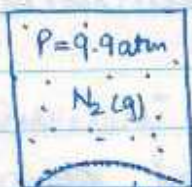
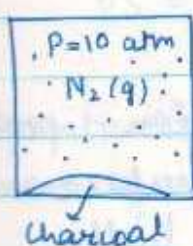


Surface Chemistry

• It is branch of chemistry which deals with phenomena taking place at surface or interface.
(gas-gas interface is not possible).
eg. rusting & crystallisation.

* Adsorption : Accumulation of molecular species on surface of substance as a result conc. of species at surface becomes more than its conc. in the bulk.



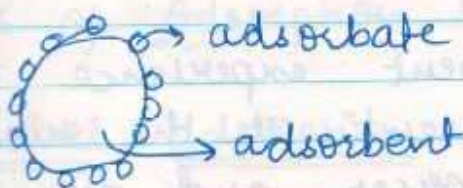
↳ charcoal

$$PV = nRT$$
$$\downarrow P = \frac{n}{V} \times \frac{RT}{1}$$

- eg. - Dye solⁿ + charcoal
- Gases + charcoal
- Raw sugar + animal charcoal
- Water vapours + silica gel.

* Adsorbate : Substances which get adsorbed.

* Adsorbent : Substances on which adsorbate gets adsorbed.



* Absorption : Conc. of substance will be same throughout.

For eg,

- CaCl_2 absorbs water vapour.

Note: rate of adsorption decreases with time while rate of absorption remains same throughout.

* Sorption : When both adsorption and absorption take place simultaneously.

For eg,

- when a chalk is placed in any solution particles of dye (ink) get adsorbed on its surface while particles of solvent get absorbed in bulk.

* Desorption : Removal of adsorbate particles from surface of adsorbent.

* Negative adsorption : Particles of solvent get adsorbed. As a result conc. of solute in solⁿ increases.

• Why adsorption takes place?

→ Particles present in adsorbent experience zero net force but particles present at the surface experience net inward forces and due to these unbalanced forces or rigid wall forces, those particles at surface attract other particles. As a

decrease in surface energy takes place in form of heat released so adsorption is exothermic process.

• Thermodynamics of adsorption :-

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

where,

ΔG = change in Gibbs free energy

ΔH = " in Enthalpy

T = Temp.

ΔS = Change in entropy / randomness

For spontaneous Process, $\Delta G < 0$

For non-spont. process, $\Delta G > 0$

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

spontaneity is driven by

a) decrease in enthalpy

b) increase in randomness.

During adsorption, entropy $\downarrow \Rightarrow \Delta S$ is -ve, still adsorption takes place, it means it is driven by enthalpy factor.

• Types of Adsorption :-

i) Physical adsorption or physisorption :-

In it particles of adsorbate & adsorbent are held together by weak Vanderwaal forces.

- Characteristics of Physisorption :

a) It lacks specificity.

→ Physical adsorption is not specific in nature.

For eg.

Charcoal can adsorb any of gases given



b) Extent of adsorption will depend on nature of adsorbate.

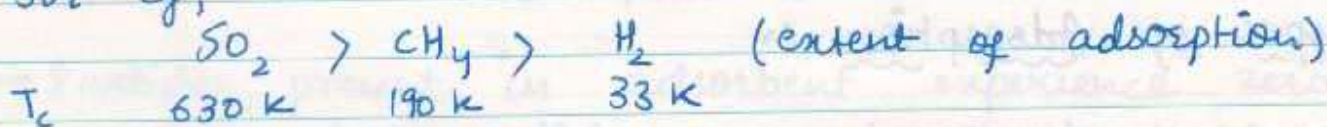
→ Easily liquifiable gases are adsorbed to a larger extent.

$$T_c = \frac{8}{27} \frac{a}{b^2}$$

$$T_c \propto a$$

Larger the value of T_c , larger will be the forces of attraction & more easily a gas can be liquified.

For eg,



For non-polar gases,

$a \propto$ Molar Mass

In polar & non-polar generally polar has larger value of a .

$$a_{\text{NH}_3} > a_{\text{N}_2}$$

$$a_{\text{H}_2\text{O}} > a_{\text{N}_2}$$

c) It is reversible in nature.

d) Physical adsorption follows the Charlier's principle.



→ As we $\uparrow P$, extent of adsorption \uparrow while on $\downarrow P$, extent will \downarrow .

→ on $\uparrow T$, extent of adsorption \downarrow

e) Extent of Adsorption will increase on increasing surface area of adsorbent.

f) Enthalpy change will be of order 20 to 40 kJ/mol.

g) It is multilayered phenomenon.

ii] Chemical Adsorption / Chemisorption :-

● Particles of adsorbate & adsorbent are held together by chemical bonds.

a) It is highly specific in nature.

