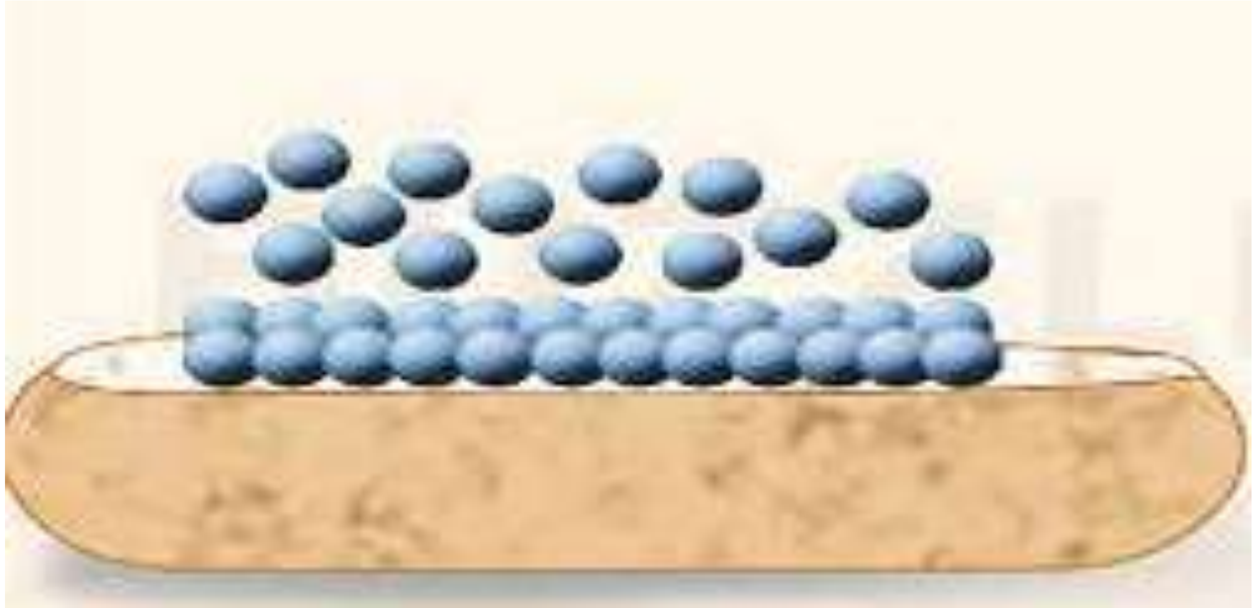
ADSORPTION



PRESENTED BY
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- ADSORPTION AND ABSORPTION
- BASICS OF ADSORPTION
- PHYSISORPTION AND CHEMISORPTION
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- IUPAC CLASSIFICATION OF ADSORPTION ISOTHERMS
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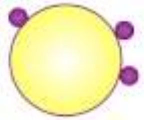
DIFFERENCE BETWEEN ADSORPTION AND ABSORPTION



ADSORPTION

- Molecules adhere to the surface of the material
- It is a surface phenomenon
- Adsorption of water vapours on silica gel in air conditioners

ABSORPTION

- Molecules are drawn into the material
- It is a bulk phenomenon
- Absorption of water in a sponge

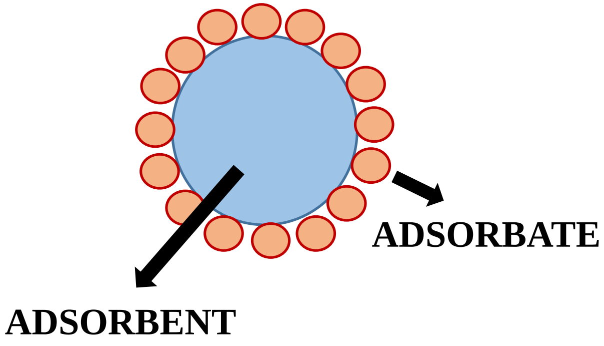
BASICS OF ADSORPTION

- **Adsorption** is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface.

- ADSORBATE – The substance which is adsorbed on the surface.

- ADSORBENT- The substance on which adsorption takes place.

