Maa Omwati Degree Collage
Hassanpur

NOTES

Subject: - Physical Chemistry,

B.Sc. Sem: - 6^{th}

Seesion: 2020-21

Section-A B.Sc IIIrd Year (1)

Electronic Spectroscopy

Physical Chemistry VIth Sem.

INTRODUCTION :→

When the molecules absorbs energy in microwave region the transitions in rotational energy levels take place and rotational spectra are observed. Vibrational spectra are obtained by the transition of the molecule in vibrational energy level when it absorbs energy in infrared region When a molecule absorbs energy in the visible region or ultraviolet region, it jumps from one electronic level to another. So electronic spectra of the molecules are observed in visible and ultraviolet region of the electromagnetic spectrum.

BORN - OPPENHEIMER APPROXIMATION:

Born and Oppenheimer put forward an approximation in 1927 which states that the translational motion of the molecule, vibrational & rotational motion of the nuclei within the molecule may be treated separately from the motion

of the electrons.

According to this approximation the total energy of a molecule is given by

$$E = E_{tr} + E_{rot} + E_{vib} + E_{el}$$

i.e the energy of the molecule is sum of translational energy, rotational energy E_{rot}, vibrational energy E_{vib} & electronic energy E_{el}. Now, the translation energy is not quantised whereas all other energies are quantised.

Magnitude of translational energy is negligibly small, so Born-Oppenheimer approximation can be written as -

$$E = E_{rot} + E_{vib} + E_{el}$$

Potential Energy Curves for Electronic States -

For a diatomic molecule, the average electronic potential energy is a function of internuclear separation & is represented by the Morse Potential function given as -

$$V(r) = D_e [1 - e^{-\beta(r-r_e)}]^2$$

where D_e = Dissociation energy of the molecule

β = A constant for a given electronic state

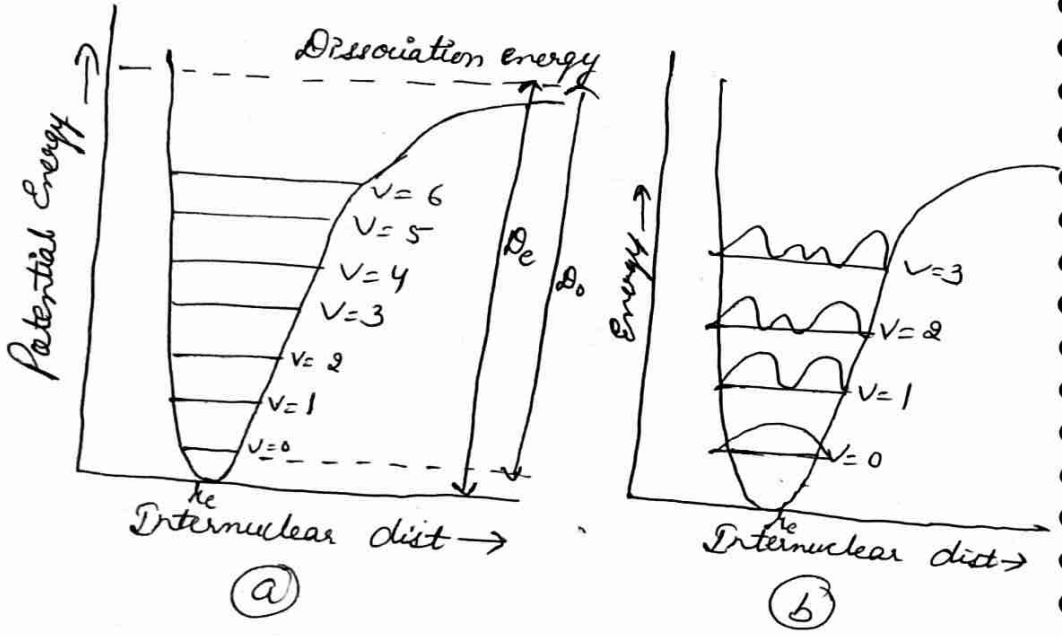
r = Internuclear distance

r_e = Equilibrium internuclear distance

A potential energy curve for a diatomic molecule is obtained by plotting electronic potential energy against the internuclear distance between two atoms. A potential energy curve of diatomic molecule is shown in fig a.. Each electronic state is made up of vibrational levels indicated by horizontal lines and indicated vibrational quantum number. Each vibrational level is associated with rotational level. It is clear from the curve that potential energy decrease as the internuclear distance

between them is decreased.

The potential energy is minimum at equilibrium distance r_e. At the equilibrium distance r_e, the atoms are vibrating thus their potential energy also keeps on oscillating about the minimum value.

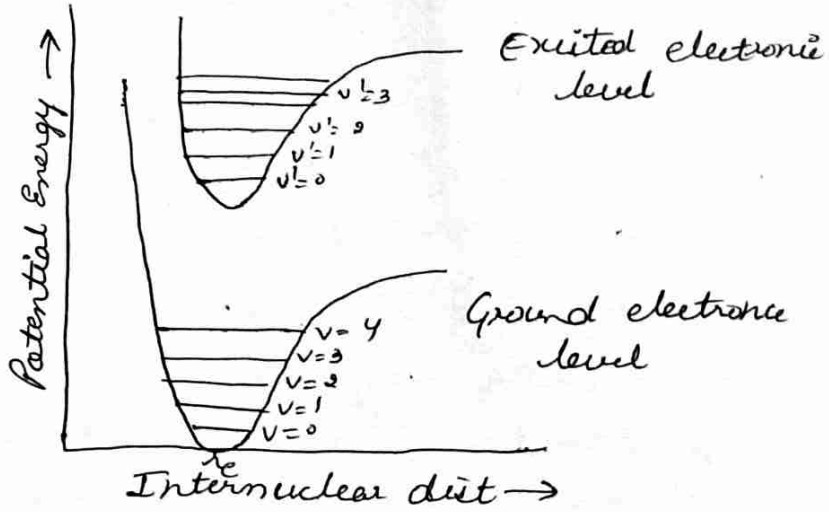


(a) (b)

The probability of finding the molecule in a vibrational level is indicated by probability distribution curve in various vibrational state in fig. (b) According to quantum theory for V=0, the molecule is most likely to be found at the centre of the ground vibrational level.

whereas for higher levels, V = 1, 2, 3 etc. the probability of finding the molecule is high at the extreme positions.

The potential energy curves for ground & excited electronic states of a diatomic molecule as shown in graph C



In this graph upper state curve is also represented by a Morse curve similar to that in the ground electronic state. However the two curves differ from each other with respect to the position of minimum in the potential energy curve. The minimum energy point (r'_e) for excited state is at a larger internuclear distance than r_e the ground electronic state.

This is because the bonding in the excited state is weaker than in the ground state. If sufficient amount of energy is supplied the molecule jumps to higher electronic state causing an electronic transition. The transition between these electronic levels take place according to Franck - Condon principle.

* FRANCK - CONDON PRINCIPLE :

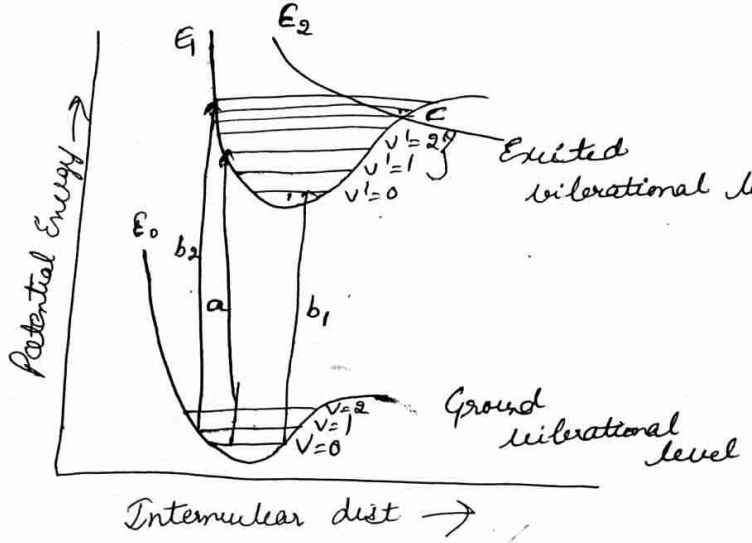
The relative intensity of lines in electronic spectra may be explained in terms of Franck - Condon principle which states that an electronic transition takes place so fast that a vibrating molecule does not change its internuclear distance during the transition.

This principle states that the movement of nuclei is negligible during an electronic transition. That means the time required for an electronic transition is so short that the nuclei do not have

time to change their position. This principle is closely related to Born-Oppenheimer approximation. Therefore during absorption of radiation the molecule gets excited to different energy state. Represented by a different potential energy curve. The internuclear distance in the excited state is the same as in the ground state at the time of electronic transition. Hence according to Franck-Condon principle there is no appreciable change in the internuclear distance during the transition. There are no selection rules for Δv and the transition will occur at the positions where wave function is maximum.

If the internuclear distance in ground state and excited state is equal then the most probable transition is from $v=0$ to $v'=0$. However, if the internuclear distance in excited state is slightly greater than in $v=0$ ground state then the most probable transition guided by Franck-Condon principle is from $V=0$ to $V=2$ i.e. This transition has maximum intensity.

The other dist transition have lesser probability and thus have lesser intensities as compared to intensity of $0 \rightarrow 2$ transition. These less probable transitions occur from from first excited vibrational level of ground electronic state.



These are shown by vertical lines b_1 & b_2. The transition b_1 ends at lowest vibrational level ($V=0$) of the first excited state. This transition is from a stable ground electronic state to a stable excited electronic state. This results in a spectrum consisting of discontinuous bands having structure. While transition b_2 excites

the molecule to a point where the excited molecule has energy more than its own dissociation energy. From such states the molecule will dissociate into atoms. The atoms which are formed may have any value of kinetic energy. Thus they undergo transition which are not quantised resulting into a continuous region or continuum in the spectrum which has no fine structure. The point at which the continuum ~~in the spectrum~~ starts is called the convergence limit

The molecule can also undergo dissociation if it gets excited to a level E_1 but during the course of transition it may shift from stable E_1 curve to unstable E_2 curve above the point C where the potential energy curves E_1 & E_2 cross each other. At an internuclear dist. corresponding to point C, the molecule undergoes a cross over from one state to another without energy change and continues to dissociate. This type of behaviour is referred to as predissociation. The region of predissociation shows a diffused

appearance in the spectrum.

* Some terms in Electronic Spectroscopy.

* **Parity :→** When the molecule has a center of symmetry. as in the term parity is used for molecular orbitals of Homonuclear diatomic molecules. It refers to the behaviour of an orbital with respect to inversion We start from any point in the molecular orbital & travel equal distance through the center of the molecule to the other side. This process is called inversion If the sign of wave function of molecular orbital does not changes on inversion it is said to have even parity & is denoted by 'g' (gerade) If the sign of wave function of the orbital changes on inversion it is said to have odd parity & is denoted by u (ungerade)

* **Multiplicity of state:→**

Multiplicity of an electronic state is given by $2S+1$, where S is the total spin quantum number. If all the electrons in an electronic state are paired then $S=0$, thus multiplicity of the state $(2\times 0+1)=1$ It is called singlet state If there is one unpaired electron in the electronic state, then $S=\frac{1}{2}$ & multiplicity $\left(2\times\frac{1}{2}+1\right)=2$, it is called doublet state If there are two unpaired electrons in an electronic in the state then $S=1$, multiplicity $=(2S+1)=3$. It is called triplet state.

* **Term Symbols for diatomic molecules:→**

For homonuclear diatomic molecules, the term symbol is written as.

$$^{2S+1}\Lambda_{g/u}^{(+/-)}$$

* **Atomic term Symbol :→**

For atoms

$$^{2S+1}L_J$$

For Molecules

$$^{2S+1}\Lambda_J$$

L =	0	1	2	3	4	5
	S	P	D	F	G	H

Λ =	0	1	2	3
	Σ	Π	Δ	Φ

$J = L - S$ (orbital is less than half filled)

$L + S$ (more than half filled)

Half filled → If e^- is less than 7 e^-.

Full filled → If more than 7 e^-

Eg- p^1 (p orbital have 1 e^-)

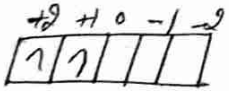
$S = \frac{1}{2}$, $L = \Sigma m_l = 1$

$J = L - S$, $1 - \frac{1}{2} = \frac{1}{2}$

$2S+1$, $2 \times \frac{1}{2} + 1 = 2$

$^2P_{1/2}$

Eg d^2



$L = \Sigma m_l = 2+1 = 3$

$S = \frac{1}{2} + \frac{1}{2} = 1$, $2S+1$, $2 \times 1 + 1 = 3$

$J = L - S$

$3 - 1 = 2$

$^3F_2$

* For homoatomic diatomic molecule-

L =	0	1	2	3
Spectroscopic state	Σ	Π	Δ	Φ

$2S+1 \Lambda_{g/u}$

Electronic configuration upto 14 e^- species or 14 e^-

$(\sigma 1S)_g (\sigma^* 1S)_u (\sigma 2S)_g (\sigma^* 2S)_u (\pi_u 2P_x = \pi 2P_y)_u$

$(\sigma_g 2P_z) (\pi_g^* 2P_x = \pi^1 2P_y)_g (\sigma^* 2P_z)_u$

Electronic configuration more than 14 e^-

$(\sigma 1S)_g (\sigma^* 1S)_u (\sigma 2S)_g (\sigma^* 2S)_u (\sigma_g 2P_z)$

$(\pi_u 2P_x = \pi 2P_y)_u (\pi_g^* 2P_x = \pi^* 2P_y)_g (\sigma^* 2P_z)_u$

Rules:→ ① If symbol is Σ then only (+) & (-) subscript are used.

② g & u is referred to the orbital of last electron filled.

③ (-) subscript will be written only when the e^- is filled in π orbital.

