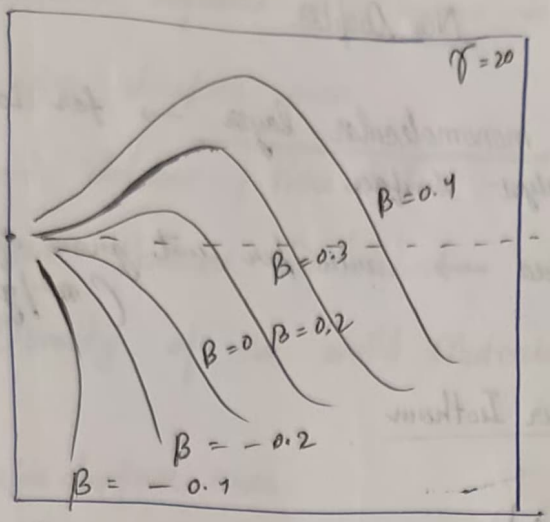


β : + → Exothermic

β : − → Endothermic

β . 0 → Isothermal

Physical significance

Endothermic → inside the pellet temp^{r} ↓, rxn becomes the controlling factor. (rate of rxn ↓)

↳ conv^{n} inside pellet is less than surface, rxn is controlling factor.

Exothermic :- temp^{r} inside pore is so high that the conv^{n} inside pore is changed by heat effect. The conv^{n} inside pore becomes greater than the surface conv^{n}, the heat inside the pore can't be released, so it remains inside the pore, which leads to change in conv^{n} pattern also heat accumulation inside pore may lead to :-

(1) melting of catalyst surface

(2) less selectivity, due to ↑ in no. of side rxns.

New Chapter

(*). Adsorption to be of monomolecular layer → for Langmuir Isotherm on the Catalyst Surface.

Specific Surface area → area per unit gram of catalyst (m^2/g-cat.)

Recapitulation of Langmuir Isotherm

$r_a = k_1 P(1-\theta)$ $\quad \theta$ = fraction of Occupied Site

$r_d = k_2 \theta$

at Equilibrium $k_1 P(1-\theta) = k_2 \theta$

$\theta = \frac{P}{1+P}$ $\quad k_1 P - k_1 P\theta = k_2 \theta$

$\theta = \frac{k_1 P}{k_2 + k_1 P}$

$\theta = \frac{P}{P + \frac{k_2}{k_1}}$

$\theta = \frac{KP}{1+KP}$ $\quad K = \frac{k_1}{k_2}$ (absorption Equilibrium Constant)

$= \frac{v}{v_m}$

v = volume of gas adsorbed at any time.

v_m = volume of gas adsorbed at monomolecular layer formation

External Surface area per unit volume of a solid sphere, if the diameter is d_p is $\frac{\pi d^2}{\frac{\pi}{6} d_p^3} = \frac{6}{d_p}$

If the particle density is ρ_p, then specific Surface area (sa/ unit mass)

$S_g = \frac{6}{d_p \rho_p}$

Important Properties Required to be known to obtain the facts :-

1. Specific Surface area
2. Void Volume / Pore Volume
3. Pore Volume Distribution
4. Density of the Solid Material

1 Specific Surface area.

N_2 → physical adsorption on Catalyst surface.

(*) Pressure < 1 atm & at just above the boiling point of N_2 (-195.8°C)

N_2 will get adsorbed on all the area (active + inactive).

