 m)2	square mile, mi2	2.590
2.47x10^{4}	square meter, m2	acre	4.05x10^{3}
10.76	square meter, m2	square foot, ft2	9.29x10^{2}
1.55x10^{3}	square millimeter, mm2 (10 3 m)2	square inch, in2	645
Volume			
9.73x10^{3}	cubic meter, m3	acre-inch	102.8
35.3	cubic meter, m3	cubic foot, ft3	2.83x10^{2}
6.10x10^{4}	cubic meter, m3	cubic inch, in3	1.64x10^{5}
2.84x10^{2}	liter, L (10 3 m3)	bushel, bu	35.24
1.057	liter, L (10 3 m3)	quart (liquid), qt	0.946
3.53x10^{2}	liter, L (10 3 m3)	cubic foot, ft3	28.3
0.265	liter, L (10 3 m3)	gallon	3.78
33.78	liter, L (10 3 m3)	ounce (fluid), oz	2.96x10^{2}
2.11	liter, L (10 3 m3)	pint (fluid), pt	0.473
Mass			
2.20x10^{3}	gram, g (10 3 kg)	pound, lb	454
3.52x10^{2}	gram, g (10 3 kg)	ounce (avdp), oz	28.4
2.205	kilogram, kg	pound, lb	0.454
0.01	kilogram, kg	quintal (metric), q	100
1.10x10^{3}	kilogram, kg	ton (2000 lb), ton	907
1.102	megagram, Mg (tonne)	ton (U.S.), ton	0.907
1.102	tonne, t	ton (U.S.), ton	0.907

Pressure			
9.90	megapascal, MPa (106Pa)	atmosphere	0.101
10	megapascal, MPa (106Pa)	bar	0.1
1.00	megagram per cubic meter, Mg m 3	gram per cubic centimeter, g cm 3	1.00
2.09 x10^{2}	pascal, Pa	pound per square foot, lb ft 2	47.9
1.45x 10^{4}	pascal, Pa	pound per square inch, lb in 2	6.90 x10^{3}

1.6 SUMMARY

In this chapter you have studied Use the SI system, know the SI base units, Recognize unit prefixes and their abbreviations, Convert measurements from SI units to English and from one prefixed unit to another. With the help of unit and dimensions we can derive the various derivations by making use units and converted units.

1.7 TERMINAL QUESTIONS

A. Short answers type questions:

1. What is the importance of base units?
2. Does the measurement of a physical quantity depend upon the system of units used?

B. Objective type questions:

1. In the S.I. system, the unit of temperature is-

(A) Degree centigrade (B) Kelvin

(C) Degree Celsius (D) degree Fahrenheit

2. In the S.I. unit of energy is-

(A) Erg (B) calorie (C) joule (D) electron volt

3. If Force = (x/density) +Cis dimensionally correct, the dimension of x are -

(A) MLT_{-2} (B) MLT_{-3} (C) $ML_{2}T_{-3}$ (D) $M_{2}L_{-2}T_{-2}$

4. Intensity of electric current is expressed in

A. Volts B. Watts C. Amperes D. Joules

5. One Newton force equals.

A. 10^5 dynes B. 10^4 dynes C. 10^3 dynes D. 10^2 dynes

6. In S.I. system, the symbol for density is

A. N/m^3 B. kg/m^3 C. m^3/s D. kg

7. The thickness of a micron, is

A. 10^{-3} m B. 10^{-6} m C. 10^{-9} m D. 10^{-12} m

8. The fundamental units in S.I. system are the same as that of

A. C.G.S. units B. F.P.S. units C. M.K.S. units D. None of these

9. Pick up the correct statement from the following:

A. In S.I. system, surface tension is expressed in Newton per meter

B. In S.I. system, force is expressed in Newton

C. In S.I. system, power is expressed in watts

D. All the above.

10. 100 kN/m^2 pressure is equal to

A. 1 atm

B. 1 bar

C. 1 m bar

D. 1 mm Hg

Answers

1. B. 2 C. 3. A 4.C 5. A 6. 7. B 8. C 9. E 10. B

References:

1. H. A. Radi and J. O. Rasmussen, *Principles of Physics*, Undergraduate Lecture Notes in Physics, DOI: 10.1007/978-3-642-23026-4_1, Springer-Verlag Berlin Heidelberg 2013.

2. Kenneth Butcher Linda Crown Elizabeth J. Gentry Weights and Measures Division Technology Services

UNIT 2: GASEOUS STATE-I

CONTENTS

2.1 OBJECTIVES

All matter exists in three common state of matter; these common states are solid, liquid and gas. A particle level representation of gaseous, liquid and solid states is shown in Fig 2.1

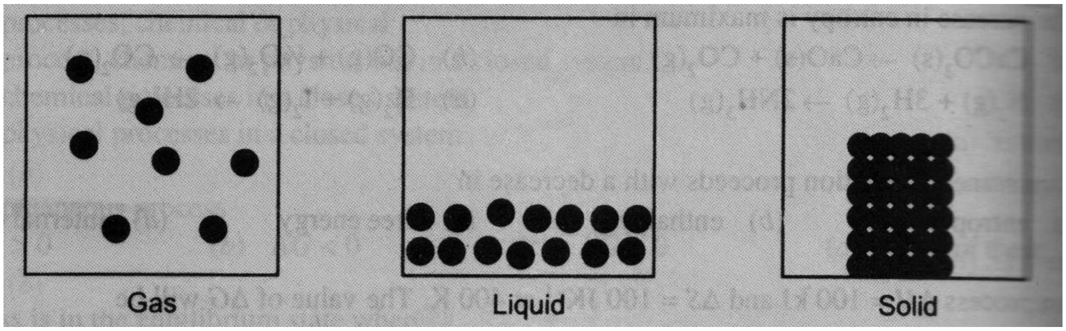


Fig- 2.1 Three states of matter

The smallest structural unit of all chemical substances in these states is molecule. How the molecules are arranged in a solid, liquid and gas, is the fundamental question before a chemist. It is the ‘molecular model’ of matter in these states which determine their physical behaviour. The theory which visualises that all substances, whether solids, liquids or gases are made of molecules in motion is called kinetic molecular theory of matter.

On the basis of kinetic molecular theory of matter and with the help of our knowledge of intermolecular forces, it has now become possible to bring out the distinguishing characteristics of three states of matter. These states can be considered to arise as a result of competition between two opposing molecular forces, namely, the forces of attraction which tend to hold the molecules together, and the disruptive forces due to thermal energy of molecules.

2.2 INTRODUCTION

Amongst the three common states of matter, the gaseous state is simplest. The laws of gaseous behaviour are more uniform and are better understood. The well known laws of gaseous behaviour are Boyle's law, Charle's law Graham's law, Dalton's law and Avogadro's law. There was no theoretical background to justify them. In the nineteenth century, however, Kronig, Clausius, Maxwell and Boltzmann developed a theory known as kinetic molecular theory of gases, which provided sound theoretical basis for the various gas laws.

As you have studied in the article 2.1 that there are two opposite molecular forces, the forces of attraction and the disruptive forces operating between molecules. If the thermal energy is much greater than the forces of attraction, then we have matter in its gaseous state.

In contrast with solids and liquids gases occupy the same volume as that of the closed vessel, they are characterised by low density and high compressibility.

The characteristic properties of gases are given below.

1. No definite shape and volume. Gases occupy all available space i.e. the shape and volume of the container in which they are filled.
2. Expansibility. Gases have limitless expansibility. They expand to fill the entire vessel they are placed in.
3. Compressibility. Gases are easily compressed by application of pressure.
4. Diffusibility. Gases can diffuse rapidly through each other to form a homogeneous mixture.
5. Pressure. Gases exert pressure on the walls of the container in all direction. You can site the example of a gas balloon.
6. Effect of heat. When a gas confined in a vessel is heated, its pressure increases. Upon heating in a vessel fitted with a piston, volume of the gas increases.

2.3 POSTULATES OF KINETIC THEORY OF GASES

It was earlier observed that the gas laws were based on experimental observations. The theoretical foundation or mathematical representation was missing. However several workers studied the properties of gases and found that the gases are essentially composed of freely moving molecules. The basic ideas of the workers were mentioned to explain the behaviour of the gases called the kinetic theory of gases. This theory succeeded to attain a rigid mathematical form due to the efforts of Joule, Kronig, Clausius, Maxwell, Boltzmann and many others. The main postulates of kinetic theory of gases may be given as follows.

1. Every gas consists of large number of tiny particles called point masses i.e. the actual volume of molecules is negligible when compared to the total volume of the gas. For the same gas, all molecules are of same size and mass.
2. The gas molecules are always in a state of rapid zig-zag motion in all directions. These molecules collide with each other and with the walls of the containing vessel.
3. A molecule moves in a straight line with uniform velocity between two collisions.
4. The molecular collisions are perfectly elastic so that there is no net loss of energy when the gas molecules collide with one another or against the walls of the vessel.

   Suppose two molecules collide having same mass m. Before collision the velocity of one molecule is v_1 and velocity of other molecule is v_2 and after collision the velocity of the molecules changes from $v_1$to $v_1^{/}$ and from v_2 to $v_2^{/}$ then if the collisions are elastic there is no loss of kinetic energy. This can be expressed as follows.

   Total kinetic energy of two molecules before collision is

   $\frac{1}{2} m_1 v_1^2 + 1/2\ m_2 v_2^2$

   And after collision total kinetic energy of both the molecules is

   $\frac{1}{2} m_1 v_1^{/2} + \frac{1}{2} m\ v_2^{/2}$

   If $\frac{1}{2} m_1 v_1^2 + 1/2\ m_2 v_2^2 = \frac{1}{2} m_1 v_1^{/2} + \frac{1}{2} m_2 v_2^{/2}$

   i.e. total kinetic energy before collision is equal to total kinetic energy after collision then the collision is said to be an elastic collision.
5. There are no attractive forces operating between molecules or between molecules and the walls of the vessel in which the gas has been contained. The molecule move independently of one another.
6. The pressure of the gas is the hits recorded by the molecules on the walls of the container in which the gas is contained.
7. The average kinetic energy of gas molecules is directly proportional to absolute temperature. This means that the average kinetic energy of molecules is the same at a given temperature.

   This must be clear to you that all the above postulates are applicable to ideal gases only i.e. the gas which obey Boyle's and Charle's law under all conditions of temperature and pressure. These are only approximately valid for real gases.

2.3.1 Derivation of kinetic gas equation

Suppose a volume of gas enclosed in a cubical vessel (fig 2.2) at a fixed temperature.

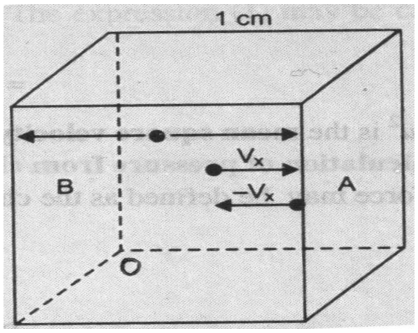


fig 2.2

Suppose that :

the length of each side of cube = l cm
the number of gas molecules = n
the mass of one molecule = m
the velocity of a molecule = v

Let us consider one single molecule of a gas can be evaluated by calculating the momentum during collisions.

According to kinetic model the molecules of the gas are moving in straight lines in all possible directions. They collide with one another frequently as also with the walls of the container. Since their mutual collisions are perfectly elastic and do not involve the loss of energy, these may be neglected. Here we will, therefore, assume that gas molecules move in all directions but rebound whenever they strike the wall of the container. Now you proceed to derive kinetic gas equation in the following steps

According to the kinetic theory, a molecule of a gas can move with velocity v in any direction velocity is a vector quantity can be resolved into components v_x, v_y, v_z along the X, Y and Z axes. These components are related to velocity v by the following expression.

$$v^2 = v_x^2 + v_y^2 + v_z^2 \qquad \text{.........................(1)}$$

Let us consider a molecule moving in ox direction between opposite faces A and B. It will strike the face A with velocity v_x and rebound with velocity $-v_x$. To hit the same face again the molecule must travel l cm to

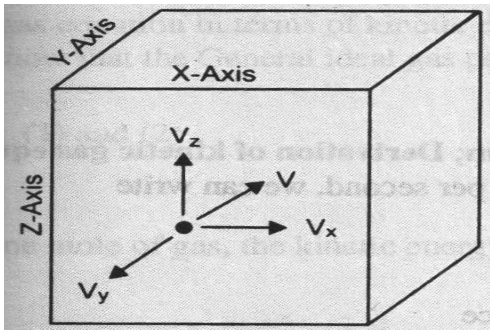


Fig 2.3

Collide with opposite face B and then again l cm to return to face A. Therefore time taken between two collisions can be calculated as follows

The molecule travels v_x cm in 1 sec

hence 1 cm in $1/v_x$ sec

And 2l cm in $2l/v_x$ sec ....(2)

In $2l/v_x$ sec molecule suffers 1 collision

In 1 sec no of collisions = $v_x/2l$ ....(3)

Each impact of the molecule on the face A causes a change of momentum which is mass x velocity.

Momentum of the molecule before impact = mv_x

Momentum of the molecule after impact = $-mv_x$

Hence change of momentum = $mv_x - (-mv_x) = 2mv_x$

But the number of collision per second on face A= $v_x/2l$

Therefore total change of momentum per second on face A caused by one

Molecule = $2mv_x \times v_x/2l$

= mv_x^2/l ....(4)

As there are two faces along x- direction, total change of momentum per second considering both the faces along x-direction will be

$2mv_x^2/l$ ....(5)

This is change of momentum caused by one molecule along x-direction. The change of momentum caused by one molecule along y- direction per second will be $2mv_y^2/l$

and change of momentum caused by one molecule along z- direction per second will be $2mv_z^2/l$

Total change of momentum caused by one molecule considering along three direction will be

$2mv_x^2/l + 2mv_y^2/l + 2mv_z^2/l$

$= 2m/l\ (v_x^2+v_y^2+v_z^2)$

$= 2mv^2/l$ ....(6)

Since there are n molecules in the vessel then total change of momentum due to n molecules will be

$2mnv^2/l$ ....(7)

v^2 = mean square velocity

Since change of momentum per second is force

Hence force = $2mnv^2/l$

Since pressure = Total force/Total area

Since there are six faces in a cube, area of each cube is l^2. Hence total area is $6l^2$

Then pressure = $2mnv^2/l \times 1/6l^2$

= $mnv^2/3l^2$

As l^2 = volume V

Hence pressure $P= 1/3\ mnv^2/V$ ....(8)

This is known as Kinetic gas equation. This equation has been derived for a cubical vessel. It is equally valid for vessel of any shape. The available volume in the vessel may be considered as made up of large number of infinitesimally small cubes, for each of them the equation is valid.

2.3.2 Derivation of gas laws from kinetic gas equation

2.3.2.1 Boyle's law

From his observations Boyle's in 1660 formulated a generalisation known as Boyle's law. Boyle's law states that at constant temperature, the volume of a given mass of gas is inversely proportional to its pressure.

According to kinetic theory, kinetic energy is directly proportional to temperature (in absolute scale).

Hence $\frac{1}{2} mnv^2 \propto T$

Or $\frac{1}{2} mnv^2 = KT$ (K is constant)

$3/2 \times 1/3\ mnv^2 = KT$

$1/3\ mnv^2 = 2/3\ KT$

As $1/3\ mnv^2 = PV$

So $PV = 2/3\ KT$

At constant temperature PV= constant which is Boyle's law

2.3.2.2 Charle's law : for a definite quantity of gas at constant pressure, its volume is directly proportional to the absolute temperature. It was established in 1787.

From above discussion

$V = 2/3\ KT/P$

At constant pressure

$V = \text{constant} \times T$

Or $V \propto T$ when P is constant.

This is Charle's law

2.3.2.3 Avogadro's law: It is states that equal volume of gases at same temperature and pressure contain equal number of molecules.

Suppose there are two gases for first gas mass of one molecule is m_1, velocity is v_1 and number of molecules are n_1. And for the second gas mass of one molecule is m_2, velocity is v_2 and number of molecules are n_2

Then for first gas $PV = 1/3\ m_1n_1v_1^2$

For second gas $PV = 1/3\ m_2n_2v_2^2$

As pressure and volume are same for both gases

Hence $1/3\ m_1n_1v_1^2 = 1/3\ m_2n_2v_2^2$

Or $m_1n_1v_1^2 = m_2n_2v_2^2$ -------------(9)

If temperature is same average kinetic energy per molecule will be same for both gases that means

$\frac{1}{2} m_1v_1^2 = \frac{1}{2} m_2v_2^2$ ----------------(10)

Comparing (9) and (10)

$n_1 = n_2$, this is **Avogadro's law**

2.3.2.4 Graham's law of diffusion (1829) – It states that rate of diffusion of a gas is inversely proportional to square root of density of the gas at constant pressure.

if m_1 and m_2 are masses and v_1 and v_2 the velocities of molecules of gas 1 and 2 respectively, then at same pressure and volume.

$PV_1 = 1/3\ m_1n_1v_1^2$

$v_1 = 3PV_1/m_1n_1$

$= 3p/d_1$

As m_1n_1/V_1 is total mass of gas and mass divided by volume equal to density of the gas equal to d

For second gas $v_2 = 3p/d_2$

$v_1/v_2 = d_2/d_1$

Since rate of diffusion is directly proportional to velocity. Hence

$$r \propto v$$

$$r_1/r_2 \propto d_2/d_1$$

This is Graham's law of diffusion

2.3.2.5 Dalton's law of partial pressure: If two or more gases which do not react with each other are mixed, then total pressure will be sum of their individual pressures.

suppose n_1 molecule each of mass m_1 of gas A are contained in a vessel of volume V then from kinetic gas equation $P_a = m_1 n_1 v_1^2/3V$

Now suppose n_2 molecules of each of mass m_2 of gas B are contained in the same vessel at the same temperature when there is no gas present at that time

Then the pressure $P_b = m_2 n_2 v_2^2/3V$

If both the gases are present in the same vessel at the same time, the total pressure P is given by

$$P = m_1 n_1 v_1^2/3V + m_2 n_2 v_2^2/3V$$

$$= P_a + P_b$$

This is Dalton's law of partial pressure.

2.3.2.6 The combined gas law: Boyle's law and Charle's law can be combined into a single relationship called the combined gas law.

Boyle's law $V \propto 1/P$
Charle's law $V \propto T$
or $V \propto T/P$
or $V = KT/P$ (K is constant)
or $PV = KT$

The value of constant K in this equation depends upon

(i) quantity of gas
(ii) the units in which P, V and T are expressed.

Avogadro's law states that one gram molecule of all gases under the same conditions of pressure and temperature occupies the same volume. So that the value of K will be the same for all gases if in every case one gram molecule of the gas is taken. When this is done, K is replaced by R which is known as universal gas constant.

Hence $PV = RT$ for n moles $PV = nRT$

2.4 DEVIATION FROM IDEAL BEHAVIOUR

An ideal gas is one which obeys the gas laws for the equation PV = RT at all pressures and temperatures. However no gas is ideal. They approach perfection as the temperature gets farther from their boiling points. Thus the gases H_2, N_2 and CO_2 which fail to obey the ideal-gas equation are termed as non ideal or real gases

The extent to which a real gas depart from ideal behaviour may be depicted in terms of a function called compressibility factor, denoted by Z.

It is defined

$$Z = PV/RT$$

The deviation from ideality may be shown by a plot of compressibility factor, Z against P.

For an ideal gas Z =1. For real gases the deviation from ideal behaviour will be determined by the value of Z being greater or less than unity.

2.4.1 Effect of pressure

Fig 2.4 shows the compressibility factor Z, plotted against pressure for H_2, N_2 and CO_2 at constant temperature.

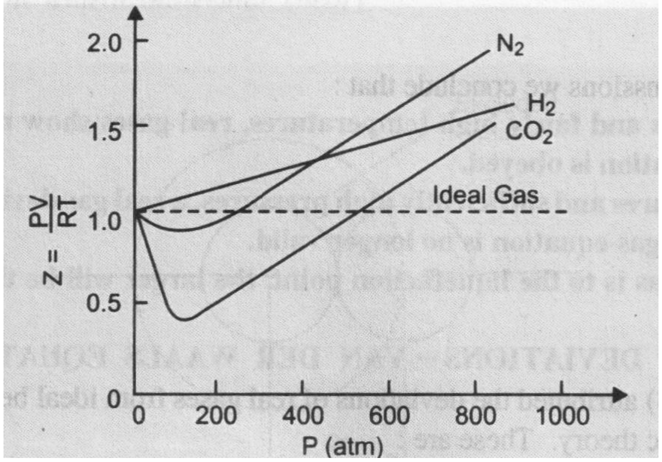


Fig 2.4

At very low pressure for all these gases Z is approximately one. This indicates that all real gases exhibit ideal behaviour (upto 10 atm). For hydrogen curve lies above ideal gas curve at all pressure.

For nitrogen and carbon di-oxide, Z first decreases. It passes to a minimum then increases continuously with increase of pressure. For gas like CO_2 the dip in the curve is greatest as it is most easily liquified.

2.4.2 Effect of temperature:

Fig 2.5 shows plot of Z against P at different temperature for N_2. It is clear

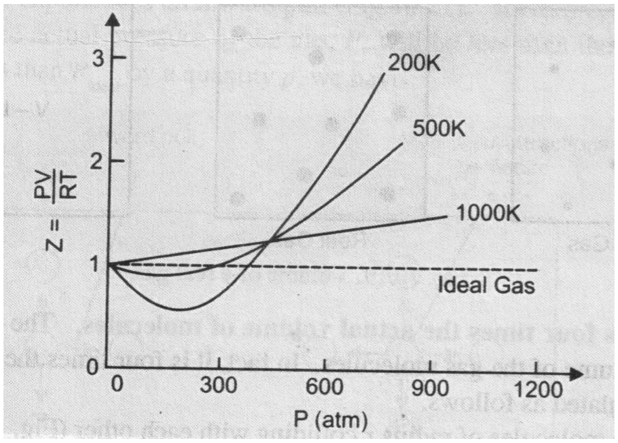


Fig 2.5

from the plot that at low temperature deviation are more and at high temperature the gas tends to become ideal.

2.5 VON DER WAAL'S EQUATION OF STATE

Von der Waal's 1873 studied the postulates of kinetic theory in detail and found that there are two faulty postulates.

(i) The molecules in a gas are point masses and possess no volume.

(ii) There are no intermolecular attractions in a gas.

Von der Waal's was the first to introduce systematically the correction terms due to the above two invalid assumptions in the ideal gas equation PV = nRT. His corrections are given below.

2.5.1 Volume correction

Volume of the gas in the available space for the movement of gas molecules. Volume V of an ideal gas is the same as the volume of the container. The dot molecule of ideal gas has zero-volume and the entire space in the container is available for their movement. But von der Waals assume that molecules of real gas are rigid spherical particles which posses a definite volume. The volume of real gas is, therefore ideal volume minus the volume occupied by gas molecules (Fig 2.6). If b is the effective volume of molecules per mole of the gas then corrected volume should be $V-b = V_{ideal}$ For n moles $V_{ideal} = V-nb$ b is also known as excluded volume.

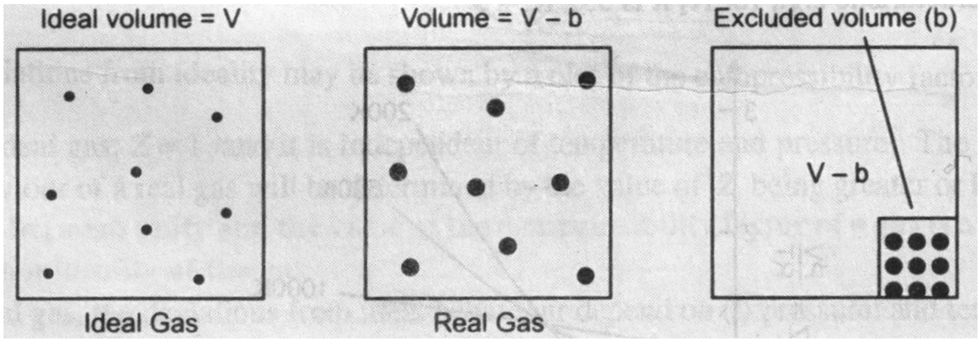


Fig 2.6

Now let us consider two molecules of radius r colliding with each other (Fig 2.7) Obviously they cannot approach each other closer than a

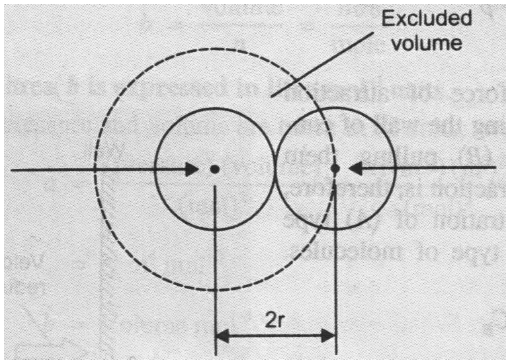


Fig 2.7

Therefore, the space indicated by the dotted sphere having radius 2r will not be available to all other molecules of the gas. In other words the dotted space is excluded volume per pair of molecules. Thus,

Excluded volume for two molecules $= 4/3\ \pi(2r)^3$
$= 8x4/3\pi r^3$
Excluded volume per molecule $= ½\ 8x4/3\pi r^3$
$= 4x\ 4/3\ \pi r^3$
$= b$
For n moles it is $nx4x\ 4/3\pi r^3$
$= nb$

2.5.2 Pressure correction

A molecule in the interior of a gas is attracted by other molecules on all sides. These attractive forces cancel out. But a molecule about to strike the wall of the vessel is attracted by molecules on one side only. Hence it experiences an inward pull (fig 2.8) due to unbalanced forces.

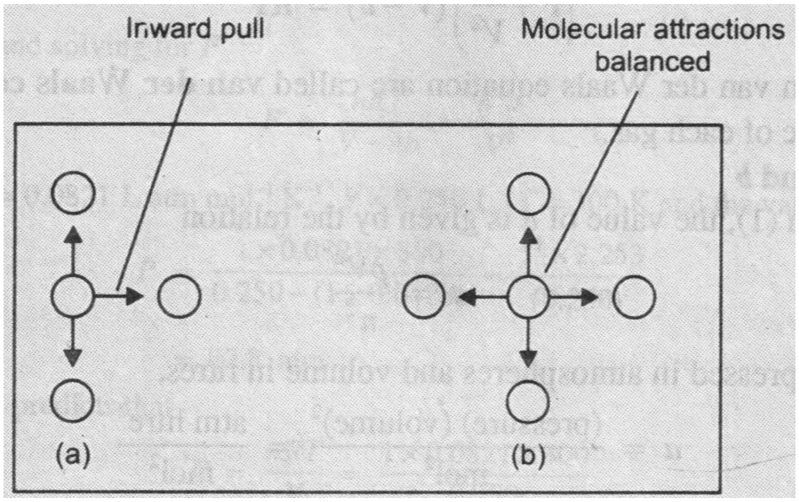


Fig 2.8

Therefore, it strikes the wall with reduced velocity and the actual pressure of the gas P, will be less than ideal pressure if the pressure P, is less than P_{ideal} by a quantity p, we have

$$P = P_{ideal} - p$$

Or $$P_{ideal} = P + p$$

The value of p is determined by the force of attraction between molecules (A) stricking the wall of the container and molecules (B) pulling them inward (Fig 2.9).

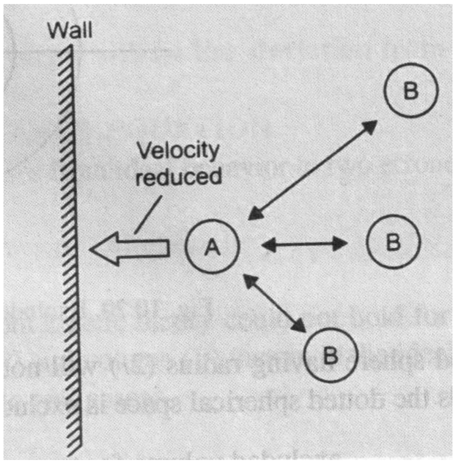


Fig 2.9

The net force of attraction is, therefore, is proportional to the concentration of (A) type molecules and also of (B) type of molecules:

That is $p \propto C_A . C_B$

$\propto A \frac{n}{V} \times \frac{n}{V}$

$p = an^2 / v^2$

n = total number of gas molecules in volume V.

Hence ideal pressure

$P_i = P + an^2/V^2$

Substituting the value of corrected volume and pressure in the ideal gas equation PV = nRT, we have

$$(P + n^2a/V^2)(V - nb) = nRT$$

This is equation for n moles for one mole

We have

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

von der Waal's equation can justify the deviations from ideal gas behaviour as given below

The equation can be written as

$PV - Pb + a/V - ab/V^2 = RT = P_iV_i$

As ab/V^2 is very small quantity it can be neglected

We get

$PV - Pb + a/V = P_iV_i$

(i) At low pressure Pb is small as compared to a/v

We have $PV + a/V = P_iV_i$

Or $PV = P_iV_i - a/V$

That means observed product PV is less then P_iV_i, the product of pressure and volume if the gas were ideal.

(ii) At high pressure, the term Pb over weighs the term a/v

Then the equation can be written as

$PV - Pb = P_iV_i$

$PV = P_iV_i + Pb$

That is observed product PV is greater than P_iV_i

(iii) At high temperature as V is large, Pb and a/V will be negligibly small.

We have $PV = P_iV_i$

(iv) Exceptional behaviour of hydrogen. This is due to the very small mass of the hydrogen molecule due to which the forces of attraction between molecules are almost negligible. Therefore neglecting the term a/V

We have

$$PV = P_iV_i + P_b$$

Therefore in the case of hydrogen even at low pressure PV is greater than P_iV_i.

2.6 ISOTHERM OF CARBON DIOXIDE- CRITICAL PHENOMENON

Isotherm means pressure volume curve at constant temperature. For ideal gas the product of PV is constant and hence the isotherm would be rectangular hyperbola. (Fig 2.10). For most of the gases at normal temperature the shape of P,V curve is the same as it is for carbon dioxide gas.

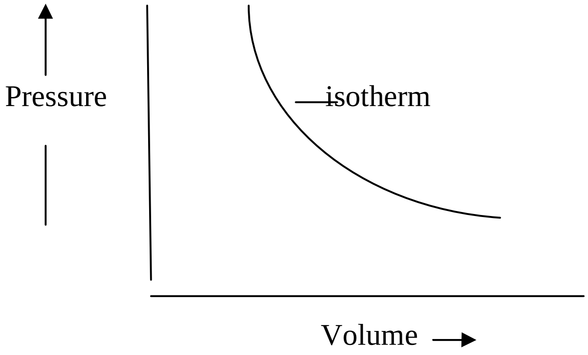


Fig 2.10 Pressure volume curve at a given temperature

Andrews in 1869 determined the isotherm of carbon dioxide at different temperatures. The isotherms of carbon dioxide determined by him at different temperature are shown in fig 2.11. Consider the first Isotherm at 13.1^0C.

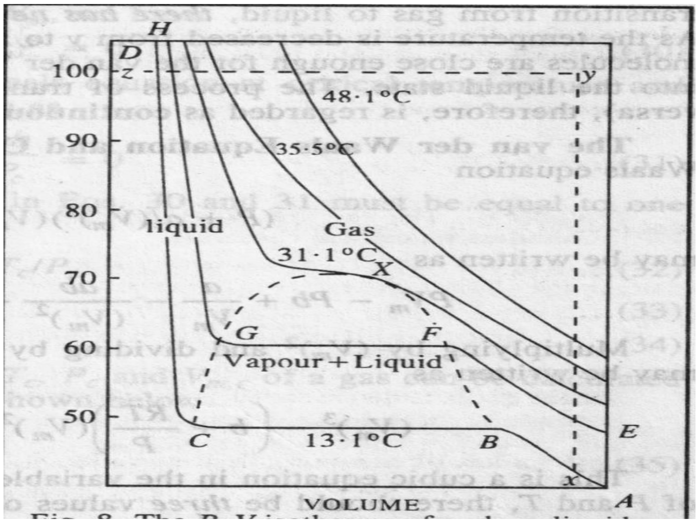


Fig 2.11 P-V isotherms of carbon dioxide

The point A represents carbon di-oxide in the gaseous state occupying a certain volume under a certain pressure. On increasing the pressure its volume diminishes as is indicated by the curve AB. At B liquification of gas commences and there after a rapid decrease in volume takes place at the same pressure as more and more of gas is converted into the liquid state. At C, the gas has been completely liquified. Now, as the liquid is only slightly compressible further increase of pressure produces only a very small decrease in volume. This is shown by a steep line CD which is almost vertical.

Thus along AB, carbon dioxide exists as gas; along BC, it exists partly as gas and partly as liquid while along CD, it exists entirely as liquid.

The curve EFGH at 21.5^0C shows a similar behaviour except that now the liquification commences at higher pressure and the horizontal portion FG, representing decrease in volume, becomes smaller. At still higher temperature, the horizontal portion of the curve becomes shorter and shorter until at 31.1^0C it reduces just to a point represented by X.

The curve passing through this point X marks the boundary between gaseous carbon dioxide and on the right and liquid carbon dioxide on the left.

Andrews noted that above 31.1^0C there was no possibility of liquefaction of carbon dioxide how great the pressure is applied. At this temperature the gas is in critical state. The point X is then called the **critical point**. The isotherm passing through this point is called the **critical isotherm** and the temperature corresponding to this isotherm (31.1^0C) is called **critical temperature.**

The critical phenomenon observed by Andrews in connection with carbon dioxide may be observed with any other gas. The pressure required to liquefy the gas at critical temperature is called the **critical pressure** and the volume occupied by one mole of the gas under these conditions is called **critical volume**.

2.7 CONTINUITY OF STATE

A careful examination of the isotherm plotted in fig 2.11 shows that it is possible to convert liquid carbondioxide into gas and vice-versa, without any discontinuity that is without having at any time more than one phase present, on joining the end of the horizontal portion of the various isotherm, a bonding curve CGXFB represented by the dotted line is obtained. At the top lies the critical point X, with in the area of the boundary curve, both liquid and gaseous state can coexist but outside this area either liquid or gaseous state alone can exist. Because of this coexistence curve, it is possible to distinguish between the two states of matter, namely, gas and liquid. However in practice this is not always true because it is possible to convert matter from one state into another without any sharp discontinuity. This can be done as shown in fig 2.11.

(i) Increase the temperature of the gas keeping volume constant. The pressure rises along xy.

(ii) Having reached y, the pressure is kept constant and the gas is cooled; this decrease the volume along the line yz.

Thus we have passed from x to z without the gradual change as it occurs along the line BC, ie condensation in the usual sense of the term did not occur. Point 2 could be said to represent a highly compressed gaseous state of the substance. Whether we refer to the state in the region of point z as liquid state or as highly compressed gaseous state depends purely upon which of the two view points happens to be convenient at the moment. Thus, in the absence of the surface of discontinuity, there is no way of distinguishing between liquid and gas.

2.3.5 Von der Waals equation and critical state Thomas in 1871 studied the isotherms of carbon dioxide drawn by Andrews. He suggested that there should be no sharp points in the isotherms below the critical temperature. These isotherms should really exhibit a complete continuity of state from gas to liquid. This he showed by a theoretical wavy curve.

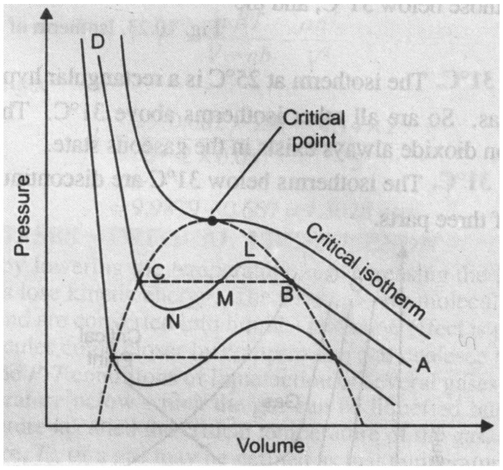


Fig 2.12 P-V isotherm of carbon dioxide

The curve MLB in fig 2.12 represents a gas compressed in a way that would remain stable. The curve MNC represents a superheated liquid. This type of discontinuity of state is predicted by von der Waals cubic equation.

According to it, for any given values of P and T there should be three values of v. These values are indicated by B, M and C of the curve. The three values of v become closer as the horizontal part of the isotherm. At the critical point, these values become identical. This enables the calculation of critical temperature, critical pressure and critical volume in terms of von der Waals constants.

The von der Waals equation may be written as

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

$PV - Pb + a/V - ab/V^2 = RT$

Or $PV^3 - (RT+Pb)V^2 + aV-ab = 0$

At critical point $V= V_c$ (V_c = critical volume)

$V-V_c = 0$

$(V-Vc)^3 =0$

$V^3 - 3V^2V_c + 3VV_c^2 - V_c^3 = 0$ . ...(1)

Thus at the critical point von der Waals equation gives

$V^3 - (RT_c /P+b) V^2 +(a/P_c)V - ab/P_c =0$ ....(2)

Equating coefficients in (1) and (2)

$3V_c = RT_c/P_c + b$ ....(3)

$3V_c^2 = a/P_c$ ....(4)

$V_c^3 = ab/P_c$ ....(5)

From (4) and (5)

$V_c = 3b$ ....(6)

Substituting this value in (4) we get

$P_c = a/27b^2$ ....(7)

Substituting the value of Pc and Vc in equation (3)

$T_c = 8a/27Rb$ ....(8)

Knowing the value of a and b, the critical constants can easily calculated. Conversely, since P_c and T_c can often be determined experimentally with some ease, these values may be employed to calculate the constants a and b.

$a= 3V_c^2P_c$ and $b = V_c/3$

The actual determination of critical constants is often a task of considerable difficulty of these critical pressure and critical temperature can be measured relatively easily with the help of Cagniard de la Tour's apparatus. The most accurate method for determining critical volume in due to Amagat.

2.8 REDUCED EQUATION OF STATE

An equation which expresses the relation between pressure volume and temperature of a gas is called the equation of state or the characteristic equation. If we express the actual pressure, volume and temperature as fractions of the critical pressure, volume and temperature respectively, we get the reduced equation of state.

If the values of pressure, volume and temperature be expressed as fractions of the corresponding critical values, we get

$P/P_c = \pi$, $V/V_c = \phi$, $T/T_c = \theta$

Where π, ϕ and θ are termed the reduced pressure, reduced volume and reduced temperature respectively.

From above $P= \pi P_c$, $V= \phi V_c$ and $T= \theta T_c$

If we replace P, V and T by πP_c, ϕV_c and T_c respectively in von der Waals equation

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

We get $\{\pi Pc + a/(\phi Vc)^2\}\{\phi Vc - b\} = R\theta Tc$

Substituting the value of $V_c= 3b$, $P_c=a/27b^2$

And $T_c = 8a/27Rb$ we get

$\{\pi \frac{a}{27b2} + a/9\phi^2b^2\}\{3\phi b-b\} = R\theta \frac{8a}{27Rb}$

Dividing the above equation throughout by a/27b

We get $\{\pi+3/\phi^2\}\{3\phi-1\} = 8\theta$

This equation is known as von der Waals reduced equation of state.

2.9 LAW OF CORRESPONDING STATES

Van der Waals reduced equation of state is given by

$\{\pi + 3/\phi^2\}\{3\phi-1\} = 8\theta$ ....(9)

In this equation the quantities a, b P_c, V_c and T_c which are characteristic of a given gas have cancelled out, thus making it applicable to all substances in the liquid or gaseous state, irrespective of their specific nature. From equation (9) it is clear that when two substances have the same reduced temperature and pressure they will have the same reduced volume. This is known as the law of corresponding states. When two or more substances are at the same reduced temperature and pressure, they are said to be in corresponding state.

In actual practice, the above reduced equation of state is not directly used. One makes use of graphs between compressibility factor z and reduced pressure at different reduced temperature. The same graphs are applicable to all gases. This can be seen from the following considerations.

Since $Z= PV/RT = \pi P_c.\phi V_c/R\theta T_c$

If we put the values of P_c, V_c and T_c

We get $Z= \frac{3\pi\phi}{8\theta}$ ....(8)

According to law of corresponding states, if two gases have the same reduced temperature and reduced pressure they will have the same reduced volume. The right hand side of the equation (8) is independent of the nature of gas and Z is same for all gases.

In practice this means that the properties of liquids should be determined at the same reduced temperature because pressure has very slight effect on them. Since it is found that boiling points of liquids are approximately $(2/3)^{rd}$ of the critical temperature, it follows that liquids are at their boiling points approximately in corresponding states. Therefore, in studies the relation between the physical properties of liquids and chemical constitutions, the physical properties may be conveniently determined at the boiling points of liquids.

2.10 SUMMARY

In this chapter you have studied different gas laws, namely: Boyle’s law, Charle’s law, Avogadros law, Graham’s law of diffusion and Dalton’s law of partial pressures. The postulates of kinetic theory are important as they are useful in deriving kinetic gas equation. By making use of this equation the different gas laws has been proved.

Deviations from ideal behaviour and von der Waals equation has been discussed in detail. Though you have studied real gas equation i.e. von der Waals equation detail and their equation is useful to discuss the deviation from ideal behaviour, there are some other equations of state also namely –

Dieterics equation, Berthelet equation, Kammerling equation.

2.11 TERMINAL QUESTIONS

(A) Multiple Choice Questions

1. Mathematically, Boyle’s law can be expressed as

(a) $V \alpha \frac{1}{P}$ (b) $V= \frac{K}{P}$ (c) VP=K (d) All of these ans (d)

2. Which of the following is the correct mathematical relation for Charle's law at constant pressure.

   (a) $V \alpha T$ (b) $V \alpha t$ (c) $V=Kt$ (d) None of these. ans (a)

3. The Average kinetic energy of gas molecule is

   (a) inversely proportional to its temperature.

   (b) directly proportional to its temperature.

   (c) equal to the square of its temperature.

   (d) directly proportional to the square root of its absolute temperature.

   ans (b)

4. The compressibility factor Z is given by

(a) $Z= PV/RT^2$ (b) $Z= PV/2RT$ (c) $Z=PV/RT$ (d) $Z=2PV/RT$ ans (c)

5. Which of the following gases will have the lowest rate of diffusion.

(a) H_2 (b) N_2 (c) F_2 (d) O_2 ans (c)

(B) Short answer questions

1.Define the following terms

(a) Critical temperature.

(b) Graham's law of diffusion

(c) Boyle's law

(d) Charle's law

2. Write two postulates of kinetic theory of gases.

3. Write a short note on critical constants.

4. Write a note on exceptional behaviour of hydrogen as given by von der Waals.

5. Write von der Waals equation for n moles of a gas.

(C) Long answer questions

1. Discuss the causes of deviation from ideal behaviour. How they are accounted for in the von der Waals equation?
2. What are the postulates of kinetic theory of gases and show how they are justified?
3. Derive the kinetic gas equation for an ideal gas.
4. What are the limitations for equation PV=RT? What improvements have been suggested by von der Waals?
5. State and explain the principle of corresponding states. Derive an expression interconnecting critical pressure, critical volume and critical temperature.
6. (a) For ammonia gas von der Waals constants a and b are 4.0 litre^2 atm mole^{-2} and 0.036 litre mole^{-1} respectively, calculate critical volume. (R=0.0821 litre atm degree^{-1}). (hint $V_c=3b$)

   (b) Obtain the relation

   $RT_c/P_cV_c = 8/3$

UNIT 3: GASEOUS STATE-II

CONTENTS:

3.1 OBJECTIVE

Till now you have studied the various postulates of kinetic theory of gases, the kinetic gas equation and derivation of various gas laws by making use of kinetic gas equation. Thought the kinetic gas equation is useful in deriving the gas law but at high pressure and at low temperature there are considerable deviations from ideal gas behaviour.

These derivations have been explained by Van der Waal and the Van der Waal’s equation explains the deviations by applying pressure and volume corrections. The law of corresponding state and its consequences have been discussed in this chapter.

3.2 INTRODUCTION

Though gas molecules possess very high velocity and because of collisions the velocity of gas molecules changes in a very short span but velocity can be easily calculated from kinetic gas equation. In this unit you will study different types of velocities their correlation and calculation, collision diameter, collision number, free path and various methods of liquefaction of gases will be discussed in this chapter. It will also we very interesting to study how molecular velocities are distributed i.e. Maxwell’s equation for distribution of velocities.

3.3 DISTRIBUTION OF MOLECULAR VELOCITIES

All the molecules constituting a given quantity of any gas do not possess the same velocity. Even a single molecule cannot maintain the same velocity for any length of time. As it collides with another molecule the kinetic energies and the velocities of two are redistributed and a consequence change in velocity takes place. In fact the velocity of a molecule changes after a span of less than 10^{-9} seconds, thus making it difficult to know the speed of a single molecule. Since number of molecule is very large, a fraction of molecule will have the same particular velocity. In this way there is a broad distribution of velocities over different fraction of molecules. In 1860 James Clark Maxwell calculated the distribution of velocities from the laws of probability. He derived the following equation for the distribution of molecular velocities.

$$\frac{dNc}{N} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e \frac{-Mc2}{2RT} c^2 dc \qquad ......(1)$$

Where dN_c = number of molecules having velocities between c and (c+dc)

N= total number of molecules

M= molar mass

T= temperature in absolute scale.

This relation is called Maxwell’s law of distribution of velocities. The ratio dN_c /n gives the fraction of the total number of molecules having velocities between c and (c+dc).

Maxwell plotted such fractions against velocity possessed by the molecules. The curve so obtained illustrate the salient features of Maxwell distribution of velocities. Fig 3.1 shows the distribution of velocities in nitrogen gas, N_2 at 300K and 600K. It is noticed that:

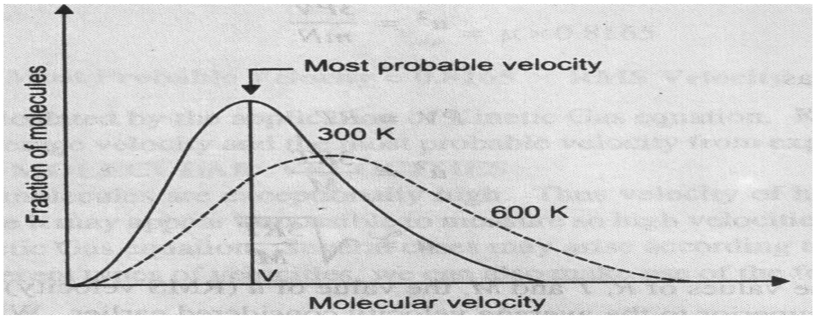


Fig 3.1 Distribution of molecular velocities at two temperatures.

1. A very small fraction of molecules has either very low (close to zero) or very high velocities (i.e. velocity greater than a high value).
2. A large majority of the molecules have a velocity in a relatively small range of variation more or less around the peak of the curve.

   The velocity represented by maximum number of molecules of a gas at a given temperature is called most probable velocity. This corresponds to the highest point on the curve.
3. At higher temperature, the whole curve shifts to the right (dotted curve at 600K). This shows that at higher temperature more molecules have higher velocities and fewer molecules have lower velocities.

3.4 DIFFERENT KIND OF VELOCITIES

3.4 .1 Root mean square velocity: Velocity v which if possessed by each of the n molecules of the gas leads to correct calculation of total kinetic energy of the gas is known as root mean square velocity.

$$\text{Total kinetic energy} = n\frac{1}{2}mv^2 \qquad ....(2)$$

We will proceed to test the validity of the above equation (2) mathematically.

Out of the total number of molecules n contained in the given sample of gas, let n_1, molecules have velocity v_1, n_2 molecules have velocity v_2 and so on then,

$$n= n_1+n_2+n_3 \qquad ....(3)$$

the total kinetic energy KE of the n molecules is the sum of the kinetic energies of the individual molecules.

Thus

$$KE= n_1 \times 1/2\, m_1 v_1^2+n_2\, 1/2 m_2 v_2^2 +......$$

$$½\, n\, v^2=n_1 \times 1/2\, m_1 v_1^2+n_2\, 1/2 m_2 v_2^2 +.... \qquad ....(4)$$

$$n\, v_2 = n_1 v_1 + n_2 v_2^2 +........ \qquad .... (5)$$

$$v^2 = \frac{n_1 v_1^2 + n_2 v_2^2 +........}{n} \qquad ....(6)$$

thus v^2 is the mean of squares of the velocities of all the n molecules in the gas and is termed as mean square velocity.

$$\text{So } v = \sqrt{\frac{n_1 v_1^2+ n_2 v_2^2}{}} + ... \qquad .... (7)$$

Here v is root of the mean of squares of velocities and is called root mean square velocity and is often written simply as rms velocity. Its value can be calculated as

$$v_{rms} = \sqrt{3RT/M}$$

.................(8)

3.4.2 Average velocity

The average velocity is given by the arithmetic mean of different velocities possessed by the molecules of the gas at a given temperature.

Suppose one molecule is moving with velocity v_1, one molecule with velocity v_2, third molecule with velocity v_3 and so on. Then total velocity will be

$$v_1 + v_2 + v_3 \ldots\ldots\ldots\ldots\ldots\ldots$$

There are total of n molecules

The $$v_a = \frac{v_1 + v_2 + v_3 \ldots\ldots\ldots}{n}$$

its value can be calculated as $v_a = \left(\frac{2RT}{M}\right)^{1/2}$ ....(9)

This is average velocity represented by v_a

3.4.3 Most probable velocity

Velocity possessed by most number of molecules is known as most probable velocity. (Fig 3.1)

Most probable velocity

$$v_{mp} = (8RT/\pi M)^{1/2} \quad \text{....(10)}$$

It is found that

$v_{rms} > v_a > v_{mp}$

$v_{rms} : v_a : v_{mp} = 1.0:0.92:0.82$

3.5 QUALITATIVE DISCUSSION OF MAXWELL'S DISTRIBUTION OF VELOCITIES

Though molecules of the gas moves with very high velocity and the velocity changes because of collisions with in very short time span, but with the help of Maxwell's distribution law and molecular kinetic energy molecular velocity can be calculated. It will be clear to you when you study numerical problems.

3.5.1 Effect of temperature on velocity distribution

It is clear from fig 3.1 that the velocity distribution of molecules in gas is influenced by a rise in temperature. At a higher temperature (600K) the curve maintains the same general trend of distribution. However, it becomes more flattened with the peak shifting to a higher velocity region. In other words, there is more even distribution of velocities about 'most probable velocity' and the number of molecules having velocities near this value becomes more. Thus higher the temperature, higher is the most probable velocity.

3.6 COLLISION NUMBER/COLLISION DIAMETER

The kinetic theory of gases treats molecule as point masses. When two such molecules approach each other, a point is reached at which they cannot come closer beyond a certain distance.

The closest distance between the centres of the two molecules taking part in collision is called the collision diameter. It is denoted by σ.

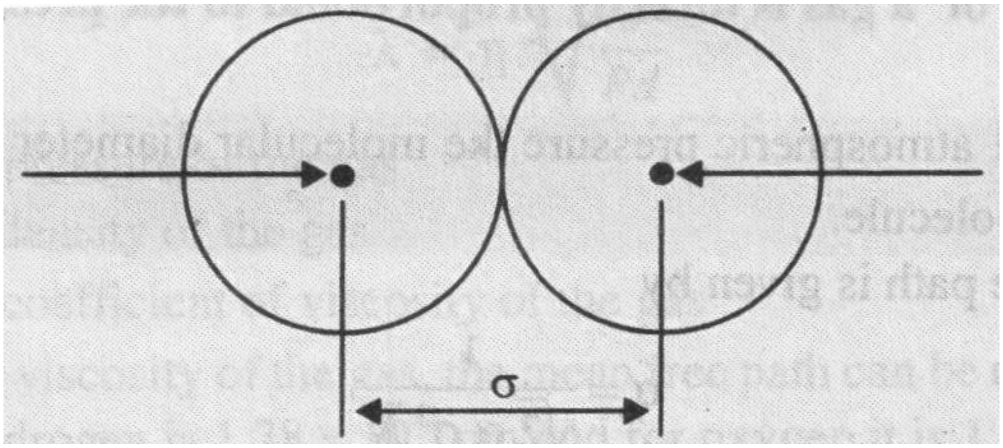


Fig 3.2

Whenever the distance between the centres of two molecules is σ, a collision occurs. The collision diameter can be determined from viscosity measurements. The collision diameter of hydrogen is 2.74A^0 and that of oxygen is 3.61A^0.

3.7 COLLISION FREQUENCY

The collision frequency of a gas is defined as:

The number of collisions taking place per second per unit volume (c.c.) of the gas.

Let a gas contain N molecules per cc. From kinetic considerations it has been established that the number of molecules, n, with which a simple molecule will collide per second, is given by the relation

$$n = \sqrt{2}\pi v_a \sigma^2 N \qquad \text{......(11)}$$

where v_a = average velocity and σ =collision diameter.

If the total number of collisions taking place per second is denoted by z we have

$$z = \sqrt{2}\pi v_a \sigma^2 N \times N$$

$$= \sqrt{2}\pi v_a \sigma^2 N^2 \qquad \text{....(12)}$$

Since each collision involves two molecules, the number of collision per second per cc, of the gas will be z/2

Hence the collision frequency $= \dfrac{\sqrt{2}\pi v_a \sigma^2 N^2}{2}$

$$= \frac{\pi v_a \sigma^2 N^2}{\sqrt{2}} \qquad \text{...(13)}$$

Evidently, the collision frequency of a gas increases with increase in temperature, molecular size and the number of molecules per c.c.

3.7.1 Effect of temperature on collision frequency

We know collision frequency is given by

$$z = \frac{\pi v_a \sigma^2 N^2}{\sqrt{2}} \qquad \text{......(14)}$$

From the equation it is clear

$z\ \alpha\ v_a$

But $v_a\ \alpha\ \sqrt{T}$ (from equation 9)

Hence $z\ \alpha\ \sqrt{T}$

Hence collision frequency is directly proportional to square root of temperature.

3.7.2 Effect of pressure on collision frequency

From equation (14)

$z\ \alpha\ N^2$

Where N is number of molecules per cc.

But we know $P\ \alpha\ N$

Hence $z\ \alpha\ P^2$

Thus collision frequency is directly proportional to the square of pressure of the gas.

3.8 MEAN FREE PATH

A very important quantity in kinetic theory of gases is the mean free path. At a given temperature, a molecule travels in straight line before collision with another molecule.

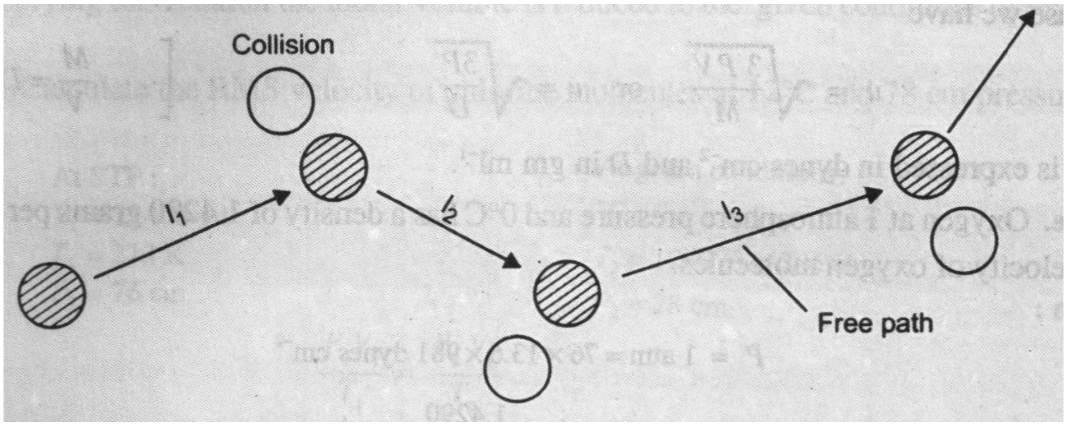


Fig 3.3 Mean free path

The distance travelled by the molecule before collision is termed free path. The mean distance travelled by a gas molecule between two successive collisions is called the mean free path. It is denoted by λ. If l_1, l_2, l_3 are the free paths for a molecule of a gas, its free path

$$\lambda = \frac{l_1+l_2+l_3 ......l_n}{n} \qquad ....(15)$$

Where n is number of molecules with which the molecule collides. Evidently, the molecular collisions will be less at a lower pressure or lower density and longer will be the mean free path. Mean free path is also related with viscosity of the gas.

$$\lambda = \acute{\eta}\sqrt{3}/P_d$$

where p= pressure of the gas

$\acute{\eta}$ = coefficient of viscosity of the gas

d = density of the gas

From the above equation it is clear that by the determination of viscosity mean per path can be calculated. At NTP the mean free path for hydrogen is 1.78×10^{-5} cm and for oxygen 1.0×10^{-5} cm.

