PHYSICAL CHEMISTRY

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(MSC - CHEMISTRY)

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UNIT - I
THERMODYNAMICS

LESSON-I

FIRST AND SECOND LAWS OF THERMODYNAMICS AND ENTROPY

1.1 (i) Review Of First And Second Laws of Thermodynamics And Their applications

Thermodynamics (Greek word meaning heat power) deals with the study of

(i) the relationship between heat and other forms of energy.
(ii) the inter-conversion of one form of energy into another form.
(iii) the efficiency and the work obtainable from such conversions.

Thermodynamics basically deals with few fundamental generalizations. The zeroth, first, and second laws of thermodynamics are the result of a number of experiments conducted by engineers, physicists, chemists and other scientists over many years. The third law is a restriction on the entropy value under certain conditions.

Variety of scientists are interested in different aspects. For example, an engineer may be interested in combustion of fuel and energy derived from this process. The chemist is interested in knowing whether a reaction is spontaneous or otherwise. The laws of thermodynamics are base on experience; they are so universal and hence they need no tests of validity. The conclusions drawn from quantitative expression of these laws are quite sound.

Thermodynamics is primarily concerned with systems at equilibrium. Since the methods of thermodynamics are being applied to systems that are not in equilibrium also, one now makes the distinction between equilibrium or reversible thermodynamics and non-equilibrium or irreversible thermodynamics. The equilibrium thermodynamics is based on properties that are easily observed and are familiar to us (macroscopic properties) such as pressure, temperature etc. and is independent of atomistic or molecular nature of matter. This is a serious limitation in the sense that though the observed macroscopic properties are due to microscopic constituents, this fact is ignored. Another limitation is the inability of thermodynamics to predict how fast a thermodynamically feasible reaction can approach the equilibrium state. In fact, time is not a variable in thermodynamics, since the systems under consideration are assumed to be in equilibrium. It is mainly concerned with initial and final states of a system and not about what happens in between (i.e.) the mechanism of the reaction. However it is possible to estimate the rate constant from statistical thermodynamics using certain models.

THE TERMINOLOGY OF THERMODYNAMICS.

The two laws have been quantified by the application of relatively simple mathematical procedures and thus thermodynamics is not abstract logic but an exact science. Consequently it is founded on precise definitions of various terms used.

A *system* is a portion of the universe under study, which is separated from the remainder of the universe by real or imaginary *boundaries.* The system may be subjected to an experimental or theoretical investigation. Other systems or the rest of the universe, which may or may not interact by exchange of matter and/or energy with the system under consideration are treated collectively as *surroundings.* However it is convenient to regard the surroundings as the region in the immediate vicinity of the boundaries of the system, so that one can monitor the changes that take place in both, the system and the surroundings.

A system can be characterized in terms of certain observable properties of bulk matter (macroscopic properties). These properties are referred to as *state variables* or *thermodynamics variables*. Examples of such variables are pressure, volume, temperature and composition. In absence of electrical, magnetic, gravitational and other such effects these four properties can be used to describe the system completely. It is not always used to specify all the four.

The state variables are of two kinds, one dependent on the mass or the quantity of the material and the other independent on the mass of the material. The former are called *extensive properties* and the latter are called *intensive properties*. If a system is divided into many parts, the total value of the extensive property is given by the sum of the values of separate properties into which the system has been divided, i.e., extensive properties are additive in nature. Intensive properties are not additive .The value of an intensive property is same in any part of the homogenous system at equilibrium. It is because temperature and pressure are intensive that these are frequently used as state variables to describe the state of a system. It will also be seen that any extensive property referred to unit amount i.e. 1 mole or 1 gram becomes intensive. For example, mass and volume are extensive but mass per unit volume i.e. density and mass per unit volume per unit mass, specific volume are intensive. Heat capacity is extensive but specific heat is intensive. Thus the ration of two extensive properties is an intensive property. The ratio of two intensive properties remains an intensive property, molar volume/temperature for an ideal gas.

Thermodynamic Equilibrium:

Thermodynamics is concerned with a study of systems in equilibrium if the observable properties of the system do not change with time. When a system is in thermodynamic equilibrium it will also be thermal, mechanical and chemical equilibrium. When the values of its intensive properties such as temperature and pressure are uniform in any part of a system, it is said to be in thermal and mechanical equilibrium.

State Function:

The state variables considered so far as P, V and T are also called state functions ot thermodynamic properties. A state function is a property of a system which has a definite value for each state and does not depend on the path or manner in which a particular state is reached or the past history of the system. Besides P, V and T, the laws of thermodynamics have led to the formulation of important functions such as internal energy (U), enthalpy (H), entropy (S), free energy (G) etc. Some important functions of state functions are summarized below.

i) When a system goes over from state A (initial state) to the state B (final state) the change in the state function, for example E, computed by subtraction the initial value from the final value will always be the same. A finite change in a state function, like prefixing the symbol " Δ "indicates internal energy.

$$\Delta E = E_B - E_A$$

$$= E_{\text{final state}} - E_{\text{initial state}} \text{ or } E_f - E_i \qquad \text{------(1.1)}$$

Any infinitesimal change in the state function such as E is given by dE. The total change in going from A to B can be expressed as an integer

$$\int_A^B dE = Eb - Ea = \Delta E. \qquad \text{---------(1.2)}$$

(ii) Any infinitesimal change in a state function can be expressed as an *exact* or *complete* or *total differential.* If any thermodynamic property such as volume (V) is a single valued function of variables such as P, T, any change in volume, ΔV from state 1 to state 2 can be written as

$\Delta V = f(P_2, T_2) - f(P_1, T_1) = V_2 - V_1$

$$dV = (\partial V/\partial P)_T * dP + (\partial V/\partial T)_P * dT \quad \text{-------}(1.3)$$

(iii) Euler's criterion of integratability or the reciprocity relationship should hold good for an infinitesimal change to be an exact differential. Eq. (1.3) can be written as

$$dV = MdP + NdT \quad \text{----------}(1.4)$$

where M and N are functions of P and T and are given by

$$M = (\partial V/\partial P)T \text{ and } N = (\partial V/\partial T)P \quad \text{-----------------}(1.5)$$

According to Euler's relationship

$$(\partial M/\partial T)P = (\partial N/\partial P)T \quad \text{------------------}(1.6)$$

(iv) In any cyclic process, the system is brought back to its initial state. Since the state function has a definite value for a given state, this means that in a cyclic process, the change in any state function is zero. This is mathematically represented as

$$.\int dE = 0$$

Here the. $\int$ symbol represents integration around a cyclic path.

WORK:

A system may interact with its surroundings and transfer its energy in the form of work. *Work is defined as the product of external force applied and the displacement in the direction of applied force.* Work is the result of action against an opposing force. In the absence of an opposing force, any movement does not produce work. For example, if a compressed gas is made to push a piston with a platform containing weights (**w**) and if the platform is lifted or raised through a height, *h*, the work done by the system is **w*h*=mg *h*** joule (**J**), where g is the acceleration due to gravity in metres per second squared and **m** is the mass in kg.

ENERGY:

Energy is the ability of the system to do work. It may take various forms such as kinetic energy of a body in motion, potential energy due to its position, thermal energy as measured by its temperature etc. Energy is a property of a system. No system has either heat or work contained in it. The transfer of energy from one system to another may appear as heat or work. All forms of energy have the same dimensions, mass $(\text{length})^2$ $(\text{time})^{-2}$. and can be expressed in the units, erg, joule, calorie, litre atmosphere, and electron volt.

One Joule **J** = One Newton metre, Nm= One volt-coulomb.

One bar $= 10^5\ \text{Nm}^{-2} = 10^5\ \text{Pa}$

One atm = 760 mm of mercury = 760 Torr.

$= 1.013 \times 10^5\ \text{Nm}^{-2} = 101.3\ \text{kPa} = 14.7\ \text{psi} = 1.013\ \text{bar}$

One torr $= 1.332\ \text{Nm}^{-2}$

One electron volt mol^{-1} $(1\text{eVmol}^{-1}) = 96.74\ \text{kJmol}^{-1} \simeq 100\text{kJmol}^{-1}$

One wave number in cm^{-1} (Kayser) is equivalent to 12.5 J mol^{-1}

One litre $= 1000\text{cm}^3 = \text{One dm}^3 = 10^{-3}\ \text{m}^3$.(one dm = .1m)

In order to indicate the direction of energy transfer in the form of heat or work between a system and surroundings, the following convention is used. Work done by the system *i.e.,* expansion of a gas against opposing pressure is negative and work done on the system *i.e.,* compression of gas by applying external pressure is positive.

THE FIRST LAW OF THERMODYNAMICS

Principle of conservation of energy

In 1798 Count Rumford observed tat heat developed during boring of a canon was related to the mechanical work involved. J.P. Joule established that when 4.184 joule of work of any kind is converted to heat, 1 calorie of heat is evolved. This relationship is known as mechanical equivalent of heat. Thus observation together with the failure to create machine that can produce one type of energy without the expenditure of an equivalent amount of energy *(perpetual motion of first kind)* led to the enunciation of the first law. This is essentially the principle of conservation of energy and can be stated in number of ways.

'Although energy may be converted from one form into another, it can neither be created nor destroyed'

Or

'Whenever a certain quantity of energy in one form is produced, an exactly equivalent amount of energy in another form must be used up'

Or

'the total energy of an isolated system must remain constant, though one form of energy may change into another.'

If the system and the surroundings are taken together, one need not consider any qualification, the total energy may be conserved.

According to Einstein, a certain quantity of mass (**m**) can be converted into energy (E) as defined by the equation $E = \mathbf{m}c^2$, where c is the velocity of light. In this process energy is created by the destruction of a certain mass and thus appears to contradict the principle of conservation of energy. Actually one should consider conservation both in terms of mass and energy. The first law should therefore be stated that ***'in an isolated system the mass and energy remaining constant'.*** This definition is most significant in nuclear reactions where the conversion of mass to energy is appreciable. However, chemical thermodynamics is concerned with chemical reactions where the first law can be considered in terms of conservation of energy alone since mass changes are not significant. For example, the energy change corresponding to a difference in mass of one mg (10^{-6} kg) is approximately 1.0×10^{-23} kg m^2 s^{-2} or **J**.

A system can be considered to be endowed with a certain amount of energy, as evidenced by its ability to transfer its energy in the form of heat or work when it is linked to its surroundings. This energy called the internal energy includes all forms of energy other than resulting from the position in space. Any change in energy due to position in a force field or due to motion of a system as a whole is not taken into consideration. The internal energy (E) includes vibrational, rotational, electronic, translational etc. energies E depends on P, V, T, mass and composition. Though the absolute value of E cannot be measured, changes in E can be measured in terms of the heat and work exchanged with the surroundings.

Mathematical formulation of the first law

Let a closed system absorb a certain quantity of heat q, from the surroundings. As a result of this, the internal energy of the system is increased. The system is able to do work $-w$ on the surroundings. If ΔE is the change in the internal energy of the system, according to the first law of thermodynamics

$$q = \Delta E - w \quad \text{-------}(1.7)$$

$$\Delta E = q_{ta} + w_{on} \quad \text{-------}(1.8)$$

Here q_{ta} is the thermal energy (heat) added to the system and w_{on} the work done on the system.

For infinitesimal changes eqn (1.8) can be written as

$$dE = \delta q_{ta} + \delta w_{on} \quad \text{--------}(1.9)$$

According to the eqn (1.8) for a closed system, an increase in the internal energy (ΔE_{sys}) is equal to the sum of heat *absorbed by the system* (q is positive) and the work done on the system (w is positive). One should use eqn (1.8) after affixing appropriate signs for q and w. For example, if a system does 500kJ of work on the surroundings work done by the system is –500kJ. If in addition it loses 100kJ of energy in the form of heat to the surroundings, the change in the internal energy (ΔE_{sys}), is equal to (-100-500) equal to (-600kJ). The internal energy of the system *decreases* by 600kJ. In all thermodynamic calculations one focuses attention on the changes that take place in the system unless otherwise stated. w includes all possible type of work.

That E is a state function as defined by eqns (1.8) and (1.9) can be shown as follows: Consider any system represented by the point A in the P-V diagram. Let the final state be represented by B. Consider the change in state from A to B by path I. From the first law,

$$\Delta E \text{ (path I)} = q_I + w_I \quad \text{-----------}(1.10)$$

For the same change by path II.

$$\Delta E \text{ (path II)} = q_{II} + w_{II} \quad \text{-----------}(1.11)$$

In eqns (1.10) and (1.11), q and w refer to the heat absorbed and the work done by the system respectively. From the principle of conservation of energy, the total energy absorbed by the system must be equal to the total work done by the system.

$$q_I + q_{II} = -(w_I + w_{II}) \quad \text{-------}(1.12)$$

$$(q_I + w_I) + (q_{II} + w_{II}) = 0 \quad \text{-------}(1.13)$$

$$\Delta E \text{ (path I)} + \Delta E \text{ (path II)} = 0 \quad \text{-------}(1.14)$$

In going from A to B and from B to A a cyclic process has been gone through and we find that $\int dE = 0$. Hence E is a state function, though q and w are path-defined functions.

APPLICATIONS OF THE FIRST LAW:

1.Change Of Phase:

A change of phase is always isothermal and isobaric; for instance water boils at a fixed temperature for a fixed pressure. During the change of phase some heat flows into the system or out of it. Let us consider the vaporization of m gm of a liquid. If v_1 and v_2 represent the specific volumes of the liquid and vapour phases respectively at the same pressure P and temperature T, the work done in the vapourization is $W=Pm(v_2-v_1)$.

If L is the latent heat of vapourization of the liquid at temperature T, the heat flow into the system is

$$Q=mL \qquad \text{-----------(1.15)}$$

The change in the internal energy in the process is

$$\Delta U=Q\text{-}mL\text{-}Pm(v_2-v_1) \qquad \text{---------(1.16)}$$

The change in internal energy per unit mass is

$$\Delta U/m=L-P(v_2-v_1) \qquad \text{---------(1.17)}$$

2.Free Expansion of a Gas-Joule's Experiment

Chamber A containing a gas is connected by a stop-cock (initially close) to another chamber B which is evacuated, the whole apparatus being enclosed in some thermally insulating material. (Fig). When the stopcock is opened, the gas rushes into chamber B, expanding freely into vacuum. Though expansion takes place, the gas does no external work because the pressure $P=0$ in chamber B. The expansion is adiabatic, hence

$W=0$ and $Q=0$

Therefore, $\Delta E=0$

There is no change in the internal energy of the gas. Unlike other processes, a free expansion cannot be made quasistatic because as soon as the stopcock is opened a finite pressure difference exists and the system is not in mechanical equilibrium. A free expansion is always irreversible, the gas passing through non-equilibrium states till the final equilibrium state is reached.

3.Heat Capacity and Specific Heat:

In general heat transfer between a system and its surroundings is accompanied by a change of temperature of the system, provided no phase change takes place. If a heat flow of Q units into the system causes its temperature to change by ΔT, the mean capacity of the system for the given process is defined as

$$\bar{C}=Q/\Delta T \qquad \text{------------(1.18)}$$

As Q decreases, ΔT also decreases and the ratio approaches the instantaneous value of the heat-capacity

$$C'=\lim_{\Delta T\to 0} \delta Q/\Delta T \qquad \text{-----------(1.19)}$$

The ratio $\delta Q/dT$ is not a derivative of Q with respect to T since Q is not a function of T, nor is it a thermodynamic co-ordinate of the system. δQ is a small quantity of heat flow into the system, whose temperature changes by dT. An extensive quantity C' represents the heat capacity for a given system. A more meaningful quantity is the heat capacity per unit mass or the specific heat as it is characteristic of the material of the system. If the mass of the system is M units the specific heat is

$$c=C'/M=\delta Q/dT. \qquad \text{-------------(1.20)}$$

THE SECOND LAW OF THERMODYNAMICS

The need for a second law:

The first law of thermodynamics asserts that in any energy conversion process, one form of energy must be converted into an equivalent amount of another form of energy. It is not converted with whether such conversions are possible and if so to what extent. For example, whether heat 'flows' from a hotter body to a colder one or vice versa, heat lost must be equal to the heat gained according to the first law, but the first law does not specify in which direction the heat will flow. In Nature many systems are known in which the direction of heat can be predicted. Heat flows from a hotter body to colder body till they reach a common temperature. A gas at high pressure spontaneously expands into a region of lower pressure till the pressure is uniform throughout. Such processes occur by themselves without the aid of external agency. These are called spontaneous or natural processes. For example, once water flows down a hill, it does not spontaneously flow up the hill. However, it can be pumped back to the top of the hill, but only at the expense of some mechanical work or other form of work. Similarly, heat by itself cannot pass from a colder to hotter body. A reaction that is spontaneous cannot be reversed except with the aid of an external agency. Thus, the process in which systems proceed from non-equilibrium to equilibrium conditions spontaneously are called *thermodynamically irreversible* or *irreversible processes.*

The first law enabled the introduction of two state functions E and H. Since it was observed that most of the chemical reactions that occurred spontaneously were exothermic, Thomson and Berthelot believed that a reaction would proceed in that direction in which heat would be evolved (ΔH negative). However, it is found that many chemical reactions, such as the formation of HI, NO etc., do take place, though endothermic in nature. Therefore the enthalpy change is not a sufficient criterion to indicate the direction of a reaction. Consequently, there is a need to formulate other laws base on our experience, which now can lead to criteria that will be useful in deducing the conditions for equilibrium and spontaneity.

A system approaching an equilibrium state can be made to do work. The expansion of a gas from high pressure to low pressure region may be used to push a piston. Similarly, the spontaneous flow of heat from hotter region to a colder region may be made to do work by using a device referred to as heat engine. In an isothermal reversible expansion of n ideal gas, the gas absorbs a quantity of heat, q and does the work of expansion, $-w$. Since E=0, it follows that $q=w$. In other words heat is apparently completely converted into work. Hence, for the reversible expansion compression cycle, the net work done as well as net heat absorbed will be zero. Thus no heat engine operating in an isothermal reversible cycle can convert heat into work. Had this been possible one would have invented a *perpetual motion machine of second hand.* However, in practice this is found to be impossible. The absence of perpetual motion of the second kind has provided the basis for the second law of thermodynamics.

THE SECOND LAW:

The second law has been stated in various forms. Some of these are given below.

(i) ***'It is not possible to convert heat into work by means of an isothermal cycle'***

(ii) ***Clausius stated the law, as 'Heat will not flow from a colder body to a warmer body without the expenditure of work'.***

(iii) The Kelvin Planck statement is ***'It is impossible to construct a machine operating in cycles, which will produce no effect other than absorption of heat from a reservoir and its conversion into an equivalent amount of work'.*** According to this statement, heat exchange with a *single reservoir* cannot be harnessed to do mechanical work.

APPLICATIONS:

The efficiency of a heat engine:

The efficiency or the conversion factor, ε, of a heat engine is defined as the fraction of heat absorbed from a high temperature reservoir that can be converted to work. *The efficiency is defined as the ratio of net work done by the gas in a cycle (-w) and the heat absorbed (Qz) from the source.* Since efficiency refers to *positive* work output from a cycle, $|w|$ is used.

$$\varepsilon = (\text{work output})/(\text{work input}) = |w|/Qz \quad \text{----------(1.21)}$$

The source of this heat (thermal energy) might be the burning of oil or gas or coal to heat the boiler to a temperature, *T2.*

$$\varepsilon = (R(T_2-T_1)\ln(Vb/Va))/(RT_2\ln(Vb/Va)) = (T_2-T_1)/T_2 \quad \text{----------}$$

(1.22)

From eqn.(1.22) It is seen that

(i) T_2 being $> T_1$, ε can never be greater than 1(*i.e.,*) ε *is <1,* as long as T1 is not zero. This means that heat absorbed is not completely converted to work. Nature has thus put a limitation on the conversion of heat to work.

(ii) ε depends mainly on (T_2-T_1), and is independent of the nature of the working substance. For a given temperature of the source, the temperature of the sink should be as low as possible for ε to be reasonably high. ε will be unity when $T_1 = 0$(*i.e.,*) when the temperature of the sink is absolutely zero (-273.16°C). This is not feasible.

Generally, working at a temperature lower than atmospheric temperature poses problems like proper insulation and so the temperature of the insulation is fixed as the room or atmospheric temperature. In such a case, for an engine to be very efficient,T2 should be as high as possible so that (T2 –T1) is large. It is for this reason that superheated steam or a working substance with a high boiling point is used in the conversion of heat into work.

(iii) When $T_2 = T_1$, $w=0$(*i.e.,*) no net work can be obtained from an engine operating in a cycle under isothermal conditions.

(iv) From eqn (1.22). $-w = RT2\ln(Vb/Va) + RT1\ln(Vd/Vc)$

Hence, $=-wI-wIII=Q2+Q1$

$\varepsilon=(Q2+Q1)/Q2$ ------------(1.23)

Heat Pump and refrigerator

A heat engine absorbs heat from a source, gives out heat to the sink and does work to the surroundings. Since the Carnot cycle is reversible it is possible to go through the reverse cycle. The heat and work terms are equal in magnitude to those in the forward cycle but have opposite signs under these conditions. In this reverse cycle, a certain quantity of heat Q_1 is absorbed from the sink and at the expense of work w, a quantity of heat Q_2 is given out to the source.

The efficiency is expressed in the same manner whether the Carnot engine is run in the forward or in the reverse direction (Carnot Theorem). As per the agreed convention Q_1 is positive and Q_2 is negative, and since the work is done on the system, w is positive. Work done is a maximum only when the heat is absorbed reversibly and isothermally and it follows that the efficiency is a maximum only for a reversible change. In other words for engine run under irreversible conditions, the efficiency will be less.

Since in this process the sink is cooled, this cycle is called the refrigeration cycle and since the heat is transformed from the sink to the source, the engine is also called the heat pump.

If the process is to supply heat to the higher temperature the device is called a heat pump. For example, in winter a heat pump supplies heat to a room to maintain normal temperature by withdrawing heat from the outside cold air. If the purpose is to cool the interior by withdrawing heat from a body at low temperature, the device is called a refrigerator. Refrigerator and air conditioners are rated in terms of tons of refrigeration. A 1.00-ton Air-Conditioner is capable of removing 12600 KJ of energy per hour. A 1.00 ton refrigerator extracts in a day an amount of heat just enough to freeze 1.00 ton of water at 0^0 C.

Domestic Refrigerators are heat pumps in which an electric motor supplies the work required to remove heat from the refrigerator to the air outside. The efficiency of the refrigerator called the coefficient of performance (ŋ) is also given by an expression similar to equation (1.22). Some authors call the reciprocal of ŋ as the coefficient of performance.

Ŋ = Work done on the engine

Heat absorbed from the sink.

The work done on the refrigeration engine in the cycle is numerical equal but opposite in sign to the work done by the engine in the forward cycle. Hence ,

$w = R(T_2 - T_1) \ln(V_b/Va)$

$= R(T_2 - T_1) \ln(Vc/Vd)$ ----------(1.24)

In the refrigeration cycle, the sink gives out heat, which is numerical equal but opposite in sign to the heat absorbed by the sink (Q1) in the forward cycle

Heat given out by the sink is $-Q_1$ and so

$Q_1 = -R T_1 \ln(Vc/Vd)$ or

$= RT_1 \ln(Vc/Vd)$

$ŋ = w/Q_1 = R(T_2 - T_1) \ln(Vc/Vd) / RT_1 \ln(Vc/Vd)$ or

$w/Q_1 = T_2 - T_1/T_1$

$w = Q_1 (T_2 - T_1)/T_1$ ------------(1.25)

This equation applies only for reversible conditions.

The thermodynamic scale of temperature.

The efficiency of a Carnot engine depends only on the temperatures of the source and the sink and not on the nature of the working substance. Kelvin in 1848 suggested that the efficiency of a reversible engine can be used as the basis of a *thermodynamic scale of temperature, which* will be independent of the nature of the material used. In this scale, the temperature of each reservoir is defined in terms of quantities proportional to the quantity of the heat transferred to or from the reversible cycle.

Let Q_1 be the *numerical* value of the heat *transferred from the source* and Q_2 be the *numerical* value of the heat *transferred* to the sink. Here the signs of Q_1 and Q_2 are not taken into the consideration. According to Kelvin,

$$Q_1/Q_2=\theta_1/\theta_2 \qquad \text{---------(1.26)}$$

Where θ_1 and θ_2 are the temperature of the source and the sink in the thermodynamic scale. Subtracting each side of eqn (1.26) from 1.

$$1-(Q_1/Q_2)=1-(\theta_1/\theta_2)$$

or $(Q_2-Q_1)/Q_2=(\theta_2-\theta_1)/\theta_2$

Q is the amount of heat taken up from the source and Q is the amount of heat rejected to the sink. Hence (Q_2-Q_1) represents the quantity of the heat that has actually been converted into work, *w*. Hence

$$\varepsilon=(w/Q_2)=(Q_2-Q_1)/Q_2=(\theta_2-\theta_1)/\theta_2$$

$\varepsilon=1$ when θ is zero in this Kelvin scale of temperature. $\varepsilon=1$ when T, the temperature in the absolute scale is zero. It is seen that the zero of the absolute scale and the Kelvin scale become identical.

LESSON II

2.i. The Concept of Entropy

From eqns (1.22) and (1.23) the efficiency of a reversible engine is

$$(Q_2+Q_1)/Q_2=(T_2-T_1)/T_2$$

or $Q_1/T_1=-(Q_2/T_2)$ or $(Q_1/T_1)+(Q_2/T_2)=0$ --------(2.1)

Here Q_1 and Q_2 are the numerical values. Actually Q_1 is positive and Q_2 is negative.

Eqn (2.1) applies to a heat engine working between two reservoirs and can be written as.

$$\Sigma\, Q_{rev}/T=0 \qquad \text{---------(2.2)}$$

The term Q_{rev} is used to indicate that the heat exchange should be carried out reversibly. Any cyclic process carried out reversibly can be considered to be made up of large number of Carnot cycles..

The area in the figure representing a cyclic process ABA can be divided into a large number of Carnot cycles by a series of isothermal and adiabatic steps. For each such Carnot cycle eqn (2.2) holds good. The adiabatic portions of such cycles need not be considered since no heat is exchanged. If for the first cycle, q_a and q_a' are the heat exchanges in the isothermal portions of the cycle, the temperature being T_a and T'_a respectively.

$(q_a/T_a) + (q'_a/T'_a)=0$ ----------(2.3)

q_a and q'_a have opposite signs.

Similarly, for the second cycle,

$(q'_a/T'_a) + (q_b/T_b)=0$ and so on.. -----------(2.4)

q'_a and q_b have same signs.

Starting from A and traversing all the cycles down to B and then back to A, it is seen that all the isothermals inside the cycle cancel out, since each isothermal is traversed in opposite direction during the cycle ABA. The zigzag boundaries of these Carnot cycles appear to constitute very nearly the cycle ABA. Thus for the entire cycle made up of Carnot cycles,

$(q_a/T_a) + \quad (q_b/T_b) + \ldots\ldots \quad (q'_a/T'_a) + (q'_b/T'_b) + \ldots=0$ --------- (2.5)

By considering the cycle to be made up of very large number of infinitely small Carnot cycles, the outside boundary of the zigzag curve can be made to coincide with ABA itself. In such a case, the summation can be replaced by a cyclic integral.

$\Sigma\,(q_{rev}/T)=0$ or $\int(\delta q_{rev}/T)=0$ ------------(2.6)

From eqn.(2.6) it is seen that the cyclic integral is zero and so $(\delta q_{rev}/T)$ has the qualities of the differential of a state function. Clausius called this function *entropy* (Gk. Transformation) since entropy is related to the transformation of heat to work. It is represented by the symbol 'S'. The increase in entropy, dS accompanying an infinitesimal reversible and isothermal change is given by the ratio of $\delta q_{rev.}$ the heat absorbed in the reversible process, and T, the absolute temperature at which the change takes place.

$dS=\delta q_{rev}/T.$ -------------(2.7)

The evaluation of entropy changes

This is possible only if the reversible processes are considered, since eqn. (2.7) contains the term q_{rev} and δq_{rev}. However, since S is a state function, ΔS is independent of the path taken. Hence even for irreversible processes between state A and the state B, if somehpw or the other a reversible path is conceived between the same two states, ΔS can be calculated by imagining the process to have taken place reversibly.

2.(*ii*). Entropy Changes in isolated systems in reversible and irreversible Process

Entropy change in reversible processes

S being a state function, for any cyclic process, $\Delta S=0$ for the system. If the surroundings are considered, in a reversible process, the system absorbs a certain quantity of heat Q_{rev} from the surroundings, the temperature of which differs infinitesimally from that of the system. At every stage of the reversible process the heat absorbed (Q is positive) by the system is equal in magnitude to the heat given out(Q is negative) by the surroundings and both are at practically the same temperature T.

Hence ΔS (system)=- ΔS (surroundings).

Therefore ΔS (system)+ ΔS (surroundings) = ΔS (isolated system)=0

Since the temperature remains practically constant at every stage of the reversible process, it can be considered isothermal. In every reversible process, the entropy of the isolated system remains constant since there is no gain or loss of heat. If one part of the isolated system increases in entropy the entropy of the remaining part of the system must decrease by an equal amount, in a reversible process. For *reversible* adiabatic changes, the heat absorbed being zero, ΔS will also be zero. For the surroundings also, ΔS is zero since no heat is given out or absorbed by the surroundings. Thus, reversible adiabatic processes are *isentropic.* Even if Q is zero and the process is irreversible, only if the heat change Q in the imaginary reversible path for the same transformation is zero will the process be isentropic.

(ii) Entropy change in irreversible processes

Reversible processes are useful for theoretical calculations but all real processes are irreversible. For a reversible cyclic process

$$\int q_{rev}/T = 0 \qquad \text{--------(2.8)}$$

For a cyclic process in which a part of it is irreversible, Clausius showed that

$$\int \delta q/T < 0 \qquad \text{----------(2.9)}$$

Equation (2.9) is called the inequality of Clausius

Considering the efficiencies of a reversible and an irreversible engine between the same two temperatures can show this. In the case of a reversible engine, the efficiency is a maximum and is given by $(T_2-T_1)/T_2$ .The efficiency of an irreversible engine is $(Q_2+Q_1)/Q_2$

$$(Q_2+Q_1)/Q_2 < (T_2-T_1)/T_2 \quad \text{------}(2.10)$$

$$Q_1/Q_2 < -(T_1/T_2) \quad \text{------}(2.11)$$

$$Q_1/T_1 < -(Q_2/T_2) \quad \text{------}(2.12)$$

$$(Q_1/T_1) + (Q_2/T_2) < 0 \quad \text{-------}(2.13)$$

$$\Sigma\,(Q/T) < 0 \text{ (irreversible)}$$

Any cycle, which is completely or partly irreversible, may be considered to be made up of a large number of Carnot cycles. Hence

$$\int \delta q_{irr}/T < 0 \quad \textbf{for an irreversible cycle} \quad \text{-----}(2.14).$$

Equation (2.6) and (2.14) can be combined as

$$\int \delta q/T < 0 \textbf{ for irreversible and } = 0 \textbf{ for reversible process.} \quad \text{----}(2.15)$$

In this expression the ' = ' refers to a reversible process and ' < ' applies to an irreversible process.

It is also known that δw_{rev} the work done by the system in a reversible process is numerically greater than that for a corresponding irreversible process (i.e.,)

$$-\delta w_{rev} > -\delta w_{irrev}$$

However dE for the system is the same whether the process is reversible or irreversible, since E is a state function. From the first law,

$$dE = \delta q_{rev} + \delta w_{rev} \quad \text{-------}(2.16)$$

$$dE = \delta q_{irrev} + \delta w_{irrev} \quad \text{--------}(2.17)$$

$$\delta q_{rev} + \delta w_{rev} = \delta q_{irrev} + \delta w_{irrev} \quad \text{--------}(2.18)$$

$$\delta q_{rev} - \delta q_{irrev} = -\delta w_{rev} + \delta w_{irrev} = -\delta w_{rev} - (-\delta w_{irrev}) \quad \text{---------}(2.19)$$

Since the R.H.S. is positive

$$\delta q_{rev} > \delta q_{irrev} \quad (2.20)$$

From the definition of dS,

$$dS = \delta q_{rev}/T = (dE - \delta w_{rev})/T \quad (2.21)$$

From the equation (2.21),

$$\delta q_{rev}/T > \delta q_{irrev}/T \quad (2.22)$$

$$dS > \delta q_{irrev}/T, \quad (2.23)$$

$$dS > (dE - \delta w_{irrev})/T \quad (2.24)$$

Equations (2.23) and (2.24) are also other ways of expressing the inequality of Clausius. In an isolated system, there is no exchange of matter and energy between a system and its surroundings. Hence, $\delta q = \delta w = 0$ and $dE = 0$. Therefore $dS_{rev} = 0$ and $\Delta S_{rev} = 0$.But, for the irreversible process from equation (2.24) $dS_{irrev} > 0$ and $\Delta S_{irrev} > 0$. These statements are applicable to isolated systems. From equation Δ S (system) =Δ S (surroundings) for a reversible process. For an irreversible process between the same initial and final statesΔS (system) will be same both for reversible and irreversible processes. However, ΔS (surrounding) will be different for reversible and irreversible processes.

2.(iii). Entropy of mixing of real gases.

When two or more gases are brought into contact they mix spontaneously by diffusion. Such a spontaneous process is accompanied by an increase in entropy.

Let n_A moles of gas A and n_B moles of gas B be mixed at a constant temperature, T and pressure, P. the entropies of the gases before mixing are given by

$$S_A = n_A[(c_p)_A \ln T - R \ln p + (S_0)_A] \text{ and} \quad (2.25)$$

$$S_B = n_B[(c_p)_B \ln T - R \ln p + (S_0)_B] \quad (2.26)$$

Here the subscripts refer to the indicated gases and S_0 is the integration constant. In the mixture, let the partial pressure of A be p_A and that of B be p_B, such that

$$P = p_A + p_B \quad (2.27)$$

After mixing the entropies of A and B are given by equation (2.28) and (2.29)

$$S_{A(mix)} = n_A[(c_p)_A \ln T - R \ln p_A + (S_0)_A] \text{ and} \quad (2.28)$$

$$S_{B(mix)} = n_B[(c_p)_B \ln T - R \ln p_B + (S_0)_B] \quad (2.29)$$

The entropy change, ΔS_{mix}

$$\Delta S_{mix} = [S_{A(mix)} + S_{B(mix)}] - (S_A + S_B)$$

$$= -n_A R \ln(p_A/p) - n_B R \ln(p_B/p) \quad (2.30)$$

The mole fractions of A and B, x_A and x_B respectively, are given by

$$x_A = p_A/p \quad \text{and} \quad x_B = p_B/p$$

$$\Delta S_{mix} = -n_A R \ln(x_A) - n_B R \ln(x_B) \qquad (2.31)$$

In equation since x_A and x_B are both less than 1, ΔS_{mix} the entropy of mixing, is positive. Equation (2.31), can be expressed as

$$\boldsymbol{\Delta S_{mix} = -R\, \Sigma_i\, n_i \ln x_i} \qquad \textbf{(2.32)}$$

The entropy of mixing for a total of 1 mole of the mixture is

$$\boldsymbol{\Delta S = -R\, \Sigma^i_1\, n_i \ln x_i} \qquad \textbf{(2.33)}$$

ENTROPY AS A MEASURE OF DISORDER :

It is seen that in spontaneous processes and processes like mixing of gases by diffusion, vaporization of a liquid etc. there is always an increase in entropy. These are also accompanied by an increased randomness of distribution or disorder. In the fusion process a solid (a highly ordered state) changes over to a slightly disordered state (i.e) the liquid state. In the vaporization process, however, the liquid goes over to a highly random and disordered gaseous or vapor state. It is seen that

ΔS (vaporization) > ΔS (fusion). It is thus possible to regard S as a measure of disorder, chaos or random arrangement of molecules in the system. Since all naturally occurring processes are spontaneous, they are all accompanied by a net increase in entropy. Hence, for every spontaneous change-taking place in the universe (isolated system), the entropy of the universe is increasing. This led Clausius to state the second law as, the entropy of the universe always tends to maximum.

LESSON –III

FREE ENERGY FUNCTIONS

3. (i). Concept and significance of Helmholtz and Gibbs free energy Functions.

It has already been seen that entropy is a measure of unavailable energy. If Q is the total amount of heat absorbed by a system at constant temperature, T, and if S is the entropy of the system, TS represents the amount of heat degraded or not available for conversion into work. Thus the amount of the energy, E, available for conversion into work is given by,

$$E = Q - TS \qquad \text{-------}(3.1)$$

If Q is the heat absorbed at constant volume *i.e.* E, the free energy is called the *Helmholtz free energy* or the *Helmholtz function* or more usually the *work function* and is given by symbol A [Arbeit = work (German)]. Thus,

$$A = E - TS \qquad \text{-------}(3.2)$$

From the equation (3.2) , it is seen that since E, T, and S are state functions, A is also one. The reason for calling this as the work function is that it can be identified with the maximum work that can be done in an isothermal reversible process. For a finite change under reversible and isothermal conditions eqn (3.2) can be written as,

$$\Delta A = \Delta E - T\Delta S \qquad \text{----------}(3.3)$$

For a reversible isothermal process, $T\Delta S = q_{rev}$ and so $\Delta A = \Delta E - q_{rev}$

From the I law, $\Delta E = q_{rev} + w_{rev}$ and so it is seen that

$$\Delta A = w_{rev} \text{ or } w_{max} \qquad \text{--------}(3.4)$$

$$-(\Delta A) = -w_{max} \qquad \text{----------}(3.5)$$

The decrease in the Helmholtz function is thus equal to the maximum work which a system can do under isothermal and reversible conditions. This work comprises all forms of work including that of expansion. It is to be noted that any given process, isothermal or otherwise, will be accompanied by a change in the property A, but it is only for an isothermal reversible process that the change in A can be identified with the maximum work.

If the heat is absorbed at constant pressure, Q = H and the free energy under these conditions is called the *Gibbs free energy* or *Gibbs potential. It is simply called the free energy* and denoted by G. It is defined by eqn (3.6)

$$G= H- TS \qquad \text{-------(3.6)}$$

It is seen that G is also a state function. Its significance can be understood form the following discussion. For a finite change in the state of a system at constant pressure and temperature eqn (3.6) can be written as

$$\Delta G = \Delta H- T\Delta S \qquad \text{--------(3.7)}$$

Since, $\Delta H =\Delta E + P\Delta V$ --------(3.8)

$$\Delta G = \Delta E + P\Delta V - T\Delta S \qquad \text{--------(3.9)}$$

In eqn (3.9) , $\Delta E- T\Delta S = \Delta A$ and so it can be written as

$$\Delta G = \Delta A + P\Delta V \qquad \text{-------(3.10)}$$

It is seen that A is related to G in the same manner as E to H. For a reversible isothermal process, $\Delta A= w_{max.}$ It is seen that $\Delta G = w_{max} + P\Delta V$ or

$$-(\Delta G) = -w_{max} - P\Delta V \qquad \text{--------(3.11)}$$

In eqn (3.11) , w_{max} represents the total reversible work that is available and may include all kinds of work such as work expansion, electrical work, surface work etc. that the system is capable of doing on the surroundings. Since $P\Delta V$ is the work of expansion, eqn (3.11) can be written as ,

$$-(\Delta G) = -(w_{total} - w_{expansion}) =w_{net} \qquad \text{---------(3.12)}$$

For any system at constant temperature

$$\Delta A= \Delta E- T\Delta S \qquad \text{--------(3.13)}$$

$$\Delta G = \Delta H- T\Delta S \qquad \text{---------(3.14)}$$

If an ideal gas undergoes an isothermal change without any phase transformation (for example, isothermal expansion or compression) ΔH *and* ΔE *will be zero. So in such a case* $\Delta A= \Delta G$.