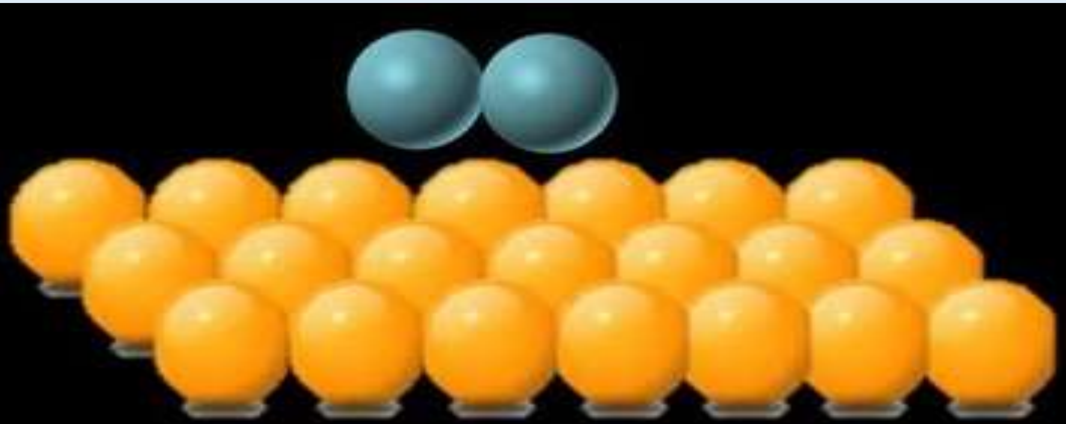
- **DRIVING FORCE OF ADSORPTION :** The surface of solids have unbalanced forces which results in higher surface energy. So the surface always has tendency to attract other molecules so as to balance the forces and lower down its energy.



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

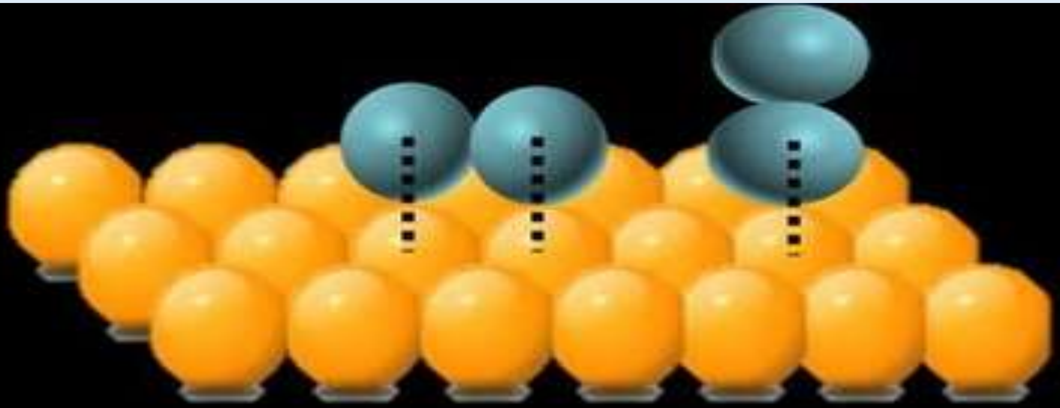
- For a spontaneous process, ΔG is negative. ΔS is negative because disorderness is decreasing. As a result ΔH is also negative , so adsorption is an exothermic process.

DIFFERENCE BETWEEN PHYSISORPTION AND CHEMISORPTION



PHYSISORPTION

- Adsorbate and adsorbent interact by weak Vander waal’s forces.
- Heat of adsorption is low.
- Non-specific in nature.
- Decreases with increase of temperature at constant pressure.
- Multilayer formation (BET).



CHEMISORPTION

- Adsorbed molecule react chemically with surface.
- Heat of adsorption is high.
- Highly specific in nature.
- First increases and then decreases with increase of temperature at constant pressure.
- Monolayer formation.

ADSORPTION ISOTHERMS

- The variation of θ with pressure at a chosen temperature is called the **adsorption isotherm.**

LANGMUIR ADSORPTION ISOTHERM

Gas adsorbed on solid surface.

Assumptions are -

- Gas behaves ideally.
- Monolayer formation only.
- All sites are equivalent and surface is uniform.
- No interactions between adsorbed molecules.

$$\textbf{A(g) + M(surface)} \leftrightarrow \textbf{AM(surface)}$$

k_a : Rate constant for adsorption
k_d : Rate constant for desorption.

