

# **C23J – SURFACES**

## **ADSORPTION AT SOLIDS**

**SOLID: ADSORBENT**

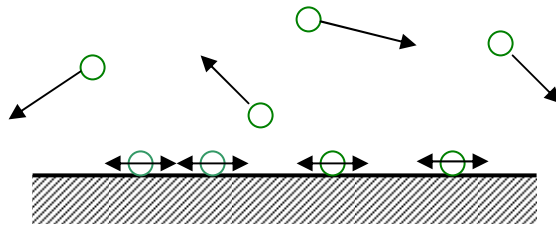
**GAS/SOLUTE: ADSORBATE**

### **APPLICATIONS IN:**

- **HETEROGENEOUS CATALYSIS**  
(E.G., HYDROGENATION OF ALKENES,  
CRACKING OF CRUDE OIL OVER SILICA-  
ALUMINA : ZEOLITES)
- **WASTEWATER TREATMENT**
- **ENVIRONMENTAL CHEMISTRY**  
(E.G., LEACHING OF PESTICIDES IN SOIL,  
CHELATION OF METAL IONS IN HUMIC ACIDS)
- **CHROMATOGRAPHY**

Finely divided solids possess a very high SPECIFIC  
SURFACE AREA (SSA) / m<sup>2</sup> g<sup>-1</sup>

(activated C : ~ 1000 ; Si gel : ~ 500)



Extent of adsorption depends on : T, P (gas) or conc.  
(solvent).

Adsorption is spontaneous process, therefore

$$(\Delta \bar{G}_{ads})_{T,P} < 0$$

(adsorption *equilibrium* if  $(\Delta \bar{G}_{ads})_{T,P} = 0$ )

On the other hand, the adsorbed state is more “ordered”  
(2D vs 3D), hence

$$\Delta \bar{S}_{ads} < 0 \quad (\text{non-dissociative adsorption})$$

$$\Delta \bar{G}_{ads} = \Delta \bar{H}_{ads} - T\Delta \bar{S}_{ads} < 0$$

$$\Delta \bar{H}_{ads} < T\Delta \bar{S}_{ads} < 0 \quad \longrightarrow \quad \text{non-dissociative} \\
\text{adsorption } \textit{exothermic}$$

**Exception: Dissociative adsorption (e.g., H<sub>2</sub> on glass  
————→ 2 H(ads) )**

$\Delta\bar{S}_{ads} > 0$  ,  $\Delta\bar{H}_{ads} > 0$  (*endothermic* adsorption), such  
that  $\Delta\bar{G}_{ads} < 0$

**Two types of adsorption, based on  $|\Delta\bar{H}_{ads}|$  :**

**PHYSICAL**  
(*physisorption*;  
e.g., N<sub>2</sub> on C)

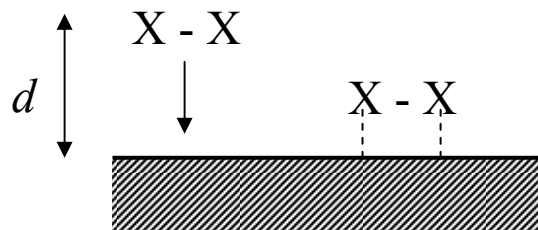
- non-specific (dispersion, electrostatic) forces
- $-\Delta\bar{H}_{ads} < 40 \text{ kJ mol}^{-1}$
- reversible
- multilayer adsorption

**CHEMICAL**  
(*chemisorption*;  
e.g., C<sub>6</sub>H<sub>6</sub> on Pd)

- covalent bonds between adsorbate and adsorbent
- $|\Delta\bar{H}_{ads}| > 80 \text{ kJ mol}^{-1}$
- often irreversible  
(C + O<sub>2</sub>(ads) —→ CO, CO<sub>2</sub> at high T)
- monolayer adsorption

