TRINITY COLLEGE FOR WOMEN NAMAKKAL

Department of Chemistry

PHYSICAL CHEMISTRY

ADSORPTION

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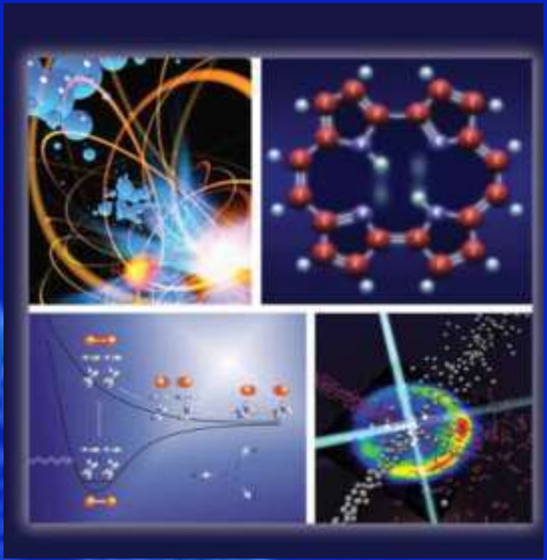
AP/Chemistry

What is chemistry?

Chemistry is the study of matter -Its composition, structure ,properties, transformation from one form to another, and the energy that accompanies its transformation.

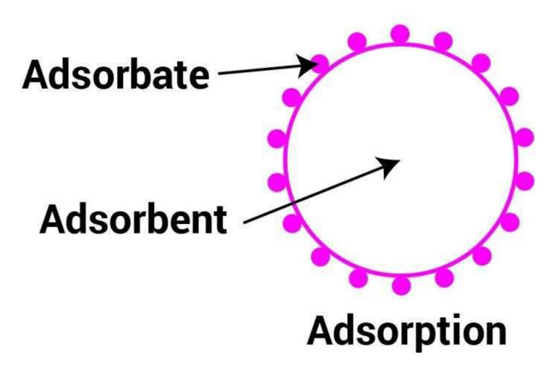


What is meant by physical chemistry?

It is concerned with the study of matter and energy and the relationship between them.

ADSORPTION : BAS IC

A mass transfer process which involves the accumulation of substance at the interface of two phases,such as, liquid-liquid ,gas-liquid,gas-solid,or Liquid-solid interface.



ADSORBATE- the substance which is adsorbed on the surface

ADSORBENT- the substance on which surface the adsorbate is adsorbed

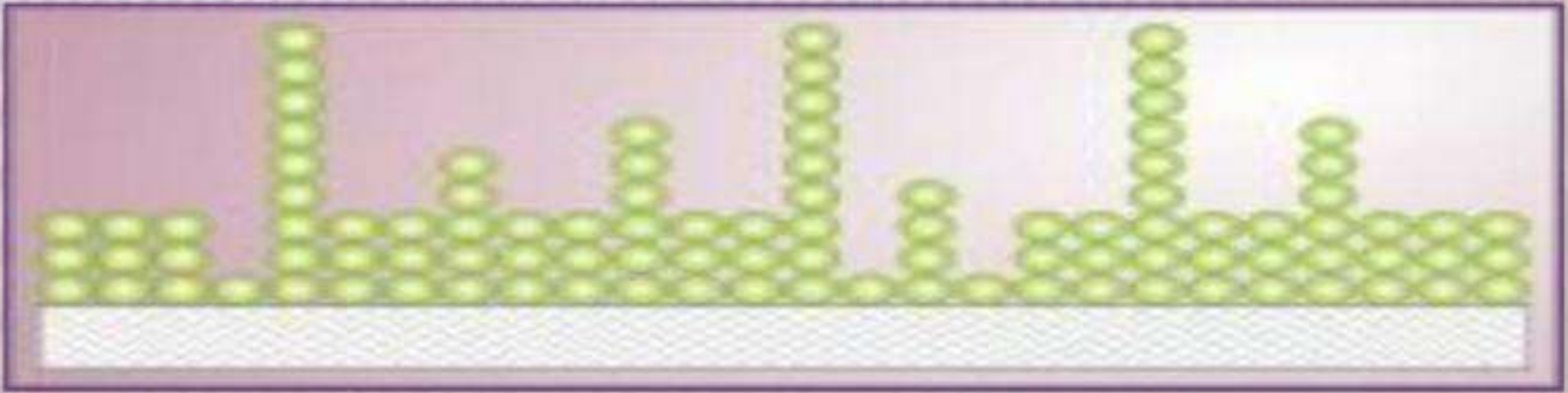
ADSORPTION is a spontaneous process i.e. Del G is negative

