

Behaviour of Gases —

All matter exist in three state gas liquid & solid. The molecular representation of gaseous liquid & solid state.

A solid has molecules atoms or ions arranged in a certain order in fixed positions in the crystal lattice. The particle in a solid are not free to move about but vibrate in their fixed position. but in liquid state the space b/w the molecules, ions permit the movement of molecule through out the liquid.

In gaseous state the molecule are not arranged in fixed manner, they can move randomly.

General characteristic of gases —

i) Expansibility —

Gases have limitless expansibility. They expand to fill the entire vessel they are placed in.

2.

Compressibility

Gases are easily compressed by application of pressure to a movable piston fitted in the container.

3.

Diffusibility

Gases can diffuse rapidly through each other to form a homogenous mixture.

4.

Pressure

Gases exert pressure on the wall of the container in all direction.

5. Effect of heat

When a gas is confined in vessel is heated, its pressure increased upon heating in a vessel fitted with a piston, volume of the gas is increased.

Above properties of gases can be easily explained by the kinetic molecular theory.

The Gas law

The volume of a given sample of a gas depends on the temperature and pressure applied to it. any change in temp. or pressure will affect the volume of gas.

The relationship, which describe the general behaviour of gases are called the gas law.

BOYLE'S LAW

In 1660 Robert Boyle found out experimentally the change in volume of a gas sample with pressure at room temp. from thus observations he formulated a generalization known as Boyle's law, it states that at constant temp. the volume of a fixed mass of a gas is inversely proportional to its pressure.

Thus Boyle's law may be expressed mathematically as,

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

where,

$$PV = k$$

$P = \text{Pressure of gas}$
 $V = \text{Volume of gas}$

if the pressure of gas becomes P_1 to P_2 then the volume of gas becomes V_1 to V_2 then,

$$P_1 V_1 = P_2 V_2$$

The relationship is useful for the determination of a gas at any pressure if its volume at any other pressure is known.

CHARLE'S Law

In 1787 Jacques Charles investigated the effect of change of temperature on the volume of fixed amount of gas at constant pressure.

- He established a generalization which is called charle's law.
- it states that at constant pressure the volume of a fixed mass of a gas is directly proportional to the kelvin temp. of absolute temp.
- if the absolute temp. is double then the volume is double.

charle's law may be expressed mathematically as

$$V \propto T \quad \text{Where } k = \text{constant}$$

$$V = kT$$

$$k = \frac{V}{T}$$

if V_1, T_1 are the initial volume and temp. of a given mass of gas and constant pressure V_2, T_2 if it is the new values we can write

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

The combine Gas law

Boyle's law & charle's law can be combined into a single relationship called the combine gas law.

Boyle's law $V \propto \frac{1}{P}$ where $T, n \rightarrow \text{constant}$

charle's law $V \propto T$ where $P, n = \text{constant}$

Therefore $\boxed{V \propto \frac{T}{P}}$

The combined law can be stated as for a fixed mass of a gas the volume is directly proportional to kelvin temp. & inversely proportional to the pressure.

if k be the proportionality constant.

$$\text{Then } V = \frac{kT}{P}$$

where n is constant

$$\frac{PV}{T} = k$$

if the pressure, volume & temp. of a gas be changed from P_1, V_1 and T_1 to P_2, V_2 and T_2 then-

$$\frac{P_1 V_1}{T_1} = k = \frac{P_2 V_2}{T_2}$$

$$\boxed{\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}}$$

AVOGADRO Law

Equal volume of the gases at the same temp. and pressure contain equal number of mole or molecules.

if the molar amount is double then the volume is double

$$V \propto n$$

$$V = AN$$

where $T \& P$ is constant

$$\boxed{\frac{V}{n} = A}$$

For any two gases which volume V_1, V_2 and
moles n_1, n_2 at constant temp. of pressure
then, $\frac{V_1}{n_1} = \frac{V_2}{n_2}$

If $V_1 = V_2$ then
 $n_1 = n_2$

The ideal gas equation

Three simple gas law that is Boyle's law $\propto \frac{1}{P}$

Charles law — $V \propto T$
And Avogadro law — $V \propto n$

These three law can be combination in to a
single gas law i.e.

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

This is called the

universal gas law.

→ it is also called ideal gas law.
→ As it applies to all gases which exhibit
ideal behaviour. i.e. obey the gas law
perfectly.

→ The ideal gas law may be stated as the volume
of a given amount of gas is directly proportional
to the number of moles of gas directly
proportional to the temp. and inversely
proportional to the pressure.

$$V = \frac{RNT}{P}$$

$PV = nRT$ — (i) R is a gas constant

The equation (i) is called the ideal gas equation.
or simply the general the gas equation.
→ The ideal gas equation holds fairly accurately
for all gas at low pressure.

For one mole of a gas the ideal gas equation is
reduced to $P = RT$. (Where $n=1$)

The numerical value of $R = \frac{PV}{nT}$

Kinetic molecular theory of Gas

Kinetic theory

→ Maxwell and Boltzman (1859) developed a
mathematical theory to explain the behavior of
gas and the gas law.

→ It is based on the fundamental concept that a
gas is made of a large number of molecules in
perpetual motion. Hence the theory is called the
kinetic molecular theory or simply the kinetic
theory of gases.

Assumptions of the kinetic molecular theory

- A gas consists of extremely small discrete particles called molecules dispersed throughout the container.
- The actual volume of the molecule is negligible compared to the total volume of the gas.

• Gas molecules are in constant random motion with high velocities. They move in straight lines with uniform velocity and change direction, on collision with other molecules or the walls of the container.

• The distance between the molecules are very large and it is assumed that van der waals attractive forces b/w them do not exist. Thus the gas molecules can move freely, independent of each other.

• All collisions are perfectly elastic. Hence, there is no loss of the kinetic energy of a molecule during a collision.

• The pressure of a gas is caused by the hits accorded by molecules on the walls of the container.

• The average kinetic energy of $\left[\frac{1}{2}mv^2\right]$ of the gas molecules is directly proportional to absolute temp.

This implies that average kinetic energy of molecules is the same at a given temp.

Deviation from ideal behaviour

→ An ideal gas is one which obeys the gas laws on the gas equation $PV = RT$ at all pressures and temperatures.

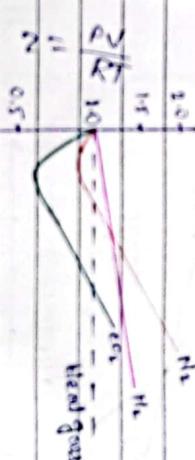
However, no gas is ideal. Almost all gases

show significant deviations from the ideal behaviour. Thus the gases H₂, N₂ and CO₂ which fail to obey the ideal gas equation are termed nonideal or real gases.

Compressibility factor

The extent to which a real gas departs from the ideal behaviour may be depicted in terms of a new function called as compressibility factor, denoted by Z. It is defined as -

$$Z = \frac{PV}{RT}$$



Z vs P plot for H₂ and He at 298K

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

For an ideal gas $Z=1$ and it is independent of temperature and pressure. The deviations from ideal behaviour of a real gas will be determined by the value of Z being greater or less than 1.

The difference b/w unity and the value of compressibility factor of a gas is a measure of the degree of nonideality of the gas.

Effect of temp. on deviation —

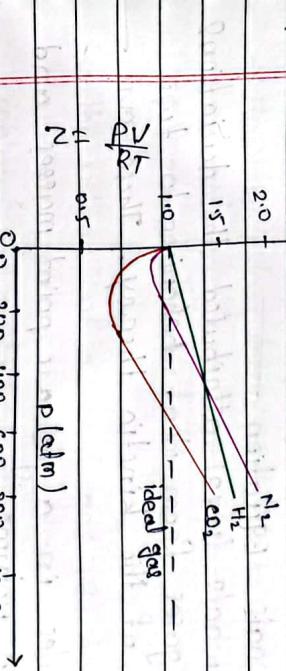
For a real gas the deviation from ideal behaviour depends on pressure and temperature. This will be illustrated by examining the compressibility curves of some gases discussed below with the variation of pressure & temp.

Effect of pressure variation in deviation

When we plot a graph between compressibility factor Z plotted against pressure for H_2 , N_2 & CO_2 at a constant temp.



2. Z versus P plots for N_2 at different temp.



As the temp. is raised, the dip in the curve decreases. At the certain temp., the minimum in the curve vanishes and the curve remaining horizontal for an appreciable range of pressure.

- At very low pressure for all three gases Z is approximately equal to one. This indicates

that at low pressure, real gases exhibit nearly ideal behaviour. As the pressure increased, H_2 shows a continuous increase in Z .

Thus the H_2 curve lies above the ideal gas curve at all pressure for N_2 & CO_2 .

Z is first decreases. If pressure goes to through a minimum then increase continuously with p .

Conclusion —

Conclusion —

- At this temp. PV/RT is almost unity and the Boyle's law is obeyed. Hence the temp. for the gas is called Boyle's temperature.
- At the low pressure and fairly high temp. real gases show nearly ideal behaviour and the

Volume Contraction

ideal-gas equation is obeyed.
 At low temp. and sufficiently high pressure
 a real gas deviates significantly from ideality
 and the ideal-gas equation is no longer valid.

The closer the gas is to the liquefaction point,
 the larger will be the deviation from the ideal
 behaviour.

Explanation of Deviation

Vander waals Equation —
 Van Den waals (1873) attributed the deviation of real gases from ideal behavior to two postulates of the kinetic theory. These are —

→ Volume v of an ideal gas is the same as the volume of the container. The del molecules of ideal gas have zero-volume and the entire space in the container is available for their movement.

→ However van den waals assumed the molecules of a real gas are rigid spherical particles which possess a definite volume.

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

(2) There are no intermolecular attraction in a gas.

Therefore, the ideal gas equation derived from kinetic theory could not hold for real gases.