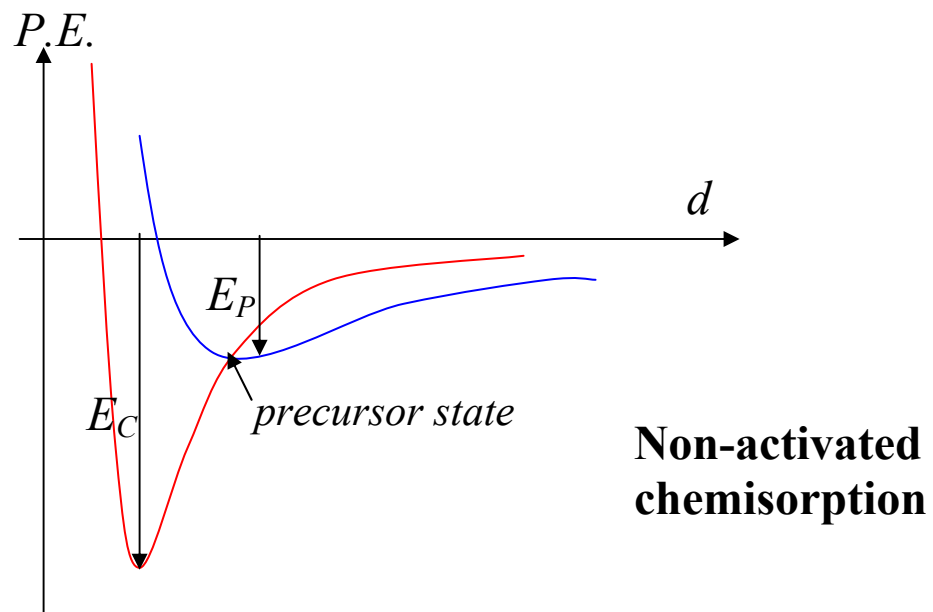
# ENERGETICS OF ADSORPTION

Adsorbate is diatom  $X_2$

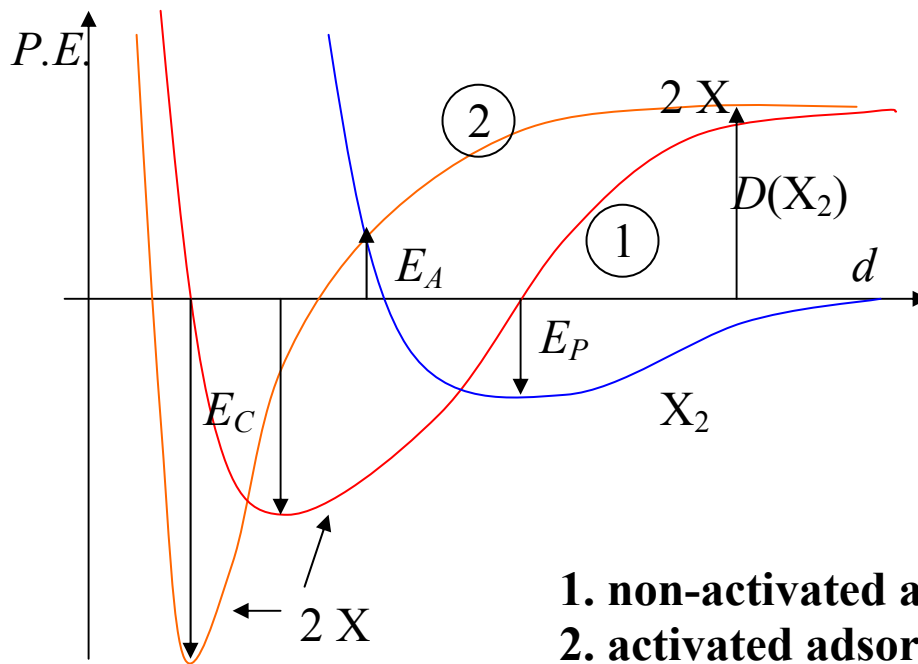


Potential energy diagram:

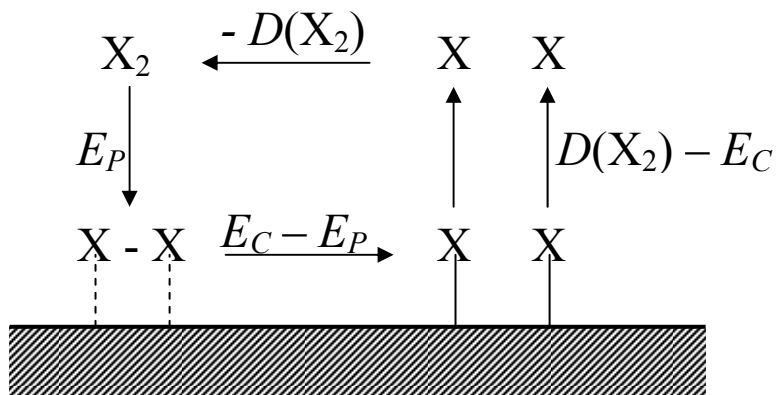
## 1. Non-dissociative adsorption



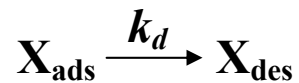
## 2. Dissociative (chemical) adsorption



1. non-activated adsorption
2. activated adsorption  
( $H_2$  on  $Cu$ ,  $E_A \sim 20 \text{ kJ mol}^{-1}$ )



## KINETICS OF DESORPTION/ADSORPTION



$k_d / s^{-1}$  : desorption rate constant

Arrhenius:  $k_d = A \exp(-E_d/RT)$

$A \sim$  vibrational frequency

Residence time  $\sim$  half-life  $t_{1/2} = \frac{\ln 2}{k_d} = \frac{\ln 2}{A} \exp(E_d / RT)$

$\tau_0 = \ln 2 / A$  : average time between two successive attempts to escape from surface

$E_d / \text{kJ mol}^{-1} = 25 \longrightarrow t_{1/2} \sim 10^{-8} \text{ s}$  (physisorption)

100  $\longrightarrow \sim 1 \text{ hr}$  (chemisorption)

## ANALYTICAL ASPECTS OF ADSORPTION

Quantitative measures of adsorption:

