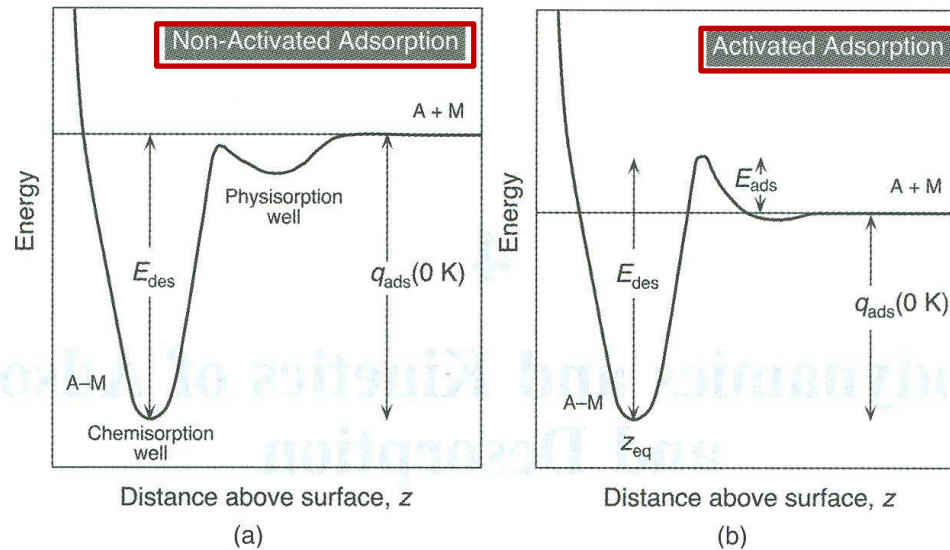


# Thermodynamics & Kinetics of Adsorption & Desorption

1. Thermodynamics of ad/desorption (4.1)
2. Kinetics of adsorption (4.5)
3. Adsorption isotherm from kinetics (4.6)
4. Rate of desorption (4.4)
5. Temperature programmed desorption (4.7)

# Thermodynamics of ad/desorption (4.1)

## Binding energies and activation barriers



**Figure 4.1** One-dimensional potential energy curves for molecular adsorption: (a) nonactivated adsorption; (b) activated adsorption.  $E_{ads}$ ,  $E_{des}$ , adsorption activation energy and desorption activation energy, respectively;  $q_{ads}$ , heat released by adsorption;  $z_{eq}$ , adsorbate-surface bond length.

- In non-dissociative, non-activated adsorption,  $E_{ads} = 0$  (ads activation E)  
 Adsorption bond binding energy (bond strength)  $\epsilon(M-A) = E_{des}$   
 $\epsilon(M-A) = q_{ads}$  (heat released by adsorption)

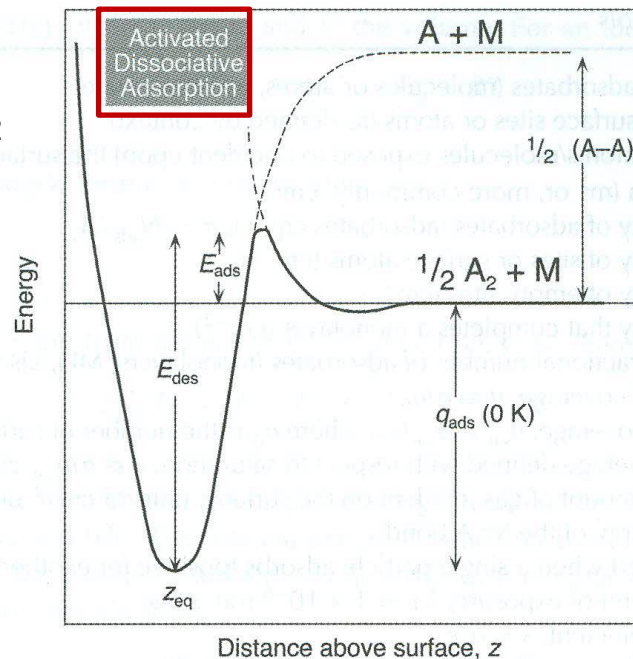
- For activated adsorption,  $E_{ads} > 0$   
 $E_{des} = E_{ads} + \epsilon(M-A)$ ,  
 $\epsilon(M-A) = q_{ads} = E_{des} - E_{ads}$

- In dissociative adsorption, the intramolecular adsorbate bond with dissociation energy  $\epsilon(\text{A-A})$  is also broken,

$$\epsilon(\text{M-A}) = \frac{1}{2}(E_{\text{des}} - E_{\text{ads}} + \epsilon(\text{A-A}))$$

$$q_{\text{ads}} = 2\epsilon(\text{M-A}) - \epsilon(\text{A-A})$$

Adsorption of a diatomic molecule  $\text{A}_2$



**Figure 4.2** Activated dissociative adsorption.  $E_{\text{ads}}$ ,  $E_{\text{des}}$ , adsorption activation energy and desorption activation energy, respectively;  $q_{\text{ads}}$ , heat released by adsorption;  $z_{\text{eq}}$ , adsorbate-surface bond length.

# Thermodynamic quantities

- Gibbs (free) energy,  $G$ ,  $\Delta G < 0$  (spontaneous process)  
$$\Delta G = \Delta H - T\Delta S$$
- Adsorption (e.g. chemisorption)  $\rightarrow$  usually exothermic process  $\rightarrow \Delta S < 0$  (gas in 2D),  $\Delta G < 0$  (constant  $T$  &  $P$ , free energy $\downarrow$ , spontaneous)  $\rightarrow \Delta G = \Delta H - T\Delta S \rightarrow \Delta H < 0$  (exothermic) (or  $\Delta_{\text{ads}}H < 0$ )
- Temperature $\downarrow \rightarrow$  Adsorption $\uparrow$
- exception: dissociate adsorbates & high translational mobility on the surface ( $\Delta S > 0$ ). Repulsion between adsorbates by coverage $\uparrow \rightarrow$  less exothermic  
  
e.g.,  $\text{H}_2$  on glass: endothermic,  $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{glass})$ ,  $\Delta S > 0 \rightarrow \Delta H > 0$

**Table 4.1** Definition of symbols

---

$N_{\text{ads}}$	Number of adsorbates (molecules or atoms, as appropriate)
$N_0$	Number of surface sites or atoms (as defined by context)
$N_{\text{exp}}$	Number of atoms/molecules exposed to (incident upon) the surface
$A_s$	Surface area ( $\text{m}^2$ or, more commonly, $\text{cm}^2$ )
$\sigma$	Areal density of adsorbates (adsorbates $\text{cm}^{-2}$ ), $\sigma = N_{\text{ads}}/A_s$
$\sigma_0$	Areal density of sites or surface atoms ( $\text{cm}^{-2}$ )
$\sigma_*$	Areal density of empty sites ( $\text{cm}^{-2}$ )
$\sigma_{\text{sat}}$	Areal density that completes a monolayer ( $\text{cm}^{-2}$ )
$\theta$	Coverage, fractional number of adsorbates (monolayers, ML), also sometimes called fractional coverage, $\theta \equiv \sigma/\sigma_0$
$\theta_{\text{sat}}$	Saturation coverage, $\theta_{\text{sat}} \equiv \sigma_{\text{sat}}/\sigma_0$ , where $\sigma_0$ is the number of surface atoms
$\delta$	Relative coverage defined with respect to saturation, $\delta \equiv \sigma/\sigma_{\text{sat}} \equiv \theta/\theta_{\text{sat}}$
$\varepsilon$	Exposure, amount of gas incident on the surface, units of $\text{cm}^{-2}$ or Langmuir
$\varepsilon(\text{M-A})$	Binding energy of the M-A bond
$q_{\text{ads}}$	Heat released when a single particle adsorbs (positive for exothermic)
L	Langmuir, unit of exposure, $1 \text{ L} = 1 \times 10^{-6} \text{ torr} \times 1 \text{ s}$
$s$	Sticking coefficient, $s = \sigma/\varepsilon$
	Integral sticking coefficient: total coverage divided by exposure, meaningful only if $s$ is constant or as $\theta \rightarrow 0$ ML
	Instantaneous or differential sticking coefficient at coverage $\theta$ $s(\theta) = dN_{\text{ads}}/dN_{\text{exp}} = d\sigma/d\varepsilon$ , evaluated at a specific value of $\theta$
$s_0$	Initial sticking coefficient, sticking coefficient as $\theta \rightarrow 0$ ML

---

# Adsorption enthalpy & heat of adsorption

- Enthalpy  $H = U + PV$  (U: internal energy)
- For an ideal gas in molar units,  $H_g = U_g + P_g V_g = U_g + RT$
- For the adsorbed gas, the PV term is negligible,  $H_a = U_a$
- The enthalpy change in going from the gas to the adsorbed phase

$$\Delta_{\text{ads}} H = H_a - H_g = U_a - U_g - RT$$

- In Fig. 4.1, 4.2  $\rightarrow$  internal energy of the system is zero at infinite separation and 0 K (internal energy depend on the sum of translational, rotational, vibrational energy of the gas (or adsorbate))
  - $-q_{\text{ads}} = U_a - U_g$  and  $q_c = RT$  ( $q_c$ : heat of compression from gas(finite volume) into adsorbed layer(volume = 0))
- c.f. heat of adsorption( $q_{\text{ads}}$ ): a **positive** quantity for exothermic adsorption  
adsorption enthalpy( $\Delta_{\text{ads}} H$ ): a **negative** quantity for exothermic adsorption



In general, the heat of adsorption is a coverage dependent quantity, hence

$$-\Delta_{\text{ads}}H(\theta) = q_{\text{ads}}(\theta) + q_{\text{c}}(\theta) = q_{\text{st}}(\theta) \quad (4.1.14)$$

where  $q_{\text{st}}(\theta)$  is the isosteric heat of adsorption,  $\Delta_{\text{ads}}H(\theta)$  is the differential adsorption enthalpy and  $q_{\text{ads}}(\theta)$  is the differential heat of adsorption. At room temperature  $q_{\text{c}}$  is only  $2.5 \text{ kJ mol}^{-1}$ , hence in practice it is usually negligible.

The isosteric heat of adsorption is defined through the Clausius-Clapeyron equation,

$$q_{\text{st}}(\theta) = RT^2 \left( \frac{\partial \ln p}{\partial T} \right)_{\theta} = -R \left( \frac{\partial \ln p}{\partial (1/T)} \right)_{\theta} = -\Delta_{\text{ads}}H \quad (4.1.15)$$

where  $p$  is the equilibrium pressure that maintains a coverage  $\theta$  at temperature  $T$ . It can be shown [5] that the heat measured in a single crystal adsorption calorimetry experiment is the isosteric heat of adsorption.

