Director of Distance & Continuing Education

Manonmaniam Sundaranar University

Tirunelveli-627012

OPEN LEARNING AND DISTANCE LEARNING (ODL) PROGRAMME

(for those who joined the programmes from the academic year 2025-2026)

B.Sc Chemistry

Course material- Physical Chemistry – I

Course code- JMCH53

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PHYSICAL CHEMISTRY – I

UNIT-I

Thermodynamics-III

Free energy and work functions – Need for free energy functions, Gibbs free energy, Helmholtz free energy – their variation with temperature, pressure and volume, criteria for spontaneity; Gibbs- Helmholtz equation – derivations and applications; Maxwell relationships, thermodynamic equations of state; Thermodynamics of mixing of ideal gases, Ellingham Diagram-application.

Partial molar properties – chemical potential, Gibbs Duhem equation, variation of chemical potential with temperature and pressure, chemical potential of a system of ideal gases, Gibbs-Duhem –Margules equation.

UNIT-II

Chemical Kinetics

Rate of reaction – Average and instantaneous rates, factors influencing rate of reaction - molecularity of a reaction - rate equation - order of reaction. Order and molecularity of simple and complex reactions, Rate laws- Rate constants – derivation of rate constants and characteristics for zero, first order, second and third order (equal initial concentration) – Derivation of time for half change with examples. Methods of determination of order of Volumetry, manometry and polarimetry.

Effect of temperature on reaction rate – temperature coefficient – concept of activation energy – Arrhenius equation. Theories of reaction rates – Collision theory – derivation of rate constant of bimolecular gaseous reaction – Failure of collision theory. Lindemann’s theory of unimolecular reaction.Theory of absolute reaction rates–Derivation of rate constant for a bimolecular reaction – significance of entropy and free energy of activation. Comparison of collision theory and ARRT.

Complex reactions–reversible and parallel reactions (noderivation and only examples) – kinetics of consecutive reactions–steady state approximation.

UNIT-III

Adsorption – Chemical and physical adsorption and their general characteristics – distinction between them. Different types of isotherms – Freund lich and Langmuir. Adsorption and their limitations–BET theory, kinetics of enzyme catalyzed reaction – Michaelis-Menten and Briggs

- Haldene equation – Line weaver- Burk plot – inhibition – reversible – competitive, non competitive and un competitive (no derivation of rate equations)

Catalysis – general characteristics of catalytic reactions, autocatalysis, promoters, negative catalysis, poisoning of a catalyst – theories of homogenous and heterogeneous catalysis – Kinetics of Acid– base and enzyme catalysis. Heterogenous catalysis.

UNIT-IV

Colloids and Surface Chemistry

Colloids: Types of Colloids, Characteristics of Colloids (Lyophilic and Lyophobic sols), Preparation of Sols - Dispersion methods, aggregation methods, Properties of Sols - Optical properties, Electrical properties - Electrical double layer, Electro Kinetic properties- Electro-osmosis, Electrophoresis, Coagulation or precipitation, Stability of sols, associated colloids, Emulsions, Gels-preparation of Gels, Applications of colloids,

Macromolecules: Molecular weight of Macromolecules - Number average molecular weight – average molecular weight, Determination of Molecular weight of molecules.

UNIT-V

Photo chemistry

Laws of photo chemistry – Lambert – Beer, Grotthus – Draper and Stark – Einstein. Quantum efficiency. Photochemical reactions – rate law – Kinetics of H_2-Cl_2, H_2-Br_2 and H_2-I_2 reactions, comparison between thermal and photo chemical reactions.

Fluorescence–applications including fluorimetry – sensitised fluorescence, phosphorescence – applications – chemiluminescence and photo sensitisation– examples Chemistry of Vision– 11cis retinal– vitamin A as a precursor colour perception of vision.

Recommended Text:

1. B.R. Puriand L.R. Sharma, Principles of Physical Chemistry, Shoban Lal Nagin Chand and Co., forty eighth edition, 2021.
2. Peter Atkins, and JuliodePaula, James Keeler, Physical Chemistry, Oxford University press, International eleventh edition, 2018.
3. Arun Bahl, B.S. Bahl, G.D. Tuli Essentials of physical chemistry,28thedition, 2019, S.Chand & Co.
4. S.K. Dograand S. Dogra, Physical Chemistry through Problems: New Age International, fourth edition, 1996.
5. J. Rajaramand J.C. Kuriacose, Thermodynamics, Shoban Lal. Nagi Chand and CO., 1986.

PHYSICAL CHEMISTRY – I - JMCH53

UNIT-I

Thermodynamics-III

Free Energy and Work Functions

Heat content (H), internal energy (E) and entropy (S), there are two other thermodynamic functions depending upon the state of the system which utilize E, H or S in their derivation and are more convenient for use. These are Work and Free energy functions represented by A and G respectively.

The Work Function

The work function (A) is defined by

$A = E – TS$

Where, E is the energy content of the system, T is its absolute temperature and S its entropy. Since E, T and S depend upon the thermodynamic state of the system only and not on its previous history, it is evident that the function A is also a single valued function of the state of the system. Consider an isothermal change at temperature T from the initial state indicated by subscript 1 to the final state indicated by subscript 2, so that

$A_1 = E_1 – TS_1$ ...(1)

and $A_2 = E_2 – TS_2$ ...(2)

Subtracting (1) from (2), we have:

$A_2 – A_1 = (E_2 – E_1) – T (S_2 – S_1)$ or

$\Delta A = \Delta E – T\Delta S$ ------(3)

where ΔA is the increase in function A, ΔE is the corresponding increase in internal energy and ΔS is the increase in the entropy of the system. Since $\Delta S = q_{rev}/T$ where q_{rev} is the heat taken up when the change is carried out in a reversible manner at a constant temperature, we have:

$\Delta A = \Delta E – qrev$ -----(4)

According to the first law of thermodynamics, $\Delta E = (q_{rev} – w_{rev})$

or $- w_{rev} = \Delta E - q_{rev}$ ...(5)

Substituting this value in equation (4), we get

$- \Delta A = w_{rev}$

i.e., decrease in the work function A in any process at constant temperature gives the maximum work that can be obtained from the system during any change.

Free energy change

Free Energy change

Enthalpy. $H = E + pV$.

$$G = H - TS$$

$$G = E + PV - TS$$

As in the intial and final states $G_1, G_2, H_1, H_2, S_1, S_2$ respectively,

$$G_1 = H_1 - TS_1 \; ; \; G_2 = H_2 - TS_2$$

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

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

$$\therefore \Delta E + W = T\Delta S$$

$$\boxed{\Delta E - T\Delta S = -W}$$

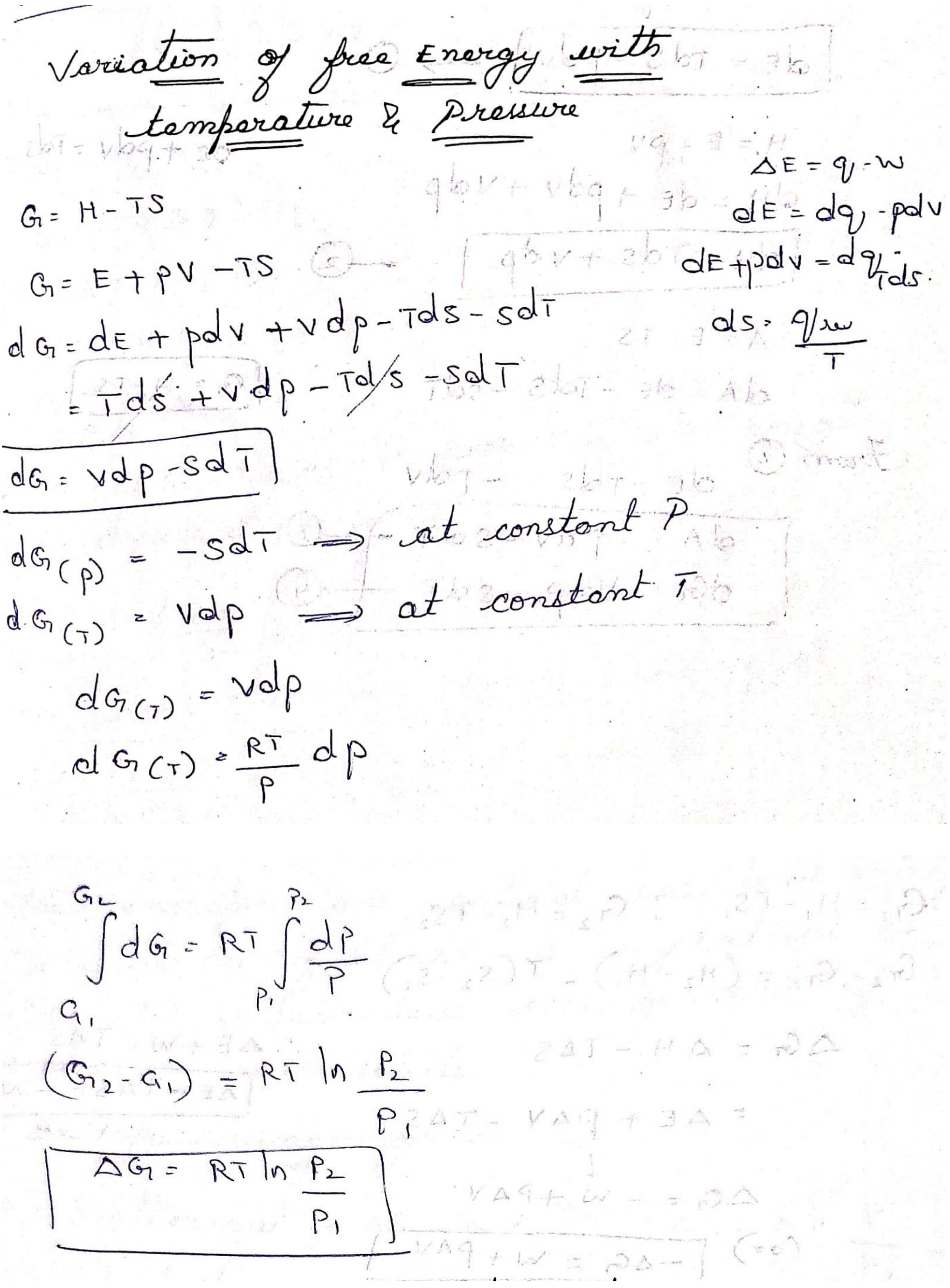
$$= \Delta E + P\Delta V - T\Delta S$$

$$\Delta G = -W + P\Delta V$$

(or) $$\boxed{-\Delta G = W + P\Delta V}$$

The decrease of free energy will give maximum work done other than the work done by exchange of Volume. It shows it is a reversible process.

Variation of free energy with temperature, pressure



Variation of free Energy with temperature & Pressure

$\Delta E = q - w$

$dE = dq - pdv$

$dE + pdv = dq = Tds$

$ds = \frac{q_{rev}}{T}$

$G = H - TS$

$G = E + pV - TS$

$dG = dE + pdv + vdp - Tds - sdT$

$= \cancel{Tds} + vdp - \cancel{Tds} - sdT$

$$\boxed{dG = vdp - sdT}$$

$dG_{(p)} = -SdT \Longrightarrow$ at constant P

$dG_{(T)} = Vdp \Longrightarrow$ at constant T

$dG_{(T)} = vdp$

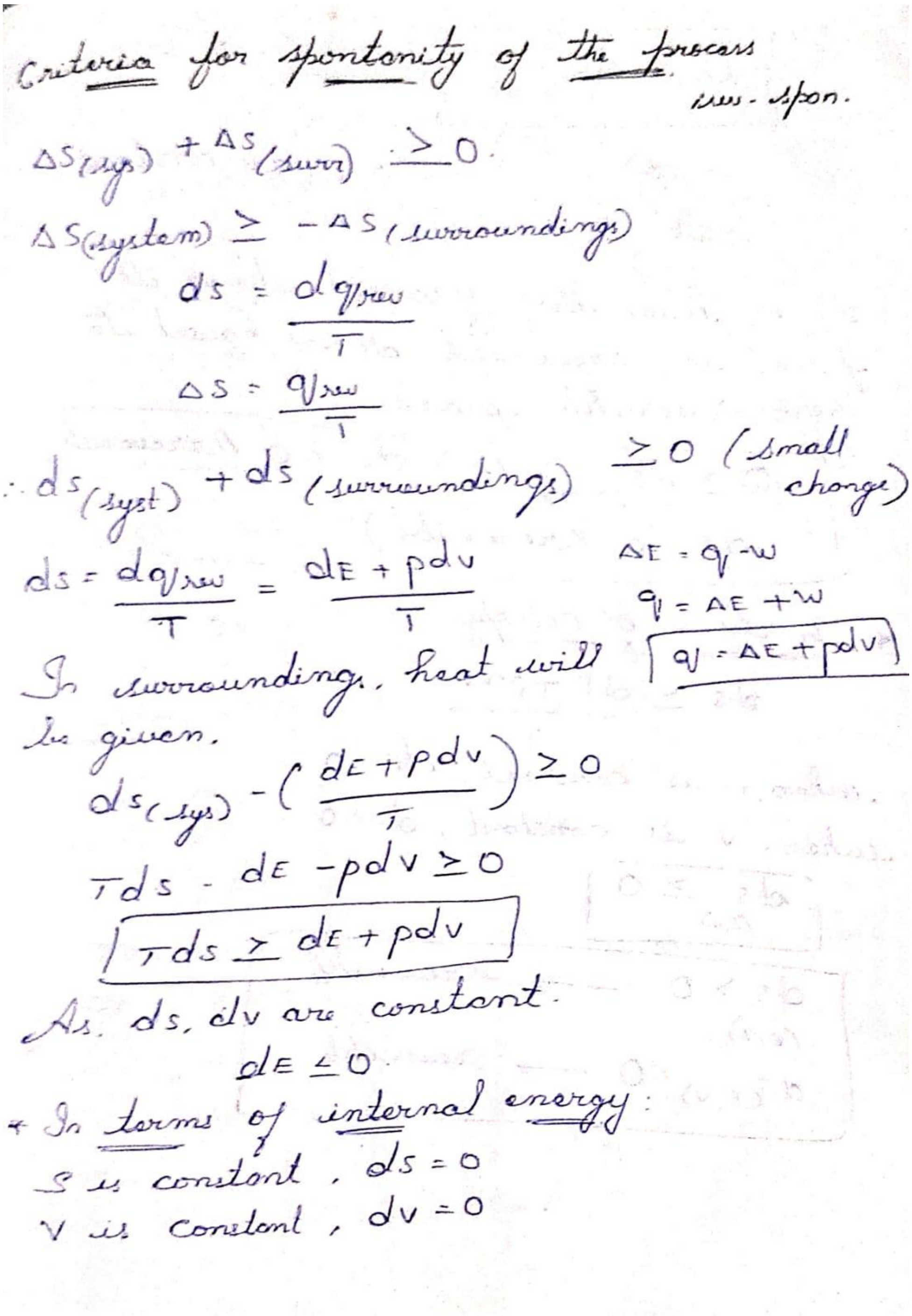
$dG_{(T)} = \frac{RT}{p} dp$

$$\int_{G_1}^{G_2} dG = RT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$(G_2 - G_1) = RT \ln \frac{P_2}{P_1}$$

$$\boxed{\Delta G = RT \ln \frac{P_2}{P_1}}$$

Criteria for spontaneity



Criteria for spontonity of the process

irrev. - spon.

$\Delta S_{(sys)} + \Delta S_{(surr)} \geq 0$.

$\Delta S_{(system)} \geq -\Delta S_{(surroundings)}$

$$ds = \frac{dq_{rev}}{T}$$

$$\Delta S = \frac{q_{rev}}{T}$$

$\therefore ds_{(syst)} + ds_{(surroundings)} \geq 0$ (small change)

$$ds = \frac{dq_{rev}}{T} = \frac{dE + pdv}{T}$$

$\Delta E = q - w$

$q = \Delta E + w$

$\boxed{q = \Delta E + pdv}$

In surroundings, heat will be given.

$$ds_{(sys)} - \left(\frac{dE + pdv}{T}\right) \geq 0$$

$$Tds - dE - pdv \geq 0$$

$$\boxed{Tds \geq dE + pdv}$$

As, ds, dv are constant.

$$dE \leq 0.$$

+ In terms of internal energy:

S is constant, $ds = 0$

V is constant, $dv = 0$

$$\boxed{0 \geq dE_{(V,S)}}$$

(or) V, S are constant.

$$dE_{(V,S)} \leq 0$$

dE is lesser than zero, it shows the process is irreversible dE is equal to zero, reversible process.

$0 \geq dE_{(S,V)}$ (or) $dE < 0$ (irreversible)

$dE = 0$ (reversible)

* In terms of Entropy:

$$dS \geq \frac{dE + PdV}{T}$$

when, E is constant, $dE = 0$

when, V is constant, $dV = 0$

$$\therefore \boxed{dS_{(E,V)} \geq 0}$$

$dS_{(E,V)} > 0 \longrightarrow$ irreversible

$dS_{(E,V)} = 0 \longrightarrow$ reversible.

In terms of Enthalpy:-

$$H = E + PV$$

$$dH = dE + pdv + vdp$$

$$dH - vdp = dE - pdv \qquad \boxed{dE + pdv \le Tds}$$

$$dH - vdp \le Tds$$

$$Tds \ge dH - vdp$$

$$\boxed{dH_{(p,s)} \le 0}$$

$$\boxed{\begin{array}{l} dH_{(p,s)} < 0 \longrightarrow \text{irreversible} \\ dH_{(p,s)} = 0 \longrightarrow \text{reversible} \end{array}}$$

In terms of work function:

$$A = E - TS$$

$$dA = dE - Tds - sdT$$

$$\boxed{dE + pdV \le Tds}$$

$$Tds = dE - dA - sdT \qquad Tds = dE + pdV$$

$$\cancel{dE} + pdV \le \cancel{dE} - dA - sdT$$

$$pdV \le -dA - SdT$$

$$pdV \ge dA + SdT$$

when, V is constant $pdV = 0$

when, T is constant $SdT = 0$

$$\therefore dA_{(V,T)} \le 0$$

$dA < 0 \rightarrow$ irreversible

$dA = 0 \rightarrow$ reversible

In <u>terms</u> of <u>free</u> energy.

$$G = H - TS$$

$$G = \Delta E + pV - TS$$

$$\Delta G = dE + pdV + Vdp - Tds - sdT$$

$$dE + pdV \le Tds$$

$$dG - Vdp + Tds + sdT = dE + pdV$$

$$dG - Vdp + T\cancel{ds} + sdT = T\cancel{ds}$$

$$dG - Vdp + sdT \le 0$$

$$dG \le Vdp \mp sdT$$

when, p is constant $Vdp = 0$

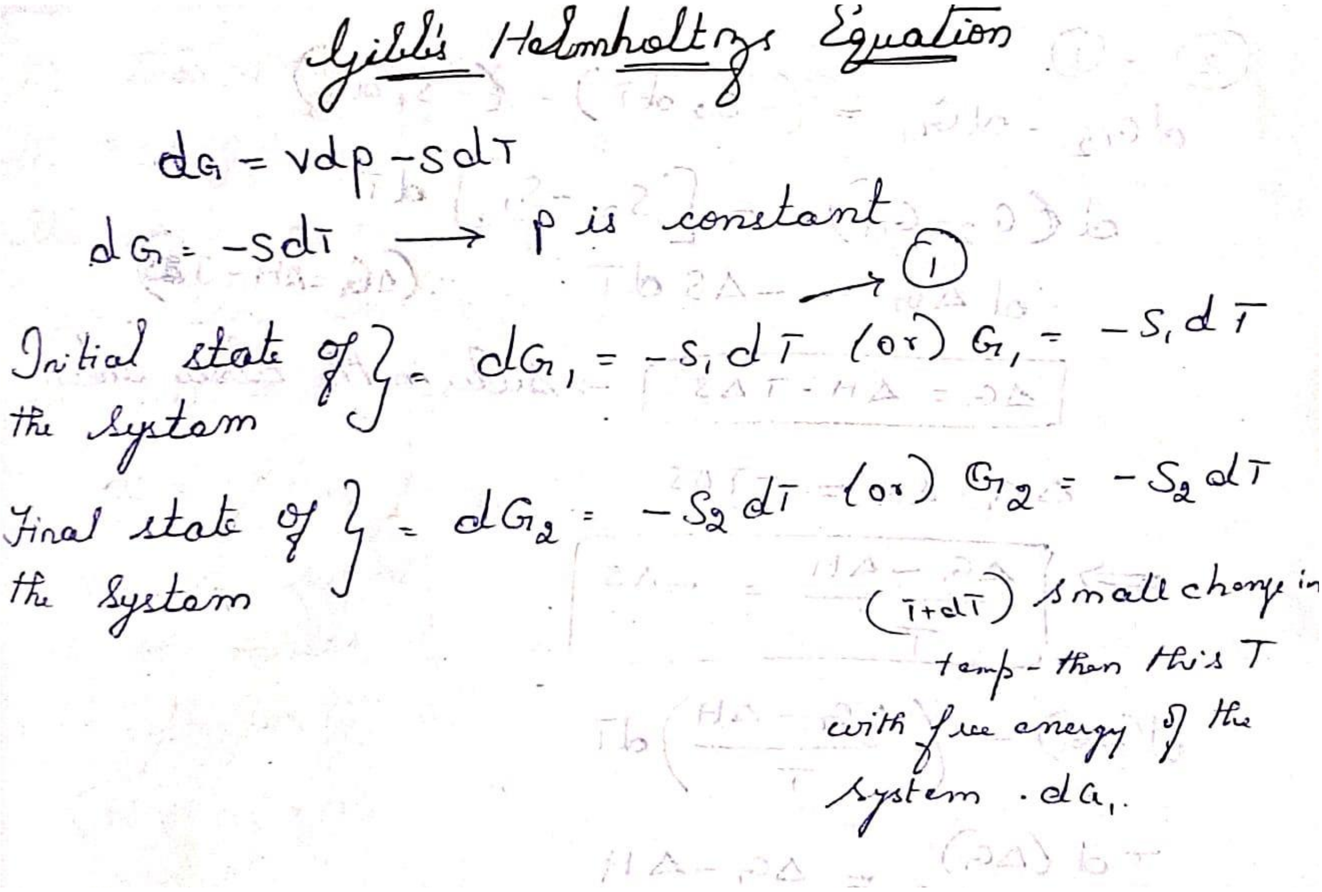
T is constant $sdT = 0$

$$dG_{(p,T)} \le 0$$

$dG_{(p,T)} < 0 \rightarrow$ irreversible

$dG_{(p,T)} = 0 \longrightarrow$ reversible

Gibbs-Helmholtz equation



Gibb's Helmholtz's Equation

$dG = vdp - SdT$

$dG = -SdT \longrightarrow$ p is constant.

$\longrightarrow$ ①

Initial state of the System } = $dG_1 = -S_1 dT$ (or) $G_1 = -S_1 dT$

Final state of the System } = $dG_2 = -S_2 dT$ (or) $G_2 = -S_2 dT$

$(T+dT)$ small change in temp - then this T with free energy of the system . dG_1.

when there is a small change in temperatur the T of the system is $T+dT$ & the free energy of a system i.e., dG_1

G_2 is the final free energy of a system & keeping P as a constant ~~of~~ & entropy is S_2.

If there is a small change in (T), the (T) of the system is $T+dT$ & the free energy of the final system is dG_2.

$$\boxed{dG_2 = -S_2\, dT} \rightarrow ②$$

② − ①

$$dG_2 - dG_1 = (-S_2 dT) - (-S_1 dT)$$

$$d(G_2 - G_1) = -[S_2 - S_1]\, dT$$

$$d\,\Delta G = -\Delta S\, dT \qquad \therefore (\Delta G = \Delta H - T\Delta S)$$

$$\boxed{\Delta G = \Delta H - T\Delta S} \rightarrow \text{Sub. in the above value.}$$

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

$$\Longrightarrow \boxed{\frac{\Delta G - \Delta H}{T} = -\Delta S}$$

$$d(\Delta G) = \left(\frac{\Delta G - \Delta H}{T}\right) dT$$

$$T\frac{d(\Delta G)}{dT} = \Delta G - \Delta H$$

$$\boxed{\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P} \rightarrow \text{Gibbs Helmholtz Eqn.}$$

Applications.

change of free energy can be calculated, provided work. the values of ΔH & free energy

$$\boxed{\Delta A = \Delta E + T\left(\frac{\partial \Delta A}{\partial T}\right)_V}$$

At constant volume, the Gibbs Helmholtz's equation become $\Delta A = \Delta E + T\left(\frac{\partial (\Delta A)}{\partial T}\right)_V$

Maxwell relationships

Maxwell Relationship

$\Delta E = q - w$

$dq = Tds$.

$dE = dq - dw$

$$\boxed{dE = TdS - pdv} \longrightarrow ①$$

$H = E + pv$

$dE + pdv = Tds$

$dH = dE + pdv + vdp$

$$\boxed{dH = Tds + vdp} \longrightarrow ②$$

$A = E - TS$

$\boxed{G = H - TS}$

$dA = dE - Tds - sdT$

From ① $dE - Tds = -pdv$

$$dA = -pdv - sdT \longrightarrow ③$$

$$dG = Vdp - sdT \longrightarrow ④$$

From eqn. ①.

$$dE = Tds - pdv$$

$$(dE)_V = Tds$$

$$\left(\frac{dE}{ds}\right)_V = T \rightarrow ⓐ$$

$$dE = Tds - pdv$$

$$(dE)_S = -pdv$$

$$\left(\frac{dE}{dv}\right)_S = -P \rightarrow ⓑ$$

Keeping entropy as constant

ⓐ

$$\frac{\partial^2 E}{\partial S \, \partial V} = \left(\frac{\partial T}{\partial V}\right)_S \rightarrow ⓒ$$

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

ⓑ $V = \text{const}$.

$$\frac{\partial^2 E}{\partial V . \partial S} = -\left(\frac{\partial P}{\partial S}\right)_V \rightarrow ⓓ$$

when we compare. c & d LHS are equal ∴ RHS are also equal.

From eqn. ②

$$dH = Tds + Vdp$$

At const (s), $Tds = 0$

$$dH = Vdp$$

$$\left(\frac{dH}{dp}\right)_S = V$$

$$dH = Tds + Vdp$$

At const (P), $Vdp = 0$

$$dH = Tds$$

$$\left(\frac{dH}{ds}\right)_P = T$$

Since, LHS are equal, RHS are also equal

Again differentiating.

$$\frac{\partial^2 H}{\partial p . \partial S} = \left(\frac{\partial V}{\partial S}\right)_P \qquad \frac{\partial^2 H}{\partial S . \partial P} = \left(\frac{\partial T}{\partial P}\right)_S$$

Since LHS & are equal. RHS are also equal.

$$\boxed{\therefore \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S} \longrightarrow ②$$

From eqn. ③

$dA = -pdV - s\,dT$

At const. (V) $-pdV = 0$

$dA = -s\,dT$

$$\left(\frac{dA}{dT}\right)_V = -S$$

$dA = -pdV - s\,dT$

At const. (T) $(-s\,dT) = 0$

$dA = -pdV$

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

$$\frac{\partial^2 A}{\partial T\,\partial V} = \left(-\frac{\partial S}{\partial V}\right)_T \qquad \frac{\partial^2 A}{\partial V \cdot \partial T} = \left(\frac{-\partial S}{\partial T}\right)_V$$

Since, LHS are equal, RHS are also equal,

$$\boxed{\cancel{-}\left(\frac{\partial S}{\partial V}\right)_T = \cancel{-}\left(\frac{\partial P}{\partial T}\right)_V} \text{ ——— ③}$$

From eqn. ④.

$dG = Vdp - s\,dT$

At const. P, $Vdp = 0$

$dG = -s\,dT$

$$\left(\frac{dG}{dT}\right)_P = -S$$

$dG = Vdp - s\,dT$

At Const T, $s\,dT = 0$

$dG = Vdp$

$$\left(\frac{dG}{dp}\right)_T = V$$

$$\frac{\partial^2 G}{\partial T \cdot \partial P} = -\left(\frac{\partial S}{\partial P}\right)_T \qquad \frac{\partial^2 G}{\partial P \cdot \partial T} = \left(\frac{\partial V}{\partial T}\right)_P$$

Since, LHS are equal, RHS are also equal.

$$\boxed{-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P} \text{ ——— ④}$$

Taking eqn. ① & ②

$dE = TdS - pdV$

$dH = TdS + Vdp$

$dE = TdS - pdV$

$dV = 0$

$$\boxed{\left(\frac{\partial E}{\partial S}\right)_V = T} \longrightarrow ⓐ$$

$dH = TdS + Vdp$

$$\boxed{dH = TdS}$$

$$\boxed{\left(\frac{\partial H}{\partial S}\right)_p = T} \longrightarrow ⓑ$$

RHS are also equal, so, LHS are equal on comparing a, b.

$$\therefore \left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p \longrightarrow ⑤$$

Taking ① & ③

$dE = TdS - pdV$

At constant Entropy

$$\boxed{dS = 0}$$

$$\boxed{\left(\frac{\partial E}{\partial V}\right)_S = -p} - ⓐ$$

$dA = -pdV - SdT$

At cont T

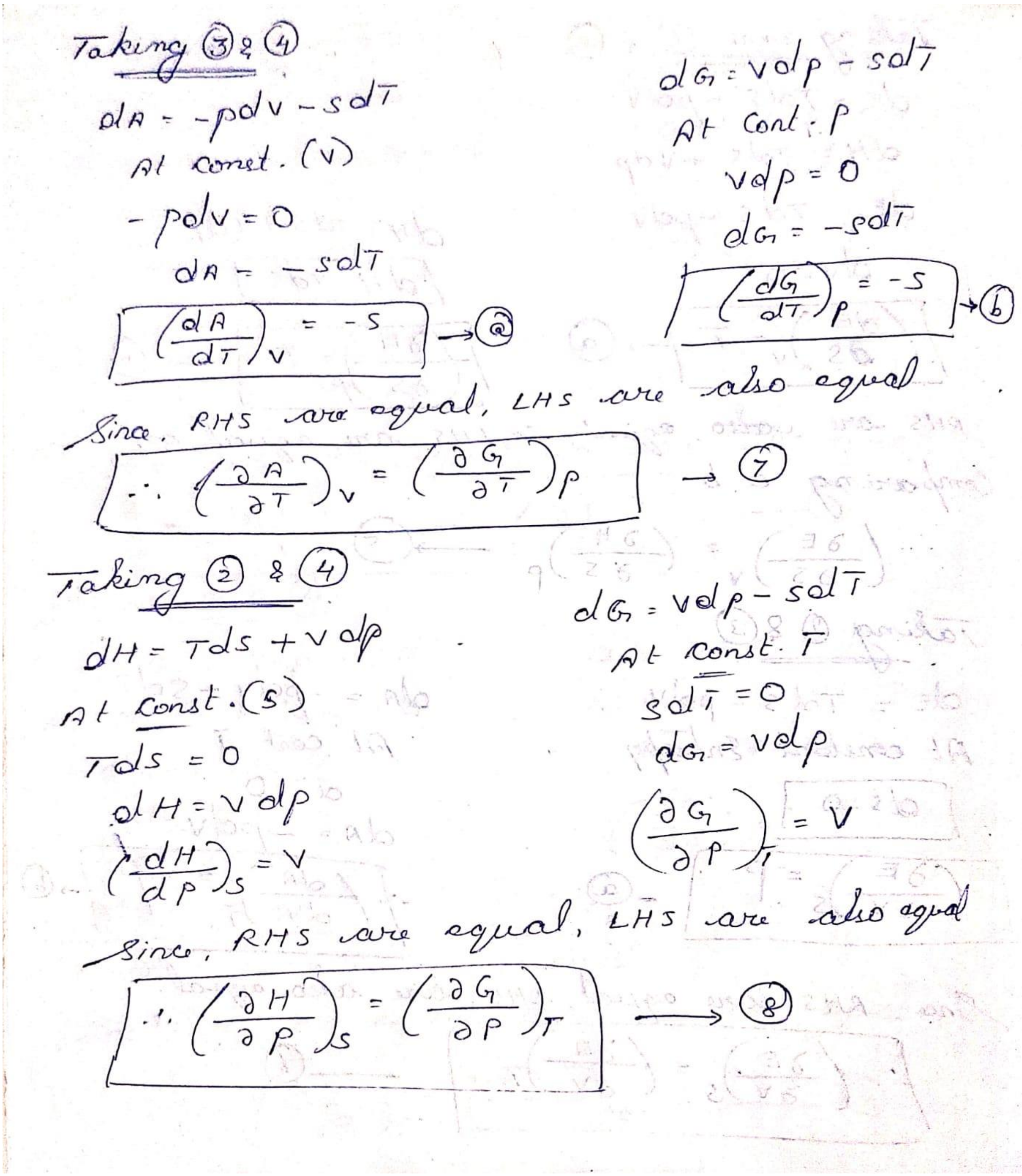
$dT = 0$

$dA = -pdV$

$$\therefore \boxed{\left(\frac{dA}{dV}\right)_T = -p} \rightarrow ⓑ$$

Since, RHS are equal, LHS are also equal.

$$\boxed{\therefore \left(\frac{\partial E}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T} \text{———} ⑥$$



Taking ③ & ④

$dA = -pdv - sdT$

At Const. (V)

$-pdv = 0$

$dA = -sdT$

$$\boxed{\left(\frac{dA}{dT}\right)_V = -S} \rightarrow ⓐ$$

$dG = vdp - sdT$

At Cont : P

$vdp = 0$

$dG = -sdT$

$$\boxed{\left(\frac{dG}{dT}\right)_P = -S} \rightarrow ⓑ$$

Since, RHS are equal, LHS are also equal.

$$\boxed{\therefore \left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P} \rightarrow ⑦$$

Taking ② & ④

$dH = Tds + v\,dp$

At Const. (S)

$Tds = 0$

$dH = v\,dp$

$$\left(\frac{dH}{dp}\right)_S = V$$

$dG = vdp - sdT$

At Const. T

$sdT = 0$

$dG = vdp$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

Since, RHS are equal, LHS are also equal

$$\boxed{\therefore \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T} \longrightarrow ⑧$$

Thermodynamics of mixing of ideal gases

The thermodynamics of mixing ideal gases describes a spontaneous process where the entropy of mixing and the Gibbs free energy of mixing. The process is driven by an increase in entropy (disorder) at constant temperature and pressure.

Ideal Behavior: Because ideal gas molecules do not interact, mixing does not change the internal energy or enthalpy of the components, resulting in $\Delta H_{mix} = 0$ and $\Delta U_{mix} = 0$

Entropy of Mixing (ΔSmix): Always positive, calculated as ΔSmix= -R Σ ni ln yi, where ni is moles and yi is the mole fraction. This indicates increased disorder.

Gibbs Free Energy of Mixing (ΔGmix): Always negative, calculated as ΔGmix = RT Σ ni ln yi. Since yi < 1, ln yi is negative, making ΔGmix negative, confirming the process is spontaneous.

Volume Change (ΔVmix): The total volume of the mixture is the sum of the volumes of the individual components before mixing (ΔVmix = 0).

Partial Pressure: Each gas expands to fill the total volume, reducing its partial pressure to P_i = yi P_{total}

Ellingham Diagram-application

Definitions

The Gibbs free energy (ΔG) of a reaction is a measure of the thermodynamic driving force that makes a reaction occur. A negative value for ΔG indicates that a reaction can proceed spontaneously without external inputs, while a positive value indicates that it will not. The equation for Gibbs free energy is:

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

Where, ΔH is the enthalpy, T is absolute temperature, and ΔS is entropy. The enthalpy (ΔH) is a measure of the actual energy that is liberated when the reaction occurs (the “heat of reaction”). If it is negative, then the reaction gives off energy, while if it is positive the reaction requires energy. The entropy (ΔS) is a measure of the change in the possibilities for disorder in the products compared to the reactants. For example, if a solid (an ordered state) reacts with a liquid (a somewhat less ordered state) to form a gas (a highly disordered state), there is normally a large positive change in the entropy for the reaction.