Therefore, the volume of a real gas is, therefore, ideal volume minus the volume occupied by the gas molecule. ($v - b$)

If b is the effective volume of molecules per mole of the gas, the volume in the ideal gas equation is corrected as — $v = v - b$

or

the excluded volume

Volume of real gas per n moles of the gas the corrected volume is $(v = v - nb)$

→ Van den waals pointed out that both the pressure & volume factors in the ideal gas equation needed correction in order to make it applicable to real gas.

Where b is termed the excluded volume which is constant & characteristic for each gas.



(i)

(ii)

Graph of contraction

The excluded volume is not equal to the actual volume of the gas molecule, in fact it is four times the actual volume of molecules and can not be calculated as follows.

Let us consider two molecules of radius r colliding with each other. Obviously, they cannot approach each other closer than a distance $(2r)$ apart.

Therefore, the space indicated by the dotted spherical space is excluded volume for a pair of molecules. Thus—

Excluded volume for two molecules = $4/3 \pi (2r)^3$

Excluded volume per molecule $V = \frac{1}{2} \times \left[\frac{4}{3} \pi r^3 \right]$

$$= 4V_m$$

where V_m = Actual volume of the single molecule.

Therefore, in general excluded volume of the gas molecules is four times the actual volume of molecules.

Pressure correction

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

Thus, if P is the wall with reduced velocity and the actual pressure of the gas is, will be less than the ideal pressure.

If the actual pressure P , is less than P_{ideal} by a quantity ρ , we have,

$$\rho = P_{ideal} - P$$

P is determined by the force of attraction b/w molecule (A) shrinking the wall of container and the molecule (B) pulling them inward.

The rd. force of attraction is, therefore proportional to the concentration of (A) type molecules and also of (B) type of molecule

That is Pressure

$$P = \frac{n^2}{V^2} \times \frac{1}{2} k T$$

Where n is total number of gas molecule in volume and a is proportionality constant characteristic of the gas. The pressure P is the ideal gas equation is corrected as—

$$\frac{P + \alpha n^2}{V^2}$$

P_{atm} n mole of gas.

Jordan Waals Equation

Substituting the values of corrected pressure and volume of ideal gas equation

$$P = nRT$$

We have,

$$\left[P + \frac{\alpha n^2}{V^2} \right] (V - nb) = nRT$$

This is known as Van den waal equation
 P_{atm} n mole of a gas. n mole of gas

($n=1$)

Van den waal equation becomes =

$$\left[P + \frac{\alpha}{V^2} \right] (V - b) = RT$$

Constant A & B in Van den waal equation are called Van den waal constant.
 This constant are characteristic of each gas.

Determination of a and b

From the expression (1), the value of a is given by the relation,

$$a = \frac{P_{\text{atm}} V^2}{n^2}$$

expressed in atmospheres and volume in liters.

$$a = \frac{(P_{\text{atm}})(V_{\text{atm}})^2}{n^2} \Rightarrow \text{atm}^2 \text{ m}^{-2}$$

Thus a is expressed in atm liter² mol⁻² units.

Since,

$$b = \frac{\text{Volume}}{n} \Rightarrow \frac{\text{litter}}{\text{mol}}$$

if volume is expressed in liters, b is expressed in liter mol⁻¹ units.

Limitations of Van den waals Equations

Van den waal equation explains satisfactorily the general behavior of real gases. It is valid over a wide range of pressure and temp.
 However it fails to give exact agreement with experimental data at very high pressures and low temperatures.

Dielectric (1922) proposed a modified Van den waal's equation. This is known as dielectric equation for 1 mol of gas it may be stated as

$$P(V-b) = RT e^{-\alpha V}$$

here the term a & b have same significance as in Van den waal equation.



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UNIT-2

Liquid State

A liquid may be defined — A collection of molecule help close to each other and exerting random motion through intervening spaces.

Most of the physical properties of liquids are actually controlled by the strengths of intermolecular attractive forces.

Intermolecular forces in liquid

Intermolecular forces in liquids are collectively called Van der waals forces. These forces are essentially electrical in nature and result from the attraction of charges of opposite sign.

The principal kind of intermolecular attraction are —

- Dipole - Dipole attraction
- London forces
- Hydrogen bonding

Dipole - Dipole attraction

Dipole - Dipole attraction occurs between polar molecules that are polar. This requires the presence of polar bonds and unsymmetrical molecules.

These molecules have a permanent separation of positive and negative charge. In illustration the H and of HCl is permanently slightly positive charge.

→ The Cl end of HCl has a permanent slight negative charge.

→ The H atom in one molecule is attached to the Cl in a neighbour.

→ The intermolecular force is weak compared to a covalent bond, but their dipole-dipole interaction is one of the stronger intermolecular attractions.

2. London forces —

London dispersion forces exist in non-polar molecules. These forces result from temporary charge in balance. The temporary charge exists because the electrons in a molecular ion move randomly in the structure.

→ The nucleus of one atom attracts electrons from the neighbouring atom at the same time the electrons in one particle repel the electrons in the neighbour and create a shield (weird in charged in balance).

→ This temporary charge is on one molecule. This atom attracts opposite charge in near atom by molecule or atom.

→ A local slight positive charge (δ^+) (δ^-) in one molecule will be attracted to a temporary slight negative charge (δ^-) (δ^+) in another molecule.



Hydrogen bonding

Hydrogen bonding is a very type of intermolecular attraction.

→ There are two requirements —

• Covalent bond b/w a H-atom and either Fluorine, oxygen or Nitrogen.
• Interaction of the hydrogen atom in this kind of polar bond with a lone pair of electrons on a near by atom like Fluorine, O or N.

H

Surface tension

This properties of liquid arises from the intermolecular forces of attraction. A molecule in the interior of a liquid is attacked equally in all directions by the molecules around it.

→ A molecule on the surface of a liquid is attacked only side ways and toward the interior. The forces on the side being direction, counter balanced. The surface molecule is, adsorbed only inward the liquid.

Thus there is a tendency on the part of the surface molecule to go in to the bulk of the liquid.

→ The liquid surface is therefore under tension and tends to contract to the smallest possible area.

in order to have the minimum number of molecules at the surface.

if we assume this reason in air, drops of a liquid assume spherical shapes because for a given volume a sphere has minimum surface area.

The surface tension (γ) is defined as the force in dynes acting along the surface of liquid at right angle to any line drawn in length.

Unit of surface tension

The unit of surface tension is C.G.S system is dyne/cm.

In S.I. system the unit is N/m.

Effect of temp. on Surface tension

A change in temp. causes a change in surface tension of a liquid when temp. increases there is an increasing kinetic energy of liquid molecules. Thus by decreasing intermolecular forces, it results in decrease in the inward pull functioning on the surface of liquid as a result surface tension decreases with increasing $\text{[T]} \text{Temp}$.

Determination of Surface tension - Capillary rise method

The methods commonly employed for the determination of surface tension are -

1) Capillary rise method

A capillary tube of radius r is vertically inserted in to a liquid.

The liquid rises to a height h and forms a concave meniscus. The surface tension γ acting along the inner circumference of tube exactly supports the weight of the liquid column, by definition, surface tension is force per unit area acting and a tangent to the meniscus surface if the angle b/w the tangent and the tube wall is θ , the vertical component of the surface tension is $\gamma \cos \theta$.

\rightarrow The total surface tension along the circular contact line of meniscus is $2\pi r \sin \theta$. Thus

force upward force is equal to $2\pi r \cos \theta$ where,

r is radius of the capillary.
for most liquids θ is nearly 0° of contact angle, the upward force is reduced to $2\pi r$.
 \rightarrow The downward force on the liquid column is due to its weight which is $m \times g$ or density $\rho \times g$ where,

d is the density of the liquid

or upward force is equal to downward force

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

In order to know the value of η the value of η was found with the help of a travelling microscope and density bottle a pyknometer.

Measurement of Viscosity by Ostwald method

Viscosity of a liquid can be determined with the help of Poiseuille's equation.

Poiseuille's expression which governs the flow of liquid through a capillary may be written as, $\eta = \frac{\pi P r^4 l}{8 \nu}$

where V is the volume of the liquid flowing

to capillary and t in time t , P the pressure head are the radius of tube

and its length.

The experimental measurement of P is difficult. Therefor it is not possible to find the absolute coefficient of viscosity (η) straight away from Poiseuille's equation.

Ordinarily, The viscosity of liquid is determined with respect to that of water it called relative viscosity.

Let us define the rate of flow of a fluid volume (V) of the two liquid through the same capillary.

The expression for relative viscosity (η_1/η_2) can be derived from the equation $\eta_1 = \frac{P_1 t_1}{8 \nu} \cdot \frac{\pi r^4 l}{V}$

$$\frac{\eta_1}{\eta_2} = \frac{P_1 t_1}{8 \nu} \cdot \frac{\pi r^4 l}{V} \cdot \frac{8 \nu}{\pi r^4 l} \cdot \frac{P_2 t_2}{V}$$

Since the pressure head is proportional to density (d) of the liquid from equation (1)

we have

$$\frac{\eta_1}{\eta_2} = \frac{d_1}{d_2}$$

Substituting the value of viscosity coefficient of water that is η_2 is equal to 1 we can find the absolute viscosity of given liquid i.e. (η_1)

Viscosity

A liquid may be considered to be consisting of molecules arranged one over the other. When a shearing force is applied to a liquid it flows. However the force of friction by the layers offers resistance to this flow. we can say viscosity of a liquid is a measure of its frictional resistance.

Let us examine the liquid flowing on a glass surface.

The molecular layer in contact with the stationary surface has zero velocity. The successive layers above it move with increasing velocities in the direction of flow.

$$ds \rightarrow v \rightarrow \text{viscosity}$$

$$\text{oooooooo} \cdot v \rightarrow$$

Now consider two adjacent moving layers of a liquid, let these be separated by the distance ds and have

The force of friction resulting the relative motion of the two layers is directly proportional to the area A and the velocity difference dv , while it is inversely proportional to distance b/w the layers.

$$f \propto \frac{Adv}{ds}$$

$$f = \frac{Adv}{ds}$$

$$= \frac{F}{A} \frac{dv}{dv}$$

where η is the proportional constant if it is known as the coefficient of viscosity or simply viscosity of a liquid.

or as a specific value for a given liquid at the same temp.