The rate of change of surface coverage due to adsorption is proportional to the partial pressure P of A and the number of vacant sites $(1 - \theta)$:

$$d\theta/dt = k_a P (1 - \theta)$$

The rate of change of θ due to desorption is proportional to the number of adsorbed species θ:

$$d\theta/dt = -k_d \theta$$

At equilibrium there is no net change
(that is, the sum of these two rates is zero)

$$\theta = \frac{Kp}{1 + Kp} \qquad K = \frac{k_a}{k_d}$$

- CASE 1 – At low P 1+KP —> 1 **$\theta \approx KP$**

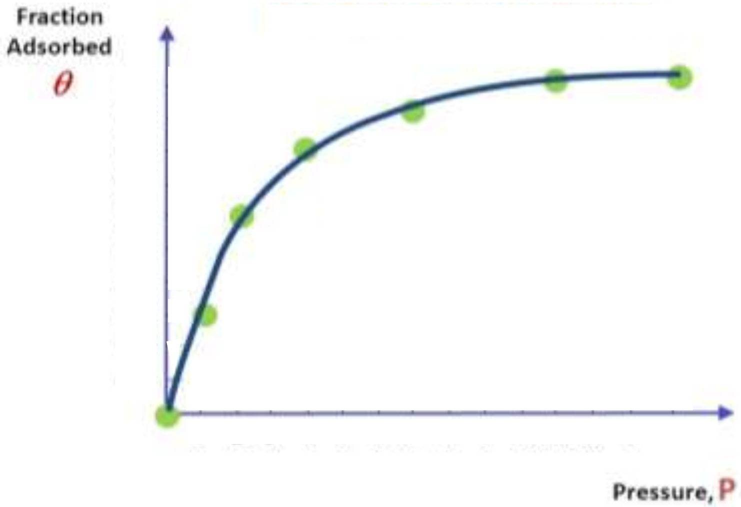
So θ directly proportional to P at low pressure

- CASE 2 – At high P 1+KP —> KP **$\theta \approx$ constant**

- CASE 3 – At intermdiate P

$x/m = K P^{1/n}$ K and n are constant and depends on adsorbate and adsorbent

1/n lie between 0 and 1

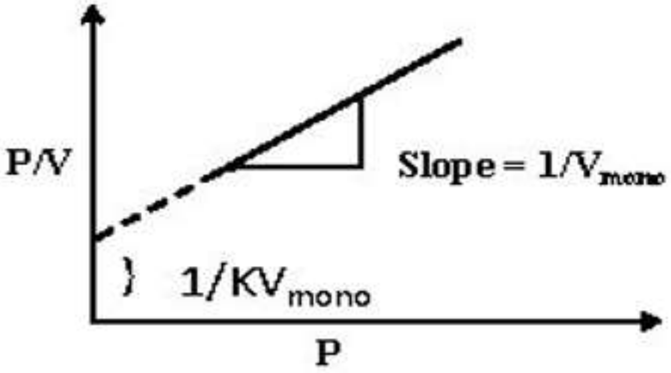


CASE 3 is called **Freundlich isotherm** (a special case of Langmuir isotherm).

➢ ALTERNATE FORM OF LANGMUIR ADSORPTION EQUATION:

$$\frac{P}{V} = \frac{P}{V_{mono}} + \frac{1}{KV_{mono}}$$

$$slope = \frac{1}{V_{mono}} \quad \text{and} \quad Intercept = \frac{1}{KV_{mono}}$$

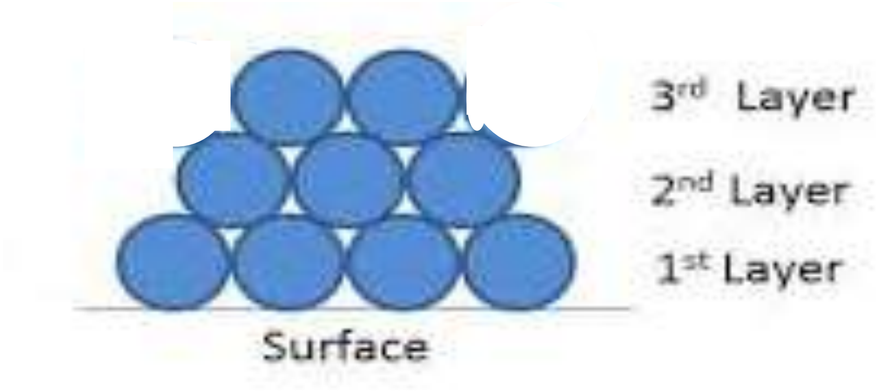


BET THEORY

- This was given by Brunauer , Emmett and Teller in 1938.