④ If two e^- lies in different orbital then

$g \times g = g$, $g \times u = u$, $u \times u = g$

Eg- He_2^+

Electronic Configuration- $\sigma_g 1s^2\ \sigma_u^* 1s^1$

$S = \frac{1}{2}$ $2S+1$, $2\times\frac{1}{2}+1 = 2$

$^2\Sigma_u^+$ → bcz last orbital is u.

Eg- O_2

$O_2 = 16e^-$

$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ (\pi_u 2p_x = \pi_u 2p_y)\ (\pi^* 2p_x' = \pi^* 2p_y')\ \sigma^* 2p_z$

p_x p_z p_y

1 | 1

$+1$ 0 -1

$S = 1$

$L = +1 - 1 = 0$

$g \times g = g$

$^3\Sigma_g^-$

* Selection Rule for Electronic Transition :-

(1) Spin Selection Rule :→

According to this rule the electronic transition can take place only between the energy levels of same multiplicity. There can be no change in the multiplicity during an electronic transition $\Delta S = 0$

Therefore singlet → singlet state transition & triplet → triplet state transition are allowed while the transition from singlet → triplet state are forbidden.

(2) Total orbital angular momentum selection rule : →

According to this rule the change in total orbital angular moment i.e $\Delta\Lambda = 0, \pm 1$.

Thus transition such as $\Sigma \to \Sigma$, $\Pi \to \Pi$, $\Delta \to \Delta$ are allowed because in these transition $\Delta\Lambda = 0$. In addition, the transition such as $\Sigma \to \Pi$, $\Pi \to \Sigma$, $\Pi \to \Delta$ etc are also allowed because they correspond to $\Delta\Lambda = \pm 1$.

However transition are like $\Delta \to \Sigma$ is forbidden

(3) Parity selection rule or Laporte selection rule : →

For an electronic transition to be allowed the parity of the molecular orbital must change during the transition. Thus the transition $g \to u$ or $u \to g$ are allowed

whereas the transition $g \rightarrow g$ or $u \rightarrow u$ are allowed.

(4) Restrictions on symmetry changes during transition :→

The Σ^+ states can undergo transition only to Σ^- states. Thus the transition $\Sigma^+ \rightarrow \Sigma^+$ & $\Sigma^- \rightarrow \Sigma^-$ are allowed while $\Sigma^+ \rightarrow \Sigma^-$ are forbidden.

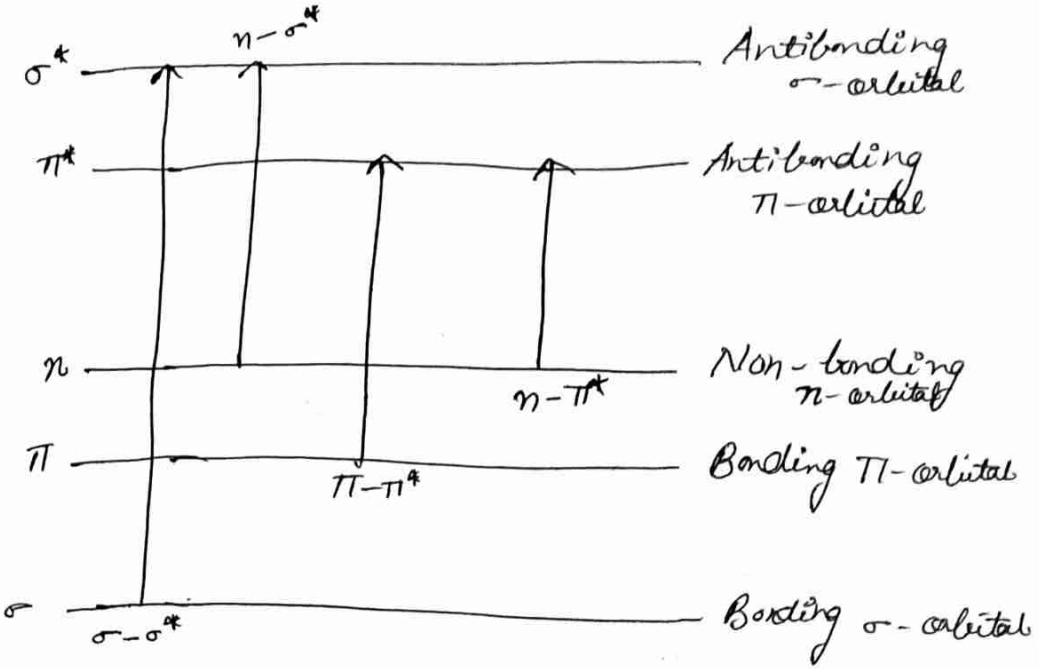
(5) The selection rules for the rotational and vibrational transitions which accompany the electronic transition are

$$\Delta J = \pm 1$$
$$\Delta V = \text{not restricted}$$

where J is the rotational quantum number & V is vibrational quantum number.

* Transition involved in MO :→

i) $\sigma - \sigma^*$ Transition :→ The transition from bonding molecular σ-orbital to antibonding molecular σ^* orbital is called as $\sigma - \sigma^*$ transition. These type of transition usually occurs in saturated hydrocarbons. The energy required for these transition is very high as sigma bonds are very strong & hence occur at very short wavelength.



ii) $n - \sigma^*$ transition :→ The transition occurs in saturated organic compounds having hetero atom containing atleast a lone pair of electron. Such as N, O or X. These transition are of lower energy than σ to σ^* transitions and are sensitive to hydrogen bonding.

iii) $\pi - \pi^*$ transition :→ The transition of electron from π- molecular orbital to antibonding π^* molecular orbital is called as $\pi - \pi^*$ transition. These type of transition usually occurs in unsaturated compounds such as alkene, alkyne etc. These transitions are of lower energy than either of σ to σ^* & n to σ^* transition.

iv) $n - \pi^*$ transition :→ The transition of electrons from non-bonding molecular orbitals to an antibonding π^* molecular orbital is called as $n - \pi^*$ transition. These type of transition usually occur in aldehyde, ketones, amides etc. These transition are usually of lower energy & a symmetry forbidden transition.

* Chromophores :→ Chromophore may be defined as an isolated functional group (not present in conjugation with other group) which shows a characteristics absorption in visible region. eg nitro compounds are usually yellow in colour, here nitro group is a Chromophore.

Auxochrome :→ is an atom or a group of atoms which does not show an absorption band on its own, but when it is attached to a chromophore it shifts to the absorption to a longer wavelength and increases the intensity of the absorption band. Eg- OH, $-NH_2$, $-OR$, halogens etc. These groups contain lone pairs of electrons which conjugate with the chromophore and a shift in wavelength of absorption band is observed.

* Extent of conjugation :—

In highly conjugated system the π-electrons are delocalised over the entire molecule. It is found that in such cases the absorption band shifts to longer wavelength as the extent of conjugation increases. Eg- β-carotene has very long conjugated system & shows a band at 240-280 nm in the visible region as a result it appears yellow in colour.

* Intensity of Electronic Bands :-

The intensity of an electronic band depends upon the extent of overlap of wave function of molecular orbitals in the ground & excited states. Greater the overlap of these wave functions higher in the intensity. in the electronic band. In $n \to \pi^*$ transitions there is poor overlap of wave functions in ground & excited state As a result the intensity of the transition is very less. Whereas in $\pi \to \pi^*$ transitions the overlap of wave function is excellent, therefore the band produced due to these transition is more intense than that given by $n \to \pi^*$ transition. Also in acidic medium, the lone pair of e^- becomes protonated Hence $n \to \pi^*$ band completely disappears.

Section-B. B.Sc IIIrd Year (1)

PHOTOCHEMISTRY VIth Sem

Photochemistry :→ The study of rates & mechanism of reactions resulting from the exposure of a system to the radiation lying in the visible and ultraviolet region.

* When a molecule absorbs photon of sufficient energy & gets excited and ultimately converts into products The reactions which occur with the absorption of radiations are called photochemical Chemical.

* Interaction of Radiation with Matter :→

When a substance is exposed to radiation, its molecules absorb photons of sufficient energy & gets excited to higher electronic states.

Photoprocess are of two types-

i) Photophysical Process

ii) Photochemical Process

Photophysical Process are the process which take place on absorption of light but do not result in any chemical change.

If the radiation of sufficient energy then the electrons may jump out from the atoms and the effect is called photo-electric effect.

The photo-activated molecule may collide with the surrounding molecules & lose energy in the form of heat. This type of energy decay does not involve emission of light is called radiationless decay & non-radiative emission.

(ii) Photochemical Process or Photochemical reaction :— occur when the reactant molecules are activated by the radiation of sufficient energy resulting into chemical reaction.

✱ Photochemical reaction - occur when the reactant molecules are activated by the radiation of sufficient energy resulting into chemical reaction.

- Photochemical reaction between hydrogen and chlorine to form hydrogen chloride.

$$H_2 + Cl_2 \xrightarrow{light} 2HCl$$

✱ Thermal Reactions	Photochemical Reactions
✱ These reactions can occur even in dark. Light is not an essential requirement for these reactions.	✱ These reactions proceed only in the presence of light and involve absorption of light
✱ In thermal reactions the energy of activation is provided by inter-molecular collisions.	✱ In these reactions the energy of activation is gained through the absorption of photons of visible or UV light.
✱ Thermal Reactions are always accompained by decrease in free energy ($\Delta G = -ve$)	✱ The free energy change (ΔG) may not be always negative for photochemical reaction. Eg- Ozonisation of oxygen is spontaneous even when the change in free energy is positive $3O_2 \xrightleftharpoons{h\nu} 2O_3$ ($\Delta G = +ve$)
✱ The rate of thermal reaction depends on temperature.	✱ The rate of photochemical reaction is independent of temp. However the rate of a photochemical reaction depends upon the intensity of electromagnetic

* Lambert's law :→

According to this law when a beam of monochromatic radiation passes through a homogeneous, the rate of decrease of intensity of the radiation with the thickness of absorbing medium is proportional to the intensity of the incident light

Mathematically-

$$-\frac{dI}{dx} \propto I$$

$$-\frac{dI}{dx} = KI \quad -(1)$$

where dI = decrease in the intensity of light after passing through small thickness of the medium

dx = the thickness of the medium

I = the intensity of incident light just before entering the medium.

K = Const of proportionality called absorption coefficient

Eqn (1) can be written as-

$$\frac{dI}{I} = -K dx \quad -(2)$$

$x = 0, I = I_0$

$x = x, I = I$

Integrating eqn (2) $x = 0$ to x & $I = I_0$ to I (3)

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_{x=0}^{x} K dx$$

$$[\ln I]_{I_0}^{I} = -K[x]_0^x$$

$$(\ln I - \ln I_0) = -K[x-0]$$

$$\ln \frac{I}{I_0} = -Kx$$

$$\frac{I}{I_0} = e^{-Kx} \qquad \boxed{I = I_0 e^{-Kx}} \quad -(4)$$

Eqn (4) is called by Lambert's law.

Intensity of light absorbed-

$$I_a = I_0 - I$$

$$I_a = I_0 - I_0 e^{-Kx} \quad -(5)$$

Eqn (3) can be written as-

$$2.303 \log \frac{I}{I_0} = -Kx$$

$$\log \frac{I}{I_0} = -\frac{Kx}{2.303} = -K'x \quad -(6)$$

$K' = \frac{K}{2.303}$ is called the absorption coefficient or extinction coefficient or absorptivity

Eqn (6) can be written as

$$\log \frac{I}{I_0} = -K'x$$

$$\frac{I}{I_0} = 10^{-K'x}$$

$$I = I_0 \times 10^{-k'x}$$

* Transmittance :→ It is the ratio of intensity (I) of the transmitted light from the medium to the intensity (I_0) of the incident light i.e the fraction of incident light transmitted by the medium of thickness x.

$$T = \frac{I}{I_0}$$

* Absorbance (A) or Optical Density (D) or Extinction (E) :→
It is defined as the logarithm of the reciprocal of transmittance i.e $\log 1/T$ or $\log I_0/I$.

Absorbance (A) = Optical density (D) = Extinction (E) = $\log \frac{1}{T} = \log \frac{I_0}{I}$

* Beer's law :→ When a monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of the light with the thickness of the solution is proportional to the intensity of the incident light as well as to the concentration of the solution.

$$-\frac{dI}{dx} \propto I \propto c$$

$$-\frac{dI}{dx} = \varepsilon I c \quad \text{—(1)}$$

where ε (epsylon) is the constant of proportionality and is called molar absorption coefficient.

$$\frac{dI}{I} = -\varepsilon c\, dx \quad \text{—(2)}$$

On integrating eqn (2)

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_0^x \varepsilon c\, dx \quad \text{—(3)}$$

$$[\ln I]_{I_0}^{I} = \varepsilon [x]_0^x c$$

$$-[\ln I - \ln I_0] = \varepsilon [x-0] c$$

$$\ln \frac{I}{I_0} = -\varepsilon c x$$

$$\frac{I}{I_0} = e^{-\varepsilon c x} \qquad I = I_0 \times e^{-\varepsilon c x}$$

Limitation of Beer's law–

(1) This law holds good only for monochromatic light
(2) This law is applicable only to dilute solutions. At higher concentrations deviation are observed
(3) The law holds at const. temp. An increase in temp. shifts the absorption band towards longer wavelength

* Laws of Photochemistry :→

① Grotthus- Draper Law - This law is also said to be the first law of photochemistry. It was given by Grotthus and proved experimentally by Draper in 1841. It states that

When light is incident on a body, a part of it is reflected, a part is transmitted & rest of it is absorbed. It is only the portion of light which is absorbed can bring about a chemical change i.e a chemical can be produced in a system only by those radiations which are absorbed.