Construction of an Ellingham Diagram

An Ellingham diagram is a plot of ΔG versus temperature. Since ΔH and ΔS are essentially constant with temperature unless a phase change occurs, the free energy versus temperature plot can be drawn as a series of straight lines, where ΔS is the slope and ΔH is the y-intercept. The slope of the line changes when any of the materials involved melt or vaporize. Free energy of formation is negative for most metal oxides, and so the diagram is drawn with $\Delta G=0$ at the top of the diagram, and the values of ΔG shown are all negative numbers. Temperatures where either the metal or oxide melt or vaporize are marked on the diagram. The Ellingham diagram shown is for metals reacting to form oxides (similar diagrams can also be drawn for metals reacting with sulphur, chlorine, etc., but the oxide form of the diagram is most common). The oxygen partial pressure is taken as 1 atmosphere, and all of the reactions are normalized to consume one mole of O_2. The majority of the lines slope upwards, because both the metal and the oxide are present as condensed phases (solid or liquid). The reactions are therefore reacting a gas with a condensed phase to make another condensed phase, which reduces the entropy. A notable exception to this is the oxidation of solid carbon. The line for the reaction

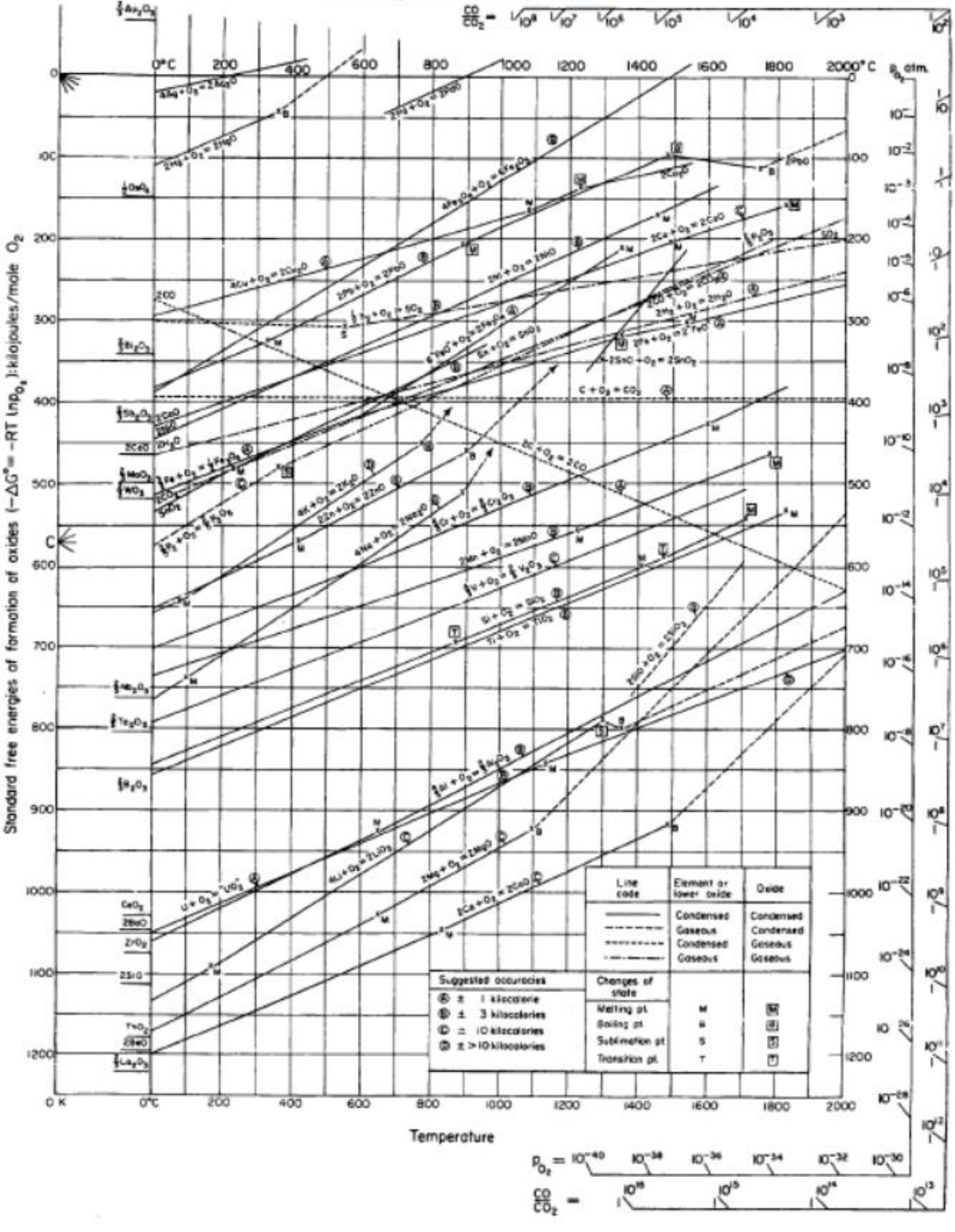
$C+O_2 ==> CO_2$

is a solid reacting with a mole of gas to produce a mole of gas, and so there is little change in entropy and the line is nearly horizontal. For the reaction

$2C+O_2 ==> 2CO$

We, have a solid reacting with a gas to produce two moles of gas, and so there is a substantial increase in entropy and the line slopes rather sharply downward. Similar behavior can be seen in parts of the lines for lead and lithium, both of which have oxides that boil at slightly lower temperatures than the metal does.

Ellingham Diagrams



There are three main uses of the Ellingham diagram:

1. Determine the relative ease of reducing a given metallic oxide to metal;

2. Determine the partial pressure of oxygen that is in equilibrium with a metal oxide at a given temperature; and

3. Determine the ratio of carbon monoxide to carbon dioxide that will be able to reduce the oxide to metal at a given temperature.

Chemical Potential

Partial Molar Properties

We have so far studied the thermodynamic systems in which there was a change in thermodynamic properties with the variation of one or more state variables. In such systems there was no transfer of mass taking place (closed systems). For studying the systems containing two or more phases or components G.N. Lewis introduced the concept of partial molar properties as in these cases both mass and composition vary (open systems). Consider any extensive thermodynamic property X of such a system, the value of which is determined by the temperature, pressure and the amounts of various constituents present. Let the system consist of J constituents and let n_1, n_2, n_3 .... n_j be the number of moles of the various constituents present. Evidently X must be a function of P, T and the number of moles of various constituents present, i.e.

$X = f(T, P, n_1, n_2, n_3 \dots n_j)$ ...(1)

If there is a small change in the temperature and pressure of the system as well as the amounts of its constituents, the change in the property X is given by

$$
\begin{aligned}
dX = {} & \left(\frac{\delta X}{\delta T}\right)_{P \; n_1, n_2 \dots n_j} dT + \left(\frac{\delta X}{\delta p}\right)_{T \; n_1, n_2 \dots n_j} dp + \left(\frac{dX}{\delta n}\right)_{T,P \; n_2 \dots n_j} dn_1 \\
& + \left(\frac{\delta X}{\delta n_2}\right)_{T,P \; n_1, n_3 \dots n_j} dn_2 + \left(\frac{\delta X}{\delta n_3}\right)_{T,P \; n_1, n_2 \dots n_j} dn_3 + \dots + \\
& \left(\frac{\delta X}{\delta n_j}\right)_{T,P \; n_1, n_2 \dots} dn_j \qquad \dots(ii)
\end{aligned}
$$

The quantity $[\frac{\delta X}{\delta n_1}]_{T,P,n2\ldots nj}$

is called partial molar property for the constituent 1. It is represented by writing a bar over its symbol for the particular property i.e. X so that

$$\bar{X}_1 = \left(\frac{\delta X}{\delta n_1}\right)_{T,P,n_2 \ldots n_j} \quad ; \bar{X}_2 = \left(\frac{\delta X}{\delta n_2}\right)_{T,P,n_1,n_3 \ldots n_j}$$

The equation (*ii*) may be written as :

$$dX = \left(\frac{\delta X}{\delta T}\right)_{P,\ n_1,n_2 \ldots n_j} dT + \bar{X} = \left(\frac{\delta X}{\delta P}\right)_{T,\ n_1,n_2 \ldots n_j} dP$$
$$+ \bar{X}_1\, dn_1 + \bar{X}_2\, dn_2 + \bar{X}_3\, dn_3 + \ldots \bar{X}_j\, dn_j$$

If the temperature and the pressure of the system are kept constant dT and dP are zero so that

$$dX = \bar{X}_1\, dn_1 + \bar{X}_2\, dn_2 + \ldots \bar{X}_j\, dn_j \qquad \ldots(iii)$$

and this on integration for a system of definite composition represented by the number of moles n_1, n_2 ..... n_j gives

$$X = n_1\bar{X}_1 + n_2\bar{X} + n_3\bar{X}_3 + \ldots n_j\bar{X}_j \qquad \ldots(iv)$$

ie., the partial molal property X of any constituent may be regarded as the contribution of 1 mole of that constituent to the total value of the property of the system under specified conditions.

Gibbs Duhem Equation

It has already been discussed that free energy G is an intensive thermodynamic property. It can be determined by fixing the variables T, P and number of moles of various constituents (composition of the mixture under study). Mathematically, we can write.

$$G = f\,(T, P, n_1, n_2 \ldots n_j) \qquad \ldots(i)$$

where n_1, n_2 .... n_j are the number of moles of various constituents.
Differentiating equation (i), we get

$$dG = \left(\frac{\delta G}{\delta T}\right)_{P,\ n_1,n_2 \ldots n_j} dT + \left(\frac{\delta G}{\delta P}\right)_{T,\ n_1,n_2 \ldots n_j} dP +$$
$$\left(\frac{\delta G}{\delta n_1}\right)_{T,P,\ n_2 \ldots n_j} dn_1 + \left(\frac{\delta G}{\delta n_2}\right)_{T,P,\ n_1 \ldots n_j} dn_2 + \left(\frac{\delta G}{\delta n_j}\right)_{T_1,P,\ n_1 \ldots n_{j-1}} dn_j$$

We know the chemical potential is given by

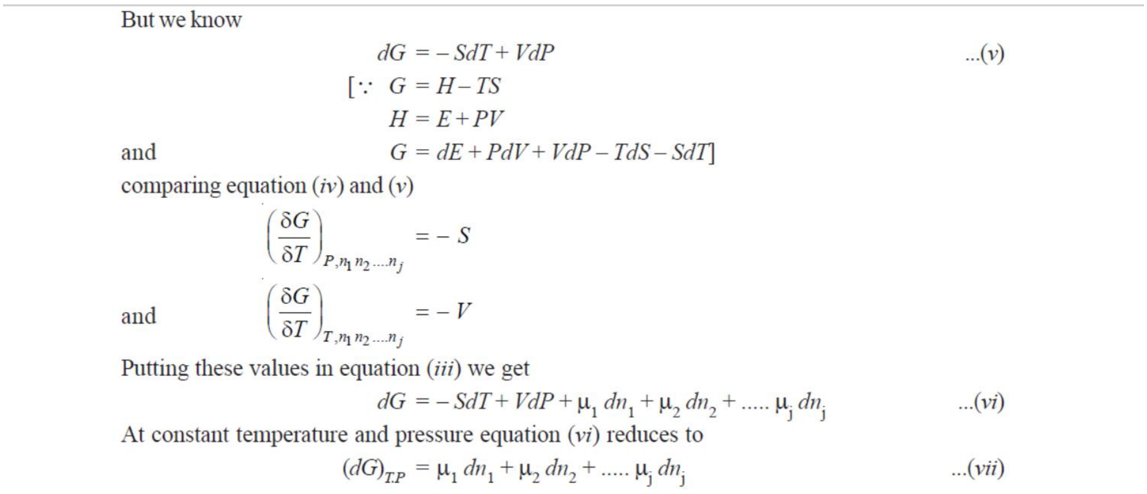
$$\mu_i = \left(\frac{\delta G}{\delta n_i}\right)_{T,P,n_1,n_2 \ldots} = \bar{G}_1$$

Substituting in equation (*ii*) we get

$$dG = \left(\frac{\delta G}{\delta T}\right)_{P,\ n_1,n_2 \ldots n_j} dT + \left(\frac{\delta G}{\delta P}\right)_{T,\ n_1,n_2 \ldots n_j} dP + \mu_1\, dn_1, + \mu_2\, dn_2, + \ldots + \mu_j\, dn_j \qquad \ldots(iii)$$

For a closed system there is no change in the composition and equation (*iii*) reduces to

$$dG = \left(\frac{\delta G}{\delta T}\right)_{P,\ n_1,n_2 \ldots n_j} dT + \left(\frac{\delta G}{\delta P}\right)_{T,\ n_1,n_2 \ldots n_j} dP \qquad \ldots(iv)$$



But we know

$$dG = -SdT + VdP \qquad ...(v)$$

$$\left[\because \; G = H - TS \right.$$

$$H = E + PV$$

and

$$\left. G = dE + PdV + VdP - TdS - SdT \right]$$

comparing equation (*iv*) and (*v*)

$$\left(\frac{\delta G}{\delta T}\right)_{P, n_1 n_2 \ldots n_j} = -S$$

and

$$\left(\frac{\delta G}{\delta T}\right)_{T, n_1 n_2 \ldots n_j} = -V$$

Putting these values in equation (*iii*) we get

$$dG = -SdT + VdP + \mu_1 \, dn_1 + \mu_2 \, dn_2 + \ldots . \, \mu_j \, dn_j \qquad ...(vi)$$

At constant temperature and pressure equation (*vi*) reduces to

$$(dG)_{T.P} = \mu_1 \, dn_1 + \mu_2 \, dn_2 + \ldots . \, \mu_j \, dn_j \qquad ...(vii)$$

Integrating equation (vii) we get the following for a system of definite composition

$(G)T.P = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \ldots . \mu j \, nj$ ...(viii)

Differentiating equation (viii) we get

$(dG)T.P = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \ldots . \mu j \, dnj + nj \, d\mu j$ ...(ix)

Comparing equation (vii) and (ix) we get

$n_1 d \mu_1 + n_2 d \mu_2 + \ldots . njd \mu j = 0$

or $\Sigma \, njd \, \mu j = 0$ ...(x)

Equation (x) is called Gibbs Duhem equation. It is applicable to a system at constant temperature and pressure.

Variation of Chemical Potential with Temperature and Pressure

(*a*) With Temperature

We know that chemical potential of a constituent *i* in a system is given by

$$\mu_i = \left(\frac{\delta G}{\delta n_i}\right)_{T,P,n_1....n_j} = \bar{G}_i \qquad ...(i)$$

Differentiating equation (*i*) w.r.t. *T* at constant pressure *P*, we get

$$\left(\frac{\delta \mu_i}{\delta T}\right)_{P,n_1 n_2....n_j} = \frac{\delta^2 G}{\delta n_i \delta T} \qquad ...(ii)$$

We also know that

$$\left(\frac{\delta G}{\delta T}\right)_{P,n_1 n_2....n_j} = S \qquad ...(iii)$$

Differentiating equation (*iii*) w.r.t. n_j at constant temperature and pressure.

$$-\left(\frac{\delta S}{\delta n_i}\right)_{T,P,n_1....n_j} = \frac{\delta^2 G}{\delta T \delta n_i} \qquad ...(iv)$$

Comparing equation (*ii*) and (*iv*), we have

$$\left(\frac{\delta \mu_i}{\delta T}\right)_{P,n_1 n_2....n_j} = \left(\frac{\delta S}{\delta n_i}\right)_{T,P,n_1....n_j} = \bar{S}_i$$

[By definition of Partial Molal Property]

Thus

$$\left(\frac{\delta \mu_i}{\delta T}\right)_{P,n_1 n_2....n_j} = \bar{S}_i = \text{Partial Molal Entropy}$$

This equation gives the variation of chemical potential of any constituent *i* with temperature.

(*b*) With Pressure

By definition, chemical potential is given by

$$\mu_i = \left(\frac{\delta G}{\delta n_i}\right)_{T,P,n_1....n_j} = \bar{G}_i \qquad ...(i)$$

Differentiating equation (*i*) w.r.t. pressure at constant temperature

$$\left(\frac{\delta \mu_i}{\delta P}\right)_{T,n_1 n_2....n_j} = \frac{\delta^2 G}{\delta n_i \delta P} \qquad ...(ii)$$

But we know that

$$\left(\frac{\delta G}{\delta P}\right)_{T,n_1 n_2....n_j} = V \qquad ...(iii)$$

Differentiating equation (*iii*) w.r.t. n_i at constant *T*, *P* and n_j

$$\left(\frac{\delta V}{\delta n_i}\right)_{T,P,n_1 n_2....n_j} = \frac{\delta^2 G}{\delta P \delta n_i} = \bar{V}_i \qquad ...(iv)$$

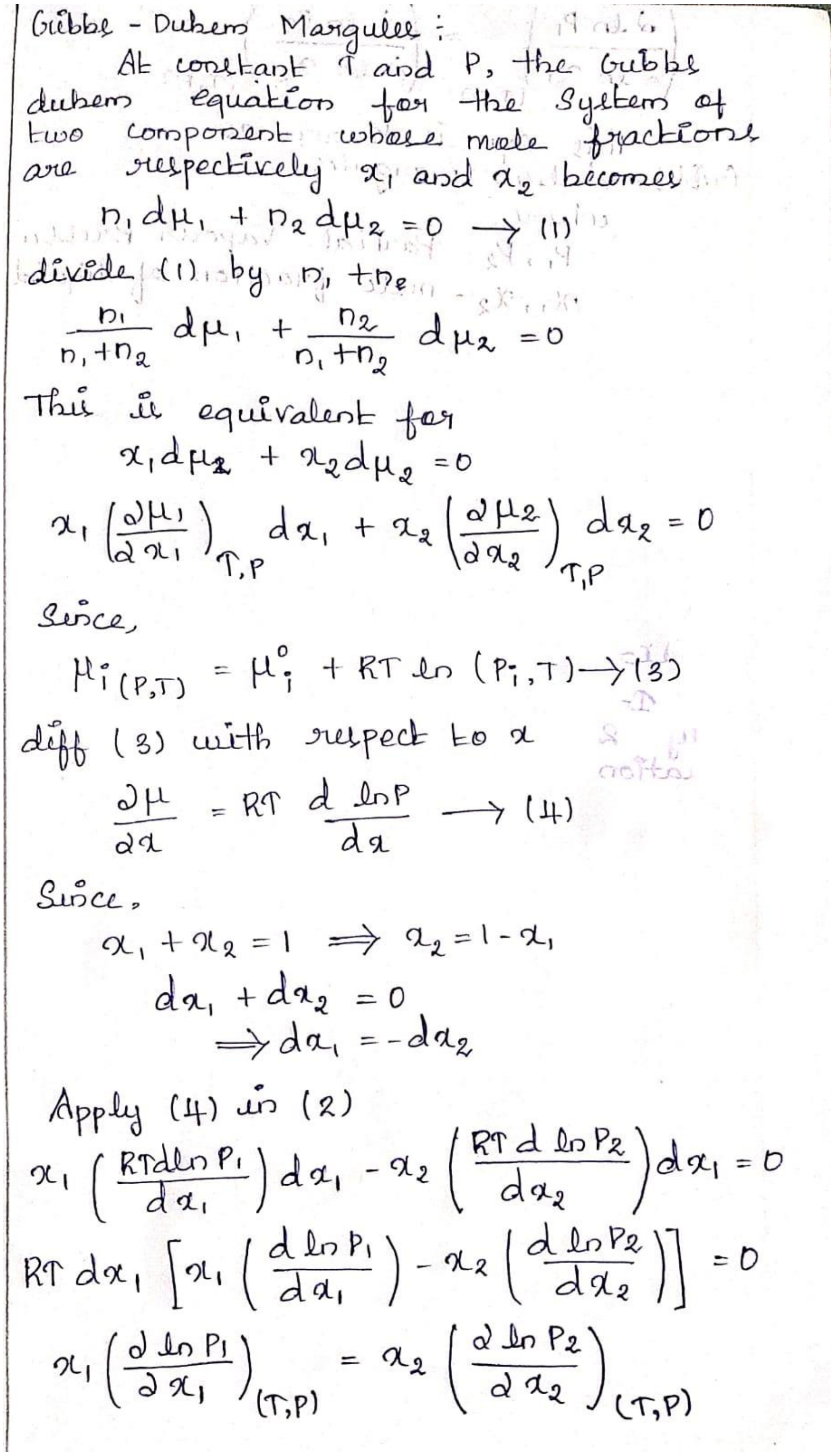
(By definition of Partial Molal Property)

Comparing equations (*ii*) and (*iv*)

$$\left(\frac{\delta \mu_i}{\delta P}\right)_{T,n_1 n_2....n_j} = \bar{V}_i = \text{Partial Molal Volume} \qquad ...(v)$$

Equation (*v*) gives the variation of Chemical potential of any constituent *i* with pressure. From this equation we can define the partial molar volume of a constituent *i* as the rate of change of chemical potential of a constituent *i* with pressure at constant temperature.

Gibbs – Duhem Margules Equation:



Gibbs - Duhem Margules :

At constant T and P, the Gibbs duhem equation for the system of two component whose mole fractions are respectively x_1 and x_2 becomes

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \rightarrow (1)$$

divide (1) by $n_1 + n_2$

$$\frac{n_1}{n_1+n_2} d\mu_1 + \frac{n_2}{n_1+n_2} d\mu_2 = 0$$

This is equivalent for

$$x_1 d\mu_2 + x_2 d\mu_2 = 0$$

$$x_1 \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} dx_1 + x_2 \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} dx_2 = 0$$

Since,

$$\mu_{i\,(P,T)} = \mu_i^0 + RT \ln (P_i, T) \rightarrow (3)$$

diff (3) with respect to x

$$\frac{\partial \mu}{\partial x} = RT \frac{d \ln P}{dx} \longrightarrow (4)$$

Since,

$$x_1 + x_2 = 1 \implies x_2 = 1 - x_1$$

$$dx_1 + dx_2 = 0$$

$$\implies dx_1 = -dx_2$$

Apply (4) in (2)

$$x_1 \left(\frac{RT d\ln P_1}{dx_1}\right) dx_1 - x_2 \left(\frac{RT\, d \ln P_2}{dx_2}\right) dx_1 = 0$$

$$RT\, dx_1 \left[x_1 \left(\frac{d \ln P_1}{dx_1}\right) - x_2 \left(\frac{d \ln P_2}{dx_2}\right)\right] = 0$$

$$x_1 \left(\frac{\partial \ln P_1}{\partial x_1}\right)_{(T,P)} = x_2 \left(\frac{\partial \ln P_2}{\partial x_2}\right)_{(T,P)}$$

$$\left(\frac{\partial \ln P_1}{\partial \ln x_1}\right)_{(T,P)} = \left(\frac{\partial \ln P_2}{\partial \ln x_2}\right)_{(T,P)}$$

This eqn is known as Gibbs-duhem margules.

where,

P_1, P_2 - Partial Vapour Pressure

x_1, x_2 - mole fraction of liquid.

UNIT-II

Chemical Kinetics

Rate of reaction

The branch of Physical chemistry which deals with the rate of reactions is called Chemical Kinetics. The study of Chemical Kinetics includes :

(1) The rate of the reactions and rate laws.

(2) The factors as temperature, pressure, concentration and catalyst, that influence the rate of a reaction.

(3) The mechanism or the sequence of steps by which a reaction occurs.

The knowledge of the rate of reactions is very valuable to understand the chemical of reactions. It is also of great importance in selecting optimum conditions for an industrial process so that it proceeds at a rate to give maximum yield.

Reaction Rate

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

$A \longrightarrow B$

The concentration of the reactant A decreases and that of B increases as time passes. The rate of reactions is defined as the change in concentration of any of reactant or products per unit time. For the given reaction the rate of reaction may be equal to the rate of disappearance of A which is equal to the rate of appearance of B.

Thus rate of reaction = rate of disappearance of A

= rate of appearance of B

$$\text{rate} = -\frac{d\,[A]}{dt}$$

$$= \frac{d\,[B]}{dt}$$

where, [ ] represents the concentration in moles per litre whereas ‘d’ represents infinitesimally small change in concentration. Negative sign shows the concentration of the reactant A decreases whereas the positive sign indicates the increase in concentration of the product B.

Units of Rate

Reactions rate has the units of concentration divided by time. We express concentrations in moles per litre (mol/litre or mol/1 or mol 1^{-1}) but time may be given in any convenient unit second (s), minutes (min), hours (h), days (d) or possible years. Therefore, the units of reaction rates may be

mole/litre sec or mol 1^{-1} s

mole/litre min or mol 1^{-1} $\min^{-1}$

mole/litre hour or mol 1^{-1} h^{-1} and, so on

Average Rate of Reaction is a Function of Time

Let us consider the reaction between carbon monoxide (CO) and nitrogen dioxide.

$CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$

The average rate of reaction may be expressed as

rate = $\frac{-\Delta[CO]}{\Delta t} = \frac{d[CO]}{dt}$

The concentration of CO was found experimentally every 10 seconds. The results of such an experiment are listed below.

Conc. of CO	0.100	0.067	0.050	0.040	0.033
Time (sec)	0	10	20	30	40

The results are also shown graphically in Fig. 2.1. As the reaction proceeds the concentration of CO decreases rapidly in the initial stages of the reaction. Then the concentration of CO decreases more and more slowly. Obviously the rate of reaction is a function of time. Over the first 10 seconds, the average rate is,

$\frac{-d[CO]}{dt} = \frac{-(0.067-0.100)}{(10-0)} = \frac{0.033}{10}$ =0.0033 mol $l^{-1}s^{-1}$

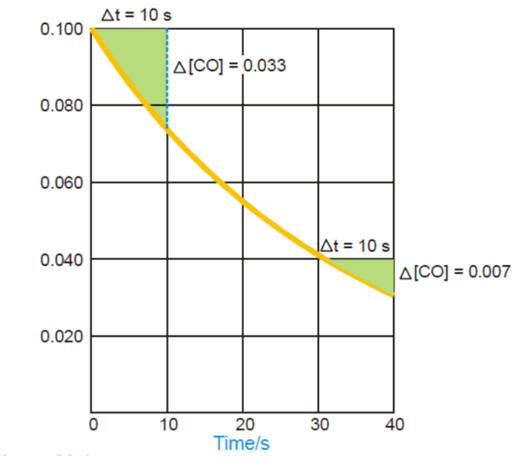


Figure 2.1: Graph of CO concentrations versus time. The average rate is equal to the slope of the curve. The average rates for the first 10 and the last 10 seconds are shown.

In the time interval between 30 and 40 seconds, the average rate is much smaller.

$\frac{-d[CO]}{dt} = \frac{-(0.033-0.040)}{(40-30)} = \frac{0.007}{10} = 0.0007 \text{ mol L}^{-1} \text{ s}^{-1}$

The reaction in indeed slowing down with time. We shall see that average rates are not always useful. They cover a large time interval during which the rate of reaction changes significantly. So, a better way to estimate the rate of reaction, we need to make the time interval as small as possible.

Instantaneous Rate of Reaction

The average rates obtained by finding the slope of the curve are not always useful. They cover a large time interval during which the rate of reaction changes significantly. So, a better way to estimate the rate of a reaction is to make the time interval as small as possible. If the interval be infinitesimally small (that is as Δt approaches zero), the rate is referred to as the instantaneous rate and is written in calculus as

$$\text{Rate} = \frac{d[\,]_t}{dt}$$

where [ ]t is the concentration at time t. In the present case, the instantaneous rate = $-\frac{d\,[CO]t}{dt}$

Thus at any time the instantaneous rate is equal to the slope of a straight line drawn tangent to the curve at that time. For example, in Fig. 2.2 the instantaneous rate at 10 seconds is found to be 0.0022 mol l^{-1} s^{-1}.

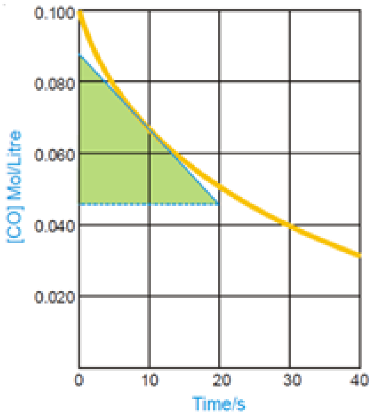


Figure 2.2: The slope of tangent at 10 seconds is equal to the instantaneous rate.

Rate Law

At a fixed temperature the rate of a given reaction depends on concentration of reactants. The exact relation between concentration and rate is determined by measuring the reaction rate with different initial reactant concentrations. By a study of numerous reactions it is shown that: the rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power. Thus for a substance A undergoing reaction,

rate $\text{rate} \propto [A]^n$

or $\text{rate} = k\,[A]^n$ ...(1)

For a reaction

$2A + B \longrightarrow \text{products}$

the reaction rate with respect to A or B is determined by varying the concentration of one reactant, keeping that of the other constant. Thus the rate of reaction may be expressed as

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

Expressions such as (1) and (2) tell the relation between the rate of a reaction and reactant concentrations. An expression which shows how the reaction rate is related to concentrations is called the rate law or rate equation. The power (exponent) of concentration n or m in the rate law is usually a small whole number integer (1, 2, 3) or fractional. The proportionality constant k is called the rate constant for the reaction.

Examples of rate law:

REACTIONS	RATE LAW
(1) $2N_2O_5 \longrightarrow 4\ NO_2 + O_2$	rate = $k\ [N_2O_5]$
(2) $H_2 + I_2 \longrightarrow 2HI$	rate = $k\ [H_2]\ [I_2]$
(3) $2NO_2 \longrightarrow 2NO + O_2$	rate = $k\ [NO_2]_2$
(4) $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$	rate = $k\ [H_2]\ [NO]_2$

In these rate laws where the quotient or concentration is not shown, it is understood to be 1. That is $[H_2]^1 = [H_2]$.

It is apparent that the rate law for a reaction must be determined by experiment. It cannot be written by merely looking at the equation with a background of our knowledge of Law of Mass Action. However, for some elementary reactions the powers in the rate law may correspond to coefficients in the chemical equation. But usually the powers of concentration in the rate law are different from coefficients. Thus for the reaction (4) above, the rate is found to be proportional to $[H_2]$ although the quotient of H_2 in the equation is 2. For NO the rate is proportional to $[NO]^2$ and power '2' corresponds to the coefficient.

Order of a Reaction

The order of a reaction is defined as the sum of the powers of concentrations in the rate law. Let us consider the example of a reaction which has the rate law

$$\text{rate} = k\ [A]^m\ [B]^n \qquad ...(1)$$

The order of such a reaction is (m + n).

The order of a reaction can also be defined with respect to a single reactant. Thus the reaction order with respect to A is m and with respect to B it is n. The overall order of reaction (m + n) may range from 1 to 3 and can be fractional.

Examples of reaction order:

RATE LAW	REACTION ORDER
rate = $k\ [N_2O_5]$	1
rate = $k\ [H_2]\ [I_2]$	1 + 1 = 2
rate = $k\ [NO_2]_2$	2
rate = $k\ [[H_2]\ [NO]_2$	1 + 2 = 3
rate = $k\ [CHCl_3]\ [Cl_2]_{1/2}$	$1 + 1/2 = 1\frac{1}{2}$

Reactions may be classified according to the order. If in the rate law (1) above

m + n = 1, it is first order reaction

m + n = 2, it is second order reaction

m + n = 3, it is third order reaction

Zero Order Reaction

A reactant whose concentration does not affect the reaction rate is not included in the rate law. In effect, the concentration of such a reactant has the power 0. Thus [A]0 = 1. A zero order reaction is one whose rate is independent of concentration. For example, the rate law for the reaction

$NO_2 + CO \longrightarrow NO + CO_2$

at 200° C is

rate = k $[NO_2]_2$

Here the rate does not depend on [CO], so this is not included in the rate law and the power of [CO] is understood to be zero. The reaction is zeroth order with respect to CO. The reaction is second order with respect to $[NO_2]$. The overall reaction order is 2 + 0 = 2.

Molecularity of a Reaction

Chemical reactions may be classed into two types :

(a) Elementary reactions

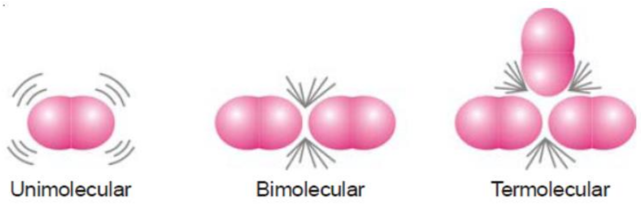
(b) Complex reactions

An elementary reaction is a simple reaction which occurs in a single step.

A complex reaction is that which occurs in two or more steps.

Molecularity of an Elementary Reaction

The molecularity of an elementary reaction is defined as: the number of reactant molecules involved in a reaction.

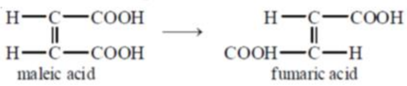


Thus the molecularity of an elementary reaction is 1, 2, 3, etc., according as one, two or three reactant molecules are participating in the reaction. The elementary reactions having molecularity 1, 2 and 3 are called unimolecular, bimolecular and termolecular respectively. Thus we have:

(a) Unimolecular reactions : (molecularity = 1)

$A \longrightarrow$ product

Examples are : (i) $Br_2 \longrightarrow 2Br$

ii) 

(b) Bimolecular reactions : (molecularity = 2)

$A + B \longrightarrow$ products

$A + A \longrightarrow$ products

Examples are :

(i) $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

Ethyl acetate acetic acid ethyl alcohol

(c) Termolecular reactions : (molecularity = 3)

$A + B + C \longrightarrow$ products

Examples are :

$2NO + O_2 \longrightarrow 2NO_2$

$2NO + Cl_2 \longrightarrow 2NOCl$

Molecularity of a Complex Reaction

Most chemical reactions are complex reactions. These occur in a series of steps. Each step is an elementary reaction. The stepwise sequence of elementary reactions that convert reactions to products is called the mechanism of the reaction. In any mechanism, some of the steps will be fast, others will be slow. A reaction can proceed no faster than its slowest step. Thus the slowest step is the rate determining step of the reaction. The decomposition of N_2O_5,

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

is an example of a complex reaction. It occurs by the following steps:

Step 1 $2N_2O_5 \longrightarrow 2NO_2 + 2NO_3$ (slow)

Step 2 $NO_2 + NO_3 \longrightarrow NO + NO_2 + O_2$ (slow)

Step 3 $NO + NO_3 \longrightarrow 2NO_2$ (fast)

Overall reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$

Each elementary reaction has its own molecularity equal to the number of molecules or atoms participating in it. It is meaningless to give the molecularity of the overall reaction because it is made of several elementary reactions, each, perhaps with a different molecularity. At best could be thought of as: the number of molecules or atoms taking part in the rate-determining step. Thus step 2 in the above mechanism is rate-determining and has molecularity ‘2’ which could be considered as the molecularity of the decomposition reaction of N_2O_5.

Molecularity versus Order of Reaction

The term molecularity is often confused with order of a reaction. The total number of molecules or atoms which take part in a reaction as represented by the chemical equation, is known as the molecularity of reaction. The sum of the powers to which the concentrations are raised in the rate law is known as the order of reaction.

Molecularity and Order are Identical for Elementary Reactions or Steps

The rate of an elementary reaction is proportional to the number of collisions between molecules (or atoms) of reactions. The number of collisions in turn is proportional to the concentration of each reactant molecule (or atom). Thus for a reaction.

$2A + B \longrightarrow$ products

$$\text{rate} \propto [A]\,[A]\,[B]$$

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

Two molecules of A and one molecule of B are participating in the reaction and, therefore, molecularity of the reaction is 2 + 1 = 3. The sum of powers in the rate law is 2 + 1 and hence the reaction order is also 3. Thus the molecularity and order for an elementary reaction are equal.

Molecularity and Order for Elementary Reactions.

Reactions	Molecularity	Rate law	Order
$A \longrightarrow$ products	1	rate = $k\,[A]$	1
$A + A \longrightarrow$ products	2	rate = $k\,[A]^2$	2
$A + B \longrightarrow$ products	2	rate = $k\,[A]\,[B]$	2
$A + 2B \longrightarrow$ products	3	rate = $k\,[A]\,[B]^2$	3
$A + B + C \longrightarrow$ products	3	rate = $k\,[A]\,[B]\,[C]$	3

Differences Between Order and Molecularity

Order of a Reaction	Molecularity of a Reaction
It is the sum of powers of the concentration terms in the rate law expression.	It is number of reacting species undergoing simultaneous collision in the elementary or simple reaction.
It is an experimentally determined value.	It is a theoretical concept.
It can have fractional value	It is always a whole number.
It can assume zero value.	It cannot have zero value.
Order of a reaction can change with the conditions such as pressure, temperature, concentration.	Molecularity is invariant for a chemical equation.

Zero Order Reactions

In a zero order reaction, rate is independent of the concentration of the reactions. Let us consider a zero-order reaction of the type

$A \longrightarrow$ Products

	A	Products
Initial conc.	a	0
Final conc.	$a - x$	x

Rate of the reaction = $\frac{-d[A]}{dt} = k_o[A]^o$ or

$$\frac{dx}{dt} = \frac{-d(a-x)}{dt} = k_o\,(a-x)^o = k_o$$

On integrating we get,

$$k_o = \frac{x}{t} \text{ or } x = k_o t$$

where, *k*0 is the rate constant of a zero-order reaction, the unit of which is concentration per unit time. In zero order reaction, the rate constant is equal to the rate of reaction at all concentrations.