→ For eg,

O_2 combines with metals while H_2 combines with transition metal.

b) Extent of adsorption also depends on nature of adsorbate.

c) It is irreversible in nature.

d) On \uparrow temp. (in low temp. range) extent of adsorption \uparrow coz that energy is used to provide necessary activation energy.

e) On \uparrow P, Extent \uparrow but on \downarrow P it will not change.

f) ~~E~~ Enthalpy change will be of order 80-240 kJ/mol

g) On \uparrow SA of adsorbent, adsorption will \uparrow

h) It is unilayer phenomena.

Note : Physisorption of gas adsorbed at low temp. may get converted into chemisorption at high temp.

• Freundlich adsorption isotherm (1909) :→

Freundlich proposed a relationship b/w extent of gases adsorbed on a solid surface and pressure of gas.

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

where,

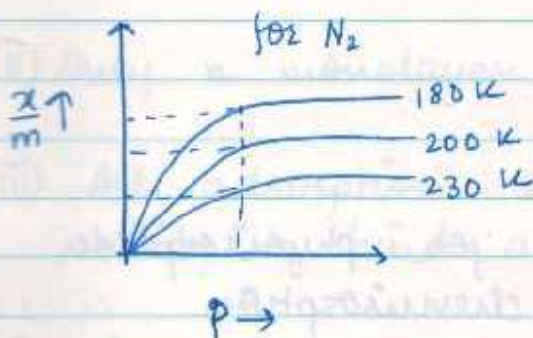
$\frac{x}{m}$ → extent of adsorption

k → constant

P → Partial pressure of gas at eq.

x → mass of adsorbate

m → mass of adsorbent



Probable values ⇒ $(0 < \frac{1}{n} < 1)$

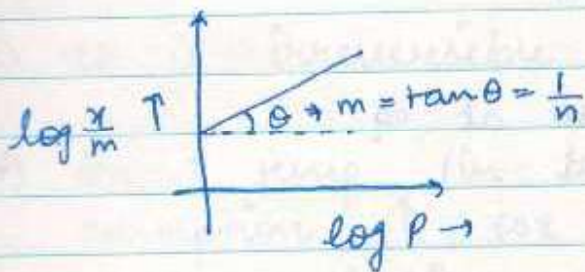
Calculation of 'n' :-

If a graph is plotted b/w $\log \frac{x}{m}$ v/s $\log P$ & it comes out to be straight line then gas is said to be following Freundlich adsorption isotherm. Value of 'n' can be calculated from slope of this line.

$$\frac{x}{m} = kP^{1/n}$$

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

\downarrow \downarrow \downarrow \downarrow
y = c + m x



Limitations,

- Freundlich fails at high pressure
- He's isotherm gives good results for physisorption but it is not suitable for chemisorption.

Adsorption of solute from solution :-

Exact mechanism is not known for this adsorption but still there are certain observations.

i) On $\uparrow T$, $\frac{x}{m} \downarrow$

ii) On \uparrow surface area of adsorbent, $\frac{x}{m} \uparrow$

iii) $\frac{x}{m}$ depends on nature of adsorbate

iv) $\frac{x}{m}$ also depends on conc. of solⁿ at Eq.

$$\frac{x}{m} = K C^{1/n}$$

where,

$C \rightarrow$ conc. of solⁿ at Eq.

Langmuir adsorption isotherm (1916):

It is based on KTG.

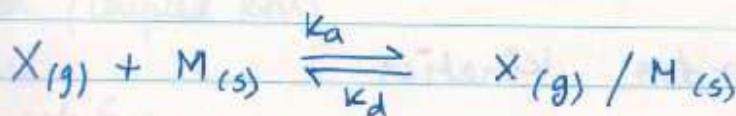
Assumptions,

i) all gases are considered as ideal

ii) Only a monolayer is formed

iii) All adsorption sites are equivalent w.r.t. their ability to bind a particular adsorbate particle.

iv) Once the adsorbate molecules are adsorbed, they become localised.



Let θ be the fraction of sites occupied.