② Stark - Einstein law of Photochemical Equivalence :→

The second law of photochemistry was put forward by Einstein & Stark. It states that

In a photochemical reaction, each reacting atom or molecule absorb one photon of light which causes the reaction.

$$E = h\nu$$

where h is the Planck's const and ν is the frequency of absorbed radiation

$$AB + h\nu \longrightarrow AB^*$$

(Reactant molecule) (Activated reactant molecule)

Energy of activation of 1 mole of molecules is given by

$$E = Nh\nu \quad , \quad \nu = c/\lambda$$

$$E = \frac{Nhc}{\lambda}$$

Einstein is the quantity of energy absorbed per mole of the reacting substance or one mole of photons during the primary photochemical process

Units of value of Einstein

C.G.S unit for E

$$E = \frac{2.86}{\lambda} \text{ cal per mol}$$

If λ is taken in Angstrom unit then eqn is

$$1 \text{ Å} = 10^{-8} \text{ cm}$$

$$E = \frac{2.86}{\lambda} \times 10^{8} \text{ cal per mol or cal einstein}^{-1}$$

$$E = \frac{2.86}{\lambda} \times 10^{5} \text{ K cal per mol or K cal einstein}^{-1}$$

S.I unit for E

$$E = \frac{11.97}{\lambda} \times 10^{-5} \text{ KJ mol}^{-1} \text{ or KJ einstein}^{-1}$$

* Quantum Yield :→ According to Einstein law, every reacting molecule absorbs one quantum of radiation. Had this law been correct, then the number of reacting molecules should be equal to the number of quantas absorbed. In many cases where a small amount of light radiation absorbed brings about a large amount of reaction while in many cases, it is reverse, i.e large amount of light absorbed brings about only a small amount of reaction. These observations can be explained by assuming that all molecules present do not absorb radiation but only a few of them absorb the radiation and get activated. These activated molecules react with other molecules and bring about a large amount of chemical reaction. The first step in which light radiation is absorbed by an atom or molecule is called the primary step or primary process & the second step involving the reaction is called secondary step or secondary process.

The quantum efficiency or quantum yield of a photochemical process -

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{No. of photons absorbed in the same time}}$$

$$= \frac{\text{No. of mole reacting in a given time}}{\text{No. of Einstein absorbed in the same time}}$$

Factors Affecting quantum Yield :→

(1) Those in which the quantum yield is a small integer. such as 1, 2, 3 etc for example, dissociation of HI or HBr, ozonization of oxygen or combination of sulphur dioxide and chlorine etc.

(2) Those in which the quantum yield is less than 1 Eg- dissociation of ammonia, nitrogen dioxide or acetone vapours and transformation of maleic acid into fumeric acid etc.

(3) Those in which the quantum yield is extremely high. Eg- Combination of carbon-monoxide and chlorine and of hydrogen & Chlorine.

i) Primary Process :→ In this process, the light radiation is absorbed by an atom or a molecules to convert into in excited state.

$$A + h\nu \longrightarrow A^*$$

A → Atom or molecule
$h\nu$ → One quanta of light
A^* → Excited state or Excited molecule

The molecule which absorb light may get dissociated yielding atoms or free radicals.

ii) Secondary Process :→ The species formed in the primary proces may undergo further reaction which are called secondary process.

The secondary proces may involve one or more than one step. Sometimes, the secondary proces initiates a chain reaction. Such reaction may results in very high or very low quantum yield.

* Reason for low quantum yield :→ Primary Process.

Sometimes the excited molecules may get deactivated before they form product. This lowers the quantum yield & the reasons are :→

① Excited molecules collide with non-excited molecules which causes excited molecule to lose their energy.

② The primary photochemical process may get reversed

③ The dissociated fragments may recombine to form the original molecule

* High Quantum Yield :→ This law of photochemical equivalence fails in reaction where the number of reactant molecules undergoing reaction by absorption of one quantum of light is more than one. The quantum yield will be high if more than one mole of reactant molecule react on absorption of one einstein of energy. High quantum yield is explained on the basis of reaction taking place in secondary process

* Luminescence :→ The glow produced in a body by methods other than the action of heat i.e the production of cold light is called luminescence and the body emitting the cold light is called luminescent.

Luminescence is of three types -

(1) Chemiluminescence :→ is defined as the production of light by a chemical reaction & is the reverse of a photochemical reaction. The essential condition for the reaction to be chemiluminescent is that it must sufficient energy to raise at least one of the reactants or intermediates to an electronically excited state so that as it returns to the ground state, it emits energy in the form of radiation. Example of chemiluminescent rxn are→

i) Oxidation - reduction reaction of hydrazide.

ii) Oxidation of decaying wood containing certain forms of bacteria.

iii) Electron transfer reaction.

(2) Fluorescence :→ Certain substances like dyes such as fluorescein etc. when exposed to light or some other radiation absorb the energy & then immediately or instantaneously start re-emitting the energy. Such substances are called fluorescent substances & the phenomenon is called fluorescence.

Fluorescence starts as soon as the substance is exposed to light & it stops as soon as the light is cut off.

Eg - i) certain organic dyes such as eosin, fluorescein.

ii) fluorite, CaF_2.

iii) a solution of chlorophyll in ether.

iv) vapours of sodium, mercury, iodine etc.

(3) Phosphorescence :→ There are certain substances which when exposed to light or certain other radiation continue to glow for sometime even after the incident radiation is cut off. Such substances are called phosphorescent substances or simply phosphors and the phenomenon is called phosphorescence. Phosphorescence is generally caused by ultraviolet or visible light & is generally shown by solids because in solids, the molecules have least freedom of motion because of which the electrons continue jumping back slowly for quite sometime. Zinc sulphide and sulphides of alkaline earth metals are

* Kinetics of Quenching of Fluorescence
Stern – Volmer Equation :→

Fluorescence occurs due to the absorption of energy by the molecules because of which molecules get activated & immediately re-emit energy. If these excited molecules get deactivated, the fluorescence stops & the phenomenon is called quenching. The substances which are responsible for quenching are called quencher & are normally represented as Q.

The quenching of fluorescence takes place because of transfer of energy from the excited state species to the molecule with which it collides. Quenching may occur any of the following two ways-

i) when the activated molecule changes from singlet excited state to the triplet excited state species This phenomenon is called internal quenching

ii) It may also result from the presence of externally added species which takes up energy from excited state molecule. This phenomenon is called external quenching (9)
If Q is the quencher, then the process from activation to deactivation by following steps-

$A + h\nu \longrightarrow A^*$ [Photoactivation]

$A^* \xrightarrow{K_1} A + h\nu'$ [Fluorescence]

$A^* \xrightarrow[ISC]{k_2} A$ [Internal quenching]

$A^* + Q \xrightarrow{k_3} A + Q'$ [External quenching]

Steady state principle is applied

$$I_a = k_1[A^*] + k_2[A^*] + k_3[A^*][Q]$$

where I_a is the intensity of light absorbed

Quantum Yield of fluorescence is -

$$\phi_f = \frac{I_f}{I_a} = \frac{k_1[A^*]}{k_1[A^*] + k_2[A^*] + k_3[A^*][Q]}$$

$$\phi_f = \frac{k_1}{k_1 + k_2 + k_3[Q]} \quad [A^* \text{ is common}]$$

In the absence of the quencher,

$$\phi_f^\circ = \frac{k_1[A^*]}{k_1[A^*] + k_2[A^*]} = \frac{k_1}{k_1 + k_2}$$

$$\frac{\phi_f^\circ}{\phi_f} = \frac{k_1}{k_1 + k_2} \times \frac{k_1 + k_2 + k_3[Q]}{k_1}$$

$$= 1 + \frac{k_3}{k_1+k_2}[Q]$$

Putting $\frac{1}{k_1+k_2} = \tau$, we get

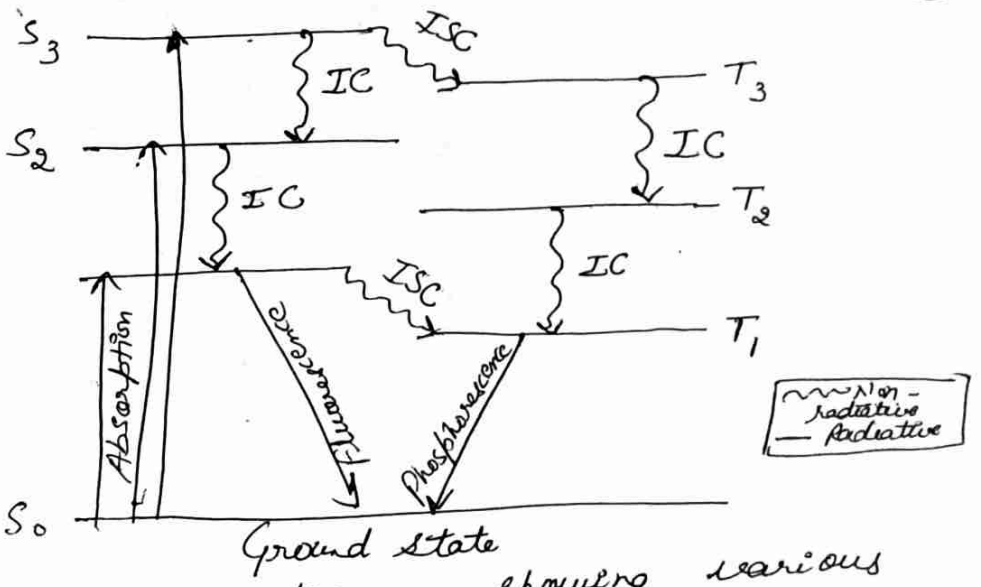
$$\frac{\phi_f^\circ}{\phi_f} = 1 + k_3\tau[Q]$$

$$\boxed{\frac{\phi_f^\circ}{\phi_f} = 1 + K_{SV}[Q]}$$

This equation is known as Stern-Volmer eqn & K_{SV} is called Stern-Volmer constant

* The Re-emission of energy by a Molecule – The Jablonski Diagram: →

The light absorbed may not always cause a photochemical reaction. A molecule after absorbing a photon gets promoted to an excited state The life time is an excited state is about 10^{-7} to 10^{-8} seconds therefore, the excited molecule must return to the ground state



Jabalonski diagram showing various photophysical process

$$A + h\nu \rightarrow A^*$$

where A^* is an excited molecule which may occupy singlet state S_1, S_2, S_3. The activated molecule returns to the ground state by losing energy through following type of processes.

(1) Non-radiative transitions (Internal conversion and intersystem crossing) – These transitions involve the return of the excited molecule from higher excited states (S_3, S_2 or T_3, T_2) to the first excited state (S_1 or T_1). These transition do not involve emission of radiation

hence they are termed as non-radiative or radiationless transition. The excess energy is lost only in the form of heat due to collisions with other molecules. This process is called internal conversion

The molecules may also lose excess energy by transitions from excited singlet to excited triplet state $S_2 \rightarrow T_2$, $S_1 \rightarrow T_1$ etc This process is termed as inter-system crossing

(2) Radiative Transitions :→

Fluorescence & Phosphorescence. These transitions involve the return of the excited molecule from singlet excited state S_1 & triplet excited state T_1 to the ground state S_0. The transition from $S_1 \rightarrow S_0$ is spin allowed transition. The instantaneous emission of radiation in this transition is called fluorescence

Whereas the transition from the triplet excited state T_1 to the ground state S_0 It is slow because it is a spin forbidden transition. The emission of radiation in this transition is called phosphorescence

In case of fluorescence & phosphorescence, the emitted radiation has frequency lower than that of exciting radiation. This is because a part of energy is lost as heat energy during internal conversion & inter-system crossing. As a result, the energy of emitted radiation is lower, & hence fluorescence & phosphorescence occur at lower frequencies than that of absorbed radiation.

* Energy Transfer in Photochemical Reactions — Photosensitization :→

The substance which itself does not undergo any chemical change but initiates a photochemical reaction in another substance is called photosensitizer. This process is called photosensitization & such reactions are called photosensitized reactions

Eg. Dissociation of Ethylene

$Hg + h\nu \rightarrow Hg^*$ (Mercury atoms act as photosensi-

$Hg^* + C_2H_2 \rightarrow C_2H_4^* + Hg$

* Photochemical Equilibrium or Photostationary state :→

Some photochemical reactions are reversible in nature In these reactions the forward step is a photochemical proces whereas the backward step may be either a photochemical or a thermal reaction.

$$A \underset{\text{light}}{\overset{\text{light}}{\rightleftharpoons}} B \qquad \text{or} \qquad A \underset{\text{thermal}}{\overset{\text{light}}{\rightleftharpoons}} B$$

During the course of reaction, a stage may be reached when the rate of forward reaction becomes equal to the rate of backward reaction. After this state, the light absorbed causes no further chemical change. This is the state of photochemical equilibrium or photostationary state

Eg.- Photochemical decomposition of Sulphur dioxide

$$2SO_3 \underset{\text{light}}{\overset{\text{light}}{\rightleftharpoons}} 2SO_2 + O_2$$

* Photoinhibitors :→ There are certain substances in whose presence the quantum yield of some photochemical reactions become less. For example, in the photosynthesis of HCl, even small traces of oxygen reduces the quantum yield of photochemical reactions are considerably. Such substances in whose presence the quantum yield of photochemical reactions are considerably reduced are called photoinhibitors. It is believed that lowering of quantum yield is due to the fact that photoinhibitors react with the chain propagating atoms or radicals resulting into chain termination. Substances like nitric oxide, sulphur dioxide or propylene etc act as photoinhibitors

Section-C

Physical Chemistry

Solution Dilute Solution & Colligative Properties

Solution :- A solution is a homogeneous mixture of two or more substances whose composition can be varied with in certain limits.

* The component present in greater amount in a solution is called solvent & the component present in smaller amount in the solution is called solute.

* Mass percentage :- is defined as the mass of solute present in 100 g of the solution.

$$\text{Mass \% of component} = \frac{\text{Mass of solute}}{\text{Mass of soln}} \times 100$$

$$\text{Mass \% of B} = \frac{W_B}{W_A + W_B} \times 100$$

* Volume percentage – $\frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$

Volume % of $B = \frac{V_B}{V_A + V_B} \times 100$

* Parts per million (ppm) -

$ppm = \frac{\text{Mass of solute}}{\text{Total mass of Soln}} \times 10^6 = \frac{w_B}{w_A + w_B} \times 10^6$

* Strength of a solution -

$\text{Strength } (S) = \frac{\text{Mass of solute}}{\text{Volume of Soln}} \times 1000$

* Molarity - It is defined as no. of moles of the solute present in one litre of Soln

$M = \frac{w_B \times 1000}{M_B \times V(ml)}$

* Molality (m) $= \frac{w_B \times 1000}{M_B \times w_A (g)}$

* Normality (N) $= \frac{w(g) \times 1000}{(\text{Eq. Mass})_B \times V}$

* Mole fraction -

Mole fraction of Solvent $(x_A) = \frac{n_A}{n_A + n_A}$

$x_B = \frac{n_B}{n}$

Ideal solution :→ A solution is said to be an ideal solution if The solution obey Raoult's law at every range of concentration.