ASSUMPTIONS ARE-

- Multilayers are formed.
- All surface sites are uniform and localised.
- Adsorption at one site does not affect adsorption at another site.
- Surface area for nth layer α θ_{n-1}
- ΔH_1 = constant
- Heat of adsorption in succeeding layers is equal = Energy of liquifaction



$$\frac{V}{V_{\mathrm{mon}}} = \frac{cz}{(1-z)\{1-(1-c)z\}} \qquad \text{with} \quad z = \frac{p}{p^{*}}$$

$$c = \mathrm{e}^{(\Delta_{\mathrm{des}}H^{\ominus} - \Delta_{\mathrm{vap}}H^{\ominus})/RT}$$

p* is the equilibrium vapour presure of liquid above the layer of adsorbate

V_{mon} is the volume corresponding to monolayer coverage

c is a constant which is large when the enthalpy of desorption from a monolayer is large compared with the enthalpy of vaporization of the liquid adsorbate

$$A(g) + S \rightleftharpoons \boxed{AS} \quad \text{first} \quad K_1 = \frac{\theta_1}{\theta_v P}$$

$$A(g) + AS \rightleftharpoons A_2S \quad K_2 = \frac{\theta_2}{\theta_1 P}$$

$$A(g) + A_2S \rightleftharpoons A_3S \quad K_3 = \frac{\theta_3}{\theta_2 P}$$

ΔH_1, ΔH_2 ---- ΔH_n

$$K_n = \frac{\theta_n}{\theta_{n-1} P}$$

$$(K_1) \quad \boxed{K_2 = K_3 = K_n} = K$$

$$\underset{P^\circ}{A(g)} \rightleftharpoons A\,(liq.)$$

$$K_L = \frac{1}{P^\circ}$$

$$\theta_2 = \theta_1 P K_2$$

$$= \boxed{\theta_1 PK = \theta_2}$$

$$\theta_n = \theta_1 P$$

$$\theta_3 = \theta_2 KP$$

$$= \theta_1 (KP)^2$$

$$\boxed{\theta_n = \theta_1 (KP)^{n-1}}$$

sum of all = 1.

$$1 = \theta_v + \theta_2 + \theta_2 ------$$

$$1 = \theta_v + \sum_{i=1} \theta_i$$

$$= \theta_v + \sum_{i=1} \theta_1 \underbrace{(KP)}_{x}{}^{i-1}$$

$$= \theta_v + \theta_1 (1 + x + x^2 + x^3 ---)$$

$$1 + x + x^2 + x^3 --- x^n = \frac{1}{1-x}$$

$$1 = \theta_v + \frac{\theta_1}{1-x}$$

$$\theta = ,$$

$$K = \frac{\theta_1}{\theta_v P}$$

$$\theta_v = \frac{\theta_1}{K_1 P} \times \frac{K}{K}$$

$$= \frac{\theta_1}{\frac{K_1}{K} PK}$$

$$= \frac{\theta_1}{cPK}.$$

$$c = \frac{K_1}{K}$$

$$= \frac{\theta_1}{c\underbrace{PK}_{x}} + \frac{\theta_1}{1-x}$$

$$= \theta_1 \left(\frac{1}{cx} + \frac{1}{1-x} \right)$$

$$\boxed{\theta_1 = \frac{cx(1-x)}{1 + (c-1)x}}$$

N → Total no. of molecules adsorbed per unit mass.

C_s → Total no. of surface sites per unit mass

$$N = C_s \sum_i i\,\theta_i$$

$$\theta_i = \theta_1 (KP)^{i-1} = \theta_1 x^{i-1}$$

$$N = C_s \theta_1 \sum_{i=1} i x^{i-1}$$

$$= C_s \theta_1 (1 + 2x + 3x^2 + -----)$$

$$(1 + 2x + 3x^2 ---) = \frac{d}{dx}(1 + x + x^2 + x^3 ---) = \frac{d}{dx} \frac{1}{(1-x)}$$

