

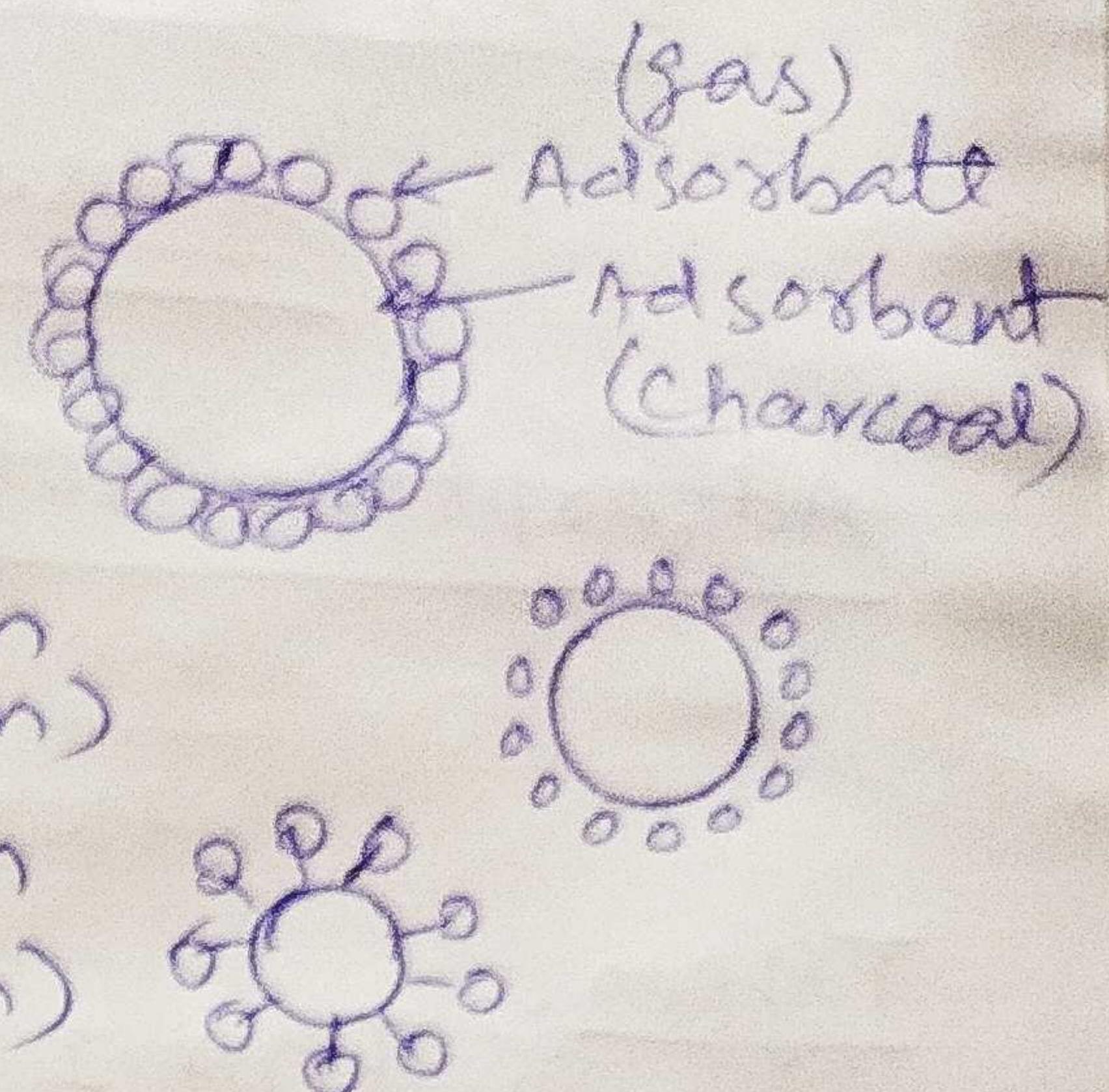
Adsorption

6D

- A surface phenomena
- Exothermic process, $\Delta H = -ve$

→ Types: (a) physical adsorption
(Physical adsorption)

(b) chemical adsorption
(Chemisorption)



Physisorption vs. Chemisorption

1. Nature of force:

Physisorption

Physical force
(Weak Vanderwaal)
force

Chemisorption

chemical force
(chemical bond)