One final quantity of interest is the integral adsorption enthalpy. This represents the total enthalpy change (generally in molar units) recorded when the coverage changes from zero to some final value  $\theta_{\text{f}}$ . The integral adsorption enthalpy is related to the heat of adsorption by

$$\Delta_{\text{ads}}H_{\text{int}} = \frac{\int_0^{\theta_{\text{f}}} -q_{\text{ads}}(\theta) d\theta}{\int_0^{\theta_{\text{f}}} d\theta} \quad (4.1.16)$$

## Isosteric enthalpy(heat) of adsorption

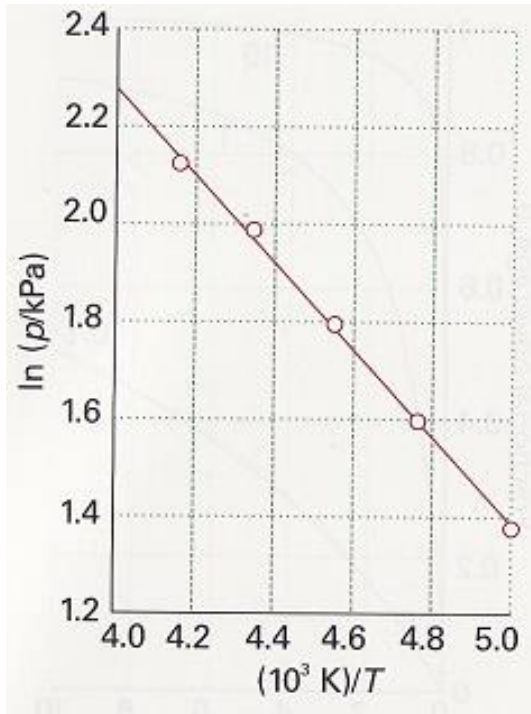
- $dG = Vdp - SdT$ , and  $d(\Delta G) = \Delta Vdp - \Delta SdT$  for any change
- At equilibrium,  $\Delta Vdp - \Delta SdT = 0$ .
- $\Delta V = V_{ad} - V_g \sim -nRT/p$
- $(\partial p / \partial T)_\theta = \Delta S / \Delta V = - (\Delta H/T) / (nRT/p) = - p \Delta H / nRT^2$  at constant  $\theta$
- $d \ln p = (\Delta H_{ad}/R) d(1/T) \rightarrow$  slope of  $(\ln p) - (1/T)$  plot gives  $\Delta H_{ad}/R$
  
- In genera,  $\Delta H_{ad}$  is coverage-dependent because of
  - 1) Heterogeneity of the adsorption sites
  - 2) Lateral interaction between adjacent adsorbates

cf. isotheric: constant adsorption

isotheric enthalpy: standard enthalpy of adsorption at fixed coverage

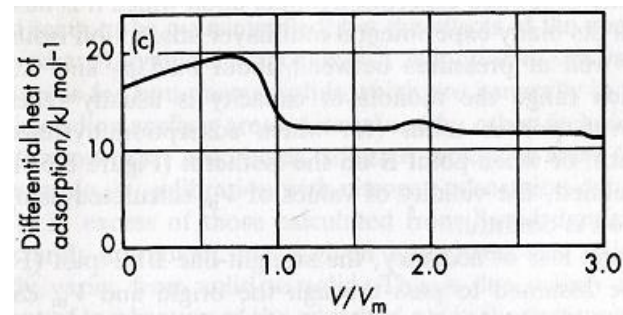
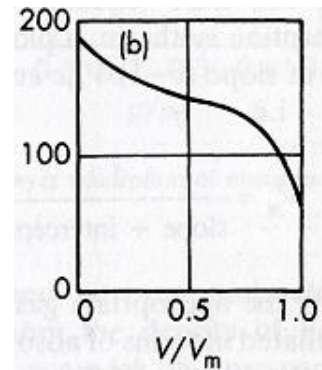
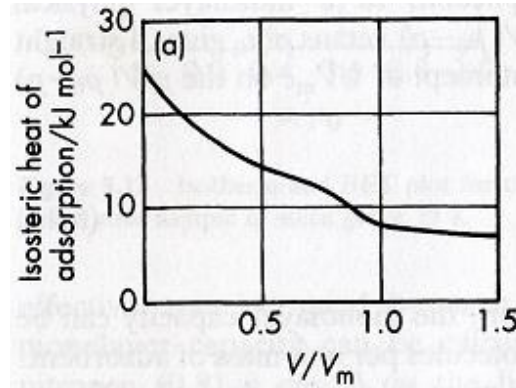


# Isosteric enthalpy(heat) of adsorption



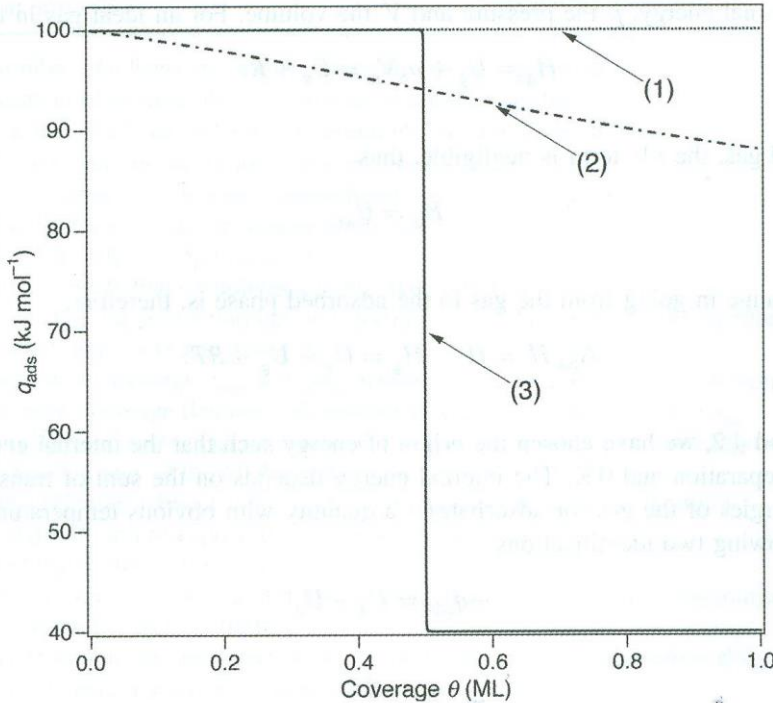
CO on charcoal

$$\Delta H_{\text{ad}} = -7.52 \text{ kJ/mol}$$



- Physisorbed  $\text{N}_2$  on rutile  $\text{TiO}_2$  at 85 K
- Chemisorbed H on W
- Physisorbed Kr on graphitized carbon black

# Heat of adsorption ( $q_{\text{ads}}$ ) vs. coverage ( $\theta$ )



**Figure 4.3** Three different behaviours of the heat of adsorption,  $q_{\text{ads}}$ , as a function of coverage,  $\theta$ . Case (1): the surface is composed of one and only one type of non-interacting site. Case (2):  $q_{\text{ads}}$  decreases linearly with  $\theta$ . Case 3: the surface is composed of two types of sites with different binding energies that fill sequentially. As shown in §4.3, case 3 can also arise from strong lateral interactions.

- **Case (1)**: one type of surface site, all these sites adsorb particles independently  $\rightarrow q_{\text{ads}}$  is constant,  $\Delta_{\text{ads}} H_{\text{int}} = -q_{\text{ads}}$
- **Case (3)**: surface has two independent adsorption sites with different characteristic adsorption energies that fill sequentially  $\rightarrow$  step-like behavior

- **Case (2)**: chemisorption involves charge transfer, and the capacity of a surface to accept or donate charge is limited  $\rightarrow$  as more and more particles adsorb, the ability of the surface to bind additional adsorbate likely drops  $\rightarrow q_{\text{ads}}$  drops with increasing  $\theta$ . In addition,  $\theta \uparrow \rightarrow$  distance between adsorbates  $\downarrow \rightarrow$  lateral interaction  $\uparrow \rightarrow q_{\text{ads}}$  changes as a function of  $\theta$

# Kinetics of adsorption (4.5)

Langmuir model assumes that

- Uniform adsorption site (all sites are equivalent & surface is uniform)
- Adsorption energy independent of  $\theta$  (no interaction between adsorbates)
- No surface diffusion
- Monolayer coverage (adsorption can't proceed beyond monolayer coverage)

$A(g) + * \rightarrow A(ad)$  : non-dissociative

\*: surface,  $k_a$ : adsorption rate const,  $k_d$ : desorption rate const

The rate of change of the surface coverage,

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

$k_a = Z_w s_0/p$  (or  $k_a \rightarrow k_a p$ ),  $s_0$  = initial sticking probability,

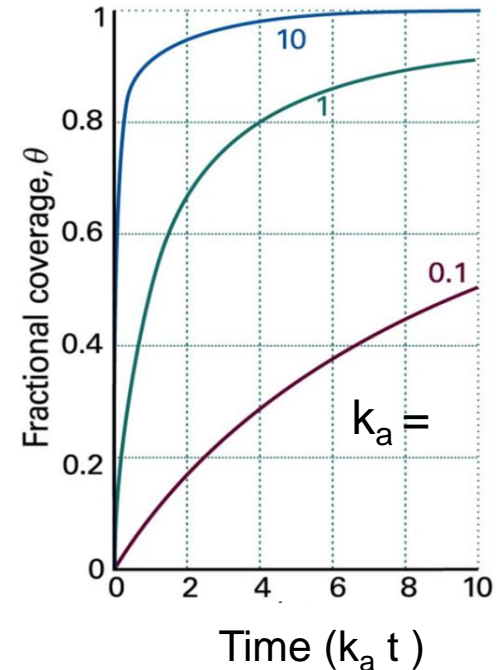
flux  $Z_w = p/\sqrt{2\pi m k_B T}$ ,  $(1 - \theta)$ : vacant site

$p$ : pressure of A,  $s = s_0(1 - \theta)$

cf. consider adsorption may be activated, rate,

$$r_{ads} = k_a(1 - \theta)\exp(-E_{ads}/RT)$$

$$\theta(t) = 1 - \exp(-k_a t)$$





$$d\theta/dt = k_a p (1 - \theta)^2$$

$$k_a = 2 Z_w s_0 / p \quad (\text{or } k_a \rightarrow k_a p)$$

$$s = s_0 (1 - \theta)^2$$

$$\theta(t) = k_a t / (1 + k_a t)$$

cf. consider adsorption may be activated,  
rate,

$$r_{\text{ads}} = k_a (1 - \theta)^2 \exp(-E_{\text{ads}}/RT)$$

Dissociative adsorption: surface coverage depends more weakly on pressure than for non-dissociative adsorption