ADSORPTION is an exothermis process i.e. Del H is negative

ADSORPTION : PRINCIPLE

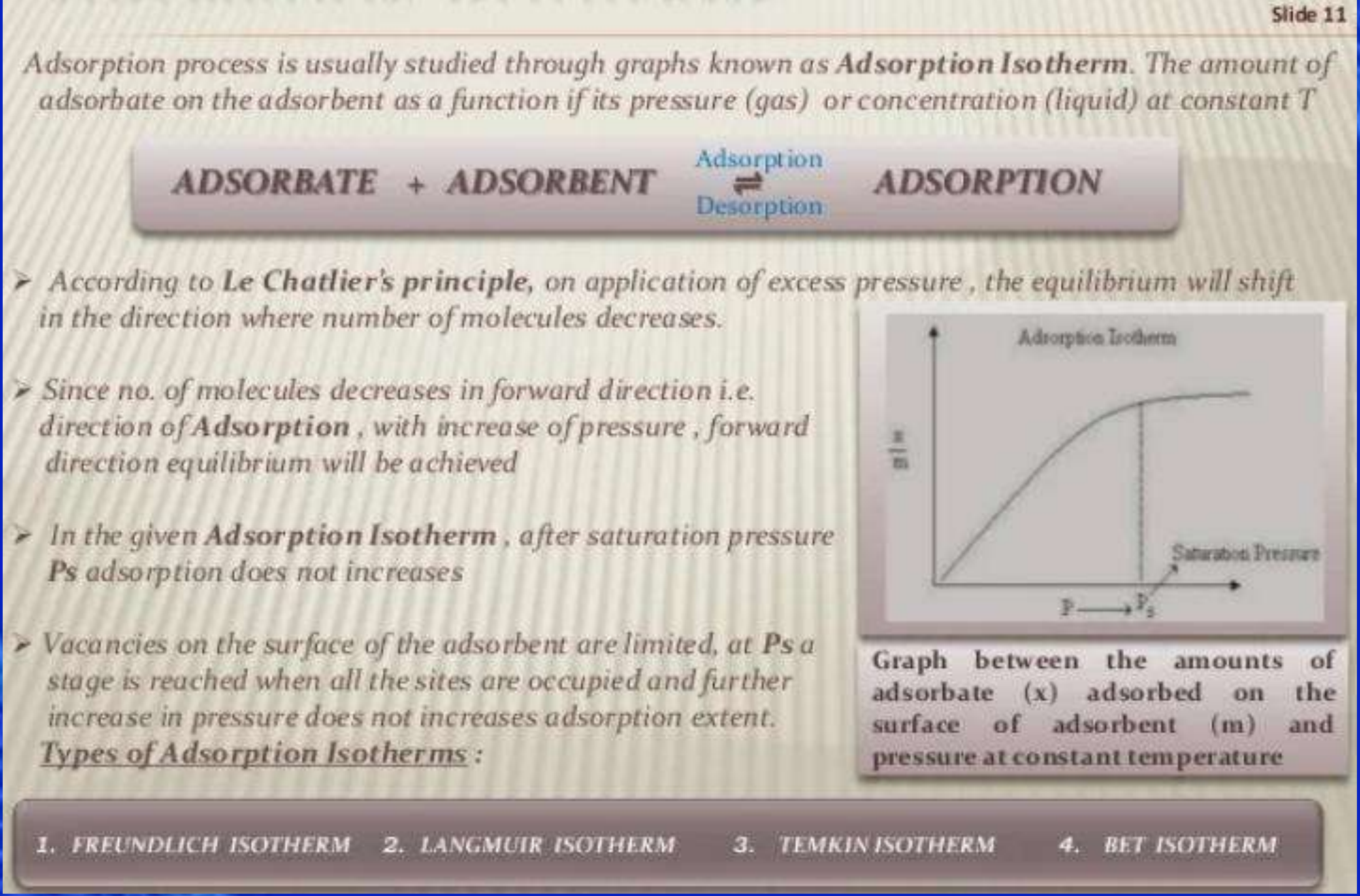
Driving Force for Adsorption

Adsorption is a surface phenomenon and consequence of surface energy
The surface of a liquid or solid is in a state of strain or unsaturation which results i
unbalanced residual force at the surface
These unbalanced residual forces results in higher surface energy. Consequently, the surface of liquids/ solids always have a tendency to attract and retain the molecular species with which it comes in contact. This tendency is responsible for the phenomenon of
Adsorption



Brunauer, Emmett and Teller's model of multilayer adsorption is a random distribution of molecules on the material surface.