**# moles of adsorbate per gram of adsorbent** :  $X / m$

(in mol g<sup>-1</sup>)

or, in the case of adsorption from the gas phase,

**adsorption volume ( $V$ ) per gram of adsorbent**, where

$$V = (n_{ads}RT/P)/m$$

evaluated at STP (25°C, 1 atm), i.e.  $V = (n_{ads} \times 22.4 \text{ dm}^3)/m$

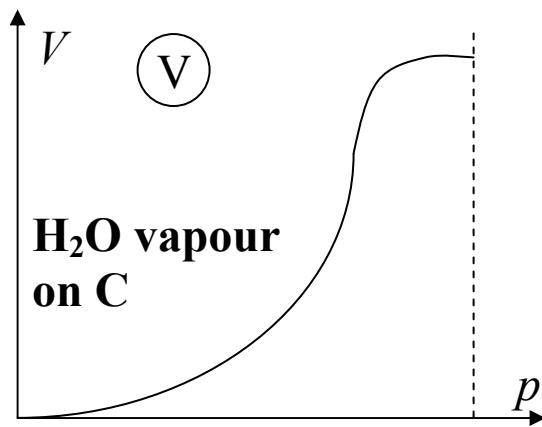
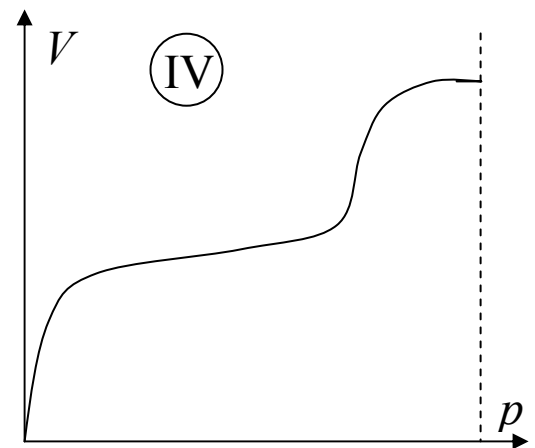
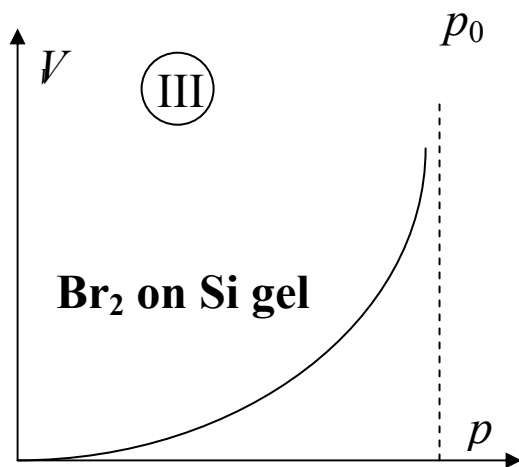
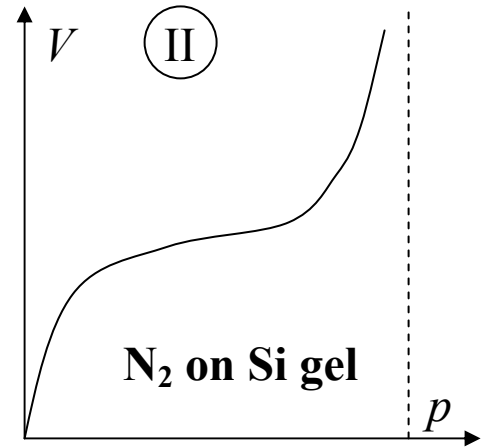
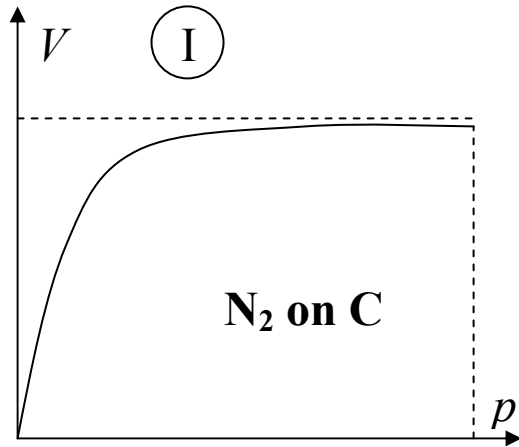
$$V = V(T,P) \quad \text{gas} \longrightarrow \text{solid}$$

