Lecture Note #4

Adsorption & desorption at solid surfaces

Reading: Shaw, ch. 5

I. Adsorption: basic concepts

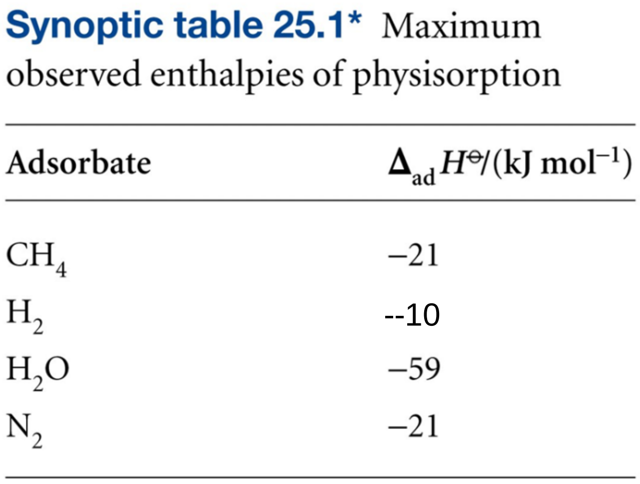
1. Physisorption vs. Chemisorption

Physisorption

- Van der Waals interaction
- Small adsorption energy: ≤ 20 kJ/mole
- Similar to condensation
- Multilayer adsorption possible
- No charge transfer
- Substrate non-specific

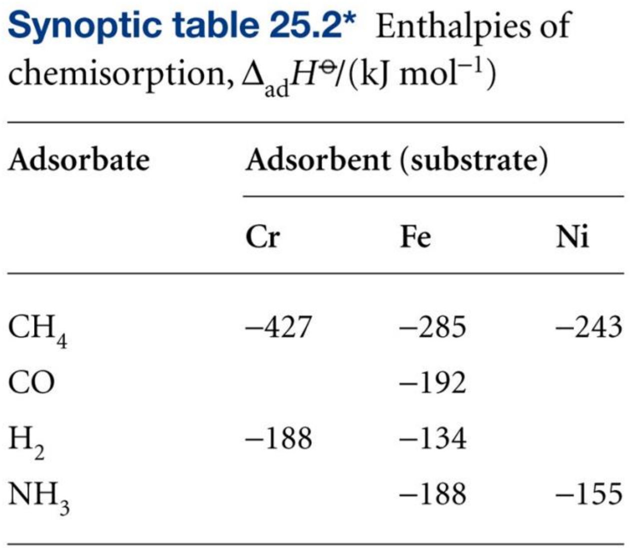
Chemisorption

- Chemical bonding
- Large adsorption energy: ≥ 200 kJ/mole
- Charge transfer : work function change
- Limited to a monolayer
- Substrate specific
- Gas specific



Synoptic table 25.1* Maximum observed enthalpies of physisorption

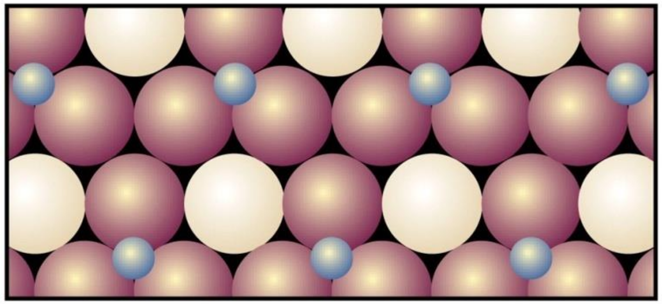
Adsorbate	$\Delta_{ad}H^{\ominus}/(\mathrm{kJ\ mol^{-1}})$
CH_4	−21
H_2	--10
H_2O	−59
N_2	−21



Synoptic table 25.2* Enthalpies of chemisorption, $\Delta_{ad}H^{\ominus}/(\mathrm{kJ\ mol^{-1}})$

Adsorbate	Adsorbent (substrate)		
	Cr	Fe	Ni
CH_4	−427	−285	−243
CO		−192	
H_2	−188	−134	
NH_3		−188	−155

Terminology



- Adsorption site density

N_s = # of sites /cm^2 ~ 10^{15} /cm^2

- Coverage

fractional coverage $\theta = N_s / N$
saturation coverage : $\theta_s = 1$

- Wall collision rate Z_w

Z_w = # molecules striking a surface /cm^2. s
$Z_w = P / (2\pi\, mkT)^{1/2}$ ~ 10^{15} molecules /cm^2. s
@ 10^{-6} Torr and 298 K
1 L (Langmuir) = 10^{-6} Torr.s of gas exposure.

$$Z_w = \int\int \mathcal{N} f(v)\, v \cos\theta dS\, dv d\Omega \,/\, dS$$

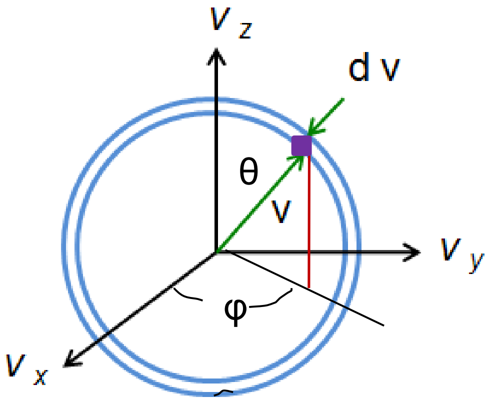
- Monolayer completion time ~ 1sec @ 10^{-6} Torr

Another way to obtain $f(v)dv$

- Consider 1D velocity distribution $f_x(v_x)dv_x$
- $\varepsilon = \frac{1}{2} mv_x^2$ is non-degenerate, so $g = 1$ for all v_x
- According to the Boltzmann distribution law,

  $f_x(v_x)dv_x = (m/ 2\pi kT)^{1/2} \exp(-\frac{1}{2} mv_x^2 /kT)\, dv_x$

  cf: $\int_{-\infty}^{\infty} \exp(-\frac{1}{2} mv_x^2 /kT)\, dv_x = (2\pi kT/m)^{1/2}$
- $\langle v_x \rangle = (2kT/\pi m)^{1/2}$



velocity space

- $f_x(v_x)$, $f_y(v_y)$, and $f_z(v_z)$ are independent with one another and have the same function.
- $f_x(v_x)\, f_y(v_y)\, f_z(v_z)\, dv_x dv_y dv_z$

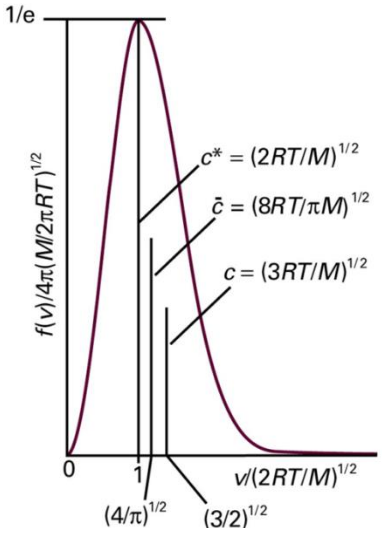
  $= (m/2\pi kT)^{3/2} \exp\{-\frac{1}{2} m(v_x^2 + v_y^2 + v_z^2)/kT\}\, dv_x dv_y dv_z$

- Expressing it in polar coordinate (v,θ,φ),

  $f(v,\theta,\varphi)\, dv d\theta d\varphi = (m/2\pi kT)^{3/2} \exp(-\frac{1}{2} mv^2)/kT)\, v^2\, dv \sin\theta\, d\theta\, d\varphi$
- Integrating over $d\theta$ and $d\varphi$,

  $f(v)\, dv = 4\pi\, (m/ 2\pi kT)^{3/2} \exp(-\frac{1}{2} mv^2)/kT)\, v^2\, dv$

  $= 4\pi\, (M /2\pi RT)^{3/2} \exp(-\frac{1}{2} mv^2)/kT)\, v^2\, dv$; text eq. (20.4)



- Mean speed $\bar{c} = \langle v \rangle = \int_{0,\infty} v\, f(v)\, dv = (8RT/\pi M)^{1/2}$
- Most probable speed $c^* = (2RT/M)^{1/2}$; $df/dv\big|_{v=c^*} = 0$
- Root mean square speed $c_{rms} = (\langle v^2 \rangle)^{1/2} = (3RT/M)^{1/2}$

2. Kinetics of Adsorption

Langmuir model assumes that

- Uniform adsorption site
- Adsorption energy independent of θ
- No surface diffusion