ADSORPTION ISOTHERM



Adsorption process is usually studied through graphs known as ***Adsorption Isotherm****. The amount of adsorbate on the adsorbent as a function if its pressure (gas) or concentration (liquid) at constant T*

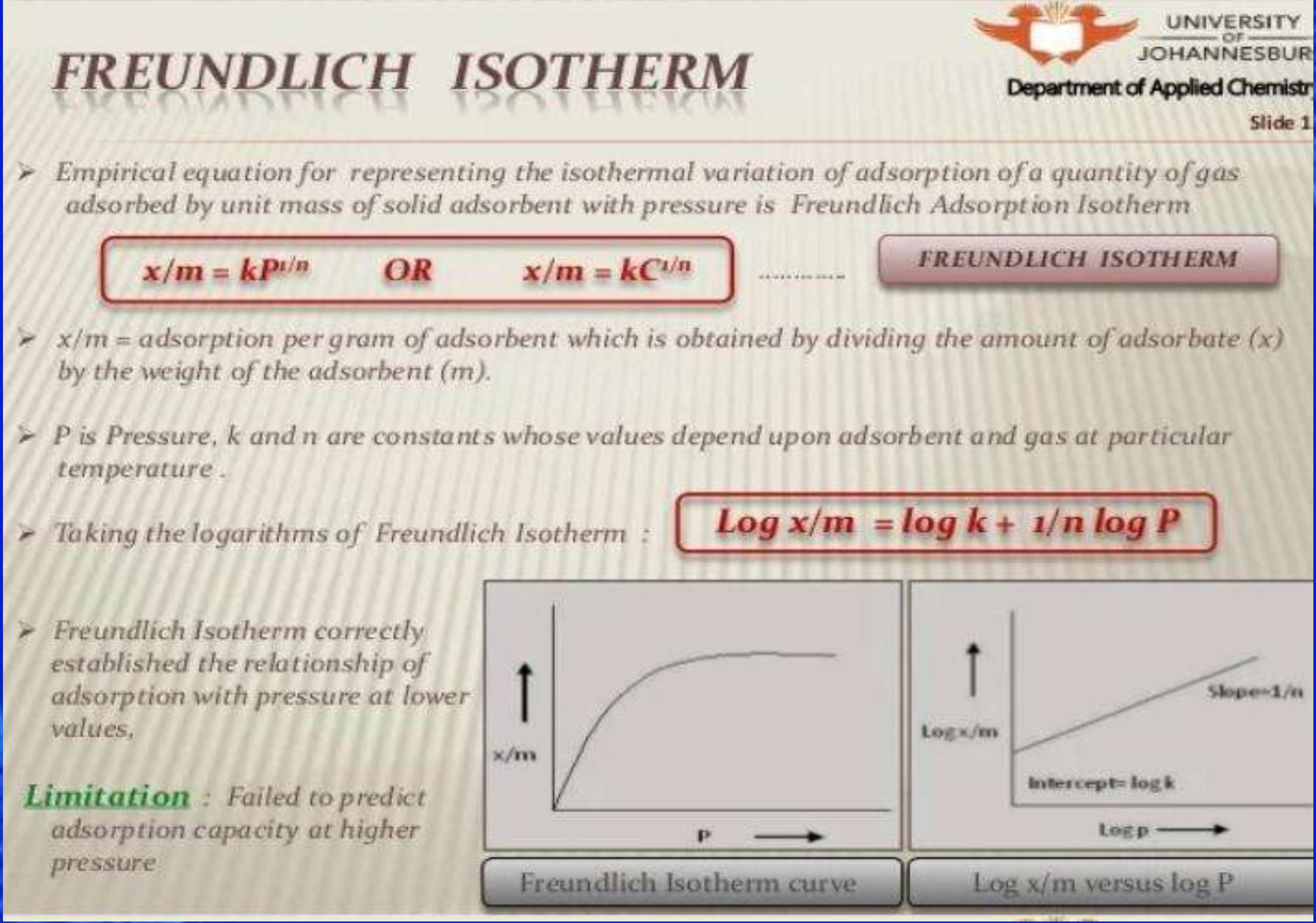
$$\text{ADSORBATE} + \text{ADSORBENT} \underset{\text{Desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} \text{ADSORPTION}$$