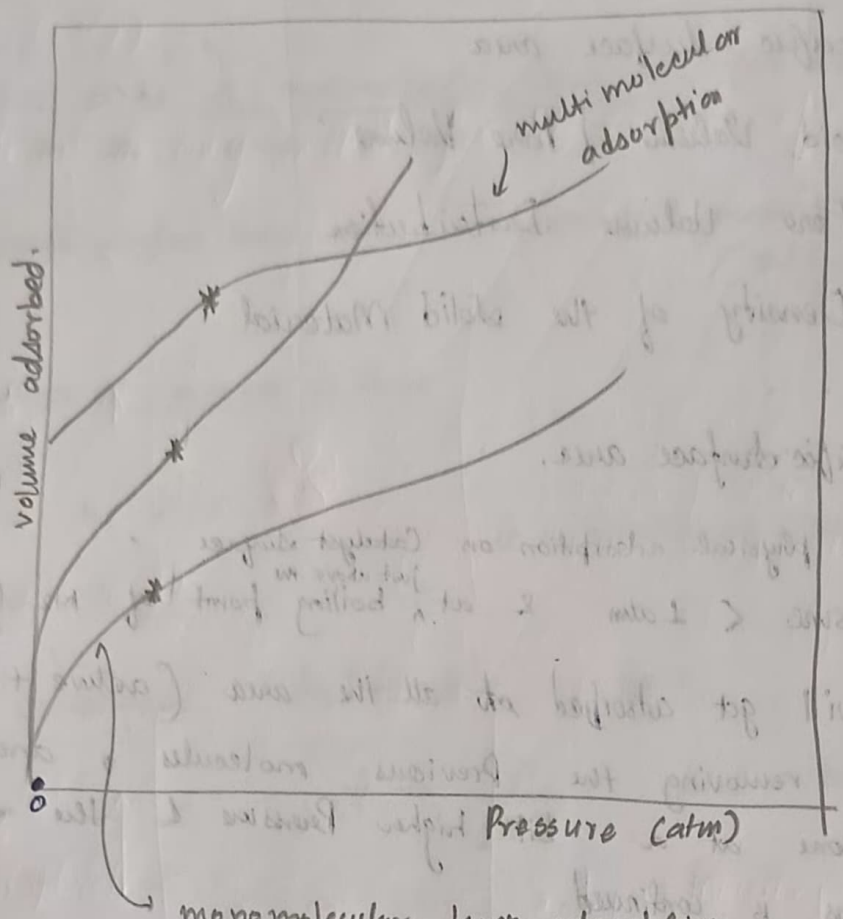
After removing the previous molecules, another adsorption is done at a bit higher Pressure & the same process is continued.

↓

So we get an isotherm. (different Pressures for Physical adsorption but same temperature)

This is called Brunauer - Emmet - Teller Surface area determination. (BET)

After few changes, Helium was also used. Helium + N_2 mixture (where P_{N_2} can be varied) is passed on a solid surface. N_2 is adsorbed. A stream of He is passed at higher temp over it. So N_2 molecules desorb from the surface.



$$\frac{KP}{1+KP} = \frac{v}{v_m}$$

$$\frac{1}{KP} + 1 = \frac{v_m}{v}$$

$$\boxed{\frac{P}{v} = \frac{1}{Kv_m} + \frac{P}{v_m}} \quad (I)$$

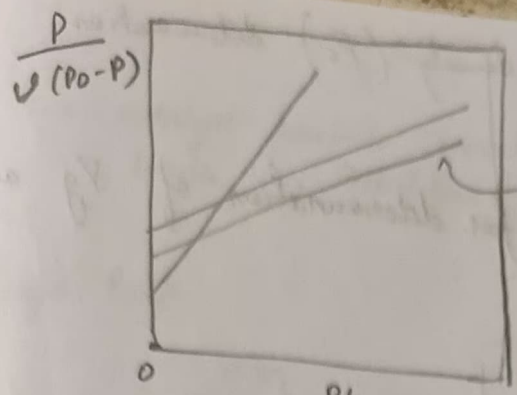
Langmuir Isotherm for monolayer Adsorption

(*) for multilayer adsorption

$$\frac{P}{v(P_0 - P)} = \frac{1}{v_m C} + \frac{(C-1)P}{C v_m P_0}$$

C = a constant for specific gas adsorption and at a constant temperature

v → multilayer volume
v_m → monolayer volume
P → partial Pressure
P_0 → saturation Pressure



$I = \frac{1}{v_m C}$

$S = \frac{C-1}{C v_m}$

$V_m = \frac{1}{I+C}$

I = Interapt

S = Slope

α = area occupied by one molecule.

$S_g = \left(\frac{v_m N_0}{V}\right)\alpha$ → avogadro no.

→ 22.4 lt.