3.8.1 Effect of temperature on mean free path

The ideal gas equation is $PV = nRT$ ....(16)

Where n is number of moles given by

n = No of molecules / Avogadro's number = N/N_0

Substituting the value of n in equation (16)

$PV = N/N_0 \times RT$

or $N/V = (PN_0)/RT$

At constant pressure $N \alpha \frac{1}{T}$ ....(17)

The mean free path is given by

λ = Distance Travelled by the molecule per second / Number of collisions per cc.

$= v/\sqrt{\pi}\sigma^2 v N$ ....(18)

Combining equation (17) and equation 18

$\lambda \alpha T$

Thus mean free path is directly proportional to the absolute temperature.

3.8.2 Effect of pressure on mean free path

We know that the pressure of a gas at certain temperature is directly proportional to the number of molecules cc. that is,

$P \alpha N$

and mean free path is $\lambda = 1/\sqrt{2}\pi\sigma^2 N$

Hence we get

$\lambda \alpha 1/P$

Thus mean free path is inversely proportional to the pressure of a gas at constant temperature.

3.9 LIQUIFICATION OF GASES

The general behaviour of gases with the decrease of temperature with increase of pressure is shown by the Andrew isotherm of carbon dioxide. You have studied these in chapter 2.3.3 and shown in fig 2.10.

It is clear from Andrews isotherm, it is necessary to cool a gas below its critical temperature before it can be liquified. In the case of gases like ammonia, Chlorine, sulphur dioxide or carbon dioxide, which has a fairly high critical temperature (table 3.1), by the application of pressure gas can be liquified.

Gas	Critical temperature (K)
He	5.2
Ne	44.2
H_2	33.0
O_2	154.8
N_2	126.2

CO_2	304.2
NH_3	405.0

Table 3.1 Critical temperature of various gases

Gases such as hydrogen, oxygen, helium and nitrogen have low critical temperature. So these gases cannot be liquified by this simple technique. These gases can be liquified if they first cooled below these respective critical temperature.

Two principles are usually applied in cooling gases below these critical temperature.

3.10 JOULE-THOMSON'S EFFECT

Joule and Thomson observed that when a gas under high pressure is made to expand into a region of low pressure it suffers a fall in temperature. This phenomenon is known as Joule-Thomson effect.

The Joule-Thomson effect offers further support to the view that attractive forces attractive forces do exist between gas molecules. As the gas expands, the molecules fall apart one another. Therefore, work has to be

done in order to overcome the cohesive or attractive forces which tend to hold the molecules together. Thus work is done by the system at the expense of the kinetic energy of the gaseous molecules. Consequently, the kinetic energy decreases and since it is proportional to temperature cooling results.

Experiments have shown that gases become cooler during the Joule-Thomson expansion only when they are below a certain temperature known as inversion temperature T_i. The inversion temperature is characteristic of each gas. The inversion temperature is related to von der Waals constants a and b of the gas concerned by the expression

$$T_i = 2a/Rb$$

At the inversion temperature there is no Joule-Thomson effect. If the temperature is above inversion temperature then after passing into lower pressure region there will be rise of temperature end if it takes place below the inversion temperature there is fall of temperature.

In most gases, the inversion temperature lies within the range of ordinary temperatures. Hence they get cooled in Joule-Thomson expansion. Hydrogen and helium, however, have very low inversion temperature. Thus at ordinary temperatures these gases get warmed up instead of getting cooled at the Joule-Thomson expansion. If these gases are first cooled to their respective inversion temperatures, then these gases also get cooled an expansion in accordance with the Joule-Thomson effect.

Adiabatic expansion involving mechanical work:

When a gas is made to expand against pressure it does some work as in the case of an engine, it does some external work also at the expense of its kinetic energy which decreases. Hence, there is a fall of temperature.

3.10.1 Methods of liquefaction

From the above discussion it is clear to you that two conditions which tend to change a gas into the liquid state are low temperature and high pressure. If a gas is cooled below its critical temperature and subjected to adequate pressure, it liquefies.

The various methods employed for the liquification of gases depend on the technique used to attain low temperature. The three important methods are

(i) Faraday's method in which cooling is done with a freezing mixture.

(ii) Linde's method in which compressed gas is released at a narrow jet (Joule-Thomson effect).

(iii) Claude's method in which gas is allowed to do mechanical work.

3.10.2 Faraday's method- Faraday (1823) used freezing mixture of ice with various salts for external cooling of gases.

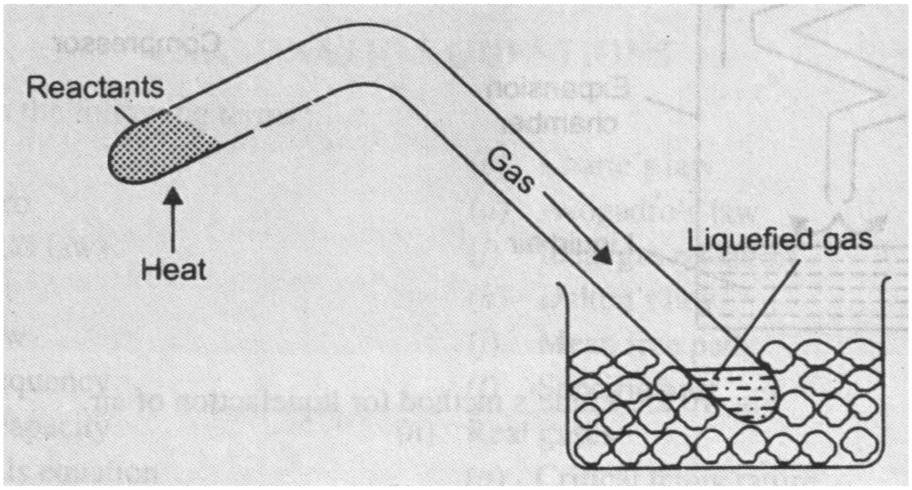


Fig 3.3 Faraday's method for the liquefication of gases

The melting of ice and dissolution of salts both are endothermic processes. The temperature of the mixture is lowered up to a temperature when the solution becomes saturated.

Faraday succeeded in liquefying a number of gases such as SO_2, CO_2, NO, Cl_2 by this method. He used V-shaped tube in one arm of which gas was prepared. In the other arm the gas was liquefied under its own pressure.

The gases liquefied by this method had their critical temperature above or just below the ordinary atmospheric temperature. The gases like N_2, O_2 and H_2 having low critical points could not be liquefied by this method.

3.10.3 Linde's method

Linde's (1895) used Joule-Thomson effect as the basis for liquefaction of gases. When a compressed gas is allowed to expand into vacuum or a region of low pressure, it produces intense cooling.

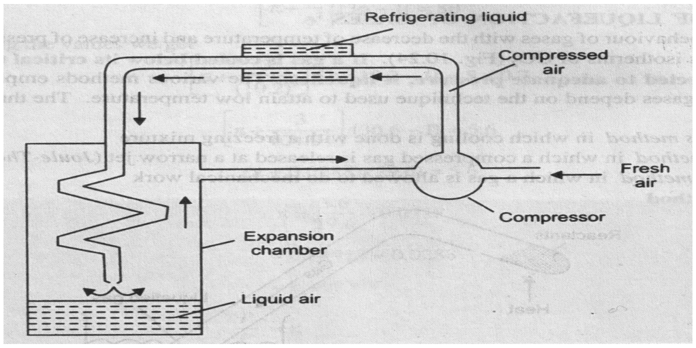


Fig 3.4 Linde's method for liquefication of air

In a compressed gas molecules are very close and attraction between them are appreciable. As the gas expands, the molecules move apart. In doing so, the intermolecular attraction must be overcome. The energy for it is taken from the gas itself which is thereby cooled.

Linde used an apparatus worked on the above principle to the liquefication of air as shown in **Fig 3.4**. Pure dry air is compressed to about 200 atmospheres. It is passed through a pipe cooled by a refrigerating liquid such as ammonia. By doing this the heat of compression is removed. The compressed air is then passed into a spiral pipe with a jet at the lower end. The free expansions of air at the jet result in a considerable drop of temperature. The cooled air which is now at about one atmosphere pressure passed up the expansion chamber. It further cools the incoming air of the spiral tube and returns to the compressor. By repeating the process of compression and expansion a temperature low enough to liquefy air is reached. The liquefied air collects at the bottom of the expansion chamber.

3.10.4 Claude's method

In this method the compressed air is allowed to do mechanical work by driving an engine. The energy for it comes from the gas itself.

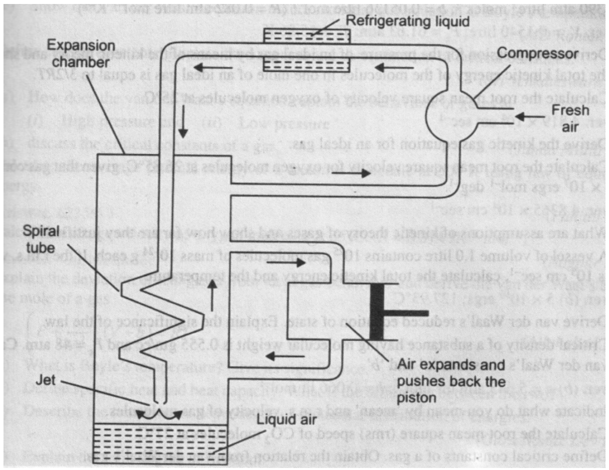


Fig 3.5 Claude's method for liquefication of air

Thus in Claude's method the gas is cooled not only by overcoming the intermolecular forces but also by performance of work. That is why the cooling produced greater than in Linde's method.

Claude's apparatus is shown in fig 3.5 for liquefication of air. Dry air is compressed to about 200 atmospheres. It is passed through a tube cooled by refrigerating liquid to remove any heat produced during compression. The tube carrying the compressed air then enters the expansion chamber. At this stage it bifurcates and a part of this air passes through a side tube into the cylinder of an engine. Here it expands and pushes back the piston. Now it is clear that the air does mechanical work and it cools. The air then enters the expansion chamber and cools the

incoming air through the spiral tube. The air undergoes further cooling by expansion at the jet and liquefies. The gas escaping liquefaction goes back to the compressor and the whole process is repeated over and over again.

Paramagnetic cooling:

It was shown by Debye on theoretical grounds that a very close approach to absolute zero was possible by adiabatic demagnetisation of a paramagnetic salt. When a paramagnetic substance is magnetised, external work is done by it and its temperature rises. But when it is demagnetised external work is done by it and its temperature falls.

In this method a temperature of the order of 0.002K has been attained.

3.11 SUMMARY

Most characteristic property of gases is that their molecules lie for apart from each other and are in continuous motion. Each molecules, therefore leads almost an independent existence. This property is so when temperature is high and pressure is low.

Till now you have studied that a gas is said to be an ideal gas if it obeys Boyle's law and Charle's law rigidly for all values of temperature and pressure. In other words a perfect gas is one which strictly follows the general gas equation PV= nRT, since both the laws are contained in it. Actually no gas is perfect. They approach ideal behaviour as the temperature gets farther from their boiling points, so that at ordinary temperature the most nearly perfect gases are those like hydrogen and nitrogen which have very low boiling points.

The study of kinetic theory of gases enables us to calculate molecular velocities. Which is otherwise very difficult to determine because gas molecule possess very high velocity and because of collisions the velocity changes with in very small time.

3.12 TERMINAL QUESTIONS

(A) Multiple Choice Questions

1. A real gas most closely approaches the behaviour of a perfect gas under the condition of

(a) High pressure and low temperature.
(b) Low pressure and high temperature.
(c) Low pressure and low temperature.
(d) High temperature and high pressure. ans (b)

2. The compressibility factor of a perfect gas is

(a) Zero (b) One (c) more than one (d) Less than one.

ans (b)

1. The root mean square velocity of a gas molecule is given by

(a) $v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$ (b) $v_{\text{rms}} = \sqrt{\frac{2RT}{M}}$

(b) (c) $v_{\text{rms}} = \sqrt{\frac{3RT}{\pi M}}$ (d) $v_{\text{rms}} = \sqrt{\frac{2RT}{\pi M}}$ ans (a)

2. The free path is the distance travelled by the molecule

(a) Before collision (b) in one second
(b) After collision (d) in one minute

ans (a)

3. Compressibility factor is represented as

(a) $Z=\frac{PV}{RT2}$ (b) $Z=\frac{RT}{PV}$ (c) $Z=\frac{2PV}{RT}$ (d) $Z=\frac{PV}{RT}$ ans (d)

4. How many molecules are present in 0.2 g of hydrogen?

(a) $6.023\text{x}10^{23}$ (b) $6.032\text{x}10^{22}$ (c) $3.0125\text{x}10^{23}$ (d) $3.0125\text{x}10^{22}$

ans (b)

(B) Short Answer Questions

1. Define the following terms.

(a) Root mean square velocity.

(b) Most probable velocity.

(c) Average velocity.

2. Define mean free path

3. Write a note on collision number

4. Explain the significance of von der Waal's constant

5. Define law of corresponding states

6. Write a note on volume correction in von der Waal's equation.

(C) Long Answer Questions

1. Narrate the various methods of producing cold, and show how these have been used in liquefaction of gases.

2 (a) Define Joule-Thomson effect. Explain inversion temperature. How is it related to von der Waal's constants.

(b) The von der Waal's constants a and b for a gas are 0.045 dm atm mole^{-2} and 0.026 dm3 mole^{-1} respectively. Calculate the inversion temperature of the gas. (hint $Ti=\frac{2a}{Rb}$)

Ans 42.16K

3. (a) State Maxwell's law or distribution of velocities. How does a change in temperature influence this distribution?

(b) Define three different types of velocities. How are the related with each other?

4 (a) Define the terms:

(i) Critical temperature.

(ii) Boyles temperature.

(iii) Conversion temperature.

(b) Write a note on collision diameter.

……………..

UNIT 4: LIQUID STATE

CONTENTS:

4.1 OBJECTIVE

The matter exists in three states. The solid state in crystalline form exhibits a complete orderly arrangement of molecules atoms or ions as the case may be. The gaseous state exhibits complete disorder or randomness. The liquid state lies in between these two extreme order and disorder.

The definite and ordered arrangement of the constituents of a solid extends over a large distance. This is termed as long range order. The liquids exhibit only a short range order while gases show no order at all.

A liquid may be regarded as a condensed gas or molten solid. In a solid the molecules are rigidly fixed and, therefore, it has a definite shape and a definite volume. In a gas, on the other hand the molecules have random motion and, therefore, it has neither a definite shape nor a definite volume. In a liquid the molecules are not as rigidly fixed as in solids. They have some freedom of motion which, however, is much more restricted than that in gases. A liquid, therefore has a definite volume although not a definite shape. It is much less compressible and are far denser than gases.

4.2 INTRODUCTION

As you have studied in the previous unit (i.e. unit 3), liquids can be obtained from gases by cooling the latter below their respective critical temperature followed by the treatment of high pressure. Effect of cooling is to decrease the thermal energies of molecules and the effect of pressure is to decrease the volume of the system so as to allow the molecules to come closer, thereby increasing the force of attraction amongst them. Alternatively, liquids can be obtained by heating solids upto or beyond their melting points. Thus we see the properties of liquids lie in between those of solids and gases. For example liquids are less compressible than gases but a little more compressible than solids. They are less dense than solid but more dense than gases. The two important properties of liquids, namely, the fixed volume but no fixed shape arises mainly because of the following two facts

(1) The energies binding the molecules are larger than their average thermal energy.
(2) Their binding energies are not strong enough to stop the motion of the molecules altogether, as in the case of solids, with the result that molecules can move from one place to another but cannot escape from the liquid unless they are present at the surface.

4.3 INTERMOLECULAR FORCES

Since the molecules in a liquid are not far apart from each other, the intermolecular forces are fairly strong. The characteristic properties of liquid arise from the nature and the magnitude of these intermolecular forces.

Intermolecular forces in liquids are collectively called von der Waal's forces. These forces are essentially electrical in nature and result from the attraction of charges of opposite sign. The principle kinds of intermolecular forces are:

(i) Dipole-dipole interaction
(ii) London forces
(iii) Hydrogen bonding.

4.3.1 Dipole-dipole interaction

We have seen that HCl is an example of a polar molecule. Such molecule have a partial positive charge at one end and a partial negative charge at the other.

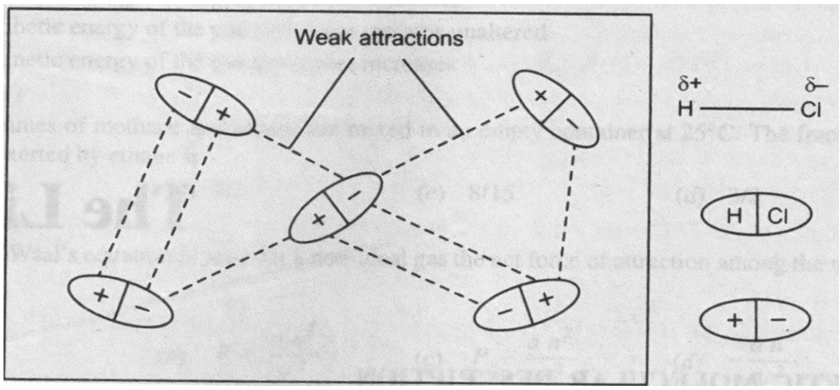


Fig 4.1 Weak attraction between polar HCl molecules

They are called dipoles. The positive end of one dipole attracts the negative end of the other. The thermal energy of molecules tends to disturb these attractions but still there exists a net attraction between the polar molecules. These forces are referred to as dipole-dipole attractions. Generally such attractions are about 1% as strong as covalent bond. It is to be noted that the attractions between the opposite poles are greater than repulsive forces between like poles. Thus these molecules have a net attraction to each other.

4.3.2 London forces

In 1930 Fritz London first offered a simple explanation of weak forces between nonpolar molecules or atoms. In a molecule (or atom) electrons are constantly moving. Most of the time electrons in the molecules could not be visualized as distributed symmetrically. However according to the principle of probability, for an instant the electrons may concentrate on one side of the molecule than the other. This causes the molecule (A) to become momentarily polar and we call it instant dipole.

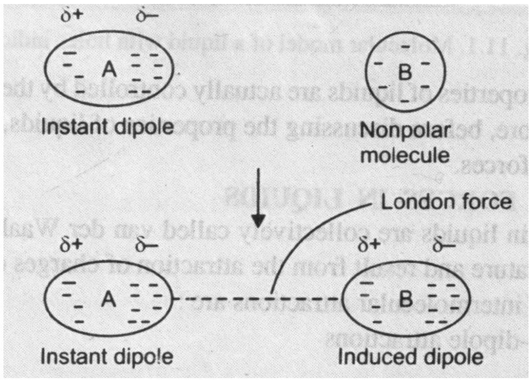


fig 4.2 Explanation of London forces

The negative side of the instantaneous dipole repels the electrons of an adjacent molecule (B). As a result the second molecule B also becomes a dipole by induced polarity. This is called induced dipole **Fig 4.2.**

The instantaneous dipole A and the induced dipole B will now attract each other. Because the electrons keep moving an instant dipole may vanish the next moment and new are produced. This continual process produces a weak overall attraction between molecules of liquid.

The momentary attraction between the molecules of liquid caused by instantaneous-dipole and **induced- dipole attractions are called London forces.** These London forces are present in polar molecules also in addition to other von der Waal's forces.

The strength of the London forces depends as to how easily the electron cloud in a particular molecule is deformed. This is determined by the number of electrons and also on the size of the molecule. Thus Argon (-245.9^{0}C) with a greater number of electron and larger molecular weight has a higher boiling point than helium (-268.9^{0}C).

4.3.3 Hydrogen bonding

In compounds of hydrogen with strongly electronegative elements, such as fluorine, oxygen and nitrogen, the electron pair shared between the two atoms lies far away from the hydrogen atom as a result of which the hydrogen atom becomes highly electropositive with respect to other atom which become electronegative. This phenomenon of charge separation

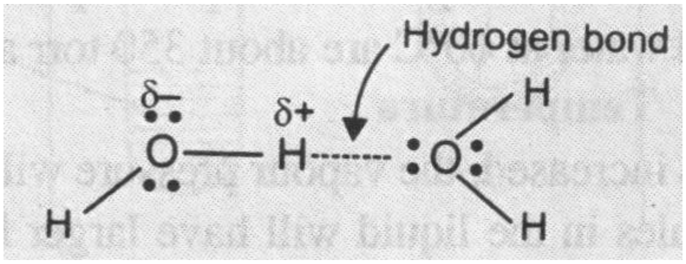


Fig 4.3 Hydrogen bond

in water is represented as shown in the fig 4.3. The electronegativity difference in H and O is so large that the electron pair in the covalent bond, H-O is shifted toward O. It leaves a partial positive charge on the H atom. This leads to a strong electrostatic attraction between positively charged H atom and an unshared electron pair on the O atom of another molecule. Thus you can understand that two or more molecules may associate together to form large cluster of molecule. This is shown below for the association of several molecules of hydrogen fluoride.

...$H^{+\delta}$ –$F^{-\delta}$ .....$H^{+\delta}$ –$F^{-\delta}$ ......$H^{+\delta}$ –$F^{-\delta}$ .....

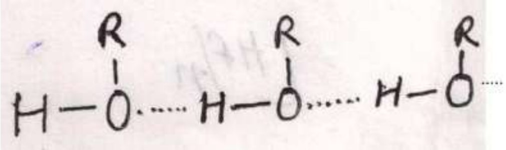
In this case, while the length of covalent bond between H and F atoms is found to be $1.00A^0$, the length of the hydrogen bond between H and F atoms of neighbouring molecules has been found to be $1.55A^0$. this cluster of HF molecules may be described as $(HF)_n$

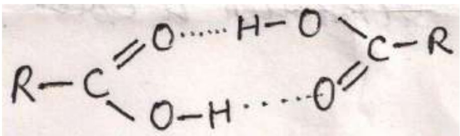
The attractive force which binds hydrogen atom of one molecule with electronegative atom of another molecule, generally of the same substance is known as the hydrogen bond.

The hydrogen bonding is the strongest of all intermolecular forces including the dipole-dipole attractions and London forces.

In the above discussion you have seen that cluster of HF molecule is described as $(HF)_n$ and cluster of water molecule may be described as $(H_2O)_n$

Alcohols and carboxylic acids also form associated molecules for the same reason, as shown below





Alchohols **Carboxylic Acids**

4.4 STRUCTURE OF LIQUIDS

In a liquid, the molecules are not as rigidly fixed an in solid. They have some freedom of motion which, however, is much less than that in a gas. Liquids resemble solids in being compact, incompressible and in having a definite volume. These properties are indicative of a regular structure in liquids similar to that in solids.

From X-ray diffraction technique, it has been found that the resemblance of liquid state with solid state is valid with in a small range; i.e. within only small distance from a given molecule. In other words the regularly ordered structure which exists in crystalline solids is of short range in liquids. It means it exists in only within a short distance from any given molecule. A solid possesses short range as well as long range order since the ordered structure extends regularly throughout the whole crystal.

Now it should be clear to you that

(i) A gas consists of molecules separated wide apart in empty space. The molecules are free to move about throughout the container.

(ii) A liquid has molecule touching each other. However, the intermolecular space, permit the movement of molecule throughout the liquid.

(iii) A solid has molecules, atoms or ions arranged in a certain order in fixed position in the crystal lattice. The particles in a solid are not free to move about but vibrate in their fixed position.

4.5 CHARACTERISTIC PROPERTIES OF LIQUIDS

As you have studied earlier in this unit that the properties of liquids arise from

(i) The nature and

(ii) The magnitude of intermolecular forces of attraction existing between their molecules. The important properties of liquids are

1. Vapour pressure
2. Surface tension
3. Viscosity
4. Refraction

Now you will study these properties in detail

4.5.1 Vapour pressure

When a liquid is an open vessel, it evaporates. You have studied in the gases unit, that the gas molecules have a particular velocity. This is so in case of liquids also. Only a few liquid molecules have lower or higher velocity, i.e. lower or higher kinetic energies. The energy distribution of molecules in a liquid is shown in Fig 4.4.

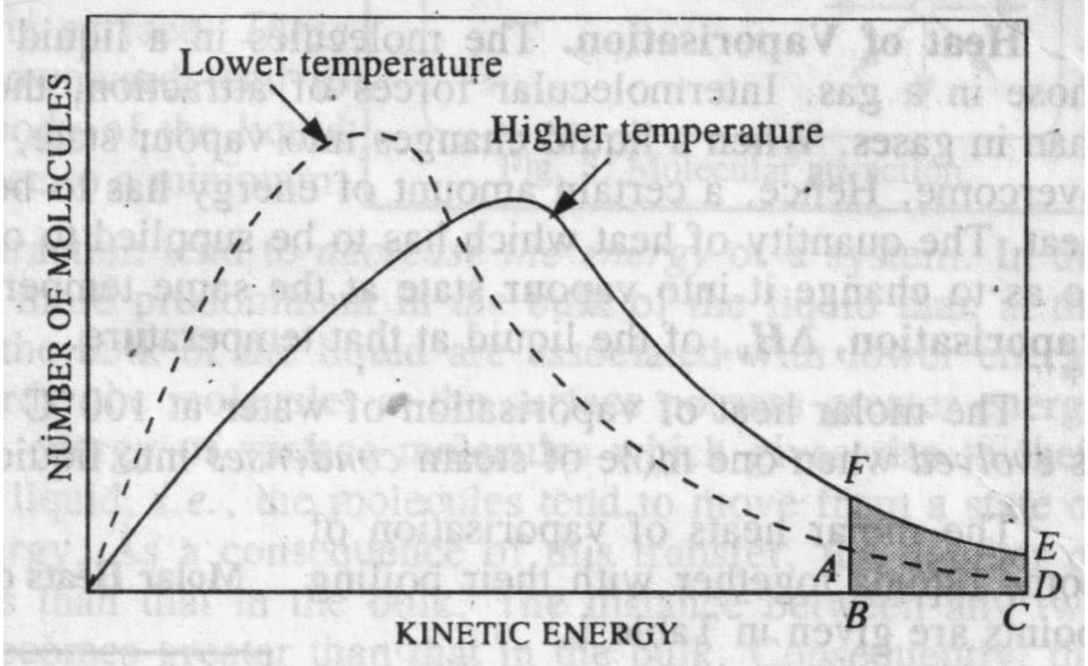


Fig 4.4 energy distribution of molecules of a liquid

It is clear from the **Fig 4.4** that the number of molecules with high kinetic energies, as shown by the shaded portion ABCD of the dotted curve is very small. This number, however, increases with rise in temperature, as shown by the shaded portion FBCE of the bold line curve.

When a liquid is placed in an open vessel it evaporates. The molecules in the liquid are moving with different kinetic energies. The molecules that possess above average kinetic energies can overcome the intermolecular forces that hold them in the liquid. These energies molecules escape from the surface as vapour. This process by which molecules of a liquid goes into gaseous state is called vaporisation or evaporation. The reverse process whereby gas molecules become liquid is called condensation.

When a liquid is place in a closed vessel, the molecules with high kinetic energies escape into space above the liquid as shown in fig 4.5. as the number of molecule in the gas phase increases, some of them strike the liquid surface and are recaptured (condensation).

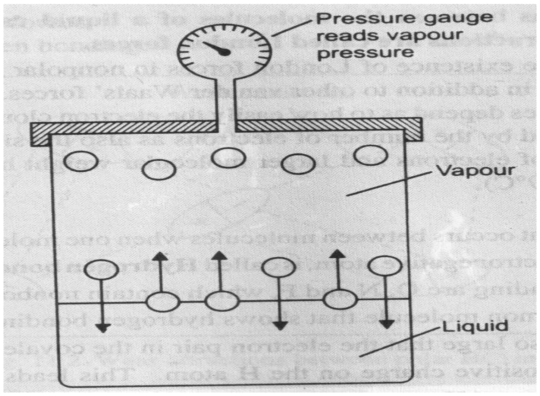


Fig 4.5 Illustration of vapour pressure

A stage comes when the number of molecules escaping from the liquid is equal to the number of molecules returning to the liquid. Thus a dynamic equilibrium is established between the liquid and the vapour at a given temperature.

$$\text{Liquid} \rightleftarrows \text{vapour}$$

Now the concentration of the vapour in the space above the liquid will remain unchanged with lapse of time. Hence the vapour will exert a definite pressure at the equilibrium. Hence vapour pressure of a liquid defined as:

The pressure exerted by the vapour in equilibrium with the liquid at a fixed temperature is the vapour pressure of the liquid.

As the temperature rises, the number of molecules escaping from the liquid surface increases as there in increase in the number of vapour molecules in the space above the liquid when equilibrium is attained.

Hence vapour pressure of the liquid increases with increase of temperature.

4.5.1.1 Determination of vapour pressure

(a) Static method:

A simple apparatus used in this method is shown in fig 4.6. a sufficient amount of the liquid whose vapour pressure is to be determined in placed in the bulb connected to a mercury manometer and a vacuum pump.

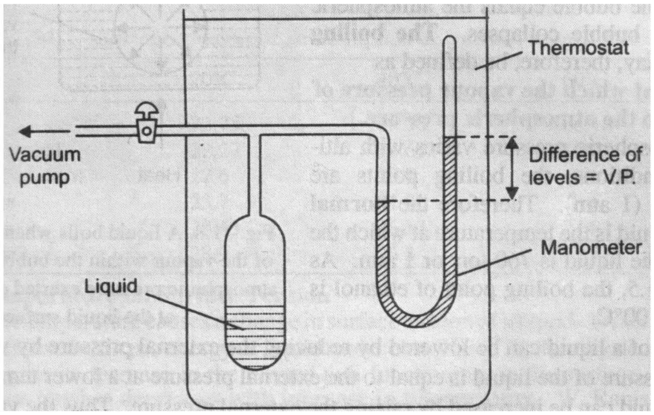


Fig 4.6 Determination of vapour pressure by static method

All the air from the bulb is removed by working the vacuum pump and the stopcock closed. A part of liquid evaporates. The system is then maintained at a fixed temperature for enough time so that equilibrium is attained. The difference in the levels of mercury in the manometer is equal to vapour pressure of the liquid. This method is used for liquids having vapour pressure up to one atmosphere.

(b) Dynamic method:

The apparatus used for the dynamic method is shown in fig 4.7.

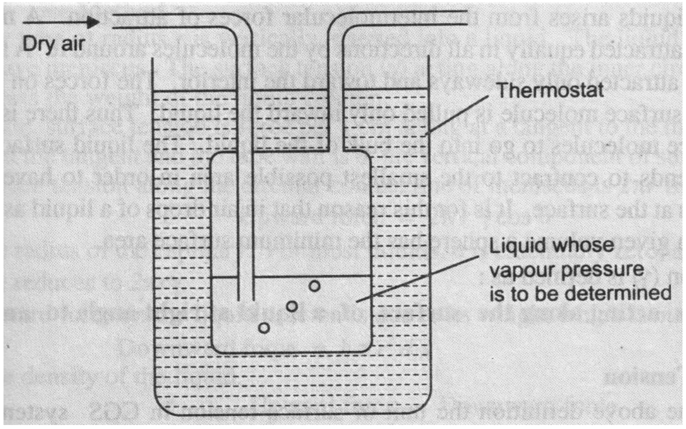


Fig 4.7 Dynamic method

An inert gas is passed through the given liquid at a constant temperature (T). The gas saturated with the vapour of the liquid leaves the flask at the exit tube. If V is the volume of the gas passed and m the loss in weight of the liquid the vapour pressure is given by the expression.

$$\text{Vapour pressure} = \frac{m}{MV}\ RT$$

Where M is the molecular weight of the liquid and R the gas constant. This method is particularly useful for liquids of very low vapour pressure

4.5.2 Surface tension

The existence of strong intermolecular forces of attraction in liquids gives rise to a property known as surface tension. The phenomenon of surface tension can be described as follows.

A molecule in the interior of a liquid is attracted equally in all directions by the molecules around it. A molecule in the surface of a liquid is attracted only sideways and towards the interior. The forces on the sides being counterbalanced, the surface is pulled only inward the liquid. These unbalanced attractive forces acting downward tend to draw the surface molecules into the body of the liquid and, therefore, tend to reduce the surface to minimum. The liquid then behaves as if it were under a strain or tension. It is this force which is called surface tension. It may be defined as **"the force in dynes acting on the surface of the liquid at right angles to one centimetre length of the surface".** It is represented by a symbol γ (gama).

In CGS system the unit of surface tension is dynes per centimetre (dyne cm^{-1}). In SI system, the unit is Newton per metre (Nm^{-1}). Both these units are related as follows

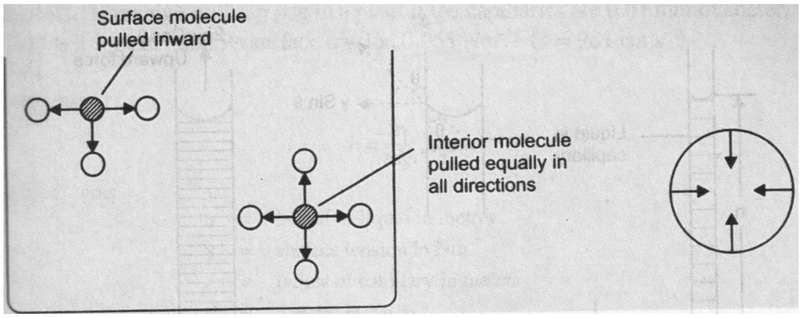


Fig 4.8 molecular attractions

$$\text{Surface energy} = \frac{\text{amount of work done}}{\text{amount of area extended}} = \frac{\text{forcexdistance}}{\text{area}}$$

Hence in CGS units we have

$$\text{Surface energy} = \frac{\text{dyn x cm}}{\text{cm}^2} = \text{dyn x cm}^{-1} = \text{surface tension}$$

In SI units we have

$$\text{Surface energy} = \frac{\text{N x m}}{\text{m}^2} = \text{Nm}^{-1}$$

obviously,

$$1 \text{ dyne cm}^{-1} = (10^{-5}\text{N})(10^{-2}\text{m})^{-1}$$
$$= 10^{-3}\text{Nm}^{-1}$$

4.5.2.1 Effect of temperature on surface tension

When temperature increases, there is increase in kinetic energy of liquid molecules (KE α T) thereby decreasing intermolecular forces. It results in decrease in inward pull functioning on the surface of the liquid. That means you can say surface tension decreases with increase in temperature. As surface tension arises of the attractional forces operating between the molecules, Ramsay and Shields gave the following relationship between the surface tension of a liquid and its temperature.

$$\gamma(M/d)^{2/3} = k(t_c\text{-}t\text{-}6)$$

where k is constant

t_c is critical temperature and t any other temperature γ $(M/d)^{2/3}$ represents molar surface energy of liquid.

4.5.2.2 Determination of surface tension

(i) Capillary rise method:

In this method a capillary tube of radius r is vertically inserted into the liquid. The liquid rises to a height h and form a concave meniscus.

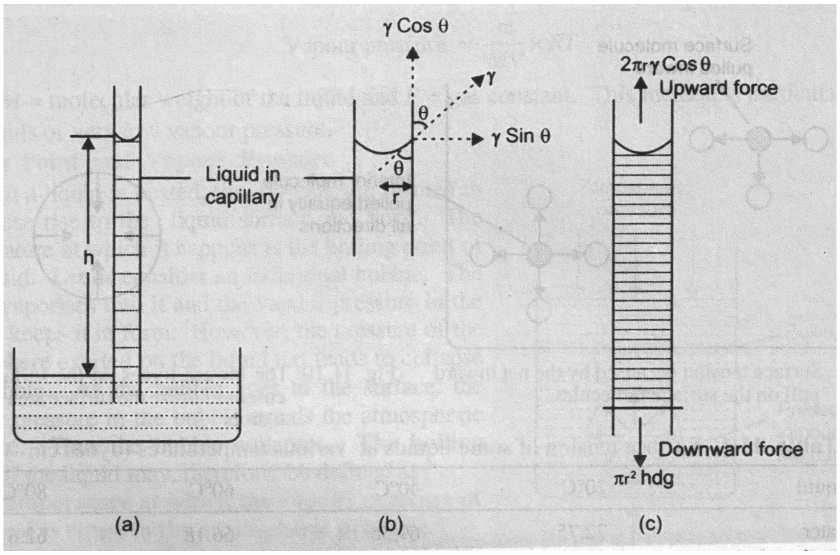


Fig 4.9 capillary rise method of surface tension

The surface tension γ acting in the inner circumference of the tube exactly supports the weight of the liquid column. By definition, surface tension is force per 1 cm acting at a tangent to the meniscus surface. If the angle between the tangent and the tube wall is θ, the vertical component of surface tension is $\gamma \cos\theta$. The total surface tension along the circular contact line of meniscus is $2\pi r$ times.

Therefore upward force = $2\pi r\gamma\cos\theta$

Where r is radius of capillary. For most liquids, θ is essentially zero, and $\cos\theta=1$ then the upward force reduces to $2\pi r\gamma$

The downward force on the liquid column is due to its weight which is mass x g, thus downward force is $h\pi r^2 dg$, where d is density of the liquid

Now upward force = downward force

$$2\pi r\gamma = h\pi r^2 dg$$

$$\gamma = hrdg/2 \text{ dynes/cm}$$

once r, h and d are known γ can be calculated.

(ii) **Drop weight/ number method:**

When a liquid is allowed to flow very slowly through a capillary tube a drop will form which will increase upto a certain point and then fall. If the radius of the end of the tube be r, the total surface tension supporting the drop will be $\gamma 2\pi r$. The drop falls down when its weight W is just equal to this force. Hence we have

$$\gamma 2\pi r = W = mg$$

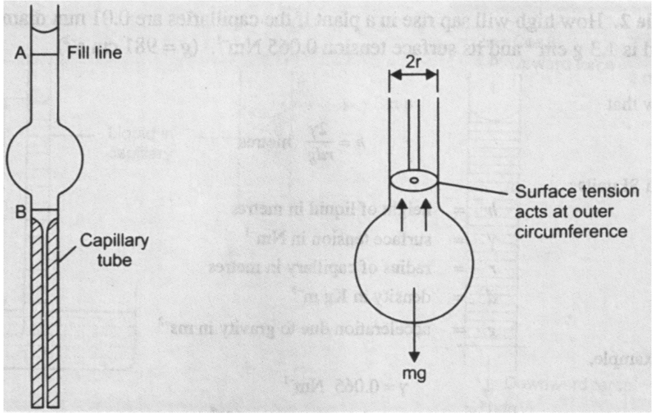


Fig 4.10 determination of surface tension by drop-pipette

The apparatus employed is a glass pipette with a capillary at the lower part. This is called a drop pipette or stalagmometer. It is cleaned, dried and filled with the experimental liquid, say upto the mark A. **(Fig 4.10)**. Then the surface tension is determined by any of the following two methods.

(a) Drop weight method:

About 20 drops of the given liquid are received from the drop-pipette in a weighing bottle and weighed. Thus weight of one drop is found. The drop-pipette is again cleaned and dried. It is filled with the second reference liquid (say water) and weight of one drop is determined as before.

Then we have

$m_1g = 2\pi r\, \gamma_1$ and $m_2g = 2\pi r\, \gamma_2$

$$\gamma_1/\gamma_2 = \frac{m1}{m2}$$

Thus knowing the surface tension of one liquid, the surface tension of other liquid can be found.

(b) Drop number method:

The drop pipette is filled up to the mark A with the liquid whose surface tension is be determined. The numbers of drops are counted as the meniscus passes from A to B. Similarly the pipette is filled with the reference liquid as the meniscus passes from A to B. Let n_1 and n_2 be the number of drops produced by the same volume V of the two liquids. Thus,

the volume of drop of the experimental liquids = V/n_1

mass of one drop of this liquid = $V/n_1 \, x d_1$

where d_1 is its density.

Similarly the mass of one drop of reference liquid = V/n_2 x d_2

Then we have $\gamma_1/\gamma_2 = \frac{(V/n_1)d_1}{(V/n_2)d_2} = \frac{n_2 d_1}{n_1 d_2}$

The density d_1 can be determined by density bottle, once γ_2 and d_2 are known γ_1 can be calculated.

For most liquids surface tension at room temperature vary between 27 and 42 dynes cm^{-1}. For water however, γ is 72.8 dynes cm^{-1} at 20^0C.

This high value is obviously due to strong intermolecular forces which exists in water as a result of extensive hydrogen bonding.

4.5.2.3 Surface tension and chemical constitution

From the study of a large number of liquids, Maclead (1923) showed that

$$\frac{\gamma^{1/4}}{D-d} = C \qquad \text{...........(1)}$$

Where γ is surface tension of the liquid, D its density and d density of vapour at the same temperature, C is a constant. Sugden (1924) modified this equation by multiplying both sides by M, the molecular weight of the liquid

$$M.\gamma^{1/4}/D\text{-}d = MC = [P] \qquad \text{.....(2)}$$

The quantity P, which is a constant for a liquid, was given the name parachor. As d is negligible as compared to D equation (2) reduces to

$$M\gamma^{1/4}/D = [P]$$

or $$M/D\gamma^{1/4} = [P]$$

$$V\gamma^{1/4} = [P] \qquad \text{........(3)}$$

Where γ is molar volume of the liquid. If surface tension γ is unity then V= [P]

Thus parachor may be defined as the molar volume of a liquid at a temperature at which its surface tension is unity.

Use of parachor in elucidating molecular structure:

Sugden examined the experimental parachor values of several organic compounds of known molecular structure. He showed that parachor is both additive and constitutive property. That is parachor of an individual compound can be expressed as sum of

(i) Atomic parachors: which are the contributions of each of the atoms present in the molecule.

(ii) Structural parachors: which are the contributions of various bonds, rings and other structural factors present in the molecule. By correlating the experimental values of parachor with molecular structure, Sugden (1924) calculated the atomic and structural parameters. These values were further revised by Vogel (1948) on the basis of more accurate measurements of surface tension table 4.1.

Atom	Parachor	Bonder ring	parachor
C	8.6	single bond	0
H	15.7	double bond	19.9
O	20.0	coordinate bond	0
N	12.5	3-member ring	12.3
Cl	55.2	6- member ring	1.4
S	48.2	= CO	44.4

Table 4.1

You will see now that how these values are useful in elucidating molecular structure.

(i) Structure of benzene:

If the Kekule formula for benzene be accepted the parachor value can be calculated by using the data:

6xc 6x8.6 = 51.6
6H 6x15.7 = 94.2
3 = 3x19.9 = 59.7
6 member ring = 1.4
Total parachor value = **206.9**

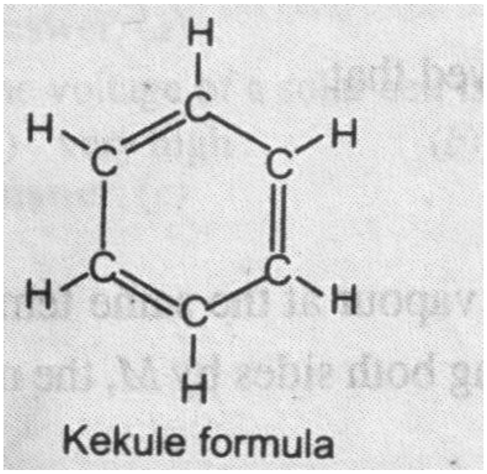


Fig 4.11

Experimental value of parachor of benzene is 206.2 since the calculated value tallys with that determined by experiment, the Kekule structure for benzene is supported.

(ii) Structure of quinone:

The two possible structural proposed for quinine are

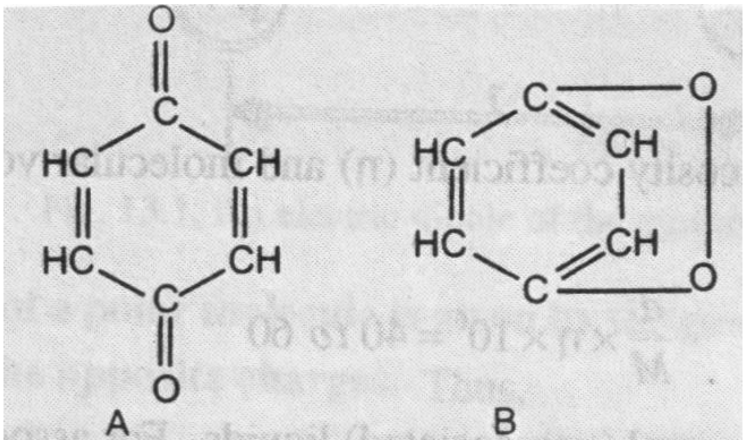


Fig 4.12

The parachor calculated for the two structure are:

	Structure A			Structure B	
6C	6x8.6	= 51.6	6C	6x8.6	=51.6
4H	4x15.7	= 62.8	4H	4x15.7	= 62.8
2O	2x19.8	= 39.6	2O	2x19.8	= 39.6
4(=)	4x19.9	= 79.6	3(=)	3x19.9	= 59.7
1 six member ring		= 1.4	2 six member ring		2.8
	Total	235.0		Total	216.5

The observed value for quinine is 236.8 and hence the formula A represents correctly the structure of its molecule.

4.5.3 Viscosity

Some liquids flow more rapidly than others. In other words, liquid molecules pose resistance to the flow of one layer over the other. This property of liquids which determines their flow is termed viscosity. The property of the liquid which determines its flow is called viscosity of the liquid.

The resistance to flow of one layer of liquid molecules over another depends on the following factors.

1. The intermolecular attractive forces do not permit a free flow of molecules in a liquid. The strength of intermolecular forces gives a rough major of the viscosity of the liquids.
2. The molecular weight or mass of the molecules of a liquid also determines flow of the liquid. Thus heavier the molecule of a given liquid the greater will be its viscosity.
3. Structure and shape of the molecules of a liquid place an important role in influencing its viscosity. Liquids with the large irregularly shaped molecules are generally known to be more viscous than those with small and symmetrical molecule. Since only hard symmetrical molecules have perfectly elastic collision, the large and irregular molecules will have less elastic molecules amongst themselves. Thus collisions between large molecules involves the loss of kinetic energy and as a consequence the intermolecular forces dominating the molecules tends to stick together. This increases the viscosity of the liquid.

4. An increase in temperature decreases the viscosity of the liquid, the molecular motion increases at the expense of cohesive forces causing resistance to flow.
5. The increase of pressure goes to strengthen the cohesive forces between molecules. Hence with increase of pressure the viscosity of a given liquid increases somewhat. The flow is a characteristic property of liquids. Let us consider flow of a liquid. A liquid may be considered to be consisting of molecular layers arranged one over the other. When shearing force is applied, it flows.

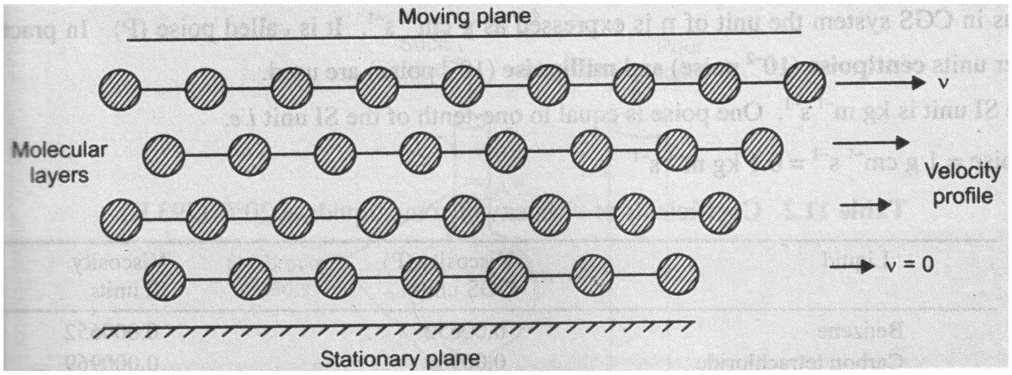


Fig 4.13 flow of liquid on a glass surface

However the force of friction between the layers offers resistance to this flow. Viscosity of a liquid is a measure of its frictional resistance.

Let us examine a liquid flowing on a glass surface. The molecular layer in contact with the stationary surface has zero velocity. The successive layers above it move with increasingly higher velocities in the direction of the flow.

Now consider two adjacent moving layers of a liquid (fig 4.11). Let these be separated by a distance dx having velocity difference dv. The force of friction (F) resisting the relative motion of the two layers is directly proportional to the area A and velocity difference dv, while it is inversely proportional to the distance between the layers dx.

Hence $F \,\alpha\, A\, dv/dx$

$= ή\, A\, dv/dx$

or $ή = F/A \times dx/dv$

where ή (eta) is the proportionality constant. It is known as coefficient of viscosity or simply viscosity of a liquid. It may be defined by the above equation as:

the force of resistance per unit area which will maintain unit different of velocity between two layers which are unit distance apart.

Unit of viscosity:

$\eta = F/A \times dv/dx$

= force/area x distance/velocity

= mass x length x $\text{time}^{-2}/\text{length}^{2}$ X length/length/time

= mass x length^{-1} x time^{-1}

In CGS system the unit of ή is expressed as g $cm^{-1}s^{-1}$, it is called poise. In practice smaller units centipoise (10^{-2} poise) and millipoise (10^{-3} poise) are used.

A liquid is said to have coefficient of viscosity as one poise when a force of one dyne maintains a velocity difference of one centimetre per second between two parallel layers of the liquid one cm apart and have an area of contact equal to on square cm. **The reciprocal of viscosity is known as fluidity.**

4.5.3.1 Effect of temperature on viscosity

As the temperature increases, the molecular motion increases at the expense of cohesive forces causing resistance to flow. Therefore, the viscosity of liquids is found to decrease by 1 to 2 per cent for each degree rise of temperature.

4.5.3.2 Determination of viscosity

The apparatus used for determination of viscosity in the laboratory is knwon as Ostwald's viscometer. A simple form of Ostwald viscometer is shown in fig 4.14, the left- hand limb is essentially a pipette with two celibration marks A and B. A length of capillary tube joins the pipette to the bulb D in the right-hand limb.

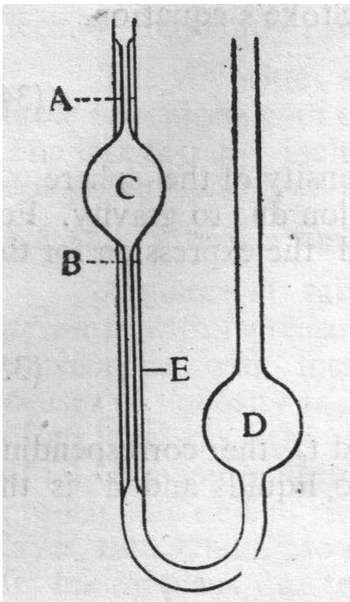


Fig 4.14 Ostwald viscometer

A definite volume of liquid (say about 25 ml) is poured into the bulb D with a pipette. The liquid is sucked up near to the top of the left-hand limb with the help of rubber tubing attached to it. The liquid is then released to flow back into the bulb D. the time t_1 to flow from A to B is noted with a stopwatch. Then the apparatus is cleaned and the experiment is repeated with water taking about the same volume. The time of flow of water t_2 from A to B is recorded. The density of the liquid d and that of water d_w are determined with the help of density bottle. The relative viscosity is calculated from the expression

$$\eta/\eta_w = dt_1/d_wt_2$$

where is η is coefficient of viscosity of the experimental liquid and η_w is the coefficient of viscosity of water. Knowing the value of coefficient of viscosity of water η_w at the temperature of experiment, the absolute viscosity coefficient η of the given liquid can be found.

4.5.3.3 Viscosity and chemical constitution

As you know viscosity is largely due to intermolecular attractions which resist the flow of liquid. Therefore some sort of relationship between viscosity and molecular structure should be there. Viscosity is also dependent on the shape, size and mass of the liquid molecules. The following general rules have been discovered.

(i) Dunstan Rule:

Dunstan in 1909 showed that coefficient of viscosity η and molecular volume (d/M) were related as $d/M \times \eta \times 10^6 = 40$ to 60

This expression holds only for normal (unassociated) liquids for associated liquids the value is much higher than 60. For example the value for benzene is 73 and for water it is 559 and for ethanol it is 189. This shows benzene is a normal liquid while water and ethanol are associated liquids.

(ii) Molar Viscosity:

The product of molar surface and viscosity is termed as molar viscosity. That is

molar viscosity = molar surface x viscosity

$= (M/d)^{2/3}$ x ή

Thorpe and Rodger (1894) found that molar viscosity is an additive property at the boiling point. They worked out the molar viscosity contributions of several atoms (C, H, O, S, etc) and groups. From these, they calculated the molar viscosity of liquid from its proposed structure. By tallying this value with the experimental one, they were able to ascertain the structure.

(iii) Rheochor:

Newton Friend (1943) showed that if molecular volume (M/d) be multiplied by the eighth root of the coefficient of viscosity it gives a constant value [R], it is termed as Rheochor

$M/d \times \eta^{1/8} = R$

Like parachor, rheochor is both additive and constitutive property.

4.6 REFRACTIVE INDEX

4.6.1 Definition

When a ray of light passes from air into denser medium say a liquid, it is bent or refracted towards the normal. The ratio of the sine of angle of incidence and the sine of angle of refraction is constant and characteristic of that liquid. This is known as Snell's law. **The constant ratio n is called refractive index of the liquid** and may be written as

$$\sin i/\sin r = n$$

The ratio of sines of the angles of incidence and refraction is identical with the ratio of the velocity of light in two media.

Thus
$$n = \sin i/\sin r = \frac{\text{velocity in air}}{\text{velocity in liquid}}$$

when a ray of light passes from a rarer to denser medium it can be shown form law of refraction that

$$\frac{\sin i}{\sin r} = \frac{n2}{n1}$$

n1 is refractive index of rarer medium

n2 is refractive index of denser medium

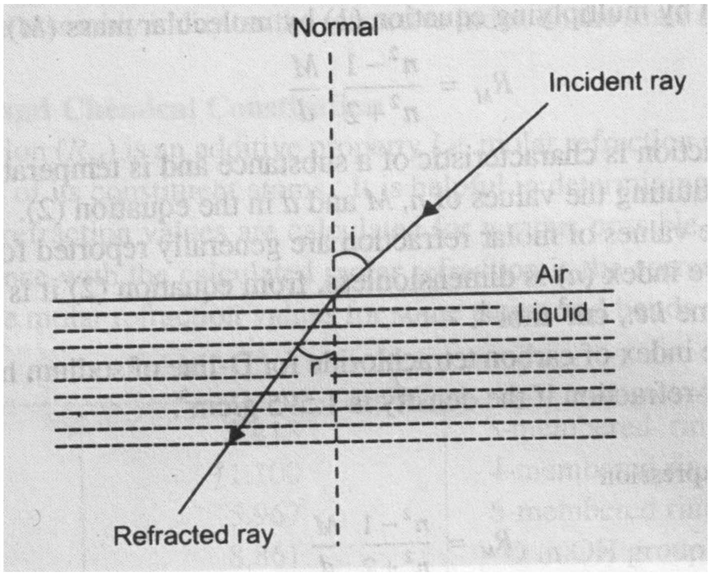


Fig 4.15

4.6.2 Determination of refractive index

The instruments used for determining refractive index are known as refractometers.

Pulfrich-refractometer:

This refractometer is very accurate and simple in principle. It is indicated diagrammatically in fig 4.16. The main part of the instrument

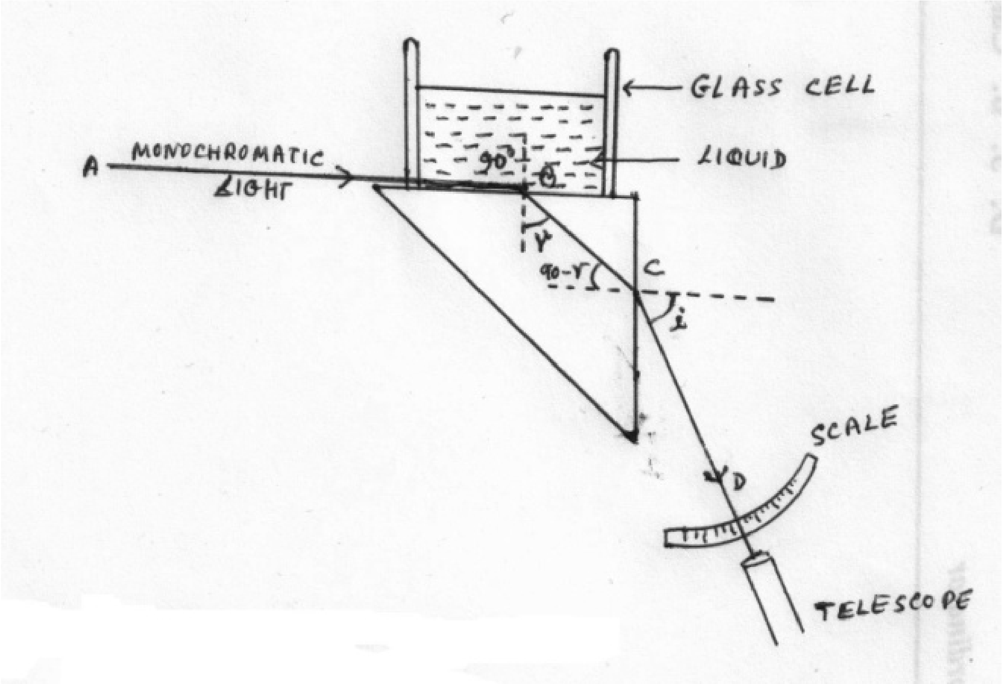


Fig 4.16 The optical system of Pulfrich refractometer

is a right angled glass prism with a small glass cell connected to its top. The liquid under examination is placed in the cell and a beam of monochromatic light is made to enter the liquid at an angle of 90^0 along the surface between the liquid and the prism. If the telescope is moved to make an angle with the horizontal which is less than i no light can reach it. At this angle i a sharp boundary between a dark and a bright field can be seen through the telescope.

