

Catalyst

A catalyst is defined as a substance which alters the rate of a chemical reaction, itself remaining chemically unchanged at the end of the reaction. The process is called Catalysis.

- * A catalyst may increase or decrease the rate of reaction.
- ⇒ which increases rate of reaction is called Positive catalyst and process is called Positive catalysis or simply catalysis
- ⇒ A catalyst retards the rate of reaction is called negative catalyst and process is called negative catalysis.

Types of catalysis

There are two main types of catalysis

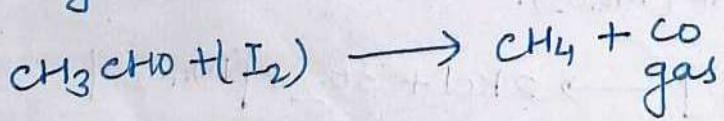
- (a) Homogeneous catalysis
- (b) Heterogeneous Catalysis
- (c) Enzyme catalysis

(a) Homogeneous catalysis:

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

Example of Homogeneous catalysis in Gas Phase

- (a) Decomposition of acetaldehyde CH_3CHO with iodine(I_2) catalyst



(b) Example of homogeneous catalysis in solution Phase:

Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst

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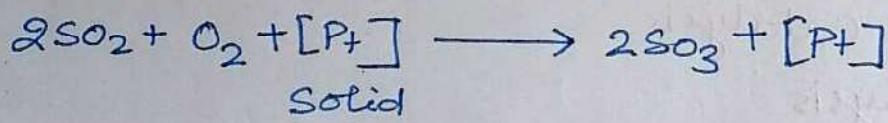


Heterogeneous catalysis

The catalysis in which the catalyst is in a different Physical Phase from the reactant is termed Heterogeneous catalysis. In this catalysis reactants are in the gas phase while the catalyst is a solid. This process is also called contact catalysis since the reaction occurs by contact of reactant with the catalyst surface.

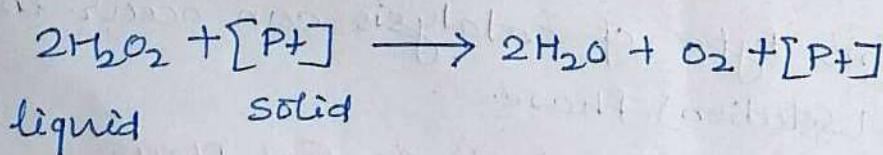
(1) Example of heterogeneous catalysis with gaseous reactant

Combination of sulphur dioxide (SO_2) and oxygen in the presence of finely divided platinum or vanadium pentoxide, V_2O_5



(2) Heterogeneous catalysis with liquid reactants

The decomposition of aqueous solution of hydrogen peroxide (H_2O_2) is catalyzed by manganese dioxide (MnO_2) or platinum in colloidal form



(3) Heterogeneous catalysis with solid reactants

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

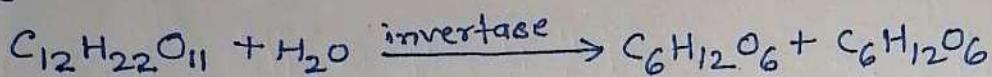


Enzyme Catalysis

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Enzymes are protein molecules which act as catalyst to speed up organic reactions in living cells. The catalysis brought about by enzymes is known as Enzyme catalysis or biocatalysis.

e.g.: Inversion of cane sugar ($C_{12}H_{22}O_{11}$) by Invertase present in yeast



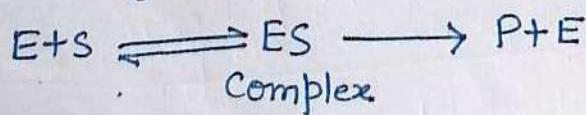
(b) conversion of glucose into ethanol by zymase present in yeast



Mechanism of Enzyme catalysis

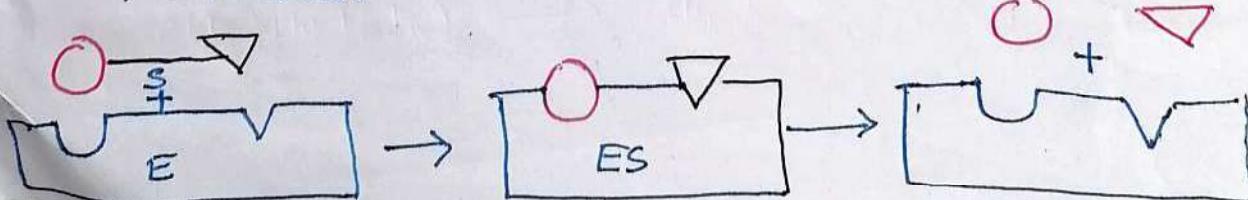
The long chains of the enzyme (protein) molecules are coiled on each other to make a rigid colloidal particle with cavities on its surface. These cavities which are of characteristic shape and abound in active groups (NH_2 , $COOH$, SH , OH) are termed Active centers. The molecules of substrate which have complementary shape, fit into these cavities just as key fits into lock (Lock-and-key theory). By virtue of the presence of active groups, the enzyme forms an activated complex with the substrate which at once decomposes to yield the product.

Michaelis and Menten proposed the following mechanism for enzyme catalysis



where E = enzyme, S = substrate (Reactant) ES = Activated complex

P = Product



Characteristics of Enzyme catalysis

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In general, enzymes behave like inorganic heterogeneous catalysts. However, they are unique in their efficiency and high degree of specificity. Some more important features of enzyme catalysis are listed below.

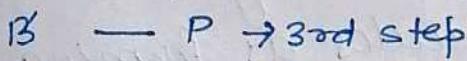
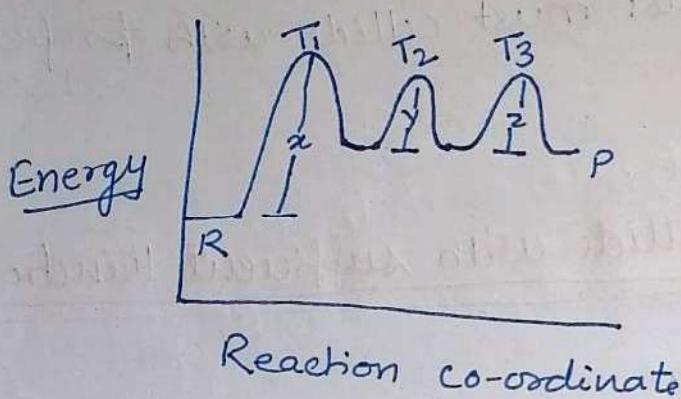
Enzyme

(i)

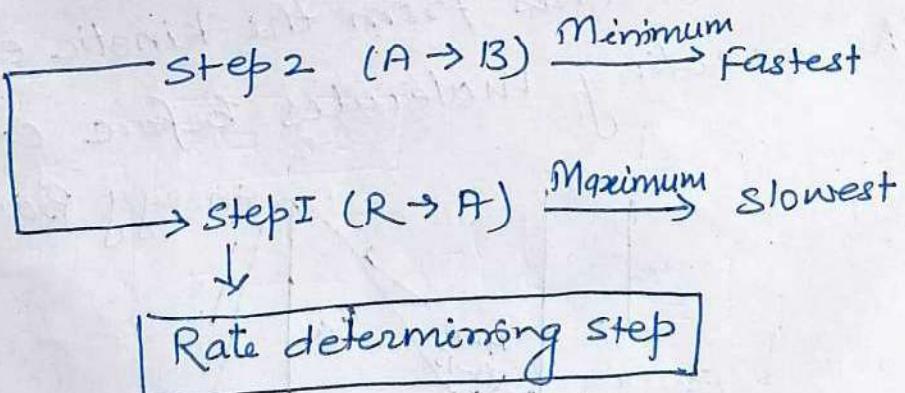
Complex reaction:

(5)

Complex reaction proceed in a series of steps instead of a single and rate all over reaction is in accordance with stoichiometric equation for that reaction or such reaction occur in several steps where each step is elementary. Which molecularity is not defined but molecularity of each step can be defined and it's rate depends on slowest step of the reaction



Activation energy



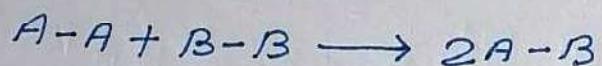
Theories of chemical kinetic

According to this theory a chemical reaction takes place only by collision between the reacting molecules. The two main conditions for a collision between the reacting molecules to be productive are:

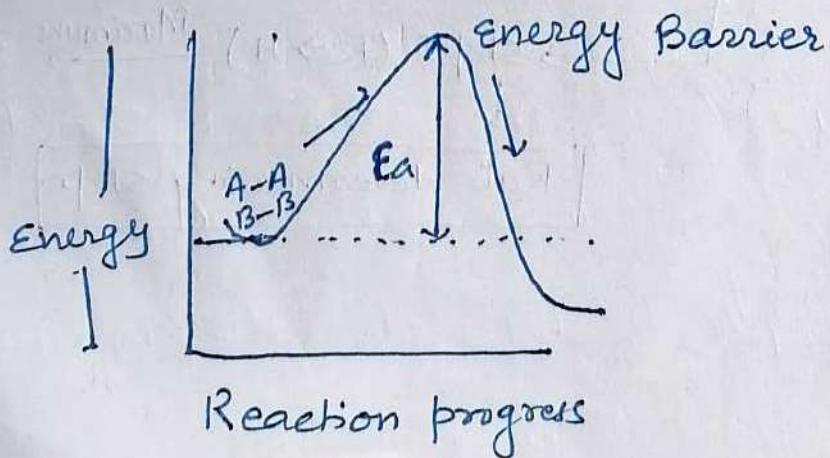
- (1) The colliding molecules must possess sufficient kinetic energy to cause a reaction
- (2) The reacting molecules must collide with proper orientation.