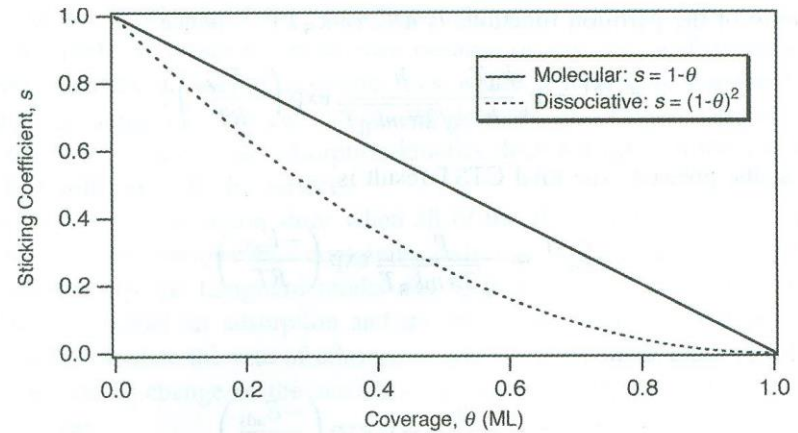


Figure 4.6 Langmuir models (molecular and dissociative) of the sticking coefficient,  $s$ , as a function of coverage,  $\theta$ .

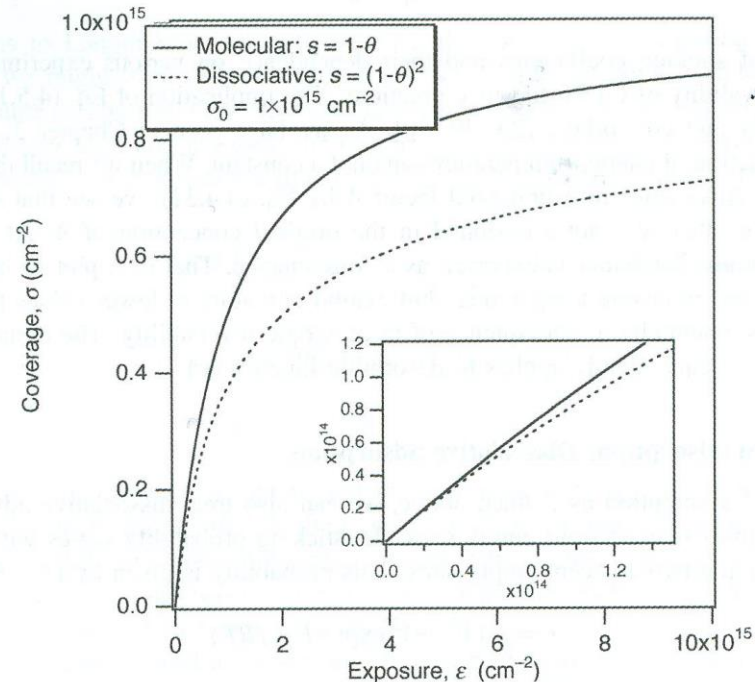
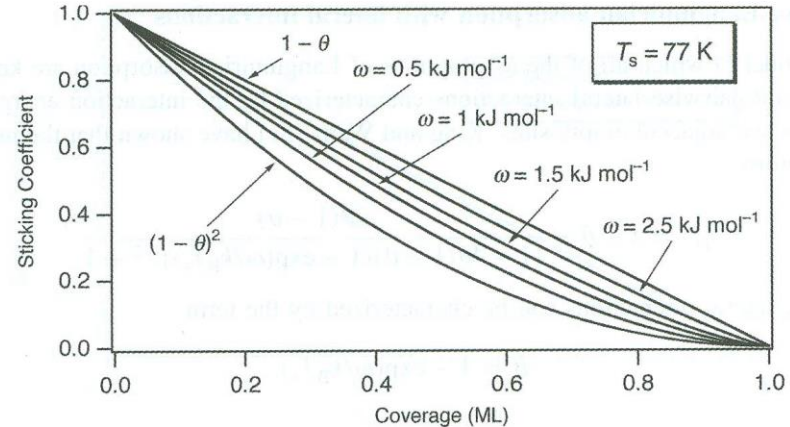


Figure 4.7 Langmuir models (molecular and dissociative) of coverage,  $\sigma$ , as a function of exposure,  $\epsilon$ .

# Dissociative Langmuir adsorption with lateral interaction

$$s = s_0 (1 - \theta)^2$$

Interaction energy  $w$



**Figure 4.8** The effect of lateral interactions on the dissociative sticking coefficient as a function of interaction strength,  $w$ , and coverage  $\theta$  at a fixed surface temperature  $T_s = 77$  K.

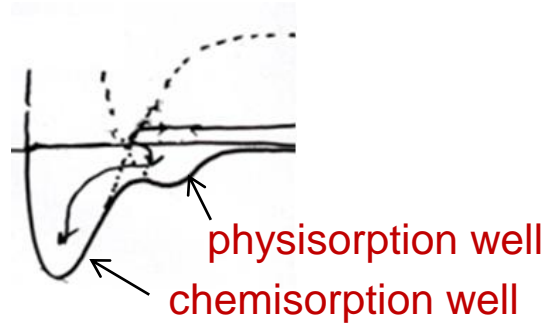
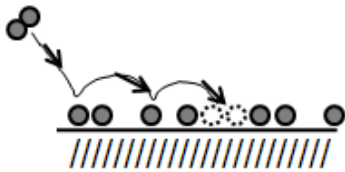
- For large repulsive interactions,  $w \ll 0$   
dissociative adsorption  $\rightarrow$  minimum 2 sites needed
 
$$s = s_0(1 - 2\theta) \quad \text{for } \theta < 0.5$$

$$s = 0 \quad \text{for } \theta \geq 0.5$$
- For large attractive interactions,  $w \gg 1$   
same as non-dissociative adsorption  
(the adsorbate coalesce into close-packed islands)
 
$$s = s_0(1 - \theta) \quad \text{for } \theta < 0.5$$
- Intermediate value of  $w$  (Fig. 4.8)



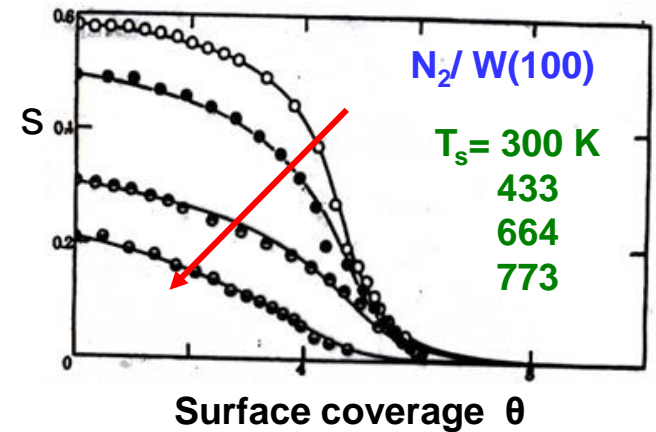
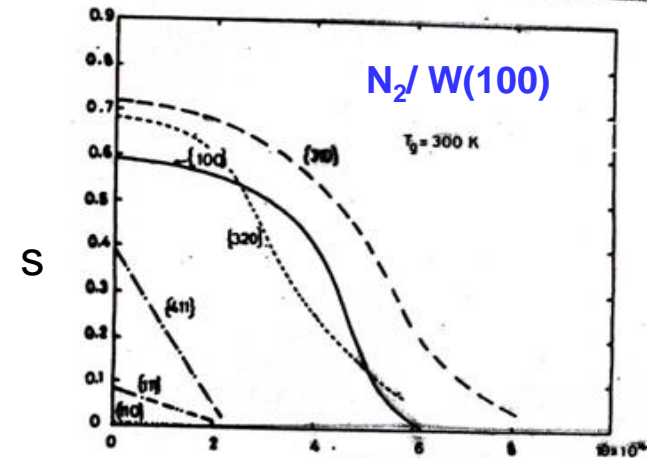
# Precursor-mediated adsorption

- Marked deviation from Langmuir adsorption  
Langmuir adsorption;  $s = s_0 (1 - \theta)^2$
- Coverage-insensitive  $s$
- Decrease in  $s$  with  $T \uparrow$ : re-evaporation of the precursor state

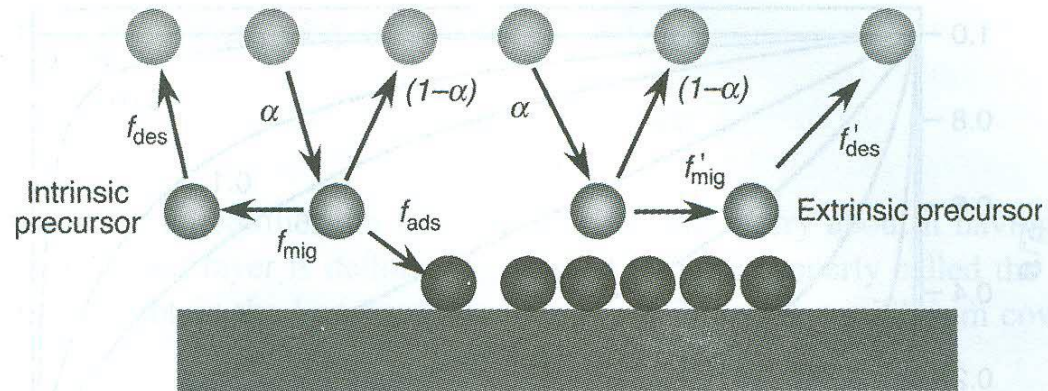


- Trapping in the physisorption well
- Precursor hopping on the surface to find an empty site  $\rightarrow$  increase in  $s$
- Re-evaporation of the precursor due to a finite surface lifetime  $\tau$ ;  $\tau = \tau_0 \exp(-E_d/RT)$

Non-dissociative  $s = s_0 (1 - \theta)^2$







**Figure 4.10** The Kisliuk model of precursor mediated adsorption. Incident molecules trap into intrinsic or extrinsic precursors. Thereafter, sticking becomes a competitive process between desorption out of the precursor and transfer into the stable chemisorbed state.  $\alpha$  is the probability to enter into the precursor state.

$$K = f'_d / (f_a + f_d)$$

Empty site:

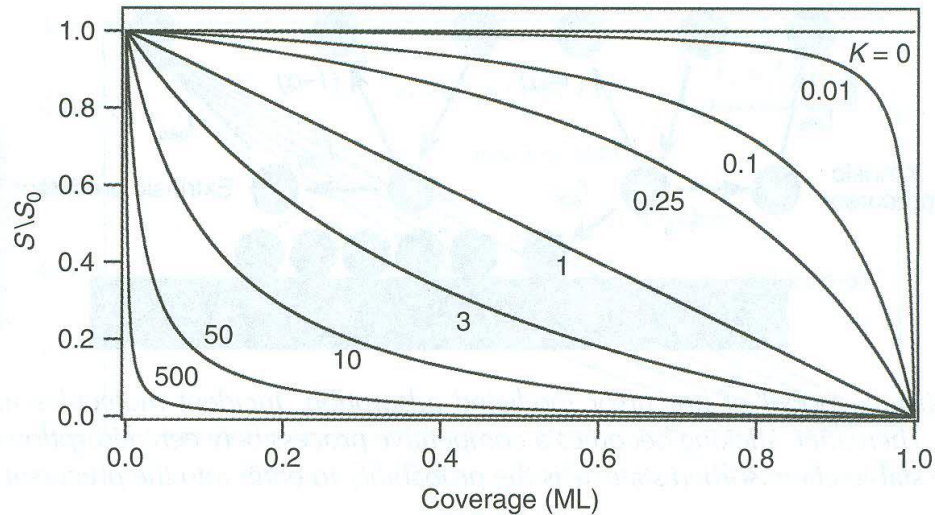
Adsorption probability  $f_a$

Desorption probability  $f_d$

Occupied site:

Desorption probability:  $f'_d$

$$S(\theta)/S_0 = \{1 + K[(1/\theta) - 1]\}^{-1}$$



**Figure 4.11** The change of sticking coefficient,  $s$ , with coverage for precursor mediated adsorption is characterized by the parameter  $K$ . For  $K = 0$ , the sticking coefficient is constant, whereas for  $K = 1$  it drops linearly with coverage as in Langmuirian adsorption. Large values of  $K$  decrease  $s$  relative to Langmuirian adsorption.

# Adsorption isotherms from kinetics (4.6)

Adsorption-desorption equilibrium



- $d\theta/dt = k_a p(1 - \theta) - k_d \theta$
- The desorption rate constant  
 $k_d = k_d^0 \exp(-E_d/RT)$
- At equilibrium,  $d\theta/dt = 0$ ,

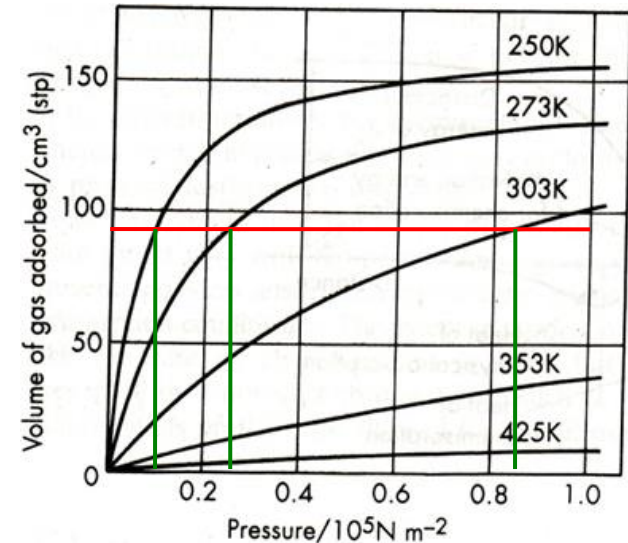
$$\theta = K(T) p / [1 + K(T) p]$$

where  $K = k_a / k_d$ : equilibrium constant

- As  $p \rightarrow \infty$ ,  $\theta \rightarrow 1$
- $\theta - P$  plot at constant  $T$  is called **Langmuir isotherm**
- $T \downarrow \rightarrow$  adsorption  $\uparrow$  ( $\Delta H_{ads} < 0$ )
- As seen in the Fig., the coverage  $\theta$  depends **more sensitively** on  $T$  than on  $p$

Dissociative,  $d\theta/dt = k_a p(1 - \theta)^2 - k_d \theta^2 \rightarrow \theta = (Kp)^{1/2} / [1 + (Kp)^{1/2}]$

$NH_3$ / charcoal



cf. adsorption isotherm: coverage change by pressure at a temperature

# Measurement of adsorption isotherm

## Volumetric measurement

-to determine specific surface area of solids from gas adsorption

$$\theta = K(T) p / [1 + K(T) p]$$

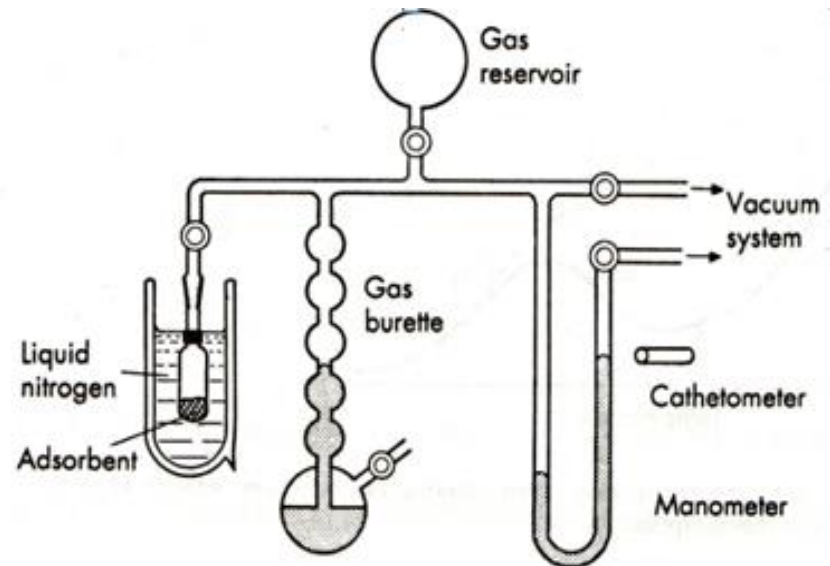
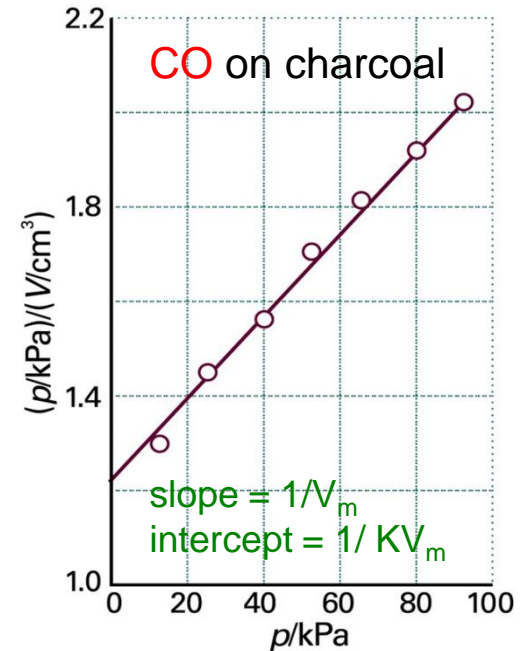
$\theta = V/V_m$  measured as a volume change, where  $V$  is the volume of gas adsorbed and  $V_m$  is the saturation volume (corresponding to complete coverage)

$$V/V_m = Kp / (1 + Kp),$$

$$P/V = (1 + Kp) / K V_m = p/V_m + 1/KV_m$$

$p/V$  vs.  $p$  plot gives a straight line

Slope =  $1/V_m$  and intercept =  $1/KV_m$

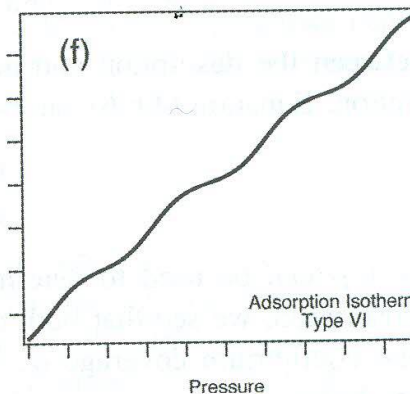
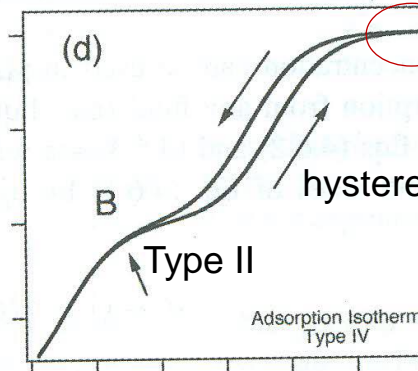
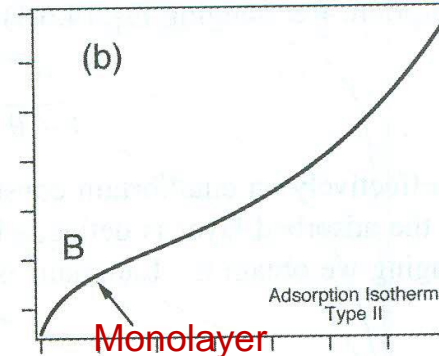
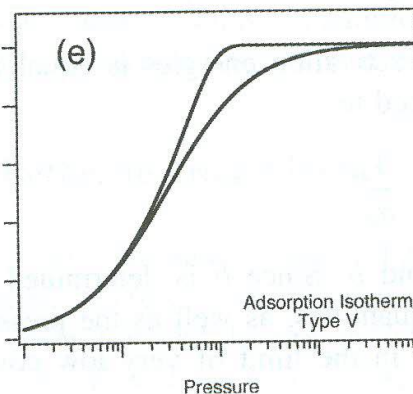
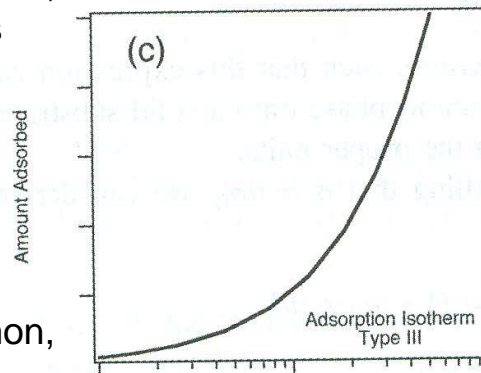
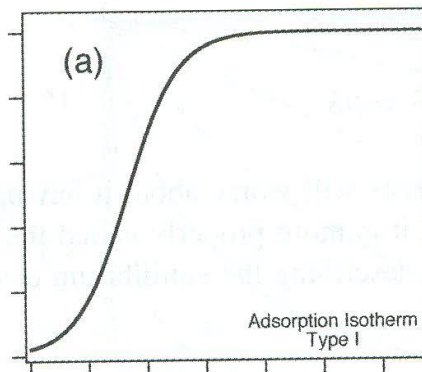