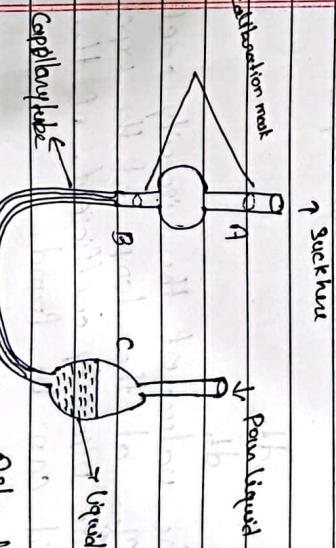
i) may be defined from eqn ① .

The force of resistance per unit area which will maintain the unit velocity difference b/w two layers of liquid at a unit difference b/w each other.

The reciprocal of viscosity is called fluidity and is denoted by $\phi = \frac{1}{\eta}$

units of viscosity

The dimensions of the coefficient viscosity (η) may be derived from equation ④ i.e $\eta = \frac{F}{A} \frac{dv}{dv}$



Ostwald viscometer

A simple form of Ostwald viscometer shown in above figure. The left hand limb is evacuated a pipette by two calibration mark a & b. A length of a capillary tube joins the pipette to a bulb c in the right hand limb.

Thus in C.G.S system the unit of η is expressed as $\text{g cm}^{-2}\text{s}^{-1}$. It is also called poise. In practice smaller unit centipoise [10^{-2}] and millipoise [10^{-3}] are used.

\rightarrow The S.T. unit is kg m s^{-1} poise is equal to 1/10 of the S.T. unit
 $1 \text{ poise} = 1951 \text{ cm}^{-1} = 0.1 \text{ kg m}^{-1}\text{s}^{-1}$

Ostwald viscometer

The apparatus commonly used for the determination of relative viscosity of a liquid is known as an Ostwald viscometer or simply viscometer.

- A definite volume of a liquid is poured in the bulb C with a pipette the liquid is sucked up near to the top of left limb with the help of a rubber tubing attached to it.
- The liquid is then released to flow back in the bulb C the time t_1 from A to B is noted with stop watch. Then the apparatus is cleaned and experiment repeated with water, taking about the same volume.
 - The time of flow of water is from A to B is recorded. The density of liquid (ρ_l) and water (ρ_w) are determined with the help of a pycnometer meter.
 - The relative viscosity coefficient is, calculated 'calibrated' from the expression.

$$m_r = \frac{t_w}{dt_h}$$

knowing the values of the viscosity coefficient of water at the temp. of the experiment and absolute viscosity coefficient of the given liquid can be found.

Solution

Solution is the homogeneous mixture of two or more substance in same different physical phases like Solute and solvent.

Solvent is the compound component which is present in large quantity while the other compound is known as solute.

If water is used as a solvent the solution is called aqueous soln and

Depending upon the amount of solute dissolve in a solvent we have the following types of solution.

Unsaturated Solution

A solution in which more solute can be dissolve without raising temp. is called an unsaturated solution.

Saturated Solution

A solution in which no solute particle can dissolve further at the given temp. is called a saturated solution.

Supersaturated Solution

A solution which contain more solute particle than would be necessary to saturated at a given temp. is called supersaturated solution.

Method of expressing conc. of solution

Percentage by weight —

it is define as the amount of solute percentage in 100 gm of solution.

$$\text{Wt}.\% = \frac{\text{wt. of solute}}{\text{wt. of solution}} \times 100$$

$$\text{Wt}.\% = \frac{m}{M} \times 100$$

Percentage by volume —

it is define as the volume of solute in ml present in 100 ml soln.

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

Percentage by mass by volume —

it is define as the mass of solute in 100 ml of solution.

$$\text{M/V}\% = \frac{\text{mass of solute}}{\text{Volume of solution}} \times 100$$

Strength and concentration —

it is define as the amount of the solute in gm percentage in liter of solution.

Molarity —

it is define as no. of moles of the solute present in liter of solvent. it is denoted by 'm'.

$$\text{Molarity} = \frac{\text{no. of moles of solute}}{\text{Volume of soln}}$$

Normality —

it is define as no. of gram equivalent of solute per liter of soln. it is denoted by 'N'.

Parts per million (ppm) —

when the solute is present in trace quantity of the solute

in gram present in 10⁶ g of solution.

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

Mole fraction —

it is define as the no. of moles of a component to the total no. of moles of the component.

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

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

Molality —

it is define as the no. of moles of the solute present in kg of solvent. it is denoted by 'm'.

$$\text{molality} = \frac{\text{no. of moles of solute}}{\text{wt. of soln}} \text{ or } \frac{\text{no. of moles of solute}}{\text{mass of soln}}$$

Ideal soln

An ideal solution is one in which the molecule attract one another with equal force irrespective of their nature. Thus, a soln composed of two component A & B will be an ideal one if the forces b/w A & A, B & B should be same. An ideal solution possess the following characteristic.

→ Volume change of mixing should be zero.

→ Heat change on mixing should be zero.

→ There should be no chemical b/w solvnt & solute.

→ Solute molecules should not dissociated in the ideal soln.

→ Solute molecules should not associated in the ideal soln.



Total Pressure,

$$P = P_A + P_B$$

$$P = x_A P^{\circ}_A + x_B P^{\circ}_B$$

Ideal solution must obey Raoult's law of all concentration. The following are some properties of ideal soln.

- Benzene and Toluene
- Carbon tetrachloride & tetrachloride

Raoult's law

Alc to this law partial pressure of any volatile constituent of a solution at a constant temp. is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in the solution.

Let a mixture (soln) be prepared by mixing n_A mole of liquid A & n_B mole of liquid B. Let P_A and P_B be the partial pressure of constituent A & B in solution and P_A° and P_B° the vapour pressure in pure state respectively.

Thus Alc to Raoult's law

$$P_A = \frac{n_A}{n_A + n_B} P^{\circ}_A \Rightarrow \text{Mole fraction of } A \times P^{\circ}_A = x_A P^{\circ}_A$$

$$P_B = \frac{n_B}{n_A + n_B} P^{\circ}_B \Rightarrow \text{Mole fraction of } B \times P^{\circ}_B = x_B P^{\circ}_B$$

This law infct is the measure desig factor whether a solution will be ideal or non ideal. Ideal soln obey Raoult's law and every range of conc. Non ideal soln don't obey Raoult's law they show either true or negative deviation from Raoult's law

Ideal Soln.

Positive Deviation

Negative Deviation

\Rightarrow Obey's Raoult's law Don't obey Don't obey Raoult's
at every stage Raoult's law low
of concentration.

$$\Rightarrow \Delta H_{mix} = 0 \quad \Delta H_{mix} > 0 \quad \Delta H_{mix} < 0$$

\Rightarrow dilute heat Endothermic dilute Exothermic dilute
endowed heat ion heat is ion heat is
heat due to absorbed. evolved

$\Rightarrow \Delta V_{mix} = 0$ total $\Rightarrow \Delta V_{mix} > 0$ volume $\Delta V_{mix} < 0$ volume
volume of soln is increase when is decrease during
equal to some distribution. distribution.

of volume the endothermic exothermic

$$\begin{aligned} \Rightarrow P &= P_A + P_B = P_A > P^* A X_A & P_A < P^* A X_A \\ P_A X_A + P_B X_B & P_B > P^* B X_B & P_A X_A + P_B X_B < P_A X_A + P_B X_B \\ i.e. P_A &= P^* A X_A & P_A X_A + P_B X_B \\ P_B &= P^* B X_B & P_A X_A + P_B X_B \end{aligned}$$

End distribution Sloe distribution

\rightarrow A-A, A-B, B-B A-B attraction. A-A attractive

attraction force should increase force should be
an interaction, like that A-B & A-B greater than A-B if
be same. attractive forces, A-B attraction force
i.e. A-B are A-B have different A-B have different
radical in pair. If A-B have different
radical in pair. If A-B have different slope most
slope most characteristic

Escape tendency

A-B shape easily Escaping tendency of A-B should showing larger escape of both compound
be same in pair because unlike A-B is liquid

liquid and its expected value, showing lower
with low vapour pressure
than expected.

high



Solution of Gases in Liquid

The solubility of gas in a liquid ~~is proportional~~ depends on the conc. of dissolved gas in a liquid when it is in equilibrium with some of the pure gas above this soln.

Ex- pharmaceutical aerosol containing hydrogen also be considered as solution of the gases in liquid.

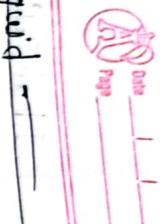
Factors affecting solubility of gases in liquid

The solubility of gas in a solvent depends on temp. pressure presence of salts and chemical rxn. if any bds the gas and the solvent.

Effect of pressure

The pressure of the gas above the solution is important in gaseous soln since this significant changes there significant changes in solubility of dissolved gas. The effect of pressure on the solubility of the gas is given by Henry's law which states that in dilute solution the mass of the gas which dissolve in a given volume of a liquid at a constant temp. is directly proportional to the gas.

According to Henry's law



Where,

C is the conc. of dissolved gas in gram per liter of solvent.

P is the 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.

is the proportionality constant and is referred to as the solubility coefficient

The solubility of gases is generally increase with increase pressure and on the decrease on the pressure a solubility decrease and the gases escape.

Effect of temperature

Solubility of most gases decrease with a rise in temperature because of the greater tendency of the gases to expand in comparison to the solvent. It is therefore essential that caution must be exercised when opening the container containing gaseous soln under elevated temp. it is better to reduce the temp. by immersing an ice cold water before opening such container.

Effect of electrolytes and non-electrolyte

Solubility of gases in a solvent is generally reduced by the addition of electrolytes such



such as sugar. This is referred as colligating out. This is due to more affinity b/w the solvent and the electrolyte as non-electrolyte than b/w the solvent & solute and the gas.