For a ray of light passing from the liquid into the prism, if r be the angle of refraction when the angle of incidence is 90^0 we have alredy stated that $\sin r = n_1 / n_2$ ....(1)

Where n_1 is the refractive index of the liquid and n_2 is that of glass prism. It is also clear to you from the fig 4.16 that

$$\sin i/\sin(90-r) = n_2 \quad \text{...........(2)}$$

$$\text{or} \quad \sin i/\cos r = n_2 \quad \text{...........(3)}$$

$$\text{or} \quad \cos r = \sin i/n_2 \quad \text{............(4)}$$

But $\sin r = \sqrt{(1-\cos^2 r)}$

substituting the value of cos r in equation (4)

we get

$$\sin r = \sqrt{(1-\sin^2 i/n_2^2)} \quad \text{...................(5)}$$

From equation (1) we get

$$n_1 = n_2 \sin r$$

$$= \sqrt{n_2^2-\sin^2 i}$$

If the refractive index n_2 of the glass is known and angle i is measured n_1 the refractive index n_1 of liquid can be calculated.

4.6.3 Refractive index and chemical constitution

Lorenz and Lozentz (1880) purely from theoretical considerations derived the following relation for refracting power of substance

$$R = \frac{n^2-1}{n^2+2} \times \frac{1}{d} \quad \text{.......(1)}$$

where R is specific refraction, d the density and n the refractive index. The value of R was constant at all temperatures.

Molar refraction:

It is defined as the product of specific refraction and molecular mass. Thus molar refraction is obtained by multiplying equation (1) by molecular mass (M).

$$R_M = \frac{n^2-1}{n^2+2} \times \frac{M}{d} \quad \text{..............(2)}$$

The value of molar refraction is characteristic of a substance and is independent of temperature. Since it depends on wavelength of light, the values of molar refraction are generally reported for D-line of sodium.

Molar refraction R_M is an additive and constitutive property. The molar refraction of a molecule is thus a sum of the contributions of the atoms (atomic refraction) and bonds (bond refraction). From the observed value of R_M of appropriate known compounds, the atomic refractions of different elements and bonds have been worked out.

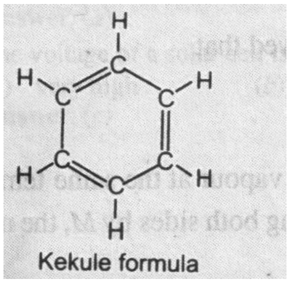
Carbon C	2.418	3-membered ring	0.710
Hydrogen H	1.100	4- membered ring	0.480
Chlorine Cl	5.967	6- membered ring	0.15
Bromine Br	8.861	O in OH group	1.525
Iodine I	13.900	O in C=O group	2.211
Double bond	1.733	O in ethers	1.64
Triple bond	2.398		

Table 4.1 some atomic and bond refractions

Now we will have some examples for you to illustrate the use of molar refractions in elucidating molecular structure

(i) Benzene :

The molar refraction of benzene (C_6H_6) on the basis of much disputed Kekule formula may be calculated as:



6C = 6x2.591 = 15.546
6H = 6x1.028 = 6.168
3C=C = 3x1.575 =4.725
One 6 C ring ` = -0.150
Total R_M = 26.289cm^3 $mole^{-1}$

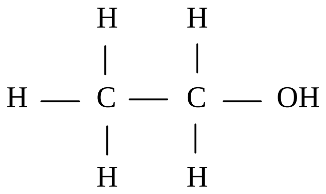
The observed value of R_M for benzene is 25.93. this is in good agreement with the calculated value. Hence the Kekule formula for benzene is supported.

Now let us take the example of ethyl alcohol (CH_3CH_2OH). Its refractive index is 1.3611 and its density is 0.7885 g cm^{-3}. The molar mass of ethyl alcohol is 46. The molar refraction can be calculated from the formula, and the value comes out equal to 12.9105 cm^3 mol^{-1}.

Let us compute now the value of molar refraction using the values from table 4.1.

Contribution of 6 hydrogens = 6x1.028 = 6.168
Contribution of 2 carbons = 2x2.591 = 5.182
Contribution of O in OH group = 1.525
Total contribution 12.875 cm^3 mol^{-1}

This value is in close agreement with the value calculated above, therefore the correct structure of ethyl alcohol is



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & OH \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

(ii) Optical exaltation:

A compound containing conjugate double bonds (C=C-C=C) has a higher observed value of R_M than that calculated from atomic and bond refractions. The molar refraction is thus said to be exalted (raised) by the presence of conjugate double bond and the phenomenon is called optical exaltation. For example, for Hexatriene $CH_2 = CH - CH=CH - CH=CH_2$ the observed value of R_M is 30.58 cm^3 $mole^{-1}$ as against the calculated value 28.28 cm^3 $mole^{-1}$.

If present in closed structure as benzene, the conjugated double bonds do not cause exaltation.

4.7 LIQUID CRYSTALS

4.7.1 Definition

There are certain solids which on heating undergo two sharp phase changes one after the other. They first fuse sharply yielding turbid liquids and again equally sharply at higher temperature yielding clear liquids. These changes get reversed on cooling at the same temperature. The turbid liquid show anisotropy i.e. they have different physical properties from different directions. Anisotropy is particularly seen in the optical behaviour of liquids. In an anisotropic substance, the physical property are different in different direction. On the other hand true liquids are isotropic ie same physical properties in different directions. As anisotropic properties are associated with crystalline state, the turbid liquids are known as liquid crystals.

This liquid crystal term, however, is not satisfactory since the substances in this state do not have properties of crystalline state. Actually, they are more like liquids in having properties like mobility, surface tension, viscosity etc. Amongst other names that have been suggested are crystalline liquids and anisotropic liquids, but these are also not satisfactory. The term mesomorphic state (meaning intermediate form) probably fits best. But, the older term liquid crystal continues to be used even in the present day literature.

Substances which show the above behaviour are usually some long chain organic molecules either terminating in groups such as-OR, -COOR or having groups like –C=N-,-N=NO-,-C=C- in the middle. The first solid showing this peculiar property was discovered in 1888 was cholesteryl benzoate $C_6H_5COOC_{27}H_{45}$. It fuses sharply at 145^0C to form turbid liquid and on further heating changes into clear liquid at 178^0C. If we cool, the above changes are reversed i.e., the clear liquid when cooled first changes into turbid state at 178^0C and then into the solid state at 145^0C

Later on, p-azoxyanisole and p-azoxyphenetone were found to exhibit the same properties. In 1991 P.G. De Genees, a French physicist got the Nobel Prize in Physics for contribution to liquid crystals and polymers.

$$\underset{\text{Solid}}{\text{p-cholesteryl benzoate(pcb)}} \overset{145^0C}{\rightleftharpoons} \underset{\text{liquid crystal}}{\text{p.c.b.}} \overset{178^0C}{\rightleftharpoons} \underset{\text{liquid}}{\text{p.c.b.}}$$

Solid state → **Liquid crystal** → **Liquid state**

One such substance that forms liquid crystal is p-ozoxyanisole (Fig 4.17)

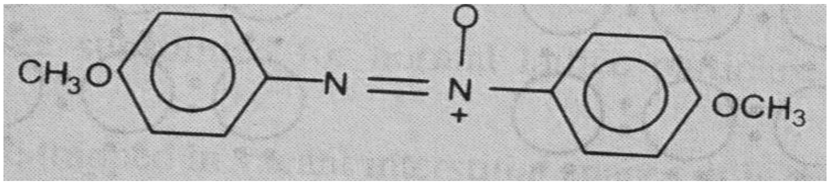


Fig 4.17 p-Ozosyanisole

4.8 STRUCTURE OF LIQUID CRYSTALS

In a liquid the moleucules have random arrangement and they are able to move fast each other. In a solid crystal the molecules have an ordered arrangement and are in fixed positions. In a liquid crystal, however, molecules are arranged parallel to each other and can flow like a liquid. **Thus liquid crystals have the fluidity of a liquid and optical properties of solid crystals.**

Accordingly to their molecular arrangement, the liquid crystals are classified into three types

(i) Nematic liquid crystals:

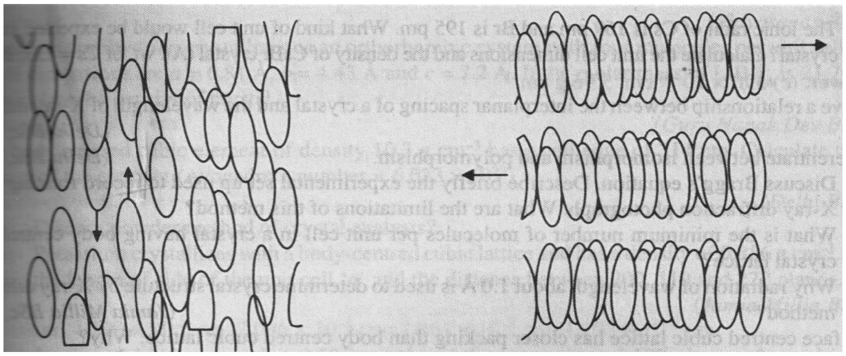
in nematic liquid crystals molecules are parallel to each other like soda straws but they are free to slide or roll individually.

(ii) Smetic liquid crystals:

The molecules in this type of liquid crystals are also parallel but these are arranged in layers. These layers can slide past each other (Fig 4.18).

(iii) Cholesteric liquid crystals:

As in nematic crystals in this type liquid crystals the molecules are parallel but arranged in layers. The molecules in successive layers are slightly rotated with respect to the layers above and below so as to form spiral structure.



Nematic liquid crystal **Smetic liquid crystal**

Fig 4.18

Application of liquid crystals:

On account of their remarkable optical and electrical properties, liquid crystal found several practical applications. Some of these are given below.

Number display:

When a thin layer of nematic liquid crystal is placed between two electrodes and an electrical field is applied, the polar molecules are pulled out of alignment. This cause the crystal to be opaque. Transparency returns when electrical signal is removed. This property is used in the number displays of digital watches, calculators, and other instruments.

Monitoring body temperature:

Like the solid crystals, liquid crystals can diffract light. Only one of the wavelengths of the white light is refracted by the crystal which appears coloured. As the temperature changes the distance between the layers of molecules also changes. Therefore the colours of the reflected light changes correspondingly. These colesteric liquid crystal undergoes a series of colour changes with temperature. These crystals are used in indicator tapes to monitor body temperature or to spot areas of overheating in mechanical systems.

4.9 SUMMARY

In this unit you have studied liquid state in detail. Various properties of liquids such as vapour pressure, surface tension, viscosity and refractive index have been discussed and also their usefulness to elucidating molecular structure.

The difference between liquid, liquid crystal and solid state have been discussed and also liquid crystal in detail.

Thought the study of the parachor, molecular viscosity, molar refraction etc. Are useful in elucidating molecular structure of compounds, but they give some rough idea about molecular structure. Mass Spectra, I.R., NMR are the latest methods/techniques for elucidating molecular structure of organic compounds accurately.

4.10 TERMINAL QUESTIONS

(A) Multiple Choice Questions:

1. The reciprocal of viscosity is known as:

(a) Anti viscosity (b) intrinsic viscosity

(c) Reduced viscosity (d) Fluidity

Ans (d)

2. The molecules which have partial positive charge at one end and partial negative charge at the other are called:

(a) ion pairs (b) charged molecules

(c) dipole (d) electric molecule

Ans (c)

3. With the rise of temperature the surface tension of a liquid:

(a) Increases (b) decreases

(c) remains the same (d) none of the above

Ans (b)

4. The unit in which surface tension is measured is:

(a) dyne cm (b) dyne cm^{-1}

(c) $dyne^{-1}$ cm (d) $dyne^{-1}$ cm^{-1}

Ans (b)

5. Which of the following liquids has maximum viscosity:

(a) water (b) ethyl alcohol

(c) Acetone (d) glycerine

Ans (d)

6. Small droplets are spherical in shape. It is due to:

(a) High viscosity

(b) their tendency to acquire minimum surface area

(c) Less viscosity

(d) their tendency to acquire maximum surface area

Ans (b)

(B) Short Answer Questions:

1. Define surface tension. What is its unit?
2. How does vapour pressure varies with temperature.
3. Explain why
   (i) Drops of liquids are spherical in shape.
   (ii) At the boiling point, the temperature of liquid does not rise although it is being heated.
   (iii) Glycerol is more viscous than water.
4. Write a note on specific refraction.
5. Write a note on liquid crystals.
6. Explain the term viscosity of a liquid.

(C) Long Answer Questions:

1. Define the terms surface tension and surface energy. Discuss capillary rise method for determination of surface tension in the laboratory.
2. What are liquid crystals? How are they classified? How would you account for turbidity observed in liquid crystals? What are the uses of liquid crystals?
3. Why do you use the same viscometer for the liquid and water during the experimental determination of the viscosity of the liquid by Ostwald viscometer? Describe the experiment.
4. Write a note on parachor. How parachor is useful in elucidating molecular structure of compounds at 20^0C toluene rises 1.95 cm in the capillary tube of radius of 0.3412 mm. Calculate the surface tension of toluene. The density of toluene at 20^0C is 0.866 cc

   Hint : use the formula $\gamma = \frac{\underline{hrdg}}{2}$ dynes/c

5. (a) Define viscosity of a liquid. What is the effect of temperature on viscosity?

(c) Water passes through a viscometer in 30 seconds and ethanol in 175 seconds at 20^0C. If the density of water is 0.998g/cm^3, density of ethanol is 0.790g/cm^3 and viscosity of water is 0.01008 poise, calculate the viscosity of ethanol.

(Hint : use formula $\eta = \eta_w dt_1/dwt_2$

ans 0.01747 poise)

6. Write notes on the following

(a) Vapour pressure

(b) Optical oxaltation

(c) Ramsay- Shields equation

....

UNIT 5: SOLID STATE

CONTENTS:

5.1 OBJECTIVES

In gaseous state you have studied that if thermal energy is much greater than the forces of attraction then we have matter in gaseous state. Molecules in gaseous state move with very large speeds and because of very small attraction forces, the gas molecules move practically independent of one another.

In the liquid state the forces of attraction are greater than the thermal energy. You have also studied that molecules in liquid state too have kinetic energy, they cannot move very far away because of the larger forces of attraction amongst them. Because of this property, liquids have definite volume, but they do not have definite shape. Liquids also resemble gases in their ability to flow. Gaseous and liquid states are, therefore, both classified as fluids.

Out of the three states of matter, solids are characterised by incompressibility, rigidity and mechanical strength.

The molecules, atoms or ions in solids are closely packed.

5.2 INTRODUCTION

It is clear to you now that intermolecular attraction is minimum in the gaseous state and this disappears completely when the gas in ideal. The interaction is stronger in liquids and is strongest in solids. Thermal motion of the molecules increases or decreases by raising or lowering of temperature. The attractive interaction between the molecules tries to keep them together and the thermal motion is opposed to that. Hence, it is possible to change a substance from one state to another by changing its temperature.

A true solid possesses the following characteristics

(a) A sharp melting point
(b) A characteristic heat of fusion
(c) General incompressibility
(d) A definite three-dimensional arrangement

Hence solids are characterised by high density and low compressibility compared to those of the gas phase. In solids, atoms, ions and molecules are held together by relatively strong chemical forces- ionic bond, covalent bond, or by intermolecular von der Waal’s forces. They do not translate although they vibrate to some extent on their fixed positions. This explains why solids are rigid and have definite shape.

5.3 DEFINITION

Solids can generally be classified into two broad categories:

(i) Crystalline solids
(ii) Amorphous solids

A crystalline solid exists as small crystals, each crystal having a characteristic geometrical shape. In a crystal, the atoms, molecules or ions are arranged in a regular, repeating three-dimensionl pattern called the crystal lattice. examples are sugar, salt etc. An amorphous solid has atoms, molecules or ions arranged at random and lacks the ordered crystalline lattice. Examples of amorphous solids are rubber, plastics and glass. In their disordered structure, amorphous solids are regarded as supercooled liquids with high viscosity. The liquid nature of glass is sometimes apparent in very old window panes that have become slightly thicker at the bottom due to gradual downward flow.

Anisotropy and isotropy:

Amorphous substances differ from crystalline solids and resemble liquids in another important aspect. Their properties such as electrical conductivity, thermal conductivity mechanical strength and refractive index are same in all directions. Amorphous substances are said to isotropic. Liquids and gases are also isotropic. Crystalline solids on the other hand are anisotropic, because their physical properties are different in different directions. For example the velocity of light through a crystal varies with the direction in which it is measured. Thus, a ray of light enter such a crystal may split up into two components each following different velocity. This phenomenon is known as double refraction. This can be shown in fig 5.1 in which simple two-dimensional arrangement of

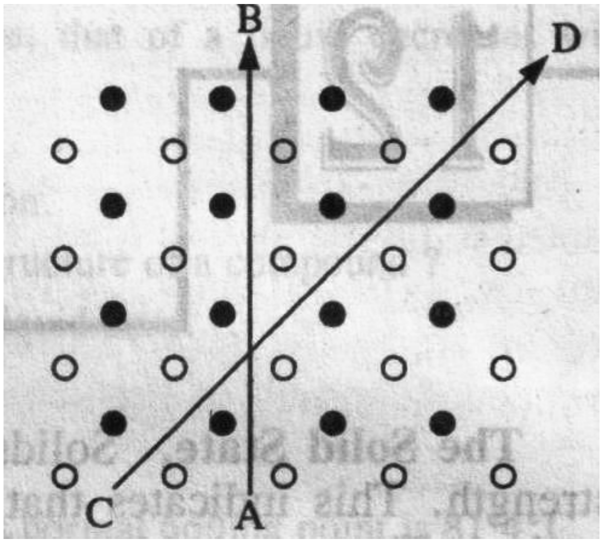


Fig 5.1 Anisotropy in crystals is due to different arrangement of particles in different directions

only two different kinds of atoms is depicted if the properties are measured along the direction indicated by the slanting line CD, they will be different from those measured in the direction indicated by the vertical line AB. The reason is that while in the first case, each row is made up of alternate types of atoms, in the second case; each row is made up of one type of atoms only. In amorphous solids, atoms or molecules are arranged at random and in a disorderly manner and, therefore all directions are identical and all properties are alike in all directions.

5.4 DEFINITION OF SPACE LATTICE AND UNIT CELL

Crystals are bound by surface which is usually planner. These surfaces are called faces and where two faces intersect an edge is formed. The angle between the normals to the two intersecting faces is the interfacial angle or the angle between any two faces is called interfacial angle. Although the size of the faces or even shapes of crystals of one and the same substances may vary widely with the condition of formation or other factors, yet the interfacial angles

between any two corresponding faces of the crystal remain invariably the same throughout. This is shown in fig 5.2. Now it is clear to you that although the external shape is different yet the interfacial angles are the same.

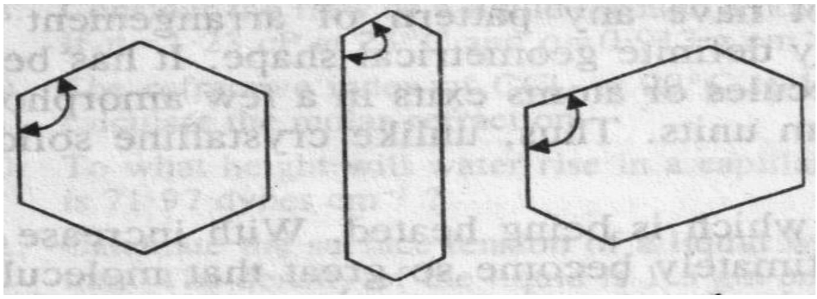


Fig 5.2 Constancy of interfacial angle

Space lattice

Rather than drawing the entire pattern, it is much more convenient to represent the unit of pattern by a point. Each point then represents the position of an atom, ion, molecule or group of ions and molecules. The regular three-dimensional arrangement of identical points in space gives rise to what is known as space lattice or crystal lattice (Fig 5.3) the positions occupied by the particles in the space lattice are called lattice sites or lattice points.

Unit cell:

It is defined as "the smallest geometrical portion of the crystal, which when repeated in three dimensional, would generate the complete crystal". Each unit cell, in turn, must be constituted of atoms, molecules or ions, as the case may be and arranged to give the particular geometrical configuration of the crystal.

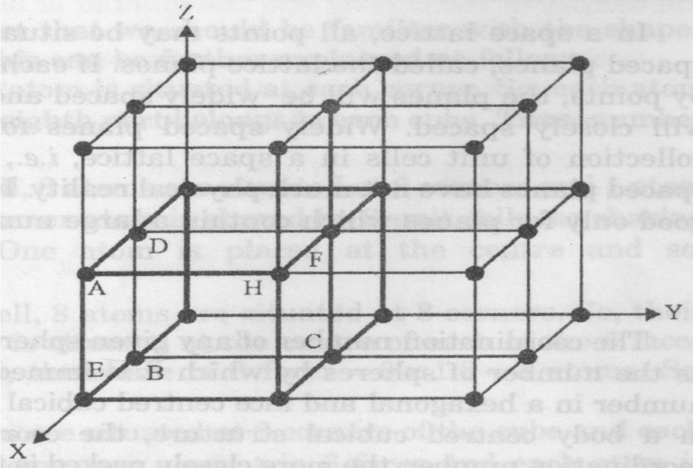


Fig 5.3 Space latice

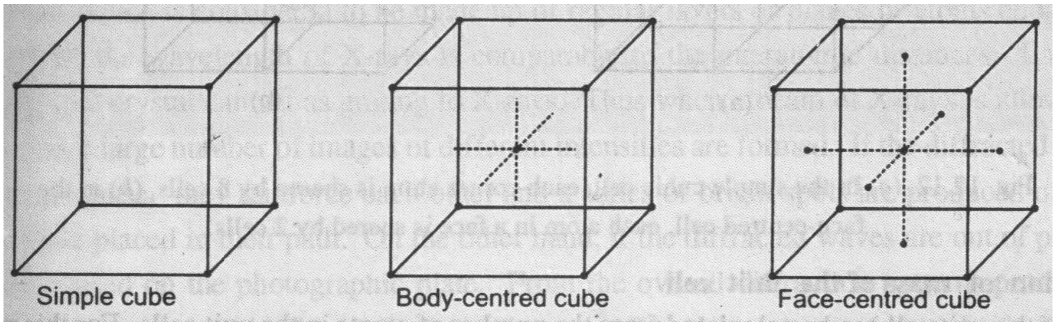
Unit cells are of following types;

(a) Simple or primitive unit cell (P): The simplest unit cell which has the lattice points at the corners is called a simple or primitive unit cell. It is denoted by P.

(b) Non primitive or multiple unit cell: When unit cell contains more than one lattice points, it is called non primitive or multiple unit cell. It is further divided into the following three categories:

(i) Face centred unit cell (F):

When a unit cell, besides the points present at the corners of the unit cell,



(a) (b) (c)

Fig 5.4 Three cubic unit cells

There is one point at the centre of each face, it is called face centred arrangement or face centred unit cell. It is denoted by F.

(ii) Body centred unit cell (I):

When in a unit cell, besides the points at the corners of the cell, there is one point at the centre with in its body, it is called body-centred arrangement or body-centred with cell. It is denoted by I.

(iii) Side centre or end face unit cell:

When in a unit cell, besides the points at the corners of the cell, the points are located at the centre of any two parallel faces of the unit cell, it is called side-centred or end face unit cell. It is denoted by c.

5.5 LAWS OF CRYSTALLOGRAPHY

There are three laws of crystallography which deal with the interfacial angles and the rational indices.

5.5.1 Law of constancy of interfacial angle

The crystal may be smaller or bigger in size and may be prepared by any method, but the interfacial angles are always the same.

5.5.2 Law of rational indices

Now it will be clear to you that crystal lattice consists of unit cells arranged in parallel planes. Thus each crystal plane lies parallel to the crystal face as also to the unit cell face. These planes cut the three axes along the three crystallographic axes (ox, oy, oz), Hauy proposed that a given crystal plane could be described in terms of intercepts along the axes. The reciprocals of these intercepts are small whole numbers, these numbers h,k and l are called Miller indices after the name of British Scientist W.H. Miller. Thus Miller indices of a plane may be defined as the reciprocals of the intercepts which the plane makes will the axes.

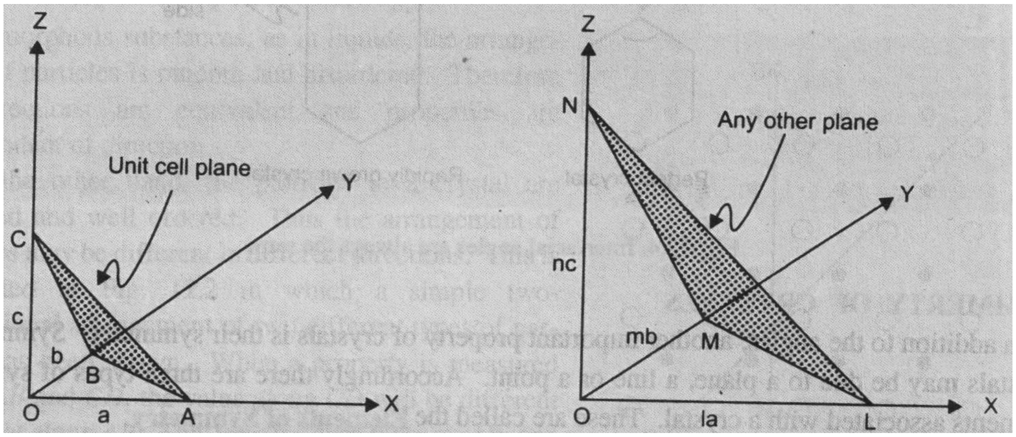


Fig 5.5 A unit cell plane intercepts the axes to give interests a, b and c

Any other plane intercepts the axes to give intercepts equal to la, mb and nc

For example let us consider a crystal system with the axes OX, OY and OZ. In fig 5.4 ABC represents a unit cell surface while LMN in fig 5.5 depicts another crystal plane under study

The intercepts of the unit plane are OA, OB and OC which have the length a,b and c respectively. The intercepts of the plane under study are OL, OM and ON. These can be expressed as multiples of the intercepts a,b,c i.e. la, mb and nc. Here l m and n are either integral whole numbers or fraction of whole numbers. The reciprocal of these numbers are written together in brackets (h,k.l) to give the Miller indices of the plane under study.

To find the Miller indices proceed as follows.

(i) Write the intercepts as multiples of a,b,c say la, mb, nc
(ii) Take the reciprocals of l, m and n
(iii) Clear fraction to get whole numbers h,k,l.
(iv) Miller indices to the plane are (h,k,l).

Example: calculate the Miller indices of crystal planes which cut through the crystal axes at

(i) 2a, 3b, c (ii) 6a, 5b, 3c

(i)					(ii)			
a	b	c				a	b	c
2	3	1	intercepts			6	3	3
½	1/3	1	reciprocals			1/6	1/3	1/3
3	2	6	clear fraction			1	2	2

Hence Miller indices are (326) hence Miller indices are (122)

5.5.3 Law of symmetry

Besides the interfacial angles, another important property of crystals is their symmetry. The law of symmetry states that:

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

Symmetry in crystals may be with respect to a plane, a line or a point, accordingly there are three types of symmetry associated with a crystal.

5.5.3.1 Plane of symmetry

When an imaginary plane can divided a crystal into two parts such that one is the exact mirror image of the other, the crystal is said to have a plane of symmetry.

5.5.3.2 Axis of symmetry

An axis of symmetry is a line about which the crystal is rotated such that it presents the similar appearance more than once during complete rotation i.e. rotation through an angle of 3600. Depending upon its nature, a crystal may have 2-fold, 3-fold, 4-fold or 6-fold axes of rotation.

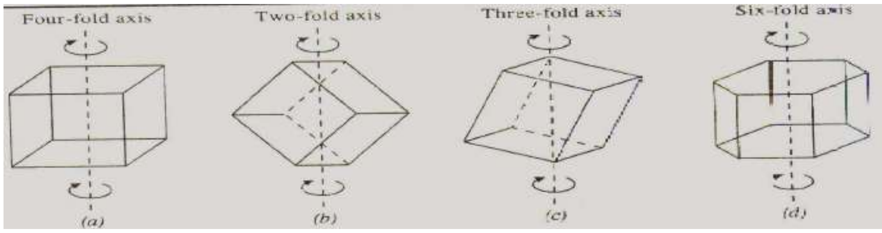
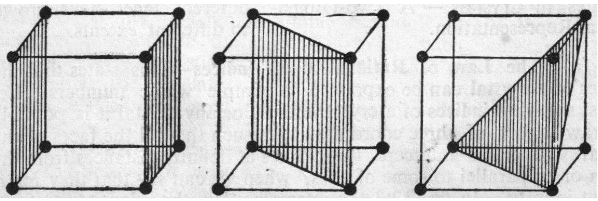


Fig 5.6 various axes of symmetry

For example in the case of a cube, an axis passing perpendicularly through the centre is such that when the cube is rotated it presents similar appearance in three rotation of 90^0 each and the same appearance after the fourth rotation, such an axis is called a four-fold or tetrad axis (fig 5.6(a)). If the same similar appearance is repeated after an angle of 180^0, the axis is called two-fold or diad axis (fig 5.6(b)). In the same way, if the same or similar appearance is repeated after an angle of 120^0, the axis is called a three-fold or triad axis (fig 5.6(c)). If the same or similar axis is repeated after an angle of 60^0, as in the case of a hexagonal crystal, the axis is called six-fold or hexad axis (fig 5.6(d)). In general, if the same or similar appearance of a crystal is repeated on rotation through an angle of 360/n, around an imaginary axis, the axis is called an n-fold axis.



100, 110 and 111 planes of a crystal

100 plane 110 plane 111 planes

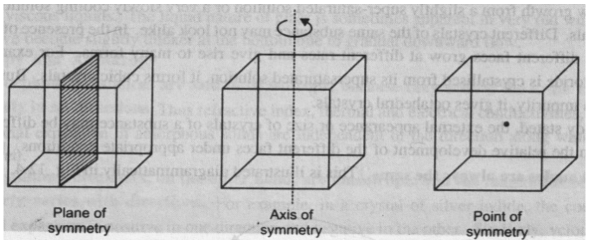


Fig 5.8 three cubic unit cells

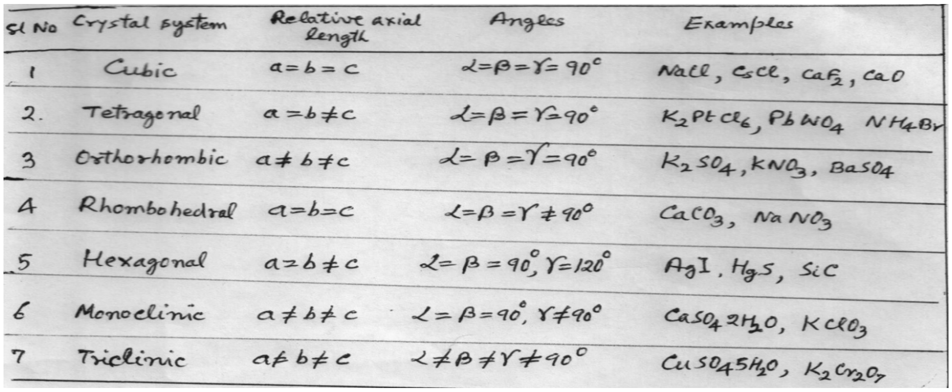
5.5.3.3 Centre of Symmetry

It is a pound at the centre of the crystal so that any line drawn through it will meet the surface of the crystal at equal distance on either side.

It may be pointed out that a crystal may have number of planes or axis of symmetry but it has only one centre of symmetry.

5.6 SYMMETRY ELEMENTS OF A CRYSTAL

Any crystal or any molecule of the crystal will have some combinations of symmetry elements. These combinations of symmetry elements are known as point groups. These points groups are called classes or systems.



Sl No	Crystal system	Relative axial length	Angles	Examples
1	Cubic	$a=b=c$	$\alpha=\beta=\gamma=90^\circ$	$NaCl$, $CsCl$, CaF_2, CaO
2.	Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90^\circ$	K_2PtCl_6, $PbWO_4$ NH_4Br
3	Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90^\circ$	K_2SO_4, KNO_3, $BaSO_4$
4	Rhombohedral	$a=b=c$	$\alpha=\beta=\gamma\neq 90^\circ$	$CaCO_3$, $NaNO_3$
5	Hexagonal	$a=b\neq c$	$\alpha=\beta=90^\circ, \gamma=120^\circ$	AgI, HgS, SiC
6	Monoclinic	$a\neq b\neq c$	$\alpha=\beta=90^\circ, \gamma\neq 90^\circ$	$CaSO_4 2H_2O$, $KClO_3$
7	Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90^\circ$	$CuSO_4 5H_2O$, $K_2Cr_2O_7$

Table 5.1 seven crystal systems

A careful study of the geometrical structure of crystals reveals that there are 230 crystal forms, which may be grouped into 32 classes. These 32 classes in turn may be referred into to seven crystal systems. These

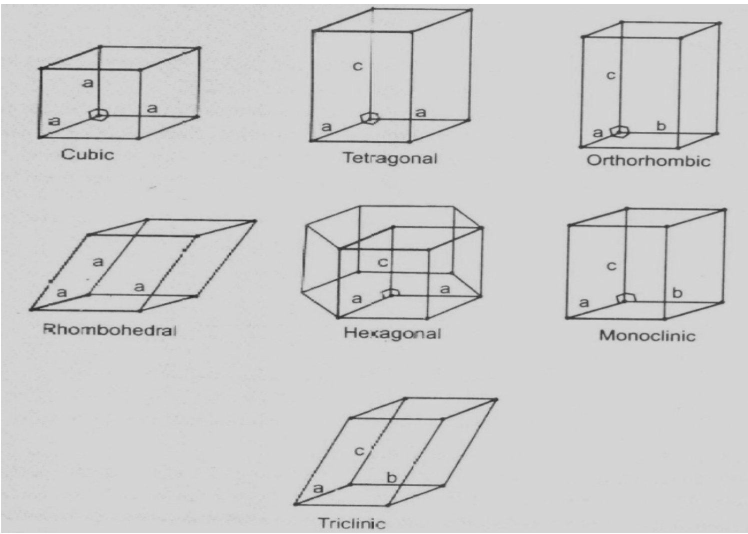


Fig 5.7 seven crystal systems

Crystal systems differ in length of the unit cell edges (a, b and c fig 5.1) and the angles between the unit cell edges.

5.7 LATTICE SITES AND COORDINATION NUMBER

From the above discussion it may be clearly understood that it is possible to have lattice sites other than the corners of the geometrical patterns. In fact for the simplest lattice system, i.e., the cube, there may be three possibilities. These possibilities are named as ‘simple cubic’, ‘body centred cubic’ and ‘face centred cubic’ depending upon the lattice sites being disposed in space in a manner that a particle is situated at any of these is surrounded in an identical manner by other particles of the lattice. In the simple cubic lattice, fig 5.6(a), the particles are occupying only the corners of the cube. The body centred cubic lattice fig 5.6 (b) has particle at the centre of the cube in addition to the four occupied corners. But in face-centred cubic lattice fig 5.6 (c) there is one lattice site at each of the six faces of the cube apart from the four corner sites.

Let us now calculate the number of particles, atoms or ions

(i) In simple cubic unit cell one particle is situated at each corner and there are eight corners in the unit cell. So each corner atom is shared by 8 unit cells, hence share of each unit cell is one-eighth. Thus number of particles in one unit cell is, z =1/8x8=1 particle.

(ii) In body centred cubic unit cell, 8 particles are situated at 8 corners and one particle at the centre of the cube. As each corner is shared by eight unit cells, so sharing of 8 corners=8x1/8=1 particle. One particle in the centre of the unit cell and hence z=1+1=2 particles.

(iii) In face centred cubic unit cell, 8 particles are situated at eight corners. So their share is 8x1/8=1 particle. One particle is situated at the centre of the 6 faces which is shared by 2 unit cells. So, the share of 6 faces=6x1/2=3 particles. So z =1+3=4 particles.

Coordination number

Coordination number or legancy is defined as the number of particles immediately adjacent to each particle in the crystal lattice.

If you carefully examine a given space lattice, in simple cubic lattice each particle is adjourned by six other particles and so the coordination number of simple cubic system is six. The coordination number of body-centred cubic system is eight and that of face-centred cubic system is 12 respectively.

5.8 X-RAY DIFFRACTION OF CRYSTALS

You know that when x-rays were first investigated, problem arose of measuring their wave length. It is a well known fact that, if light is allowed to strike a surface consisting either of a series of edges or lines spaced closely enough to be of the same order of magnitudes as that of the wavelength of light, the beam of light is diffracted. And the various radiations are dispersed into a series of spectra known as, first, second, third etc. order of spectra. Further, there is definite relation between the angle of diffraction, the wavelength of radiation and the spacing of the lines on the ruled grating. Since x-rays are of the same nature as light, it should be theoretically possible to determine the wavelength of this radiation in the same way. However it is impossible by any mechanical means to rule a grating as fine as that required, namely one with 10^8 lines per centimeter. For this purpose Laue (1912) suggested that crystal can act as grating to x-rays as wavelength of x-rays is comparable to the interatomic distance. When a beam of x-rays is allowed to fall on a crystal, a large number of images of different intensities are formed. If the diffracted waves are in the same phase, they reinforce each other and a series of bright spots are produced on a photographic plate placed in their path. On the other hand, if the diffracted waves are out of phase, dark spots are caused on the photographic plate (fig 5.8). From the overall diffraction pattern produced by a crystal, can arrive at the detailed information regarding the position of particles in the crystal.

5.8.1 Bragg’s equation

Bragg’s pointed that the scattering of x-rays by crystal could be taken to be equivalent to reflection from successive planes of atoms in the crystal. However the reflection of x-rays can take place only at certain angles which are dependent on wavelength of the x-rays and the distance between the planes of the crystal. The fundamental equation which gives a simple relation between the wave length of x-rays, the interplaner distance in the crystal and the angle of reflection is known is known as Bragg’s equation. This equation can be derided as follows.

The horizontal lines represent parallel planes in the crystal structure separated from one another by a distance d. suppose a beam of x-rays incident at an angle falls on the crystal. Some of them will be reflected from uppermost plane at the same angle, while the other will be absorbed and get reflected from successive planes, as shown in

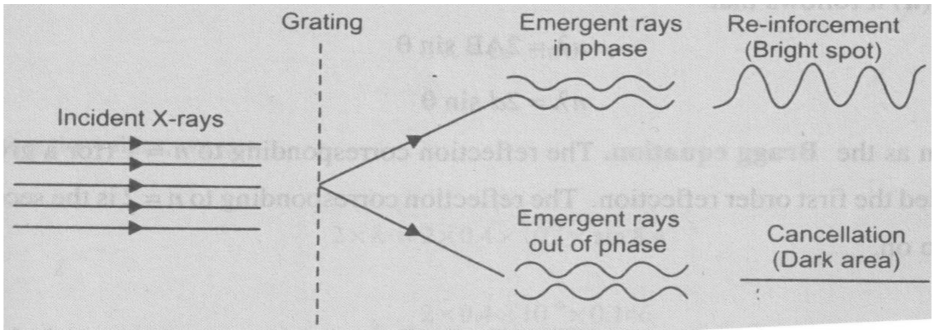


Fig 5.8 diffraction patterns produced by crystals

Let the planes ABC and DEF drawn perpendicular to the incident and reflected beams, respectively. The waves reflected from different planes will be in phase will one another only if the difference in the path length of the wave reflected from the successive planes is equal to an integral number of wavelengths. Drawing perpendicular OL and OM to the incident and reflected beams, it will be seen that the path difference in the wavelength, say δ of the wave reflected from the first two planes is given by

$$\delta = LN + NM \qquad \text{............ (1)}$$

This should be equal to a whole number multiple of wavelength
λ, i.e.

$$n\lambda = LN + NM \qquad \text{..................(2)}$$

Since the two triangle ONL and ONM are congruent LN=NM

$$n\lambda = 2LN = 2d\sin\theta \qquad \text{............(3)}$$

Equation (3) is known as Bragg's equation.

For a given set of lattice planes, d has a fixed value.

Therefore possibility of getting maximum diffraction (i.e., the possibility of getting reflected waves in phase with one another) depends upon θ. If θ is increased gradually, a number of positions will be found at which the reflection will be maximum. At these positions, n will have values 1,2,3,4...etc. generally, in experiments on x-ray diffractions, any set as equal to 1. If λ in known, it is possible to determine d, the distance between atomic planes in the crystal by determining θ experimentally. Thus if d is known λ can be calculated.

Measurement of diffraction angle:

The x-ray diffraction techniques used in the study of crystals are of two types known as rotating crystal method and powder method. Both these techniques make use of the x-ray spectrometer, the setting of which for the former technique is shown in Fig 5.8.

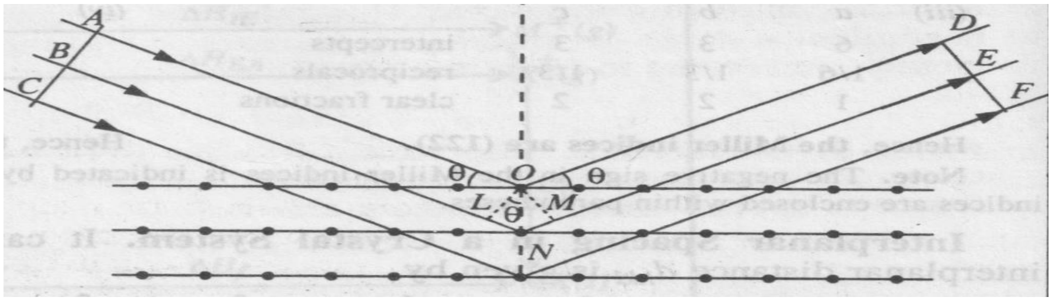


Fig 5.9 x-ray diffraction by crystals

5.8.2 Rotating crystal method

x-ray generated in the tube T are passed through a slit so as to obtain a narrow beam which is then allowed to strike a single crystal C mounted on the turn table. The crystal is rotated gradually by means of the turn table so as to increase the glancing angle at which x-rays are incident at the exposed phase of the crystal. The intensities of the refracted rays are measured on a recording device R. The recording device may be either a photographic plate or an ionisation chamber. The angle for which reflections are maximum give the value of θ. The process is carried out for each plane of the crystal. The lowest angle at which maximum reflection occurs corresponds to n=1. This is called first order reflection. The next higher angle at which maximum reflection occurs again, corresponds to n=2. This is second order reflection, and so on.

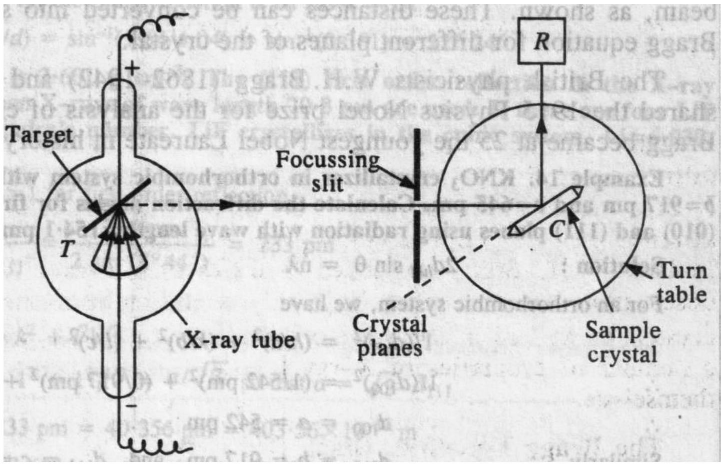


Fig 5.10 Rotating crystal method

5.8.3 Powder Method

Power method is the simplest technique for obtaining x-ray diffraction. It was first used by P.J.W. Debye and P. Scherer. Instead of taking a single crystal having a definite orientation to the impinging x-rays, we can take a mass of finely divided crystal with random orientation

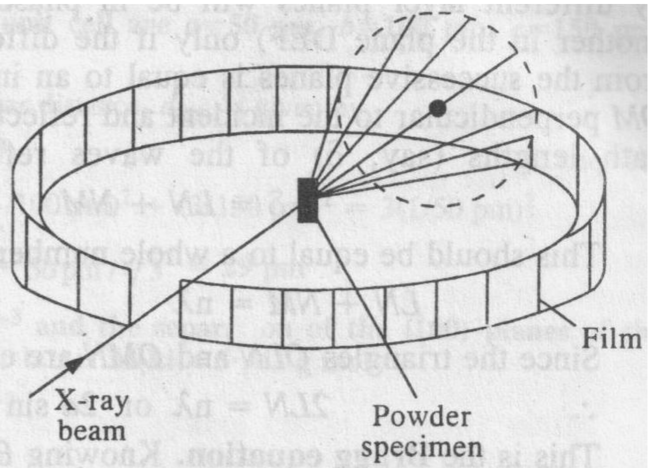


Fig 5.11 The powder method

This method is better adopted due to its simplicity and versatility. In this method, the crystal sample is need not to be taken in large quantity but a little as one milligram of the material is sufficient for study. The power, in fact consists of many small crystals which are oriented in all possible directions. As a result of this x-rays are scattered from all set of planes (e.g., 100,110, etc.). The scattered rays are detected by using an x-ray sensitive film. The principle is shown in Fig 5.9. A narrow beam of x-rays is allowed to fall on the powder. The diffracted x-rays strike a strip of photographic film arranged in the form of circular arc, as shown in the Fig 5.11.

In this method no rotation is necessary since the powder sample already contains microcrystal arranged in all possible orientations. Hence, a large number of them will have their lattice planes in correct positions for maximum x-ray reflection to occur. As a result of this we get lighted areas in the form of arcs of lines at different distances from the incident been as shown. These distances can be converted into scattering angles to be used in the Bragg's equation for different planes of crystals.

5.9 STRUCTURE OF CRYSTAL SYSTEM NaCl, KCl and CsCl

Structure of NaCl crystal

The ionic crystal of NaCl is shown in Fig 5.12. Each sodium ion is surrounding by six chloride ions and each chloride ions is surrounded by six sodium ions. The maximum intensity of reflection occurs at the glancing angle of 5.9^0, 8.4^0 and 5.2^0 for 100, 110 and 111 planes, respectively for first order reflection.

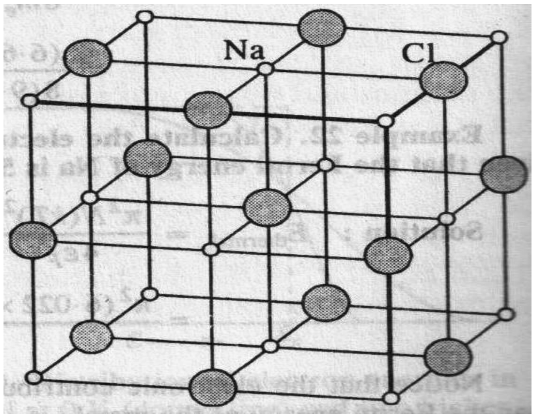


Fig 5.12 Structure of NaCl crystals

We know that,

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

or $$\frac{1}{d} = 2\,\frac{\sin\theta}{n\lambda}$$

Therefore for a particular order of reflection

$$d \,\alpha 1/\sin\theta$$

If only first order reflection are considered than,

$$d_{100}:d_{110}:d_{111} = 1/\sin 5.9^0 : 1/\sin 8.4^0 : 1/\sin 5.2^0$$

$$= 1/0.103 : 1/0.146 : 1/0.091$$

$$= 1:0.704:1.155$$

For face-centred cubic system the planes can be passed through the atom having Miller indices 100, 110 and 111 at the relative spacing a/2:a/2√2: a/√3

So $d_{100}:d_{110}:d_{111} = a/2:a/2\sqrt{2}:a/\sqrt{3}$

$= 1:0.707:1.154$

This ratio is almost identical with the ratio we have calculated from experimental observations. Hence NaCl crystal is face-centred cubic system.

Structure of KCl crystal

On investigating the KCl crystal ,the maximum reflection of x-rays, corresponding to first order reflections are observed to occur at the glancing angles of 5.38^0, 7.61^0 and 9.38^0 for (100),(110) and (111) faces, respectively,

Therefore,

$d_{100}:d_{110}:d_{111}= 1/\sin 5.38^0:1/\sin 7.61^0:1/\sin 9.38^0$

$= 1:0.704:0.575$

For the simple cubic system the planes can be passed through the atoms having Miller indices (100),(110) and (111) and the relative spacing for the unit cell is a:a/√2:a/√3

So $d_{100}:d_{110}:d_{111}= 1:0.707:0.577$

Therefore, KCl crystal has a simple cubic lattice.

Potassium Chloride is isomorphous with sodium chloride. The explanation for this apparent anomaly is very simple and can be explained on the basis that the x-rays scattering power for an atom or ion is governed by the number of extra-planetary electrons. viz. atomic number.

The atomic numbers of potassium (K=19) and chlorine (Cl=17) are not very different and the x-rays are unable to detect any difference between the two kinds of atoms. If we imagine all the atoms to be identical, it is evident that face-centred arrangement has become a simple cubic arrangement. This is the reason for the KCl spectrum corresponding apparently to the simple cubic lattice. With KCl, the structure is face-centred, but the face-centred characteristics are marked by the fact that the two types of atoms composing the substance have nearly the same atomic numbers and atomic weights (K=39, Cl=35.5). But in the case of sodium chloride the atomic numbers differ considerably (Na=11, Cl=17), and so their scattering powers are different and hence the true structure as two interpenetrating face-centred lattices become apparent. It is only the (111) face spectra which allows us to distinguish between the simple cubic lattice and the face-centred cubic lattice.

Structure of CsCl crystal

Cesium chloride, CsCl, has a body centred cubic structure. In its crystal lattice, each

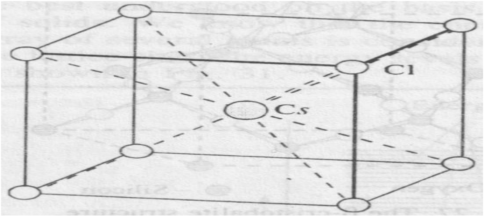


Fig 5.13 Cesium chloride crystal lattice

Cs^+ ion is surrounded by 8 Cl^- ions and its coordination number is 8. The value of distance between Cs^+ ion and Cl^- ion as determined by Bragg's spectrometer is 3.510^0A Fig 5.11.

The **diamond lattice** consists of a series of atoms, each of which is placed between four neighbours. The latter occupies the angular points of a regular tetrahedral, while atom under consideration lies in the centre. The type of structure runs throughout the crystal. The C-C bond distance is 0.154 nm. The whole lattice is continuous Fig 5.14. The diamond crystal is regarded as giant molecule. The crystal is very hard because the covalent links runs without a break throughout the whole crystal. The crystal can be cut only by breaking the covalent links. High melting point can also be explained by stating that the atoms are very firmly attached within the crystal.

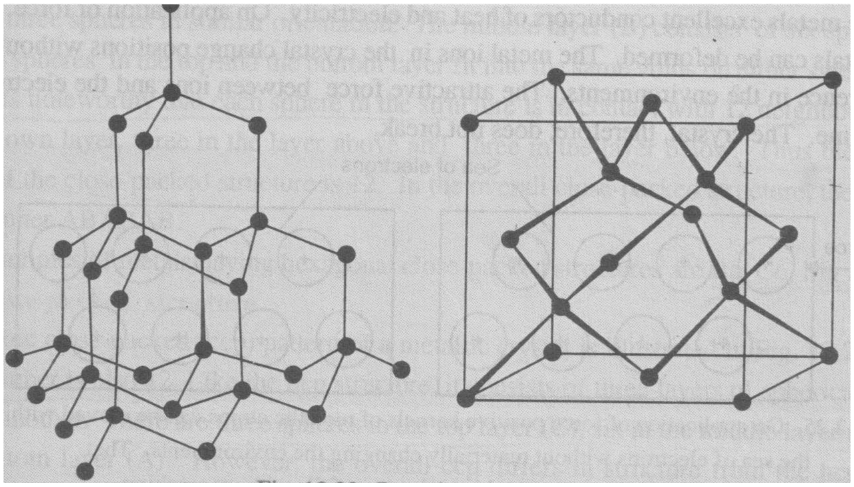


Fig 5.15 crystal structure of diamond

Though diamond and graphite are both covalent crystals. The great difference between graphite and diamond can be understood in terms of the crystal lattice. Graphite has hexagonal networks in sheets like benzene rings. The distance between atoms in the plain is 142 pm but the distance between these atomic layer planes is 335 pm. In two directions the carbon atoms are tightly held as in diamond, but in the third direction, the force of attractions appreciably less. As a result one layer can slip over the other. The crystal are flatty.

Examples:

Q.1 At what angle (θ will x-rays of wavelength $1.542x10^{-10}$m, be reflected by plains separated by $3.5x10^{-10}$m.

Solution:

From Bragg's equation $2d\sin\theta=n\lambda$

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

$\theta=\sin^{-1}n\lambda/2d$

$\theta= \sin^{-1} 1x1.542x10^{-10}/2x3.5x10^{-10}$

$=12.73^0$ ans

Q.2 Metallic gold Au=197 is face centred cubic lattice. Calculate (a) how many atoms occupy the gold unit cell and (b) what is the mass number of a gold unit cells.

Solution:

Corner atom is shared by 8 unit cells, hence share of one unit cell is 1/8, for 8 corners 1/8x8=1 atom

There are six faces, each contain 1 atom and share of one unit cell is ½ and for six faces $\frac{1}{2}$ x 6=3 atoms

So 1+3=4 atoms occupy the gold unit cells.

Mass of gold atom = $\frac{molar\ mass}{Avagadro\ number}$

= 197g/mole/6.022x10^{23} Au atoms/mole x1/4

= 8.178x10^{-23}gans

Q.3 Diffraction angle 2θ=16.8^0. for a crystal having interplaner distance in the crystal is 0.400mm when second order reflaction was observed. Calculate the wavelength of the x-rays used.

Solution:

Given that n=2, d=0.400nm = 0.4x10^{-9}m, 2θ=16.8^0 , so θ=8.4^0

Now 2dsinθ=nλ

λ=2/2x0.4x10^{-9}xsin8.4^{0}m

= 0.4x10^{-9}x0.146m

=0.584x10^{-10}m

=0.584A^0 ans

5.10 BORN HABER CYCLE

(determination of lattice energy of an ionic crystal)

5.10.1 Lattice energy

The positive and negative ions in an ionic crystal are held together by electrostatic forces. The bond energy is expressed in terms of the lattice energy.

5.10.2 Definition

The change in enthalpy (heat change) that occurs when 1 mole of a solid crystalline substance is formed from its gaseous ions is known as lattice energy.

Born-Haber cycle is used to determine the lattice energy of a ionic solid. The lattice energy of sodium chloride, for example is the change in enthalpy, ΔH^0, when Na^+ and Cl^- ions in the gas phase come together to form 1 mole of NaCl crystal.

Process of obtaining sodium chloride can be obtained in the following steps:

(a) Conversion of sodium metal to gaseous atoms (sublimation), energy required for this sublimation process is ΔH=S

$$Na(s) \longrightarrow Na(g),\ \Delta H=S$$

(b) Conversion of gaseous sodium to sodium ions by loosing electron. Energy required for ionisation is I.

$$Na(g) \longrightarrow Na^+(g) + e^-,\ \Delta H=I$$

(c) Dissociation of chlorine molecule to chlorine atoms. Energy required for this process is $\frac{1}{2}$ D as half molecule is dissociated

$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$, $\Delta H= \frac{1}{2}D$

(d) Chlorine atoms gain electron to form chloride ions. Energy released is the electron affinity E.

$Cl(g) + e^- \longrightarrow Cl^-(g)$, $\Delta H=-E$

(e) Sodium and chloride ions get together and form the crystal lattice. Energy released in this process is known as lattice energy and is equal to U.

$Na^+(g) + Cl^-(g) \longrightarrow NaCl\ (s)$. $\Delta H=-U$

The enthalpy change for the direct formation of sodium chloride for sodium metal and chlorine is heat of formation ΔH^0. This amount of heat is released in this process.