2. Specificity:

no specificity

specificity

3. Reversibility:

Reversible

is there

Irreversible

4. Heat of adsorption:

low

(20-40 J/mole)

more

(40-400 J/mole)

5. Effect of Temp :

Decreases

Increases

6. Effect of Pressure: $P \uparrow$ Ads \uparrow

No effect

7. Activation energy: not essential/ High

8. Nature of layers: Multilayer

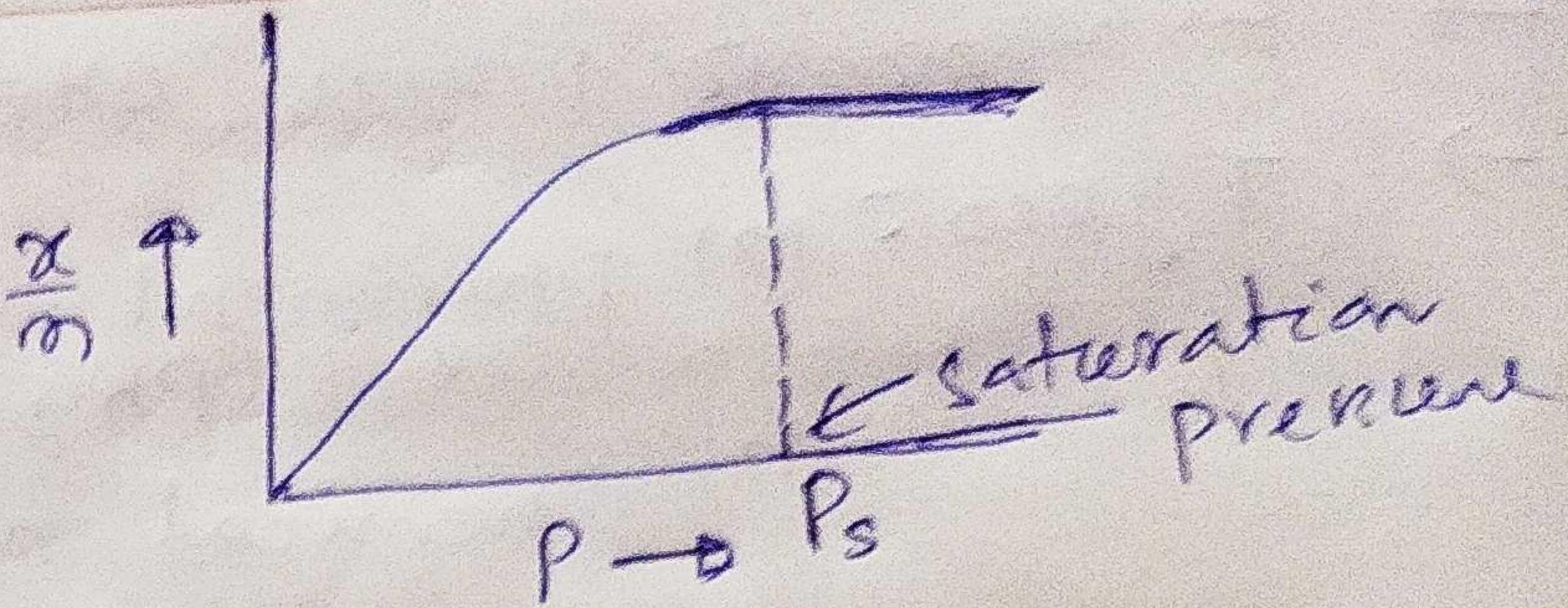
Monolayer