3.(ii). Maxwell's Partial relations

The state functions, E, H, P, V, A, T, G and S are related by means of four fundamental equations (*i*) to (*iv*)

(*i*) $dU = TdS – PdV$

(*ii*) $dH=dU+ PdV+ VdP = TdS + VdP$

(iii) **$dA = -PdV - SdT$**

(iv) **$dG = VdP - SdT$**

These equations *(i)* to *(iv)* are of form $dx = Mdy + Ndz$, where x is a single valued function of variables y and z(*i.e.*) a thermodynamic property of a closed system and dx is an exact differential. M and N are also functions of y and z such that

$$\mathbf{(\partial x/\partial y)_z = M \text{ and } (\partial x/\partial z)_y = N} \qquad \text{---------(3.15)}$$

$$\mathbf{(\partial M/\partial z)_y = (\partial^2 x/\partial z\partial y) \text{ and}} \qquad \text{---------(3.16)}$$

$$\mathbf{(\partial N/\partial y)_z = (\partial^2 x/\partial y\partial z)} \qquad \text{---------(3.17)}$$

It follows from Euler's criterion that

$$\mathbf{(\partial M/\partial z)_y = (\partial N/\partial y)_z} \qquad \text{---------(3.18)}$$

From eqn,

$$\mathbf{dE = TdS - PdV} \qquad \text{---------(3.19)}$$

$M = T$, $N = -P$, $x = U$, $y = S$ and $z = V$

Hence according to eqn (3.18),

$$\mathbf{(\partial T/\partial S)_S = -(\partial P/\partial V)_V} \qquad \text{---------(3.20)}$$

From eqn *(ii)*,

$$\mathbf{(\partial T/\partial P)_S = (\partial V/\partial S)} \qquad \text{---------(3.21)}$$

From eqn *(iii)*,

$$\mathbf{(\partial P/\partial T)_V = (\partial S/\partial V)_P} \qquad \text{---------(3.22)}$$

From eqn *(iv)*,

$$\mathbf{-(\partial S/\partial P)_T = (\partial V/\partial T)_P} \qquad \text{---------(3.23)}$$

Equations (3.20) to (3.23) are called *Maxwell equations or relationships.* All of these contain entropy term, which is a measure of spontaneity. In these equations it will be noticed that P and V, S and T occur in pairs diagonally opposite to each other on either side of the equation. On each side of the equation the state function occurring in the denominator of the equation on the opposite side is held constant. Maxwell equations are quite useful since entropy is expressed in terms of measurable state functions.

3.(iii) The Gibbs – Helmholtz equation:

For a closed system

$$\mathbf{dG = VdP - SdT} \qquad \text{------------(3.31)}$$

At constant pressure

$$dG = -SdT \quad \text{------------}(3.32)$$

Suppose G_1 the free energy of a system in state 1 at a temperature T K. If the temperature is changed by dT, the free energy would become $G_1 + dG_1$ at the temperature, (T + dT)K.

If the same system in state 2 has a free energy of G_2 at a temperature T the free energy in state 2 has a temperature (T + dT) will be $(G_2 + dG_2)$.

At constant pressure

$$dG_1 = -S_1dT \quad \text{------------}(3.33)$$

$$dG_2 = -S_2dT \quad \text{------------}(3.34)$$

$$(dG_2 - dG_1)_P = -(S_2 - S_1)dT \quad \text{------------}(3.35)$$

G_2-G_1 is equal to ΔG is the change in the free energy as the system transforms isothermally at T K from state 1 to state 2. $(dG_2 - dG_1)_P$ is the change in ΔG because the system in undergoing the transformation at (T + dT) K instead of T K.

$$(dG_2 - dG_1) = d(\Delta G) = -S\ dT \quad \text{------------}(3.36)$$

$$(d(\Delta G)/dT)_P = -\Delta S \quad \text{------------}(3.37)$$

The Gibbs-Helmholtz equation is obtained by substituting this value of ΔS in the defining equation for ΔG.

$$\Delta G = \Delta H - T\Delta S \quad \text{------------}(3.14)$$

$$\Delta G = \Delta H + T(\partial(\Delta G)/\partial T)_P \quad \text{------------}(3.38)$$

One of the most convenient applications of this equation is for a reaction taking place in an electro-chemical cell. ΔG for a chemical reaction can be calculated by allowing the same reaction to occur in electro-chemical cells whose E.M.F, E can be measured accurately. The E.M.F is equal to $-\Delta G/nF$ where n is the number of electrons involved in the reaction as represented by the balanced chemical equation and F, the Faraday. If E is determined at various temperatures, the variation in E with temperature or the temperature co-efficient of the E.M.F. which is related to $(\partial(\Delta G)/\partial T)_P$ can be determined. Once, ΔG at the desired temperature can be calculated.

Another form of Gibbs-Helmholtz equation can be derived as follows. Dividing eqn (3.38) by $-T^2$

$$-\Delta G/T^2 = -\Delta H/T^2 - 1/T(\partial(\Delta G)/\partial T)_P \quad \text{------------}(3.39)$$

Since,

$$\partial/\partial T\ (1/T) = -1/T^2$$

$$\Delta G\ \partial/\partial T\ (1/T) + 1/T(\partial(\Delta G)/\partial T)_P = -\Delta H/T^2 \quad \text{------------}(3.40)$$

Considering the L.H.S as the differential product *uv*.

$$[udv + vdu] = d(uv) \qquad \text{------------}(3.41)$$

Substituting $u = \Delta G$ and $v = 1/T$ eqn (3.40) can be written as

$$1/T(\partial(\Delta G)/\partial T)_P = -\Delta H/T^2 \qquad \text{------------}(3.42)$$

Since the pressure is kept constant one can write

$$d(\Delta G/T) = -\Delta H(dT/T^2) \qquad \text{------------}(3.43)$$

If ΔH is assumed to be constant in the temperature interval T_2 to T_1, this equation can be integrated between T_1 and T_2.

$$\int_{\Delta G_1}^{\Delta G_2} d(\Delta G/T) = \Delta H \int_{T_1}^{T_2} -dT/T^2 \text{ or} \qquad \text{------------}(3.44)$$

$$\Delta G_2/T_2 - \Delta G_1/T_1 = \Delta H\,(T_2 - T_1)/T_1T_2 \qquad \text{------------}(3.45)$$

This equation is useful in the calculating ΔG at any other temperature, provided that all other quantities are known.

Equations (3.14), (3.38), (3.42) and analogous equations involving the work function A instead of G are called **Gibbs – Helmholtz** equations

3.(iv).Criteria of equilibrium and spontaneity

From eqn (2.23), considering a spontaneous (irreversible)process occurring in the system taken alone

$$TdS > \delta q \qquad \text{---------}(3.24)$$

And for a reversible process $TdS = \delta q$. From the I law $\delta q = dE - \delta w$ and since $-\delta w = PdV$, $\delta q = dE + PdV$ for system in which only P-V work is done.

$$TdS > dE + PdV \text{ (irreversible process)} \qquad \text{---------}(3.25)$$

$$TdS = dE + PdV \text{ (reversible process)} \qquad \text{---------}(3.26)$$

$$TdS-(dE + PdV) \geq 0 \qquad \text{---------}(3.27)$$

At constant pressure $d(PV) = PdV$ and at constant temperature $d(TS) = TdS$. So at constant tempetrature and pressure eqn (3.27) can be written as

$$d(TS)_T - d[E+PV]_P \geq 0$$

$$d(TS)_T - d(H)_P \geq 0$$

$$-d(H-TS)_{T,P} \geq 0$$

$$-(dG)_{T,P} \geq 0 \qquad \text{-----------------(3.28)}$$

For a finite change, $(\Delta G)_{T.P}=0$ (rev) and $(\Delta G)_{T,P}<0$ (irrev).The equality applies to a reversible(equilibrium) process and the inequality to an irreversible process. In a similar fashion it can be shown that $(\Delta A)_{T.V}\leq 0$ (irrev) and $(\Delta A)_{T.V}=0$ (rev). From eqn (3.25), if the volume is constant (dV=0),$TdS-dE\geq 0$. For an isothermal process, d(TS) = TdS and so this equation can be written as

$$d(TS)_T - d[E]_V \geq 0$$

$$-d(E-TS)_{T,V} \geq 0$$

$$d(E-TS)_{T,V} \leq 0$$

$$(dA)=0(\text{rev}) \text{ and } (dA)<0(\text{irrev}) \qquad \text{-------(3.29)}$$

Most of the chemical reactions and physical transformations take place under conditions of constant T and P. Hence eqn (3.29) is most commonly used. For a system in equilibrium at a given temperature and pressure, the free energy must be minimum. For a spontaneous process occurring at constant T and P, ΔG must be negative. Thus we have a convenient test that can be applied to system alone to find out whether a process is feasible or not.

Standard free energies

G is a state function and the sign and magnitude of ΔG is a measure of the spontaneity of the process. As in the case of ΔH, ΔG also is dependent only on the initial and final states and not on the number and nature of stages through which a given reaction may pass. So calculations of the type using Hess's law can be carried out using ΔG values. As in the case of ΔH, it is preferred to have tabulated values of ΔG_f^0, standard free energies of formation . *The standard free energy formation of a compound is defined as the free energy change accompanying the formation of 1 mole of a compound from the constituent elements, the reactants and the products being in their respective standard states , at 1 atm and 298K. For the purpose of evaluating free energies of compounds, it is assumed that the free energies of all elements in their standard state are equal to zero, at 298K.* The standard states for solid and liquid elements are their pure and stable forms at 1 atm. For gaseous elements the standard states are the ideal gases are 1 atm pressure.

The literature values are always given at 298K. This convention that G_f^0 for an element in its standard state means that the standard free energy of a compound is equal to its standard free energy of formation (*i.e.*)

$$G^0_{\text{comp}} = \Delta G^0_{f\,(\text{compound})} \qquad \text{----------(3.30)}$$

3

3. (v). Free Energy Changes in Ideal Gases

The free energy changes for isothermal processes involving ideal gases can be calculated from Equations (5.21) and (5.27)

$$(dA)_T = - P.dV$$

$$\therefore (\triangle A)T = - f^{V2}$$

Where V_1 and V_2 are the initial and final volumes respectively. But for one mole of an ideal gas, $P = RT/V$.

In the case of Gibbs free energy,

Where P_1 and P_2 are the initial and final pressures. For one mole of an ideal gas, Since one mole of ideal gas is under consideration, in an isotermal process, $P_1.V_1 = P_2.V_2$. Hence it follows that for one mole of an ideal gas,

$$(\triangle A)_T = (\triangle G)_T$$

LESSON-IV

APPLICATIONS OF FREE ENERGY FUNCTIONS.

4. (i) Free energy change accompanying a chemical reaction : Van' t Hoff Reaction Isotherm :

The quantitative expression for the Le Chatlier's principle as applied to the effect of temperature is called the Van't Hoff equation (also called the reaction isochore, since it was originally derived for constant volume processes). For a reaction involving ideal gases in the standard state of 1.013 X 10^5 Nm^{-2} , ΔG^0 and K_p are related by equation 11.8.

$$\Delta G^0 = -RT \ln K_p \qquad \text{---------(4.1)}$$

The effect of temperature on K_p can be obtained by differentiating equation (1) with respect to temperature at constant pressure

$$[\partial(\Delta G^0)/\partial T]_P = -R\ln K_P - RT\,[\partial \ln K_P/\partial T]_P \qquad \text{--------(4.2)}$$

Multiplying through out by T,

$$T\,[\partial(\Delta G^0)/\partial T]_P = -RT\ln K_P - RT^2\,[\partial \ln K_P/\partial T]_P \qquad \text{--------(4.3)}$$

Since $[\partial(\Delta G^0)/\partial T]_P = -\Delta S^0$, eqn. (4.3) can be written as,

$$-T\Delta S^0 = \Delta G^0 - RT^2\,[\partial \ln K_P/\partial T]_P \qquad \text{--------(4.4)}$$

From the Gibbs-Helmholtz equation, at constant temperature, the substances taking part in the process being at their standard states.

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

K_P being independent of P , the partial notation and the condition of constant pressure are not necessary. Hence eqn. (4.4) can be written as

$$(d\ln K_P/dT) = (\Delta H^0/RT^2) \qquad \text{------------(4.5)}$$

In eqn. (4.5), ΔH^0 is the enthalpy change for the reaction, the reactants and products being in their standard states. In general, the enthalpy change does not vary appreciably with pressure and ΔH^0 can be replaced by ΔH, the enthalpy change of the reaction at moderate pressures Eqn. (4.5) can thus be written as

$$(d\ln K_P/dT) = \Delta H/RT^2 \qquad \text{-----------(4.6)}$$

and is known as the Vant's Hoff equation. Since K_P and K_c are related as $K_P = K_c\,(RT)^{\Delta n}$ taking logarithms,

$$\ln K_P = \ln K_c + \Delta n \ln R + \Delta n \ln T$$

$$[\partial \ln K_P / \partial T]_P = [\partial \ln K_c / \partial T]_P + \Delta n/T$$

From eqn. ,

$$\Delta H^0 / RT^2 = [d \ln K_c / \partial T]_P + \Delta n/T$$

$$[d \ln K_c / dT]_P = (\Delta H^0 - \Delta n\,(RT)) / RT^2$$

From eqn. , $\Delta H^0 = \Delta U^0 + \Delta n\,(RT)$ .So it is seen that

$$\mathbf{[d \ln K_c / dT] = \Delta U^0 / RT^2} \qquad \text{-------------(4.7)}$$

Eqn. (4.7) is called that van't Hoff reaction isochore or equation.

Van't Hoff Reaction Isotherm :

Consider the general reaction

$$aA + bB = l\,L + mM$$

taking place at a given temperature and pressure

$$(\Delta G)_{T,P} = G_{\text{Products}} - G_{\text{Reactants}}$$

$$= (l\,\mu_L + m\,\mu_M) - (a\,\mu_A + b\,\mu_B)$$

The chemical potential of any component j is given by

$$\mu_j = \mu^0_j = RT \ln a_j$$

Where μ^0_j is the chemical potential of j in the standard state. Hence,

$$\mathbf{(\Delta G)_{T,P} = (\Delta G^0)_{T,P} + RT \ln (a^l_L\, a^m_M / a^a_A\, a^b_B)} \qquad \text{----------(4.8)}$$

In eqn. (4.7) the activities refer to any arbitrarily chosen quantities. Substituting for ΔG^0 and indicating activities as equilibrium values by introducing the suffix 'e', eqn. (4.8) becomes,

$$(\Delta G)_{T,P} = -RT \ln ((a^l_L)_e (a^m_M)_e / (a^a_A)_e (a^b_B)_e) + RT \ln (a^l_L\, a^m_M / a^a_A\, a^b_B) \text{ or,}$$

$$\mathbf{(\Delta G)_{T,P} = -RT \ln K_a + RT \ln Q} \qquad \text{------------(4.9)}$$

Equation (4.9) is called the van't Hoff reaction isotherm. The function Q, called the reaction quotient, has the same form as K_a but the activities are arbitrary values whereas for K_a, the activities refer to equilibrium values. The reaction isotherm gives the increase of free energy accompanying the transfer of reactants at any specified activities

(concentrations) to products at specified activities (concentrations). If, however the arbitrary activities are chosen to correspond to the equilibrium values,
$\Delta G = 0$, since K_a ~~and~~ Q become identical.

It is necessary to specify the standard states employed since the actual values of the activities and of the equilibrium constant depend on the choice of the standard state. The same standard state is usually chosen for K_a and Q. for reactions involving gases, the standard state is that of unit fugacity i.e., ideal gases at $1.013 \times 10^5 \text{ Nm}^{-2}$. for ideal gases, the fugacities can be replaced by partial pressures and so eqn. (4.9) can also be written as

$$\Delta G = -RT \ln K_P + RT \ln Q_P \quad \text{------------(4.10)}$$

where the concentrations of the reactants and products are expressed in terms of the partial pressures. Similar equations can be written for different standard states.

The importance of the isotherm lies in the fact that it can be predict in which direction a reaction would proceed under a given set of conditions. For a reaction to proceed spontaneously $(\Delta G)_{T,P}$ may be < 0. If it is positive under a given set of conditions, the reaction cannot possibly take place under these conditions, though it may do so, if the conditions are suitably altered. It is seen from eqn. (4.9) that the sign of (ΔG) depends upon the relative values of K and Q. If eqn. (4.9) is written as

$$(\Delta G) = RT \ln (Q/K_a) \quad \text{------------(4.11)}$$

it is seen that if $Q > K_a$, (ΔG) is positive and for(ΔG) to be negative the arbitrary concentrations should be chosen to make $Q < K_a$. Another way in which (ΔG) can be made negative is to make use of the fact that the value of K_a is affected by changes in temperatures. If at a given temperature $K_a < Q$, (ΔG) is positive. However as temperature is altered suitably (increased for an endothermic reaction and decreased for an exothermic reaction), K_a becomes greater than Q and (ΔG) becomes negative.

4. (ii). Partial Molar Quantities – Chemical Potential.

Although the concept of partial molar quantities is employed in connection with thermodynamic properties other than the free energy, the partial molar free energy is used so frequently that it is necessary to introduce some of the general ideas here.

The results obtained in thermodynamics so far are based on the supposition that the system under consideration is a closed one, that is, one of constant mass. The change of any thermodynamic property is then due to a change in the state of the system, and not to the addition or removal of matter. In the study of systems consisting of two or more substances, i.e., solutions, and of heterogeneous systems containing two or more phases, is necessary to consider open systems, where composition and mass may vary. In this connection the concept of partial molar properties, as developed by G.N.Lewis (1907), is of great significance.

Consider any thermodynamic extensive property, such as volume, free energy, entropy, energy content, etc., the value of which, for a homogeneous system, is completely determined by the state of the system, e.g., the temperature, pressure, and the amounts of the various constituents present; thus, G is a function represented by

$$G = f(T, P, n_1, n_2, \ldots, n_i, \ldots) \quad \text{---} \quad (4.12)$$

Where $n_1, n_2, n_3 \ldots n_i$ are the numbers of moles of the respective constituents, 1,2,3...i... of the system as well as in the amounts of its constituents. The change in the property G is given by

$$dG = (\partial G/\partial T)_{P,n1,n2}\, dT + (\partial G/\partial P)_{T,n1,n2}\, dP + (\partial G/\partial n_1)_{T,P,n2}\, dn_1 + \ldots\ldots$$

(4.13)

The derivative $(\partial G/\partial n_1)_{T.P.n2}$ is called the **partial molar property** for the constituent I, and it is represented by writing a bar over the symbol for the particular property, i.e., G_1, so that

$$G_1 = (\partial G/\partial n_1)_{T,P,n2} \qquad G_2 = (\partial G/\partial n_2)_{T,P,n1} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4.14)$$

It is thus possible to write equation (4.14) in the form

$$dG = (\partial G/\partial T)_{P,n1,n2}\, dT + (\partial G/\partial P)_{T,n1,n2}\, dP + G_1\, dn_1 + G_2\, dn_2 \quad \text{-----} \quad (4.15)$$

Gibbs –Duhem equation.

If the temperature and pressure of the system are maintained constant, dT and dP at zero, so that

$$dG_{T,P} = G_1\, dn_1 + G_2\, dn_2 + \ldots\ldots\ldots + G_i\, dn_i \quad \text{-------} \quad (4.16)$$

Which gives, upon integration, for a system of definite composition, represented by the numbers of moles

$$G_{T,P,N} = n_1G_1 + n_2G_2 + \ldots\ldots \qquad \text{--------} \ (4.17)$$

By general differentiation of equation, at constant temperature and pressure but varying composition, it is seen that

$$dG_{T,P} = (n_1\,dG_1 + G_1\,dn_1) + (n_2\,dG_2 + G_2\,dn_2) + \ldots\ldots$$
$$= (n_1\,dG_1 + n_2\,dG_2 + \ldots..) + (G_1\,dn_1 + G_2\,dn_2 + \ldots..) \qquad \text{--------}(4.18)$$

Comparing this result with equation (4.19), it follows that at a given temperature and pressure

$$n_1\,dG_1 + n_2\,dG_2 + \ldots..+ n_i\,dG_i = 0 \qquad \text{--------}(4.20)$$

Which must obviously apply to a system of definite composition. This simple relationship is the basis of the important Gibbs – Duhem equation, first derived by J.W. Gibbs and later, independently, by P. Duhem.

PARTIAL MOLAR FREE ENERGY :

4. (iii).THE CHEMICAL POTENTIAL.

Although the partial molar quantities of various thermodynamic properties will be considered in the course of this book, the discussion at present will be restricted mainly to the consideration of the partial molar free energy, that is, for the *i*th constituent. This quantity is, for present purposes, identical with the function described by J.W.Gibbs, known as the molar chemical potential or, in brief, the chemical potential, and which is represented by the symbol. Hence, by the definition given above, the partial molar free energy or chemical potential of a constituent of a mixture is

$$(\partial F/\partial n_i)_{T,P,n1,n1,\ldots\ldots} = F_i = \mu_i \qquad \text{---------} \ \text{-}(4.21)$$

it is thus possible to rewrite equation (4.21), replacing G by F, and using μ for a partial molar quantities, to give

$$dF = (\partial F/\partial T)_{P,N}\,dT + (\partial F/\partial P)_{T,N}\,dP + \mu_1\,dn_1 + \mu_2\,dn_2 + \ldots\ldots + \mu_i\,dn_i \ \ldots.. \qquad \text{-------}(4.22)$$

4. (iv). VARIATION OF CHEMICAL POTENTIAL WITH TEMPERATURE AND PRESSURE:

The variation of the chemical potential of any constituent of a system with temperature may be derived by differentiating equation (4.21) with respect to temperature, and equation (4.23) with respect to n_i; the results are

$$(\partial F/\partial T)_{P,N} = -S \qquad \text{--------} \quad (4.23)$$

$$(\partial^2 F/\partial n_2\,\partial T) = (\partial \mu_i/\partial T)_{P,N} \qquad \text{----------}(4.24)$$

$$(\partial^2 F/\partial T\,\partial n_i) = -(\,\partial S/\partial n_i)_{T,P,ni} = -S_i \qquad \text{----------}(4.25)$$

the latter being equal to the partial molar entropy, by definition. Since dF is a complete differential, the order of differentiation is immaterial, and hence equations – (4.24) and (4.25) are equivalent, so that

$$(\partial \mu_i/\partial T)_{P,N} = -S_i \qquad \text{----------}\ (4.26)$$

F = H – TS, and differentiation with respect to n_i, the temperature, pressure and the numbers of the other constituents remaining constants, gives

$$(\partial F/\partial n_i)_{T,P,n1\ldots} = (\partial H/\partial n_i)_{T,P,n1\ldots\ldots} - T(\partial S/\partial n_i)_{T,P,n1,\ldots.}$$

Or, in alternative symbols,

$$\mu_i = F_i = H_i - TS_i$$

If the expression for the partial molar entropy give by equation (4.26) is introduced, it is seen that

$$H_i = \mu_i - T(\partial \mu_i/\partial T)_{P,N} \qquad \text{-------}(4.27)$$

Which is a form of the Gibbs-Helmholtz equation. Upon dividing both sides of equation (4.27) by T^2 , the result , is

$$(\partial(\mu_i/T)/\,\partial T)_{P,N} = -\,(H_i/T^2) \qquad \text{---------------}(4.28)$$

This equation is particularly useful for expressing the variation of the chemical potential with temperature, at constant pressure and composition, of any constituent of a gaseous, liquid or solid solutions.

The effect of pressure on chemical potential may be derived by differentiating equation (4.21) with respect to pressure and (4.24) with respect to pressure; it is seen that

$$(\partial F/\partial n_i\,\partial P) = (\partial \mu_i/\partial P)_{T,N} \qquad \text{----------(4.29)}$$

$$(\partial F/\partial P\,\partial n_i) = (\partial V/\partial n_i)_{T,P,n1.....} = V_i \qquad \text{----------(4.30)}$$

So that

$$(\partial \mu_i/\partial P)_{T,N} = V_i \qquad \text{-------------(4.31)}$$

The rate of change of chemical potential with pressure of a particular constituent of a system, at constant temperature, is thus equal to the partial molar volume of that constituent.

For a system of ideal gases, a further development of equation (4.31) is possible. For any constituent *i* of a mixture of ideal gases of total volume V, the equation of state is $p_i V = n_i RT$,where n_i is the number of moles of that constituent present in the mixture and the p_i is its partial pressure; hence,

$$V = n_i R\, T/p_i \qquad \text{------------(4.32)}$$

The partial molar volume is then given by differentiating with respect to n_i all the other n's remaining unchanged, at constant temperature and pressure; thus,

$$n_i = (\partial V/\partial n_i)_{T,P,n,.....} = RT/P_i \qquad \text{-------(4.33)}$$

It can also be shown that

$$(\partial \mu_i/\partial P)_{T,N} = RT/P_i \qquad \text{------(4.34)}$$

THERMODYNAMICS OF PHASE EQUILIBRIA

4.(v). CLAPEYRON EQUATION ;

Consider any system consisting of two phases e.g., liquid and vapour, of a single substance in equilibrium at constant temperature. Suppose that a small amount of one phase is transferred to the other; it follows, therefore, that the corresponding free energy is zero. As long as both the phases are present, an appreciable transfer, e.g., of 1 mole, from one phase to the other, will not disturb the equilibrium at constant temperature and pressure. For example, if liquid water and its vapour are in equilibrium, a large amount of water can be transferred from one phase to other, at constant temperature and pressure, without affecting the state of equilibrium. It is therefore, possible to utilize eqn*, viz.,

$$\Delta F = 0 \qquad (4.35)$$

where ΔF is the free energy change accompanying the process under consideration. If F_A is the molar free energy of the substance in one phase eg., liquid, and F_B is that in the other, e.g., vapour, the transfer of 1 mole of liquid to the vapour state is companied by an increase F_B and a decrease in F_A in the free energy; thus,

$$\Delta F = \Delta F_B - \Delta F_A \qquad (4.36)$$

Since, this is zero,when the system is in equilibrium it follows that

$$F_B = F_A$$

In other words, *whenever two phases of the same single substance are in equilibrium, at a given temperature and pressure, the molar free energy is the same in each phase.* This conclusion can be extended to three phases, which is the maximum number that can co-exist in equilibrium for a system of one component

Since the molar free energy of a given substance is the same in two phases A and B of a one component system at equilibrium, it follows that if the temperature and pressure are altered infinitesimally, the system remaining in equilibrium under the new conditions, the change in the free energy must be the same in each phase i.e.,

$$dF_A = dF_B \qquad (4.37)$$

In a phase change there is no work done other than work of expansion, and so it is permissible to use equation (4), namely

$$dF_A = V_A\,dp - S_A\,dT \text{ and } dF_B = V_B\,dp - S_B\,dT$$

Since dF_A is equal to dF_B

$$V_A\,dp - S_A\,dT = V_B\,dp - S_B\,dT$$

Therefore, $$(dp/dT) = (S_B - S_A)/(V_B - V_A) = (\Delta S/\Delta V) \qquad \text{------(4.38)}$$

the terms ΔS is the entropy increase for the transfer of a specified quantity; e.g., 1 mole, of substance from phase A to Phase B, and hence it is equal to (ΔH/T), where ΔH is here the molar latent heat of the phase change taking place at the temperature T; making this substitution, equation (4.32) becomes

$$(dP/dT) = (\Delta H/T\Delta V) \qquad \text{----------(4.39)}$$

where ΔV is the difference of the molar volumes in the two phases. This expression is a form of the equation first derived by B.P.E. Clapeyron ; it gives the variation of the equilibrium pressure with temperature for any two phases of a given substance.

THE CLAUSIUS – CLAPEYRON EQUATION :

If the temperature is not too near the critical point, the volume of the liquid, i.e., V_l is small in comparison with that of the vapor, i.e.,V_v at the same temperature and pressure; hence, $V_v - V_l$ may be replaced by V_v .

$$(dp/dT) = (\Delta H/T(V_v - V_l)) \qquad \text{--------------(4.40)}$$

or $$(dp/dT) = (\Delta H/TV_v) \qquad \text{--------------(4.41)}$$

further, in regions well below the critical point, the vapor pressure is relatively small, so that where V_v is the molar volume of the vapor and p is its pressure at the temperature T. Substituting RT/p for V_v in equation (4.39), this becomes

$$1/p\ (dp/dT) = (\Delta H_v/RT^2)$$

$$\mathbf{d(\ln p)/dT = (\Delta H_v/RT^2)} \qquad \text{-------(4.42)}$$

this expression is sometimes referred to as the Clausius – Clapeyron equation, for it was first derived by R.Clausius (1850), in the course of a comprehensive discussion of the Clapeyron equation, although the Clausius – Clapeyron equation is approximate, for it neglects the volume of the liquid and supposes ideal behavior of the vapor, it has the advantage of great simplicity. In the calculation of dp/dT from a knowledge of the heat of vaporization, or vice versa, it is not necessary to use the volumes of the liquid and vapor. However, as may be expected, the results are less accurate than those derived from the latter expressions.

INTEGRATION OF THE CLAUSIUS – CLAPEYRON EQUATION :

A particular advantage of the Clausius – Clapeyron equation is the readiness with which it can be integrated; thus, if the heat of vaporization is assumed to be independent of temperature, integration of equation (4.40) between the temperature limits of T_1 and T_2 and the corresponding vapor pressures p_1 and p_2 gives

$$\begin{aligned}\ln (p_2/p_1) &= -\Delta H_v/R\,(1/T_1-1/T_2)\\ &= \Delta H_v/R\,(T_2-T_1)/T_1T_2 \qquad \text{----------(4.43)}\end{aligned}$$

if ΔH is expressed in cal.mole $^{-1}$, then R will be 1.987 cal. Deg. $^{-1}$ mole $^{-1}$, and hence, after converting the logarithms, equation (4.41) becomes

$$\log (p_2/p_1)= \Delta H_v/4.576\,(T_2-T_1)/T_1\,T_2 \qquad \text{---------------(4.44)}$$

recalling that 4.576 arises from the product of the logarithm conversion factor (2.303) and the value of R, i.e., 1.987, in cal. deg. $^{-1}$ mole $^{-1}$. This equation may be used to calculate the heat of vaporization if the vapor pressures of the liquid at two adjacent temperatures are known. Because ΔH_v is not really independent of temperature, as was assumed in the integration of equation (4.40), the value obtained is actually a mean for the given temperature range. Alternatively, if a mean heat of vaporization is available, the vapor pressure at one temperature (or boiling point at a given pressure) can be calculated (approximately) if that at another is known.

CONDITIONS OF EQUILIBRIUM :

If a system of several phases consists of more than one component, then the equilibrium condition of equal molar free energies in each phase requires some modification. Because each phase may contain two or more components in different proportions, it is necessary to introduce partial molar free energies, in place of the molar free energies. Consider a closed system of P phases, indicated by the letters a,b,…,P, containing a total of C components, designated by 1,2,….,C, in equilibrium at constant pressure and temperature which are the same for all the phases. The chemical potentials, or partial molar free energies, of the various components in the P phases may be represented by

Suppose various small amounts dn moles of the components are transferred from one phase to another, the temperature and pressure remaining constant; the whole closed system is in equilibrium, and so according to equation (4.43) the sum of all the μdn terms for all the phases will be zero.

$$\Sigma \mu_i dn_i = 0 \qquad \text{--------(4.45)}$$

It follows therefore that

$$\mu_{1(a)}\, dn_{1(a)} + \mu_{1(b)}\, dn_{1(b)} + \ldots\ldots\ldots + \mu_{1(p)}\, dn_{1(p)}$$

$$\mu_{2(a)}\, dn_{2(a)} + \mu_{2(b)}\, dn_{2(b)} + \ldots\ldots\ldots\ldots + \mu_{2(p)}\, dn_{2(p)}$$

$$\cdot$$

$$\cdot$$

$$\cdot$$

$$\mu_{c(a)}\, dn_{c(a)} + \mu_{c(b)}\, dn_{c(b)} + \ldots\ldots\ldots\ldots\ldots + \mu_{c(p)}\, dn_{c(p)} = 0 \qquad \text{------------(4.46)}$$

at equilibrium, the total mass of each component will be constant will be constant, since the whole system is a closed one; hence,

$$dn_{1(a)} + dn_{1(b)} + \dots\dots\dots + dn_{1(p)} = 0$$

$$dn_{2(a)} + dn_{2(b)} + \dots\dots\dots + dn_{2(p)} = 0$$

$$\cdot$$

$$\cdot$$

$$dn_{c(a)} + dn_{c(b)} + \dots\dots\dots + dn_{c(p)} = 0 \qquad \text{------------}(4.47)$$

if the expression in equation (4.44) is to remain zero for all possible variations dn in the numbers of moles of the components, subject only to the restrictions represented by the equations (4.41), it is essential that

$$\mu_{1(a)} = \mu_{1(b)} = \dots\dots\dots = \mu_{1(p)}$$

$$\mu_{2(a)} = \mu_{2(b)} = \dots\dots\dots = \mu_{2(p)}$$

$$\cdot$$

$$\cdot$$

$$\cdot$$

$$\mu_{c(a)} = \mu_{c(b)} = \dots\dots\dots = \mu_{c(p)} \qquad \text{------------}(4.48)$$

It is seen, therefore, that when a system consisting of a number of phases containing several components is in complete equilibrium, at a definite temperature and pressure which are uniform throughout, the chemical potential of each component is the same in all the phases. It amy be noted that in the special case of a single component, the partial molar free energy (or chemical potential) is equal to the molar free energy, and the equations (4.46) become identical with (4.35)

If the phases of a system are not in equilibrium, the chemical potential of the components will not be the same in each phase. There will then be a tendency for each component, for which such a difference exists, to pass spontaneously from the phase in which its chemical potential is higher to that in which it is lower, until the vaslues become identical in the two phases. In other words, matter tends to flow spontaneously from a region of higher to one of lower chemical potential. There is thus seen to be an analogy between chemical potential and other forms of potential, e.g., electrical potential, energy potential. etc.

4. (vi). THERMODYNAMIC DERIVATION OF PHASE RULE :

By means of the conclusion reached in the preceding section, it is possible to derive the familiar phase rule, which gives the relationship between the number of components and phases in equilibrium in a system, and the number of variables, i.e., the degrees of freedom, which must be specified in order to define the system completely. The composition of a phase containing C components is given by C – 1 concentration terms, for if the concentrations of all but one of the component known, that of the last component must be equal to the remainder. Hence, for the compositions of P phases to be defined it is necessary to state P (C – 1) concentration terms. The total number of concentration variables of the system is thus P (C – 1). In addition to the composition, the uniform temperature and pressure of the system must be specified, and assuming that no other factors, such as surface or electrical effects, influence the equilibrium, it follows that

$$\text{Total number of variables} = P(C-1)+2$$

The fact of the closed system being in equilibrium, at a given temperature and pressure, leads to the result represented in the equations (4.42); this is equivalent to set of C (P–1) independent equations which automatically fix C (P – 1) of the possible variables. The number of variables remaining undetermined is then [P (C – 1) + 2] – C (P – 1) = C – P + 2. In order to define the system completely, therefore, this number of variables must be arbitrarily fixed, and hence must be equal to the number of degrees of freedom (F), or variance, of the system; hence,

$$F = C - P + 2, \qquad \text{---} \quad (4.49)$$

Which is the phase rule derived by J.W.Gibbs.

Thermodynamic Derivation of Phase Rule

The Phase Rule is given by the Equation F = C-P+2, Where represents The number of degrees of freedom, C, the number of components, and P, the number of phases. This can be derived thermodynamically, based on concept of chemical potential.

Let us imagine a system consisting of Components, 1,2,3,.C. distributed among the phases, a,b,c, ...P. Let $\mu_{1(a)}$, $\mu_{1(b)}$, $\mu_{1(c)}$,.. $\mu_{1(p)}$, etc., represent the chemical potentials of the component 1 in the phases a,b,c,..P and let the corresponding values for the other components be $\mu_{2(a)}$, $\mu_{2(b)}$, $\mu_{2(c)}$,$\mu_{2(p)}$,….,etc.

(Fig .4.1.)

Component / Phase	1	2	3	…	C
a	$M_{1(a)}$	$M_{2(a)}$	$M_{3(a)}$	…	$M_{c(a)}$
b	$M_{1(b)}$	$M_{2(b)}$	$M_{3(b)}$	…	$M_{c(b)}$
C	$M_{1(c)}$	$M_{2(c)}$	$M_{3(c)}$	…	$M_{c(c)}$
⋮	⋮	⋮	⋮	⋮	⋮
P	$M_{1(p)}$	$M_{2(p)}$	$M_{3(p)}$	…	$M_{c(p)}$

The composition of each phase can be defined by (C – 1) concentration terms. (Since the total number of components is a constant, it is not necessary to know all the concentration terms: it is sufficient if (C – 1) conceptration terms are known.) Hence for P phases, the total number of concentration terms will be p.(C – 1). In addition to these, the system will have two more variables, namely, the temperature and pressure. Hence the total number of variables for the system is P(c – 1) +2.

Out of these total number of variables, some variables are fixed by the equilibrium state of the system. For Calculating this fixed number of variables, let us imagine that a small quantity d_{n1} of component 1 is transferred from phase a to phaseb. Then the change in chemical potential will be

$$\mu_{1(b)}.d_{n1} - \mu_{1(a)}.d_{n1}$$

(4.50)

But for a system at constant pressure and temperature, according to Equation ($\Sigma \mu_1 dn_1 = 0$)

$$\mu_{1(b)}.d_{n1} - \mu_{1(a)}.d_{n1} = 0$$

(4.51)

$$\mu_{1(a)} = \mu_{1(b)}$$

(4.52)

Further, considering the transfer of dn1 moles of component 1 from phase b to c, the following relation will be obtained

$$\mu_{1(b)} = \mu_{1(c)}$$

(4.53)

Similarly,

$$\mu_{1(c)} = \mu_{1(d)}$$

(4.54)

Thus if two phases a and þ are under consideration, one Equation (4.52) defines the system and for three phases, two Equations (4.52) (4.53) and define the system will be (P-1) for a single component. Consequently, for C components, the number of equations which define the equilibrium state of the system will be C.(P – 1). The number of degrees of freedom is equal to the total number of variable minus the number of fixed variables, or

$$F = P(C-1)+2-C(P-1) = C-P+2 \qquad (4.55)$$

Which is nothing but the equation representing the phase rule.

4. (vii) Thermodynamic Derivation of Raoult's law

W. Henry (1803) was the first to establish quantitative relationship between the solubility of a gas and its pressure, and this relationship is known as Henry's Law which states that at a fixed temperature, the mass of a gas dissolved in a given quantity of a solvent is proportional to its partial pressure. That is,

$$m = K.P \qquad (4.56)$$

where m is the mass of the gas, p is the partial pressure and K is the proportionality constant. Equation (4.56) may also be written as.

4

$$\frac{W_B}{W_A} = K' . P_B \qquad (4..57)$$

$$\frac{W_B / M_B}{W_A / M_A} = K'' . P_B \qquad (4.58)$$

Or

$$\frac{n_B}{n_A} = K'' P_B \qquad (4.59)$$

where W_A, M_A and n_A represent the weight, molecular weight and number of moles, respectively, of the solvent and W_B, M_B and n_B are the corresponding values of these quantities for the gas, P_B is the pressure of the gas and K'' is a constant. If the solution is dilute, i.e., $n_A > n_B$, Equation (4.59) may be written as.

$$\frac{n_B}{n_A + n_B} = K'' . P_B \qquad (4.60)$$

But the left-hand side of Equation (4.60) represents the mole fraction of the gaseous solute in the solution, x_B. Hence

$$x_B = K'' . P_B \qquad (4.61)$$

Thus, the solubility of a gas, expressed as mole fraction, is proportional to the pressure of the gas and Equation (4.61) may be considered as the ideal form of Henry's law.

The applicability of Equation (4.61) may also be considered from a different point of view, wherein P_B may be regarded as the vapour pressure of a volative solute whose mole fraction in the solution is x_B, and Henry's law may also be stated as *in a dilute solution, the vapour pressure of a solute is proportional to its mole fraction.*

Taking logarithms on both sides, Equation ( ) Becomes

$$\text{In } x_B = \text{In } K'' + \text{In } P_B \qquad (4.62)$$

So that on differentiation

$$\text{d In } x_B = \text{d In } P_B \qquad (4.63)$$

or

$$\frac{\text{d ln P}_\text{B}}{\text{d ln x}_\text{B}} = 1 \qquad (4.64)$$

Now, assuming that the solvent and solute of a solution are represented by *A* and *B*, at **constant** temperature and pressure,

$$\text{dG} = \mu_A \,.\, \text{d}n_A + \mu_B \,.\, \text{d}n_B \qquad (4.65)$$

according to Equation ($\text{dG} = \mu_1 \,.\, \text{d}n_1 + \mu_2 \,.\, \text{d}n_2 + \ldots$). But general differentiation of Equation ($\text{G} = \mu_1 \,.\, n_1 + \mu_2 \,.\, n_2 + \ldots.$) gives

$$\text{dG} = \mu_A \,.\, \text{d}n_A + n_A \,.\, \text{d}\,\mu_A + \mu_B \,.\, \text{d}n_B + n_B \,.\, \text{d}\,\mu_B \qquad (4.66)$$

Comparing Equations (4.66) and (4.67), it follows that

$$n_A \,.\, \text{d}\mu_A + n_B \,.\, \mu_B = 0 \qquad (4.67)$$

or

$$n_A \,.\, \text{d}\mu_A = - \; n_B \,.\, \text{d}\mu_B \qquad (4.68)$$

The relationship represented by Equation (4.68) is known as the Gibbs-Duhem equation.