First order reactions

Let us consider a first order reaction

$A \longrightarrow$ products

Suppose that at the beginning of the reaction (t = 0), the concentration of A is a moles litre–1. If after time t, x moles of A have changed, the concentration of A is a – x. We know that for a first order reaction, the rate of reaction, dx/dt, is directly proportional to the concentration of the reactant. Thus,

$\frac{dx}{dt} = k(a - x)$ or

$\frac{dx}{a-x} = kdt$ ----------(1)

Integration of the expression (1) gives

$\int \frac{dx}{a-x} = \int kdt$

Or $-\ln(a-x) = kt + I$ -------(2)

Where I is the constant of integration. The constant k may be evaluated by putting t = 0 and x = 0.

Thus, $I = -\ln a$

Substituting for I in equation (2)

$\ln \frac{a}{a-x} = kt$ -------(3)

or $k = \frac{1}{t} \ln \frac{a}{a-x}$

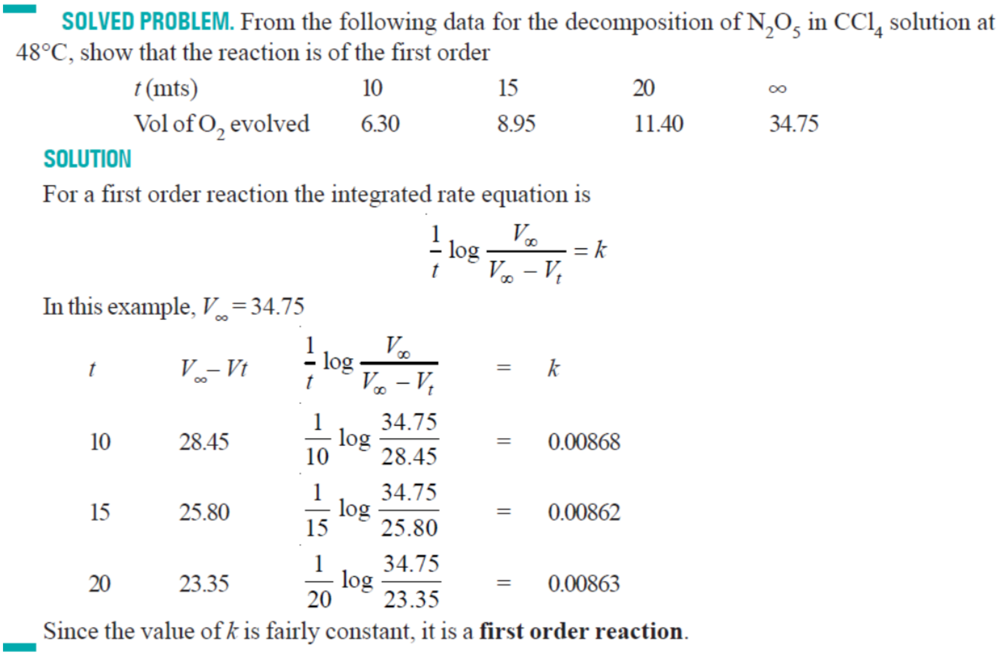
Changing into common logarithms

$K = \frac{2.303}{t} \log \frac{a}{a-x}$

The value of k can be found by substituting the values of a and (a – x) determined experimentally at time interval t during the course of the reaction. Sometimes the integrated rate law in the following form is also used:

$$k = \frac{2.303}{t2 - t1} \log \frac{(a - x1)}{(a - x2)}$$

Where, x_1 and x_2 are the amounts decomposed at time intervals t_1 and t_2 respectively from the start.



SOLVED PROBLEM. From the following data for the decomposition of N_2O_5 in CCl_4 solution at 48°C, show that the reaction is of the first order

t (mts)	10	15	20	∞
Vol of O_2 evolved	6.30	8.95	11.40	34.75

SOLUTION

For a first order reaction the integrated rate equation is

$$\frac{1}{t} \log \frac{V_\infty}{V_\infty - V_t} = k$$

In this example, $V_\infty = 34.75$

t	$V_\infty - Vt$	$\frac{1}{t} \log \frac{V_\infty}{V_\infty - V_t}$	=	k
10	28.45	$\frac{1}{10} \log \frac{34.75}{28.45}$	=	0.00868
15	25.80	$\frac{1}{15} \log \frac{34.75}{25.80}$	=	0.00862
20	23.35	$\frac{1}{20} \log \frac{34.75}{23.35}$	=	0.00863

Since the value of k is fairly constant, it is a **first order reaction**.

Second Order Reactions

Let us take a second order reaction of the type

$2A \longrightarrow$ products

Suppose the initial concentration of A is a moles litre–1. If after time t, x moles of A have reacted, the concentration of A is (a – x). We know that for such a second order reaction, rate of reaction is proportional to the square of the concentration of the reactant. Thus,

$$\frac{dx}{dt} = k(a - x)^2 \text{ --------(1)}$$

where k is the rate constant, Rearranging equation (1), we have

$$\frac{dx}{(a-x)2} = kdt \text{ ---------(2)}$$

On integration, it gives

$$\frac{1}{a-x} = kt + I \text{ -------------(3)}$$

Where, I is the integration constant. I can be evaluated by putting $x = 0$ and $t = 0$. Thus, I= 1/a

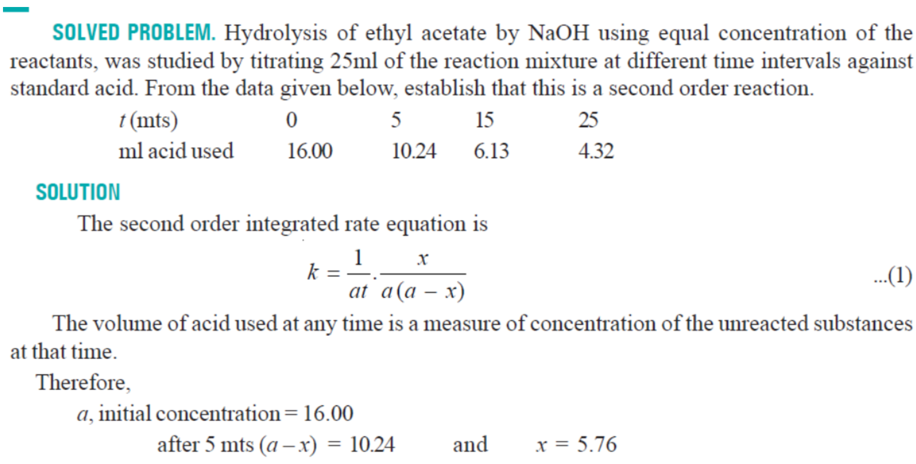
Substituting for I in equation (3)

$$\frac{1}{a-x} = kt + \frac{dy}{dx}\frac{1}{a}$$

Kt = $\frac{1}{a-x} - \frac{1}{a}$

Thus, k = $\frac{1}{t} \cdot \frac{x}{a(a-x)}$

This is the integrated rate equation for a second order reaction.



SOLVED PROBLEM. Hydrolysis of ethyl acetate by NaOH using equal concentration of the reactants, was studied by titrating 25ml of the reaction mixture at different time intervals against standard acid. From the data given below, establish that this is a second order reaction.

t (mts)	0	5	15	25
ml acid used	16.00	10.24	6.13	4.32

SOLUTION

The second order integrated rate equation is

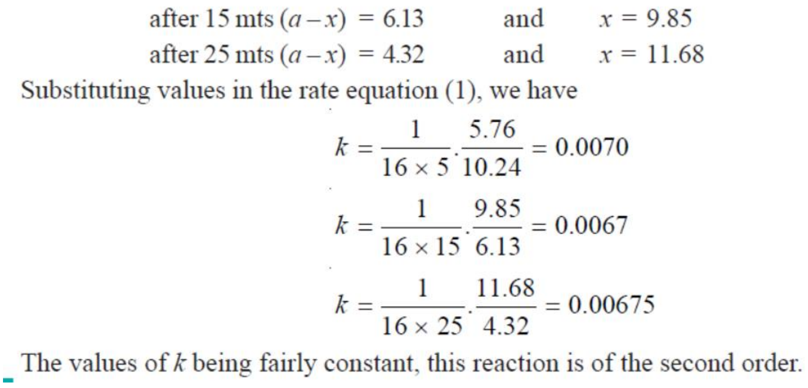
$$k = \frac{1}{at} \cdot \frac{x}{a(a-x)} \qquad \text{...(1)}$$

The volume of acid used at any time is a measure of concentration of the unreacted substances at that time.

Therefore,

a, initial concentration = 16.00

after 5 mts $(a-x) = 10.24$ and $x = 5.76$



after 15 mts $(a-x) = 6.13$ and $x = 9.85$

after 25 mts $(a-x) = 4.32$ and $x = 11.68$

Substituting values in the rate equation (1), we have

$$k = \frac{1}{16 \times 5} \cdot \frac{5.76}{10.24} = 0.0070$$

$$k = \frac{1}{16 \times 15} \cdot \frac{9.85}{6.13} = 0.0067$$

$$k = \frac{1}{16 \times 25} \cdot \frac{11.68}{4.32} = 0.00675$$

The values of k being fairly constant, this reaction is of the second order.

Third Order Reactions

Let us consider a simple third order reaction of the type

3A $\longrightarrow$ products

Let the initial concentration of A be a moles litre^{-1} and after time t, x, moles have reacted. Therefore, the concentration of A becomes (a – x). The rate law may be written as:

$\frac{dx}{dt} = k\ (a - x)^3$ -------(1)

Rearranging equation (1), we have,

$\frac{dx}{(a-x)3} = k\ dt$ --------------(2)

On integration, it gives,

$\frac{1}{2(a-x)2} = k\ t + I$ -------------(3)

Where, I is the integration constant. I can be evaluated by putting x = 0 and t = 0. Thus,

$I = \frac{1}{2a^2}$

By substituting the value of I in (3), we can write

$Kt = \frac{1}{2(a-x)} - \frac{1}{2a^2}$

Therefore, $k = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}$

This is the integrated rate equation for a third order reaction.

Units of Rate Constant

The units of rate constant for different orders of reactions are different.

Units of Zero order Rate constant

For a zero order reaction, the rate constant k is given by the expression

$K = \frac{d[A]}{dt} = \frac{mole}{litre}$.

Thus the units of k are

mol l^{-1} $time^{-1}$

Time may be given in seconds, minutes, days or years.

Units of First order Rate constant

The rate constant of a first order reaction is given by,

$K = \frac{2.303}{t} \log \frac{[A]_o}{[A]_t}$

Thus the rate constant for the first order reaction is independent of the concentration. It has the unit $time^{-1}$

Units of Second order Rate constant

The rate constant for a second order reaction is expressed as

$K = \frac{1}{t} \cdot \frac{x}{[A]_o\ ([A]_o - x)}$ or $\frac{concentration}{concentration\ .concentration} \cdot \frac{1}{time}$

$$\frac{1}{concentration} \cdot \frac{1}{time}$$

$\frac{1}{mole/litre} \cdot \frac{1}{time}$ = mol^{-1} l time $^{-1}$

Thus the units for k for a second order reactions are mol^{-1} 1 time^{-1}

Units of Third order Rate constant

The rate constant for a third order reaction is

$K = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2\,(a-x)^2}$

$K = \frac{concentration \times concentration}{(concentration)^2 \times (concentration)^2} \times \frac{1}{time}$

$K = \frac{1}{(concentration)^2} \times \frac{1}{time}$

$$\frac{1}{(\frac{mole}{litre})^2} \times \frac{1}{time}$$

Thus the units of k for third order reaction are mol^{-2} l^2 time^{-1}

Half–Life of a Reaction

Reaction rates can also be expressed in terms of half-life or half-life period. It is defined as: the time required for the concentration of a reactant to decrease to half its initial value. In other words, half-life is the time required for one-half of the reaction to be completed. It is represented by the symbol $t_{1/2}$ or $t_{0.5}$.

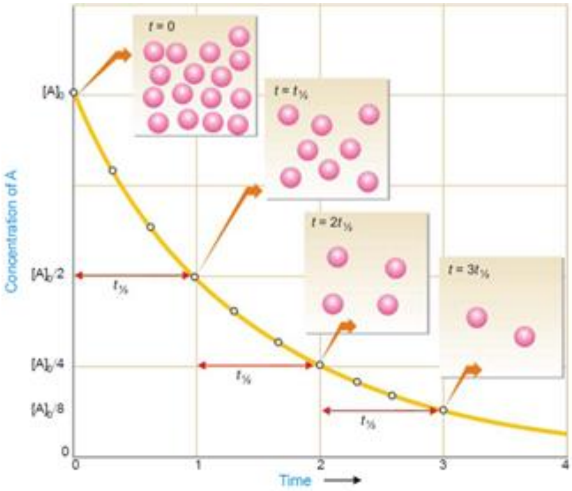


Figure 2.3: First-order half-life. Concentration of a reactant A as a function of time for a first-order reaction. The concentration falls from its initial value, $[A]_o$, to $[A]_o$ /2 after one half-life, to $[A]_o$ /4 after a second half-life, to $[A]_o$ /8 after a third half-life, and so on. For a first-order reaction, each half-life represents an equal amount of time.

Calculation of Half-life of a First order Reaction

The integrated rate equation (4) for a first order reaction can be stated as:

$$K = \frac{2.303}{t}\log\frac{[A]_o}{[A]}$$

Where, $[A]_0$ is initial concentration and [A] is concentration at any time t. Half-life, $t_{1/2}$, itime when initial concentration reduces to ½ ie.,

$[A] = \frac{1}{2}\ [A]_o$

Substituting values in the integrated rate equation, we have

$K = \frac{2.303}{t1/2}\log\frac{[A]_o}{1/2[A]_o} = \ \frac{2.303}{t1/2}\log 2$

$t_{1/2} = \frac{2.303}{k}\log 2 = \ \frac{2.303}{k}\ \times 0.3010$ or

$t_{½} = 0.693 / k$

It is clear from this relation that:

(1) half-life for a first order reaction is independent of the initial concentration.

(2) it is inversely proportional ot k, the rate-constant.

Calculation of Time for Completing any Fraction of the Reaction

As for half-change, we can calculate the time required for completion of any fraction of the reaction. For illustration, let us calculate the time in which two-third of the reaction is completed. First order integrated rate equation is

$t = \frac{2.303}{k}\log\frac{[A]_o}{[A]}$

Here, the initial concentration has 2/3 reacted reducing it to 1/3. Thus,

$[A] = \frac{1}{3}\ [A]_o$

Substituting values in the rate equation

$t_{¾} = \frac{2.303}{k}\log\frac{[A]_o}{1/3[A]_o} = \ \frac{2.303}{k}\log 3$

$= \frac{2.303}{k} \times 0.4771$

SOLVED PROBLEM 1. Compound A decomposes to form B and C the reaction is first order. At 25°C the rate constant for the reaction is 0.450 s^{-1}. What is the half-life of A at 25°C ?

SOLUTION

We know that for a first order reaction, half-life $t_{1/2}$, is given by the expression

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

where k = rate constant

Substituting the value of $k = 0.450\ s^{-1}$, we have

$$t_{1/2} = \frac{0.693}{0.450\,s^{-1}} = \mathbf{1.54\ s}$$

Thus half-life of the reaction $A \rightarrow B + C$ is 1.54 seconds.

SOLVED PROBLEM 2. The half-life of a substance in a first order reaction is 15 minutes. Calculate the rate constant.

SOLUTION

For a first order reaction

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

Putting $t_{1/2}$ = 15 min in the expression and solving for k, we have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{15\,\text{min}} = \mathbf{4.62 \times 10^{-2}\ min^{-1}}$$

SOLVED PROBLEM 3. For the reaction

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

the rate is directly proportional to $[N_2O_5]$. At 45°C, 90% of the N_2O_5 reacts in 3600 seconds. Find the value of the rate constant k.

SOLUTION

Since rate is $\propto [N_2O_5]$ it is first order reaction. The integrated rate equation is

$$k = \frac{2.303}{t} \log \frac{[N_2O_5]_0}{[N_2O_5]}$$

When 90% of N_2O_5 has reacted, the initial concentration is reduced to $\frac{1}{10}$ That is,

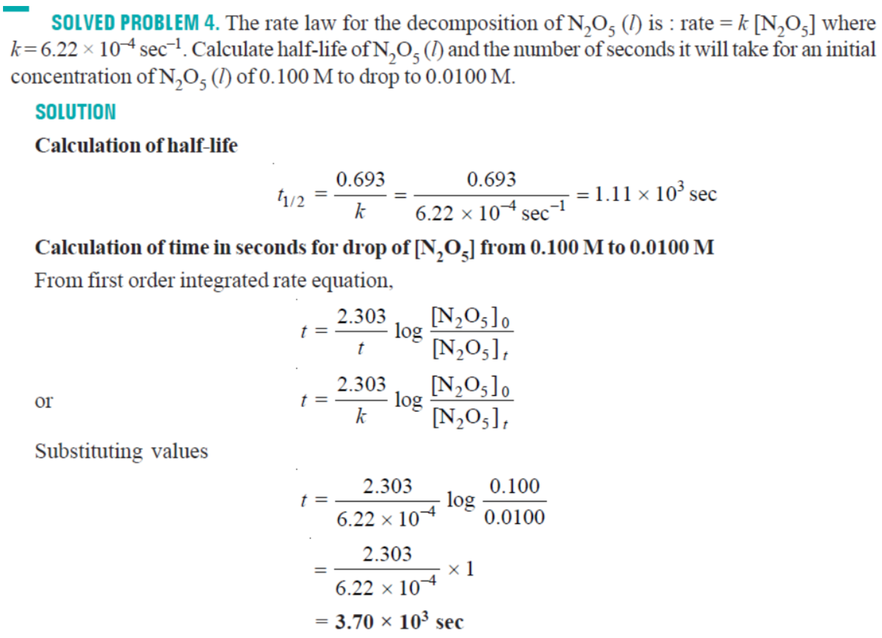
$$[N_2O_5] = \frac{1}{10}[N_2O_5]_0$$

Substituting values in the rate equation,

$$k = \frac{2.303}{3600} \log \frac{[N_2O_5]_0}{\frac{1}{10}[N_2O_5]_0}$$

$$= \frac{2.303}{3600} \log 10 = \frac{2.303}{3600} \times 1$$

Thus $$k = \frac{2.303}{3600} = \mathbf{6.40 \times 10^{-4}\ s^{-1}}$$



SOLVED PROBLEM 4. The rate law for the decomposition of N_2O_5 (*l*) is : rate = *k* [N_2O_5] where $k = 6.22 \times 10^{-4}$ sec^{-1}. Calculate half-life of N_2O_5 (*l*) and the number of seconds it will take for an initial concentration of N_2O_5 (*l*) of 0.100 M to drop to 0.0100 M.

SOLUTION

Calculation of half-life

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.22 \times 10^{-4}\ \text{sec}^{-1}} = 1.11 \times 10^3\ \text{sec}$$

Calculation of time in seconds for drop of [N_2O_5] from 0.100 M to 0.0100 M

From first order integrated rate equation,

$$t = \frac{2.303}{t} \log \frac{[N_2O_5]_0}{[N_2O_5]_t}$$

or

$$t = \frac{2.303}{k} \log \frac{[N_2O_5]_0}{[N_2O_5]_t}$$

Substituting values

$$t = \frac{2.303}{6.22 \times 10^{-4}} \log \frac{0.100}{0.0100}$$

$$= \frac{2.303}{6.22 \times 10^{-4}} \times 1$$

$$= \mathbf{3.70 \times 10^3\ sec}$$

Half-life for a Second order Reaction

For the simple second order reaction 2A → Products, the integrated rate equation is

$$kt = \frac{1}{[A]} - \frac{1}{[A]_o}$$

where, $[A]_0$ is the initial concentration and [A] is the concentration when time t has elapsed. When one-half life has elapsed.

$[A] = \frac{1}{2} = [A]_o$ and we have

$$kt_{1/2} = \frac{1}{1/2[A]_o} - \frac{1}{[A]_o} \quad \text{or}$$

$$kt_{1/2} = \frac{2}{[A]_o} - \frac{1}{[A]_o}$$

Solving for $t_{1/2}$ we find that

$$t_{½} = \frac{1}{k\,[A]_o}$$

As in case of a first order reaction, half-life for a second order reaction is inversely proportional to rate constant k. While half-life of a first order reaction is independent of initial concentration, half-life of a second order reaction depends on initial concentration. This fact can be used to distinguish between a first order and a second order reaction.

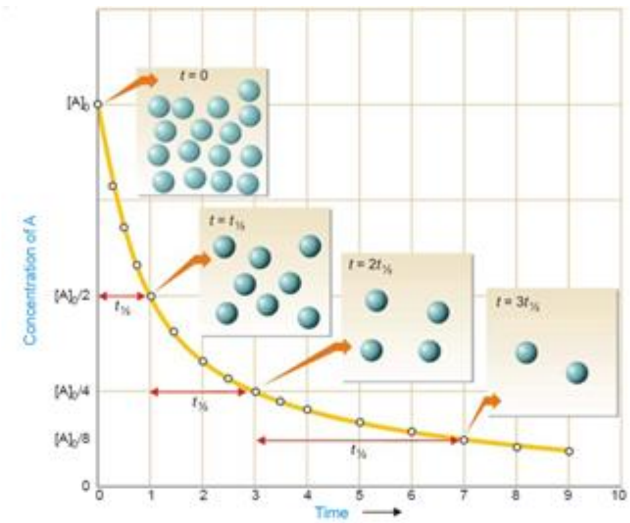


Figure 2.4: Second-order half-life. Concentration of a reactant A as a function of time for a second-order reaction. Note that each half-life is twice as long as the preceding one because $t = 1/k[A]_0$ and the concentration of A at the beginning of each successive half-life is smaller by a factor of 2.

Collision Theory of Reaction Rates

According to this theory, a chemical reaction takes place only by collisions between the reacting molecules. But not all collisions are effective. Only a small fraction of the collisions produce a reaction. The two main conditions for a collision between the reacting molecules to be productive are:

(1) The colliding molecules must posses sufficient kinetic energy to cause a reaction.

(2) The reacting molecules must collide with proper orientation.

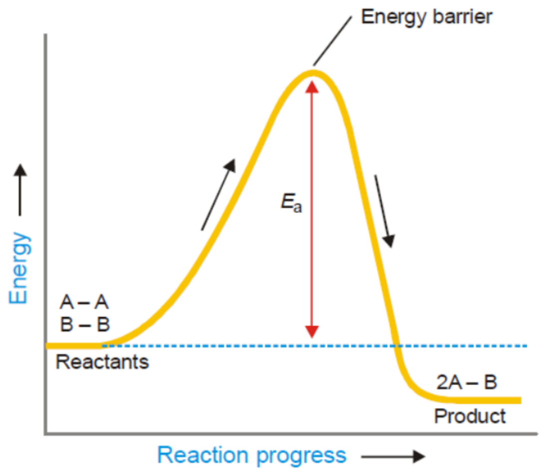
Now let us have a closer look at these two postulates of the collision theory.

(1) *The molecules must collide with sufficient kinetic energy*

Let us consider a reaction

$A-A + B-B \longrightarrow 2A-B$

A chemical reaction occurs by breaking bonds between the atoms of the reacting molecules and forming new bonds in the product molecules. The energy for the breaking of bonds comes from the kinetic energy possessed by the reacting molecules before the collision. Fig. 2.5 shows the energy of molecules A_2 and B_2 as the reaction $A_2 + B_2 \rightarrow 2AB$ progresses.



Figur 2.5: The energy of the colliding molecules as the reaction A + $B_2 \longrightarrow$ 2AB proceeds. The activation energy E_a provides the energy barrier.

The Fig. 2.5 also shows the activation energy, Ea, that is the minimum energy necessary to cause a reaction between the colliding molecules. Only the molecules that collide with a kinetic energy greater than Ea, are able to get over the barrier and react. The molecules colliding with kinetic energies less that Ea fail to surmount the barrier. The collisions between them are unproductive and the molecules simply bounce off one another.

(2) *The molecules must collide with correct orientation*

The reactant molecules must collide with favourable orientation (relative position). The correct orientation is that which ensure direct contact between the atoms involved in the breaking and forming of bonds. (Fig. 2.6) From the above discussion it is clear that: Only the molecules colliding with kinetic energy greater that Ea and with correct orientation can cause reaction.

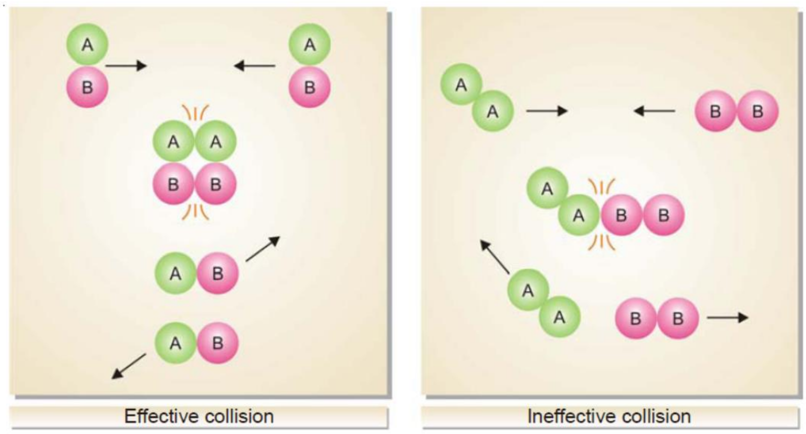


Figure 2.6: Orientations of reacting molecules A and B which lead to an effective and ineffective collision.

Collision Theory and Reaction Rate Expression

Taking into account the two postulates of the collision theory, the reaction rate for the elementary process.

$A + B \longrightarrow C + D$

is given by the expression, rate = f × p × z

where, f = fraction of molecules which possess sufficient energy to react; p = probable fraction of collisions with effective orientations, and z = collision frequency.

Effect of Increase of Temperature on Reaction Rate

It has been found that generally an increase of temperature increases the rate of reaction. As a rule, an increase of temperature by 10°C doubles the reaction rate. Thus the ratio of rate constants of a reaction at two different temperatures differing by 10 degree is known as Temperature Coefficient.

i.e., Temperature Coefficient = $\frac{k_{35^o}}{k_{25^o}} = \frac{k_{308}}{k_{298}}$ = 2 to 3

It has been found that generally an increase of temperature increases the rate of reaction. As a rule, an increase of temperature by 10°C doubles the reaction rate.

Temperature Dependence of Reaction Rate and Arrhenius Equation

We know that the kinetic energy of a gas is directly proportional to its temperature. Thus as the temperature of a system is increased, more and more molecules will acquire necessary energy greater that Ea to cause productive collisions. This increases the rate of the reaction.

In 1889, Arrhenius suggested as simple relationship between the rate constant, k, for a reaction and the temperature of the system.

k $= Ae^{-Ea}/RT$ -----------(1)

This is called the Arrhenius equation in which A is an experimentally determined quantity, E_a is the activation energy, R is the gas constant, and T is Kelvin temperature.

Taking natural logs of each side of the Arrhenius equation, it can be put in a more useful form:

ln k = $-\frac{E_a}{RT} + \ln A$ --------------(2)

$\log k = \frac{-E_a}{2.303\ RT} + \log A$ -----------(3)

If k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively, we can derive

$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R}[\frac{T2-T1}{T1\ T2}]$ ------------(4)

Arrhenius equation is valuable because it can be used to calculate the activation energy, Ea if the experimental value of the rate constant, k, is known.

Calculation of Ea Using Arrhenius Equation

In slightly rearranged form Arrhenius equation (2) can be written as

$$\begin{array}{ccccccc} 1\mathrm{n}\ k & = & -\frac{E_a}{R} & \left(\frac{1}{T}\right) & + & 1\mathrm{n}\ A & \\ \uparrow & & \uparrow & & & \uparrow & \\ y & = & mx & & + & b & \end{array} \qquad ...(3)$$

You can see that the equation (3) is that of a straight line, y = mx + b. The two variables in this equation are 1n k and 1/T. Thus if we plot the natural logarithm of k against 1/T, we get a straight line (Fig. 2.7). From the slope of the line, we can calculate the value of Ea.

Slope = $-\frac{E_a}{RT}$

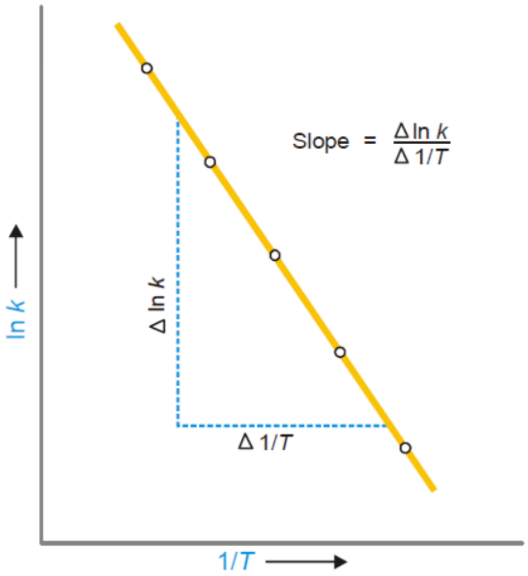
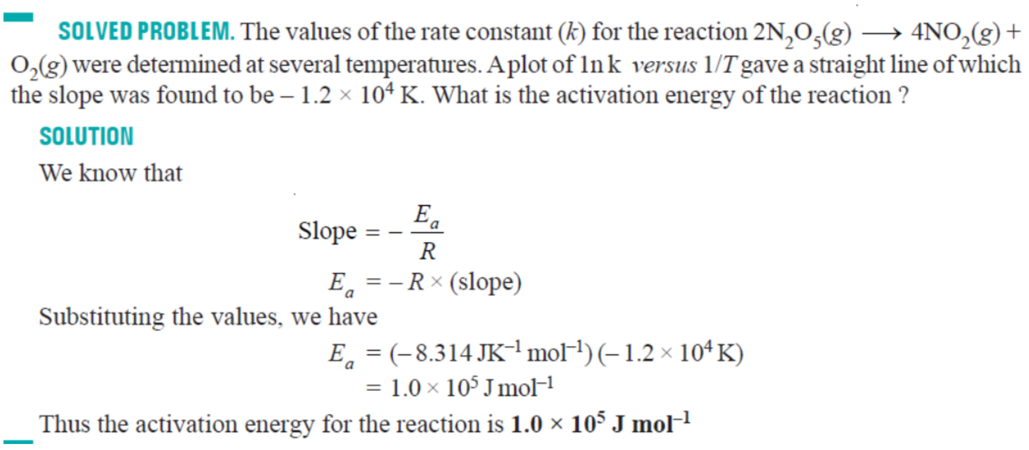


Figure 2.7: The plot of In k versus I/T gives a straight line. The slope of line ΔIn k/Δ I/T gives Ea using the expression given above.



SOLVED PROBLEM. The values of the rate constant (k) for the reaction $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ were determined at several temperatures. A plot of ln k *versus* $1/T$ gave a straight line of which the slope was found to be -1.2×10^4 K. What is the activation energy of the reaction ?

SOLUTION

We know that

$$\text{Slope} = -\frac{E_a}{R}$$

$$E_a = -R \times (\text{slope})$$

Substituting the values, we have

$$E_a = (-8.314\ \text{JK}^{-1}\ \text{mol}^{-1})(-1.2 \times 10^4\ \text{K})$$

$$= 1.0 \times 10^5\ \text{J mol}^{-1}$$

Thus the activation energy for the reaction is **1.0×10^5 J mol^{-1}**

Calculation of Ea from the Values of k at Two Temperatures

The rate constant, k, is measured at two temperatures. Ea, is then calculated using the formula that can be derived as follows from equation (3) above.

At temperature T_1, where the rate constant is k_1,

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \text{--------(1)}$$

At temperature T_2, where the rate constant is k_2,

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \quad \text{--------(2)}$$

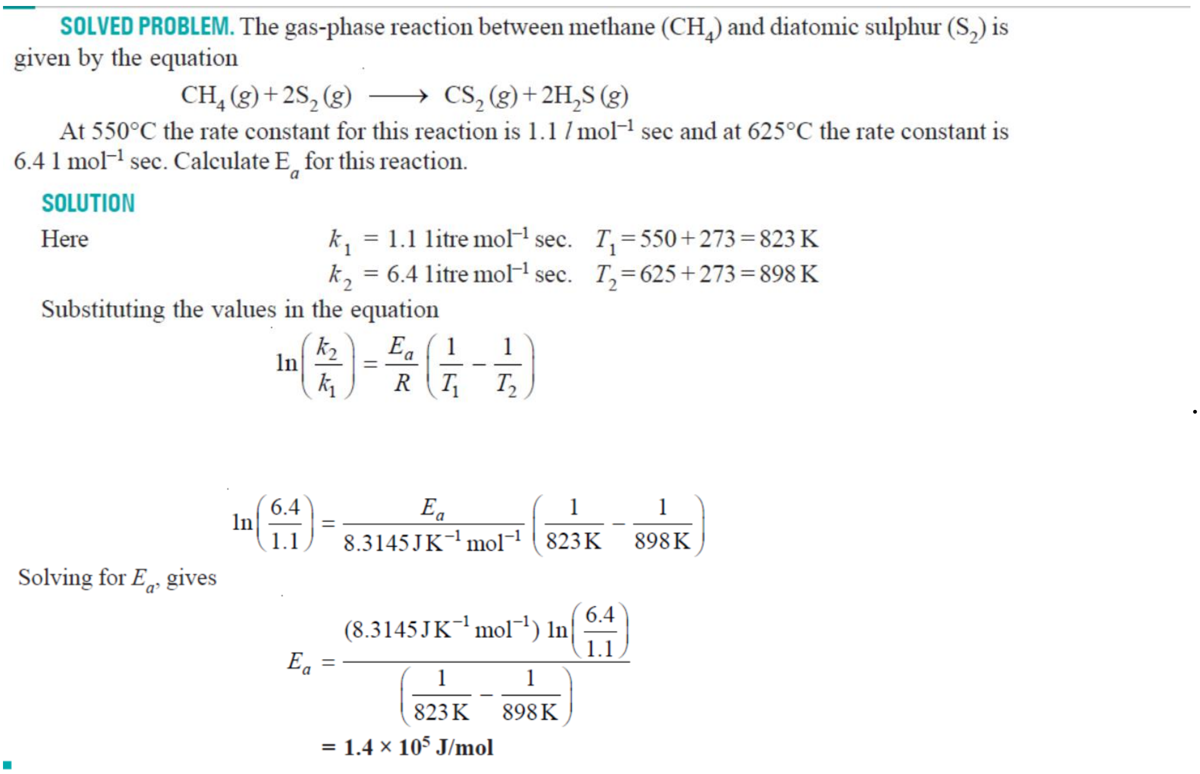
Subtracting the equation (1) from the equation (2), we have

$$\ln k_2 - \ln k_1 = [-\frac{E_a}{RT_2} + \ln A] - [-\frac{E_a}{RT_1} + \ln A\ ]$$

$$= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

$$\ln [\frac{k_2}{k_1} = \frac{E_a}{R}\ [\frac{1}{T_1} - \frac{1}{T_2}] \text{ or } \log\frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\ [\frac{T_2 - T_1}{T_1 T_2}]$$

Thus the values of k_1 and k_2 measured at T_1 and T_2 can be used to find E_a



SOLVED PROBLEM. The gas-phase reaction between methane (CH_4) and diatomic sulphur (S_2) is given by the equation

$$CH_4\,(g) + 2S_2\,(g) \longrightarrow CS_2\,(g) + 2H_2S\,(g)$$

At 550°C the rate constant for this reaction is 1.1 l mol^{-1} sec and at 625°C the rate constant is 6.4 1 mol^{-1} sec. Calculate E_a for this reaction.

SOLUTION

Here k_1 = 1.1 litre mol^{-1} sec. $T_1 = 550 + 273 = 823\,K$

k_2 = 6.4 litre mol^{-1} sec. $T_2 = 625 + 273 = 898\,K$

Substituting the values in the equation

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{6.4}{1.1}\right) = \frac{E_a}{8.3145\,J\,K^{-1}\,mol^{-1}}\left(\frac{1}{823\,K} - \frac{1}{898\,K}\right)$$

Solving for E_a, gives

$$E_a = \frac{(8.3145\,J\,K^{-1}\,mol^{-1})\,\ln\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{823\,K} - \frac{1}{898\,K}\right)}$$

$$\mathbf{= 1.4 \times 10^5\ J/mol}$$

Limitations of the Collision Theory

The collision theory of reaction rates is logical and correct. However, it has been oversimplified and suffers from the following weaknesses.

(1) The theory applies to simple gaseous reactions only. It is also valid for solutions in which the reacting species exist as simple molecules.

(2) The values of rate constant calculated from the collision theory expression (Arrhenius equation) are in agreement with the experimental values only for simple bimolecular reactions. For reactions involving complex molecules, the experimental rate constants are quite different from the calculated values.

(3) There is no method for determining the steric effect (p) for a reaction whose rate constant has not been determined experimentally.

(4) In the collision theory it is supposed that only the kinetic energy of the colliding molecules contributes to the energy required for surmounting the energy barrier. There is no reason why the rotational and vibrational energies of molecules should be ignored.