$\Delta H_{mix} = 0$, neither heat is evolved nor absorbed during dissolution.

$\Delta V_{mix} = 0$, total volume of solution is equal to sum of volumes of the components

$P = P_A + P_B = P_A^\circ x_A + P_B^\circ x_B$ i.e $P_A = P_A^\circ x_A$

$P_B = P_B^\circ x_B$

A-A, A-B, B-B interactions should be same. i.e A & B are identical in shape size & character.

Escaping tendency of 'A' & 'B' should be same in pure liquids & in the solution.

Eg - i) n-hexane + n-heptane.

ii) benzene + toluene

iii) ethyl bromide + ethyl iodide

iv) Chlorobenzene + bromobenzene

* Non-Ideal solution :→ A solution is said to be non-ideal solution if -

① The solution do not obey Raoult's law

② $\Delta H_{mix} > 0$ or $\Delta H_{mix} < 0$ heat is increased or evolved during dissolution.

③ $\Delta V_{mix} > 0$ or $\Delta V_{mix} < 0$ volume is increased or decreased during dissolution.

④ $P_A > P_A^\circ X_A$; $P_B > P_B^\circ X_B$ $\therefore P_A + P_B > P_A^\circ X_A + P_B^\circ X_B$

$P_A < P_A^\circ X_A$; $P_B < P_B^\circ X_B$ $\therefore P_A + P_B < P_A^\circ X_A + P_B^\circ X_B$

⑤ A-B attractive force should be weaker or stronger than A-A & B-B attractive forces.

⑥ Escaping tendency of 'A' & 'B' different than those in pure liquids & in the solution.

Eg. Acetone + Ethanol
Acetone + benzene
water + Ethanol

* Chemical Potential or Partial Molar Free Energy :→

$$X = f(T, P, n_1, n_2, n_3 \ldots n_i) \quad -①$$

$$dX = \left[\frac{\partial X}{\partial T}\right]_{P,n,n_2\ldots} dT + \left[\frac{\partial X}{\partial P}\right]_{T,n,n_2\ldots} dP + \left[\frac{\partial X}{\partial n_1}\right]_{T,P,n_2,3\ldots} dn_1 + \left[\frac{\partial X}{\partial n_2}\right] dn_2 + \ldots \quad -②$$

③

When temp. & pressure is kept constant,

Eqn ② becomes -

$$(dX)_{T,P} = \left[\frac{\partial X}{\partial n_1}\right]_{T,P,n_2,n_3\ldots} dn_1 + \left[\frac{\partial X}{\partial n_2}\right]_{T,P,n_1,n_3\ldots} dn_2 + \ldots \quad -③$$

$$\left[\frac{\partial X}{\partial n_1}\right]_{T,P,n_2,3\ldots} = \bar{X}_1$$

$$\left[\frac{\partial X}{\partial n_2}\right]_{T,P,n_1,3\ldots} = \bar{X}_2$$

For ith constituent, we can write

$$\left[\frac{\partial X}{\partial n_i}\right]_{T,P,n_1,n_2\ldots} = \bar{X}_i$$

Partial molar free energy also called chemical potential represented by symbol μ

$$\mu_i = \bar{G}_i = \left[\frac{\partial G}{\partial n_i}\right]_{T,P,n_1,n_2\ldots}$$

$$\mu = (\partial G)_{T,P,n_1,n_2\ldots}$$

At const T & P taking free energy as the extensive property eqn ② can be written as -

$$(dG)_{T,P} = \left[\frac{\partial G}{\partial n_1}\right]_{T,P,n_2,n_3\ldots} dn_1 + \left[\frac{\partial G}{\partial n_2}\right]_{T,P,n_1,n_3\ldots} dn_2 + \ldots$$

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \ldots$$

$$G_{T,P,N} = n_1\mu_1 + n_2\mu_2 + \ldots$$

pressure of that component in the pure state.

Let us consider a mixture of the components miscible volatile liquid A & B having mole fraction x_A & x_B. Their partial pressure P_A & P_B. the vapour pressure in the pure state P°_A & P°_B.

According to Raoult's law

$$P_A = x_A P^\circ_A \quad \text{—(1)}$$

$$P_B = x_B P^\circ_B \quad \text{—(2)}$$

If P is the total pressure then.

$$P = P_A + P_B$$

$$P = x_A P^\circ_A + x_B P^\circ_B \quad \text{—(3)}$$

$$x_A + x_B = 1$$

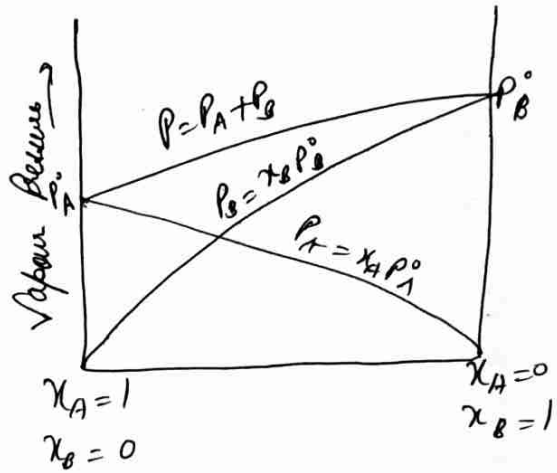
$$x_A = 1 - x_B \quad \text{—(4)}$$

Put eqn (4) in (3)

$$P = (1 - x_B) P^\circ_A + x_B P^\circ_B$$

$$P^\circ_A - x_B P^\circ_A + x_B P^\circ_B$$

$$\boxed{P = P^\circ_A + x_B (P^\circ_B - P^\circ_A)}$$



* Raoult's law for non-volatile solution :→

The vapour pressure of a solution containing non-volatile is directly proportional to the mole fraction of the solvent

$$P_A \propto x_A$$

$$P_A = K x_A$$

Let us consider a solution containing non volatile solute so that the pressure of the solution is equal to the vapour pressure in pure state multiplied by the mole fraction of the solvent

$$P_S = \chi_1 P^\circ \quad -(1)$$

$$\frac{P_S}{P_0} = \chi_1 \quad -(2)$$

$$\frac{P_S}{P_0} = \frac{n_1}{n_1+n_2} \quad -(3)$$

Subtracting both side by 1 in eqn (3)

$$1 - \frac{P_S}{P_0} = 1 - \frac{n_1}{n_1+n_2}$$

$$\frac{P_0 - P_S}{P_0} = \frac{n_1+n_2-n_1}{n_1+n_2}$$

$$\boxed{\frac{P^\circ - P_S}{P^\circ} = \frac{n_2}{n_1+n_2} = \chi_2}$$

$P^\circ - P_S = \Delta P$ (lowering of vapour pressure

$$\boxed{\frac{\Delta P}{P^\circ} = \frac{n_2}{n_1+n_2} = \chi_2}$$

where as the ratio $\Delta P / P^\circ$ is called relative lowering of vapour pressure

Colligative Properties :→ The property which depends upon amount of solute or the no. of moles of solute but do not depend upon nature of solute are called colligative properties

i) Relative lowering of vapour pressure
ii) Osmotic pressure
iii) Elevation in boiling point
iv) Depression in freezing point

Relative lowering of vapour pressure :-

For a solution of non-volatile solute (relative lowering of vapour pressure is equal to the no. of moles of solute)

$$\frac{\Delta P}{P^\circ} = \chi_2$$

$\Delta P = (P^\circ - P_S)$ Lowering of vapour pressure

P° = Vapour pressure of pure solvent

χ_2 = mole fraction.

It is a colligative property because it depends upon the no of moles of solution

& independent to their nature

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n_2}{n_1 + n_2}$$

$$\frac{P^\circ - P_s}{P^\circ} = \frac{\frac{w_2}{M_2}}{\frac{w_1}{M_1} + \frac{w_2}{M_2}}$$

for a dilute solution n_2 can be neglected as comparison with n_1

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n_2}{n_1}$$

$$\boxed{\frac{P^\circ - P_s}{P^\circ} = \frac{w_2}{M_2} \times \frac{M_1}{w_1}}$$

ii) Osmotic Pressure :-

Osmosis - The flow of the solution through a semipermeable membrane from pure solvent to solution or from a dilute solution to concentration solution is termed osmosis.

Osmotic pressure may be defined as equilibrium hydrostatic pressure of the column set up as a of osmosis.

Osmotic Pressure $\pi \propto C$

$\pi \propto T$

$\pi \propto C \times T$

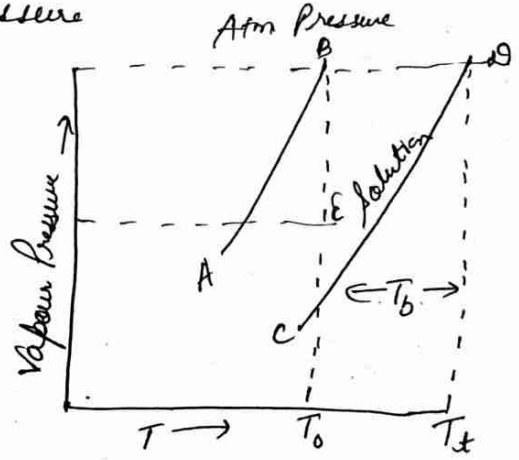
$\pi = CRT$ (R = Const)

$C = n/V$, $\pi = \frac{n}{V} RT$

$$\boxed{\pi = \frac{w}{MV} RT}$$

iii) Elevation in boiling point :-

The boiling point of the liquid is the temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure



$\Delta T_b = T_b - T_b^\circ$

T_b = boiling point of solution

T_b° = boiling point of pure solvent

ΔT_b = Elevation in boiling point

$\Delta T_b \propto m$ (m = Molarity)

$\Delta T_b = k_b m$

where k_b = Constant known as elevation or Ebullioscopic Const

Ebullioscopic Constant –

$\Delta T_b = k_b \times m$ If $m = 1$ unit

$\Delta T_b = k_b$

Molal or ebullioscopic const. may be defined as the elevation in boiling point when the molarity is taken as unit

$$\Delta T_b = k_b \times \frac{W_2}{M} \times \frac{1000}{W_1}$$

iv) Depression in freezing point :–

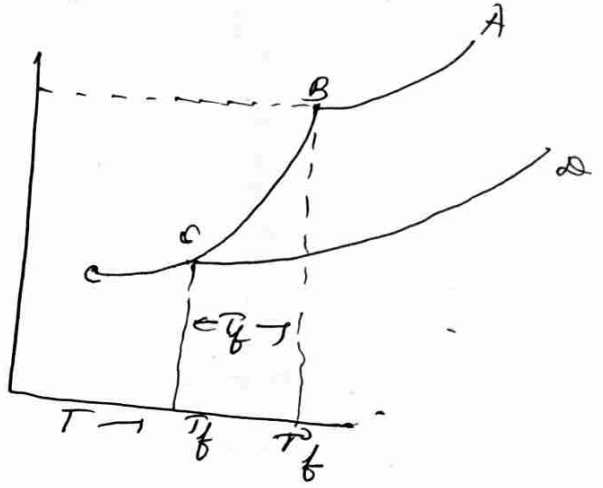
Freezing point of the substance is the temperature at which the solid or the liquid forms of the substance are in equilibrium

$\Delta T_f = T_f^\circ - T_f$

ΔT_f is depression in freezing point

T_f° = freezing point of pure solvent

T_f = freezing point of solution



$\Delta T_f \propto m$

$\Delta T_f = k_f \times m$

k_f = Constant known as molal depression Constant or cryoscopic constant

Cryoscopic Constant –

$\Delta T_f = k_f \times m$

if $m = 1$

$\Delta T_f = k_f$

Cryoscopic Const may be defined as the depression of freezing point when the

molality of the solution is ... and

$$\Delta T_f = K_f \times \frac{w_2}{M} \times \frac{1000}{w_1}$$

NOTE- Molarity is preferred over molality because molality does not involve volume & it temp. independent, therefor it is preferred over molarity for expressing the concentration of a solution.