(1) The molecule must collide with sufficient kinetic energy

Let us consider a reaction



A chemical reaction occurs by breaking bonds between the atoms of the reacting molecules as forming new bonds in product molecules. The energy for the breaking of bonds comes from the kinetic energy possessed by the reacting molecules before collision.



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The figure shows the activation energy, E_a that is the minimum energy necessary to cause a reaction between the colliding molecules. Only the molecules colliding with kinetic energies greater than E_a are able to get over the barrier and react and whose kinetic energy less than E_a fail to surmount the barrier and this type of collisions are unproductive.

(2) The molecule must collide with correct orientation \Rightarrow

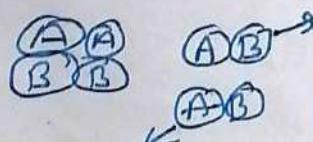
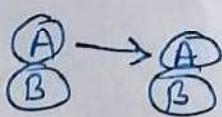
The reactant molecules must collide with favorable orientation. The correct orientation is that which ensure direct contact between the atoms involved in the breaking and forming of bond i.e. only the molecule colliding with kinetic energy greater than E_a (activation energy) and with correct orientation can cause reaction. Let's suppose



Then the reaction rate of elementary process is given by the expression

$$\text{rate} = f \times P \times z$$

f = fraction of molecule which possess sufficient energy to react, P = probable fraction of collision with effective orientations and z = collision frequency.



(1) Explain the Zeroth law of Thermodynamics! 19

Ans: The term zeroth law was coined by Ralph H. Fowler. The zeroth law of thermodynamics tells us the concept of temperature. The law states that if two bodies are each in thermal equilibrium with third one, then they are in thermal equilibrium with each other. Thermal equilibrium is a system whose macroscopic properties like pressure, temperature, volume etc are not changing in time.

2. What is Phase rule or Gibbs phase rule.

Ans: In 1875 Josiah Willard Gibbs published a general principle governing system in thermodynamic equilibrium called the Phase rule in a paper titled "On the Equilibrium of Heterogeneous substances".

It can mathematically represented as

$$P+F=C+2$$

where

P = The number of Phases of material

F = The number of degrees of freedom

C = The number of component of a system

2 = represents two variables (Pressure & temperature)

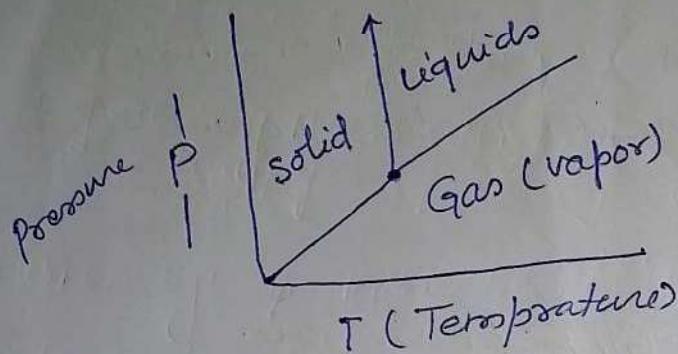
Phase: A region of material that is chemically uniform, physically distinct and mechanically separable.

component: Minimum number of independent species necessary to define the composition of all phases of the system.

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Degree of freedom:

The number of extensive variables that are independent of each other or in other words the number of thermodynamics variables which can be specified independently without changing the phase in equilibrium.



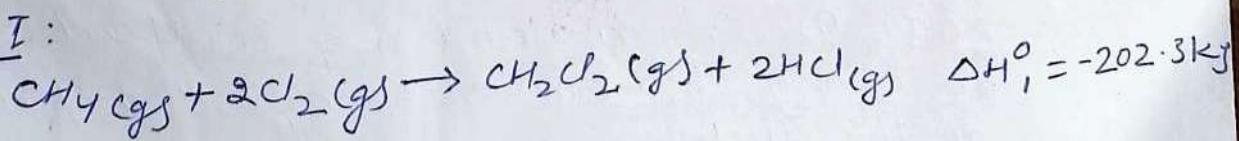
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③ Define Hess's law

Ans: Hess's law of heat summation states that for a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall equation is the sum of enthalpy changes for the individual steps. or in other words the change in enthalpy in a chemical reaction, at a constant pressure is not dependent on the process, and only dependent on the initial and final states of the chemical reaction. Hess's law can be seen as an application of the principle of conservation of energy.

e.g. consider the following two routes for preparation of methylene chloride (CH_2Cl_2) from the reaction between methane (CH_4) and chlorine (Cl_2)

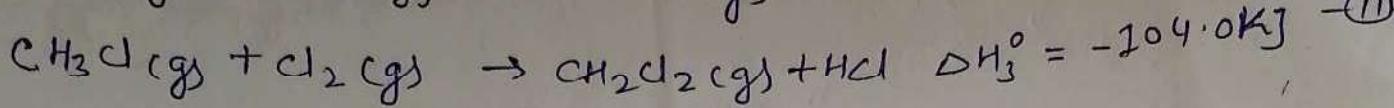
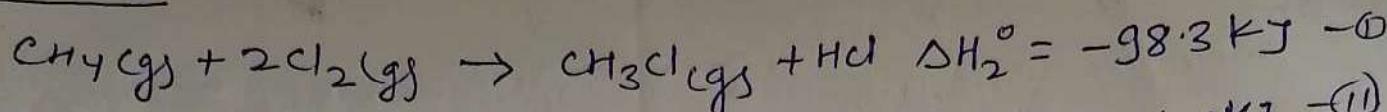
Route I:



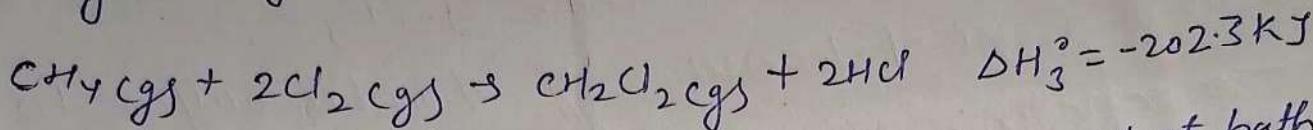
Route II

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(3)



Adding change in enthalpy of both step



Thus it can be clearly seen that no matter what path we follow, the total enthalpy change in the reaction is always the same

$$\Delta H_1^\circ = \Delta H_2^\circ + \Delta H_3^\circ = -202.3 \text{ kJ}$$

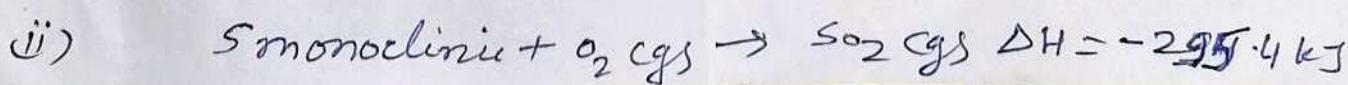
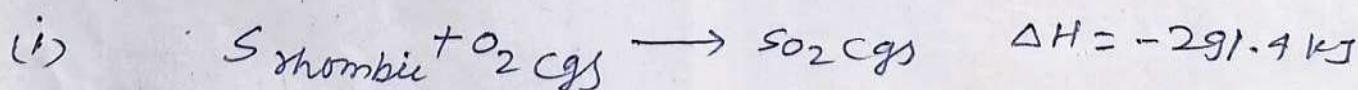
Application of Hess's law

- (1) Determination of heat of formation of substance which otherwise cannot be measured experimentally:

Substances like methane, ~~CO~~, CO, benzene etc cannot be prepared by uniting their elements. Therefore it is not possible to measure the heats of formation of such compounds directly. These can be determined indirectly by using Hess's law.