Dividing both sides of Equation (4.67) by $(n_A + n_B)$ which is equal to the total number of moles, we get.

$$\frac{n_B}{(n_A+n_B)} . d\mu_A = - \frac{n_B}{(n_A+n_B)} . d\mu_B \qquad (4.69)$$

or

$$x_A . d\mu_A = - x_B . d\mu_B \qquad (4.70)$$

where x_A and x_B are the mole fractions of A and B respectively.

Dividing both sides of euqtion by dx_A,

$$x_A \frac{d\mu_A}{dx_A} = x_B \frac{d\mu_B}{dx_A} \qquad (4.71)$$

But since $x_A = (1-x_B)$, $dx_A = - dx_B$, so that Equation (4.71) becomes

$$x_A \frac{d\mu_A}{dx_A} = x_B \frac{d\mu_B}{dx_B} \qquad (4.71)$$

or

$$\frac{d\mu_A}{d\ln x_A} = \frac{- d\mu_B}{d \ln x_B} \qquad (4.72)$$

Assuming that the vapours of the two components A and B behave like ideal gases,

$$\mu_A = \mu_{0(A)} + RT \text{ In } P_A \qquad (4.73)$$

And

$$\mu_B = \mu_{0(B)} + RT \text{ In } P_B \qquad (4.74)$$

according to Equation ($\mu = \mu_0 + RT. \ln P$) Hence

$$d\mu_A = RT \text{ In } P_A \qquad (4.75)$$

And

$$d\mu_B = RT \text{ In } P_B \qquad (4.76)$$

substituting there values of $d\mu_A$ and $d\mu_B$ in Equations (4.71)

$$x_A \frac{d \ln P_A}{d x_A} = x_B \frac{d \ln P_B}{dx_B} \qquad (4.77)$$

$$\frac{d \ln P_A}{d \ln x_A} = \frac{d \ln P_B}{d \ln x_B} \qquad (4.78)$$

Equations (4.77) and (4.78) are the alternative forms of a general equation called the Duhem-Margules equation, first derived by Gibbs (1876) and later, independently by Duhem, Margules and Lehfeldt.

From a comparison of Equations (4.131), and (4.64) it follows that.

$$\frac{d \ln P_A}{d \ln x_A} = 1 \qquad (4.79)$$

so that

$$d \text{ In } P_A = d \text{ In } x_A \qquad (4.80)$$

or

$$\text{In } P_A + K_1 = \text{In } x_A + K_2 \qquad (4.81)$$

Where K_1 and K_2 are the integration constants. Extracting out the logarithms.

$$P_A = K \,.\, x_A \qquad (4.82)$$

Where K is a constant. When $x_A = 1$, that is, for the pure solvent, Hence $K = P^0$, where P^0 is the vapour pressure of the pure solvent.

$$P_A = P^0 \,.\, x_A \qquad (4.83)$$

Equation (4.83) represents a general law known as **Raoult's law** which may be stated as : ***the vapour pressure of a solvent in a solution is directly proportional to the mole fraction of the solvent.***

MODEL QUESTIONS :

Short answer questions

1. Define first and second laws of the thermodynamics.
2. What do you understand by the term entropy
3. Derive clapeyron equation
4. Derive Gibbs – Helmhotz equation
5. Write a note on chemical potential
6. What are the criteria of equilibrium and spontaneity.

Long answer questions:

1. Derive phase rule thermodynamically
2. derive Vant Hoff equation
3. Discuss the entropy changes in isolated systems in reversible and irreversible process
4. Derive Gibbs – Duhem equation

UNIT - II

LESSON – 1

RADIOACTIVE DECAY AND NUCLEAR STABILITY

An element is said to be radioactive if the nuclei of its atoms keep disintegrating spontaneously thereby transforming in to a different element with the emission of nuclear particles. These are about 2000 radio nuclides as against 275 stable nuclides. The properties of the radiations from the various radioactive elements were investigated in detail by Ernest Rutherford, Becquerel, Madame Curie and others. Three different types of radiations - α, β and γ with different characteristics of range, penetration and charge were identified.

2.1 (i). Radioactive Decay :

The number of atoms of a radioactive substance decaying per unit time is called the rate of decay. The following are some of the important modes of nuclear decay.

Type	General nuclear reaction	Example
α - decay	${}^{A}_{Z}X \rightarrow {}^{A-4}_{Z-2}Y + \alpha$	${}^{226}_{88}Ra \rightarrow {}^{222}_{86}Rn + {}^{4}_{2}He(\alpha)$
β - decay	${}^{A}_{Z}X \rightarrow {}^{A}_{Z+1}Y + \beta^{-} + \nu^{-}$	${}^{32}_{15}P \rightarrow {}^{32}_{16}S + \beta^{-} + \nu^{-}$
β+ - decay	${}^{A}_{Z}X \rightarrow {}^{A}_{Z-1}Y + \beta^{-} + \nu$	${}^{22}_{11}Na \rightarrow {}^{22}_{10}Ne + \beta^{+} + \nu^{-}$
Electron capture	${}^{A}_{Z}X + e \rightarrow {}^{A}_{Z-1}Y + \nu$	${}^{55}_{26}Fe + e \rightarrow {}^{55}_{25}Mn + \nu$

The rate of decay of a radio element at any instant is proportional to the number of its atoms present at that instant. As the decay proceeds, the number of the atoms decrease and so does the rate of decay. The Kinetics of decay follows the first order rate law

$$-\frac{dn}{dt} = \lambda N \qquad \ldots \qquad (1)$$

Where λ is a proportionality constant; known as the decay constant having the dimensions of time^{-1}. The number of atoms of a substance decaying per unit time dN / dt, called the activity of the substance, is always proportional to the total number of atoms N present at time t.

Rearranging the equation 1 as:

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

On integration, $\ln N = -\lambda t + C$

Where C is the integration constant whose value is revealed if we put N = No for t = o, thus

$$\ln N_0 = O + C$$

Replacing C by its value, we finally get

$$\ln N = -\lambda t + \ln No$$

$$\ln(N/No) = -\lambda t$$

$$N = No.\, e^{-\lambda t} \ \ldots\ldots\ldots\ldots \quad (2)$$

where No and N are the numbers of atoms of the parent element remaining at time zero and t respectively. The exponential nature of the decay rate is revealed by fig .1, By converting Logarithms into ordinary logarithms Equation 2 can be written as

$$\log N = \log\ N_0 - 0.4343\ \lambda t \ldots\ldots (3)$$

This expression means that if the logarithm of N, the number of atoms present at any time, is plotted against the time, the results should fall on a straight line. The slope of this line will be equal to – 0.4343λ and hence it can be used to obtain the value of λ, the decay constant for the given radio element.

Units of Radioactivity :

The activity of one gram of ^{226}Ra is considered the unit of radioactivity and is called Curie (Ci) which is 3.7×10^{10} disintegrations per sec. The S I unit of radioactivity is the becquerel (Bq) which is defined as the activity due to disintegration per second . Hence $1Ci = 3.7 \times 10^{10} Bq$.

2.1 (ii). Half-life -- Determination of Half – life :

A quantity more frequently used to characterise a radio element is its half life period. ($T_{½}$) It is defined as the time needed for a given amount of the radio element to decay exactly to half its initial value. Its relation to λ is revealed when we make

N = No / 2 in equation . . . . . .(3)

$$\text{Log } ½ = -\ 0.4343\ \lambda T_{1/2}$$

$$T_{½} = \frac{0.693}{\Lambda} \ \ldots\ldots\ldots (4)$$

The half life of the radio element can thus be obtained directly from λ, the decay constant.

Generally no two radionuclides have identical half – life values. Thus a radioactive element can be identified by its characteristic half – life. The half life of most of the radionuclides vary from 4.2 x 10^{-6} sec (^{210} Po) to 1.39x 10^{10} y (^{232} Th) . There are two commonly used methods for the determination of half – life values namely graphical method and the specific activity method.

Graphical Method :

The rate at which particles are emitted in a small time interval may be taken as proportional to the number N of active atoms remaining at that instant of this rate, which can be determined by automatic counting instruments, measured after time t , is represented by I_t then equation (3) may be written as

$$\log I_t = \log I_g - 0.4343\,\lambda t\,\ldots\ldots\,(5)$$

Where I_t which need not be known, is the disintegration rate at zero time. Half lives having moderate values ranging from few seconds to a few years, can be determined by using the relationship (5). The values of log. I_t plotted against time on a semi log graph yeild a straight line as shown in the fig .2. The slope of this line give the decay constant from which T $_{½}$ can be calculated.

Specific Activity method :

The activity A of a radioactive substance is the quantity that is usually measured experimentally. It is the rate of decay of the number of disintegrations per unit time is given by

$$A = \left| dN / dt \right| = \lambda N$$

For practical purposes, specific activity is used which is defined as the activity per unit mass of material. The specific activity method is used for determining very long half – lives in which the activity does not decrease during the period of measurement . The number of atoms present in a radioactive substance is determined by an analytical method and the number of atoms decaying per unit time is measured. The decay constant (λ) can be determined by the relationship.

$$\lambda = \frac{\text{Number of atoms decaying per unit time}}{\text{Number of atoms present}}$$

From this relationship the half – life can be calculated. The graphical and the specific activity methods are not suitable for determining extermely short half - lives, for which special methods have to be employed.

2.1 (iii). Radioactive Equilibrium – Conditions for Different Equilibria

In many cases radioactive decay leads to the production of a radioactive daughter with a characteristic activity of its own. Let us take the case of a chain consisting of a parent substance A with a decay constant λ_A that decays to a daughter substance with a decay constant λ_B, which is unstable and decays to a stable species C ,. The steps are

$$A \xrightarrow{\lambda_A} B \xrightarrow{\lambda_B} C$$

The rate at which the number of daughter atoms builds up is equal to the ratio of their formation from the decaying parent atoms less the rate of their own decay. If N_A and N_B are the number of parent and daughter atoms respectively which are present at time t and N_A^o and $N_B^{\ o}$, the corresponding number of atoms present at time t = O
Then,

$$\frac{dN_B}{dt} = \lambda_A N_A - \lambda_B N_B$$

$$\text{Since } N_A = N_A^{\ O}\ e^{(-\lambda_A t)}$$

$$\text{We have } \frac{dN_B}{dt} = \lambda_A N_A^o\, e^{-\lambda_A t} - \lambda_B N_B$$

By integrating this equation, we get the number of daughter atoms N_B which are present at time t as

$$N_B = N_A^{\ O} \frac{\lambda_A}{\lambda_B - \lambda_A} \left[e^{-\lambda At} - e^{-\lambda B t} \right] + N^o_B\, e^{-\lambda_B t} \qquad \ldots\ldots.(6)$$

On the right hand side of equation (6) the first term gives the growth of the daughter from the parents and its decay, while the second term represent the concentration of the daughter present initially at time t =o, of N_B^o in zero, then

$$N_B = N_A^{\ O} \frac{\lambda_A}{\lambda_B - \lambda_A} \left[e^{-\lambda_A t} - e^{-\lambda_B t} \right] \ldots\ldots (7)$$

Depending on the relative magnitudes of λ_A and λ_B and assuming the daughter activities initially present to be zero ($N_B^{\ o} = O$) , some important condition can be drawn from equation. . . . . .. (7)

If the parent is long lived than the daughter ($\lambda_A < \lambda_B$) and if t is sufficiently large, the second term of equation (7) i $e^{-\lambda_B t}$ vanishes, Then we have

$$N_B = \frac{\lambda_A}{\lambda_B - \lambda_A} N_A^{o} e^{-\lambda_A t} \qquad \ldots\ldots\ldots\ldots\ldots(8)$$

Since $N_A^{O} e^{-\lambda_A t} = N_A$, We obtain

$$\frac{N_B}{N_A} = \frac{\lambda_A}{\lambda_B - \lambda_A} \qquad \ldots\ldots\ldots\ldots\ldots(8)$$

It is evident from equation (8) that the ratio of the number of daughter atoms to parent atoms becomes constant, and the rate of decay of the daughter is now determined by the rate of decay of the parent. This state is called the transient equilibrium and is shown in fig 3 . A limiting case of transient equilibrium occurs when the half life of the parent is considerably greater than that of the daughter ($\lambda_B << \lambda_A$). Under there condition equation (8)became,

$$\frac{N_B}{N_A} = \frac{\lambda_A}{\lambda_B} \qquad \ldots\ldots\ldots\ldots(9)$$

This means that a sufficiently long time interval has elapsed, the ratio of the daughter atoms to the parent atoms will remain constant. This is known as secular equilibrium and is illustrated in fig 4,

If the parent has a short half life compared with that of the daughter ($\lambda_A > \lambda_B$)equation (7) simplifies to

$$N_B = N_A^{O} e^{-\lambda_B t} \qquad \ldots\ldots\ldots\ldots(10)$$

This means that N_A^{O} parent atoms very rapidly decay to an equal number of daughter atoms which in turn decay at a rate characteristic of the daughter. This is called the state of no equilibrium and is shown in fig 5.

Example of the foregoing three types of equilibrium are.

Secular equilibrium :

(i). $^{238}U \xrightarrow{4.5 \times 10^{9} Y} {}^{234}Th \xrightarrow{241\ d}$

(ii). $^{90}Sr \xrightarrow{28.1Y} {}^{90}Y \xrightarrow{64.1\ h}$

Transient Equilibrium

(i). $^{140}Ba \xrightarrow{12.8\ d} {}^{140}La \xrightarrow{40.2\ h}$

(ii). $^{212}Pb \xrightarrow{19.7min} {}^{212}Bi \xrightarrow{60.5\ min}$

No - Equilibrium

(i). $^{218}Pb \xrightarrow{3.05\ m} {}^{214}Pb \xrightarrow{26.8min}$

(ii). $^{210}Tl \xrightarrow{1.32\ min} {}^{210}Pb \xrightarrow{22y}$

2.1 (iv). Nuclear Stability - Simple Theories of Nuclear Stability

A study of the characteristic of a large number of stable and radioactive element shows the following to be some of the important factors involved .

1. Even – odd nature of the number of protons and neutrons.

A plot of the number of neutrons N versus the number of protons Z for various stable nuclides (fig 6) known as segre chart , provides some useful information relating to stability of nuclides O up to Z = 2O the number of neutrons and protons is almost equal. Beyond this value the nuclei contain more neutrons than protons. This is because the coulombic repulsion between the protons in the nucleus becomes more prominent as the mass number (A) increases, There by requiring the addition of extra neutrons to counter balance it .

2. The neutron to proton ratio N / Z

Except in the case of light or ordinary hydrogen H, all other nuclides contain both neutrons and protons . A look at the stable nuclides shows that the radio N / Z in them is 1. The ratio is 1 in all the light stable nuclides up to $^{40}{}_{20}Ca$ and thereafter the ratio is > 1 for heavy nuclei. The segre chart shows that a large number of elements have several stable isotopes and the curve is in the nature of a strip or zone which widens out higher Z values. All the stable nuclides fall with in this zone and it is significant that nuclides falling outside the zone are invariably radioactive. Those lying above the zone are richer in neutrons than required for stability and they display a tendency to have one neutron transformed in to a proton (β^- activity) and thus approach the zone of stability. The reverse holds good for nuclides lying below the zone which are deficient in neutrons and they exhibit β^+ or electron capture radioactivity by which a proton is converted in to a neutron. Thus an optimum N / Z ratio appears to be another factor responsible for nuclear stability.

Simple theories of nuclear structure :

The concept of a nucleus being composed of protons and neutrons confined within a small volume requires that same force with properties quite different from those of electrostatic forces operate. This force must be such that it attracts the protons to each other nullifying their mutual electrostatic repulsion and must also act on the neutrons. A fundamentally different force involving protons and neutrons called the nuclear force is supposed to operate between them. In 1935, H Yullawa suggested that the forces between nucleons might arise as a result of an exchange of a practicle called μ - meson or muon. The actual exchange particle was discovered in 1947 and is called π – meson or peron.

Because of the difficulty in explaining quantitatively the forces between nucleons, another approach to the problem of the atomic nucleus is to set up a model which will account for the behaviour of the nucleus as a whole. Several models of the nucleus have been developed which can be divided into two categories. In the first categories, called liquid drop model, it is assumed that there exists a strong interaction among all the nucleons. The second category compresses the independent particle model which is called the shell model. It assumes that each nucleon moves independently of the others in a nuclear patented well. The neutrons and protons are arranged in pairs having opposite spin and the nuclear properties depend only on one or two unpaired nucleons that occupy the highest energy levels. We now briefly out line the features of both the models.

2.1 (v). Liquid Drop Model :

The liquid drop model first proposed by Bohr in 1936 and later developed by Bohr and wheeler in 1939, considers the nucleons analogous to a small drop of liquid in which the nucleons are held together by short range attractive forces. In the ground state, the nucleus is spherical in shape and the nucleons like the molecules in a liquid drop, are in constant motion. If the total energy of the nucleons is increased by bombardment with a particle, the binding energy is rapidly shared among the other nucleon. As a consequence, large statistical fluctuations may occur in the energies of the individual nucleons and it becomes possible for sufficient energy to be concentrated on one particle in order to enable it to escape from the nucleus resulting in a nuclear reaction. Sometimes, the concentration of energy on one particle may also cause the elongation of the nucleus into a dumbbell shape, which when sufficiently large, could lead to fission.

We can calculate the binding energy (in MeV) of the nucleus using the liquid drop model and a semi empirical equation has been proposed

$$BE = 14.1\,A - 13\,A^{2/3} - \frac{0.6\,Z^2}{A^{1/3}} - \frac{20\,(A-2\,Z)^2}{A} \pm \frac{125}{A}$$

The five terms on the right hand side of this equation are related to a particular nuclear property which affects the binding energy.

The first term indicates that the binding energy is nearly proportional to the number of nucleons. The second term represents the reduction in the binding energy in proportion to the nuclear surface area. The third term specifies the decrease in the binding energy arising as a result of the coulombic repulsion between the protons which is proportional to Z^r / R or $Z^r / A^{1/3}$. The fourth term accounts for the decrease in the binding energy due to excess neutrons over protons. The last term represents an odd – even effect and accounts for the increased stability due to the pairing of nucleons. The value is positive for even nuclides, zero for odd–even and even–odd nuclides and negative for odd–odd nuclides.

2.1 (vi). Shell Model :

Some nuclear properties were found to exhibit marked discontinuities near certain even values of the proton or neutron number of 2,8,20,50,82 and 126 which are called magic numbers. A few general observations corresponding to the magic numbers are

(1) Elements with Z as a magic number have a large number of isotopes compared to their immediate neighbours. For example, tin (Z =50) has ten stable isotopes and calcium (Z = 20) has six.

(2) The stable end product of the three main natural radioactive series in Pb (Z = 82)

(3) Nuclides with Z or N or particularly both Z and N, corresponding to magic numbers, are the most abundant in their mass range (e.g., ${}^{16}_{8}O$).

(4) Nuclides with N equal to magic numbers have very low neutron capture cross–section where as those with one neutron less than the magic number have very high neutron capture cross sections.

These observations suggest a possibility of an energy level arrangement in the nucleus which is similar to that of electrons in an atom.

The shell model assumes that the nucleons are distributed in a series of discrete energy level satisfying certain quantum–mechanical conditions like the electrons in the outer sphere. As the capacity of each level is reached, a closed shell is formed, the protons and neutrons being in separate shells. It is also referred to as the single particle model as this model considers the motions of individual nucleons.

Model Questions:

1. Write short notes on nuclear stability?
2. Define half-life, average life and decay constant?
3. Discuss the methods for the determination of half-life?
4. Explain the simple therioes of Nuclear structure.

LESSON - 2

TYPES OF DECAY AND COUNTING TECHNIQUES

Radioactive Decay Processes

2.2.(i) α – DECAY

α – decay has been observed for all the elements beyond lead and for some nuclides of intermediate masses (e.g., $^{142}_{58}Ce$ and $^{141}_{60}Nd$).

The energies of α – particles range from 1.5 MeV ($^{142}_{58}Ce$, $t_{1/2} = 5 \times 10^{15}$ y) to 8.75 MeV ($^{212}_{84}Po$, $t_{1/2} = 3 \times 10^{-7}$ sec). H. Geiger and J.M. Nuttall were the first to observe that nuclides emitting α – particles with high energies have shorter half-lives. They showed that when the logarithm of the range R of the α – particles is plotted against the logarithm of the decay constant (λ), a series of straight lines are obtained as expressed by the relationship

$$\log \lambda = A \log R + B,$$

where A and B are constants. This relationship can also be expressed as a relation between ~~the decay~~ constant and the energy E of the α – particles:

$$\log \lambda = A' \; ' \log E + B \;,$$

where A and B are another set of constants. The experimentally determined value of the α – particle energy (E_α) is less than its disintegration energy (E) because some energy is used during the recoil (E_r) of the daughter nucleus. Thus,

$$E = E_\alpha + E_r = E_\alpha \left(\frac{M_\alpha + M_r}{M_r} \right)$$

Where M_α and M_r are the masses of the α – particle and the recoil nucleus, respectively.

The computation of α – particle energies shows that the α – particles are monoenergetic in a few cases, but, in most instances, they consist of two or more groups. Further, γ – rays are simultaneously emitted with some or all of them.

G.Gamow demonstrated the manner in which the energies of the α – particles and γ-rays could be correlated in terms of nuclear energy levels. When the daughter nucleus formed as a result of α – emission is in an excited state, it goes to the ground state by the emission of one or more γ-rays. From a knowledge of the α – and the γ-energies, a decay scheme can be constructed. Figure 2.1 gives a scheme for the α – decay of $^{226}{}_{90}$ Th to $^{222}{}_{88}$ Ra.

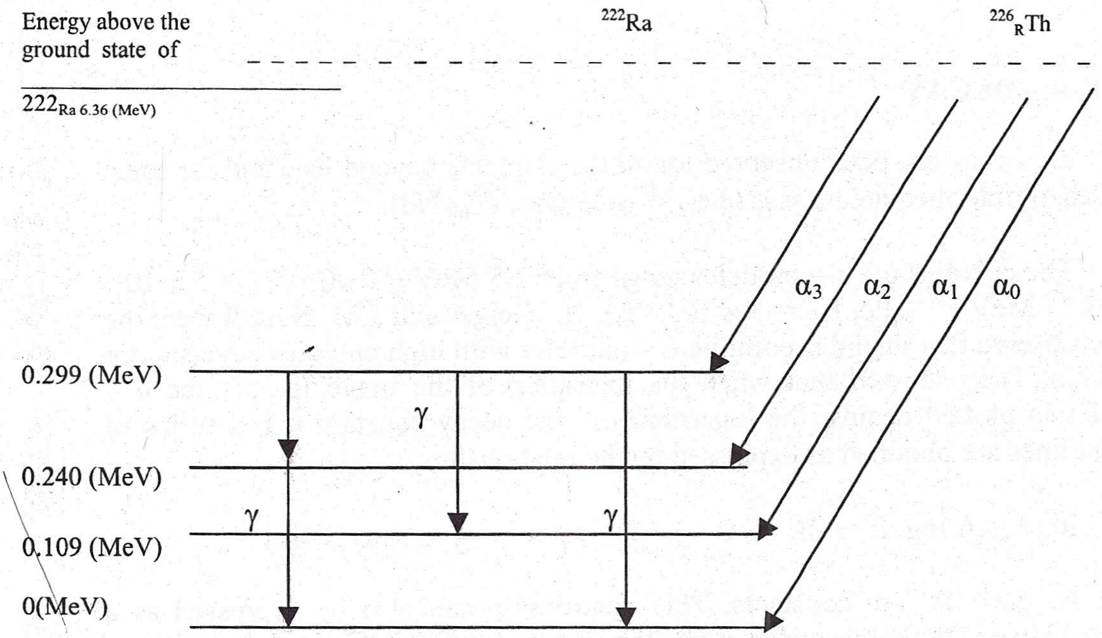


Fig. 2.1 α -decay sheme for 226 Th

2.2 (ii) α – DECAY THEORY

A charged α – particle has to surmount the potential barrier in order to enter the nucleus Similarly, in order escape from the nucleus, the α – particle has to surmount the potential barrier. Let us consider an example. An α – particle coming out of the ^{238}U nucleus has an energy less than 5 MeV. Although the height of the potential barrier is about 24 MeV, the α – particle still manages to escape from the nucleus. An explanation for this phenomenon was provided by G. Gamow and by R.W. Gurney and E.U. Condon in 1982 on the basis of quantum mechanical theory. According to this explanation, the α – particle is formed inside the nucleus represented by the potential well and is assumed to oscillate back and forth by bouncing off the walls (see Fig. 2.3). According to classical mechanics, the particle will never be able to escape from the potential well unless it has an energy equal to the height of the barrier. In quantum mechanical terms, however, there is a finite probability that particle will penetrate the barrier (called tunnel effect). Based on these considerations, a complex equation can be derived for the probability of an α – particle with a given energy escaping when it reaches the external surface of the nucleus. As a fair approximation, we may state that this probability is greater (1) the closer the energy of the α – particle relative to the top of the barrier and (2) the smaller the thickness of the barrier at a point corresponding to the given energy value. It is evident from Fig. 2.3 that the higher the energy, the lesser the thickness of the barrier. Consequently, the higher the energy of the α – particle, the greater the likelihood of its being emitted from the nucleus. Thus, we see that nuclides with high decay constants emit α – particles having high energies and long ranges, whereas the long – lived nuclides emit α – particles with low energies and short ranges, as observed by Geiger and Nuttall. It should be noted that this explanation essentially applies only to even-even nuclides.

2.2 (iii) β – DECAY

β – decay includes three processes : (1) the emission of a positive electron, i.e., β^+ (positron); (2) the emission of a negative electron, i.e., β^- (negatron); and (3) the capture of an orbital atomic electron (electron capture) by the nucleus. In the first and the third processes, the atomic number (Z) becomes one unit smaller, whereas in the second process, it becomes one unit greater. The mass number (A), however, remains the same in all the three cases. Nuclides with an excess of protons or neturons over the stable N/Z ratio tend to decay by the conversion of either a neutron into a proton causing (β-) emission or a proton into a neutron causing (β+)- emission for example,

$$^{30}_{15}P \longrightarrow {}^{30}_{14}Si + {}^{0}_{+1}e,$$

$$^{31}_{15}P \quad \text{(Stable)},$$

$$^{32}_{15}P \longrightarrow {}^{32}_{16}S + {}^{0}_{-1}e.$$

Although there is no change in the mass number, there is a definite decrease in the mass in both the (β –)-and (β+)-decay processes. The mass and energy balance of the (β –)- emission process is given by

$$m_n(^{A}_{Z}X) = m_n({}_{Z+1}{}^{A}Y) + m_e + Q,$$

where m_n is the nuclear mass and m_e the electron rest mass, in practice, the nuclear masses are replaced by the atomic masses so that the aforestated equation becomes

$$m(^{A}_{Z}X) = m({}_{Z+1}{}^{A}Y) + m_e + Q.$$

Q is positive when

$m(^{A}{}_{Z}X) > m(_{Z+1}{}^{A}Y) + m_e,$

which represents the conditions for negatron emission.
For (β^+)-emission the mass balance equation is

$$m_n\,(^{A}{}_{Z}X) = m_n\,(_{Z-1}{}^{A}Y) + 2m_e + Q.$$

(For maintaining neutrality, Y loses one orbital electron, making a deficit of $2m_e$ in all). Thus, for favourable (β^+)-emission the condition is

$$m(^{A}{}_{Z}X) > m(_{Z-1}{}^{A}Y) + 2m_e.$$

Since the energy equivalent of $2m_e$ is 1.022 MeV, the condition for the (β^+)-emission process is

$$m(^{A}{}_{Z}X) - m(_{Z-1}{}^{A}Y) > 1.022 \text{ MeV}.$$

In some cases, it is found that

$$m(^{A}{}_{Z}X) - m(_{Z-1}{}^{A}Y) > 1.022 \text{ MeV}.$$

As illustrated by the hypothetical reaction

$$^{37}{}_{18}\text{Ar} \longrightarrow {}^{37}{}_{17}\text{Cl} + {}_{+1}{}^{0}\text{e}.$$

36.96677 amu 36.96589 amu 0.00055 amu

Form this equation, we see that the mass difference between the parent and the daughter is 0.00088 amu (< $2m_e$), which rules out (β^+)-emission. The transition from Ar to Cl, therefore, occurs by orbital electron capture according to the reaction.

$$^{37}{}_{18}\text{Ar} + {}_{-1}{}^{0}\text{e} \longrightarrow {}^{37}{}_{17}\text{Cl}.$$

2.2. (iv) β – SPECTRA

The total energy emitted during β – decay can be calculated from the mass difference between the parent nuclide and the daughter nuclide, and is normally expected to appear as the kinetic energy of the emitted β – particle. However, the overwhelming proportion of β – particles, from any β-active source, exhibit a continuous energy unlike α – particles which have discrete energies. If the relative number of β – particles possessing a particular value of energy is plotted against this energy, the points lie on a curve, as given in Fig. 5.2. Only a small fraction of the β-particles possess the maximum energy E_{max} (also known as the end-point energy) corresponding to the energy theoretically available to the β-particles.

Yet another problem encountered was regarding the conservation of spin angular momentum. It has been established that the atomic nucleus does not contain free electrons, but only neutrons and protons. Hence, the electrons that are emitted as (β^-)-particles by radioactive nuclides must result from the spontaneous conversion of a neutron into a proton and an electron according to the scheme.

$${}^1_0n \rightarrow {}^1_1H + {}^0_1e.$$

it has further been established that the spin components of the neutron, proton and electron can be + ½ (h/2π) or –½ (h/2π). Obviously, the spin angular momentum is not conserved in this process.

The solution to the foregoing apparent anomaly was provided by W. Pauli in 1930, who postulated the simultaneous formation of a new particle, which he called the neutrino, along with the emission of a β-particle, According to him, the particle has a spin of ½ (h/2π), zero charge and near zero rest. The energy difference between E_{max} and the energy carried by a particular β-particle is the energy with which the neutrino is simultaneously emitted along with the β-particle. The neutrino cannot be easily detected because it carries no charge and does not interact with matter. The experimental evidence for the existence of the neutrino was, however, obtained by F. Reines and C.L. Cowan in 1953. The particle emitted along with a (β^-)-particle was found to be an antineutrino (ν), according to the scheme.

$${}_0^1n \rightarrow {}_1^1H + {}_{-1}^0e + \tilde{\upsilon}.$$

On the other hand, a neutrino (ν) is emitted during (β^+)-emission and during electron capture processes. The reactions are.

$${}_1^1H \rightarrow {}_0 1_n + {}_0^{+1}e + \nu.$$

$${}_1^1H + {}_0^{-1}e \rightarrow {}_1^0n + \nu.$$

It should be noted that the difference between a neutrino and an antineutrino arises from the sign of their spins.

β-decay energies vary from 0.02 MeV to 13.7 MeV with half-lives ranging from 5 X 10^{14}y to 0.02 sec. B.W. Sargent attempted to relate the β-decay constant to E_{max} in a manner analogous to the Geiger-Nuttall rule. A plot of log λ versus log E_{max}

gives a number of near straight lines, known a sargent curves, each line *representing a type of β-transition radiation from the nucleus.* But primary capture

process creates a vacancy in the K-shell, which is filled by an electron from shell of a lower binding energy (e.g., L-shell). This cause the release of a high amount of energy which appears as an X-ray photon. Alternatively the high energy released may be transferred directly to another electron in an outer shell, causing its ejection from the atom. This is called the Auger effect. These secondary effects enable the detection of the electron capture process by a suitable detector.

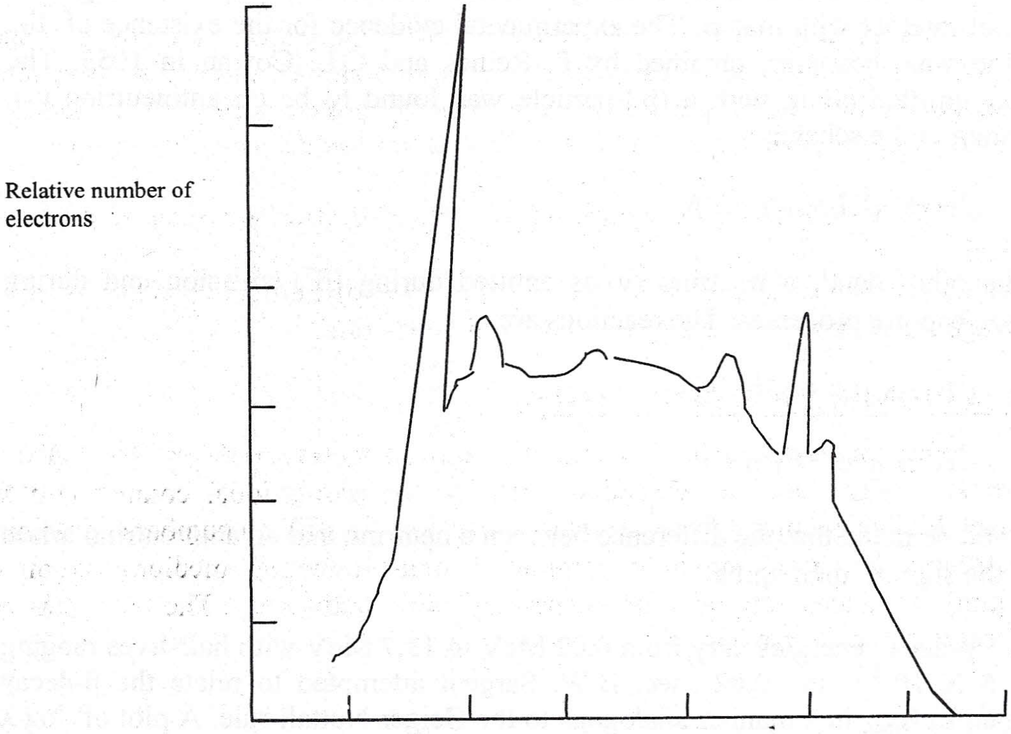
2.2 (v) γ -DECAY

α-and β – decays frequently produce nuclei in excited states which decay to ground states by the emission of energy as one or more γ – photons, which are very, short wavelength electromagnetic radiations. This process is so fast that the half-life of α-emission (10^{-15} sec) cannot be measured.

In some cases, the energy possessed by a γ – photon is transferred directly to the orbital electron, causing its expulsion. This process is known as internal conversion. In contrast to the β-particles, the conversion electrons are monoenergetic (there is no emission of a neutrino) and give discrete line spectra. The peaks in the β-spectrum of ^{131}I in Fig.2.2 are due to the conversion electrons. The vacancy left in

Energy (keV)

Fig. 2.2 -spectrum of 131 I (peaks due to internal conversion electrons).



the electron shell is then filled by an electron from the outer shell, the transition causing an X-ray emission. Alternatively, auger electrons emission may occur.

In some instances, the nucleus may remain in the excited state for a measurable length of time(>0.1 sec). This excited state is called the metastable state. The metastable and the ground state together are called the isomeric states of the nucleus (nuclear isomerism). These two states are both isobaric and isotopic. Nuclear isomerism arises when a nucleus is in an excited state having a nuclear angular momentum that is much higher than that of the ground state such that γ-transition is forbidden. Conditions for nuclear isomerism obtain among nuclides with odd Z or odd N just before the closed shells of 50, 82 or 126 nucleons.

2.2 (vi) COUNTING TECHNIQUIES

An instrument that measure radiations consists of two parts, namely, the detector and the measuring system. The output from the detector if fed into the measuring system. All types of detector used for the detection and measurement of radiation are based on the interaction of the radiations with the matter they transverse. Such an interaction produces either an ionization effect. One particular group of detectors is classified under *ionization detectors* . These detectors are devices in which the electric charge of the ion-pairs formed through radiation interactions is collected and electronically amplified.

The passage of radiation through certain inorganic materials produces excited atomic states, whereas in certain organic materials molecular vibrational states get excited. In both cases, the light that is emitted during de-excitation is converted into electric pulses and fed to the *scintillation detectors*.

The measuring system consists of electronic circuits which amplify and record
radiation emission (also called *event*) in the form of individual pulses or as an average effect produced as a result of several interaction.

(a)GAS IONIZATION DETECTORS

Gas ionization detectors were the earliest to be employed for radiation detections. They are the ionization chamber, the proportional counter and the Geiger-Müller counter. These detectors consist of gas-filled chambers containing electrodes. The gas, which is normally a non-conducting medium (argon or helium), produces ion-pairs on interaction with radiation . The ion-pairs are collected at the electrodes by applying a potential between them and the electric pulse thereby generated is amplified and measured.

The essential differences among the aforestated ionization detectors can be highlighted through a schematic diagram of a gas ionization detector (see Fig.2.3). This detector consists of a central anode that is well insulated from the chamber wall which acts as the cathode. An electronic voltmeter is connected in parallel to a resistance in order to measure the electric pulse produced by the ionizing. The inozation chamber is filled with a gas at a pressure of 1 atm or less.

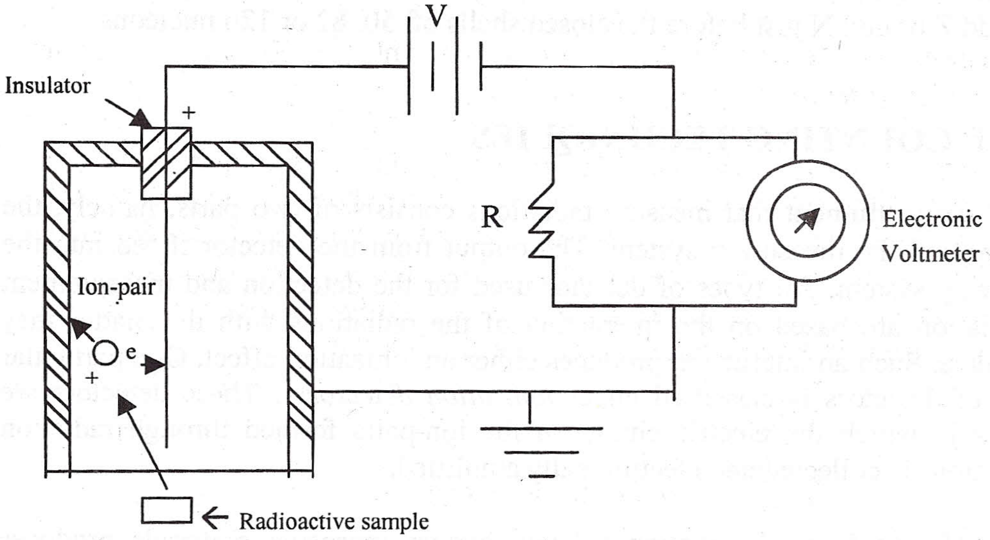


Fig : 2.3. Schematic Diagram of gas ionization detector.

Let us suppose that some degree of ionization occurs in the gas due to the passage of a charged particle causing the formation of a few ion-pairs. By plotting the number of ion-pairs collected at the electrodes as a function of the applied voltage across them, we get a curve of the type shown in Fig. 2.4. In Region I, the voltage is too low to cause the separation of all the ion-pairs for their collection at the electrodes. Consequently, some of the ion-pairs recombine to give a low charge collection. As the voltage is increased, the electric field proportionately increases till all ion-pairs produced are collected at the electrodes to give a saturation current. This occurs over Region II, known as the *ionization chamber region* (also called zero amplification region) , in which the ionization chambers are operated.

When the voltage is further increased (Region III), a new type of behaviour is observed. Following a primary ionization event, the acceleration of electrons from the site of the ion-pair production towards the anode becomes greater than before. As a result of the more intense field, ion-pairs receive sufficient energy to create, in turn , new ion-pairs. This phenomenon is known as *gas multiplication.* Consequently, the size of the output Pulse is proportional to the number of primary electrons and also to the gas multiplication factor. This region is known as the *proportional region,* in which the proportional counters operate.