# Classifications of adsorption isotherms

Langmuir isotherm  
Monolayer, chemisorption, Microporous solids (activated carbons, zeolites, porous oxides)

Not common, multilayer

Not common, type III with porous adsorbents



Monolayer adsorption + multilayer condensation, non-porous solids

Capillary condensation in mesoporous

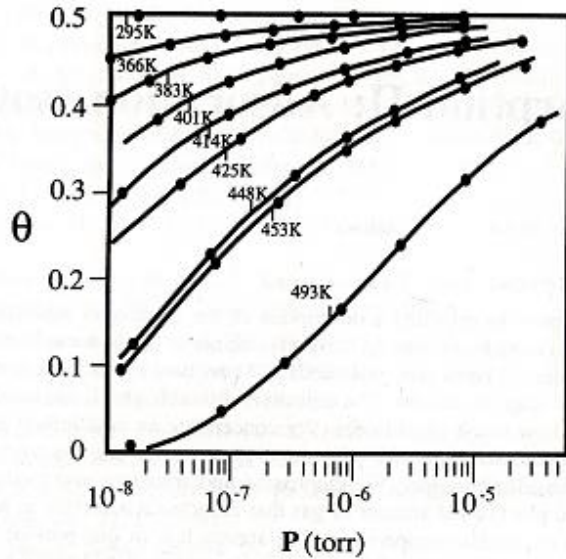
Mesoporous industrial adsorbents

Stepwise multilayer adsorption on a uniform non-porous surface

**Figure 4.12** The six types of physisorption isotherms in which coverage (either relative coverage  $\theta$  or absolute coverage  $\sigma$ ) is plotted against pressure,  $p$ , of a gaseous adsorbing species (or concentration,  $c$ , of a species dissolved in a liquid solution). The coverage is often expressed as specific coverage, that is, coverage per unit mass of the substrate.

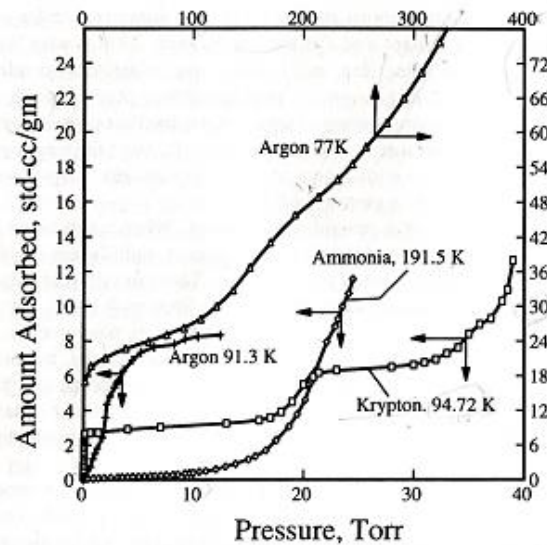


# Examples of adsorption isotherms

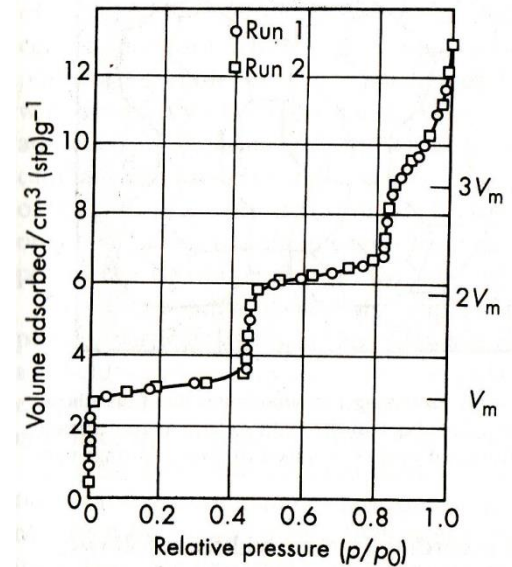


CO/Pd(111)

temp  $\uparrow$   $\rightarrow$   
Langmuir  
isotherm



Ar, NH<sub>3</sub> /carbon black

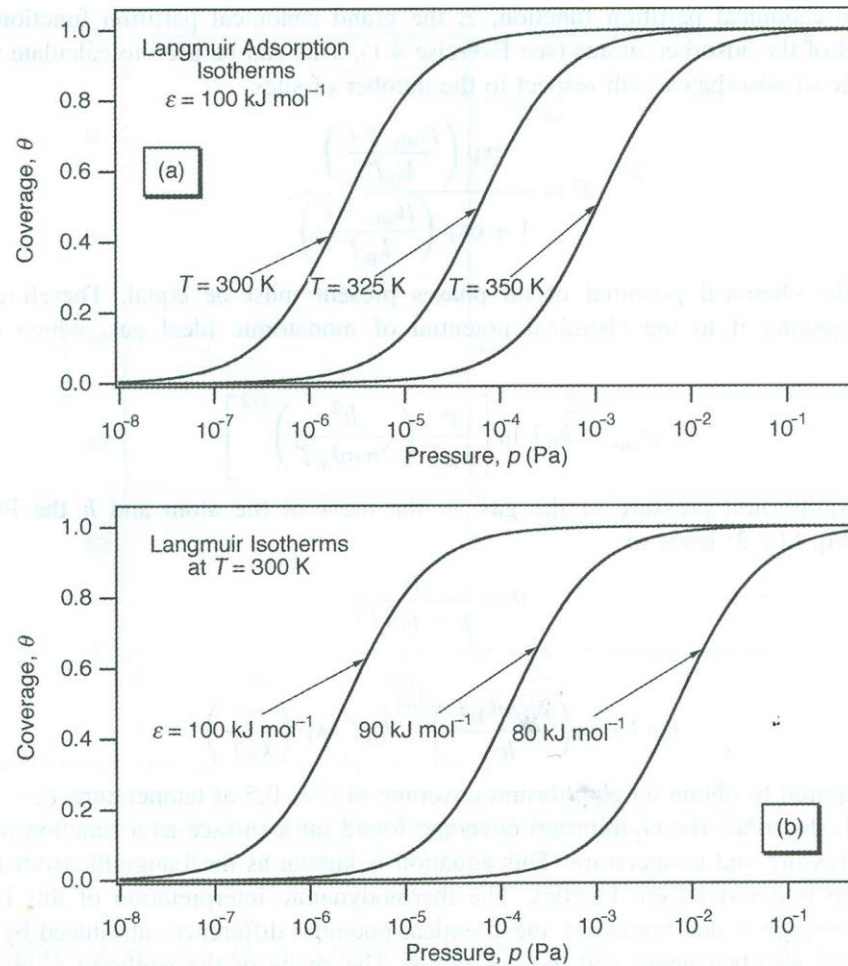


Kr /carbon black

Stepwise isotherms  $\rightarrow$   
uniform solid surface  
(each layer  $\rightarrow$   
complete monolayer

\* carbon black graphitized at 3000 K

# Langmuir adsorption isotherm



Other isotherms:  
Freundlich adsorption isotherm

$$V = kp^{1/n}, \quad k, n: \text{const}$$

$$\text{Log } V = \text{log } k + (1/n)\text{ln } p$$

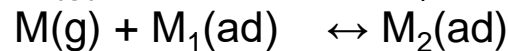
**Figure 4.4** Langmuir isotherms exhibit a dependence on the temperature and binding energy. (a) Constant heat of adsorption for various temperatures  $T$ . (b) Constant temperature for various adsorption energies  $\epsilon$ .



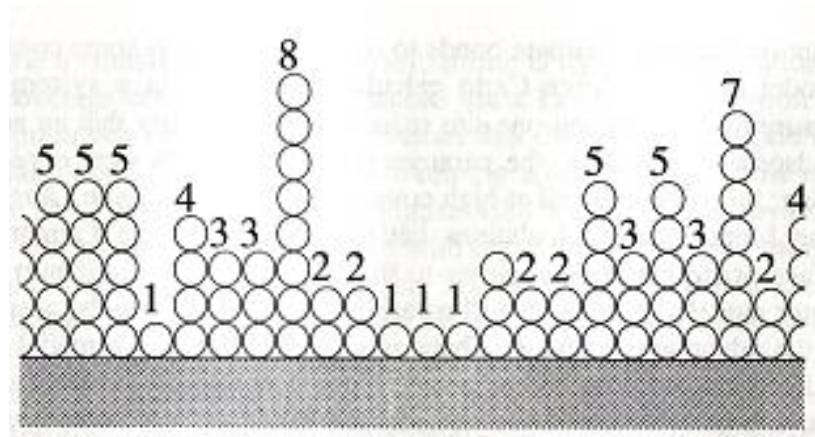
# Multilayer physisorption

**BET isotherm:** Brunnauer, Emmett, Teller

- Langmuir adsorption extended to allow multilayer adsorption
- **Equilibrium maintained between the adjacent layers**
- $\Delta H^\circ_{\text{des}}$  for the first layer and  $\Delta H^\circ_{\text{vap}}$  ( $=\Delta H_L$ ) for the multilayers
- **used for surface area measurements**



....