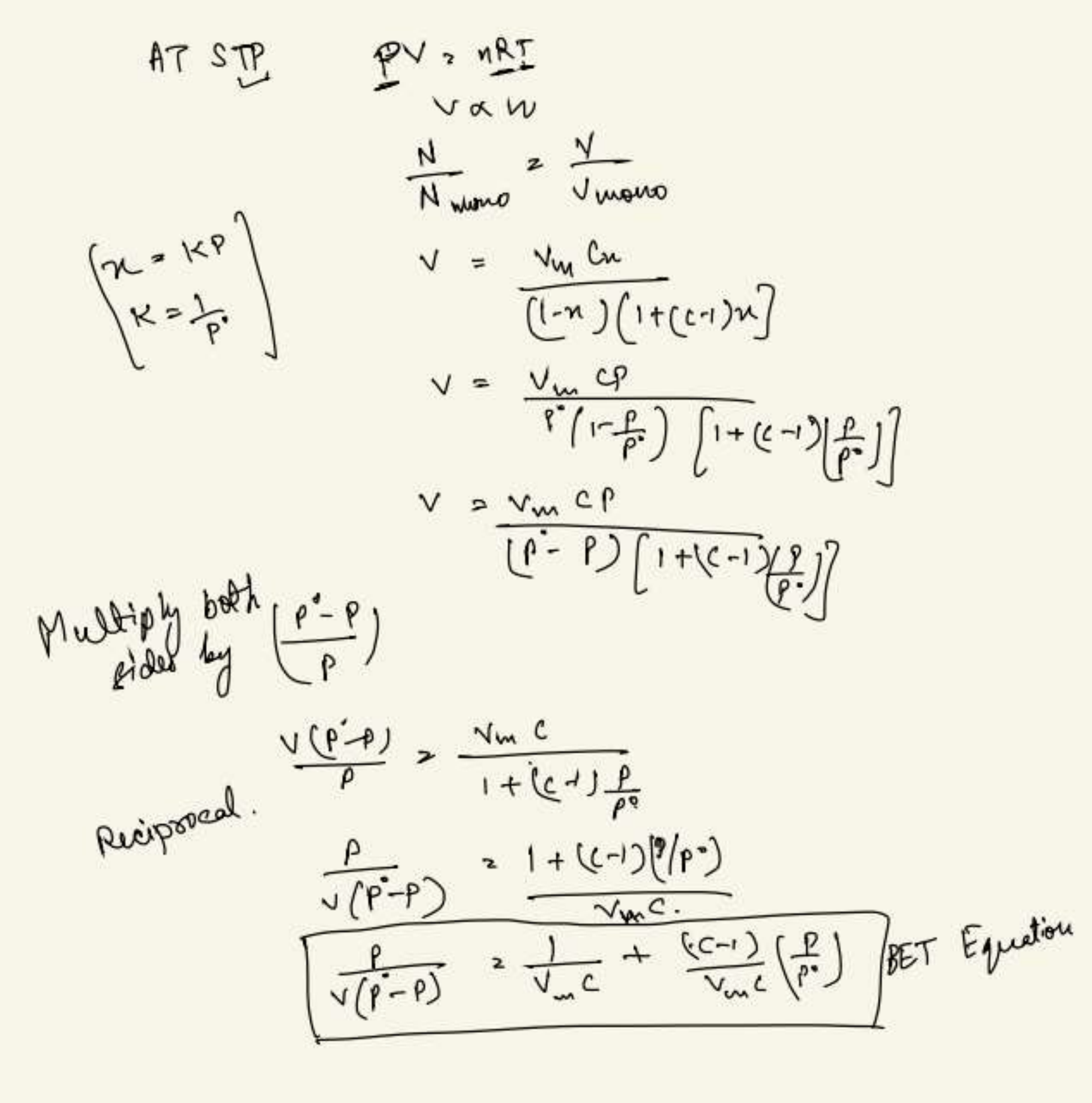
$$= \boxed{\frac{1}{(1-x)^2}}$$

$$N = \frac{C_s \theta_1}{(1-x)^2}$$

$$\boxed{N_m = C_s}$$

$$N = \frac{N_m \theta_1}{(1-x)^2}$$

$$N = \frac{N_m cx}{(1-x)[1 + (c-1)x]}$$



AT STP $\quad \underline{P}V = n\underline{RT}$

$$V \propto W$$

$$\frac{N}{N_{mono}} = \frac{V}{V_{mono}}$$

$$\begin{bmatrix} x = KP \\ K = \frac{1}{P^\circ} \end{bmatrix}$$

$$V = \frac{V_m C x}{(1-x)\left(1+(c-1)x\right)}$$

$$V = \frac{V_m C P}{P^\circ\left(1-\frac{P}{P^\circ}\right)\left[1+(c-1)\left[\frac{P}{P^\circ}\right]\right]}$$

$$V = \frac{V_m C P}{(P^\circ - P)\left[1+(c-1)\left(\frac{P}{P^\circ}\right)\right]}$$