4. Effect of chemical reaction

Henry's law generally applies to gases that are only slightly soluble in solvent and thus don't react in any way with this solvent. chemical can b/w a gas and a solvent greatly increase the solubility of the gases in the solvent.

Hydrogen chloride gas reacts with water by hydrogen bonding when it dissolved in water. This increases the solubility of HCl gas in water.

~~Colligative properties of dilute soln~~
A dil. soln is one in which the amount of the solute is very small in comparison to the amount of the solvent. Since most of the ideal behaviour of the heat and volume changes accompanying the mixing of solute and solvent are negligible for all practical purpose.

→ Dil. soln obey Raoult's law

Dilute soln containing non-volatile solute exhibit some special properties which depend 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—

- Lowering in vapour pressure
- Elevation in the boiling point
- Depression in the freezing point
- Osmotic pressure

Look the diagram for detail

Decreasing in vapour pressure
When a non-volatile solid is added to a solvent, the vapour pressure is lowered due to following reasons—

- 1) Percent surface area occupied by the solvent decreases. Thus the rate of evaporation and vapour pressure decreases. The solute molecule occupies the surface so the percent surface area occupied by the solvent decrease.
- 2) According to Raoult's law evaporation of like a non-volatile solute is dissolved in liquid its density increase. Thus both both

of evaporation and vapour pressure lowered if P^o is the vapour pressure of the pure solvent and P^o_s is the vapour pressure of pure solvent and P^o_s is the vapour pressure of the solution the difference $(P^o - P_s)$ is termed lowering in vapour pressure and the ratio $\left[\frac{P^o - P_s}{P^o} \right]_s$ is termed relative lowering in up.

Ale to Raoult's law —

$$\frac{P_{\text{solvent}}}{P_{\text{solution}}} = \frac{P^o_{\text{solvent}}}{P^o_{\text{solution}}} \times \frac{x_{\text{solvent}}}{x_{\text{solution}}}$$

But if the solute used is non-volatile only pressure from solvent can be considered.

So,

$$P_{\text{solution}} = P^o_{\text{solvent}} \times x_{\text{solvent}}$$

- on the other hand

$$x_1 + x_2 = 1 \quad x_1 = \text{mole fraction of solute}$$

$$P^o = P^o(1 - x_2) \quad x_2 = \text{mole fraction of solute}$$

$$P^o = P^o - P^o x_2$$

$x_1 + x_2 = 1$ $x_1 = \text{mole fraction of solute}$

$$\frac{P^o - P}{P^o} = \frac{\Delta P}{P^o} = x_2 = \frac{n_2}{n_1 + n_2}$$

Elevation of Boiling Point —

Evallioscopy — The boiling point of a liquid is the temp. 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 temp. of the ~~solute~~ when its vapour pressure will be equal to the atmospheric pressure will be higher than the temp. of pure solvent.

$\Delta P = P^o - P$ is the lowering of the vapour pressure lowering.

\rightarrow The relative vapour pressure lowering depends only on the mole fraction of the solute.

x_n that is on the number of solute particles in a definite volume of solution. Therefore the relative vapour pressure lowering is a colligative property.

x_n that is on the number of solute particles in a definite volume of solution.

Therefore the relative vapour pressure lowering is a colligative property.

* The boiling point is defined as the temp. at which the v.p. of a liquid equals the atmospheric pressure.

→ Due to vapour pressure lowering, a solution will require a higher temp. to reach its boiling point than the pure solvent.

$$T - T_0 = \Delta T_b$$

$$\Delta T_b = k_b x_m$$

$$P_A = P_A^{\circ} x_A$$

For ideal behaviour of solution, solubility

solute must be same in nature.

Property of ideal Solution—

- 1) Ideal solution must be obey Raoult's law.
- 2) When component's are mixed together their force of interaction are not changed.
means A - B interaction, A - A interaction and B - B interaction must have same.

- 3) Two components which is present in solution their structure and polarity must have similar.
- 4) When components are mixed together then change in volume is zero.



- 5) When components are mixed together then change in enthalpy is zero.

$$\Delta H_{\text{mixing}} = 0 \quad [\text{Change in heat}]$$

A — Benzene & Toluene

n-hexane & n-heptane

Ethyl bromide & Ethyl iodide

Bromobenzene & Toluobenzene

Non-ideal Solution

A solution whose component is different in nature is known as ideal soln. Such type of solution is not obey the Raoult's law.
→ Doesn't obey Raoult's law means $p_A \neq p_{A^{\text{ext}}}$ and $p_B \neq p_{B^{\text{ext}}}$

- A → B interaction is A → B interaction and $\Delta H_{\text{mix}} \neq 0$
- if two components are mixed together then change in volume is not zero.
- if two components are mixed together then change in mixture is not zero.

Conductance of Electrolytes

The power of electrolytes to conduct electric current is termed conductivity or conductance like metallic conductors electrolyte obeys Ohm's law.

According to this law the current I flowing through a metallic conductor given by the relation $I = \frac{V}{R}$ or $R = \frac{V}{I}$

where V is the potential difference at two ends and R is the resistance measured in ohm.

Positive deviation from Raoult's law of non-ideal solution.

The resistance of R of a conductor is directly proportional to its length and inversely proportional to the area of its cross section.

The resistance R of a conductor is directly proportional to its length and inversely proportional to the area of its cross section.

That is $R \propto \frac{l}{A}$

$$R = \rho \times \frac{l}{A}$$

where ρ = is a constant and is called resistivity or specific resistance.

if values depends upon the material of a conductor.

Simply we can write

$$P = R \frac{A}{l} \quad \text{if } l = 1 \text{ cm} \text{ & } A = 1 \text{ cm}^2$$

then $R = P$

Thus its follows that the specific resistance of a conductor is the resistance in a column 1cm² cube of it which offers to the passage of electricity

Specific Conductance

The power of a substance to conduct electricity or conductivity is

converse of resistance.
The reciprocal of specific resistance is term specific conductance or specific conductivity.

It may defined as the conductance of 1cm³ of an electrolyte

The specific conductance is denoted by the symbol k (kappa) thus,

$$k = \frac{1}{R} = \frac{I}{V} \times A$$

Unit of Specific Conductance

Specific conductance is generally expressed in reciprocal ohm cm⁻¹ or mho cm⁻¹ or siemens cm⁻¹

its unit can be derived as follows $k = \frac{1}{R} \frac{l}{A}$

$$= \frac{C}{\Omega \cdot m} = \text{mho cm}^{-1}$$

The internationally recommended unit of $\text{a}^{\prime}(\text{mho})$ is siemens (S).

Then we can express k as S cm^{-1}

* Equivalent Conductance

The conductance of n electrolytes obtained by dissolving in equivalent of it one in 1 cm^3 of water is Nec cm^{-1}



CHEMICAL KINETICS

Rate Law

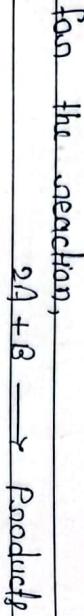
At a fixed temperature the rate of a given reaction depends on conc. of reactants.

→ The exact relation between conc. and rate is determined by measuring the reaction rate with different initial reactant conc.

The rate of reaction is directly proportional to the reactant conc. each conc. being raised to some power.

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

$$\text{rate} = k[A]^n \quad \text{--- (i)}$$



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

$$\text{rate} = k[A]^m[B]^n \quad \text{--- (ii)}$$

An expression which shows how the reaction rate is related to concentrations is called the rate law or rate equation.

1) The rate of appearance of product = rate of disappearance of reactant.



Conc. of reactant A decrease

With time

Conc. of product B increase

With time

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

Chemical kinetics

is the part of chemical science dealing with the study of —

a) Rate of chemical rxn

b) the factors which affect the rxn rate.

Reaction Rate

$$\text{Rate of Reaction} = \frac{\text{change in conc.}}{\text{change in time}}$$

Rate of chemical rxn = change in conc. [mol/l] of a reactant or product with time. (s, min, hr)

Rate with respect to A

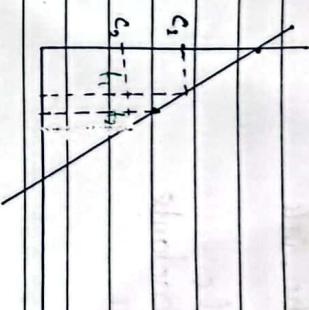
$$\text{Rate} = \frac{\text{change in conc. } A}{\text{change in time}} = \frac{\text{conc. } A_2 - \text{conc. } A_1}{t_2 - t_1}$$

$$= \frac{\Delta[A]}{\Delta t}$$

Rate with respect to B

$$\text{Rate} = \frac{\text{change in conc. } B}{\text{change in time}} = \frac{\text{conc. } B_2 - \text{conc. } B_1}{t_2 - t_1}$$

$$= \frac{\Delta[B]}{\Delta t}$$



* Chemical kinetics —

Chemical kinetics is the branch of physical chemistry which deals with a study of the speed of chemical reactions. Such studies also enable us to understand the mechanism by which the reaction occurs.

Thus in chemical kinetics we can also determine the rate of chemical reactions.

Homogeneous Reaction —

Average Rate of Reaction decreases with time as conc. of reactants decrease.

Instantaneous Rate change in the conc. of reactants as products at a given instant of time.

Slope of a tangent line to the curve of a conc. versus time plot.

$$\text{Slope} = \frac{C_2 - C_1}{t_2 - t_1}$$

$$\text{Average velocity} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[C]}{\Delta t}$$

Factors Affecting The rate



Date _____
Page _____



Date _____
Page _____

- 1) Nature of Reactants
- 2) Surface area of Reactants
- 3) Conc. of Reaction
- 4) Temperature
- 5) Catalyst

Concentration of Reaction / Reactant

- Surface area of a solid can be increased by sub-division i.e. dividing the bigger particles in smaller.