(*) $\frac{v_m N_0}{V}$ = no. of molecules adsorbed in monolayer adsorption

α is taken as projected area (actual contact area be determined

$$\alpha = 1.09 \left[\frac{M}{N\rho}\right]^{2/3}$$

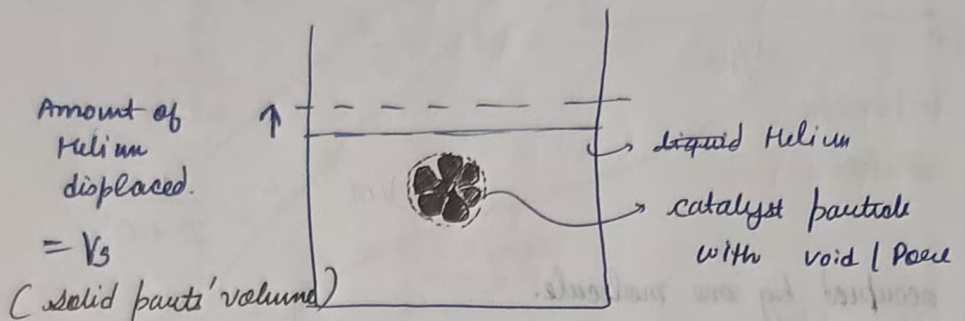
M = mol. wt of the gas.

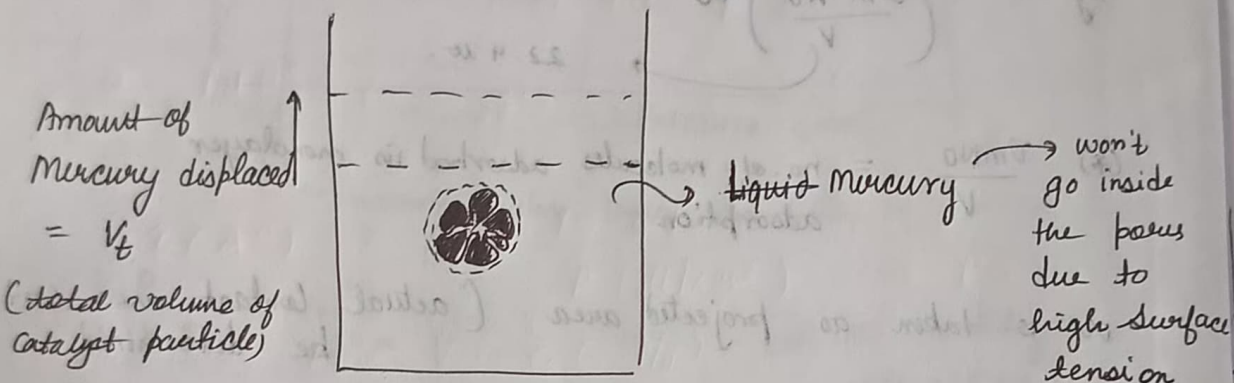
ρ = Density of the molecules

No = avogadro's number

Void Volume and Solid density (ρ_s) determination.
(V_g)

⇒ Helium Mercury method for determination of V_g and ρ_s





$$V_t - V_s = V_g \cdot (\text{Pore volume per unit wt of catalyst})$$

$$\text{Void fraction } (\varepsilon_p) = \frac{\text{Void Volume}}{\text{Total Volume}}$$

$$= \frac{m_p V_g}{m_p V_g + m_p \left(\frac{1}{\rho_s}\right)}$$

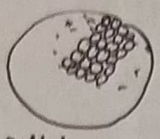
$$= \frac{V_g \rho_s}{1 + V_g \rho_s}$$

SS

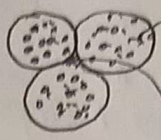
$\frac{1}{16}^{th}$ inch — $\frac{1}{2}$ inch

↳ catalyst particle Characteristic Length in Packed Bed Reactor.