Region IV, where there is a step rise in the number of ion-pairs, is known as the *limited proportionality region.*

When the voltage is further raised (Region V), the gas multiplication factor increases to a point where the counter becomes completely non-proportional in its response. At this stage, the discharge spreads along the entire length of the anode and the final pulse size becomes independent of the primary ionization. This region is known as the *Geiger-Muller region.* A further increase of voltage (Region VI) results in a continuous discharge in the detector.

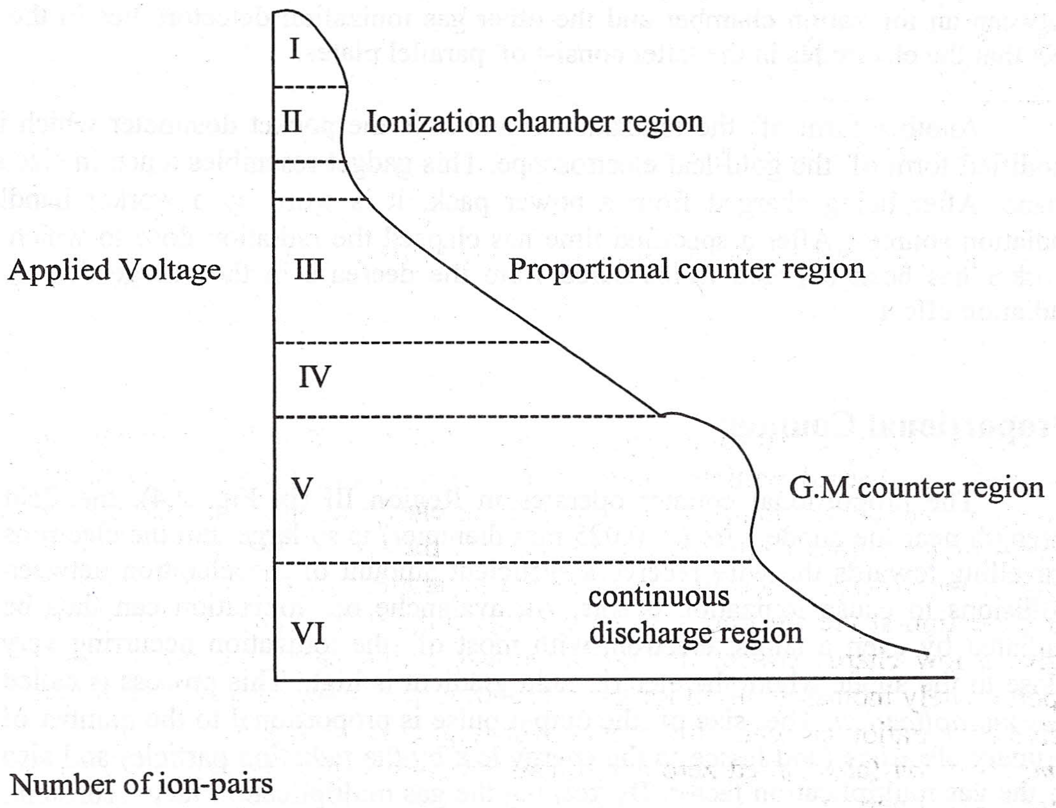


Fig. 2.4 Variation of Number of ion-pairs in gas ionization detector as function of applied voltage.

We now proceed to briefly describe the gas ionization detectors and also the solid-state and scintillation detectors.

Ionization Chamber.

The ionization chamber is versatile because of the simplicity of its operation. Moreover, it can be designed in various sizes and shapes. This detector contains air or an inert gas mixture at a pressure above the atmospheric pressure. The drawback that this instrument suffers from is that it can be used only when very strong activities are to be measured as the output current is very small (10^{-15} A) and, hence, difficult to measure accurately. Since only individual α – particles can produce a sufficient degree of ionization that can be detected as individual events, the ionization chamber is generally useful for α – particle counting. In addition, if the chamber is large enough for the α – particle to dissipate all its energy, the pulse size becomes a function of the initial α – particle energy, and the system can be used to measure α – particle energies. Since the specific ionizations of β - particles and γ – photons are considerably less than those of the α – particles, they cannot be detected using an ionization chamber. The integrated effect of several β - particles and γ – photons can, however, be measured by suitably modifying the circuit. The primary construction difference between an ionization chamber and the other gas ionization detectors lies in the fact that the electrodes in the latter consist of parallel plates.

Another form of the ionization chamber is the pocket dosimeter which is a modified form of the gold-leaf electroscope. This gadget resembles a pen in size and shape. After being charged from a power pack, it is worn by a worker handling radiation sources. After a specified time has elapsed the radiation dose to which the worker has been exposed is measured from the decrease in the charge due to the radiation effect.

Proportional Counter

The proportional counter operates in Region III (in Fig. 2.4). the field strength near the anode wire (0.025 mm diameter) is so large that the electrons travelling towards the wire receive a sufficient amount of acceleration between collisions to cause ionization events. An avalanche of ionization can thus be initiated by even a single electron, with most of the ionization occurring very close to the anode where the electric field gradient is high. This process is called *gas multiplication*. The size of the output pulse is proportional to the number of primary electrons (and hence to the energy lost by the radiation particle) and also to the gas multiplication factor. By keeping the gas multiplication factor constant, i.e., by employing a very stable high-voltage supply, the energy of a particle can be measured using the proportional counter.

Proportional counters are often used for detecting and counting of α – and β – particles. The active sample may be placed inside or outside the counter. Air is removed by means of a continuous flow of a gas mixture containing 90 % argon and 10 % methane or 90 % helium and 4 % isobutane. (Domestic cooking gas also can be used). Fig. 7.3 illustrates a gas flow proportional counter inside which the source can be mounted. Such counters are useful for counting α – particles and low-energy β – particles (e.g., ^{14}C and ^{35}S). If the range of the α – or β – particles is less than the dimensions of the counter, these counters can be used for counting almost 50 % of these particles emitted in a 2π geometry. By combining two of these counters (4π geometry), we can make very precise absolute activity measurements.

Geiger–Muller Counter

The Geiger-Miller (G-M) counter is one of the earliest counting devices. During operation, the electric field near the anode wire is maintained at such a value that the avalanche of electrons is independent of the primary ionization. However, special precautions have to be taken to prevent the avalanche from turning into a continuous discharge, the free electrons formed in the avalanche, as a result of the primary ionization, are collected quickly at anode, because of their greater mobility. The positive ions, however, move slowly to the cathode, where they either combine with electrons drawn from the cathode or emit photons that liberate photoelectrons, which cause another avalanche (secondary ionization), leading to the repetition of the process. This effect is prevented by adding a polyatomic gas or vapour such as ethyl alcohol to the argon gas. The positive argon ions are neutralized by removing the electrons from the alcohol molecules. The alcohol ions, in turn, reach the cathode where they get neutralized by the electrons from the cathode walls. The energy of neutralization decomposes the alcohol molecules rather than cause a further avalanche of electrons. This process is called chemical quenching or self-quenching. In view of the fact that the quenching agent (alcohol) gets used up, the G-M counter has a limited life. Halogens also are used as quenching agents instead of alcohol. The advantage is that the halogen, after dissociation, reconstitutes itself and, consequently, the life of the G-M counter becomes theoretically infinite. However, the characteristics of a halogen-quenched counter are poorer.

Following the detection of an ionization event, the entire length of the anode of the G-M counter is surrounded by a dense sheath of positive ions, which reduces the electric field strength. Consequently, the counter will not respond to a second ionization event before these positive ions drift away from the anode. This interval is known as the *dead-time* of the counter. The time required for the complete recovery of the pulse size after the end of the dead-time interval is known as the recovery time and the sum of the dead-time and the recovery time is known as the resolving time of the counter (see Fig. 2.5). The resolving time is variable in the same counter, depending upon the life of the counter. This variation leads to counting errors. These errors are avoided by electronically fixing the inoperative period of the detection system at a predetermined value that is greater than the resolving time of the counter. This value could vary from

300 μ sec to 600 μ sec. The relation between the true number of counts per unit time (R) and the number of observed counts (r) is given by

$$R = \frac{r}{1 - r\tau}$$

where τ is the resolving time. By using this equation, we can determine the true number of counts in a counting operation.

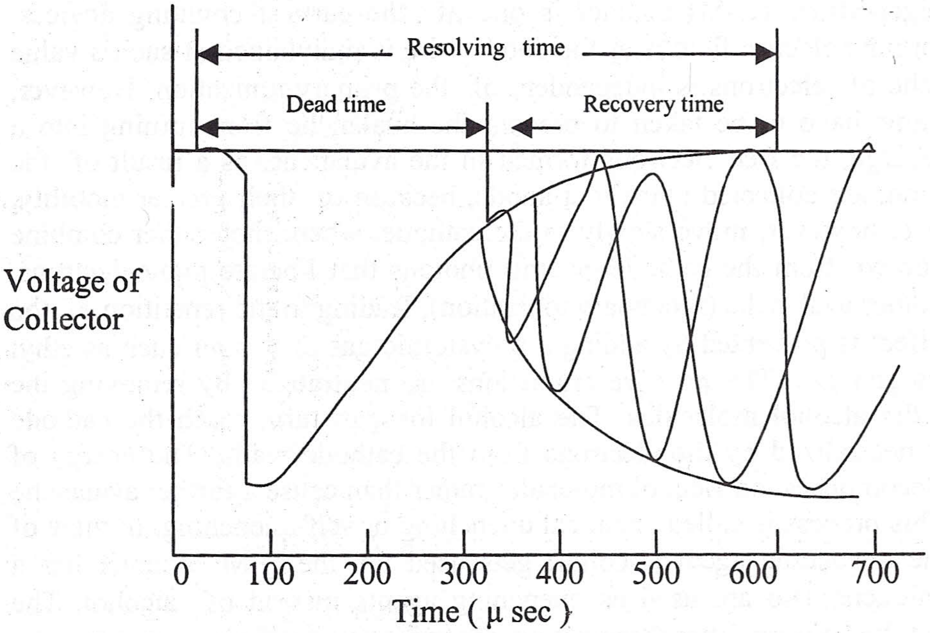
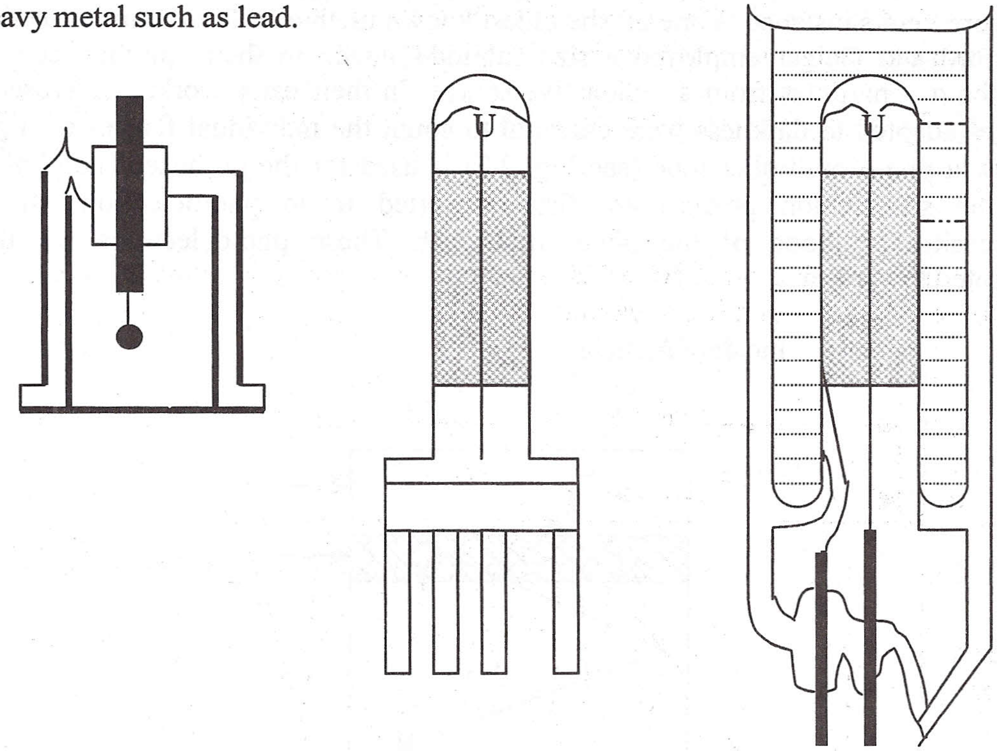


Fig. 2.5 Dead-time, Recovery time and resolving time.

The main advantage of the G-M counter is that it produces large pulses which require very little further amplification. Moreover, this counter is inexpensive, reliable and simple and can be fabricated in a variety of shapes depending on the specific use (see Fig. 2.6 (a-d). For example, it can be used for counting liquid samples, for flow counting, for mineral surveying and as a portable laboratory instrument. The chief disadvantage of the G-M counter is that it gives no information on the identity or the energy of the detected particle.

The most important feature of the G-M counter is its efficiency in β – detection. The counting efficiency in the thin end-window type of counter approaches 100%, except in the case of low-energy β – particles.

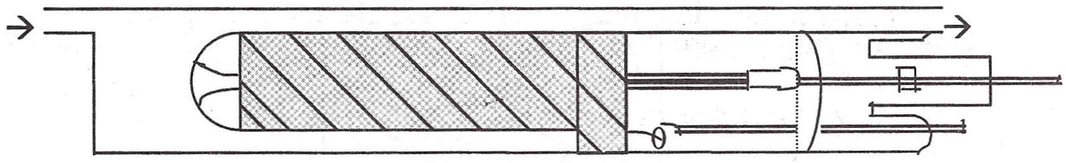
The detection of γ – rays and X – rays by the G-M counter is achieved through the secondary Compton electrons produced by the radiation due to the interaction with any portion of the metal cathode. In this case, the cathode is made of a heavy metal such as lead.



(a) End-window counter

(b) Liquid immersion counter

(c) Liquid counter



(d) Flow counter

Fig. 2.6 Common types of Geiger-Miller Detectors.

(b) SCINTILLATION COUNTERS

The detection of nuclear radiation by recording the scintillations in a phosphorescent substance is one of the oldest known methods of radiation detection. Rutherford and Geiger employed a size sulphide screen in their spinthariscope to count the α – particles from a radioactive source. In their early work, a microscope and eyes adapted to darkness were essential to count the individual flashes of light, but now a photo multiplier tube (see Fig. 2.7) is used for the purpose. The photons from the scintillation process are first converted in to photoelectrons in the photosensitive cathode of the photo multiplier. These photoelectrons are then accelerated towards a

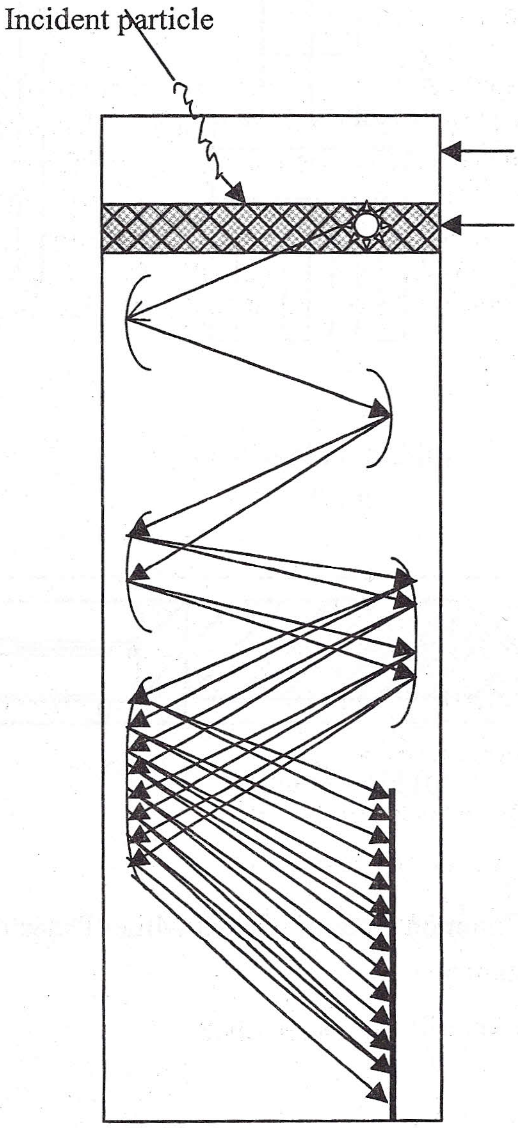


Fig 2.7 Scintillation detector

specially prepared photoactive dynode by applying a suitable voltage, When these electrons strike the dynode, electron multiplication occurs through the generation of secondary electrons. This multiplication process is repeated in several dynode stages in order to achieve a significant electric pulse at the final collecting dynode. To a good approximation, the size of the pulse output is proportional to the energy deposited by the particle or by the γ – photon in the scintillation detector, provided the detector is, large enough to stop all the incident radiation. The scintillation detector is, therefore, specially useful for measuring the energies of radiation, i.e., spectrometry.

The most common scintillator for γ – detection is sodium iodide crystal activated with thallium [NaI (Tl)]. Organic crystals such as anthracene and trans – stilbene are used for β – Particle detection and zinc sulphide phosphor is employed for α – particle detection.

Another useful application of the scintillation detector is liquid scintillation counting, in which the radioactive sample is dissolved in the solution of a scintillator. This counting method is particularly useful in the case of low-energy β – emittes such as ^{14}C and ^{3}H, leading to 100% detection efficiency. Some commonly used liquid scintillators are *p*-terphenyl, 2, 5 – diphenyl oxazole (PPO) and 2,2' – phenylene bis – (5-phenyl oxazole) (POPOP) which are dissolved in suitable solvents such as xylene, toluene and phenyl cyclohexane.

Model Questions

1. Discus the theory of Alpha Decay ?
2. What do you understand by the term internal conversation ?
3. Discus the different types of β – Decay processes.
4. Discus the salient features of β – Spectra.
5. Write notice on γ – Decay processes.
6. How does the behavior of G.M Counter differ from that of a proportional counter ?
7. Write notice on Scintillation detectors ?

LESSON - 3

ARTIFICIAL RADIOACTIVITY

2.3 (i). Energies of Nuclear Transformations

A nuclear reaction is a process in which one nuclide is converted to another by interaction with another nuclide. The first ever nuclear reaction in the laboratory was carried out by Rutherford in 1919 when he bombarded nitrogen with α – particles.

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \qquad {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

Where $^{14}_{7}N$ and $^{4}_{2}He$ are called target nucleus and projectile particle respectively and $^{17}_{8}O$ and $^{1}_{1}H$ are product nucleus and ejectile particle. Nuclear reactions are represented in an abridged form, the projectile particle and ejectile particle given in the parentheses between the target and the product nuclides. Thus the above reaction can be represented as $^{14}_{7}N$ (α, p) $^{17}_{8}O$. This is called Bethe's notation of nuclear reactions.

2.3 (ii). Q-Value, Potential Barriers, Threshold Energy Calculations.

As in Chemical reactions, Nuclear reactions also involve energy changes represented by the symbol Q. If Q is negative, the reaction is called endoergic (i.e.,) energy is absorbed, and if Q is positive, the reaction is called exoergic i.e., energy is released. The value of Q can be determined from the difference in the total mass of the reactions and the products of the reaction. Let us consider the reaction.

$$\begin{array}{ccccccc} ^{14}_{7}\mathrm{N} & + & ^{4}_{2}\mathrm{He} & & ^{17}_{8}\mathrm{O} & + & {}_{1}^{1}\mathrm{H} + Q \\ 14.003074 & & 4.002603 & & 16.999133 & & 1.007825 \\ \text{amu} & & \text{amu} & & \text{amu} & & \text{amu} \end{array}$$

The total mass of the reactions is 18.005677 amu and the total mass of the products is 18.00698 amu. Therefore, the mass deference is –0.001281 amu. Therefore, the value of Q is –0.001281 X 931.5 or –1.192 MeV. Since Q is negative the reaction is endoergic and the energy required for the reaction is made available in the form of kinetic energy associated with the α – particle. Q values are expressed in energy units most commonly in MeV per atom.

As per the Q value, nuclear reaction should occur when λ- particle with an energy or 1.193 MeV strikes the nitrogen nucleus. The composite nucleus does not remain at rest but moves forward with certain kinetic energy when λ- particle interacts with the nucleus. The minimum energy required for the reaction to occur is therefore grater than the Q value. This energy is called the threshold energy (E_{th}) which can be calculated from the law of conservation of momentum.

If a practicle of mass m and Velocity v strikes head of a nucleus of mass m and is absorbed, the product nucleus whose mass is (m + M) moves in the same direction as the incident particle with the velocity V, then

$$mv = (m+M)V$$

$$V = \frac{mv}{m.+M}$$

At the threshold energy (E_{th}), the minimum kinetic energy $\frac{1}{2} mv^2$ of the projectile needed for the excitation of the compound nucleus is

$$\frac{1}{2} mv^2 = -Q + \frac{1}{2}(m+M)V^2$$

$$\text{Therefore } -Q = \frac{1}{2} mv^2 - \frac{1}{2}(m+M)V^2$$

$$= \frac{1}{2} mv^2 - \frac{m^2 v^2}{m+M}$$

$$\text{Therefore } -Q = \frac{1}{2} mv^2 \; \frac{M}{m+M}$$

$$-Q = E_{th}\left[M / m+N\right] \text{ Where } E_{th} = \frac{1}{2} mv^2$$

$$E_{th} = -Q\left[M + m / M\right]$$

The negative sign on the right hand side of the equation indicates that E_{th} has to be supplied from outside for the reaction to occur. For the reaction under consideration, the threshold energy E_{th} is therefore.

$$E_{th} = -\left[-1.192 / 14\right] 18 = 1.53 \text{ MeV}$$

The threshold energy is of significance only for endoergic reactions and for potential barrier penetration.

The factor that has to be taken into consideration in the case of reactions involving charged particles is the potential barrier. This barrier arises because of the Coulombic repulsion between charged particles as they approach each other. The height of the coulombic barrier is given by the equation

$$\text{Barrier height, } E_B = \frac{1.44 Z_1 Z_2}{R_1 + R_2} \text{ MeV}$$

Substituting the values for $^{14}_{7}N$ and $^{4}_{2}He$ in this equation, we get the barrier height between the two nuclei as 3.2 MeV. An α - practical must therefore have at least (18 / 14) 3.2 or 4.0 MeV energy for the reaction to occur. In order to bring about reactions between charged particles and heavier elements, it became necessary to accelerate the charged particles to higher energy.

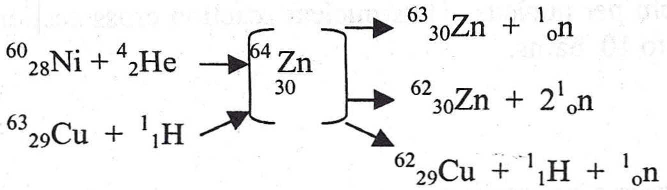
2.3. (iii). Mechanism of nuclear reactions, Compound Nucleus Theory

In nuclear reactions involving particles of not too high energy, e.g., less than 50 MeV, the first stage in the majority of instances is that the target nuclear complexity absorbs the projectile to form what is called a compound nucleus. Before it can unite with the target to form compound nucleus, the incident particle must overcome or penetrate the barrier due to electrostatic forces of repulsion. The compound nucleus thus formed possess a high excitation energy, which is equal to the kinetic energy of the projectile plus its binding energy. This excitation energy is of the order of several MeV. This energy is rapidly, shared among the nucleons present in the compound nucleus. This distribution of energy takes place continuously and in the course of time, one particular nucleon or combination of nucleons in the compound nuclear acquires sufficient energy to permit it to escape, leaving a more stable residual nucleus. The average life time of compound nucleus is estimated to be about 10^{-14} see or less.

These are two important aspects of the emission of particles from a compound nucleus which are considered to be the criteria for the formation of a compound nucleus. First the particles are emitted from the target almost equally in all directions. Second, the emitted particles do not all have exactly the same energy. As the nucleus bounce about in the process of the distribution of excitation energy, there is a variation in their individual kinetic energy and the probability that at least one nucleon acquires sufficient kinetic energy to escape from the nucleus is high. Such a nucleon evaporates from the nucleus in the same manner as a molecule does from a liquid surface. The reaction under consideration may be written as

$$^{14}_{7}N + ^{4}_{2}He \quad [^{18}_{9}F] \quad ^{17}_{8}O + ^{1}H + Q$$

Where $[^{18}_{9}F]$ denotes the compound nucleus. Because of its relatively long life time, the compound nucleus forgets the history of its formation. Its mode of disintegration depends on several factors such as its excitation energy, the heights of the potential barriers for different reactions and the stabilities of the residual nuclei but not on its mode of formation. ^{64}Zn compound nucleus can be obtained in two different ways, that is



and the relative yields of ^{63}Zn, ^{63}Zn and ^{63}Cu depend on the aforementioned factors but not on the mode of formation of the compound nucleus.

2.3 (iv). Nuclear Reaction Cross Section

The probability of a nuclear reaction can be defined in terms of the number of particles emitted or nuclei undergoing transmutation for a specified number of incident particles. It is expressed in terms of a quantity called nuclear reaction cross section. It represents the effective area of cross section of single nuclear of a given species for a particular reaction. Thus, when the probability of the process is high, the nuclear reaction cross section will be large, on the other hand, when the probability is low, the cross section will be small.

If I is the number of incident particles introducing in a given time a certain area of target material, containing N_a target nuclei per sq. cm, and A is the number of these nuclei that undergo interaction in the specified time, then the nuclear cross section , expressed as sq. cm per nucleus is defined by

$$= \frac{A}{N_a I} \quad \text{sq cm per nuclear}$$

When the nuclear cross section for a particular reaction is required, it is necessary to determine the number of nuclei taking part, either by counting the particles or by determining the number of product nuclei formed. If I_o is the number of incident particles, in a narrow beam, falling in a given time on the target material which is in the form of a sheet of thickness x cm, and I is the corresponding number of these particles emerging from the other side of the sheet in the narrow beam, the difference $I_o - I$ has been removed in various nuclear reaction, then

$$\frac{I}{I_o} = e^{-Nx}$$

When N is the number of target nuclei per cc, e is the base of natural logarithms and is the total nuclear cross section. Hence it is possible to determine from measurements of the intensity of the beam of incident particles before and after passage through the target material. The experimental values for values are usually in the vicinity of 10^{-25} to 10^{-23} sq cm per nucleus. The unit of nuclear reaction cross section is barn which is equal to 10^{-24} sq cm per nucleus. Thus nuclear reaction cross sections are frequently in the range of 0.1 to 10 barns.

Model Questions:

1. Write notes on a) Nuclear reaction cross section.
   b) Potential barrier

2. Discuss about the Compound Nucleus theory.

LESSON - 4

APPLICATIONS OF RADIO ISOTOPES

The applications of radioisotopes can be classified into three categories.

i). Applications in which the nuclear properties of the isotope of an element serve as an indicator to the behaviour of the chemical species (tracer methods)

ii). Applications in which the age of a sample is determined by estimating a specific isotope in the sample (dating techniques).

iii). Applications in which radioisotopes act as radiation sources to produce a change in a material .

2.4. (i). Basic Assumptions for Tracer Use

The uniqueness of the tracer method lies in the high degree of sensitivity of the detection methods used for estimating very low concentration of radioactive elements. An isotopic tracer enables us to follow the chemical transformation of an element or a compound or a group of which the tracer constitutes a part. Consequently, isotopic, tracers find extensive use in the fields of chemistry, agriculture, biology and medicine. The following are some of the basic assumptions for selecting an appropriate tracer.

(1). The tracer should be chemically identical with the stable isotope of the element.

(2). The tracer must have a half–life which is long enough to allow its activity to be followed, but short enough not to present a long term hazard

(3). The amount of activity used should be minimum, constant with the requirement for accurate measurements.

In situations where a stable radio isotope is not available, its rare stable isotope (^{2}H, ^{14}C, ^{15}N, ^{18}O) is used as tracer. In such an event, the mass spectrometric detection method is employed.

2.4. (ii). Radiometric Analysis

Radiometric titrations employ radioisotopes to indicate the end point by sudden release to or absorption from the solution activity. For instance, in the reaction of silver ion by chloride ions labelled with ^{36}Cl, the solution remains inactive till the end point is reached as all the activity is removed as Ag Cl precipitate. The end point is indicated by a sudden release of activity into supernatant solution which keeps increasing thereafter (Fig. . . .) on the contrary, if the silver ions had been labelled with ^{110}Ag, the solution remains active, though decreasingly so ,and the end point corresponds to a constant minimum activity. (Fig . . . .) in either case, the end point corresponds to sharp inflection in the activity, versus titre value. Another important application of release of radioactivity is in the determination of the pollutant SO_2 in air samples. The given air sample is bubbled through a solution of potassium iodate, labelled with ^{131}I. This releases radio iodide quantitatively as per the reaction.

$$^{5}SO_2 + 2K^{131}IO_3 + 4H_2O \longrightarrow K_2SO_4 + 4H_2SO_4 + {}^{131}I_2$$

A chloroform extract of the I_2 is counted for the activity which is related to the SO_2 content in the air sample.

2.4. (iii). Isotope Dilution Analysis :

Isotope dilution analysis is based on the change in specific activity caused by mixing the labelled and inactive forms of component that is to be estimated. A pure labelled form of the component of mass W_o and activity A_o, giving a specific active S_o is added to the sample to be analysed after ensuing that the labelled component and the unknown component (x) have been completely mixed, the combined component is separated in a pure form and its specific activity (S_x) is determined. If W_x is the weight of the component present in the sample, the specific activity S_x is given by

$$S_x = \frac{A}{W_o + W_x} \quad \ldots\ldots (1)$$

The specific activity of pure compound S_o is given by

$$S_o = \frac{A_o}{W_o} \quad \ldots\ldots (2)$$

From equation 1 and 2, we get the weight W_x of the unknown component as

$$W_x = W_o \left[S_o / S_x - 1 \right]$$

The isotope dilution analysis is of particular advantage in situations where the quantitative separation of the desired component is not feasible. Numerous applications of the isotope dilution technique include the analysis of substances such as petroleum products, isomeric mixtures, biological samples.

2.4. (iv). Applications of Radio Isotopes in Reaction Kinetics, Mechanism

(i). Esterification : It is difficult to show experimentally whether the water eliminated in an esterification reaction is formed from the OH of the alcohol and H of the acid or it is the other way corresponding to the upper and lower bracketing in the following equation

$$RC\,H_2COOH + HOCH_3 \qquad RCH_2COOCH_3 + H_2O$$

By using $CH_3\,{}^{18}OH$, Hwas found that the ${}^{18}O$ goes into the ester showing that it is the alcohol which contributes H and the acid the OH, corresponding to the lower braketing in the above reaction.

(ii). The mechanism of electron transfer reaction between Cr^{2+} and $[\,Co\,(NH_3)_5Cl]^{+2}$ can be understood by labelling chlorine (${}^{36}Cl$) in the complex ion. The product $[Cr\,Cl\,]^{+22}$

ion is found to contain all the activity. From this observation the mechanism.

$$Cr+^{2+}\left[Co\,(NH_3)_5\,{}^{36}Cl\right]^{+2} \rightleftharpoons \left[Cr = {}^{36}Cl - Co\,(NH_3)_5\right]^{+4} \rightleftharpoons \left[Cr\ {}^{36}Cl\right]^{+2} +$$

$$\left[Co\,(NH_3)_5\right]^{+2}$$

has been proposed. An alternative possibility is that another anionic solute species (OH^-) could act as the bridge for electron transfer (represented by broken line) when the reaction is repeated without active chlorine in the cobalt complex but with active chlorine in the solution, no activity is found in the $[Cr\ Cl]^{2+}$ species, which confirms that the electron transfer proceeds according to the earlier mechanism.

(iii) Decomposition of H_2O_2 by PbO_2. The net reaction here is

$$PbO_2 + H_2O_2 \quad PbO + H_2O + O_2$$

The earlier idea was that of the reactants provides an atom of oxygen to yield the molecular. However, when ^{18}O labelled $H_2\,O_2$ was used, the resulting oxygen had all the ^{18}O, none remaining with the water. This shows that the molecular oxygen formed comes wholly from the $H_2\,O_2$ as shown below .

$$O = Pb = O + H - O - O - H \quad PbO + H_2O + O_2$$

(iv). Oxidation of CO by air in the presence of catalyst MnO_2
The earlier idea of this reaction was

$$CO + MnO_2 \quad CO_2 + MnO$$
$$MnO + O\ (air) \quad MnO_2$$

Labelling MnO_2 with ^{18}O should that the resulting CO_2 had none of the enrichment in ^{18}O which remained wholly with the catalyst suggesting that the oxidation is directly between the reactions, thus

$$CO + O\ (air) + [\,Mn^{18}O_2] \quad CO_2 + Mn^{18}O_2$$

2.4. (v). Structural Studies :

When two or more atoms of the same element are present in molecule, the question of their structural equivalence or otherwise can be achieved by the labelling technique.

(i) Phosphorous pentachloride: To know whether all the five chlorine atoms in PCl_5 occupy structurally equivalent positions or not, the substance is synthesised using PCl_3 and Cl_2 with its radioisotope ^{36}Cl.

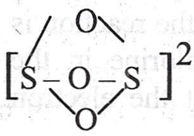
$$PCl_3 + {}^{36}Cl_2 \quad P^{36}\,Cl_5$$

Subsequently, the product is hydrolysed when the following reaction takes place

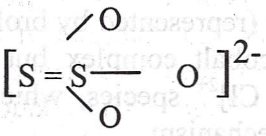
$$P^{36}\,Cl_5 + H_2O \quad POCl_3 + 2H\ {}^{36}Cl$$

Experimentally, it was found that all the radioactivity remained with the HCl and none with $POCl_3$ it is obvious that two Cl atoms in PCl_5 occupy positions different from the rest of the three Cl atoms. This agrees with trigonal bipyramidal structure accepted for PCl_5 with three Cl atoms in the equatorial plane and two along the vertices.

(iii) Thiosulphate ion : Two structures for the thiosulphate ion can be increased.

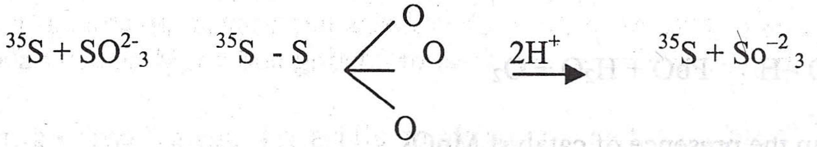


(a) Equivalent positions



(b) Non – Equivalent positions

The problem is to know which of the structures (a) and (b) is correct. This has been solved by preparing thiosulphate from sulphur resoled with ^{35}S and sulphate and decomposed with an acid. It can be seen that all the activity is found in the sulphur and none in the sulphur dioxide, providing that the two sulphur atoms in the thiosulphate are not equivalent and do not interchanging in the molecule. The reaction is



2.4. (vi). Medicine, Agriculture and Industry

By using the tracer method, we can observe the behaviour and follow the reaction paths of the molecules involved in biological processes. The development has led to great advances in the feeds of medicine and agriculture with regard to heart diseases, Cancer, the metabolism of nutrients and hormones and the rate of uptake of nutrients, water and minerals by plants and organisms.

Medical Applications :

The tracer method is now an invariable tool in designing and treating certain diseases. Radio nuclides such as ^{131}I, ^{32}P, ^{198}Au, ^{51}Cr, ^{59} Fe and ^{24} Na find extensive use as tracers for this purpose. Some times it becomes necessary for a surgeon to know the amount of blood in a patient. The surplus way of assessing the volume of blood in a person is by the technique of isotope dilution. Brain tumors are difficult to locate it is known that certain dyes as fluorescin, rose bengal are preferentially adsorbed by cancerous cells. The technique is to label the dye with ^{131}I as divodoflueorescein and scan the entire space around the skill by special counters. By this, it may be possible to locate the tumour fairly closely.

Thyroid gland located at the base of the neck takes up inorganic iodide from the blood stream. After concentrating and storing the iodide, the gland gradually releases the iodine into the blood stream as protein–bound iodine. The condition of the thyroid is clearly revealed by admistering a light dose radio iodine (^{131}I) to the patient and monitoring the variation in its activity in the neck region. The obstruction of blood in the circulatory system can be understood by studying the time taken by a sample of ^{24}NaCl solution that has been injected into the blood stream to reach another part or the body.

Agricultural Applications

Labelled fertilisers are correctly used in studies conducted on the role of nutrient elements such as phosphorus, calcium and sulphur which yield basic data on the optimum use of fertilisers and the mode of their application to the soil. Heritable variation occur spontaneously in all living organisms due to mutation of genes. In the case of plants, it is established that the frequency of mutations can be enhanced by exposing the seeds and other parts of the plants to high does of γ radiation. These studies have led to the birth of new technology called genetic engineering which offers the possibilities directed, specific genetic alterations to select and combine different desired characteristics in plant crops by using radiation in a controlled way. It is not always possible to effectively combat predatory insects with pesticides only. It is necessary to know their migration and breeding habits. It is possible to obtain the data in this regard by labelling the insects with ^{32} P or ^{60} Co to follow the migration of the labelled insects. These spots once located, are sprayed with suitable insecticides and predators are thus destroyed.

Industrial Applications

A non–destructive method of measuring the thickness of coatings or layers, levels of liquids in satic contains, layers of textiles, paper rubber sheets has been in practice in many industries using usually ^{90}Sr beta source below the sheet or coating and a GM detector above it.

When two surface of same or deferent metals or alloys rub against each other, as during the motion of one relative to the other, friction develops and trace amount are transferred from one surface to the other and the surface wear out. The presence of a lubricant reduces the friction and wear out. It is different by normal chemical analysis to know the trace amounts of matter lost by friction. This can be achieved by tracer analysis . This technique finds application in some automobile industries for assessing the wear out of piston rings.

The kinetic energy of nuclear radiation may be transformed into thermal or radiant energy which can be used to produce electrical power through energy conservation techniques.

2.4. (vii). Radiocarbon dating :

In the atmosphere, the reaction between neutrons produced by cosmic rays and nitrogen forms ^{14}C

$$^{14}N_7 + {}_0{}^1n \quad {}^{14}{}_0C + {}^1{}_1H$$

In this reaction, ^{14}C is produced at the rate of approximately 2 atoms / cm^2 / sec and decays to ^{14}N through weak negatron emission with a half–life of 5760y. The production and decay of ^{14}C in the atmosphere are assumed to have reached equilibrium conditions ^{14}C is evenly mixed with the CO_2 in the air and forms a part of the carbon cycle, coming to equilibrium with living matter (e.g. plant). However when plant dies, it no longer absorbs

CO_2 from the atmosphere, the equilibrium ^{14}C quantity trapped in the plant begins to decay with its characteristic half–life. By measuring the specific activity of carbon in terms of ^{14}C in a piece of wood, we can back calculate the time t when the ^{14}C content would have been the same as we now find in the living wood by using the equation .

$$T = \frac{2.303}{\lambda} \log \frac{A_o}{A}$$

Where A_o is the specific activity of the present day ^{14}C in the atmosphere, A is the present day specific activity of ^{14}C in the wood and λ the decay constant of ^{14}C. The procedure for the ^{14}C measurement is to take a known amount of the specimen, convert its carbon content into carbon dioxide or acetylene and count the specific activity of ^{14}C by special counting techniques. This procedure is found reliable in case of the specimens that are a few thousand years old.

Model Questions:

1. Explain the principle of isotopic dilution analysis and discuss its application in trace analysis with example.
2. Discuss the applications of radio isotopes in medicine, agricultural and in the study of mechanism of chemical reactions.
3. Write notes on Radio carbon dating.

LESSON - 5

SOLID STATE

2.5. (i)Bragg's equation

Bragg's pointed out that scattering of X-rays by crystals could be considered as reflection from successive planes of atoms in the crystal. However, unlike reflection of ordinary light, the reflection of X-rays can take place only at certain angles which are determined by wavelength of X-rays and the distance between the planes in the crystal. The relation between wavelength and this angle and interplanar distance, d, is called Bragg's equation (Fig. 1).

The horizontal lines represent parallel planes in the crystal structure, separated from one another by the distance, d. Suppose a beam of X rays falls on the crystal at a glancing angle θ, as shown. Some of these rays will be reflected from the upper plane at the same angle, θ, while some others will be absorbed and get reflected from successive layers. Let planes, ABC and DEF be drawn perpendicular to the incident and reflected beams respectively. The waves reflected by different planes will be in phase with one another only if the difference in the path lengths of waves reflected from the successive planes is equal to an integral number of wavelengths. Drawing OL and OM perpendicular to the incident and reflected beams, it will be seen that the difference in the path length δ of the waves reflected from the first two planes is equal to ZM + NM.