Nature of Reactants —

- Rate of Homogeneous Reaction is higher than the Heterogeneous reactions.

- Rate depends on the physical state of reactants. If, liquid / gas / solid

- Rate depends on the number of collisions an encounter by the reacting species

Surface Area of Reactants —

Heterogeneous reaction

- occurs at interface of two phases of reactants

- If one reactant is solid, rate increases with increase in surface area of solid phase reactant.

- Surface area increases + area of contact

- blue reactant increase, Rate of encounter

- blue reactant increase — Rate increases.

Nature of reactants —

- * A chemical reaction involves the rearrangement of atoms by the reacting molecules to the product.
- Old bonds are broken and new bonds are formed
- the nature and the strength of the bonds in reactant molecule greatly influence the rate of transformation of product.

Temperature

Temperature In the most cases, the rate of a reaction in a homogeneous system is approximately doubled on tripled by an increase the temp. of only 10°C . In some cases the rise in reaction rates are even higher.

When the reaction is increased the temp. of sun is increased.

Order of reaction

The order is the number of conc. terms on which reaction rate of a reaction depends on the first power of the conc. of reactant.

Suppose,



$$\text{Rate of reaction} \propto (A)^m (B)^n (C)^l$$

Order of reaction $\rightarrow m+n+l$

If $\text{Rate} = kC^2$

Then the rxn is said to be first order.

When the rate is proportional to the product of two reactant conc. or the square of the conc. of a reactant, the reaction is of the second order.

Molecularity of a reaction

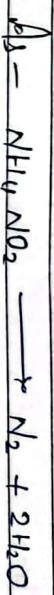
The molecularity of a reaction is defined as the number of molecules or atoms which take part in the process of chemical change / reaction.

~~order reaction~~

The term unimolecular was used for all first order reactions, the term bimolecular for reactions involving in the process of a chemical change.

The term unimolecular was used for all first order reactions, the term bimolecular for

order reactions.



$$\text{Molecularity of this rxn} = 1$$



$$\text{Molecularity of this rxn} = 2$$

Primary & Complex Reaction

Primary & Elementary Reactions

That rxn which is complete in only one step, and the molecularity of that rxn is maximum i.e. known as primary reaction.

Complex Reactions

Such rxn which is not complete in one step, but complete in several steps, then such rxn is called complex rxn.

Complex reaction is that which occurs in two or more steps

* Order of rxn will be 0, 1, 2, 3 or fractional

The term unimolecular was used for all first

~~order reaction~~

* High molecularity of reaction is very rare.

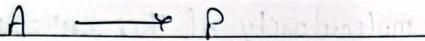
The molecularity of reaction with high molecularity can be explained on the basis of the kinetic molecular theory.

$$N_2 + O_2 \rightarrow NO + NO$$

2

Zero order reaction

A chemical reaction whose rate does not depend on conc. of reactants is called a zero order chemical reaction.



$$\begin{aligned} t = 0 & \quad \text{conc.} = [A]_0 \\ t = t & \quad \text{conc.} = [A] \end{aligned}$$

for zero order

$$\text{rate} \propto [A]^0$$

$$\text{rate} = k[A]^0 \quad (i)$$

$$\text{rate} = -\frac{d[A]}{dt} \quad (ii)$$

$$\text{from equ. } (i) \neq (ii)$$

$$\Rightarrow k[A]^0 = -\frac{d[A]}{dt} \quad \therefore [A]^0 = 1$$

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

$$\Rightarrow -kdt = -d[A] \quad (iii)$$

On integrate both side of eqn (iii)

$$-\int kdt = \int d[A]$$

$$[A] = -kt + c \quad (iv)$$

if $t = 0$ & $[A] = [A]^0$ then,

$$[A]^0 = kt_0 + c$$

$$[A]^0 = c$$

Zero Order Reaction

A chemical reaction whose rate does not depends on conc. of reactants is called a zero-order chemical reaction.



$$\begin{aligned} \text{When, } t = 0 & \quad \text{conc.} = [A]^0 \\ t = t & \quad \text{conc.} = [A] \end{aligned}$$

for the zero order reaction, rate of reaction

$$\text{rate} = k[A]^0 \quad (i)$$

change in the conc. of (rate of reaction) reactant.

$$\text{rate} = -\frac{d[A]}{dt} \quad (ii)$$

$$\text{for equ. } (i) \neq (ii)$$

$$\Rightarrow k[A]^0 = -\frac{d[A]}{dt} \quad \therefore [A]^0 = 1$$

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

$$\Rightarrow -kdt = d[A]$$

$$\Rightarrow -\int kdt = \int d[A]$$

$$\Rightarrow -kt + c = [A] \quad (iv)$$

When c is Integral Constant,
if $t = 0$ and $[A] = [A]^0$.

Put the value of eqn (iv)

$$\Rightarrow [A] = -kt + c$$

$$\Rightarrow [A]^0 = -k \times 0 + c$$

$$\Rightarrow c = [A]^0$$

Again put the value of c in eqn

$$\Rightarrow [A] = -kt + [A]^0$$

$$\Rightarrow [A] = -kt + [A]^0$$

$$\Rightarrow k_t = [A]^0 - [A]$$

$$\Rightarrow k = \frac{[A]^0 - [A]}{t} \quad \text{(v)}$$

$k = \text{Initial conc.} - \text{End conc.}$

Time

if we put Initial conc. $[A]_0 = a \text{ mol l}^{-1}$
And, After t time conc. is $(a-x) = [A] \text{ mol l}^{-1}$
then,

$$k_t = a - (a-x)$$

$$k_t = \frac{x}{t} \rightarrow 0$$

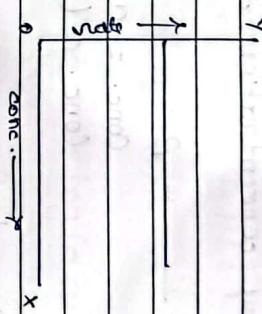
for zero order reaction.

if we plot a graph of conc. of time
we find a straight line $y = mx + c$
and slope is $-k$

y

$[A]^0$

$k = \text{slop}$

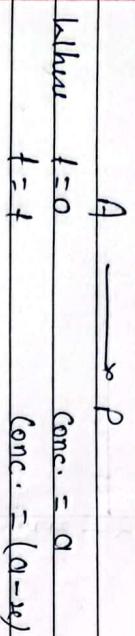


if we plot the graph b/w rate and conc.
then we found straight parallel with concentration.



First order Reaction

A chemical reaction in which rate of a reaction is proportional to the primary concentration of reactant.



For the first order reaction,

rate of rxn,

$$\therefore -\frac{dx}{dt} \propto (a-x) \quad \text{(i)}$$

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

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

Where k is constant, known as rate constant.

Integrate both side

$$\int \frac{dx}{(a-x)} = kxdt$$

$$\therefore -\log(a-x) = kt + c \quad \text{(ii)}$$

If $t=0$, then $x=0$

Put the value of $t=0$ in eqn (i)

$$-\log(a-0) = kx_0 + c$$

$$c = -\log a$$

Put the value of c in eqn (i)

$$-\log(a-x) = kt + c$$

$$\Rightarrow -\log(a-x) = kt + [-\log a]$$

$$\Rightarrow -\log(a-x) = kt - \log a$$

$$\Rightarrow \log a - \log(a-x) = kt$$

$$\Rightarrow \log \frac{a}{a-x} = kt$$

$$\log \frac{a}{a-x} = kt$$

$$\Rightarrow 2.303 \log_{10} \frac{a}{a-x} = kt$$

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$

it is known as
first order of rxn.

Rate constant

$$k = \frac{2.303}{t} \log \left(\frac{a_0}{a-x} \right)$$

Thus the rate constant for the "First order rxn" is independent of the conc. it has unit time.

Second Order Reaction

in which rate of a reaction is proportional to the ^{primary} concentration of reactant.



where

$$t = 0 \quad \text{Conc.} = a$$

$$t = t \quad \text{Conc.} = a - u$$

for the second order reaction,

$$\Rightarrow \frac{dt}{dt} \propto (a - u)^2 \quad \text{(i)}$$

$$\Rightarrow \frac{dt}{dt} = k(a - u)^2 \quad \text{(ii)}$$

$$\Rightarrow \frac{dt}{(a - u)^2} = k dt$$

On integration both side,

$$\Rightarrow \int \frac{dt}{(a - u)^2} = \int k dt$$

$$\Rightarrow (a - u)^{-2+1} = kt + c$$

$$\Rightarrow (a - u)^{-1} = kt + c$$

$$\Rightarrow \frac{1}{(a - u)} = kt + c \quad \text{(iii)}$$

where c is integral constant.

If we put $u = 0$ & $t = 0$ thus,

$$\Rightarrow \frac{1}{(a - 0)} = kt + c$$

$$\Rightarrow \frac{1}{(a - 0)} = k \cdot 0 + c \Rightarrow c = \frac{1}{a}$$

$$c = \frac{1}{a}$$

Put the value of c in eqn (iii)

$$\Rightarrow \frac{1}{(a - u)} = kt + \frac{1}{a}$$

$$kt = \frac{1}{a} - \frac{1}{(a - u)}$$

$$kt = \frac{1}{a(a - u)}$$

$$k = \frac{1}{t} \cdot \frac{1}{a(a - u)}$$

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

Rate Constant —

$$k = \frac{1}{t} \cdot \frac{1}{a(a - u)}$$

= Concentration \times Concentration \times Time

= conc. \times time \Rightarrow mol/liter \times time

$$\text{mol}^{-1} \text{dm}^{-3}$$

Thus the unit of k for a second order reaction are $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$

Third Order Reaction

A chemical reaction which rate of a reaction is proportional to the triply concentration of reactant.



$$\begin{aligned} t = 0 & \quad \text{Conc.} = a \\ t = t & \quad \text{Conc.} = a - rt \end{aligned}$$

For the third order reaction,

$$\text{rate of reaction} =$$

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

$$\Rightarrow \frac{dx}{dt} = k(a-x)^3 \quad \text{(i)}$$

Rearranging equation (i), we have,

$$\Rightarrow \frac{dx}{(a-x)^3} = kdt$$

On integrating both sides,

$$\Rightarrow \int \frac{dx}{(a-x)^3} = \int kdt$$

$$\Rightarrow \int (a-x)^{-3} dx = \int k dt$$

$$\Rightarrow 2(a-x)^{-2} = kt + C$$

$$\Rightarrow \frac{1}{2(a-x)^2} = kt + C \quad \text{(ii)}$$

Where C is integral constant
if $x = 0$, $t = 0$

Put the value of x of t in eqn. (ii)

$$\Rightarrow \frac{1}{2(a^2 - 2x^2)} = kt + C$$

$$\Rightarrow \frac{1}{2(a^2 - 2x^2)} = k0 + C$$

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

Again put the value of C in eqn. (ii)

$$\Rightarrow \frac{1}{2(a-x)^2} = kt + \frac{1}{2a^2}$$

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

$$kt = \frac{a^2 - a^2 - x^2 - 2ax}{2a^2(a-x)^2}$$

$$kt = \frac{2(a^2 - ax - x^2)}{4a^2(a-x)^2}$$

This is third order reaction.