- (2) Determination of Heat Transition

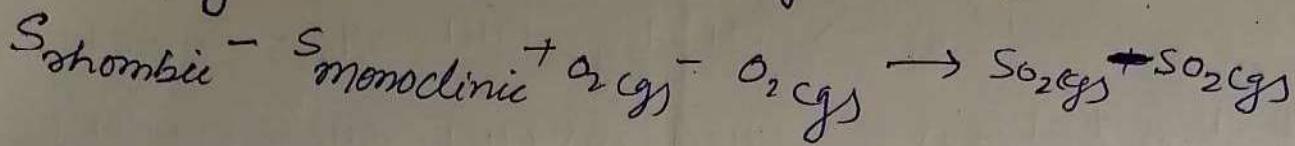
The heat of transition of one allotropic form to another can also be calculated ^{with} the help of Hess's law. For example the enthalpy of transition from monoclinic sulfur to rhombic sulfur can be calculated for their heats of combustion which are



Subtracting eq. ⑪ from (i) we get

(4)

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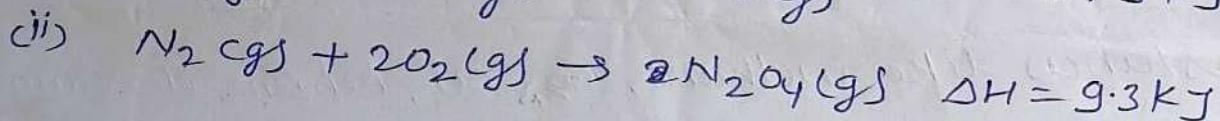
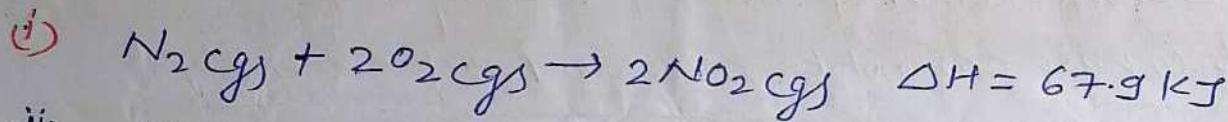
$$\Delta H = -291.4 - (-295.4)$$

$$\Delta H = 4.0 \text{ kJ}$$

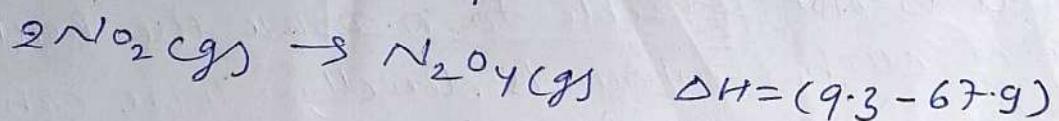
Thus heat of transition of shombe sulfur to monoclinic sulfur is 4.0 kJ

(3) Determination of heats of various reactions:

By using Hess's law we can calculate the heats or enthalpies of many reactions which otherwise cannot be measured directly. For example, from the following equations the enthalpy of dimerization of NO_2 can be calculated



Subtracting eq. i) from eq. ii) we have



$$= -58.6 \text{ kJ}$$

Thus the heat of dimerization of NO_2 is -58.6 kJ

Adsorption:

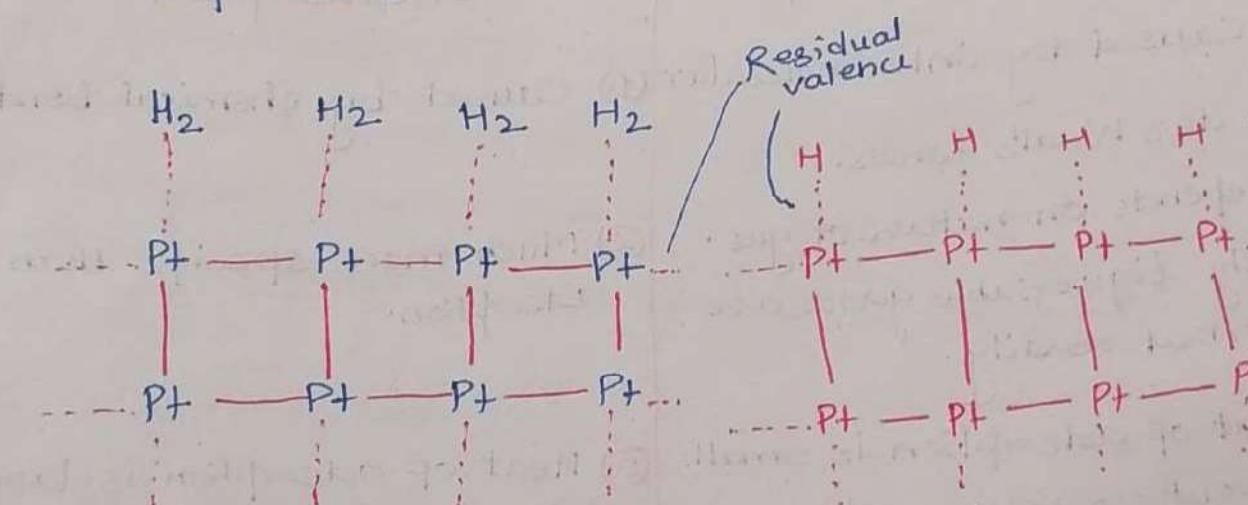
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The phenomenon of concentration of molecule of a gas or liquid at a solid surface is called adsorption.

The substance that deposits at the surface is called Adsorbate and the solid on whose surface the deposition occurs, is called the Adsorbent.

* Mechanism of Adsorption:

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



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

* Types of Adsorption

The adsorption of a gas onto solid surface is mainly of two types

- (a) Physical Adsorption: \Rightarrow This is due to the gas molecules being held to the solid surface by van der Waal's

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attractive forces. g_t is also referred to as van der Waal's Adsorption.
e.g. adsorption of hydrogen or oxygen on charcoal is Physical Adsorption.

④ Chemical Adsorption or Chemisorption:

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In this kind of adsorption, the gas molecules or atoms are held to the solid surface by chemical bonds. These bond may be covalent or ionic in nature.

e.g. hydrogen is chemisorbed on nickel.

Comparison of Physical adsorption and chemisorption

Physical adsorption

Chemisorption

- | | |
|---|--|
| (1) Caused by intermolecular Van der Waal's forces. | (1) Caused by chemical bond formation. |
| (2) Depends on nature of gas. Easily liquefiable gases are adsorbed readily. | (2) Much more specific than physical adsorption. |
| (3) Heat of adsorption is small (about $20.93 \text{ kJ mol}^{-1}$) | (3) Heat of adsorption is large ($83.74 - 418.68 \text{ kJ mol}^{-1}$) |
| (4) g_t is reversible | (4) g_t is irreversible |
| (5) Occurs rapidly at low temperature; decreases with increasing temperature. | (5) Increases with increase of temperature. |
| (6) Increase of pressure increases adsorption; decrease of pressure causes desorption | 6. Change of pressure has no such effect |
| (7) Forms multimolecular layers on adsorbent surface | (7) Forms unimolecular layer |

Factors affecting the extent of gas-solid adsorption

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The extent to which adsorption will happen on a solid surface depends on following factors.

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(1) Nature of adsorbent: ⇒

The adsorption of the gas depends

on the nature of the adsorbent. A gas can be adsorbed on different adsorbent surfaces in different amounts. e.g

Hydrogen is weakly adsorbed on the alumina surface whereas it is strongly adsorbed on the nickel surface under certain conditions.

(2) Surface Area: Adsorption being a surface phenomenon,

the extent of adsorption depends on the surface area.

Increase in the surface area of the adsorbent, increases the total amount of gas adsorbed. So finely divided solids and some porous substances are good adsorbents.

(3) Nature of the gas:

In general, if a gas is more liquefiable it will be more easily absorbed. For example like NH_3 , HCl , Cl_2 , CO_2 which can be liquefied easily are more readily adsorbed on the solids surface, rather than permanent gases like O_2 , H_2 etc

(4) Heats of Adsorption:

Heat of adsorption is defined as the energy liberated

when 1 gm mole of a gas is adsorbed on the solid surface. In physical adsorption, gas molecules concentrate on the solid surface. Thus it is similar to the condensation of a gas to liquid. Therefore, adsorption like condensation is an exothermic process. When the temperature increases the kinetic energy of the gas molecules also increases which results in more number of collisions between the molecules.

and the gas.

(5) Effect of Pressure:

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on the solid surface, there is a fixed number of adsorption sites where gas molecules can be adsorbed. Initially when the pressure has increased the rate of adsorption increases due to an increase in the gas molecules striking on the surface. Thus, an increase in the pressure increases the rate of adsorption linearly. But after sometime, it will reach a point when the pressure has no effect on the rate of adsorption as the number of adsorption sites is fixed and no more adsorption can happen in those sites. Hence, at that point, the extent of adsorption will be independent of the pressure.

(6) Effect of temperature:

Physical adsorption occurs rapidly at low temperature ~~at~~ and chemisorption like most chemical changes, generally with temperature. Thus a rise of temperature can often cause physical adsorption to change to chemisorption. Nitrogen for example is physically adsorbed on iron at 463 K but chemisorbed to form a nitride at 773 K.

ADSORPTION ISOTHERMS

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An adsorption isotherm is a graph that represents the variation in the amount of adsorbate (x) adsorbed on the surface of the adsorbent with the change in pressure at a constant temperature.