$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$, $\Delta H=- \Delta H^0$

Equating these two we get,

$$- \Delta H^0 = S+I+ \frac{1}{2} D-E-U$$

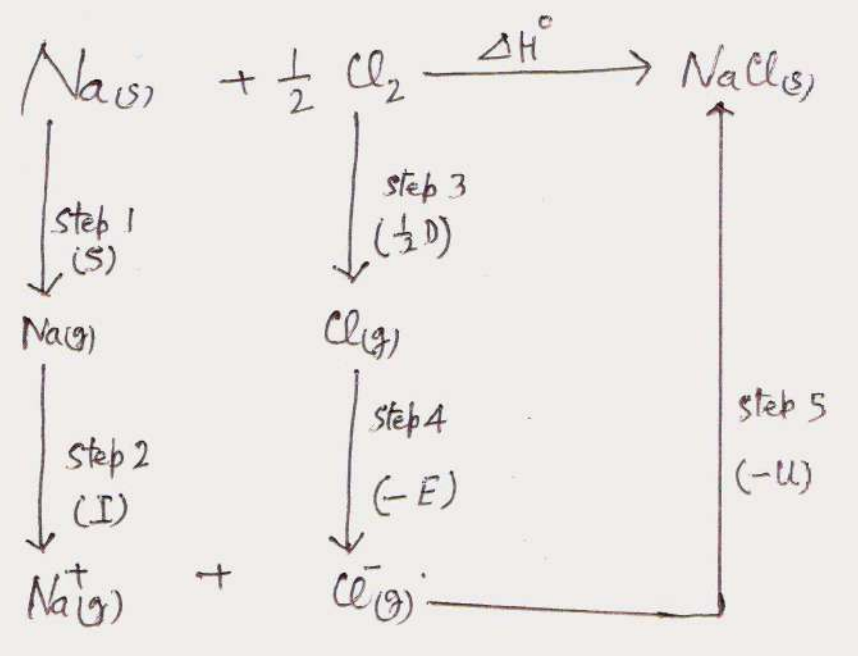


Fig 5.16 Born-Haber cycle

The cycle of changes shown in Fig 5.16 is called Born-Haber Cycle named after Max Born and Fritz Haber, who used this method for calculating lattice energies of crystals. Thus lattice energy U can be calculated from the above equation.

5.11 SUMMARY

In this unit you have studied details of solid state in general and crystalline state in particular. You have studied difference between crystalline state and amorphous state, the various law of crystallography. The importance of Bragg's Equation which can be used for calculating Avogadro's number. In molecular crystals the forces which hold the constituents of von der Waals type. These are weaker because of which molecular crystals are soft and having law melting points example are CO_2, CCl_4, Ar and most of the organic compounds.

In ionic crystals forces involved are electrostatic and these are stronger. Therefore, the ionic crystals are strong and likely to be brittle. The melting points are high, which decreases with increasing size of ions. In covalent crystals, the forces involved are of chemical nature (covalent bonds). They are strong, and consequently the crystals are strong and hard,

with high melting points examples are diamond, silicon, etc. In metallic crystals, electrons are held loosely and hence they are good conduction of electricity. Metallic crystals can be bond and are also strong.

5.12 TERMINAL QUESTIONS

(A) Multiple choice questions:

Q.1 Tetragonal crystal system has the following unit of dimensions

(a) $a \neq b \neq c$ and $\alpha=\beta=\gamma=90^0$ (b) $a=b\neq c$ and $\alpha=\beta=\gamma=90^0$

(c) $a=b\neq c$ and $\alpha=\beta=90^0$, $\gamma=120^0$ (d) $a=b=c$ and $\alpha=\beta=\gamma=90^0$

ans (b)

Q.2 In the crystal of C_SCl, the nearest neighbours of each C_S^+ ion are :

(a) six Cl^- ions (b) six C_S^+ ions

(c) eight Cl^- ions (d) six Cl^- ions ans (c)

Q.3 The Bragg's equation for diffraction of x-rays is:

(a) $n\lambda=d \sin\theta$ (b) $n=2d\frac{\sin\theta}{\lambda}$

(c) $n\lambda=2d^2 \sin \theta$ (d) $n\lambda^2 = 2d \sin \theta$ ans (b)

Q.4 Which is incorrect for hexagonal crystal system

(a) $a=b=c$ (b) $a=b\neq c$

(c) $\alpha=\beta=90^0$, $\gamma=120^0$ (d) none of these ans (a)

Q.5 The total number of atoms in a body-centred cubic unit cell each:

(a) 1 (b) 2 (c) 3 (d) 4 ans (b)

(B) Short Answer questions

Q.1 Explain the terms anisotropy and isotropy

Q.2 Account for the following:

"Graphite and Diamond are both allotropic forms of carbon yet graphite is soft while diamond is hard."

Q.3 Why is rotation of crystal is not necessary in power method for the determination of crystal structure?

Q.4 Write a short note on rational intercepts.

Q.5 Define the terms:

(i) unit cells (ii) plane of symmetry (iii) law of constancy of interfacial angle.

(C) Essay type questions

Q.1 Derive Bragg's equation for diffraction of x-rays by a crystal lattice. How is this equation used in elucidating the crystal structure?

Q.2 (i) Derive the equation $2d \sin \theta= n\lambda$

(ii) Draw structure of NaCl crystal.

Q.3 Write notes of the following:

(a) Laws of crystallography
(b) Anisotropy and isotropy
(c) Power method for the determination of crystal structure.

Q.4 (a) Differentiate between crystalline and amorphous solids.
(b) What is lattice energy? How lattice energy can be determined by Born-Haber cycle?

Q.5 (a) Enumerate various elements of symmetry of a cubic type unit cell.
(b) Draw diagrams to represent:
(i) Face centred cubic lattice.
(ii) Body centred cubic lattice.

Source of Study Material

1. Essentials of Physical Chemistry By B.S. Bahl, Arun Bahl, G.D. Tuli
2. Principles of Physical Chemistry by Puri and Sharma
3. Under graduate Physical Chemistry by J.N. Gurtu

Books recommended for further study-

1. Physical Chemisty By Walter J. Moore
2. Elements of Physical Chemistry By B.R. Puri, L.R. Sharma & M.S. Pathania
3. A textbook of physical chemistry By K.L. Kapoor.

UNIT 6: CHEMICAL KINETICS-I

CONTENTS:

6.1 OBJECTIVES

The chemical reactions can be classified into following categories on the basis of their speed:

(a) Fast reactions which proceed at very fast speed and it is practically very difficult to measure the speed of such reactions. Examples of fast reactions include

(i) Neutralisation of acids and bases

(ii) Organic substitution reactions

(iii) Explosive reactions of oxygen with hydrogen and hydrocarbons. The rates of such reactions can be measured by using special methods.

(b) Extremely slow reactions which proceed at a very slow speed and the speed is so slow that it not possible to measure the speed of such reactions. Rusting of iron is very slow reaction.

(c) Reaction which precede a measurable speed. These reactions are utilized in the study of chemical kinetics.

Examples are Inversion of cane sugar, saponification of ethyle acetate etc. The significance of study of kinetics of reactions is many fold. It provides very important information on how chemical reactions occur and what is their mechanism. The knowledge of rate of reaction is very valuable for the success of an industrial process where it is imperative to second optimum conditions of the reactions involved when these reactions proceed at a rate so as to give maximum yield.

6.2 INTRODUCTION

The branch of physical chemistry which deals with the speed or rate at which a reaction occurs is called chemical kinetics. **Chemical Kinetics is the study of rate of a reaction under different conditions like different concentrations, pressures,**

temperatures, catalyst, pH, dielectric constant of the medium, free radical scavengers, neutral salts etc and suggesting a suitable mechanism for the reaction.

Chemical kinetics constitutes an important topic in physical chemistry. It concerns itself with measurement of rates of reactions proceding under given condition of temperature, pressure and concentration.

The study of chemical kinetics has been highly useful in determining the factors which influence rate of reaction as well as in understanding mechanism of a number of chemical reactions. The experimental data have led to the development of the modern theories of chemical reactivity of molecules.

6.3 CHEMICAL KINETICS AND ITS SCOPE

6.3.1 Scope of chemical kinetics

Thermodynamics predicts that at room temperature hydrogen and oxygen react to form water, all the reactants being essentially converted into products. When we carry out the experiment we find that the reaction proceeds so slowly that unless we are willing to wait indefinitely, practically no water results. On the other hand, experiment shows that N_2O_4 decomposes into NO_2 under atmospheric conditions almost instantaneously even though $-\triangle G^0$, which is a measure of spontaneity of a reaction, is far less for the decomposition of N_2O_4 than that for the reaction between hydrogen and oxygen to form water.

Above two examples suggest that there is essentially no correlation between thermodynamic instability and the rate of the chemical reaction. In fact, the rate of a reaction depends upon structural and energetic factors which are not uniquely specified by thermodynamic quantities such as the free energy change. Hence, chemical kinetics is a technique complementary to thermodynamics for studying a given reaction.

The first stage in studying the rate and the mechanism of a chemical reaction is the determination of overall stoichiometry of the reaction and to identify any side-reaction. The next step involves the determination of the change of the concentration of the reactant and product species with time. Since the reaction rate depends sharply on temperature, the temperature of the reacting mixture must be kept constant.

Several experimental techniques have been developed to monitor the concentration of the reactants and products and their variation with time. The selection of a typical method depends on the nature of the species involved and how rapidly their concentration change. For reactions that are relatively slow, conductometric, poteniometric, optical methods, polarimetry and spectrophotometry are used. The time taken for reactions to reach completion varies widely, from femtoseconds (1fs = 10^{-15} s) to days.

For reactions in which one or more products are gases, the reaction rate involves monitoring pressure as in the reaction :

$$N_2O_5\,(g) \longrightarrow 2NO_2\,(g) + O_2(g).$$

For optical method involves monitoring optical activitiy.
Reactions in solution involving ionic species may be studied by monitoring their conductivity. The change in EMF of an electrochemical reaction can be followed potentiometrically. Spectrophotometry, the measurement of intensity of absorbtion in a particular spectral region is widely used to monitor concentration. Reactions that involve a change in concentration of H^+ ions may be studied by monitoring pH of the solution with a glass electrode. Other methods of monitoring the composition include the detection of fluorescence and phosphorescence, mass spectrometry, gas chromatography and magnetic resonance.

In a real time analysis the composition of reaction mixture is analysed while the reaction is in progress by direct spectroscopic observation. In the quenching method, the reaction is stopped after being allowed to proceed for a certain time and the composition is analysed. The entire reaction mixture may be quenched either by sudden cooling or by adding to it a large volume of solvent. This method is applicable for reactions that are slow enough for there to be little reaction during the time it takes to quench the reaction mixture.

Femtochemistry has emersed as the most exciting field for investigating extremely fast reactions whose time-scale is of the order of femtoseconds. This method is due to A.H. Zewail, who was awarded Nobel Prize of chemistry in 1999.

Femtochemistry is extremely useful for studying biological processes such as the energy converting processes of photosynthesis and photostimulated processes of vision in which the primary energy and electron-transfer reactions occur on the femtosecond or picosecond time-scale.

6.3.2 Rate of a reaction

The rate of a reaction tells us to what speed the reaction occurs. Let us consider a simple reaction-

$A \longrightarrow B$

The concentration of A decreases and that that of B increases with time. The rate of a reaction is defined as the change in concentration of any

of reactant or product with time. As you know during the progress of a reaction the concentration of A keeps on falling with time. The rate of reaction at any given instant is given by the expression-

$r = -dC_A/dt = kC_A$ ……………………….(1)

where $-dC_A$ is very small decrease in concentration of A in a very small time interval dt, C_A gives the concentration of the reactant A at a given instant and k is constant called the rate constant or velocity of the reaction.

Now the concentration of product B increases with time. Hence rate of reaction can also be expressed in terms of increase in concentration of the product B as well. Thus

$r = dC_B/dt = kC_A$ ………………………….(2)

where dC_B is very small increase in the concentration of product B in a very small time interval of time dt.

Now it should be clear to you from (1) and (2)

$r= - dC_A/dt =dC_B/dt= kC_A$

and for a reaction $A+B \xrightarrow{\qquad} M+N$

the rate can be expressed

$r= -dC_A/dt = -dC_B/dt = dC_M/dt=dC_N/dt=kC_AC_B$ ………………(3)

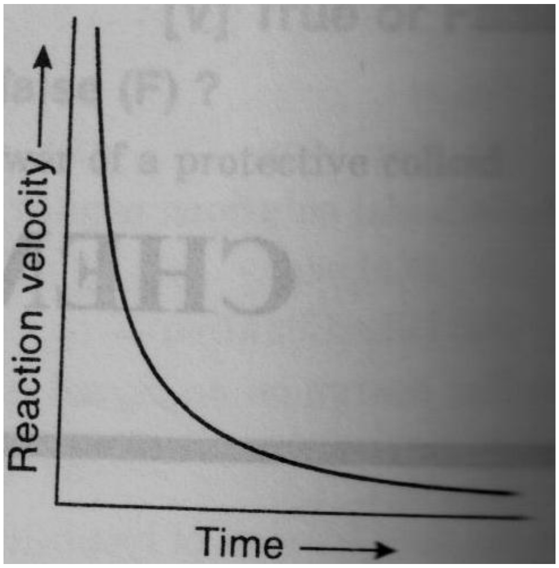


Fig-6.1

As the reaction proceeds the reactants are consumed where by their molecular concentration decreases. Hence the rate of a chemical reaction will also decrease with time. The graph between reaction velocity and time will be as shown in the fig. (6.1). Now it should be clear to you that reaction velocity is maximum to start with and then falls gradually with time. The reaction velocity become so slow in the latter states that it takes a

very long time for the reaction to be completed. It can be safely assumed that in the latter stages the reaction is nearly complete.

Now let us consider a reaction-

$aA+bB \xrightarrow{\qquad} cC+dD$

In this reaction a moles of A reacts with b moles of B to form c moles of C and d moles of D. the rates of such a reaction can be expressed either in terms of decrease in concentration of a reactant per mole or increase in concentration of a product per mole. Thus we can write as follows:

r= -1/a dC_A/dt = -1/b dC_B/dt =1/c dC_C/dt = $1/dC_D/dt$ = k $C^a_A C^b_B$

6.3.3 Units of rate

Reaction rate has the units of concentration divided by time. We express concentration in moles per litre (mole/litre) but time may be given in any convenient unit second(s), minutes (min), hours (h) days (d) or possibly years. Therefore, the units of reaction rates may be

mole/litre/sec or mole $l^{-1}s^{-1}$

mole/litre/ minute mol $l^{-1}m^{-1}$ and so on

6.3.4 Factors affecting reaction velocity

There are a number of factors which affect the rate of a reaction, the most important of them are:

(a) Effect of concentration: The rate of a chemical reaction is influenced by the no. of collisions per second between the reacting molecules. On increasing the concentration of the reactant, the number of collisions will increase and the rate of reaction will increase and on decreasing the concentration the rate will decrease.

(b) Effect of nature of reactants: Reactions between polar or ionic molecules occur almost instantaneously. Those reactions in which the bonds are arranged or electrons are transferred takes a comparatively longer time than the reaction between ionic molecules.

You can cite the examples of neutralisation reactions or double displacement reactions which are very fast while the oxidation reduction reactions are slower.

(c) Effect of catalyst: A catalyst can increase or decrease the rate of a chemical reaction. For example the combination of hydrogen and oxygen to form water is slow at ordinary temperature, while it proceeds rapidly in presence of platinum.

(d) Effect of surface area of reactant: Surface area of reactants is of importance only for heterogeneous reactions. As particle size decreases, surface area for the same mass increases. The smaller particle thus reacts more rapidly than the larger particles. For example, burning of coal dust in air takes place more rapidly than large lump of coal.

(e) Effect of temperature: With the exception of few reactions, the rate of reaction is increased considerably with an increase of temperature. Generally the rate of a reaction is almost doubled or tribled by an increase of 10^0C in temperature.

$$\frac{\text{Rate of reaction at } 35^0C}{\text{Rate of reaction at } 25^0C} = \frac{K_{35}}{K_{25}} = 2 \text{ to } 3$$

6.3.5 Order of reaction and molecularity

The total number of reactant particles involved in the overall reaction, is called as molecularity of a reaction

Thus in the reaction -

$N_2O_5\,(g) \longrightarrow 2NO_2\,(g)+1/2O_2(g)$ it is unimolecular

$2HI\,(g) \longrightarrow H_2(g) + I_2(g)$ it is bimolecular

and $2NO\,(g) + O_2(g) \longrightarrow 2NO_2$ it is trimolecular

Order of reaction depends only on the reactants upon which the rate of reaction depends. It means that order is in those reactants only, by changing whose concentration, the rate of reaction changes.

If reaction rate is independent of reactant concentration, the order is zero in that reactant.

We can say that "Order is the sum of powers of concentration of reactants as given in a rate law or rate equation or rate expression for the reaction under consideration".

A reaction is said to be first order if its rate r (or dx/dt) is given by the following rate expression -

$$R = dx/dt = kC_a$$

The reaction is of second order and third order if its rate expressions are given by Eqn. (i) and (ii) respectively

$$dx/dt = kCa^2 \quad \text{or} \quad kC_aC_b \quad \ldots\ldots\ldots\ldots\ldots\ldots(i)$$

$$dx/dt = kCa^3 \quad \text{or} \quad kC_a^{\,2}C_b \text{ or } kC_aC_b^{\,2} \quad \ldots\ldots\ldots\ldots\ldots\ldots(ii)$$

The subscripts a, b and c stand for various reactants A, B and C respectively. When the rate expression is given by

$$dx/dt = kC_a^{\,n}{}_1\, C_b^{\,n}{}_2 C_c^{\,n}{}_3$$

The order of reaction as a whole n is given by $n= n_1+n_2+n_3$…………

The molecularity of any process can only be small position integers, while order of reaction can have zero as well as fractional values.

Difference between order of reaction and molecularity:

	Molecularity	Order of reaction
1	It is equal to the number of molecules of reactants which take part in a chemical reaction.	1. It is equal to some of the power of the molar concentration of the reactants in the rate expression.

2	It is theoretical concept.	2. It is an experimentally determined quantity, which is obtained from the rate for the overall reaction. It depends on rate determining step in the reaction mechanism.
3	It is always a whole number.	3. It may be negative, zero or fractional value generally not more than 3.
4	It is obtained from a single balanced chemical equation.	4. It cannot be obtained from a balanced chemical equation
5	It does not reveal anything about reaction mechanism.	5. It reveals some basic facts about a reaction mechanism.

Table 6.1

6.4. ZERO, FIRST, SECOND AND THIRD ORDER REACTIONS

(1) Zero order reaction

Reactions, in which the reaction rate does not depend upon the initial concentration of the reactant, are said to be zero order reactions. The Law of mass action fails in these reactions

$$A \longrightarrow B$$

$$\frac{d\,[A]}{dt} = kA^0 = k$$

Examples of zero order reactions:

1. Thermal decomposition of hydrogen iodide at gold surface is found to be of zero order

$$2HI \longrightarrow H_2 + I_2$$

2. The decomposition of ammonia on platinum surface at 800^{0}C in kinetically of zero order.

$$NH_3 \longrightarrow N_2 + 3H_2$$

3. The phosphine decomposition on the surface of molybdenum or tungsten at high pressure is of zero order.

$$2PH_3 \longrightarrow 2\,P + 3H_2$$

(2) First order reaction

A first order reaction is that in which the sum of powers to which the concentrations of reactants must be raised while expressing the reaction rate, is one.

Expression for first order reaction is given by

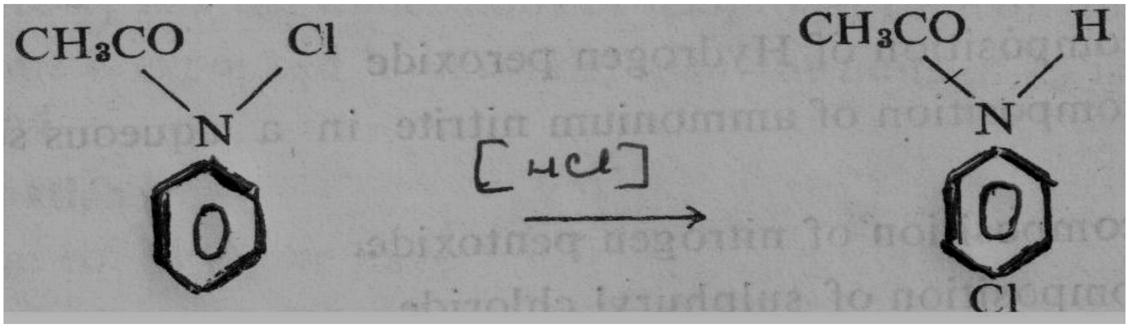
$$A \longrightarrow \text{products}$$

A	P	
a	0	initially
a-x	x	after time t

rate expression is given as

$r = -d[A]/dt$
$= d[P]/dt$
$= dx/dt$
$=k[A]$
$= kC_A$
$= k. A$ (at zero time)
$=k (a-x)$ (at t time)

Example is conversion of N-chloroacetamide into parachloroacctanicide



(3) Second order reaction

A second order reaction is that in which the sum of powers to which the concentrations of reactants must be raised while expressing the reaction rate, is two.

$dx/dt = kC^2_A$ for reaction $2A \longrightarrow$ products

and $dx/dt = kC_AC_B$ for reaction $A+B \longrightarrow$ products

Example of second order reactions are :

Hydrolysis of an ester by an alkali (Saponification of ester)

$CH_3COOC_2H_5+NaOH \longrightarrow CH_3COONa+C_2H_5OH$

(4) Third order reaction

Definition of third order reaction:

A third order reaction is that in which the sum of powers to which the concentrations of reactants must be raised while expressing the reaction rate, is three.

Reactions of third and higher order are rare, but there are infact reactions which are definitely of third or sometimes higher order. This is due to the effect that the probability of three molecules coming to a single point simultaneously is must less as compared to unimolecular and bimolecular reactions.

In a reaction of the third order the number of molecules where concentration alters as a result of chemical change is three, and the change may belong to any of the following types

$A + A + A \longrightarrow$ products

$A + A + B \longrightarrow$ products

$A + B + C \longrightarrow$ products

Note: Above given examples are of elementary reactions i.e. reactions in which order and molecularity are same and there is a single step mechanism. For complex reactions (involving more than one step in mechanism and difference in molecularity and order), order may be 3 even if the number of reactants is more than 3.

Examples of third order reaction is

(i) $2\ FeCl_3+SnCl_2 \longrightarrow 2\ FeCl_2+SnCl_4$
(ii) $O_2+2NO \longrightarrow 2NO_2$
(iii) $2NO + Cl_2 \longrightarrow 2NOCl$

(5) Pseudo molecular reactions [pseudo means false]

These are the reactions in which order and molecularity are different. These reactions are named after the order and not after the molecularity. Eg. if molecularity is 2 and order is 1 than the reaction is called as pseudo first order reaction.

There are several reactions which obey first order rate equation although in reality they are bi-or tri-molecular.

For example, consider the hydrolysis of methyl acetate in presence of an acid

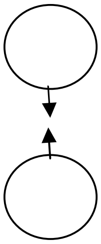
$$CH_3COOCH_3+H_2O(Excess) \longrightarrow CH_3COOH+CH_3OH$$

Here molecularity is 2, while order is one in ester and zero in water i.e. overall order is 1 + 0 = 1. The order becomes zero in the reactant which is taken in excess, because the overall rate of reaction does not depend upon the reactant taken in excess. If we will change the concentration of reactant taken in excess, there will not be any change in its being in excess.

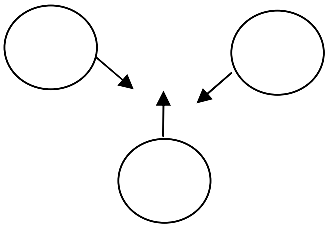
Why high molecularity reaction are rare

Most of the reactions involve one, two or at the most three molecules. The reactions involving four or more molecules are rare. This can be explained on kinetic molecular theory. According to this theory, the rate of a chemical reaction is proportional to the number of collisions taking place between the reacting molecules. The chances of simultaneous collision of reacting molecules will go on decreasing will increase in number of molecules. Thus the possibility of three molecules colliding is much less than in case of bimolecular collision. For a reaction of molecularity 4, the four molecules must come closer and collide will one another at the same time.

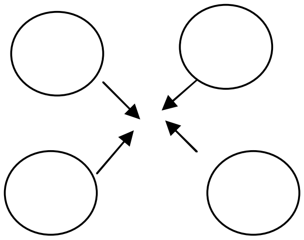
The possibility of their doing so is much less than even in the case of termolecular reactions. Hence the reactions involving many molecules proceed through a series of steps, each involving two, three or less number of molecules. Such a reaction is called complex reaction and the slowest step determines the overall rate of reaction.



less common



rare



Common

Molecularity of a complex reaction:

Most chemical reactions are complex reactions. These occur in a series of steps. Each step is an elementary reaction. The stepwise sequence of elementary reactions that convert-reactants to products is called the mechanism of the reaction. In any mechanism, some of the steps will be fast other will be slow. A reaction can proceed no faster than its slowest step. Thus the slowest step is rate determining step of the reaction.

The decomposition of N_2O_5

$2N_2O_5 \longrightarrow 4\,NO_2+O_2$ is an example of complex reaction.

It occurs by the following steps

Step I : $2N_2O_5 \longrightarrow 2NO_2+2NO_3$ (slow)

StepII : $NO_2+NO_3 \longrightarrow NO+NO_2+O_2$ (slow)

Step III : $NO+NO_3 \longrightarrow 2NO_2$ (fast)

Adding all the three steps

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

Each elementary reaction has its own molecularity, equal to number of molecules or atoms participating in it. It is meaningless to give the molecularity of the overall reaction because it is made of several elementary reactions, each perhaps with different moelcularity. At best it could be thought of as:

"The number of molecules or atoms taking part in the rate determining step."

Thus step 2 in the above mechanism is rate determining step and has molecularity, '2' which could be considered as the molecularity of the decomposition reaction of N_2O_5. As slowest step is the rate determining step. In such complex reactions the molecularity of slowest i.e. the rate determining step, is called as order of reaction. e.g. for decomposition of n_2o_5, the molecularity is 2 but order is one.

And thermal decomposition of acetaldehyde:

$2CH_3CHO \longrightarrow 2CH_4+2CO$

6.5 INTEGRATED LAW FOR ZERO AND FIRST ORDER REACTION

(1) Integrated law for zero order reaction

Let us consider a reaction

$A \longrightarrow B$

a 0 initially

a-x x after time t

For a zero order reaction the reaction velocity at any time t is given by -

$dx/dt = k$ (constant)

$dx = kdt$

$\int dx = \int kdt$

$x = kt + I$ (I is integration constant)

when $t=0$ $x=0$ hence $I=0$

so we have $x=kt$

this is general rate expression for zero order reaction.

Unit of zero order reaction:

The unit of zero order rate constant is that of concentration x time^{-1} (as $k=x/t$). Hence unit of k will be mole/litre time $^{-1}$ or mole lit^{-1} time^{-1}. Examples are given earlier.

6.6 RATE EXPRESSION FOR FIRST ORDER REACTION

As we know that a first order reaction is that in which the reaction rate is determined by the change of the one concentration term of reactant only.

Let us consider a first order reaction

$A \longrightarrow B$

A 0 (initially)

a-x x (after time t)

Suppose the initial concentration of the reaction A be a mole/litre.

Let x mole/litre of A decompose after time t leaving behind (a-x) mole/litre of A, the amout of B formed will be x mole/litre.

The rate of first order reaction is proportional to the concentration of A at any particular time. Therefore

$dx/dt = kC_A$ ………………....(1)

where k is rate constant or velocity constant.

$dx/dt = k(a-x)$ …………..(2)

$dx/a-x = kdt$ ……………..…..(3)

$\int dx/a-x = \int kdt$ …………..(4)

integrating equation (4) we get

$-\log_e(a-x) = kt+I$ (I= constant of integration) ………(5)

When t=0 x=0 then
$-\log_e a = I$
Then equation (5) becomes
$\log_e a - \log_e (a-x) = kt$
or $kt = \log_e a/a-x$
$k = 2.303/t \log_{10} a/(a-x)$ ………………………..…(6)

It is clear from equation (6) that if we plot $\log_{10} a/a-x$ against time t a straight line passing through the origin is obtained with a slope of 2.303/k.

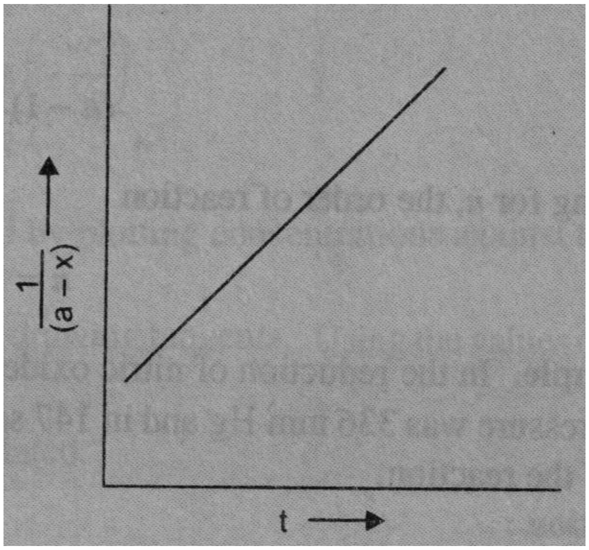


Fig 6.3

Unit of velocity constant of first order reaction:

As the rate constant for first order reaction is $k=1/t \ln (a/a-x)$, hence unit will be
1 concentration
time concentration
i.e. 1/time
or $time^{-1}$

6.7 SUMMARY

In this chapter you have studied different definitions associated with chemical kinetics, rate laws for zero, first, second and third order reaction and will examples also rate laws for zero order and first order reaction. The difference between order of reaction and molecularity has been discussed. The factors affecting rate of a reaction have also been studied namely the factors are temperature, pressure, concentration, catalyst and surface area.

The first stage in studying the rate and mechanism of a chemical reaction is the determination of the overall stoichiometry of the reaction and to identify any side reaction. The next step involves the determination of the change of the concentration of the reactant and product species with time. The reaction rate depends sharply on temperature; the temperature of the reaction mixture must be kept constant.

6.8 TERMINAL QUESTIONS

(A) Multiple Choice Questions

Q.1 The reaction A+B+C $\longrightarrow$ Products is found to obey the rate law.

$r = d[A]/dt = k[A]^2[B]^{3/2}[C]^{-1/2}$ the overall order of reaction is

(a) 7/2 (b) 5/2 (c) 3 (d) 1 ans (c)

Q.2 If the rate of reaction is given by $r = k[A]^2[B]^{1/2}$

The overall order of reaction is

(a) 5/2 (b) ½ (c) 2 (d) 1 ans (a)

Q.3 Which reaction is pseudo-unimolecular reaction?

(a) $H_2+Cl_2 \longrightarrow 2HCl$ (b) Acid-catalyzed hydrolysis of an ester.

(c) Base-catalyzed hydrolysis of an ester.

(d) $N_2O_5 \longrightarrow N_2O_4 + 1/2O_2$ ans (b)

Q.4 **Choose the correct statement:**

(a) The rate of a reaction decreases with T

(b) Order is always equal to molecularity

(c) Catalyst is always essential for a reaction

(d) For a zero order reaction the concentration of product increase linearly will time. ans(d)

Q.5 **Choose the correct statement:**

(a) The rate of reaction decreases with T

(b) Order of reaction is equal to molecularity of a reaction.

(c) The units of first order rate consistent are mole lit S^{-2}

(d) $t_{1/2}$ of the first order reaction is independent of initial concentration.

ans (d)

Q.6 Reaction rates can change with

(a) Temperature

(b) The addition of a catalyst

(c) Reactant concentration

(d) all of these

ans (d)

(B) Short Answer Questions:

Q.1 Derive mathematical expression for the rate constant of a reaction $A \longrightarrow$ products of the first order.

Q.2 Distinguish between reaction rate and rate constant.

Q.3 Explain why the rate of reaction cannot be measured by dividing the total amount of a substance reacted by the total time taken.

(C) Long answer/essay type questions questions:

Q.1. Explain the following terms.

(a) Rate of reaction (b) Molecularity of a reaction
(c) Order of reaction (d) Rate constant.

Q.2 What are different factors which affect the rate of a reaction, explain.

Q.3 What is meant by the terms rate constant and order of reaction?

Starting from the rate equations derive the units of the rate constant (k) for a zero order and first order reaction.

Q.4 Distinguish between molecularity and order of reaction. Why high molecularity reactions are rare explain?

UNIT 7: CHEMICAL KINETICS-II

CONTENTS:

7.1 OBJECTIVES

In the previous chapter you have studied that kinetics is important topic of physical chemistry. It concerns will measurement of rates of reactions proceeding under given condition of temperature, pressure and concentration. The study of this subject has been highly useful in determining the factor which influence rates of reactions as well as in understanding mechanism of a number of chemical reactions.

In this chapter we will study rate law for zero and first order reaction, half life period of a reaction mean life, radioactive decay as a first order reaction, concept of energy of activation and its importance some method of determining rate of a reaction.

7.2 INTRODUCTION

Not all chemical reaction proceeds to completion. In most reactions two or more substances react to form products which themselves react to give back the original substances. Thus A and B may react to form C and D which react together to form A and B.

$A+B \longrightarrow C+D$ (forward reaction)
$C+D \longrightarrow A+B$ (backward reaction)

A reaction which can go in the forward and backward direction simultaneously is called reversible reaction.

Let us consider a reaction

$$A+B \rightleftharpoons C+D$$

If you start with A and B in a closed vessel, the forward reaction proceed to form C and D. the concentration of A and B decreases and those of C and D increases continuously. As a result the rate of forward reaction decreases and rate of backward reaction increases. Eventually, the rate of two opposing reactions equals and the system attains equilibrium.

We assume that a chemical reaction occurs as a result of collision between the reacting molecules. Although some of these collision are ineffective, the chemical change produced is proportional to number of collision actually taking

place. Thus at a fixed temperature the rate of a reaction is determined by number of collision between the reactant molecules present in unit volume.

Now let us consider four boxes of one cubic centimeter volume; containing different number of reacting molecules A and B **(figure 7.1)**. they undergo collisions to form products C and D, the rate of reaction being governed by the number of possible collisions between them.

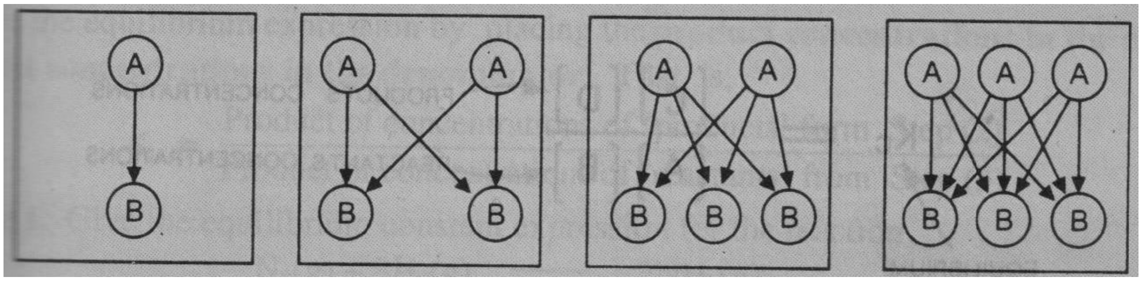


Fig-7.1

In the first box there is one molecule of A and one molecule of B and the possibilities of collision at any extent is 1x1=1. In the second box the number of molecules of A and B are two each and the possibilities of collision are 2x2=4. In the third box there are two molecules of A and three molecules of B, the number of possibilities of collisions between A and B are increased to 3x2=6. In the fourth box the possibilities of number of collision between A and B are 3x3=9.

Since the rate of reaction is determined by molecular impacts, it is proportional to moles per unit volume i.e. , molar concentration. Thus we can write

Rate of reaction ά [A][B]

= k[A][B]

The above concept is for equilibrium reactions. But most chemical reactions are spontaneous reactions. These reactions occur from left to right till all the reactants are converted to products. A spontaneous reaction may be slow or it may be fast.

Rate law of zero order reaction

Order of reaction:In the study of chemical kinetics, reactions are generally classified in terms of their order. The order of reaction is defined

as the number of molecules whose concentration determine the rate of chemical reaction at a given temperature. We may define order of reaction as sum of powers to which the concentration (or pressure in case of gases) terms are raised in order to determine the rate of the reaction.

Thus a reaction is said to be zero order if the rate reaction is written as $r= k_0$. If the rate expression is expressed of the type $r=k_1C_A$. if the rate is given by the expression of the type $r=k_2\, C_AC_B$ and for third order rate expression is given by the expression of the type $r= k_3C_AC_BC_C$ or $r=k_3C_A{}^2C_B$ and so on.

7.3 RATE EXPRESSION FOR ZERO ORDER REACTION

As you have studied that rate expression:

$A \longrightarrow$ products is given by $-dC_A/dt = r = kC_A = dP_A/dt$

As the reaction progresses the concentration of reactant keeps on falling will time hence there is negative sign. Where $- dC_A$ is very small decrease in concentration of A in an infinitesimally small time interest dt, C_A gives the concentration of the reactant A at the given instant and k is constant called rate constant or velocity of the reaction.

For a reaction

$A+B \longrightarrow L+M$

$r= -dC_A/dt = -dC_B/dt = dC_l/dt = dC_M/dt = kC_AC_B$

Now consider a reaction $aA+bB \longrightarrow lL + mM$

The rate of this can be written as $r= kC_A{}^aC_B{}^b$

The rate of such as reaction is to be expressed in terms of fall of concentration of a reactant per mole or increase in concentration of product per mole. According you can express

$r= -1/a\, dC_A/dt = -1/b\, dC_B/dt = 1/l\, dC_L/dt =1/m\, dC_M/dt.$

There are reactions in which reaction rate is not affected by charges in concentration of one or more reactant. These are called zero order reactions. In these reactions, the rate may be determined by some other limiting factor such as the amount of catalyst used in a catalytic reaction or the intensity of light absorbed in a photochemical reaction. Mathematically for a zero order reaction.

$A \longrightarrow P$

A 0 initially

The reaction velocity at any time t is given by

$dx/dt = k_0$ (constant)

$dx= k_0/dt$

$\int dx =\int k_0dt$

$x= k_0t + I$ (I= constant of integration)

when $t=0; x=0$

then $I=0$.

Hence we get $x=k_0t$

7.3.1 Characteristic of zero order reactions

(i) As $k_0 = x/t$; hence unit of zero order rate constant is that of concentration x time^{-1}. As concentration is generally expressed as mole per litre then unit of k_0 will be mole lit^{-1} time^{-1}.

(ii) Concentration of the product increases linearly with time so as plot of x against time t will be straight line passing through the origin.

7.3.2 Example of zero order reaction

Photochemical reaction between H_2 and Cl_2 over water (saturated with HCl) surface is of zero order.

Now let us consider a reaction $NO_2 + CO \longrightarrow NO + CO_2$ at 200^{0}C

Its rate = $k[NO_2]^2$

Here the rate does not depend on [CO] so this is not included in the rate law and the power of [CO] is understood to be zero. The reaction is zeroth order with respect to CO. The reaction is second order with respect to $[NO_2]$.

7.4 RATE LAW FOR FIRST ORDER REACTION

7.4.1 First order reaction

In a reaction of first order only one molecule is necessary for the reaction to proceed.

The change may be represented in the general form

$$A \longrightarrow \text{Products}$$

Let *a* be the concentration of A in gm mole per litre initially. After time t suppose the concentration is (a-x) gm moles per litre. According to the law of mass action the reaction velocity at any time t is given by the expression.

$dx/dt = k (a-x)$.

To get the value of k the velocity coefficient we integrate the expression-

$\int dx/a-x = \int kdt$

$\log (a-x) = kt+I$ (I= constant of integration)

when t=0; x=0

Hence $- \log a = I$

$-\log (a-x) = kt - \log a$

$\log a - \log (a-x) = kt$

$\log_e a/a-x = kt$

$k=1/t \log_e a/a-x$

$= 2.303/t \log_{10} (a/a-x)$

This is equation for a reaction of the first order.

When experimental values of a, x and t are inserted in the equation the value of k always comes out to be constant, if the reaction under examination is first order.

Following important conclusions can be drawn out from the study of the equation

(i) The time taken for the completion for the same fraction of change independent of initial concentration.

At half change $x=a/2$

$k=2.303/t \log_{10} (a/a-a/2)$

$=2.303/t \log_{10} a/(2a-a)/2$

$=2.303/t =\log_{10}2a/a$

$=2.303/t \log_{10} 2 = 2.303/t X .3010$

or $t= 2.303X\log_{10}2$

So t is independent of a i.e initial concentration

(ii) A change in concentration unit will not alter the velocity coefficient

$k= 1/t \log_e ma/m(a-x)$

$=1/t \log_e (a/a-x)$

7.4.2 Unit of first order rate constant

$r= -d[A]/dt =k_1[A]$

$k_1 = -1/[A] d[A]/dt$

$$\text{So units of } k_1 = \frac{1}{\text{mole per litre}} \times \frac{\text{mole per litre}}{\text{time}}$$

$$= \text{time}^{-1}$$

So units of first order rate constant are time^{-1} ie per second, per minute, per hour per day etc.

7.4.3 Half life time of a reaction

The time required for the half completion of a reaction is called half life time of a reaction. Half life time of a reaction is represented by $t_{1/2}$.

Half life time for a first order reaction is represented as-

$k_1 = 1/t_{1/2} \log_e a/(a-a/2)$

$= 1/t_{1/2} \log_e 2$

$= 1/t_{1/2} 2.303\log_{10}2$

$= 1/t_{1/2} 2.303X.3010$

$= .693/t ½$

or $t_{1/2} = 0.693/ k$

It is clear from the above discussion that

(i) Half life of a first order reaction is independent of the initial concentration.

(ii) Half life is inversely proportional to k.

Now you can calculate the time for completing any fraction of the reaction by making use of first order reaction.

We know $k= 2.303/t \log a/a-x$

Let us calculate the time in which one third of a reaction is completed.

$k = 2.303/t \log a/(a-a/3)$

$= 2.303/t \log 3a/2a$

$= 2.303 \log 3/2$

$= 2.303/t (\log 3-\log 2)$

If we have to calculate the time in which two third of a reaction is completed we proceed as under-

k = 2.303/t log a/(a-2/3a)
= 2.303/t log q/(3a-2a)/3a
= 2.303/t log 3

And half life period you can studied earlier.

7.4.4 Determination of order of reaction

(i) Integration method (Substitution in the equation)

This method consists in actually carrying out the change with known quantities of the reactants and nothing the progress of the reaction by analyzing the reaction mixture from time to time. These values are substituted in the velocity constant equation. When the values are substituted in the expression for first order that is values of a, x and t are substituted and value of k always remains constant the reaction is of first order.

Example: A solution of H_2O_2 when titrated against $KMnO_4$ solution at different time intervals gave the following results.

Time (minutes)	0	10	20
Volume of $KMnO_4$ Used for 10 ml of H_2SO_4	23.8 me	14.7	me 9.1 ml

Show that the reaction if of first order

The integrated rate equation for first order reaction is

k= 2.303/t log a/a-x

Since volume of $KMnO_4$ used in the titration is a measure of concentration of H_2O_2 in solution.

a= 23.8
a-x = 14.7 in 10 minutes
a-x = 9.1 in 20 minutes

Substituting these values in the rate equation above we have

k = 2.303/10 log 23.8/14.7
= 0.2303 (log 23.8-log 14.7)
= 0.2303 (1.3766- 1.1673)
= 0.04794………………………..……….(1)
k = 2.303/20 log 23.8/9.1
= 0.10165 (log 23.8 – log 9.1)
= 0.10165 (1.3766 – 0.9595)
= 0.04806 ……………………………………(2)

Since the value of k is almost constant hence reaction is of first order.

7.4.5 Hydrolysis of ester catalysed by hydrogen ion

The hydrolysis of ester like methyl acetate catalysed by hydrogen ion proceeds according to the following equation. It is catalysed by mineral acids say HCl. The hydrolysis of an ester by pure water is very slow; hence it is catalysed by an acid.

$$CH_3COOCH_3+H_2O \quad H^+ \longrightarrow CH_3COO + CH_3OH$$

This equation is pseudo-unimolecular. Since active mass of water being in large excess remains constant and rate of reaction depends only on the concentration of ester. It's molecularity is two and the reaction is of first order.

To study this reaction freshly distilled methyl acetate and N/2 hydrochloric acid in separate bottles were kept in a thermostat for half an hour. When they had acquired the temperature of the bath, mix 5 ml of methyl acetate in 100 ml of N/2 HCl. Immediately withdraw 5 ml of the reaction mixture with the help of the pipette and add a few pieces of ice to freeze the equilibrium. Now titrate the solution by adding N/50 solution of NaOH from the burette using phenolphthalein as an indicator. Similarly again pipette out 5 ml of reaction mixture after five minutes and repeat the above procedure. Repeat the process after 10, 20, 30, 40 minutes and finally at the end of 24 hours. As after 24 hours the reaction is almost completed.

The amount of NaOH used is equivalent to the amount of HCl present originally and the amountof acetic acid produced in the reaction. The amount of HCl present originally can be determined by titrating against the same alkali before the start of the reaction. The amount of acetic acid produced after different intervals of time t can be determined.

The amount of acetic acid formed at the end of the reaction is equivalent to the initial amount (a) of methyl acetate. Suppose V_o, V_1 and V_∞ are the volume of N/50 NaOH solution used at zero, t and infinite time respectively.

The amount of acetic acid produced after time t i.e. value of x proportional to $(V_t - V_0)$. The initial concentration of methyl acetate i.e. value of a is proportional to $(V_\infty - V_0)$.

Therefore, amount of ester present at time t i.e.

$$a-x \quad \text{ά} \; (V_\infty - V_0) - (V_t - V_0)$$

$$\text{ά} \; V_\infty - V_t$$

Hence from first order rate expression

$$K = 2.303/t \log (V_\infty - V_0/V_\infty - V_t)$$

The value of k comes out to be constant, showing that the reaction is first order. Inversion of cane sugar into glucose and fructose is also first order reaction, here again water is in large excess and its active mass practically remain constant.

7.5 RATE OF RADIOACTIVE DISINTEGRATION

The rate of disintegration of a radioactive element is found to be independent of the temperature, pressure or its state of chemical combination. Each element disintegrates at a characteristic rate independent of all external factors. Nuclear reactions are generally first order.

Since in a radioactive transformation an atom breaks down to give one or more new atoms, it may be regarded as a chemical reaction in which one molecule changes to yield one or more products (unimolecular reaction). Let us consider an atom A changing into B.

$$A \longrightarrow B$$

a	0	initially
a-x	x	after time t

if in a small time dt, dx is the number of atoms which change, the rate of disintegration dx/dt can be expressed as:

$dx/dt = k\,(a-x)$………………….(1)

Where k is ordinarily called velocity constant and here it may well be named as disintegration constant or transformation constant.

From equation (1) it follows

$dx/a-x = kdt$ …………………..(2)

if $dt = 1$ then $dx/a-x = k$ ………(3)

Thus the disintegration constant k may be defined as the fraction of total number of atoms dx/a-x present at any time (t) which disintegrate per second. This disintegration constant k has a definite characteristic value for a particular radioactive element.

On integrating the equation (2) we have get

$\int dx/a-x = k \int dt$

$-\log_e(a-x) = kt + I$ I= integration constant (5)

When $t=0$ $x=0$

$-\log_e a = I$ (6)

Hence $\log_e a - \log_e (a-x) = kt$

$k = 1/t \log_e (a/a-x)$

$= 2.303/t \log_{10} a/(a-x)$ (7)

at half time i.e $t_{1/2} = T$ $x=a/2$

$T = 2.303/k \log a/a-a/2$

$= 2.303/k \log 2$

$= 0.693/k$ (8)

It is clear from the above that for a particular radioactive disintegration the value of $t_{1/2}$ is independent of amount of the substance present and depends only on k. the time $t_{1/2}$ required for the disappearance of one half of the original amount of the radioactive substance is called its half life period.

The statement that half life period of say radium is 1600 years means after 1600 years any given quantity of radium will disintegrate to half of it.

7.5.1 Average life

The reciprocal of the disintegration constant k gives the average life of the disintegrating atom.

Hence $\lambda = 1/k = T/0.693$

$= 1.44T$

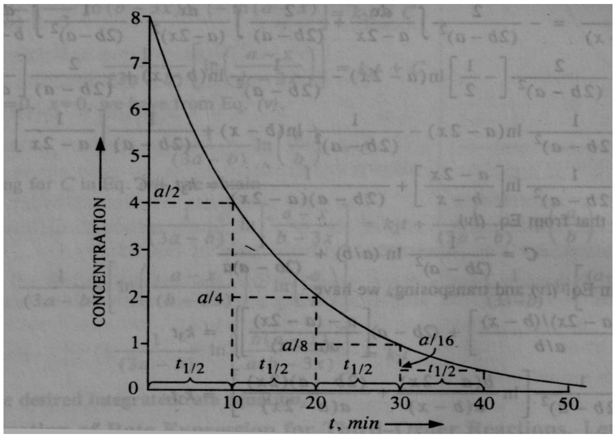


Fig-7.2

7.6 CONCEPT OF ACTIVATION ENERGY

7.6.1 Effect of temperature on reaction rate

Temperature coefficient of a reaction:

Now let us consider effect of temperature on reaction rates

It has been found that generally an increase of temperature increases the rate of reaction. The ratio of rate constants of a reaction at two temperatures differing by 10^0C is known as temperature coefficient of the reaction. The temperatures usually selected for this purpose are 25^0C and 35^0C. Thus

$$\text{Temperature coefficient} = \frac{\text{Rate at } 35^0\text{C}}{\text{Rate at } 25^0\text{C}} = \frac{k_{35}}{k_{25}}$$

The value of temperature coefficient for most of the reactants is close to 2 and in some cases it approaches to 3.

$$\text{Hence temperature coefficient} = \frac{\text{Rate at } \quad 35^0\text{C}}{\text{Rate at } \quad 25^0\text{C}} = \frac{k_{35}}{k_{25}} = 2 \text{ to } 3$$

7.7 COLLISION THEORY OF REACTION RATE

Now let us study why such small rise of temperature speeds up a reaction to such a large extent. This can be explained on the basis of collision theory.

According to collision theory for chemical reaction to occur, there must be collisions between reacting molecules. But all collisions are not effective. Only a small fraction of collisions produce a reaction. Two main conditions for a collision between the reacting molecules to be productive are-

(i) The colliding molecules must possess sufficient kinetic energy to cause a reaction.

(ii) The reacting molecules must collide will proper orientation.

The molecules must collide with sufficient energy:

Let us consider a reaction

$$A\text{-}B + B\text{-}B \longrightarrow 2\ A\text{-}B$$

A chemical reaction occurs by breaking bonds between the atoms of reacting molecules and forming new bonds in the product molecules. For ***breaking the bonds energy is required and in forming the bonds energy is liberated.*** The energy for breaking the bonds comes from the kinetic energy possessed by the reacting molecules, before the collision.

The (figure 7.3) shows the energy of molecules A_2 and B_2 as the reaction

A_2+B_2 $\longrightarrow$ 2AB progresses.

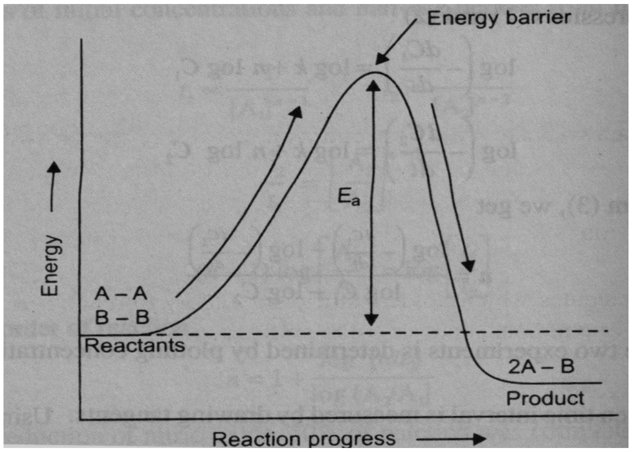
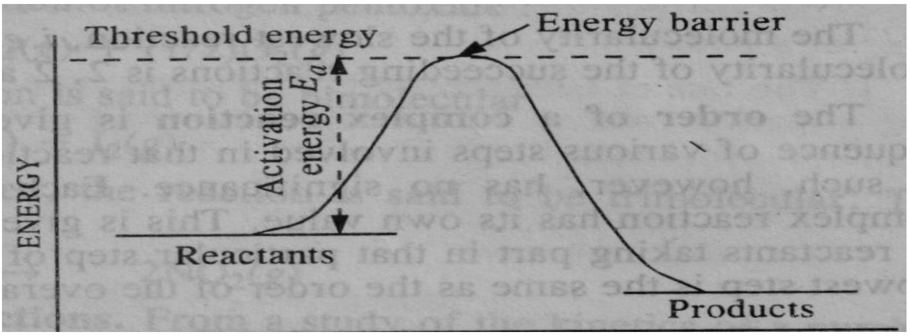


Fig 7.3

The figure 7.3 also shows the activation energy E_a, that is minimum energy required to cause a reaction between the colliding molecules. Only the molecules that collide will a kinetic energy greater than E_a are able to get over the barrier and react. The molecules colliding will kinetic energies less than E_a fail to cross the barrier.

As you have studied till now that for a reaction to occur there must be collision between molecules. And most of the collisions are ineffective. According to collision theory those collision results in chemical reaction in which the colliding molecules are associated with a certain minimum energy called threshold energy



Reaction progress $\longrightarrow$

Fig- 7.4

Hence there is certain minimum energy called threshold energy which the colliding molecules must acquire before they are capable of reacting. Most of the molecules have much less kinetic energy than the threshold energy. The excess energy that the reactant molecules having energy less than the threshold energy must acquire in order to react to yield products is known as activation energy.

That means

Activation energy = threshold energy – energy possessed by the molecules.

Now you must have followed from the above discussion that there is energy barrier placed between reactants and products (fig 7.4) The barrier has to be crossed before reactants can yield product.

7.8 EFFECT OF CATALYST

As you have studied earlier a catalyst is a substance that can increase the rate of a reaction but which itself remains unchanged in amount and chemical composition at the end of the reaction. When a catalyst is added, a new reaction path with a lower energy barrier is provided (dotted curve in the fig 7.5). Since the energy barrier is reduced in magnitude, a larger number of molecules of the reactants can get over it. This increases the rate of the reaction.

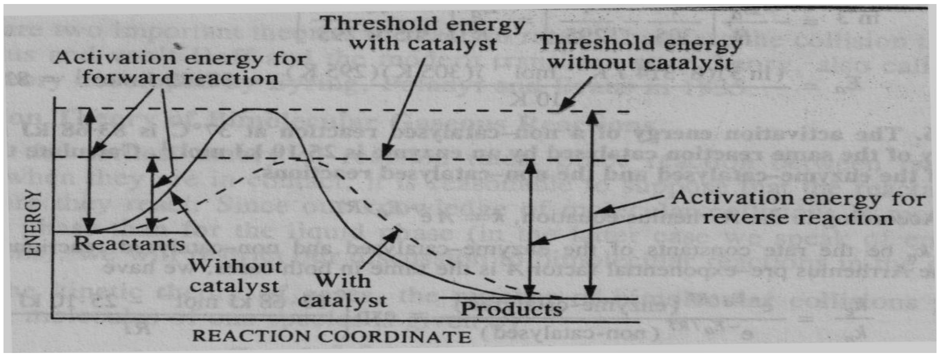


Fig- 7.5

7.9 ARRHENIUS EQUATION

For the effect of temperature Arrhenius proposed and empirical equation which is useful in calculating energy of activation of a reaction

$k = Ae^{-Ea/RT}$ ……………………….(9)

Where E_a is called Arrhenius activation energy at temperature T, k is rate constant and A is called the Arrhenius pre exponential factor, a has the same units as the rate constant k. the units of k for a first order reaction are S^{-1} which is units of frequency. Hence A is also called the frequency factor, Ea and A are called Arrhenius parameters.

Taking logs of equation (9) we have

$\ln k = \ln A - E_a/RT$ ……………….(10)

A plot of lnk against reciprocal of absolute temperature (1/T) gives a straight line with slope = $-E_a/R$ and intercept = lnA, and hence energy of activation E_a be obtained.

Differentiating equation (10) with respect to temperature, we get

$d\ln k/dT = E_a/RT^2$ …………………(11)

Integrating equation (11) between temperature T_1 and T_2 when the corresponding rate constants are k_1 and k_2 respectively assuming that Ea is constant over the entire range we get-

$\ln k_2/k_1 = E_a/R[T_2-T_1/T_1\ T_2]$ ………………(12)

or $\log_{10} k_2/k_1 = E_a/2.303R\ \ [T_2-T_1/T_1\ T_2]$

This is the integrated Arrhenius equation. Thus knowing the rate constants at two temperature the energy of activation Ea can be calculated.