# BET equation

- Extension of Langmuir equation beyond the 1<sup>st</sup> layer
- Equilibrium between adjacent layers
- The rate of coverage change for each layer is zero
- The 1<sup>st</sup> layer may be chemisorption, but the 2<sup>nd</sup> layer and beyond are always physisorption → Therefore, different  $k_a$  and  $k_d$  values may be involved
- At equilibrium

$$d\theta_0/dt = -k_a p \theta_0 + k_d \theta_1 = 0$$

$$d\theta_1/dt = k_a p \theta_0 - k_d \theta_1 - k'_a p \theta_1 + k'_d \theta_2 = 0$$

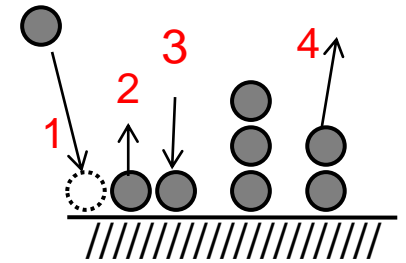
$$d\theta_2/dt = k'_a p \theta_1 - k'_d \theta_2 - k'_a p \theta_2 + k'_d \theta_3 = 0$$

.....

$$d\theta_{n-1}/dt = k'_a p \theta_{n-2} - k'_d \theta_{n-1} - k'_a p \theta_{n-1} + k'_d \theta_n = 0$$

- $k_a = Z_w s_0$ ,  $k_d = v \exp(-\Delta H_{des}/RT)$  for the 1<sup>st</sup> layer
- $k'_a = Z_w s'_0$ ,  $k'_d = v' \exp(-\Delta H_{vap}/RT)$  for the 2<sup>nd</sup> layer and beyond.
- For multilayer adsorption  $s_0 \sim s'_0$  and  $v \sim v'$ . Then,  $k_a \sim k'_a$
- But  $E_{des}$  can be much larger than  $E'_{des}$ , hence  $k_d$  much smaller than  $k'_d$

$$d\theta_1/dt = 1 - 2 + 3 - 4$$



$\Delta H_{des}$  : 1<sup>st</sup> layer

$\Delta H_{vap}$  : multilayer

- Let  $k_a/k_d = K$ ,  $k'_a/k'_d = K'$ , and  
 $c = K / K' = (k_a/k_d) / (k'_a/k'_d) \sim k'_d/k_d = \exp(\Delta H_{des} - \Delta H_{vap}) / RT$

$$\theta_1 = (k_a/k_d) p \theta_0 = K p \theta_0 = c K' p \theta_0$$

$$\theta_2 = [(k_d + k'_a p) \theta_1 - k_a p \theta_0] / k'_d = (1/c + K' p) \theta_1 - K' p \theta_0 = c (K' p)^2 \theta_0$$

$$\theta_3 = [(k'_d + k'_a p) \theta_2 - k'_a p \theta_1] / k'_d = (1 + K' p) \theta_2 - K' p \theta_1 = c (K' p)^3 \theta_0$$

.....

$$\theta_n = (1 + K' p) \theta_{n-1} - K' p \theta_{n-2} = c (K' p)^{n-1} \theta_0 + (K' p)_n \theta_0 - c (K' p)^{n-1} \theta_0 = c (K' p)^n \theta_0$$

$$(1) \theta_0 + \theta_1 + \dots + \theta_n (n \rightarrow \infty) = 1$$

$$\rightarrow \theta_0 + c K' p [1 + K p + (K' p)^2 + (K' p)^3 + \dots] \theta_0 = 1 \rightarrow \theta_0 [1 + c K' p / (1 - K' p)] = 1$$

$$\rightarrow \theta_0 = 1 / [1 + c K' p / (1 - K' p)] = (1 - K' p) / [1 + (c - 1) K' p]$$

$$(2) V/V_m = \theta_1 + 2 \theta_2 + \dots + n \theta_n = c [K' p + 2 (K' p)^2 + 3 (K' p)^3 + \dots] \theta_0$$

$$= (1 - K' p) c K' p / [1 + (c - 1) K' p] (1 - K' p)^2$$

$$\text{cf: } 1 + x + x^2 + \dots = d(x + x^2 + x^3 + \dots) / dx = d[x / (1 - x)] / dx = 1 / (1 - x)^2$$

- When  $p = p_0$  (saturation vapor pressure), adsorption and desorption can take place at all sites. Therefore,  $k'_a p_0 (\theta_0 + \theta_1 + \dots + \theta_n) = k'_d (\theta_0 + \theta_1 + \dots + \theta_n) \rightarrow k'_a p_0 = k'_d \rightarrow K' = 1/p_0$  and  $K' p = p/p_0$  (3)
- $V/V_m = (1 - K' p) c K' p / [1 + (c - 1) K' p] (1 - K' p)^2$  from (2) and (3)  
 $= c (p/p_0) / [1 + (c - 1) p/p_0] (1 - p/p_0) = V/V_m = c p p_0 / [p_0 + (c - 1) p] (p_0 - p)$
- Rearranging,  $[p_0 + (c - 1) p] / c p_0 V_m = p / V (p_0 - p) \rightarrow$

$$p / [V (p_0 - p)] = 1 / c V_m + [(c - 1) / c V_m] (p / p_0); \quad y = a + b x \text{ type}$$

# BET equation

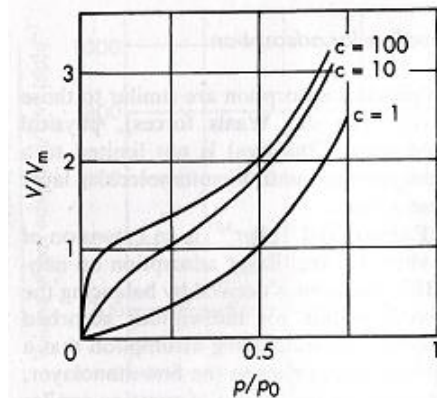
$p/V(p_0-p)$  vs.  $p/p_0$  plot gives a **straight line**

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m c} + \frac{(c-1)p}{V_m c p_0}$$

Intercept =  $1/cV_m$

$$V_m = \frac{1}{\text{slope} + \text{intercept}}$$

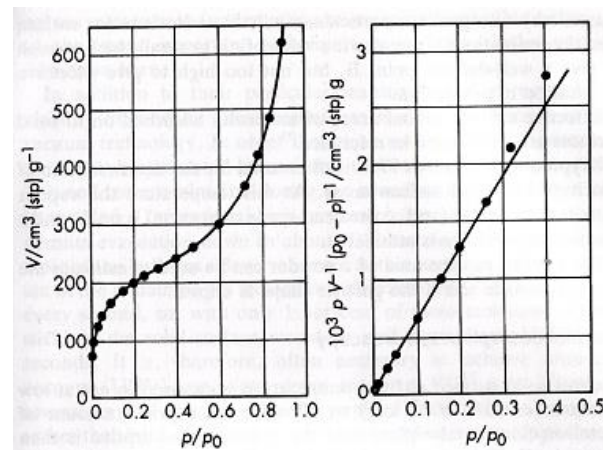
$V_m$  = monolayer capacity,  $p_0$ : saturation vapor pressure  
 $c = \exp(\Delta H_{\text{des}} - \Delta H_{\text{vap}}) / RT$



$N_2$ / silica gel @ 77 K

Text book:  $V, V_m \rightarrow n$  (amount adsorbed, moles per unit mass of the porous material),  $n_m$  (the monolayer capacity)

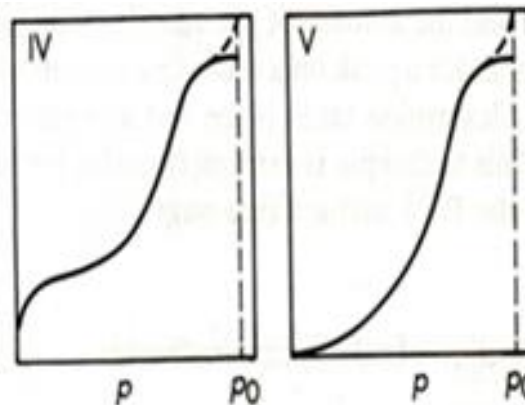
BET surface area,  $A = n_m N_A a_m$   
 $a_m$ : cross sectional area ( $N_2$  (at 77K) = 0.162 nm<sup>2</sup>)



For a **porous solid**

$$V = \frac{V_m c x}{(1-x)} \cdot \frac{1 - (n+1)x^n + nx^{n+1}}{1 + (c-1)x - cx^{n+1}}$$

where  $n$  is related to the pore size and  $x = p/p_0$   
 $n=1$ : Langmuir isotherm,  $n = \infty$ : BET isotherm



# Classifications of adsorption isotherms

## Brunner classification

Type I: Langmuir adsorption

Type II: monolayer + multilayer

Type III: multilayer adsorption

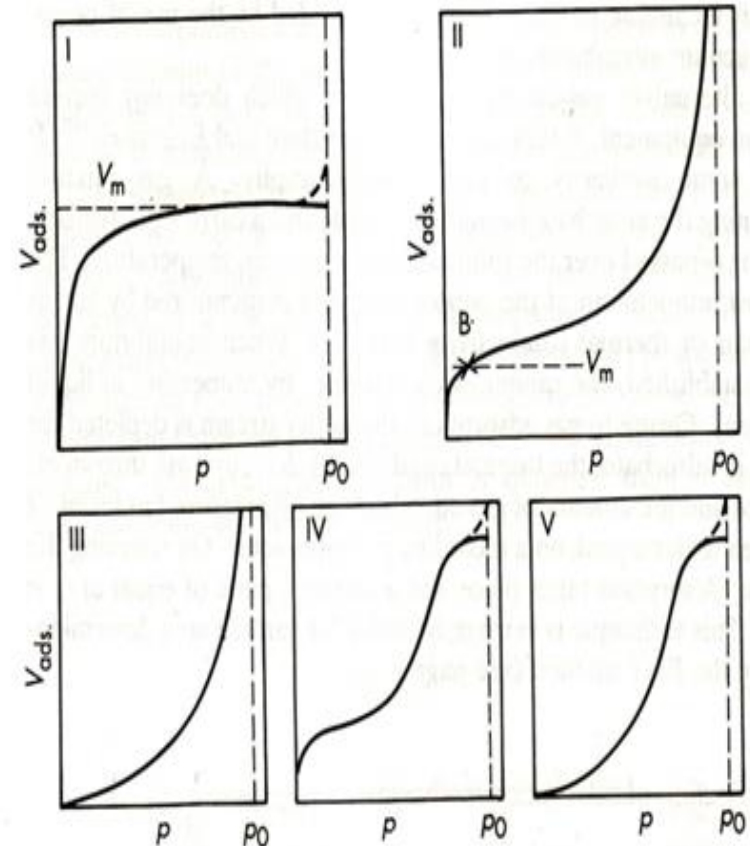
Type IV: Type II on porous solids

Type V: Type III on a porous adsorbent

- Finite pore volume limits the max  $V_{\text{ads}}$
- Type II & IV:  $\Delta H_{\text{des}} \gg \Delta H_{\text{vap}}$
- Type III & V:  $\Delta H_{\text{des}} \sim \Delta H_{\text{vap}}$