(5) The collision theory is silent on the cleavage and formation of bonds involved in the reaction. The various drawbacks in the simple collision theory do not appear in the modern transition-state theory.

Transition State Theory or Absolute Reaction Rate Theory (ARRT)

The transition state or activated complex theory was developed by Henry Erying (1935). This theory is also called the absolute rate theory because with its help it is possible to get the absolute value of the rate constant. The transition state theory assume that simply a collision between the reactant molecules does not really causes a reaction. During the collision, the reactant molecules form a transition state or activated complex which decomposes to give the products.

Thus,

$$\underset{\text{Reactants}}{A + B\text{—}C} \longrightarrow \underset{\text{Activated complex}}{ABC^{\ddagger}} \longrightarrow \underset{\text{Products}}{A \text{ — } B + C}$$

The double dagger superscript (‡) is used to identify the activated complex.

The transition state theory may be summarised as follows:

(1) In a collision, the fast approaching reactant molecules (A and BC) slow down due to gradual repulsion between their electron clouds. In the process the kinetic energy of the two molecules is converted into potential energy.

(2) As the molecules come close, the interpenetration of their electron clouds occurs which allows the rearrangement of valence electrons.

(3) A partial bond is formed between the atoms A and B with corresponding weakening of B – C bond. This leads to formation of an activated complex or transition state. The activated complex is momentary and decomposes to give the products (A–B + C).

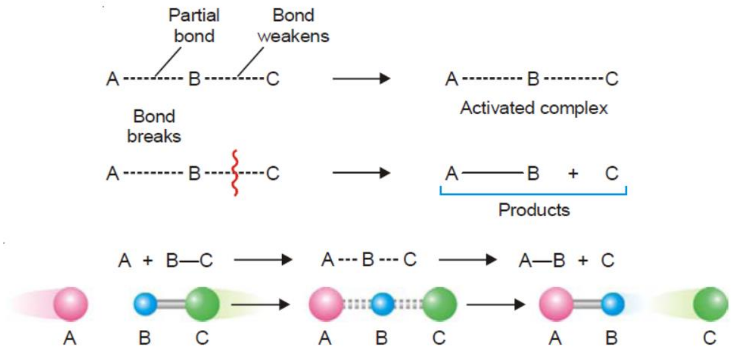


Fig. 2.8: The activated complex theory may be illustrated by the reaction energy diagram

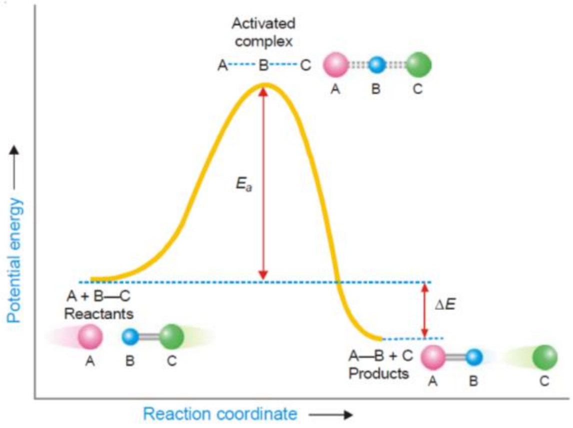


Figure 2.9: Change of potential energy during a collision between the reactant molecules for an exothermic reaction.

Here the potential energy of the system undergoing reaction is plotted against the reaction coordinate (the progress of the reaction). The difference in the potential energy between the reactants and the activated complex is the activation energy, Ea. The reactants must have this minimum energy to undergo the reaction through the transition state. As evident from the energy diagram, energy is required by the reactants to reach the transition state. Also, the energy is obtained in passing from the transition state to the products. If the potential energy of the products is less than that of the reactants (Fig. 2.10) the energy obtained in going from the activated complex to products will be more than the activation energy (Ea). Thus such a reaction will be exothermic.

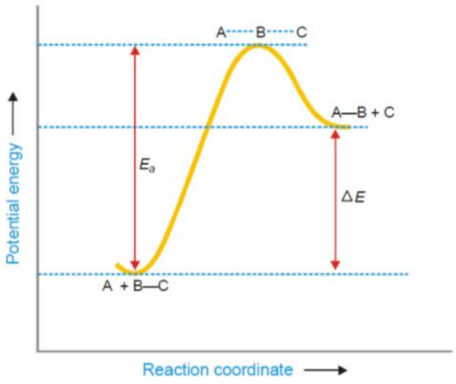


Figure 2.10: A potential energy diagram for an endothermic reaction.

On the other hand, if the potential energy of the products is greater than that of the reactants, the energy released in going from the activated complex to products will be less than the activation energy and the reaction will be endothermic.

Activation Energy and Catalysis

We know that for each reaction a certain energy barrier must be surmounted. As shown in the energy diagram shown in Fig. 2.8, the reactant molecules must possess the activation energy, Ea, for the reaction to occur.

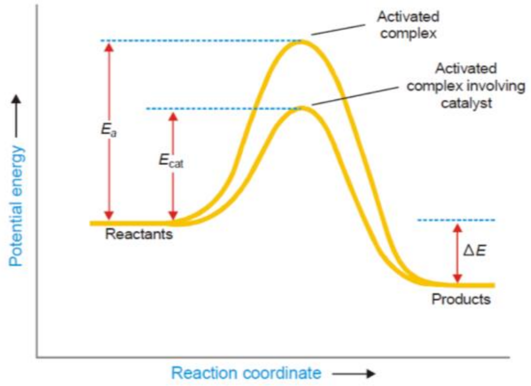


Figure 2.8: Energy diagram for a catalysed and uncatalysed reaction showing a lowering of activation energy by a catalyst.

The catalyst functions by providing another pathway with lower activation energy, Ecat. Thus a much large number of collisions becomes effective at a given temperature. Since the rate of reaction is proportional to effective collisions, the presence of a catalyst makes the reaction go faster, other conditions remaining the same. It may be noted from the above diagram that although a catalyst lowers the activation energy, the energy difference, ΔE, between products and reactants remains the same.

Lindeman's Theory of Unimolecular Reactions

A number of unimolecular reactions, for example,

$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

are found to be of the first order. It is difficult to account for such reactions using the collision theory and the absolute reaction rate theory. If two molecules must collide in order to provide necessary activation energy, a second order rate law should result. In 1922, Lindeman explained this anomaly by assuming that there existed a time lag between activation and reaction of molecules. During this time lag, the activated molecules could either react or be deactivated. Thus,

$A + A \longrightarrow A + A^*$ activation ...(1)

A + A* ──→ A + A deactivation ...(2)

A* ──→ products reaction ...(3)

If the time lag is long, step (3) is slow, the reaction should follow first order kinetics. However, if A reacts as soon as formed, step (2) is the slow step, then the reaction should be second order. The proof of Lindeman’s theory is provided by studying the effect of change of pressure on the reaction. At high pressure the rate of deactivation will be dominant. On the other hand, at sufficiently low pressure all the activated molecules will react before they can be deactivated. Therefore the reaction kinetics should change from first order to second order with decreasing pressure. Several gases are known to exhibit this behaviour.

Simultaneous Reactions

Sometimes there are some side reactions accompanying the main chemical reaction. Such reactions are known as complex reactions as these do not take place in a single step. In other words, such complex reactions proceed in a series of steps instead of a single step and the rate of overall reaction is in accordance with the stoichiometric equation for that reaction. Generally, following types of complications occur.

(1) Consecutive reactions

(2) Parallel reactions

(3) Reversible or opposing reactions

These are discussed as follows:

(1) Consecutive Reactions

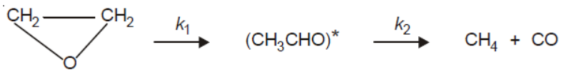
The reactions in which the final product is formed through one or more intermediate steps are called consecutive reactions. These are also known as sequential reactions.

Examples of first order consecutive reactions

(*a*) Decomposition of dimethyl ether is gaseous phase

$$CH_3COCH_3 \xrightarrow{k_1} CH_4 + HCHO \xrightarrow{k_2} H_2 + CO$$

(*b*) Decomposition of Ethylene oxide



(*c*) Any radioactive decay of the type

$$^{218}_{84}Po \xrightarrow{-\alpha} {}^{214}_{82}Pb \xrightarrow{-\beta} {}^{214}_{83}Bi \xrightarrow{-\beta} {}^{214}_{84}Po$$

Kinetics of consecutive reactions

In such reactions the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction. Various step reactions can be written for the overall reaction as shown below:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

	A	B	C
Initial concentration	$[A]_o$	0	0
Concentration after time t	[A]	[B]	[C]

In the above reaction the product C is formed from the reactant A through intermediate B. In this reaction each stage has its own different rate constants k_1 for the first step and k_2 for the second step. The net or overall rate of reaction depends upon the magnitude of these two rate constants. The initial concentration and concentration after time t are shown below each species in above reaction under consideration.

$$[A]_0 = [A] + [B] + [C]$$

The differential rate expressions are,

$$\frac{-d[A]}{dt} = k_1 [A]$$

$$\frac{d\,[B]}{dt} = k_1\,[A] - k_2\,[B]$$

$$\frac{d(C)}{dt} = k_2\,[B]$$

During the course of the reaction the concentration of A, B and C vary as shown in the Fig. 2.9

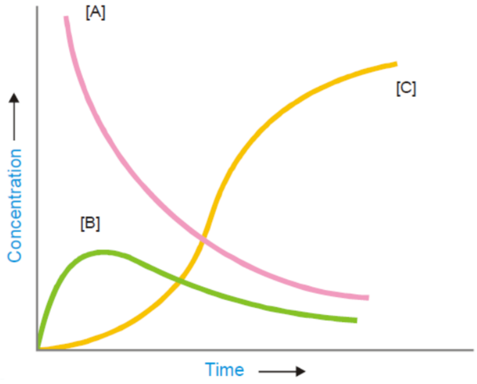


Figure 2.9: Variation of concentration of reactants and products in a consecutive reaction.

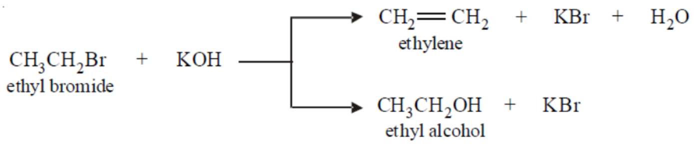
From the Fig 2.9 it is clear that the concentration of A decreases exponentially, the concentration of B first increases and then decreases and that of C increases (from zero) with time and finally attains the value equal to $[A]_0$ (initial concentration A) when all A has changed into the final product C.

(2) Parallel or Side Reactions

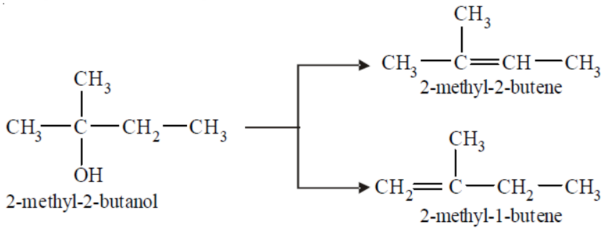
In these reactions the reacting substance follows two or more paths to give two or more products. The preferential rate of such may be changed by varying the conditions like pressure, temperature or catalyst. The reaction in which the maximum yield of the products is obtained is called the main or major reaction while the other reaction (or reactions) are called side or parallel reactions.

Examples of Parallel or Side Reaction

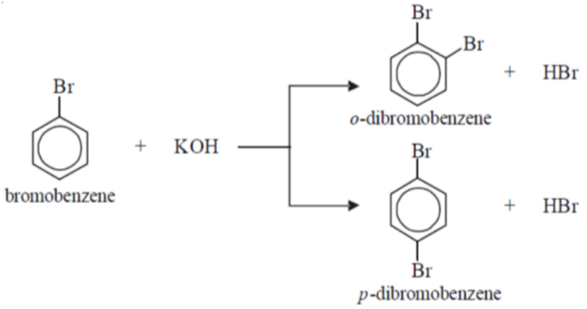
(*a*) Reaction of ethyl bromide with potassium hydroxide



(*b*) Dehydration of 2-methyl–2–butanol



(*c*) Bromination of bromobenzene



(3) Reversible or Opposing Reactions

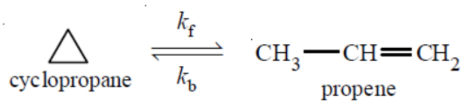
In reversible or opposing reactions the products formed also react to give back the reactants. Initially, the rate of forward reaction is very large which decreases with passage of time and the rate of backward or reverse reaction is zero which increases with passage of them. A stage is reached when two rates become equal. This situation is called the chemical equilibrium. It is dynamic in nature i.e., all the species are reaching at the rate at which they are being formed.

Examples of Reversible or Opposing Reactions

(*a*) Dissociation of hydrogen iodides

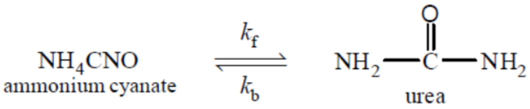
$$2HI \underset{k_b}{\overset{k_f}{\rightleftharpoons}} H_2 + I_2$$

(*b*) Isomerisation of cyclopropane into propene



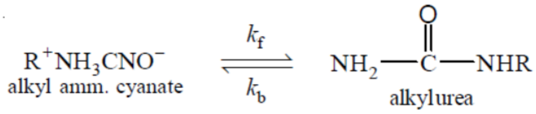
$$\underset{\text{cyclopropane}}{\triangle} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{\text{propene}}{CH_3-CH=CH_2}$$

(*c*) Isomerisation of ammonium cyanate into urea in aqueous solution.



$$\underset{\text{ammonium cyanate}}{NH_4CNO} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{\text{urea}}{NH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2}$$

(*d*) Isomerisation of alkyl ammonium cyanate into substituted urea in aqueous solution



$$\underset{\text{alkyl amm. cyanate}}{R^+NH_3CNO^-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{\text{alkylurea}}{NH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NHR}$$

(*e*) Reaction between gaseous CO and NO_2

$$CO(g) + NO_2(g) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CO_2(g) + NO(g)$$

UNIT-III

Adsorption

When a solid surface is exposed to a gas or a liquid, molecules from the gas or the solution phase accumulate or concentrate at the surface.

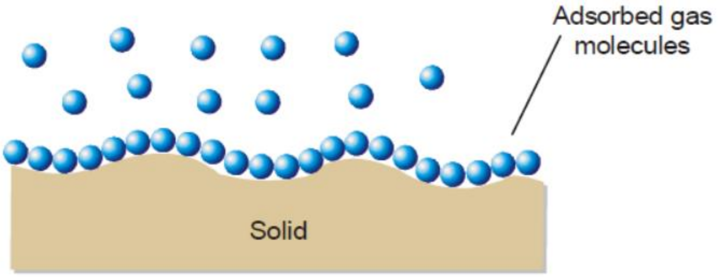


Figure 3.1: Adsorption of a gas at a solid surface.

The phenomenon of concentration of molecules of a gas or liquid at a solid surface is called adsorption. The substance that deposits at the surface is called Adsorbate and the solid on whose surface the deposition occurs is called the Adsorbent.

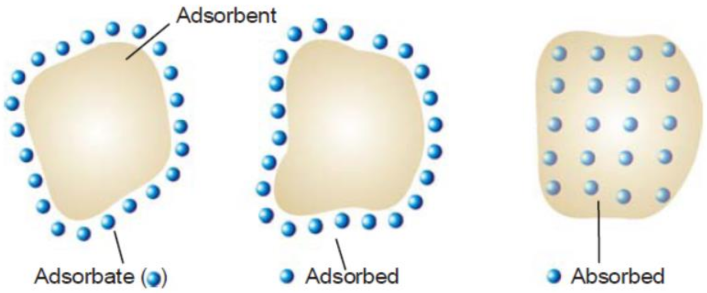


Figure 3.2: Adsorption versus absorption.

Examples of Adsorption

(1) Adsorption of a dye by a charcoal. If finely divided charcoal is stirred into a dilute solution of methylene blue (an organic dye), the depth of colour of the solution decreases appreciably. The dye molecules have been adsorbed by charcoal particles.

(2) Adsorption of a gas by charcoal. If a gas (SO_2, Cl_2, NH_3) is treated with powdered charcoal in a closed vessel, the gas pressure is found to decrease. The gas molecules concentrate on charcoal surface and are said to be adsorbed.

Adsorption versus Absorption

The term ‘adsorption’ must be carefully distinguished from another like-sounding term ‘absorption’. While adsorption implies deposition at the surface only, absorption implies penetration into the body of the solid (Fig. 3.2). For illustration a chalk crayon when dipped in ink adsorbs the latter and on breaking it is found to be white from within. On the other hand, water is absorbed by a sponge and is distributed throughout the sponge uniformly. Both adsorption and absorption often take place side by side. It is thus difficult to distinguish between the two processes experimentally. Mc. Bain introduced the general term Sorption which includes both the adsorption and absorption.

Mechanism of Adsorption

Atoms or molecules of a solid surface behave like the surface molecules of a liquid. These are not surrounded by atoms or molecules of their kind. Therefore, they have unbalanced or residual attractive forces on the surface which can hold adsorbate particles.

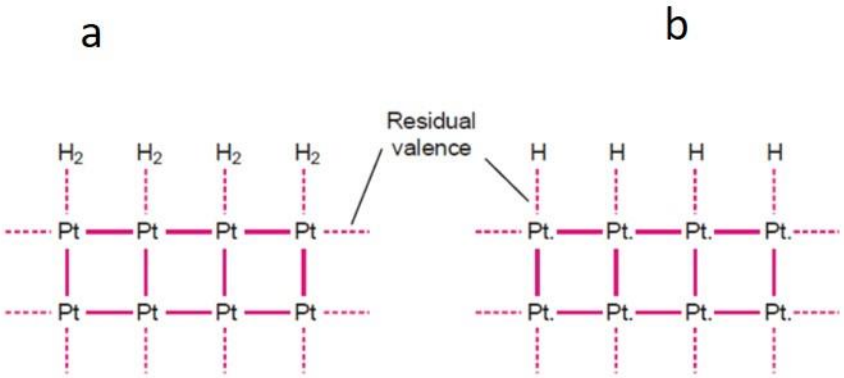


Figure 3.3: a) Hydrogen adsorbed molecularly on platinum and b) Hydrogen adsorbed atomically on platinum.

The adsorbed atoms or molecules can be held on the surface of a metal such as platinum (Pt) by physical van der Waal’s force or chemical forces due to residual valence bonds. Thus the adsorption of hydrogen on platinum may take place in two ways (molecularly or atomically as shown above).

Types of Adsorption

The adsorption of a gas into a solid surface is mainly of two types:

(a) Physical Adsorption

This is due to the gas molecules being held to the solid surface by van der Waal's attractive forces. It is also referred to as van der Waal's Adsorption. For example, adsorption of hydrogen or oxygen on charcoal is Physical Adsorption.

(b) **Chemical Adsorption or Chemisorption**

In this kind of adsorption, the gas molecules or atoms are held to the solid surface by chemical bonds. These bonds may be covalent or ionic in nature. For example, hydrogen is chemisorbed on nickel. Hydrogen molecules is first adsorbed by van der Waal's forces and then dissociates. The hydrogen atoms are thus chemisorbed on nickel.

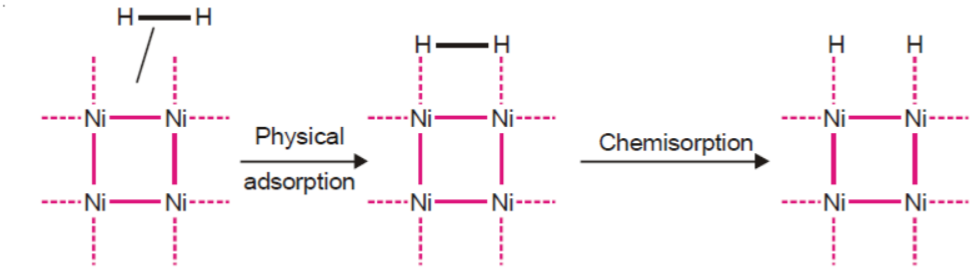


Figure 3.4: Hydrogen dissociates before it is chemisorbed on nickel.

Characteristic Features

The adsorption of gases by solid adsorbents has certain characteristic feature. Physical adsorption and chemisorption are found to differ in many respects.

(1) Adsorption and Surface area

Adsorption being a surface phenomenon, the extent of adsorption depends on the surface area. Increase in the surface area of the adsorbent, increases the total amount of the gas adsorbed. Thus finely divided metals (nickel, platinum) and porous substances (charcoal, silica gel) provide a large surface area and are best solid adsorbents.

(2) Nature of Gas

The amount of gas adsorbed by a solid depends on the nature of the gas. In general, more easily liquefiable a gas is (i.e., higher its critical temperature), the more readily will it be adsorbed. Thus 1 g of activated charcoal adsorbs 380 ml of sulphur dioxide (critical temperature 157°C), 16 ml of methane (critical temperature – 83°C) and 4.5 ml of hydrogen (critical temperature – 20°C). Chemisorption on the other hand, is much more specific than physical adsorption.

However, it will not occur when there is some possibility of chemical action between the gas adsorbed and the solid.

(3) Heats of Adsorption

Heat of adsorption is defined as the energy liberated when 1 gm mole of a gas is adsorbed on the solid surface. In physical adsorption, gas molecules concentrate on the solid surface. Thus it is similar to the condensation of a gas to liquid. Therefore, adsorption like condensation is an exothermic process. Since the attractions between gas molecules and solid surface are due to relatively weak van der Waal's forces, heats of adsorption are small (about 5 kcal mol^{-1}). In chemisorption the attractive forces are due to the formation of true chemical bonds. Therefore, the heats of adsorption are large (20 to 100 kcal mol^{-1}).

(4) Reversible character

Physical adsorption is a reversible process. The gas adsorbed onto a solid can be removed (desorbed) under reverse conditions of temperature and pressure. Thus, Chemisorption, on the contrary, is not reversible because a surface compound is formed.

$$\text{Gas} \rightleftharpoons \text{Gas/Solid} + \text{Heat}$$

(5) Effect of temperature

Physical adsorption occurs rapidly at low temperature and decreases with increasing temperature (Le Chatelier's Principle). Chemisorption, like most chemical changes, generally increase with temperature. Thus a rise of temperature can often cause physical adsorption to change to chemisorption. Nitrogen, for example, is physically adsorbed on iron at 190°C but chemisorbed to form a nitride at 500°C.

(6) Effect of pressure

Since a dynamic equilibrium exists between the adsorbed gas and the gas in contact with the solid. Le Chatelier's Principle is applied. Actually it has been found that increase of pressure leads to increase of adsorption and decrease of pressure causes desorption.

(7) Thickness of Adsorbed layer of gas

From a study of the isotherms relating to the amount of gas adsorbed to the equilibrium pressure, Langmuir showed that at low pressure, the physically adsorbed gas forms only one molecular thick layer. However, above a certain pressure, multi-molecular thick layer is formed.

Comparison of Physical Adsorption and chemical Adsorption

Physical Adsorption	Chemical Adsorption
Caused by intermolecular van der Waal's forces.	Caused by chemical bond formation.
Depends on nature of gas. Easily liquefiable gases are adsorbed readily.	Much more specific than physical Adsorption.
Heat of adsorption is small (about 5 kcal mol^{-1}).	Heat of adsorption is large (20–100 kcal mol^{-1}).
Reversible.	Irreversible.
Occurs rapidly at low temperature; decreases with increasing temperature.	Increases with increase of temperature.
Increase of pressure increases adsorption; decrease of pressure causes desorption.	Change of pressure has no such effects.
Forms multimolecular layers on adsorbent surface.	Forms unimolecular layer.

Adsorption Isotherms

The adsorption of a gas on a solid adsorbent in a closed vessel is a reversible process.

Free Gas $\rightleftarrows$ Gas adsorbed on solid

The amount of the gas adsorbed depends on equilibrium pressure (P) and temperature. The relationship between the equilibrium pressure of a gas and its amount adsorbed on the solid adsorbent at any constant temperature is called an Adsorption isotherm. It may be given in the form of an equation or graphical curve.

Freundlich Adsorption Isotherm

Freundlich proposed an empirical relation in the form of a mathematical equation.

$$\frac{w}{m} = k\,P^{1/n}$$

Where, w is the mass of the gas adsorbed on a mass m of adsorbent at a pressure P; k and n are constants depending on the nature of the gas and the adsorbent and on temperature. This relation is generally represented in the form of a curve obtained by plotting the mass of the gas adsorbed per unit mass of adsorbent (w/m) against equilibrium pressure.

Freundlich isotherm is not applicable at high pressures. Taking logarithms on both sides of Freundlich equation, we have

$$\log w/m = logk + \frac{1}{n}\log P$$

This is equation for a straight line. Thus a plot of log (w/m) against log P should be a straight line with slope 1/n and intercept log k. However, it is actually found that the plots were straight lines at low pressures, while at higher pressure they showed a slight curvature, especially at low temperature. This indicated that Freundlich equation is approximate and does not apply to adsorption of gases by solids at higher pressures.

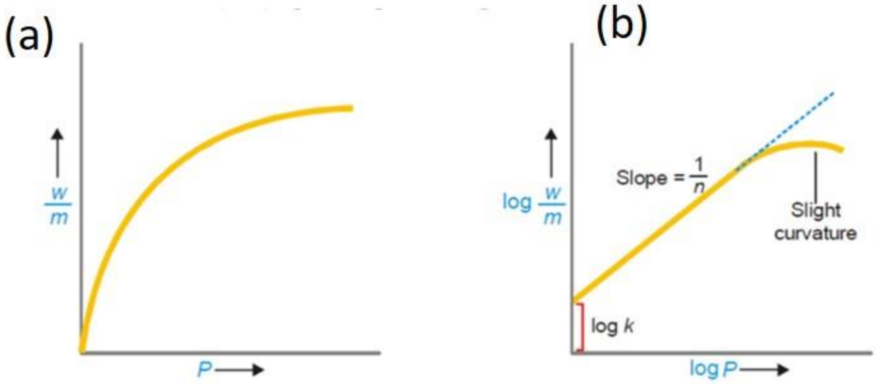


Figure 3.5: (a) Freundlich isotherm; a plot of mass of adsorbed gas per unit mass of adsorbent. (b) Plot of log w/m against log P shows slight curvature at higher pressures.

Langmuir Adsorption Isotherm

Langmuir (1916) derived a simple adsorption isotherm based on theoretical considerations. It was named after him.

Assumptions

Langmuir made the following assumptions.

(1) The layer of the gas adsorbed on the solid adsorbent is one-molecule thick.

(2) The adsorbed layer is uniform all over the adsorbent.

(3) There is no interaction between the adjacent adsorbed molecules.

Derivation of Langmuir Isotherm

Langmuir considered that the gas molecules strike a solid surface and are thus adsorbed. Some of these molecules then evaporate or are ‘desorbed’ fairly rapidly. A dynamic equilibrium is eventually established between the two opposing processes, adsorption and desorption. If θ is the fraction of the total surface covered by the adsorbed molecules, the fraction of the naked area is (1 – θ). The rate of desorption (Rd) is proportional to the covered surface θ. Therefore,

$R_d = k_d \theta$

Where, kd is the rate constant for the desorption process. The rate of adsorption (Ra) is proportional to the available naked surface $(1 - \theta)$ and the pressure (P) of the gas.

$Ra = ka\ (1 - \theta)\ P$

Where, ka is rate constant for the adsorption process.

At equilibrium the rate of desorption is equal to the rate of adsorption. That is,

$K_d\ \theta = k_a\ (1-\theta)\ P$

$$\Theta = \frac{kaP}{ka+ka\ P}$$

$$\Theta = \frac{(ka\ /kd)\ P}{1 + (Ka\ /\ kd\ )\ P}$$

$$\Theta = \frac{K\ P}{1 + K\ P}$$

Where, K is the equilibrium constant and is referred to as the adsorption coefficient. The amount of the gas adsorbed per gram of the adsorbent, x, is proportional to θ.

Hence, $x\ \alpha\ \frac{K\ P}{1+K\ P}$

$$X = K'\ \frac{K\ P}{1 + K\ P} \qquad \text{---------}\ (1)$$

Where, K' is a new constant. Equation (1) gives the relation between the amounts of gas adsorbed to the pressure of the gas at constant temperature and is known as Langmuir Adsorption isotherm. In order to test the Langmuir isotherm, equation (1) is rearranged so that

$$\frac{P}{x} = \frac{1}{K'} + \frac{P}{K''}\text{------------}(2)$$

Where, K" constant = K'/K.

The equation (2) is similar to an equation for a straight line. Thus if P/x is plotted against P, we should get a straight line with slope 1/K" and the intercept 1/K'. It was found in most cases that the actual curves were straight lines. Thus Langmuir isotherm stood verified.

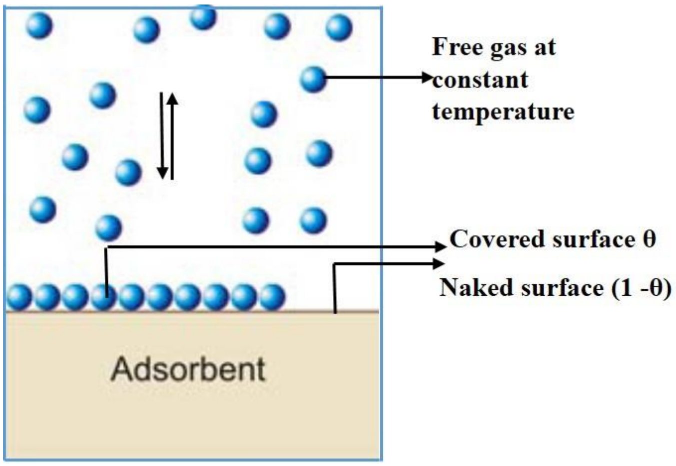


Figure 3.6: Dynamic equilibrium exists between free molecules and those adsorbed on the fraction of adsorbent surface.

Langmuir Isotherm holds at low pressures but fails at high pressures

As stated above, Langmuir Adsorption isotherm may be written as

$$\frac{P}{x} = \frac{1}{K'} + \frac{P}{K''}$$

If the pressure (P) is very low, the factor P/K" may be ignored and the isotherm assumes the form

x = K' P (at low pressure)

If the pressure (P) is very high, the factor 1/K' may be ignored and the isotherm becomes

x = K" (at high pressure)

Hence, at low pressures, the amount of gas adsorbed (x) is directly proportional to pressure (P).

At high pressures the mass adsorbed reaches a constant value K" when the adsorbent surface is completely covered with a unimolecular layer of the gas. At this stage adsorption is independent of pressure.

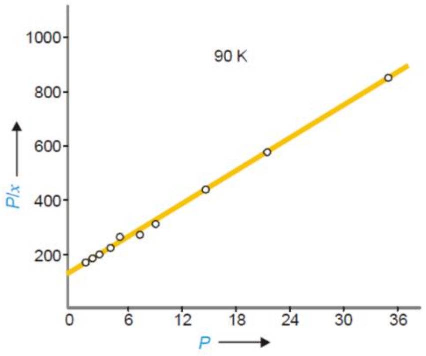


Figure 3.7: Verification of Langmuir isotherm for adsorption of N2 on mica at 90 K.

BET theory

- This equation is an extention of the interpretation of the monomolecular layer adsorption.
- The derivation is based on the same kinetic picture and the assumption that the condensation forces are the principle forces (or) the main force is adsorption
- As in langomuer theory the rate of evaporation from the first layer is equal to the rate of condensation on each bare (or) uncovered surface.
- Additionally the rate of evaporation from each successiting layer is equal to the rate of condensation and proceeding layer.
- The heat of adsorption is expontially involved and each of the equilibrium evaporation rate expression.
- The heat of adsorption in each layer other than the first is equal to the heat of liquification of the bulk adsorbate material.

BET eqn. is derived based on the above postulates

- Let $S_0, S_1, S_2 \cdots S_i$ represent surface area of the adsorbent that is covered by $S_0, = 1, 2, 3 \cdots i$ layers of the adsorbed molecule.

At equilibrium S_0 must remain constant the rate of condensation on the bare surface is equal to the rate of evaporation from the first layer.

The rate of adsorption (or) condensation is proportional to the pressure of the gas.

Rate of condensation directly proportion to $S_0 p$. Rate of condensation $\propto S_0 p$.

$$\text{Rate of condensation} = a_1 S_0 p \quad ①$$

where a_1 is the proportionality constant

The rate of evaporation is proportional to the surface which is covered that is $k_2 S_1$

$$\text{The rate of evaporation} = b_1 S_1 e^{-E/RT} \quad ②$$

According to postulates rate of condensation is equal to rate of evaporation

$$a_1 p s_0 = b_1 S_1 e^{-E_1/RT} \quad ③$$

$$a_2 p S_1 = b_2 S_2 e^{-E_2/RT} \quad ④$$

$$a_3 p S_2 = b_3 S_3 e^{-E_3/RT} \quad ⑤$$

$$\vdots$$

$$a_i p S_{i-1} = b_i S_i e^{-E_i/RT} \quad ⑥$$

The total surface area of the catalyst is given by
adsorbent

$$A = \sum_{i=0}^{\infty} S_i \quad ⑦$$

The total Volume adsorbed is gn. by adsorbate

$$V = V_0 \sum_{i=0}^{\infty} i S_i \quad ⑧$$

⑧/⑦ $$V/A = \frac{V_0 \sum_{i=0}^{\infty} i S_i}{\sum_{i=0}^{\infty} S_i} \quad (\text{or})$$

$$\frac{V}{AV_0} = \frac{\sum_{i=0}^{\infty} i S_i}{\sum_{i=0}^{\infty} S_i}$$

where AV_0 = Volume of the gas adsorbed, when the entire adsorbent surface is covered with the complete unimolecular layer.

$$\frac{V}{AV_0} = \frac{V}{V_m} = \frac{\sum_{i=0}^{\infty} i S_i}{\sum_{i=0}^{\infty} S_i} \quad Ⓐ$$

V_m = adsorbent

In order to simplify the equation, two assumptions are made here,

i) $E_1 = E_2 = E_3 \cdots = E_i = E_L \rightarrow E_L$

ii) $b_2/a_2 = b_3/a_3 \cdots b_i/a_i = g$

take eqn. ③

$$b_1 S_1 e^{-E_1/RT} = a_1 p S_0$$

$$S_1 = \frac{(a_1/b_1) p S_0}{e^{-E_1/RT}} = \frac{a_1}{b_1} p S_0 e^{E_1/RT}$$

$$= \left(\frac{p}{g}\right) e^{E_1/RT} S_0 \qquad \left(\begin{matrix} b_1/a_1 = g. \\ a_1/b_1 = 1/g \end{matrix}\right)$$

②

$$S_1 = \left(P/g\right) e^{E_1/RT} S_0$$

$$\boxed{S_1 = y S_0} \quad \text{where } \left(y = P/g \; e^{E_1/RT}\right)$$

eqn. ④

$$b_2 S_2 e^{-E_2/RT} = a_2 P S_1$$

$$S_2 = \frac{(a_2/b_2) P S_1}{e^{-E_2/RT}} = (a_2/b_2) P S_1 e^{E_2/RT}$$

$$S_2 = (P/g) e^{E_2/RT} S_1 \qquad y = (P/g) e^{E_2/RT}$$

$$S_2 = x S_1$$

$$\boxed{S_2 = xy S_0}$$

$$\boxed{S_3 = x^2 y S_0}$$

$$\left(\cancel{x^i}\right. \quad \boxed{\frac{x^i}{x} = x^{i-1}} = \left(\frac{x^i}{x}\right) = x^{i-1} \qquad \boxed{x^{i-1} = x^i, x^{-1} = x^i x^1/x}$$

$$\boxed{x^{-1} = x^i \cdot x^{-1} \quad = (y/x}$$

$$S_i = x^{i-1} y S_0$$

$$S_i = x^i \left(y/x\right) S_0$$

$$S_i = x^i \left(y/x\right) S_0 \quad (\text{where } (y/x) = c)$$

$$\boxed{S_i = x^i c S_0}$$

Substituted the value of S_i in eqn. Ⓐ.

$$\frac{V}{AV_0} = \frac{V}{V_m} = \frac{\sum_{i=0}^{\infty} i S_i}{\sum_{i=0}^{\infty} S_i} \quad \text{— Ⓐ}$$

$$\frac{V}{V_m} = \frac{\sum_{i=0}^{\infty} i x^i c S_0}{\sum_{i=0}^{\infty} x^i c S_0} \rightarrow \left(S_i = x^i c S_0\right.$$

[illegible]

$$= \frac{c S_0 \sum_{i=0}^{\infty} i x^i}{S_0 + \sum_{i=1}^{\infty} S_i}$$

$$\boxed{\sum_{i=0}^{\infty} x^i c S_0 = S_0 + \sum_{i=1}^{\infty} S_i}$$

Formula

(Substitute $S_i = x^i c S_0$)

$$= S_0 + \sum_{i=1}^{\infty} x^i c S_0$$

$$= S_0 \left(1 + \sum_{i=1}^{\infty} c x^i\right)$$

$$\frac{V}{V_m} = \frac{c S_0 \sum_{i=0}^{\infty} i x^i}{S_0 \left(1 + c \sum_{i=1}^{\infty} x^i\right)}$$

formula

$$\boxed{\sum_{i=0}^{\infty} i x^i = \frac{x}{[1-x]^2} \qquad \sum_{i=1}^{\infty} x^i = \frac{x}{(1-x)}}$$

$$\frac{V}{V_m} = \frac{c\, x/(1-x)^2}{1 + cx/(1-x)} = \frac{cx/(1-x)^2}{\dfrac{(1-x) + cx}{(1-x)}}$$

$$= \frac{cx\,\cancel{(1-x)}}{[(1-x) + cx]\,(1-x)^{\cancel{2}}}$$

$$\frac{V}{V_m} = \frac{cx}{(1-x+cx)(1-x)}$$

$$= \frac{cx}{((cx-x+1)(1-x))} \xrightarrow{\text{Rearrange}}$$

$$(c-1)(x+1)$$
$$cx + c - x - 1$$
$$c(x+1) - 1(x+1)$$
$$(c-1)(x+1)$$

$$\frac{V}{V_m} = \frac{cx}{((c-1)(x+1)(1-x))}$$

$$V = \frac{V_m\, cx}{(1-x)\,[1 + (c-1)x]}$$

$$V(1-x)[1+(c-1)x] = V_m\, cx$$

$$1 + (c-1)x \,/\, V_m c = \frac{x}{(1-x)V}$$

$$\frac{1}{V_m c} + \frac{(c-1)x}{V_m c} = \frac{x}{(1-x)V}$$

The aquation called as the BET equation. If N number of adsorbed layer is there, the BET eqn. becomes

$$V/V_m = \frac{cx}{(1-x)} \left\{ \frac{1 - (n+1)x^n + n x^{n+1}}{1 + (c-1)x - c x^{n-1}} \right\}$$

Limitation of BET eqn: BET eqn. fails below a relative pressure P/P_0 of 0.05 and it also fails when it is above 0.35. The assumbion that the adsorbate has liquid property is not correct therefore this equation needs some modification.