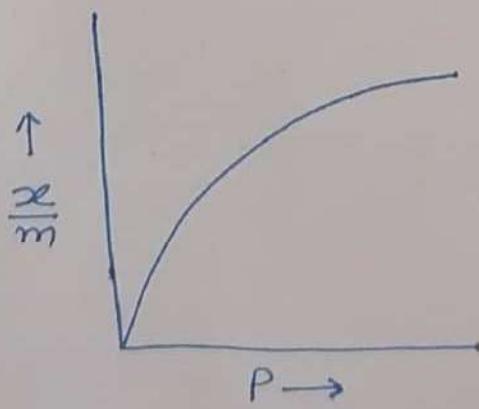
Freundlich Adsorption Isotherm

In 1909, German scientist Freundlich provided an empirical relationship between the amount of gas adsorbed by a unit mass of solid adsorbent and pressure at a particular temperature. It is expressed using the following equation

$$\frac{x}{m} = k \cdot P^{1/n} \quad (n > 1)$$

where ' x ' is the mass of the gas adsorbed on mass ' m ' of the adsorbent at pressure ' P '. ' k ' and ' n ' are constants that depend on the nature of the adsorbent and the gas at particular temperature.

The mass of the gas adsorbed per gram of the adsorbent is plotted against pressure in the form of a curve to show the relationship. Here, at a fixed pressure, physical adsorption decreases with increase in temperature. The curve reaches saturation at high pressure.



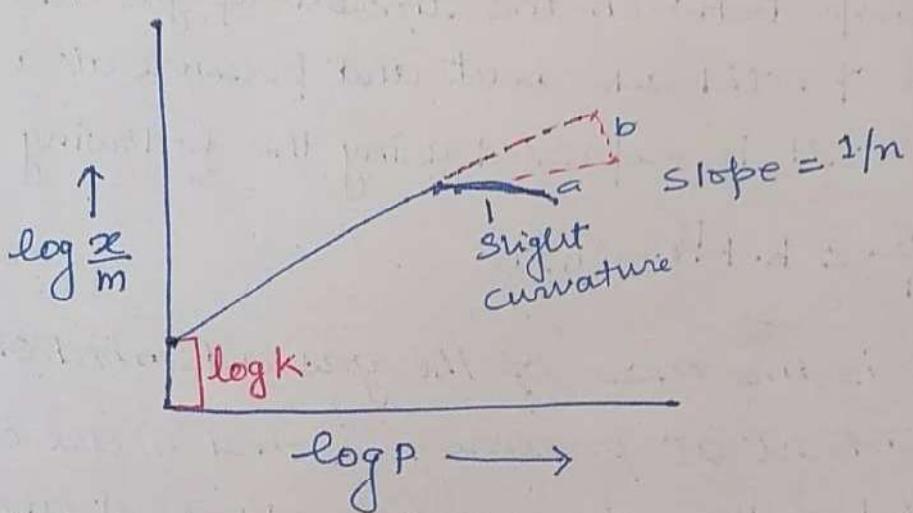
- Freundlich isotherm: a plot of mass of adsorbed gas per unit mass of adsorbent

Now if we take the log of the above equation

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log P$$

To test the validity of Freundlich isotherm, we can plot $\log \frac{x}{m}$ on the y-axis and $\log P$ on the x-axis.

If the plot shows a straight line, then the Freundlich isotherm is valid, otherwise it is not. The slope of the straight line gives the value of $1/n$, while the intercept on the y-axis gives the value of $\log K$.



It is actually found that the plots were straight lines at low pressure, while at higher pressure they showed a slight curvature, especially at low temperature. This indicated that Freundlich equation is approximate and does not apply to adsorption of gases by solid at higher pressure.

LANGMUIR ADSORPTION ISOTHERM

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In 1916 Langmuir derived a simple adsorption isotherm based on theoretical consideration. It was named after him.

Assumption:

Langmuir made the following assumptions.

- (1) The layer of the gas adsorbed on the solid adsorbent is one-molecule thick.
- (2) The adsorbed layer is uniform all over the adsorbent.
- (3) There is no interaction between the adjacent adsorbed molecule.

Derivation of Langmuir Isotherm:

Langmuir considered that the gas molecules strike a solid surface and are thus adsorbed. Some of these molecules then evaporate are 'desorbed' rapidly. A dynamic equilibrium is eventually established between the two opposing processes, adsorption and desorption.

If Θ is the fraction of total surface covered by the adsorbed molecules, the fraction of the naked area is $(1-\Theta)$. The rate of desorption (R_d) is proportional to the covered surface Θ . Therefore

$$R_d = k_d \Theta$$

where k_d is the rate constant for the desorption process. The rate of adsorption (R_a) is proportional to the available naked $(1-\Theta)$ and the pressure (P) of the gas.

$$R_a = k_a (1-\Theta) P$$

where k_a is rate constant for the adsorption process.

(3)

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

$$K_d \Theta = K_a (1-\Theta) P$$

$$\Theta = \frac{K_a P}{K_d + K_a P}$$

or

$$\Theta = \frac{(K_a/K_d)P}{1+(K_a/K_d)P}$$

$$\Theta = \frac{KP}{1+KP}$$

Where K is the equilibrium constant and is referred to as the adsorption coefficient.

The amount of the gas adsorbed per gram of the adsorbent α is proportional to Θ

Hence

$$\alpha \propto \frac{KP}{1+KP}$$

$$\alpha = K' \frac{KP}{1+KP}$$

$$\alpha = K' \frac{KP}{1+KP} \quad \dots \dots \dots \quad (1)$$

where ' K' ' is a new constant. Equation(1) gives the relation between the amount of gas adsorbed to the pressure of the gas at constant temperature and is known as Langmuir Adsorption isotherm.

In order to test the Langmuir isotherm, equation (1) is rearranged so that

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

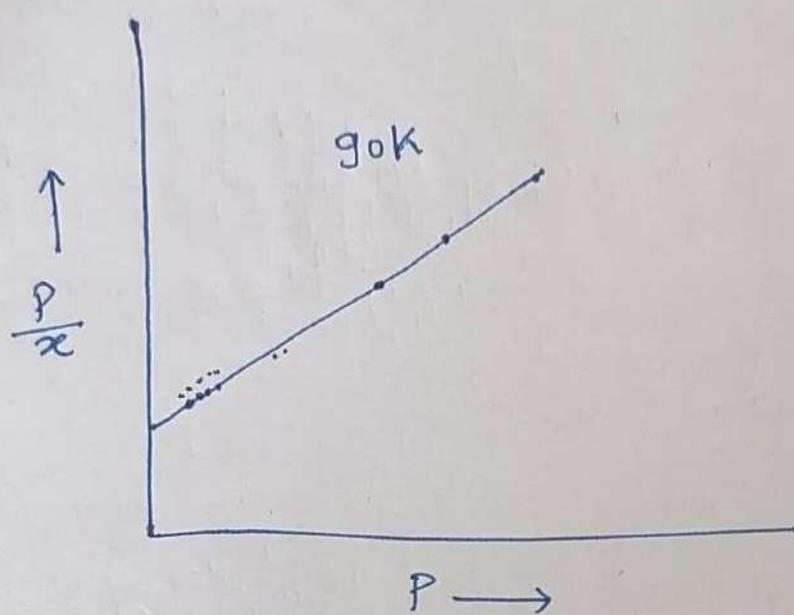
→ (2)

where K'' constant = K'/K

The equation (2) is similar to an equation for a straight line. Thus if P/α is plotted against P , we should get a straight line with slope $1/K''$ and intercept $1/K'$. It was found in

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most cases that the actual curves were straight line.
Thus Langmuir isotherm stand verified.



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

Langmuir isotherm holds at low pressures but fails at high pressures.

As stated above, Langmuir Adsorption isotherm may be written as

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

if pressure is very low then the factor P/K'' may be ignored.

$$x = K'P$$

if the pressure is very high $1/K'$ may be ignored.

$$x = K''$$

Hence at low pressure the amount of gas adsorbed (x) is directly proportional to pressure. At high pressure the mass adsorbed reaches a constant value K'' when the adsorbent surface is completely covered with a unimolecular layer of the gas. At this stage adsorption is independent of pressure.

Gibbs Free energy:

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The Gibbs free energy of a system at any moment in time is defined as the enthalpy of the system minus the product of the temperature times the entropy of the system

$$G = H - TS$$

G = Gibbs free energy (kJ mol^{-1})

H = heat of combustion, enthalpy (kJ mol^{-1})

T = Temperature (kelvin)

S = entropy ($\text{J}^\circ \text{K}^{-1}$)

The change in the Gibbs free energy of the system that occurs during a reaction is therefore equal to the change in the enthalpy of the system minus the change in the product of the temperature times the entropy of the system

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

If the reaction is run at constant temperature, this equation can written as follows

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

If ΔG is less than 0 ($\Delta G < 0$) for any reaction, reaction will be favorable or spontaneous and if $\Delta G > 0$ reaction will be unfavorable or non-spontaneous.

Spontaneous chemical reactions:

A spontaneous reaction is a reaction that favors the formation of products at the conditions under which the reaction is occurring. The entropy of the system increases during a combustion reaction. The combination of energy decreases and entropy increases dictates that combustion reactions are spontaneous reactions.