(i.e.) $n\lambda = LM + NM$

Since the triangles OLN and OMN are congruent, $LN = NM = d \sin \theta$

$\therefore n\lambda = 2d \operatorname{Sin} \theta$

This is the Bragg's equation. If θ, n and λ are shown the interplaner spacing, d, can be calculated.

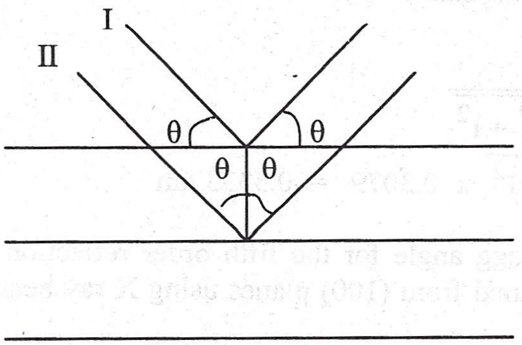


Fig. 1

Determination of crystal structure

Bragg's equation is the basis for the investigation of crystal structure. For monochromatic X-radiation, λ has a fixed value; for given lattice d is also fixed. Therefore, the possibility of getting maximum reflection ((i.e.) the possibility of getting reflected waves in phase with each other, depends on θ. If θ is increased gradually, a number of positions will be found in the X-ray pattern at which maxima are noticed. At these positions, n will have values equal to 1, 2, 3, 4 etc. For given 'n' if θ and λ is known, d is obtained by determining θ. There are two commonly used technique, the rotating crystal technique and the powder method. Both involve the use X ray spectrometer.

In the rotating crystal method, X rays generated in the tube are passed through a slit so as to obtain a narrow beam which is then allowed to strike a single crystal mounted on the turn table. The crystal is rotated gradually to increase the glancing angle at which the X-rays are incident at the exposed face of the crystal. The intensities of the reflected rays are measured on a recording device. The angle at which reflection maximum is observed gives θ. The process is carried out for each face of crystal. The lowest angle corresponds to n = 1. This is the first order reflection. The next higher angles for the given face correspond to higher orders n = 2, 3, etc. The disadvantage of the method is, it requires a large single crystal which is difficult to develop.

Powder Method

The powder method is more widely used for crystals with cubic symmetry. The powder consists of many tiny crystals oriented in all possible directions. As a result of this, X rays are scattered from all sets of planes (100, 110 etc.). The scattered rays are detected using X-ray sensitive film. The substance to be examined is finely powdered and kept in the form of a cylinder inside a thin glass tube. 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 a circular arc. In this method no rotation is necessary since the powdered sample already contain microcrystals arranged in all possible directions. Hence a large number of them will have their lattice planes in correct positions for X ray reflection to occur.

e.g. The d_{111} spacing for crystalline potassium is 0.3079 nm. Determine the length of the unit cell

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

$$a^2 = \sqrt{1^2 + 1^2 + 1^2} \times 0.3079 = 0.5333 \text{ nm}$$

eg. Calculate the Bragg angle for the fifth order reflection of cubic crystal that would be obtained from (100) planes using X ray beam of wavelength 1.54 Å given d

= 4.076 Å

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

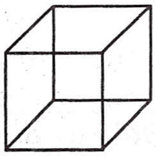
$$\sin\theta = \frac{n\lambda}{2d} = \frac{5 \times 1.54}{2 \times 4.078} = 0.944$$

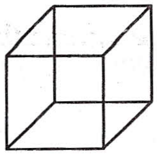
$$\theta = 87.9^{o}$$

2.5. (ii) Bravais Lattices

A crystal is a regular three-dimensional design and is a consequence of regular arrangement of atoms, ions or molecules of which it is built up. The design is composed of identical points ((i.e.) atoms or groups) forming three-dimensional net work of cells, which divide the space into equal volumes with no space excluded. This is possible only when the points are so arranged that each point has exactly the same surroundings as any similar point. The points with identical surroundings are called lattice points and the three-dimensional arrays of such points are called space lattices. Because of the regularity in distribution of points in space lattice, its essential geometry can be determined by vector lengths a, b, c and interfacial angles α, β, γ. These quantities constituting the lattice parameters describe the unit cell or the smallest repeating unit of the lattice when translated along the axes of the lattice a unit cell gives rise to actual crystal.

Bravais showed, from the geometrical considerations, that there can be only 14 different ways in which similar points can be arranged in a three-dimensional space. Thus the total number of space lattices will be fourteen obtained from the possible seven crystal systems. The Bravais space lattices associated with various crystal systems are shown below (Fig. 1).





The parameters and interfacial angles are summarized in the following table.

	Crystal system	Bravais Lattices	Parameters of unit cell	
			Intercepts	Crystal angles
1.	Cubic	Primitive Face centered Body centered 3	a = b = c	$\alpha = \beta = \gamma = 90^o$
2.	Orthorhombic	Primitive Face centred Body centred End-centred 4	a + b = c	$\alpha = \beta = \gamma = 90^o$
3.	Tetragonal	Primitive Body centered 2	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^o$
4	Monoclinic	Primitive End-centred 2	$a \neq b \neq c$	$\alpha = \gamma = 90^o$ $\beta \neq \gamma \neq 90^o$
5	Triclinic	Primitive 1	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^o$
6	Hexagonal	Primitive 1	$a = b \neq c$	$\alpha = \beta = 90^o$ $\gamma = 120^o$
7.	Octahedral	Primitive 1		

The Law of Rational Indices

This law states that the intercepts of any face of crystal along the crystallographic axes are either equal to unit intercepts (a, b, c) or some single whole number multiples of them. (i.e) (na, n'b, n"c) where n, n', n" are simple integers. Let OX, OY, OZ represent the three crystallographic axes and ABC a unit plane and the unit intercepts will be a, b, c. According to the above law, the intercept of any face such as KLM, with the same three axes will be simple whole number multiples of a, b, c.

2.5. (iii) Miller Indices – Labelling of Planes

Any particular face of a crystal is represented by reciprocals of the multiples of unit intercepts. Let us say for the face, KLM the reciprocals are ½, ½, 1/3. Evidently the reciprocals are in the ratio 3 : 3 : 2. These numbers are known as Miller indices of the face KLM, which is now designated as (332) face. For the unit plane the intercepts a, b, c are all unity. The plane will be (111) plane. Suppose a face cuts only two axes OX, OY and does not cut the third axes OZ, *running parallel* to it. If the intercepts on OX, OY are say 2 and 3 multiples of a and b and intercept on OZ will be ∞. The reciprocals will be ½, 1/3 and 0. The Miller indices are 3 : 2 : 0 and the plane will be designated (320). In general the Miller indices of a plane are denoted as (h k l).

Diffraction of X-rays by crystals

Laue suggested that crystals diffract X-rays because the wavelength of x rays is in the same order as the interatomic distances in crystal (10^{-8} cm). This leads to the possibility of determining structures and dimensions of crystals through X-ray study.

2.5. (vi). CRYSTAL DEFECTS – SCHOTTKY AND FRENKEL DEFECTS

We think of an ideal crystal as a three dimensional array of atoms with perfectly regular periodicity in all directions. But such a perfection is not found in real crystals. The crystal has many types of defects. The defects increase with increasing temperature. If the energy required to form a certain type of point defect in a lattice is known the equilibrium number of such defects (n) at a given temperature can be calculated

$$\frac{n}{N} = e^{-Q/RT}$$

In this N is the total number of lattice positions Q is the work required to produce one mole of vacancies or defects.

Point Defects

These imperfections are localized about a specific lattice point and involve only few atoms. Various types of point defects may occur in a crystal.

Vacancies

These are vacant lattice sites from which atoms are missing. Vacancies may be formed from solidification and crystal growth. They can also be produced by raising the temperature. Vacancies produce local distortions since they allow surrounding atoms to approach slightly closer than normal.

Impurity atoms

Atoms may occupy positions between atoms of ideal crystal. Because of this also a strain is produced. The interstitial atom may be an impurity atom. The impurity atom may also occupy normal positions causing distortion due to difference in the size between impurity atom and actual atom.

Frenkel Defect

A vacancy defect and interstitial defect may occur in combination which is known as Frenkel defect. This comes about when an atom is displaced from its normal position into interestecies of the structure (Fig. 4).

Schottky Defect

In a metal, a Schottky defect is simply a vacant lattice site. In an ionic crystal this defect occurs in the form of pairs of cation and anion vacancies. In alkali halides at room temperature about 1 in 10^6 anions and cations are absent.

Nonstoichiometric compounds

The presence of vacancies or interstetialcies in a compound can result in composition differing slightly from the true composition. Since overall electrical neutrality must be maintained it is obvious that some cations must have extra charge. For example in FeO, CoO, NiO there are vacant cation positions. In such cases the there should be an equivalent increase in positive change (p type). In the case of missing anion positions like NaCl, KCl, UO_2 etc., there must be equivalent number of free electrons (n type). The band structure of n type and p-type are shown below

Conduction band
0 0 0 0 0 0
Value band
n-type

Conduction band
+ + + + +
Value band
p-type

The n type and p-type structures are responsible for semi-conductivity.

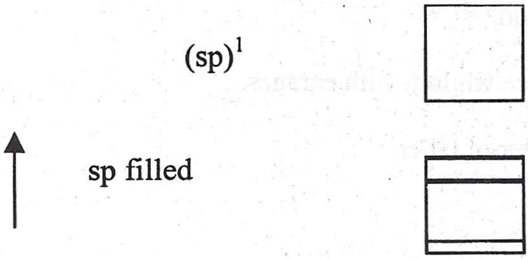
The presence of defects may also lead to photoconductivity and photovoltaic effect. Photoconductivity is the conductivity induced by absorption of light energy. E.g. Cu_2O, chlorophyll. The photovoltaic effect is the generation of EMF by the absorption of light e.g. Cu=Cu_2O Function.

2.5. (vii). Conductors – Semiconductors and Insulators

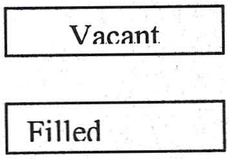
Ionic conductivity of ionic solids is due to lattice defects. In perfect crystal all ions are firmly anchored so that they could be dislodged only by the absorption of enormous electric field. Then they are poor conductors. If a defect is present the ionic solid has increased conductivity. For example if there is vacancy, ion movement is facilitated. The defects can move through whole crystal.

Suppose in a solid system there are N atoms. For each energy level in the isolated atom which accommodates two electrons there is in the solid an energy bond containing N levels each of which can accommodate 2 electrons. This energy band has a definite width a fact which implies that N levels within the band are closely spaced. Let us take the example of sodium atom with the electronic configuration $1s^2$ $2s^2$ $2P^6$ $3s^1$. The filled 1s, 2s are 2p bands are screened by valence electrons and hence are not influenced by the corresponding electron in other atoms. But the levels in the valence shell are influenced by presence of other atoms and split into bands. The N valence electrons fill the lowest levels available which results in partial filling of both 3s and 3p bands. The overlapping of s and p bands is a characteristic structure of metals. Since these are only partially filled the metals are associated with high conductivity. Even in the case of metals like Ca in which there are two electrons in outer most s orbital the top of s band overlaps with that of bottom of p band (empty). Hence there is room for movement of electrons in outermost orbitals giving high conductivity for Ca.

In the case of insulators the vacant band is very much separated in energy from the filled band. For example in the case of diamond the s band which holds 2 electrons and p band which holds 6 electrons interact to form the distinct bands each of which holds 4 electrons per atom. These are sp and $(sp)^1$.



The four electrons per atom in diamond exactly fill the lower band separated by large energy gap from unfilled $(sp)^1$. In the case of sodium chloride crystal eight electrons occupy 3s, 3p bands of Cl^- the 3s band of Na^+, which has a higher energy, is vacant



The filled bands are separated from empty band by an energy gap so that only sodium chloride is an insulator.

Semiconductors

Semiconductors have low conductivity and the conductivity increases with temperature. It may be noted that the conductivity of highly conducting metals decreases with increase in temperature.

Since Si has electronic structure similar to diamond, pure silicon is an insulator. Suppose some silicon atoms are replaced by (doped) phosphorus atoms with one more electron than silicon, the extra electrons due to phosphorus atoms occupy the impurity levels as shown below. They are located slightly below the empty levels of Si since the energy gap between these n levels and empty band of Si is not very much. Increase in temperature can push them into empty conduction band. Hence conductance will increase with temperature.

Suppose that instead of phosphorus atoms, atoms like boron atoms with one electron less than Si are introduced. The impurity levels are vacant since boron has one electron less. These impurity levels are placed slightly above the filled band of silicon. Electron from the filled band can be excited thermally to the impurity levels where they are bound to boron atoms to produce B^- in lattice. The holes that are left in the band, therefore, effectively carry a positive charge and can move under the influence of applied field carrying current. This type of semi conductor is called p-type semiconductor.

Similar n-type, p-type semiconductors can be obtained by introducing non-stoichiometry also as illustrated earlier.

Solid State chemistry

Short Answer Questions

1. Derive Braggs Equation.

2. What are bravais lattice whilom with enrages.

3. Discuss the stling upper of taller

UNIT - III

ELECTROCHEMISTRY

LESSON - 1

CONDUCTANCE, TRANSPORT NUMBERS & BEHAVIOUR OF ELECTROLYTES

1. (i). Specific and equivalent conductance, variation with concentration

The resistance 'R' of a material, is proportional to the length and inversely proportional to the area of cross section; $R = \frac{sl}{a}$ where l is the length and a is the area of cross section, s is called the specific resistance (resistance of material of unit length and unit area of cross section). Resistance is measured in terms of Ohms.

The reciprocal of resistance is conductance measured on Mhos and reciprocal of specific resistance is called specific conductance.

The conductance of different solutions are to be compared and investigated. Because the conductance depends on the concentrations it is necessary to determine the conductance of solution containing are gram equivalent of the solute which is called equivalent conductance. The conductance of a solution containing are gram mol is called molar conductance. The equivalent conductance and molar conductance are more useful in comparing conductances of different solutions.

In order to work out relationship between specific conductance and equivalent conductance, imagine 1 cc of solution of electrolyte between electrodes 1 cm apart. The cross sectional area of solution is 1 sq. cm. The conductance of the solution is therefore specific conductance because we are having 1 cm cube of the material. Suppose that 1 cc of the solution contains one gm equivalent of the electrolyte dissolved in it. Then according to definition the conductance of the solution will be equal to the equivalent conductance Λ. Conductance = equivalent conducts Λ = specific conductance K in this case. Suppose the solution is diluted to 1000 cc. We are having 100 cm cubes of material. The conductance of the resulting solution will be 1000 times specific conductance. But even now, as the solution contains only 1 gm equivalent of the electrolyte between electrodes, the conductance will still be equivalent conductance Λ. Thus in this case equivalent conductance $\Lambda = 1000$ x spc. Conductance. In general $\Lambda = k\varphi$. Where φ is the volume containing 1 gm equivalent of electrolyte.

Suppose the concentration of a solution of is C gm equivalent for litre. Then volume containing one gram equivalent is 1/C litre or 1000/C cc.

$$\therefore \Lambda = K\frac{1000}{C}$$

1.(ii) Cell constant

The specific conductance is conductance of one cm cube of material. Therefore the conductance measured will be specific conductance if electrodes are exactly 1 sq. cm in area and 1 cm apart. If not, the value of the conductance obtained will have to be multiplied by a factor to get the specific conductance. This factor is called cell constant. This is obtained by using standard KCl solution.

$$\text{Cell constant} = \frac{\text{Specific conductance of the standard KCl solution}}{\text{measured conductance of the same solution}}$$

Variation of equivalent conductance with concentration

The equivalent conductance Λ of a solution increases with dilution. The equivalent conductance is a measure of conducting power which increases with dilution because dilution increases ionization. The variation of Λ with concentration is shown in Fig. 1. The Λ at zero concentration, Λo (i.e.) at infinite dilution can be obtained by extrapolation of the curve to zero concentration in the case of a strong electrolyte like KCl. But in the case of weak electrolyte the ionization of the electrolyte is never complete. The graph also illustrates this; it is impossible to obtain limiting value of Λ by extrapolating the curve. (Fig. 1)

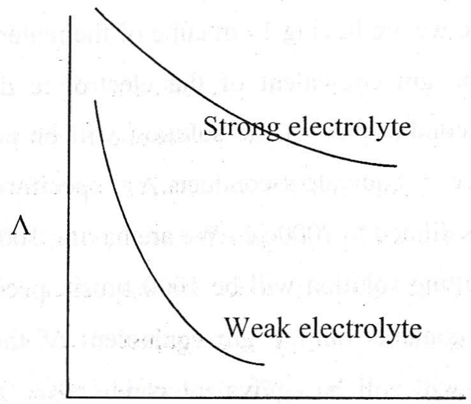
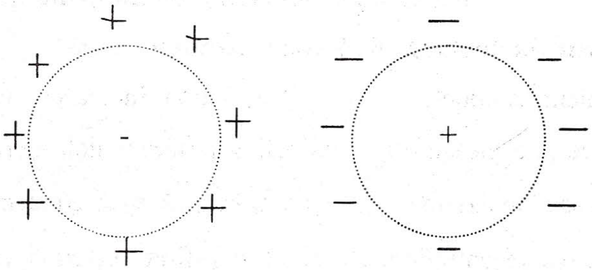


Fig. 1. Concentration

1. (iii) Anomalous behaviour of Strong Electrolytes – Debye – Huckel Equation

In the case of strong electrolytes, the ionization is complete in the solution. It is surprising that Λ decreases with increase in the concentration or increases with increasing dilution, making the behavior of the strong electrolytes anomalous. Debye and Huckel suggested that increase of equivalent conductance with dilution in the case of strong electrolytes is due to increase in the mobility of ions due to weaker interionic attraction. At high dilution the cations and anions will be far apart, their interionic forces being negligible. They make full contribution to conductance. As the concentration increases, the oppositely charged ions come closer. The inter ionic attractions between cations and anions reduces the ionic mobilities (i.e) conductance.

Each ion can be considered to be considered to be in an atmosphere of opposite ions produced due to cation-anion, attractive forces. The atmosphere has spherical symmetry in the absence of an applied field.---



Where an EMF is applied, ion and the oppositely charged ionic atmosphere move in opposite directions and the ionic atmosphere imposes a drag reducing the mobility. The greater the concentration, greater will be the thickness of the ionic atmosphere and the greater will be the drag and lower will be the mobility and conductance. This effect is called asymmetry effect.

Another factor that slows down the movement of the ions at higher concentration arises from the tendency of the ionic atmosphere being solvated – being associated with water molecules. These water molecules associated with the ionic atmosphere also move along with the ionic atmospheric. If the ion is positively charged, the ionic atmosphere being negatively charged moves in opposite direction along with water of hydration. Thus the positive ion is moving against a tide of water molecules. This also results in decreased ionic mobility. This effect is called the electrophoretic effect.

The asymmetric effect and electrophoretic effects have been mathematically treated and Debye and Huckel evolved the following equation including both these effects.

$$\Lambda = \Lambda_o - [\frac{82.4}{(DT)^{1/2}\eta} + \frac{8.2 \times 10^5}{(DT)^{3/2}}] \sqrt{C}$$

Where D is the dielectric constant η is viscosity, T is temperature and C is concentration of the electrolyte in water.

A plot of Λ vs. $\sqrt{C}$ showed be linear. This has been checked in the case of a number of uni-univalent electrolytes and found to be true upto a concentration of 0.02 N. At higher concentrations, deviations are observed which have been attributed to approximations involved in the derivation of the equation

ELECTROCHEMICAL CELLS AND CONCENTRATION CELLS

1. (iv) Nernst Equation

Consider a general reaction whose free energy change is converted into electrical energy through forming a cell with EMF, E.

$$aA + bB + \longrightarrow pP + qQ + \ldots$$

The reaction isotherm for this process is given by

$$\Delta G = \Delta G^o + RT\ln \frac{a_P^a\, a_Q^q \ldots}{a_A^a\, a_B^b}$$

Here ΔG is the free energy change under given experimental conditions and ΔG^o is the standard free energy change when all the materials, A,B .... P, Q ... are present at unit activities at temperature 25°C.

The free energy change is related to the EMF by the equation

$$\Delta G = -nFE$$

$$\Delta G^o = -nFE^o$$

In these equations n is the number of electrons involved in the reaction, F is the Faraday (96500 coulombs) and E^0, the EMF of the cell under standard conditions.

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_P^p\, a_Q^q}{a_A^a\, a_B^b}$$

The equation is called the Nernst equation used to calculate the EMF of a cell.

Consider the reaction $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ forming the basis for the Daniel cell.

The application of the Nenst equation gives

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{Zn^{2+}}\, a_{Cu}}{a_{Zn}\, a_{Cu^{2+}}}$$

The activities of Zn and Cu which are in metallic state are taken as unity

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

n = No. of electrons involved in the reaction = 2

In this cell Zn undergoes oxidation to Zn^{2+} and Cu^{2+} is reduced to Cu. Hence, the overall reaction can be split up into two half reactions one involving oxidation and the other involving the reduction.

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

$$\begin{array}{l} Cu^{2+} + 2e \rightarrow Cu \\ \hline Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \end{array}$$

Each of these half reactions can be seen to involve oxidized form and reduced form or two different oxidation states of the same element. This involves the couples Cu^{2+}/Cu and Zn^{2+}/Zn (i.e.) two different states of Cu on one side and those of Zn on the other.

A potential is developed when the oxidized and reduced form (or) two different oxidation states of a system are in contact with each other (e.g. Cu^{2+}/Cu, Zn^{2+}/Cu, quinone hydroquinone etc.) and the potential is called oxidation - reduction or redox potential When the oxidized and reduced form (and H^+ or OH^- ion if present) or the different oxidation states (and H^+ or OH^- if present) are at unit activities and the temperature is maintained at 25° the potential is called standard oxidation – reduction or standard redox potential.

The redox potential is called reduction potential of the half reaction is expressed as reduction

$$Zn + 2e \longrightarrow Zn \qquad E^0_{Zn^{2+}/Zn} = -0.76V$$

If the half reaction is expressed as oxidation the redox potential is an oxidation potential

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

$$E^o_{Zn, Zn^{2+}} = 0.76V$$

The standard EMF of the cell is given by taking the algebraic sum of standard oxidation potential for the oxidation half reaction and standard reduction potential of the reduction half reaction.

$$Zn \longrightarrow Zn^{2+} + 2e \qquad E^{0}_{Zn,Zn^{2+}} = 0.76V$$

$$Cu^{2+} + 2e \rightarrow Cu \qquad E^{0}_{Cu^{2+},Cu} = 0.34V$$

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \qquad E^{0} = 0.76 + 0.34 = 1.10\ V$$

Standard free energy change for this reaction $= \Delta G^0 = -nFE^o$

$= -2 \times 96500\ (\text{Joule volt}^{-1}) \times E^o\ (V)$

$= -2 \times 96500 \times 1.1\ \text{Joules mol}^{-1}$

$= -2.123 \times 10^5\ \text{Joules mol}^{-1}$

The free energy change is negative, i.e. there is a decrease in free energy and hence this reaction is spontaneous. Therefore if ΔG^o is to be negative the standard EMF of the cell should be positive. The standard free energy change is related to equilibrium constant, K, for the reaction.

$$\Delta G^o = -RT \ln K = -nFE$$

$$\therefore \ln K = \frac{nFE^o}{RT}$$

From this equation K can be calculated for the reaction

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

$E^0 = 1.1V$

$\log K = 37.37$

$K = 2.34 \times 10^{37}$

Measurement of Redox potentials.

The redox potential of a system (i.e) a mixture of two different oxidation states of an element or a mixture of oxidized and reduced forms, can be determined by combining with a reference electrode (whose potential is known) and forming a cell. The EMF of this cell measured with a potentiometer is equal to the algebraic sum of oxidation potential at the anode and reduction potential at the cathode. The couple whose potential is to be determined and the reference electrode act as anode or cathode depending upon the relative reduction potentials of these electrodes. The one having greater reduction potential acts as cathode (right hand side of the cell) and the one having lower reduction potential acts as anode (left hand side of the cell). The reference electrodes used often are the normal hydrogen electrode, calomel electrode or silver–silver chloride electrode.

The normal hydrogen electrode involves hydrogen at a pressure of one atmosphere and a mineral acid (HCl) at unit mean activity, temperature being 25°C. If it acts as anode the electrode reaction is

$$\tfrac{1}{2}H_2 \longrightarrow H^+ + e, \quad E^0 = 0.0V$$

The potential of the normal hydrogen electrode is assumed to be zero volts.

The calomel electrode has the structure, $Hg \mid Hg_2Cl_2, KCl \mid$

(S) m

Hg_2Cl_2 being present as a paste in water (saturated with Hg_2Cl_2) and KCl is at unit activity or the system is saturated with KCl which then becomes saturated calomel electrode. Acting as anode the electrode reaction is

$$Hg + 2\,Cl^- \longrightarrow Hg_2Cl_2 + 2e$$

The silver silver chloride electrode is also a popular reference electrode involving a reaction when working in anode

$$Ag + Cl^- \longrightarrow Ag\,Cl + e$$

Electrode potential and pH

Consider a cell in which equimolecular mixture of quinone and hydroquinone (called quinhydrone) at a given pH is a cathode and saturated calamel electrode is an anode.

$Hg \mid Hg_2Cl_2\ H\,Cl \parallel Q, H_2Q \mid pt$

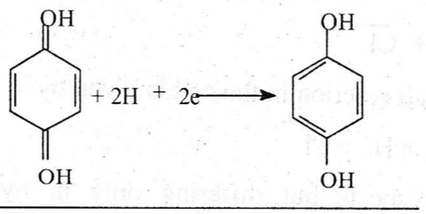
(S) H^+,

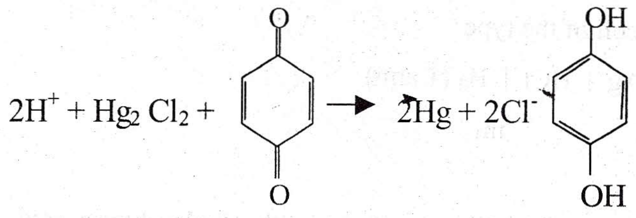
The purpose of platinum rod is not only for giving electrical connection but also due to its ability to act as an indicator electrode. Platinum rod when placed in the quinhydrone electrode or (in any other solution) assumes the potential of the system in which it is placed. It does not undergo electrode reaction. The respective electrode reaction are :

LHS anode – oxidation

$$2\,Hg + 2\,Cl \longrightarrow Hg_2\,Cl_2 + 2e$$

RHS cathode - reduction





$$E = E^0 - \frac{RT}{2F} \ln \frac{[Hg_2Cl_2][H_2Q]}{[Hg]^2 + [Cl^-]^2[H^+]^2[Q]}$$

But Cl^-, H_2Q, Hg_2Cl_2 and Q are saturated solutions and hence their activities are taken as constant at a given temperature and so is elemental mercury Hg. Hence the eq. becomes

$$E = E^{01} - \frac{RT}{2F} \ln \frac{1}{[H^+]^2} = E^{01} - \frac{RT}{2 \times 2.303F} \log_{10} \frac{1}{[H^+]^2}$$

$$= E^{01} + \frac{RT}{F} pH$$

Thus the EMF is a function of pH when the anode is SCF and cathode is a quinhydrone electrode at given pH. Thus pH determination can be accurately carried out from the EMF measurements.

CONCENTRATION CELLS

Concentration cells are the galvanic cells in which the electrical energy is derived from the free energy change when the substance is transferred from state of higher activity around one electrode to that of lower activity around another electrode. There is no net chemical reaction in the cell. Consider a cell of the type :

H_2 | H Cl | Ag Cl | Ag
(1 atm) (S)

In this cell, left hand electrode forming the anode involves the oxidation reaction.

$$\tfrac{1}{2} H_2 \longrightarrow H^+ + e$$

the right side involves the reduction

$$Ag\,Cl + e \longrightarrow Ag + \overline{Cl}$$

Combining both the reactions, the overall reaction in the cell is given by

$$\tfrac{1}{2}H_2 + Ag\,Cl \longrightarrow Ag + H^+ + \overline{Cl}$$

If two such cells identical in all respects but differing only in hydrochloric acid concentrations are combined to give a cell of the type

$$\underset{(1\ atm)}{H_2} \mid \underset{m_2}{HCl} \mid Ag \mid Ag\,Cl \mid Ag \mid \underset{m_1}{HCl} \mid H_2\,(1\ atm)$$

in which m_1 is greater than m_2, there will be an increase in the hydrochloric acid concentration through the occurrence of the reaction on the left hand side.

$$\tfrac{1}{2}H_2 + Ag\,Cl \longrightarrow HCl + Ag$$

whereas there will be decrease in hydrochloric acid reaction due to occurrence of the exactly opposite reaction on the right hand side.

$$Ag + HCl \longrightarrow Ag\,Cl + \tfrac{1}{2}H_2$$

This is due to tendency of the system to equalize [HCl]. Thus there will be no net chemical reaction in the cell. Further the two hydrochloric acid solutions are not in direct contact with each other, there is no direct movement or transfer of H^+ or $\overline{Cl}$ across the cell. The free energy changes due to these changes are given by equation

$$\Delta G_{H^+} = RTln\frac{(a_{H^+})_2}{(a_{H^+})_1}$$

$$\Delta G_{Cl} = RTln\frac{(a_{Cl^-})_2}{(a_{Cl^-})_1}$$

$$\therefore\ \Delta G = \Delta G_{H^+} + \Delta G_{Cl^-} = RTln\frac{(a_{H^+})_2\,(a_{Cl^-})_2}{(a_{H^+})_1\,(a_{Cl^-})_1}$$

But the mean activity of HCl,

$$a_\pm = (a_{H^+} \times a_{Cl^-})^{1/2}$$

∴ The equation can be written as

$$\Delta G = 2\,RTln\frac{(a_\pm)_2}{(a_\pm)_1}$$

But $\Delta G = -nFE$ where F is the Faraday, n is number of electrons involved in the reaction and E is the EMF formed due to concentration difference in HCl at each side.

$$\therefore \; E = \frac{2RT}{F} \ln \frac{(a_\pm)_1}{(a_\pm)_2}$$

In general for the electrolyte of the general type $M_{\upsilon+}A_{\upsilon-}$, where υ_+, υ_- represent respectively number of cations and anions obtained on ionization of one molecule of electrolyte

$$E = \frac{\upsilon}{\upsilon_\pm} \frac{RT}{nF} \ln \frac{(a_\pm)_1}{(a_\pm)_2}$$

This concentration cell is called concentration cell without transference, because the electrolyte solutions present on either side at different concentrations are not in direct contact with each other.

1.(v).Concentration cells with transference

Consider the modified cell in which two hydrochloric acid solutions ae in direct contact with each other as shown :

H_2 | HCl ⋮ HCl | H_2(1 atm)
(1 atm) m_2 ⋮ m_1

In this cell, let us assume m_2 is less than m_1. On the left hand electrode oxidation takes place

$$\tfrac{1}{2} H_2\,(q) \longrightarrow H^+ + e$$

On the right hand electrode reduction takes place

$$H^+ + e \longrightarrow \tfrac{1}{2} H_2$$

Since the solutions are in direct contact with each other the ions are free to move. For 1 Faraday of electricity passing through, t_H^+ gm ions of H^+ move from say left to right and t_{Cl}^{-} gm ions of $\overline{Cl}$ move from right to left. The net effect is the transfer of $(1 - t_H^+)$ gm ions of H^+ and t_{Cl}^- gm ions of $\overline{Cl}$ move from right to left. Hence the free energy change is the sum of the two free energy terms $(1 - t_{H^+})$ RT ln $\frac{(a_{H^+})_2}{(a_{H^+})_1}$ (i.e.) t_{Cl^-} RT ln $\frac{(a_{H^+})_2}{(a_{H^+})_1}$ and t_{Cl^-} RT ln $\frac{(a_{Cl^-})_2}{(a_{Cl^-})_1}$

$$\therefore \Delta G = t_{Cl^-} RT \ln \frac{(a_{H^+})_2}{(a_{H^+})_1} + t_{Cl^-} RT \ln \frac{(a_{Cl^+})_2}{(a_{Cl^-})_1}$$

$$= t_{Cl^-} RT \ln \frac{(a_{H^+})_2 \; (a_{Cl^-})_2}{(a_{H^+})_1 \; (a_{Cl^-})_1}$$

$$a_\pm = (a_{H^+} \times a_{Cl^-})^{1/2}$$

$$\therefore \; \Delta G = 2t_{Cl^-} RT \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

But $\Delta G = -nFE_t$ where E_t is he EMF developed due to the concentration difference of HCl on either side. $n = 1$ in this case.

$$\therefore E_t = \frac{2RT}{F} \ln \left(\frac{(a_\pm)_1}{(a_I)_2} \right)$$

In general for the electrolyte $M_{V+} A_{V-}$ present at different concentrations on either side of the cell

$$E_t = t_\pm \frac{\upsilon}{\upsilon_\pm} \frac{RT}{nF} \ln \left(\frac{(a_\pm)_1}{(a_I)_2} \right)$$

In this $t_\pm$ represents the transport number of ion. This cell is a concentration cell with transference because the two electrolyte solutions are in direct contact with each other.

3.2 (iv). Liquid Junction Potential

Suppose that two different concentrations of the electrolyte HCl are in direct contact with each other. The system is not stirred and is protected from the air currents.

$H^+ Cl^-$ $\qquad$ $H^+ Cl^-$

m_2 $\qquad$ m_1

Let us assume m_2 is less than m_1

There is always a tendency for the equilisation of concentrations and therefore hydrogen and chloride ions move from right to left. But H^+ ions have far higher mobility than Cl^- and hence more hydrogen ions than chloride ions would have moved from right to left at a given instant. Therefore the left hand side has developed a positive charge and right hand side has developed equivalent negative charge just like an electric condenser. Hence a potential is developed which is called liquid junction potential. If in a cell such a situation exists the liquid junction potential is in opposition to the EMF of the cell and therefore the observed EMF is different from the actual EMF by that amount. Let us assume that in the hydrochloric acid solutions in direct contact, 1 Farday of electricity is passed. Then t_H^+ gm ions move from say left to right than t_{Cl^-} gm ions of chloride move from right to left. The free energy change is equal to the sum of these two free energy changes.

$$\Delta G = t_H^+ RT \ln \frac{(a_{H^+})_1}{(a_{H^+})_2} + t_{Cl^-} RT \ln \frac{(a_{Cl^-})_2}{(a_{Cl^-})_1}$$

$$t_{H^+} = 1 - t_{Cl^-}$$

$$\Delta G = (1-t_{Cl^-}) RT \ln \frac{(a_{H^+})_1}{(a_{H^+})_2} + t_{Cl^-} RT \ln \frac{(a_{Cl^-})_2}{(a_{Cl^-})_1}$$

$$= (2t_{Cl^-} - 1)\ RT \ln \frac{(a_{H^+})_2\,(a_{Cl^-})_2}{(a_{H^+})_1\,(a_{Cl^-})_1}$$

Elimination of liquid junction potential

The liquid junction potential has to be minimized for the accurate determination of EMF. This can be effected by connecting the two sides by a salt bridge which consists of u tube filled with agar agar jel containing a high concentration of electrolyte like KCl in which the cations and anions have nearly the same ionic mobilities. The ions in the salt bridge being present at far higher concentrations than all other ions in the system carry almost all the electricity and since they have nearly the same mobility applicable liquid function potential will be extremely small.

LESSON - 2

SURFACE PHENOMENA

2. (i). SURFACE TENSION

Let us consider an interfacial region, the region in the sample where one phase ends and the other Eg: gas-liquid interface. In a liquid the molecules stick together compared to gas. Therefore the molecule in the bulk has a lower potential energy than one in free gas and it takes energy to dig out a molecule from the bulk and to deposit in gas. When a molecule is on the surface its energy is intermediate between free molecule and the molecule in the bulk. Its potential energy will be lowered if it is moved into the bulk and so the molecules are under the influence of a force which tends to draw them into bulk. This force is attractive and is called surface tension. Liquids always tend to minimize the surface to have maximum number of molecules in bulk than on surface. Hence the droplets will be spherical shape which has the minimum surface/volume ratio. But flattening does take place due to gravitational forces. Changing surface or increasing surface area means doing work. If the surface area is changed by ds work done = dw = surface tension γ x ds. The PV work given by $(-SdT + Vdp)$ is added to this. The total consequent change in chemical potential $d\mu$ is given by $d\mu = -SdT + Vdp + \gamma ds$.

2. (ii). Adsorption on Solids - Langmuir Adsorption Isotherm

Langmuir proposed that the gases when adsorbed on a solid surface form a layer which is one-molecule thick (i.e.) unimolecular films. On this basis he derived an adsorption isotherm which is called Langumuir adsorption isotherm.

The whole surface of the adsorbent is taken as one unit. Let ϑ be the fraction of the surface occupied by a gas forming unimolecular layer. Then $(1-\vartheta)$ is the fraction of the surface that is free.

Rate of adsorption is proportional to fraction of the surface that is free and available for adsorption and the pressure, P, of the gas. At the same time desorption also takes place with rate proportional to fraction of surface on which adsorption taken place.

rate of adsorption = $k_1 (1 - \vartheta) P$

rate of desorption = $k_{-1} \times \vartheta$

$k_1/k_{-1} = K$

At the equilibrium,

rate of adsorption is equal to rate of desorption

$h_1(1 - \vartheta)\ P = k_{-1}\vartheta,\ \ V = k_1/k_{-1}$

$$\therefore \vartheta = \frac{KP}{1+KP}$$

which is the equation for Langumuir adsorption isotherm. Fraction, ϑ, is proportional to amount of gas adsorbed by a definite mass m of adsorbent.

a is proportional to ϑ or $a = k_2\vartheta$

$$= \frac{h_2KP}{1+KP}$$

The amount of adsorption per gram of adsorbent (a) is represented by x/m where x is the total mass of gas adsorbed on m gram of adsorbent.

$$\therefore\ a = \frac{x}{m} = \frac{h_2KP}{1+KP}$$

At low pressure KP is negligible in comparison with 1

$$\therefore\ a = k_2KP \text{ or } \frac{x}{m} = k_2$$

(i.e.) $\frac{x}{m}$ tends to approach limiting value which means that at this stage the surface is complete by occupied hence $\frac{x}{m}$ is independent of pressure.

2. (iii). B E T Equation.

The Langmuir adsorption isotherm is based on the premise that the gas that is adsorbed on a solid surface involves only a unimolecular layer (i.e.) the layer is one molecule-thick. The adsorption is of chemisorption type involving the bond formation between molecule of the gas and the atom at the surface site. This is an oversimplification of the actual situation and Langmuir isotherm shows considerable deviation at high pressures. Brunaur, Emmett and Teller modified the theory and the BET theory involves the following principles.

1. The adsorption does not lead to a unimolecular layer but a multimolecular layer.

2. The first layer is formed by chemisorption (i.e) the bond formation between surface atom and the gas molecule.
3. The second, third etc. layers are formed by purely Van der Walls types of attraction between the molecule of the first layer and the molecule of the second layer etc.
4. Thus the heat evolved in the formation of the first layer is in the range 12-40 kcal/mole

   which corresponds to chemisorption and heats evolved in the formation of subsequent layers are about 2 kcl mol^{-1} which is due to physisorption type.

Based on these principles, the B E T adsorption equation has been developed :

$$\frac{P}{m(P_0 - p)} = \frac{1}{m_0C} + \frac{C-1}{m_0C}\ \frac{P}{P_0}$$

In this equation m is the mass of the gas adsorbed at a given pressure, P_o is the critical pressure. m_o is the mass of the gas adsorbed had it been only due to the formation of a unimolecular layer. C is a constant. A plot of $\frac{P}{m(P_0 - p)}$ Vs $\frac{P}{P_0}$ must be linear with intercept equal to $\frac{1}{m_0C}$ and slope $= \frac{C-1}{m_0C}$ and slope + intercept is equal to $\frac{1}{m_0}$ from which m_o is obtained. Thus number of molecules adsorbed on a given surface as unimoleculor layer can be obtained. If the molecular dimension are known, the surface area can be calculated.