Multiply both sides by $\left(\frac{P^\circ - P}{P}\right)$

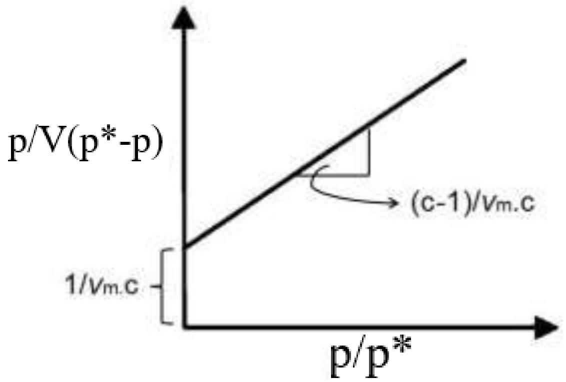
$$\frac{V(P^\circ - P)}{P} = \frac{V_m C}{1+(c-1)\frac{P}{P^\circ}}$$

Reciprocal.

$$\frac{P}{V(P^\circ - P)} = \frac{1+(c-1)(P/P^\circ)}{V_m C}$$

$$\boxed{\frac{P}{V(P^\circ - P)} = \frac{1}{V_m C} + \frac{(c-1)}{V_m C}\left(\frac{P}{P^\circ}\right)}$$ BET Equation

BET ISOTHERM



- BET isotherms rise indefinitely as the pressure is increased because there is no limit to the amount of material that may condense when multilayer coverage may occur.

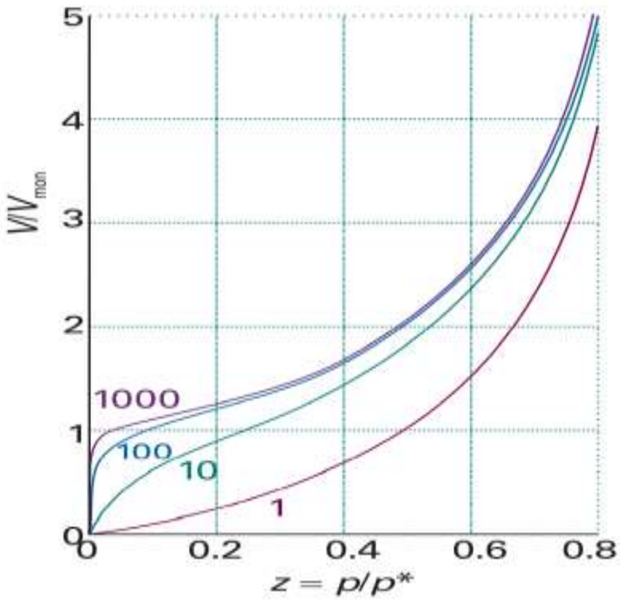
- **c** is related to the affinity of the solid with the adsorbate.

- Higher the value of c, higher is the interaction between adsorbate and the solid.