It must be clear to you that different reactions require different amount of energy activation energy. A reaction which has lower activation energy will proceed at a faster rate at a given temperature. A reaction which has higher activation energy will proceed at a slower rate.

The differences in activation energy are mainly responsible for observed difference in rate of reaction.

If the reactants posses higher total energy than the products there will be a release of energy. The reaction is said to be exothermic reaction. If the reactants possess lower total energy than the products energy will be absorbed and the reaction is said to be endothermic.

7.10 SUMMARY

From the above discussion it is clear that chemical kinetics is an important branch of chemistry. The study of a chemical reaction is of fundamental concern to a chemist from two aspects first his interest is to ascertain how fast or slow a reaction proceeds secondly one is interested to study the feasibility of a reaction between substances. And to what extent will it yield the desired products. The speed of a reaction has been studied in this unit.

Different chemical reactions and their mechanism has been studied. It is an important aspect that how chemical reaction takes place and what is the effect of temperature and other factors. The energy of activation concept is useful in the study of reactions. The activation energy depends upon the nature of the chemical bonds undergoing rupture. It is independent of initial and final energy contents of the reacting particles. The feasibility of a reaction is studied under ‘thermodynamics’.

The study of the subject has been highly useful in determining the factors which influence rates of reactions as well as in understanding mechanism of a number of chemical reactions.

The studies have also been useful in working out in conditions for getting maximum yields of several industrial products.

7.11 TERMINAL QUESTIONS

(A) Solved questions:

Q.1 The rate constant of a first order reaction is $1.54 \times 10^{-3}\ s^{-1}$
Calculate its half life time.

$t_{½} = 0.693/k_1$

$= 0.693/(1.54 \times 10^{-3}\ s^{-1})$
$= 450\ s$

Q.2 The half life of a reaction A $\longrightarrow$ B+C which obey's first order kineties, is 8:0 minutes. How long it will take for the concentration of A to reduced to 1% of it initial value

$k_1 = 0.693/t_{1/2}$

$= 0.693/8.0m$

$= 0.087 min^{-1}$

Now $k_1 = 2.303/t \log (a/a-x)$

$t = 2.303/0.087 \log(100/1)$

$= 52.93m$

Q.3 50% 0f a first order reaction is complete in 23 minutes.
Calculate the time required to complete 90% of the reaction.
$t_{1/2} = 0.693/k$
$k = 0.693/23\ m$
$= 0.03013\ m^{-1}$
For 90% completion time required can be calculated as follows:
$0.03010 = 2.303/t \log(100/10)$
As a-x= 100-90 =10
$t = 2.303/0.0310\ \log 10$
$= 76.4$ min.

(B) Short answer questions:

Q1. What do you understand by energy of activation?

Q.2 What is temperature co-efficient of a reactions?

Q.3 What is interpretation of A in Arrhenius equation?

Q.4 Write Arrhenius equation.

Q.5 If the concentrations are measured in mole per liter, time in seconds, what are the units of rate constant for :

(i) A zero order reaction.

(ii) A first order reaction.

(C) Long answer/essay type questions:

Q.1 Integrate the rate expression for a first order reaction. What is meant by half life time of a reaction?

Q.2 What is meant by reaction being of first order, second order or zero order? What are pseudo-unimolicular reactions?

Q.3 Bring out clearly the main features of the collision theory of reaction rate? What do you mean by effective collisions?

Q.4 (a) Define chemical kinetics? Describe what is meant by order of a reaction.

(b) Describe a suitable method to study the kinetics of the following reaction

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+ \text{ ions}} CH_3COOH + C_2H_5OH$$

(D) Multiple choice questions

Q.1 For a zero order reaction A $\longrightarrow$ Products $t_{1/2}$ is proportional to

(a) [A] (b) 1/[A] (c) $[A_0]^2$ (d) $1/[A_0]^2$ ans (a)

Q.2 The $t_{1/2}$ of a reaction is doubled as the initial concentration is doubled. The order of reaction is

(a) 1 (b) 0 (c) 2 (d) 1/(1/2) ans (b)

Q.3 In how many years will a 100 mg sample of ^{14}C($t_{1/2}$= 5760 years) be reduced to 25 mg.

(a) 5760 (b) 17280 (c) 11520 (d) 23040 ans (c)

Q.4 The rate constant of a gaseous reaction is 2×10^{-2} $dm^3 mole^{-1} s^{-1}$. Its value in $cm^3 mole^{-1} s^{-1}$ is –

(a) 2 (b) 0.2 (c) 20 (d) 200 ans (c)

Q.5 For a first order reaction the time required to decompose 75% is related to $t_{1/2}$

(a) $t_{75\%}=t_{1/2}$ (b) $t_{75\%} = 3t_{1/2}$ (c) $t_{75\%} = 2t_{1/2}$ (d) $t_{75\%} = 7/2\ t_{1/2}$

ans (c)

Q.6 If $E_a>E_b$; where E_a and E_b are energies of activation for forward and backward reactions respectively, then:

(a) The reaction is endothermic (b) The reaction is exothermic
(c) The reaction is chain reaction (d) The reaction is explosive.

ans (b)

Q.7 for the reaction $2A+B \longrightarrow$ Products, doubling the initial concentration of both the reactants increases the rate by a factor of 8 and doubling the concentration of B alone doubles the rate. The rate law for the reaction is –

(a) $r=k[A][B]^2$ (b) $r= k[A]^2[B]$ (c) $r= k[A][B]$ (d)$r=k[A]^2[B]^2$

and (b)

Q. 8 for a first order reaction, $A \longrightarrow$ Products, $t_{1/2}$ =100s . the rate constant for the reaction is –

(a) $6.93\text{x}10^{-2}\text{s}^{-1}$ (b) $6.93\text{x}10^{-4}\text{s}^{-1}$ (c) $6.93\text{x}10^{-3}\text{s}^{-1}$ (d) $6.93\text{x}10^{-4}\text{s}$

ans (c)

UNIT 8: COLLOIDS AND MACROMOLECULES

CONTENTS:

8.21 Terminal Questions

8.1 OBJECTIVES

Matter exists in three states. These three states are solid, liquid and gaseous state. A gas consists of molecules separated wide apart in empty state. A liquid state molecule touching each other.

Solids are characterised by incompressibility, rigidity and mechanical strength. In solid state molecules, atoms or ions that make up the solid are closely packed. They are held together by strong cohesive forces and cannot move at random.

Some substance such as suger, salts, acids and bases when dissolved in water can pass through parchment membrane and form true solutions. Whereas substances such as gelatin, albumen, glue diffuse at a slow rate. These are called colloids.

The colloidal solutions are intermediate between true solutions and suspensions.

8.2 INTRODUCTION

During his research work Thomas Graham in 1861 found that while some substances diffused readily through parchment membrane, others diffuse at slow rate. The substance which diffuse at slow rate were given the name colloids (from Greek Kolla means glue like). These observations led to the development of a new branch of knowledge known as colloidal science.

Latter many investigators including Thomas Graham realised that distinction between crystalloids and colloids was not rigid, since many crystalline substances like sulphur, carbon and salt can be converted into colloidal form by suitable means. At the same time the so called colloidal like gum and gelatin, were shown to have a crystalline structure by X-ray examination. In fact, it is now well known that one and the same substance may show colloidal behaviour at one time and crystalloidal behaviour at another time depending upon the prevailing conditions for example, sodium salt of long chain fatty acids (the soaps) show colloidal character in water in which they are sparingly soluble but crystalloidal character in alcohol in which they are freely soluble. The term ‘colloidal substances’ has, therefore been discarded in favour of ‘colloidal state’ into which almost every substances can be brought by suitable means.

Hence colloidal solutions or colloidal dispersions are intermediate between true solutions and suspensions.

8.3 COLLOIDAL SYSTEMS

When the diameter of the particles of substance dispersed in a solvent ranges from about $10A^0$ to $2000A^0$, the system is said a colloidal solution, colloidal dispersion or simply a colloid, the material will particle size in the colloidal range is said to be in the colloidal state. A colloidal system is thus a two phase system consisting of a continuous phase or dispersion medium in which extremely minute particles, lying within the colloidal range of second substance termed as discontinuous phase or dispersed phase, are suspended.

Difference between suspensions, colloidal solutions and true solution

Property	Suspensions	Colloidal solutions	True solution
1.Nature	Hetrogeneous	Heterogeneous	Homogeneous
2. Size range	Greater than 2000A^0 or 200 mμ	Between 10A^0 to 2000 a^0 or 1 mμ to 200 mμ	Less than 10a^0 or 1 mμ
3. Visibility	Particles are visible under microscope even with a naked eye	Particles are visible under ultramicroscope	Particles are not visible even under ultramicroscope
4. Diffusibiltiy	Do not diffuse	Diffuse slowly	Diffuse rapidly
5. Tyndall effect and Brownian movement	Do not exhibit	Exhibit	Do not exhibit
6. Molecular weight	Low	High	Low

Table -1

8.3.1 Types of Colloidal Systems

As we have seen in the above article, a colloidal system is made of two phases, the substance distributed as the colloidal particle is called the dispersed phase, the second continuous phase in which the colloidal particles are dispersed is called the dispersion medium. If we take colloidal solution of copper in water, copper particles constitute the dispersed phase and water dispersion medium (fig 8.1).

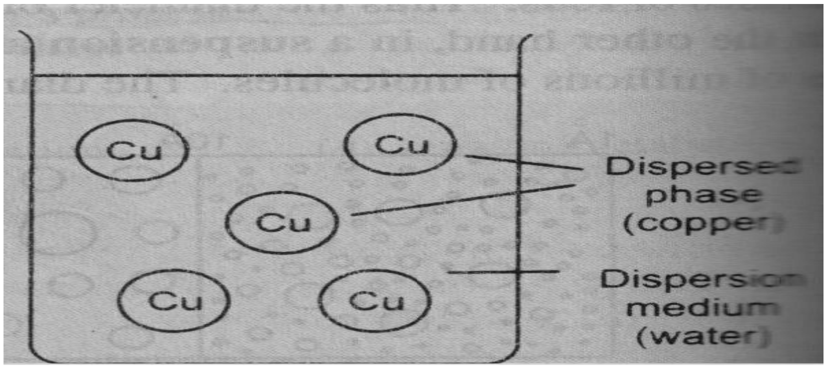


Fig 8.1

Now we see that either the dispersed phase or the dispersion medium can be gas liquid or solid, these are eight types of colloidal system possible.

A colloidal dispersion of one gas in another is not possible, since the two gases would give a homogeneous molecular mixture.

The various types of colloidal systems are given in table 2.

Dispersion medium	Name of the dispersion phase	Name of the colloidal system	Examples
1. Gas	Liquid	Liquid aerosol	Clouds, mist, fog
2. Gas	Solid	Aerosol	Smoke, dust
3. Liquid	Gas	Foam	Shaving cream, foam
4. Liquid	Liquid	Emulsions	Milk, hair cream, cod-lever oil
5. Liquid	Solid	Colloidal solutions	Colloidal gold
6. Solid	Gas	Solid foam	Foam rubber, occluded gases
7. Solid	Liquid	Gel or jelly	Butter, cheese, gels
8. Solid	Solid	Solid sol	Alloys, ruby glass (gold dispersed in glass)

Table-2

8.3.2 Classification of Colloids

Substance like metal, metal sulphides cannot be brought into the colloidal state simply by bringing them in contact with solvent, these are known as lyophobic colloids (or hydrophobic colloid if water is solvent).

Substances like proteins, starch and rubber whose molecules are large enough to be close to the lower limit of colloidal range, pass readily into colloidal state when mixed with a suitable solvent are called lyophilic colloids (or hydrophilic colloids if water is solvent).

8.3.3 Distinction between Lyophilic and Lyophobic Colloids

Property	Lyophobic sols	Lyophilic sols
Preparation	Formed by special method	Formed easily
Nature	Particles are true molecules	Particle consists of aggregate molecules
Viscosity	Viscosity is almost the same as that of the medium	Viscosity is much higher than that of the medium
Visibility	Particle can be readily detected under ultra	Particles cannot be readily detected even under

	microscope	ultramicroscope
Tyndall effect	More distinct	Less distinct
Reversibility	Lyophobic salts are irreversible	These are reversible
Surface tension	Surface tension is usually the same at that of the medium	Surface tension is generally lower than that of the medium
Migration in electric field	Particles migrate to anode or cathode	Medium particles migrate to anode or cathode, or not at all

Table -3

8.4 PREPARATION OF COLLOIDAL PARTICLES

The primary consideration in the preparation in the colloidal solution is that the dispersed particle should be $10A^0$ to $2000\ A^0$ (1 m μ to 200 mμ) the lyophilic sols can readily prepared since colloidal materials such as starch, gelatin when added to water swell up and spontaneously break into particulates of matter of colloidal range.

Lyophobic sols cannot be prepared by simple contact or slight shaking of the substance with the solvent. Svedberg (1908-1912) suggested that there are two ways for obtaining lyophobic sols.

(i) Dispersion methods

In these methods, larger lumps of the insoluble substance are pulverized by mechanical or by other means till particles of colloidal dimensions are obtained.

(ii) Condensation methods:

In these methods, a molecular on ionic distribution is first prepared then by suitable coarsening gives rise to particles of colloidal dimensions.

Dispersion methods

(i) Mechanical dispersion:

The most obvious method of dispersion consists in breaking down the courser solid particles by one chemical grinding. This is done in the so called ‘colloidal mill’ which generally consists of two metal discs held at a very small distance apart from one another which are capable of revolving at very high speed in opposite direction. The solid particles are ground down to colloidal size and are then dispersed in the liquid to give the sol.

(ii) Bredig’s are method (1898)

This method is used for preparing hydrosols of metals like gold, silver and platinum. This method consists in striking an arc between two electrodes of the metal immersed in water as shown in (fig-8.2.)

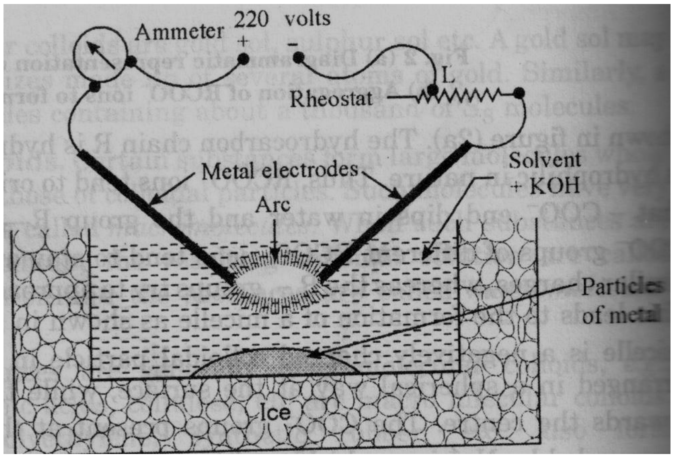


Fig-8.2

A current of one ampere and voltage of 100 volts is used. The vessel in which water is kept is surrounded by ice. On striking an arc, the vapours of metal are formed which then immediately condense to form particles of colloidal size. Sometimes it is necessary to add traces of electrolyte, say alkali hydroxide is added in water, to obtain best results.

Svedberg devised a method to obtain organo sols of metal and nonmetals. In this method electrodes are usually of iron or aluminium and an alternating current is employed. The material to be dispersed in taken in the form of granules and pasted on the electrodes (immersed in the organic medium) through which the electric current is passed.

Alternative current is used which greatly diminishes the decomposition of the liquid. Practically any metal can be obtained in the colloidal state in a liquid with which it does not react chemically.

Peptization

Peptization is a process by means of which a suitable colloidal solution can be produced from suitable substances originally present in massive forms, when the particle of colloidal size pre-exist in the substance to be dispersed.

The dispersal of a precipitated material into colloidal solution by the action of an electrolyte in solution is termed as peptization. The electrolyte used is known as peptizing agent. An electrolyte having an ion in common with the material to be dispersed is required for sol formation.

Peptization action is due to the preferential adsorption of one of the ions of the electrolyte by particles of the material. As a result of the preferential adsorption of the ion which is more closely related chemically to the precipitate, the particles acquire positive or negative charge depending upon the change on the ion adsorbed.

Because of the presence of the same type of charge, the particles of the precipitate are pushed apart. The precipitate thus gets dispersed resulting in the formation of stable sol.

Thus you can see ferric hydroxide sol is obtained when a small quantity of ferric chloride solution is added. The peptization action is due to the preferential adsorption of F_e^{3+} ion. Similary silver chloride can be converted into a sol by adding hydrochloric acid (Cl^- being common ion).

8.5 CONDENSATION METHODS

Colloidal system can be obtained by various reactions such as double decomposition, oxidation, reduction, hydrolysis etc. the conditions (temperature concentration etc.) used are such as permit the formation of sol particles but prevent the particles becoming too large and forming precipitate the unwanted ions present in the sol are removed by dialysis as these ions may eventually coagulate the sol.There are four condensation methods:-

8.5.1 (i) Double decomposition- An arsenic sulphide sol is prepared by passing a slow stream of H_2S gas through a dilute solution of arsenious oxide. This is continued till the yellow colour of the sol attains maximum intensity. Excess H_2S is removed either by passing in a stream of hydrogen or by boiling.

(ii) Reduction:

Sols of metals such as copper, silver, gold and platinum are obtained by reducing the aqueous solutions of their salts by non-electrolytes such as formaldehyde, tannin, phenyl hydrazine. carbon mono oxide and phosphorus.

Thus

$$AgNO_3\text{+tannic acid} \longrightarrow \text{Ag sol}$$

$$Aucl_3\text{+tannic acid} \longrightarrow \text{Au sol}$$

(iii) Oxidation:

A sol of sulphur can be obtained by passing hydrogen sulphide into a solution of sulpher dioxide.

$$2H_2S+SO_2 \longrightarrow 2H_2O+S\downarrow$$

(iv) Hydrolysis:

Colloidal sols of heavy metals are obtained by the hydrolysis of the solutions of their salts.

Thus when a small amount of ferric chloride is added to boiling water, a red-brown sol of ferric hydroxide obtained.

$$FeCl_3+3H_2O \longrightarrow Fe(OH)_3+3HCl.$$

8.6 PURIFICATION OF SOLS

The presence of impurities, particularly the electrolytes, renders the sols unstable. We will discuss the cause of instability latter on. These impurities must be eliminated by suitable means. The purification of sols can be accomplished by following methods.

(i) Dialysis

The purification of colloidal solution by dialysis is based on the inability of the sol particles to pass through an animal membrane or a parchment paper which allows only the molecules or ions to pass through. The vessel in which dialysis is carried out is known as a dialyser.

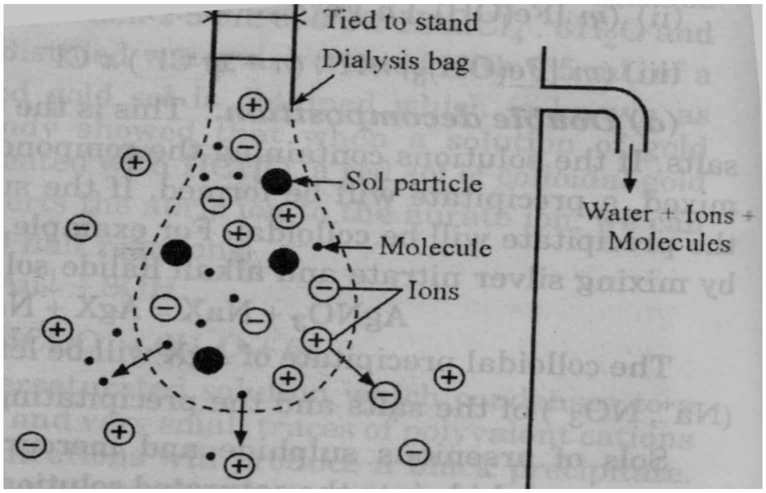


Fig-8.3

The animal membranes have very fine pours. These pores permit ions or small molecules to pass through but not the large colloidal particles when a sol containing dissolved ions (electrolyte) or molecules is placed in a bag of permeable membrane dipping in pure water, the ions diffuse through the membrane. By using continuous flow of fresh water, the concentration of electrolyte outside the membrane tends to zero. Thus diffusion of the ions into pure water remains brisk all the time and practically all the electrolyte present in the sol can be removed easily.

Ordinarily, the process of dialysis is quite slow, but it can be quickened by applying an electric field if the solution in true solution is an electrolyte. The process is then called electrodialysis.

(ii) Ultrafiltration

Ultrafiltration is a process of separating colloidal particles from the solvent and the solutes present by specially prepared filters which allows all other particles except the colloidal particles to pass through it.

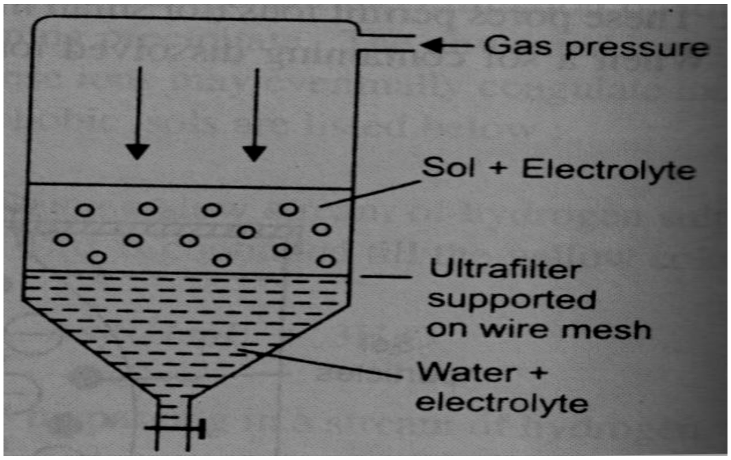


Fig-8.4

Ordinary filter papers have pours larger than 1000 mμ, so that the colloidal particles having a smaller size can easily pass through them. But if the pour's are made smaller, then the colloidal particles may be retained on the filter paper.

Ultrafiltration is a method not only for purification of the sol but also for concentrating the sol.

8.7 GENERAL PROPERTIES OF COLLOIDAL SYSTEMS

8.7.1 Heterogeneous character

As you have seen from the above discussion every colloidal system is a heterogeneous system. It consists of two phases, the dispersed phase and dispersion medium.

8.7.2 Visibility

Most of the sols appear to be true solutions with naked eye, but the colloidal particles can be seen through an ultramicroscope.

8.7.3 Colligative properties

The property which depends on the number of particles in solution and not in any way on the size or chemical nature of the particles, is known as a colligative property.

As you know that colloidal particles are aggregate of molecules, therefore all the colligative properties would be reduced. Hence colloidal systems have very low osmotic pressure, and freeze and boil at about the same temperature as the pure dispersion medium.

8.7.4 Diffusibility

The colloidal particles do not readily diffuse through a parchment paper or any other membrane.

8.8 COLOUR OF THE SOLS

The colour of the hydrophobic sol depends on the wavelength of the light scattered by the dispersed particles. The wavelength of the scattered light again depends on the size and nature of the particle. This will be clear to you with following example:

Colour of Ag sol	**Particle diameter**
Orange yellow	$6x10^{-5}$ nm
Orange red	$9x10^{-5}$ nm
Purple	$13x10^{-5}$ nm
Violet	$15x10^{-5}$ nm

This can be seen in other cases also.

8.9 OPTICAL PROPERTIES

8.9.1 Tyndall effect

In 1867 Tyndall found that when a beam of light is passed through a true solution, it cannot be seen unless the eye is placed directly in the path. But when the same light beam is passed through a colloidal dispersion it is

visible as a bright beam. The phenomenon of the scattering of light by the sol particles is called Tyndall effect. The illumination of beam or cone formed by the scattering of light by the sol particles if often called as Tyndall beam or Tyndall cone.

This phenomenon is due to the scattering of light from the surface of colloidal particles. In true solutions the particle size is very small to scatter the light and hence the beam is invisible.

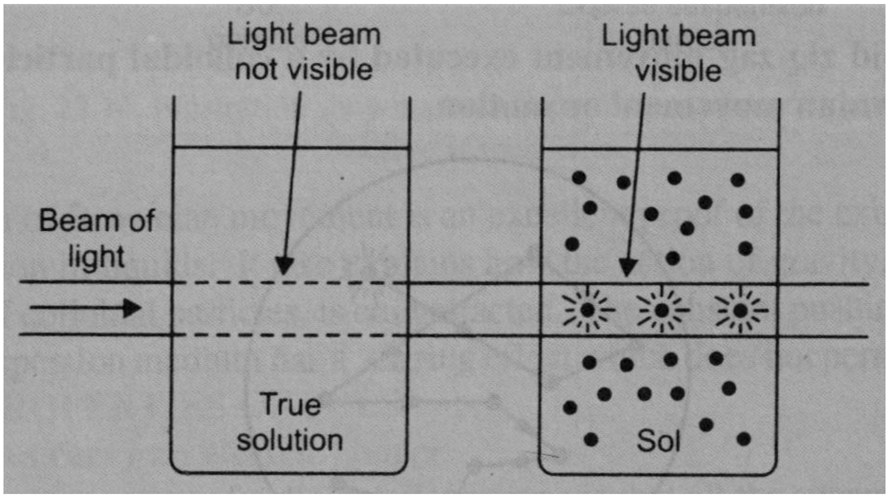


Fig-8.5

The intensity of the scattered light depends on the difference between the refractive indices of the dispersed phase and dispersion medium. In lyophobic sols, the difference is appreciable and hence the Tyndall effect is quite well-defined. In lyophilic sols the difference is small hence the Tyndall effect is much weaker.

Sol particles cannot be seen with microscope. Zsigmondy (1903) used the Tyndall phenomenon to set up an apparatus called ultramicroscope. The intense beam of light is focused on a sol contained in a glass vessel. The focus of light is then observed with a microscope at right angle to the beam individual sol particles appear as bright specks of light against a dark background. It may be noted that under the ultra microscope, the actual particles are not visible. It is the larger halos of scattered light around the particles that are visible. Thus the ultra microscope does not give any information regarding the shape and size of sol particles.

8.9.2 Kinetic properties of sols

Robert Brown an English botanist in 1827, observed that pollen grains in aqueous suspensions were in constant motion. Later when ultramicroscope was invented, it was found that particles of lyophobic sols were also in a state of ceaseless random motion similar to pollen grains. This

Kinetic activity of particles suspended in a liquid is called Brownian movement.

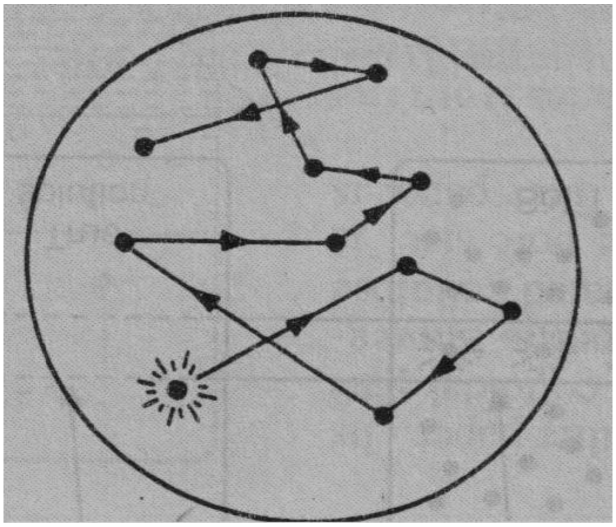


Fig-8.6 Brownian movement

The Brownian movement is independent of the nature of the colloidal particles, but was more rapid the smaller the particles and less viscous the solution. The Brownian movement is due to the bombardment of colloidal particles by molecules of dispersion medium which are in constant motion like molecules in a gas**.(fig 8.6).**

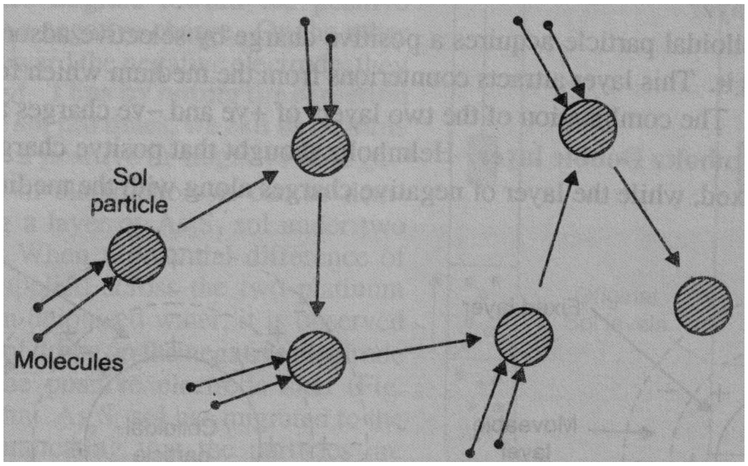


Fig- 8.7

As a result of bombardment the colloidal particle acquire almost the same amount of kinetic energy as possessed by the molecules of dispersion medium. But since the colloidal particles are considerably heavier than molecules of the dispersion medium, their movement is considerably slower than that of the molecules of the medium**. (fig 8.7).**

8.9.3 Charge on colloidal particles

The most important property of colloidal dispersions is that all the suspended particles posses either positive or negative charge. The mutual forces of repulsion between similarly charged particles prevent them from aggregating and settling under the action of gravity. This gives stability to the sol.

The origin of charge on colloidal particles:

It has been observed that sols are invariably associated will minute quantities of electrolytes and that if the latter are completely removed by persistent dialysis, the sols become unstable. It is believed therefore that charge on colloidal particles is due to preferential adsorption of either positive or negative ion on their surface.

Ferric hydroxide sol particles are positively charges because these absorbs Fe^{3+} ions from ferric chloride ($FeCl_3$) used in the preparation of the sol. Since the sol as a whole is neutral, the charge on the particle is counterbalanced by oppositely charged ions termed counterions (in this case Cl^-) furnished by the electrolyte in medium.

The negative charge on arsenic sulphide sol is due to preferential adsorption of sulphide ions on the surface of arsenic sulphide particle. Sulphide ions are furnished by ionization of hydrogen sulphide which is present in traces. Thus, in ferric hydroxide sol, ferric not chloride ions are preferred. Similarly, in arsenic sulphide sol, a sulphide ion not hydrogen ion is preferred.

8.10 ELECTRICAL DOUBLE LAYER

The surface of colloidal particle acquires a positive charge by selective adsorption of a layer of positive ions around it. This layer attracts counterions from the medium which forms a second layer of negative charges. The combination of two layers of positive and negative charges around the sol particles was called Helmholtz Double Layer**. (fig 8.8).**

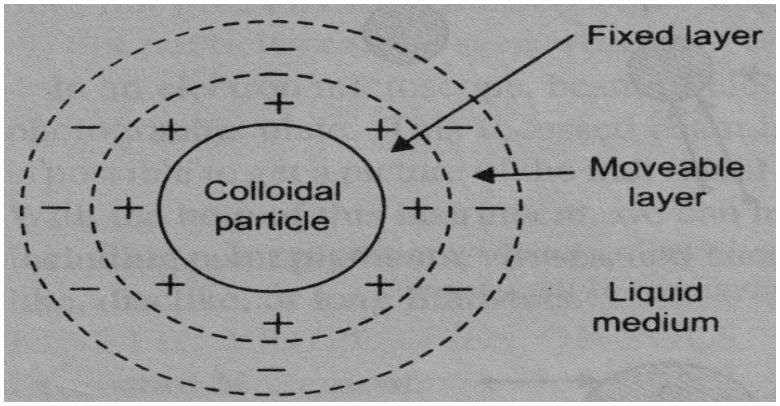


Fig-8.8

Helmholtz thought that positive charges next to the particle surface were fixed, while the layer of negative charge along with the medium were mobile. More recent considerations have shown that the double layer is made of:

(a) Compact layer of positive and negative charges which are fixed firmly on the particle surface.

(b) Diffuse layer of counter ions (negative ions) diffuse into the medium containing positive ions.

The combination of compact and diffuse layer is referred to as the Stern double layer. The diffuse layer is only loosely attached to the particle surface and moves in the opposite direction under the applied electric field. Because of the distribution of charge around the particle, there is a difference of potential between the compact layer and the bulk of solution across the diffuse layer. This is called Electro kinetic or Zeta potential.

8.11 COAGULATION

As you have already studied that stability of colloidal particle is due to the adsorption of positive or negative ion by the dispersed particles. The repulsive forces between the charged particles do not allow them to settle. If somehow, the charge is removed, there is nothing to keep the particles apart from each other. They aggregate and settle down under the action of gravity. This phenomenon of changing colloidal state to the suspended state is known as coagulation, floculation or precipitation of colloidal solution.

In case of lyophobic colloids the stability is due the electrical charge present on the colloidal particles whereas the stability of lyophilic colloid depends upon both the electrical charge and solvation. In order to cause precipitation of the dispersed particles, it is necessary that they come closer to one another and form bigger aggregates which lie outside the colloidal range.

The coagulation or precipitation of a given sol can be brought about in four ways:

(i) By addition of electrolytes
(ii) By electropholysis
(iii) By mixing oppositely charged sols
(iv) By boiling

(i) By addition of electrolytes:

When excess of an electrolyte is added to a sol the dispersed particles are precipitated. The electrolyte furnishes both positive and negative ions in the medium. The sols particles adsorb the oppositely charged ions and get discharged. The electrically neutral particles then aggregate and settle down as precipitate.

A negative ion causes the precipitation of a positively charged sol and vice versa. The effectiveness of an anion or cation to precipitate a sol will naturally depend on the magnitude of the charge or the valence of the effective ion.

From a study of the precipitating action of various electrolytes on a particular sol, Hardly and Schulz gave the following rules.

(i) Coagulation is brought about ions having opposite charge to that of the sol. Hence negative ions cause coagulation of the positively charged sol and positive ion cause coagulation of negatively charged sol. Thus $Fe(OH)_3$ sol which is positively charged is coagulated by negative ions such as Cl^-, NO_3^-, SO_4^{2-} etc. Similarly As_2S_3 sol which is negatively charged is coagulated by positive ions such as Na^+, Ba^{2+}, Mg^{2+} etc.

(ii) The higher the valency of the ion greater is its coagulating power. Thus the power of Al^{3+}, Na^+, Ba^{2+} is in the order $Al^{3+} > Ba^{2+} > Na^+$

Similarly the precipitating power of $[Fe(CN)_6]^{3-}$,Cl^- and SO_4^{2-} is in the order $Fe(CN)_6^{3-} > SO_4^{2-} > Cl^-$

Quantitatively the efficacy varies directly as the square of the valence of the ion. Thus Mg^{2+} ion is 4 times more effective and Al^{3+} ion is 9 times more effective than Na^+ ion.

8.12 PROTECTION OF COLLOIDS

Lyophobic sols are easily precipitated by small amount of electrolyte. However these sols are often stabilized by the addition of lyophilic sols. When lyophobic and lyohilic sols are mixed and lyophilic sol is in excess then the resultant sols is avoided from being coagulated. The sol now is more stable to temperature changes and is not readily precipitated by electrolytes. The lyophilic colloids thus used for protecting the lyophobic colloids are known as protective colloids. Different protective colloids have different protective powers. Zsignondy investigated the protective action quantitatively and gave the concept of gold number.

8.12.1 Gold number

Gold number may be defined as 'the weight in milligrams of protective colloid which will just stop the coagulation of 10 ml of a gold sol on adding 1 ml of 10% solution of sodium chloride'. Gold sol is ruby red in color and becomes blue on coagulation.

Gold number of protective colloids

Sl No.	Colloid	Gold number
1.	Gelatin	0.005-0.01
2.	Casein	0.1
3.	Gum Arabic	0.15-0.25
4.	Dextrin	6-20
5.	Starch	25.0

Table-4

8.13 STABILITY OF SOLS

A true colloidal solution is stable. The stability of sols is mainly due to two factors:

8.13.1 (a) Presence of charge on colloidal particles

The dispersed particles of lyophobic sols possess a like electrical charge either positive or negative, on their surface. Since like charges repel one another, the particles push from one another and resist joining together.

However by the addition of electrolyte the lyohobic sol particles are discharged and precipitated.

(b) Presence of solvent layer around sol particle

The lyophilic sols are stable for two reasons. Their particles posses a charge and in addition have a layer of solvent bound on the surface. For example, a sol particle of gelatin has a negative charge and a water layer envelopes it. When sodium chloride is added to colloidal solution of gelatin, its particles are not precipitated. The water layer around the gelatin particle does not allow the Na^+ ions to penitrate it and discharge the particle. Thus gelatin sol is not precipitated the addition of sodium chloride solution.

Now it should be clear to you that why lyophilic sols are more stable than lyophobic sols. Generally lyohobic sols are coagulated by electrolytes at 0.001-0.1M concentrations. The coagulation is irreversible process and removal of coagulating electrolyte does not allow the coagulam to be redispersed.

Lyophilic sols on the other hand are not easily coagulated. They require much higher concentration of electrolyte **(usually of the order of 1M)** for precipitation. The coagulation of lyophilic sol by the addition of electrolytes is not due to neutralization of charge on the particle.The electrolyte binds part of the water thereby getting hydrated. As a result, the polymer molecules in the lyophilic sol get dehydrated. The dehydration leads to coagulation.

Various ions are arranged in increasing order of their efficacy for coagulating a lyophobic sol in the form of series as shown below:

$Mg^{2+} > Ca^{2+} > Ba^{2+} > Na^+ > K^+$

$SO_4^{2-} > Cl^- > NO_3^- > ClO_3^- > 1^-$

8.13.2 Electrophoresis:

Since the solid particles and the liquid medium carry opposite charges, it is obvious that when an electrical field is applied, the particles and the liquid will migrate is opposite direction. The movement of sol particles under an applied electric potential is called electrophoresis or cataphoresis.

If the sol particles migrate toward the positive electrode, they carry negative charge. On the other hand, if they move toward the negative electrode they are positively charged. Thus by noting the direction of movement of the sol particles, we can determine whether they carry positive or negative charge.

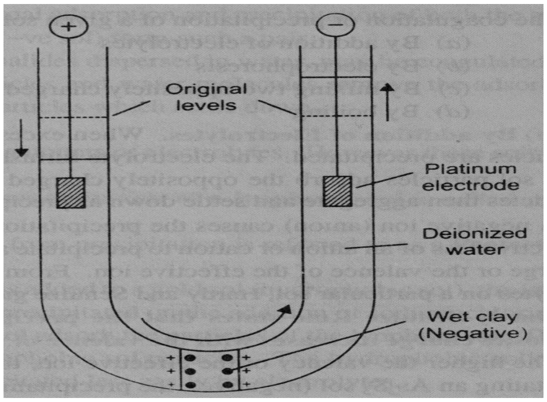


Fig-8.9

The phenomenon of electrolysis can be demonstrated by placing a layer of As_2S_3 sol under two limbs of a U-tube. When a potential difference of 100 volts is applied across the two platinum electrodes dipping in deionised water, it is observed that the level of the sol drops on the negative electrode side and rises on the positive electrode side (fig-8.9). This shows that As_2S_3 sol has migrated to the positive electrode, indicating that the particles are negatively charged. Similarly a sol of ferric hydroxide will move to the negative electrode showing that its particle carry positive charge.

Aplications of electrophoresis:

Some important applications of electrophoresis are: (1) Removal of smoke from chimney gases; (2) Removal of suspended impurities ; (3) Electroplating of rubber on metal surfaces from latex (a sol) ; (4) Painting of metal parts of cars from colloidal pigmants.

8.13.3 Electro-osmosis:

The movement of dispersion medium with respect to dispersed phase as a result of an electric field is known as electro-osmosis. Or when electrophoresis of dispersed particles in a colloidal system is prevented by suitable means, it is observed that the dispersion medium itself begins to move in an electric field. This phenomenon is called electro-osmosis.

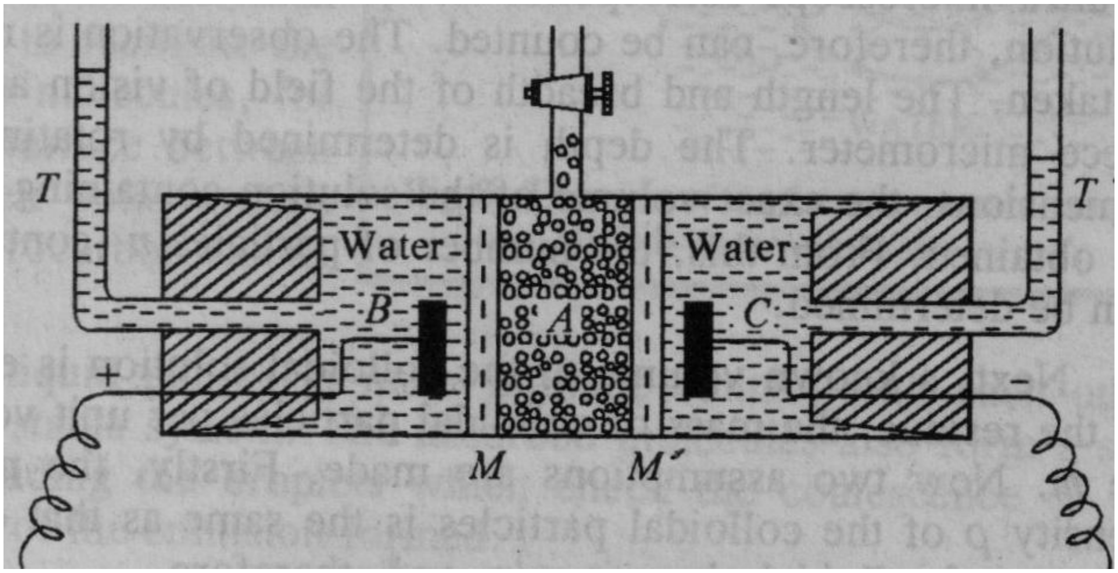


Fig-8.10

It can be observed as shown in **(fig 8.10)**

The colloidal system is put in a central chamber A which is separated from the side chambers B and C with water, by a dialysing membranes M and M^{-}. The water in the chamber B and C extends to the side tubes T and T^{-} respectively. The membrane does not allow the colloidal particles to pass through it. So when a potential difference is applied across the electrodes held close to the membranes in chambers B and C, the water starts to move. If the particles carry negative charge, the water will carry positive charge. So it would start moving towards the cathode and so the level of water in side tube ‘T^{--}’ would be observed to rise. If on the contrary the particles carry positive charge the water will carry a negative charge. The level of water will now start moving towards the anode and its level in the side tube T would start rising.

The theoretical interpretation of electro-osmosis has been given by Helmholtz, Lamb, Perrin and Smoluchowski.

Application of electro-osmosis:

(i) In the preparation of pure colloids. The case in point is the preparation of colloidal silicic acid of low molecular weight i.e. in a state of fine subdivision.

(ii) In the tanning of hides and impregnation of similar materials.

(iii) In the manufacture of gelatin for photographic emulsions. The object is to get a gelatin free from fat, mineral and reducing constituents. The phenomenon is also applied in the manufacture of high grade glue.

(iv) In the dying of peat, a process due to Schwerin.

8.14 DETERMINATION OF SIZE OF COLLOIDAL PARTICLES

There are number of methods for the determination of size of colloidal particles. Some important methods are given below-

8.14.1 Ultra-filtration method

The size of the pours of the ultrafilters can be calculated from the measurement of the pressure required to force air through the membrane saturated with water or by measuring the volume of water forced through unit area of the membrane in unit time by a known pressure. It may be repeated that in addition to the size of the particle, adsorption and electric charge will hold the particles and may simulate a lower porosity than should be present according to the size of the pours of the ultrafilters.

By finding which of the ultrafilters will just permit the particles of a sol to pass into the filtrate, while the next filter just stops the passage, the diameter of the colloidal particle can be determined, provided the particles are assumed to be spherical.

8.14.2 From Brownian movement

Colloidal particles suspended in the liquid medium exhibit Brownian motion. They tend to settle down due to gravity. Due to the influence of both these effects, the colloidal particles distribute themselves in a vertical column according to the equation:

$$\frac{2.303RT}{N} \log_{10}\left(\frac{n_1}{n_2}\right) = \frac{4}{3}\pi r^3 (h_2-h_1)(d-d^1) \text{ ……………(a)}$$

Since the number of particles n_1 and n_2 at heights h_1 and h_2 of the vertical column can be counted with the help of ultramicroscoe and densities d and d^1 of the dispersed phase and dispersion medium can be determined by

usual methods. Knowing the value of Avogadro's number (N) r the radius of the particle can be calculated.

8.14.3 From Scattering of light

Zsigmondy used ultramicroscope for determining size of colloidal particles. Each spot of light seen in an ultramicroscope, corresponds to a particle. So the number of particles in a given volume of a solution can be counted. The observation is made a number of times and an average is taken. The length and breadth of the field of vision are measured by an eye piece micrometer. The depth is measured by rotating the slit through 90^0. From this data the exact volume of the solution containing the observed number of particles can be measured. Thus the number of particles per unit volume of the solution can be calculated.

Next, a known volume of a colloidal is evaporated to dryness. From the weight of residue the mass of colloidal particles per unit volume is calculated. Let it be m gm, Now assuming the colloidal particles to be spherical and density of (d) of the colloidal particles to be the same as that in the bulk state, the volume of the colloidal phase is

$$\frac{m}{d} = \frac{4}{3}\pi r^3 n$$

Hence r can be calculated.

8.15 ASSOCIATED COLLOIDS OR COLLOIDAL ELECTROLYTES

The molecule of substances as soap and artificial detergents are smaller than the colloidal particles. However in concentrated solutions these molecules form aggregates of colloidal size.

Substances whose molecules aggregate spontaneously in a given solvent to form particles of colloidal dimensions are called associated or associated colloids.

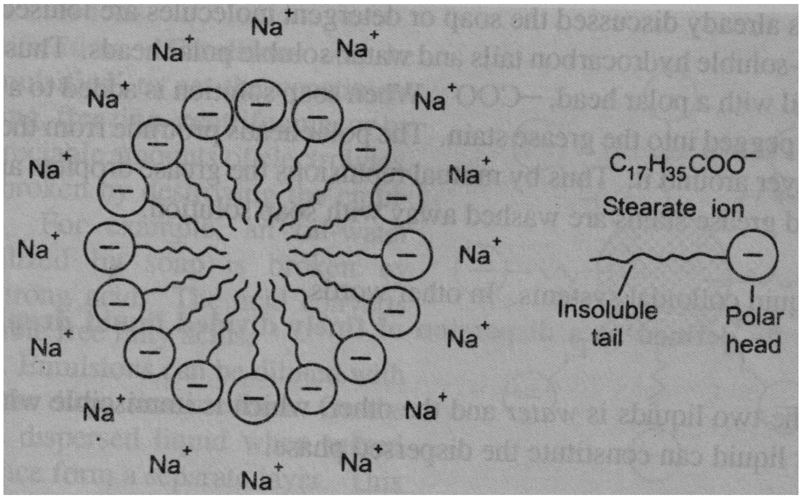


Fig-8.11

The colloidal aggregates of soap or detergent molecules formed in the solvent are referred to as micelles.

Example is sodium stearate $C_{17}H_{35}COO^{-}Na^{+}$

Explanation:

Soap or detergent molecules ionises in water to form an anion and sodium ion. Thus we get $C_{17}H_{35}COO^{-}$ ano Na^{+} ions. As many as 70 stearate ions aggregate to form a miscelle of colloidal size. The stearate ion has a long carbon chain (17 carbons) with a polar – COO^{-} group at one end. The zig zag hydrocarbon tail is shown by a wavy line and the polar head by a hollow circle. In the micelle formation, the tail being insoluble in water are directed toward the centre, while soluble polar heads are on the surface in contact with water (fig-8.11). The charge on the micelle due to the polar heads accounts for the stability of the particle.

8.16 EMULSIONS

Definition

Dispersion of finely divided liquid droplets in another liquid are called emulsion. The particles of dispersed phase in emulsions are generally bigger than those is sols and are sometimes visible under microscope. In most of the cases one of the liquid phases is an oil and the other is water. Accordingly, there are two types of emulsions: oil-in-water (O/W) type in which oil is the dispersed phase and water is the dispersion medium and water-in-oil (W/O) type in which water is the dispersed phase and oil is dispersion medium.

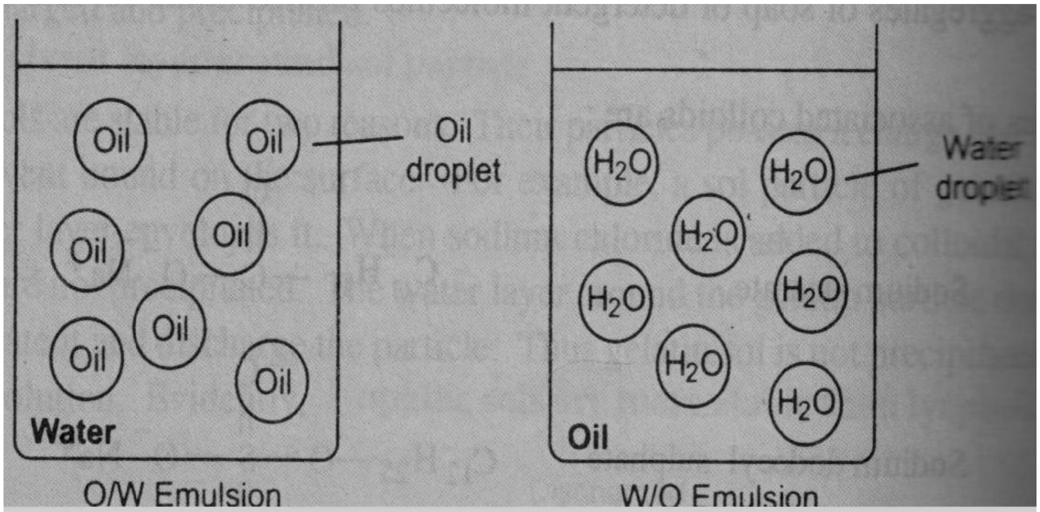


Fig-8.12

Milk is an emulsion of O/W type in which tiny droplets of fat are dispersed in water. Stiff greases are emulsions of W/O type, water being dispersed in lubricating oil.

Emulsifiers

When two imericible liquids such as a hydrocarbon oil and water are shaken together vigorously a milky looking solution result.

This is an emulsion consisting of small droplets of oil suspended in water. However the droplets remain suspended in water for a short time only. On standing the two liquids soon separate, the oil droplets rising to the top and forming a separate oil phase. This is because the cohesive forces between the molecules of each layer exceed the adhesive forces between two liquids. In

other words the emulsion formed by merely shaking the two immiscible liquids together is highly unstable. In order to get stable emulsions of fairly high concentrations it is necessary to add another substance known as emulsifier or emulsifying agent in a small quantity.

Role of emulsifier

The emulsifier concentrates at the interface and reduces surface tension on the side of one liquid which rolls into droplets. Soap for example is made of a long hydrocarbon tail, which is oil soluble, with a polar head – $COONa^+$ (water soluble).

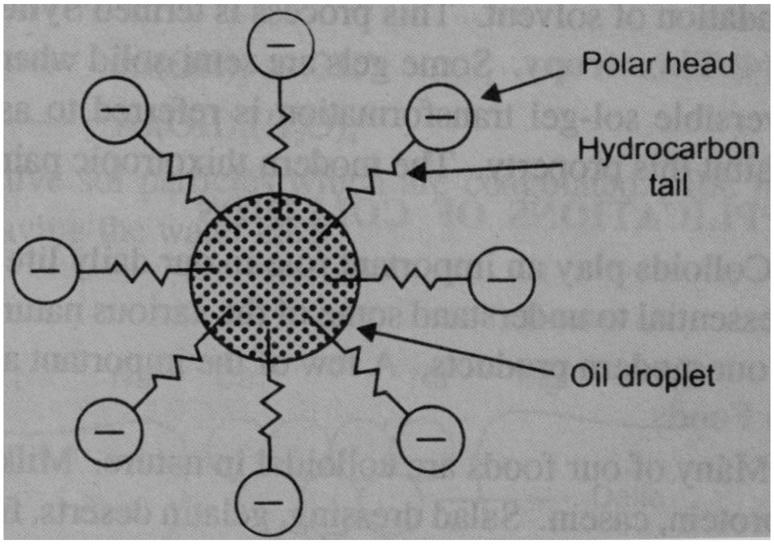


Fig 8.13

In O/W type emulsions the tail is pegged into the oil droplet which the head extends into water. Thus the soap acts as a go-between and the emulsified droplets are not allowed to coalesce.

8.17 GELS

Definition

Several lyophilic sols and a few lyophobic sols, when coagulated under certain conditions, change into a semi-rigid mass, enclosing the entire amount of the liquid with in itself. Such a product is gel. The process of transformation of a sol into a gel is known as gelation.

Gel is a colloidal solution in which a liquid is dispersed in a solid.

Elastic and non elastic gels:

There are two types of gels namely elastic gels and non-elastic gels. Elastic gels are reversible. When partially dehydrated, they change into a solid mass which however changes back into original form on simple addition of water followed by slight warming if necessary. Non-elastic gels are irreversible. When dehydrated they become glassy or change into a powder which on addition of water and followed by warming does not change back into the original gel.

Gelatin, agar-agar and starch are examples of elastic gels as they are reversible. Silica, alumina and ferric oxide gels are non-elastic as they are irreversible.

Elastic gels can imbibe water when placed in it and undergo swelling, non-elastic gels are incapable of doing so. This phenomenon is known as imbibition or swelling.

8.17.1 Sol-gel transformation

Sol transformation is a phenomenon in which a gel is formed from a sol. When a freshly prepared sol of CeO_2 containing about 10g per litre was transformed into a gel by coagulation with electrolyte. But if the sol of CeO_2 was kept for 200-300 days then it lost its power and gave a precipitate instead of a gel, by the addition of electrolytes. But in case of some lyophilic sols, such as gelatin in water, agar in water, the sol-gel transformation is well known and the transformation is reversible with in certain limits.

If gelatin sol is prepared by heating gelatin with water upto 70^0C, and it is then cooled, it is seen that the sol sets to a gel at low temperature. If the gel is again warmed, it liquefies to a sol. This process can be repeated as and when desired. This sol- gel transformation is actually reversible as long as the temperature 65^0-70^0 is not exceeded. At higher temperature the product formed are not reversible and sol-gel transformation does not take place.

8.18 APPLICATION OF COLLOIDS

Colloids play an important role in our daily life as well as in industry, agriculture, medicine and biology.

(i) Foods:

Many of our foods are colloidal in nature. Milk is an emulsion of butter fat in water protected by a protein, casein. Casein in nutrient of great value. Gelatin is added to ice cream (colloidal solution of ice in cream) as a protective agent as as to presence its smoothness.

Whipped cream, fruit jellies, salad dressings egg and a host of other materials used as food are colloidal in nature.

(ii) Medicines:

A number of medicinal and pharmaceutical preparations are emulsions. It is believed that in this form they can be more effective and are easily assimilated. Many ointments for application to skin consist of physiologically active components dissolved in oil and made into an emulsion with water.

Antibiotics such as penicillin and streptomycin are produced in colloidal form suitable for injections.

(iii) Electrical precipitation of smoke:

Smokes and dusts are a nuisance and create health problems in industrial areas. Actually those are dispersions of electrically charged colloidal particles in air.

The removal of these particles from air involves the principle of electrophoresis. The air from a furnace or industrial plant carrying these particles is passed between metal electrodes maintained at high difference of potential (about 50,000 volts). The particles are discharged and deposited as precipitates on the oppositely charged electrodes from which they can be scrapped mechanically.

(iv) Industrial goods:

Soap is a colloidal electrolyte. A series of newer detergent and wetting agents have been produced in recent years. Paints varnishes, enamals, celluloses, resins, gums, glues and other adhesives: rayon, nylon, terylene textiles, leather, paper etc. Are all colloidal in nature. Industrial processes such as tanning, dyeing, lubrication etc are all colloidal in nature.

(v) Rubber-plating:

The negatively charged particles of rubber (latex) are made to deposit on to wires or handles of various tools (in order to insulate them) by electrophoresis. The article to be rubber plated is made the anode. The rubber particles migrate in an electrical field towards the anode and get deposited on it.

(vi) Sewage disposal:

Sewage water consists of particles of dirt, rubbish, mud etc which are of colloidal dimensions and carry electrical charge and therefore do not settle down easily. On creating an electrical field in the sewage tank, these

Particles migrate to the oppositely charged electrodes, get neutralized and settle down at the bottom. This is electrophoresis property of colloids.

(vii) Detergent action of soap:

Most of the dirt and dust sticks on to grease or some oily material which somehow gathers on cloth. As grease is not easily wetted by water. It is difficult to clean the garments by water alone. The addition of soap lowers the interfacial tension between water and grease and this causes the emulsification of grease in water. The mechanical action, such as rubbing etc releases the dirt.