2. (iv). Gibbs Adsorption Equation

The consideration of changes in surface energy is essential for considering the change in free energy. This can be 'accomplished by adding the term γS in the equation for free energy. γ is the interfacial tension (i.e.) interfacial energy per Sq. cm where S is the surface area. Hence Gibbs free energy is given by

$$G = \gamma S + \mu n_1 + \mu_2 n_2$$

$$dG = \gamma ds + Sd\gamma + \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2$$

dG is also obtained adding the term γds to $- SdT + vdp$

$$dG = -Sd + vdp + \gamma ds + \mu_1 dn_1 + \mu_2 dn_2$$

Comparing the eq. are gets

$$Sd\gamma - Vdp + Sd\gamma + n_1 d\mu_1 + n_2 d\mu_2 = 0$$

At constant temperature and pressure

$$S d\gamma + n_1 d\mu_1 + n_2 d\mu_2 = 0$$

Imagine a system to be divided into two parts, one consisting of all that portion which comes under the influence of surface forces, and the other the remainder of the solution. The former may be called the surface phase and the latter the bulk phase. If n_1^0 and n_2^0 are the numbers of moles of the two components in the bulk phase corresponding to n_1, n_2 on surface phase.

The eq. $n_1^0\, d\mu_1 + n_2^0\, d\mu_2 = 0$ applies for bulk phase.

If this equation is multiplied by $\frac{n_1}{n_1^o}$ and subtracted from the equation $S d\gamma + n_1 d\mu_1 + n_2 d\mu_2 = 0$ it see that

$$S d\gamma + (n_2 - n_1 n_2^0/n_1^0)\, d\mu_2 = 0$$

$$\therefore \frac{-d\gamma}{d\mu_2} = \frac{n_2 - n_1 n_2^0/n_1^o}{S}$$

The quantity is the number moles of one component say solute associated with n_1 moles of solvent $\frac{n_1 n_2^0}{n_1^o}$ is the corresponding number of moles of solute associated with n_1 moles by solvent in the bulk phase. The quantity $\frac{n_2 - n_1 n_2^0/n_1^o}{S}$ is the number of moles of solute on surface for unit area of surface and is denoted Γ_2

$$\therefore \Gamma_2 = \frac{-d\gamma}{d\mu_2}$$

$$\mu_2^o + RT\ln a_2$$

$$\Gamma_2 = -\frac{1}{RT}\frac{d\nu}{d_{mo\mathbf{2}}} = -\frac{a_2}{RT}\frac{d\gamma}{da_2}$$

In general $\Gamma = -\frac{a_2}{RT}\frac{d\gamma}{da}$

These are the forms of Gibbs eq. In deriving this equation no assumption has been made on the system or surface. It could be a liquid solution, the surface being that between liquid and vapour or air. It could as well apply to a system involving a solution and liquid (eq. mercury) and the interface between solution and liquid, the two being immiscible.γ is now the interfacial tension. If $\frac{d\gamma}{da}$ is negative, (i.e.) change of interfacal

8)

tension with increase in solution concentration is negative, the solute reducing the interfacial tension, Γ is positive. It means the concentration of solute on the surface or interface will be more than in bulk.

LESSON - 2

ELECTRO KINETIC PHENOMENA, MICELLES AND REVERSE MICELLES

2. (v). Electro Kinetic Phenomena at Interfaces – Zeta Potentials

When a solid is in contact with a liquid, a double layer of ions appears at the surface of separation. One part of the double layer is fixed on the surface of the solid. It consists of either positive ions or negative ions. The second part consists of diffuse or mobile layer of ions which extends into in liquid phase. This layer consists of ions of both the signs but its net charge is equal and opposite to that on the fixed part of the double layer. (Fig. 1) Thus the fixed part contains positive charge and the diffuse part a net negative charge. Alternatively, the fixed part may contain negative charge and the diffuse part on equivalent positive charge. The existence of such a double layer should contain some potential like a charged condenser. The difference in potential between the two layers is called electrokinetic or zeta potential.

The zeta potential is given by the eq.

$\xi = \dfrac{4\pi e d}{D}$ when e is the basic electronic charge, D is the dielectric constant of the liquid and d is the thickness of layer. The thickness of layer and hence zeta potential decreases under the influence of ion of opposite sign. The greater the charge of the ion of the opposite sign greater will be the decrease in the value of electrokinetic or zeta potential.

2. (vi). Micelles - Determination of critical micelle concentration

Micellization involves the aggregation of 5 – 100 molecules of a surfactant to form an oligomer which is called a micelle. The surfactant molecules have long alkyl chains ending in ionizable groups or highly polar groups. The examples are sodium dodecyl sulphate (also known as sodium lauryl sulphate) which has the structure and cetyl trimethyl ammonium bromide having the structure.

The former has ionizable end group giving an anion and the latter has ionizable end group forming cation. The examples of surfactants having highly polar end group is triton-X 100 which has the structure :

That means the surfactant has apolar part due to long alkyl chain and polar part due to ionizable or highly polar end groups. When these surfactant molecules are dissolved in water, the apolar alkyl chains tend to avoid aqueous medium ( ) and align inwards forming what is known as the core of the micelle. The polar or ionizable end groups are attracted by water and therefore tend to be positioned on the surface of the micelle.

The small region of the surface of the micelle enclosing the positive charge or negative charge or polar end group is called the Stern layer. The micellization commences only after certain concentration of the surfactant is reached and this concentration is called critical micelle concentration (cmc). Sodium dodecyl sulphate has cmc in the order of 10^{-3} moles litre^{-1}. At concentrations near cmc the micelles have nearly spherical structure. As the concentration of the surfactant are increased to a high value the spherical shape changes into a rod-like structure. The rod like micelles have properties much different from the spherical micelles.

Determination of critical micelle concentration

The proportions of surfactant molecules change abruptly at the critical micelle concentration and further increase in concentration produces smaller changes. This behavior is made use of in determining the critical micelle concentration. The properties that undergo an abrupt change at the cmc are conductance, surface tension etc. CMC is often determined by determining the surface tension of the surfactant solution in water at various concentrations.

The cleaning effect of the surfactants is due to the solubilization of materials like greases oils etc. These are solubilised by the apolar part (core) of the micelle.

The micelles are known to exert catalytic action on many reactions. This is due to binding of the reactant molecules in the stern layer which is only a small fraction of the total volume. This produces a concentration effect (The increase in concentration is enormous because the reactants are partitioned from whole volume of the solution. A unimolecular reaction catalyesd by a micelle, M, can be represented by the following scheme:

$$\underset{\text{reactant}}{S} + \underset{\text{Micelle}}{M} \overset{K}{\rightleftharpoons} M.S \xrightarrow{k_m} \text{product} + M.$$

$\downarrow$ k_w (uncatalysed part)

product

The rate constant (overall) k_Ψ is given by the expression

$$k_\Psi = \frac{k_o + k_m K[M]}{1 + k_m K[M]}$$

where k_o is the rate constant for the uncatalysed reaction and k_m is the rate constant for the micellar-catalysed reaction; K is the binding constant. [M] is the concentration of the micelles in solution. to small volume fraction of the stern layer. The stern layer is also known to be associated with low dielectric constant and hence the desolvation of the reactant molecules is facilitated which is a precursor to the transition state formation in general. In general, carton – cation reactions are accelerated by anionic micelles which have a concentrated negative charge in small Stern layer thus binding the reactants and producing enormous concentration effect. The cationic micelles in turn accelerate the anion – anion reactions. For the same reason cation – anion reactions are inhibited charged micellar surface selectively bind only one of cation or anion.

2. (vii). Reverse Micelles

When a surfactant is dissolved in water, micellization commences after certain concentration called critical micelle concentration is reached. The surfactant molecules have long alkyl chains (a polar part) ending in ionizable or highly polar groups. The apolar alkyl chains are repelled by water and hence tend to escape from water pseudophase and tend align inwards forming the core of the micelle whereas ionizable or polar end groups tend to be attracted towards water and hence positioned on the surface of the micelle. The whole structure is spherical in shape at concentrations near cmc but tends to assume rod-like shape at very high concentrations.

Exactly the opposite is observed when a surfactant molecule is dissolved in an apolar liquid like liquid hydrocarbon. The long alkyl chains have affinity for the solvent whereas the ionizable or polar end groups tend to avoid the solvent bulk and are aligned inwards whereas the alkyl chains are aligned outwards towards the solvent.

The reverse micelle for ration also commences after the cmc is reached. The reverse micelle has capacity to solubilize water. When concentration of solubilized water is less than or equal to surfactant concentration, almost all the water solubilized is utilized for solvating the polar or the ionizable end groups and hence this water immobilized. This water has same special properties that distinguish this from ordinary water. The solubilized water in the Aerosol-oT reverse micelles has dielectric constant much lower than bulk water and has highly nucleophilic properties. The viscosity and density also differ considerably. The ratio of solubilized water concentration to the surfactant concentration (W) therefore decides the properties of solubilized water. As the W value increases further and the solvation of the ionizable or polar core groups is complete, the water pools are formed.

The solubilized water especially at low W values has properties akin to intracellular water and hence reverse micelle offers ambience somewhat resembling a cell. Hence the study of biometric reactions (serving as models for the enzyme catalysed reactions taking place in the living body) in the reverse micellar media gives better information of the life processes than when these reactions are investigated in conventional aqueous medium. The surfactants used to prepare the reverse micelles include Aerosol OT cetyltrimethylammonium bromide etc.,

MODEL QUESTIONS :

Short answer questions

1. Explain the term liquid junction potential.
2. Derive Nernest equation
3. Derive the relation between pH and electrode potential
4. What are reverse micelles

Essay type questions

1. Derive the equations for concentration cells with and without transference
2. Derive Gibbs adsorption equation
3. Discuss the salient feature of BET isotherm
4. Describe the method for the determination of CMC

LESSON – 1

RATES OF CHEMICAL REACTIONS
THEORIES OF REACTION RATES

4.1. (i) Zero, First and Second order Reactions

Some reactions proceed in a single step and the mechanism involves direct collisions between reactant molecules. Such reactions are called concerted processes like the reaction between a primary alkyl halide and hydroxyl ion

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$

The reaction involves nucleophilic substitution of Br^- by OH^- and the rate-determining process involves collisions involving two types of molecules and is designated as SN_2 process. Most of the reactions proceed in two or more steps and each of the steps in the mechanism is called an elementary step. The number of molecules of reactants participating in each of the elementary steps is called the molecularity of the step. For example the reaction between t-butyl bromide and OH^- proceeds according to a mechanism involving two elementary steps :

$$(CH_3)_3CBr \xrightarrow{\text{slow}} (CH_3)_3C^+ + Br^-$$

$$(CH_3)_3C^+ + OH^- \xrightarrow{\text{fast}} (CH_3)_3COH$$

The first step which is also the slow step has molecularity equal to 1 (unimolecular) whereas the second step involves the participation of two species $(CH_3)C^+$ and OH^- and has a molecularity equal to 2 (bimolecular). All elementary steps in the mechanism do not proceed with the same rate and rate of one of the steps is significantly less than the others. The overall rate is determined by slowest step(s). In the mechanism mentioned above the rate of the first step is far less than the step involving $(CH_3)_3C^+$ and OH^-. Hence, the first step is rate-determining. Applying the law of mass action we get.

$$\text{Rate} = \frac{-d}{dt}[(CH_3)_3CBr] = k[(CH_3)_3CBr] \qquad \ldots \qquad (1)$$

The rate is dependent on the first power of concentration of $(CH_3)_3CBr$ and hence called first order. The second reactant, OH^-, is present in the fast step between the carbonium ion and OH^-. Since this is present in the fast step the rate is independent of concentration of OH^- i.e. rate equation can be imagined to contain the term $[OH^-]^0$

$$\frac{-d}{dt}[(CH_3)_3CBr] = k[(CH_3)_3CBr][OH^-]^0$$

$$= k[(CH_3)_3C\ Br] \qquad -(2)$$

This means that the reaction is zero order with respect to OH^-. Since rate-determining step contain only one molecule (unimolecular), this nucleophilic substitution is called SN_1 substitution. Thus the term molecularity, is concerned with each of the elementary steps present in the mechanism. This should be distinguished from the term, stoichiometry, which gives the number of molecules of reactants participating in the overall process, that is, the balanced chemical equation.

Thus the order of the reaction is defined as the way in which rate of the reaction depends on the concentration of a reactant. If the reaction depends on the first power of concentration of the reactant, (e.g. the reaction just discussed) the order is 1. If the reaction has a rate directly proportional to the square of the concentration of a reactant, the reaction is said to obey second order kinetics with respect to this reactant and so on. In the SN_2 process, the concerted reaction between CH_3Br and OH^- involves a mechanism consisting of a single step.

$$CH_3\,Br + OH^- \longrightarrow CH_3\,OH + Br^-$$

Applying law of mass action the rate equation can be written as

$$\text{Rate} = \frac{-d}{dt}[CH_3Br] = \frac{-d}{dt}[OH^-] = k[CH_3Br][OH^-]$$

The reaction is first order in each of the reactants and the total order is 2. In general, if the reaction obeys mth order kinetics in a reactant A and nth order kinetics in the reactant B, the rate equation can be written as

$$\text{Rate} = k[A]^m[B]^n$$

Rate is defined as rate of decrease in the concentration of reactant or increase in the concentration of product with time and has the units 'moles $\text{litre}^{-1}\text{sec}^{-1}$'

$$k = \frac{\text{rate}}{[A]^m[B]^n} = \frac{\text{moles litre}^{-1}\ \text{sec}^{-1}}{(\text{moles litre}^{-1})^m(\text{moles litre}^{-1})^n}$$

$$= \text{litre}^{(m+n)-1}\ \text{mole}^{1-(m+n)}\ \text{sec}^{-1} \qquad \ldots \qquad (3)$$

For a first order process m+n = 1 and the k has the units, sec^{-1}. For a second order rate constant, m+n = 2, and k has the units, lit. $\text{mole}^{-1}\text{time}^{-1}$ and so on.

Since the rate is defined as rate of decrease in concentration of reactant, it may be expressed as $\frac{-d[A]}{dt}$ or $\frac{-d[B]}{dt}$ (-ve sign because concentration of the reactant decreases with time) or rate of increase of concentration of products (ar) $\frac{d[C]}{dt}$, or $\frac{d[D]}{dt}$ (+ sign because the concentration of product increases with time during a reaction). For a process involving 1 : 1 stoichiometry (balance equation 1)

$$A + B \rightarrow C + D$$

$$\left|\frac{-d[A]}{dt}\right| = \left|\frac{-d[B]}{dt}\right| = \frac{d[C]}{dt}, = \frac{d[B]}{dt} \qquad \ldots \qquad (4)$$

because in the balanced equation 1mole of A reacts with one mole of B producing the products C, D each one mole. If the balanced equation has the form

$$A + 3B \rightarrow 2D$$

$$\left|\frac{-d[A]}{dt}\right| = \left|\frac{1}{3}\frac{d[B]}{dt}\right| = ½\,\frac{d[D]}{dt} \qquad \ldots \qquad (5)$$

4.1. (ii). Effect of temperature on the rate of reaction

All the thermal reactions (reactions taking place in the absence of light) are influenced by temperature. A 10° rise in temperature increases the rate by 2-3 times. Thus,the temperature coefficient of reaction, which is the ratio of rate constants at temperatures differing by 10°, lies between 2 and 3. Considering a general reaction

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

The equilibrium constant which is equal to the ratio of the rate constants of forward and reverse process (k_1 and k_{-1}) varies with temperature according to Van't Hoff equation .

$$\frac{d \ln K}{dt} = \frac{\Delta E}{RT^2} \qquad \ldots \qquad (6)$$

where K is the equilibrium constant of the reaction (= k_1/k_{-1}).

$$\text{Or} \quad \frac{d \ln (k_1/k_{-1})}{dt} = \frac{E_1 - E_{-1}}{RT^2}; \text{ (where } \Delta E = E_1 - E_{-1})$$

Splitting this equation one gets

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} + \text{Constant} \qquad \ldots \qquad (7)$$

$$\frac{d \ln k_{-1}}{dt} = \frac{E_{-1}}{RT^2} + \text{Constant} \qquad \ldots \quad (8)$$

The constant has been found to be equal to zero.

In general, therefore, the dependence of rate constant, k, on temperature can be expressed by the Arrhenius equation

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \qquad \ldots \quad (9)$$

on integration one gets

$$\ln k = \frac{-E}{RT} + A \quad \text{or} \; k = A\,E^{-E/RT} \qquad \ldots \quad (10)$$

In this equation E represents the activation energy which can be defined as the minimum energy the reactant molecules must possess before they collide and form the products. The eq. 10 gives a method for experimentally determining the activation energy, E. The method consists in determining the rate constant, k, at different temperatures and plotting ln k Vs 1/T which gives a straight line with a negative slope equal to E/R from which E can be calculated. The intercept gives the value of A. For majority of the reactions, the activation energy ranges between 12 and 20 k cal mol^{-1}.

The activation energy can be determined if the two values of rate constant corresponding to two different temperatures are known. The eq. 10 gives

$$\log_e \frac{KT_1}{KT_2} = \frac{-E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \ldots \quad 11$$

and enables direct evaluation of the activation energy, E.

Example : A first order reaction is 30% complete in 100 sec at 25°C and 60% complete in 120 sec at 35°C. Calculate the activation energy.

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a - x}$$

The reaction is 30% complete in 100 sec at 25°C

$$a - x = \frac{70}{100}\,(a)$$

$$\therefore \; k = \frac{2.303}{100} \log \left(\frac{a}{\frac{70}{100} x\, a}\right) = 3.56 \times 10^{-3} \text{ sec}^{-1}$$

The reaction is 60% complete in 120 sec at 35°C

$$a - x = \frac{40}{100} a$$

$$k = \frac{2.309}{120} \log \left(\frac{a}{\frac{40}{100} x a} \right) = 7.64 \times 10^{-3} \text{ sec}^{-1}$$

$$\log \left(\frac{7.64 \times 10^{-3}}{3.56 \times 10^{-3}} \right) = \frac{-E}{2.303 \times 8.3} \left[\frac{1}{308} - \frac{1}{298} \right]$$

$$E = 5.818 \times 10^{4} \text{ Joules mol}^{-1}$$

4.1. (iii). Collision Theory

An energy barrier separates the reactant state from product state. Hence the reactants upon collision must have sufficient energy to surmount this barrier if the products are to appear. The height of the barrier, that is, the difference in the energies of the barrier and the reactants is the activation energy which must be possessed by the reactants. Hence the rate of the reaction according to the simple collision theory is given by the eq.

$$\text{rate} = Z e^{-E/RT}$$

Where Z is the collision number defined as the number of collisions taking place per cc per second. $e^{-E/RT}$ is the Boltzmann factor. It is easy to understand the direct dependence of rate on $e^{-E/RT}$ because this factor measures the probability that the reactant molecules possess energy in excess of required activation energy, E, For energizing the reactant molecules which have energy less than E, collision with molecules which have energy more than E is necessary, whose proportion is measured by $e^{-E/RT}$.

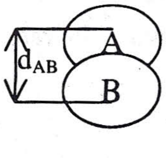
On the basis of the kinetic theory gases, the expression for Z for collisions involving same type of molecules is given by

$$Z_{AA} = 2n^2 d^2 \sqrt{\frac{\pi kt}{m}} \qquad \ldots \qquad 12$$

Where n is the number of molecules in a cubic centimeter. d is the distance between spheres where the collision occurs (assuming molecules to be hard spheres) m is the mass of the molecule and k is the Boltzmann constant. The collisions involving two different reactant molecules A and B.

$$Z_{AB} = n_A n_B d^2_{AB} \left(8 \pi RT \frac{M_A + M_B}{M_A M_B}\right)^{1/2} \qquad \ldots \qquad 13$$

In this n_A and n_B are the number of molecules present



in a c.c, d_{AB} is the distance of closest approach (equal to sum of radii of A and B assuming them to be spherical without any internal degrees of freedom).

M_A, M_B are the molecular weights of A and B and R is the gas constant.

$$\text{rate} = e^{-E/RT} \qquad \ldots \quad 14$$

$$= n_A\, n_B\, d_{AB}^2 (8\,\pi RT \frac{M_A + M_B}{M_A M_B})^{1/2}\, e^{-E/RT} \qquad \ldots \quad 15$$

$$\frac{\text{rate}}{n_A n_B} = k = d_{AB}^2 (8\,\pi RT \frac{M_A + M_B}{M_A M_B})^{1/2}$$

$$= A\ e^{-E/RT}$$

$$\text{Where } A = d_{AB}^2 (8\,\pi RT \frac{M_A + M_B}{M_A M_B})^{1/2}$$

A is the frequency factor.

If rate is expressed as number of molecules per cc reacting per second and n_A and n_B are the number of molecules per cc then A has the units

$$\frac{\text{rate}}{n_A n_B} = \frac{\text{molecule cc}^{-1}\ \text{sec}^{-1}}{(\text{molecule cc}^{-1}\ \text{sec}^{-1})\,(\text{molecule cc}^{-1}\ \text{sec}^{-1})} \qquad \ldots \quad 16$$

$$= \text{cc molecule}^{-1}\ \text{sec}^{-1}$$

because the other term $e^{-E/RT}$ is a dimensionless quantity $(e\dfrac{-\text{Joules mole}^{-1}}{\text{Joules mole}^{-1}\ \text{sec}^{-1}\ \text{x deg}^{-1}})$.

If the equation is multiplied by 10^{-3} x Avogadro's number the frequency factor will have units lit.mole^{-1}sec^{-1} which are the units of the second order rate constant in vogue.

As per the collision theory equation, the temperature dependence of rate or rate constant is mainly due to variation of the factor $e^{-E/RT}$ rather than the frequency factor or collision number because frequency factor or collision number is proportional to $T^{1/2}$ and the ratio of this factor at temperatures differing by 10^0, say at 35° and 25° is $\sqrt{\dfrac{273+35}{273+25}}$ which is equal to 1.016 where as the effect of temperature on $e^{-E/RT}$ is much more marked.

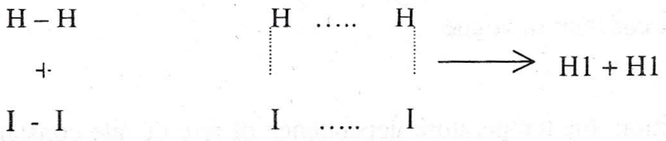
It is an easy matter to calculate the rate constant using the collision theory equation if the activation energy is known. The rate constants calculated that way is $10^3 - 10^5$ times more than the observed rate constants for reactions involving complex molecules, though for reactions between monatomic or diatomic molecules the observed and calculated rate constants are in reasonable agreement. This discrepancy has been explained by assuming that not all collisions lead to products and only those collisions in which reacting molecules are suitably oriented in space before participating in the collision give products. The fraction of successful collisions is called the probability or steric factor.

$$k = PA\,e^{-E/RT} \qquad \dots\ 17$$

The probability factor will later be shown to be related to entropy of activation. Though the introduction of probability factor appears logical it cannot explain the value greater than usual for extremely fast reactions. The failure of collision theory may also be ascribed to the fact that being derived on the basis of kinetic theory of gases, only kinetic energy of the molecules is considered whereas in the actual breaking and forming of bonds in the reaction vibrational and rotational energy changes must also be considered.

4.1. (iv) Transition state theory or theory of absolute reaction rates

The transition state theory retains the concept of collisions. The reacting molecules being associated with the necessary activation energy collide with each other and they pass through an intermediate state called the transition state which finally is transformed into stable products. The transition state is only of transitory existence ($10^{-8} - 10^{-6}$ sec) and hence cannot be isolated or its presence established by spectroscopic or other methods. It is thus only postulatory. In the transition state, the old bonds are partially broken and new bonds are partially created. This assumption is necessary because if the old bonds are to be completely disrupted before the new bonds are formed the required activation energy is enormous. But if the new bonds are imagined to be formed partially the energy requirement for making of old bonds is partially met. This can be picturised taking a simple reaction like the one between hydrogen and iodine molecules



$$\begin{array}{c} H-H \\ + \\ I-I \end{array} \qquad \begin{array}{ccc} H & \cdots\cdots & H \\ \vdots & & \vdots \\ I & \cdots\cdots & I \end{array} \longrightarrow H1 + H1$$

The transition state has higher energy compared to reactants and products and it is customary to illustrate these energy changes through the reaction profile which is a plot of energy versus reaction coordinate. The reaction coordinate is the configuration of minimum energy i.e. set of parameters like vibrational frequencies, bond angles etc. which give minimum energy at a given instant. The activation energy, E, should be taken as the difference between the energies of the transition state and the reactant state. Once the reactants have been transformed into the intermediate transition state, the transition state has to translate (traverse) the length of the energy barrier, δ. The transition state is in equilibrium with the reactant molecules A and B.

$$A + B \rightleftharpoons AB^{\neq} \longrightarrow \text{products}$$

The symbol '$\neq$' is used to denote the transition state. The transition state may traverse the length of the energy barrier δ and form products or it may return to the initial reactant state. The rate of formation of products is therefore proportional to concentration of transition state, $C^{\neq}$, that translates the distance of the energy barrier, δ, and also frequency of crossing the barrier. The value $C^{\pm}$ is obtained by multiplying the total concentration of transition $C_{\neq}$ by the translational partition function in one dimension $\frac{(2\pi m^{\neq} kT)^{1/2}\delta}{h}$ where $m^{\neq}$ is the mass of the transition state, k is the Boltzmann constant and h is the plank's constant. '$C_{\neq}$' can be obtained by using the equilibrium constant of equilibrium between transition state $AB^{\neq}$ and the reactants A and B.

$$K^{\neq} = \frac{C_{\neq}}{C_A C_B} \quad \text{or } C_{\neq} = K^{\neq} C_A C_B \qquad \ldots \qquad 18$$

$C^{\neq}$ = Concentration of transition state that traverses length of the barrier

$$= C_{\neq} \times \frac{(2\pi m^{\neq} kT)^{1/2}\delta}{h} = K^{\neq} C_A C_B \frac{(2\pi m^{\neq} kT)^{1/2}\delta}{h} \qquad \ldots \qquad 19$$

The frequency of crossing the barrier is equal to $(\frac{kT}{2\pi m^{\neq}})^{1/2} \times \frac{1}{\delta}$

Rate = Conc. Of T.S. crossing the barrier x frequency of crossing the barrier

$$= K_{\neq} C_A C_B \frac{(2\pi m^{\neq} KT)^{1/2}\delta}{h} \times (\frac{kT}{2\pi m^{\neq}})^{1/2} \times \frac{1}{\delta} \qquad \ldots \qquad 20$$

$$= \frac{kT}{h} K_{\neq} C_A C_B$$

Rate constant, k_r, is equal to $\frac{\text{rate}}{C_A C_B}$

$$\therefore k_r = \frac{kT}{h} K_{\neq} \qquad \ldots \qquad 21$$

In statistical language $k_{\neq}$ is equal to $\frac{\varphi_{\neq}}{\varphi_A \varphi_B} e^{-E/RT}$ where $\varphi_{\neq}$, φ_A, φ_B are the total partition functions of the transition state and the rectants, A and B respectively. The total partition 'φ' in each case is equal to product of translational (φ_t) vibrational (φ_v) and rotational (φ_r) partition functions

$$\varphi = \varphi_t \varphi_v \varphi_r \quad \ldots \quad 22$$

To calculate these quantities absolute physical constants like molecular dimensions, moments of inertia etc. are used. That is why the theory is also called theory of absolute reaction rates. In the calculation of rate constants, not only translational or kinetic energy but also vibrational and rotational energies are accounted for. Hence the transition state theory does not suffer the disadvantage of collision theory of reaction rates.

Thermodynamic formulation

For a reaction the transition state theory equation can be written in the form

$$k_r = \frac{kT}{h} K_{\neq} \quad \ldots \quad 21$$

Where k_r is the rate constant, k and h are Boltzmann and planck's constants and $K_{\neq}$ is the equilibrium constant for the equilibrium between reactant(s) and transition state. The free energy of activation which is the difference in the Gibbs free energies of transition state and the reactants, $\Delta G_{\neq}$, is related to K by the relation,

$$\Delta G_{\neq} = -RT \ln K_{\neq}$$

from this equation, $k_r = \frac{kT}{h} e^{-\Delta G_{\neq}/RT}$ ... 23

But $\Delta G_{\neq} = \Delta H_{\neq} - T\Delta S_{\neq}$ ... 24

Where $\Delta H_{\neq}$ and $\Delta S_{\neq}$ are the enthalpy of activation and entropy of activation defined similar to free energy of activation.

$$\therefore k_r = \frac{kT}{h} e^{\Delta S_{\neq}/R} e^{-H_{\neq}/RT} \quad \ldots \quad 25$$

According to Van't Hoff equation

$$\frac{d \ln K_{\neq}}{dT} = \frac{\Delta E_{\neq}}{RT^2} \quad \ldots \quad 26$$

Where $\Delta E_{\neq}$ is the difference in the intrinsic energies of the transition state and the reactant state. We have

$$k_r = \frac{kT}{h} K_{\neq}$$

$$\ln k_r = \ln\left(\frac{kT}{h}\right) + \ln K_{\neq}$$

$$\frac{d \ln k_r}{dT} = \frac{1}{T} + \frac{d \ln K_{\neq}}{dT} = \frac{1}{T} + \frac{\Delta E_{\neq}}{RT^2} = \frac{RT + \Delta E_{\neq}}{RT^2}$$

But $\frac{d \ln k_r}{dT} = \frac{E_o}{RT^2}$

Where E_o is the activation energy

$\therefore \frac{E_o}{RT^2} = \frac{RT + \Delta E_{\neq}}{RT^2}$ or $E_o = RT + \Delta E$

But $\Delta H_{\neq} = \Delta E_{\neq} + P\Delta V \neq$

$$\Delta E_{\neq} = \Delta H_{\neq} - P\Delta V \neq$$

where $\Delta V \neq$ is the volume of activation which is the difference in the volumes of transition state and the reactant state. But $P\Delta V \neq = \Delta n_{\neq} RT$

where $\Delta n_{\neq}$ is the change in the number of molecules when the transition state is formed from the reactants.

$$\therefore E_o = RT + \Delta H_{\neq} - P\Delta V \neq$$

For unimolecular reactions, the transition state is formed from one reactant molecule i.e., $\Delta n_{\neq} = 0$

$$\therefore \Delta H_{\neq} = E_o - RT \quad \ldots 27$$

$\therefore$From eq. (25) and (27)

$$k_r = e \frac{kT}{h} e^{\Delta S_{\neq} / R} e^{-E_o/RT} \quad \ldots 28$$

For bimolecular reactions the transition state is formed from two reactant molecules $\Delta n_{\neq} = -1$

$$\Delta H_{\neq} = E_o - 2 RT \quad \ldots 29$$

$$\text{Or } k_r = e^2 \frac{kT}{h} e^{\Delta S_{\neq} / R} e^{-E_o/RT} \quad \ldots 30$$

The eq. 28 and 30 enable the calculation of entropy of activation from the knowledge of rate constant, k_r and E_o

Significance of entropy of activation for reaction between gaseous reactants

The entropy of activation is equal to the difference in the entropy of transition state and the reactants. Since the entropy is a measure of disorderliness, entropy of activation indicates relative order or disorder of initial and transition states. For reactions between gaseous reactants no solvent is present and for the unimolecular gaseous reactions, the transition state is formed from one reactant molecule i.e. there is no change the number of molecules or number of bonds but there will be only readjustment of bonds and thi produces only a small entropy change. Hence for unimolecular gaseous reactions entropy of activation is zer or a small negative or positive value. For bimolecular gaseous reactions, the transition state is formed fro two reactant molecules and thus there is a decrease in the number of molecules and there is an increase in th orderliness or decrease in the disorderliness or entropy. Hence, in general, for bimolecular gaseous reactions a large negative entropy of activation is expected. The rate constant k_r for a bimolecular gaseous reaction is given by :

$$k_r = e^2 \frac{kT}{h} e^{\Delta S_{\neq}/R} e^{-E_0/RT} = PA\ e^{-E_0/RT} \qquad \ldots \qquad 31$$

Where A is the frequency and P is the probability factor.

$$\therefore PA = e^2 \frac{kT}{h} e^{\Delta S_{\neq}/R} \qquad \ldots \qquad 32$$

The frequency factor equal to $d^2_{AB}(8\pi RT \frac{M_A + M_B}{M_A M_B})^{1/2}$ is dependent only on the molecular dimensions and therefore a large negative value of entropy of activation means low value of probability or steric factor, P. If $\Delta S_{\neq}$ is positive higher frequency factor is obtained. Thus the probability or steric factor should be preferably linked to entropy of activation.

4.1. (v) Unimolecular Reactions – Lindemann's Theory

In a unimolecular reaction, the transition state is made of a single reactant molecule and the necessary activation energy is achieved from collisions. The molecules deficient in energy gain the necessary activation energy by colliding with molecules possessing energy in excess over the required activation energy. These energized molecules decompose directly giving products at a rate that is small compared with the rate they are de-energised by collision; a stationary concentration of these may be built up. These energized molecules are in equilibrium with normal molecules and hence their concentration is proportional to that of normal molecules. The rate of the reaction is proportional to the concentration of energized molecules which is in turn proportional to normal molecules. Therefore, the rate is proportional to the concentration of normal molecules i.e. first order in A. At very low pressures, the collisions cannot maintain a supply of energized molecules. The rate, therefore, is dependent on rate of energisation and hence proportional to square of concentration of normal molecules i.e. second order in reactant. In any case, though the reaction is unimolecular, reaction involves only binary collisions.

These results can be deduced by applying steady state technique to the mechanism :

$$A + A \underset{k\text{-}1}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{k_2} \text{products}$$

According to the Bodenstain's steady state approximation, once the steady state is reached, the concentration of the energized molecule is constant because the rate of their formation is equal to the rate of their removal i.e. rate of change in concentration with time is zero.

$$\therefore \quad \frac{d.[A^*]}{dt} = 0 \qquad \ldots \quad 31$$

The rate of formation of A^* is equal to $k_1[A]^2$ and the rate of removal of A^* is equal to k_{-1} $[A^*]$ $[A] + k_2[A^*]$. At the steady state they are equal.

$$\therefore\ k_1[A]\,[A] - k_{-1}[A^*][A] - k_2[A^*] = 0$$

$$\text{or} \quad [A^*] = k_1[A][A]/(k_{-1}[A+k_2) \qquad \ldots \quad 33$$

Rate of formation of products = rate of the reaction

$$= k_2[A^*] = \frac{k_2\, k_1\, [A][A]}{k_{-1}[A] + k_2}$$

At high pressures k_2 is $<<$ k_{-1} $[A]$

$$\therefore \text{ rate } = \frac{k_2\, k_1\, [A]}{k_{-1}} = \text{ i.e. first order behaviour}$$

At low pressures $k_{-1}[A] < k_2$

$$\therefore \quad \text{Rate} = \frac{k_2\, k_1\, [A][A]}{k_2} = k_1[A]^2$$

i.e. the reaction obeys second order kinetics.

The validity of Lindemann's collision theory is shown by the observed inhibitory effect i.e. decrease in rate of a unimolecular gaseous reaction when inert gases are added to the system. These inert gas molecules also collide with the energized molecules, A* and deenergise them. Thus there is an additional step in the mechanism.

$$A^* + He \xrightarrow{k_3} A + He$$

The steady state approximation now gives

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] - k_3[A^*][He]$$

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2 + k_3[He]}$$

$$\text{Rate} = k_2[A^*] = \frac{k_2 k_1[A]^2}{k_{-1}[A] + k_2 + k_3[He]} \qquad \ldots \quad 34$$

The concentration of He is now present in the denominator and increase in [He] results therefore in decrease in rate.

Evaluation of rate constants

$$\text{Rate} = \frac{k_2 k_1[A]^2}{k_{-1}[A] + k_2}$$

The first order rate constant $k = \dfrac{\text{rate}}{[A]}$

$$k = \frac{k_2 k_1[A]}{k_{-1}[A] + k_2}$$

A plot of k vs. [A] is linear at low pressures since $k_{-1}[A] << k_2$.

As pressure is increased deviations from linearity are observed at higher pressures because $k_{-1}[A]$ cannot be neglected in comparison with k_2 and at high pressures $k_{-1}[A] >> k_2$ and the first order rate constant k is equal to $\dfrac{k_2 k_1[A]}{k_{-1}[A]} = k_2 \dfrac{k_1}{k_{-1}} = k_\infty$ i.e. k_∞ is the limiting first order rate constant at high pressures. A plot of 1/k vs 1/[A] is linear with a positive intercept

$$\frac{1}{k} = \frac{k_{-1}[A]}{k_2 k_1[A]} + \frac{k_1}{k_2 k_1[A]}$$

$$= \frac{k_{-1}}{k_2 k_1} + \frac{1}{k_2[A]} \qquad \ldots \quad 36$$

4.1. (vi) Ionic Reaction–Primary and Secondary Salt Effect

Consider a general reaction

$$A + B \underset{}{\overset{K}{\rightleftharpoons}} AB^{\pm} \longrightarrow \text{products}$$

Proceeding through the formation of the transition state $AB^{\neq}$. The equilibrium between constant transition state and reactants A and B is given by

$$K_{\neq} = \frac{a_{\neq}}{a_A a_B} = \frac{f_{\neq}C_{\neq}}{f_A C_A f_B C_B}$$

Where 'a' represents the activity and 'f' the activity coefficient

$$\therefore C\neq = C_A C_B K \frac{f_A f_B}{f_{\neq}}$$

The rate is proportional to $C\neq$

$$\therefore \quad \text{rate} = \text{Proportionality constant or } C_A C_B K\neq \frac{f_A f_B}{f_{\neq}} = C_A C_B k_o \frac{f_A f_B}{f_{\neq}}$$

$$\text{rate constant} = k_r = \frac{\text{rate}}{C_A C_B} = k_o \frac{f_A f_B}{f_{\neq}} \qquad 42$$

The activity coefficient, f, is related to the ionic strength, μ by the eq.

$$\log f_1 = - AZ_i^2 \sqrt{\mu} \qquad 43$$

Where Z_i is the charge of the ion, μ the ionic strength as a constant equal to 0.51. This equation (42) represents the Debye - Hucke limiting law which is valid us to ionic strength of the medium less than 0.005 using the eq. 42 and 43.

$$\log k_r = \log k_o + 2AZ_AZ_B\sqrt{\mu} \qquad 44$$

This equation represents the primary salt effect on rate. The effect is due to variation of activity coefficients with the ionic strength and rate is related to the activity coefficients (eq. 42). Since this equation is based on the Debye-Huckel limiting law, it is valid at ionic strengths less than 0.005. This equation correlates the rate constant of the reaction with the ionic strength. As per the equation, if the reactants A and B are both cations or both anions and Z_AZ_B is positive, the rate constant should increase with increase in μ and plot of log k_r Vs $\sqrt{\mu}$ should be linear with a positive slope eq. 2 x 0.51 x Z_AZ_B and intercept equal to log k_o can be seen to be rte constant at $\mu = 0$. k_o cannot be determined experimentally because it is impossible to carry out kinetic runs at zero ionic strength since reactants themselves contribute to the ionic strength of the medium. The examples are

$$S_2O_8^{=} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

$$[Co(NH_3)_3Br^{2+}]Hg^{2+} \xrightarrow{H^2O} [Co(NH_3)_5\,H_2O]^{3+} + Hg\,Br^+$$

For the cation – anion reaction Z_AZ_B is negative and log k_r should decrease with increasing ionic strength, μ. For example, the rate of the reaction

$Co(NH_2)Co(NH_3)_5\,Br^{2+} + OH^- \longrightarrow Co(NH_3)_5OH^{+2} + Br^-$ decreases with increasing ionic strength since $Z_AZ_B = (+2+x(-1) = -2)$ is negative. As per the equation the reaction between ion and a neutral molecule is little affected by ionic strength since Z_AZ_B is equal to zero.

The primary salt effect thus enables one to decide whether, the rate-determining step in a reaction is of cation – cation, anion – anion or cation – anion or ion-neutral molecule type.

Calculation of ionic strength

The ionic strength, μ, is given by the equation

$$\mu = \tfrac{1}{2}\,\Sigma C_iZ_i^2$$

Example : Calculate the ionic strength of 0.01M NaCl and 0.01M $AlCl_3$ solutions in water.