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

$d\theta/dt = k_a(1-\theta)$: $k_a = Z_w s_0 / N_s = k_a p$

$s_0 =$ initial sticking probability

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

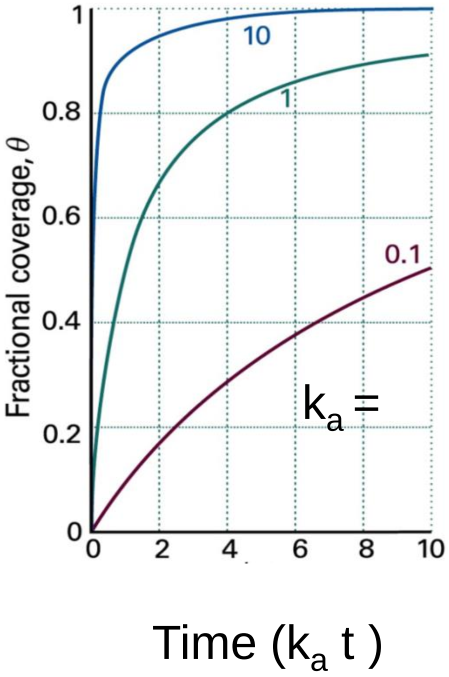
$\theta(t) = 1 - \exp(-k_a t)$

$A_2 + 2 * \rightarrow 2 A(ad)$: dissociative adsorption

- $d\theta/dt = k_a(1-\theta)^2$: $k_a = 2 Z_w s_0 / N_s$

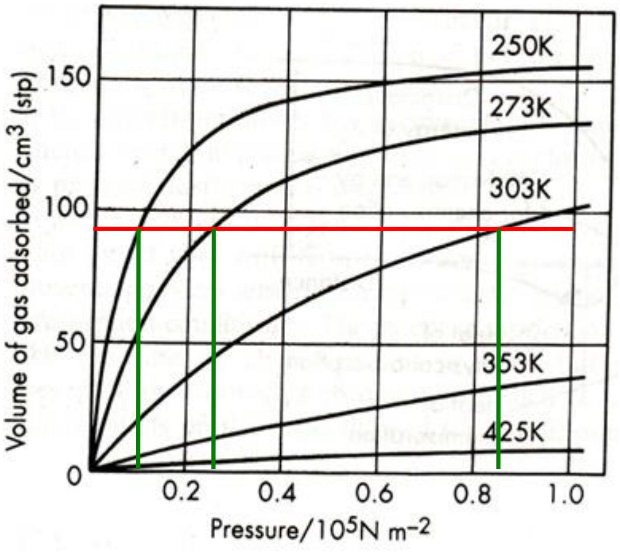
$s(\theta) = s_0(1-\theta)^2$

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



3. Reversible adsorption

NH_3/ charcoal



Adsorption-desorption equilibrium

M(g) + * ↔ M(ad)

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

at equilibrium, $d\theta/dt = 0$.

- 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 $p\rightarrow\infty$, $\theta \rightarrow 1$
- θ-P plot at constant T is called Langmuir isotherm.
- As seen in the Fig., the coverage θ depends more sensitively on T than on p.

4. Measurement of adsorption isotherm

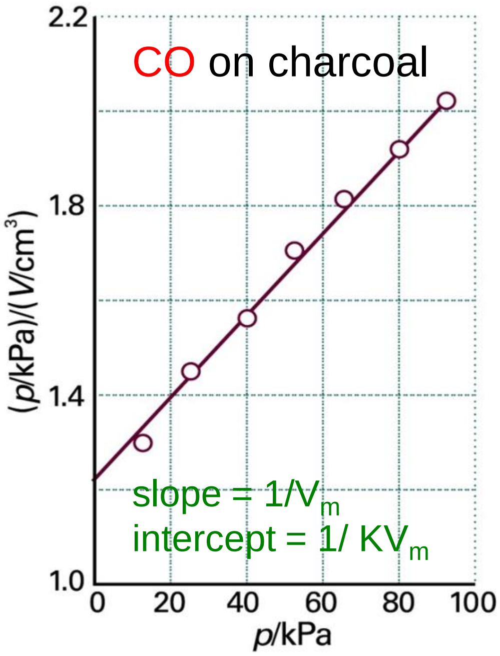
Volumetric measurement

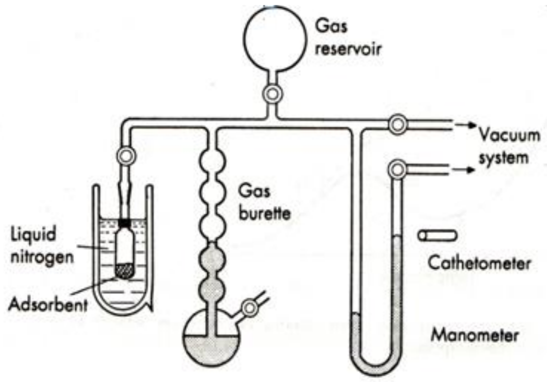
$\theta = K(T)p / \{1+K(T)\, p\}$

$\theta = p/V_m$ measured as a volume change,
where V is the volume of gas adsorbed
and V_m is the saturation volume.

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

p/V vs. p plot gives a straight line.
Slope = $1/V_m$ and intercept = $1/KV_m$

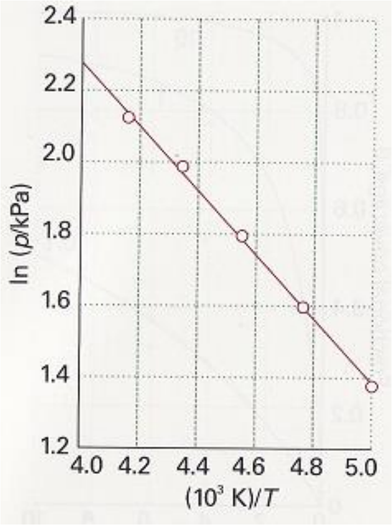




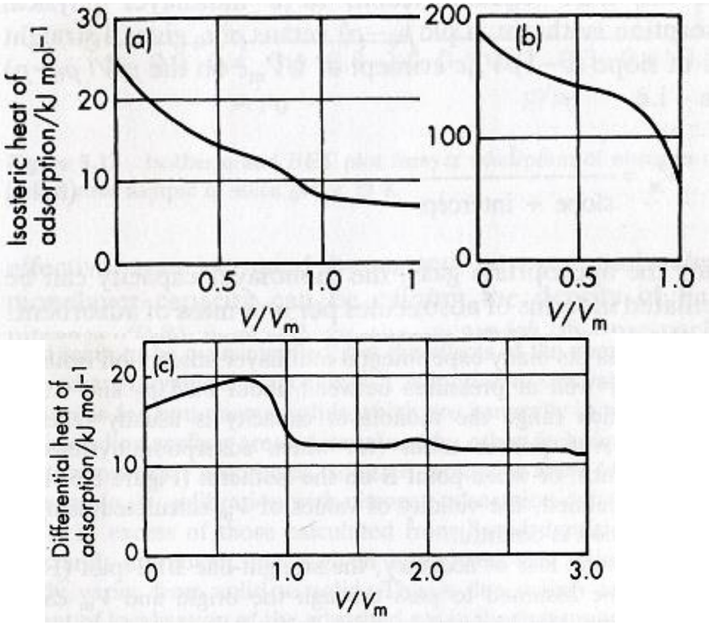
Isosteric enthalpy(heat) of adsorption

- $dG = Vdp - SdT$, and $d(\Delta G) = \Delta Vdp - \Delta S\, dT$ 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 θ.
- $d\ln p = (\Delta H_m/R)\, d(1/T) \rightarrow$ The slope of (ln p) – (1/T) plot gives $\Delta H_m/R$

- In genera, Δh_{ad} is coverage-dependent because of
  1) Heterogeneity of the adsorption sites
  2) Lateral interaction between adjacent adsorbates



CO on charcoal
$\Delta H_m = -7.52$ kJ/mol



a) Physisorbed N_2 on rutile TiO_2 at 85 K
b) Chemisorbed H on W
c) Physisorbed Kr on graphized carbon black

Sticking probability

- Sticking probability
  s = # molecules adsorbed/ # molecules impinging on a surface
- Molecular beam method, in which the partial pressure change is monitored with a QMS.