(viii) Artificial kidney machine:

Human kidneys purify blood by dialysis through natural membranes. The toxic waste products such as urea and uric acid pass through the membranes while colloid size particles of blood proteins are retained. Kidney failure therefore leads to death due to accumulation of poisonous waste products in blood. Now-a-days patient’s blood can be cleansed by shunting it into a artificial kidney machine. Here the impure blood is made to pass through a series of cellophane tubes surrounded by washing solution in water. The toxic waste chemicals diffuse across the tube walls into the washing solution. The purified blood is returned to the patient.

(ix) Formation of deltas:

The river water contains colloidal particles of sand and clay which carry negative charge. The sea water, on the other hand contains positive ions such as Na^+, Mg^+, $Ca^{2+.}$ As the river water meets sea water these ions discharge the sand or clay particles which are precipitate as deltas.

Other uses are purification of water formation of smoke screen artificial rain and many more.

8.19 MACROMOLECULES

Definition

Colloidal solutions are formed by aggregation of atoms or molecules to give paticles of colloidal size. There are substances which are themselves composed of giant molecules and dissolve in a solvent to yield colloidal solution directly. These giant molecules are termed macromelecules or polymers.

The dimensions of the macromolecules fall in a range between $10A^0$ to $10{,}000A^0$. The molar mass of polymer may vary from 5000 to several millions. Proteins, synthetic polymers (plastic), synthetic rubber, cellulose and and starch all posses macromolecules.

Solutions of macromoelcules behave like reversible colloids or lyophilic sols. They show a weak Tyndall effect and possess high viscosity. Macromolecules in solution do not carry an electric charge and do not show electrophoresis.

Research in synthetic polymer chemistry has grown at huge pace. Several industries in U.S.A. Japan and some Europian countries have specialized in the synthesis of high molar mass compounds from low molar mass compounds as starting materials. Some industries have specialized in the production of plastic, synthetic rubber, synthetic fibre, lacquers, paints varnishes, adhesives and insulators. In fact plastic industry covers several varities of systhetic polymers having wide range of properties. Some of them are superior to even gold and platinum in chemical resistance and retain their mechanical propertics even when cooled to -50^0C and heated to 500^0C. The strength of other polymers equals that of metals approaching even diamond in hardness. Some varieties of systhetic rubbers act as gas-impermeable and petrol and oil-resistant. Synthetic fibres are far stronger than natural fibres. These can be converted into crease proof fabrics and excellent artificial furs.

A major discovery in the late 1970's was the preparation of conducting organic polymers such as hydrogen derivative of polyacetylene and the one-dimensional polymers $(SN)_{x.}$

8.19.1 Molecular weight of macro molecules

The molecular weight is an important property of polymeric substances such as proteins, polymers (plastics, starch) and other macro molecules. Generally; molecules of protein or a polymer may not be of the same size. Therefore all the experimental methods of molecular weight determination will give some kind of an average value. Two types of average molecular weights have been defined.

(i) Number-average molecular weight M_N

(ii) Mass-average molecular weight M_M.

For a sample consisting of N polymer molecules containing n_1 monomer molecules of molar mass M_1, n_2 monomer molecules of molar mass M_2, etc, the number-average molecular weight is defined as

$$M_N = \frac{n_1M_1+n_2M_2+}{n_1+n_2\ldots..} = \sum niMi/ \sum ni \ldots\ldots\ldots\ldots\ldots.(1)$$

And mass-average molecular weight is

Defined as

$$M_M= \frac{n_1M_1^2+n_2M_2^2}{} +\ldots\ldots = \sum niMi^2 /\sum niMj \ldots\ldots.(2)$$

$N_1M_1+n_2M_2 +$ ……

If c denotes the concentration of polymer solution in grams per unit volume then
$Ci=\sum niMi$
so that $M_M = \sum niMi^2/\sum ci$
The mass- average molecular weight is larger than the number-average molecular weight.

Determination of molecular weight of macro-molecules:

There are a number of methods available for the determination of molecular weight of macromolecules.

(1) Osmotic pressure measurement
(2) Diffusion method
(3) Sedimentation method
(4) Viscosity determination method
(5) Light scattering method

Viscosity method:

It is a simple method for determining molecular weight of macromolecules. The pressure of macromolecules raises the viscosity of the solvent. By measuring the viscosity of pure solvent and the solution in the laboratory we can calculate the molecular weight of the polymer.

The relative viscosity of a solution of a polymer, denoted by $ή_r$ is given by the expression

$ή_r = ή/ ή_0$ ....(1)

Where ή is viscosity of the solution and $ή_0$ is viscosity of pure solvent at same temperature.

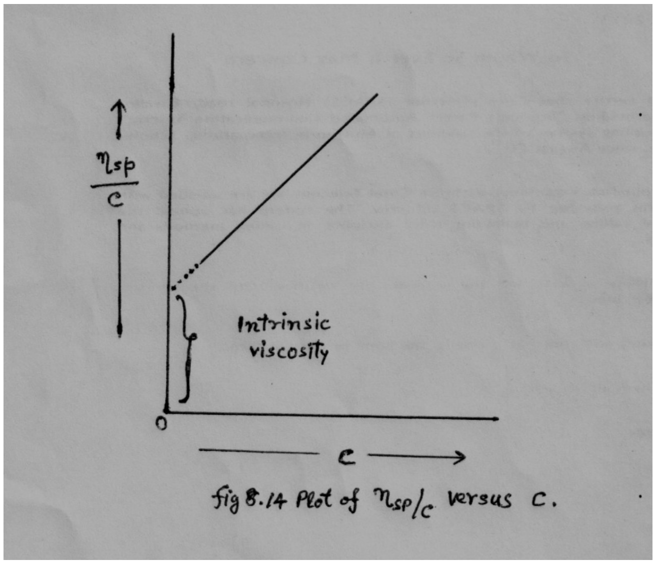


fig 8.14 Plot of η_{sp}/c versus c.

Fig 8.4

The specific viscosity, $ή_{sp}$ is given by

$ή_{sp} = ή_r - 1$ …….(2)

in terms of eqn.(1) and eqn.(2) intrinsic viscosity is defined as

$$[ή] = \lim_{c \to 0} (ή_{sp}/c)$$

where c is concentration of solute. The plot of $\acute{\eta}_{sp}/c$ against c gives a straight line. Extrapolation to c=0 yields the intrinsic viscosity.

Fig(8.4)

It was shown by Staudinger that the empirical relationship exist between intrinsic viscosity $[\acute{\eta}]$ and molecular weight [M] of high polymer

$$[\acute{\eta}] = kM^x$$

Where k and x are constant for a specific polymer in a specific solvent. Once k and x are known for a polymer solvent combination, M may be calculated.

8.20 SUMMARY

In this chapter you have studied that colloidal system is a two phase heterogeneous system in which one phase is dispersed in a fine state of subdivision in another medium termed as dispersion medium. In actual instances the size limit is not rigid and may vary on either side but most systems conform to the above description.

The wide variety of proteins obtained from the living world form the most important group of naturally occuring macromolecules. These are produced from repetitive linking of various amino acids. As a result the proteins are amphoteric in nature.

The sub-topics studied in this chapter include definition, type of colloidal systems, properties of sols. Preparation of sols, purification of sols, zeta potential, electrophoresis, electro-osmosis, coagulation of colloids, origin of charge on colloidal particles.

Emulsions and gels and their properties have also been studied in this chapter. Most important above all is wide range of uses of colloids in different areas in our daily life and industry.

8.21 TERMINAL QUESTIONS

(A) Multiple choice questions:

(1) In a true solutions, the diameter of the dispersed particles is of the range from-

(a) $1A^0$ to $10A^0$ (b) $10A_0$ to $100\ A^0$

(c) $100\ A^0$ to $200\ A^0$ (d) $200\ A^0$ to $500\ A^0$ ans(a)

(2) The precipitating power of Al^{3+}, Na^+ and Ca^{2+} is in the order

(a) $Na^+ > Ca^{2+} > Al^{3+}$ (b) $Na^+ > Al^{3+} > Ca^{2+}$

(c) $Ca^{2+} > Na^+ > Al^{3+}$ (d) $Al^{3+} > Ca^{2+} > Na^+$ ans(d)

(3) Ice cream is a dispersion of ....in cream.

(a) Water (b) Water vapour

(c) Ice (d) Cooling agent

ans(c)

(B) Short answer questions:

(1) Define the following terms:

(a) Sol (b) Gel

(c) Lyophilic Colloids (d) emulsion

(2) How are colloidal solutions classified.What is meant by colloidal state of matter.

(3) Explain why-

(a) Deltas are formed at a place where the rivers pour their water into the sea.

(b) Define number average and weight average molecular weight.

(C) Long answer questions:

Q.1 What is a molecular colloid? How does a lyophilic colloid stabilise a lyophobic one? Give an account of gold number in this respect.

Q.2 Discuss the origin of charge on a colloidal particles. What is meant by electrical double layer?

Q.3 What are lyophilic and lyophobic sols? Discuss the main differences between lyophilic and lyophobic colloids.

Q.4 Explain the following:

(a) stability of colloids

(b) Difference between gels and emulsions.

(c) The Schulze-Hardy rule of coagulation.

Q.5 Equal number of molecules with M_1=10,000 M_2=10,000. are mixed. Calculate number average molecular weight and mass average molecular weight.

Q.6 (a) What are various methods for determining size of the colloidal particles? Describe one method in detail.

(b) Write a note on Brownian movement.

UNIT 9: CATALYSIS

CONTENTS:

9.2 OBJECTIVE

It is an interesting aspect of chemistry that certain reactions which do not proceed to completion even when carried out for indefinite periods of time, get completed within a matter of few minutes when small quantity of a foreign substances added. This substance is known as catalyst. Because of this property it is important to study this topic in detail particularly for many industrial processes.

Autocatalysis:

In certain reactions, one of the product acts as a catalyst. For example, the oxidation of oxalic acid by acidified potassium permanganate becomes much more rapid due to the presence of manganese (II) ions which are formed in the reaction.

This type of reaction in which one of the products itself acts as a catalyst is known as auto-catalysis.

9.1 INTRODUCTION

There are certain reactions which do not proceed to completion even when carried out for indefinite periods of time. These reactions get completed very soon when small quantity of a foreign substance is added. Berzelius in 1836 realised that there are substances which increase the rate of a reaction without themselves being consumed. These substances are called catalyst. A catalyst is defined as a substance which increases the rate of the chemical reaction without undergoing any change and can be recovered as such at the completion of the reaction. The phenomenon of increase in the rate of a reaction with the help of the catalyst is known as catalysis.

Usually a catalyst accelerates a reaction as was originally thought by Berzelius. But a number of cases are now known where the catalyst definitely retards the progress of a reaction.

Thus a catalyst is a substance which alters the rate of a chemical reaction, itself remaining unchanged chemically at the end of the reaction. The process is called as catalysis.

Now it is evident from the above definition a catalyst may increase or decrease the rate of a reaction. A catalyst which increases the rate of a reaction is called positive catalyst and the process positive catalysis or simply catalysis. A catalyst which retards the rate of a reaction is called negative catalyst and the process negative catalysis.

The decomposition of potassium chlorate takes place much more rapidly and at a much lower temperature if a little of manganese dioxide is added to it. Manganese dioxide is not used up at all and can be recovered unchanged.

The combination of hydrogen and oxygen to form water which is slow at ordinary temperature proceeds more rapidly in the presence of platinum.

While studying chemical kinetics you have studied that when a catalyst is added a new reaction path with a lower energy barrier is provided

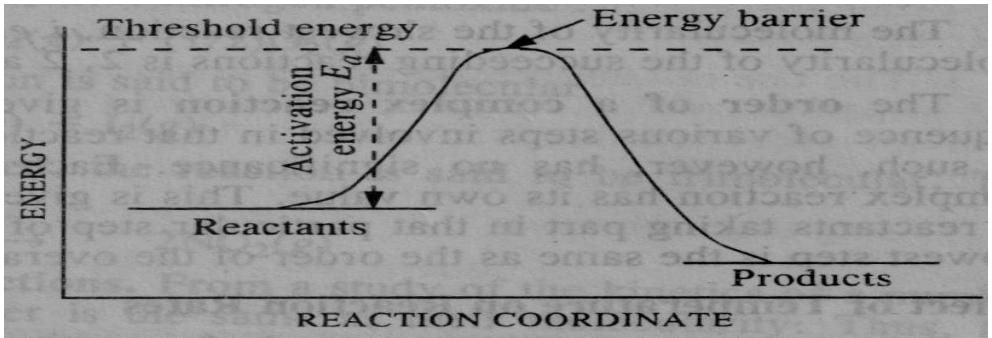


Fig. 7. The concept of energy barrier in chemical reactions

Fig-9.1

Since energy barrier is reduced in magnitude a large number of molecules of the reactants can get over it. This increases the rate of the reaction. In this case the catalyst does not alter the position of the equilibrium in a reversible reaction. It simply hastens the approach of the equilibrium by speeding up both the forward and the backward reactions. How the catalyst works you will study in this chapter later.

9.3 TYPES OF CATALYSIS

There are two types of catalysis:

(a) Homogenius catalysis
(b) Heterogenius catalysis

A third type of catalysis known as enzyme catalysis which is largely of biological interest, you will study in this chapter later on.

9.3.1 Homogenius catalysis

When the catalyst is present in the same phase as that of the reactants, the phenomenon is known as homogeneous catalysis. Following are some ***examples of homogeneous catalysis: Gas phase:***

(i) Oxidation of sulpher dioxide (SO_2) into sulphurtrioxide (SO_3) with nitric oxide (NO) as catalyst.

$2SO_2 + O_2 + [NO] \longrightarrow 2SO_3+[NO]$

gas gas gas gas

(ii) Decomposition of acetaldehyde (CH_3CHO) with iodine (I_2) as catalyst

$CH_3CHO+[I_2] \longrightarrow CH_4+CO+[I_2]$

vapour vapour gas gas

example of homogeneous catalysis in solution phase:

Many reactions in solutions are catalysed by acids (H^+) and bases (OH^-).

(i) Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst.

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H_2SO_4} C_6H_{12}O_6 + C_6H_{12}O_6 + [H_2SO_4]$

cane sugar glucose fructose

(ii) Hydrolysis of an ester in the presence of acid or alkali

$CH_3COOC_2H_5 + H_2O \xrightarrow{H+ / OH} CH_3COOH + C_2H_5OH$

ethyl acetate acetic acid ehtenol

9.3.2 Heterogeneous catalysis

The catalysis in which the catalyst is in a different physical state from the reactants is termed as heterogeneous catalysis. The most important of such reactions are those in which reactants are in the gas phase while the catalyst in solid phase. This form of catalysis has great industrial importance, as you will study later in this chapter.

Example of heterogeneous catalysis

(i) Oxidation of ammonia to nitric oxide in the presence of a platinum gauze.

$$\underset{\text{gas}}{4NH_3} + \underset{\text{gas}}{5O_2} + \underset{\text{solid}}{[Pt]} \longrightarrow 4NO + 6H_2O + [Pt]$$

(ii) Combination of hydrogen and nitrogen to form ammonia in the presence of finely divided iron (Haber's process for ammonia).

$$\underset{\text{gas}}{N_2} + \underset{\text{gas}}{3H_2} + \underset{\text{solid}}{[Fe]} \longrightarrow 2NH_3 + [Fe]$$

(iii) Combination of sulphur dioxide (SO_2) and oxygen in the presence of finely divided platinum or vanadium pentoxide, V_2O_2, (Contact process for sulphuric acid).

$$\underset{\text{gas}}{2SO_2} + \underset{\text{gas}}{O_2} + \underset{\text{solid}}{[Pt]} \longrightarrow 2SO_3 + [Pt]$$

(iv) Hydrogination reaction of unsaturated organic compounds are catalysed by finely divided nickel

$$H_2C = CH_2 + H_2 + [Ni] \longrightarrow H_3C\text{-}CH_3 + [Ni]$$

(v) Decomposition of hydrogen peroxide in aqueous solution is catalysed by gold and platinum in colloidal form as well as by mercury and oxides of metals like lead, manganese cobalt, nickel etc.

$$2H_2O_2 + [Pt] \longrightarrow 2H_2O + O_2 + [Pt]$$

(vi) The decomposition of potassium chlorate is catalysed by manganese dioxide is shown below

$$2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2 + [MnO_2]$$

The above reaction is heterogeneous, though both reactants are in the same phase (solid), because every solid forms a new phase.

9.4 CHARACTERISTIC OF CATALYTIC REACTIONS

As you have studied that a catalyst remains unchanged during the chemical reaction although there are different type of catalytic reactions, the following characteristics are common to most of them. These features are often referred as the criteria of catalysis.

1. A catalyst remains unchanged in mass and chemical composition at the end of the reaction. However the catalyst may undergo a physical change. Thus granular manganese dioxide used as a catalyst in the thermal decomposition of potassium chlorate is left in a fine powder at the end of the reaction.
2. A small quantity of catalyst is generally needed to produce almost unlimited reaction. Sometime a trace of metal catalyst is required to affect very large amounts of reactants. For example one ten-millionth of its mass of finely divided platinum is all that needed to catalyse the decomposition of hydrogen peroxide.

   On the other hand, there are catalysts which need to be present in relatively large amount to be effective. Thus in Friedel-Crafts reaction,

$$C_6H_6 + C_2H_5Cl \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HCl + [AlCl_3]$$

Anhydrous aluminium chloride functions as a catalyst effectively when present to the extent of 30 per cent of the mass of benzene.

3. A catalyst is more effective when finely divided in heterogeneous catalysis; the solid catalyst is more effective when in a state of fine subdivision that it is used in bulk. Finely divided nickel is more effective as catalyst than lump of solid nickel.

4. A catalyst is specific in action. While a particular catalyst works for one reaction it will not necessarily work for another reaction. Different catalysts can bring about completely different reactions for the same reaction. For example ethanol gives ethene when passed over hot aluminum oxide.

$$C_2H_5OH + [Al_2O_3] \longrightarrow C_2H_4 + H_2O + [Al_2O_3]$$

But with hot copper it gives ethanol (CH_3CHO).

$$C_2H_5OH + [Cu] \longrightarrow CH_3CHO + H_2 + [Cu]$$

5. A catalyst cannot in general initiate a reaction.

As you have studied earlier that in most cases a catalyst speeds up a reaction already in progress and does not start the reaction but there are certain reactions where the reactants do not combine for very long time.

For example a mixture of hydrogen and oxygen which remains unchanged almost indefinitely at room temperature can be brought to reaction by the catalyst platinum black in a few seconds.

$$H_2 + O_2 \xrightarrow{\text{room temp.}} \text{No reaction}$$

$$2H_2 + O_2 \xrightarrow{\text{Pt black}} 2H_2O$$

This is because the reacting molecules do not possess minimum kinetic energies for successful collsion.The molecules rebound from collisions without reacting at all. But in the presence of the catalyst they get sufficient energies after reacting with catalyst and are now in a position to give products after further collision with other molecules.

6. A catalyst does not affect the final position of equilibrium although it shortens the time required to establish the equilibrium. It means that in a reversible reaction the catalyst accelerates the forward and reverse reactions equally. Thus the ratio of the rates of two opposing reactions i.e. equilibrium constant remains unchanged.

The effect of a catalyst on the time required for equilibrium to be established for the reaction

$$A + B \rightleftharpoons C + D$$

is shown in fig-9.2

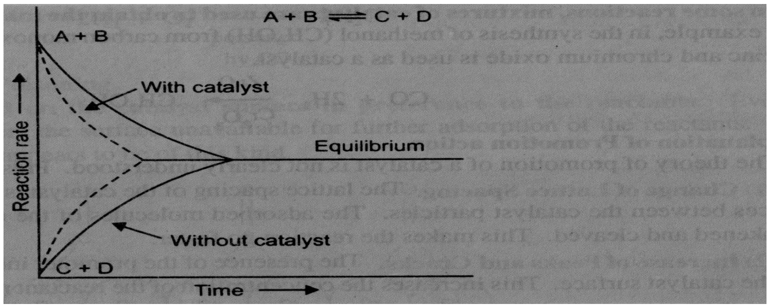


Fig-9.2

To start with the concentration of A and B are at the maximum and hence rate of forward reaction is maximum. As the time passes the rate of reaction decreases till the equilibrium is established. For the reverse reaction the initial concentration of C and D are zero and the rate of reaction is lowest. As the time passed the rate of reaction increases till the equilibrium is established. Similar curves of the rates of reactions with the catalyst show that the rates of the forward reaction and the reverse reaction are altered equally but the equilibrium is established in a much shorter time.

7. The catalyst cannot alter the nature of products of the reaction. The combination of hydrogen and nitrogen under suitable conditions results invariably in the formation of ammonia whether a catalyst is added or not.

8. Change of temperature alters the rate of a catalytic reaction as it would do for the same reaction with a catalyst. You have already studied in your earlier classes the effect of temperature on reversible reactions under Le Chatelier's Principle, which says that ***"If equilibrium is subjected to a stress, the equilibrium shifts in such a way as to reduce the stress".***

Some catalysts are, however, physically altered by a rise in temperature and hence their catalytic activity may be decreased. This is particularly true with colloidal solutions like that of platinum, since a rise of temperature may cause their coagulation. In such a case the rate of reaction increases up to certain point and then gradually decreases. The rate of reaction is maximum at a particular temperature called the ***optimum temperature.***

9.5 PROMOTERS

It has been observed in a number of cases that the activity of a catalyst is considerably increased by the addition of a second substance which by itself has no catalytic property. Such a substance which promotes the activity of catalyst is called promoter. Thus molybdenum (Mo) or aluminium oxide (Al_2O_3) promotes the activity of iron catalyst in the Haber synthesis for the manufacture of ammonia.

$$N_2 + 3H_2 \xrightarrow[+Mo]{Fe} 2\,NH_3$$

In the synthesis of methanol (CH_3OH) from carbon monoxide and hydrogen, a mixture of zinc oxide and chromium oxide is used as catalyst.

$$CO + 2H_2 \xrightarrow[Cr_2O_3]{ZnO} CH_3OH$$

Explanation of promoter action

The action of promoter is not clearly known, this action may be because of the following points:

(1) Change of lattice spacing:

The lattice spacing of the catalyst is changed. Thus enhancing the spaces between catalyst particles. The adsorbed molecules of the reactant (say H_2) are further weakened and cleaved. This makes the reaction go faster (fig 9.3).

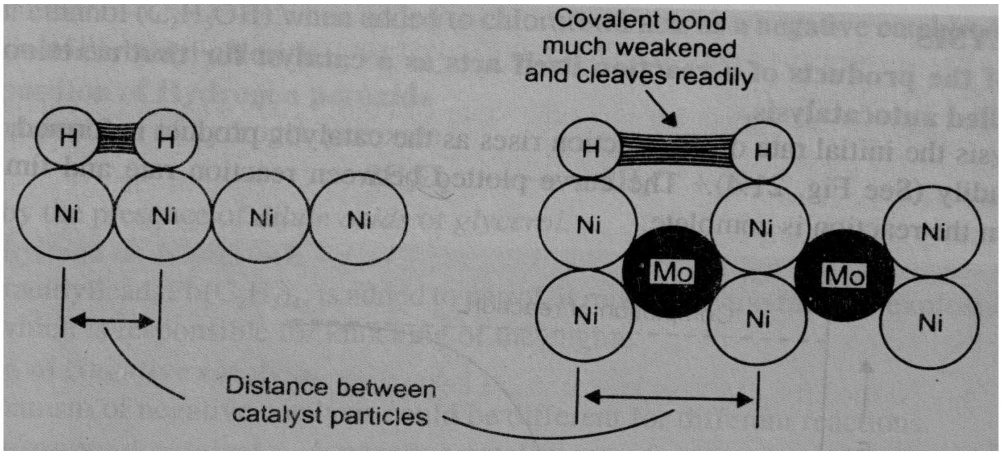


Fig-9.3

(2) Increased peaks and cracks:

The presence of promoter increases the peaks and cracks on the catalyst surface. This increases the concentration of the reactant molecules and hence the rate of reaction.

9.6 CATALYTIC POISONING

A substance which destroys the activity of the catalyst to accelerate a reaction is called a poison and the process and the process is called catalytic poisoning.

Example of catalytic poisoning

(i) The platinum catalyst used in the oxidation of sulphurdioxide is poisoned by arsenic oxide (AS_2O_3).

$$SO_2 + O_2 \xrightarrow[\text{Poisoned By } As_2O_3]{Pt} 2SO_3$$

(ii) The iron catalyst used in the synthesis of ammonia is poisoned by H_2S

$$N_2 + 2H_2 \xrightarrow[\text{Poisoned by } H_2S]{Fe} 2NH_3$$

(iii) The platinum catalyst used in the oxidation of hydrogen is poisoned by carbon monoxide.

$$2H_2 + O_2 \xrightarrow[\text{Poisoned by CO}]{Pt} 2H_2O$$

Explanation of catalytic poisoning

(i) The poison is adsorbed on the catalyst surface is presence of the reactants. It has been found that even a monolayer renders the surface unavailable for further adsorption of the reactants. The poisoning by As_2O_3 or CO appears to be of this kind.

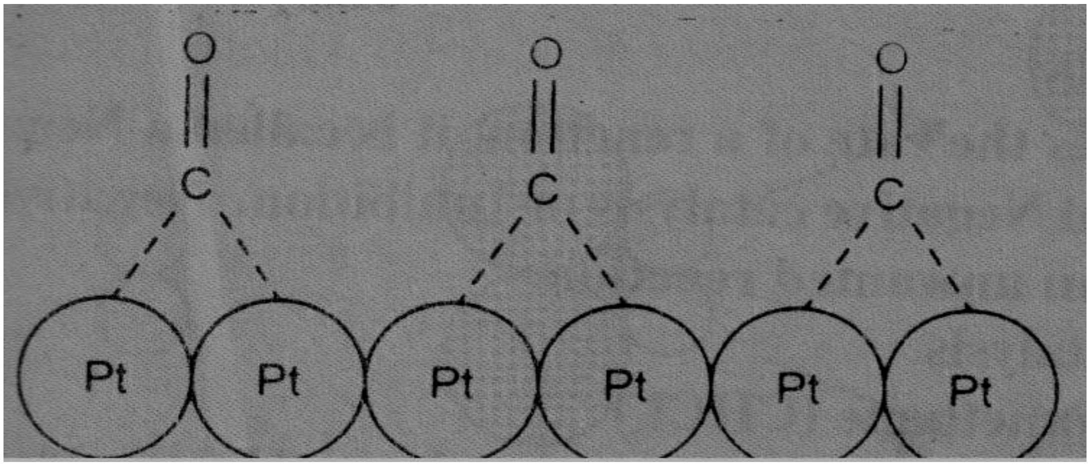


Fig -9.4

(ii) The catalyst may combine chemically with the impurity. The poisoning of iron catalyst by H_2S falls in this class.

$$Fe + H_2S \longrightarrow FeS + H_2$$

9.7 NEGATIVE CATALYSIS

In some cases it has been found that a catalyst instead of speeding up a reaction may actually retard it. Such substances are called negative catalysts or inhibitors. The negative catalysts are of great use when it is desired to slow down altogether a particular reaction.

(i) In the decomposition of hydrogen peroxide a small amount of acetanilide or glycerine when added slow down the reaction.

(ii) When tetraethyl lead $Pb(C_2H_5)_4$ is added to petrol it retards the too rapid or explosive combustion of the fuel which is responsible for knocking of the engine.

Explanation of negative catalysis

Negative action of substances to catalyst could be different for different reactions.

(i) By poisoning the catalyst:

The negative catalyst may function by poisoning a catalyst which already happens to be present in the reaction mixture. For example the traces of alkali dissolved from the glass of a container, catalyse the decomposition of hydrogen peroxide (H_2O_2). But the addition of an acid would destroy the alkali catalyst thus prevents decomposition.

(ii) By breaking the chain reaction:

In some cases negative catalysis are believed to operate by breaking the chain of reaction. For example, the combination of hydrogen (H_2) and chlorine (Cl_2) which is a chain reaction is negatively catalysed by nitrogen trichloride (NCl_3).

$$Cl_2 \longrightarrow Cl^* + Cl^*$$
$$H_2 + Cl^* \longrightarrow HCl + H^*$$
$$H^* + Cl_2 \longrightarrow HCl + Cl^*$$

NCl_3 breaks the chain of reactions by absorbing the propagating species (Cl*) and the reaction stops.

$$NCl_3 + Cl^* \longrightarrow \tfrac{1}{2} N_2 + 2Cl_2$$

9.8 THEORIES OF CATALYSIS

9.8.1 Theories of homogeneous catalysis

It is believed that in homogeneous catalysis, a reactive intermediate compound is first formed by the interaction of one of the reactants with catalyst. The intermediate compound then reacts with the other reactant or reactants giving the final product and at the same time regenerating the catalyst in its original form.

(i) The combination of sulphur dioxide and oxygen, catalysed by nitric oxide gas, is represented as under:

$$\underset{\text{catalyst}}{2NO} + \underset{\text{one reactant}}{O_2} \longrightarrow \underset{\text{intermediate compound}}{2NO_2} \qquad \ldots\ldots\ldots\ldots(1)$$

$$\underset{\text{intermediate compound}}{2NO_2} + \underset{\text{second reactant}}{2SO_2} \longrightarrow \underset{\text{product}}{2SO_3} + \underset{\text{catalyst regenerated}}{2NO} \qquad \ldots\ldots\ldots(2)$$

The reaction would have taken place in the absence of catalyst shown below:

$$2SO_2 + O_2 \longrightarrow 2SO_3 \qquad \ldots\ldots\ \ldots\ldots\ldots\ldots(3)$$

The reaction represented by equation (2) takes place much more rapidly than that represented by equation (3). This explains the catalytic effect of nitric oxide.

(ii) Preparation of diethyl ether $(C_2H_5)_2O$ from ethanol (C_2H_5OH) using sulphuric acid as catalyst can be explained as:

$$\underset{\text{reactant first molecule}}{C_2H_5OH} + \underset{\text{catalyst}}{H_2SO_4} \longrightarrow \underset{\text{intermediate compound}}{C_2H_5HSO_4} + H_2O$$

$$\underset{\text{Intermediate compound}}{C_2H_5HSO_4} + \underset{\text{reactant second molecule}}{C_2H_5OH} \longrightarrow \underset{\text{product}}{(C_2H_5)_2O} + \underset{\text{catalyst regenerated}}{H_2SO_4}$$

(iii) Thermal decomposition of potassium chlorate ($KClO_3$) in presence of manganese dioxide can be explained as:

$$2KClO_3 + 6MnO_2 \longrightarrow \underset{\text{Intermediate compound}}{6MnO_3} + 2KCl$$

$$6\,MnO_3 \longrightarrow 6\,MnO_2 + 3O_2$$

9.8.2 Theories of heterogeneous catalysis

In homogeneous catalysis the intermediate compound formation theory is applicable. The second theory known as adsorption theory, is applicable to heterogeneous catalysis in most of the cases.

According to this theory catalyst functions by adsorption of the reacting molecules. This theory was originated by Faraday in 1833. He suggested that the reacting gases collect on the surface of the solid to form a film. As the concentration of reactants is high in the film, the reaction takes place at a faster rate in the presence of the solid than its absence. Now the formation of such gaseous films on the solid surface is well established by the researches of Langmuir and others.

four steps can be put forwarded for heterogeneous catalysis. For example, if the general reaction is

$$A_{(g)} + B_{(g)} \xrightarrow{\text{catalyst}} C_{(g)} + D_{(g)}$$

$$\underset{\text{reactants}}{A+B} + \underset{\text{catalyst}}{M} \longrightarrow \underset{\text{products}}{C + D} + \underset{\text{catalyst}}{M}$$

$$\underset{\text{one reactant}}{A} + \underset{\text{catalyst}}{M} \longrightarrow \underset{\text{intermediate}}{AM}$$

$$\underset{\text{intermediate}}{AM} + \underset{\text{other reactant}}{B} \longrightarrow \underset{\text{product}}{C + D} + \underset{\text{catalyst}}{M}$$

Step-1 Adsorption of reactant molecules:

The reactant molecules A and B strike the catalyst surface. They are held up at the surface by weak von der Waal's forces (Physical adsorption) or by partial chemical bonds (chemical adsorption).

Step-2 Formation of activated complex:

The particles of the reactants adjacent to one another join to form an intermediate complex (A-B). The activated complex is constable. It has very short existence.

Step-3 Decomposition of activated complex:

The activated complex breaks to form the products C and D. The separated particles of the products hold to the catalyst surface by partial chemical bonds.

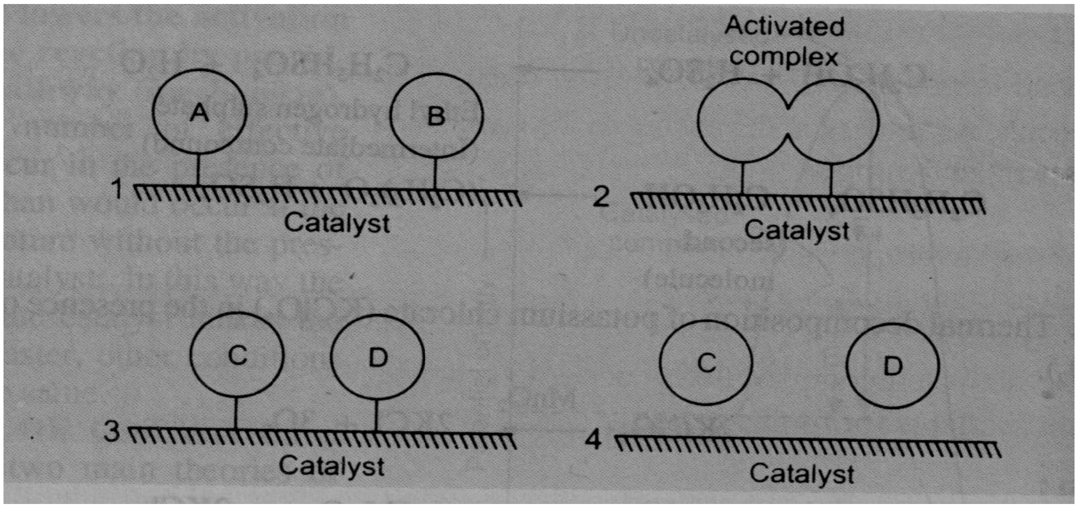


Fig-9.5

Step-4 Desorption of products:

The particles of products are desorbed or released from the surface. They are stable and can lead an independent existence.

The mechanism of contact catalysis may vary in details, depending on the nature of reactants.

Let us consider the example of hydrogenation of ethene in presence of nikel. In this case, ethene adds hydrogen in the presence of nickel as a catalyst to yield ethane.

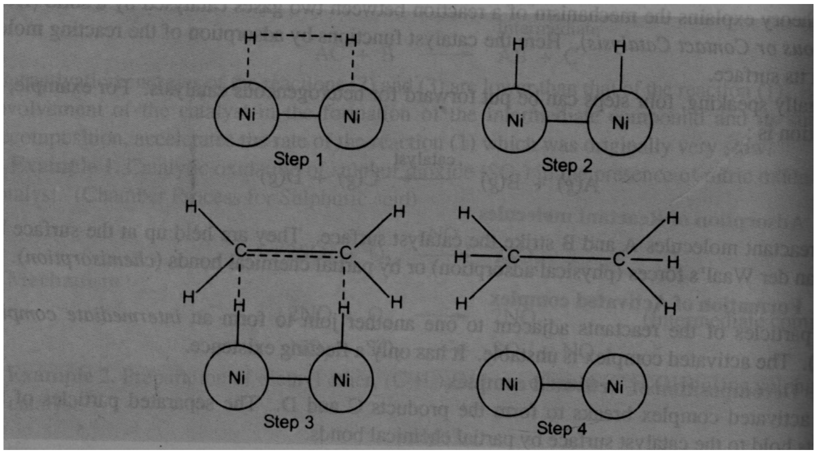


Fig-9.6 (a), 9.6 (b), 9.6 (c) & 9.6 (d)

The functioning of catalyst in this reaction is as follows:

Step-1 Adsorption of hydrogen molecules:

Hydrogen molecules are adsorbed on the nickel surface due to residual valence bonds of the nickel atoms **(fig 9.6a)**

Step-2 H-H bonds are broken:

The H-H bond is smaller than Ni-Ni bond. Therefore, the H-H bond of the adsorbed hydrogen molecule is stretched and weakened. The weakened bond breaks, separating the hydrogen atoms. The separated hydrogen atoms are held to the nickel surface by chemical bonds (fig- 9.6 b).

Step-3 Formation of the activated complex:

The chemisorbed hydrogen atoms then attach to ethene molecule by partial chemical bonds. Therefore, unstable activated complex is formed (**fig 9.6c).**

Step-4 Decomposition of activated complex and desorption of ethane molecule:

The unstable activated complex decomposes to form ethane molecule. The freed catalyst surface is again available for further action **(fig 9.6d)** In the case of reaction between sulphur dioxide and oxygen in the presence of platinum catalyst, the molecules are first adsorbed at adjacent points and then those possessing sufficient energy react with the surface of the catalyst yielding an adsorbed activated complex. The complex then readily dcomposes to give sulphur dioxide which gets readily desorbed.

If one of the reactants is adsorbed strongly on the solid, it will cover most of the surface of the catalyst leaving very little space for the adsorption of the second reactant. The formation of activated complex, therefore, will be slowed down. At the same time, if one of the reactants is adsorbed to a small extent, the catalytic effect will be negligible. For efficient catalysis, therefore, it is desirable that both the reacting gases should be adsorbed appreciably. At the same time it is essential that the products of the reaction are desorbed readily from the surface so that necessary space for the adsorption of the reacting molecules is made available once again.

If the reaction involves only one molecular species for example the decomposition of ammonia gas on the surface of tungsten or that of hydrogen iodide on platinum, it should be adsorbed strongly so that the 'adsorbed activated complex' is formed readily and the reaction is quickened.

9.8.3 Active centres on catalyst surface

The catalyst surface has unbalanced chemical bonds on it. The reactant gaseous molecules are adsorbed on the surface by these free bonds. This accelerates the rate of a reaction. The distribution of free bonds on the catalyst surface is not uniform. These are crowded at peaks, cracks and corners of the catalyst. **(fig 9.7)** The catalytic activity due to adsorption of reacting molecules is maximum at these spots.

These are therefore referred at the active centres.

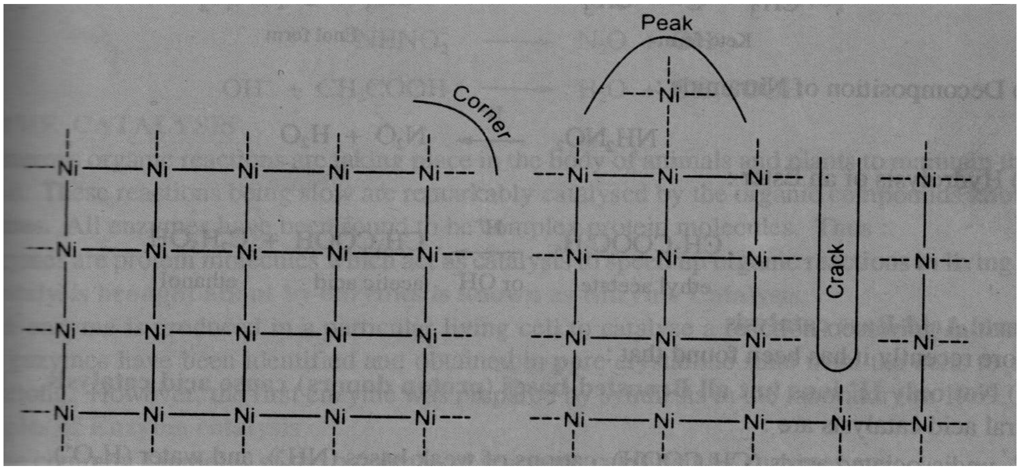


Fig-9.7

The active centres increase the rate of reaction not only by increasing the concentration of the reactants but they also activate the molecule adsorbed at two such centres by stretching it.

9.8.4 The adsorption theory explains catalytic activity

(i) Metals in a state of fine subdivision or colloidal form are rich in free valance bonds and hence they are more efficient catalysts than the metal in lumps.

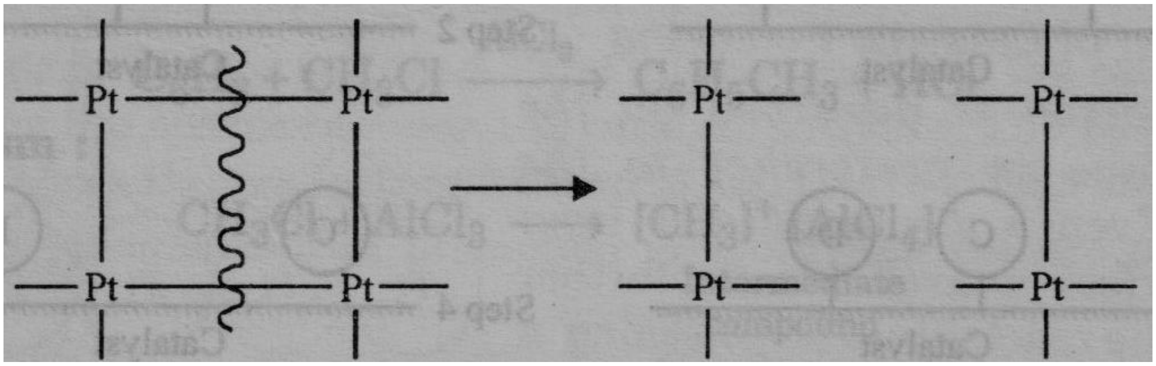


Fig-9.8

(ii) A promoter increases the valance bonds on the catalyst surface by changing the crystal lattice and thereby increasing the active centres. **(fig- 9.8).**

(iii) Catalytic poisoning occurs because the so called poison blocks the free valence bonds on its surface by preferential adsorption or by chemical combination.

9.9 ACTIVATION ENERGY AND CATALYSIS

As you have studied in chemical kinetics a reaction occurs by the collision between the reactant molecules (or ions). At ordinary temperature, the molecules do not possess enough energy and hence collisions are not effective. However, when the temperature of the system raised, the kinetic energy of the molecules increases. But the molecules do not react unless they attain minimum amount of energy.

The minimum amount of energy required to cause a chemical reaction is known as activation energy.

The activated molecules on collision first form an activated complex. As a result of breaking of old bonds and forming of new bonds the activated complex dissociates to yield product molecules.

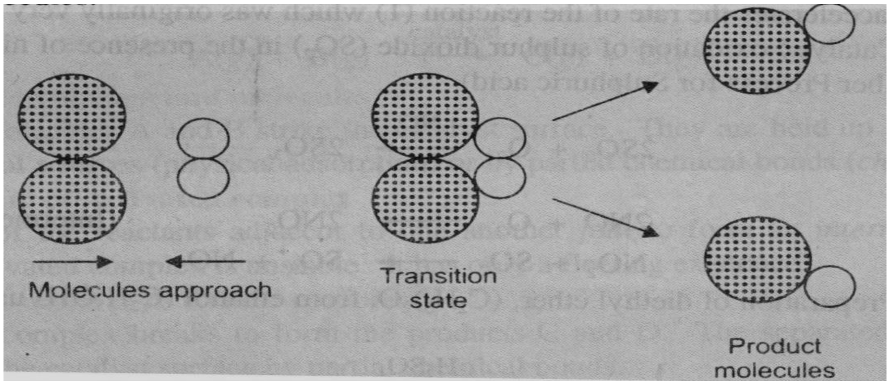


Fig-9.9

A catalyst lowers the activation energy of the reaction by providing a new pathway **(fig 9.10)**. Thus larger number of effective collisions occurs in the presence of the catalyst, than would occur at the same temperature without the presence of catalyst. In this way the presence of catalyst makes the reaction go faster, other condition remaining the same.

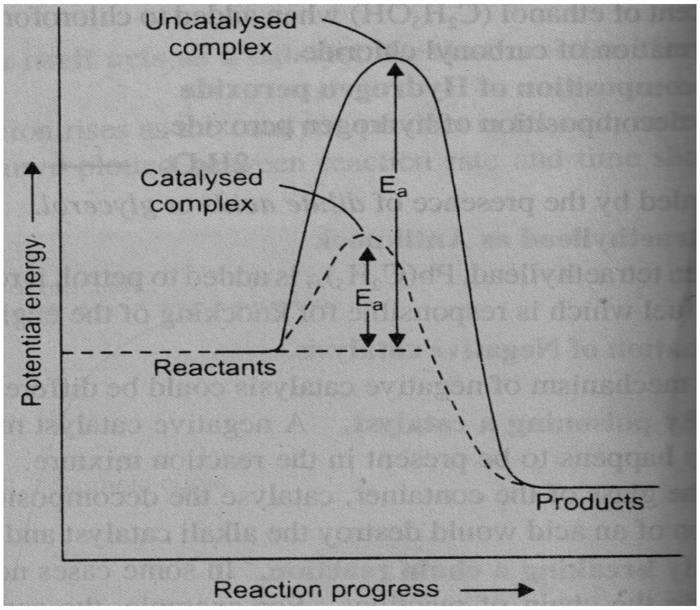


Fig-9.10

9.10 ACID-BASE CATALYSIS

9.10.1 Definition

There are a number of homogeneous catalytic reactions which are brought about by acids and bases. The subject of acid-base catalysis therefore has assumed a special importance.

Arrhenius pointed out that acid catalysis was, infact, brought about by H^+ ions supplied by strong acids, while base catalysis was caused by OH^- ions supplied by strong bases.

The catalytic effect of the dilute mineral acids on

(i) The inversion of sucrose has been well known for a long time:

$$\underset{\text{sucrose}}{C_{12}H_{22}O11} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

(ii) Decomposition of nitramide catalysed by H^+ ion takes place as follows:

$$NH_2NO_2 \xrightarrow{H+} N_2O + H_2O$$

(iii) Hydrolysis of nitrile, first to amino acid and then to ammonium salt of the corresponding fatty acid,is catalysed by acid and bases.

$$\underset{\text{nitrile}}{RCN + H_2O} \xrightarrow{H^+/OH^-} \underset{\text{amide}}{RCONH_2}$$

$$\underset{\text{amide}}{RCONH_2 + H_2O} \xrightarrow{H^+/OH^-} \underset{\text{Ammonium salt}}{RCOONH_4}$$

(iv) Hydrolysis of an ester to give corresponding acid and alcohol is accelerated in the presence of acids.

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} \; H^+ \longrightarrow \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethanol}}{C_2H_5OH}$$

The recent work has shown that in the reactions catalysed by acids not only hydrogen ions but also undissociated acids even cations of weak bases (such as NH_4^+), in short, all substances which have tendency to give up proton, can show catalytic activity. Similarly in the reactions catalysed by bases, not also undissociated bases and even anions of weak acid (such as CH_3COO^-), can function as catalysts. It is this discovery which leads to the development of modern concept of acids and bases.

According to this concept, a reaction which is catalysed by an acid is also catalysed by any substance which defined as a substance which has a tendency to lose a proton. This is known as general acid catalysis and an acid is defined as a substance which has a tendency to lose a proton. Similarly, a reaction, which is catalysed by a base, is also catalysed by all substances which has tendency to gain a proton. This is known as general base catalysis and a base is defined as a substance which has tendency to gain a proton.

Some reaction such as mutarotation of glucose, hydrolysis of nitriles and esters and enolisation of acetone are catalysed by both acids and bases.

9.10.2 Theory of acid base catalysis

Careful experiments have shown that the catalytic activity of an acid (or a base) for the given reaction depends upon its readiness to lose (or gain) a proton. Therefore the mechanism of acid-base catalysis appears to involve loosing or gaining of protons. It is believed that a complex is formed first by the transfer of proton (from the acid catalyst) to the reactant molecule. This process, which is slow and determines the rate of the reaction, is followed by a rapid internal rearrangement giving rise to the product. The proton set free in this rearrangement is removed by the base catalyst.

Following are few examples considered to illustrate the mechanism of acid-base catalysis.

(i) **Mutarotation of glucose:**

Let GH represent ά - glucose and HG its isomer,

ß - glucose. The catalysed transformation of ά - glucose into ß - glucose may be represented as below:

$$H^+ + GH \longrightarrow HGH^+ \xrightarrow{\text{rearrangement}} HG + H^+$$

Proton supplied the intermediate ß

glucose proton

by acid catalyst complex

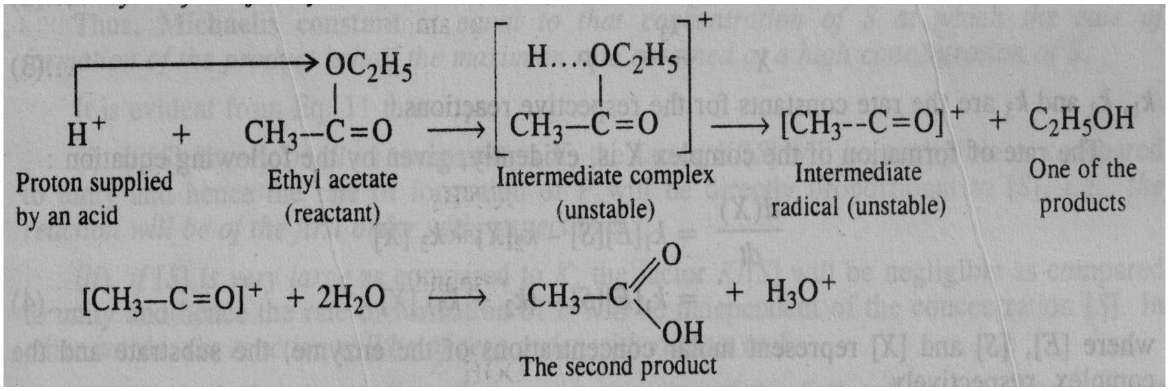
(product) removed by

base catalyst

the rate of mutarotation of glucose is very small in pyridine, a base, and also in cresol, an acid, but is appreciably high in a mixture of two solvents.

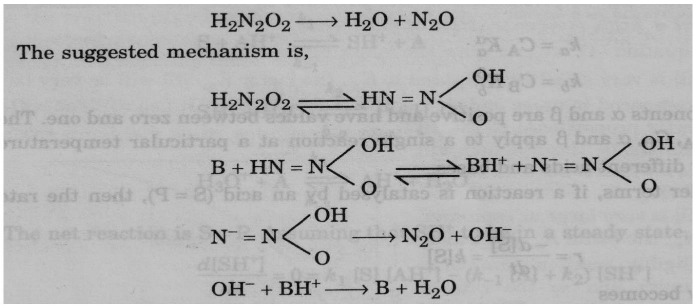
(ii) **Hydrolysis of ethyle acetate:**

The acid catalysed hydrolysis of ethyl acetate proceed in the following steps.



Evidently, one out of the two molecules of water acts as a base as it takes up the proton.

(iii) **An example of a base catalysed reaction is given by the decomposition of nitramide:**



9.11 ENZYME CATALYSIS (BIOCHEMICAL CATALYSIS)

9.11.1 Definition

Enzymes are complex nitrogeneous organic compounds. They are produced in living cells of plants and animals. When dissolved in water they produce colloidal solution, hence they behave as very active catalysts in certain biochemical reactions. They are thus known as biochemical catalysts and the phenomenon itself is known as biochemical catalysis.

Enzyme is proteins having high molar mass of the order of 10,000 or even more. Each enzyme can catalyse a specific reaction.

9.11.2 Characteristics of enzyme catalysis

(i) Enzymes form a colloidal solution in water and hence they are very active catalysts.

(ii) Like inorganic catalysts they cannot disturb the final state of equilibrium of a reversible reaction.

(iii) They are highly specific in nature, i.e. , one catalyst cannot catalyse more than one reaction.

(iv) They are highly specific to temperature. The optimum temperature of their activity is 35^0C to 40^0C. They are deactivated at 70^0C.

(v) Their activity is increased in the presence of certain substances known as co-enzymes.

(vi) A small quantity of enzyme catalyst is sufficient for a large change.
(vii) They are destroyed by U.V. rays.
(viii) Their efficiency is decreased in the presence of electrolytes.

9.11.3 Examples of enzyme catalysis

(i) Conversion of starch into maltose sugar:

The enzyme diastate produced in the germinated barley seeds converts starch into maltose sugar.

$$2\,(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{diastase}} nC_{12}H_{22}O_{11}$$

(ii) The enzyme zymase produced by living yeast cells converts glucose into ethyl alcohol.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} \underset{\text{ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

(iii) The enzyme urease present in soyabean hydrolyses urea into ammonia.

$$\underset{\text{urea}}{NH_2\,CONH_2} + H2 \xrightarrow{\text{urease}} \underset{\text{ammonia}}{2NH_3 + CO_2}$$

(iv) Canesugar converted into glucose and fructose by the enzyme invertase.

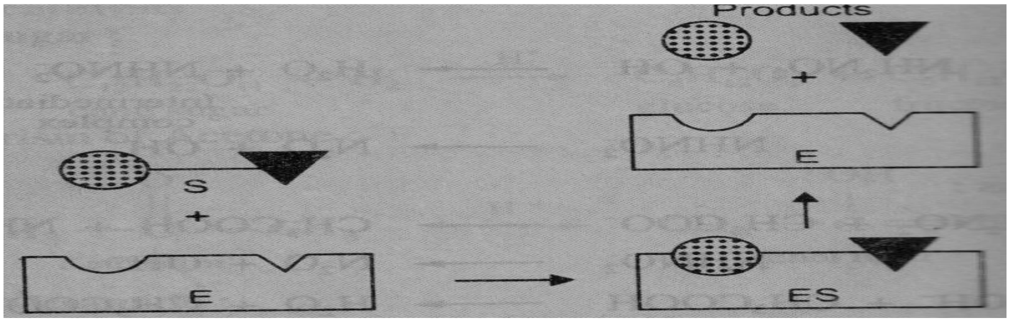
$$\underset{\text{canesugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

The catalytic activity of enzymes is due to their capacity to lower the activation energy for a particular reaction.

9.11.4 Mechanism of enzyme catalysis

The long chain of the enzyme (protein) molecules is coiled on each other to make a rigid colloidal particle with cavities on its surface. These cavitites which are of chacteristic shape and abound in active group (NH_2, COOH, OH, SH), are termed as active centres. The molecules of substrate (reactant) which has complementary shape, fit into these cavities just as key fits into a lock (lock and key theory). By virtue of the presence of active groups, the enzyme forms an activated complex with the substrate which at once decomposes to yield the products. Thus the substrate molecules enter the cavities, forms complex and reacts and at once the products get out of the cavities.

Michaelis and Menton (1913) preposed the following mechanism for enzyme catalysis



E=Enzyme S= substrat (reactant) ES = activated complex P=product

Fig-9.11

9.11.5 Kinetics of enzyme catalysis:

A reactant in enzyme catalysed reaction is known as substrate. According to mechanism of enzyme catalysis, the enzyme combines with the substrate to form a complex as suggested by Henry (1903). He also suggested that this complex remains in equilibrium with the enzyme and the substrate. Later on in 1925 Briggs and Haldane showed that a steady state treatment could be easily applied to the kinetics of enzymes. Some photochemical reactions and some enzymic reactions are reactions of zero order. With S representing the substrate E the enzyme, ES enzyme-substrate complex and the products, the mechanism of the enzyme catalysed reaction is presumed to be adequately represented by

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_3} E + P$$

Where k_1, k_2 and k_3 are the rate constant for the respective reactions.

By adopting steady state concept we can determine the order of reaction of enzyme catalysed reactions.

9.12 INDUSTRIAL APPLICATION OF CATALYSIS

The following are a few important examples of heterogeneous catalytic reactions of industrial importance.

1. Haber's process for manufacture of ammonia

   $$N_2 + 2H_2 \xrightarrow{Fe/MO} 2NH_3$$

   Finely divided iron and molybdenum (as promoter) 200 atm. pressure and temperature range is 400^0C – 500^0C are applied in this process.

2. The manufacture of chlorine by Deacon's process.

   $$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2$$

   In this case cupric chloride is catalyst and excess of air functions as promoter. The temperature should be 500^0C.

3. Ostwald's process for the manufacture of HNO_3.

   $$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$
   $$2NO + O_2 \longrightarrow 2NO_2$$
   $$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

   Conditions for better yield are platinised asbestos as catalyst + excess of air (as promoter) and temperature 300^0C.

4. Manufacture of hydrogen by Bosch's process.

   $$\underset{\text{water gas}}{(CO + H_2)} + H_2 \longrightarrow CO_2 + H_2$$

   In this process ferric oxide acts as catalyst, chromic oxide as promoter and temperature is maintained between 400^0C- 600^0C.