9. Surface Area (SA): $SA \uparrow$ Ads \uparrow

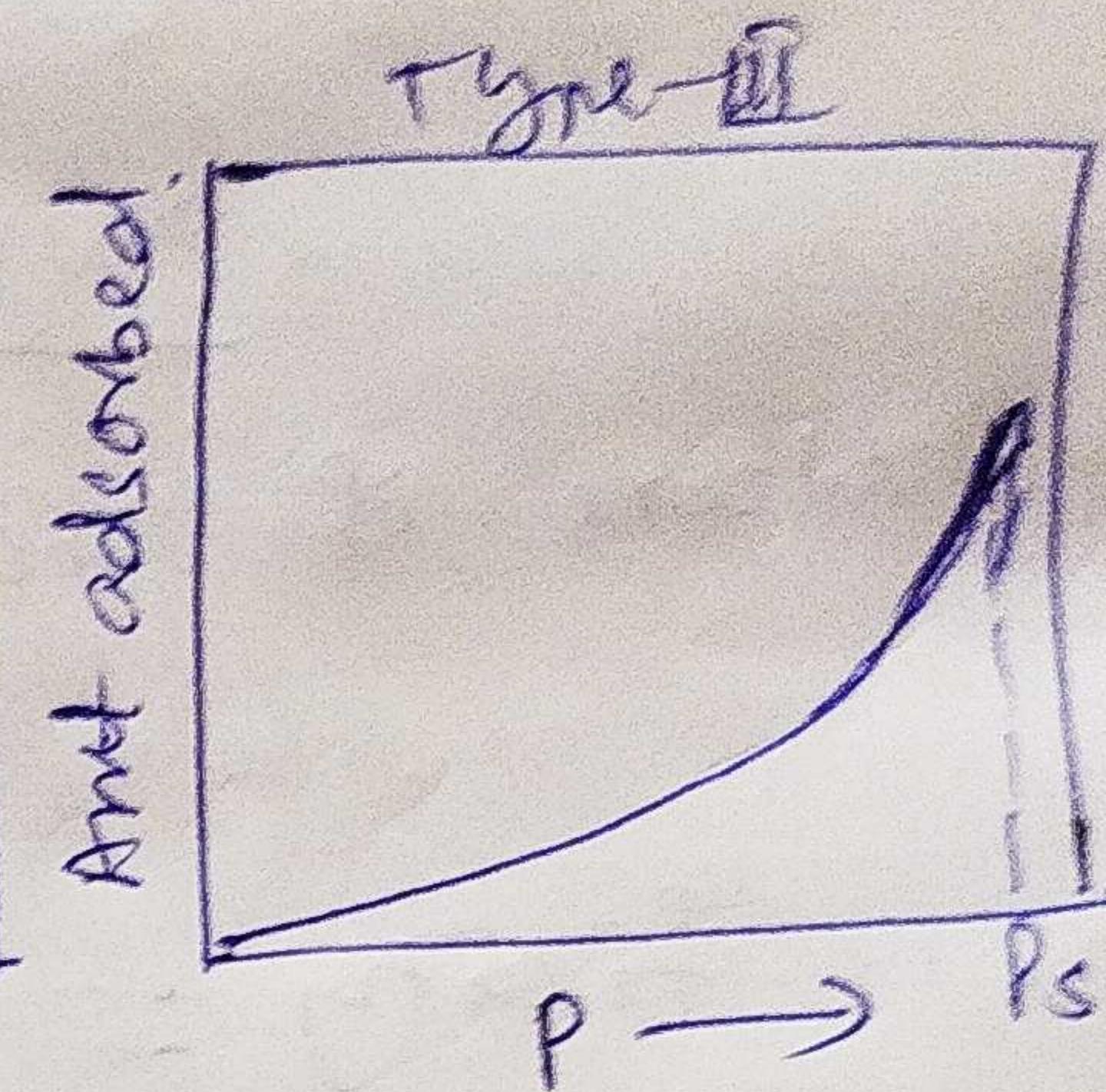
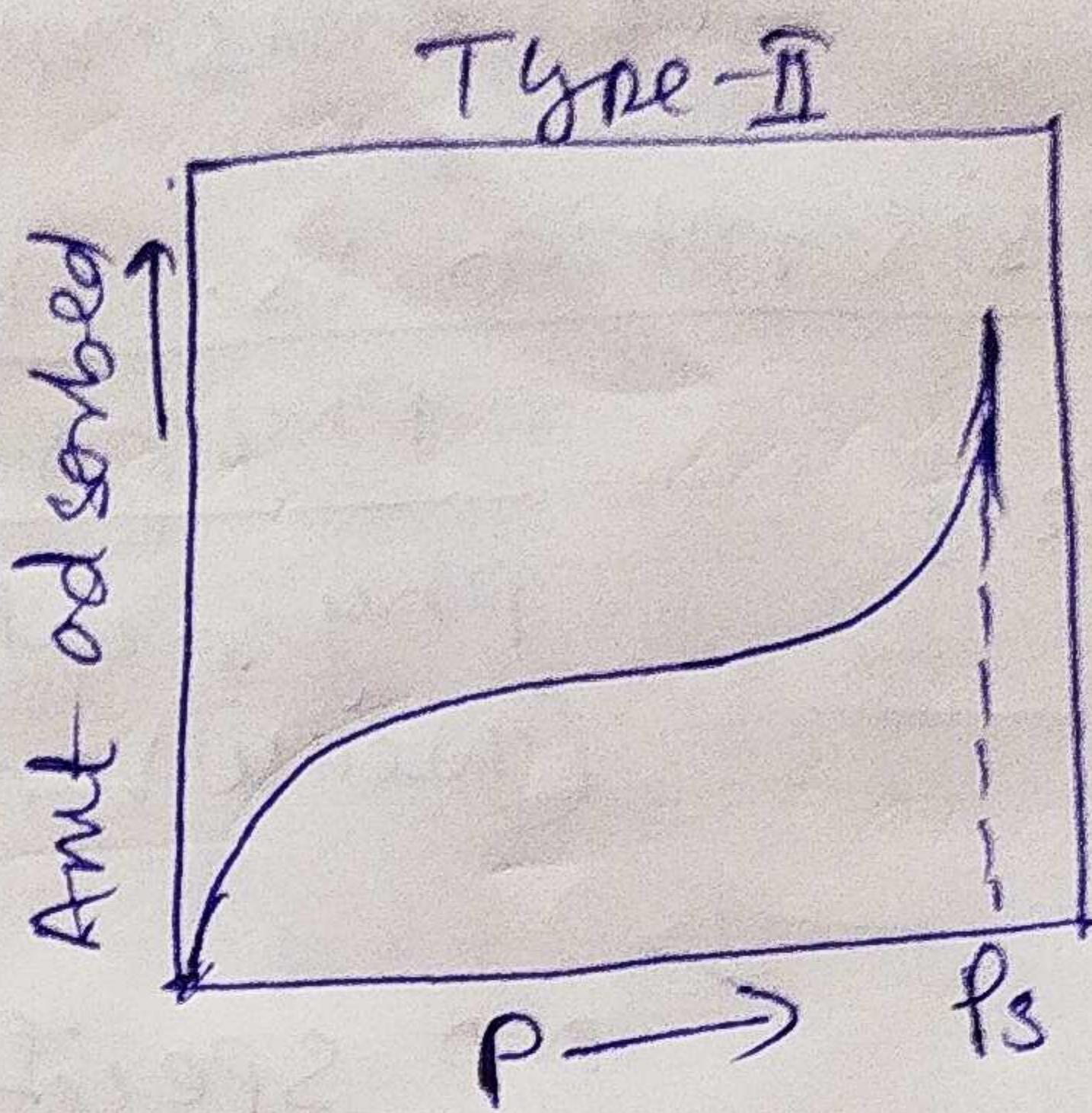
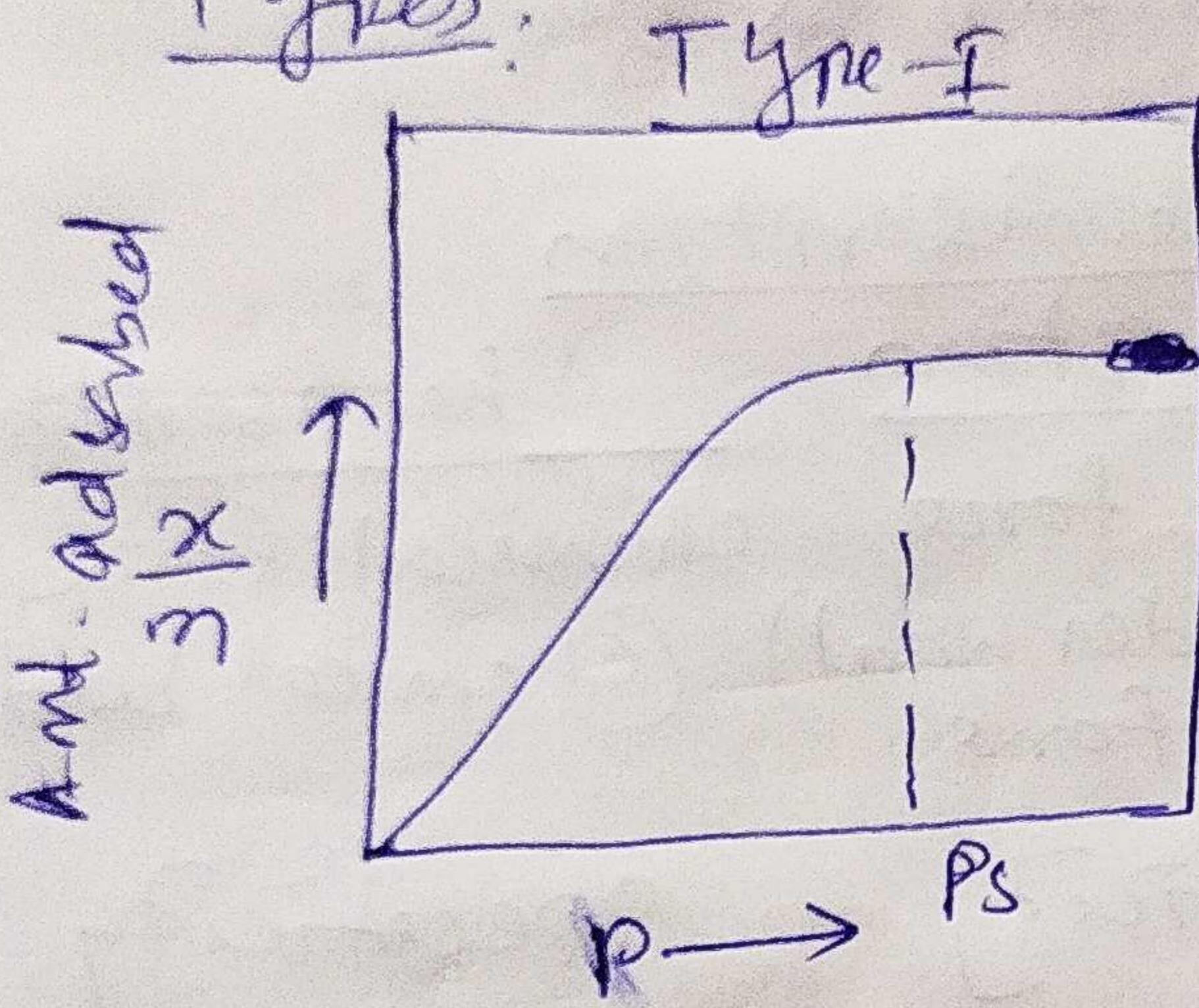
$SA \uparrow$ Ads \uparrow