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In other words entropy can be defined as for a ~~reversible~~ reversible change taking place at a fixed temperature (T), the change in entropy (ΔS) is equal to heat energy absorbed or evolved divided by the temperature T . That is

$$\boxed{\Delta S = \frac{q}{T}}$$

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If heat is absorbed, then ΔS is positive and there will be increase in entropy. If heat is evolved ΔS is negative and there is a decrease in entropy. The unit of entropy is calories per degree per mole i.e. $\text{cal mol}^{-1} \text{K}^{-1}$ and in SI unit it is Joules per mole per degree i.e. $\text{J mol}^{-1} \text{K}^{-1}$.

Enthalpy

The total heat content of a system at constant pressure is equivalent to the internal energy E plus the PV energy. This is called enthalpy of the system and is represented by the symbol H .

$$H = E + PV \quad \text{where } E = \text{internal energy}$$

P = Pressure

V = Volume

If ΔH be the difference of enthalpy of a system in final state (H_2) and in the initial state (H_1).

$$\Delta H = H_2 - H_1$$

$$\Delta H = (E_2 + P_2 V_2) - (E_1 + P_1 V_1)$$

$$\Delta H = (E_2 - E_1) + (P_2 V_2 - P_1 V_1)$$

$\Delta H = \Delta E + \Delta PV$ if P is constant while gas is expanding

$$\boxed{\Delta H = \Delta E + P\Delta V}$$

Ideal Gas Law : - The ideal gas law is the equation of state of a hypothetical ideal gas. It is a good approximation of the behaviour of many gases under many conditions, although it has several limitations.

Boyle's Law :- states that for a given mass of gas held at a constant temperature the gas pressure is inversely proportional to the gas volume.

Charles Law :- states that for a given fixed mass of gas held at a constant pressure the gas volume is directly proportional to the gas temperature.

Ideal Gas Law :- The ideal gas law states that the product of the pressure and the volume of one gram molecule of an ideal gas is equal to the product of the absolute temperature of the gas and the universal gas constant. $PV=nRT$ where,

P is the pressure.

V is the volume.

n is the amount of substance.

R is the ideal gas constant.

Derivation of the Ideal Gas Law :-

The ideal gas law is derived from the observational work of Robert Boyle, Gay-Lussac and Amedeo Avogadro. Combining their observations into a single expression, we arrive at the Ideal gas equation, which describes all the relationships simultaneously.

The three individual expressions are as follows:

Boyle's Law

$$V \propto \frac{1}{P}$$

Charles's Law

$$V \propto T$$

Avagadro's Law

$$V \propto n$$

Combining these three expressions, we get

$$V = \frac{RnT}{P} = \frac{nRT}{P}$$

The above equation shows that volume is proportional to the number of moles and the temperature while inversely proportional to the pressure.

This expression can be rewritten as follows:

Multiplying both sides of the equation by P to clear off the fraction, we get

$$PV = nRT$$

The above equation is known as the ideal gas equation.

Properties of ideal gases :-

- An ideal gas can not be liquefied because the gaseous molecule has no intermolecular attraction.
- The coefficient of thermal expansion(α) depends on the temperature of the gases and does not depend on nature.
- The coefficient of compressibility(β) similarly depends on the pressure and will be the same for all gases.

- When pressure is plotted against volume at a constant temperature a rectangular hyperbola curve is obtained according to Boyle's law.
- When PV is plotted against pressure at a constant temperature a straight line parallel plot is obtained.
- If the ideal gas passes through a porous plug from higher pressure to lower pressure within the insulated enclosure, there will be no change in the specific heat or temperature. This confirms that the ideal gases have no intermolecular attraction.

Properties of real gases :-

- Real gas could be liquefied because the gaseous molecule has the property of intermolecular attraction which helps to coalesce the molecule .
- The coefficient of thermal expansion (α) depends on the nature of the gaseous molecule .
- The coefficient of compressibility (P) was also found to depend on the nature of the gases .
- When pressure is plotted against volume a rectangular hyperbola curve is obtained only at a high temperature above the critical temperature.
- But a temperature below the critical temperature (T_c), the molecule can be liquefied after certain pressure depends on temperature. Liquid and gas can be indistinguishable properties in the critical point of the gases. When PV is plotted against pressure for real or Van der Waals gases, the Amagat curve is obtained.
- Real gases pass through porous plugs from higher pressure to lower pressure within the insulated enclosure, there occurs a change of temperature.
- Real gases have intermolecular attraction and when expanded, the molecules have to spend more kinetic energy to overcome intermolecular attraction. Therefore, the temperature drops down.

What is Critical Pressure ?

The critical pressure of a substance is the pressure that must be applied in order to liquefy that substance at its critical temperature. For example, 217.7 atmospheres of pressure must be applied to water in order to liquefy it at its critical temperature (which is 647.09 Kelvin).

Define Critical Temperature ?

Critical temperature (of a substance) can be defined as the highest possible temperature value at which the substance can exist as a liquid. At temperatures

above the critical temperature of a given gaseous substance, it can no longer be liquified, regardless of the amount pressure applied to it.

Consequences of the Absorption of Light :-

- Light is a form of energy. According to the principle of photochemical activation , only that part of the light which is absorbed by any system can cause photochemical change or reaction. However, it is not essential that every time, the energy which is absorbed by any system can bring about a photochemical reaction. Absorption of light means absorption of radiation energy. Absorption of radiation energy by a substance may lead to the following changes:
- **Thermal Change** :- The kinetic energy of the molecules may be increased giving rise to an increase in temperature. i.e., heat will be generated.
- **Excitation** : The internal energy of the molecules or atoms may be raised. This will result in elevating the electrons to higher energy levels. In spectroscopic terminology, it is assumed that the atoms or molecules are raised from the ground state energy levels to the excited state energy levels.
- **Dissociation** : The molecule breaks down to form smaller molecules, atoms or free radicals. Excitation and dissociation may occur simultaneously.
- **Emission** : Part of the absorbed radiation may be re-emitted giving rise to fluorescence or phosphorescence.
- The first of the four processes are not important when visible and ultraviolet light are considered. When the light of shorter wavelengths is used, in addition to the above processes ionisation and physical interaction of the photons and matter become also prominent.

Debye law of the strong electrolyte :- Debye-Hilckel limiting law that depicts the behaviour of strong electrolytes. The non-ideal behaviour of strong electrolytes, his mathematical treatment considers that each ion is encompassed by an ionic cloud of oppositely charged ions, which retards the motion of ions in the medium. The theory provides a method for calculation of activity coefficients, understanding of diffusion in ionic media, change in the rate of ionic reactions upon addition of salts, and biochemical reactions.

Debye Huckel Law :- In the year 1926, Debye and Huckel modified the theory and Onsager modified it further but all the postulates and original theory were retained. It was assumed that the electric field causes the distortion of the charge cloud from the spherical symmetry. After taking this into account, together with some specific requirements of moving ions like viscosity and electrophoretic effects. Onsager helped to derive a theoretical expression to give an empirical relation that is called kohlrausch's law for the molar conductivity λ_m .

$$\lambda_m = \lambda^\circ m - Kc\sqrt{v}$$

$\lambda^\circ m$ is the limiting molar conductivity, K is an empirical constant and c is the electrolyte concentration. The limit of the infinite dilution means limiting. Onsager express it through-

$$\lambda_m = \lambda^\circ m - (A + B\lambda^\circ m)c\sqrt{v}$$

Here, A and B are constants that are dependent only on known quantities like temperature, charges on the ions, and the dielectric constant and viscosity of the solvent. This is known as the Debye-Huckel-Onsager equation.

Kinetic Theory of Gases Postulates :-

The kinetic theory of gas postulates is useful in the understanding of the macroscopic properties from the microscopic properties.

- Gases consist of a large number of tiny particles (atoms and molecules). These particles are extremely small compared to the distance between the particles. The size of the individual particle is considered negligible and most of the volume occupied by the gas is empty space.
- These molecules are in constant random motion which results in colliding with each other and with the walls of the container. As the gas molecules collide with the walls of a container, the molecules impart some momentum to the walls. Basically, this results in the production of a force that can be measured. So, if we divide this force by the area it is defined to be the pressure.
- The collisions between the molecules and the walls are perfectly elastic. That means when the molecules collide they do not lose kinetic energy. Molecules never slow down and will stay at the same speed.
- The average kinetic energy of the gas particles changes with temperature i.e the higher the temperature, the higher the average kinetic energy of the gas.
- The molecules do not exert any force of attraction or repulsion on one another except during collisions.

Deviation of real gases from ideal behaviour :-

All the gas molecules obey the ideal gas laws only under special conditions of low pressures and high temperatures. The deviations of the real gases, from the ideal gas behaviour, is traced mainly to wrong or incorrect assumptions in the postulates.

They are,

- The particles are point charges and have no volume: Then, it should be possible to compress the gases to zero volume. But, gases cannot be compressed to zero volume indicates that particles do have volume though small and cannot be neglected.
- Particles are independent and do not interact: Particles do interact depending upon their nature. The interactions affect the pressure of the gas. Volume and the interactions differ from gas to gas. Many gas laws have been developed for the real gases incorporating correction factors in the pressure and volume of the gases.

What is Van der Waals equation ?