Kinetics of Enzyme catalysed reaction

Mechanism and kinetics of Enzyme Catalyst reaction :

* Enzymes are proteins which are having high molar mass in the range of 10000 or even more than that and are derived from living organism.

* Each enzyme can Catalyst a specific reaction.

For example, the enzyme diatase produced in the germinated barley seeds converts starch into maltose.

* In 1913, Biochemists L. Michaelis and Ms. Menton proposed a mechanism for the kinetics of enzyme catalyst reaction.

The following steps are :

Step 1 : Formation of enzyme substrate Complex.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

Enzyme Substrate Enzyme-substrate Complex.

Step 2 : Decomposition of enzyme substrate Complex

$$ES \xrightarrow{k_2} P + E$$

where, 'E' ⇒ Free enzyme
'S' ⇒ Substrate
'ES' ⇒ Enzyme substrate complex
'P' ⇒ Product

The rate constant of this reaction is,

$$r = k_2 [ES] \quad \text{———} \; ①$$

The overall reaction ($S \longrightarrow P$), the enzyme is Consumed in step 1 and it is regenerated in step 2.

By applying the steady state of approximation (s.s.a) we the rate of formation (forward reaction) is equal to the rate of decomposition (backward reaction)

$$r \Rightarrow \underbrace{k_1[E][S]}_{r_f} - \underbrace{k_{-1}[ES] - k_2[ES]}_{r_b} = 0 \qquad ②$$

$$k_1[E][S] = k_{-1}[ES] + k_2[ES] \qquad ③$$

$$k_1[E][S] = [ES](k_{-1} + k_2) \qquad ④$$

The Concentration of enzyme [E] cannot be measured experimentally. In order to find out the equilibrium between the free and the bounded enzyme, it is given by enzyme - Conservation equation.

$$(i) \quad [E_0] = [E] + [ES] \qquad ⑤$$

where, $[E_0]$ ⇒ total enzyme Concentration

$[E]$ ⇒ Concentration of free enzyme

$[ES]$ ⇒ Concentration of bounded enzyme

$$[E] = [E_0] - [ES] \qquad ⑥$$

sub the value of Concentration of E in equation ④,

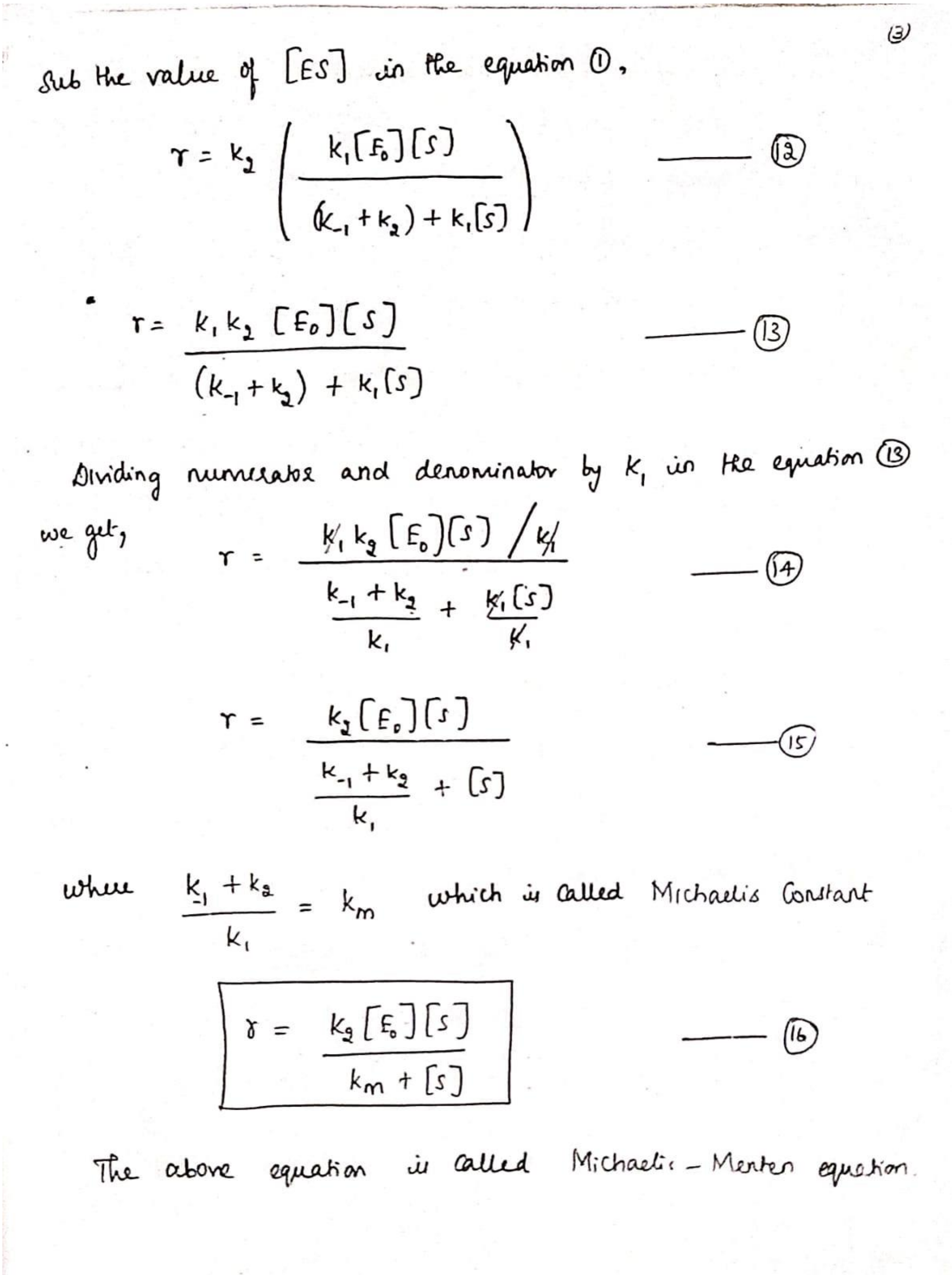
$$k_1\{[E_0] - [ES]\}.[S] = [ES](k_{-1} + k_2) \qquad ⑦$$

$$k_1[E_0][S] - k_1[ES][S] = [ES](k_{-1} + k_2) \qquad ⑧$$

$$k_1[E_0][S] = [ES](k_{-1} + k_2) + k_1[ES][S] \qquad ⑨$$

$$k_1[E_0][S] = [ES]\left((k_{-1} + k_2) + k_1[S]\right) \qquad ⑩$$

$$[ES] = \frac{k_1[E_0][S]}{(k_{-1} + k_2) + k_1[S]} \qquad ⑪$$



(3)

Sub the value of $[ES]$ in the equation ①,

$$r = k_2 \left(\frac{k_1 [E_0][S]}{(k_{-1} + k_2) + k_1 [S]} \right) \quad \text{———} ⑫$$

$$r = \frac{k_1 k_2 [E_0][S]}{(k_{-1} + k_2) + k_1 [S]} \quad \text{———} ⑬$$

Dividing numerator and denominator by k_1 in the equation ⑬ we get,

$$r = \frac{\cancel{k_1} k_2 [E_0][S] / \cancel{k_1}}{\frac{k_{-1} + k_2}{k_1} + \frac{\cancel{k_1}[S]}{\cancel{k_1}}} \quad \text{———} ⑭$$

$$r = \frac{k_2 [E_0][S]}{\frac{k_{-1} + k_2}{k_1} + [S]} \quad \text{———} ⑮$$

where $\frac{k_{-1} + k_2}{k_1} = k_m$ which is called Michaelis Constant

$$\boxed{r = \frac{k_2 [E_0][S]}{k_m + [S]}} \quad \text{———} ⑯$$

The above equation is called Michaelis – Menten equation.

Briggs - Haldene equation

In 1925, G. E. Briggs and J. B. S. Haldane refined the Michaelis-Menten equation by introducing the steady-state approximation. Their derivation is the standard mathematical model used for enzyme kinetics.

The Equation The Briggs-Haldane equation relates the initial reaction rate (\(v\)) to the substrate concentration ([S])

v= Vmax[S] / Km + [S]

Vmax: The maximum velocity achieved by the system at saturating substrate concentrations

Km (Michaelis Constant): The substrate concentration at which the reaction rate is half of Vmax.

Main differences from Michaelis-Menten

While the algebraic form is identical to the 1913 Michaelis-Menten equation, the interpretation of the parameters differs based on the underlying assumptions:

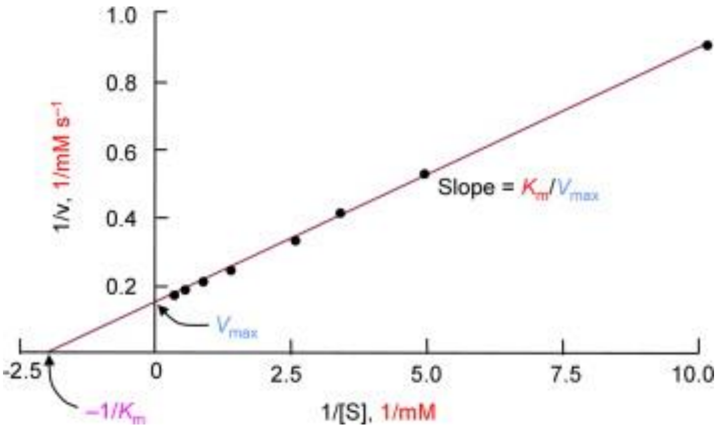
Feature	Michaelis-Menten (1913)	Briggs-Haldane (1925)
Core Assumption	Rapid Equilibrium: The enzyme and substrate reach equilibrium with the complex (EScap E cap S ES) much faster than the product is formed.	Steady-State: The concentration of the \(ES\) complex remains constant (\(d[ES]/dt=0\)) during the measured period.
Definition of Km	\(K_{m}\approx K_{d}=\frac{k_{-1}}{k_{1}}\) (the dissociation constant).	(K_{m}=\frac{k_{-1}+k_{2}}{k_{1}}\) (includes the rate of product formation).
Applicability	Limited to cases where product formation is very slow (k2≪k-1k sub 2 is much less than k sub negative 1 $k2 \ll k-1$).	Valid for almost all enzyme-catalyzed reactions, regardless of relative rate constants.

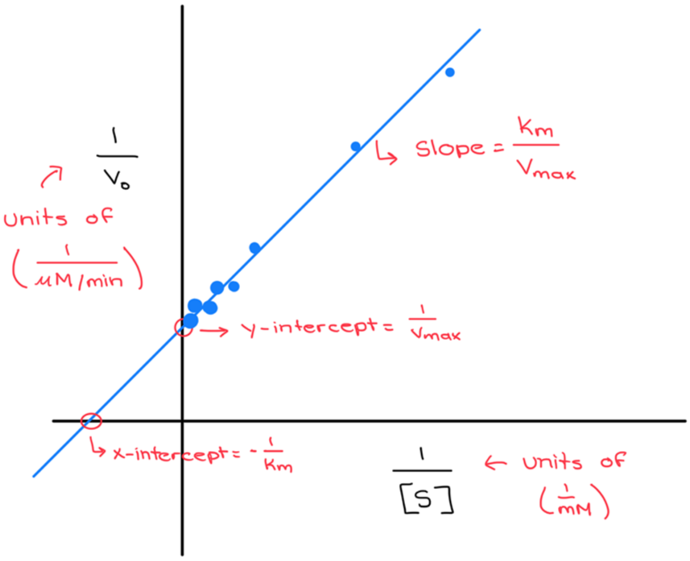
Derivation Context

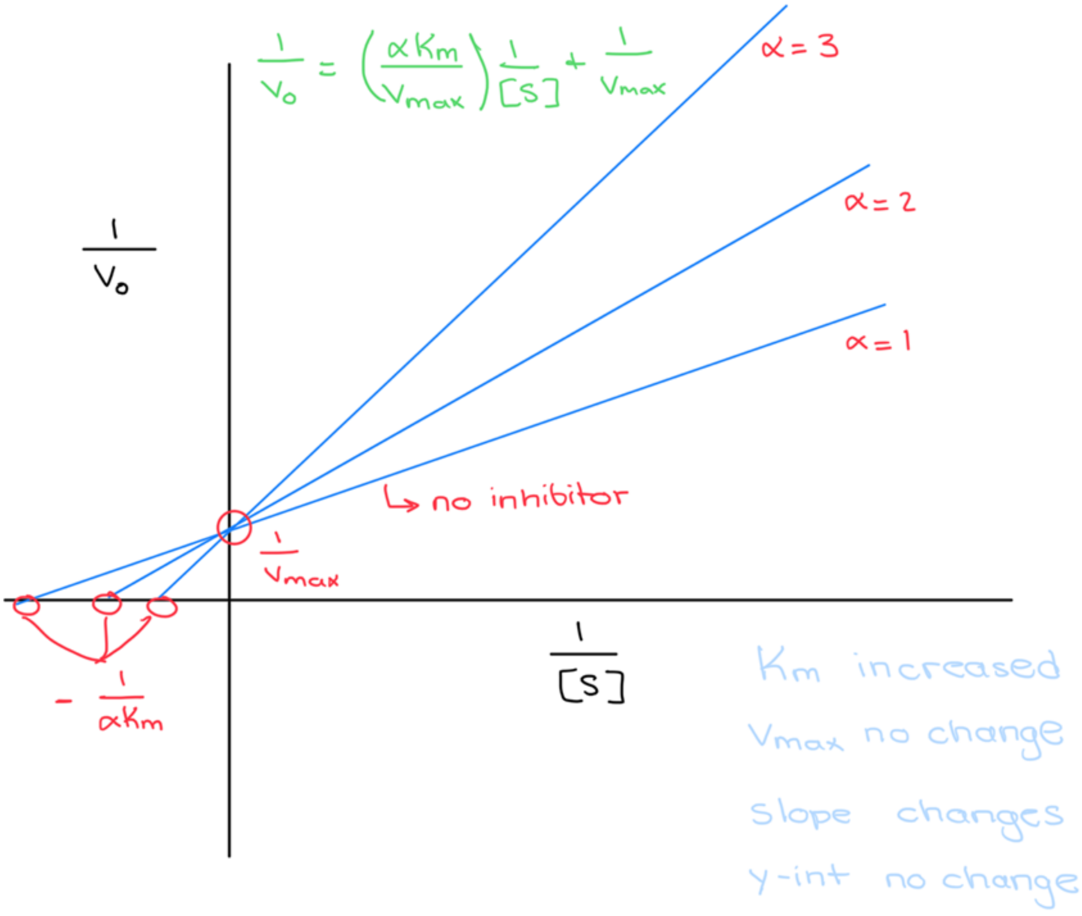
The derivation considers a simple one-intermediate reaction: By assuming the ES complex is consumed as fast as it is produced, Briggs and Haldane were able to solve for the reaction velocity without requiring the complex to be in true chemical equilibrium with the free substrate

Line weaver- Burk plot

In chemical kinetics, the Lineweaver–Burk plot (or double reciprocal plot) is a graphical method used to analyze enzyme kinetics by linearizing the Michaelis–Menten equation. It was developed by Hans Lineweaver and Dean Burk in 1934 to more easily determine the kinetic parameters of an enzyme-catalyzed reaction







The plot is derived by taking the reciprocal of both sides of the Michaelis-Menten equation:

$\frac{1}{\vartheta} = \frac{Km}{Vmax} \cdot \frac{1}{[S]} + \frac{1}{Vmax}$

This matches the standard straight-line equation y=mx+c, where:

Y:1/υ (Reciprocal of reaction velocity)

x: 1/ [S] (Reciprocal of substrate concentration)

m (slope): Km/Vmax

c(y-intercept):1/Vmax

x-intercept:-1/Km

Uses

Determining Vmax and Km: By plotting experimental data, researchers can extrapolate the line to find the intercepts, allowing direct calculation of the maximum velocity Vmax and the Michaelis constant Km.

Identifying Inhibition Types: The plot is a powerful tool for distinguishing between different types of Enzyme Inhibition:

Competitive Inhibition: Increases the slope and shifts the x-intercept closer to zero, but leaves the y-intercept (1/Vmax) unchanged.

Non-competitive Inhibition: Increases the slope and the y-intercept, but leaves the x-intercept (-1/Km) unchanged.

Uncompetitive Inhibition: Shifts both intercepts, resulting in a line parallel to the uninhibited one.

Limitations:

Error Amplification: Taking reciprocals can disproportionately weight experimental errors, especially at low substrate concentrations where the values are naturally less precise.

Inhibition – reversible – competitive

The reversible competitive inhibition is a mechanism where an inhibitor molecule competes with a substrate for binding to the same active site on an enzyme. Because the inhibitor binds non-covalently, the process is reversible, and the inhibitor can be displaced by increasing the concentration of the substrate

Non competitive and un competitive

Non-competitive inhibition (specifically enzyme kinetics) involves an inhibitor binding to a site other than the active site, changing the enzyme's shape to reduce efficiency, while uncompetitive inhibition occurs when the inhibitor binds only to the already-formed enzyme-substrate (ES) complex, preventing product release and slowing the reaction, common in multi-substrate reactions. The key difference: noncompetitive can bind free enzyme or ES complex (affecting (Vmax), while uncompetitive only binds the ES complex (also reducing Vmax, but affecting Km differently).

Catalysis

A catalyst is defined as a substance which alters the rate of a chemical reaction, itself remaining chemically unchanged at the end of the reaction. The process is called Catalysis. As evident from the above definition, a catalyst may increase or decrease the rate of a reaction. A catalyst which enhances the rate of a reaction is called a Positive catalyst and the process Positive catalysis or simply Catalysis. A catalyst which retards the rate of a reaction is called a Negative catalyst and the process Negative catalysis.

General characteristics of catalytic reactions

(1) A catalyst remains unchanged in mass and chemical composition at the end of the reaction

Qualitative and quantitative analysis show that a catalyst undergoes no change in mass of chemical nature. However, it may undergo a physical change. Thus granular manganese dioxide (MnO_2) used as a catalyst in the thermal decomposing of potassium chlorate is left as a fine powder at the end to the reaction.

(2) A small quantity of catalyst is generally needed to produce almost unlimited reaction

Sometimes a trace of a metal catalyst is required to affect very large amounts of reactants. For example, one ten-millionth of its mass of finely divided platinum is all that is needed to catalyse the decomposition of hydrogen peroxide. On the other hand, there are catalysts which need to be present in relatively large amount to be effective. Thus in Friedel-Crafts reaction,

$$C_6H_6 + C_2H_5Cl\ AlCl_3 \longrightarrow C_6H_5C_2H_5 + HCl$$

anhydrous aluminium chloride functions as a catalyst effectively when present to the extent of 30 per cent of the mass of benzene. For the acid and alkaline hydrolysis of an ester, the rate of reaction is proportional to the concentration of the catalyst (H^+ or OH^-).

$$RCOOR + H_2O \xrightarrow{H^+ \text{ or } OH^-} RCOOH + R'OH$$

ester

(3) A catalyst is more effective when finely divided

In heterogeneous catalysis, the solid catalyst is more effective when in a state of fine subdivision than it is used in bulk. Thus a lump of platinum will have much less catalytic activity than colloidal or platinised asbestos. Finely divided nickel is a better catalyst than lumps of solid nickel.

(4) A catalyst is specific in its action

While a particular catalyst works for one reaction, it will not necessarily work for another reaction. Different catalysts, moreover, can bring about completely different reactions for the same substance. For example, ethanol (C_2H_5OH) gives ethene (C_2H_4) when passed over hot aluminium oxide,

$$C_2H_5OH \xrightarrow{Al_2O_3} CH_2{=}CH_2 + H_2O \qquad \text{(Dehydration)}$$

ethene

but with hot copper it gives ethanal (CH_3CHO).

$C_2H_5OH \xrightarrow{\text{Cu}} CH_3CHO + H_2$ (Dehydrogenation)

ethanal

(5) A catalyst cannot, in general, initiate a reaction

In most cases a catalyst speeds up a reaction already in progress and does not initiate (or start) the reaction. But there are certain reactions where the reactants do not combine for very long period (perhaps years). For example, a mixture of hydrogen and oxygen, which remains unchanged almost indefinitely at room temperature, can be brought to reaction by the catalyst platinum black in a few seconds.

$H_2 + O_2 \xrightarrow{\text{room temperature}}$ No reaction

$2H_2 + O_2 \xrightarrow{\text{Pt black}}$ 2H2O

Thus it is now considered that the catalyst can initiate a reaction. According to this view, the reacting molecules (in the absence of catalyst) do not possess minimum kinetic energies for successful collisions. The molecules rebound from collision without reacting at all.

(6) A catalyst does not affect the final position of equilibrium, although it shortens the time required to establish the equilibrium

It implies that in a reversible reaction the catalyst accelerates the forward and the reverse reactions equally. Thus the ratio of the rates of two opposing reactions i.e., the equilibrium constant, remains unchanged. The effect of a catalyst on the time required for equilibrium to be established for the reaction.

$A + B \rightleftharpoons C + D$

is illustrated in Fig. 3.8. To start with the concentrations of A and B are at the maximum and hence the rate of forward reaction is maximum. As the time passes the rate of the reaction decreases till the equilibrium is established. For the reverse reaction the initial concentrations of C and D are zero and the rate of reaction is lowest. At the time passes, the rate of reaction increases till the equilibrium is established. Similar curves of the rates of reactions with the catalyst show that the rates of the forward reaction and the reverse reaction are altered equally but the equilibrium is established in a much shorter time. For example, in the Haber Process for ammonia,

$N_2 + 3H_2 \xrightleftharpoons{\text{Fe}} 2NH_3$

the reaction is very slow. In the presence of the catalyst, the equilibrium is reached much sooner but the percentage yield remains unchanged. The iron catalyst shortens the time to attain equilibrium but cannot alter the percentage yield.

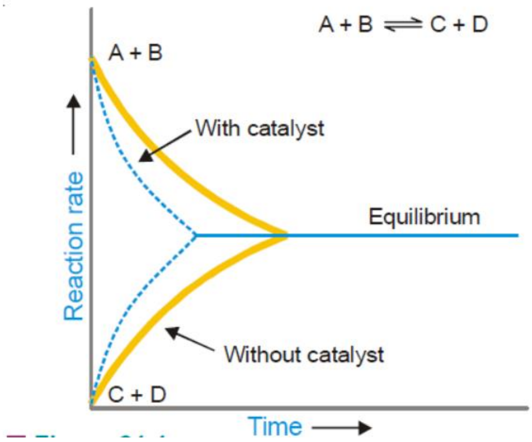


Figure 3.8: The effect of a catalyst on the time required for the equilibrium to be established.

Energy considerations also show that the final state of equilibrium cannot be changed by the catalyst. Suppose the catalyst accelerates the forward reaction more than the reverse reaction. This will shift the equilibrium point, which cannot happen without the supply of energy to the system. But a catalyst unchanged in mass and composition at the end of the reaction, cannot supply the required energy.

(7) Change of temperature alters the rate of a catalytic reaction as it would do for the same reaction without a catalyst

We have already studied the effect of temperature change on reversible reactions under Le Chatelier principle. Some catalysts are, however, physically altered by a rise in temperature and hence their catalytic activity may be decreased. This is particularly true with colloidal solutions like that of platinum, since a rise in the temperature may cause their coagulation. In such a case the rate of reaction increases up to a certain point and then gradually decreases. The rate of reaction is maximum at a particular temperature called the optimum temperature.

Autocatalysis

When one of the products of reaction itself acts as a catalyst for that reaction the phenomenon is called Autocatalysis. In autocatalysis the initial rate of the reaction rises as the catalytic product is formed, instead of decreasing steadily (Fig.3.9). The curve plotted between reaction rate and time shows a maximum when the reaction is complete.

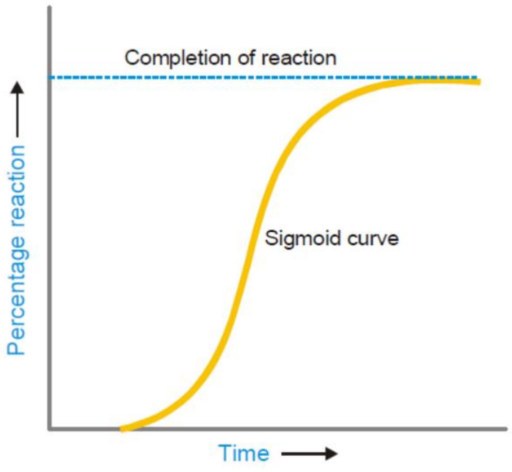


Figure 3.9: Curve showing the rise of rate of reaction with time.

Examples of Autocatalysis

(1) *Hydrolysis of an Ester*. The hydrolysis of ethyl acetate forms acetic acid (CH_3COOH) and ethanol. Of these products, acetic acid acts as a catalyst for the reaction.

$$CH_3COOC_2H_5 + H_2O \xrightarrow[\text{catalyst}]{} CH_3COOH + C_2H_5OH$$

(2) *Oxidation of Oxalic acid*. When oxalic acid is oxidised by acidified potassium permanganate, manganous sulphate produced during the reaction acts as a catalyst for the reaction.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \xrightarrow[\text{catalyst}]{} 2MnSO_4 + K_2SO_4 + 8H_2O + 10CO_2$$

(3) *Decomposition of Arsine*. The free arsenic produced by the decomposition of arsine (AsH_3) Auto catalyses the reaction.

$$2AsH_3 \xrightarrow[\text{catalyst}]{} 2As + 3H_2$$

Promoters

The activity of a catalyst can often be increased by addition of a small quantity of a second material. This second substance is either not a catalyst itself for the reaction or it may be a feeble catalyst. A substance which, though itself not a catalyst, promotes the activity of a catalyst is called a promoter.

Example of Promoters

Molybdenum (Mo) or aluminium oxide (Al_2O_3) promotes the activity of iron catalyst in the Haber synthesis for the manufacture of ammonia.

$$N_2 + 3H_2 \underset{+Mo}{\overset{Fe}{\rightleftharpoons}} 2NH_3$$

In some reactions, mixtures of catalysts are used to obtain the maximum catalytic efficiency. For example, in the synthesis of methanol (CH_3OH) from carbon monoxide and hydrogen, a mixture of zinc and chromium oxide is used as a catalyst.

$$CO + 2H_2 \xrightarrow[Cr_2O3]{Zno} CH_3OH$$

Explanation of Promotion Action

(1) Change of Lattice Spacing. The lattice spacing of the catalyst is changed thus enhancing the spaces between the catalyst particles. The absorbed molecules of the reactant (say H_2) are further weakened and cleaved. This makes are reaction go faster.

(2) Increase of Peaks and Cracks. The presence of the promoter increases the peaks and cracks on the catalyst surface. This increases the concentration of the reactant molecules and hence the rate of reaction. The phenomenon of promotion is a common feature of heterogeneous catalysis.

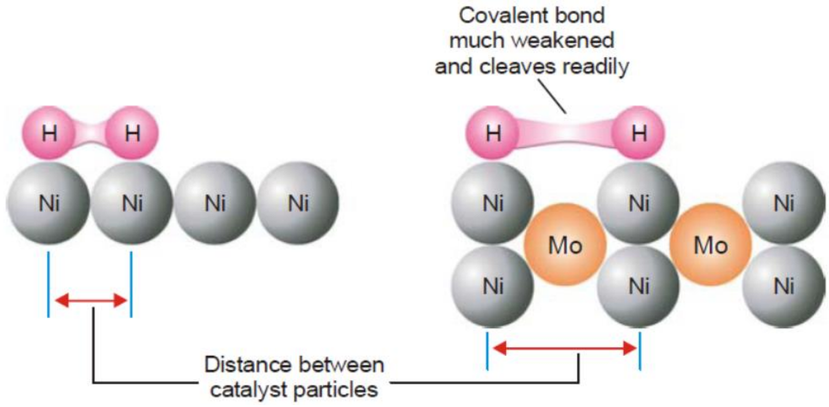


Figure 3.10: Change of crystal lattice spacing of catalyst (makes the reaction faster).

Negative Catalysis

When a catalyst reduces the rate of a reaction, it is called a Negative catalyst or Inhibitor. This phenomenon is called Negative catalysis or Inhibition. Negative catalysis is useful to slow down or stop altogether an unwanted reaction.

Examples of Negative Catalysis

(1) *Oxidation of Trichloromethane ($CHCl_3$)*

Trichloromethane (or chloroform) is used as anaesthetic. Upon oxidation by air it forms carbonyl chloride ($COCl_2$) which is a poisonous substance.

$4CHCl_3 + 3O_2 \longrightarrow 4COCl_2 + 2H_2O + 2Cl_2$

2 per cent of ethanol (C_2H_5OH) when added to chloroform acts as a negative catalyst and suppresses the formation of carbon chloride.

(2) *Decomposition of Hydrogen peroxide*

The decomposition of hydrogen peroxide,

$2H_2O_2 \longrightarrow 2H_2O + O_2$

is retarded by the presence of dilute acids or glycerol.

(3*) Tetraethyllead as Antiknock*

When tetraethyllead, $Pb(C_2H_5)_4$, is added to petrol, it retards the too repaid or explosive combustion of the fuel which is responsible for knocking of the engine.

Explanation of Negative Catalysis

The mechanism of negative catalysis could be different for different reactions.

(1) By poisoning a catalyst. A negative catalyst may function by poisoning a catalyst which already happens to be present in the reaction mixture. For example, the traces of alkali dissolved from the glass of the container, catalyse the decomposition of hydrogen peroxide (H_2O_2). But the addition of an acid would destroy the alkali catalyst and thus prevent decomposition.

(2) By breaking a chain reaction. In some cases negative catalysts are believed to operate by breaking the chain of reactions. For example, the combination of H_2 and Cl_2, which is a chain reaction, is negatively catalysed by nitrogen trichloride (NCl_3).

$Cl_2 \longrightarrow Cl^{\cdot\cdot} + Cl^{\cdot\cdot}$

$H_2 + Cl^{\cdot\cdot} \longrightarrow HCl + H^{\cdot\cdot}$

$H^{\cdot\cdot} + Cl_2 \longrightarrow HCl + H^{\cdot\cdot}$

NCl_3 breaks the chain of reactions by absorbing the propagating species (Cl), and the reaction stops.

$NCl_3 + Cl^{\cdot\cdot} \longrightarrow \frac{1}{2} N_2 + 2Cl_2$

Poisoning of a Catalyst

Very often a heterogeneous catalyst in rendered ineffective by the presence of small amounts of impurities in the reactants. A substance which destroys the activity of the catalyst to accelerate a reaction, is called a poison and the process is called Catalytic poisoning.

Examples of Catalytic Poisoning

(1) The platinum catalyst used in the oxidation of sulphur dioxide (Contact Process), is poisoned by arsenic oxide (As_2O_3)

$$SO_2 + O_2 \xrightarrow[Pt\ \&\ As_2O_3]{} 2SO_3$$

(2) The iron catalyst used in the synthesis of ammonia (Haber Process) is poisoned by H_2S.

$$N_2 + 3H_2 \xrightarrow{Fe\ \&\ H_2S} 2NH_3$$

(3) The platinum catalyst used in the oxidation of hydrogen is poisoned by carbon monoxide.

$$2H_2 + O_2 \xrightarrow{Pt/CO} 2H_2O$$

Explanation

The poison is adsorbed on the catalyst surface in preference to the reactants. Even a monomolecular layer renders the surface unavailable for further adsorption of the reactants. The poisoning by As_2O_3 or CO appears to be of this kind.

(2) The catalyst may combine chemically with the impurity. The poisoning of iron catalyst by H_2S falls in this class.

$$Fe + H_2S \longrightarrow FeS + H_2$$

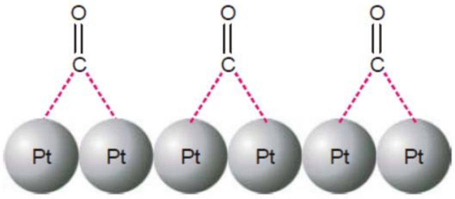


Figure 3.11: Poisoning of platinum catalyst by carbon monoxide.

Homogeneous Catalysis

In homogeneous catalysis, the catalyst is in the same phase as the reactants and is evenly distributed throughout. This type of catalysis can occur in gas phase or the liquid (solution) phase.

Examples of Homogeneous Catalysis in Gas Phase

(a) Oxidation of sulphur dioxide (SO_2) to sulphur trioxide (SO3) with nitric oxide (NO) as catalyst,

$2SO_2 + O_2 + [NO] \longrightarrow 2SO_3 + [NO]$
gas gas gas gas

(b) Decomposition of acetaldehyde (CH_3CHO) with iodine (I_2) as catalyst,

$CH_3CHO + (I_2) \longrightarrow CH_4 + CO$

vapour vapour gas gas

Examples of Homogeneous Catalysis in Solution Phase

Many reactions in solutions are catalysed by acids (H^+) and bases ($OH^–$).

(a) Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst,

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H_2SO_4} C_6H_{12}O_6 + C_6H_{12}O_6 + [H_2SO_4]$
cane sugar glucose fructose

(b) Hydrolysis of an ester in the presence of acid or alkali,

$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+/OH^-} CH_3COOH + C_2H_5OH$

ethyl acetate acetic acid ethanol

(c) Decomposition of hydrogen peroxide (H2O2) in the presence of iodide ion ($I^–$) as catalyst,

$2H_2O_2 \xrightarrow{-I} 2H_2O + O_2$

Heterogeneous Catalysis

The catalysis in which the catalyst is in a different physical phase from the reactants is termed Heterogeneous catalysis. The most important of such reactions are those in which the reactants are in the gas phase while the catalyst is a solid. The process is also called Contact catalysis since the reaction occurs by contact of reactants with the catalyst surface. In contact catalysis, usually the catalyst is a finely divided metal or a gauze. This form of catalysis has great industrial importance.

Examples of Heterogeneous Catalysis

Some examples of heterogeneous catalysis with reactants in the gas, liquid or the solid phase are

listed below.

(1) Heterogeneous catalysis with gaseous reactants (Contact catalysis)

(a) Combination of sulphur dioxide (SO_2) and oxygen in the presence of finely divided platinum or vanadium pentoxide, V_2O_5, (Contact Process for Sulphuric acid).

$2SO_2 + O_2 + [Pt] \longrightarrow 2SO_3 + [Pt]$

gas gas solid

(b) Combination of nitrogen and hydrogen to form ammonia in the presence of finely divided iron, (Haber Process for Ammonia).

$N_2 + 3H_2 + [Fe] \longrightarrow 2NH_3 + [Fe]$

gas gas solid

(c) Oxidation of ammonia to nitric oxide (NO) in the presence of platinum gauze (a stage in manufacture of Nitric acid).