$$X/m = X/m(T,c) \quad \text{solution} \longrightarrow \text{solid}$$

$$X = V_{soln}(c_{ini} - c_{fin}) \quad (c_{fin} = c)$$

$T$  constant:  $V(P)$  or  $X/m(c)$  : *adsorption isotherms*

## Five different types of isotherms (physisorption)



$p_0$  = saturation pressure

**I: monolayer adsorption**

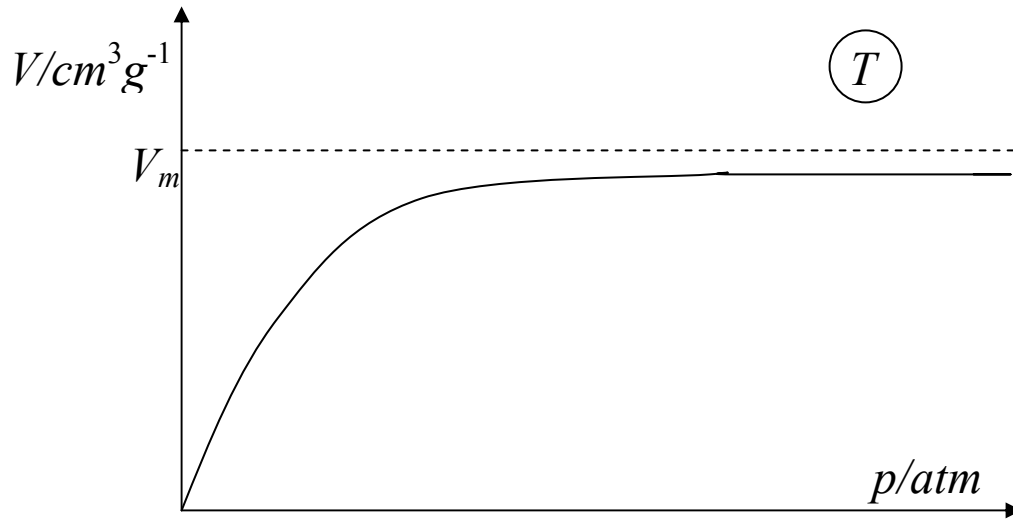
**II: adsorbate - adsorbent interaction**  
**> adsorbate - adsorbate interaction** } **multi-**  
**layer**  
**ads.**

**III: <**

**IV, V: similar to II, III; adsorption at *porous* solids**  
**(“capillary condensation”)**

## TYPE I ISOTHERMS: THE LANGMUIR MODEL

### Monolayer adsorption (Chemi/Physisorption)



#### Model assumptions:

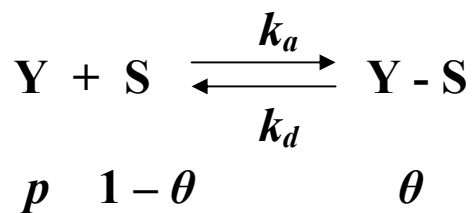
- (1) Uniform surface with  $N$  adsorption sites per  $\text{cm}^2$
- (2) No interference of adsorption properties between sites
- (3) One molecule per site
- (4) Molar heat of adsorption  $\Delta\bar{H}_{ads}$  independent of fractional coverage  $\theta$
- (5) No dissociation

**Fractional coverage**  $\theta = (\# \text{ sites occupied per cm}^2) / N$

$$= V / V_m \quad (\text{gas/solid})$$

$$= X / X_m \quad (\text{solution/solid})$$

**Kinetic scheme:**



**Equilibrium : rate of adsorption = rate of desorption**

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

**(Adsorption from solution: replace  $p$  by  $c$ )**

$$K p = \theta / (1 - \theta)$$

$$K(T) = k_a / k_d \quad \text{adsorption constant (in atm}^{-1} \text{ or M}^{-1}\text{)}$$

$$\boxed{\theta(T, p) = \frac{Kp}{1 + Kp}}$$

**Langmuir isotherm ( $T$  const.)**

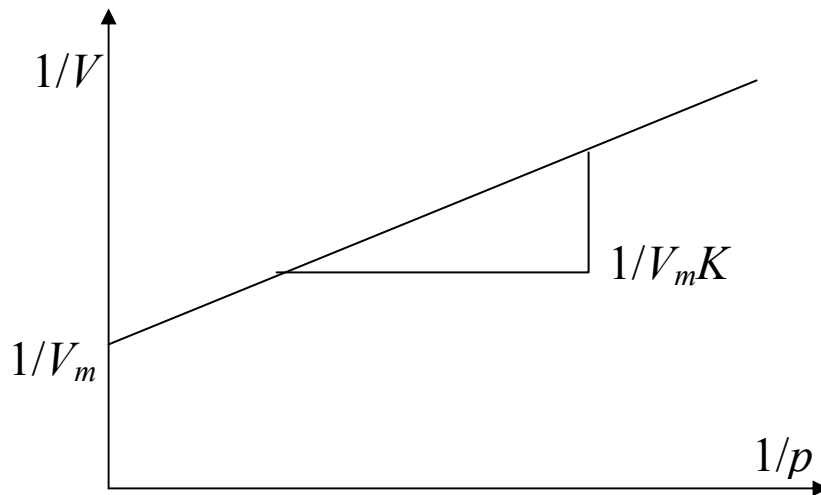
**$p$  small:  $\theta \sim Kp$**

**$p \longrightarrow \infty : \theta \longrightarrow 1$**

**In terms of adsorption volume:**

$$V = \frac{V_m K p}{1 + K p} \quad \longrightarrow \quad \frac{1}{V} = \frac{1}{V_m} + \frac{1}{V_m K} \cdot \frac{1}{p}$$

$\uparrow$   $\uparrow$

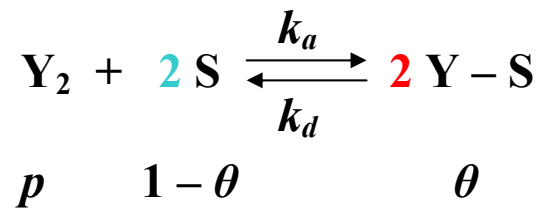
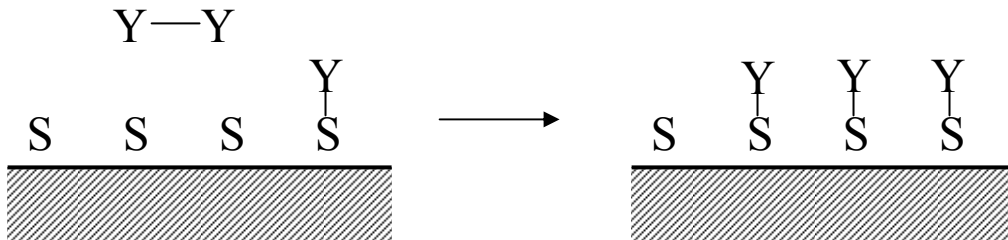