* Experimental
* Thermodynamic Derivation for the expression for Relative lowering of Vapour Pressure :→

Solution $\underset{\rightleftharpoons}{\text{At const T\&P}}$ Vapour

Under this condition, the chemical potential of the solvent in the liquid phase i.e in the solution is equal to that of the solvent in the vapour phase-

$$\mu_1^l = \mu_1^v \quad \text{—(1)}$$

1 indicate solvent, l is for liquid phase & v is for vapour phase

$$d\mu_1^l = d\mu_1^v \quad \text{—(2)}$$

$$d\mu_1^l = f(T, P, x_1)$$

$$d\mu_1^l = \left(\frac{\partial \mu_1^l}{\partial T}\right)_{P,x} dT + \left(\frac{\partial \mu_1^l}{\partial P}\right)_{T,x_1} dP + \left(\frac{\partial \mu_1^l}{\partial x_1}\right) dx_1 \quad \text{—(3)}$$

At const T & P

$$(d\mu_1^l)_{T,P} = \left(\frac{\partial \mu_1^l}{\partial x_1}\right) dx_1 \quad \text{—(4)}$$

For ideal solvent

$$\mu_1^l = (\mu_1^\circ)^l + RT \ln x_1 \quad \text{—(4)}$$

$$d\mu_1^l = d(RT \ln x_1) = RT\, d \ln x_1 = RT \frac{dx_1}{x_1} \quad \text{—(5)}$$

$$\frac{d\mu_1^l}{dx_1} = \frac{RT}{x_1} \quad \text{—(6)}$$

Chemical Potential of the solvent in the vapour phase depends only on T & P

$$\mu_1^v = f(T, P)$$

$$d\mu_1^v = \left(\frac{\partial \mu_1^v}{\partial T}\right)_P dT + \left(\frac{\partial \mu_1^v}{\partial P}\right)_T dP \quad \text{—(7)}$$

At const temp.-

$$d\mu_1^v = \left(\frac{\partial \mu_1^v}{\partial P}\right) dP \quad \text{—(8)}$$

$\frac{\partial \mu_1^v}{\partial P} = \bar{V}_1$ called partial molar volume. Eqn (9) becomes

$$d\mu_1^v = \bar{V}_1 \, dP \quad -(9)$$

For a dilute solution $\bar{V} = V_1^\circ$ molar volume of the solvent

$$d\mu_1^v = V_1^\circ dP \quad -(10)$$

Solvent vapour present in equilibrium with the solution vapour present in eqn behave like an ideal gas -

$$V_0' = RT / P_1 \quad -(a)$$

Put eqn (a) in (10)

$$d\mu_1^v = RT \frac{dP_1}{P_1} \quad -(11)$$

From eqn (2)

$$d\mu_1^l = d\mu_1^v \quad -(b)$$

Put eqn (5) & (11) in (b)

$$RT \frac{dx_1}{x_1} = RT \frac{dP_1}{P_1}$$

$$\frac{dx_1}{x_1} = \frac{dP_1}{P_1} \quad -(12)$$

For a binary solution having x_1 as the mole fraction of the solvent & x_2

$$x_1 + x_2 = 1 \quad / \quad x_1 = 1 - x_2 \quad -(c) \quad (10)$$

$$dx_1 + dx_2 = 0$$

$$dx_1 = -dx_2$$

Put eqn (c) in (12)

$$\frac{dP}{P_1} = \frac{dx_2}{1 - x_2}$$

Integrating this equation -

$$\int_{P_1^\circ}^{P_1} \frac{dP}{P_1} = \int_{x_2=0}^{x_2=x_2} \frac{dx_2}{1-x_2}$$

$$\ln (P_1 / P_1^\circ) = \ln (1 - x_2)$$

$$P_1 / P_1^\circ = 1 - x_2 = x_1$$

$$\boxed{P_1 = x_1 P_1^\circ} \quad -(13)$$

* Thermodynamic Derivation for Osmotic pressure :→

Chemical potential of solvent in compartment A is greater than its chemical potential in the solution in compartment B.

$$\mu_1^A > \mu_1^B \quad -(1)$$

$$\mu_1(T, P) = \mu_1(T, P + \pi)$$

$$\mu_1 = f(T, P, x_1)$$

$$d\mu_1 = \left(\frac{\partial \mu_1}{\partial T}\right)_{P,x_1} dT + \left(\frac{\partial \mu_1}{\partial P}\right)_{T,x_1} dP + \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} dx_1 \quad -(3)$$

At const Temp. $dT = 0$

$$d\mu_1 = \left(\frac{\partial \mu_1}{\partial P}\right)_{T,x_1} dP + \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} dx_1 \quad -(4)$$

From thermodynamics, we have

$$\left(\frac{\partial \mu_1}{\partial P}\right)_{T,x_1} = \bar{V}_1 = V_1^\circ \quad -(5)$$

$\bar{V}_1$ is the partial molar volume of the solvent & is equal to molar volume of solvent (V_1°). When the soln is dilute

$$\mu_1 = \mu_1^\circ + RT \ln x_1$$

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} = \frac{RT}{x_1} \quad -(6)$$

Put eqn (5) & (6) in (4)

$$d\mu_1 = V_1^\circ dP + \frac{RT}{x_1} dx_1$$

$$= V_1^\circ dP + RT\, d\ln x_1 \quad -(7)$$

Integrating eqn (7)

(11)

$$\int_P^{P+\Pi} d\mu_1 = V_1^\circ \int_P^{P+\Pi} dP + RT \int_{x_1=1}^{x_1=x_1} d\ln x_1 \quad -(7)$$

$$\mu_1(T, P+\Pi) - \mu_1(T,P) = V_1^\circ (P+\Pi-P) + RT \ln x_1 \quad -(8)$$

Eqn (8) becomes

$$0 = V_1^\circ (P+\Pi-P) + RT \ln x_1$$

$$RT \ln x_1 = -V_1^\circ \Pi \quad -(9)$$

For a dilute solution $x_2 << 1$

$$\ln x_1 = -x_2 \quad -(10) \quad (x_1 + x_2 = 1,\ x_1 = 1 - x_2)$$

Put Eqn (10) in (9)

$$-x_2 RT = -V_1^\circ \Pi$$

$$\Pi V_1^\circ = x_2 RT \quad -(11)$$

$$x_2 = \frac{n_2}{n_1+n_2} = \frac{n_2}{n_1} \text{ for dilute solution}$$

Eqn (11) comes

$$\Pi V_1^\circ = \frac{n_2}{n_1} RT \text{ or } n_1 \Pi V_1^\circ = n_2 RT \quad -(12)$$

Total Volume. $V = n_1 V_1 + n_2 V_2$

But for dilute solution $n_2 = 0$

$$V = n_1 V_1^\circ \text{ or } V_1^\circ = \frac{V}{n_1} \quad -(13)$$

Put eqn (13) in (11)

$$n_1 \Pi \frac{V}{n_1} = n_2 RT$$

$$\Pi = \frac{n_2}{V} RT$$

$$\Pi = C RT$$

* Thermodynamic Derivation of Elev... in Boiling Point :-

Solution ⇌ Vapour

By Clausius - Clapeyron equation -

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad -(1)$$

$$\ln \frac{P^\circ}{P_S} = \frac{\Delta H_v}{R}\left[\frac{1}{T_0} - \frac{1}{T_S}\right]$$

$$\ln \frac{P^\circ}{P_S} = \frac{\Delta H_v}{R}\left[\frac{T_S - T_0}{T_S T_0}\right]$$

$$\ln \frac{P^\circ}{P_S} = \frac{\Delta H_v}{R}\left[\frac{\Delta T_b}{T_S T_0}\right] \quad -(2)$$

For a dilute solution boiling point of solution (T_S) is nearly equal to the boiling point of the solvent (T_0)

Eqⁿ (2) can be written as -

$$\ln \frac{P^\circ}{P_S} = \frac{\Delta H_v}{R} \times \frac{\Delta T_b}{T_0^2}$$

By Raoult's law -

$$\frac{P^\circ - P_S}{P^\circ} = x_2$$

$$\frac{P_S}{P^\circ} = 1 - x_2$$

$$\ln \frac{P_S}{P^\circ} = \ln (1 - x_2)$$

$$\ln \frac{P^\circ}{P_S} = -\ln (1 - x_2) \quad -(5)$$

For a dilute solution, the concentration of solute is very small $x_2 << 1$, therefore the term in $(1 - x_2)$ can be expanded as infinite series as

$$\ln (1 - x_2) = -x_2 - \frac{1}{2}x_2^2 - \frac{1}{3}x_2^3 + \cdots$$

$x_2 << 1$ therefore x_2^2 & x_2^3 are smaller quantity which can be neglected

$$\ln (1 - x_2) = -x_2$$

$$-\ln (1 - x_2) = x_2 \quad -(6)$$

$(1 - x_2)$ can be expanded as infinite series

$$\ln (1 - x_2) = -x_2 - \frac{1}{2}x_2^2 - \frac{1}{3}x_2^3 - \cdots$$

Put (6) eqⁿ in (5)

$$\ln \frac{P^\circ}{P^S} = x_2 \quad -(7)$$

Comparing eqⁿ (3) & (7)

$$x_2 = \frac{\Delta H_v}{R} \times \frac{\Delta T_b}{T_0^2}$$

$$\boxed{\Delta T_b = \frac{R T_0^2 x_2}{\Delta H_v}} \quad -(8)$$

We know that

$$x_2 = \frac{n_2}{n_1 + n_2} \quad -(9)$$

$$n_1 = w_1/M_1 \,, \; n_2 = w_2/M_2$$

Put in eqn (9) n_1 & n_2

$$x_2 = \frac{w_2/M_2}{w_1/M_1 + w_2/M_2}$$

For dilute solution $w_2/M_2 << w_1/M_1$, thus w_2/M_2 may be neglected in denominator compared to w_1/M_1

$$x_2 = \frac{w_2/M_2}{w_1/M_1} \quad -(10)$$

Put eqn (10) in (8)

$$\Delta T_b = \frac{RT_0^2}{\Delta H_v} \times \frac{w_2 M_1}{w_1 M_2} \quad -(11)$$

$$l_v = \frac{\Delta H_v}{M_1} \quad -(12)$$

Put eqn (12) in (8)

$$\Delta T_b = \frac{RT_0^2}{l_v} \cdot \frac{w_2}{M_2} \quad -(13)$$

$$m = \frac{w_2}{M_2} \times \frac{1000}{w_1} \;\Rightarrow\; \frac{w_2}{w_1 M_2} = \frac{m}{1000} \quad -(14)$$

By eqn (14) eqn (13) comes

$$\Delta T_b = \frac{RT_0^2}{1000 l_v} \cdot m \quad -(15)$$

When $k_b = \frac{RT_b^2}{1000 l_v}$ $\quad -(16)$

Put eqn (16) in (15)

$$\boxed{\Delta T_b = k_b m}$$

* Thermodynamic Derivation of Depression in Freezing point :→

According to clausius – Clapeyron eqn.

$$\ln \frac{P^\circ}{P} = \frac{\Delta H_s}{R}\left[\frac{1}{T_s} - \frac{1}{T_0}\right] \quad -(1)$$

where H_s rep. the molar heat of sublimation of solid solvent

$$\ln \frac{P^\circ}{P} = \frac{\Delta H_s}{R} \times \frac{T_0 - T_s}{T_s T_0} = \frac{\Delta H_s}{R} \times \frac{\Delta T_f}{T_s T_0} \quad -(2)$$

$$\ln \frac{P_s}{P} = \frac{\Delta H_v}{R}\left(\frac{1}{T_s} - \frac{1}{T_0}\right)$$

$$= \frac{\Delta H_v}{R} \times \frac{T_0 - T_s}{T_s T_0} = \frac{\Delta H_v}{R} \cdot \frac{\Delta T_f}{T_s T_0} \quad -(3)$$

For dilute solution $T_S = T_0$

$$\frac{\ln P_S}{P_0} = \frac{\Delta H_V}{R} \cdot \frac{\Delta T_f}{T_0^2} \quad -(4)$$

$$\ln \frac{P^\circ}{P} - \ln \frac{P_S}{P} = \frac{\Delta H_S}{R} \times \frac{\Delta T_f}{T_0^2} - \frac{\Delta H_V}{R} \times \frac{\Delta T_f}{T_0^2}$$

$$\ln (P^\circ - \ln P) - (\ln P_S - \ln P) = \frac{\Delta T_f}{RT_0^2} (\Delta H_S - \Delta H_V)$$

$$\ln P^\circ - \ln P_S = \frac{\Delta T_f}{RT_0^2} (\Delta H_S - \Delta H_V)$$

$$\ln \frac{P^\circ}{P_S} = \frac{\Delta T_f}{RT_0^2} \Delta H_f$$

As we know

$$\frac{P^\circ - P_S}{P^\circ} = x_2$$

$$1 - \frac{P_S}{P^\circ} = x_2$$

$$\frac{P_S}{P^\circ} = 1 - x_2$$

$$\ln \frac{P_S}{P_0} = \ln (1 - x_2)$$

$$\ln \frac{P^\circ}{P_S} = -\ln (1 - x_2)$$

The term $(1 - x_2)$ can be expanded as infinite series

$$\ln (1 - x_2) = -x_2 - \frac{1}{2} x_2^2 - \frac{1}{3} x_2^3$$

x_2^2 & x_2^3 are small quantities which can be neglected.

$$\ln (1 - x_2) = -x_2$$

$$-\ln (1 - x_2) = x_2 \quad -(8)$$

Put eqn (8) in (7)

$$\ln \frac{P^\circ}{P_S} = x_2 \quad -(9)$$

Put eqn (9) in (5)

$$x_2 = \frac{\Delta T_f}{RT_0^2} \Delta H_f$$

$$\boxed{\Delta T_f = \frac{RT_0^2}{\Delta H_f} \times x_2} \quad -(10)$$

$$x_2 = \frac{n_2}{n_1 + n_2} \quad -(11)$$

$$n_1 = w/M_1 \quad , \quad n_2 = w_2/M_2$$

$$x_2 = \frac{w_2/M_2}{w_1/M_1 + w_2/M_2}$$

For dilute solution w_2/M_2 may be neglected

$$x_2 = \frac{w_2/M_2}{w_1/M_1} \quad -(12)$$

Put eqn (12) in (10)

$$\Delta T_f = \frac{RT_0^2}{\Delta H_f} \times \frac{w_2 M_1}{w_1 M_2} \quad -(13)$$

When $\frac{\Delta H_f}{M_1} = l_f$

Then eqn (13) comes.

$$\Delta T_f = \frac{RT_0^2}{l_f} \times \frac{w_2}{w_1 M_2} \quad \text{—(14)}$$

$$m = \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

$$\frac{w_2}{w_1 \times M_2} = \frac{m}{1000} \quad \text{—(15)}$$

By eqn (15) eqn (14) comes

$$\Delta T_f = \frac{RT_0^2}{l_f} \cdot \frac{m}{1000}$$

$$\Delta T_f = \frac{RT_0^2}{1000 l_f} \cdot m$$

where $k_f = \frac{RT_0^2}{1000 l_f}$

Then, $\boxed{\Delta T_f = k_f m}$

* Experimental determination of lowering of vapour pressure :→

(i) Differential manometer method (*static method*) : In this method, the difference in the vapour pressures of the solvent and the solution, *i.e.* $(p^\circ - p_s)$ is measured by a *differential manometer* (Fig. 12). The manometer is filled with a suitable liquid of low density. Pure solvent is taken in one bulb and the solution is taken in the other. The apparatus is kept in a thermostat at constant temperature. Taps T_1 and T_2 are opened and the apparatus is connected to vacuum pump. The air present in the apparatus is slowly evacuated and the taps are then closed. The difference in the levels of the liquid in the two arms of the manometer directly gives $(p^\circ - p_s)$.