$4NH_3 + 5O_2 + [Pt] \longrightarrow 4NO + 6H_2O + [Pt]$
gas gas solid

(d) Hydrogenation reactions of unsaturated organic compounds are catalysed by finely divided nickel.
$H_2C{=}CH_2 + H_2 + [Ni] \longrightarrow H_3C{-}CH_3 + [Ni]$

ethene(gas) gas solid ethane(gas)

Vegetable oils are triesters of glycerol with higher unsaturated acid (oleic acid). When hydrogen is passed through the vegetable oils in the presence of nickel, the carbon-carbon double bonds of the acid portions are hydrogenated to yield solid fats (Vanaspati ghee).

(2) *Heterogeneous catalysis with liquid reactants*

(i) The decomposition of aqueous solutions of hydrogen peroxide (H_2O_2) is catalysed by manganese dioxide (MnO_2) or platinum in colloidal form,

$2H_2O_2 + [Pt] \longrightarrow 2H_2O + O_2 + [Pt]$

Liquid solid

(ii) Benzene and ethanoyl chloride (CH_3COCl) react in the presence of anhydrous aluminium chloride to form phenyl methyl ketone ($C_6H_5COCH_3$),

$C_6H_6 + CH_3COCl + [AlCl_3] \longrightarrow C_6H_5COCH_3 + HCl + [AlCl_3]$
liquid liquid solid

(3) Heterogeneous catalysis with solid reactants

The decomposition of potassium chlorate ($KClO_3$) is catalysed by manganese dioxide (MnO_2).

$2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2 + [MnO_2]$
solid solid

Acid–Base Catalysis

A number of homogeneous catalytic reactions are known which are catalysed by acids or bases, or both acids and bases. These are often referred to as Acid-Base catalysts. Arrhenius pointed out that acid catalysis was, in fact, brought about by H^+ ions supplied by strong acids, while base catalysis was caused by $OH^–$ ions supplied by strong bases.

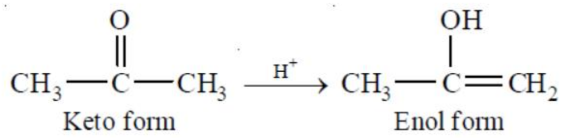
Examples of Acid-Base catalysis

(1) Inversion of Cane sugar:

$C_{12}H_{22}O_{11} + H_2 \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

cane sugar glucose fructose

(2) Keto-Enol tautomerism of Acetone:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{H^+} CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2$$

(3) Decomposition of Nitramide:

$NH_2NO_2 \xrightarrow{H^+} N_2O + H_2O$

(4) Hydrolysis of an Ester:

$CH_3COOC_2H_5 \xrightarrow{H^+ \text{ or } OH^-} CH_3COOH + C_2H_5OH$
ethyl acetate acetic acid ethanol

General Acid-Base catalysis

More recently it has been found that :

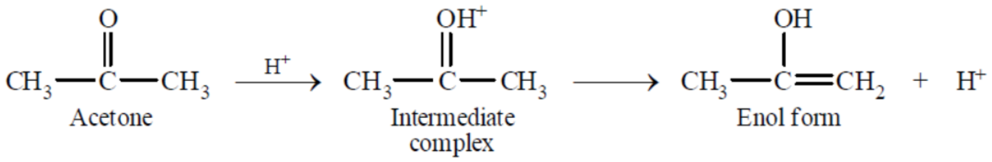
(a) Not only H+ ions but all Bronsted bases (proton donors) cause acid catalysis. Thus the general acid catalysts are : H+, undissociated acids (CH3COOH), cations of weak bases (NH^+_4) and water (H2O).

(b) Not only $OH^–$ ions but all Bronsted bases (proton acceptors) act as base catalyst. Thus the general base catalysts are : $OH^–$, undissociated bases, anions of weak acids (CH3COO–) and water (H_2O). The catalysis brought about by general acids and bases is termed General Acid-Base catalysis. For elucidation, decomposition of nitramide is also catalysed by acetate ions ($CH_3COO^–$).

$$NH_2NO_2 \xrightarrow{CH_3COO^-} N_2O + H_2O$$

Mechanism of Acid-Base catalysis

(*a*) In acid catalysis, the H^+ (or a proton donated by Bronsted acid) forms an intermediate complex with the reactant, which then reacts to give back the proton. For example, the mechanism of keto-enol tautomerism of acetone is:



(b) In base catalysis, the OH– ion (or any Bronsted base) accepts a proton from the reactant to form an intermediate complex which then reacts or decomposes to regenerate the OH– (or Bronsted base). For example, the decomposition of nitramide by OH– ions and CH3COO– ions may be explained as follows:

(i) By $OH^–$ ions:

$$NH_2NO_2 + OH^- \longrightarrow H_2O + \underset{\text{Intermediate complex}}{NHNO_2^-}$$

$$NHNO_2^- \longrightarrow N_2O + OH^-$$

(ii) By $CH_3COO^–$ ions:

$$NH_2NO_2 + CH_3COO^- \longrightarrow CH_3COOH + NHNO_2^-$$

$$NHNO_2^- \longrightarrow N_2O + OH^-$$

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

Enzyme Catalysis

Numerous organic reactions are taking place in the body of animals and plants to maintain the life process. These reactions being slow remarkably catalysed by the organic compounds known as Enzymes. All enzymes have been found to be complex protein molecules. Thus, Enzymes are protein molecules which act as catalysts to speed up organic reactions in living cells. The catalysis brought about by enzymes is known as Enzyme Catalysis. Each enzyme is produced in a particular living cell to catalyse a reaction occurring in that cell. Many enzymes have been identified and obtained in pure crystalline state from the cells to which they belong. However the first enzyme as prepared by synthesis in the laboratory in 1969.

Examples of Enzyme Catalysis

Some common examples of the biochemical reactions catalysed by enzymes are:

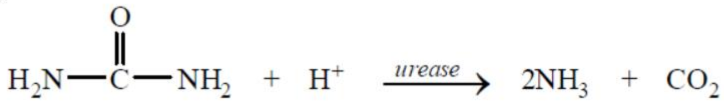
(1) Inversion of cane sugar ($C_{12}H_{22}O_{11}$) by Invertase present in yeast,

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

(2) Conversion of glucose into ethanol by Zymase present in yeast,

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{ethanol}}{2C_2H_5OH} + 2CO_2$$

(3) Hydrolysis of urea ($H_2N—CO—NH_2$) by Urease present in soya bean,



$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + H^+ \xrightarrow{urease} 2NH_3 + CO_2$$

Mechanism of Enzyme Catalysis

The long chains of the enzyme (protein) molecules are coiled on each other to make a rigid colloidal particle with cavities on its surface. These cavities which are of characteristic shape and abound in active groups (NH_2, COOH, SH, OH)] are termed Active centres. The molecules of substrate which have complementary shape, fit into these cavities just as key fits into a lock (Lock-and- Key theory). By virtue of the presence of active groups, the enzyme forms an activated complex with the substrate which at once decomposes to yield the products. Thus the substrate molecules enters the cavities, forms complex and reacts, and at once the products get out of the cavities. Michaelis and Menten (1913) proposed the following mechanism for enzyme catalysis (Fig 3.12)

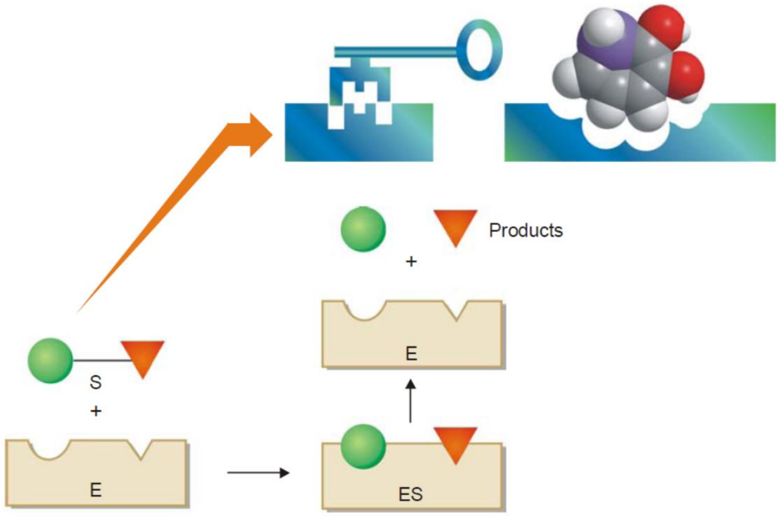


Figure 3.12: Illustration of the lock-and-key model of enzyme catalysis.

$$E + S \rightleftharpoons \underset{\text{complex}}{ES} \longrightarrow P + E$$

where E = enzyme; S = substrate (reactant); ES = activated complex; P = products

UNIT-IV

Colloids and Surface Chemistry

Colloids

In a true solution as sugar or salt in water, the solute particles are dispersed in the solvent as single molecules or ions. Thus the diameter of the dispersed particles ranges from 1Å to 10 Å. On the other hand, in a suspension as sand stirred into water, the dispersed particles are aggregates of millions of molecules. The diameter of these particles is of the order 2,000 Å or more.

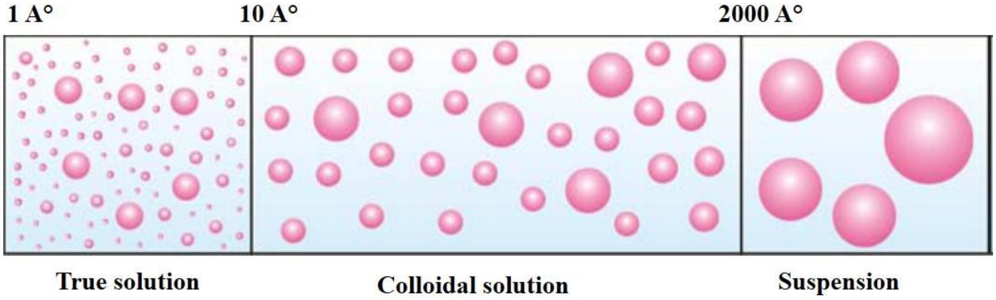


Figure 4.1: Particle size (indicated by diameter) range of true solution, colloidal dispersion, and suspension.

The colloidal solutions or colloidal dispersions are intermediate between true solutions and suspensions. In other words, the diameter of the dispersed particles in a colloidal dispersion is more than that of the solute particles in a true solution and smaller than that of a suspension. When the diameter of the particles of a substance dispersed in a solvent ranges from about 10 Å to 2,000 Å, the system is termed a colloidal solution, colloidal dispersion, or simply a colloid. The material with particle size in the colloidal range is said to be in the colloidal state.

Figure 4.2: Common examples of colloids.

The colloidal particles are not necessarily corpuscular in shape. In fact, these may be rod-like, disc-like, thin films, or long filaments. For matter in the form of corpuscles, the diameter gives a measure of the particle size. However, in other cases one of the dimensions (length, width and thickness) has to be in the colloidal range for the material to be classed as colloidal. A system with at least one dimension (length, width, or thickness) of the dispersed particles in the range 10 Å to 2,000 Å, is classed as a colloidal dispersion.

Types of colloidal systems

As we have seen above, a colloidal system is made of two phases. The substance distributed as the colloidal particles is called the Dispersed phase. The second continuous phase in which the colloidal particles are dispersed is called the Dispersion medium. For example, for a colloidal solution of copper in water, copper particles constitute the dispersed phase and water the dispersion medium.

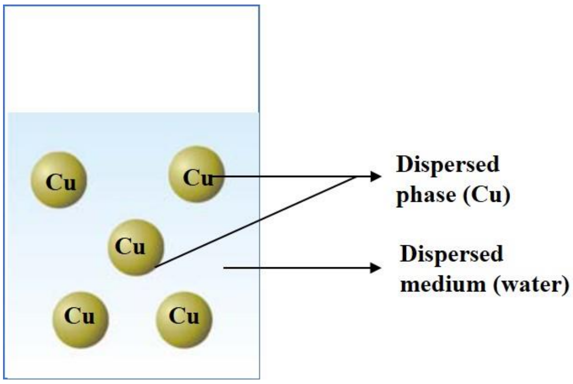


Figure 4.3: A colloidal solution of Cu in water.

A colloidal system is made of a dispersed phase and the dispersion medium. Because either the dispersed phase or the dispersion medium can be a gas, liquid or solid, there are eight types of colloidal systems possible. A colloidal dispersion of one gas in another is not possible since the two gases would give a homogeneous molecular mixture.

Colloidal systems which consist of a solid substance dispersed in a liquid are frequently referred to as Sols or Colloidal solution. The colloidal solutions in water as the dispersion medium are termed as Hydrosols or Aquasols. When the dispersions medium is alcohol or benzene, the sols are referred to as Alcosols and Benzosols respectively. The various types of colloidal systems are listed in Table. 4.1.

Table 4.1: Various types of colloidal systems

Type name	Dispersed phase	Dispersed medium	Examples
Foam	gas	liquid	whipped cream, shaving cream, soda-water
Solid foam	gas	solid	froth cork, pumice stone, foam rubber
Aerosol	liquid	gas	fog, mist, clouds
Emulsion	liquid	liquid	milk, hair cream
Solid emulsion (gel)	liquid	solid	butter, cheese
Smoke	solid	gas	dust, soot in air
Sol	solid	liquid	paint, ink, colloidal gold
Solid sol	solid	solid	ruby glass (gold dispersed in glass), alloys.

Characteristics of Colloids

Sols are colloidal systems in which a solid is dispersed in a liquid. These can be subdivided into two classes:

(a) Lyophilic sols (solvent-loving)

(b) Lyophobic sols (solvent-hating)

Lyophilic sols are those in which the dispersed phase exhibits a definite affinity for the medium or the solvent.

The examples of lyophilic sols are dispersions of starch, gum, and protein in water.

Lyophobic sols are those in which the dispersed phase has no attraction for the medium or the solvent. The examples of lyophobic sols are dispersion of gold, iron (III) hydroxide and sulphur in water. The affinity or attraction of the sol particles for the medium, in a lyophilic sol, is due to hydrogen bonding with water. If the dispersed phase is a protein (as in egg) hydrogen bonding takes place between water molecules and the amino groups ($-NH-$, $-NH_2$) of the protein molecule. In a dispersion of starch in water, hydrogen bonding occurs between water molecules and the – OH groups of the starch molecule. There are no similar forces of attraction when sulphur or gold is dispersed in water.

Characteristics of lyophilic and lyophobic sols

Some features of lyophilic and lyophobic sols are listed below.

(1) Ease of preparation

Lyophilic sols can be obtained straightaway by mixing the material (starch, protein) with a suitable solvent. The giant molecules of the material are of colloidal size and these at once pass into the colloidal form on account of interaction with the solvent. Lyophobic sols are not obtained by simply mixing the solid material with the solvent.

(2) Charge on particles

Particles of a hydrophilic sol may have little or no charge at all. Particles of a hydrophobic sol carry positive or negative charge which gives them stability.

(3) Solvation

Hydrophilic sol particles are generally solvated. That is, they are surrounded by an adsorbed layer of the dispersion medium which does not permit them to come together and coagulate. Hydration of gelatin is an example. There is no solvation of the hydrophobic sol particles for want of interaction with the medium.

(4) Viscosity

Lyophilic sols are viscous as the particle size increases due to solvation, and the proportion of free medium decreases. Warm solutions of the dispersed phase on cooling set to a gel e.g., preparation of table jelly. Viscosity of hydrophobic sol is almost the same as of the dispersion medium itself.

(5) Precipitation

Lyophilic sols are precipitated (or coagulated) only by high concentration of the electrolytes when the sol particles are dissolved. Lyophobic sols are precipitated even by low concentration of electrolytes, the protective layer being absent.

(6) Reversibility

The dispersed phase of lyophilic sols when separated by coagulation or by evaporation of the medium, can be reconverted into the colloidal form just on mixing with the dispersion medium. Therefore this type of sols are designated as Reversible sols. On the other hand, the lyophobic sols once precipitated cannot be reformed merely by mixing with dispersion medium. These are, therefore, called Irreversible sols.

(7) Tyndall effect

On account of relatively small particle size, lyophilic sols do not scatter light and show no Tyndall effect. Lyophobic sol particles are large enough to exhibit tyndall effect.

(8) Migration in electronic field

Lyophilic sol particles (proteins) migrate to anode or cathode, or not at all, when placed in electric field. Lyophobic sol particles move either to anode or cathode, according as they carry negative or positive charge.

Comparison of lyophilic and lyophobic sols

Lyophilic Sols	Lyophobic Sols
Prepared by direct mixing with dispersion medium	Not prepared by direct mixing with the medium
Little or no charge on particles	Particles carry positive or negative charge
Particles generally solvated	No solvation of particles
Viscosity higher than dispersion medium; set to a gel.	Viscosity almost the same as of medium; do not set to a gel.
Precipitated by high concentration of Electrolytes	Precipitated by low concentration of Electrolytes
Reversible	Irrerversible
Do not exhibit Tyndall effect	Exhibit Tyndall effect
Particles migrate to anode or cathode, or not at all	Particles migrate to either anode or cathode

Preparation of Sols

Lyophilic sols may be prepared by simply warming the solid with the liquid dispersion medium e.g., starch with water. On the other hand, lyophobic sols have to be prepared by special methods. These methods fall into two categories:

(a) Dispersion Methods in which larger macro-sized particles are broken down to colloidal size.

(b) Aggregation Methods in which colloidal size particles are built up by aggregating single ions or molecules.

Dispersion methods

In these methods, material in bulk is dispersed in another medium.

(1) Mechanical dispersion using colloid mill

The solid along with the liquid dispersion medium is fed into a Colloid mill. The mill consists of two steel plates nearly touching each other and rotating in opposite directions with high speed. The solid particles are ground down to colloidal size and are then dispersed in the liquid to give the sol. ‘Colloidal graphite’ (a lubricant) and printing inks are made by this method. Recently, mercury sol has been prepared by disintegrating a layer of mercury into sol particles in water by means of ultrasonic vibrations.

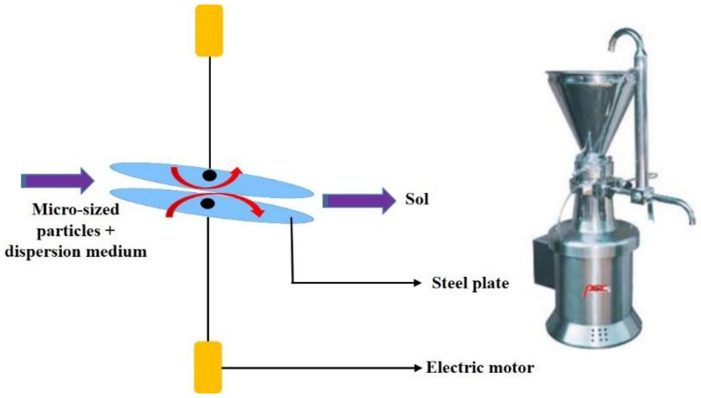


Figure 4.4: A colloid mill

(2) Bredig’s Arc Method

It is used for preparing hydrosols of metals e.g., silver, gold and platinum. An arc is struck between the two metal electrodes held close together beneath de-ionized water. The water is kept cold by immersing the container in ice/water bath and a trace of alkali (KOH) is added. The intense heat of the spark across the electrodes vaporises some of the metal and the vapour condenses under water. Thus the atoms of the metal present in the vapour aggregate to form colloidal particles in water. Since the metal has been ultimately converted into sol particles (via metal vapour), this method has been treated as of dispersion. Non-metal sols can be made by suspending coarse particles of the substance in the dispersion medium and striking an arc between iron electrodes.

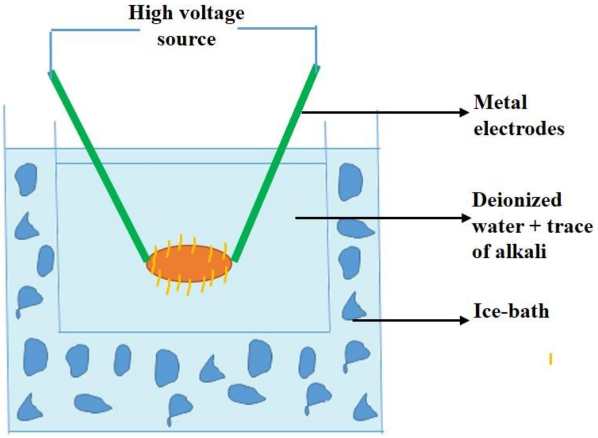


Figure 4.5: Bredig's Arc method

(3) By Peptization

Some freshly precipitated ionic solids are dispersed into colloidal solution in water by the addition of small quantities of electrolytes, particularly those containing a common ion. The precipitate adsorbs the common ions and electrically charged particles then split from the precipitate as colloidal particles. The dispersal of a precipitated material into colloidal solution by the action of an electrolyte in solution, is termed peptization. The electrolyte used is called a peptizing agent. Peptization is the reverse of coagulation of a sol.

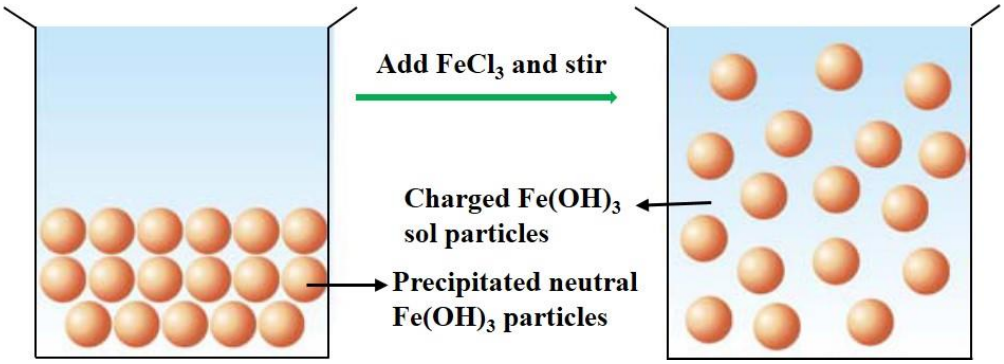


Figure 4.6: Sol of ferric hydroxide is obtained by stirring fresh precipitate of ferric hydroxide with a small amount of $FeCl_3$.

Examples of preparation of sols by peptization

(1) Silver chloride, Ag^+Cl^-, can be converted into a sol by adding hydrochloric acid (Cl^- being common ion.)

(2) Ferric hydroxide, $Fe(OH)_3$, yields a sol by adding ferric chloride (Fe^{3+} being common ion).

Aggregation methods

These methods consists of chemical reactions or change of solvent whereby the atoms or molecules of the dispersed phase appearing first, coalesce or aggregate to form colloidal particles. The conditions (temperature, concentration, etc.) used are such as permit the formation of sol particles but prevent the particles becoming too large and forming precipitate. The unwanted ions (spectator ions) present in the sol are removed by dialysis as these ions may eventually coagulate the sol. The important methods for preparing hydrophobic sols are as follows:

(1) Double Decomposition

An arsenic sulphide (As2S3) sol is prepared by passing a slow stream of hydrogen sulphide gas through a cold solution of arsenious oxide (As2O3). This is continued till the yellow colour of the sol attains maximum intensity.

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3\ (sol) + 3H_2O$$

Excess hydrogen sulphide (electrolyte) is removed by passing in a stream of hydrogen.

(2) Reduction

Silver sols and gold sols can be obtained by treating dilute solutions of silver nitrate or gold chloride with organic reducing agents like tannic acid or methanal (HCHO)

$$AgNO_3 + \text{tannic acid} \longrightarrow \text{Ag sol}$$

$$AuCl_3 + \text{tannic acid} \longrightarrow \text{Au sol}$$

(3) Oxidation

A sol of sulphur is produced by passing hydrogen sulphide into a solution of sulphur dioxide.

$$2H_2S + SO_2 \longrightarrow 2H_2O + S\downarrow$$

In qualitative analysis, sulphur sol is frequently encountered when H_2S is passed through the solution to precipitate group 2 metals if an oxidizing agent (chromate or ferric ions) happen to be present. It can be removed by boiling (to coagulate the sulphur) and filtering through two filter papers folded together.

(4) Hydrolysis

Sols of the hydroxides of iron, chromium and aluminium are readily prepared by the hydrolysis of salts of the respective metals. In order to obtain a red sol of ferric hydroxide, a few drops of 30% ferric chloride solution is added to a large volume of almost boiling water and stirred with a glass rod.

$$FeCl_3 + 3H_2O \longrightarrow \underset{\text{red sol}}{Fe(OH)_3} + 3HCl$$

(5) Change of Solvent

When a solution of sulphur or resin in ethanol is added to an excess of water, the sulphur or resin sol is formed owing to decrease in solubility. The substance is present in molecular state in ethanol but on transference to water, the molecules precipitate out to form colloidal particles.

Properties of sols–their colour

The colour of a hydrophobic sol depends on the wavelength of the light scattered by the dispersed particles. The wavelength of the scattered light again depends on the size and the nature of the particles.

Table 4.2: Colour and its corresponding particle size in the case of silver sols

Colour of Ag-Sol	Particle Diameter
Orange-yellow	6×10^{-5} mm
Orange-red	9×10^{-5} mm
Purple	13×10^{-5} mm
Violet	15×10^{-5} mm

Optical Properties of Sols

(1) Sols exhibit Tyndall effect

When a strong beam of light is passed through a sol and viewed at right angles, the path of light shows up as a hazy beam or cone. This is due to the fact that sol particles absorb light energy andthen emit it in all directions in space. This ‘scattering of light’, as it is called, illuminates the path ofthe beam in the colloidal dispersion. The phenomenon of the scattering of light by the sol particles is called Tyndall effect. The illuminated beam or cone formed by the scattering of light by the sol particles is often referred as Tyndall beam or Tyndall cone. The hazy illumination of the light beam from the film projector in a smoke-filled theatre or the light beams from the headlights of car on a dusty road, are familiar examples of the Tyndall effect.

If the sol particles are large enough, the sol may even appear turbid in ordinary light as a result of Tyndall scattering. True solutions do not show Tyndall effect. Since ions or solute molecules are too small to scatter light, the beam of light passing through a true solution is not visible when viewed from the side. Thus Tyndall effect can be used to distinguish a colloidal solution from a true solution.

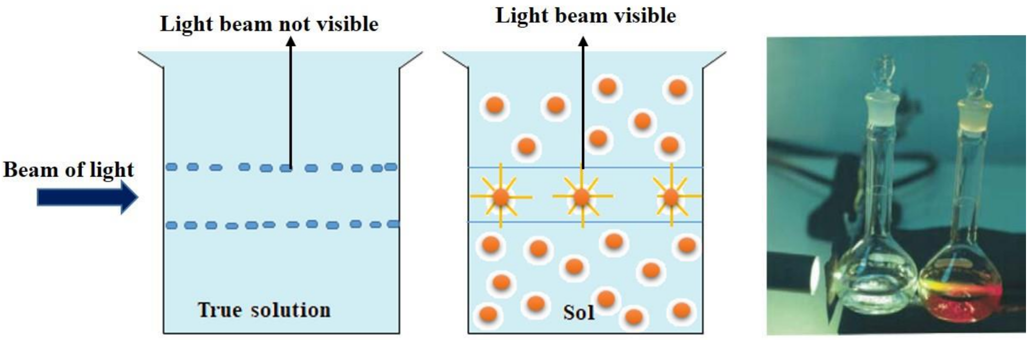


Figure 4.7: Tyndall effect (illustration).

Figure 4.8:Tyndall effect in nature.

(2) Ultramicroscope shows up the presence of individual particles

Sol particles cannot be seen with a microscope. Zsigmondy (1903) used the Tyndall phenomenon to set up an apparatus named as the ultramicroscope. An intense beam of light is focussed on a sol contained in a glass vessel. The focus of light is then observed with a microscope at right angles to the beam. Individual sol particles appear as bright specks of light against a dark background (dispersion medium). It may be noted that under the ultramicroscope, the actual particles are not visible. It is the larger halos of scattered light around the particles that are visible. Thus an ultra-microscope does not give any information regarding the shape and size of the sol particles.

(3) Sol particles can be seen with an Electron microscope

In an electron microscope, beam of electrons is focussed by electric and magnetic fields on to a photographic plate. This focussed beam is allowed to pass through a film of sol particles. Thus it is possible to get a picture of the individual particles showing a magnification of the order of 10,000. With the help of this instrument, we can have an idea of the size and shape of several sol particles including paint pigments, viruses, and bacteria. These particles have been found to be spheroid, rod-like, disc-like, or long filaments.

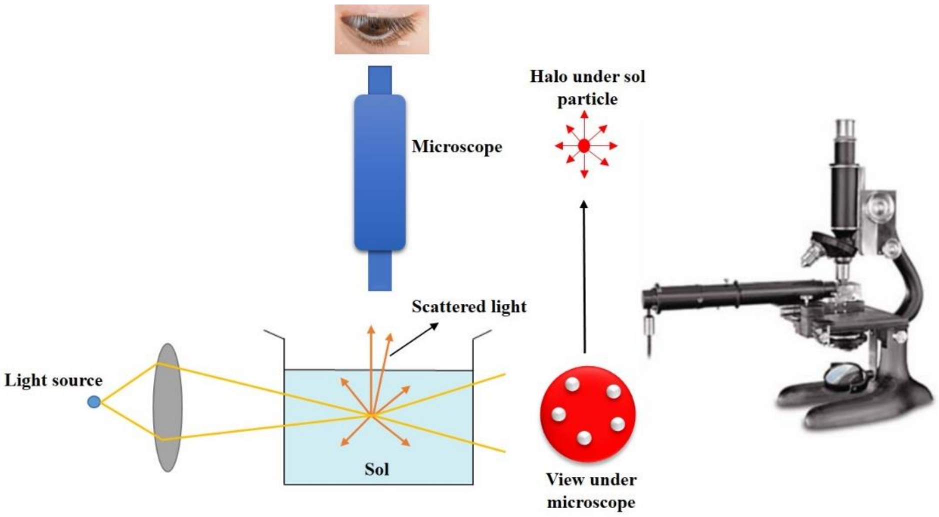


Figure 4.8: Principle of the Ultra-microscope.

Electrical Properties of Sols

(1) The sol particles carry an electric charge

The most important property of colloidal dispersions is that all the suspended particles posses either a positive or a negative charge. The mutual forces of repulsion between similarly charged particles prevent them from aggregating and settling under the action of gravity. This gives stability to the sol. The sol particles acquire positive or negative charge by preferential adsorption of positive or negative ions from the dispersion medium. For example, a ferric hydroxide sol particles are positively charged because these adsorb Fe3+ ions from ferric chloride ($FeCl_3$) used in the preparation of the sol. Since the sol as a whole is neutral, the charge on the particle is counterbalanced by oppositely charged ions termed counter ions (in this case Cl^-) furnished by the electrolyte in medium.

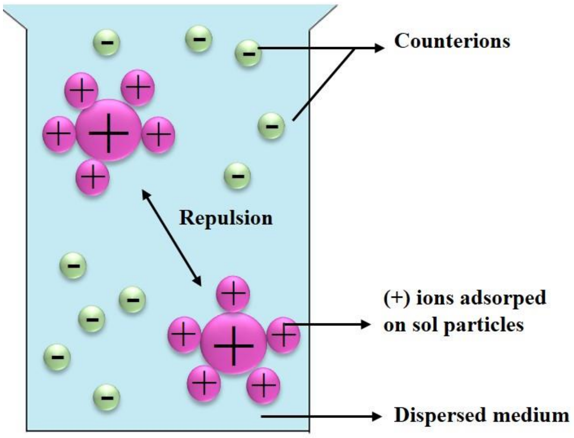


Figure 4.9: Adsorption of ions from dispersion medium gives charge to Sol particles which do not settle on account of mutual repulsions.

Electrical Double layer

The surface of colloidal particle acquires a positive charge by selective adsorption of a layer of positive ions around it. This layer attracts counterions from the medium which form a second layer of negative charges. The combination of the two layer of +ve and –ve charges around the sol particle was called Helmholtz Double layer. Helmholtz thought that positive charges next to the particle surface were fixed, while the layer of negative charges along with the medium were mobile. More recent considerations have shown that the double layer is made of:

(a) a Compact layer of positive and negative charges which are fixed firmly on the particle surface.

(b) a Diffuse layer of counterions (negative ions) diffused into the medium containing positive ions.

The combination of the compact and diffuse layer is referred to as the Stern Double layer after the colloid chemist who first realised its significance. The diffuse layer is only loosely attached to the particle surface and moves in the opposite direction under an applied electric field. Because of the distribution of the charge around the particle, there I a difference in potential between the compact layer and the bulk of solution across the diffuse layer. This is called by Electrokinetic or Zeta potential. The presence of the double layer accounts for the electrical properties : (a) Electro-osmosis and (b) Cataphoresis of colloids. It has been made possible to estimate the magnitude of the zeta potential with the help of these properties.

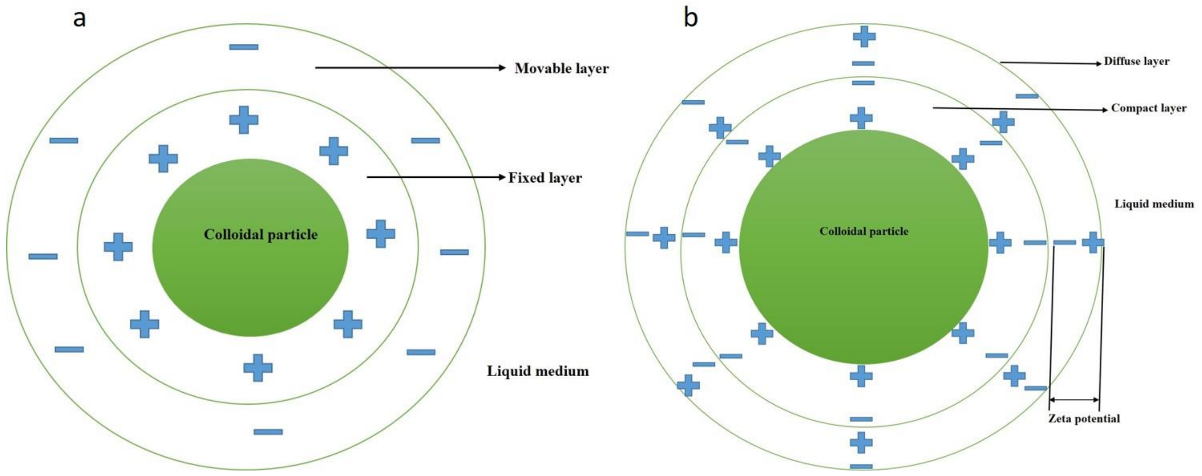


Figure 4.10: a) Helmholtz double layer. b) The electrical double layer (Stern).

2) *Electro-osmosis*

A sol is electrically neutral. Therefore the dispersion medium carries an equal but opposite charge to that of the dispersed particles. Thus the medium will move in opposite direction to the dispersed phase under the influence of applied electric potential. When the dispersed phase is kept, stationary, the medium is actually found to move to the electrode of opposite sign that its own. The movement of the dispersion medium under the influence of applied potential is known as electroosmosis. Electro-osmosis is a direct consequence of the existence of zeta potential between the sol particles and the medium. When the applied pressure exceeds the zeta potential, that diffuse layer moves and causes electro-osmosis. The phenomenon of electro-osmosis can be demonstrated by using a U-tube in which a plug of wet clay (a negative colloid) is fixed (Fig. 4.11). The two limbs of the tube are filled with water to the same level. The platinum electrodes are immersed in water and potential applied across them. It will be observed that water level rises on the cathode side and falls on anode side. This movement of the medium towards the negative electrode, shows that the charge on the medium is positive. Similarly, for a positively charged colloid electro-osmosis will take place in the reverse direction. Technically the phenomenon has been applied in the removal of water from peat, in dewatering of moist clay and in drying dye pastes.

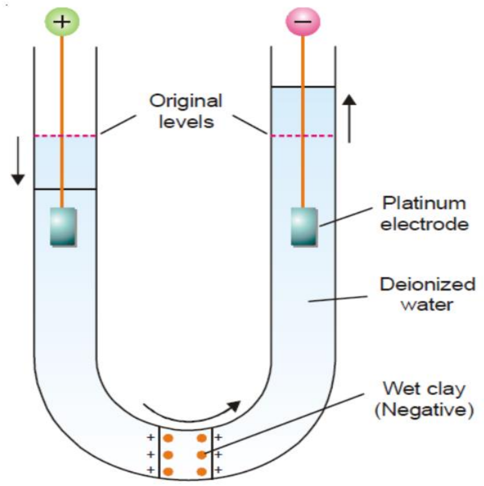


Figure 4.11: Illustration of Electro-osmosis.