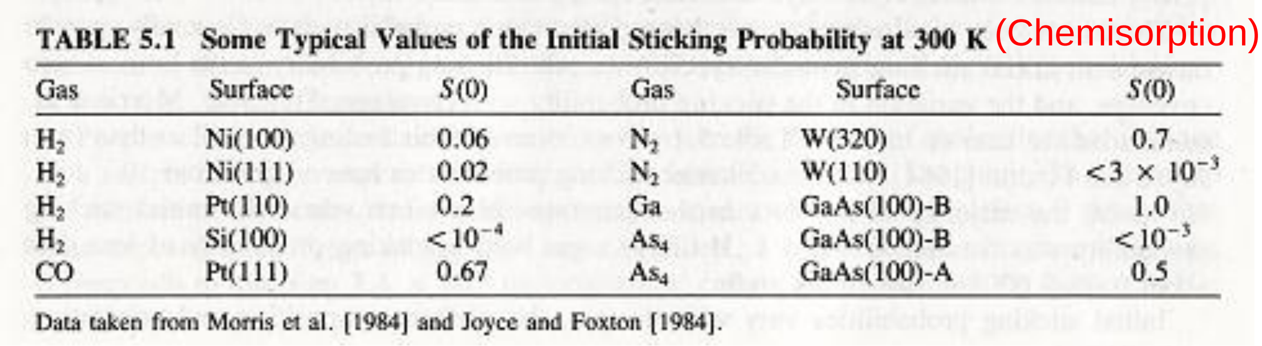


TABLE 5.1 Some Typical Values of the Initial Sticking Probability at 300 K (Chemisorption)

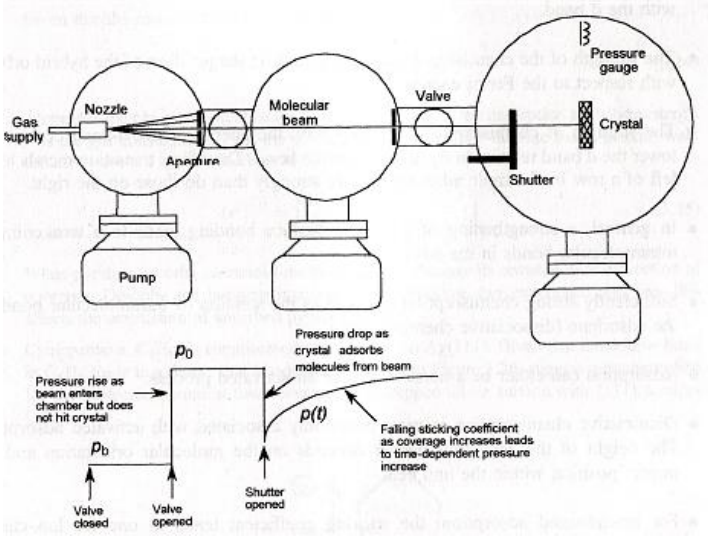
Gas	Surface	$S(0)$	Gas	Surface	$S(0)$
H_2	Ni(100)	0.06	N_2	W(320)	0.7
H_2	Ni(111)	0.02	N_2	W(110)	$<3 \times 10^{-3}$
H_2	Pt(110)	0.2	Ga	GaAs(100)-B	1.0
H_2	Si(100)	$<10^{-4}$	As_4	GaAs(100)-B	$<10^{-3}$
CO	Pt(111)	0.67	As_4	GaAs(100)-A	0.5

Data taken from Morris et al. [1984] and Joyce and Foxton [1984].

$$s(t) = \frac{p_0 - p(t)}{p_0 - p_b}$$

Factors influencing s_0 in chemisorption

- Gas- surface combination
- Efficiency of energy transfer in gas-surface collisions
- Surface orientation of the surface for a given single crystal material
- Presence of an energy barrier for dissociative adsorption: activated adsorption



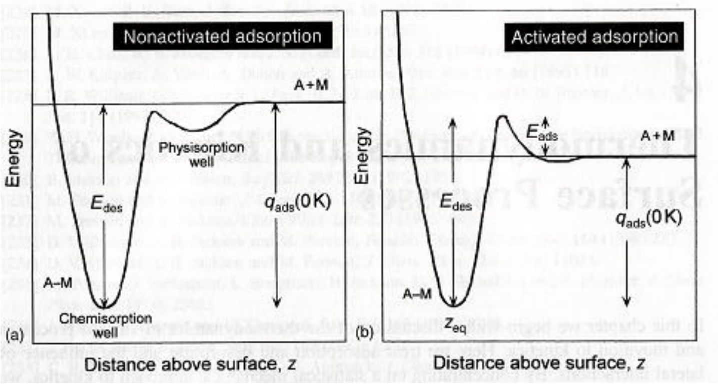
5. Activated adsorption

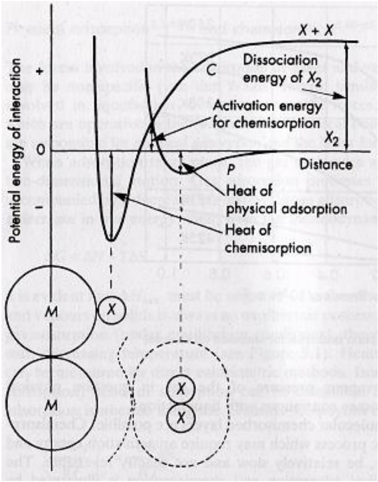
$X_2 \text{ (g)} \rightarrow 2\ X_{ad}$

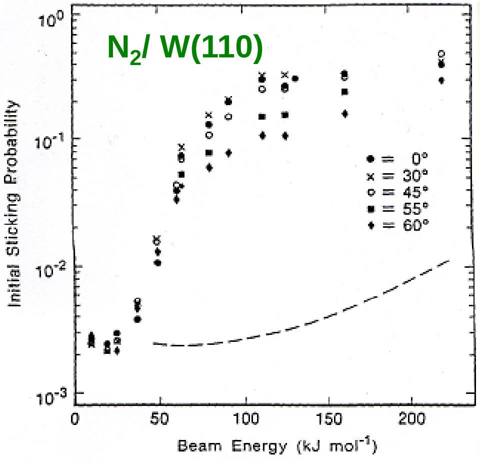
- Important process in heterogeneous catalysis
- Very small s_0 due to the presence of an adsorption barrier

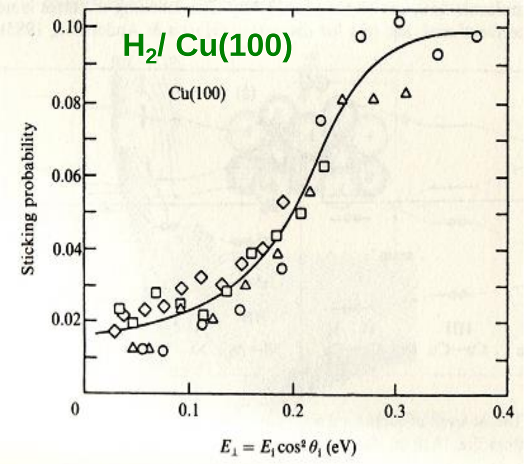
- A fast N_2 can overcome the barrier to directly populate the atomic state.

- A large kinetic energy dependence of s_0



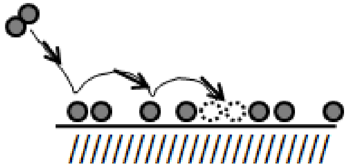


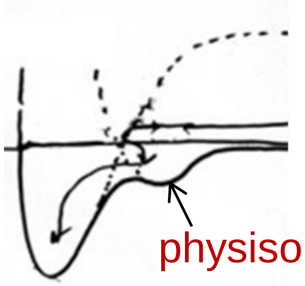

N2/ W(110)


H2/ Cu(100)

6. Precursor-controlled adsorption

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

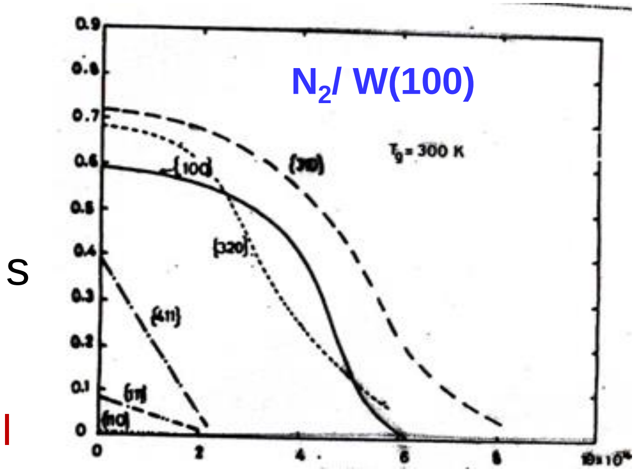


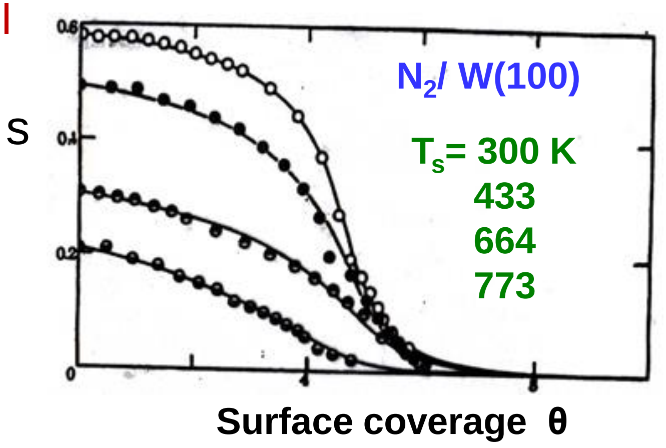


physisorption well

chemisorption well

N_2 (g) → 2 N_{ad}



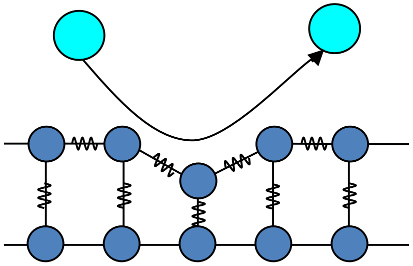


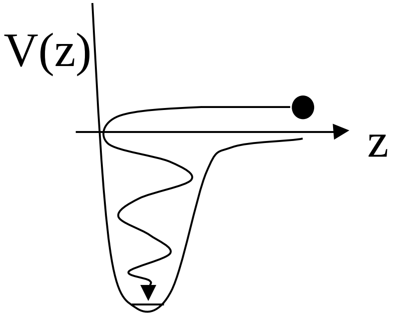
N_2(g) ↔ N_2(ad) → 2 N(ad)