**$V_m = 1 / \text{intercept}$        $K = \text{intercept} / \text{slope}$**

**Alternatively:  $\frac{p}{V} = \frac{1}{V_m K} + \frac{p}{V_m}$**

**Graph of  $p/V$  vs  $p$  has slope =  $1/V_m$ , intercept =  $1/V_m K$**

## Dissociative adsorption



**Adsorption equilibrium:**

$$k_a p (1 - \theta)^2 = k_d \theta^2$$

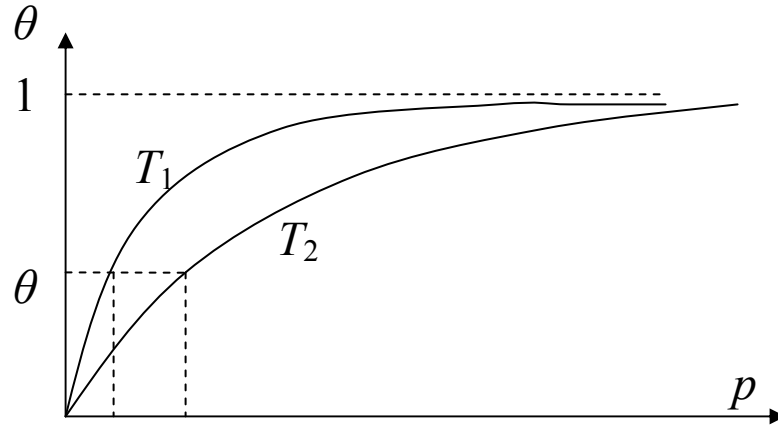
**Thus:** 
$$Kp = \left( \frac{\theta}{1 - \theta} \right)^2$$

**from which we obtain:**

$$\boxed{\theta(T, p) = \frac{\sqrt{Kp}}{1 + \sqrt{Kp}}} \quad (K = K(T))$$



## EFFECT OF TEMPERATURE ON ADSORPTION



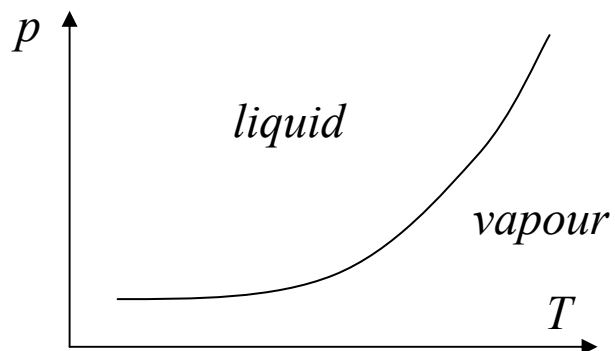
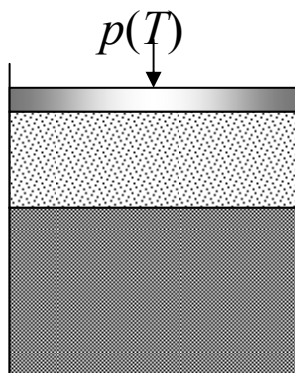
$T_2 > T_1$  : **exothermic** adsorption ( $\Delta\bar{H}_{ads} < 0$ )

$T_2 < T_1$  : **endothermic** adsorption ( $\Delta\bar{H}_{ads} > 0$ )

**Adsorption equilibrium**

$$\theta = \theta(T, p) \longrightarrow p = p(T, \theta) \longrightarrow \left( \frac{\partial p}{\partial T} \right)_{\theta}$$

**Liquid / vapour equilibrium :  $p = p(T)$**



**Assume vapour behaves like ideal gas, and use**

$$\bar{V}_{vap} \gg \bar{V}_{liq} \longrightarrow \Delta\bar{V} \cong RT / p$$

$$\left(\frac{dp}{dT}\right)_{sat} = \frac{p\Delta\bar{H}_{vap}}{RT^2} \quad \text{Clausius-Clapeyron eqn}$$

$$\Rightarrow \frac{dp}{p} = \frac{\Delta\bar{H}_{vap}}{R} \frac{dT}{T^2} \quad \text{or} \quad d \ln p = -\frac{\Delta\bar{H}_{vap}}{R} d\left(\frac{1}{T}\right)$$

$$\Rightarrow \frac{d \ln p}{d(1/T)} = -\frac{\Delta\bar{H}_{vap}}{R}$$

**Analogy with adsorption:**

**evaporation**  $\longleftrightarrow$  **desorption**

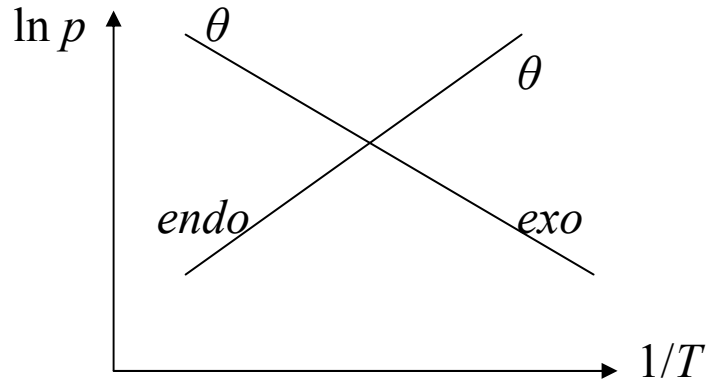
$$\Delta\bar{H}_{vap} \longleftrightarrow \Delta\bar{H}_{des} = -\Delta\bar{H}_{ads}$$