Catalyst Pellets



Catalyst pellets



(*) Bidispersed Pore system

→ micropores (inside the particles)

→ macropore (between the particles)

Pore Volume Distribution According to the pore Radius

1. Mercury Penetration Method. (for Higher radii)
2. Nitrogen desorption Method (below $10^{\circ}A^{\circ}$) $200^{\circ}A^{\circ}$ – ($<10A^{\circ}$)

Above $200\,A^{\circ}$, influence of radius on pressure decrement is not much)

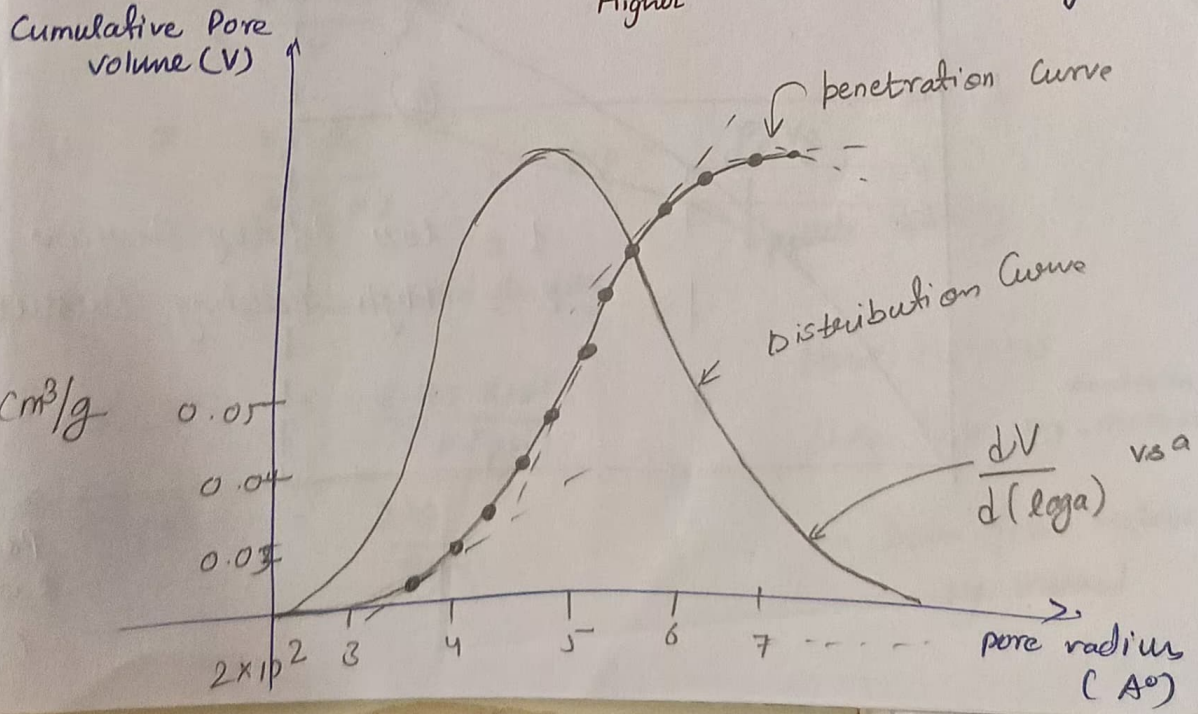
Pore size : $100\,A^{\circ} \longrightarrow 10\,A^{\circ}$

adsorb N_2 first

Now we desorb the N_2 adsorbed. [We are decreasing the Pressure to desorb the gas]

Lower Pore Radius → ~~more~~ Lower Pressure required (more gradient)

Higher Pore Radius → ~~Lower~~ Higher Pressure Required (less gradient)



Cumulative Volume → Sum of Volumes

$\pi a^2 P = -2\pi a \sigma \cos\theta$

$\pi a^2 P$ — applied force in the pore having radius a (A°); P = Pressure applied