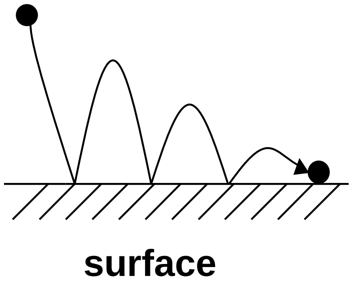
- Trapping in the physisorption well
- Precursor hopping on the surface to find an empty site → increase in s
- Re-evaporation of the precursor due to a finite surface lifetime τ ; **$\tau = \tau_0 \exp(-E_d/RT)$**

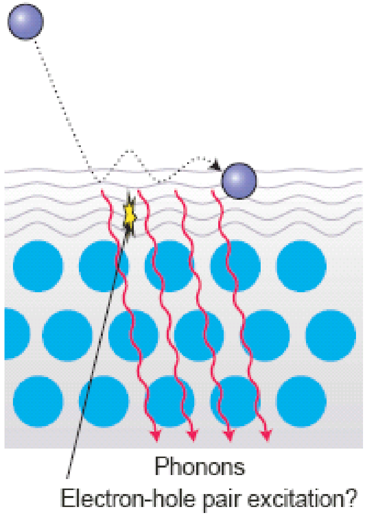
II. Adsorption dynamics

- The outcome of the gas-surface collisions;
  1) Trapping: becoming a bound state after the 1st collision
  2) Direct reflection to the gas phase
- The trapping probability is determined by the amount of the energy transfer to the surface.
- Energy transfer occurs via multiphonon excitations.









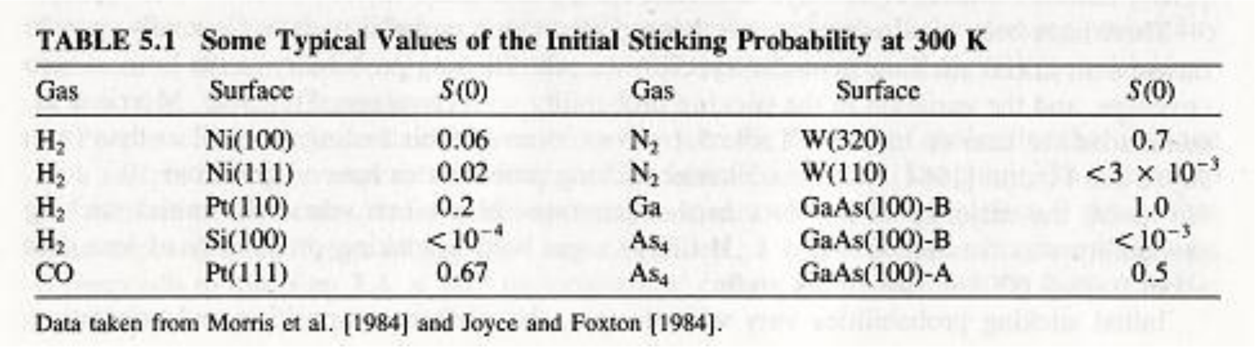


TABLE 5.1 Some Typical Values of the Initial Sticking Probability at 300 K

Gas	Surface	$S(0)$	Gas	Surface	$S(0)$
H_2	Ni(100)	0.06	N_2	W(320)	0.7
H_2	Ni(111)	0.02	N_2	W(110)	$<3 \times 10^{-3}$
H_2	Pt(110)	0.2	Ga	GaAs(100)-B	1.0
H_2	Si(100)	$<10^{-4}$	As_4	GaAs(100)-B	$<10^{-3}$
CO	Pt(111)	0.67	As_4	GaAs(100)-A	0.5

Data taken from Morris et al. [1984] and Joyce and Foxton [1984].

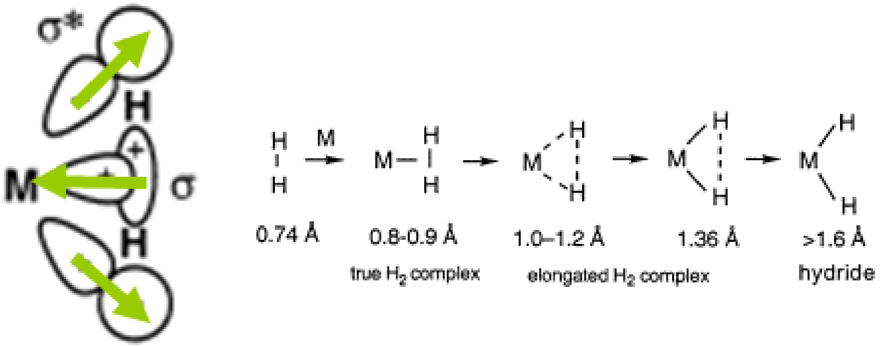
Chemisorption bonding of H_2 and CO(NO)

- Charge transfer : work function change
- e^- donation + backdonation
- Orbital symmetry

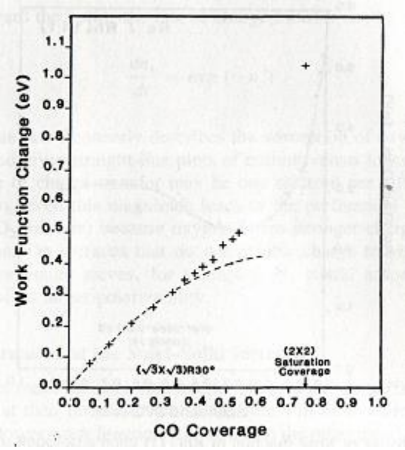
- Transition metal : d-band metal
- Noble metal: sp-band metal

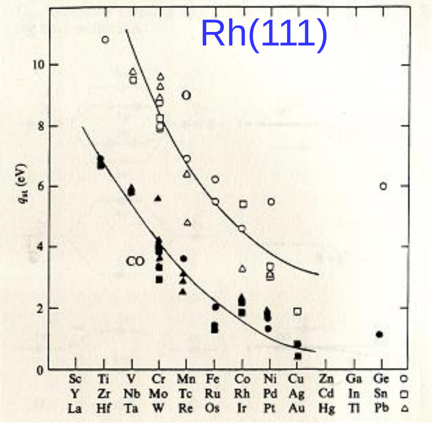
- Heat of adsorption: bond strength
- Dissociation
- Activated adsorption

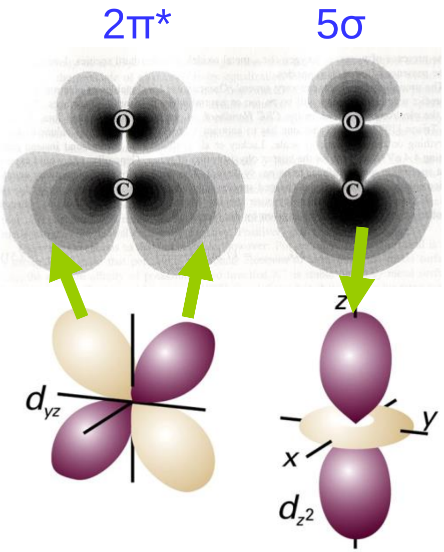
Kubas interaction



Heat of adsorption of CO



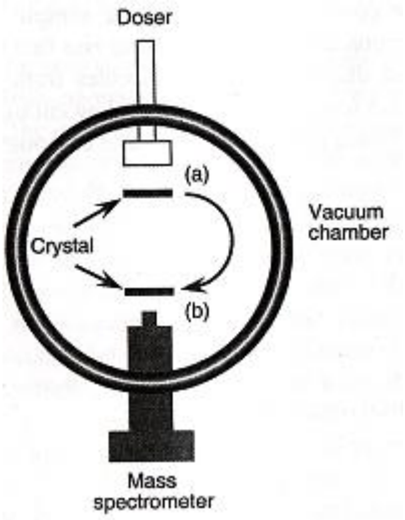




III. Desorption

- Reverse process of adsorption
- Thermal desorption by phonon anihilation
- Temperature programmed desorption (TPD)

information available: surface coverage,
desorption kinetics, adsorption energy,



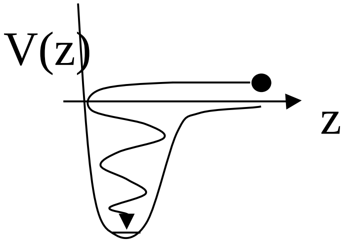
Desorption rate

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

n = 0 : 0^{th}-order desorption

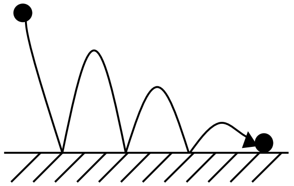
n = 1 : 1^{th}-order desorption : $M(ad) \rightarrow M(g)$