*at certain  $\theta$*

$$\therefore \boxed{\left(\frac{\partial \ln p}{\partial(1/T)}\right)_{\theta} = \frac{\Delta\bar{H}_{ads,\theta}}{R}}$$

$\rightarrow$  **isosteric heat of adsorption**  
(in  $\text{kJ mol}^{-1}$ )

**Adsorption from solution onto solid :  $p \longrightarrow c$**



**Application to the Langmuir isotherm (*non-dissociative* case) :**

$$Kp = \frac{\theta}{1-\theta}$$

$$\Rightarrow \ln p = \ln\left(\frac{\theta}{1-\theta}\right) - \ln K(T)$$

$$\Rightarrow \left(\frac{\partial \ln p}{\partial (1/T)}\right)_{\theta} = -\frac{d \ln K}{d(1/T)} = \frac{\Delta \bar{H}_{ads}}{R}$$

**independent of  $\theta$  , so Langmuir's model assumption (4) redundant (consequence of assumption (2))**

**This result remains valid for *dissociative* adsorption ( $(\theta / (1 - \theta))^2$  i.s.o.  $\theta / (1 - \theta)$ )**

**Correction of Langmuir model for interactions between neighbouring adsorbate molecules**

$$Kp = \frac{\theta}{1-\theta} \exp(B\theta/T) \quad \text{Fowler-Frumkin isotherm}$$

( $B/T$  : interaction parameter ;  $B < 0$  : attraction  
 $B > 0$  : repulsion  
 $B = 0$  : no interaction)

$$\Rightarrow \ln p = \ln\left(\frac{\theta}{1-\theta}\right) - \ln K(T) + B\theta/T$$

$$\Rightarrow \left(\frac{\partial \ln p}{\partial(1/T)}\right)_{\theta} = -\frac{d \ln K}{d(1/T)} + B\theta$$

$$= \frac{\Delta\bar{H}_{ads,\theta}}{R}$$

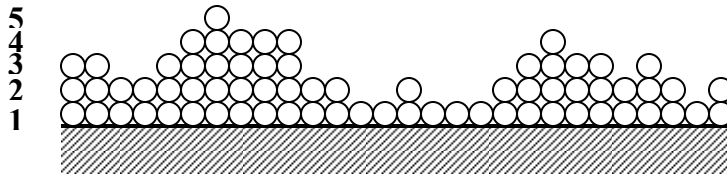
**Thus,  $\Delta\bar{H}_{ads,\theta}$  may become  $> 0$  for  $B$  sufficiently  $> 0$  in the case of non-dissociative adsorption.**

$$B = \frac{1}{R} \frac{d\Delta\bar{H}_{ads,\theta}}{d\theta}$$

# MULTILAYER ADSORPTION

## Model assumptions:

- (1) smooth, uniform surface
- (2) same number of adsorbate molecules in each layer when full
- (3) no lateral interactions
- (4)  $\Delta\bar{H}_{ads,1} \neq \Delta\bar{H}_{ads,2} = \Delta\bar{H}_{ads,3} = \dots \cong -\Delta\bar{H}_{vap}$  (bulk)
- (5) dynamic equilibrium between adjacent layers
- (6) non-dissociative adsorption



Coverage :  $\theta = V / V_m$

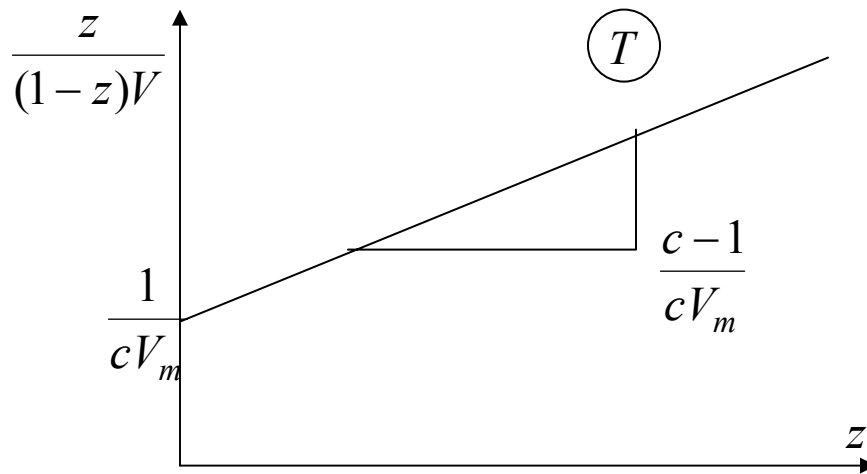
$V_m$  = adsorption volume (STP) occupied by molecules covering a *monolayer* (so  $\theta$  may now become  $> 1!$ )

2 equilibrium constants:

$$K_1(T) = \frac{k_a^{(1)}}{k_d^{(1)}} = \frac{\theta_1}{\theta_2}$$

$K_2(T)$  defined analogously for layers 2, 3,...