Half-life of a Reaction

- The time required for the concentration of a reactant to decrease to the half-life initial value.
- H is denoted by the symbol $t_{1/2}$ up to 5

Half life for zero order kinetic

$$k = \frac{x}{t_{1/2}} \rightarrow \text{Initial Concentration}$$

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

Half life for first order Reaction

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

Substituting value in the integrated rate

$$\text{Equation, } k = \frac{2.303}{t_{1/2}} \log \frac{a}{a-x}$$

$$= \frac{2.303}{t_{1/2}} \log 2$$

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

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

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

Half life for a Second Order Reaction

for 2nd order the integrated rate equation is-

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

When one-half life has elapsed
 $(a-x) = \frac{1}{2}a$

And, we have

$$kt_{1/2} = \frac{1}{\frac{1}{2}a} - \frac{1}{a}$$

$$kt_{1/2} = \frac{2}{a} - \frac{1}{a}$$

Solving for $t_{1/2}$ we get

$$t_{1/2} = \frac{1}{ka}$$

half life for a 2nd order reaction depends on initial concentration

Half life for 3rd order Reaction -

For 3rd order the integrated rate equation is

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

$$\text{or } 2k_i t_{1/2} = \frac{1}{(a-x)^2} - \frac{1}{a^2}$$

$$2k_i t_{1/2} = \frac{1}{\left(\frac{a}{2}\right)^2} - \frac{1}{a^2}$$

$$\text{rate} = k'[A][B]$$

$$2k_i t_{1/2} = \frac{4}{a^2} - \frac{1}{a^2}$$

$$t_{1/2} = \frac{3}{2k(a)^2}$$

$$\text{or } t_{1/2} = \frac{1.5}{k(a)^2}$$

✓ Pseudo-order Reaction

→ A reaction in which one of the reactant is present in large excess. Since it is an elementary reaction, its rate law can be written as

→ The experimental order which is not the actual one is referred to as the pseudo order. Let us consider a reaction,



in which the reactant B is present in large excess. Since it is an elementary reaction, its rate law can be written as

$$\text{rate} = k[A][B]$$

As B is present in large excess, its concentration remains practically constant in the course of reaction. Thus the rate law can be written as

$$\text{rate} = k'[A]$$

$$k' = k_B$$

Thus the actual order of the reaction is second-order but in practice it will be first-order. Therefore the reaction is said to have a pseudo-first order.

Complex Reaction

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 as such reaction occurs in several steps where each step is elementary. Which molecularity is not defined but molecularity of each step can be defined and its rate depends on slowest step of the reaction.

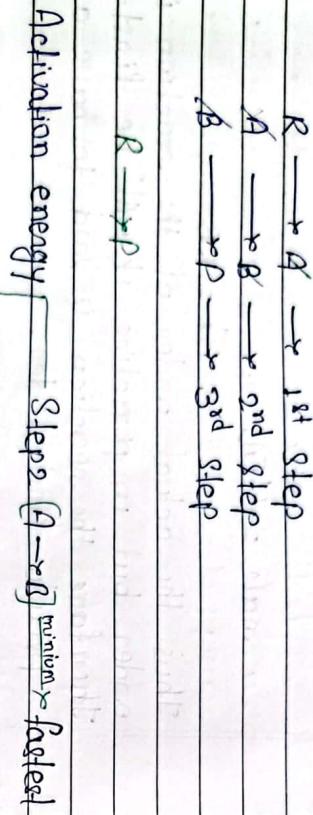
2) The reacting molecules must collide with proper orientation.

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 or 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.



Activation energy

Step $[R \rightarrow A]$ minimum → fastest

Rate determining Step

✓ # Theories of Chemical Kinetics

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

1. The colliding molecules must possess sufficient kinetic energy to cause a reaction.

The figure shows the activation energy. E_a is the minimum energy necessary to cause a reaction b/w 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 pass the barrier and thus type of collisions are unproductive.

2. The molecule must collide with correct orientation

The reaction molecules must collide with favourable orientation. The correct orientation is that which ensure direct contact b/w 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 orientation and

z = Collision frequency.

Catalyst

A catalyst is defined as a substance which alters the rate of a chemical reaction, if self remaining chemically unchanged at the end of the reaction. This process is called catalysis.

* A catalyst may increase or decrease the rate of reaction.

→ which increase rate of reaction is called positive catalyst and process is called positive catalysis or simply catalysis

→ A catalyst which the rate of reaction is called negative catalyst and process is called negative catalysis.

Types of Catalyst

There are two main types of catalysis —

- Homogeneous Catalysis
- Heterogeneous Catalysis
- Enzyme Catalysis

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 liquid (solution) phase.

Example of Heterogeneous Catalysis in Gas-Phase

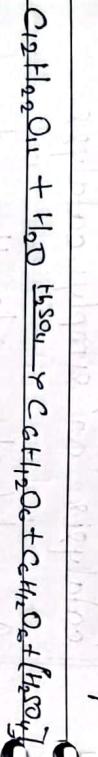
- Phase →

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



- b) Example of homogeneous catalysis in solution phase

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



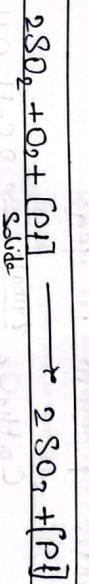
Heterogeneous Catalysis

The catalyst in which the catalyst is in a different physical phase from the reactant is termed heterogeneous catalyst. In this catalysis reaction one in the gas phase while the catalyst is a solid. This process is also called contact catalyst since the reaction occurs by contact of reactant with the catalyst surface.

- c) Example of heterogeneous catalysis with gaseous reactant

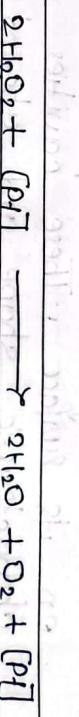
- Combination of Sulfur dioxide (SO_2) and oxygen in the presence of finely divided

platinum or vanadium pentoxide V_2O_5



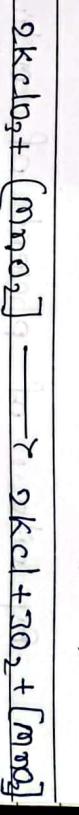
- d) Heterogeneous Catalysis with liquid reactants

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



- e) Heterogeneous Catalysis with solid reactants

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

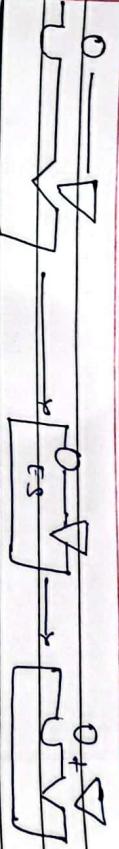


Enzyme Catalysis | Biological Catalysis

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

- f) - Inversion of cane-sugar $[\text{C}_12\text{H}_{22}\text{O}_11]$ 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 characteristic shape and abound in active groups $[NH_2, COOH, SH, OH]$ are termed Active center sites. 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 presence of active groups the enzyme forms an activated complex with the substrate which at once decomposes to yield the product.

Michaelis & Menten proposed the following mechanism for zymase catalysis:

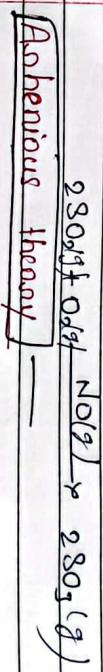


where,

E = Enzyme, S = Substrate (Reactant)
 ES \rightarrow Activated complex, P = Product.

(a) Homogeneous Catalysed

Example of homogeneous catalysis In the lead chamber process during the manufacture of sulphuric acid, the presence of nitric oxide gas helps in catalysing the sulphur dioxide.



Adsorption

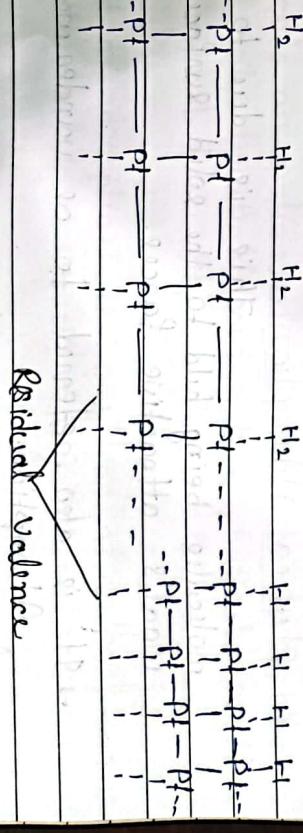
The phenomenon of concentration of molecule of a gas on liquid or solid surface is called adsorption.

Langmuir Adsorption Isotherm

- ① The adsorbed molecules do not interact with one another.
- ② The enthalpy of adsorption is independent of the surface coverage.
- ③ There are a finite number of surface sites where a molecule can absorb.
- ④ The layer of the adsorbed gas is unimolecular.