NaCl $C_{Na^+} = 0.01$, $C_{Cl^-} = 0.01$

$$\mu = \tfrac{1}{2}\,(0.01 \times (-1)^2 + 0.01 \times (-1)^2) = 0.01$$

$\therefore$ ionic strength of uniunivalent electrolyte is equal to concentration Al Cl_3 $C_{Al^{3+}} = 0.01$. $C_{Cl^-} = 0.03$

($\therefore$ 1 mole of $AlCl_3$ gives 3 Cl^- ions)

$$\therefore \mu = \tfrac{1}{2}\,[0.01 \times (+3)^2 + 0.03 \times (-1)^2] - 0.06$$

Eg. The rate constant of the reaction

$$S_2O_8^{--} + I^- \longrightarrow$$

Is 1.05 litre $mol^{-1}sec^{-1}$ at $\mu = 0.00245$. Calculate the rate constant of the reaction at μ equal to 0.01245.

$$\log k = \log k_a + 2 \times 0.51 \times (-2)(-1)\sqrt{\mu}$$

$$\log (1.05) = \log k_o + 2 \times 0.51 \times (-2)(-1)\sqrt{0.00245}$$

$$\therefore \log k_o = -0.0886$$

At $\mu = 0.01245$

$$\log k = \log k_o + 2 \times 0.51 \times (-2)(-1)\sqrt{0.01245} = 0.1390$$

$$\therefore k = 1.37 \text{ litre } ml^{-1}sec^{-1} \text{ at } \mu = 0.01245.$$

Secondary salt effect

The secondary salt effect is connected mainly with acid base catalysis and is less direct than the primary salt effect. The secondary salt effect is due to variation of activity coefficients with change in ionic strength and consequent change in the concentration of the catalyst (H^+ ion). The change in the concentration of the catalyst results in change in rate. Consider a hydrogen ion-catalysed reaction whose rate constant, k_n is related the hydrogen ion concentration C_{H^+} by the equation :

$$K_r = kC_{H^+}$$

The hydrogen ion has, as its source, the acid HA which ionizes according to :

$$HA \xrightleftharpoons{ka} \overset{+}{H} + \bar{A}$$

$$K_a = \frac{a_{H^+} \text{ x } a_{A^-}}{a_{HA}} = \frac{C_H + C_{A^-}}{C_{HA}} \frac{f_H \, f_{A^-}}{f_{HA}}$$

$$\text{Or } C_{H^+} = K_a \frac{f_H \; H^*}{f_{H^+} \; x \; f_{A^-}} \text{ x } \frac{C_{HA}}{C_{A^-}}$$

In this study, the ratio of concentrations of acid HA to its salt (A^-) is kept constant.

$$\therefore C_{H^+} = \text{constant} \frac{f_{HA}}{f_H + f_{A^-}} \quad \text{where constant} = K_a \frac{C_{HA}}{C_{A^-}}$$

$$k_r = k \text{ constant} \frac{f_{HA}}{f_{H^+} \text{ x } f_{A^-}} = k_o \frac{f_{HA}}{f_{H^+} \text{ x } f_{A^-}} \qquad \dots \quad 46$$

$$\therefore \; \log k_r = \log k_o + \log f_{HA} - \log f_{A^-} - \log f_{H^+} \qquad \dots \quad 47$$

Using the equation for Debye-Huckel limiting law – $\log f_i = AZ_i^2 \sqrt{u}$ where A is a constant equal to 0.51, Z_i is the charge of the ion and μ is the ionic strength 3.

$- \log f_{A^-} = A(-1)^2 \sqrt{\mu}$, $- \log f_{H^+} = A(+1)^2 \sqrt{\mu}$ and $\log f_{HA} = - A(0)^2 \sqrt{\mu} = 0$

because Z_{HA} the charge of the undissociated acid = 0.

∴ The equation becomes

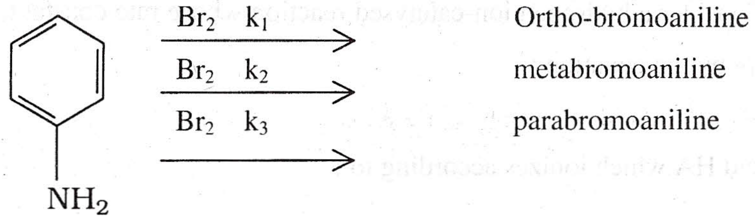
$$\log k_r = \log k_o + 2A\sqrt{u} \qquad 48$$

This represents the equation for secondary salt effect for the H^+ ion catalysed reaction.

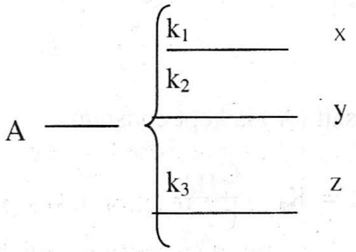
4.1 (vii). Complex Reactions – opposing, Parallel and Consecutive Reactions (First Order Type)

Parallel reactions

It is often observed that the substances may undergo several reactions simultaneously the concentration of products at a given instant being dependent on the rate constants of the reactions. For example bromine can react with aniline in three different ways simultaneously forming ortho meta and para bromoderivatives.



The derivation of the rate-law is quite simple. Taking general case of a reactant undergoing three different reactions simultaneously. The rate of decrease in the concentration can be written as



$$\frac{-d[A]}{dt} = k_1[A] + k_2[A] + k_3[A]$$

where [A] is the instantaneous concentration of A at time 't'

$$-\int \frac{d[A]}{[A]} = \int k_1 + k_2 + k_3)\, dt$$

$$-\ln A = (k_1 + k_2 + k_3)\, t + I$$

At zero time no product is formed and no reaction has taken place i.e. $[A] = [A]_o$

or $- \ln[A]_o = (k_1 + k_2 + k_3) \times t + I$

$\therefore$ I = integration constant = $- \ln [A]_o$

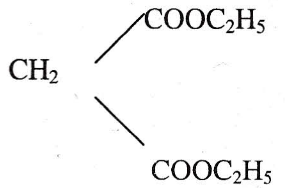
or $- \ln[A] = (k_1 + k_2 + k_3)\ 1 - \ln[A]_o$

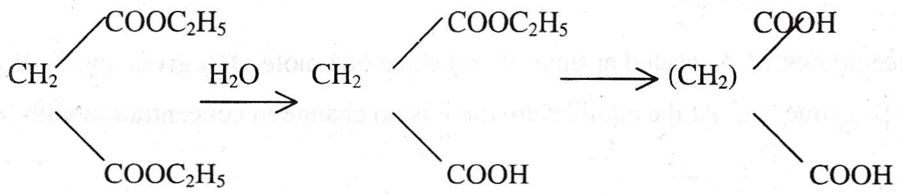
$$(k_1 + k_2 + k_3) = \frac{1}{t} \ln \frac{[A]_\infty}{[A]} \qquad \ldots\ 37$$

The products x, y, z are present in the concentration ratio $k_1 : k_2 : k_3$

Consecutive Reaction

Most of the chemical reactions proceed forming intermediates which undergo reactions consecutively giving final product(s). For example the ester


$CH_2(COOC_2H_5)_2$ may be hydrolysed consecutively as follows :



In these reactions if the first step is slow and the other steps are fast, the overall rate of the reaction is equal to the rate of the slow step and simple kinetics are observed though the reaction takes place in several stages. Fortunately this is the case with many reactions making the kinetic investigation simple. If these elementary steps in the mechanism proceed with comparable rates there will be no single rate-determining step and the analysis of the rate-data has to be carried out using a different technique. For example taking the ease of the simplest consecutive process,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

the following rate equations are easy to set up.

$$\frac{-d[A]}{dt} = k_1 [A] \qquad [A] = [A]_o e^{-kt}$$

where [A] is the concentration of A at time 't'

$$\frac{-d[B]}{dt} = k_1 [A] - k_2 [B]$$

$$= k_1[A]_o e^{-kt} - k_2[B]$$

$$\text{or} \quad \frac{d[B]}{dt} + k_2[B\} = k_1[A]_o e^{-kt}$$

$$[B] = \frac{k_1 [A]_o}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}] \qquad \ldots \quad 38$$

Opposing Reactions

The simplest possible case of the opposing reactions is the unimolecular are :

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

The following rate equations can be set up from this mechanism

$$\frac{dx}{dt} = k_1 (a - x) - k_{-1} x$$

where 'x' is the concentration of A reacted at time 't' and since one mole of A gives one mole of B, x will be the concentration of B at time 't'. At the equilibrium there is no change in concentration with time

$$\text{i.e. } \frac{dx}{dt} = 0$$

$\therefore$ $k_1 (a - x_e) - k_{-1} x_e = 0$ Where $(a - x_e)$ is the equilibrium concentration of A and x_e is the equilibrium concentration of B.

$$k_1 = \frac{k_1(a - x_e)}{x_e}$$

using equation …..

$$\frac{dx}{dt} = k_1(a - x) - \frac{k_1 (a - x_e) x}{x_e}$$

$$= \frac{k_1 a}{x_e} (x_e - x) \quad \text{or}$$

$$\int \frac{dx}{(x_e - x)} = \int \frac{k_1 a}{x_e} dt$$

$$- \ln (x_e - x) = \frac{k_1 a}{x_e} t + I$$

'I' can be calculated by taking the boundary condition that at t = 0, x = 0.

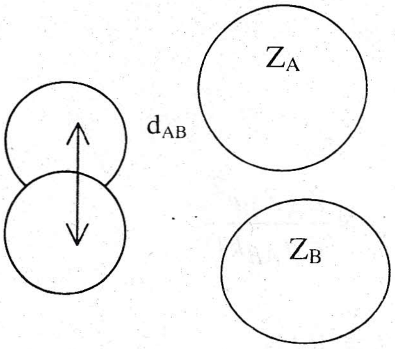
Therefore $I = - \ln x_e$. This leads to the relation :

$$\frac{k_1 a}{x_e} = 1/t \ln \left(\frac{x_e}{x_e - x} \right)$$

Effect of Dielectric Constant on Reactions between Ionic Reactants

It is a common experience that the reaction between ions is markedly influenced by solvent. The most important property of solvent to reckon with is the dielectric constant of the solvent. The greater the dielectric constant, more polar is the solvent. The reaction between two cationic or two anionic reactants proceed in solvents of higher dielectric constant with greater facility. The cation-anion reactions are accelerated by decrease in the dielectric constant of the medium. The mathematical relation between rate constant and the dielectric constant can be easily derived and interpreted.

Consider the reaction between two ionic reactants A and B with charges Z_A and Z_B. Before collision, the reactants are at distance from each other and they are brought into proximity with each other to effect the collisions. The electrostatic force, f, between the reactants is given by :



$$f = \frac{Z_A Z_B e^2}{Ex^2}$$

where is the basic electronic charge E is the dielectric constant and x is the distance between A and B

The work done for bringing together though a distance dx is dw = - f.dx

For collision they are to be brought from ∞ to the distance of closest approach, d_{AB}, in the collision, and the work done is obtained from

$$\int_{\infty}^{d_{AB}} dW = W = -\int_{\infty}^{d_{AB}} \frac{Z_A Z_B e^2}{Ex^2} = \frac{Z_A Z_B e^2}{Ed_{AB}} \quad \dots \quad 40$$

The negative sign is used because x decreases by dx when the ions move together.

This work is equal to electrostatic contribution to the free energy of activation. But this calculation has been made for individual ions. To calculate the same per mole the quantity must be multiplied by Avogadro number, N

$$\therefore\ \Delta^{\neq}_{es} = \frac{N Z_A Z_B e^2}{E d_{AB}} \qquad \ldots \qquad 41$$

There is also the nonelectrostatic term, $\Delta G^{\neq}_{nes}$,and the total free energy of activation $\Delta G_{\neq}$ is equal to sum of

$\Delta G^{\neq}_{\neq es}$ and $\Delta G^{\neq}_{\neq nes}$

$$\therefore \Delta G_{\neq} = \Delta G_{\neq nes} + \frac{N Z_A Z_B e^2}{E d_{AB}}$$

But $\Delta G_{\neq}$ is related to the rate constant, k_r by the eq.

$$k_r = \frac{kT}{h} e^{-\Delta G_{\neq} / RT}$$

$$\ln k_r = \frac{kT}{h} - \frac{\Delta G_{\neq}}{RT} = -\left(\frac{\Delta G_{\neq}}{R}\right)_{nes} + \ln \frac{kT}{h} - N \frac{Z_A Z_B e^2}{\varepsilon d_{AB} kT}$$

$$\text{(or)} \quad \ln k_r = \ln k_0 - \frac{Z_A Z_B e^2}{\varepsilon d_{AB} kT} \qquad \therefore K = R / N$$

where $\ln k_0 = -\Delta G_{\neq} / RT + \ln kT/h$

To study the effect of solvent on rate constant, the rate constant is determined for the same reaction in solvents of different dielectric constant. As per the eq. 41 plot of $\ln k_r$ vs $\frac{1}{E}$ should be linear with slope equal to

$\frac{N Z_A Z_B e^2}{\varepsilon d_{AB} RT}$, from which the distance of closest approach d_{AB}, is calculated. The slope will have a positive or negative sign according as both the reactants have same charge, i.e. $Z_A Z_B$ is positive or $Z_A Z_B$ is negative. In the former case the slope will be negative and in k_r increases with increasing dielectric constant. I.e. rate increases with increasing dielectric constant. If $Z_a Z_B$ is negative the slope will be positive and such reactions take place with greater ease in solvents of lower dielectric constant.

Short answer questions

1. Explain the significance of the probability factor.
2. Describe how the activation energy is experimentally determined
3. Explain the terms, molecularity, rate-determining step and order. Explain the origin of the terms 'SN_1' and 'SN_2' processes.
4. A reaction between two reactants A and B obeys first order kinetics in A and zero order kinetics in B. Suggest a suitable mechanism.
5. Discuss the significance of Boltzmann.factor in the collision theory equation
6. Discuss the weaknesses of collision theory of reaction rates. How are they overcome in the transition state theory?
7. Discuss the significance of entropy of activation
8. Predict the effect of ionic strength and dielectric constant on the following reactions

$$Co(NH_3)_5Cl^{2+} + OH^- \longrightarrow Co(NH_3)_5\,OH^{2+} + Cl^-$$

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

$$Co(NH_3)_5\,Cl^{2+} + Hg^{2+} \xrightarrow{H_2O} Co(NH_3)_5\,H_2O^{3+} + Hg\,O^+$$

Long answer questions

1. Discuss critically the collision theory of reaction rates and its weaknesses. Explain how the defects of collision theory are overcome with transition state theory
2. Derive the equation for primary salt effect. Explain its mechanistic applications.

LESSON - 2

CHAIN REACTIONS – BRANCHING CHAIN REACTIONS

The chain reactions differ from the nonchain reactions in that the products are not obtained by direct collisions between the reactants ; one of the reactants undergoes a reaction forming an intermediate (which is often an atom or a free radical) which then reacts with the other reactant producing a product and a second intermediate. The second intermediate then reacts to produce a product and regenerating the first intermediate. These chains can propogate till they undergo chain terminating reactions. For example, the hydrogen-chlorine reaction proceeds according to the following mechanism.

$Cl_2 \longrightarrow 2\,Cl$ (initiation), $Cl + H_2 \longrightarrow HCl + H$ (propagation)

$H + Cl_2 \longrightarrow HCl + Cl$ (propagation), $Cl + X \longrightarrow ClX$

$H + O_2 \longrightarrow HO_2$, $Cl + O_2 \longrightarrow Cl\,O_2$ (termination steps)

The intermediates are called chain carriers.

Since the products are not obtained by direct collisions between the reactants but require the formation of chain carriers, whose concentration is zero initially, a certain time lag occurs before the build up of appreciable rate of formation of products.

The rate of formation of products is zero at zero time because the chain carriers are not present initially. The rate subsequently reaches a maximum after certain time (called the induction period) and then decreases with time. For a non chain reaction involving direct collisions between the reactants, the rate is maximum at zero time because the number of collisions directly dependent on the concentrations of the reactants is maximum at zero time decreasing with time, the rate with decrease in the concentrations of the reactants. Chain reactions involve multi step mechanisms, leading to complicated rate-laws and orders.

The mechanisms of chain reactions have a definite pattern further distinguishing them from non-chain processes. The mechanisms invariably involve an initiation step in which the chain carriers are generated and propagation step in which the products are formed and the initial chain carrier is regenerated and termination reaction in which the chain reactions undergo secondary reaction resulting in the termination or shortening of chains. Some chain reactions, called the branched chain reactions, also involve branching steps in which more chain carriers are produced than are consumed. Thus, in hydrogen – oxygen reaction which is a branched chain reaction, there are branching step like

$H + O_2 \longrightarrow OH + O$, $O + H_2 \longrightarrow HO + H$

In these steps though the chain carrier H (or O) is consumed, two more chain carriers OH and O are produced. This results in an enormous increase in the rate of reaction leading to explosion. Other examples of this type are oxidation of phosphorus and alkanes with oxygen.

All these features of chain reactions can be generalized, a general mechanism can be envisaged and rate-law can be determined for this general mechanism. Assuming that a chain carrier, R, is generated in the initiation, the features of chain reactions can be summarized in the following general scheme.

$\xrightarrow{V_i} R$ (Initiation) ... 1

$k \xrightarrow{k_b} \alpha R$ (branching) ... 2

$R + \ldots \xrightarrow{k_p} R + \text{product}$ (propagation) ... 3

$R \xrightarrow{k_g}$ termination in gaseous phase (homogeneous termination) ... 4

$R \xrightarrow{k_S}$ termination on surface (heterogeneous termination) ... 5

In this mechanism, the propagation steps are summarized into one step. R represents the chain carrier(s) which is an atom or a free radical.

The rate-law can be derived using the steady state approximation first enunciated by Bodensteim. According to this approximation

$$\frac{d[R]}{dt} = 0 \qquad \ldots \quad 1$$

i.e., rate of change of concentration of the chain carrier, R, with respect to time is zero. This postulate is tenable in the case of highly reactive intermediates like atoms, free radicals, unstable oxidation states etc. The eq. is a situation under steady state conditions where the sum of rates of formation minus sum of rates of removal in all the steps in the scheme of mechanism is equal to zero. Expressed mathematically

$$\frac{d[R]}{dt} = V_i + (\alpha - 1)\, k_b [R] - k_S [R] - k_g [R] = 0 \qquad \ldots \quad (2)$$

In this equation V_i is the rate of formation of the chain carrier in the initiation step, k_b, k_s, k_g are the rate constants of branching, surface – catalysed termination and gas phase termination corresponding to the steps 2, 5 and 4 in the mechanism. For calculating the rate of change of concentration of R, step 3 need not be considered because it is a propogation step in which the chain carrier, though consumed, is ultimately regenerated using the eq. 2, the concentration of the chain carrier R, [R], can be obtained.

$$[R] = \frac{V_1}{k_s + k_g - (\alpha - 1)\, k_b} \qquad \ldots \quad 3$$

The products are formed in the propogation step (step 3) and rate of the chain reaction is equal to rate of formation of products, $\frac{d[\text{products}]}{dt}$

$$\frac{d[\text{products}]}{dt} = k_P[R] = \frac{k_P V i}{k_s + k_g - (\alpha - 1) k_r} \quad \ldots \quad 4$$

This is a general rate-law for a chain process. One can understand many facets of chain reactions from eq. 4. The rate of chain reaction undergoes a decrease in value as the termination becomes more prominent (i.e.) as $(k_S + k_g)$ increases k_b is positive or zero and α (number of chain carriers produced in the branching step) is always greater than 1. Therefore $-(\alpha - 1)K_b^k$ is a negative term which being present in the denominator, reduces the value of denominator i.e. increases the rate. In other words, greater the contribution of branching, higher will be the rate of the chain reaction. Under the limits where $(k_s + k_g)$ and the negative term $-(\alpha - 1)\, k_b$ approach each other the rate becomes extremely high i.e. explosion occurs. This is called an explosion limit. Such reactions become explosively fast at these limits which can be experimentally determined. Such reactions, are called branched chain reactions, the explosive rates being due to presence of branching steps. The most extensively investigated branched chain reaction is the reaction between hydrogen and oxygen. The reaction has been shown to proceed according to the following mechanism.

$H_2 \longrightarrow 2H$ ... 1

$H + O_2 \longrightarrow OH + O$ ... 2

$O + H_2 \longrightarrow OH + H$ ... 3

$HO_2 \longrightarrow$ removal at surface ... 4

$HO_2 + H_2 \longrightarrow H_2O + OH$ ... 5

$OH + H_2 \longrightarrow H_2O + H$ ... 6

$H \longrightarrow$ removal at surface ... 7

$OH \longrightarrow$ removal at surface ... 8

The steps 1 and 5 and 6 are respectively the initiation and propagation steps. Steps 2 and 3 are the branching steps (α = 2) and steps 7 and 8 are the termination steps. In addition, though not shown in the mechanism, there will be termination steps in gas phase not influenced by surface. The termination steps 7 and 8 are catalysed by the material of the vessel in which the reactants are mixed.

There are two explosion limits recognized for the reaction, the lower explosion limit (i.e. the pressure condition in the low pressure region where the reaction becomes explosively fast) and the higher explosion limit (the pressure condition at with the high pressure region). At both these limiting pressure conditions $k_S + k_g$ and the negative term – $(\alpha - 1)\ k_l$ in the denominator of eq. 4 are very nearly equal to each other.

These can be interpreted as follows. The reactant gases are mixed in stoichiometric ratio. When they are mixed at very low pressures the radicals do not undergo many collisions among themselves under these low pressure conditions and have ample opportunity to reach the surface of the vessel which catalyses the termination i.e. k_g is negligible compared to k_S. As pressure increases k_S decreases and at certain values of pressure k_S approaches $-(\alpha\text{-}1)\ k_b$ leading to explosion. This is the lower explosion limit. At high pressures k_S is very small compared to k_g which assumes a large value due to increased number of collisions between radicals due to high pressure. Under these conditions, as pressure decrease, k_g decreases and at a particular value of pressure k_g approaches – $(\alpha - 1)\ k_b$ resulting in explosion because the value of the denominator of eq. 4 assumes a very small value under these conditions. A third explosion limit has also been found which is however a thermal limit.

Chain length

The chain length can be defined as the number of propogation steps undergone before termination takes place. For example in hydrogen chlorine reaction the termination steps are less prominent than propagation steps, the rate of propagation being far more than the rate of termination. Therefore a single atom of chlorine can produce large number of HCl molecules and the chain length is as high as 10^5. The experimental definition of chain length provides an easy experimental method for the determination of chain length. According to this definition chain length is the ratio of overall rate of chain reaction to rate of initiation.

Hydrogen – Halogen Reactions

These classical reactions have been subject of extensive investigation and the results have been found to be of immense use in understanding the chain mechanisms. Interestingly, the hydrogen – iodine reaction proceeds through non chain mechanism and the products are the result of direct collisions between hydrogen and iodine molecules. On the other hand, the hydrogen – chlorine and the hydrogen – bromine reactions proceed through a chain mechanism. This has been explained by calculating the activation energies of both chain and non chain mechanisms of each of these three reactions. The results indicate involvement of higher activation energy for chain mechanism compared to non chain mechanism in the case of hydrogen – iodine reaction whereas the chain mechanism involves lower activation energy than a non chain process in the case of hydrogen – chlorine and hydrogen bromine reactions. Contribution of chain mechanism to rate of $H_2 - I_2$ reaction is negligible compared to that of non chain mechanism whereas the reverse is the case for $H_2 - Cl_2$ and $H_2 - Br_2$ reactions.

4.2. (i). Derivation of rate law of The Hydrogen-Bromine Reaction

The hydrogen-bromine reaction also proceeds according to chain mechanism but the mechanism differs from that of hydrogen – chlorine reaction in that it has the step H + HBr $\longrightarrow$ H_2 + Br. The step H + HCl $\longrightarrow$ H_2+Cl is not possible because of high stability of HCl molecule.

$$Br_2 \xrightarrow{k_1} 2\,Br$$

$$\left.\begin{array}{l} Br + H_2 \xrightarrow{k_2} HBr + H \\ \\ H + Br_2 \xrightarrow{k_3} HBr + Br \end{array}\right\} \text{Propagation}$$

$$H + HBr \xrightarrow{k_4} H_2 + Br$$

$$2\,Br \xrightarrow{k_5} Br_2 \qquad \text{Termination}$$

The rate-law can be derived by applying steady state hypothesis to the chain carriers Br and H atoms. The equations can be written as follows :

$$\frac{d[Br]}{dt} = 2k_1[Br_2] - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - k_5[Br]^2 = 0 \quad \ldots \quad (10)$$

$$\frac{d[H]}{dt} = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] = 0 \quad \ldots \quad (11)$$

Adding the right hand sides of eq. 10 and 11 we get

$$2k_1[Br_2] - k_5[Br]^2 = 0$$

$$\therefore \quad [Br] = \left(\frac{2k_1}{k_5}\right)^{1/2} [Br_2]^{1/2}$$

Substituting the expression for [Br] in eq. and solving for the concentration hydrogen atom, [H] we get

$$[H] = \frac{k_2(2k_1/k_5)^{1/2}\,[H_2][Br_2]}{k_3[Br_2] + k_4[HBr]}$$

The rate of the reaction which is equal to $\frac{d[HBr]}{dt}$ is given by eq.

$$\frac{d[HBr]}{dt} = k_3\,[Br][H_2] - k_3\,[H]\,[Br] - k_4[H][HBr]$$

Substituting the expression for [H] and [Br] in this equation and simplifying, the final rate-law is obtained

$$\frac{d[HBr]}{dt} = \frac{k_2\,(2k_1/k_5)^{1/2}\,[h_2][Br_2]}{1 + k_4[HBr]/k_3[Br_2]} \quad \ldots\ 12$$

This equation agrees with the empirical rate-law obtained from the experimental results.

4.2 (ii). Derivation of rate law of Hydrogen chlorine reaction

The hydrogen chlorine reaction gives very complicated kinetic pattern not only due to the operation of a chain mechanism but also due to sensitivity of kinetics to the presence of oxygen and other impurities. These impurities have large inhibitory effect on rate increasing the termination of chains. In the absence of oxygen, rate becomes extremely high. Gohring has given a satisfactory mechanism for the chain reaction in the presence of light which only is responsible for the photochemical initiation of chains.

$$Cl_2 + h\upsilon \xrightarrow{k_1} 2\,Cl \qquad \text{Initiation} \quad \ldots\ 1$$

$$\left.\begin{aligned} Cl + H_2 &\xrightarrow{k_2} HCl + H \quad \ldots\ 2 \\ H + Cl_2 &\xrightarrow{k_3} HCl + Cl \quad \ldots\ 3 \end{aligned}\right\} \text{Porpagation}$$

$$\left.\begin{aligned} H + O_2 &\xrightarrow{k_4} HO_2 \quad \ldots\ 4 \\ Cl + O_2 &\xrightarrow{k_5} ClO_2 \quad \ldots\ 5 \\ Cl + X &\xrightarrow{k_6} ClX \quad \ldots\ 6 \end{aligned}\right\}$$

The rate of formation of Cl atom is equal to twice the rate of decomposition of Cl_2 since 2 Cl atoms are produced on decomposition of one molecule of chlorine. The rate of photochemical decomposition of molecular chlorine is equated to the intensity of the radiation (I) and therefore the rate of formation of Cl atoms is equal to 2. The rate-law can be derived by applying steady state, hypothesis to the chain carriers, Cl and H atoms. At the steady state the rate of there formation of Cl or H atom is equal to rate of removal and hence rate of change of Cl atom or H atom is (i.e.) $\frac{d[Cl]}{dt}$ or $\frac{d[H]}{dt}$ is equal to the difference between their formation and rate of removal which is equal to zero. For example the chlorine atom is formed in steps (1), (3) and removed in steps (2), (5) and (6)

the rate of formation of Cl atom $= 2I + k_3[H][Cl_2]$

and the rate of removal of Cl atom $= k_2[Cl][H_2] + k_5[Cl][O_2] \pm k_6[Cl][X]$

$$\therefore \frac{d[Cl]}{dt} = 2I + k_3[H][Cl_2] - k_2[Cl][H_2] - k_5[Cl][O_2] - k_6[Cl][X] = 0$$

on the same lines $\frac{d[H]}{dt} = k_2[Cl][H_2] - k_3[H][Cl_2] - k_4[H][O_2]$

The expressions for concentration of [Cl] can be obtained from both these equations and the expressions can be equated

$$[Cl] = \frac{2I + k_3[H][Cl_2]}{(k_2[H_2] + k_5[O_2] + k_6[X])}$$

$$[Cl] = \frac{k_2[H][Cl_2] + k_4[H][O_2]}{k_2[H_2]}$$

The expression can be equated and solved for the concentration of H atom [H]

$$[H] = \frac{2I\, k_2[H_2]}{k_3 k_6[Cl][x] + [O_2](k_2 k_4[H_2] + k_3 k_5[Cl_2] + k_4 k_6[x])}$$

The expression for [Cl] can be obtained by substituting for [H] the right hand expression in one of these equations and simplifying. The rate of the reaction is equal to rate of formation of the product [HCl] which is given by eq.

$$\frac{d[HCl]}{dt} = k_2[Cl][H_2] + k_3[H][Cl_2]$$

It has been found that k_2 is far less than k_3 and hence the contribution of k_2 term to rate can be neglected.

$$\therefore \frac{d[HCl]}{dt} = k_3[H][Cl_2]$$

Substituting for [H] from eq. (9) one gets

$$\frac{d(Hd)}{dt} = \frac{2k_2 k_3[H_2][Cl_2]I}{k_3 k_6[Cl_2][x] + [O_2](k_2 k_4[H_2] + k_3 k_5[Cl_2] + k_4 k_6[x])}$$

The rate-law for thermal reaction can be obtained by substituting I by $k_1[Cl_2]$. The rate law then is given by

$$\frac{d\,(Hd)}{dt} = \frac{2k_1k_2\,k_3\,[H_2\,][Cl_2\,]^{\,2}}{k_3\,k_6\,[Cl_2\,][x]+[O_2\,](k_2\,k_4\,[H_2\,]+k_3\,k_5\,[Cl_2\,]+k_4\,k_6\,[x])}$$

4.2. (iii). Derivation of rate law of Decomposition of Acetaldehyde

The decomposition of acetaldehyde in the gaseous state over a wide range of temperatures and pressures follows three-halves order kinetics and the kinetics were interpreted on the basis of the following chain mechanism.

$$CH_3CHO \xrightarrow{k_1} CH_3 + CHO$$ Initiation

$$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$$

$$CH_3CO \xrightarrow{k_3} CH_3 + CO$$

$$\left.\begin{matrix} \\ \\ \end{matrix}\right\}$$ Propagation

$$2CH_3 \xrightarrow{k_4} C_2H_6$$ Termination.

In this mechanism the chain carriers are CH_3 and CH_3CO free radicals and applying steady state hypothesis with respect to both of them, the following equations can be derived.

$$\frac{d[CH_3]}{dt} = k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3[CH_3CO] - k_4[CH_3]^2 = 0 \ldots (5)$$

$$\frac{d[CH_3CO]}{dt} = k_2[CH_3][CH_3CHO] - k_3[CH_3CO] = 0 \quad \ldots \qquad (6)$$

Adding of both the equations one gets

$$K_1[CH_3CHO] - k_4[CH_3]^2 = 0 \qquad \text{or}$$

$$[CH_3] = \left(\frac{k_1}{k_4}\right)^{1/2} [CH_3CHO]^{1/2} \qquad \ldots \quad (7)$$

rate of the reaction can be taken as rate of formation of the product CH_4 i.e. $\frac{d[CH_4]}{dt}$ and the rate law is obtained by using

$$\frac{d[CH_4]}{dt} = k_3[CH_3][CH_3CHO]$$

from eq. 7 the expression for the term $[CH_3]$ can be substituted

$$\therefore \frac{d[CH_4]}{dt} = k_3 \left(\frac{k_1}{k_4}\right)^{1/2} [CH_3CHO]^{3/2} \qquad \ldots \quad 8$$

The rate equation elegantly explain the observed 3/2 order kinetics in acetaldehyde. The overall 3/2 order rate constant is equal to

$$\frac{d[CH_4]}{dt} \times \frac{1}{[CHCHO]^{3/2}} = k = k_2 \left(\frac{k_1}{k_4}\right)^{1/2}$$

Differentiating with respect to temperature

$$\frac{d \ln k}{dT} = \frac{d \ln k_2}{dT} + \frac{1}{2}\left(\frac{d \ln k_1}{dT} - \frac{d \ln k_4}{dt}\right)$$

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$ Where E is the overall activation energy and this is given by

$$\frac{E}{RT^2} = \frac{E_2}{RT^2} + \frac{1}{2}\left(\frac{E_1}{RT^2} - \frac{E_4}{RT^2}\right)$$

$$\text{or} \quad E = E_2 + ½ (E_1 - E_4)$$

Model Questions

Chain Reactions

1. Define Chain length.
2. Discuss the mechanistic difference between Chain and non chain reactions.
3. Explain the conditions for explosion.
4. Discuss the explosion limits of hydrogen – oxygen reaction.
5. What is branched chain reaction. Discuss the features of branched chains.

Long Answers Questions

6. Discuss the distinguishing factures of chain reaction. Derive a rate – law for a general chain mechanism and discuss the explosion limits.

7. Derive rate – laws for hydrogen – chlorine or reaction.

LESSON - 3

CATALYSIS

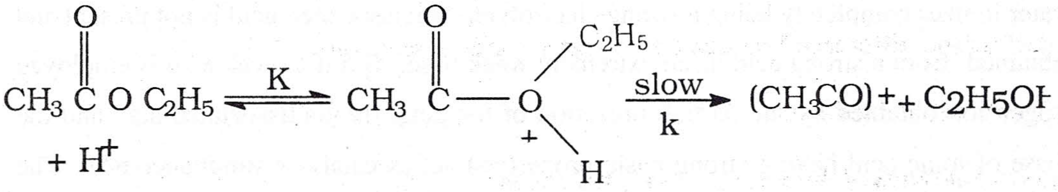
4.3. (i) Introduction

A catalyst enhances the rate of a chemical reaction without itself undergoing a permanent chemical change. It means that the concentration of the catalyst must be the same before the occurrence of a reaction and at the end of the reaction. Because the catalyst is not consumed it does not add or remove the energy from the system. That is the standard free energy change is the same for a catalysed and uncatalysed reactions. The standard free energy change is related to the equilibrium constant of the reaction by the eq. (1).

$$\Delta G^\circ = -RT \ln K \qquad \ldots \quad (1)$$

Hence if ΔG° is the same for both catalysed and uncatalysed reactions, the equilibrium constant, K (which measures the position of the equilibrium) is also the same. The catalyst only speeds up the attainment of equilibrium. Therefore it should catalyse both forward and reversible processes of a reversible reaction such that (k_1/k_{-1}) is a constant equal to equilibrium constant, k_1 and k_{-1} being rate constants of forward and reverse reactions in the equilibrium.

Though the catalyst concentration remains unaltered during the reaction it participates in the mechanism and enters the rate equation. That is why the rate of the reaction depends on the catalyst concentration. For example the hydrolysis of ethyl acetate, the catalyst hydrogen ion protonates the ester the protonated ester undergoing acyl-oxygen scission in the rate determining step producing $[CH_3CO]^+$ which in a fast step interacts with water producing the final product CH_3COOH.



$$CH_3\overset{O}{\overset{\|}{C}}OC_2H_5 + H^+ \overset{K}{\rightleftharpoons} CH_3\overset{O}{\overset{\|}{C}}-\overset{+}{O}(C_2H_5)(H) \xrightarrow[k]{slow} (CH_3CO)^+ + C_2H_5OH$$

$$(CH_3CO)^+ \xrightarrow[fast]{H_2O} CH_3COOH + H^+$$

$$K = \frac{[I]}{[Ester][H^+]} \quad \text{or} \quad [I] = K[Ester][H^+]$$

$$\text{rate} = k[I] = kK[Ester][H^+]$$

Thus the rate is proportional to first power of the catalyst concentration. The catalyst, H^+ ion, is ultimately regenerated.

The main function of the catalyst is therefore to provide an alternative pathway or mechanism such that the catalyst enables the lowering of activation energy. If the activation energy decreases, the rate of the reaction increases. The catalyst may interact and participate in the mechanism in many ways. For example when H^+ ion protonates a molecule the atoms to be protonated having lone pairs of electrons like O atom or N atom ('O' in ester). The addition of a positive charge disturbs the electron's density distribution in the bonds around making the bonds unstable and rendering the reactant very reactive. Thus in the nitration of benzene the catalyst H^+ interacts with nitric acid producing NO_2^+ whichis more reactive than HNO_3 and can react with benzene more easily than HNO_3 itself.

$$HNO_3 + H^+ \longrightarrow NO_2^+ + H_2O$$

$$NO_2^+ + C_6H_6 \longrightarrow C_6H_5NO_2 + H^+$$

The catalyst may in some cases produces an unstable oxidation state by reacting with one of the reactants and this unstable state may react with the second reactant with greater ease.

$$Ce(IV) + Ag(I) \longrightarrow Ce(III) + Ag(II)$$

Intermediate unstable oxidant

State

$$Ag(II) + Tl(I) \longrightarrow Ag(II) + Tl(II)$$

$$Ce(IV) + Tl(II) \longrightarrow Ce(III) + Tl(III)$$

If a strong acid like hydrochloric acid is acting as a catalyst, there is only the effect of H^+ ion since hydrochloric acid in water ionizes completely being a strong electrolyte. Undissociated acid is not present and the conjugate base, obtained from a strong acid, is an extremely weak base. But if a weak acid is employed as a catalyst, the hydrogen ion obtained by the partial ionization of the acid, the undissociated acid and the anion (the conjugate base of ionic acid having strong basic properties) act as catalysts simultaneously. The rate constant can be expressed as a sum of all these components.

$$k = k_{H_2O} + k_{H^+}[H]^+ + k_{HA}[HA] + k_A[A^-] \qquad \ldots 2$$

k_{H^+}, k_{HAC}, k_{AC^-} are the rate constants of H^+ catalysed, undissociated acid catalysed and anion ion – catalysed components of the overall rate.

k_{H_2O} *and* k_{H^+} will be the same whether it is weak acid or strong acid like HCl. In the case of strong acid like HCl there will be no component due to $[A^-]$ because the enjoyed base (A^-) of story acid in very wecn.

$$k = k_{H_2O} + k_{H^+} [H^+] \quad \ldots \quad 3$$

If k is determined at different concentration of HCl and k is plotted vs [HCl] a straight line with slope equal to k_H^+ and intercept equal to k_{H_2O} will be obtained. Thus k_{H^+} and k_{H_2O} are determined. Now the rate constant, k, is determined at different concentrations of the weak acid HA taking care to see that the concentrations of HA and A^- (taken in the form of, say, sodium salt of HA) maintained such that [A] | [HA] is constant and equal to value of q.

$$[A^-] \mid [HA] = q \qquad [A^-] = q\,[HA] \quad \ldots \quad 4$$

Substituting the value of [A] in eq. 2 we get

$$k = k_{H_2O} + k_{H^+} [H^+] + k_{HA}[HA] + q\,k_{A^-} [A^-].$$

Since HA is a weak acid and $[HA] \mid [A^-]$ is maintained constant pH i.e. $[H^+]$ is constant according to Henderson equation

$$pH = pKa + \ln \frac{[A^-]}{[HA]} \quad \ldots \quad 5$$

Therefore if k is plotted against [HA] again a straight line is obtained as per eq. 3. The slope is equal to $k_{HA} + q\,k_{A^-}$ and intercept is equal to

$k_{H_2O} + k_{H^+} [H^+]$. If the slope is determined taking different ratios, q_+, then k_{HA} and k_{A^-} can be determined solving simultaneous equations. Thus the values of k_{H_2O}, k_{H^+}, k_{HA} and k_{A^-} can be determined for given acid catalyst.

4.3. (ii) Bronsted Catalysis Law

In most of the cases, the hydrogen ion obtained by the ionization of acid catalyst or hydroxyl ion obtained by the ionization of base are strong catalyzing species rather than the undissociated acid or undissociated base respectively. Hence the rate constant is related to the ionization constant K_a of acid or K_b of a base catalyst. This has been expressed in the form of Bronsted catalysis law :

$$k = G_a K_a^{\alpha} \quad \text{(for acid catalysis)}$$

$$k = G_b K_b^{\beta} \quad \text{(for base catalysis)}$$

i.e. G_a, G_b, α and β are constants and k is the observed rate constant in the presence of an acid catalyst or a base catalyst. It can be seen that acids or bases having higher ionization constants have better catalytic effect. It should also be noted that the acid and base catalysis are not associated with much specificity of catalyt, unlike enzyme catalysis which is highly specific.