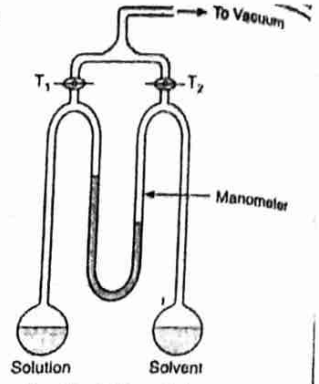


Fig. 12. Differential manometer

(ii) Ostwald and Walker's Method (*dynamic method or transpiration method*). This method is also named as *Gas saturation method*. It is most widely used method for measurement of the lowering of vapour pressure. The apparatus, as shown in Fig. 13 consists of a set of bulbs and U-shaped calcium chloride tubes.

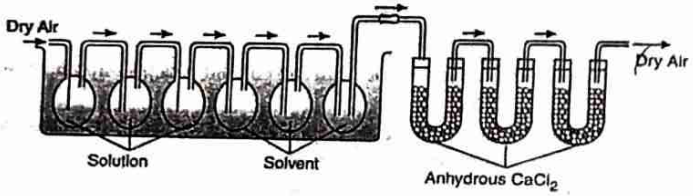


Fig. 13. Experimental set up for Ostwald and Walker's method

To start the experiment, the weight of bulbs containing solution and solvent and calcium chloride tubes is taken. The solution and solvent bulbs are placed in a thermostat to maintain the required temperature. A stream of dry air is passed through bulbs containing solution, then through bulbs containing solvent and finally through anhydrous calcium chloride which can absorb the solvent. As the air passes through the solution, it absorbs the amount of vapour present over the solution till its pressure becomes equal to the vapour pressure of the solution. As a result, a loss in weight of solution bulbs takes place. Thus,

Loss in the weight of solution bulbs $(w_1) \propto$ *vapour pressure of solution* p_s

or $w_1 \propto p_s$ ...(16)

The moist air passes through solvent tubes and takes up solvent vapours and solvent tubes show loss in weight. Here,

Loss in weight of solvent bulbs $(w_2) \propto$ *vapour pressure of solvent–vapour pressure of solution.*

i.e. $w_2 \propto (p^\circ - p_s)$ ...(17)

Combining equations (16) and (17) we can write

Total loss of weight of solution bulbs and solvent bulbs

$(w_1 + w_2) \propto p_s + (p^\circ - p_s) = p^\circ$ ...(18)

or $w_1 + w_2 \propto p^\circ$ ...(19)

From equations (17) and (19), we can write

$$\frac{p^\circ - p_s}{p^\circ} = \frac{w_2}{w_1 + w_2} = \frac{\text{Loss in weight of solvent bulbs}}{\text{Total loss in weight of solution bulbs and solvent bulbs}}$$

As already mentioned, if water is used as solvent, then, anhydrous calcium chloride absorbs the entire solvent in the end. Then,

The increase in weight of calcium chloride tubes (w_3) $\propto p^\circ$ ...(20)

The combining equations (17) and (20) we can write,

$$\boxed{\frac{p^\circ - p_s}{p^\circ} = \frac{w_2}{w_3} = \frac{\text{Loss in weight of solvent bulbs}}{\text{Gain in weight of calcium chloride tubes}}}$$

3.18.13 Experimental determination of Osmotic pressure

Berkeley and Hartley's Method

The principle of this method is to apply an external pressure on the solution which is just sufficient to prevent the entry of the solvent into the solution through the semipermeable membrane. The apparatus used for measuring osmotic pressure is shown in Fig. 18.

Fig. 18. Berkeley and Hartley apparatus for measuring osmotic pressure.

It consists of a porous tube (A) lined with semi-permeable membrane of copper ferrocyanide. The porous tube is fitted into an outer gun metal vessel which is fitted with a piston and a pressure gauge. The porous tube is fitted with a water reservoir on one side and a capillary indicator T on the other side. Solvent is put in the porous tube and the outer cylinder is filled with the solution, the osmotic pressure of which is to be measured. Solvent placed in the porous tube tends to pass into the solution through the semi-permeable membrane due to which the level of capillary indicator moves downwards. External pressure is now applied on the piston so that the solvent level in the capillary indicator remains constant. The pressure which is equal to the osmotic pressure is recorded from the pressure gauge.

This method is an improvement over the other two methods in the following respects :

(i) In this method the external pressure balances the osmotic pressure, as a result the strain on the membrane is not so much as in other methods.

(ii) The equilibrium is reached more quickly so the time taken for measurement of osmotic pressure is lesser than other methods.

(iii) The concentration of the solution does not change during measurement because the osmosis of solvent into solution is stopped by applying external pressure.

If w grams of solute are dissolved in V litres of solution and M is the molecular mass of solute, then, the number of moles of solute is given as, $n = \frac{w}{M}$

Substituting the value of n in equation $\pi = \frac{n_2}{V} RT$,

$$\pi = \frac{wRT}{VM}$$

or

$$M = \frac{wRT}{V\pi}$$

Thus measuring osmotic pressure π of a solution containing w grams of the solute dissolved in V litres of solution at a particular temperature T, the molecular mass of the solute can be calculated. The value of R = 0.0821 litre atm degree^{-1} mole^{-1}, when π is taken in atmospheres.

It is important to note that *osmotic pressure measurement is usually not preferred for determining the molecular masses. For most of compounds, the osmotic pressures are so high that they cannot be easily measured. For such compounds, depression in freezing point data is preferred for the determination of their molecular masses. On the other hand for macromolecules like polymers, the depression in freezing point and other colligative properties are too small to be measured. However, osmotic pressures of such compounds are appreciable and can be easily measured. Hence osmotic pressure method is best suitable for determination of molecular masses of macromolecules like polymers and proteins etc.*

Experimental determination of elevation in boiling point :→
The elevation of boiling point of solution containing non-volatile solute can be determined by the difference between boiling point of pure solvent

The values of elevation in boiling point i.e. ΔT_b are usually very small. So to measure the small differences in temperature with high precision, *differential thermometers* are used. For this purpose Beckmann thermometer is used.

It is designed to measure small changes in temperature and not the absolute temperature of solvent or solution itself. It consists of a large bulb B at the bottom of a fine long capillary tube A. There is a small reservoir R of mercury at the top. The amount of mercury in the reservoir can be increased or decreased by tapping the thermometer gently. As the bulb B is large so a small change in temperature causes appreciable movement of mercury in the capillary, hence measuring the temperature changes with precision. The complete scale is callibrated from 0 to 6 K and each small division can read upto 0.01°.

The thermometer is gently tapped to increase or decrease the amount of mercury in the reservoir. In this way the initial reading in the capillary can be adjusted at any desired point on the scale when the thermometer is placed in boiling or freezing solvent or solution.

Following methods are most commonly used methods for determination of elevation in boiling point.

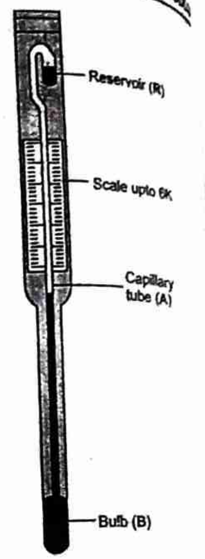


Fig. 20. Beckmann thermometer

(I) Landsberger's Method

This method is based on the principle of heating the solvent or solution to its boiling point by passing hot vapours of the pure solvent into it. The heating is done slowly so that superheating of the solvent or the solution does not take place.

The Landsberger's apparatus used for this purpose is shown in Fig. 21. It consists of following parts :

(*i*) A round bottomed *boiling flask* A in which pure solvent is boiling.

(*ii*) A *delivery tube* B which has a bulb at the end with holes known as the (*rose-head*) C to carry out uniform heating.

(*iii*) An *inner boiling tube* D which is graduated in ml and has a hole H. It holds the thermometer T reading correctly upto one-tenth of a degree. The middle portion of the tube is blown into bulb E.

(*iv*) The *hot vapour Jacket* F surrounding the inner boiling tube. The outer vessel has a side tube G which is connected to condenser.

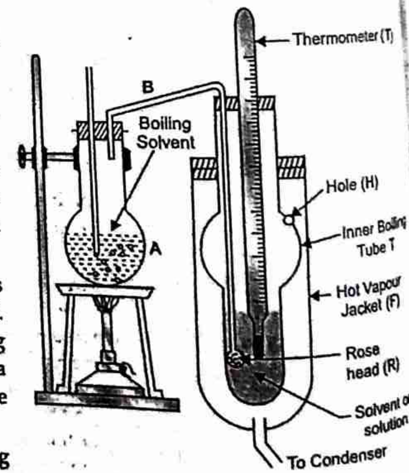


Fig. 21. Landsberger's apparatus for determination of elevation in boiling point.

Procedure

(i) Small amount of the pure solvent is taken in the inner boiling tube D.

(ii) Pure solvent is heated to its boiling point in the boiling flask A to get a steady flow of solvent vapours. The hot vapours are bubbled into the inner boiling tube D through the rose-head R which ensures the uniform heating of the solvent. As soon as the solvent begins to boil, the temperature becomes constant and the thermometer reading is noted. This gives the boiling point T_0 of the pure solvent. The uncondensed vapours escape into the outer Jacket F through the hole H.

(iii) The flow of vapours through the solvent is stopped for a while and an accurately weighed amount of solute is introduced into the inner tube D. Vapours of the boiling solvent are again passed into the solution and its boiling point (T_1) is noted. The difference of the two temperatures ($T_1 - T_0$) gives the elevation in boiling point (ΔT_b).

(iv) The volume of the solution (V) is noted directly from the graduated tube D. The mass of the solvent (W_1) is calculated by multiplying this volume by its density.

Knowing the masses of solute (W_2), and the solvent (W_1), the elevation in boiling point (ΔT_b), the molecular mass of solute (M_2) can be calculated using following equation

$$M_2 = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1}$$

Sources of error

Some errors that can occur in this method are

(i) There are chances of superheating of solvent and the solution.

(ii) It is difficult to know the composition of the solution at its boiling point.

(iii) The boiling points measurements are made at a surface 3-4 cm below the liquid surfaces. Therefore, an error may occur due to hydrostatic pressure of this liquid column.

The boiling points measured by this method were about 0.1° higher than expected values.

(ii) Cottrell's Method

To eliminate the sources of error in landsberger's method, Cottrell designed the apparatus shown in Fig. 22.

The Cottrell apparatus consists of a boiling tube in which pure solvent is taken. To maintain a continous stream of vapours, a small pieces of porcelain are put into the liquid. An inverted funnel with side tubes is placed in the liquid in a way that its side tubes open above the level of the liquid. A thermometer that can read accurately upto one-tenth of a degree is fitted in the boiling tube in a way that the vapours of the liquid are sprayed on the bulb of the thermometer. The side tube of the boiling tube is fitted with a condenser.

A known mass W_1 of the solvent is taken in the boiling tube and is gently heated and the liquid starts boiling. The vapours of the boiling solvent rise through the funnel and

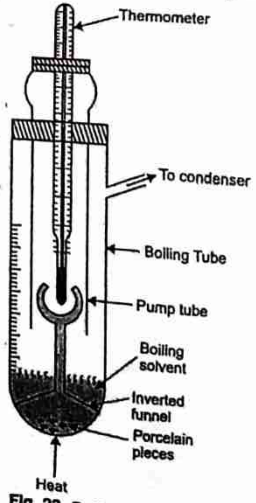


Fig. 22. Cottrell apparatus

are sprayed on the thermometer after passing through the side tube. This constant temperature indicates the boiling point of the solvent (T_0).

A known mass of solute W_2 is added to the solvent and the boiling point of the solution T_1 is noted as before. The difference in boiling points ($T_1 - T_0 = \Delta T_b$) gives the elevation of the boiling point. Knowing W_1, W_2, ΔT_b and K_b, the molecular mass of the solute can be calculated.

The advantages of Cottrell's method

(i) In this method superheating does not take place because the vapours of the boiling liquid are sprayed on the bulb of thermometer after passing through an inverted funnel and the side tubes.

(ii) The composition of the solution at boiling point remains unchanged because no solvent is lost by evaporation. The vapour gets condensed in the condenser and flows back into the solution.

(iii) The hollow stopper fitted in the boiling tube prevents the contact of cold condensate with the thermometer.

It may be noted in Cottrell's apparatus that with Beckmann's thermometer is used, it is inserted in place of ordinary thermometer, only when a constant boiling point temperature has been reached for the solvent at the given temperature, the Beckmann thermometer is set so that the level of mercury

3.20.7 Experimental determination of depression in freezing point

The most commonly used methods for finding the depression in freezing point are described below :

(a) Beckmann's Method

This is the most commonly used method for finding the depression in freezing point of a solution. The apparatus used for the purpose is shown in Fig. 24. It consists of the following parts :

(*i*) The *inner freezing tube* A in which a known weight of the solvent is taken. This tube is fitted with Beckmann thermometer T and a stirrer C. It has a side tube S for the addition of solute.

(*ii*) The *outer glass tube* B that surrounds the inner tube. This serves as an air jacket and ensures a slow and uniform rate of cooling of the liquid in the inner tube.

(*iii*) A *glass vessel* D covered with a lid and contains freezing mixture. It is provided with a stirrer.

Fig. 24. Beckmann's apparatus for the determination of depression in freezing point.

Procedure

(*i*) A known weight of solvent is taken in freezing tube A and its approximate freezing point is determined by placing the tube A directly into the freezing mixture.

(*ii*) The frozen solvent is melted and the tube A is placed in outer tube surrounded by freezing mixture.

(*iii*) The liquid is allowed to cooled till the temperature falls to approximately 0.5° below the approximate freezing point of the solvent. In this process the solvent has been supercooled without undergoing solidification.