- *According to* ***Le Chatlier's principle****, on application of excess pressure , the equilibrium will shift in the direction where number of molecules decreases.*
- *Since no. of molecules decreases in forward direction i.e. direction of* ***Adsorption*** *, with increase of pressure , forward direction equilibrium will be achieved*
- *In the given* ***Adsorption Isotherm*** *, after saturation pressure* ***Ps*** *adsorption does not increases*
- *Vacancies on the surface of the adsorbent are limited, at* ***Ps*** *a stage is reached when all the sites are occupied and further increase in pressure does not increases adsorption extent.*

Graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature

<u>Types of Adsorption Isotherms</u> *:*

1. FREUNDLICH ISOTHERM
2. LANGMUIR ISOTHERM
3. TEMKIN ISOTHERM
4. BET ISOTHERM



FREUNDLICH ISOTHERM

- *Empirical equation for representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure is Freundlich Adsorption Isotherm*

$x/m = kP^{1/n}$ **OR** $x/m = kC^{1/n}$ ………… **FREUNDLICH ISOTHERM**

- *x/m = adsorption per gram of adsorbent which is obtained by dividing the amount of adsorbate (x) by the weight of the adsorbent (m).*
- *P is Pressure, k and n are constants whose values depend upon adsorbent and gas at particular temperature .*
- *Taking the logarithms of Freundlich Isotherm :* $\text{Log } x/m = \log k + 1/n \log P$
- *Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values,*

Limitation : *Failed to predict adsorption capacity at higher pressure*

Freundlich Isotherm curve

Log x/m versus log P

LANGMUIR ISOTHERM

In 1916, Langmuir proposed another Isotherm : ***Langmuir Adsorption isotherm***

- *Based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecule.*

$$A(g) + M\ (surface) \rightleftharpoons AM(surface) \quad \text{..........................}$$

A(g) = unadsorbed gaseous molecules M(surface) = unoccupied adsorbent surface AM(surface) = Adsorbed gaseous molecules

- *The extent of surface coverage is normally expressed as the fractional coverage, θ*

θ = number of adsorption sites occupied / number of adsorption sites available

- *The rate of change of surface coverage due to adsorption is proportional to the partial pressure **p** of gas & the number of vacant sites **$N(1-\theta)$**, where **N** is the total number of sites, **k_a** & **k_d** rate constants for adsorption & desorption*

$$d\theta/dt = k_a pN(1-\theta) \quad \text{..........................}$$

Rate of Adsorption

- *The rate of change of θ due to desorption is proportional to the number of adsorbed species, **$N\theta$***

$$d\theta/dt = -k_d N\theta \quad \text{..........................}$$

Rate of Desorption

- *At equilibrium there is no net change (that is, the sum of these two rates is zero), and solving for θ gives the* ***Langmuir Isotherm****, where* $K = (ka / kd)$

$$\boxed{\theta = Kp / (1 + Kp)}$$ …………… **LANGMUIR ISOTHERM**

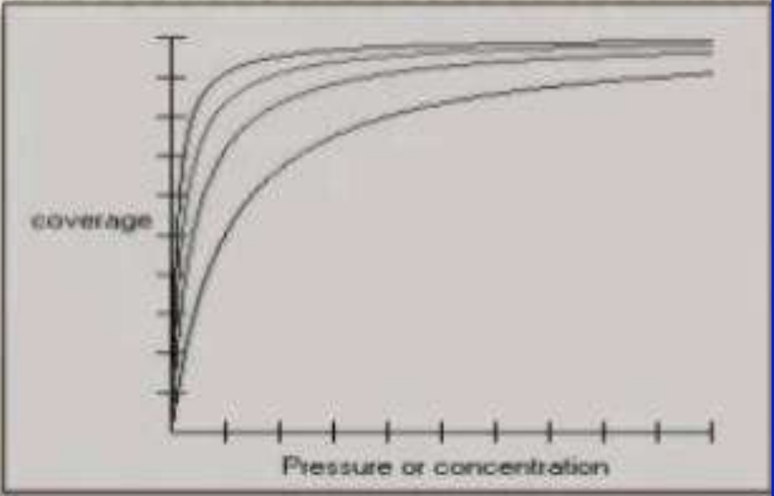
- *At lower pressure, Kp is so small that factor (1 + Kp) in denominator can almost be ignored & Langmuir equation reduces to :*

$$\theta = Kp$$

- *At higher pressure , Kp is so large that factor (1 + Kp) in denominator is nearly equal to Kp & Langmuir equation reduces to :*

$$\theta = Kp / Kp = 1$$

Limitation : *Valid at low Pressures only*



Langmuir isotherm for different values of K

THANK YOU

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