4.3. (iii) General Mechanism of Acid Catalysis

The acid catalysed reaction, in general, involves a transfer of proton to the reactant (substrate) from the acid (BH^+). The protonated substrate undergoes the reaction which is the rate determining stage ultimately producing the products and the hydrogen ion is released. The hydrogen ion may be taken up by water present in the medium or by the conjugate base (B)of the acid catalyst. If the hydrogen ion is taken up by water forming H_3O^+ the mechanism is called protolytic mechanism.

Scheme I

$$S + BH^+ \underset{k_{-1}}{\xrightarrow{k_1}} SH^+ + B \qquad \ldots \qquad (1)$$

$$SH^+ + H_2O \xrightarrow{k_2} \text{products} + H_3O^+ \qquad \ldots \qquad (2)$$

Acid – Base Catalysis - Protolytic mechanism

The derivation of the rate-equation for this mechanism is carried out by applying steady state approximation with respect to the intermediate, SH^+ (i.e.)

$$\frac{d}{dt}[SH^+] = k_1[S][BH^+] - k_{-1}[SH^+][B] - k_2[SH^+] = 0$$

$$\text{or} \qquad [SH^+] = \frac{k_1[S][BH^+]}{k_{-1}[B] + k_2}$$

The rate of the reaction, defined as rate of formation of products is given by the eq.

$$\text{rate} = k_2[SH^+] = \frac{k_1 k_2 [S][BH^+]}{k_{-1}[B] + k_2}$$

Now two situations have been envisaged, depending upon the relative magnitudes of k_2 and $k_{-1}[B]$. If k_2 is negligibly small conferred to $k_{-1}[B]$, the intermediate, SH^+, is called Arrhenius complex and the rate law assumes the form.

$$\text{rate} = \frac{k_1 k_2 [S][BH]}{k_{-1}[B]}$$

of the ionization of equilibrium of the acid catalyst, BH^+, is considered,

$$BH^+ \underset{}{\overset{Ka}{\rightleftharpoons}} B + H^+$$

$$K_a = \frac{[B][H^+]}{[BH^+]} \quad \text{or} \quad \frac{[BH^+]}{[B]} = \frac{[H^+]}{K_a}$$

$$\text{rate} = \frac{k_1 k_2 [S][H^+]}{k_{-1}\, K_a} \qquad \dots \quad 6$$

The rate is directly proportional $[H^+]$ i.e. the reaction involves only H^+ as the catalyst but not BH^+, the undissociated acid. If $k_{-1}[B]$ is far less than k_2 the rate law becomes

$$\text{rate} = k_1 [S][BH^+] \qquad \dots \quad 7$$

The rate is directly proportional to the concentrationof the undissociated acid catalyst, BH^+.

If the hydrogen ion released, after the products are formed, is taken up by the conjugate base of the acid catalyst, B, the mechanism is called prototropic mechanism.

Scheme – II

$$S + BH^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + B \qquad .. \quad 1$$

$$SH^+ + B \xrightarrow{k_2} \text{products} + BH^+ \qquad \dots \quad 2$$

Applying the steady state hypothesis with respect to the intermediate, SH^+, one gets

$$\frac{d}{dt}[SH^+] = k_1[S][BH^+] - k_{-1}[SH^+][B] - k_2[SH^+] = 0$$

$$\text{or } [SH^+] = \frac{k_1 [S][BH^+]}{k_{-1}[B] + k_2[B]}$$

rate = rate of formation of products (step 2)

$$= k_2\,[SH^+][B] = \frac{k_2k_1\,[S][BH^+]}{k_{-1}[B]+k_2[B]}$$

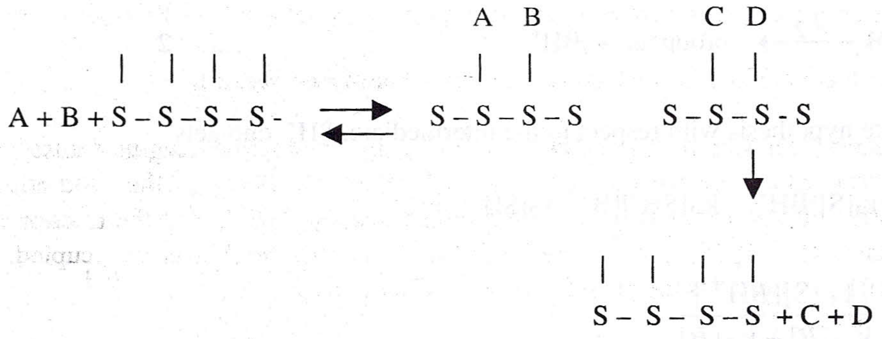
$$= \frac{k_2k_1}{k_{-1}+k_2}\,[S][BH^+] \qquad \ldots\ 8$$

The reaction involves the undissociated acid, BH^+ as catalyzing species.

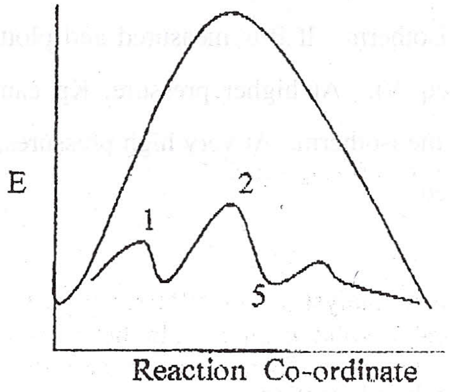
4.3. (iv). Heterogeneous catalysis

In heterogeneous catalysis, the reactants and catalyst are in different phases. Industially important reactions genuinely involve gaseous reactants and a solid catalyst. In heterogeneous or homogeneous catalysis, the acceleration is due to modification of the mechanism in such a way, that the catalysed reaction has lower activation energy. A decrease in activation energy by a even few kilocalories will produce an enormous increase in rate. The nature of the heterogeneous catalysis can be understood in simplest terms through the chemisorption of the reactant molecules on the surface sites or active sites of the catalyst. A definite chemical bond is formed between catalyst site and the the reactant. However, the binding of the reactant molecules must take place at the adjacent active sites of the catalyst the distance between them being in the range of angstrom units. Thus the reactant molecules are brought to close proximity. Further, when a bond, however weak, is formed between the catalyst surface atom and the reactant, the electron density distribution in the bonds in the molecule is disturbed thus weakening the bonds and rendering the reactant molecule more reactive. The adsorption of reactant molecule or adjacent sites is also a necessary requirement for interaction between them. At the same time product molecules formed after the reaction between reactant molecules should not form strong bonds with the catalyst atoms because then they do not be desorb easily making room for fresh reactant molecules. The product should not poison the surface. Thus the heterogeneous catalysed reaction involves the following steps.

1. Diffusion of the reactants on to the surface of the catalyst.
2. Adsorption of the reactant molecules on adjacent sites
3. Actual chemical reaction between the adsorbed reactant molecules forming products
4. Desorption of the product molecules
5. Diffusion of the product molecules into the bulk



4.3. (v) Reaction profile of the catalysed reaction



Reaction Profile of the Catalyzed Reaction.

These steps can be illustrated in the reaction profile of the catalysed reaction. The chemi-sorption itself is a chemical reaction and the transition state for this is represented by peak 1. Then adsorbed reactants are formed which undergo actual chemical reaction through the transition state (2) forming products (still in adsorbed state) which have the energy represented by 5. The desorption of the products is also a chemical reaction involving the breaking of bonds between product molecules and catalyst surface atoms. At any stage in the catalysed rection, the activation energy will be less than that in the uncatalysed reaction.

Nature of active centers

It was originally thought that atom present on surface peaks or apices are most active but it has because clear that active centers may also be certain crystal imperfections or lattice defects. The crystal defects acting as active centers can be illustrated by the inability of copper prepared electrilytically to act as catalyst because, the solid copper obtained this way has a regular crystal structure without many defects. But catalytically active copper can be prepared by passing ammonia at 820°C over copper. In this case, as a result of decomposition of ammonia on copper and partial formation of copper nitride which, being unstable decomposes producing copper atoms in an irregular manner producing crystal defects.

These copper atoms do not enter the regular crystal lattice and remain on surface. These form active centers and have strong catalytic action on the dehydrogenation of alcohols $RCH_2OH \xrightarrow{Cu} RCHO$

4.3. (vi) Deviation of Rate Equations of Heterogeneous – Catalysed Reactions

The mathematical derivation of rate-laws is possible by employing Langmuir adsorption theory to the adsorption of the reactants. The basic assumption of Longmuir's theory is that the adsorption of the reactant on catalyst surface involves the formation of a unimolecular film. If θ is the fraction of the surface occupied by the reactant, $(1 - \theta)$ is equal to the fraction of the surface that is unoccupied. The rate of adsorption $= k_1 [1 - \theta)] p$ where p is the pressure of the reactant gas.
The rate of desorption $= k_{-1}\theta$

At the equilibrium ;

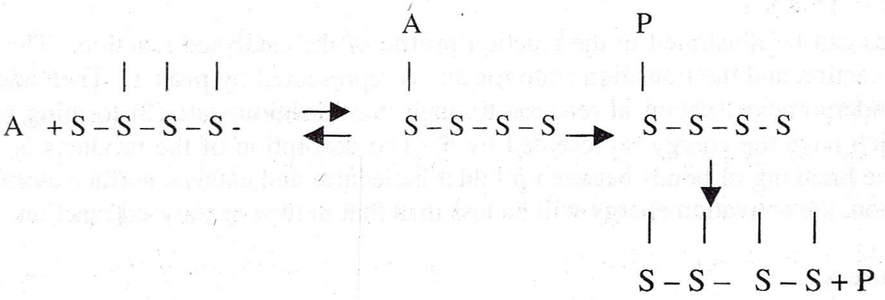
$$K_1 (1 - \theta) p = k_{-1}\theta, \quad k_1/k_{-1} = K$$

$$\theta = \frac{Kp}{1 + Kp} \qquad \ldots \quad 9$$

is the equation for Langmuir adsorption isotherm. If θ is measured and plotted Vs. pressure, the plot is initially linear. (because $KP << 1$ in the eq. 9). At higher pressure, Kp cannot be neglected in comparison with 1 and this gives the curved part of the isotherm. At very high pressures, $KP >> 1$ and $\theta = 1$. At this high pressures the surface completely occupied.

Unimolecular reactions

Consider a unimolecular heterogeneous catalysed reaction



$$\text{The rate of reaction} = \frac{-d[A]}{dt} = k\theta = \frac{kKp}{1 + Kp} \qquad \ldots \quad 10$$

At very low pressure $KP << 1$, rate is proportional to pressure (i.e. concentration) and this gives first order behavior. At very high pressure $KP >> 1$ and rate = k = constant.

This situation represents zero order behavior. At intermediate pressures, fractional order behavior is noticed.

The examples of reaction reflecting this pattern include decomposition of phosphine on glass surface and tungsten surface, decomposition of stilbene on antimony surface, decomposition of nitrous oxide, decomposition of formic acid on silver, gold, TiU_2 etc.

Considering a first order reaction on a catalyst surface

$$\text{rate} = kKP$$

$$k_r = kK$$

$$\frac{d \ln k_r}{dT} = \frac{d \ln k}{dT} + \frac{d \ln K}{dT}$$

K being the equilibrium constant $\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$ where ΔH heat is the heat liberated due to the adsorption of the reactant on catalyst surface

$\frac{d \ln k}{dT} = \frac{E_o}{RT^2}$ when E_o is the activation energy of the catalysed reaction

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad \therefore E_o = E - \Delta H$$

This equation shows that in the presence of the catalyst the observed activation is less by an amount equal to heat of adsorption.

4.3 (vii) Poisoning of catalyst

If along with the reactant an indifferent gas is also adsorbed there will be a competition between reactant and the foreign gas molecules for the active centers and fewer sites will be available for the ractant molecules. In this way the reaction is inhibited and this is the poisoning of the catalyst surface by poison gas. If the pressures of the reactant and foreign gases are P and P' and fraction of surface occupied by them are θ and θ' respectively.

Rate of adsorption of reactant gas : $k_1 (1-\theta) P$

Rate of desorption of reacting gas : $k_{-1} \theta$

rate of adsorption of poison gas : $k_1' (1 - \theta - \theta') P'$

rate of desorption of poison gas : $k_{-1}' \theta'$

and $K = \frac{k_1}{k_{-1}}$ $K^1 = \frac{k_1}{k_{-1}}$

using these equations it can seen that

$$\theta = \frac{KP}{1 + KP + K'P'},$$

$$\theta' = \frac{K'P'}{1 + KP + K'P'}$$

$$\text{rate} = k\theta = \frac{kKP}{1 + KP + K'P'} \qquad \ldots \quad 11$$

If the foreign gas is absorbed more strongly than the reactant gas, which is often the case, KP << K'P'

1 << K'P'

$$\therefore \theta = \frac{kKP}{K'P'}$$

$$k_r = \text{rate} \times \frac{P'}{P} = \frac{KK}{K'}$$

Taking logarithms and differentiating with respect to temperature

$$\ln k_r = \ln k - \ln K + \ln K'$$

$$\frac{d \ln k_r}{dT} = \frac{d \ln k}{dT} - \frac{d \ln K}{dT} + \frac{d \ln K'}{dT}$$

(or) $$\frac{E_o}{RT^2} = \frac{E}{RT^2} - \frac{\Delta H}{RT^2} + \frac{\Delta H'}{RT^2}$$

$$E_o = E - \Delta H + \Delta H'$$

Thus the poison increases the activation energy by value of its heat of adsorption ΔH'.

4.3. (viii) Catalysis of oxidation – reduction reactions

The catalysis of the oxidation – reduction reactions have some common features. These reactions are catalysed by substances capable of undergoing a change in oxidation state giving an unstable oxidation state with high reactivity and this is responsible for the acceleration. It is not, therefore, surprising that most of the catalysts are the transition metal compounds which can undergo change in the oxidation state giving an intermediate with unstable oxidation state. Thus an element capable of existing in several oxidation states, one of them being highly reactive, gives a catalyst accelerating a redox reaction.

The reduction of iron (III) by vanadium (III) is slow and is catalysed by Cu (II). The catalysis can be explained by the following mechanism.

$$\text{Cu (II)} + \text{V (III)} \longrightarrow \text{Cu (I)} + \text{V (IV)}$$

$$\text{Cu (I)} + \text{Fe (III)} \longrightarrow \text{Cu (II)} + \text{Fe (II)}$$

In this reaction, the catalyst Cu (II) reacts with V(III) producing the highly react intermediate Cu (I) which reacts with Fe (III) with greater ease than V (III) and produces Fe (II) and the catalyst Cu (II) is regenerated. In the mechanism, the second step is faster.

The oxidation of thallium (I) by Ce (IV) is quite slow and is catalysed by Ag (I). In this, Ce (IV) on interacting with Ag (I) produces the unstable oxidation state Ag (II) which easily oxidizes thallium (I) to thallium (II). Thallium (II) further oxidized by Ce (IV) to thallium (III).

$$\text{Ce (IV)} + \text{Ag (I)} \rightleftharpoons \text{Ce (III)} + \text{Ag (II)}$$

$$\text{Ag (II)} + \text{Tl (I)} \longrightarrow \text{Ag (I)} + \text{Tl (II)}$$

$$\text{Ce (IV)} + \text{Tl (II)} \xrightarrow{\text{fast}} \text{Ce (III)} + \text{Tl (III)}.$$

It is not necessary that the catalysts should be transition, inner transition or coinage metal ions. Any ion which produces a reactive oxidation state is a potential catalyst. Thus I^- catalyses the oxidation of As (III) by Ce (IV). The catalysis can be traced to the highly reactive oxidation state I^+ formed by interaction between Ce (IV) and I^-

$$\text{Ce (IV)} + I^- \longrightarrow \text{Ce (III)} + I$$

$$\text{Ce (IV)} + I \longrightarrow \text{Ce (III)} + I^{+1}$$

$$I^{+1} + \text{As (III)} \longrightarrow I^- + \text{As (V)}$$

LESSON - 4

Photochemistry

Photochemistry is the study of effect of light on the chemical reactions. The light energy used will be in the ultraviolet or visible regions. The effect of higher energy radiations on chemical reactions like the effect of γ-rays is a separate discipline called radiation chemistry.

The most important requirement for the light energy to have effect on chemical reactions is that the light energy that is incident on the reactant must be absorbed by the reactant. If the energy of the light radiation is equal to or greater than the bond dissociation energy then the bonds are, in general, homolytically broken resulting in a chemical reaction. In many photochemical reactions, the free radicals forming on homolytic rupture are detectable by spectroscopic (esr) or other means. If the energy of the light radiation is such that the bonds cannot be broken, the absorbed energy is reemitted in the form of fluorescence or phosphorescence involving no permanent chemical change and hence these phenomena are called photophysical processes.

Eg: Will mercury light source operating at 254 nm be effective in breaking C=O bond in acetone Given bond energy of C = O bond is 728 KJ mol^{-1}.

The energy for breaking Avogadro number of C = O bonds 728 KJml^{-1}

$$\therefore \text{energy for one bond} = \frac{728}{6.023x10^{23}} = \frac{hC}{\lambda} = \frac{6.626x10^{34} \text{ x } 3 \text{ x } 10^{8}}{\lambda}$$

$\therefore \lambda = 1.64 \text{ x } 10^{-7}\text{m} = 164 \text{ nm} <$ wave length from merely lent

The energy of mercury light is 254 nm since λ and E are inversely related ($E = hC/\lambda$) the energy of the mercury lamp is not sufficient to break the C = O bond in acetone.

4.4. (i). Laws of Photochemistry

Photochemistry is concerned with the effect of light energy on chemical reactions the light energy being in the ultra violet and visible regions (200 – 800 nm). The effect of light is felt only if the light energy is absorbed by the reacting substances and this is governed by certain laws. The first law is the Lambert's law which states that when a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of the medium is proportional to the intensity of the radiation.

$-\frac{dI}{dt} = kI$ where t is the thickness and I is the intensity of radiation after passing through medium.

$$-\int \frac{dI}{I} = \int k\,dt, \quad -\ln I = kt + \text{constant}$$

Assuming that at t = 0

$I = I_o$ (the intensity of light before entering the medium)

$$\therefore \ln \frac{I}{I_0} = -kt \quad \text{or } I = I_0 e^{-kt} \qquad (1)$$

The intensity of radiation absorbed $= I_0 - I$

$= I_0 - I_0 e^{-kt}$

$= I_0 (1 - e^{-kt})$

Beer's law

According to this law, when a beam of monochromatic rdiation is passed through a solution of an absorbing substance the rate of decrease in intensity of radiation with thickness is proportional to concentration of the solution and intensity of radiation

$$-\frac{dI}{dt} = k'IC$$

$$-\int \frac{dI}{I} = \int k'C\,dt$$

or $-\ln I = k'Ct$ + constant of integration assuming that t = 0, $I = I_o$(intensity of radiation before entering the solution). Hence the integration constant is equal to I_0

$$\therefore \ln \frac{I}{I_0} = k'Ct$$

$$\log \left(\frac{I}{I_0}\right) = -\frac{k'}{2.303} Ct = -\varepsilon Ct$$

$$\text{or } \log \left(\frac{I_0}{I}\right) = \varepsilon Ct = \text{Optical density or absorbance} \qquad (2)$$

ε represents the molar extinction coefficient which has the units, litre $mol^{-1}cm^{-1}$. The ratio, I/I_0 is called the transmittance (T) and represents the fraction of total light transmitted and it is easy to see that absorbance or optical density is equal to log (1/T).

Eg. : A substance is dissolved in water to give concentration equal to 0.001M and transmits 90% of light in a path of 1 cm. What should be concentration if it has to transmit10% of light absorbance

$-\log\left(\frac{90}{100}\right) = \varepsilon \times 0.001 \times 1$ $\varepsilon = 45.8$ litre $mol^{-1}cm^{-1}$. If 10% is transmitted the absorbance is –

$\log\left(\frac{10}{100}\right) = \varepsilon C t = 45.8 \times C \times 1$

$\therefore C = 0.021801M$

The Grothus – Draper law touches the more fundamental requirement for any photochemical process. The law states that for the light energy to have photochemical effect it should be absorbed by the reactant. However, it does not mean that the light energy can bring about a reaction if it is absorbed. The energy of light absorbed must be at least equal to the energy of the bond that is broken in the reaction. If the energy of the incident light is less than the bond energy, the absorbed light is remitted in the form of fluorescence or phosphorescence.

The Stark-Enistein Law of Photochemical Equivalence

According to this law, each molecule of the reacting substance absorbs one quantum of radiation for reaction; the term quantum yield is defined as

$$\text{Quantum yield} = \frac{\text{Number of molecules reacted}}{\text{numberof quanta absorbed}}$$

$$= \frac{\text{number molecules reactd per second}}{\text{number of quanta absorbed per second}} = \frac{\text{rate of reaction}}{\text{Intensity of light absorbed}}$$

$$= \frac{\text{numbr of moles reacted}}{\text{number of equisteins absorbed}} \qquad (3)$$

Energy of one Avogadro number of quanta of light is called one Einstein.

One Einstein $= 6.013 \times 10^{23} \times h\upsilon$

Where υ is the frequency of light

Eg. Calculate the energy of one Einstein of radiation of the wavelength 2537 Å

$$\text{Energy of one Einstein} = N h \upsilon = \frac{N h C}{\lambda}$$

$$= \frac{6.023 \times 10^{23} \times 6.626 \times 10^{-34}\ \text{Joule - Sec} \times 3 \times 10^{8}\ m\ sec^{-1}}{2537 \times 10^{-8} \times 10^{-2}\ m}$$

$= 4.719 \times 10^{5}$ Joule mol^{-1}

eg. Photobromination of cinnamic acid to produce dibromocinnamic acid is carried out in the presence of light of wavelength 440 nm using light intensity of 1.5×10^{-3} Js^{-1}. An exposure of 20 min resulted in a decrese of 0.075 milli mole of Br_2. Calculate the quantum yield.

$$\text{Energy of one quantum of light} = \frac{h\,C}{\lambda}$$

$$= \frac{6.626 \times 10^{-34}\ \text{J.S} \times 3.10^{8}\ \text{m S}^{-1}}{440 \times 10^{-9}\ \text{m}} = 4.517 \times 10^{-19}\ \text{joules}$$

Intensity of light = $1.5 \times 10^{-3} J\, S^{-1}$

$\therefore$ Energy absorbed in 20 x 60 Sec = $1.5 \times 10^{-3} \times 20 \times 60$ Joules.

$$\text{No. of quanta in the energy} = \frac{1.5 \times 10^{-3} \times 20 \times 60}{4.517 \times 10^{-19}} = 3.98 \times 10^{18}$$

$$\text{quantum yield} = \frac{0.075 \times 6.023 \times 10^{23} \times 10^{-3}}{3.98 \times 10^{18}} = 11.3$$

PHOTOPHYSICAL EFFECTS

Fluorescence

In the ground state which is a singlet state the molecules are mostly in the ground vibrational state (vibrational quantum number, V = 0). The ratio of number of molecules in higher vibrational state (V = 1) to the total number of molecule is equal to $e^{-E/RT}$. ΔE is in the order of 10^3 cm^{-1} and the ratio at 27^0C comes to $e^{-h\upsilon/kT} = 0.008$.

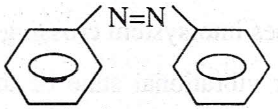
The existence in the higher vibrational state will be almost negligible. When the molecule absorbs the light energy, it is excited to higher electronic state within 10^{-15}s. On the other hand, the time period for the vibration is 10^{-13}s (i.e.) the movement nuclei is hundred times slower. As a consequence, the internuclear distance does not change immediatly after excitation. Usually, this internuclear distance will be less than the equlibrium internuclear distance in the excited state and hence the molecule will be in the higher vibrational state of the excited state and now the molecule loses this excess vibrational energy in the form of heat by collision with the molecules of the medium and comes down to the ground vibrational state (V = 0) of excited singlet state without emitting light. This is called internal conversion. From this state (S_1) the molecule may come down to ground singlet state (S_o) emitting fluorescence or may exchange the energy with the medium through internal conversion. Usually internal conversion from S_1 to S_o state is slow compared to the same process in higher energy states.

4.4. (ii). Fluorescence

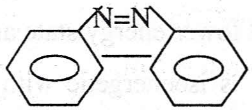
In the ground state, which is a singlet state, the molecule is in the lowest vibration state (V = 0 where V is vibrational quantum number) and the electronic transition (transition to higher electronic state) takes place within 10^{-15} second. On the other hand, vibrational changes require 10^{-13} s. As a consequence, the internuclear distances do not change during the absorption. Hence transition can be represented by a vertical line parallel to potential energy axis. This is the basis for the Franck-Condon principle according to which electronic transitions are so fast in comparison with the nuclear motion that immediately after the transition, the nuclei have nearly the same relative position and momentum as they did just before the transition. Since usually, in the excited electronic state, the equilibrium internuclear distance is greater than in the ground electronic state, the molecule does not immediately attain the equilibrium internuclear distance corresponding to the excited state and hence the molecule is in the higher vibrational state of the excited state. There, the molecule is subjected to collisions with its environment and loses the vibrational energy and goes to the lowest vibrational state in the excited state. It has a life time in the order of 10^{-8} s and undergoes spontaneous emission and returns to the ground state. The downward step also occurs vertically in accordance with the Franck-Condon principle and a series of lines appear in the fluorescence spectrum. The vibrational structure of this spectrum is characteristic of lower electronic state (in contrast to the structure of the absorption spectra). If the internuclear distances do not differ very much, the absorption and emission spectra look like mirror images.

In the case of poly atomic molecules, the energy of the fluorescence is less than the energy of the incident radiation. In the case of atoms the energy of fluorescent radiation is the same as that of incident radiation and this type of fluorescence in the case of monoatomic substances is called resonance fluorescence. The emission of fluorescence stops once the incident radiation is cut off which distinguishes fluorescence from phosphorescence. In the case of phosphorescence, the emission continues for some more time after the incident radiation is cut off.

Though every substance should exhibit fluorescence it is not observed in the case of a large number of compounds. Fluorescence is observed in those organic molecules which have rigid frame work and not many loosely coupled substituents through which Vibrational energy can flow out in the form of thermal radiation and molecule comes down to ground electronic state without emiting light. For example phenolphthalein or azobenzene do not fluoresce whereas the closely related rigid structures fluorescein dye, and azophenanthrene give fluorescence.



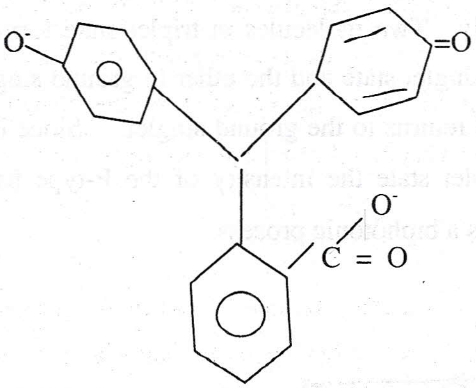
Azobenzene

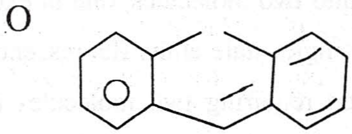


aza phenanthrene

This is also further illustrated by the increasing fluorescence as one goes from benzene to naphthalene to anthracene. Introduction of electron-donating substituents in the molecule enhances fluorescence.

Eg. –OH, $-NH_2$, etc. Electron-withdrawing substituents have the opposite effect. For example benzene is fluorescent whereas benzoic acid is not. The phenomenon of fluorescence is of utmost importance in the analytical estimations because fluorescence intensity is a function of concentration and forms the basis of fluorimetric analysis. This technique is especially useful in the analysis of vitamins and drugs. Usually fluorometric analysis enables the assay of these materials even when present at very low concentrations.





Phenolphthalein

Delayed Fluorescence

The phenomenon involves only singlet – singlet transition but not triplet – singlet transition. There are two types of delayed fluorescence Viz. ε-type delayed fluorescence and the P-type delayed fluorescence. The ε-type is temperature – dependent and is not observed at very low temperatures. The P-type is independent of temperature. The intensity of ε-type delayed fluorescence varies as the first power of intensity of incident radiation whereas the P-type displays the square dependence. The ε-type was first observed with the dye Eosin whereas the P-type was observed with the hydrocarbon, pyrene. To understand the mechanism of the delayed fluorescence, consider a molecule like pyrene or Eosin which absorbs the relevant light energy. On absorbing the quantum, the molecule is lifted to excited singlet state. In this state, the molecule goes to the higher vibrational level due to the operation of Franck – Condon principle. Subsequently it comes down to the lowest vibrational state. At this point, it is equienergetic with the triplet state which is at some what lower energy state and undergoes intersystem crossing to triplet state. The lowest vibrational state of singlet is isoenergetic with the higher vibrational state of the triplet state. Hence the molecule crosses over to higher vibrational state of the triplet, loses the excess vibrational energy and drops down to the lowest vibrational level of the triplet state. If the triplet to ground singlet transition is very slow the molecule may receive some energy from the medium in the form of heat and may return to the higher vibrational state in the triplet which is isoenergetic with excited singlet and hence the molecule may cross over back to excited singlet state and finally comes down to ground singlet state emitting the ε-type delayed fluorescence. For this to take place the medium must have sufficient energy to lift the molecule in the lowest vibrational state of triplet to higher vibrational level which is isoenergetic with excited singlet state. Then, only crossing over back to excited singlet state is possible. That is why the ε-type delayed fluorescence is temperature dependent.

In the case of P-type delayed fluorescence the molecule in the ground vibrational level of the triplet state does not go back to excited singlet state directly. Two molecules in triplet state form a dimer which then decomposes into two molecules, one in excited singlet state and the other in ground singlet state. The molecule in excited singlet state emits fluorescence and returns to the ground singlet. Since is for this process a dimer is needed requiring two molecules in triplet state the intensity of the P-type has square dependence on the intensity of the incident radiation (i.e.) it is a biphotonic process.

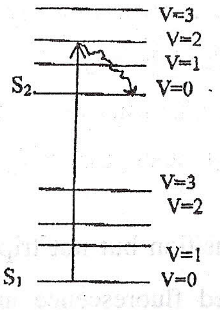


Fig 4

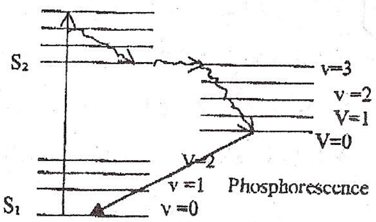


Fig 5

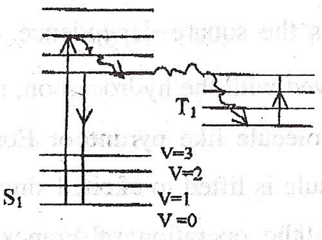


Fig 6

$$2T \qquad T_2$$
$$T_2 \longrightarrow S_1 + S_o$$
$$S_1 \longrightarrow S_o + h\upsilon'$$

This requires no uptake of energy from the medium and hence it is temperature – independent.

4.4 (iv). Inter system crossing and phosphorescence Emission

Suppose a molecule has, in addition to excited singlet state, another excited state which is a triplet state, there may be equienergetic points for both these excited states. At these points the molecules may switch over from singlet to triplet state. The triplet state will usually be less in energy than the singlet state and hence when switching occurs the molecule goes to the higher vibrational state of the triplet state and there it may lose the excess vibrational energy to the surroundings and reaching the ground vibrational state of the triplet state. The singlet – to – triplet conversion is called intersystem crossing. In most molecules switching over from singlet (paired spins) to triplet (two unpaired spins) is forbidden, but in some molecules it is weakly allowed. This happens when the molecule contains a heavy atom, giving rise to strong spin – orbit interactions and this can reverse the relative orientations of the spins of electrons. However, the transition is slow phosphorescence which is due to this transition, therefore has low rate constant and has less intensity. This is also the reason why emission of phosphorescence persists for some more time even after the incident radiation is cut off, unlike in fluorescence. In the case of fluorescence, the emission ceases immediately after the incident radiation is cut off. Further, the intensity of the phosphorescence will be higher in solid state than in liquid state, because the deactivating collisions with triplet state than now less in number. Since there are two unpaired electrons in the triplet state, the molecule in such a state has paramagnetic properties.

4.4 (v). Chemiluminescence

Chemiluminescence may be defined as emission of light radiation as a result of chemical reaction at temperatures when light rays are not normally expected. The chemiluminescence is due to formation of products in excited state and when they return to ground state they emit light.

A classical example is that when atomic hydrogen comes into contact with mercury surface, blue luminescence appears with a resonance line at 2537Å characteristic of mercury along with band spectrum due to HgH. The process may be explained according to the following mechanism. Hg H is formed which acts as a third body for combination of H atoms and the excited Hg H is formed

$$\text{Hg H} + \text{H} + \text{H} \longrightarrow \text{Hg H}^* + H_2$$

$$\text{Hg H} + \text{Hg H}^* \longrightarrow H_2 + \text{Hg} + \text{Hg}(\beta P_1)$$

Chemiluminescence is also observed when alkali metal vapours react with halogens and with organic halides and low pressures. In order to account for the observation it is necessary to postulate that Na_2 molecule combine with Cl atoms which liberates sufficient energy to excite NaCl molecule which then excites sodium atom.

$$\text{NaCl}^* + \text{Na} \longrightarrow \text{NaCl} + \text{Na}^*$$

The excited Na* atom emits its characteristic spectrum.

Grignard reagents emit chemiluminescence when they are oxidized by air in ethereal solution. The luminescence is greenish blue and contains a single broad band. Only Grignard reagents in which magnesium atom is attached to unsaturated carbon atom are chemiluminescent in solution but in solid state both aliphatic and aromatic compounds exhibit this phenomenon.

Another classical reaction is the oxidation of 5-aminophthalic hydrazide with hydrogen peroxide in which chemiluminescence is observed.

Bioluminescence is due to chemiluminescence in biological reactions most well-known among which is the oxidation of luciferin by atmospheric oxygen in the presence of the enzyme iuciferase.

4.4. (vi). Quantum yield – Reaction with High and low Quantum yields

According to Einstein's law of photochemical equivalence, each reacting molecule absorbs one quantum of radiation. The quantum yield which is defined as number of molecules reacting divided by number of quanta absorbed should be equal to one for a primary photochemical process in which the quantum is involved. In many reactions in addition to a primary photochemical process there will also be secondary thermal steps and this is the reason why the quantum yield is different from one for many reactions. For chain reactions for example the quantum yield could be very high because for one chain carrier species produced in the initiation step which is a primary photochemical step, several reactant molecules react in the secondary thermal propogation steps since the chain carrier is regenerated.

$Cl_2 + h\upsilon \longrightarrow 2\,Cl$ Primary photochemical step

$$\left.\begin{array}{l} Cl + H_2 \longrightarrow HCl + H \\ H + Cl_2 \longrightarrow HCl + Cl \end{array}\right\}$$

Secondary thermal propagation Step

$Cl \longrightarrow$ termination

Had it not been due to termination of chains the quantum yield should have been extremely high. In the case of the hydrogen-chlorine reaction the quantum yield, which is a measure of chain length, is 10^6 in the absence of O_2 (i.e.)10^6 reactant molecules are undergoing reaction for a quantum of light absorbed. This is due to low rates of termination steps. If the termination steps are fast, the chain length will be small and so is the quantum yield. For the hydrogen-bromine reaction, the quantum yield is less because of the preponderance of termination steps. In the photochemical oxidation of sodium sulphite solution, in the presence of 0.1M benzyl alcohol as inhibitor (terminator of chains) 128 molecules of sulphite are oxidized. At the same time one molecule of benzyl alcohol is oxidized for 58 molecules of sulphite. Hence, if the alcohol is the terminator of chains, the chain should involve 58 molecules following the primary absorption of light. Therefore 125/58 = 2 chains must be involved for absorption of each quantum.

In the $H_2 - I_2$ reaction the quantum yield is 2 and this can be accounted for by the following mechanism.

$$HI \xrightarrow{h\upsilon} H + I$$

$$H + HI \longrightarrow H_2 + I$$

$$I + I \longrightarrow I_2$$

Two molecules of HI decompose for one quantum of light is absorbed.

4.4 (vii) Kinetics of collisional quenching - Stern – Volmer Equation

The medium may also contain molecules or ions which colliding with the excited state will extract the energy and deactivate them. This may involve transient formation of complex between the excited state and the quencher. The mathematical relation showing the effect of quencher on the intensity of fluorescence has been derived by Stern and Volmer and is called the Stern-Volmer equation. The following scheme represents the various processes involved.

$$S_0 \xrightarrow{h\upsilon} S_1 \quad \text{Rate of excitation = I (intensity of light)}$$

$$S_1 \xrightarrow{k_{IC}} S_0 + \text{heat}$$

$$S_1 \xrightarrow{k_{ISC}} T_1$$

$$S_1 \xrightarrow{k_f} S_0 + h\upsilon'$$

In the scheme, molecule in ground state, excited singlet state and triplet state is denoted as S_o, S_1 and T_1. k_{IC}, k_{ISC} and k_f refer to rate constants of internal conversion, intersystem crossing and fluorescence emission.

The concentration of the molecules in the excited state $[S_1]$ is calculated by applying steady state approximation with respect to the excited state S_1.

According to this $\frac{d[S_1]}{dt} = 0 =$ rate formation – rate of removal

Rate of formation is equated to the intensity of the incident light, I and rate of removal = $(k_{IC}[S_1] + k_{ISe}[S_1] + k_f[S_1])$

$\therefore I - (k_{IC}[S_1] + k_{Ise}[S_1] + k_f[S_1[) = 0$

$$\text{or } [S_1] = \frac{I}{k_{IC} + k_{ISC} + k_f}$$

$$\text{Rate of fluorescence} = k_f[S_1] = \frac{k_f I}{k_{IC} + k_{SC} + k_f}$$

The quantum yield of fluorescence

$$\phi_o = \frac{\text{rate of fluorescence}}{\text{Intensity}} = \frac{k_f}{k_{IC} + k_{IC} + k_f}$$

In the presence of quencher, the step $S_1 + Q \xrightarrow{h_Q} S_0 + Q +$ heat is to be added to this scheme.

$$S_o + h_0 \longrightarrow S_1$$

$$S_1 \xrightarrow{h_{IC}} S_0 + \text{heat}$$

$$S_1 \xrightarrow{h_{ISC}} T_1$$

$$S_1 \xrightarrow{h_f} S_0 + h\upsilon'$$

$$S_1 + Q \xrightarrow{k_Q} S_0 + Q + \text{heat}$$

$$\frac{d[S_1\}}{dt} = 0 = I - (k_{ISC} + k_{ISC} + k_f + k_\varphi[\varphi]$$

$$\text{or } [S_1] = \frac{I}{k_{IC} + k_{ISC} + k_f + k_\varphi[\varphi]}$$

Where $[\varphi]$ is the concentration of quencher

$$\text{Rate of fluorescence} = k_f[S_1] = \frac{k_f f}{k_{IC} + k_{ISC} + k_f + k_\varphi[\varphi]}$$

$$\text{Quantum yield in the presence of quencher } \varphi = \frac{\text{rate of fluorescence}}{\text{Intensity}}$$

$$= \frac{k_f f}{k_{IC} + k_{ISC} + k_f + k_\varphi [\varphi]} \qquad (5)$$

The quantum yield, φ, is determined in the presence of different concentrations of quencher and ϕ_o / ϕ is calculated in each case and plotted against [φ]

$$\frac{\phi_u}{\phi} = \frac{k_{IC} + k_{ISC} + k_f + k_\varphi[\varphi]}{k_{IC} + k_{IS} + f}$$

$$= 1 + \frac{k_\varphi[\phi]}{k_{IC} + k_{ISC} + k_f} \qquad (6)$$

The equation (6) is called Stern-Volmer equation. A straight line is obtained with slope equal to $h_\varphi / (k_{IC} + k_{ISC} + k_f)$ and intercept equal to unity

$k_\varphi / (k_{IC} + k_{ISC} + k_f)$ is called Stern – Volmer constant $\frac{I}{k_{IC} + k_{ISC} + k_f}$ is equal to life time of the excited state in the absence of quencher. The rate constant k_φ is a function of ionic strength. And when Bronsted equation is applied one gets

$$\log k_\varphi = \log k_Q^0 + 0.5\, \delta Z^2 \sqrt{\mu}$$

Where $\Delta Z^2 = Z^2_{A\varphi} - (Z^2_A + Z^2_\varphi]$

$Z_{A\varphi}$ is Z_A are Z_φ being the charges of Aφ, A and φ respectively.

MODEL QUESTIONS

Short answer questions