3) Electrophoresis or Cataphoresis

If electric potential is applied across two platinum electrodes dipping in a hydrophilic sol, the dispersed particles move toward one or the other electrode. The movement of sol particles under an applied electric potential is called electrophoresis or cataphoresis. If the sol particles migrate toward the positive electrode, they carry a negative charge. On the other hand, if they move toward the negative electrode, they are positively charged. Thus by noting the direction of movement of the sol particles, we can determine whether they carry a positive or negative charge. The phenomenon of electrophoresis can be demonstrated by placing a layer of As_2S_3 sol under two limbs of a U-tube. When a potential difference of about 100 volts is applied across the two platinum electrodes dipping in deionised water, it is observed that the level of the sol drops on the negative electrode side and rises on the positive electrode side (Fig. 4.12). This shows that As_2S_3 sol has migrated to the positive electrode, indicating that the particles are negatively charged. Similarly, a sol of ferric hydroxide will move to the negative electrode, showing that its particles carry positive charge. Using water as the dispersion medium, the charge on the particles of some common sols determined by electrophoresis is given below.

Negatively Charged	**Positively Charged**
Metals *e.g.*, Au, Ag, Pt	Ferric hydroxide
Arsenic sulphide	Aluminium hydroxide
Starch	Basic dyes
Clay	Haemoglobin

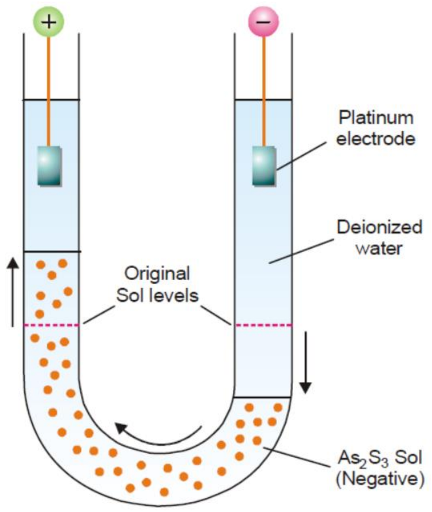


Figure 4.12: Electrophoresis of a Sol.

Applications. Some important applications of electrophoresis are:

(1) Removal of smoke from chimney gases

(2) Removal of suspended impurities

(3) Electro-plating of rubber on metal surfaces from latex (a sol)

(4) Painting of metal parts of cars from colloidal pigments

(4) Coagulation or Precipitation

We know that the stability of a lyophobic sol is due to the adsorption of positive or negative ions by the dispersed particles. The repulsive forces between the charged particles do not allow them to settle. If, somehow, the charge is removed, there is nothing to keep the particles apart from each other. They aggregate (or flocculate) and settle down under the action of gravity. The flocculation and settling down of the discharged sol particles is called coagulation or precipitation of the sol. The coagulation or precipitation of a given sol can be brought about in four ways:

(a) By addition of electrolytes

(b) By electrophoresis

(c) By mixing two oppositely charged sols

(d) By boiling

(a) *By addition of Electrolytes*. When excess of an electrolyte is added to a sol, the dispersed particles are precipitated. The electrolyte furnishes both positive and negative ions in the medium. The sol particles adsorb the oppositely charged ions and get discharged. The electrically neutral particles then aggregate and settle down as precipitate (Fig. 4.13).

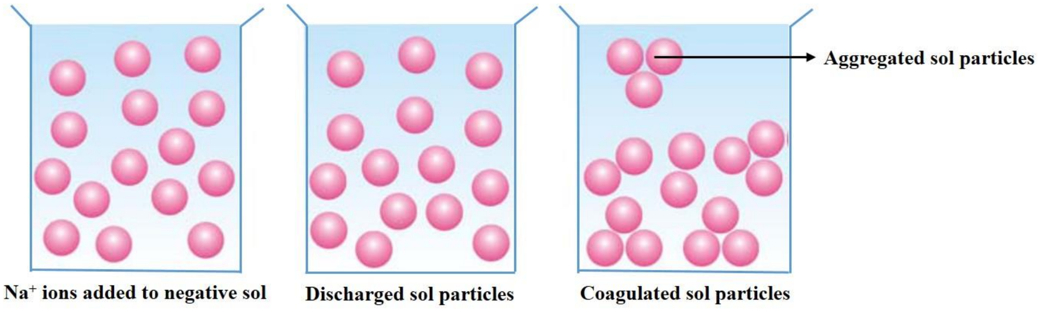


Figure 4.13: Coagulation of a Sol (illustration).

A negative ion (anion) causes the precipitation of a positively charged sol, and vice versa. The effectiveness of an anion or cation to precipitate a sol, will naturally depend on the magnitude of the charge or valence of the effective ion. From a study of the precipitating action of various electrolytes on particular sol, Hardy and Schulze gave a general rule. Hardy-Schulze Rule states that the precipitating effect of an ion on dispersed phase of opposite charge increases with the valence of the ion. The higher the valency of the effective ion, the greater is its precipitating power. Thus for precipitating an As_2S_3 sol (negative), the precipitating power of Al3+ , Ba2+, Na+ ions is in the order $Al^{3+} > Ba^{2+} > Na^+$

Similarly, for precipitating $Fe(OH)_3$ sol (positive), the precipitating power of cations $[Fe(CN)_6]^{3-}$, SO_4 , Cl^- is in the order. $[Fe(CN)_6]^{3-} > SO_4{}^{2-} > Cl^-$

The precipitation power of an electrolyte or ion is experimentally determined by finding the minimum concentration in millimoles per litre required to cause the precipitation of a sol in 2 hours. This is called the Flocculation value. The smaller the flocculation value the higher the precipitating power of an ion.

Table 4.3: Flocculation Values

($Fe(OH)_3$ Sol (+ve)		**As_2S_3 Sol (–ve)**	
Electrolyte	**Concentration (millimoles/litre)**	**Electrolyte**	**Concentration (millimoles/litre)**
NaCl, (Cl^-)	9.3	NaCl, (Na^+)	51
KCl, (Cl^-)	9.0	KCl, (K^+)	50

K_2SO_4 , (SO_4)	0.20	$BaCl_2$, (Ba^{2+})	0.69
$K_3Fe(CN)_6$, $[Fe(CN)_6]^{3-}$	0.096	$AlCl_3$, (Al^{3+})	0.093

It may be noted how rapidly the precipitation power increases with the increases of valence. The ratio for the mono-, di-, and trivalent anion or cation are approximately 1:40:90 for $Fe(OH)_3$ sol and 1:70:500 for the As_2S_3 sol.

(b) *By Electrophoresis*. In electrophoresis the charged sol particles migrate to the electrode of opposite sign. As they come in contact with the electrode, the particles are discharged and precipitated.

(c) *By mixing two oppositely charged sols*. The mutual coagulation of two sols of opposite charge can be effected by mixing them. The positive particles of one sol are attracted by the negative particles of the second sol. This is followed by mutual adsorption and precipitation of both the sols. Ferric hydroxide (+ve sol) and arsenious sulphide (–ve sol) form such a pair.

(d) *By boiling*. Sols such as sulphur and silver halides dispersed in water, may be coagulated by boiling. Increased collisions between the sol particles and water molecules remove the adsorbed electrolyte. This takes away the charge from the particles which settle down.

Stability of Sols

A true colloidal solution is stable. Its particles do not ever coalesce and separate out. The stability of sols is mainly due to two factors:

(1) Presence of like charge on sol particles

The dispersed particles of a hydrophobic sol possess a like electrical charge (all positive or all negative) on their surface. Since like charges repel one another, the particles push away from one another and resist joining together. However, when an electrolyte is added to a hydrophobic sol, the particles are discharged and precipitated.

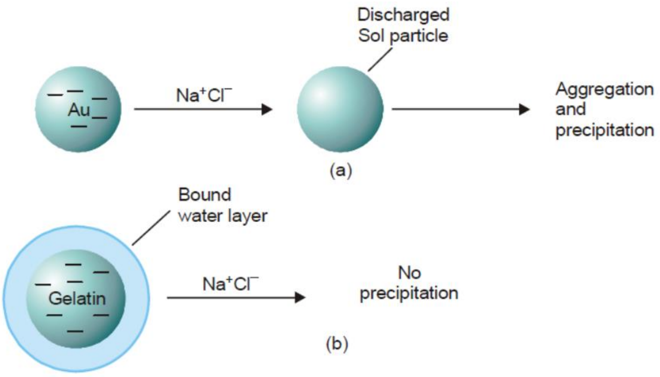


Figure 4.14: (a) A negatively charged gold particle is precipitated by Na ions; (b) The water layer around gelatin particle does not allow Na ions to penetrate and discharge the particle.

(2) Presence of Solvent layer around sol particle

The lyophilic sols are stable for two reasons. Their particles possess a charge and in addition have a layer of the solvent bound on the surface. For example, a sol particle of gelatin has a negative charge and a water layer envelopes it. When sodium chloride is added to colloidal solution of gelatin, its particles are not precipitated. The water layer around the gelatin particle does not allow the Na^+ ions to penetrate it and discharge the particle. The gelatin sol is not precipitated by addition of sodium chloride solution. Evidently, lyophilic sols are more stable than lyophobic sols.

Associated Colloids

The molecules of substances as soaps and artificial detergents are smaller than the colloidal particles. However in concentrated solutions these molecules form aggregates of colloidal size. Substances whose molecules aggregate spontaneously in a given solvent to form particles of colloidal dimensions are called Associated or Association Colloids.

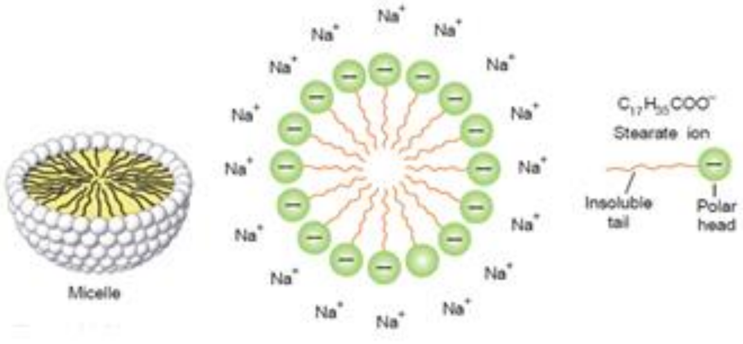
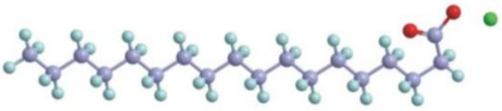


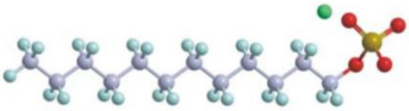
Figure 4.15: A soap micelle.

The colloidal aggregates of soap or detergent molecules formed in the solvent are referred to as micelles. Some examples of associated colloids are:

$C_{17}H_{35}\text{—}CO\bar{O}Na^{+}$
Sodium stearate



$C_{12}H_{25}\text{—}SO_2\bar{O}Na^{+}$
Sodium dodecyl sulphate



Explanation. Soap or detergent molecule ionises in water to form an anion and sodium ion. Thus sodium stearate (a typical soap) furnishes stearate anion and sodium ion in aqueous solution.

$C_{17}H_{35}COO^{-}\,Na^{+} \longrightarrow C_{17}H_{35}COO^{-} + Na^{+}$

Sodium stearate Stearate ion

As many as 70 stearate ions aggregate to form a micelle of colloidal size. The stearate ion has a long hydrocarbon chain (17 carbons) with a polar —COO– group at one end. The zig zag hydrocarbon tail is shown by a wavy line and the polar head by a hollow circle. In the micelle formation, the tails being insoluble in water are directed toward the centre, while the soluble polar heads are on the surface in contact with water (Fig. 4.15). The charge on the micelle due to the polar heads accounts for the stability of the particle.

Cleansing Action of Soaps and Detergents

The cleansing action of soap is due to

(1) Solubilisation of grease into the micelle

(2) Emulsification of grease

Solubilisation. In relatively strong solution the soap (or detergent) anions spontaneously form a micelle. The hydrocarbon tails are in the interior of the micelle and COO– ions on the surface. The grease stain is thus absorbed into the interior of the micelle which behaves like liquid hydrocarbons. As the stain is detached from the fabric, the dirt particles sticking to the stain are also removed.

Emulsification. As already discussed the soap or detergent molecules are ionised in water. The anions are made of oil-soluble hydrocarbon tails and water-soluble polar heads. Thus soap anion has a long hydrocarbon tail with a polar head, —COO–. When soap solution is added to a fabric, the tails of the soap anions are pegged into the grease stain. The polar heads protrude from the grease surface and form a charged layer around it. Thus by mutual repulsions the grease droplets are suspended in water. The emulsified grease stains are washed away with soap solution.

Emulsions

These are liquid-liquid colloidal systems. In other words, an emulsion may be defined as a dispersion of finely divided liquid droplets in another liquid. Generally one of the two liquids is water and the other, which is immiscible with water, is designated as oil. Either liquid can constitute the dispersed phase.

Types of Emulsions

There are two types of emulsions. (a) Oil-in-Water type (O/W type) ; (b) Water-in-Oil type (W/O type)

Examples of Emulsions

(1) Milk is an emulsion of O/W type. Tiny droplets of liquid fat are dispersed in water.

(2) Stiff greases are emulsions of W/O type, water being dispersed in lubricating oil.

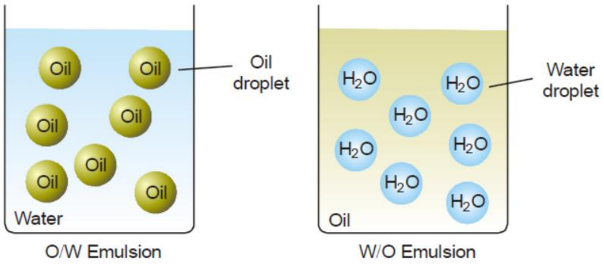


Figure 4.16: Two types of Emulsions.

Preparation of Emulsions

The dispersal of a liquid in the form of an emulsion is called emulsification. This can be done by agitating a small proportion of one liquid with the bulk of the other. It is better accomplished by passing a mixture of the two liquid through a colloid mill known as homogenizer. The emulsions obtained simply by shaking the two liquids are unstable. The droplets of the dispersed phase coalesce and form a separate layer. To have a stable emulsion, small amount of a third substance called the Emulsifier or Emulsifying agent is added during the preparation. This is usually a soap, synthetic detergent, or a hydrophilic colloid.

Role of Emulsifier

The emulsifier concentrates at the interface and reduces surface tension on the side of one liquid which rolls into droplets. Soap, for example, is made of a long hydrocarbon tail (oil soluble) with a polar head —COO^-Na^+ (water soluble). In O/W type emulsion the tail is pegged into the oil droplet, while the head extends into water. Thus the soap acts as go-between and the emulsified droplets are not allowed to coalesce.

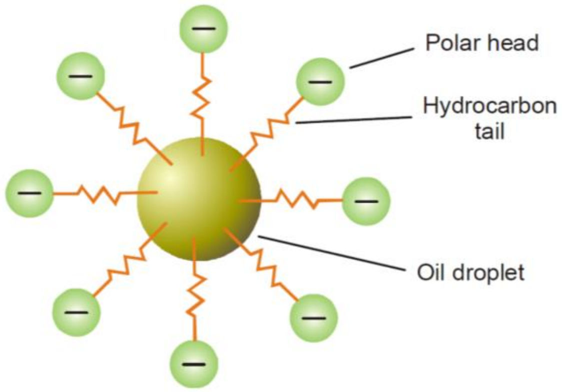


Figure 4.17: Role of emulsifier (Soap).

Properties of Emulsions

(1) Demulsification. Emulsions can be broken or ‘demulsified’ to get the constituent liquids by heating, freezing, centrifuging, or by addition of appreciable amounts of electrolytes. They are also broken by destroying the emulsifying agent. For example, an oil-water emulsion stabilized by soap is broken by addition of a strong acid. The acid converts soap into insoluble free fatty acids.

(2) Dilution. Emulsions can be diluted with any amount of the dispersion medium. On the other hand the dispersed liquid when mixed with it will at once form a separate layer. This property of emulsions is used to detect the type of a given emulsion.

Gels

A gel is a jelly-like colloidal system in which a liquid is dispersed in a solid medium. For example, when a warm sol of gelatin is cooled, it sets to a semisolid mass which is a gel. The process of a gel formation is known as Gelation.

Explanation. Gelation may be thought of as partial coagulation of a sol. The coagulating sol particles first unite to form long thread-like chains. These chains are then interlocked to form a solid framework. The liquid dispersion medium gets trapped in the cavities of this framework. The resulting semisolid porous mass has a gel structure. A sponge soaked in water is an illustration of gel structure.

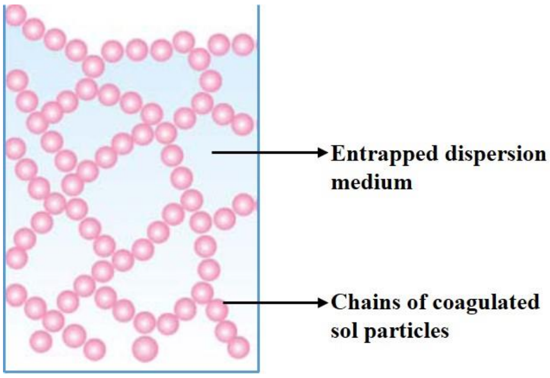


Figure 4.18: The network of the coagulated sol particles enclosing liquid, forming a gel.

Two types of Gels

Gels may be classified into two types:

(*a*) *Elastic gels* are those which possess the property of elasticity. They change their shape on applying force and return to original shape when the force is removed. Gelatin, starch and soaps are examples of substances which form elastic gels. Elastic gels are obtained by cooling fairly concentrated lyophilic sols. The linkages between the molecules (particles) are due to electrical attraction and are not rigid.

(*b*) *Non-elastic gels* are those which are rigid *e.g.*, silica gel. These are prepared by appropriate chemical action. Thus silica gel is produced by adding concentrated hydrochloric acid to sodium silicate solution of the correct concentration. The resulting molecules of silicic acid polymerise to form silica gel. It has a network linked by covalent bonds which give a strong and rigid structure.

Properties of Gels

(1) Hydration.A completely dehydrated elastic gel can be regenerated by addition of water. But once a nonelastic gel is freed from moisture, addition of water will not bring about gelation.

(2) Swelling. Partially dehydrate elastic gels imbibe water when immersed in the solvent. This causes increase in the volume of the gel and process is called Swelling.

(3) Syneresis. Many inorganic gels on standing undergo shrinkage which is accompanied by exudation of solvent. This process is termed Syneresis.

(4) Thixotropy. Some gels are semisolid when at rest but revert to liquid sol on agitation. This reversible sol-gel transformation is referred to as Thixotropy. Iron oxide and silver oxide gels exhibit this property. The modern thixotropic paints are also an example.

Applications of Colloids

Colloids play an important role in our daily life and industry. A knowledge of colloid chemistry is essential to understand some of the various natural phenomena around us. Colloids make up some of our modern products. A few of the important applications of colloids are listed below.

(1) *Foods*

Many of our foods are colloidal in nature. Milk is an emulsion of butterfat in water protected by a protein, casein. Salad dressing, gelatin deserts, fruit jellies and whipped cream are other examples. Ice cream is a dispersion of ice in cream. Bread is a dispersion of air in baked dough.

(2) *Medicines*

Colloidal medicines being finely divided, are more effective and are easily absorbed in our system. Halibut-liver oil and cod-liver that we take are, in fact, the emulsions of the respective oils in water. Many ointments for application to skin consist of physiologically active components dissolved in oil and made into an emulsion with water. Antibiotics such as penicillin and streptomycin are produced in colloidal form suitable for injections.

3) *Non-drip or thixotropic paints*

All paints are colloidal dispersions of solid pigments in a liquid medium. The modern nondrip or thixotropic paints also contain long-chain polymers. At rest, the chains of molecules are coiled and entrap much dispersion medium. Thus the paint is a semisolid gel structure. When shearing stress is applied with a paint brush, the coiled molecules straighten and the entrapped medium is released. As soon as the brush is removed, the liquid paint reverts to the semisolid form. This renders the paint ‘non-drip’.

(4) *Electrical precipitation of smoke*

The smoke coming from industrial plants is a colloidal dispersion of solid particles (carbon, arsenic compounds, cement dust) in air. It is a nuisance and pollutes the atmosphere. Therefore, before allowing the smoke to escape into air, it is treated by Cottrell Precipitator (Fig. 4.19). The smoke is let past a series of sharp points charged to a high potential (20,000 to 70,000 V). The points discharge high velocity electrons that ionise molecules in air. Smoke particles adsorb these positive ions and become charged. The charged particles are attracted to the oppositely charged electrodes and get precipitated. The gases that leave the Cottrell precipitator are thus freed from smoke. In addition, valuable materials may be recovered from the precipitated smoke. For example, arsenic oxide is mainly recovered from the smelter smoke by this method.

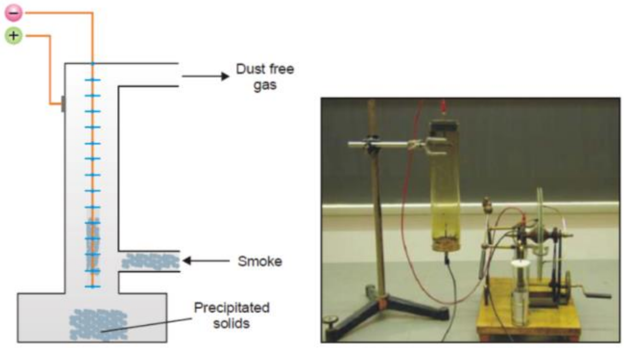


Figure 4.19: Cottrell Smoke precipitator.

(5) *Clarification of Municipal water*

The municipal water obtained from natural sources often contains colloidal particles. The process of coagulation is used to remove these. The sol particles carry a negative charge. When aluminium sulphate (alum) is added to water, a gelatinous precipitate of hydrated aluminium hydroxide (floc) is formed,

$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+$
$Al(OH)3+ + 4H2O + H^+ \longrightarrow Al(OH)3(H2O)^{4+}$

The positively charged floc attracts to it negative sol particles which are coagulated. The floc along with the suspended matter comes down, leaving the water clear.

(6) *Formation of Delta*

The river water contains colloidal particles of sand and clay which carry negative charge. The sea water, on the other hand, contains positive ions such as Na^+, Mg^{2+}, $Ca2^+$. As the river water meets sea water, these ions discharge the sand or clay particles which are precipitated as delta.

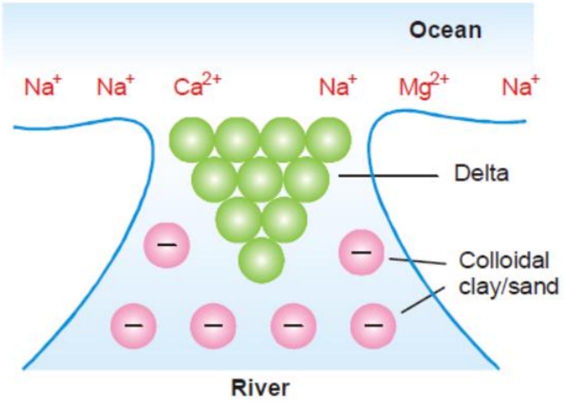


Figure 4.20: Formation of Delta.

(7) Artificial Kidney machine

The human kidneys purify the blood by dialysis through natural membranes. The toxic waste products such as urea and uric acid pass through the membranes, while colloidal-sized particles of blood proteins (haemoglobin) are retained. Kidney failure, therefore, leads to death due to accumulation of poisonous waste products in blood. Now-a-days, the patient's blood can be cleansed by shunting it into an 'artificial kidney machine'. Here the impure blood is made to pass through a series of cellophane tubes surrounded by a washing solution in water. The toxic waste chemicals (urea, uric acid) diffuse across the tube walls into the washing solution. The purified blood is returned to the patient. The use of artificial kidney machine saves the life of thousands of persons each year.

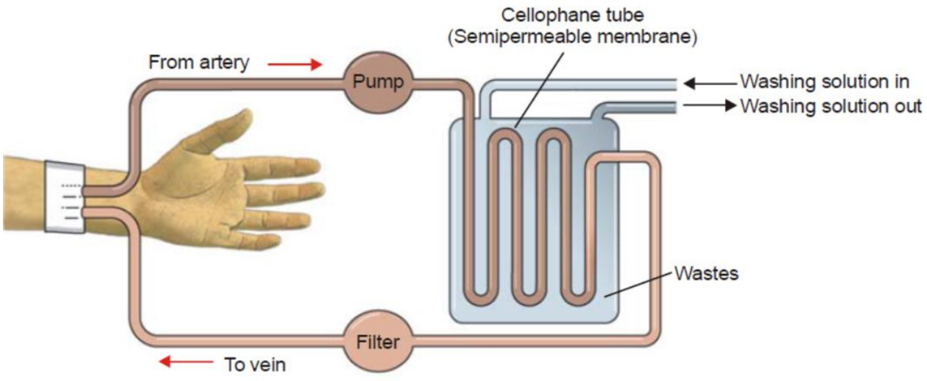


Figure 4.21: An artificial kidney machine for purification of blood by dialysis.

(8) *Adsorption indicators*

These indicators function by preferential adsorption of ions onto sol particles. Fluorescein (Na^+Fl) is an example of adsorption indicator which is used for the titration of sodium chloride solution against silver nitrate solution. When silver nitrate solution is run into a solution of sodium chloride containing a little fluorescein, a white precipitate of silver chloride is first formed. At the end-point, the white precipitate turns sharply pink.

Explanation. The indicator fluorescein is a dye ($Na^+Fl^–$) which gives coloured anion $Fl^–$ in aqueous solution. The white precipitate of silver chloride formed by running $AgNO_3$ solution into NaCl solution is partially colloidal in nature.

(a) Before the end-point, $Cl^–$ ions are in excess. The AgCl sol particles adsorb these ions and become negatively charged. The negative $AgCl/Cl^–$ particles cannot adsorb the coloured fluorescein anions ($Fl^–$) due to electrostatic repulsion. Thus the precipitate remains white.

(b) After the end-point, Ag^+ ions become in excess. AgCl sol particles adsorb these and acquire positive charge. The positive $AgCl/Ag^+$ particles now attract the coloured fluorescein anions (Fl^-) and turn rose-red. Thus the end-point is marked by white precipitate changing to pink.

(9) Blue colour of the sky

This is an application of Tyndall effect. The upper atmosphere contains colloidal dust or ice particles dispersed in air. As the sun rays enter the atmosphere (Fig. 4.22) these strike the colloidal particles. The particles absorb sunlight and scatter light of blue colour (4600–5100Å). The light that is incident at earth's surface is considerably reddened due to the removal of most of the blue light in the upper atmosphere.

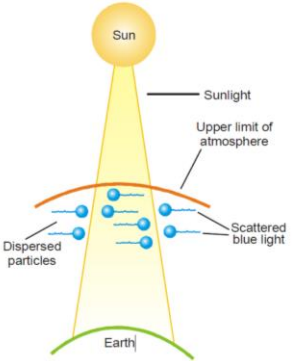


Figure 4.22: Blue colour of sky (illustration).

Macromolecules:

Colloidal solutions are formed by aggregation of atoms or molecules to give particles of colloidal size. Yet there are substances which are themselves composed of giant molecules and dissolve in a solvent to yield colloidal solutions directly. These giant molecules are termed macromolecules. The dimensions of the macromolecules fall in a range between 10Å and 10,000Å. Proteins (gelatin), synthetic polymers (plastics), synthetic rubber, cellulose and starch all possess macromolecules. Solutions of macromolecules behave like reversible colloids or lyophilic sols. They show a weak Tyndall effect and possess high viscosity. Macromolecules in solution do not carry an electric charge and do not show electrophoresis.

Molecular weight of Macromolecules

The molecular weight is an important property of polymeric substances such as proteins, polymers (plastics, starch) and other macromolecules. Generally, molecules of a protein or a polymer may not be of the same size. Therefore all the experimental methods of molecular weight determination will give some kind of an average value. Two types of average molecular weights have been defined.

(1) Number average molecular weight. It is defined as:

$$M_n = \frac{\text{Total weight, } W}{\text{Total number of particles}}$$

$$\overline{M}_n = \frac{n_1M_1 + n_2M_2 + ...}{n_1 + n_2 + ...}$$

$$\overline{M}_n = \frac{\Sigma n_iM_i}{\Sigma n_i}$$

niMi stands for the weight of macromolecules numbering ni and having molecular weight Mi. The experimental methods based on properties which depend on the number of particles present e.g., osmotic pressure, yield number average molecular weight.

(2) Weight average molecular weight. It is defined as:

$$\overline{M}_w = \frac{m_1M_1 + m_2M_2 + ...}{m_1 + m_2 + ...} = \frac{\Sigma m_iM_i}{\Sigma m_i}$$

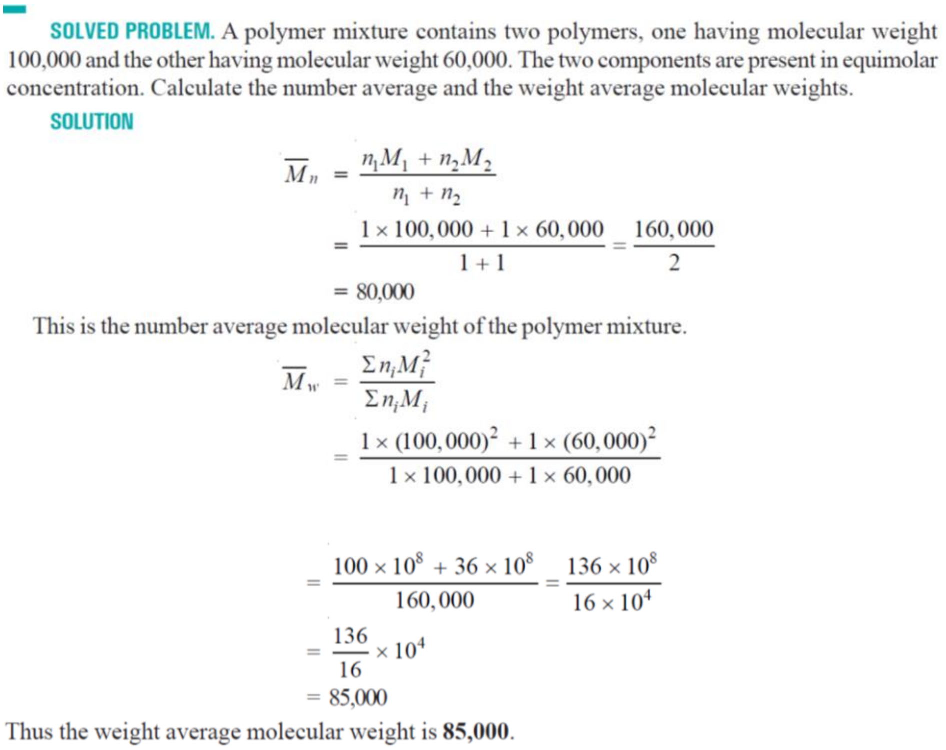
Where, m1, m2, etc. represent mass of macromolecules having molecular weights M1, M2, etc. respectively.

$$W_i = n_i M_i$$

$$\overline{M}_v = \frac{n_1M_1^2 + n_2M_2^2 + ...}{n_1M_1 + n_2M_2 + ...}$$

$$\overline{M}_v = \frac{\Sigma n_iM_i^2}{\Sigma n_iM_i}$$

Molecular weights determined by methods based on properties dependent on the mass of the particles are the weight average molecular weights. According to the definitions set out here, Mw > Mn . The two are equal only when all particles are identical in weight



SOLVED PROBLEM. A polymer mixture contains two polymers, one having molecular weight 100,000 and the other having molecular weight 60,000. The two components are present in equimolar concentration. Calculate the number average and the weight average molecular weights.

SOLUTION

$$\overline{M}_n = \frac{n_1M_1 + n_2M_2}{n_1 + n_2}$$

$$= \frac{1 \times 100,000 + 1 \times 60,000}{1+1} = \frac{160,000}{2}$$

$$= 80,000$$

This is the number average molecular weight of the polymer mixture.

$$\overline{M}_w = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i}$$

$$= \frac{1 \times (100,000)^2 + 1 \times (60,000)^2}{1 \times 100,000 + 1 \times 60,000}$$

$$= \frac{100 \times 10^8 + 36 \times 10^8}{160,000} = \frac{136 \times 10^8}{16 \times 10^4}$$

$$= \frac{136}{16} \times 10^4$$

$$= 85,000$$

Thus the weight average molecular weight is **85,000**.

Determination of Molecular Weights of Macromolecules

(1) *Osmotic Pressure Method*

The van’t Hoff equation for dilute solutions may be written as:

$$p = \frac{c}{M} RT$$

$$\frac{p}{c} = \frac{RT}{M}$$

where p = osmotic pressure, atm ; c = concentration of solution gl^{-1}; R = gas constant, 0.08205 l atm deg^{-1} mol^{-1}; T = kelvin temperature ; M = molecular weight of the solute (polymer). In actual determination of molecular weight of a high polymer, osmotic pressure (p) of a series of small concentrations (c) is measured with the help of a special Osmometer shown in Fig. 4.23(b). The plot of p/c against c is a straight line (Fig. 4.23 (a)).

It is extrapolated to zero concentration. This gives RT/M as the intercept from which the molecular weight can be calculated.

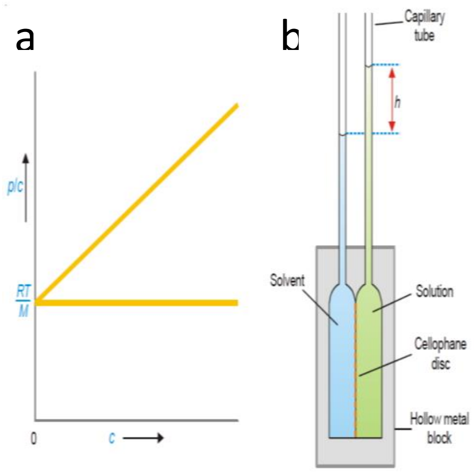


Figure 4.23 a) Plot p/c versus *c*: giving intercept = RT/M b) Fuos-Mead Osmometer for measuring osmotic pressure of polymer solution.

Fuos-Mead Osmometer

It is a modern device for measuring the osmotic pressure of polymer solutions (Fig. 4.23 (b)). It consists of two hollow metal blocks holding a cellophane disc in between. Each block carries a capillary tube. The hollow metal compartments are charged with solvent and solution through the side-tubes (not shown). Osmosis occurs across the semipermeable membrane (cellophane disc). The height of the solution in the capillary (h) is read off differentially to eliminate surface tension effect.

(2) *Viscosity method*

It is a very convenient method for determining the molecular weights of macromolecules in solution. The addition of macromolecules to a solvent increases its viscosity over that of pure solvent. The relative viscosity of a solution of a polymer, denoted by ηr, is given by the expression.

$$\eta = \frac{\eta}{\eta_o} \quad \text{--------------(1)}$$

Where, η is viscosity of solution and η0 that of the solvent at the same temperature. The specific viscosity, denoted by ηsp , is given by

$\eta sp = \eta r - 1$ ---------(2)

In terms of (1) and (2), the intrinsic viscosity is defined as

$[\eta] = \lim_{c \to 0} (\eta sp/c)$

Where, c is the concentration of the solute. The plot ηsp/c against η gives a straight line. Extrapolation to c = 0 yields the intrinsic viscosity.
It was shown by staudinger that an empirical relationship exists between intrinsic viscosity [η] and the molecular weight [M] of the high polymer.

$[\eta] = kM^a$

Where, k and a are constants for a specific polymer in a specific solvent. Once k and a are known for a polymer solvent combination, M may be calculated from a determination of the value of intrinsic viscosity. The viscosity measurements yield the weight average molecular weight of a macromolecular substance.

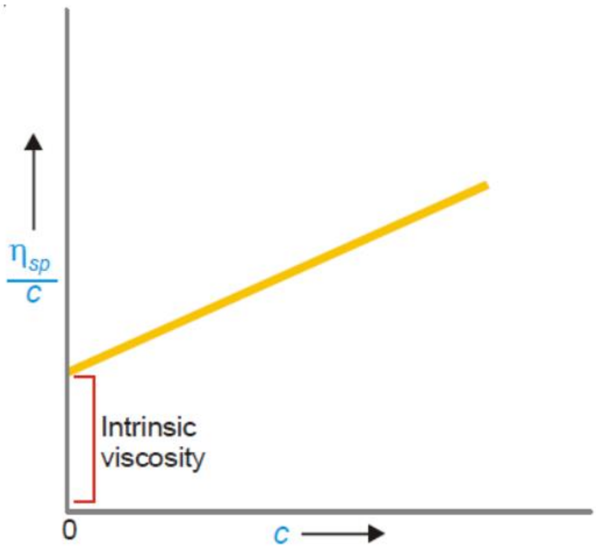


Figure 4.24: Plot of η_{sp} /c versus c.