n = 2 : 2^{th}-order desorption : $2\,A(ad) \rightarrow A_2\,(g)$



$k_d = k_d^{\,0}\,\exp(-\,E_{des}/\,RT)$

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



surface

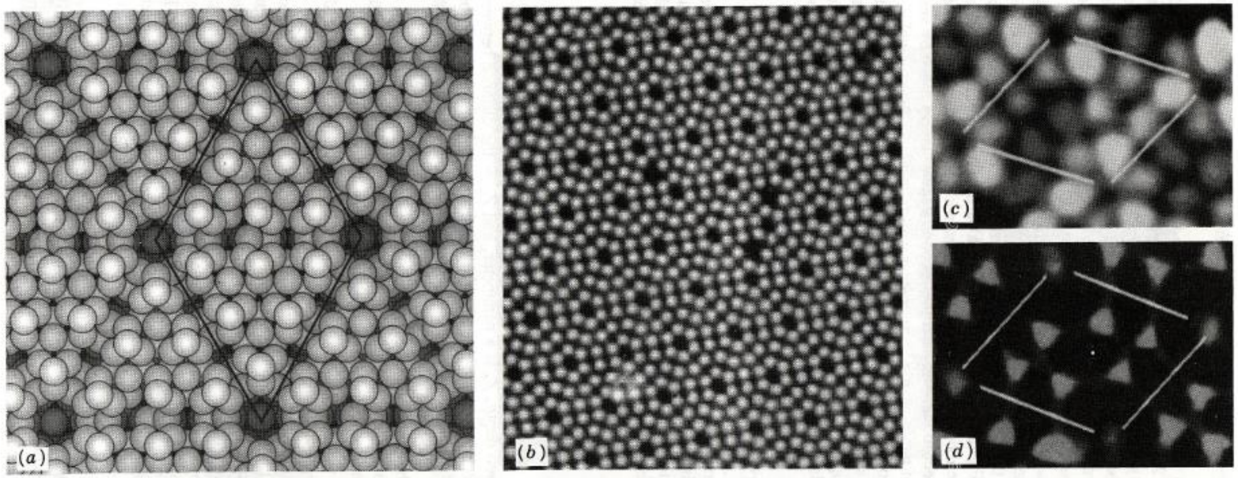


Figure 2.47 (*a*) A schematic of the (7x7) reconstruction of Si(111). (*b*) An STM image of the (7x7) surface. (*c*), (*d*) Images of the dangling bonds in the (1x1) surface. (From Trump et al. [1988].)

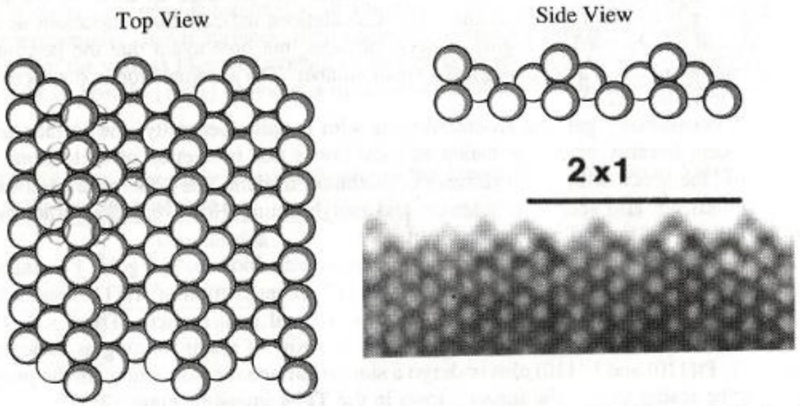
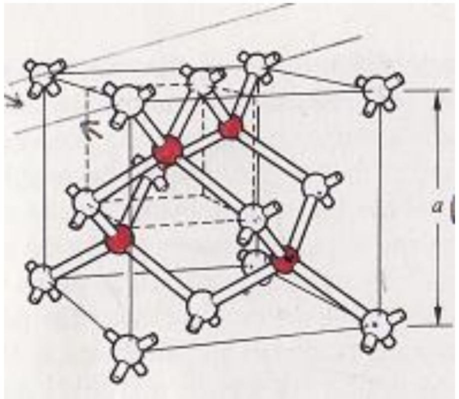


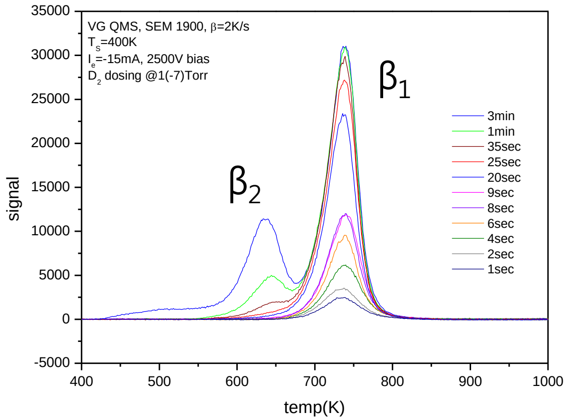
Figure 2.52 A schematic of the (2x1) reconstructon of Au(110) and a TEM image that looks down the surface. (The TEM image is from Marks and Smith [1983]. Reprinted with permission from *Nature* **303,** 316 (1983). © 1983 McMillan Magazines Limited.)

1. Example of TPD spectra: H/Si(100)

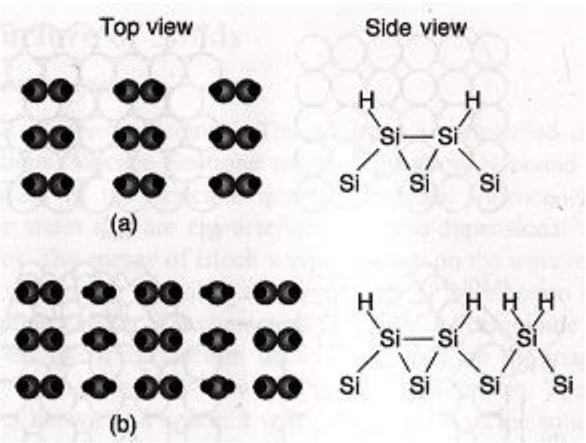


Unreconstructed Si(100)

D atom beam dosing



saturation β_1 coverage = 6.683×10^{14} H atoms/cm^2

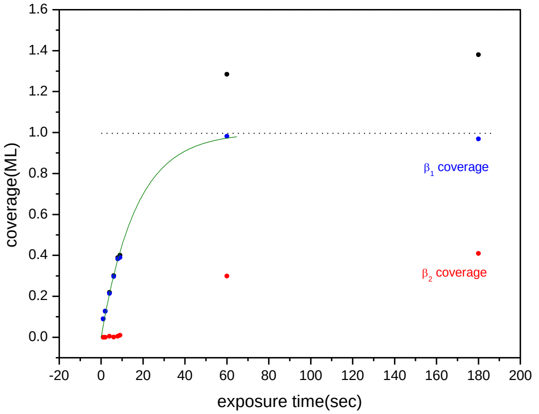


β_1 state

monohydride (1 ML)
(2x1)

β_2 state

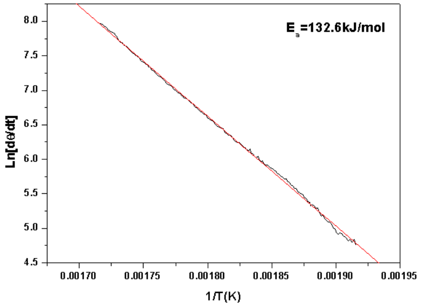
dihydride (1⅓ ML)
(3x1)