Adsorption Isotherm & its types

Adsorption Isotherm

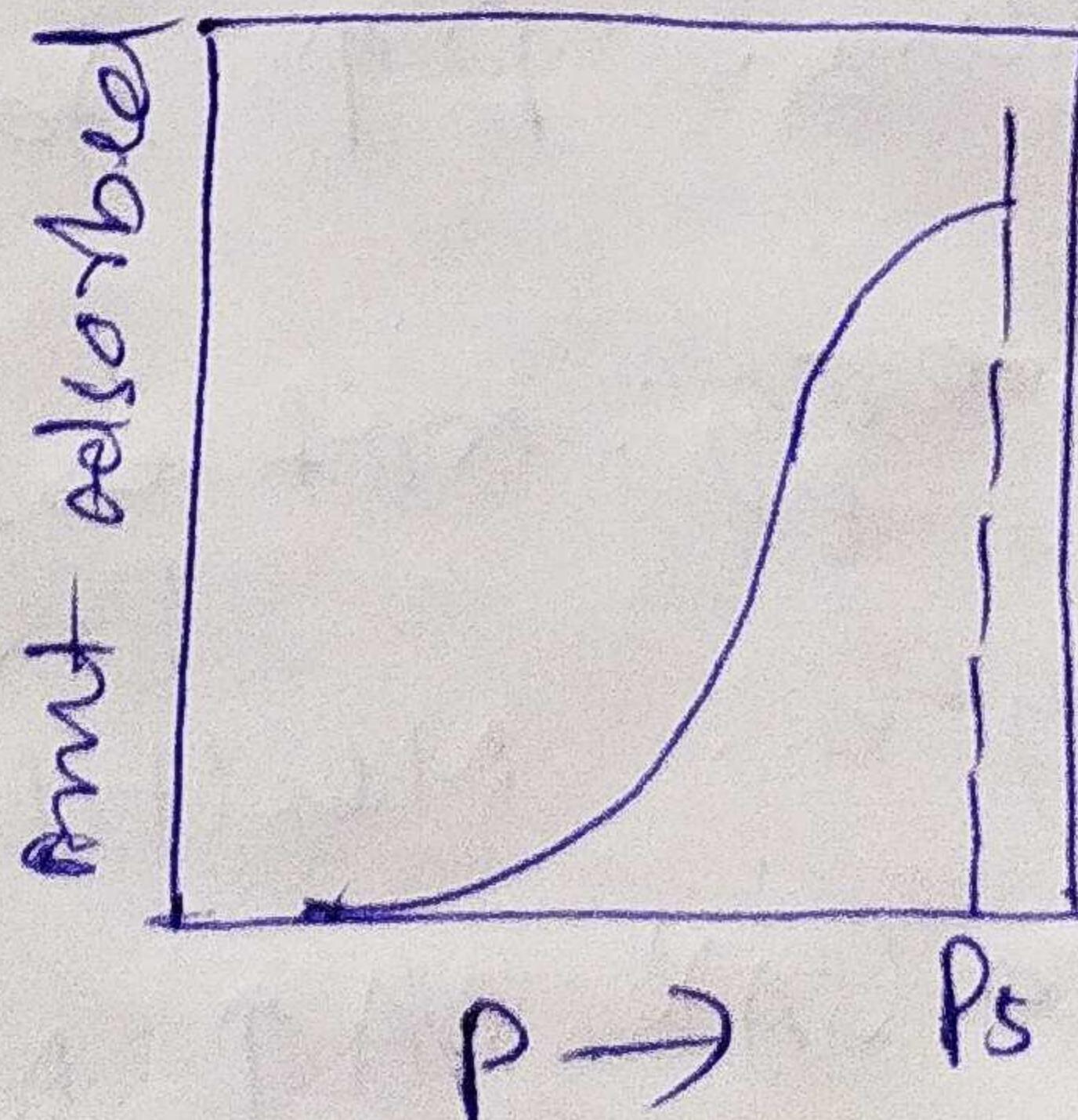
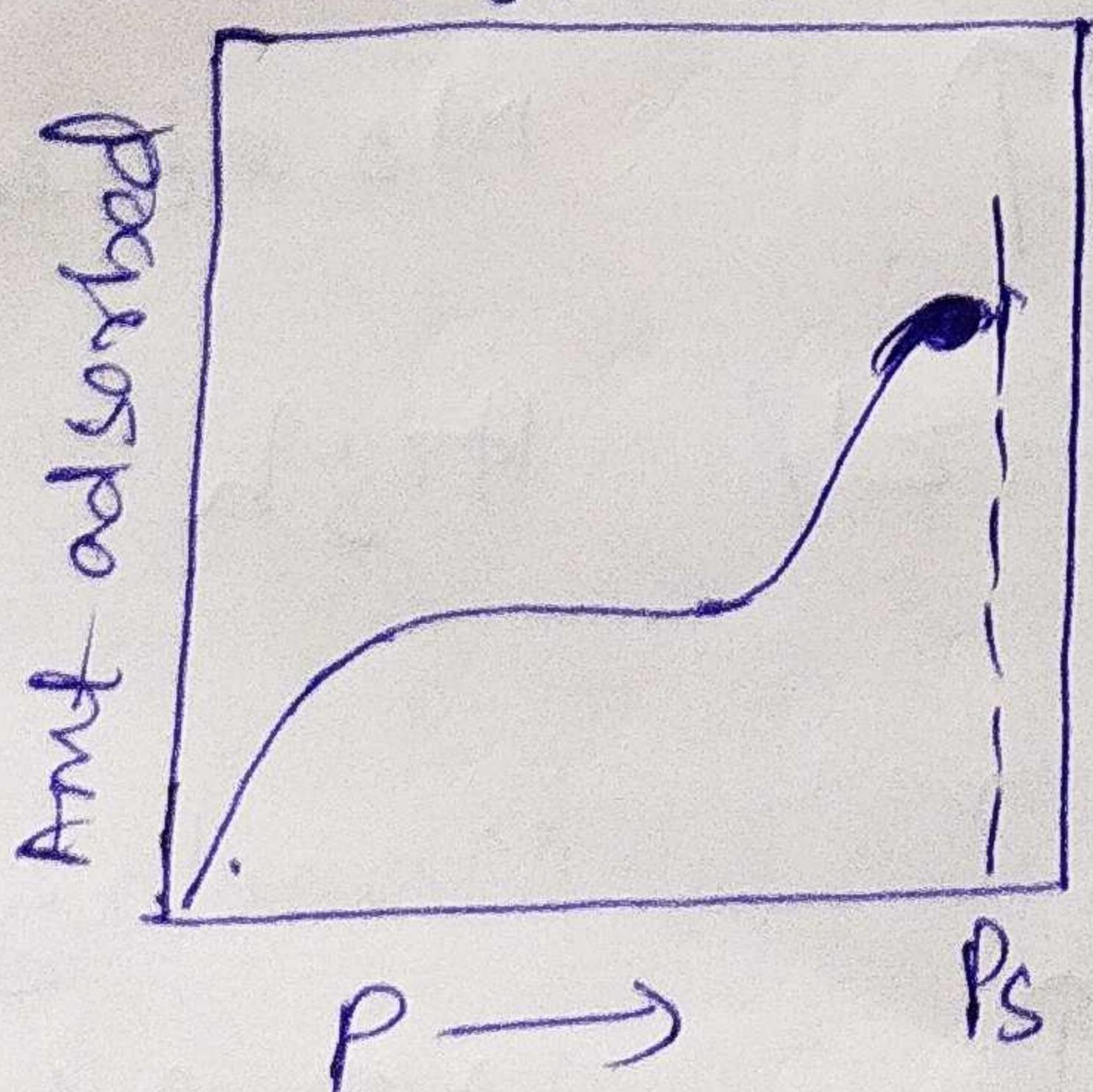