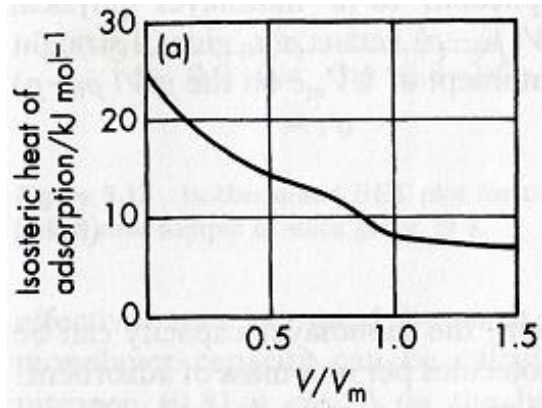
Physical adsorption

1. Monolayer adsorption
2. Multilayer adsorption
3. Condensation in pores or capillaries

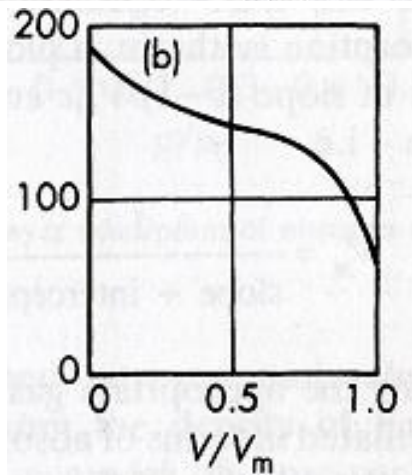


$p_0$  = saturation vapor pressure

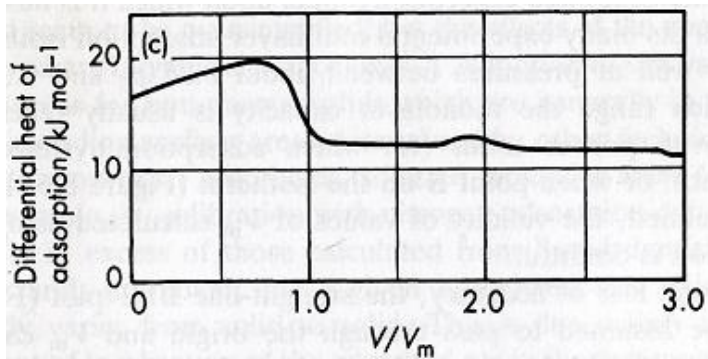
# Isosteric enthalpy(heat) of adsorption



$\theta \uparrow \rightarrow \Delta H_{ad}$  less exothermic  $\rightarrow$  repulsive, BET equation



Approach to 1 ML  $\rightarrow \Delta H_{ad} \downarrow \rightarrow$  Langmuir equation



Up to 1 ML  $\rightarrow$  interaction between adsorbates  $\rightarrow$  more exothermic

- Physisorbed N<sub>2</sub> on rutile TiO<sub>2</sub> at 85 K
- Chemisorbed H on W
- Physisorbed Kr on graphitized carbon black (monomolecular layer)



# Capillary Condensation

Porosity may result from

- 1) Gas evolution during the formation of the solid
- 2) Fibrous structure
- 3) Compaction of particulate solid

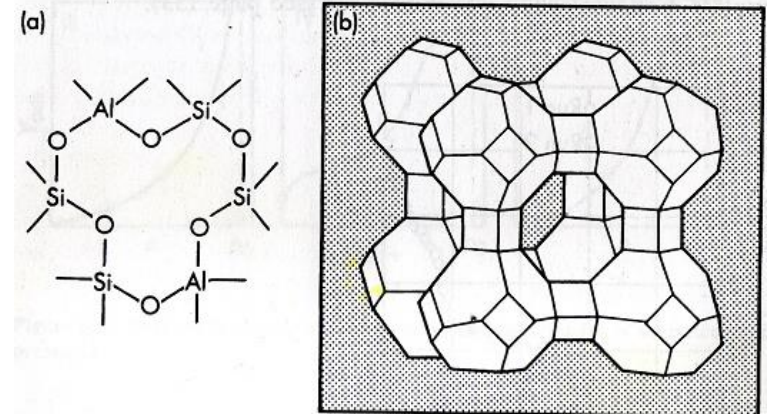
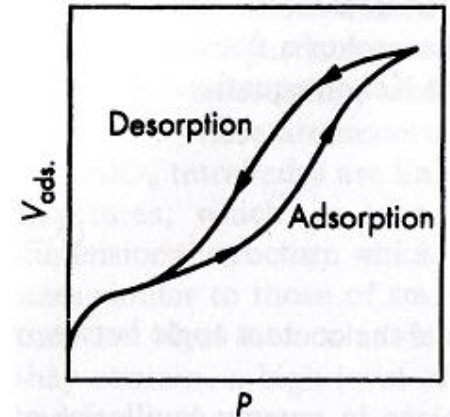
Representative example: Zeolites

- Natural or synthetic materials
- $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra are linked by sharing O atoms
- 3D structure containing regular channels and cavities of sizes similar to those of small and medium-sized molecules

Classification of pores

- Micropores: width < 2nm
- Mesopores: width = 2nm ~ 50 nm
- Macropores: width > 50 nm

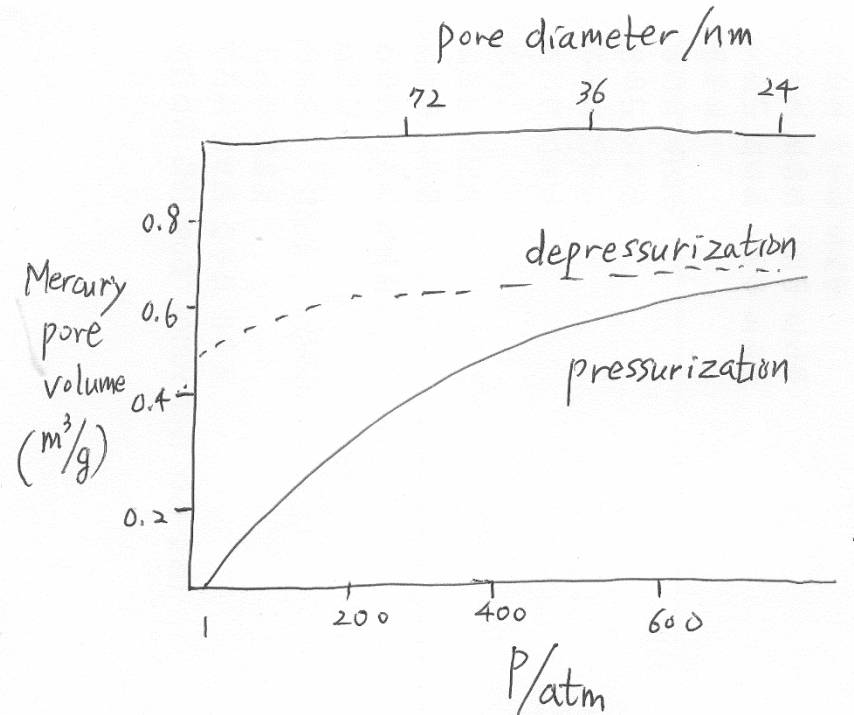
Hysteresis loop  
in physisorption



**Figure 5.7** Zeolite structure. (a) 6-ring containing two aluminium and four silicon tetrahedral centres. (b) Zeolite A structure. Each of the eight sodalite units depicted contains 24 aluminium or silicon tetrahedral centres arranged to give six 4-rings plus eight 6-rings

# Pore size distribution: Mercury intrusion porosimetry

- Volume of mercury (contact angle  $\sim 140^\circ$ ) into pores as a function of pressure
  - Pore size distribution,  $p = 2\gamma\cos\theta/r$
- $r > 2\gamma\cos\theta/p \rightarrow$  filling pores,  $p \uparrow \rightarrow$  filling in smaller  $r$  pores  $\rightarrow$  volume  $\uparrow$



# Rate of desorption (4.4)

- Reverse process of adsorption
- Thermal desorption by phonon annihilation
- Temperature programmed desorption (TPD)  
→ **information available**: surface coverage, desorption kinetics, adsorption energy

## Desorption rate

$$d\theta/dt = k_d \theta^n$$

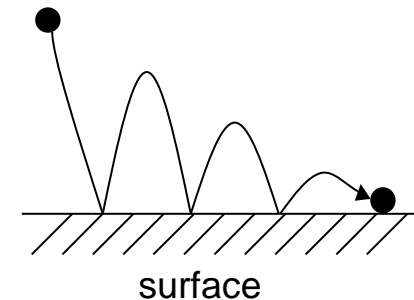
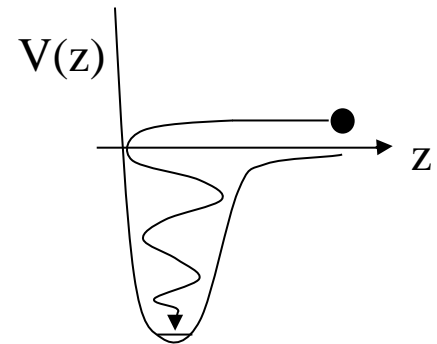
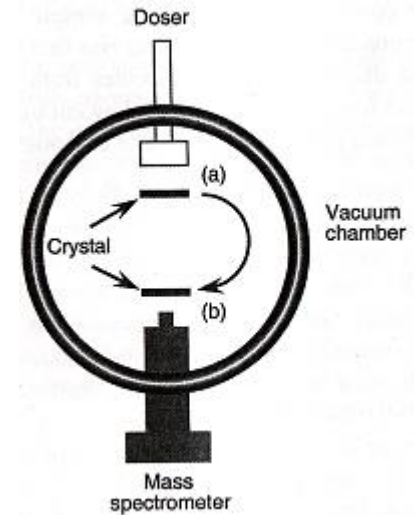
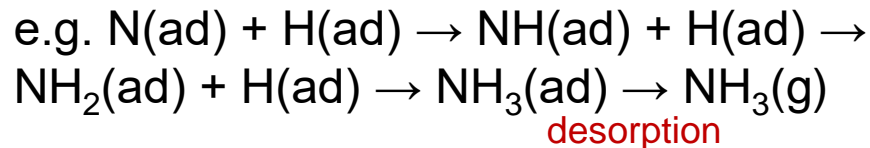
$n = 0$  : 0<sup>th</sup>-order desorption

$n = 1$  : 1<sup>th</sup>-order desorption :  $M(ad) \rightarrow M(g)$

$n = 2$  : 2<sup>th</sup>-order desorption :  $2 A(ad) \rightarrow A_2(g)$

$k_d = k_d^0 \exp(-E_{des}/RT)$  **desorption: always activated**

$T = T_0 (1 + \beta t)$ , where the heating rate  $\beta = 0.1 \sim 10$  K/s



# Temperature programmed desorption (TPD) (4.7)

$$\frac{E_d}{RT_p^2} = \frac{n\nu^n}{\beta} \theta_p^{n-1} \exp\left(\frac{-E_d}{RT_p}\right) \quad (4.7.10)$$