$V_m = 1 / (\text{slope} + \text{intercept}) \longrightarrow \# \text{ adsorption sites}$

$c(T) = 1 + (\text{slope} / \text{intercept}) \longrightarrow \Delta \bar{H}_{ads,1}$

**Determination of specific surface area**

**SSA = adsorbent area / adsorbent mass**

$$= N_A n_{max} a / m = N_A V_m a / (22.4 \text{ dm}^3 m)$$

$N_A = 6.0 \times 10^{23} \text{ mol}^{-1}$ ,  $a = \text{area} / \text{adsorbate molecule}$



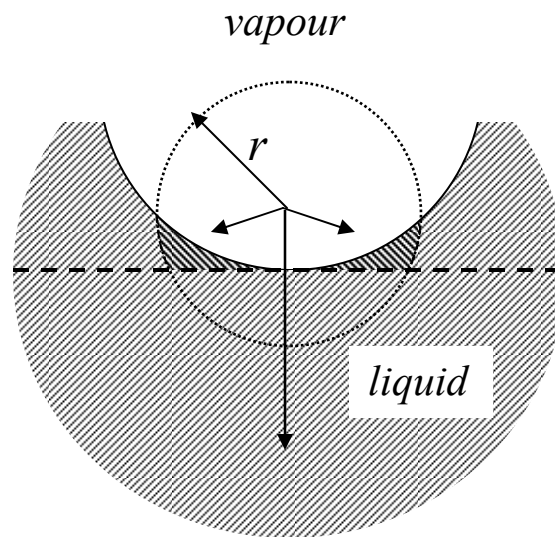
## SORPTION AT POROUS SOLIDS : TYPE IV ISOTHERMS

Adsorption or liquid / vapour equilibrium :

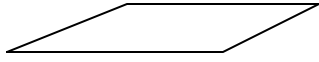
rate of evaporation = rate of condensation

Rates depend on:  $T$  and  $p$  (condensation)

$T$  and *curvature* (evaporation)

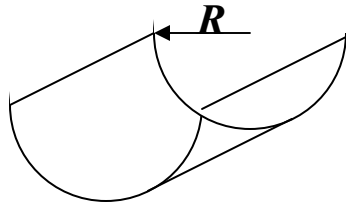


Inward pull is stronger over a hollow meniscus than over a planar surface ( $r$  = radius of sphere of attraction), hence, at a given  $T$ , the rate of evaporation is *less* than at a planar surface. Equilibrium vapour pressure  $p$  is therefore *lower*.



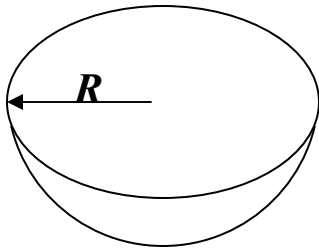
$$p_0(R = \infty)$$

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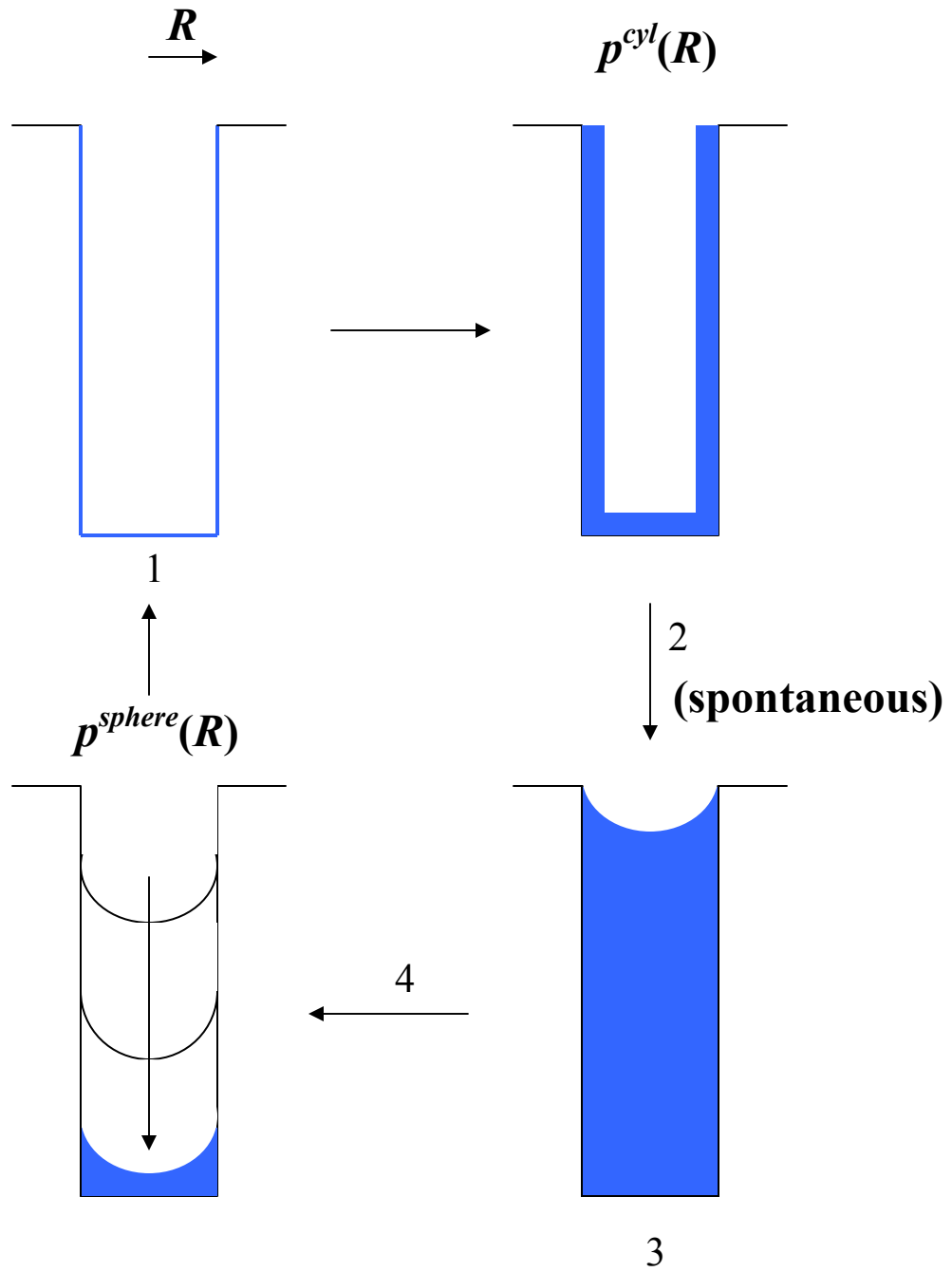