(*iv*) Vigorous stirring of supercooled liquid is done to introduce solidification. When the solidification starts, the temperature rises and then becomes constant. This is the accurate freezing point of the solvent (T_f). *This temperature is taken using a thermometer that can read upto one-tenth of a degree.*

(*v*) Now one-tenth thermometer is replaced by Beckmann thermometer. The thermometer is set such that at the freezing point of pure solvent, the mercury thread in the capillary stands at the top of the scale.

(*vi*) The freezing tube A is taken out and the solvent is remelted. A known quantity of solute is added and dissolved by stirring to obtain a solution. Now the freezing point of the solution is determined in the same way as that of the solvent. The difference between the two freezing points gives the depression in freezing point.

Knowing the weights of the solute and the solvent and the depression in the freezing point, the molecular mass of the solute can be calculated by using the expression

$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1}$$

To obtain accurate results following precautions should be observed :

(*i*) The temperature of cooling vessel should be 4° to 5° below the freezing point of the liquid.

(*ii*) The stirring should be uniformly done.

(*iii*) The supercooling should not exceed 0.5°C.

Rast's Camphor Method

The depression in freezing point is directly proportional to the value of molal depression constant *i.e.* K_f. Rast's method is based on the fact that the value of K_f for camphor is 40, so a solution of a substance in camphor will show large freezing point depression which can be read easily using an ordinary thermometers. *This method is used for determination of molecular mass of solutes which are soluble in molten camphor.* The procedure involves following steps :

(*i*) Pure camphor is powdered and filled in a capillary tube sealed at the lower end. This is tied along a thermometer and suspended in a glycerol bath or concentrated sulphuric acid bath.

(*ii*) The melting point of camphor is recorded. This is the melting point of pure solvent (T_f).

(*iii*) A known weight of solute is mixed with a known quantity of camphor and is melted to form a homogeneous mixture. It is then cooled. On solidification, the mixture is powdered and introduced into a capillary tube and its melting point determined. The difference in two melting points gives ΔT_f. Now-a-days, the electrical heating apparatus is used for determination of melting points of camphor and its mixture with the given solute.

Section-D B.Sc - VI^th Sem. Physical Chemistry (1)

Phase Equilibrium

* Phase :- A phase may be defined as i) homogeneous & physically distinct part of a heterogeneous system separated by a well defined boundary ii) physically & chemically different from other parts of a system & mechanically separable from other parts of the system

i) A system containing only liquid water is a one phase system $P=1$

ii) A system containing liquid water & water vapour is a two phase system $P=2$

* Component :- The term component is defined as for a system in equilibrium it is the minimum number of independent chemical constituents in terms of which the composition of each phase can be expressed either

directly or in terms of a chemical equation zero & negative values are permitted.

* Water system is one component system & calcium carbonate is two component system.

* Degree of Freedom :→

The degree of freedom may be defined as the number of variables, such as temperature, pressure & concentration which can be varied independently without altering the number of phases.

Degree of freedom is represented by F in the phase rule equation $F = C - P + 2$

* Gibbs Phase Rule :→

J. Willard Gibbs put forward a relationship between the number of phases P, number of components C & the number of degree of freedom F

which must be specified in order to define a heterogeneous system. This relation is known as phase rule.

$$F = C - P + 2$$

Derivation of Phase rule :—

Consider a heterogeneous system having P phases ($P_1, P_2, P_3 \ldots P_n$) & components ($C_1, C_2, C_3 \ldots C_x$)

Degree of freedom = (Total number of variables - No. of relations b/w variables at equilibrium)

Phase P_4	C_1	C_2	C_3 ——	C_x
	‖	‖	‖	‖
Phase P_3	C_1	C_2	C_3 ——	C_x
	‖	‖	‖	‖
Phase P_2	C_1	C_2	C_3 ——	C_x
	‖	‖	‖	‖
Phase P_1	C_1	C_2	C_3 ——	C_x

The total no. of variables can be calculated as follows—

i) Temperature - At equilibrium each

phase has the same temperature, there is one temp. variable for whole of the system.

ii) Pressure – At equilibrium each phase has the same pressure, there is one pressure variable for whole of the system.

iii) Composition :– Suppose there are two components A & B in a single phase. If the molar concentration of A is known, the molar concentration of B can be simply obtained by difference. Single phase containing three components can be defined, if concentration of two components are given. Hence a single phase containing C components can be defined by (C-1) conc. terms.

Total no. of variables = P(C-1) + 1 + 1
(for composition) (for Temp.) (for P)

= P(C-1) + 2

According to thermodynamics, the chemical potential μ of a component is same in all phases when the system is in equilibrium.

$$(\mu_i)_A = (\mu_i)_B = (\mu_i)_C$$

$$(\mu_i)_A = (\mu_i)_B$$

$$(\mu_i)_A = (\mu_i)_C$$

No. of relationship at equilibrium = C(P-1)

F = (Total no of independent variables) – (No. of relationships b/w variables at equilibrium)

= [P(C-1) + 2] – [C(P-1)]

= PC – P + 2 – PC + C

$$\boxed{F = C - P + 2}$$

THE WATER SYSTEM

Under normal conditions water exists in phases namely liquid water, ice and water vapour.

$$\text{ice } (s) \rightleftharpoons \text{water } (l) \rightleftharpoons \text{water vapour } (g)$$

All these phases can be represented by single constituent 'water' so it is a one component system.

Various phases which can exist in equilibrium are

$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

$$H_2O\ (s) \rightleftharpoons H_2O\ (g)$$

$$H_2O\ (s) \rightleftharpoons H_2O\ (l)$$

$$H_2O\ (s) \rightleftharpoons H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

The number of phases which can exist at any time depends on the conditions of temperature and pressure. The phase diagram or pressure-temperature, P-T diagram of water system is shown in Fig. 2. This phase diagram consists of

(*i*) Three curves OA, OB and OC.

(*ii*) Curve OA′ for metastable equilibrium

(*iii*) Three areas AOC, AOB, BOC.

(*iv*) A point O called the triple point.

Fig. 2. The phase diagram for water system

1. Curves

(i) Curve OA, the vapour pressure curve of water. Curve OA separates the liquid water from water vapour region. It represents equilibrium between liquid water and water vapour at different temperatures and is known as *vapour pressure curve*. Above this curve liquid water alone exists and below it only water vapour exists. At any point on this curve, the two phases water liquid and water vapour exist in equilibrium. The curve starts from point O, the freezing point of water and terminates at A, the critical point above which the liquid does not exist. At this point A, the critical temperature is 374°C and critical pressure is 218 atm. At point A the liquid and vapour phases are indistinguishable and there is only one phase. The degree of freedom of water system as given by phase rule is one.

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

This can be well explained by considering any point on curve OA. Note that for a given value of pressure, there is a fixed value of temperature. That means if pressure is kept constant and the temperature is raised, then vapour phase will disappear. Similarly if temperature is increased then liquid phase will disappear. So to define the system completely along this curve it is required to mention pressure or temperature of the system, or we can say if pressure is fixed, the temperature becomes automatically fixed.

Hence water-vapour system along curve OA is univariant as predicted by the phase rule.

The slope of curve OA *i.e.* dP/dT is positive which indicates that vapour pressure of water increases with temperature. This fact can be explained by Clausius-Clapeyron equation.

$$\frac{dP}{dT} = \frac{\Delta H_f}{T(V_g - V_s)}$$

where ΔH_f = Molar heat of fusion of water

V_g = Molar volume of water vapour

V_s = Molar volume of ice

Since ΔH_f is +ve and $V_g > V_s \therefore V_g - V_s$ is +ve

$$\therefore \quad \frac{dP}{dT} = +ve$$

(ii) Curve OA', the metastable curve vapour pressure curve for supercooled water. If liquid water on the curve OA is carefully supercooled, then it is possible that the ice may not appear at triple point O and we may get liquid water below its freezing point. The water is then said to be supercooled and the curve OA' represents the vapour pressure curve of supercooled water, the curve OA' represents the **metastable equilibrium** between liquid water and vapour phase. If a small crystal of ice is added to the supercooled liquid, the liquid at once solidifies and changes into ice and the curve OA' merges into curve OB. *It is seen in the phase diagram that the curve OA' lies above the curve OB. Consequently, the vapour pressure of the metastable system is higher than that of the stable system (along curve OB) at the same temperature.*

(iii) Curve OB, *the sublimation curve of ice*. Curve OB represents equilibrium between ice and vapour at various temperatures and pressures. The curve starts from point O, the freezing point of water and terminates at absolute zero (– 273°C) where vapour phase does not exist. It shows that as the temperature is lowered the vapour pressure of ice tends to be negligible. All along the curve there can be only one value of pressure for a given temperature and vice versa, or we can say that the system is univariant along curve OB. It also follows from the phase rule equation

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

The slope of curve OB is positive indicating that the vapour pressure of ice increases with temperature. This can be explained by Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H_f}{T(V_g - V_l)} = \frac{+ve}{+ve} = +ve$$

(iv) Curve OC, the melting point curve of ice. The curve AD divides the solid ice region from the liquid water region. It represents equilibrium between ice and liquid at different temperatures. Here ice and water coexist in equilibrium. It shows how the melting point of ice or the freezing point of water varies with the pressure. In other words, it shows the effect of pressure on the melting point of ice. The curve OC *is inclined towards the pressure axis i.e., the slope of curve OC is negative* which indicates that the melting point of ice is lowered by increase of pressure. This fact follows from Clausius-Clapeyron equation, which is

$$\frac{dP}{dT} = \frac{\Delta H_f}{T(V_l - V_s)} \quad \text{or} \quad \frac{dT}{dP} = \frac{T(V_l - V_s)}{\Delta H_f} = \frac{-ve}{+ve} = \text{negative}$$

The volume of ice V_s is less than the volume of water V_l, therefore, the term on right hand side of above expression is negative. Hence *dT/dP has a negative sign; the negative sign indicates that the melting point of ice decreases by increase of pressure.*

At 1 atmospheric pressure the line to the temperature axis meets the fusion curve at 0°C which is the freezing point of ice while at a higher pressure P_2 the melting point is T_2°C which is less than 0·0023°C.

There is no upper limit for the curve OC. At higher pressures different structural forms of ice come into existence because the bonds between water molecules are modified by high pressure. These forms of ice have been found to exist at pressures above 2500 atmospheres and temperature – 22°C. At any point on the curve OC, there are two phases ice and water are present. Hence the system is univariant as shown by the phase rule.

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

2. Areas AOC, AOB and BOC

The areas AOC, AOB and BOC in the phase diagram show the conditions of pressure and temperature at which a single phase ice, water or vapour can exist. In area AOC the single phase liquid water is present. In area BOC there is only ice whereas the area below the curve AOB contains only water vapour. It is necessary to specify both temperature and pressure to define a system in these areas. For example, in area AOB, point *d* can be completely defined if pressure, P_1 and temperature T_1 are stated. Thus, the system has two degrees of freedom (or it is bivariant).

Similarly, within single phase areas AOC and BOC the system is *bivariant*. In other words, we can say that in these areas pressure and temperature can be independently varied within the area without any change of phase taking place. Hence, *these areas are bivariant systems*. It also follows from phase rule equation,

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

Thus to specify the system at any point in these areas, both the temperature and pressure must be fixed. In other words, the system in these areas has two degrees of freedom *i.e.* it is bivariant.

3. Triple point 'O'

Point 'O' in the phase diagram represents triple point of water system. The curves OA, OB and OC meet at the triple point. At this point all the three phases *i.e.* ice, water and water vapour exist in equilibrium only one such point is possible.

It represents a non-variant system *i.e.* zero degree of freedom. It is not necessary to specify either temperature or pressure under these conditions because there is only one temperature and one possible pressure at which all the three phases can exist together in equilibrium.

This point corresponds to a definite temperature 0.0098°C and a definite pressure of 4.58 mm. If either pressure or temperature is changed, one of the phase will disappear. Thus on changing the condition of temperature or pressure, one of the three phases will disappear. So at triple point O, there is **zero degree of freedom** hence, the system is invariant or non-variant at triple point O. According to phase rule equation,

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

PHASE DIAGRAM FOR SULPHUR SYSTEM

It is a one component system comprising of four phases. The four phases are :

(*i*) Rhombic sulphur S_R (solid)

(*ii*) Monoclinic sulphur, S_M (solid)

(*iii*) Sulphur liquid, S_L

(*iv*) Sulphur vapour, S_V.

The two crystalline forms of sulphur namely rhombic sulphur (S_R) and monoclinic sulphur (S_M) exist in equilibrium with each other at a transition temperature 95.6°C. The rhombic sulphur is stable below 95.6°C whereas monoclinic sulphur is stable above this temperature. At 120°C the monoclinic sulphur melts into sulphur liquid, thus

$$S_R \overset{95.6°C}{\rightleftharpoons} S_M \overset{120°C}{\rightleftharpoons} S_L$$

It may be noted that all the four phases of sulphur cannot coexist. This is forbidden by the phase rule equation as follows :

$$F = C - P + 2$$

Sulphur is one component system $\therefore C = 1$

There are four phases. So $P = 4$

Then $F = 1 - 4 + 2 = -1$

$F = -1$ is not possible. However when $F = 0$ and $C = 1$ then the phase rule equation becomes

$$0 = 1 - P + 2$$

or $P = 3$

Thus the maximum number of phases that can coexist is three. However the actual number of phases which can exist in equilibrium depends upon the conditions of temperature and pressure.

The phase diagram of sulphur is shown in Fig. 4.