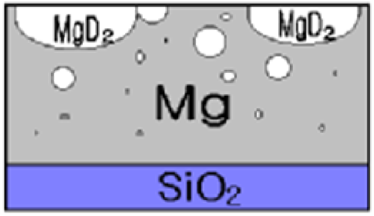


2. Desorption kinetics

A. 0th –order desorption

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





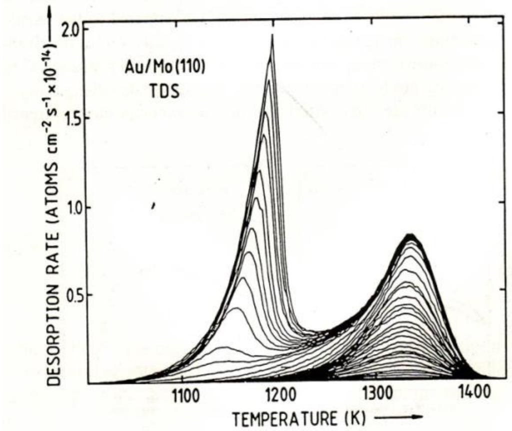
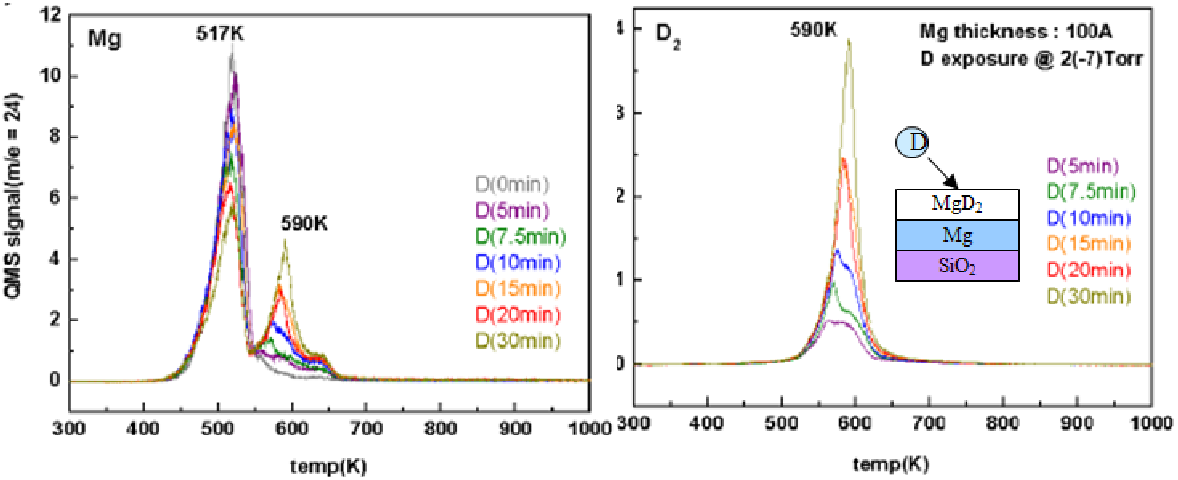


Figure 2 *Thermal desorption spectra of* Au *on* Mo(110) *in the coverage range from* 0 to 2 ML. *Heating rate* 5.2 K s^{-1}
(Reproduced with permission from *Surf. Sci.*, 1988, **195**, 207)



B. 1th –order desorption

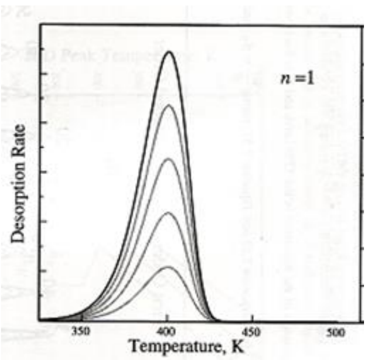
- $d\theta/dt = k_d^0 \exp(- E_{des}/ RT)\, \theta$
- The peak temperature is coverage-independent
- Asymmetric peak shape

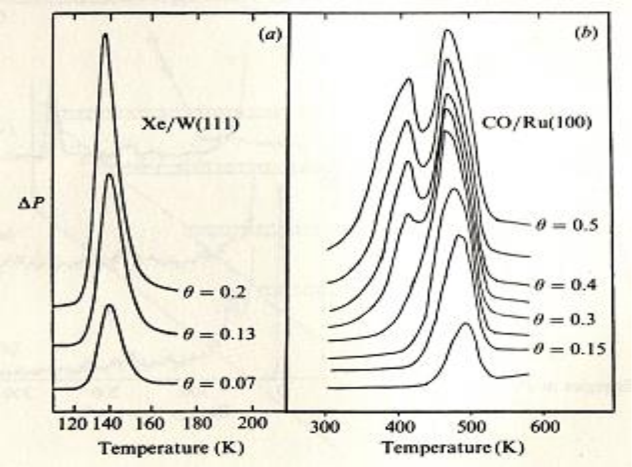
$$E_{\mathrm{des}} = RT_{\mathrm{p}}\left[\ln\left(\frac{AT_{\mathrm{p}}}{\beta}\right) - 3.46\right]$$

$\sim 31\ kT_p$

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

calculated

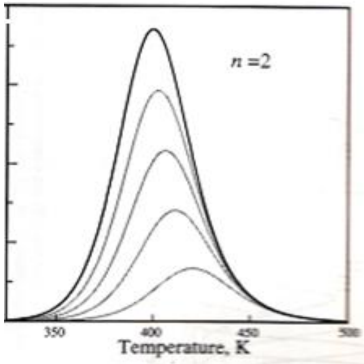


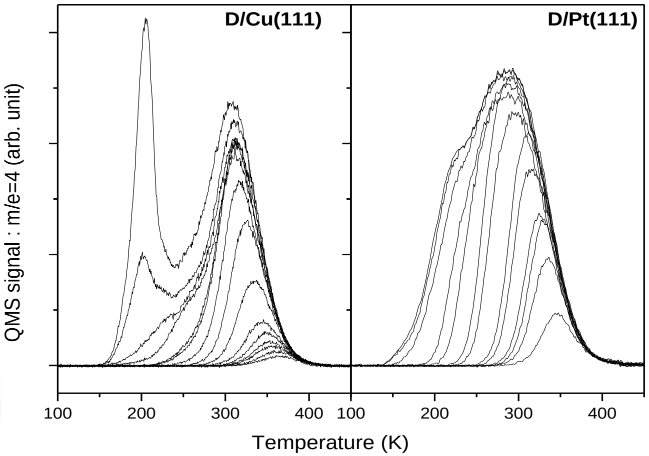


C. 2th –order desorption

- $d\theta/dt = k_d^0 \exp(- E_{des}/ RT)\, \theta$
- Peak shift to a lower T with increasing coverage
- Almost-symmetric peak

calculated

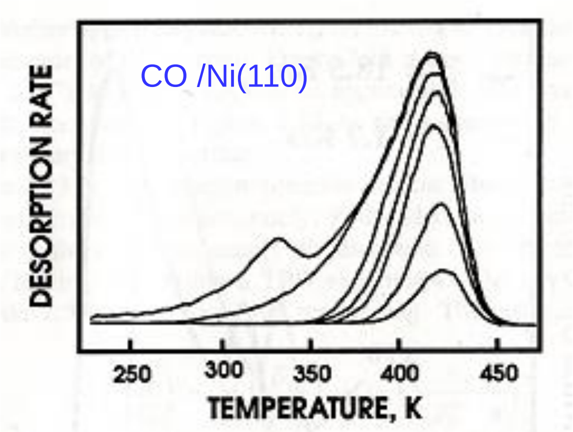


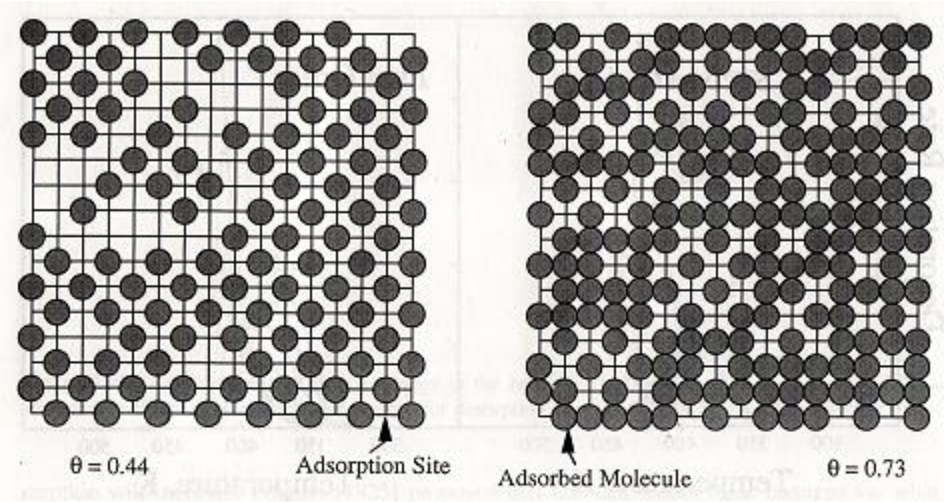


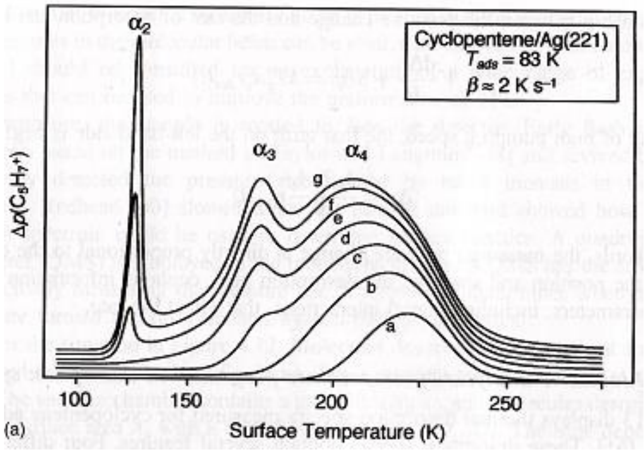
3. Deviation from simple kinetic theory

1) Adsorbate-adsorbate interaction

- Repulsive or attractive interaction.
- E_{des} is coverage-dependent.
- Repulsive interaction →
- T_p shifts to a lower T with increasing θ.