Van der 'N aals eq nation is given by modifying ideal gas law in 1873. He put the reasons for the deviations of the real gases from ideal behaviour. Van der Waals proposed that the two postulates used in the kinetic theory of gas molecules are not applicable to real gases. These two assumptions are

- The gas molecules are point masses or practically they have no volumes.
- There is no intermolecular attraction in the gas molecules.
- Van der Waals introduced the size effect and the intermolecular attraction effect of the real gases. These two effects or factors in the Van der Waals equation are arising because he considered the size and intermolecular attraction among the gas molecules.

Equation :-

Van der Waals equation is an equation relating the relationship between the pressure, volume, temperature, and amount of real gases. For a real gas containing 'n' moles, the equation is written as;

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

Where, P, V, T, n are the pressure, volume, temperature and moles of the gas. 'a' and 'b' constants specific to each gas. The equation can further be written as;

1. Cube power of volume:

$$V^3 - \left(b + \frac{RT}{P} \right) V^2 + \frac{a}{P} V - \frac{ab}{P} = 0$$

2. Reduced equation (Law of corresponding states) in terms of critical constants:

$$\left(\pi + \frac{3}{\varphi^3} \right) (3\varphi - 1) = 8\tau : \text{ where } \pi = \frac{P}{P_c}, \varphi = \frac{V}{V_c} \text{ and } \tau = \frac{T}{T_c}$$

Solution

- Solution is a homogeneous mixture of two or more substance in same or different physical phases. The substances forming solution are called component of solution i.e. solute and solvent. Solvent is the component which is present in large quantity while the other component is known as solute.
- If H_2O is used as a solvent the solution is called aqueous soln. and if not solution is called non-aqueous solution. Depending upon the amount of solute dissolved in it solvent we have the following types of solution.

(1) Unsaturated solution:-

A solution in which more solute can be dissolved without raising temperature is called an unsaturated solution.

(2) Saturated solution:-

A solution in which no solute can be dissolved further at a given temperature is called a saturated solution.

(3) Super-saturated solution:-

A solution which contains more solute than that would be necessary to saturate it at a given temperature is called super-saturated solution.

* Methods of expressing concentration of solution

(1) % / weight :-

It is defined as the amount of solute present in 100g of solution.

(2) \Rightarrow

$$\boxed{W/W \% = \frac{\text{wt. of solute}}{\text{wt. of solvent}} \times 100}$$

(2) % / volume :-

It is defined as the volume of solute in ml present in 100ml solution

*

$$\boxed{V/V \% = \frac{\text{volume of solute}}{\text{vol. of solution}} \times 100}$$

(3) % mass / volume :-

It is defined as the mass of solute in 100ml of solution.

*

$$\boxed{\% w/v = \frac{\text{mass of solute}}{\text{vol. of solution}} \times 100}$$

(4) Strength or Concentration (g/l) :-

\rightarrow It is defined as the amount of the solute in gram present in one liter of solution.

*

$$\boxed{\text{conc of solution} = \frac{\text{solute in gram}}{\text{vol. of soln in liters}}}$$

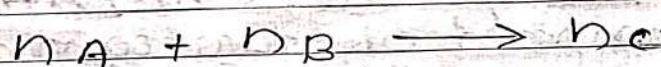
⑤ Parts per million (ppm) :-

When the solute is present in trace quantity quantities it is convenient to express the concentration in parts per million. It is defined as the quantity of solute in gram present in 10^6 gram of the soln.

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$

Mole fraction:-

It is defined as the ratio of the no. of moles of a component to the total no. of moles of the component.



$$X_A = \frac{n_A}{n_A + n_B}$$

$$X_B = \frac{n_B}{n_A + n_B}$$

~~H₂O 100
Monomer~~

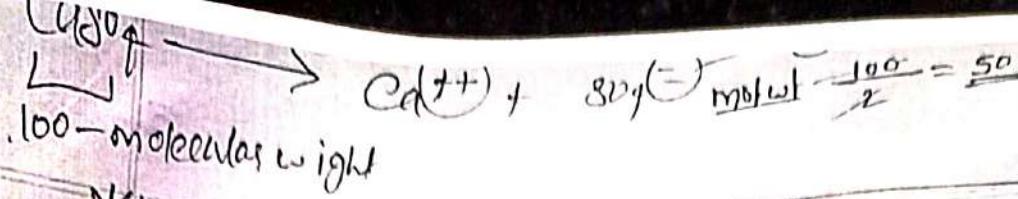
Molarity:-

It is defined as the no. of moles of the solute present in 1 kg of solvent it is denoted by "m".

$$\text{Molarity} = \frac{\text{no. of moles of solute}}{\text{wt (kg) of solution}}$$

Molality:-

It is defined as the no. of moles of the solute present in 1 litre of solvent it is denoted by "M".



* **Molarity** = $\frac{\text{no. of moles of solute}}{\text{volume of solution in litres}}$

* **Normality**:-

It is defined as no. of gram equivalent of solute per litre of solution. It is denoted by "N".

* **Normality** = $\frac{\text{no. of gram equivalent}}{\text{no. of volume of solution}}$

* **Ideal Solution**:-

An ideal solution is one in which the molecule attract one another with equal force irrespective to their nature thus a solution composed of two components A and B will be an ideal (1) if the forces b/w A & A, B & B should be same.

→ An ideal solution passes the following characteristics

(1) * Volume change of mixing should be zero (0).

$$|\Delta V_{\text{mix}} = 0|$$

(2) * Heat change on mixing should be zero (0).

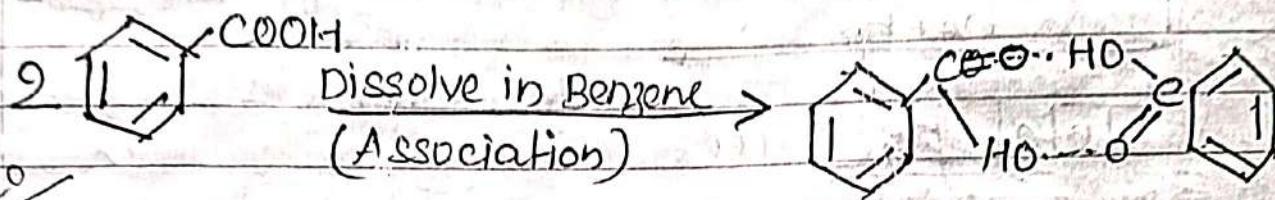
$$|\Delta H_{\text{mix}} = 0|$$

(3) * There should be no chemical rxn b/w solvent

and solute.

(4) Solute molecules should not dissociate in the ideal solution.

(5) Solute molecules should not associate in ideal solution.



Ideal solution must obey Raoult's Law at all concentrations. The following are some of the binary mixtures which show the properties of ideal solution.

(A) Benzene & Toluene

(B) Carbon tetrachloride & Chloro tetrachloride

Raoult's law :-

According to this law, the partial pressure of any volatile constituents of a solution at a constant temperature is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in ~~this~~ this solution.

→ Let a mixture (solution) be prepared by mixing n_A mole of liquid A and n_B mole of liquid B. Let P_A and P_B be the partial pressure of two constituents A & B. In solution and $P^{\circ}A$ and $P^{\circ}B$ the vapour pressure in pure state respectively.

Thus according to Raoult's law

$$P_A = \frac{n_A}{n_A + n_B} P^{\circ}_A \quad \left[= \text{mole fraction of A} \times P^{\circ}_A = X_A P^{\circ}_A \right]$$

$$P_B = \frac{n_B}{n_A + n_B} P^{\circ}_B \quad \left[\text{mole fraction of B} \times P^{\circ}_B = X_B P^{\circ}_B \right]$$