$\frac{\alpha}{m} = \frac{k_1 k_2 p}{1 + k_1 p}$

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



The adsorbed atoms on molecules can be held on the surface of a metal such as platinum (Pt) by physical Vanden-waals force or chemical force 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 molecule being held to the solid surface by vander waal's attractive force.

H is also adsorbed to a vanderwaal's

Adsorption

A) Adsorption of hydrogen on oxygen on charcoal is physical adsorptio.

Types of Adsorption

The adsorption of a gas mainly of two types.

A) Physical Adsorption

This is due to the gas molecule being held to the solid surface by vander waal's attractive forces.

H is also referred to as vander waal's Adsorption.

A) adsorption of hydrogen on oxygen on charcoal is physical adsorptio.

Hydrogen on charcoal is adsorbed by vander waal's attractive force.

b) Chemical adsorption or chemisorption

In this kind of adsorption, The gas molecules being held to the solid surface by vander waal's attractive force.

or alone are held to the solid surface by

chemical bonds.

Hydrogen is chemisorbed on nickel in nature

Hydrogen is chemisorbed on nickel.

* Composition of physical adsorption & chemisorption

i) Caused by intermolecular ii) Caused by chemical vanderwaal's force . bond formation.

iii) Depends on nature of

iii) Much more specific gas easily liquefiable gases than physical adsorption. one adsorbed readily

iii) Heat of adsorption is small [about 20.93 kJ/mol^2] [range $(23.74 - 43.63 \text{ kJ/mol}^2)$]

iv) it is reversible . if is irreversible

v) occurs rapidly at low vi) increase with increase temperature, decrease with of temperature increasing temperature

Surface Area

v) Increase of pressure change of pressure increase adsorption has no such effect decrease of pressure cause desorption

vii) same multimolecular forms unimolecular layer on adsorbent surface

Factors affecting the extent of gas-solid adsorption
The extent to which adsorption will happen on a solid surface depends on following:

viii) Nature of adsorbent

The adsorption of the gas depends on the nature of the adsorbent.
A gas can be adsorbed on different adsorbent surface in different amount.

Ex

Hydrogen is weakly adsorbed on the alumina surface where as it strongly increases 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.

- adsorbed on the nickel surface under certain condition.

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

ix) Nature of the gas

In general if a gas is more liquefiable it will be more easily absorbed.

x) An example

like NH_3 , HCl , Cl_2 , CO_2 which can be liquified easily are more readily adsorbed on the solid surface rather than permanent gases like O_2 , H_2 etc.

Heat of Adsorption

Heat of adsorption is defined as the energy liberated when 1 gm mole of gas is adsorbed on the solid surface.

→ In physical adsorption, gas molecule concentrated on the solid surface. Thus it is similar to the condensation of a gas to liquid.

→ Thus pure adsorption like condensation of a gas to liquid is an exothermic process.

→ When the temp. increased the kinetic energy of the gas molecule also increased, which results in more no. of collision b/w the molecules of the gas.

Effect of pressure

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 absorption increased due to an increase in the gas molecule striking on the surface.

Thus an increase in the

pressure increases the rate of adsorption linearly, but after 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 these sites. Hence,

At the point extent of adsorption will be independent of the pressure.

Effect of temp

physical adsorption occurs rapidly at low temp. and chemisorption like most chemical change, generally with temp.

thus a rise of temp can often cause physical adsorption to change to chemisorption. \rightarrow Nitrogen for example is physically adsorbed on iron at 463 K but chemisorbed to form a nitride at 773 K

Adsorption Isotherme

An adsorption isotherms is a graph that represents the variation in the amount of adsorbate adsorbed on the surface of the adsorbent with the change in pressure at a constant temp.

Freundlich Adsorption Isotherm

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

$$\frac{M}{m} = k p^{\frac{1}{n}}$$

Amount of adsorbate P
mass m of adsorbent

where 'M' is the mass of the gas adsorbed on mass 'm' of the adsorbent at pressure 'P', 'k' and 'n' are constant that depends on the nature of the adsorbent and the gas at particular temp.

The mass of the gas adsorbed per gram of the adsorbent is plotted against pressure in the form of a curve for the relationship. Here,

At a fixed pressure, physical adsorption decreases with increase in temp. The curve reaches saturation at high pressure

$$\frac{m}{M}$$

$P \rightarrow$

\rightarrow Freundlich Isotherm: A plot of mass of adsorbed gas per unit mass of adsorbent.

Now if we take the log of the above equation,

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

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

\rightarrow The slope of straight line gives the value of $1/n$, while the intercept on the y-axis gives the value of $\log K$.

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Tangmuir Adsorption Isotherm

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

Assumption —

Langmuir made the following assumptions if the plot shows a straight line the Freundlich isotherm is valid, otherwise it is not.

- The layer of the gas adsorbed on the solid adsorbent is one molecule thick.
- The adsorbed layer is uniform all over the adsorbent.

(3) There is no interaction b/w 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 when evaporate are desorbed, rapidly. A dynamic equilibrium is eventually established b/w 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 area $(1-\theta)$ and the pressure P of the gas.

Hence,

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

$$\theta = k' \frac{KP}{1+KP}$$

$$\theta = k' \frac{KP}{1+KP} \quad (1)$$

Where 'K' is a new constant (Equation is given). The relation b/w the amount of gas adsorbed to the pressure of the gas at constant temperature and is known as Langmuir Adsorption isotherm.

→ At equilibrium the rate of desorption is equal to the rate of adsorption that is

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

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

$$\theta = \frac{k_a P}{k_d + k_a P}$$

$$\text{or, } \theta = \frac{(k_a/k_d)P}{1 + (k_a/k_d)P}$$

The equation ② is similar to an equation for a straight line. Thus if θ/P is plotted against P , we should get a straight

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

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

The amount of the gas adsorbed per gram of the adsorbent is proportional to θ .

line with slope $1/k'$ and intercept $1/k''$. It was found in most cases that the actual curves were straight line. Thus Langmuir isotherm is often satisfied.



Verification of Langmuir isotherm holds at low pressure but fails at high pressure.

As stated above Langmuir above Langmuir Adsorption isotherm may be written as -

$$\frac{P}{n} = \frac{1}{k'} + \frac{P}{k''}$$

If pressure is very low then the factor P/k'' may be ignored.

$$x = k'P$$

If the pressure is very less k'/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 of adsorbed reaches a constant value k' when the adsorbent surface is completely covered with a unimolecular layer of the gas.

A) thus stage adsorption is independent of pressure.

Only Question —

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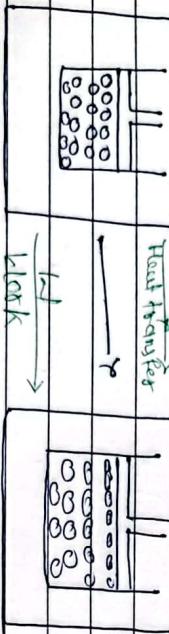
In other words, heat energy can never be converted completely into work and it is also —

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Q1) Discuss first and second laws of thermodynamics. Explain entropy and enthalpy. Illustrate Gibbs free energy and spontaneous chemical reaction.

First law of thermodynamics —

The first law of thermodynamics states that energy can neither be created nor if be destroyed, but can only be transformed from one form to another. Put another way, the law states that the total energy of an isolated system remain constant though it may change from one form to another.



Since the flow of heat following the temperature gradient, the heat absorbed (Θ_2) and heat rejected (Θ_1) can be related directly to temp. T_2 and T_1 respectively as —

$$\text{Efficiency} = \frac{W}{\Theta_2} = \frac{\Theta_2 - \Theta_1}{\Theta_2}$$

and $\frac{\Theta_2}{\Theta_1} = \frac{T_2}{T_1}$

$\Delta E = q - w$,
q - the amount of heat supplied

w - work done by the system

Second law of thermodynamics —

It state that, while all other forms of energy can be completely converted to heat the complete conversion of heat into any other form of energy cannot take place without leaving some changes in the system.

— and it is also isothermally unavailable for doing work. The fraction of heat that a machine can convert into work is known as its efficiency.

If we consider a hypothetical steam engine operating reversible b/w an upper temp. T_2 and a lower temp. T_1 . It absorbs heat Θ_2 from the hot boiler our source and by means of the working substance, steam, it converts that quality Θ_2 into work, and rejects heat Θ_1 to the cold reservoir or sink. The efficiency of such an engine can be given by the expression.

$\text{Efficiency} = \frac{W}{\Theta_2} = \frac{\Theta_2 - \Theta_1}{\Theta_2}$

$$\frac{\Theta_2}{\Theta_1} = \frac{T_2}{T_1}$$

By combining the above equation, we can write Entropy —

Entropy Entropy is a thermodynamic state quantity that is measure of the random or disorder of the molecules of the system. The entropy of a system is a state function and depends only on the initial & final state.

of the system.

The change in entropy ΔS for any process in given by the equation -

$$\Delta S = S_{final} - S_{initial}$$

Gibbs free energy —

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.

$$G_f = H - TS$$

G_f - Gibbs free energy kJ mol^{-1}
 H - heat of combustion, enthalpy kJ mol^{-1}

T - Temperature kelvin
R - Entropy $\text{J mol}^{-1} \text{K}^{-1}$

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. the change in the product of the temperature times the entropy of the system.

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

If ΔG_f is less than 0 ($\Delta G_f < 0$) for any reaction, reaction will be favourable or spontaneous and if $\Delta G_f > 0$ reaction will be unfavourable or non-spontaneous.

Spontaneous Chemical Reaction —

A spontaneous reaction is a reaction that favours the formation of products at the conditions under which the reaction is occurring. The entropy of the system increasing during a combustion reaction.

→ The combination of energy decrease, entropy increase indicates that combustion reactions are spontaneous.