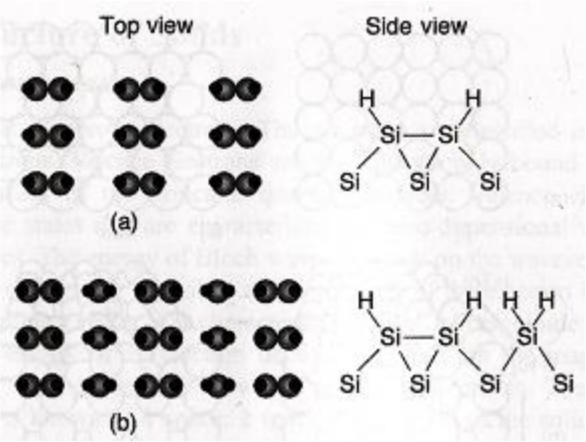
2) Pre-pairing of atoms

- 2 A(ad) → A(ad)-A(ad) → A_2 (g)

- No direct bonding between A(ad)'s.
- Occupy the adjacent sites.

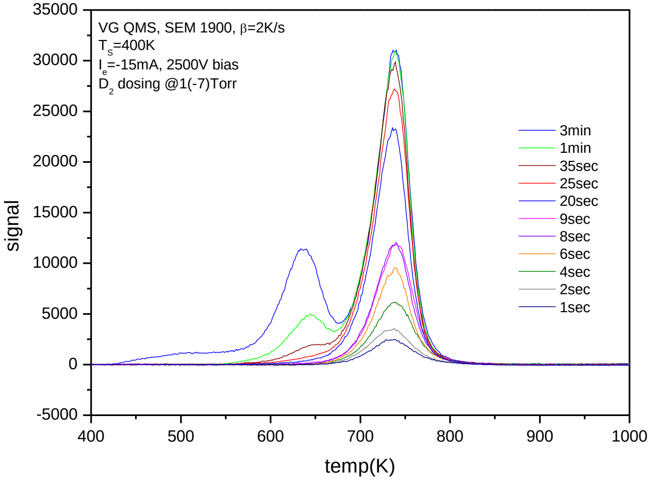
- 2 H(ad)/ Si(100) → H(ad)-H(ad) (pair) → H_2 (g).
- No T_p shift with coverage.

- 2 H(ad) occupy the Si dimer sites.



β_1 state (1 ML)

monohydride (2x1)



IV. Adsorption isotherms

1. Brunner clasification

Type I: Langmuir adsorption

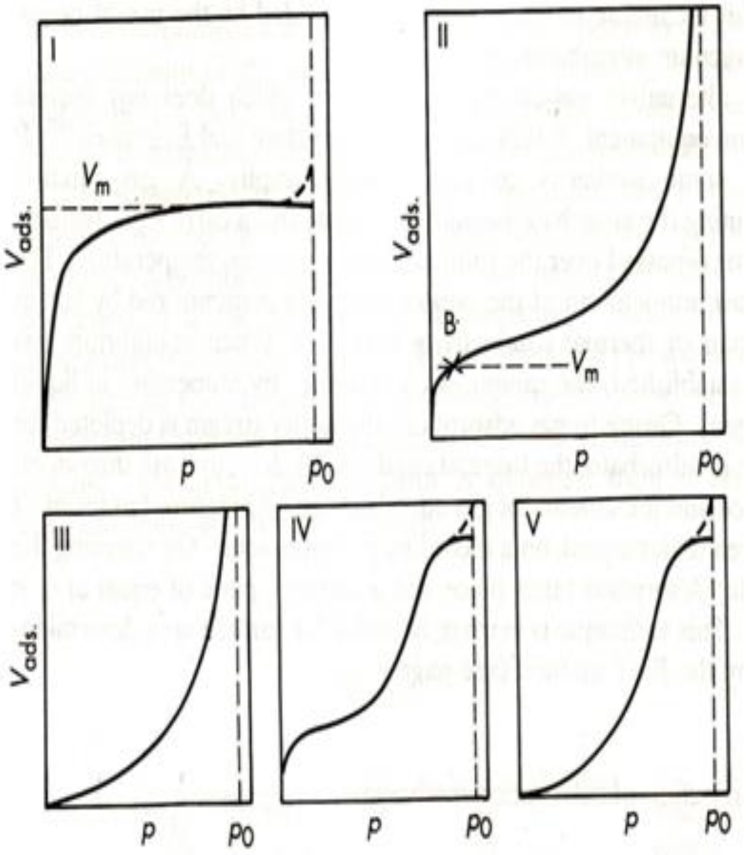
Type II: monolayer + multilayer

Type III: multilayer adsorption

Type IV: Type II

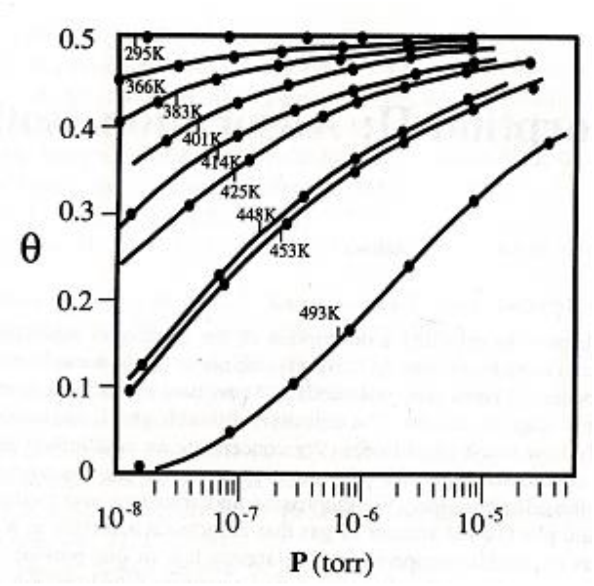
Type V: Type III on a porous adsorbent

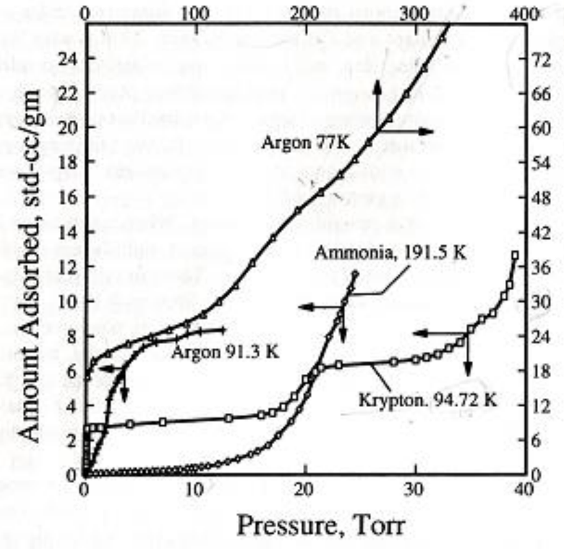
- Finite pore volume limits the max. V_{ads}.
- Type II & IV: $\Delta H_{des} >> \Delta H_{vap}$
- Type III & V: $\Delta H_{des} \sim \Delta H_{vap}$

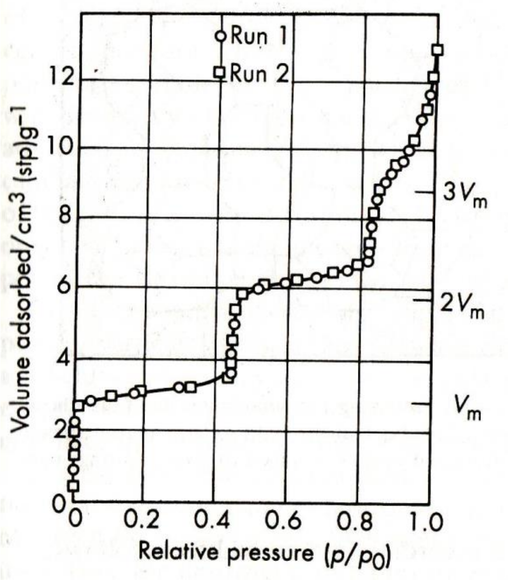


p_0 = saturation vapor pressure

Examples of adsorption isotherms







CO/Pd(111)

Ar, NH3 /carbon black

Kr /carbon black

* carbon black graphitized at 3000 K

2. Multilayer physisorption

BET isotherm: Brunnauer, Emmett, Teller

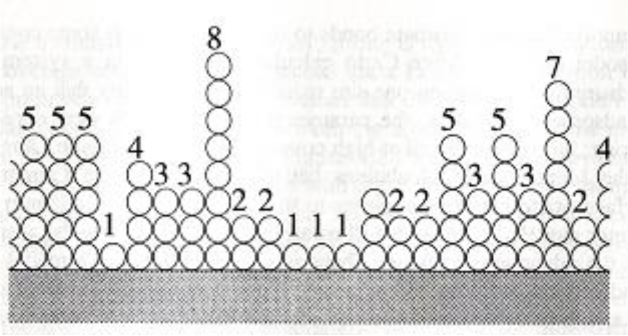
- Langmuir adsorption extended to allow multilayer adsorption
- Equilibrium maintained between the adjacent layers
- $\Delta H^o_{\mathbf{ads}}$ for the first layer and $\Delta H^o_{\mathbf{vap}}$ for the multilayers
- used for surface area measurements.