Total pressure

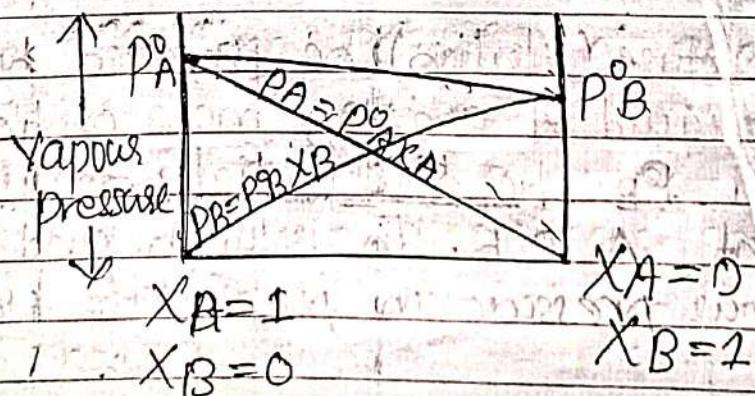
$$P = P_A + P_B$$

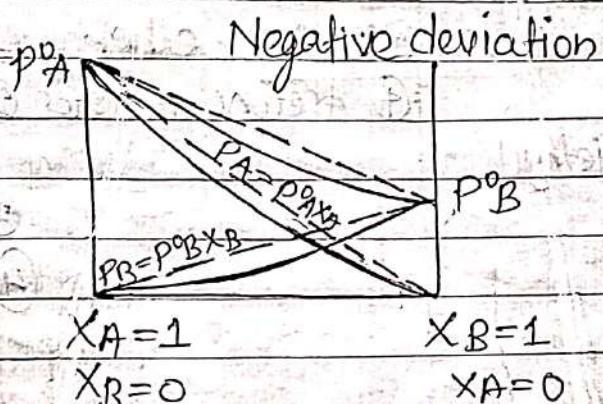
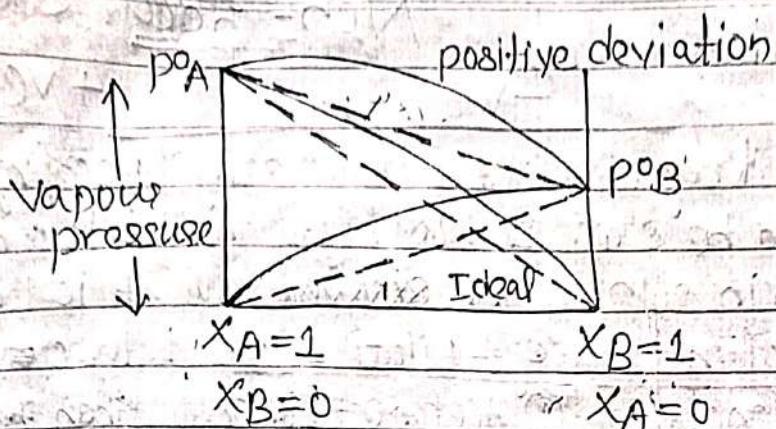
$$P = X_A P^{\circ}_A + X_B P^{\circ}_B$$

→ This law in fact is the major deciding factor whether a solution will be ideal or non-ideal. Ideal solution obey Raoult's law at every range of concentration. Non-ideal solution don't obey Raoult's law, they show either +ve or -ve deviation from Raoult's law.

Ideal or Non-Ideal Solution:-

Ideal deviation:-





Ideal solution - $\Delta H_{mix} = 0$

Non-ideal solution - $\nabla \neq 0$

(i) Obey Raoult's law every range of concentration

Don't obey Raoult's law.

Don't obey Raoult's law.

(ii) $\Delta H_{mix} = 0$ either heat is evolved or released

$\Delta H_{mix} > 0$, Endothermic, dissociation heat is absorbed

$\Delta H_{mix} < 0$, Exothermic dissociation heat is released.

(iii) $\Delta V_{mix} = 0$ total volume of soln is equal to sum of value of the component.

$\Delta V_{mix} > 0$ volume increases after dissolution.

$\Delta V_{mix} < 0$ volume decreases after dissolution.

(iv) $P = P_A + P_B = P_A^0 X_A + P_B^0 X_B$ i.e. $P_A = P_A^0 X_A - P_B = P_B^0 X_B$

$P_A > P_A^0 X_A$
 $P_B > P_B^0 X_B$
 $P_A + P_B > P_A^0 X_A + P_B^0 X_B$

$P_A < P_A^0 X_A$, $P_B < P_B^0 X_B$
 $P_A + P_B < P_A^0 X_A + P_B^0 X_B$

(v) A-A, A-B, B-B attractive forces of interaction should be same that is A & B are identical and same size and character.

A, B attractive force AB attractive force should be weaker than A-B, B-B attractive force A & B have different size, shape & character.

A-A, B-B attractive force A & B have different size, shape and character.

Ideal solution

Non-Ideal solution

-ve

+ve

- (vi) Escaping tendency of A and B should be same in pure liq. and in solns.
e.g.- Dilute solns.

- ① Benzene + Toluene
- ② N-hexane + N-heptane
- ③ Chlorobenzene + Bromobenzene
- ④ Ethyl bromide + ethyl iodide

A & B escape easily showing higher than the expected value
e.g.- Dilute solns.

- ① Acetone + Ethanol
- ② water + Methanol
- ③ water + ethanol
- ④ Acetone + water

Escaping tendency both components A & B is lowered than lower evap. pres.

- than the expected value
- e.g.-
- ① Acetone + Aniline
- ② Acetone + Chloroform
- ③ water + HCl
- ④ Acetic acid + pyridine.

* Solution of gases in liquid:-

→ The solubility of gas in a liquid represent the concentration of dissolved gas in a liquid when it is in equilibrium with some of the pure gas about this solution.

Eg:- Pharmaceutical aerosols containing hydrogen also be considered as solution of the gases in liquid.

* Factors affecting solubility of gases in liquid:-

→ This solubility of gas in a solvent depend on temperature, pressure, presence of salts and chemical reaction. If any between the gas and the solvent.

Effect of Pressure:

The pressure of the gas above the solution, since this significant changes this these significant changes the solubility of the dissolved gas. The effect of pressure on the solubility of the gas is given by Henry's law which states that in a dilute solution the mass of the gas which dissolves in a given volume of a liquid at a constant temperature is directly proportional to the partial pressure of the gas.

A/C to Henry's law

$$C \propto P$$

$$C = kP$$

\approx low

- C is the conc of dissolved gas in grams per liter of solvent.
- P is partial pressure in mm of Hg of the undissolved gas above the solution can be obtained by subtracting the vapour pressure of the solvent from the total pressure.
- C is the proportionality constant and is referred to as the solubility coefficient.

(1) The solubility of gases generally increases with increase pressure and on the release on the pressure a solubility decrease and the gases escape.

(2) Effect of Temperature:-

Solubility of most gases decreases with a rise in temperature because of

The greater tendency of the gases to expand is comprison to the solvent. It is therefore essential that caution must be exercised when opening the containers containing gaseous soln under elevated temperature. It is better to reduce the temperature by immersing an ice coated water before opening such containers.

③ Effect of electrolytes and non-electrolytes:-

→ Solubility of gases in a solvent is generally reduced by the addition of electrolytes such as sugars. This is referred as salting out. This is due to more affinity between the solvent and the electrolyte or non-electrolyte than between the solvent and the gas.

④ Effect of chemical rxns:-

→ Henry's law generally applies to gases that are only slightly soluble in solvent and then don't react in anyway with this solvent. Chemical rxn between a gas and a solvent greatly increases the solubility of the gases in the solvent.

for e.g. - Hydrogen chloride gas reacts with water by Hydrogen bonding when it dissolved in water. This increases the solubility of HCl gas in water.

⑤ Colligative properties of dilute soln:-

A dilute soln is one in which the amount of the solute is very small in comparison to the

amount of the solvent. The dilute soln show more or less ideal behaviour as the heat and volume changes accompanying the mixing of solute and solvent are negligible for all practical purpose.

→ Dilute soln obey Raoult's law.

→ Dilute soln containing non-volatile solute exhibit some special properties which depends only upon the no. of solute particles present in the solution irrespective of their nature.

These properties are termed as colligative properties.
The colligative properties are:-

- (i) Lowering of vapour pressure.
- (ii) Elevation in the boiling point.
- (iii) Depression in the freezing point.
- (iv) Osmotic pressure.

(i) Lowering in Vapour pressure-

→ When a non-volatile solute is added to a solvent, the vapour pressure is lowered due to following reasons:-

- (1) % surface area occupied by the solvent decreases. Thus, the rate of evaporation and vapour pressure decreases. The solute molecules occupied the surface area and so the % surface area occupied by the solvent decreases.

- (2) According to Graham's law - rate of evaporation $\propto \frac{1}{\text{density}}$

→ When a non-volatile solute is dissolved in a liquid its density increases their both rate of evaporation and

Vapour pressure lowered. If P^o is the vapour pressure of the pure solvent and P_s is the vapour pressure of the solution the difference ($P^o - P_s$) is termed lowering of vapour pressure and the ratio $\frac{P^o - P_s}{P^o}$ is termed relative lowering of vapour pressure.