In other words entropy can be defined as for a reversible change taking place at a fixed temp. T. That is

$$\Delta S = \frac{Q}{T}$$

If heat is absorbed, then ΔS is positive and there will be increase in entropy. If heat is evolved as 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 S.I unit - Joules per degree i.e. $\text{J mol}^{-1} \text{K}^{-1}$

Enthalpy

The total heat content of a system at constant temp. is equivalent to the initial energy E plus the PV energy.

- This is called enthalpy of the system and is denoted by the symbol H .

$$H = E + PV$$

Where

E = initial 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 ,

$$\Delta H = [E_2 + P_1 V_2] - [E_1, P_1 V_1]$$

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

Types of System

- Open System
- closed System
- Isolated System

Open Such a system which can exchange mass & exchange energy with their surrounding known as open system.

Close Such a system which can't exchange mass only energy exchange with their surrounding known as close system.

Isolated Such a system which can't exchange mass of energy with their surrounding known as isolated system.

$$\Delta H = \Delta E + \Delta PV$$

If P is constant while gas is expanding,

$$\Delta H = \Delta E + PV$$

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

$\Delta H = \Delta E + PV$ for constant volume.

Thermodynamics

Heat in motion → System + Surrounding \rightarrow _↓ ^{part under excep system} Universe

Boundary

It can be rigid & flexible
Can be Diathermic & Adiabatic

Diathermic

→ ^{conducting} Across heat change easily.
→ ^{insulating} Across heat cannot flow.

$$\Delta Q = 0$$

Reversible Process — Such process which contains their second step of stage but contains their previous stage.



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Properties of thermodynamics —

Extensive / Qualitative Intensive

- (Amount of matter) depend → Doesn't depends upon size of sample or amount
- upon \propto [or volume of matter]
- Depend upon size of sample of matter (or nature of matter)
- Ab Mass, Volume, No. of Density, Refractive index, Specific heat capacity
- Mole, Heat capacity, Enthalpy, Entropy, Gibbs free Energy, Temperature, Pressure, Viscosity
- Concentration, Molarity

- Types of thermo-D-process —
- ① Isobaric Process — Constant pressure.
 - $\Delta P = 0$

② Isochoric Process — Constant volume.

$$\Delta V = 0$$

- ③ Isothermal Process — Constant temp.

By ~~heat~~ Spontaneous process

Spontaneous Process —

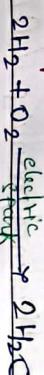
→ Any process which has tendency to occur —

- 1) By itself
- 2) By proper initiation
- 3) Under given condition

Also Spontaneous process —

- ① Sugar dissolution in water
- ② Salt dissolution in water
- ③ Evaporation of lake
- ④ Flow of heat from high temp to lower temp.
- ⑤ Diffusion of gas from higher pressure \rightarrow lower pressure
- ⑥ Melting of ice (0°C)

By proper initiation —



- ④ Adiabatic Process — $\Delta q = 0$ also Heat change
- ⑤ Cyclic Process — Such a process which occurs in several process, but at last final process is same as initial process.

First Law of Thermodynamics —

Law of Conservation of energy

Limitation of 1st law of thermodynamics

- 1) Heat can flow from hot body to cold body But not from cold body to hot body
- 2) Flow of heat [direction] not defined.
- 3) Reversibility process & spontaneity not defined.
- 4) Natural spontaneous process are irreversible.



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Non-spontaneous process

A process which has no tendency to occur.

1) By itself

2) Even after initiation

3) If continuous energy [externally] is supplied.

A —

Heat flow from body at low temp. — High temp.

Refrigerator

→ bodies cannot flow from lower height to upper height

Pump, motor etc.

Zeroth law of thermodynamics

Zeroth law of thermodynamics states that if two thermodynamic systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

it is given by R.H. Fowler in 1931

Second law of thermodynamics / Gibbs

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Enthalpy — H

Heat content of system at constant pressure.

$$\Delta H = \Delta E + \Delta nRT$$

$$H = U + PV$$

$$U \rightarrow \text{Internal energy}$$

$$P \rightarrow \text{External pressure}$$

$$V \rightarrow \text{Volume}$$

$$\Delta H = \Delta U + \Delta PV$$

$$\Delta H = \Delta U + [P_2V_2 - P_1V_1]$$

Enthalpy = Pressure \times Temperature + internal energy
At constant pressure, the enthalpy of a system is sum / addition of internal energy with the multiplication / product of pressure and volume.

$$\Delta H = H_2 - H_1 \quad (i)$$

$$H_1 = E_1 + P_1V_1$$

$$H_2 = E_2 + P_2V_2$$

Put the value of H_1 & H_2 in eqn (i)

$$\Delta H = [E_2 + P_2V_2] - [E_1 + P_1V_1]$$

$$\Delta H = (E_2 - E_1) + [P_2V_2 - P_1V_1] \quad (ii)$$

At constant pressure —

$$\text{At eqn } (ii) \quad P_2 = P_1 = P$$

$$\Delta H = \Delta E + P(V_2 - V_1)$$

$$\Delta H = \Delta E + P\Delta V$$

$$\boxed{\Delta H = \Delta E + \Delta PV}$$

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Heat Capacity

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Requirement of heat for increase of 1°C temp. of the system known as heat capacity.

If any system absorb temp. heat then increase in temp.

$$q \propto \Delta T$$

$$q = c \Delta T \quad c = \text{heat capacity constant}$$

The value of c is depend upon the size of body, state of component of body.

$$c = \frac{q}{\Delta T} \quad \text{J/K}$$

Specific Heat Capacity

Require heat for increase of 1°C temp. of the 1g of system product is known as Specific heat capacity.

$$q = c_s \Delta T \times m$$

$$c_s = \frac{q}{\Delta T \times m} \quad \text{J/K/g}$$

Entropy

S

Measurement of randomness

- P - The number of phase material
- F - The number of degree of freedom
- C = The number of component of a system
- Ω = represents two variable [pressure & temperature]

It can mathematically represented as -

$$P + F = C + 2$$

Q1 Explain the zeroth law of thermodynamics?

The term zeroth law was coined by Ralph H. Fowler in 1921.

→ The zeroth law of thermodynamics tells us the concept of temp. 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 microscope properties like pressure, temperature, volume etc. are not changing in time.

Q2 What is phase rule or Gibbs Phase rule.

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 homogeneous substance.

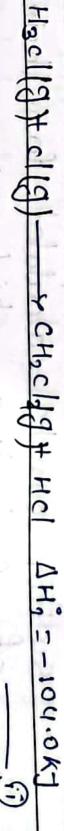
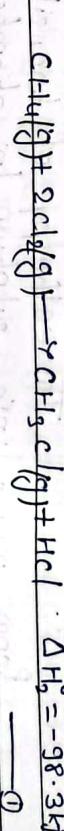
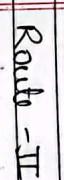
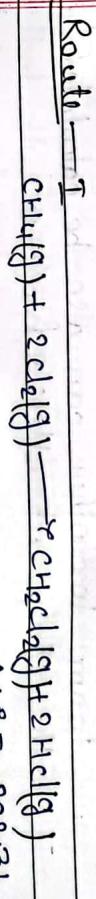
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Phase — A region of material that is chemically uniform physically distinct and mechanically separable.

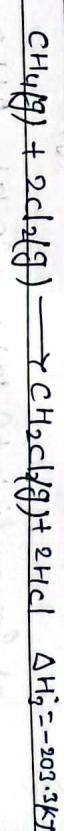
Component — Minimum number of independent species necessary to define the composition of all phase of a the system.

Degree of freedom —

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



Adding change in enthalpy of both step



Thus it can be clearly seen that no matter what path,

the total enthalpy change in the reaction is always the same

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

Application of Hess's Law

~~Solubility of solvents~~

Hess's law can be seen as an application of the principle of conservation of energy.

Qs - Considered the following two ~~route~~ method for preparation of methylene chloride (CH_2Cl_2) from the reaction blue methane (CH_4) and chlorine (Cl_2)

* Define Hess's law

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 changes for the individual steps or in other words the change in enthalpy in a chemical reaction at a constant temperature is not dependent on the process, and only dependent on the initial and final state of the chemical reaction.

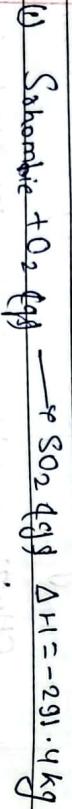
Application of Hess's law —

- Determination of heat of formation of substance which otherwise can not be measured experimentally —

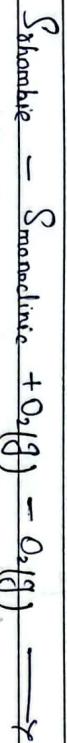
The heat of transition of one allotropic form to another can also be calculated with the help of Hess's law.

For example —

The enthalpy of transition from monoclinic sulphur to rhombic sulphur can be calculated from their heats of combustion which are



Subtracting eq ① from eq ② we get,



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

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

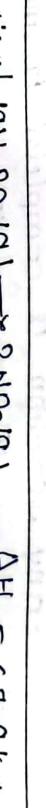
Thus heat of transition of rhombic sulphur is 4.0 kJ

3) Determination of heats of various reaction —

By using Hess's law we can calculate the heat of enthalpies of many reactions which otherwise cannot be measured directly.

For example

From the following equations that the enthalpy of dimerization of NO_2 can be calculated.



Subtracting eq ① from eq ③ we have



Thus the heat of dimerization of NO_2 is -58.6 kJ

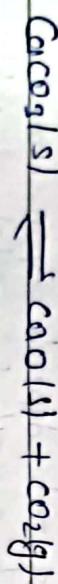
Phase

Phase may be defined as physically distinct, mechanically separable by otherwise such part of the system.

- Solid → Always form separate phase

Liquid →
if miscible → 1 phase
if immiscible → 2 phases

Gas →
Always 1 phase
Separate phase



Degree of freedom

Degree of freedom may be define as the number of intensive variable [temp., pressure, & conc.] that can be changed independently without disturbing the number of phase in equilibrium.