Types:



- Monolayer formation; → Deviation from Langmuir model → Deviation from Langmuir model
- Explained by Langmuir; → Flat region shows multilayer monolayer → NO flat means NO monolayer
- Ex: Adsorption of H_2 & N_2 ; → N_2 on I₂ at -195°C → I_2 on silica gel at 79°C
on charcoal ~ -180°C;

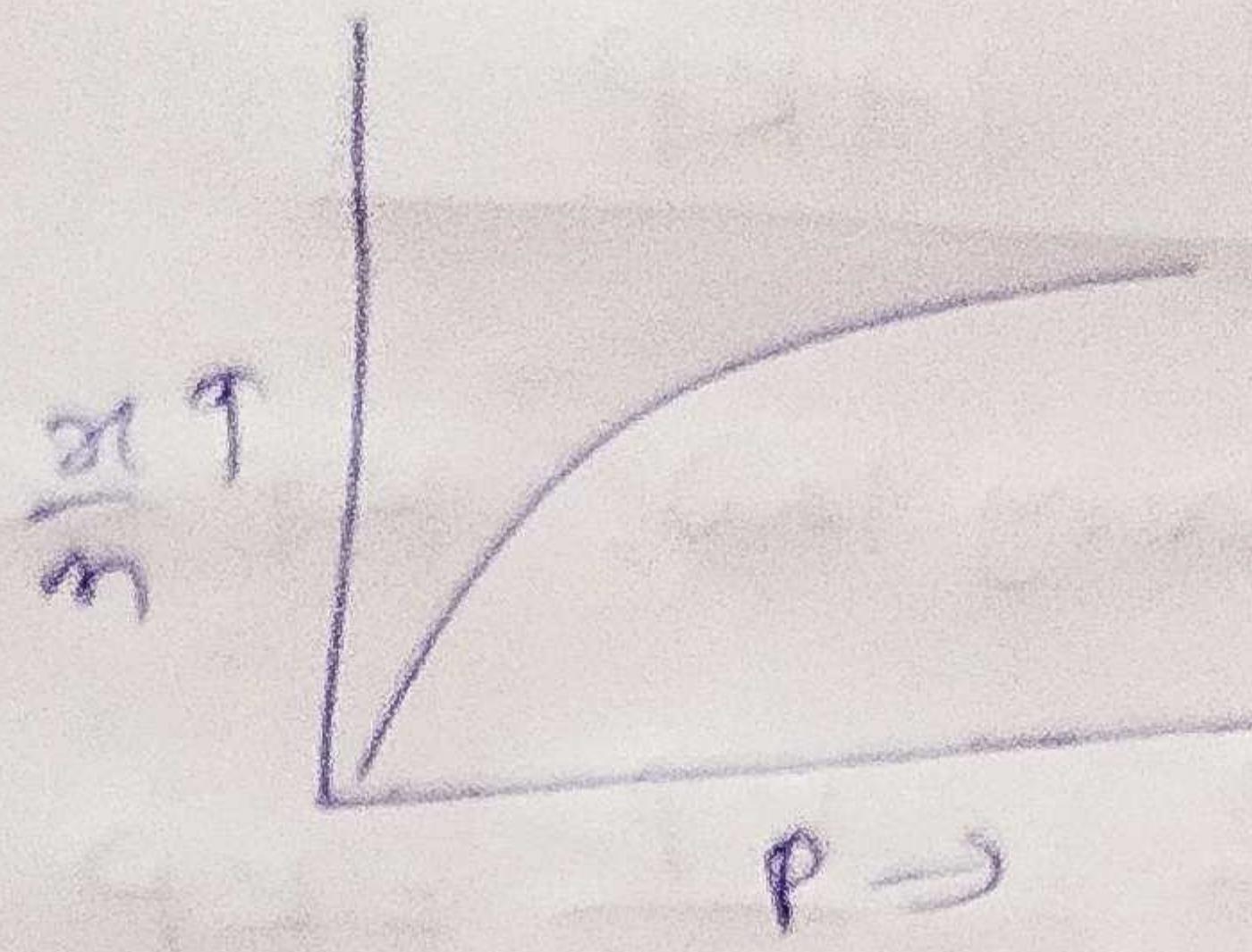
Type-IV



- Formation of monolayer → Same to type-IV
- balanced by multilayer → capillary condensation of gas
- Saturation level reaches before Ps
- C_6H_6 on Fe₂O₃ at ~50°C

Freundlich Isotherm

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



$$\Rightarrow \frac{1}{n} = 1, \quad \frac{x}{m} = K P$$

$$\Rightarrow \frac{x}{m} \propto P \text{ (1st order)}$$

$$\Rightarrow \frac{1}{n} = 0, \quad \frac{x}{m} = K$$

$$\Rightarrow \frac{x}{m} \propto P^0 \text{ (zero order)}$$

Langmuir Isotherm

Assumptions: will be discussed online during class one of that is dynamical equilibrium bet' b/w free and adsorbed adsorbates.

$$\theta = \frac{\text{Fraction of the total site(1)}}{\text{occupied}} \quad \begin{array}{c} \xrightarrow{\text{total}} \\ \xleftarrow{\theta} \end{array} \quad \begin{array}{c} \xleftarrow{\text{(1-\theta)}} \\ \xleftarrow{\text{free site}} \end{array}$$

$$(1-\theta) = \text{Free site of the total surface}$$

Rate of adsorption (R_a)

$$R_a \propto (1-\theta) P$$

$$\Rightarrow R_a = K_a (1-\theta) P - (1)$$