$$p^{cyl}(R)$$

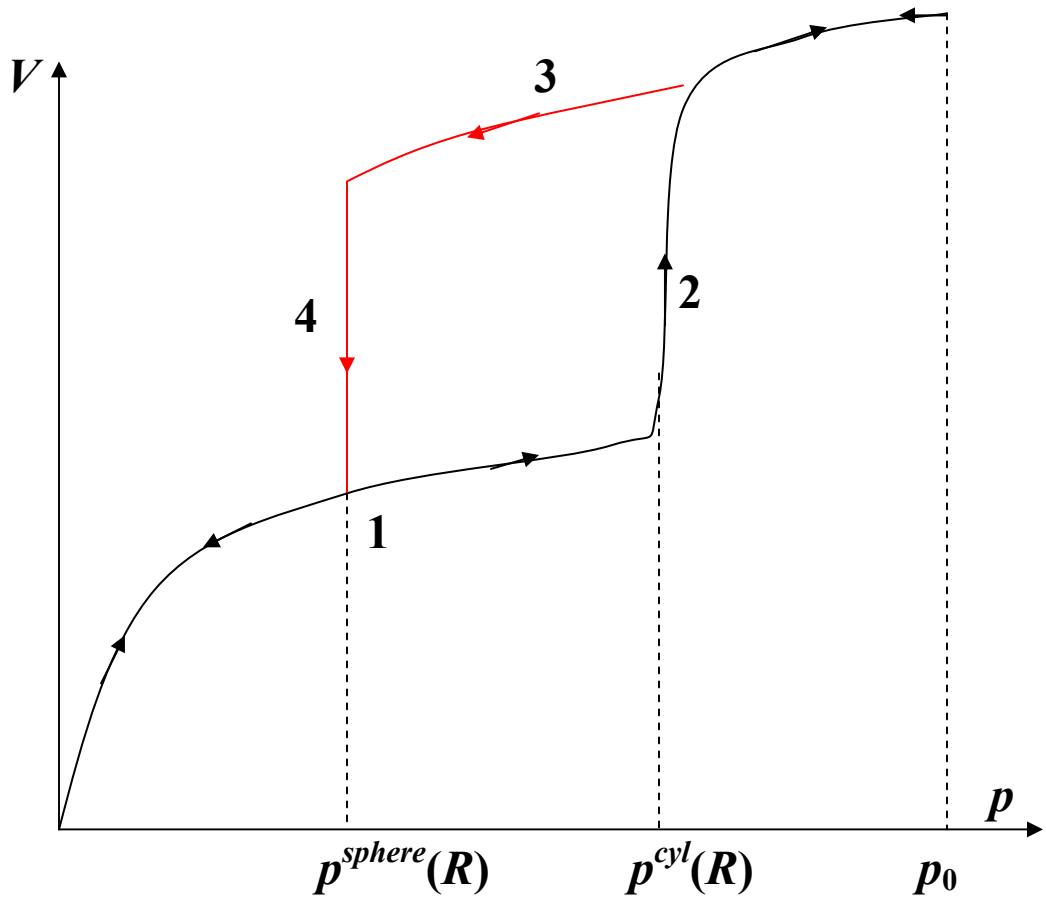
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$$p^{sphere}(R)$$



*Capillary condensation*



*“hysteresis loop”*