(3) *Svedberg's Sedimentation method*

The rate of selling or sedimentation of polymer particles under the influence of gravitation force is very slow. Svedberg devised a centrifugal machine with the help of which macromolecules could be sedimented with speed. As a result, the particles move down in the containing tube. This causes a concentration gradient in the tube. The rate, dx/dt, at which the macromolecules sediment, is given in terms of the sedimentation constant S by the following expression:

$S = \frac{dx}{dt} / \omega^2 x$

Where, x is the distance of the solute species from the centre of rotation and ω is the angular velocity. The sedimentation constant, S, is related to the molecular weight of the polymer by the expression:

$$M = \frac{SRT}{D(1-\rho/\rho')}$$

Where, ρ and ρ' are the densities of the solvent and solute respectively. The rate at which sedimentation occurs, determined experimentally, can thus be used for finding the molecular weight of macromolecules. Since the rate of sedimentation depends on the mass of the particle undergoing sedimentation, the molecular weight obtained by this method is the weight average molecular weight, $\overline{M}$ w .

(4) *Sedimentation Equilibrium method*

This method for determining molecular weight of a high polymer is quicker and convenient compared to method (3). If a sol is whirled sufficiently long in an ultracentrifuge, a stage is reached at which the sol no longer settles. At this stage an equilibrium is reached between the centrifugal force and diffusion of the material in a direction opposite to the centrifugal force. If c1 and c2 be the concentrations of the particles at points x_1 and x_2 cm from the centre of rotation, the molecular weight, M, of the high polymer is given by the relation

$$\text{In}\,\frac{c_2}{c_1} = \frac{M\omega^2(\rho-\rho')\,(x_2^2+x_1^2)}{2RT\rho}$$

$$M = \frac{2RT\rho\ln c_2/c_1}{\omega^2(\rho-\rho')\,(x_1^2-x_2^2)}$$

By determining the concentrations c_1 and c_2 at the two levels x_1 and x_2 in the settling cell at sedimentation equilibrium, M can be calculated.

UNIT-V

Photo chemistry

Photochemical Reactions

Ordinary reactions occur by absorption of heat energy from outside. The reacting molecules are energised and molecular collisions become effective. These bring about the reaction. The reactions which are caused by heat and in absence of light are called thermal or dark reactions.

On the other hand, some reactions proceed by absorption of light radiations. These belong to the visible and ultraviolet regions of the electromagnetic spectrum (2000 to 8000 Å). The reactant molecules absorbs photons of light and get excited. These excited molecules then produce the reactions. A reaction which takes place by absorption of the visible and ultraviolet radiations is called a photochemical reaction. The branch of chemistry which deals with the study of photochemical reactions is called photochemistry.

Difference Between Photochemical and Thermochemical Reactions

Photochemical Reactions	**Thermochemical Reactions**
These involve absorption of light radiations.	These reactions involve absorption or evolution of heat.
The presence of light is the primary requirement for reactions to take place.	These reactions can take place in dark as well as in light.
Temperature has a very little effect on the rate of photochemical reactions.	Temperature has a significant effect on the rate of a thermochemical reaction.
ΔG for photochemical spontaneous reactions may be +ve or –ve.	ΔG for a thermochemical reaction is always negative.
Photochemical activation is highly selective. The absorbed photon excites a particular atom or group of atoms which become site for the reaction.	Thermochemical activation is not selective in nature.

Laws of Photochemistry

There are two basic laws governing photochemical reactions:

(a) The Grothus-Draper law

(b) Lambert-Beer Law

(c) The Stark-Einstein law of Photochemical Equivalence

(a) Grothus–Draper Law

When light falls on a cell containing a reaction mixture, some light is absorbed and the remaining light is transmitted. Obviously, it is the absorbed component of light that is capable of producing the reaction. The transmitted light is ineffective chemically. Early in the 19th century, Grothus and Draper studied a number of photochemical reactions and enunciated a generalisation. This is known as Grothus-Draper law and may be stated as follows: It is only the absorbed light radiations that are effective in producing a chemical reaction. However, it does not mean that the absorption of radiation must necessarily be followed by a chemical reaction. When the conditions are not favourable for the molecules to react, the light energy remains unused. It may be re-emitted as heat or light.

The Grothus-Draper law is so simple and self-evident. But it is purely qualitative in nature. It gives no idea of the relation between the absorbed radiation and the molecules undergoing change.

(b) Lambert-Beer Law

The probability or rate of absorption is given by the Lambert-Beer Law. The Lambert law states that the *fraction of incident radiation absorbed by a transparent medium is independent of the intensity of incident radiation and that each successive layer of the medium absorbs an equal fraction of incident radiation.* The Beer law states *that the amount of radiation absorbed is proportional to the number of molecules absorbing the radiation ie., the concentration C of the absorbing species.*

$-\frac{dI}{I} = \alpha_v \, Cdl$ --------- (1)

where α_v, is the proportionality constant. The quantity Cdl, measures the amount of solute per unit area of the layer, dl being the thickness of the layer. Since

$C = \frac{mole}{volume} = \frac{mole}{area\ X\ thicheness}$

Therefore, $Cdl = {}^{mole}/_{area}$

On integrating equation (1) within the boundary conditions, we get

(i) $I = I_o$ when $l = 0$, and (ii) $I = I$, when $l = l$, we have,

$\ln I_o/I = \alpha_v Cdl$ --------------(2)

α_v known as absorption coefficient: is a function of frequency or wavelength of radiation. The final form is expressed in the decadic logarithm,

$\log I_o/I = \varepsilon_V Cl$ ---------------(3)

Where, $\varepsilon_V = \alpha_v / 2.303$, is called the molar extinction coefficient and is a function of frequency v. the concentration is expressed in moles per litre and l is the optical path length in cm. The S1 units of c, l and ε are mol dm^{-3}, m and m^2mol^{-1} respectively. I_o and I are incident and transmitted intensity respectively (Figure 5.1) . The quantity $\log I_o/I$ is commonly known as the optical density OD or absorbance A. A plot of εv (or its logarithm) vs wavelength or wavenumber gives rise to familiar absorption bands. Since

$I = I_o 10^{-\varepsilon v Cl}$ ----------------- (4)

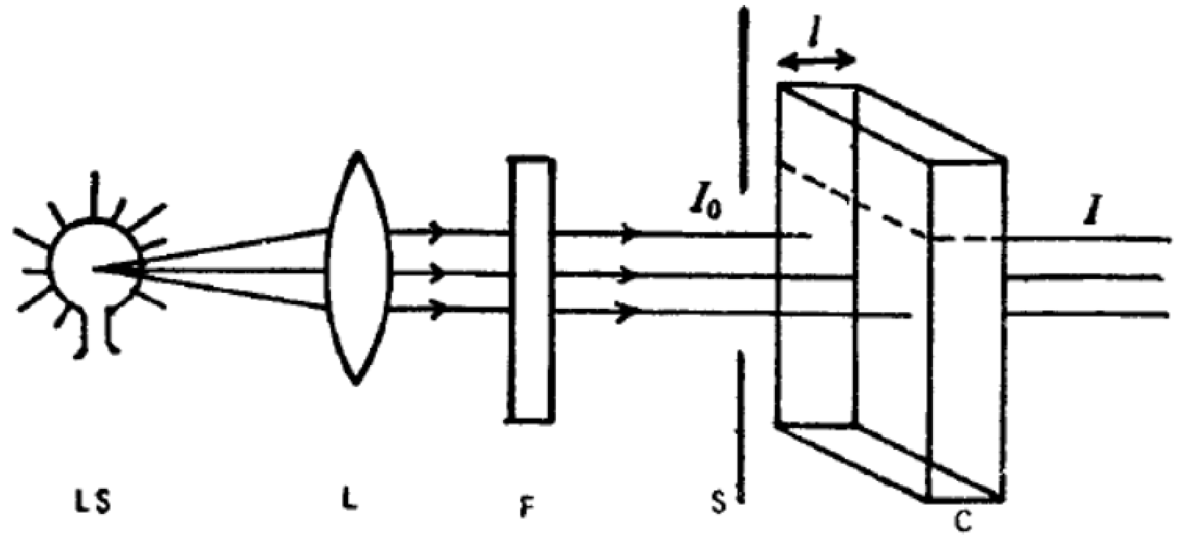


Figure 5.1: Optical arrangement for a photochemical reaction by a collimated beam of radiation of cross-sectional area A. LS = light source, L= lens, F= filter, S=collimating shield, C- reaction cell, l = optical path length, I_o = incident light intensity, I = transmitted light intensity.

The amount of light absorbed I_o, by the system is

$Io = Io - I = I_o 10^{-\varepsilon vCl}$

$= I_o (1-10^{-\varepsilon vCl})$ -------------------- (5)

For more than one absorbing components, optical density is $\Sigma_i \varepsilon_{vi} C_i l$, where ε_{vi} is the molar absorptivity at frequency $_{vi}$ for the ith component whose concentration is C_i, assuming path length to be unity. Hence the measured OD is

$OD = OD_1 + OD_2 + OD_3 + \ldots\ldots\ldots\ldots$ ------------(6)

(c) Stark-Einstein Law of Photochemical Equivalence

Stark and Einstein (1905) studied the quantitative aspect of photochemical reactions by application of Quantum theory of light. They noted that each molecule taking part in the reaction absorbs only a single quantum or photon of light. The molecule that gains one photon-equivalent energy is activated and enters into reaction. Stark and Einstein thus proposed a basic law of photochemistry which is named after them. The Stark-Einstein law of photochemical equivalence may be stated as: In a photochemical reaction, each molecule of the reacting substance absorbs a single photon of radiation causing the reaction and is activated to form the products.

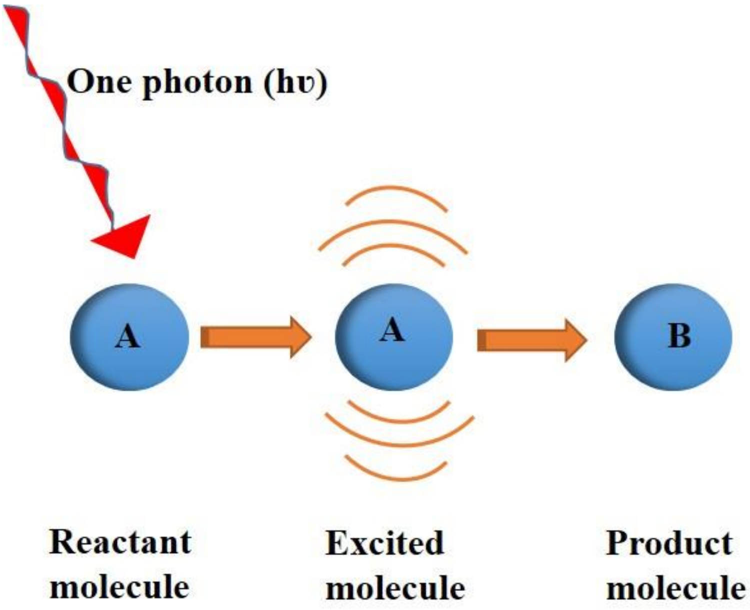


Figure 5.2: Illustration of Law of Photochemical equivalence; absorption of one photon decomposes one molecule

The law of photochemical equivalence is illustrated in Figure 5.2 where a molecule ‘A’ absorbs a photon of radiation and gets activated. The activated molecule (A*) then decomposes to yield B. We could say the same thing in equational form as:

$A + h\upsilon \rightarrow A^*$

$A^* \rightarrow B$ there overall be,

$A + h\upsilon \rightarrow B$

In practice, we use molar quantities. That is, one mole of A absorbs one mole of photons or one einstein of energy, E. The value of E can be calculated by using the expression given below:

$E = \frac{2.859}{\lambda} \times 10^5$ kcal mol^{-1}

Primary and Secondary reactions

The overall photochemical reaction may consist of :

(a) Primary reaction

(b) Secondary reactions

A primary reaction proceeds by absorption of radiation.

A secondary reaction is a thermal reaction which occurs subsequent to the primary reaction.

For example, the decomposition of HBr occurs as follows:

$HBr + hv \longrightarrow H + Br$ Primary reaction

$HBr + H \longrightarrow H_2 + Br$ Secondary reaction

$Br + Br \longrightarrow Br_2$ Secondary reaction

$2HBr + hv \longrightarrow H_2 + Br_2$ Overall reaction

Evidently, the primary reaction only obeys the law of photochemical equivalence strictly. The secondary reactions have no concern with the law.

Quantum efficiency or (Quantum yield)

It has been shown that not always a photochemical reaction obeys the Einstein law. The number of molecules reacted or decomposed is often found to be markedly different from the number of quanta or photons of radiation absorbed in a given time.

The number of molecules reacted or formed per photon of light absorbed is termed Quantum yield. It is denoted by ϕ so that,

$$\Phi = \frac{No.of\ molecules\ reacted\ or\ formed}{No..of\ photons\ absorbed}$$

For a reaction that obeys strictly the Einstein law, one molecule decomposes per photon, the quantum yield $\varphi = 1$. When two or more molecules are decomposed per photon, $\varphi > 1$ and the reaction has a high quantum yield. If the number of molecules decomposed is less than one per photon, the reaction has a low quantum yield.

Cause of high quantum yield

When one photon decomposes or forms more than one molecule, the quantum yield $\varphi > 1$ and is said to be high. The chief reasons for high quantum yield are:

(a) *Reactions subsequent to the Primary reaction*. One photon absorbed in a primary reaction dissociates one molecule of the reactant. But the excited atoms that result may start a subsequent secondary reaction in which a further molecule is decomposed Obviously, one photon of radiation has decomposed two molecules, one in the primary reaction and one in the secondary reaction. Hence the quantum yield of the overall reaction is 2.

$AB + h\nu \longrightarrow A + B$ Primary

$AB + A \longrightarrow A_2 + B$ Secondary

(b) A reaction chain forms many molecules per photon. When there are two or more reactants, a molecule of one of them absorbs a photon and dissociates (primary reaction). The excited atom that is produced starts a secondary reaction chain.

$$\begin{aligned} &A_2 + h\nu \longrightarrow 2A && \text{...(1)} && \text{Primary} \\ &A + B_2 \longrightarrow AB + B && \text{...(2)} && \left.\begin{matrix}\text{Secondary}\\ \\ \text{Reaction chain}\end{matrix}\right. \\ &B + A_2 \longrightarrow AB + A && \text{...(3)} && \end{aligned}$$

It is noteworthy that A consumed in (2) is regenerated in (3). This reaction chain continues to form two molecules each time. Thus the number of AB molecules formed in the overall reaction per photon is very large. Or that the quantum yield is extremely high.

Examples of high quantum yield

The above reasons of high quantum yield are illustrated by citing examples as below:

(i) *Decomposition of Hl.* The decomposition of hydrogen iodide is brought about by the absorption of light of less than 4000 Å. In the primary reaction, a molecule of hydrogen iodide absorbs a photon and dissociates to produce H and I. This is followed by secondary steps as shown below:

$$\begin{array}{ll} HI + hv \longrightarrow H + I \quad ...(1) & \text{Primary} \\ \left.\begin{array}{l} H + HI \longrightarrow H_2 + I \quad ...(2) \\ I + I \longrightarrow I_2 \quad ...(3) \end{array}\right] & \text{Secondary} \\ \hline 2HI + hv \longrightarrow H_2 + I_2 & \end{array}$$

In the overall reaction, two molecules of hydrogen iodide are decomposed for one photon (hv) of light absorbed. Thus the quantum yield is 2.

(ii) *Hydrogen-Chlorine reaction*. This is a well known example of a photochemical chain reaction. A mixture of hydrogen and chlorine is exposed to light of wavelength less than 4000 Å. The hydrogen and chlorine react rapidly to form hydrogen chloride. In the primary step, a molecule of chlorine absorbs a photon and dissociates into two Cl atoms. This is followed by the secondary reactions stated below:

$$\begin{array}{ll} Cl_2 + hv \longrightarrow 2Cl \quad ...(1) & \text{Primary reaction} \\ \left.\begin{array}{l} Cl + H_2 \longrightarrow HCl + H \quad ...(2) \\ H + Cl_2 \longrightarrow HCl + Cl \quad ...(3) \end{array}\right] & \text{Secondary reactions} \end{array}$$

The Cl atom used in step (2) is regenerated in step (3). Thus the steps (2) and (3) constitute a self-propagating chain reaction. This produces two molecules of HCl in each cycle. Thus one photon of light absorbed in step (1) forms a large number of HCl molecules by repetition of the reaction sequence (2) and (3). The chain reaction terminates when the Cl atoms recombine at the walls of the vessel where they lose their excess energy.

$$2Cl \xrightarrow{\text{Walls}} Cl_2$$

The number of HCl molecules formed for a photon of light is very high. The quantum yield of the reaction varies from 10^4 to 10^6.

Causes of low quantum yield

The chief reasons of low quantum yield are:

(a) *Deactivation of reacting molecules*. The excited molecules in the primary process may be deactivated before they get opportunity to react. This is caused by collisions with some inert molecules or by fluorescence.

$A + hv \longrightarrow A^*$ Activation

$A^* \longrightarrow A + hv'$ Fluorescence

(b) *Occurrence of reverse of primary reaction*. Here the primary reaction generally yields a polymer. The product then undergoes a thermal reaction giving back the reactant molecules.

$2A \xrightleftharpoons{hv} A_2$

The reverse thermal reaction proceeds till the equilibrium state is reached.

(c) Recombination of dissociated fragments. In a primary process the reactant molecules may dissociate to give smaller fragments. These fragments can recombine to give back the reactant.

$(AB) + hv \longrightarrow A + B$

$A + B \longrightarrow (AB)$

Thus the secondary reactions involving the fragments to form the product will not occur. This will greatly lower the yield.

Examples of low quantum yield

The examples listed below will illustrate the above causes of low quantum yield:

(i) *Dimerization of Anthracene*. When anthracene, $C_{14}H_{10}$, dissolved in benzene is exposed to ultraviolet light, it is converted to dianthracene, $C_{28}H_{20}$.

$2C_{14}H_{10} + hv \longrightarrow C_{28}H_{20}$

Obviously, the quantum yield should be 2 but it is actually found to be 0.5. The low quantum yield is explained as the reaction is accompanied by fluorescence which deactivates the excited anthracene molecules. Furthermore, the above reaction is reversible.

$2C_{14}H_{10} \xrightleftharpoons{h\upsilon\ /\ \text{thermal}} C_{28}H_{20}$

The transformation of the product back to the reactant occurs till a state of equilibrium is reached. This further lowers the quantum yield.

(ii) *Combination of H_2 and Br_2*. When a mixture of hydrogen and bromine is exposed to light, hydrogen bromide is formed. The reaction occurs by the following possible steps.

$$Br_2 + hv \longrightarrow 2Br \qquad ...(1) \qquad \text{Primary reaction}$$

$$Br + H_2 \longrightarrow HBr + H \qquad ...(2)$$

$$\left.\begin{array}{ll} H + Br_2 \longrightarrow HBr + Br & ...(3) \\ 2\,H + HBr \longrightarrow H + Br & ...(4) \\ Br + Br \longrightarrow Br & ...(5) \end{array}\right\} \text{Secondary reaction}$$

The reaction (2) is extremely slow. The reactions (3), (4) and (5), depend directly or indirectly on (2) and so are very slow. Therefore most of the Br atoms produced in the primary process recombine to give back Br2 molecules. Thus the HBr molecules obtained per quantum is extremely small. The quantum yield of the reaction is found to be 0.01 at ordinary temperature.

Calculation of Quantum Yield

By definition, the quantum yield, φ, of a photochemical reaction is expressed as:

$$\phi = \frac{\text{Number of molecules decomposed or formed}}{\text{Number of photons of radiation energy absorbed}}$$

or

$$\phi = \frac{\text{Number of moles decomposed or formed}}{\text{Number of moles of radiation energy absorbed}}$$

Thus we can calculate quantum yield from:

(a) The amount of the reactant decomposed in a given time and

(b) The amount of radiation energy absorbed in the same time

The radiation energy is absorbed by a chemical system as photons. Therefore we should know the energy associated with a photon or a mole of photons.

The energy of photons; Einstein

We know that the energy of a photon (or quantum), $\in$, is given by the equation.

$$\in = hv = \frac{hc}{\lambda} \qquad ...(1)$$

where h = Planck’s constant (6.624×10^{-27} erg-sec)

v = frequency of radiation

λ = wavelength of radiation

c = velocity of light (3×10^{10} cm sec^{-1})

If λ is given in cm, the energy is expressed in ergs.

The energy, E, of an Avogadro number (N) of photons is referred to as one einstein. That is,

$$E = \frac{Nhc}{\lambda} \qquad \text{...(2)}$$

Substituting the values of N ($= 6.02 \times 10^{23}$), h and c, in (2), we have

$$E = \frac{1.196 \times 10^{8}}{\lambda} \text{erg mol}^{-1}$$

If λ is expressed in Å units (1Å = 10^{-8} cm),

$$E = \frac{1.196 \times 10^{16} \text{ erg mol}^{-1}}{\lambda} \qquad \text{...(3)}$$

Since 1 cal = 4.184×10^{7} erg, energy in calories would be

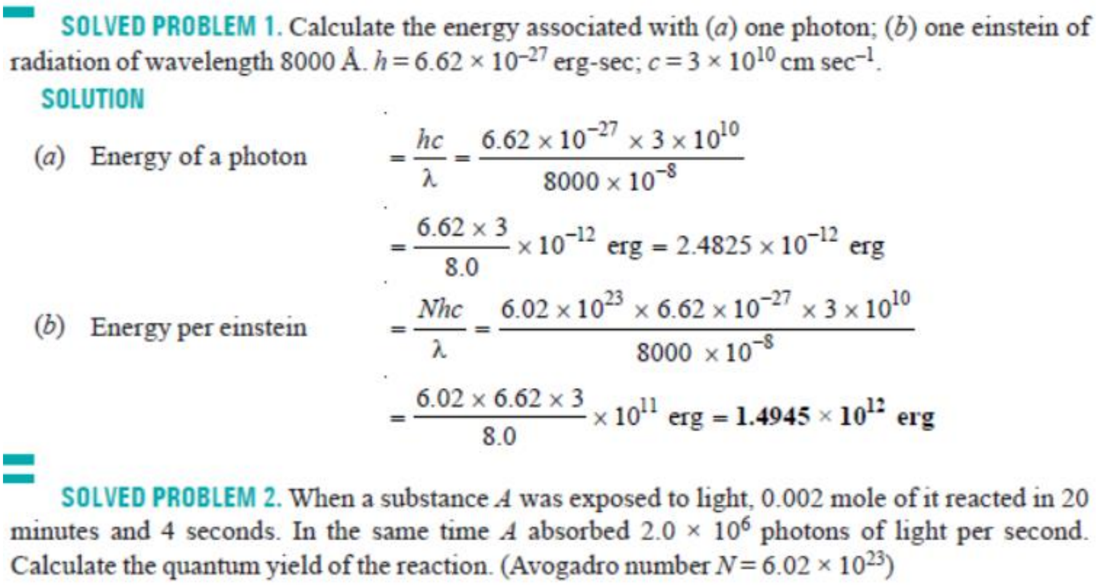
$$E = \frac{1.196 \times 10^{16}}{\lambda \times 4.184 \times 10^{7}} \qquad \text{-----------(4)}$$

$$= \frac{2.859}{\lambda} \times 10^{8} \text{ cal mol}^{-1}$$

$$E = \frac{2.859 \times 10^{5}}{\lambda} \text{ kcal mol}^{-1} \qquad \text{-----------(5)}$$

or

It is evident from (3) that the numerical value of einstein varies inversely as the wavelength of radiation. The higher the wavelength, the smaller will be the energy per einstein.



SOLVED PROBLEM 1. Calculate the energy associated with (*a*) one photon; (*b*) one einstein of radiation of wavelength 8000 Å. $h = 6.62 \times 10^{-27}$ erg-sec; $c = 3 \times 10^{10}$ cm sec^{-1}.

SOLUTION

(*a*) Energy of a photon

$$= \frac{hc}{\lambda} = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{8000 \times 10^{-8}}$$

$$= \frac{6.62 \times 3}{8.0} \times 10^{-12} \text{ erg} = 2.4825 \times 10^{-12} \text{ erg}$$

(*b*) Energy per einstein

$$= \frac{Nhc}{\lambda} = \frac{6.02 \times 10^{23} \times 6.62 \times 10^{-27} \times 3 \times 10^{10}}{8000 \times 10^{-8}}$$

$$= \frac{6.02 \times 6.62 \times 3}{8.0} \times 10^{11} \text{ erg} = \mathbf{1.4945 \times 10^{12}} \textbf{ erg}$$

SOLVED PROBLEM 2. When a substance *A* was exposed to light, 0.002 mole of it reacted in 20 minutes and 4 seconds. In the same time *A* absorbed 2.0×10^{6} photons of light per second. Calculate the quantum yield of the reaction. (Avogadro number $N = 6.02 \times 10^{23}$)

SOLUTION

Number of molecules of A reacting $= 0.002 \times N = 0.002 \times 6.02 \times 10^{23}$

Number of photons absorbed per second $= 2.0 \times 10^6$

Number of photons absorbed in 20 minutes and 4 seconds $= 2.0 \times 10^6 \times 1204$

$$\text{Quantum yield} \qquad \phi = \frac{\text{No. of molecules reacted}}{\text{No. of photons absorbed}}$$

$$= \frac{0.002 \times 6.02 \times 10^{23}}{2.0 \times 10^6 \times 1204} = \mathbf{5.00 \times 10^{11}}$$

SOLVED PROBLEM 3. When irradiated with light of 5000 Å wavelength, 1×10^{-4} mole of a substance is decomposed. How many photons are absorbed during the reaction if its quantum efficiency is 10.00. (Avogadro number $N = 6.02 \times 10^{23}$)

SOLUTION

Quantum efficiency of the reaction $= 10.00$

No. of moles decomposed $= 1 \times 10^{-4}$

No. of molecules decomposed $= 1 \times 10^{-4} \times 6.02 \times 10^{23}$

$= 6.02 \times 10^{19}$

we know that,

$$\phi = \frac{\text{No. of molecules decomposed}}{\text{No. of photons absorbed}}$$

$$= \frac{6.02 \times 10^{19}}{\text{No. of photons absorbed}}$$

$$\text{No. of photons absorbed} = \frac{6.02 \times 10^{19}}{10} = \mathbf{6.02 \times 10^{18}}$$

SOLVED PROBLEM 4. When propionaldehyde is irradiated with light of $\lambda = 3020$ Å, it is decomposed to form carbon monoxide.

$$CH_3CH_2CHO + h\nu \longrightarrow CH_3CH_3 + CO$$

The quantum yield for the reaction is 0.54. The light energy absorbed is 15000 erg mol in a given time. Find the amount of carbon monoxide formed in moles in the same time.

SOLUTION

From expression (3), we have

$$\text{one einstein } (E) = \frac{1.196 \times 10^{16}}{\lambda} \text{ erg mol}$$

$$\text{when } \lambda = 3020 \text{ Å, one einstein} = \frac{1.196 \times 10^{16}}{3020} \text{ erg mol}$$

$$\text{or} \qquad 15000 \text{ erg mol of energy} = \frac{15000 \times 3020}{1.196 \times 10^{16}} = 3.78 \times 10^{-9} \text{ einstein}$$

$$\text{But} \qquad \phi = \frac{\text{No. of moles of CO formed}}{\text{No. of einsteins absorbed}} = 0.54$$

Hence the amount of CO formed $= 0.54 \times 3.78 \times 10^{-9} =$ $\mathbf{2.04 \times 10^{-9}}$ **moles**

Photochemical reactions

There is a large variety of reactions which can occur by the absorption of photons of suitable energy. The photon energies lie mostly in the visible and ultraviolet regions. A few photochemical reactions are as follows,

1. Photochemical decomposition of hydrogen halides,

$2HI \xrightarrow{h\upsilon} H_2 + I_2$

$2HBr \xrightarrow{h\upsilon} H_2 + Br_2$

2. Photochemical Decomposition of ammonia

$2NH_3 \xrightarrow{h\upsilon} N_2 + 3H_2$

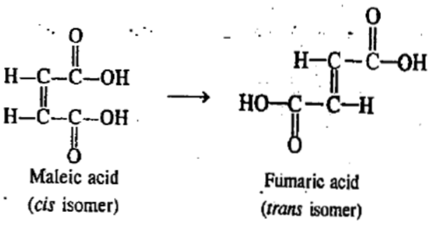
3. Photochemical Decomosition of acetone

$CH_3COCH_3 \xrightarrow{h\upsilon} C_2H_6 + CO$

4. Photochemical combination of hydrogen and halides to form hydrogen halides

$H_2 + X_2 \xrightarrow{h\upsilon} 2HX$

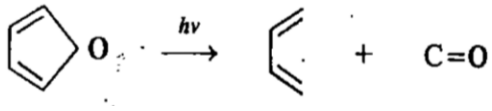
5. Isomerization of maleic acid to fumaric acid



6. Dimerization of anthracene in benzene solution in the absence of oxygen

$2CH_{14}H_{10} \xrightarrow{h\upsilon} C_{28}H_{20}$

7. Cleavage reactions - when the double bonds are suitably placed as follows



Photochemical rate law

A photochemical rate law describes how fast light-induced reactions occur, governed by Grotthuss-Draper (only absorbed light matters) and Stark-Einstein laws (one photon activates one molecule). Rates depend heavily on light intensity, not just concentration, often following power laws like Rate $\alpha\sqrt{I}$ or Rate α I, depending on whether reactants recombine bimolecularly or unimolecularly (I) after excitation.

Photophysical Processes

If the absorbed radiation is not used to cause a chemical change, it is re-emitted as light of longer wavelength. The three such photophysical processes which can occur are:

(a) Fluorescence (b) Phosphorescence (c) Chemiluminescence

Fluorescence

Certain molecules (or atoms) when exposed to light radiation of short wavelength (high frequency), emit light of longer wavelength. The process is called fluorescence and the substance that exhibits fluorescence is called florescent substance. Florescence stops as soon as the incident radiation is cut off.

Examples. (a) a solution of quinine sulphate on exposure to visible light, exhibits blue fluorescence.

(b) a solution of chlorophyll in ether shows blood red fluorescence.

Explanation- When a molecule absorbs high energy radiation, it is excited to higher energy states. Then it emits excess energy through several transitions to the ground state. Thus the excited molecule emits light of longer frequency. The colour of fluorescence depends on the wavelength of light emitted.

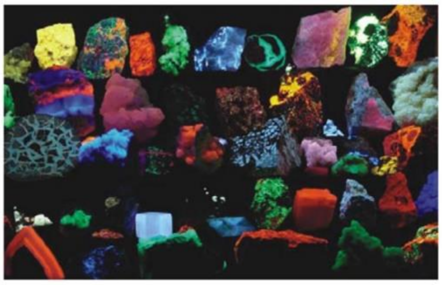


Figure 5.3: Fluorescent material shown under ultraviolet light

Figure 5.3: Tonic water is clear under normal light, but vividly fluorescent under ultraviolet light, due to the presence of the quinine used as a flavouring.

Figure 5.5: A solution of chlorophyll in ether solution shows blood red fluorescence.

Phosphorescence

When a substance absorbs radiation of high frequency and emits light even after the incident radiation is cut off, the process is called phosphorescence. The substance which shows phosphorescence is called phosphorescent substance. Phosphorescence is chiefly caused by ultraviolet and visible light. It is generally shown by solids.

Examples. (a) Sulphates of calcium, barium and strontium exhibit phosphorescence.

(b) Fluorescein in boric acid shows phosphorescence in the blue region at 5700 Å wavelength.

Explanation - As in fluorescence, a molecule absorbs light radiation and gets excited. While returning to the ground state, it emits light energy of longer wavelength. In doing so the excited molecule passes from one series of electronic states to another and gets trapped. This shows the emission of light which persists even after the removal of light source. Thus phosphorescence could be designated as delayed fluorescence.

$A + hv \longrightarrow A^* \xrightarrow{\text{slow}} hv'$

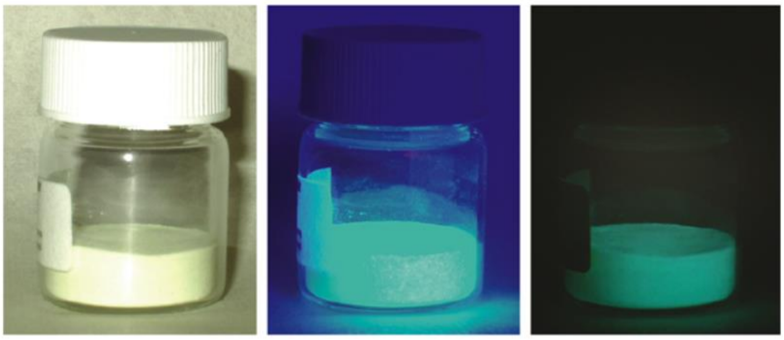


Figure 5.6: Phosphorescent powder under visible light, ultraviolet light, and total darkness

Chemiluminescence

Some chemical reactions are accompanied by the emission of visible light at ordinary temperature. The emission of light as a result of chemical action is called chemiluminescence. The reaction is referred to as a chemiluminescent reaction. Such a reaction is the reverse of a photochemical reaction which proceeds by absorption of light. The light emitted in a chemiluminescent reaction is also called ‘cold light’ because it is produced at ordinary temperature.

Figure 5.7: Chemiluminescence of fireflies and luminol

Examples. (a) The glow of fireflies due to the aerial oxidation of luciferin (a protein) in the presence of enzyme luciferase.

(b) The oxidation of 5-aminophthalic cyclic hydrazide (luminol) by hydrogen peroxide in alkaline solution, producing bright green light.

Explanation - In a chemiluminescent reaction, the energy released in the reaction makes the product molecule electronically excited. The excited molecule then gives up its excess energy as visible light while reverting to ground state.

Photo sensitisation – Examples

In chemistry, photosensitization occurs when a substance (sensitizer) absorbs light and transfers that energy to another molecule to initiate a reaction.

Chlorophyll: Acts as a sensitizer in photosynthesis, capturing solar energy and transferring it to semiconductors or chemical pathways to produce energy.

Mercury-sensitized decomposition: Mercury vapour absorbs UV light and transfers energy to hydrogen gas (H_2) to causes its dissociation.

Singlet Oxygen Generation: Dyes like Methylene Blue or Rose Bengal absorb light and transfer energy to ground-state oxygen, creating reactive singlet oxygen used in organic synthesis and photodynamic therapy.

--Chemistry of Vision & 11-cis-Retinal

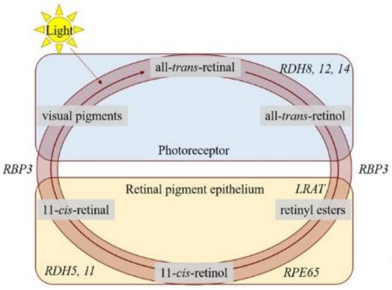
Vision begins when light strikes the retina, specifically hitting the photosensitive pigment rhodopsin found in rod cells.

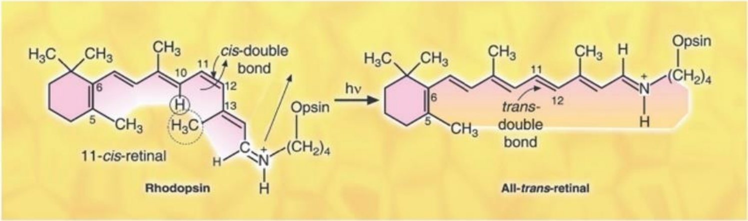
Molecular Switch: Rhodopsin consists of a protein called opsin covalently bound to 11-cis-retinal.

Photo-isomerization: When a photon is absorbed, the 11-cis-retinal undergoes a rapid geometric change, straightening into all-trans-retinal.

Signal Transduction: This change in shape (isomerization) triggers a conformational change in the opsin protein, activating a G-protein (transducin) and eventually causing a nerve impulse to be sent to the brain.

--*Vitamin A as a Precursor Vitamin A (all-trans-retinol)* is the essential building block for the visual cycle.
Biosynthesis: Humans cannot synthesize the core structure and must obtain it from diet (e.g., beta-carotene from plants).
Visual Cycle: After light "bleaches" the pigment by turning 11-cis-retinal into all-trans-retinal, the body must recycle it. All-trans-retinal is reduced back to all-trans-retinol (Vitamin A) and then enzymatically converted back to 11-cis-retinal in the retinal pigment epithelium to restart the cycle.
Deficiency: A lack of Vitamin A leads to an inability to regenerate rhodopsin, causing night blindness





--Color Perception

Color vision is facilitated by cone cells, which operate on the same 11-cis-retinal chemistry but use different types of opsin proteins.
Trichromatic Theory: Humans typically have three types of cones—Short (S), Medium (M), and Long (L) wavelength-sensitive—corresponding roughly to blue, green, and red.
Spectral Sensitivity: Each cone's opsin creates a unique chemical environment that shifts the absorption peak of the 11-cis-retinal chromophore to a specific wavelength.
Brain Integration: The brain perceives color by comparing the relative levels of activation across these three cone types.