Rate of desorption (R_d)

$$R_d \propto \theta$$

$$\Rightarrow R_d = K_d \theta - (2)$$

$$\text{At eqn, } R_a = R_d$$

$$\begin{aligned} K_a (1-\theta) P &= K_d \theta \\ \Rightarrow \frac{K_a}{K_d} &= \frac{\theta}{(1-\theta) P} \\ \Rightarrow K &= \frac{\theta}{(1-\theta) P} \\ \Rightarrow K P &= \frac{\theta}{1-\theta} \\ \Rightarrow \frac{1-\theta}{\theta} &= \frac{1}{K P} \\ \Rightarrow \frac{1}{\theta} - 1 &= \frac{1}{K P} \\ \Rightarrow \frac{1}{\theta} &= \frac{1}{K P} + 1 = \frac{1+K P}{K P}, \quad \boxed{\theta = \frac{K P}{1+K P}} \end{aligned}$$

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

Case-I: P is very low, $KP \ll 1$, $1+KP \approx 1$

$$\text{Sv, } \theta = \frac{KP}{1+KP} \approx \frac{KP}{1} = KP$$

$$\Rightarrow \theta \propto P \text{ (1st order)}$$

Case-II: P is very high, $KP \gg 1$, $1+KP \approx KP$

$$\text{Sv, } \theta = \frac{KP}{1+KP} = \frac{KP}{KP} = 1 = \text{constant (K)}$$

$$\theta = K$$

$$\Rightarrow \theta \propto P^0 \text{ (Zero order)}$$

Case-III: P is neither low nor high $\theta \uparrow$

$$\theta \propto P^\eta \text{ (Low pressure)}$$

$$\theta \propto P^0 \text{ (High pressure)}$$

$$\text{Sv } \theta \propto P^{\frac{1}{n}} \text{ (at intermediate pressures)}$$

$$\frac{1}{n} > 0 \text{ but } < 1$$

$$\text{i.e. } n > 1$$

$$\text{Sv } \theta = K P^{\frac{1}{n}}$$