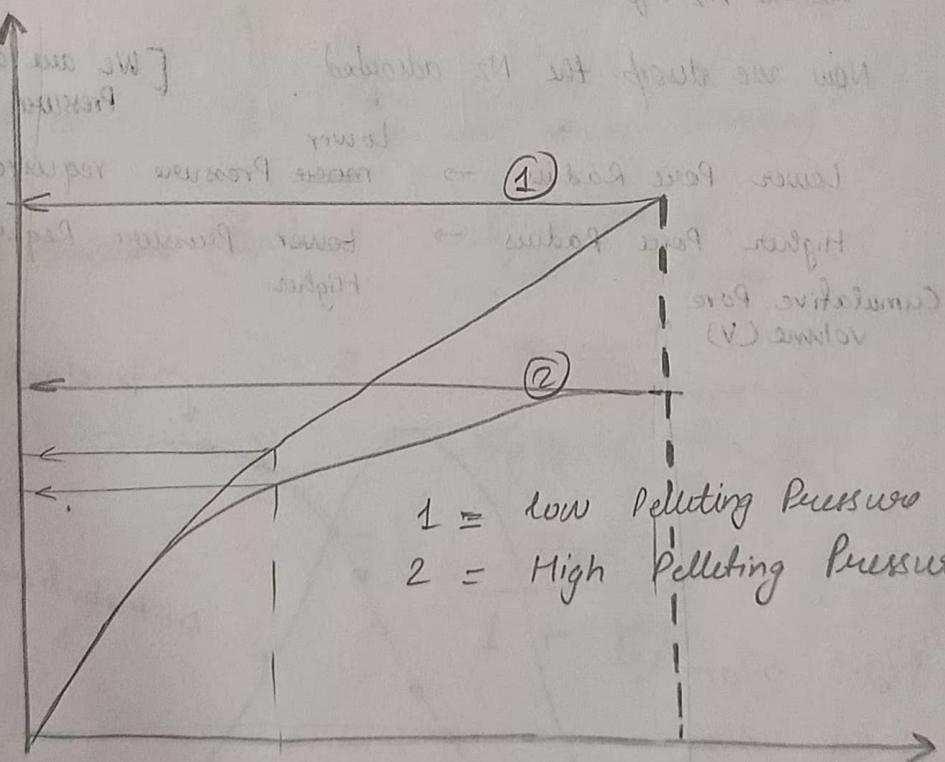
$2\pi a \sigma \cos\theta$ — force due to Surface Tension. Surface tension force for Hg to push into the pores.

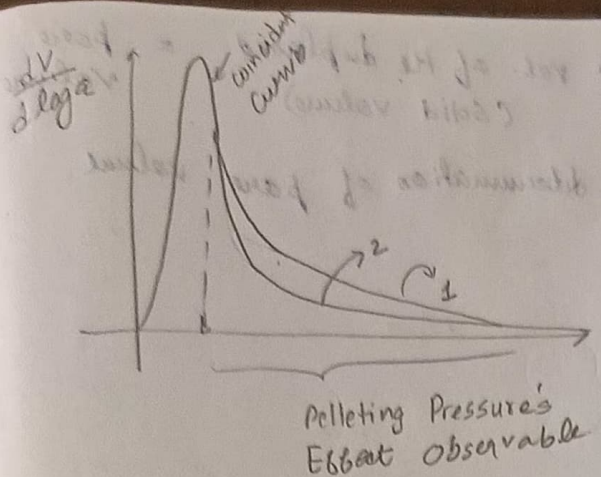
θ = contact angle b/w Hg & solid wall of the pore

$\theta = 140°$ (average)

$$a(A^\circ) = \frac{8.75 \times 10^5}{P\ (lb/cm^2)} \longrightarrow \underline{P.S\ I}$$

Cumulative Pore Volume (cm^3/g)





Wheeler's Parallel Pore Model

(Pores having same average Radius ($\bar{a}$).
Pores having same average length ($\bar{l}$)
Pores are parallel and are not interconnected to each other)

If m_p = mass of catalyst, S_g = surface area/g,
V_g = pore volume/g. n = number of pores,

$$m_p S_g = (2\pi(\bar{a})\bar{l})n$$
$$m_p V_g = (\pi(\bar{a})^2 \bar{l})n$$

$$\bar{a} = \frac{2V_g}{S_g}$$

* Remember all Equations

From Langmuir Isotherms:-

$$v_m = \frac{1}{I+S}$$

$$S_g = \left(\frac{v_m N_o}{V}\right)\alpha.$$

$$\epsilon_p = \frac{V_g \rho_s}{V_g \rho_s + 1}, \quad G_p = \rho_p V_g$$

(ρ_s: solid density; ρ_p: pellet density)

$$a(A^\circ) = \frac{8.75 \times 10^5}{P(psi)}$$

$$\bar{a}(A^\circ) = \frac{2V_g}{S_g}.$$

Pore Volume = penetration
Data from Hg injection method

- Data from Helium Hg method.

Vol of Hg displaced (Total Volume) − vol. of He displaced (Solid volume) = pore volume

In He − Hg method for determination of pore volume.