For first-order desorption

$$\frac{E_d}{RT_p^2} = \frac{\nu}{\beta} \exp\left(\frac{-E_d}{RT_p}\right) \quad (4.7.11)$$

while for second-order desorption

$$\frac{E_d}{RT_p^2} = \frac{2\nu^2}{\beta} \theta_p \exp\left(\frac{-E_d}{RT_p}\right) \quad (4.7.12)$$

## A. 0<sup>th</sup> –order desorption

- $d\theta/dt = k_d = k_d^0 \exp(-E_{des}/RT)$
- For a multilayer  $\theta = 1$
- Exponential rate increase with T  $\rightarrow$  obtain  $E_{des}$

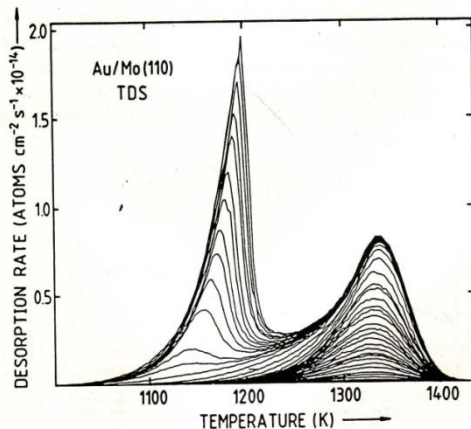
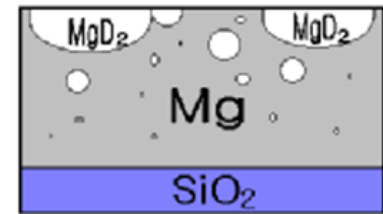
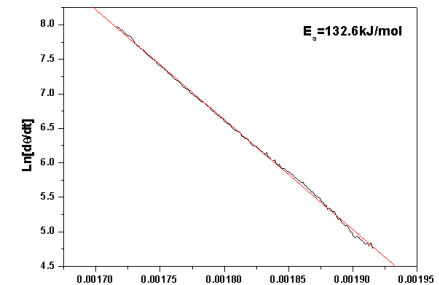
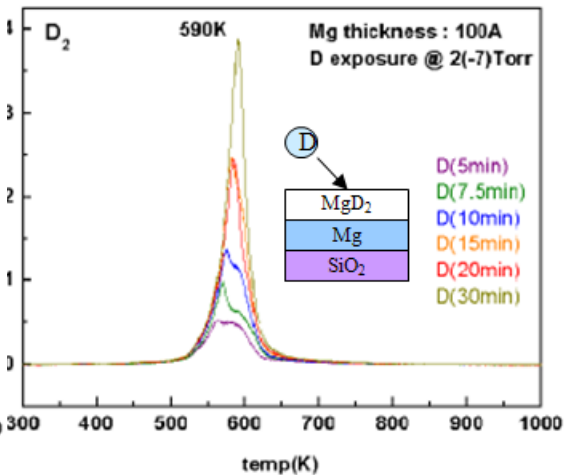
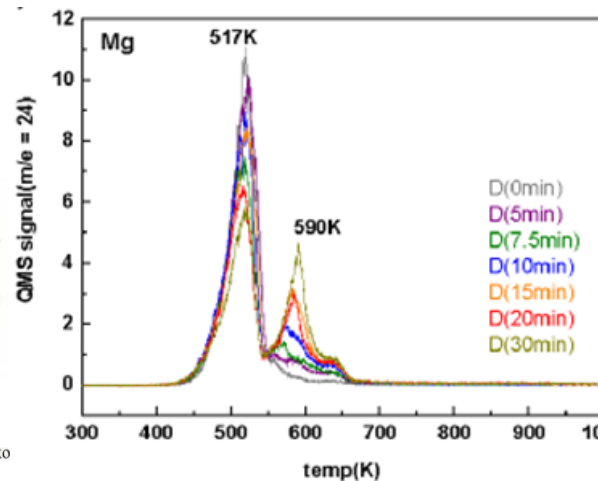


Figure 2 Thermal desorption spectra of Au on Mo(110) in the coverage range from 0 to 2 ML. Heating rate  $5.2 \text{ K s}^{-1}$   
(Reproduced with permission from *Surf. Sci.*, 1988, 195, 207)



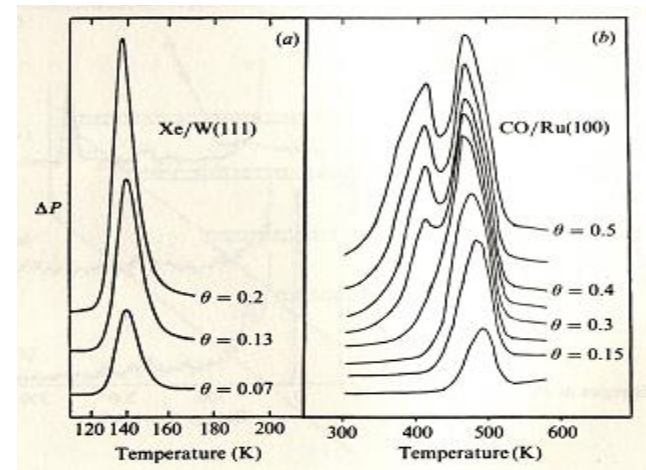
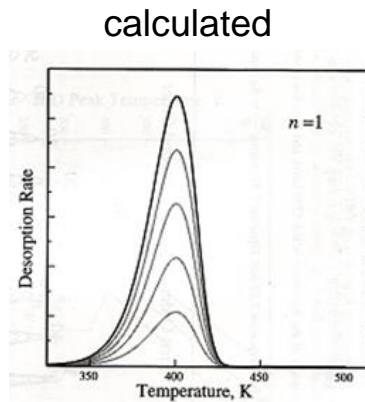
## 1<sup>st</sup> –order desorption

- The peak temperature is coverage-independent
- Asymmetric peak shape

$$E_{\text{des}} = RT_p \left[ \ln \left( \frac{AT_p}{\beta} \right) - 3.46 \right]$$

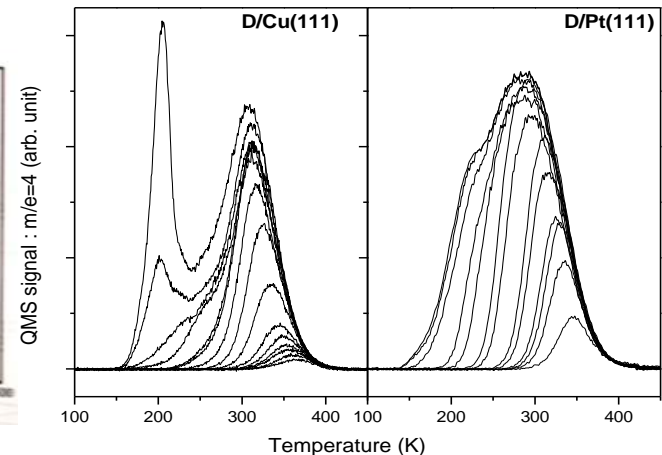
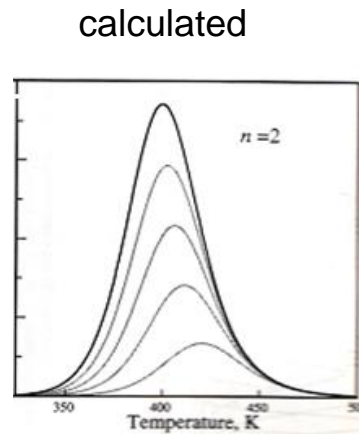
$$\sim 31 \text{ kT}_p$$

Ex:  $T_p = 300 \rightarrow E_{\text{des}} = 0.81 \text{ eV}$



## 2<sup>nd</sup> –order desorption

- Peak shift to a lower T with increasing coverage
- Almost-symmetric peak





# Summary

- Physisorption is a weak adsorption interaction in which polarization (dispersion) forces such as van der Waals interactions hold the adsorbate on the surface.
- Chemisorption is a strong adsorption interaction in which orbital overlap (sharing of electrons) leads to chemical bond formation.
- Binding sites at surfaces are separated by energy barriers. Therefore, diffusion on surfaces is an activated process.
- When the surface temperature is sufficiently high to cause rapid desorption, the adsorbed molecule may be able to enter a state with unhindered diffusion known as a 2D gas.
- The chemisorption bond is formed by hybridization of substrate electronic states with the MOs of the adsorbate.
- As a first approximation, the interaction of frontier MOs with the substrate should be considered to understand chemisorption bonding and adsorbate structure.
- On transition metals, chemisorption bond formation is conceived of as a two-step process (the d band model). In step 1, the frontier orbitals of the adsorbate are broadened and shifted by the interaction with the s band. In step 2, bonding and antibonding hybrids are formed by the interaction of the modified frontier orbitals with the d band.
- The strength of the chemisorption bond depends on the position of the hybrid orbitals with respect to  $E_F$ .
- The strength of chemisorption correlates with the energy of the d band centre. The lower the d band relative to  $E_F$ , the weaker the bond. Therefore, transition metals to the left of a row bind simple adsorbates more strongly than those on the right.
- In general, a strengthening of adsorbate-surface bonding leads to a weakening of intramolecular bonds in the adsorbate.
- Sufficiently strong chemisorption can lead to the scission of intramolecular bonds in the adsorbate (dissociative chemisorption).
- Adsorption can either be a non-activated or activated process.
- Dissociative chemisorption is most commonly associated with activated adsorption. The height of the activation barrier depends on the molecular orientation and the impact position within the unit cell.
- For non-activated adsorption, the sticking coefficient tends to one for low-energy molecules but decreases for very high-energy molecules.
- For activated adsorption, sticking can only occur if the incident molecule has sufficient energy to overcome the adsorption barrier. Molecules with energy far in excess of the barrier height may have difficulty sticking as they cannot follow the minimum energy path.
- Adsorption occurs on a multidimensional potential energy hypersurface (PES) and the effect on the sticking coefficient of placing energy in any particular degree of freedom depends on the shape of the PES.
- Adsorption can either be direct or precursor-mediated.



- Adsorption and desorption are connected by microscopic reversibility.
- In any system for which the sticking coefficient is a function of energy, the desorbed molecules do not have an energy distribution corresponding to an equilibrium distribution at the surface temperature.
- Corrugation is the variation of barrier heights across the surface.
- Whereas initial sticking coefficient values for activated adsorption may exhibit Arrhenius behaviour over some range of temperature, a more general expectation is that they follow the sigmoidal form of Eq. (3.15.3).