Rate of adsorption $(r_a) = k_a P_x (1-\theta)$

Rate of desorption $(r_d) = k_d \theta$

At equilibrium,

$$r_a = r_d$$

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

$$\Rightarrow \theta = \frac{k_a P_x}{k_d + k_a P_x}$$

$$\Rightarrow \theta = \frac{kP}{1+kP}$$

where $k = \frac{k_a}{k_d}$

Amount of adsorption $(\frac{x}{m}) \propto \theta$

$$\frac{x}{m} = k' \theta$$

$$\Rightarrow \frac{x}{m} = \frac{k' k P}{1+kP}$$

$$\Rightarrow \boxed{\frac{x}{m} = \frac{aP}{1+bP}}$$

• a & b are called langmuir constants

At low pressure

$$1+bP \approx 1$$

$$\frac{x}{m} = aP$$

First order kinetics

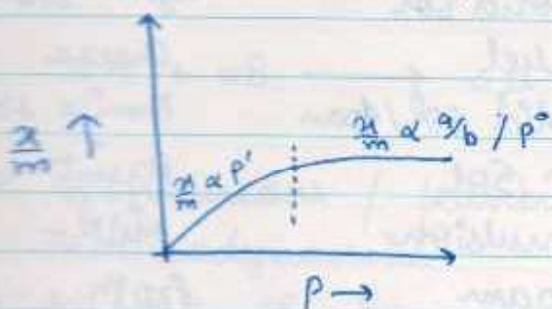
$$\boxed{\frac{x}{m} \propto P}$$

At high Pressure,

$$\frac{x}{m} = \frac{a}{p^{1/2} + b} = \frac{a}{b}$$

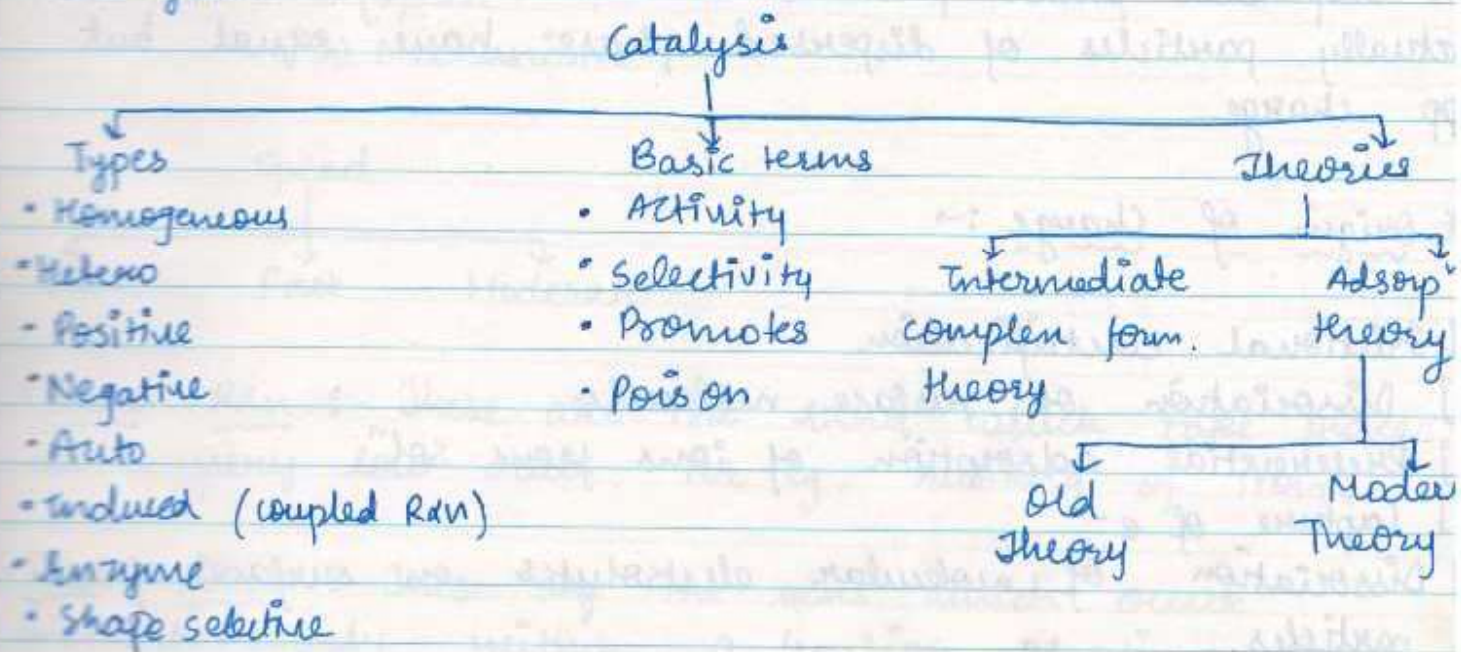
zero order kinetics

$\frac{x}{m}$ is independent of pressure



* Catalysis :

Catalysts are the substances which change rate of chemical rxn without quantitatively participating in it. & this whole phenomena is called Catalysis.



* Colloids :->

Dispersed Phase	Dispersion Medium	Colloid	Example
S	S	solid sol	lyem stones
L	S	gel	cheese
G	S	solid sol/foam	pumice stone
S	L	Sol	Paints
L	L	emulsion	Milk
G	L	Foam	foth
S	G	aerosol	Smoke, dust
L	G	aerosol	Fog, mist

* Charge on colloid :->

Colloid as a whole is neutral but generally charge on dispersed phase particles is called charge on colloid. Actually particles of dispersed phase have equal but opp. charge.

* Origin of Charge :->

- i] Frictional electrification
- ii] Dissociation of surface molecules
- iii] Preferential adsorption of ions from solⁿ
- iv] Capture of e⁻
- v] Dissociation of molecular electrolytes on surface of particles.