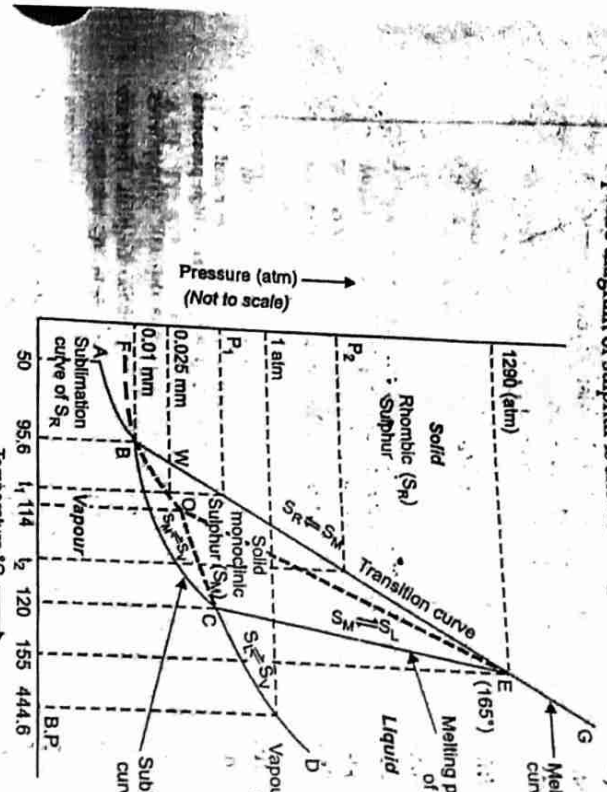


Fig. 4. Phase diagram of sulphur system

1. The curves

The diagram shows six equilibrium curves AB, BC, CD, BE, CE, EG and four metastable equilibrium curves BO, BF, CO and EO. *These curves divide the phase diagram into four areas.*

(*i*) Curve AB, *the sublimation curve of rhombic sulphur.* It shows the variation of vapour pressure of S_R with temperature. Along this curve two phases S_R and S_V are in equilibrium. The curve starts from point B, the transition temperature, (95.6°C) of S_R and S_M and terminates at A (50°C). Below point A the vapour pressure of rhombic sulphur cannot be measured. As there are two phases S_R and S_V in equilibrium along this curve so it represents a univariant system as predicted by the phase rule equation

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

(*ii*) Curve BC, *the sublimation curve of monoclinic sulphur.* It shows variation of vapour pressure of S_M with temperature. Along this curve two phases S_M and S_V are present in equilibrium with each other. The curve starts from point C (120°C) and terminates at B (95.6°C) which is the transition temperature of S_R. The system along this curve is univariant.

(*iii*) Curve CD, *the vapour pressure curve of sulphur liquid.* It shows the variation of the vapour pressure of sulphur liquid with temperature. S_L and S_V are in equilibrium along this

curve. So it is a *univariant system*. The curve starts at point C (120°C) which is the melting point of S_M and terminates at D the critical point after which only S_V exists. One atmosphere line meets this curve at temperature 444.6°C which is the boiling point of sulphur.

(iv) Curve CE, *the melting point curve of S_M*. It shows the effect of pressure on the melting point of S_M. Along this curve, the two phases S_M and S_L exist in equilibrium. The curve represents a *univariant system*. CE slopes away from the pressure axis showing that the melting point is raised by the increase in pressure. The curve ends at E, beyond which S_M does not exist.

(v) Curve EG, *the melting point curve for S_R*. Along this curve, the two phases S_R and S_L are in equilibrium. Thus the system is univariant.

(vi) Curve BE, *the transition curve*. This curve separates the regions of S_R and S_M. It represents equilibrium between the two allotropes S_R and S_M. Each point on this curve represents a definite temperature and pressure at which the two crystalline forms S_R and S_M change reversibly into one another. Curve BE represents a univariant system (F = C – P + 2 = 1 – 2 + 2 = 1).

At pressure P_1 at point W the rhombic sulphur changes into monoclinic sulphur. It corresponds to temperature t_1. Keeping pressure constant and increasing the temperature S_R changes to S_M while on decreasing the temperature S_M changes to S_R.

At temperature t_1 (when the pressure is P_1) one form changes to the other and the two are in equilibrium. This is known as the *transition point or transition temperature*, the temperature at which S_R changes into S_M reversibly at a definite pressure. Similarly t_2 is another transition temperature at pressure P_2.

The curve BE and CE slope away from pressure axis showing that the transition temperature and melting point of monoclinic sulphur increase with increasing pressure.

As the transition of one form to another form is a slow process, it is possible to go directly from S_R to S_M by rapid heating. This gives rise to four metastable curves which represent two phases in metastable equilibrium. These curves are also univariant.

(vii) Curve BO, *the metastable curve of S_R*. This is a continuation of sublimation curve AB of S_R. When S_R on the curve AB is rapidly heated then it is possible that S_M may not appear at B and we may get rhombic sulphur above the transition point. Curve BO represents the metastable equilibrium between S_R and S_V. On a slight disturbance, the curve BO merges into curve BC, the sublimation curve or vapour pressure curve of monoclinic sulphur. It represents a univariant system.

(viii) Curve BF, *the metastable vapour pressure curve of S_M*. Curve BF is a continuation of sublimation curve of S_M. If monoclinic sulphur is rapidly cooled then rhombic sulphur may not appear at point B (the transition temperature) and we may get supercooled S_M. Curve BF represents the metastable equilibrium between S_M and S_V. It represents a univariant system.

(ix) Curve CO, *the metastable vapourisation curve of sulphur liquid*. On supercooling the sulphur liquid the curve CO is obtained. It represents the metastable equilibrium between supercooled S_L and S_V. It meets the metastable vapour pressure curve of S_R at point O.

(x) Curve EO, *the metastable melting point curve for S_R*. The two metastable phases i.e. S_R and S_L are in equilibrium along this curve. The curve EO slopes away from pressure axis

showing that the melting point of S_R is increased with increasing pressure. The system is thus univariant. If liquid sulphur is cooled rapidly at a pressure higher than 1290 atm, then we can get solid rhombic sulphur without the formation of S_M. The curve ends at E where the metastable S_R disappears.

2. Areas

The phase diagram of sulphur system has four areas. These regions contain S_R, S_M, S_L and S_V. There is only one phase present in these areas so they represent bivariant systems which have two degrees of freedom.

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

These areas show the conditions of pressure and temperature at which a single phase S_R, S_M, S_L or S_V is present.

(i) Below **ABCD** the region of **sulphur vapour** S_V is present (*bivariant system*).

(ii) To the right of GECD, The region of *liquid sulphure*. S_L is present (*bivariant sysetm*).

(iii) To the left of GEBA, the region of rhombic sulphur, S_R is present. (*bivariant system*).

(iv) Area enclosed in EBC, the region of monoclinic sulphur, S_M is present (*bivariant system*).

3. The Triple Points B, C, E and metastable triple point O

Triple Point B

At this point, the curves AB, BC and BE meet. At point B, the three phases in equilibrium are S_R, S_M and S_V. At this point, if temperature or pressure is changed, one of the phases disappears. There are three phases at this point. Thus, it represents a *non-variant system*.

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

At point B, S_R is changed to S_M and this process is reversible. So the temperature corresponding to point B represents the transition temperature (95.6°C).

Triple Point C

The curves BC, CD and CE meet at this point. The three phases, S_M, S_L, S_V co-exist in equilibrium at this point. As there are three phases, the point C represents a non-variant system which is also indicated by phase rule equation

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

In this phase diagram, the temperature corresponding to point C is 120°C which is the melting point of S_M.

Triple Point E

This is the melting point of three curves CE, BE and EG, The three phases, S_R, S_M and S_V are in equilibrium at point E. The system is non-variant at this point. This point corresponds to temperature 155°C and 1290 atmosphere pressure at which the three phases S_R, S_L and S_M coexist. If one of the variables *i.e.* temperature or pressure is changed at this point, one of the phases disappears. In other words, the system has no degree of freedom.

4.9 LEAD-SILVER SYSTEM

It is a two-component system involving solid-liquid equilibrium and forms a simple eutectic. Lead and silver are the two components. The possible phases are :

(*i*) solid lead (*ii*) solid silver (*iii*) solution of molten lead and silver (*iv*) vapour

The effect of pressure on solid-liquid equilibrium is negligible because the vapour pressure of solid lead and silver is very small. Therefore, the vapour phase is ignored. Thus, lead-silver is a condensed system with three phases. Hence reduced phase rule equation F' = C – P + 1 is applicable here. The temperature composition phase diagram of the lead-silver system is shown in Fig. 11.

Fig. 11. Phase diagram of lead-silver system.

Main features of the diagram are :

(*i*) *Curves AO and BO*

(*ii*) *Eutectic point O*

(*iii*) *Area above AOB, area below AO and area below BO.*

The Curves

(i) Curve AO, the freezing point-curve of silver

Point A represents the freezing point of silver (961°C). Curve AO shows that addition of Pb to Ag decreases the freezing point of Ag. Thus, the freezing point of Ag falls along the curve AO. Along this curve solid Ag exists in equilibrium with liquid solution of Pb in Ag.

Applying reduced phase rule equation to curve AO = C – P + 1 = 2 – 2 + 1 = 1

We find it represents a univariant system. It is seen that along this curve the lead that is added goes into solution and silver separates out. The separation of silver continues till point O is reached.

At point O, the solution becomes saturated with respect to lead and no more lead dissolves into it, hence the freezing point of silver does not fall any further.

The eutectic point O at point O is fixed i.e. 97.4% Pb and 2.6% Ag. A fixed eutectic temperature (303°C) corresponds to this eutectic composition.

Metastable Triple Point Q.

This point can be reached when S_R is rapidly heated. At this point three metastable phases S_R, S_L and S_V are in equilibrium at a temperature of 114°C and 0.025 mm pressure of sulphur vapours. *It represents the melting point of* S_R *under metastable conditions.*

Since on changing any of the variable like temperature or pressure, one of the phase will disappear. Thus at this point, the system has no degree of freedom and is non-variant.

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

Thermal characteristics of phase diagram of sulphur system are summed up in Table 2.

(ii) Curve BO, the freezing point curve of lead

Point B represents the freezing point of solid lead (327°C). It is found that melting point of lead is gradually lowered by the addition of small amounts of silver. Along this curve, the silver which is added goes into solution while the separation of solid lead takes place. Therefore, along this curve, solid lead is in equilibrium with liquid solution of silver in lead of varying composition.

Applying reduced phase equation,

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

Thus, it is a *univariant system.*

(iii) Eutectic Point O

The curves AO and BO meet at point O which is called the **eutectic point.** At this point solid silver and solid lead exist in equilibrium with a the molten solution or melt. Hence there are three phases present at point O, therefore there is no degree of freedom at this point.

Applying reduced phase rule equation

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

Hence, the point O is a non-variant system. It represents the lowest possible temperature (303°C) below which liquid phase cannot exist. Below this point liquid phases cannot be enriched in any component by freezing out the other component. *Such a liquid mixture of two components (here Pb and Ag), which has the lowest freezing compared to all other liquid mixtures is a called the eutectic means easy melting. No mixture of lead and silver has a melting point lower than the eutectic temperature (303°C).*

At eutectic point the mixture freezes out completely at a constant temperature to form solid mixture having the same composition as in the liquid phase.

At this point the eutectic has fixed composition. At point O, an alloy composition 97.4% lead and 2.6% silver melts at 303°C.

It may be noted that *eutectic is not a chemical compound of lead and silver. It is a mixture of lead and silver and its composition depends on temperature.*

It the temperature is raised above the eutectic temperature, one of the phase will disappear. Whereas cooling below this temperature results in the simultaneous crystallisation of a mixture of silver and lead in the composition corresponding to point O.

(iv) Area AOC

In this region, solid Ag and liquid melt (Pb/Ag) exists. In this area two phases are present *i.e.* $P = 2$, $F = C - P + 1 = 2 - 2 + 1 = 1$, hence it is a *univariant* system. The composition of liquid melt at any point within this area can be obtained from the curve AO. At any point '*a*' in this area, solid Ag is in equilibrium with liquid melt (Pb/Ag). The composition of this melt at point '*a*' can be obtained by drawing a horizontal line *d a b* which passes through the points corresponding to different phases present in equilibrium with one another. This horizontal line is called tie line. At point *d*, almost pure Ag is present and at point *b* almost all the component is liquid melt (Pb/Ag). However the composition at point '*a*' is given by *lever rule* i.e.,

$$\frac{\text{Amount of silver}}{\text{Amount of melt}} = \frac{ad}{ab}$$

(v) Area BOD

In this region solid lead and liquid melt (Pb/Ag) exist. The composition of the liquid melt at any point within this area can be obtained as in case of area AOC.

In this area, two phases are present

i.e. $P = 2 \therefore F = C - P + 1 = 2 - 2 + 1 = 1$

Hence, this area represents a *univariant system.*

(vi) Area below line COD

In this area there are two phases, solid silver and solid lead are present $\therefore P = 2$

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

Hence this area represents *univariant system.*

In the region marked eutectic + solid Ag, there are silver crystals and solid eutectic crystals. While in the area marked eutectic + solid Pb, fine lead crystals are present alongwith eutectic crystals.

Application of lead-silver system Pattinson's Process (Desilverisation of lead)

Galena, an ore of lead is usually contaminated with 0.1 percent of silver. This lead is therefore called argentiferous lead. For separating silver from this alloy, the argentiferous lead is heated much above the melting point of lead so that the system consists of only the liquid phase represented by the point *x*, in the phase diagram (Fig. 11).

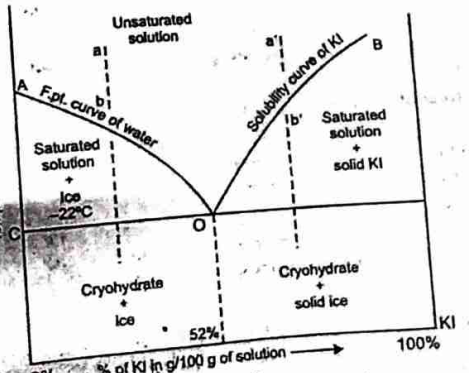


Fig. 11. Phase diagram for KI-H_2O system

The liquid solution at point *x* is cooled slowly, the temperature of liquid melt falls along the ... At soon as point *y* is reached, lead will start crystallising. As a result the residual ... becomes richer in silver. If cooling is continued, the system shifts along the curve ... with lead continuing to separate and is removed with the help of ladles. As cooling is ... the liquid solution continues to be richer in silver until at point O, the percentage of ... rises to about 2.5%. This process of removing silver is called desilverization of lead. This ... is employed in Pattinson's process for increasing the concentration of silver in the ... alloy.