5. In the manufacture of methyl alcohol from water gas

   $$\underset{\text{water gas}}{(CO + H_2)} + H_2 \longrightarrow CH_3OH$$

Zinc oxide is used as catalyst, chromic oxide as promoter pressure 200 atms. and temperature 450^0C.

6. In Chamber process for manufacture of H_2SO_4, nitric oxide is used as catalyst.

$$2SO_2 + O_2 + [NO] \xrightarrow[\text{catalyst}]{} 2SO_3 + [NO]$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

7. In the manufacture of acetic acid from acetaldehyde.

$$2CH_3CHO + O_2 \longrightarrow 2CH_3COOH$$

Vanadium oxide (V_2O_5) is used as catalyst.

9.13 SUMMARY

It is indeed, a fascinating aspect of chemistry that certain reactions which do not proceed to completion even when carried out for indefinite period of time, that completed within a matter of few minutes when small

Quantity of a catalyst is added. A catalyst provides for the reaction another path that has a lower energy of activation E_a. A Better explanation is offered by the activated complex theory on the basis of the decrease in free energy of activation. The presence of catalyst is very useful in many industrially important reactions which are either very slow or takes place at a very high temperature. Hence to decrease the cost of production it is essential to make use of a suitable catalyst.

In this chapter you have studied definition of catalysis, types of catalysis, catalytic promoters, negative catalysis, acid-base catalysis, enzyme catalysis, different theories of catalysis and uses of catalysis.

9.14 TERMINAL QUESTIONS

(A) Multiple choice questions:

Q.1 In the hydrogenation of oils the catalyst used is:

(a) Iron (b) Platinum

(c) Nickel (d) Molybdenum ans (c)

Q.2 Which of the following is most likely to increase the rate of the reaction?

(a) decreasing the temperature.

(b) increasing the volume of the vessel.

(c) reducing the activation energy.

(d) decreasing the concentration of the reactant in the reaction vessel.

ans (c)

Q.3 Which of the following statement is universally correct?

(a) A catalyst remains unchanged at the end of the reaction.

(b) A catalyst physically changes at the end of the reaction.

(c) A catalyst take part in a chemical reaction.

(d) A catalyst can induce chemical reaction. ans (a)

Q.4 A substance that retards the rate of chemical reaction in the presence of catalyst is called:

(a) An inhibitor.

(b) A positive catalyst.

(c) An autocatalyst/

(d) A promoter. ans (a)

Q.5 A catalyst

(a) may be in the same phase with the reactants or in a different phase.

(b) may accelerate a reaction.

(c) affect a reaction without being consumed in the process.

(d) all of the above. ans(d)

Q.6 The energy needed to overcome for a reaction to occur is called:

(a) activation energy.

(b) energy of vapourisation.

(c) specific heat

(d) potential energy ans (a)

(B) Short answer and very short answer type questions:

1. Define catalyst and catalysis.
2. Explain how a catalyst increases the rate of a reaction.
3. Define the terms
   - (i) catalytic promoter
   - (ii) catalyst inhibitor
   - (iii) catalytic poison
4. Explain the term homogeneous catalysis and heterogeneous catalysis.
5. What is an enzyme? Describe its characteristics?
6. Explain why solid catalysts are generally used in the finely divided state.
7. What is the role of an inhibitor in a chemical reaction?
8. Where are the following used as catalyst?
   - (i) Finely divided nickel
   - (ii) Platinum gauge
   - (iii) Ferric oxide
   - (iv) Manganese dioxide.
9. Write a note on adsorption theory of catalysis.
10. Explain with examples what is negative catalyst.

(C) Essay type or long answer questions:

1. Write a brief account of the theories of catalysis. Explain the function of active centres.
2. Write an essay on catalysis.
3. Give a brief account of adsorption theory. How does this theory explain the characteristics of contact catalysis?
4. Explain the important characteristics of enzyme catalysis with examples.
5. (a) Describe the theory of homogeneous and heterogeneous catalysis.
   (b) Give an example each for enzyme catalysis and acid base catalysis.
6. Write notes on:
   - (a) catalyst and energy of activation.
   - (b) specificity of catalytic action.
   - (c) auto catalyst.

UNIT 10: BASIC CONCEPTS OF THERMODYNAMICS

CONTENTS:

10.1 OBJECTIVES

Literally speaking thermodynamics concerns itself with the flow of heat and it deals with relation between heat and work. Heat, as we all know, is a form of energy and the conversion of heat into useful work and vice versa come under the domain of thermodynamics. The science of thermodynamics governs not only the transformation of heat into work but also includes all types of inter-conversion of one kind of energy into another; e.g., electricity into work, chemical energy to electrical energy, etc.

10.2 INTRODUCTION

The study of flow of heat or any other form of energy into or out of a system as the system undergoes a physical or chemical transformation is called thermodynamics.

The most distinguishing feature of thermodynamics, however, is its predominant concern with temperature and temperature-dependent variables.

Thermodynamics is essentially a practical science and it has its verification extending mainly to the fields of chemistry, physics and engineering. With the assistance of thermodynamics the chemist predicts the possibility of a chemical reaction or the maximum yield in a chemical process under a given set of circumstances. Using thermodynamic laws the physicist explains the phenomena where phase changes or inter-actions with radiations or electromagnetic field are involved. To the engineers it is the most powerful weapon to solve problems of power and consumptions, in the prediction of efficiencies of heat-engines and refrigerators, in the design of engines and so on.

The thermodynamic principles correlate different observable properties of a system but cannot always give us the exact magnitude of a property of the system. These relations help us in predicting the behaviour of a system or the ultimate result that a process would lead to. Thus, from thermodynamics we can predict under a set of defined conditions the maximum yield in a chemical process, but we cannot say anything about the rate of the reaction or the mechanism of the reaction.

Thermodynamics does not make any hypothesis as to the structure of matter. Thermodynamics derives from various laws, relations between properties experimentally observed but not offer any explanation as to why these properties arise in a system. The approach in thermodynamics is thus entirely different from that in the atomic constitution of matter. For example, in kinetic theory we consider the pressure of a gas is measure of the impact of the molecules on the wall per second, while in thermodynamics, pressure is a property of the state of a system. Similarly temperature is, according to kinetic theory, a measure of the average kinetic energy of the molecules while it is a simple property of state from the view-point of thermodynamics.

10.3 DEFINITION OF THERMODYNAMIC TERMS

10.3.1 Temperature

The hotness or the coldness of an object is understood fundamentally by our senses. The hotter body will have a higher temperature than the colder body. We also have another experience in nature. Suppose there are two bodies, A and B, A being hotter than B. If A is brought in contact with B, it is found that A gradually becomes colder and B becomes warmer. During this process, other changes in pressure or volume may also occur. Ultimately, we find that both A and B are equally warm, i.e. they have attained the same temperature. A and B are now said to be in thermal equilibrium. During this process, some energy (really the heat-energy) have moved from the hotter body A to the colder body B. Temperature then determines the direction in which in which heat would flow, namely, from the hotter body to colder body. In other words “temperature is the driving forces for the flow of heat.”

Zeroth law of thermodynamics:

Let us consider three systems A, B and C. Suppose A is in thermal contact with B through a diathermic wall. A diathermic wall is that which permits the systems in contact to influence each other. And again B is also in thermal contact with C (fig 10.1). Sufficient time being allowed A will be in thermal equilibrium.

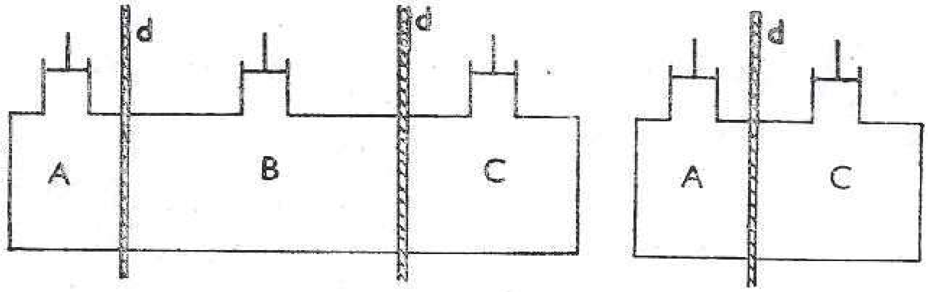


Fig 10.1 Zeroth law of thermodynamics

With B. Similarly, C will also in thermal equilibrium with B. If B is now removed and A is brought in thermal contact with C, it is found that there is no change in the coordinates of A and C. The systems A and C are in thermal equilibrium with each other. Hence

“Two systems in thermal equilibrium with a third are in thermal equilibrium with each other”. This is Zeroth law of thermodynamics.

10.3.2 System and surroundings

A system may be defined as any specified portion of matter under study which is separated from rest of the universe with a bounding surface. A system may consist of one or more substances.

The rest of the universe which might be in a position to exchange matter and energy with the system with the system is called surroundings. The real or imaginary surface separating the system from the surroundings is called the boundary. The boundary may be real or imaginary.

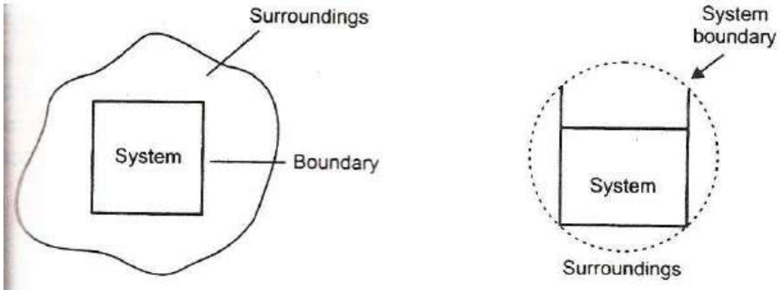


Fig 10.2 thermodynamic system and surroundings

A quantity of a gas in a closed cylinder has real and defined boundaries, but if the same gas flows through a zigzag pipe, its boundaries constantly change and have to be followed in imagination as it progresses. If say 250 ml of water contained in a beaker it will constitute a thermodynamic system. The beaker and the air in contact, are the surroundings.

If one mole of a gas confined in a cylinder fitted with a piston, is a thermodynamics system. The cylinder, the piston and all other objects outside the cylinder, form the surroundings. Here the boundary between the system (gas) and the surroundings (cylinder and piston) is clearly defined. A system and its surroundings constitute the universe.

System + surroundings = universe

10.3.3 Homogeneous and heterogeneous system

A system is said to be homogeneous if it is completely uniform throughout. In such a system there is only one phase. A phase is defined as a homogeneous, physically distinct and mechanically separable portion of a system. Examples of homogeneous system are pure single solid, liquid or gas, mixture of gases and true solution of solid in a liquid.

A system is said to be heterogeneous, when it is not uniform throughout. In such a system there are two or more phases. Examples of heterogeneous system are: ice in contact with water, ice in contact with vapour, etc. Here ice, water and vapour constitute separate phases.

10.3.4 Types of systems

There are three types of thermodynamics systems depending on the nature of boundary.

10.3.4.1Open system

A system which can exchange matter as well as energy with its surroundings is said to be an open system. Hot water contained in a beaker placed on laboratory table is an open system. Here the water vapour (matter) and also heat (energy) is transferred to the surroundings through the imaginary boundary.

10.3.4.2 Closed system A system which can exchange energy not matter with its surroundings is called a closed system. A specific quantity of hot water contained in a sealed tube in an example of a closed system. While no water vapour can escape from this system, it can transfer heat through the walls of tube to the surroundings.

10.3.4.3 Isolated system A system which can exchange neither matter nor energy with its surroundings is called an isolated system.

Let us consider a system 100 ml of water in contact with its vapour in a closed vessel which is insulated. Since the vessel is sealed, no water vapour (matter) can escape from it. Also as the vessel is insulated, no heat (energy) can be exchanged with its surroundings.

Isothermal and adiabatic systems:

If a system is maintained at a constant temperature it is termed as isothermal system. If a system is so insulated from its surroundings that no heat flows in or out of the system its termed as adiabatic system.

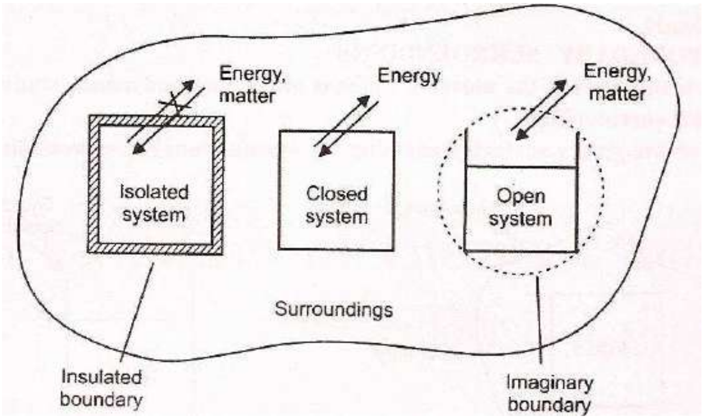


Fig 10.3 three types of thermodynamic systems

10.3.5 Intensive and extensive properties

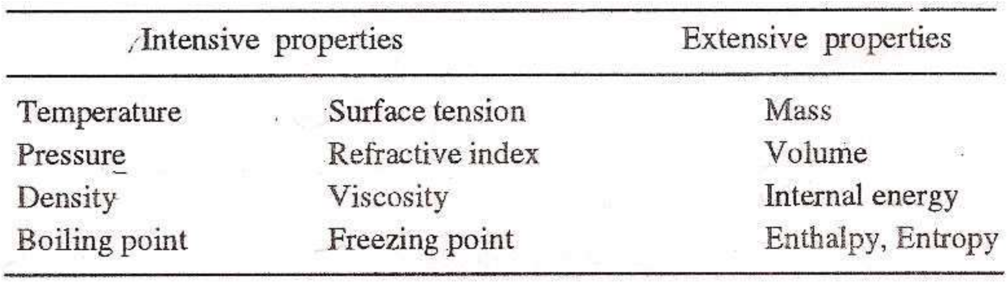
The macroscopic or bulk properties of a system (volume, pressure, mass etc.) can be devided into two classes

(a) Intensive properties

(b) Extensive properties

In intensive property of a system is that which is independent of the amount of the substance present in the system. The examples are temperature, pressure, density, concentration, viscosity. Refractive index, surface tension and specific heat.

A property that does depend on the quantity of matter present in the system is called an extensive property. Some examples of extensive properties are volume, no. of moles, enthalpy, entropy, mass and Gibbs free energy.



Intensive properties		Extensive properties
Temperature	Surface tension	Mass
Pressure	Refractive index	Volume
Density	Viscosity	Internal energy
Boiling point	Freezing point	Enthalpy, Entropy

Table 10.1 common properties of a system

10.3.6 Processes and their types

When a thermodynamic system changes from one state to another, the operation is called a process. When a system changes from one state to another it is accompanied by change in energy. In the case of open systems, there may be change of matter as well.

The following types of processes are known:

(1) Isothermal process:

A process is said to be isothermal if the temperature of the system remains constant during each state of process. For an isothermal process dT=0

(2) Adiabatic process:

A process is said be adiabatic if no heat enters or leaves the system during any step of the process. Adiabatic conditions can be approached by carrying the process in an insulated container such as 'thermos bottle.' High vacuum and highly polished surfaces help to achieve thermal insulation.

For an adiabatic process dq=0

(3) Isobaric process:

Those processes which take place at constant pressure are called isobaric processes. Heating of water to its boiling point and its vaporisation takes place at the same atmospheric pressure is an example of isobaric process.

For an isobaric process dP=0

(4) Isochoric process:

A process in which volume remains constant is known as isochoric process. The heating of a substance in a non-expanding chamber is an example of isochoric process.

For an isochoric process dV=0

(5) Cyclic process:

When a system in a given state goes through a number of different processes and finally returns to its initial state, the overall process is called a cyclic process.

For cyclic process dE=0, dH=0.

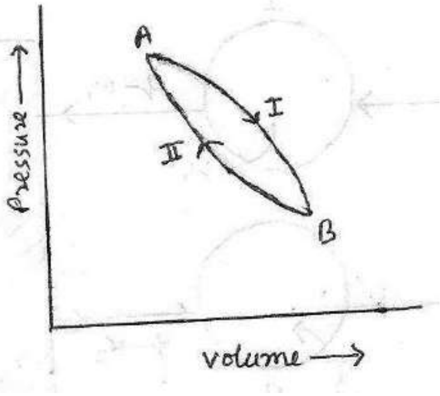


Fig 10.4 cyclic process

10.4 REVERSIBLE AND IRREVERSIBLE PROCESSES

A process carried out infinitesimally slowly and its direction at any point can be reversed by an infinitesimal change in the state of a system is a reversible process.

In fact, reversible process is considered to proceed from initial state to final state through an infinite series of infinitesimally small stages. At the initial, final and all intermediate stages, the system is in equilibrium state, this is so because an infinitesimal change in the state of the system at each intermediate step is negligible.

When a process goes from initial state to the final state in a single step and cannot be carried in the reverse order, it is said to an irreversible process. Here the system is in equilibrium state in the beginning and at the end, but not at points in between.

A reversible process cannot be realised in practice, it would require infinite time for its completion. Hence, all those reactions which occur in nature or in laboratory are irreversible. A reversible process is thus theoretical and imaginary.

Example:

Let us consider a certain quantity of gas contained in a cylinder having a weightless and frictionless piston. The expansion of the gas is carried out by two methods illustrated in fig 10.5.

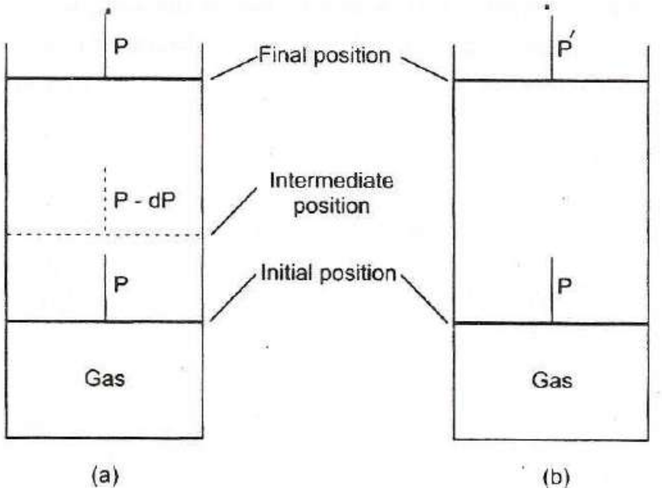


Fig 10.5 reversible expansion of a gas (a) irreversible expansion of a gas (b)

Let the pressure applied to the piston be P and this is equal to the internal pressure of the gas. Since the external and internal pressure are exactly counterbalanced, the piston remains stationary and there is no change in the volume of the gas. Now suppose the pressure on the piston is decreased by an infinitesimal amount dP. Thus the external pressure on the piston being P-dP, the piston moves up and the gas will expand by an infinitesimal small amount. The gas will, therefore, be expanded infinitely slowly i.e., by a thermodynamically reversible process. At all stages in the expansion of the gas, dP being negligibly small the gas is maintained in a state of equilibrium throughout. If at any point of the process the pressure is increased by dP, the gas would contract reversibly (Fig 10.4 a).

On the other hand, the expansion is irreversible (Fig 10.4b) if the pressure on the piston is decreased suddenly. It moves upwards rapidly in a single operation. The gas is in equilibrium state in the initial and final stages only. The expansion of the gas, in this case, takes place in an irreversible manner.

10.5 STATE OF A SYSTEM

A thermodynamic system is said to be in a certain state when all its properties are fixed. The fundamental properties which determine the states of a system are pressure (P), temperature (T), volume (V), mass and composition. Since the change in the magnitude of such properties alters the state of the system, these are referred to as **state variables or state functions or thermodynamic parameters.**

In actual practice, it is not necessary to specify all the variables because some of them are interdependent. In the case of a single gas composition is fixed, because it remains always 100 percent. Further, if the gas is ideal and one mole of gas is under examination, it obey's the equation PV=RT, where R is universal gas constant. Hence it is clear that if only two of the three variables (P,V and T) are known, the third can easily be calculated. The two variables, generally specified, are temperature and pressure. These are called **independent variables.** The third variable, **generally volume, is said to be dependent variable**, as its value depends on the value of P and T. Thus, the thermodynamic state of a system consisting of a single gaseous substance may be completely defined by specifying any two of the three variables, viz. temperature pressure and volume.

In a closed system, consisting of one or more components, mass is not a state variable.

10.6 THERMODYNAMIC EQUILIBRIUM

A system in which the state variables have constant values throughout the system is said to be in a state of thermodynamic equilibrium. In fact, the term thermodynamic equilibrium implies the existence of three kinds of equilibrium in the system. These are (i) thermal equilibrium (ii) mechanical equilibrium and (iii) chemical equilibrium.

10.6.1 Thermal equilibrium

A system is said to be in thermal equilibrium if there is no flow of heat from one portion of system to another. This is possible if the temperature remains the same throughout in all parts of the system.

10.6.2 Mechanical equilibrium

A system is said to be in mechanical equilibrium if no mechanical work is done by one part of the system on another part of the system. This is possible if the pressure remains the same throughout in all parts of the system.

10.6.3 Chemical equilibrium

A system is said to be in chemical equilibrium if the composition of the system is uniform and there is not net chemical change.

Difference between reversible and irreversible processes.

	Reversible process	**Irreversible process**
1.	It takes place in infinite number of Infinitesimally small steps and it would take infinite time to occur.	It takes place in finite time.
2.	It is an imaginary process as it assumes the presence of frictionless and weightless piston.	It is real and can be performed actually.
3.	It is an equilibrium state at all stages of of the operation.	It is an equilibrium state only at the initial and final stages of equilibrium.
4.	All changes are reversed when the process is carried out in reverse direction.	After this type of process has occurred all changes do not Return in the initial state by themselves.

5. It is extremely slow.	It proceeds at measurable speed.
6. Work done by a reversible process is greater than the corresponding irreversible process.	Work done by an irreversible process is smaller than the Corresponding reversible Process.

10.7 NATURE OF HEAT AND WORK

Whenever a system changes from one state to another, there is always a change in energy. The change in energy may appear in the form of heat, work, light etc.

We shall refer the term ‘work’ for mechanical work which is defined as

Force X work.

James Joule, in 1850, showed that there is a definite relationship between mechanical work W and heat produced H (If we rub our palms together we feel the warmth).

$$W \alpha H \qquad \text{or} \qquad W=JH$$

J is known as the joule mechanical equivalent of heat.

In CGS system the unit of energy is erg. Which is defined as the work done when a resistance of one dyne is moved through a distance of one centimetre. Since erg is small quantity, a bigger unit, called joule (=10^7 ergs) is often used.

1 joule = 10^7 ergs

For large quantities of work we often use kilojoule (kj)

1 kj= 1000J

10.7.1 Unit of heat

The unit of heat, which is used for many years is calorie (cal). A calorie is defined as the quantity of heat required to raise the temperature of one gram of water by 1^0C in the vicinity of 15^0C. Since heat and work are interrelated, s1 unit of heat is the joule (J).

1 joule = 0.2390 calorie

1 calorie = 4.184 J

or 1 kcal = 4.184 kJ

10.7.2 Sign convention of heat

The symbol of heat is q. If the heat flows from the surrounding into the system to raise the energy of the system, it is taken to be positive, +q. If heat flows from the system to the surrounding, thus lowering the energy of the system, it is taken to be negative, – q.

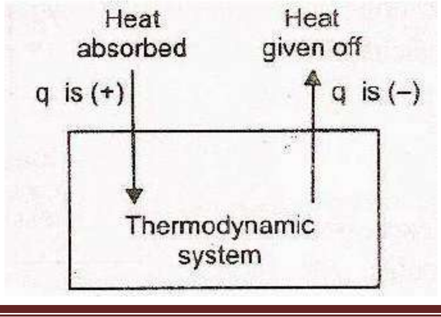


Fig 10.6 sign convention for heat flow in a thermodynamic system

10.7.3 Sign convention of work

The symbol of work is ω. If work is done on the system by the surroundings and the energy of the system is thus increased, it is taken to be positive, + ω. If work is done by the system on the surroundings and energy of the system is decreased, it is taken to be negative, -ω.

Thus we may summarise

Heat flows into the system,	q is +ve
Heat flows out of the system,	q is -ve
Heat is done on the system,	ω is +ve
Heat is done by the system,	ω is –ve

10.7.4 Pressure - volume work

As you know in physics mechanical work is defined as force multiplied by the distance through which the force acts. In elementary thermodynamics the only type of work generally considered is the work done in expansion (or compression) of a gas. This is known as pressure-volume work or PV work or expansion work.

10.7.5 Work done in reversible isothermal expansion

Consider a gas enclosed in a cylinder fitted with a weightless frictionless piston as shown in fig 10.7. The cylinder is not insulated. It is supposed to be in thermal equilibrium with the surroundings so that the temperature of the gas remains constant.

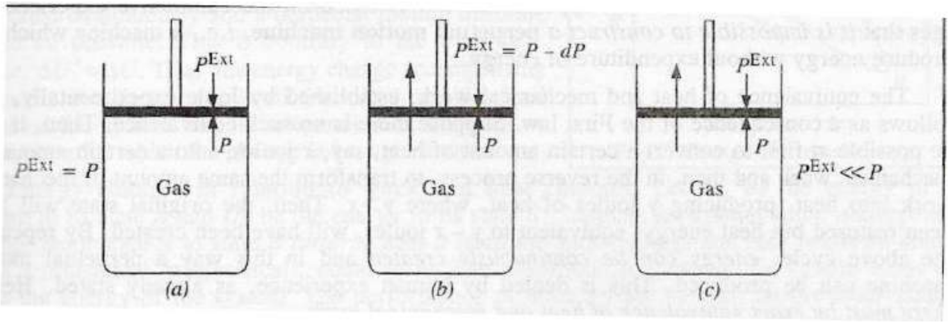


Fig 10.7 pressure volume work of a system

The external pressure on the piston is equal to the pressure of the gas within the cylinder as shown in fig 10.7 a. If the external pressure is lowered by infinitesimal amount dP that is it falls from P to P-dP fig 10.7b, the gas will expand by infinitesional volume dV, i.e., the volume changes from V to V+dV. As a result of expansion, the pressure of the gas within the cylinder falls to P-dP, i.e., it becomes again equal to external pressure. The piston then comes to rest.

If the external pressure is lowered again second time by the same infinitesimal amount dP, the gas will undergo the second infinitesimal expansion dV before the pressure again equals the new external pressure. The piston again comes to rest. The process is continued such that the external pressure is lowered by successive small amounts and, as a result, the gas undergoes a series of small successive increments of volume dV at a time.

It should be clear to you that since the system is in thermal equilibrium with the surroundings, the infinitesimally small cooling produced as a result of infinitesimally small expansion of the gas at each step, is offset by the heat absorbed from the surroundings and the temperature remains constant throughout the operation.

Since during expansion, pressure decreases and volume increases these two parameters are assigned opposite signs. The work done by the gas in an infinitesimal expansion is thus given by

$$d\omega = -(P-dP)(dV)$$

$$= -PdV \quad ....(1)$$

As the product dP.dV is neglected (both dP and dV being very very small).

The total work ω done by the gas in expansion, say from original volume V_1 to final value V_2, will be sum of the series of the terms PdV in which the pressure keeps on decreasing gradually. The result may be expressed mathematically as

$$W= -\int_{V_1}^{V_2} PdV \quad ....(2)$$

Where V_1 is the volume of the gas initial state and V_2 in the final state.

The above integral may be evaluates by substituting

P=RT/V for one mole of an ideal gas. Thus,

$$W= -RT\int_{V_1}^{V_2} \frac{dV}{V} = -RT\ln\frac{V_2}{V_1} \quad ....(3)$$

For an ideal gas $P_1V_1 = P_2V_2$, at constant temperature, the above equation may also be written as

$$W= -RT\,ln\,\frac{P_1}{P_2} \quad ....(4)$$

For n moles, the above expressions may be written as

$$W=-nRTln\frac{V_2}{V_1} = -nRT\,ln\,\frac{P_1}{P_2} \quad ....(5)$$

Since during expansion, V_2 is more than V_1 and P_2 is less than P_1, hence from equation (5) the work comes out to be negative in conformity with the convention used in this regard. When work is done by system it is taken as negative.

10.7.6 Work done in reversible isothermal compression

Now let us suppose the gas undergoes isothermal reversible compression from volume V_2 to V_1. The external pressure will now be made infinitesimally hiper than P, the pressure of the gas inside the cylinder. Let the external pressure be P+dP. There will be an infinitesimal contraction in volume, say dV, of the gas. Since during compression of gas, the pressure increases and the volume decreases, hence these two parameters are assigned opposite signs as before. Thus, the work done by the surroundings on the system for this infinitesimal step is given by

$$d\omega = -(P+dP)dV= -PdV \quad ....(6)$$

Ignoring the quantity dPdV as before.

If the compression is carried out reversibly in a series of steps from initial volume V_2 to final volume V_1, the work done ($\acute{\omega}$) by the surrounding on the gas will be given by

$$\acute{\omega} = -\int_{V_2}^{V_1} PdV \quad ....(7)$$

assuming the gas to be ideal, P as before, may be substituted by RT/V in the above equation so that

$$\acute{\omega} = -\int_{V_2}^{V_1} \frac{RT}{V} dV = -RT \int_{V_2}^{V_1} \frac{dV}{V} \quad \text{..........(8)}$$

$$= \; - RT \ln V_1/V_2 \quad \text{...........(9)}$$

$$= \; -RT \ln P_2/P_1 \quad \text{............(10)}$$

For n moles of the gas the above expression can be written as

$$\acute{\omega} = -nRT \ln V_1/V_2 = -nRT \ln P_2/P_1 \quad \text{.............(11)}$$

Since during compression, the initial volume V_2 is greater than the final volume V1 and also since the initial P_2 is less than the final pressure P_1, hence according to equation (11), the work done $\acute{\omega}$ comes out to be positive, as was chosen as a convention in this regard.

10.7.8 Work done in irreversible isothermal expansion

Suppose we have an ideal gas contained in a cylinder with a piston. This time the process of expansion of the gas is performed irreversible i.e., by instantaneously dropping the external pressure P^{ext} to the final pressure P_2. The work done by the system is now against the pressure P_2 throughout the whole expansion and is given by the following expression

Work = pressure x change of volume

$$W_{ir} = -\int dw$$

$$= -\int P^{ext} \times dV$$

$$= -\int_{V_1}^{V_2} P^{ext} dV$$

$$= -P^{ext}(V_2 - V_1) \quad \text{.................(12)}$$

Since P^{ext} is less than P_1 the work done during isothermal irreversible expansion is numerically less than the work done during reversible isothermal expansion in which P^{ext} is almost equal to P.

Now it should be clear to you that when there is free expansion that is when gas expands against zero pressure, work done will be zero.

10.8 STATE FUNCTION, EXACT AND INEXACT DIFFERENTIALS

State variables which are determined by the initial and final states of the system only and not by the path followed are called state functions. State variables which are determined or depend upon path followed are called path functions.

The state function is a property of a thermodynamic system which has a definite value for a particular state of the system. It is independent of the manner in which the state is reached. The change in the state function accompanying the change in the state of the system depends only on the initial and final states of the system and not on the path by which the change is brought about. Pressure, volume, temperature and energy are state functions. On the other hand work (ω) is not state function because the work done in a given change of state depends upon the manner in which the change is brought about. If the work is done reversibly its value is different than the value obtained irreversibly as you have seen above. And also work done would be zero if the gas expands in vacuum. First law equation ($\Delta E = q+w$), E is a definite quantity; hence if w is not a state function, q also is not a state function. Mathematically, this is expressed by saying that while the differential of energy, dE, is an exact differential, the differentials of heat and work, viz., dq and dw respectively, are inexact differentials. Exact differentials can be integrated between the appropriate limits. This cannot be done in the case of inexact differentials. Thus

$$\int_{E_1}^{E_2} dE = E_2 - E_1 \qquad \text{.....................(13)}$$

$$\text{But} \quad \int_{q_1}^{q_2} dq \neq q_2 - q_1 \text{ and } \int_{w_1}^{w_2} dw \neq w_2 - w_1 \qquad \text{..........(14)}$$

10.8.1 The Euler reciprocal relation

Let z be a state function of two independent variables x and y of the system, i.e., z=$\int(x, y)$. since z is state function, hence differential of z is an exact differential and can be written as

$$d_z = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$= M(x,y)dx + N(x,y)\,dy \qquad . \qquad \text{...........(15)}$$

$$\text{Where } M(x,y) = \left(\frac{\partial z}{\partial x}\right)_y \text{ and } N(x,y) = \left(\frac{\partial z}{\partial y}\right)_x \qquad \text{........(16)}$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x \partial y} \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial y \partial x}$$

Taking mixed second derivatives, we get –

Since $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$

Hence $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

This equation is known as Euler's reciprocal relation. This is applicable to state functions only. Since z is a state function. The finite change, Δz as the system passes from initial state A to final state B, is given by $\Delta z = z_B - z_A$

Also $\oint dz = 0$ where cyclic integral means that the system is in the same state at the end of its path as it was at the beginning, i.e., it has traversed a close path. Thus, dz is an exact differential.

10.9 SUMMARY

You have studied in this unit that thermodynamics is an important branch of chemistry which deals with energy transformation in all types of physical chemical process. In studying and evaluating the flow of energy into or out of a system it is useful to consider changes in certain properties of the system. These properties include temperature, pressure, volume and concentration of a system. Measuring the changes in these properties from the initial state to the final state, can provide information concerning changes in energy and related quantities such as heat and work.

10.10 TERMINAL QUESTIONS AND ANSWER

(A) Objective type questions:

1. Thermodynamics is applicable to
   (a) Microscopic systems only (b) macroscopic systems only
   (c) Homogeneous systems only (d) heterogeneous systems only
   Ans (b)
2. A gas contained in a cylinder fitted with a piston constitutes
   (a) An open system (b) A closed system
   (c) A heterogeneous system (d) An isolated system
   Ans (b)
3. A system that can transfer neither matter nor energy to and from its surroundings is called
   (a) an open system (b) a closed system
   (c) an isolated system (d) a heterogeneous system
   Ans (c)
4. The work differential dw is
   (a) a state function (b) an exact differential
   (c) an inexact differential (d) none of the above
   Ans (c)
5. Two moles of an ideal gas expands spontaneously into a vacuum. The work done is
   (a) 2 J (b) infinity (c) J (d) zero
   Ans (d)

(B) Short answer type questions:

6. Define the terms
   (a) Closed system
   (b) Extensive properties
   (c) Isothermal process
   (d) Ideal gas
7. Define and explain the following terms
   (a) Adiabatic process
   (b) Open and closed systems
   (c) Homogeneous and heterogeneous system
   (d) Zeroth law of thermodynamics

(C) Long answer type questions:

8 (a) Differentiate clearly between reversible and irreversible processes.
  (c) Calculate the work done in isothermal reversible explanation of an ideal gas.

9. Write notes on the following
   (a) Euler reciprocal relation
   (b) Sign convention of heat and work

(c) System and surroundings.

10. Differentiate between

(a) exact and inexact differentials
(b) homogeneous and heterogeneous systems
(c) intensive and extensive properties
(d) system and surroundings

****

UNIT 11: FIRST LAW OF THERMODYNAMICS

CONTENTS:

11.1 OBJECTIVES

Historically, the science of thermodynamics was developed to provide a better understanding of heat engines with particular reference to the conversion of heat into useful work. Thermodynamics is based on three generations, called the first, second and third law of thermodynamics. All these laws are based on human experience. There is no proof of these laws, but the results we get from these laws are always correct. All that one can say is that nothing contrary to these laws has been known to happen whenever we consider the behaviour of matter in bulk. Scientists are of the view that nothing contrary to these laws will ever be known.

11.2 INTRODUCTION

Most of the important generalisations of physical chemistry say Van't Hoff law of dilute solutions, Raoult's law of lowering vapour pressure, elevation in boiling point, lowering of melting point, distribution law, laws of thermochemistry and many more, can be deduced from the laws of thermodynamics.

Thermodynamics helps to lay down the criteria for predicting feasibility of a process, including a chemical reaction, under a given set of conditions. It also help us to determine the extent to which a process, including a chemical reaction can proceed before attainment of equilibrium.

You have studied in unit 10 that there is constant proportionality between heat and work.

$$W= JH$$

Where J is constant of proportionality between the work performed and the heat produced H, J is amount of work required to produce unit quantity of heat and it called the mechanical equivalent of heat.

In this unit you will study the origin of first law, its different consequences and other related topics.

11.3 FIRST LAW OF THERMODYNAMICS

Joule in his experiment, carried out the performance of work is diverse ways. The work was done by (a) agitating paddle wheels in a mass of water or mercury, (b) rubbing iron rings in mercury, (c) passing electricity through a wire of known resistance etc. The heat so produced was measured, latter on many workers namely Rowlands, Callender and Barnes, Laby and Hercus carried on the determination of the value of J with considerable accuracy. The accepted value of J is 4.1858×10^7 ergs per calorie.

This relation between heat and work is the origin of first law of thermodynamics. The first law can be enunciated as "If or whenever, heat is obtained from work the amount of heat produced is proportional to the work spent. There are many instances to show that not only heat can be converted into work but different form of energy are also interconvertible into one another. A given quantity of electrical energy which is comparatively easily measurable, was found to be equivalent to a definite amount of heat or mechanical work. You will study in this unit that such equivalent did not only exist between heat and work but between any two forms of energy.

Hence if

X units of energy A ≡ y units of energy B

Then mx units of energy A ≡ my units of energy B

The proportionality between quantities of two given forms of energy is universally constant and the constancy of this proportionality is essence of the first law.

The first law of thermodynamics is, in fact, an application of the broad principle known as the law of conservation of energy to the thermodynamics systems.

The first law of thermodynamics states that energy can neither be created nor destroyed, although in can be transferred from one form to another. Thus, whenever energy in one form disappears, an equal amount of energy in some other form must appear.

Since the disappearance of an amount of energy causes appearance of an equivalent amount of energy of another form, neither more nor less, we are compelled to accept that energy cannot be completely destroyed nor it can be created from nothing.

Clausius, therefore, enunciated that varied changes and transformation might occur but the total energy of the universe must remain constant, hence the first law of thermodynamics is really the law of conservation of energy.

11.4 INTERNAL ENERGY

Every substance is associated with a definite amount of energy which depends upon its chemical nature as well as upon its temperature, pressure and volume. Or by virtue of its pressure each substance is associated with certain amount of energy. This is known as internal energy of the system. This energy includes not only the translational kinetic energy of the molecules but also other molecular energies such as rotational, vibrational energies.

The total of all the possible kinds of energies of a system is called its internal energy.

The exact magnitude of this energy is not known because the chemical nature includes such factors as the translational, rotational and vibrational movements of the molecules, the manner in which the molecules are put together, the nature of the individual atoms, the arrangement and number of electrons, the energy possessed by the nucleus, etc. But, one thing is certain that the internal energy of a substance or a system is a definite quantity and it is a function only of the state (i.e., chemical nature, composition, temperature, pressure and volume) of the system at the given moment, irrespective of the manner in which that state has been brought about.

It is neither possible nor necessary to calculate the absolute value of internal energy of a system. In thermodynamics we concerned only with the energy changes when a system changes from one state to another. The amount of internal energy depends on the thermodynamics state and hence on thermodynamics parameters of the system. It is represented by E.

The internal energy is dependent on the internal structure and composition of the system. So, in a system of constant composition, the magnitude of E will depends upon other thermodynamics variables (P,V,T), any two of which may be regarded as independent variables. Thus,

E= f (P,T); or E=f (P,V), or E=f(V,T)

An explanation of the existence of the internal energy comes from the kinetic theory, the translator motion of the molecules, the vibrations and rotations of the atoms, the electronic revolutions etc. contribute to the internal energy.

11.5 INTERNAL ENERGY AND FIRST LAW OF THERMODYNAMICS

Suppose, a system is subjected to change of pressure and volume. Let the initial state is represented by A and the final state by B (fig. 11.1) and let E_A and E_B represent energies associated with the system in its state A and B

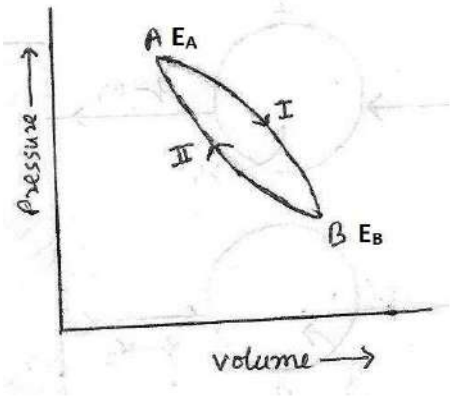


Fig 11.1 internal energy

respectively. These will be definite quantities as explained above. Then, the change in internal energy,

$$\Delta E = E_B - E_A$$

must be a definite quantity, irrespective of the path or the manner in which the change is brought about. If it were not so, it would again be possible to construct a perpetual motion machine, a machine which can produce energy without expenditure of energy. Suppose, that the system changes from state A to state B by following path I and is accompanied by change of energy equal to ΔE. Now suppose the same change of state is brought about by another path, say, path II and the change of energy is ΔE`. Suppose, ΔE >ΔE`, then coupling of these two processes:

$$A \xrightarrow{\qquad} B \text{ (by path I) and}$$

$$A \xrightarrow{\qquad} B \text{ (by path II)}$$

As shown in fig 11.1, the system would return to its initial state and at the same time a surplus of energy equal to ΔE-ΔE` would become available. By repeating the same cycle over and over again, energy would be generated continuously and a perpetual motion machine would be possible. This is contrary to the first law. Hence ΔE=ΔE`. Thus the energy change accompanying a process is a function only of the initial and the final states of the system and is independent of the path or the manner by which the change is brought about.

11.6 MATHEMATICAL STATEMENT OF THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is, in fact, an application of the broad principle known as law of conservation of energy to the thermodynamic system. It states that:

The total energy of an isolated system remains constant though it may change from one form to another.

Let us consider a system in a state A having internal energy E_A undergoing a change to a state B. During the transaction let the system absorbs a small amount of heat say q, then the net amount of energy of the system would become E_A+q. In the process of transformation, the system might have also performed some work W of any type. If E_B be the internal energy of the system at state B, then the net energy after the transformation would be E_B+W

Then from principle of conservation of energy, we clearly see

$$E_A + q = E_B + W$$

$$q = (E_B - E_A) + W = \Delta E + W$$

for infinitesimal change

$$\delta q = dE + \delta w \qquad \text{......(11.1)}$$

that is, heat taken up by a system would be equal to internal-energy increase of the system plus the work done by the system. This is mathematical statement of first law. Here E is state function hence its change is shown as dE and q, the heat supplied and w, the work obtained depends upon the path of the change, hence shown as δq and δw respectively.

Now a few comments may be made on the above equation

(a) If the system is an isolated one, so that there is no heat exchange with the surroundings, i.e., in an adiabatic process

$\delta q=0$

hence $\Delta E+W=0$

or $W= -\Delta E$ 11.2

that means the decrease in internal energy is exactly equal to the work done on the system by the surroundings.

(b) In a cyclic process, $\oint dE=0$

Hence $\oint \delta q = \oint dE+\oint \delta w$

or $\oint \delta q =\oint \delta w$ 11.3

The total work obtained is equal to the net heat supplied and no excess work can be obtained. Thus, establishes the impossibility of perpetual motion of the first kind, which is our experience.

(c) For an adiabatic process there is no change in heat gained or lost

i.e. $q=0$

Then $\Delta E= -W$ 11.4

That means the decrease in internal energy is exactly equal to work done on the system by the surroundings or we can say work is done at the expense of internal energy and internal energy will decrease.

(d) For an isobaric process there is no change in pressure, i.e., P remains constant. Hence

$\Delta E =q-W$

$=q-P\Delta V$ 11.5

11.7 *ENTHALPY OF A SYSTEM*

In a process carried out at constant volume (say in a sealed tube), the heat content of a system is the same as internal energy E, as no PV work is done. But in a constant-pressure process, the system (a gas) also expends energy in doing PV work. Therefore, total heat content of a system at constant pressure is equivalent to the internal energy E plus the PV energy. This is called enthalpy of the system and is represented by the symbol H. Thus enthalpy is defined by the equation.

$H=E+PV$ 11.6

Suppose the change of state of a system is brought about at constant pressure. In that case, there will be change of volume, let the volume increases from V_A to V_B at constant pressure P. Then the work done (W) by the system will be given by

$W= -P(V_B-V_A)$ 11.7

Substituting the value of W in equation 11.5 we have

$\Delta E = q + [-P(V_B-V_A)]$

$= q - P(V_B-V_A)$

$= q- PV_B+PV_A$ 11.8

If E_A be internal energy in the initial state aw E_B the internal energy at final state, then

$\Delta E = E_B-E_A$

So equation 11.8 becomes

$$E_B - E_A = q - PV_B + PV_A$$

$$E_B + PV_B = q + E_A + PV_A \qquad \text{................11.9}$$

As the quantity H=E+PV is known as enthalpy of the system. It represents the total energy stored in the system.

From equation 11.6 and 11.9

$$H_B = q + H_A$$

or $$q = (H_B - H_A) = \Delta H \qquad \text{................11.10}$$

Since H_B and H_A are definite quantities, it is evident that ΔH, like ΔE, is a definite quantity depending only on the initial and final states of the system. Obviously, ΔH represents increase in the enthalpy of a system when it changes from state A to state B.

Putting the value of q in equation 11.9 we get

$$E_B - E_A = \Delta H - PV_B + PV_A$$

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

$$\Delta H = \Delta E + P\Delta V \qquad \text{.....................11.11}$$

From equation 11.6 by definition of enthalpy

$$H = E + PV$$

Its differential form $dH = dE + PdV + VdP$

If a system undergoes a change at constant pressure then change in enthalpy,

$$dH_P = dE_P + PdV_P \qquad \text{.....................11.12}$$

the suffix P used to indicate constancy of pressure.

The first law states

$$\delta q = dE + \delta W \qquad \text{......................11.12a}$$

The work δW may be mechanical, electrical, chemical or any type. If we consider processes in which the entire work is mechanical, i.e., expansion or compression of the system, then δW would depend on the values P and V. Further, if the change of the system be carried out at constant pressure then,

$$\delta W_P = PdV_P$$

Hence from the first law, for change at constant pressure

$$\delta q_p = dE_P + \delta W_P = dE_P + PdV_P \qquad \text{..............11.13}$$

From equation 11.12 and equation 11.13

$$\delta qp = dH_P \qquad \text{..............11.14}$$

That is the increase in heat content of a system during a given transformation is the heat absorbed at constant pressure during the process.

11.8 RELATION BETWEEN ΔH AND ΔE

From equation 11.11

$$\Delta E = \Delta H - PdV$$

or

$$\Delta H = \Delta E + PdV \qquad \text{..........11.15}$$

This equation means when heat supplied to a system it is used in two ways (a) to increase the internal energy of the system and (b) secondly to perform some work (PdV)

If gases are involved in a reaction, they account for most of the volume change as the volumes of solids and liquids are negligibly small in comparison.

Suppose we have n_1 moles of gases before reaction and n_2 moles of gases after reaction. If we assume behaviour

$$PV_2 = n_2RT$$

and $$PV_1 = n_1RT$$

$$P(V_2-V_1) = (n_2-n_1)\, RT$$

$$P\Delta V = \Delta n\, RT$$ Δn is change in no. of moles.

Substituting this value in 11.11 we get

$$\Delta H = \Delta E + \Delta nRT$$

11.9 HEAT CAPACITY

If q amount of heat is given to a system of mass m, temperature is raised from T_1 to T_2. Then

$$q \propto (T_2-T_1)m$$

or $$q = m.C(T_2-T_1) \qquad \text{..........11.16}$$

here C is known as heat capacity of the system

If $m=1$ and $T_2-T_1=1$ then $q=C$, that means heat capacity is the amount of heat required to raise the temperature of unit mass of substance by one degree.

From eqn. 11.16 we have

$$C= q/m(T_2-T_1) \qquad \text{..........11.17}$$

When one mole is considered then

$$C= \frac{q}{T_2-T_1} = \frac{q}{\Delta T}$$

Then C is molar heat capacity

Since the heat capacity varies with temperature, hence the true molar heat capacity is defined by the differential equation.

$$C= \frac{dq}{dT} \qquad \text{.......11.18}$$

Where dq is a small quantity of heat absorbed by the system producing a small temperature rise dT.

Thus heat capacity may be defined as the ratio of the amount of heat absorbed to the rise in temperature.

From equation 11.17 it is clear that units of molar heat capacity are calorie per degree per mole (cal K^{-1} $mole^{-1}$) and in SI unit joule per degree per mole ($JK^{-1}mole^{-1}$)

It is found that amount of heat required by a system for one degree change depends upon the conditions in which the change occurs. That means heat capacity is not a state function two specific conditions are found to be very useful, whether heat is supplied at constant volume or at constant pressure.

11.9.1 Heat capacity at constant volume

As you have studied above that specific heat is amount of heat required to raise the temperature of the system by one degree. In case of solid and liquids there is very little or no change of volume when temperature is raised by an degree but in case of gases there is change of volume also. Thus if volume is kept constant heat capacity will have different value than in case pressure is kept constant.

Heat capacity at constant volume is the amount of heat required to raise the temperature of the system by one degree keeping volume constant it is denoted by c_v.

If one mole of gas is under consideration then it is molar heat capacity, defined as amount of heat required to raise the temperature of one mole of the gas by one degree at constant volume.

Molar heat at constant volume is represented as C_v.

From first law of thermodynamics

$$dq = dE + PdV$$

dividing both sides by dT we get

$$\frac{dq}{dT} = \frac{dE}{dT} + \frac{PdV}{dT}$$

At constant volume dV=0 so

$$\left(\frac{\delta q}{\delta T}\right)v = \left(\frac{\delta E}{\delta T}\right)v = C_v \qquad ....11.19$$

11.9.2 Heat capacity at constant pressure

If temperature is raised by one degree keeping the pressure constant, the amount of heat required is called heat capacity at constant pressure, denoted by C_p. If the system contains one mole of a substance then the molar heat capacity at constant pressure is C_p.

From first law of thermodynamics

$$\Delta q = dE + \delta w$$
$$= dE + PdV$$

dividing of dT

$$\frac{\partial q}{\partial T} = \frac{dE}{dT} + \frac{PdV}{dT}$$

We know H= E+ PV

$$\left(\frac{dH}{dT}\right) = \frac{dE}{dT} + \frac{d(PV)}{dT}$$

Keeping pressure constant

$$\left(\frac{\partial H}{\partial T}\right)p = \left(\frac{\partial E}{\partial T}\right)p + P\left(\frac{\partial V}{\partial T}\right)p$$

Hence $\left(\frac{\partial q}{\partial T}\right)p = \left(\frac{\partial H}{\partial T}\right)p = C_p$

Here in our discussion some times d has been written and in some cases ∂ (del) has been adopted for changes. The difference is that if we simply see the change in some property say, enthalpy with temperature we write $\frac{dH}{dT}$ but if put some restrictions, say if volume is kept constant then change in enthalpy with temperature will be $\left(\frac{dH}{dT}\right)_V$. Then $\left(\frac{dH}{dT}\right)_p$ means change in enthalpy when pressure is constant.

It is clear from the above that two heat capacities are not equal and Cp is greater than C_v by a factor which is related to the work done. At constant pressure part of heat absorbed by the system is used up in increasing the internal energy of the system and the other for doing work by the system. While at constant volume the whole of the heat absorbed is utilised in increasing the internal energy of the system as there is no work done by the system. Thus **C_p is greater than C_v.**

11.9.3 Internal energy change with volume and pressure

Gay Lussac and Joule carried out experiments to find out changes in internal energy of a gas. The experiment was very simple. As shown in fig 11.2, two containers A and B connected by a stop clock at the middle were taken and kept immersed in the water of a thermostat. Initially A was filled up with the gas and B was evacuated. When thermal equilibrium was established, the stopcock was opened and the gas passed into B. The flow continued until equilibrium was again reached. Since the gas expanded against zero pressure, no work was involved. $\delta w=0$. Very careful and repeated observations showed no change in temperature of the water in the thermostat. Hence $\delta q=0$. Yet the volume of the gas has changed. From the first law of thermodynamics we can say that

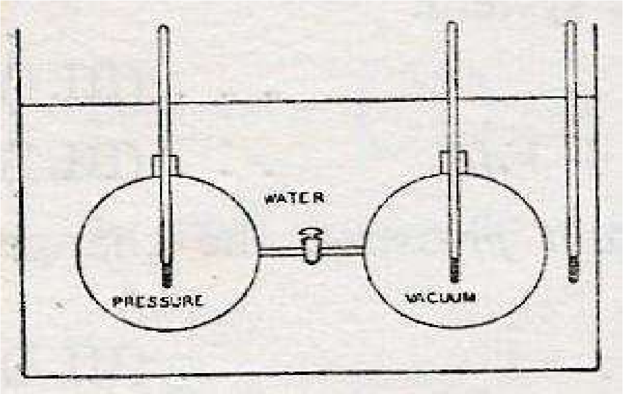


Fig 11.2 Joule's experiment

$$dE = \delta q - \delta w = 0$$

again $dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_v dT$

since $dT=0$ and $dE=0$

hence $\left(\frac{\partial E}{\partial V}\right)_T dV=0$

but $dV \neq 0$

that means $\left(\frac{\partial E}{\partial V}\right)_T =0$

$$\left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial E}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T$$

Again $\left(\frac{\partial P}{\partial V}\right)_T \neq 0$, hence $\left(\frac{\partial E}{\partial P}\right)_T =0$

We conclude $\left(\frac{\partial E}{\partial V}\right)_T =0, \left(\frac{\partial E}{\partial P}\right)_T =0$ 11.20

This is true for an ideal gas.

11.9.4 Relation between C_P and C_V

We know E=(V,T) (E is a function of volume and temperature)

Change in E can be written as

$$dE= \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT$$

dividing this equation by T and the keeping pressure constant we have

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial E}{\partial T}\right)_V \qquad .....11.21$$

As $C_P= \left(\frac{\partial H}{\partial T}\right)_P$ and $C_V=\left(\frac{\partial E}{\partial T}\right)_V$

Now $Cp- Cv = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V$

But H=E+PV

$$\left(\frac{\partial E}{\partial T}\right)_P = \frac{\partial}{\partial T}(E+PV)_P - \left(\frac{\partial E}{\partial T}\right)_V$$

$$= \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_v \qquad ......11.22$$

Putting the value of $\left(\frac{\partial E}{\partial T}\right)_P$ from equation 11.21 we get

$$C_P-C_V = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V$$

$$= \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$= \left(\frac{dV}{dT}\right)_P \left\{\left(\frac{\partial E}{\partial V}\right)_T + P\right\} \qquad ......11.23$$

This equation is generally applicable for an ideal gas

$$\left(\frac{\partial E}{\partial V}\right)_T =0$$

so $C_P-C_V = \left(\frac{\partial V}{\partial T}\right)_P .P$

As PV=RT

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

So $C_P - C_V = \frac{R}{P} P = R$ 11.24

11.10 JOULE-THOMSON EFFECT

If a gas is allowed to pass from a region of high pressure to low pressure region through a porous plug or through a narrow orifice and the system is thermally insulated, its temperature was lowered.

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure to a region of low pressure is known as Joule-Thomson effect or Joule-Kelvin effect.

11.10.1 Joule-Thomson experiment

The apparatus used by Joule and Thomson to measure the temperature change on expansion of a given volume of gas is shown in fig 11.3. An insulated tube is fitted with a porous plug in the middle and two frictionless pistons A and B on the sides. Let a volume V_1 of a gas at pressure P_1 be forced through the porous plug by a slow movement of piston A. The gas in the right-hand chamber be allowed to expand to volume V_2 and pressure P_2 by moving the piston B outward. The change in temperature is found by taking readings on two thermometers.

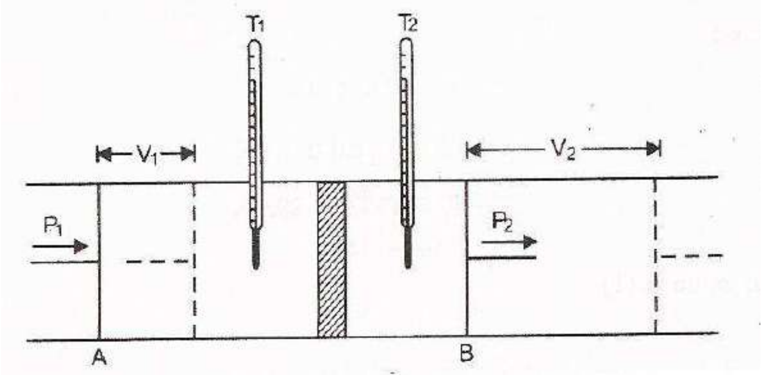


Fig 11.3 Joule Thomson experiment

Most gases were found to undergo cooling on expansion through the porous plug. Hydrogen and helium were exceptions as these gases showed a warming up instead of cooling.