According to Raoult's law →

The relative lowering in vapour pressure of a dilute solution is equal to mole fraction of solute present in the solution. If n moles of solute be dissolved in N moles of the solvent the mole fraction of solute will be $\frac{n}{n+N}$

According to Raoult's law

$$\frac{P^o - P_s}{P^o} = \frac{n}{n+N}$$

mole of solvent
mole of solute

or, it can be written as,

$$\frac{P^o}{P^o - P_s} = \frac{n+N}{n} = 1 + \frac{N}{n}$$

or,

$$\frac{P^o}{P^o - P_s} = 1 = \frac{N}{n} \quad \text{or} \quad \frac{P_s}{P^o - P_s} = \frac{n}{N}$$

or,

$$\frac{P^o - P_s}{P_s} = \frac{w_A}{m_A} \times \frac{m_B}{w_B}$$

→ After adding of non-volatile solute dissolved in a volatile solvent:

$$P_s \propto \frac{1}{\frac{n}{N}}$$

$$P_s = K \cdot \frac{N}{n+N}$$

(i)

K = proportionality factor

* For pure solvent $n=0$

$$\text{and hence, } P_0 = K \frac{N}{0+N} = K \quad \text{(ii)}$$

putting the value of K in eqn (i)

$$P_S = P_0 \frac{N}{n+N}$$

$$\frac{P_S}{P_0} = \frac{N}{n+N}$$

$$\frac{1-P_S}{P_0} = \frac{1-N}{n+N}$$

$$\left[\frac{P_0 - P_S}{P_0} = \frac{n}{n+N} \right] \quad \text{(iii)}$$

→ If a solution is made by dissolving w_B gram of solute (molecular mass m_B) in w_A gr. of the solvent (molecular mass m_A) the mole fraction of the solute will be

$$\frac{w_B}{m_B}$$

$$\frac{w_A}{m_A} + \frac{w_B}{m_B}$$

→ If the solution is very dilute w_B/m_B can be neglected in the denominator as compare to w_A/m_A then equation (iii) thus becomes,

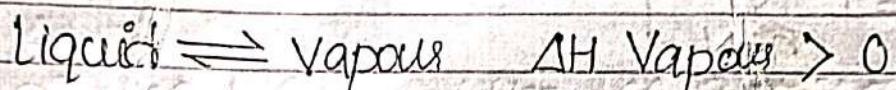
$$\left[\frac{P_0 - P_S}{P_0} = \frac{w_B \times m_A}{w_A \times m_B} \right] \quad \text{(iv)}$$

→ This relationship is useful in the determination of the molecular mass of dissolved solute by measuring relative lowering of vapour pressure.

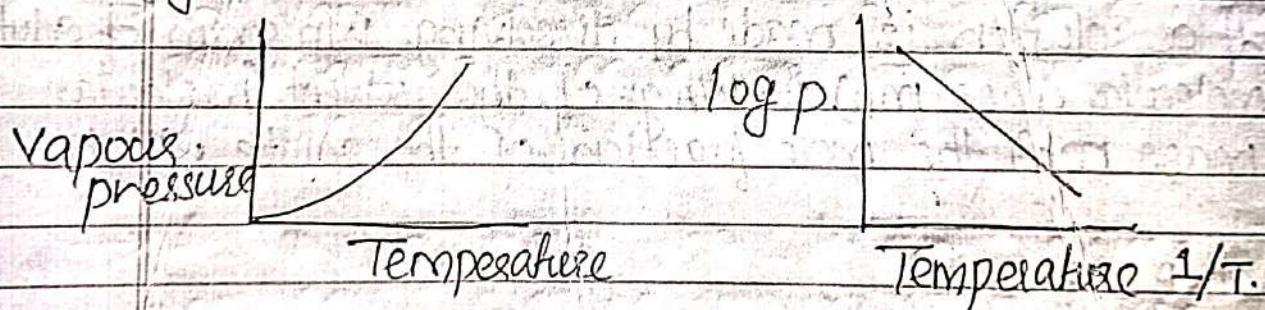
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Effect of Temperature on lowering of Vapour pressure:-

→ Vapour of liquid increases with increase in temperature.



→ Here ΔH is enthalpy of vaporization. A graphical representation of vapour pressure vs temperature is given below.



* A vapour pressure of liquid is known at a temperature. It can be calculated at another temperature using Clausius Clapeyron equation.

$$\log \left(\frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{2.303RT} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

P_1 = Vapour pressure at temperature T_1 .

P_2 = Vapour pressure at temperature T_2 .

Elevation of Boiling point :-

Evallioscopy:- The boiling point of a liquid is the temperature at which its vapour pressure is equal to the atmospheric pressure.

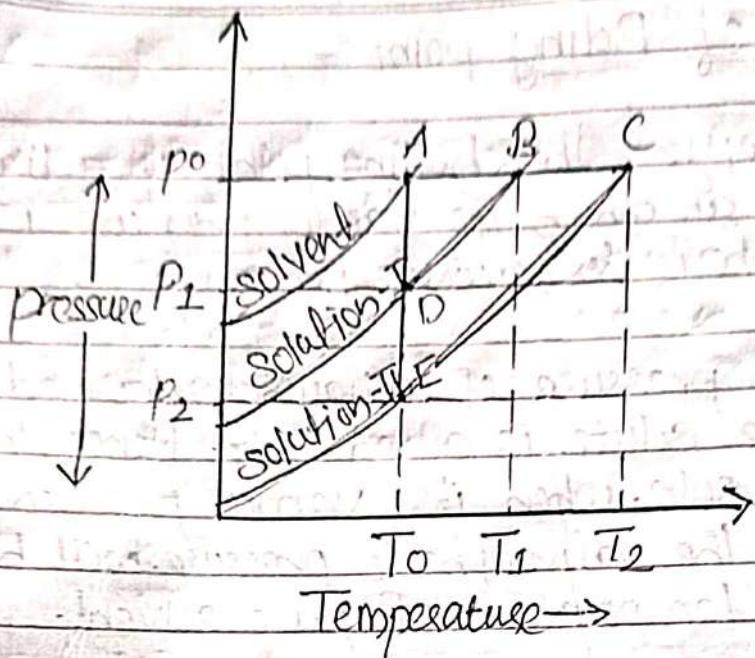
→ The vapour pressure of a liquid is lowered when a non volatile solute is added to it. Hence the temperature of the soln. when its vapour pressure will be equal to the atmospheric pressure will be higher than the temperature of pure solvent.

→ In other words the boiling point of the solvent is elevated by the addition of non-volatile solute.

→ The difference in the boiling point of the solution and the boiling point of the pure solvent is termed as elevation of boiling point.

$$\Delta T = \text{Boiling point of soln} - \text{Boiling point of pure solvent}$$

→ This can be better understand by a graph of vapour pressure against temperature for a pure solvent and two (2) solution of different concentration. The curve of the solution always lies ~~under~~ below the curve of the pure solvent.



→ The line P^o_C represent the atmospheric pressure, T_0 , T_1 and T_2 represent the boiling point of pure solvent of solution-I & solution-II respectively.

→ The vapour pressure of pure solvent solution I & solution II at temperature T are P^0 , P_1 & P_2 respectively.

→ Assuming that the solutions are very dilute this cause may be approximately taken as straight line near the boiling point, thus ΔH_{CE} & ΔH_{BI} are similar.

Therefore

$$\frac{AC}{AB} = \frac{AE}{AD}$$

$$\frac{T_2 - T_0}{T_1 - T_0} = \frac{P_0 - P_2}{P_0 - P_1}$$

$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

$$\boxed{\Delta T \propto \Delta P \propto \frac{W_B}{M_B \times W_A}} \quad \textcircled{1} \textcircled{2}$$

From Raoult's law for dilute solution.

$$\frac{P_0 - P_s}{P_0} = \frac{W_B \times M_A}{M_B \times W_A}$$

or

$$P_0 - P_s = \frac{W_B \times M_A}{W_A \times M_B} P_0$$

For the pure solvent, P_0 (its vapour pressure at the boiling point) M_A (its molecular mass) are constant.
Therefore

$$P_0 - P_s \propto \frac{W_A}{M_A \times W_A}$$

$$\Delta T = K \frac{W_B}{M_B \times W_A} \quad K = \text{elevation constant}$$

when $\frac{W_B}{M_B} = 1$ (1 mole of solute) and $W_A = 1 \text{ g}$, then,

$$\boxed{\Delta T = K}$$

→ Thus boiling point constant is equal to the elevation in boiling point which the theoretically produced when 1 mole of non-volatile solute is dissolved in 1 gram of the solute-solvent.

$$\text{of } \frac{W_B}{M_B} = 1 \text{ and } W_A = 100 \text{ g.}$$

$$\Delta T = \frac{K}{100}$$

$$\boxed{\Delta T = K'}$$

K' = molecular elevation constant.

* K' is called molecular elevation constant.
It is defined as the elevation in boiling point produced when one mole of solute is dissolved in 100 g of solvent.

$$\Delta T = \frac{K}{100}$$

$$\Delta T = K' = \frac{K}{100}$$

$$\boxed{100K' = K}$$

~~Now~~ putting this value in eqn: ①

* $\boxed{\Delta T = \frac{100K' w_B}{M_B w_A}}$

$$\text{If } \frac{w_B}{M_B} = 1 \text{ and } w_A = 1000 \text{ g}$$

This relation may also be written as

$$\boxed{\text{Then } \Delta T = \frac{K}{1000} = K_b}$$

K_b = molal elevation constant

(K_b) → It is defined as the elevation in boiling point produced when one mole of solute is dissolved 1000 g of the solvent.

$$\boxed{K = 1000 K_b}$$

NOTE

$$K_b = \frac{R K_b^2}{1000 L_v}$$

$K = \text{molar gas constant}$
 $T_b = \text{boiling point of the solvent}$
 $L_v = \text{latent heat of vaporization}$

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putting this value in eqn - (i)

$$\Delta T = \frac{1000 K_b M_A}{M_A + M_B}$$

$$\boxed{\Delta T = \text{Molality} \times K_b}$$

→ The elevation in boiling point of a solution of non-electrolyte is proportional to its molality and equimolar solution of all substances in a same solvent will show equal elevation in boiling point. This are known as Raoult's laws of elevation of boiling point.

Note: 0.515 is

→ Molal elevation constant is of water.