➢ **p*** —> ∞ , p/p* = 0

$$V/V_{mon} = \frac{Kp}{1 + Kp}$$

Similar to Langmuir Equation

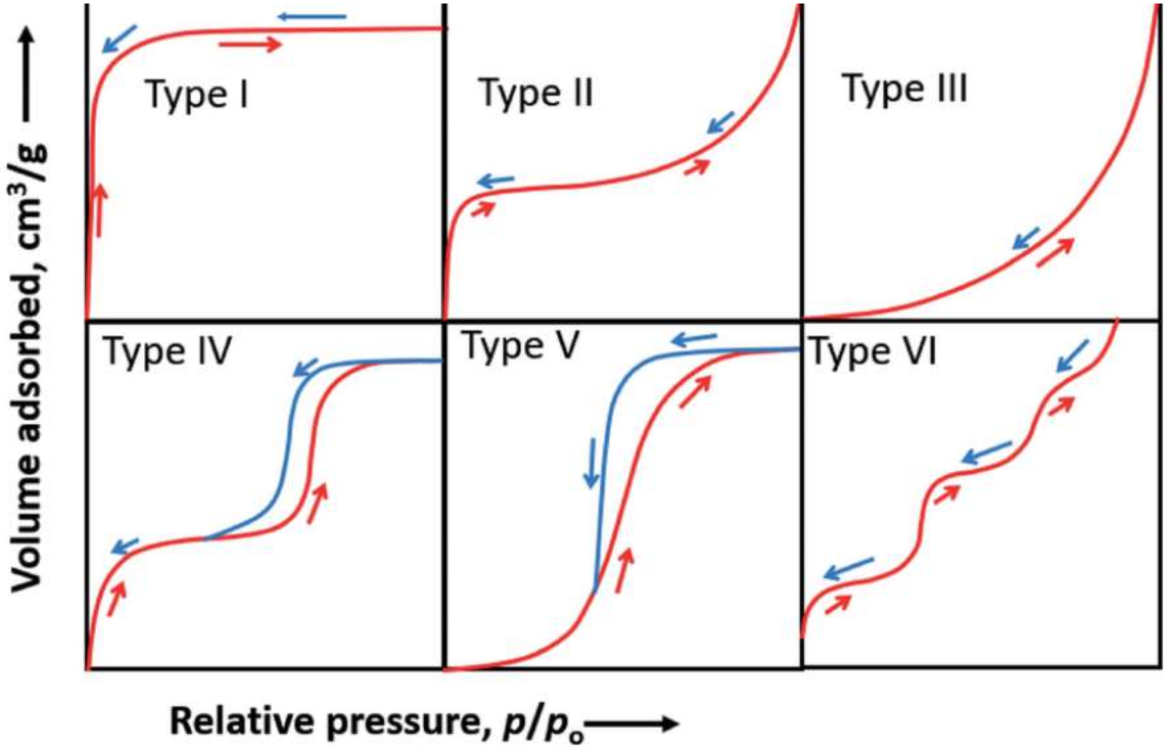


Plots of the BET isotherm for different values of c

IUPAC classification of adsorption isotherms

- IUPAC conventions have been proposed for classifying pore sizes and gas sorption isotherms that reflect the relationship between porosity and sorption.

- The six types of isotherm (IUPAC classification) are characteristic of adsorbents that are
  - ➢ microporous (type I),
  - ➢ nonporous or macroporous (types II, III, and VI),
  - ➢ mesoporous (types IV and V)



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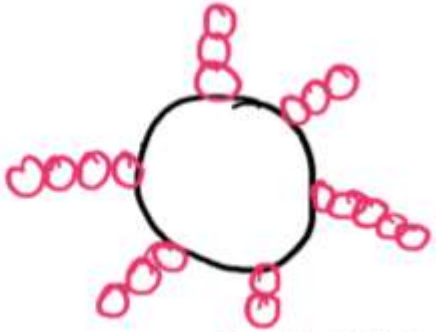
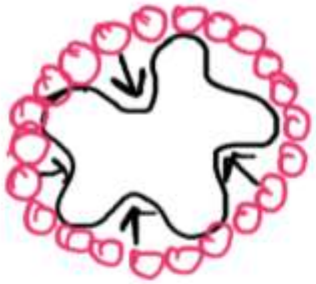
PHYSICAL SIGNIFICANCE OF TYPES OF ISOTHERMS

TYPE I
(microporous)

TYPE II
(nonporous)

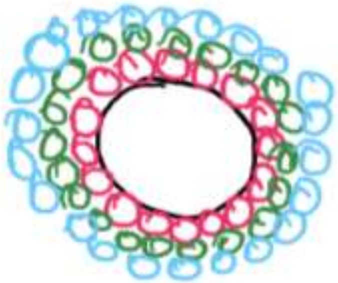


TYPE III
(macroporous)



TYPE IV
(mesoporous)

TYPE V
(mesoporous)



TYPE VI
(nonporous)

CONCLUSION

- **Freundlich isotherm fails at high pressure of gas** whereas Langmuir adsorption isotherm does not.

- **Langmuir assumes that ions are adsorbed as a monolayer on the surface**, and the maximum adsorption occurs when the surface is completely covered, whereas Freundlich has assumptions of heterogeneous surfaces with different affinities for adsorption.

- **Langmuir isotherm describes the monolayer molecular adsorption**, whereas BET isotherm describes the multilayer molecular adsorption.

- BET theory aims **to explain the physical adsorption of gas molecules on a solid surface.**

- BET serves as an important analysis technique for the measurement of the specific surface area of materials.