11.10.2 Explanation

The work done on the gas (is pressure multiplied by the change in volume) at the piston A is (P_1V_1) (As initial volume on left hand side of the plug was V_1) and work done by the gas at the piston B is P_2V_2.

So,

Work done on the system at the piston A = P_1V_1 and work done by the system at piston B = P_2V_2

Net work done by the system = $P_2V_2 – P_1V_1$

$$w= P_2V_2- P_1V_1 \qquad .....11.25$$

From first law of thermodynamics

$$\Delta E = q-w$$

But the process is adiabatic and therefore q=0

Hence, $\Delta E= -w$ and $\Delta E=E_2-E_1$

So $E_2-E_1 = -w = -(P_2V_2 + P_1V_1)$

Rearranging the terms

$$E_2 +P_2V_2 = E_1 + P_1V_1$$

As $H=E+PV$

so $H_2=H_1$

Or, $\Delta H=0$ 11.27

Thus, the Joule-Thomson expansion of a real gas occurs not with constant internal energy, but with constant enthalpy. This is therefore called isoenthalpic process.

11.10.3 Joule-Thomson coefficient

The rate of change in temperature with pressure when enthalpy remains constant is called Joule-Thomson's coefficient, μ.

$$\mu =\left(\frac{\partial T}{\partial P}\right)_H \qquad .....11.28$$

If μ is positive there is cooling effect and if μ is negative it means heating effect will be there. In most of the cases at ordinary temperature cooling effect is there but hydrogen and helium get warmed up under similar conditions. We will discuss the reason later (when we will discuss inversion temperature).

In Joule-Thomson effect gas runs from high pressure to low pressure hence dP is negative. Hence μ will be positive if dT is also negative, i.e., if temperature falls. Whether μ is positive (cooling) or negative (heating) we can explain this in the following way. We know, H(enthalpy) is a function of temperature and pressure, so

$$H=\int(P,T)$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\delta H}{\partial T}\right)_P dT \qquad ......11.29$$

In an isoenthalpic change as in Joule-Thomson effect, dH=0

$$:. \qquad \left(\frac{\partial H}{\partial T}\right)_P dT = \left(\frac{\partial H}{\partial P}\right)_T dP$$

Dividing this equation by dP and keeping enthalpy (H) constant

We get

$$\left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H = - \left(\frac{\partial H}{\partial P}\right)_T$$

$$\left(\frac{\partial T}{\partial P}\right)_H = - \left(\frac{\partial H}{\partial P}\right)_T / \left(\frac{\partial H}{\partial T}\right)_P$$

$$\mu = -\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T \qquad .....11.30$$

since $\qquad H=E+PV$

$$\mu = - \frac{1}{Cp}\frac{\partial}{\partial P}(E+PV)_T$$

$$= - \frac{1}{C_p}\left(\frac{\partial E}{\partial P}\right)_T - \frac{1}{C_p}\{(\frac{\partial}{\partial P}(PV)\}_T \qquad ......11.31$$

This relation is applicable both to ideal and also to real gases. In the case of an ideal gas, both the terms on the right-hand side separately vanish. As for and ideal gas $\left(\frac{\partial E}{\partial P}\right)_T$ =0 (equation 11.20) and PV=RT hence $\frac{\partial}{\partial P}(PV)_T = 0$,

hence μ=0

A truly ideal gas has no J.T. coefficient.

Now let us discuss the case of a real gas. We can write equation 11.31 this way

$$\mu = - \frac{1}{C_p}\left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T - \frac{1}{C_p}\{\frac{\partial}{\partial P}(PV)\}_T \qquad ....11.32$$

In this equation $(\partial E/\partial V)_T$ of a gas is usually positive, while $(\partial V/\partial P)_T$ for any gas is always negative. As a result the first term is always positive. The magnitude of second term may be negative or may be positive. At low temperature and at low pressure, $\{\partial/\partial P\ (PV)\}_T$ is negative. Under such conditions both the terms in the equation being negative, μ has a positive value and cooling will be there in Joule-Thomson's experiment.

11.10.4 Inversion temperature

The cooling effect is observed at relatively low temperatures but if the temperature be high, then instead of cooling the gas become heated, i.e., in J.T. effect μ becomes negative. For every gas there is a temperature where μ=0, when neither heating nor cooing of the gas due to passage the porous plug would occur. This is called inversion temperature T_i of the gas. The value of T_i can be calculated to be equal to

$$\frac{2a}{Rb} = T_i \qquad ......11.33$$

So if a and b for a gas are known inversion temperature can be calculated. The inversion temperature for hydrogen is -80^0C and that of helium is -240^0C.

The Joule-Thomson effect support to the view that attractive forces do exist between gas molecules. As the gas expands, the molecules fall apart from one another. Therefore, work has to be done in order to overcome the cohesive or attractive forces which tend to hold the molecules together. This work is done by the system at the expense of the kinetic energy of the gaseous molecules. Consequently, the kinetic energy decreases and since this is proportional to temperature, cooling results. It may be noted that in this case no external work has been done by the gas in expansion.

11.11 REVERSIBLE WORK: ISOTHERMAL EXPANSION, ISOTHERMAL COMPRESSION AND ADIABATIC

11.11.1 Isothermal reversible expansion

From first law of thermodynamics we know energy neither be created nor destroyed, for an isolated system total energy always remains constant. Whole universe can be divided into very large number of isolated systems, for each isolated system energy remains constant, that means total energy of universe remains constant.

The mathematical representation of first law of thermodynamics

is $\delta q = dE + \delta w$, or $q = dE + w$

Which means when δq amount of heat is given to a system it is used up in two ways, first in increasing the internal energy dE of the system and secondly to perform certain amount of work δw. Here heat absorbed (or evolved) and work done (on the system or by the system) are not state functions, they depend on the path of transformation but internal energy does not depend upon path and hence it is a state function.

Let us consider a gas enclosed in a cylinder fitted with a piston (which is weightless and frictionless) as shown in fig 11.4. The cylinder is not insulated. The external pressure P on the piston is equal to the pressure of the gas within the cylinder, as shown in fig 11.4(a). If the external pressure is lowered by infinitesimal amount dP, that means pressure is now P-dP fig 11.4(b), the gas will expand by an infinitesimal volume dV, i.e., the volume changes (increases) from V to V+dV. As a result of expansion, the pressure of the gas within the cylinder falls from P to P-dP, i.e., it becomes again equal to external pressure. The piston then comes to rest.

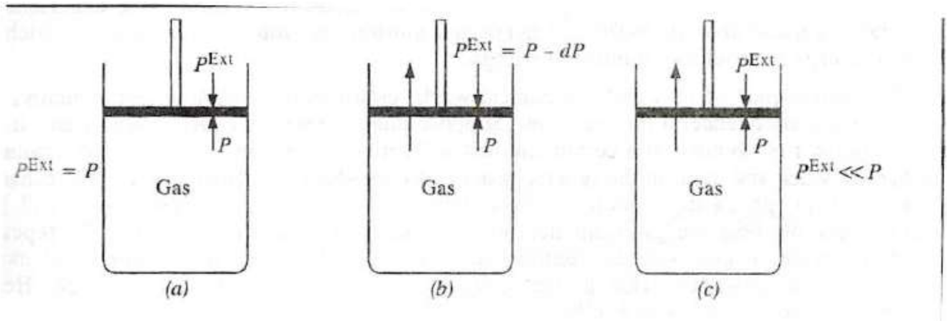


Fig 11.4 Isothermal reversible expansion work

If the external pressure is lowered again second time by the same infinitesimal amount dP, the gas will undergo the second very small expansion dV before the pressure again equals the new external pressure. The piston again comes to rest. The process is continued such that the external pressure is lowered by successive small amounts and, as a result, the gas undergoes a series of small successive increments of volume dV at a time.

Since the system is in thermal equilibrium with the surroundings, it is noted that the infinitesimally small cooling produced as a result of infinitesimally small expansion of the gas at each step, is offset by the heat absorbed from the surroundings and the temperature remains constant throughout the operation.

Work done by the gas in driving the piston upwards

$$= - (P-dP)dV$$

$$= - PdV \qquad \text{........11.34}$$

As dPdV is negligibly small and can be neglected the total work done by the gas, w in expansion from volume V_1 to volume V_2, will be sum of the series of the terms pdV in which pressure keeps on increasing gradually. The result may be expressed mathematically as

$$W= -\int_{V_1}^{V_2} PdV \qquad \text{..........11.35}$$

Where V_1 is initial volume and V_2 is volume in the final state.

As PV=RT hence

$$W= -\int_{V_1}^{V_2} \frac{RT}{V}\, dV$$

$$= -RT \text{ lm} \frac{V_2}{V_1} \qquad \text{............11.36}$$

As we know $P_1V_1 = P_2V_2$

$$W= -\text{ RT ln } P_1/P_2 \qquad \text{.............11.36}$$

For n moles the work above expression can be written as

$$W= -\text{ nRTln} \frac{V_2}{V_1} = -\text{ nRTln} \frac{P_1}{P_2} \qquad \text{..................11.37}$$

Since V_2 is greater than V_1 and P_1 is greater than P_2, it is clear from the above equation that W comes out to be negative meaning thereby that work is done by the gas.

11.11.2 Work done in isothermal reversible compression

Let us suppose the gas undergoes isothermal reversible compression from V_2 to V_1. The external pressure will now be made infinitesimally higher than P, the pressure of the gas inside the cylinder. Let the external pressure be P+dP. There will be infinitesimal contraction in volume, say dV, of the gas. Since during compression of a gas, the pressure increases and volume decreases, hence these two parameters are assigned opposite signs as before. Thus, the work done by the surroundings on the system for this infinitesimal step is given by

$$dW= = -(P-dP)dV$$

$$= - PdV \qquad \text{......11.38}$$

Ignoring the quantity dPdV, as before.

If the compression is carried out reversibly in a series of steps from initial volume V_2 to final volume V_1, the work done ω' by the surrounding on the gas will be given by

$$\omega' = -\int_{V_2}^{V_1} PdV \qquad \text{............11.39}$$

If the gas under consideration is ideal than P can be replaced by RT/V

$$\omega' = -\int_{V_2}^{V_1} \frac{RT}{V} dV$$

$$= -RT \ln \frac{V_1}{V_2}$$

$$= -RT \ln \frac{P_2}{P_1} \qquad ....11.40$$

For n moles of the gas the above expression can be written

as $$\omega' = -nRT\, ln\, \frac{V_1}{V_2} = \text{-nRT ln} \frac{P_2}{P_1} \qquad ....11.41$$

11.11.3 Maximum work

As we have discussed above, the work done by a gas during expansion is given by the product $P^{ext}\Delta V$ where ΔV is increase in volume. If the external pressure P^{ext} is only infinitesimally smaller than the pressure P of the gas (fig 11.4(b) then , expansion is said to place reversibly. If , however, the external pressure is much smaller than the gas pressure (fig 11.4 c), the expansion will take place rapidly, i.e., irreversibly and the work done for the same amount of expansion will be much smaller since P^{ext} is now much small than before. Taking the extreme case, if the external pressure is zero (i.e., the expand in vacuum) the work done will be zero. Hence, it follows that when a gas expands freely, i.e., when it expands against vacuum such that $P^{ext} =0$ no work is done by the gas.

Now it is clear from the above discussion that the magnitude of work done by a system on expansion depends upon the magnitude of opposing external pressure. The closer is the opposing pressure to the pressure of the gaseous system in the cylinder, the greater is the work performed by the system on expansion. In another words maximum work is obtained when the two opposing pressure differ only by an infinitesimal amount from each other. This condition is evidently demanded for a thermodynamically reversible process, as discussion earlier. Hence, the condition for maximum work concides with that for a thermodynamics reversibility.

11.11.4 Work done in isothermal irreversible expansion

Suppose we have an ideal gas contained in a cylinder with a piston. This time the process of expansion of the gas is performed irreversibly i.e., by instantaneously dropping the external pressure, P^{ext}, to the final pressure P_2. The work done by the system is now against the pressure P_2 throughout the whole expansion and is given by the following expression:

$$\omega = -P^{ext} \int_{V_1}^{V_2} dV$$

$$= -P_2 (V_2-V_1)$$

$$= -P_2 \, dV$$

In both the process, reversible and irreversible, the same state of the system has changed from the initial to the final state. The work done is smaller in irreversible expansion than the reversible expansion. Thus mechanical work is not a state function as it depends on the path by which the process is performed rather than on the initial and final states, it is a path function.

11.11.5 Adiabatic expansion

In adiabatic process no heat is allowed to enter or leave the system. Hence in an adiabatic system q=0. From equation 11.5

$$q= dE+w$$

or $$dE= -w \qquad ....11.42$$

since the work is done at the expense of internal energy, the internal energy of the system decreases and the temperature falls.

Let us consider one mole of an ideal gas at pressure P and volume V. For an infinitesimal increase in volume dV at pressure P the work done by the gas is –PdV. The internal energy decreases by dE, then from equation 11.42

$$dE = - PdV \qquad ....11.43$$

By definition of molar heat capacity at constant volume

$$dE = C_V \, dT \qquad ....11.44$$

From equation 11.43 and equation 11.44

$$C_V \, dT = - PdV = - \frac{RT}{V}dV \qquad \text{(gas being ideal)}$$

or $$C_V \frac{dT}{T} = - \frac{R}{V} dV$$

on integrating between limits when volume is V_1 temperature T_1 and when volume is V_2 temperature falls to T_2

$$\int_{T_1}^{T_2} Cv \frac{dT}{T} = - \int_{V_1}^{V_2} \frac{RdV}{V}$$

$$C_V \ln T_2/T_1 = -R \ln V_2/V_1$$

Since $R= C_P-C_V$ for an ideal gas we have:

$C_V \ln T_2/T_1 = -(C_P - C_V) \ln V_2/V_1$

$\ln T_2/T_1 = -\frac{C_P - C_V}{C_V} \ln V_2/V_1$ 11.45

the ratio of C_P/C_V is often written as γ (gama)

equation 11.45 then becomes

$\ln T_2/T_1 = -(\gamma - 1) \ln (V_2/V_1) = (\gamma - 1) \ln (\frac{V_1}{V_2})$

or $T_2/T_1 = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$

or $T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1}$

or $TV^{\gamma-1}$ =constant 11.46

we know $P_1V_1/T_1 = P_2V_2/T_2$

so $T_2/T_1 = P_2V_2/P_1V_1$

substituting the value of T_2/T_1 in equation 11.46 we get

$\frac{P_2V_2}{P_1V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$

or $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

or PV^{γ} = constant = K 11.47

This equation is known as adiabatic expansion ratio.

11.11.6 Calculation of dE, and dH

Calculation of ΔE

As we have studied earlier the molar heat capacity at constant volume of an ideal gas is given by

$C_V = (\frac{\partial E}{\partial T})_V$

Accordingly $dE = C_V\, dT$

And for a finite change $\Delta E = C_V\, dT$ 11.48

Calculation of ΔH

The enthalpy equation (equation 11.15) is given as

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

As $PV = RT$

$P\Delta V = R\Delta T$

So $\Delta H = \Delta E + R\Delta T$

$= (C_V\Delta T + R\Delta T)$ from equation 11.48

$= (C_v + R)\,\Delta T$

or $\Delta H = C_P\,\Delta T$ 11.49

11.12 SUMMARY

In the above discussion we have studied first law of thermodynamics and its consequences in detail. The various forms of first law of thermodynamics, various definitions, namely internal energy, enthalpy, heat capacity at constant volume, heat capacity at constant pressure, work done in reversible and irreversible processes and the difference between C_P and C_V have been discussed.

Most important of these in Joule-Thomson effect which is useful in producing low temperature or cooling. At the inversion temperature, there is no Joule-Thomson effect. If a gas under pressure passes through a porous plug and expands adiabatically into a region of very low pressure at the inversion temperature, there is neither fall nor rise of temperature. If, however the expansion takes place above the conversion temperature, there is small rise in temperature and if it takes place below the inversion temperature there is small fall of temperature.

11.13 TERMINAL QUESTIONS

(A) Objective type questions:

1. The mathematical relation for first law of thermodynamics is

(a) $\Delta E = q - w$ (b) $\Delta E = 0$ for a cyclic process

(c) $\Delta E = q$ for an isochoric process (d) All of these

Ans (d)

2. Heat capacity at constant pressure is the change in

(a) Internal energy with temperature at constant pressure.

(b) Internal energy with temperature at constant volume.

(c) Enthalpy with temperature at constant pressure.

(d) Enthalpy with temperature at constant volume.

Ans (c)

3. Which of the following is not correct?

(a) H=E+PV (b) H-E=PV

(c) H-E-PV=0 (d) H=E-PV

Ans (d)

4. The heat capacity at constant pressure is related with heat capacity at constant volume by the relation

(a) $C_P+R=w$ (b) $C_V-R=C_P$

(c) $C_P-R=C_V$ (d) $R-C_P=C_V$

Ans (c)

5. For an ideal gas Joule-Thomson coefficient is

(a) Positive (b) Negative (c) Zero

Ans (c)

(B) Short answer type questions:

6. Define molar heat capacity at constant volume and molar heat capacity at constant pressure.

7. State and explain first law of thermodynamics.

8. For an adiabatic process prove PV^{γ} = constant

9. Write a note on enthalpy and internal energy.

(C) Long answer type questions:

10. Derive expression for the work done in isothermal reversible expansion and isothermal reversible compression of an ideal gas. What is meant by maximum work.

11. (a) Give two definitions of first law of thermodynamics

(b) Calculate the work of expansion of one mole of an ideal gas at

25^0C under isothermal conditions, the pressure being changed from 1 to 5 atmosphere, given R=8.314 Joule.

12. What is Joule-Thomson effect? How do you account for it? Define inversion temperature. Show that Joule-Thomson coefficient is zero for an ideal gas.

****

UNIT 12: THERMOCHEMISTRY

CONTENTS:

12.1 INTRODUCTION

The chemical reactions are invariably accompanied by energy changes which, ordinarily, appear in the form of evolution or absorption of heat.

Thermochemistry is the branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions. The energy change that occurs in a chemical reaction is largely due to change of bond energy, i.e., change of potential energy that results from the breaking of bonds in reactants and formation of new bonds in products.

We have studied in unit 11 that every substance has a definite amount of energy known as intrinsic or internal energy, E. Its exact value cannot be determined but the change in internal energy, ΔE can be accurately measured experimentally.

When internal energy of reactants (E_r) is greater internal energy of products (E_P), the difference in internal energy, ΔE is released as heat energy.

$$\Delta E = E_{products} - E_{reactants}$$

or $$\Delta E = E_P - E_r$$

Such a reaction is called **exothermic reaction**. If the internal energy of the products (E_P) is greater than internal energy of reactants (E_r), heat is absorbed from the surroundings. Such a reaction is called **endothermic reaction**. The amount of heat released or absorbed in a chemical reaction is called the **heat of reaction**.

As we have discussed above the energy changes in chemical reactions are largely due to the breaking of existing bonds between the atoms and formation of new bonds. Thus thermochemistry provides useful information regarding bond energies.

12.2 HEAT OF REACTION

Thermochemical reactions are studied either at (a) constant volume or at (b) constant pressure. The magnitude of changes observed under the two conditions is different.

The change in internal energy (ΔE) is the heat change accompanying a chemical reaction at constant volume because no external work is performed. But at constant pressure there is change in the internal energy and work is also involved because of expansion or contraction. In the laboratory most of the chemical reactions are carried out at constant pressure (atmospheric pressure) rather than at constant volume. In order to study heat changes for reactions taking place at constant pressure and constant temperature, a new term enthalpy have been introduced.

As we have studied in unit- 11 the enthalpy of a system is defined as the sum of the internal energy and the product of its volume with pressure. That is

$$H=E+PV$$

Where H is enthalpy, E is internal energy, P is the pressure and V is the volume of the system. The term H is also called heat content.

Like internal energy enthalpy is also a state function and it is not possible to measure its absolute value. However a change in enthalpy (ΔH) accompanying a process can be measured accurately and is given by the expression.

$$\Delta E = H_{products} - H_{reactants}$$

$$= H_P - H_r$$

At constant pressure and temperature the change in the enthalpy ΔH will be equal to change in the internal energy ΔE and the work done in expansion or contraction PΔV

Hence $\Delta H = \Delta E + P\Delta V$ …………….12.1

Therefore, while heat change in a process is equal to its change in internal energy ΔE at constant volume, it gives at constant pressure the enthalpy change ΔH.

ΔE= heat change at constant volume

ΔH= heat change at constant pressure

For reactions involving solids and liquids only, the change in volume (ΔV) is very small and hence the term PXΔV is so small that it is neglected. For such reactions ΔE is equal to ΔH. In case of gases, we have to specify whether the reaction is taking place at constant pressure or at constant volume, because the value of PXΔV is appreciable. Most of such reactions are however, studied at constant pressure and change in enthalpy ΔH is involved.

12.3 EXOTHERMIC AND ENDOTHERMIC REACTIONS

Reactions that gives out heat, i.e., which are accompanied by evolution of heat, are called exothermic reactions. On the other hand the reactions which are accompanied by absorption of heat are called endothermic reactions.

Let us consider a general reaction at constant pressure

$$A+B \longrightarrow C+D$$

Suppose enthalpy of A is H_A, enthalpy of B is H_B, enthalpy of C is H_C and enthalpy of D is H_D then heat of reaction at constant pressure ΔH is equal to difference in enthalpy of the products and the reactants, i.e.,

$$\Delta H = H_{products} - H_{reactants}$$

$$= [H_C + H_D] - [H_A + H_B]$$

The value of heat of reaction ΔH may be zero, negative or positive. When ΔH is equal to zero, the enthalpy of reactants and products being the same, no heat is evolved or absorbed. In case ΔH is negative, the sum of enthalpies of the products is less than that of the reactants and the difference in enthalpy is given out in the form of heat.

Such reactions in which evolution of heat energy takes place are called **exothermic reactions**.

When ΔH is positive meaning there by, the enthalpy or heat content of the products is more than of the reactants, an equivalent heat is absorbed by the system from the surroundings.

Such reactions which are accompanied by absorption of heat are called

endothermic reactions.

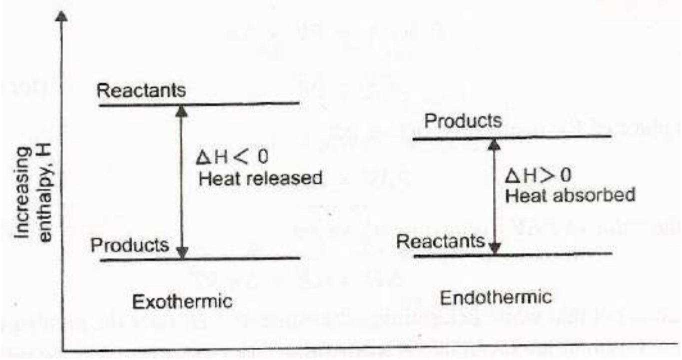


Fig 12.1 enthalpy diagram for an exothermic and endothermic reaction

Thus for an endothermic reactions $H_P > H_r$ and ΔH =+ve and for an exothermic reactions $HP < H_r$ and ΔH = -ve.

In chemistry, it is customary to represent thermochemical changes as,

For exothermic reaction: $HCl + NaOH = NaCl + H_2O + 13700$ cal

For endothermic reaction: $N_2 + O_2 = 2NO - 42000$ cal

That is, in case of heat-evolution, the quantity of heat evolved is written with the products with a positive sign. In heat absorption, the quantity of heat is written with the products with a negative sign.

Hence 13700 cal = $H_{(HCl+NaOH)} - H_{(NaCl+H_2O)}$

And -42000 cal=$H_{(N_2 + O_2)} - H_{(2NO)}$

In thermochimisty, the attention is concentrated on the system. In exothermic changes heat content or energy content of the system would diminish, in endothermic changes these would increase. Hence, we write

$HCl + NaOH = NaCl + H_2O$ $\Delta H = -13700$ cal

$N_2 + O_2 = 2\ NO$ $\Delta H = +42000$ cal

In these cases however ΔH_P and ΔH_v i.e., q_P and q_v would be equal, as there is no volume change involved. Now we take the following equation

$C_7H_8 + 9O_2 = 7CO_2 + H_2O$

In this case q_P = - 930 Kcal

q_v = -928.8 Kcal

12.4 RELATION BETWEEN ENTHALPY OF REACTION AT CONSTANT VOLUME AND AT CONSTANT PRESSURE

The quantities ΔH and ΔE are related to each other by the expression from equation 12.1 $\Delta H = \Delta E + P\Delta V$

Where ΔV is the change in volume that takes place in a given reaction.

Since $q_v = \Delta E$ and $q_p = \Delta H$

Then $q_p = q_v + P\Delta V$

for n moles of an ideal gas

$PV = nRT$

Suppose n_1 and n_2 represent the number of moles of gaseous reactants and gaseous products, respectively and suppose n_2 is greater than n_1. Then increase in number of gaseous moles = $n_2 - n_1 = \Delta n_g$

Then $P\Delta V = PV/n \; \Delta n_g = RT x \Delta n$ As $PV = nRT$

$P\Delta V = \Delta n_g RT$

Let us discuss, for example dissociation of ammonia into nitrogen and hydrogen.

$2NHO_3(g) \longrightarrow N_2(g) + \quad 3H_2(g)$

2 moles 1 mole 3 mole

$\Delta n_g = 4-2=2$

So $q_P = q_v + 2RT$

In the reaction involving combination of hydrogen and nitrogen

$2H_2(g) + \quad O_2(g) \longrightarrow 2H_2O(g)$

2 moles 1 mole 2 moles

$\Delta n = 2-3=-1$

$q_P = q_v - RT$

Since in reactions involving only solids and liquids, ΔV is negligible, $q_P=q_v$, i.e., the enthalpy of reaction at constant pressure is almost the same as the enthalpy of reaction at constant volume.

12.5 FACTORS AFFECTING HEAT OF REACTION

There are some factors which affect the quantity of heat evolved or absorbed during a physical or chemical transformation. These factors are:

(1) At constant pressure or at constant volume
(2) Physical state of reactants and products.
(3) Amount of reactants and products.
(4) Temperature.
(5) Pressure.

The physical states in a thermochemical reaction are represented by the symbols (s), (l), (g) and (aq) for solid, liquid, gas and aqueous states respectively.

Consider a reaction

$H_2 + ½\, O_2 \rightleftarrows H_2O \qquad H = -\ 68.32$ kcal

This reaction indicates that when one mole of hydrogenreacts with 0.5 mole of oxygen, one mole of water is formed and 68.32 kcal of heat is evolved at constant pressure. If two moles of hydrogen are burnt, the heat evolved would be 2x68.32 kcal. This equation is not complete thermochemical equation because it does not specify water is in the form of steam or liquid. There is difference in the value of H if water is in the liquid or gaseous state as given below.

$H_2(g) + ½\, O_2(g) \longrightarrow H_2O_{(l)}\ ; \Delta H = -\ 68.32$ kcal

And $H_2(g) + ½\, O_2(g) \longrightarrow H_2O_{(g)}\ ; \quad \Delta H = -\ 57.80$ kcal

12.6 ENTHALPY OF REACTION OR HEAT OF REACTION

The heat of reaction is simply the amount of heat absorbed or evolved in the reaction. As we know that amount of heat absorbed or evolved at constant temperature and pressure is called enthalpy. Hence the amount of heat change during a reaction at constant pressure and temperature may also be called enthalpy change. **Heat of reaction may be defined as the amount of heat absorbed or evolved in a reaction when number of moles of reactants as represented by the balanced chemical equation change completely into the products.**

It is very important to note that heat of reaction varies with change in temperature. Hence we must mention the temperature at which the reaction is taking place. It is also convenient for comparison to fix up some temperature as standard or reference. By thermodynamic convention, the state of a substance at 298K and one atmosphere pressure is taken as its standard state. The heat change accompanying a reaction taking place at 298K and one atmosphere pressure is called standard heat change or standard enthalpy change. It is denoted by ΔH^0.

12.7 VARIATION OF HEAT OF REACTION WITH TEMPERATURE

The heat of reaction changes with change in temperature of a gas due to variation in its specific heat.

The equation representing the variation of heat change of reaction with temperature is known as Kirchoff's equation.

At constant volume, the heat of reaction, ΔE, is given by the relation

$$\Delta E = E_2 - E_1$$

Where E_2 is internal energy of products and E_1 is the internal energy of reactants.

Differentiating this equation with respect to temperature keeping volume constant we get

$$\left[\frac{\partial}{\partial T}(\Delta E)\right]_v = (\partial E_2/\partial T)_v - (\partial E_1/\partial T)_v \quad \text{........12.2}$$

But we know $\frac{\partial E}{\partial T} = C_v$

Hence $$\left[\frac{\partial}{\partial T}(\Delta E)\right] = (C_v)_2 - (C_v)_1 \quad \text{...12.3}$$

$$= \Delta C_v$$

Here $(C_v)_2$ is heat capacity of products and $(C_v)_1$ is heat capacity of reactants.

On integrating the above equation between the limits T_1 and T_2 and keeping in view that when temperature is T_1 heat of reaction is ΔE_1 and when temperature is T_2 heat of reaction is ΔE_2

$$\int_{\Delta E_1}^{\Delta E_2} d(\Delta E) = \int_{T_1}^{T_2} \Delta C_v dT$$

or $\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)$ 12.4

Similarly heat of reaction at constant pressure is given by the relation.

$\Delta H = H_2 - H_1$ 12.5

Where H_2 aw H_1 are heat content or enthalpy of products and reactants respectively.

Differentiating equation 12.5 with respect to temperature at constant pressure.

$$\left[\frac{\partial}{\partial T}(\Delta H)\right]p = (\partial H_2/\partial T)\,p - \partial H_1/\partial T)\,p$$

We have

$= (C_P)_2 - (C_P)_1 = \Delta C_p$ 12.6

Here $(C_P)_2$ and $(C_P)_1$, are the heat capacities of products and reactants respectively.

or $d(\Delta H) = \Delta C_p dT$

integrating the equation between temperature T_1 and T_2

we have

$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta Cp dT$

$= \Delta C_p (T_2 - T_1)$ 12.7

The relations (12.3), (12.4), (12.6) and (12.7) were first derived by Kirchoff and are called Kirchoff's equations.

These equations are used to calculate heat of reaction at a given temperature provided heat of reaction at some other temperature and when the heat capacities of products and reactants are known.

12.8 DIFFERENT TYPES OF HEAT OF REACTION (ENTHALPY OF REACTION)

Heat of formation

The change in enthalpy that takes place when one mole of the compound is formed from its elements is known as heat of formation. It is denoted by ΔH_f. For example the heat of formation of ferrous oxide may be expressed as

$$Fe_{(s)} + S_{(s)} \longrightarrow Fe\,S_{(s)} \qquad \Delta H_f = -24.0 \text{ kcal}$$

This equation can be explained as, one mole of Fe (in solid from) reacts with one mole of sulphur (in solid form) to form one mole of ferrous sulphide (in solid form) and 24 kcal heat in evolved.

The reaction between gaseous hydrogen and gaseous chlorine to form gaseous hydrogen chloride is represented by the equation.

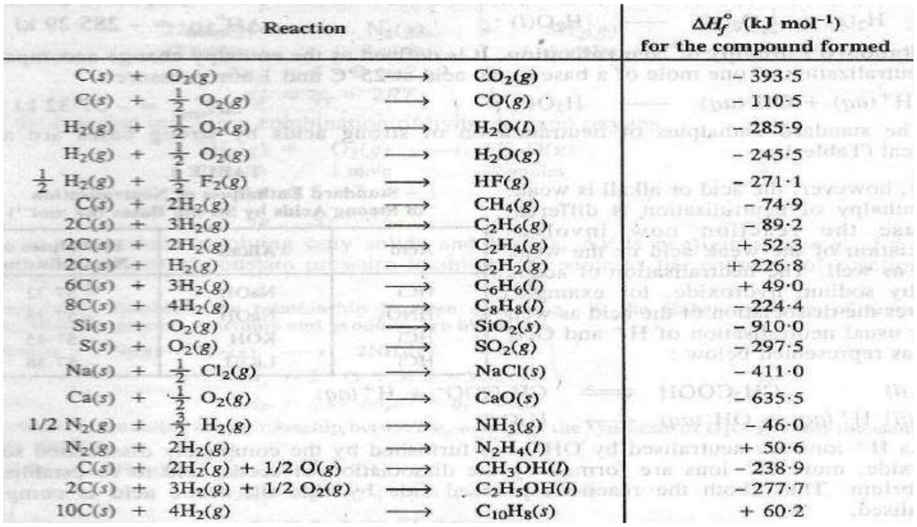
$$H_2(g) + Cl_2(g) \longrightarrow 2H\,Cl(g) \quad \Delta H= -44 \text{ kcal}$$

This equation means one mole of gaseous hydrogen reacts until one mole of gaseous chlorine to form two moles of gaseous hydrogen chloride and 44 kcal heat is evolved. It may be noted in this case that 44 kcal is not heat of formation of HCl because this amount of heat is evolved when two moles of hydrogen chloride are formed. The heat of formation of hydrogen chloride would be - 44/2= - 22 kcal and the equation can be written as

$$\tfrac{1}{2} H_2(g) + \tfrac{1}{2} Cl_2(g) \longrightarrow HCl(g) \qquad \Delta H = -22 \text{ kcal}$$

Standard heat of formation

The standard heat of formation, $\Delta H^0{}_f$, is the enthalpy change when one mole of a substance is formed from its elements in their standard states. That is all substances are at 298K and one atmosphere pressure. $\Delta H^0{}_f$ values may be exothermic or endothermic.



Reaction	ΔH_f° (kJ mol^{-1}) for the compound formed
$C(s) + O_2(g) \longrightarrow CO_2(g)$	– 393·5
$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$	– 110·5
$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$	– 285·9
$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$	– 245·5
$\frac{1}{2} H_2(g) + \frac{1}{2} F_2(g) \longrightarrow HF(g)$	– 271·1
$C(s) + 2H_2(g) \longrightarrow CH_4(g)$	– 74·9
$2C(s) + 3H_2(g) \longrightarrow C_2H_6(g)$	– 89·2
$2C(s) + 2H_2(g) \longrightarrow C_2H_4(g)$	+ 52·3
$2C(s) + H_2(g) \longrightarrow C_2H_2(g)$	+ 226·8
$6C(s) + 3H_2(g) \longrightarrow C_6H_6(l)$	+ 49·0
$8C(s) + 4H_2(g) \longrightarrow C_8H_8(l)$	– 224·4
$Si(s) + O_2(g) \longrightarrow SiO_2(s)$	– 910·0
$S(s) + O_2(g) \longrightarrow SO_2(g)$	– 297·5
$Na(s) + \frac{1}{2} Cl_2(g) \longrightarrow NaCl(s)$	– 411·0
$Ca(s) + \frac{1}{2} O_2(g) \longrightarrow CaO(s)$	– 635·5
$1/2\ N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(g)$	– 46·0
$N_2(g) + 2H_2(g) \longrightarrow N_2H_4(l)$	+ 50·6
$C(s) + 2H_2(g) + 1/2\ O(g) \longrightarrow CH_3OH(l)$	– 238·9
$2C(s) + 3H_2(g) + 1/2\ O_2(g) \longrightarrow C_2H_5OH(l)$	– 277·7
$10C(s) + 4H_2(g) \longrightarrow C_{10}H_8(s)$	+ 60·2

Table 12.1 Standard heat of formation of some common compounds

Determination of enthalpy of reaction

Enthalpies of reaction at 25^{0}C (298K) can be determined if $\Delta H^0{}_f$ of reactants and products involved in the reactions are known since

$$\Delta H^0 = \Delta H^0{}_f \text{ (products)} - \Delta H^0{}_f \text{ (reactants)}$$

By convention, ΔH^0_f values for elements in their standard states are taken as zero. This aspect has been shown in the following example.

Example: Calculate ΔH^0 for the equation

$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$ given that ΔH^0_f for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are -393.5, -111.31 and -241.80 kJ mole^{-1} respectively.

$\Delta H^0 = \Delta H^0_f$ (products)- ΔH^0_f(reactants)

$= [\Delta H^0_f\, CO(g) + \Delta H^0_f\, H_2O(g)] – [\Delta H^0_f\, CO_2(g) + \Delta H^0_f\, H_2(g)]$

$= -111.31 – 291.80 – (-393.5-0)$

$= -353.11+393.5$

$= 40.4$ kJ

12.9 HEAT OF COMBUSTION

Heat of combustion of a substance is change in enthalpy when one mole of substance is completely burnt in excess of oxygen. Heat of combustion is denoted by ΔH_C. Thus combustion of methane shown as

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + H_2O(l) \qquad \Delta H_C = -87.78$ kJ

Combustion of hydrogen similarly can be represented as

$H_2(g) + ½\, O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_C = -285.29$ kJ.

Now let us consider the following chemical equations.

$C_{(S)} + ½\, O_{2(g)} \quad CO_{(g)} \longrightarrow \qquad \Delta H =-26$ kcal ....(A)

$C_{(S)} + O2_{(g)} \longrightarrow CO_{2(g)} \qquad \Delta H =-94.3$ kcal ....(B)

It may be noted that -94.3 kcal is the heat of combustion of carbon as combustion is complete in equation (B). In the first case (A) carbon has been converted into carbon monoxide and by no means completely oxidised, it can be further oxidised to carbon dioxide.

12.10 USES OF HEAT OF COMBUSTION

(i) Calculation of heat of formation

The heat of combustion of organic compounds can be easily determined, these are employed to calculate their heat of formation.

Example : The enthalpy of combustion of glucose $C_6H_{12}O_{6(S)}$ is -2816 kJ. Heat of formation of $CO_{2(g)}$ and $H_2O_{(l)}$ are -393.5 kJ mole^{-1} and -285.9 kJ mole^{-1} respectively. Calculate the heat of formation of glucose.

Ans. We have to calculate

$$6C_{(S)} + 6H_{2(g)} + 3O_{2(g)} \longrightarrow C_6H_{12}O_6(S) \Delta H=?$$

Given that

(1) $C_6H_{12}O_6(S) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g) \Delta H= -2816kJ$

(2) $C_{(S)} + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H=-393.5$ kJ

(3) $H_2(g) + ½ O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -285.9$ kJ

Multiplying eqn.(2) by 6 and equation (3) by 6 and adding

We get

(4) $6 C_{(S)} + 6 O_{2(g)} + 6H_{2(g)} + 6/2 O_{2(g)} \longrightarrow 6 CO_{2(g)} + 6H_2O_{(l)}$

$$\Delta H = - 6x393.5-6x285.9$$

$$= -4086.4 \text{ kJ}$$

Subtracting eqn (1) from eqn (4) we get

$$6C_{(S)} + 6O_{2(g)} + 6H_{2(g)} + 3O_2 - C_6H_{12}O_6^{(S)} = 6CO_{2(g)} + 6H_2O_{(l)} - 6O_{(l)}$$

$$\Delta H = - 4076.4+2816$$

$$= - 1260.4$$

Hence $6C_{(S)} + 3O_2 + 6H_{2(g)} \quad C_6H_{12}O_{6(S)}, \longrightarrow \Delta H= - 1260.4$

So heat of formation glucose is – 1260.4 kJ

(ii) Calorific value of foods and fuels

The amount of heat produced when one gram of substance is completely burnt is known as calorific value of food or fuel efficiency.

It is expressed in cal per gram or kcal per gram or kJ per gram.

Methane has better fuel efficiency than ethane as it produces more heat per gram. It can be explained by comparing heat of combustion of methane and ethane. Heat of combustion of methane is -890.3 KJ and that of ethane is – 1559.7 KJ

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 3H_2O_{(l)} \qquad \Delta H = - 890.3 \text{ kJ}$$

and $C_2H_{6(g)} + 3/2\ O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\Delta H = -\ 1559.7$ kJ

for methane heat produced per gram is $-\frac{890.3}{16}$

$= -\ 55.64$ kJ g^{-1} and for ethane heat produced per gram

is $-\frac{1559.7}{30} = -\ 51.90$ kJg^{-1} (molecular weight of methane is 16 and that of ethane is 30). Thus methane has better fuel efficiency than ethane as it produces more heat per gram.

(iii) Deciding constitution

Heat of combustion of organic compounds is to a large extent an additive property as shown by the fact that in a homologous series the difference between the heats of combustion of successive members is nearly constant and its equal to 158 cals. Constants corresponding to the heats of combustion of various atoms and linkages have been worked out. The heat of combustion of an organic substance can be calculated from its probable structural formula by adding up the values of the constants corresponding to the atoms and linkages involved therein. If the value so obtained comes out to be the same as the experimental value of the heat of combustion of the compound, the assumed formula must be correct.

12.11 HEAT OF SOLUTION

When a substance is dissolved in a solvent heat changes are usually observed. When reaction takes place in solution, heat of solution of reactants and products must be taken into account.

The heat of solution is defined as:

The change in enthalpy when one mole of substance dissolved in a specific quantity of solvent at a given temperature. If a substance is dissolved in a solvent certain amount of heat is evolved or absorbed. If the solution is further diluted, there will be again be change in enthalpy. If we go on diluting the solution, a stage will come when further dilution produces no thermal effect. This is called the state of infinite dilution. To avoid the quantity of the solvent, we have to incorporate the idea of infinite dilution in the definition which may be stated as:

The heat of solution is the change in enthalpy when one mole of substance is dissolved in a solvent so that further dilution does not give any change in enthalpy. Thus

$$KCl_{(S)} + H_2O_{(l)} \longrightarrow KCl_{(ag)}\ \Delta H = -4.4\ \text{kcal}$$

$$MgSO_{4(S)} + H_2O(l) \longrightarrow MgSO_{4(ag)} \quad \Delta H = -20.28\ \text{kcal}$$

The heat of solution of an electrolyte may be due to energy change involved during ionisation or some hydrate formation as in sulphuric acid. Usually heat is absorbed when ions are torn apart from each other in the process of solution and heat is evolved during hydrate formation.

12.12 HEAT OF NEUTRALISATION

The change in heat content (enthalpy) of the system when one gram equivalent of an acid is neutralised by one gram equivalent of base or vice versa in dilute solution is known as heat of neutralisation.

Following are some examples of the heat of neutralisation

$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O(l) \quad \Delta H = -13.68$ kcal

$HNO_{3(aq)} + NaOH_{(aq)} \longrightarrow NaNO_{3(aq)} + H_2O(l) \quad \Delta H = -13.69$ kcal

$HNO_{3(aq)} + KOH_{aq)} \longrightarrow KNO_{3(aq)} + H_2O(l) \quad \Delta H = -13.87$ kcal

From these equations written above it is observed that heat of neutralisation of a strong acid and strong base is – 13.7 kcal. This can be explained with the help of theory of ionisation. If HA and BOH represent any strong acid and strong base respectively and equivalent amount of these in dilute solution be mixed, we have

$H^+ (aq) + A(aq) + B(aq) + OH(aq) \longrightarrow A(aq) + B(aq) + H_2O(l) \quad \Delta H = -13.7$ Kcal

Hence $H^+_{(aq)} + OH_{(aq)} \longrightarrow H_2O\ (l) \quad \Delta H = -13.7$ kcal

Thus the heat of neutralisation of an acid and a base is merely heat of formation of water from hydrogen and hydroxyl ions.

If, however, the acid or alkali is weak, the enthalpy of neutralisation is different because the reaction now involves dissociation of weak acid or weak alkali as well the neutralisation of acetic acid with sodium hydroxide, for example, involves the dissociation of the acid as well as the usual neutralisation of H^+ and OH^- ions as represented below.

(i) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
(ii) $H+ (aq) + OH (aq) \longrightarrow H_2O\ (l)$

As H^+ ions are neutralised by OH^- ions furnished by the completely dissociated sodium hydroxide, more H^+ ions are formed by the dissociation of acetic acid to re-establish the equilibrium. Thus, both the reactions proceed side by side till acetic acid is completely neutralised.

The enthalpy of neutralisation of acetic acid by sodium hydroxide has been found to be -13.2 kcal. Since the average value for the combination of H^+ and OH^- ions is taken as -13.7 kcal, the enthalpy of dissociation of acetic acid may be taken as 0.5 kcal.

The heat of dissociation of a weak acid or weak base may be defined as the change in enthalpy of the system when one mole of it is dissociation into ions.

12.13 SOME OTHER DEFINITIONS

12.13.1 Heat of fusion

Heat of fusion is defined as the heat change (or enthalpy change) when one mole of solid substance is converted into liquid state at its melting point.

$H_2O(s) \longrightarrow H_2O\ (l)$ $\Delta H=+1.43$ Kcal

Ice water

Here ice melt at 273K and change into liquid water by absorbing 1.43 kcal heat. It is found that greater the heat of fusion of a substance higher the magnitude of intermolecular forces.

12.13.2 Heat of vaporisation

The heat of vaporisation is defined as:

Change in enthalpy when one mole of liquid is converted into vapour or gaseous state at its boiling point.

For example one mole of water is converted into steam at 100^0C or 373K, the heat absorbed is 9.71 kcal which is heat of vaporisation of water.

$H_2O\ (l) \longrightarrow H_2O(g)$: $\Delta H=9.71$ Kcal

Water steam

12.13.3 Heat of sublimation

In sublimation process a solid change directly into gaseous state without changing into liquid state. Sublimation occurs at a temperature below the melting point of solid.

Heat of sublimation is defined as the enthalpy change when one mole of solid is directly converted into gaseous state at a temperature below its melting point.

For example, the heat of sublimation of iodine is 14.92 kcal per mole. It can be represented as:

$$I_2(s) \longrightarrow I_2(g) \qquad \Delta H=14.92 \text{ kcal}$$

12.13.4 Heat of transition

The change in enthalpy when one mole of an element changes from one allotropic form to another is known as heat of transition.

For example transition of diamond into amorphous carbon be represented as:

$$C_{diamond} \longrightarrow C_{amorphous} \qquad \Delta H=3.3 \text{ kcal}$$

Similarly

$$P_{white} \longrightarrow P_{red} \qquad \Delta H=-1.028 \text{ kcal}$$

12.14 HESS'S LAW OF CONSTANT HEAT SUMMATION

The energy changes accompanying chemical processes are governed by a general principle known as Hess's law. This law states that the amount of heat involved or absorbed in a process is the same whether the process takes place in two or more different ways in one step or in several steps.

Let us suppose that a substance A can be changed to Z directly.

$$A \longrightarrow Z+Q_1 \quad : \qquad \Delta H_1= -Q_1$$

Where Q_1 is the heat involved in the direct change.

When the same change is brought about in stages:

$$A \longrightarrow B+q_1 \qquad \Delta H_2= -q_1$$

$$B \longrightarrow C+q_2 \qquad \Delta H_2 = - q_2$$

$$C \longrightarrow Z+q_3 \qquad \Delta H_3 = - q_3$$

The total evolution of heat $q_1+q_2+q_3 = Q_2$

According to Hess's law $Q_1=Q_2$. If it is not so, let $Q_2>Q_1$. Then by transforming A to Z through stages and Transforming directly back to A, there would be a gain of heat energy= Q_2-Q_1. By repeating the process again and again unlimited heat energy will be developed in an isolated system. This goes against the first law of thermodynamics. Hence Q_1 must be equal to Q_2

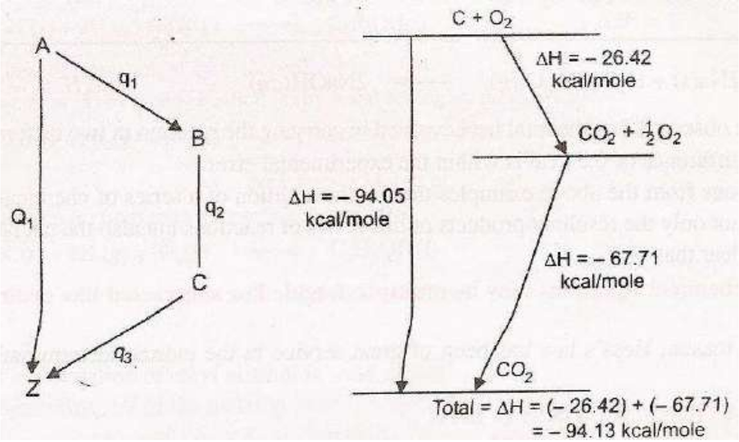


Fig 12.2 Illustration of Hess's law

Examples of Hess's:

Burning of carbon to carbon dioxide:

Carbon can be burnt to carbon dioxide directly or it may first changed to carbon monoxide which may then be oxidised to carbon dioxide.

Ist way $C_s + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -94.05$ kcal

2nd way $C(s) + ½ O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -26.42$ kcal

$CO(g) + ½ O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -67.71$ kcal

Overall change $C(s)+O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -94.1$ k cal

It is shown in fig 12.2

12.14.1 Application of Hess's law

(i) Calculation of enthalpy of reaction:

With the help of Hess's law it is possible to calculate enthalpies of many reactions which cannot be determined experimentally. For example, it is extremely difficult to measure the heat evolved when carbon burns in oxygen to form carbon monoxide.

$C(s)+ ½ O_2(g) \longrightarrow CO(g)$: $\Delta H=?$

From the Hess's law it is known that the heat evolved in the combustion of one mole carbon dioxide is same, viz whether the reaction takes place in single step as

$C_{(S)}+ O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -94.05$

or in two steps as

$$C_{(S)}+1/2\ O_2(g) \longrightarrow CO(g) \qquad \Delta H= x\ \text{kcal (say)}$$

$$CO(g)+1/2\ O_2(g) \longrightarrow CO_2(g)\ \Delta H= y\ \text{kcal (say)}$$

Although x, the heat change involved in the combustion of carbon monoxide cannot be determined easily, y, the heat change involved in the combustion of carbon monoxide to give carbon dioxide can be measured and has been found to be -67.71 kcal. According to Hess's law

$$x+y = -94.05\ \text{kcal}$$

$$\text{or } x= -94.05-67.71 = -26.34\ \text{kcal}$$

Thus, ΔH heat of combustion of carbon to give carbon monoxide is – 26.34 kcal.

(ii) Determination of enthalpy changes of slow reactions:

Hess's law is extremely useful in determining enthalpy changes of those reactions which takes place extremely slowly for example, the transformation of rhombic sulphur into monoclinic sulphur is so slow that direct measurement of enthalpy change is not possible. But the enthalpy of combustion of rhombic sulphur are known to be respectively, i.e.,

(i) $S(\text{rhombic}) +O_2(g) \longrightarrow SO_2(g)\ ; \qquad \Delta H =- 297.5\ \text{kJ}$

(ii) $S(\text{monoclinic}) + O_2(g) \rightarrow SO_2(g)\ ; \qquad \Delta H = - 300.0\ \text{kJ}$

Substracting (i) from (ii) and rearranging, we get

$$S(\text{monoclinic})\ S(\text{rhombic}); \qquad \Delta H= - 2.5\ \text{kJ}$$

or $S(\text{rhombic}) \qquad S(\text{monoclinic})\ \Delta H= 2.5\ \text{kJ}$

Thus transformation of one mole of rhombic sulphur into monoclinic sulphur is accompanied by absorption of kcal of heat.

(iii) Calculation of enthalpy of formation:

The enthalpy of formation of compounds can be calculated by the application of Hess's law when it is not possible to determine these experimentally.

For example it is impossible to determine experimentally the enthalpy of formation of benzene from its elements: carbon and hydrogen. However, it can calculate from the enthalpy of combustion of benzene and the enthalpy of formation of water and carbon dioxide. The solution is carried out in two steps

Step I

(i) $C_6H_6(l) + 15/2\ O_2(g) \longrightarrow 6CO_2 + 3H_2O\ (l)$ $\Delta H = -781.74$ kcal

(ii) $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -94.14$ kcal

(iii) $H_2O\ (g) + ½\ O_2(g) \longrightarrow H_2O\ (l)$ $\Delta H = +\ 68.40$ kcal

Step-II

(iv) $6\ C(s) + 6O_2\ (g) \longrightarrow 6CO_2(g)$; $H = -564.84$ kcal
(v) $3H_2(g) + 3/2\ O_2(g) \longrightarrow 3H_2O(l)$ $\Delta H = -205.20$ kcal

Adding (iv) and (v) and subtracting (1) we get

$6C(s) + 3H_2(g) \longrightarrow C_6H_6\ (l)$; $\Delta H = 11.70$ kcal

Thus enthalpy of formation of benzene is 11.72 Kcal.

12.15 BOND ENERGIES

Bond energy for any particular type of bond in a compound may be defined as the average amount of energy required to dissociate (i.e., break) one mole, Avogadro number of bonds of that type present in the compound. This is also called the enthalpy of formation of the bond.

Thus the bond energy of H-H bond is the energy required to break all the bonds in one mole of the gas. It is expressed in kcal per mole or kJ per mole. For example, bond energy of H-H bond is 433 kJ per mole or 103.58 kcal per mole.

Bond energies of some common bonds are given below.

(i) $H_2(g)$ $2H_g(g)$; $\longrightarrow$ $\Delta H = 433.1$ kJ
(ii) $O_2(g)$ $2O(g)$; $\longrightarrow$ $\Delta H = 489.5$ kJ
(iii) $N_2(g)$ $2N(g)$; $\longrightarrow$ $\Delta H = 937.4$ kJ
(iv) $C(s)$ $C\ (g)$; $\longrightarrow$ $\Delta H = 719.6$ kJ

Suppose we have to determine the enthalpy of formation of C-H bond in methane. We should know the enthalpy of formation of methane. This had been calculated from the enthalpy of combustion of methane to be – 74.9 kJ. Thus

(v) $C(s) + 2H_2(g) \longrightarrow CH_4(g)$; $\Delta H = -\ 74.9$ kJ

Multiplying equation (i) by 2 we have

(vi) $2H_{2(g)}$ $4H_{(g)}$; $\longrightarrow$ $\Delta H = 866.2$ kJ

Adding equation (iv) and (vi) and subtracting from equation (v) we have

$$C(g) + 2H_2(g)\ CH_4(g)\ ; \quad \longrightarrow \quad \Delta H = -1660.7\ kJ$$

It follows from above that -1660.7 kJ of energy is required to break four moles of C-H bonds in methane. Therefore the average bond energy per mole of C-H bond is -1660.7/4 = 415.2 kJ. This is also the enthalpy of formation of the C-H bond.

12.16 SUMMARY

In this unit we have studied different definitions associated with thermochemistry. As we know thermochemistry is the study of energy changes involved in chemical reactions. This study is very useful in determining enthalpy changes in various reactions. Kirchoff's equation is very useful in calculating change of enthalpy with temperature. Hess's law and bond energy calculations are utilised for various transformations.

12.17 TERMINAL QUESTIONS

(A) Objective type questions:

Q.1 Which of the following relations holds good for the reaction?

$$CO_{(g)} + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$$

(a) $\Delta H = \Delta E$ (b) $\Delta H = \Delta E + RT$

(c) $\Delta H = \Delta E + \frac{1}{2} RT$ (d) $\Delta H = \Delta E - \frac{1}{2} RT$

Ans (d)

Q.2 The change in internal energy with temperature at constant volume is given by the relation.

(a) $\Delta E = \Delta C_v(T_1 - T_2)$ (b) $\Delta E = \Delta C_P(T_2 - T_1)$

(c) $\Delta E = \Delta C_v(T_2 - T_1)$ (d) $\Delta E = \Delta C_P(T_1 - T_2)$

Ans(c)

Q.3 Which of the following always has a negative value?

(a) Heat of reaction (b) Heat of formation

(c) Heat of combustion (d) Heat of solution

Ans (c)

Q.4 The change in enthalpy that takes place when one mole of compound is formed from its elements is called:

(a) Heat of combustion (b) heat of formation of compound

(c) Heat of synthesis (d) standard heat of formation

Ans (b)

Q.5 The heat of neutralisation of strong acid and strong base is always:

(a) Zero (b) constant (c) positive (d) changing

Ans (b)

(B) Short answer type questions:

Q.6 Derive the relation between ΔH and ΔE

Q.7 What is meant by heat of formation

Q.8 Define heat of neutralisation

Q.9 Derive the relation between enthalpy of reaction at constant volume and at constant pressure.

(C) Long answer type questions:

Q.10 State Hess's law of constant heat summation. Calculate the heat of formation of acetylene from the following data:

$C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta n = -94.052$ kcal

$H_2(g) + ½\, O_2(g) \longrightarrow H_2O$; $\Delta H = -68.317$ kcal

$C_2H_2(g) + 5/2\, O_2(g) \longrightarrow 2CO_{2(g)} + H_2O(l)$; $\Lambda H= -310.615$ kcal

Q.11 (a) Explain what is meant by the term bond energy

(b) Define heat of neutralisation. Why heat of neutralisation of a strong acid and strong base is 13.69 kcal?

Q.12 Define the following terms:

(a) Thermochemistry

(b) Heat of reaction

(c) Heat of formation

(d) Thermochemical equation

****