$M(g) + * \leftrightarrow M_1(ad)$

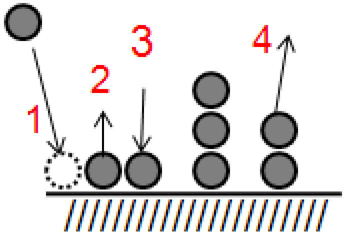
$M(g) + M_1(ad) \leftrightarrow M_2(ad)$

….

$M(g) + M_{n-1}(ad) \leftrightarrow M_n(ad)$

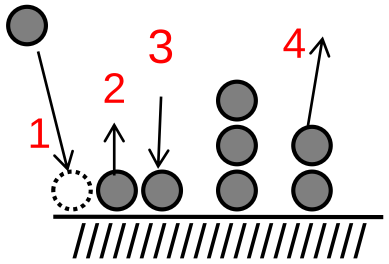


$d\theta_1/dt = 1 - 2 - 3 + 4$



BET equation

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



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

$$d\theta_0/dt = -k_a p\,\theta_0 + k_d\,\theta_1 = 0$$
$$d\theta_1/dt = k_a p\,\theta_0 - k_d\,\theta_1 - k'_a p\,\theta_1 + k'_d\,\theta_2 = 0$$
$$d\theta_2/dt = k'_a p\,\theta_1 - k'_d\,\theta_2 - k'_a p\,\theta_2 + k'_d\,\theta_3 = 0$$

…………………………

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

- $k_a = Z_w s_0$, $k_d = \nu \exp(-\Delta H_{des}/RT)$ for the 1st layer
- $k'_a = Z_w s'_0$, $k'_d = \nu' \exp(-\Delta H_{eva}/RT)$ for the 2nd layer and beyond.

- For miultilayer adsorption $s_0 \sim s'_0$ and $\boldsymbol{\nu} \sim \boldsymbol{\nu'}$. Then, $\boldsymbol{k_a \sim k'_a}$.
- But E_{des} can be much larger than E'_{des} , hence k_d much smaller than k'_d .

- **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** $=$ **$\exp(\Delta h_{des} - \Delta H_{vap})/RT$**

$$\theta_1 = (k_a/k_d)\, p\, \theta_0 = \mathbf{K}p\theta_0 = c\mathbf{K'}p\theta_0$$
$$\theta_2 = [(k_d + k'_a p)\, \theta_1 - k_a\, p\, \theta_0]/k'_d = (1/c + K'p)\, \theta_1 - K'p\, \theta_0 = c(K'p)^2\, \theta_0$$
$$\theta_3 = [(k'_d + k'_a p)\, \theta_2 - k'_a\, p\, \theta_1]/k'_d = (1 + K'p)\, \theta_2 - K'p\, \theta_1 = c(K'p)^3\, \theta_0$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$\theta_n = (1 + K'p)\, \theta_{n-1} - K'p\, \theta_{n-2} = c(K'p)^{n-1}\, \theta_0 + (K'p)_n\theta_0 - c(K'p)^{n-1}\, \theta_0 = c(K'p)^n\, \theta_0$$

(1) $\theta_0 + \theta_1 + \dots + \theta_n\ (n \to \infty) = 1$
$\to \theta_0 + cK'p\,[1 + Kp + (K'p)^2 + (K'p)^3 + \cdots]\, \theta_0 = 1 \to \theta_0\, [1 + cK'p/(1 - K'p)] = 1$
$\to \theta_0 = 1/[1 + cK'p/(1 - K'p)] = (1 - K'p)/[1 + (c-1)K'p]$

(2) $V/V_m = \theta_1 + 2\, \theta_2 \dots + n\, \theta_n = c[\,K'p + 2(K'p)^2 + 3(K'p)^3 + \cdots\,]\, \theta_0$
$= (1 - K'p)\, cK'p/[1 + (c-1)K'p]\, (1 - K'p)^2$
cf: $1 + x + x^2 + \cdots = d(x + x^2 + x^3 \cdots)/dx = d[x/(1-x)]/dx = 1/(1-x)^2$

- When $p = p_0$ (saturation vapor pressure), adsorption and desorption can take place at all sites. Therefore, $k'_a\, p_0\, (\theta_0 + \theta_1 + \dots + \theta_n) = k'_d\, (\theta_0 + \theta_1 + \dots + \theta_n) \to k'_a\, p_0 = k'_d \to$
$K' = 1/p_0$ and $K'p = p/p_0$ (3)
- $V/V_m = (1 - K'p)\, cK'p/[1 + (c-1)K'p]\, (1 - K'p)^2$ from (2) and (3)
$= c\, (p/p_0)/[1 + (c-1)p/p_0]\, (1 - p/p_0) = V/V_m = cp\, p_0/[p_0 + (c-1)p]\, (p_0 - p)$
- Rearranging, $[p_0 + (c-1)p]/c\, p_0\, V_m = p/V(p_0 - p) \to$
$\mathbf{p/V(p_0 - p)} = 1/cV_m + [(c-1)/cV_m]\, \mathbf{(p/p_0)}$; $y = a + bx$ type

$p/V(p_0-p)$ vs. p/p_0 plot gives a straight line as shown in the Figure.

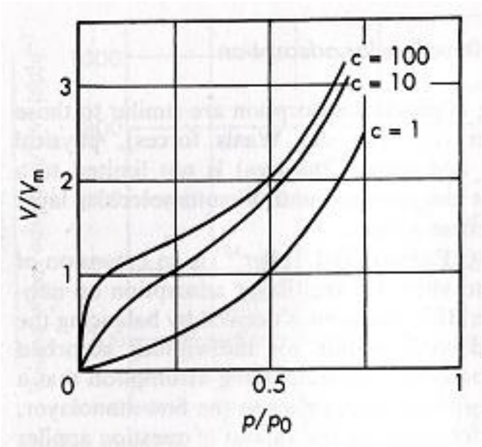
$$\frac{p}{V(p_0-p)}=\frac{1}{V_m c}+\frac{(c-1)}{V_m c}\frac{p}{p_0}$$

Intercept = $1/cV_m$

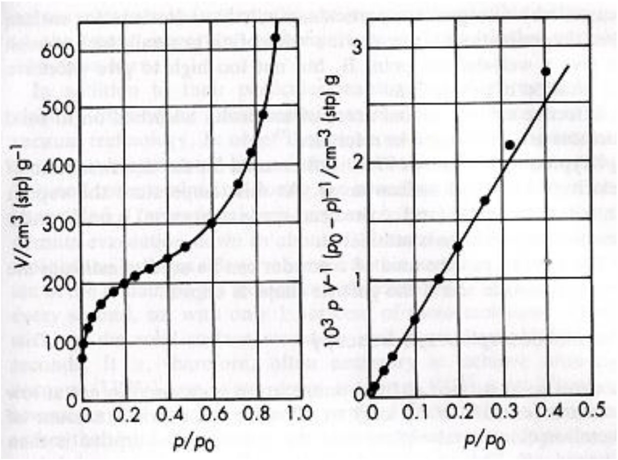
$$V_m=\frac{1}{\text{slope}+\text{intercept}}$$

V_m = monolayer capacity

$c = \exp(\Delta H_{des} - \Delta H_{vap})/RT$

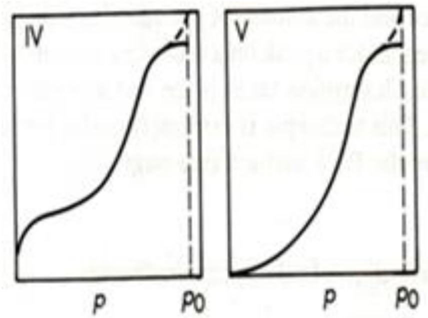


N_2/ silica gel @ 77 K



For a porous solid

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



, where n is related to the pore size and $x = p/p_0$

Capillary Condensation

Porosity may result from

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

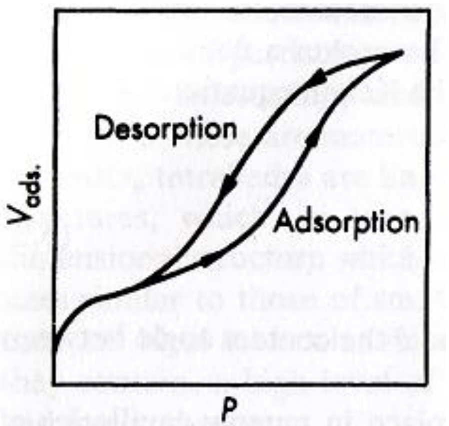
Representative example: Zeolites

- Natural or synthetic materials
- SiO_4 and AlO_4 tetrahedra are linked by sharing O atoms
- 3D structure containing regular channels and cavties of sizes similar to those of small and medium –sized molecules.

Classification of pores

- Micropore s: width < 2nm
- Mwsopores: width = 2nm ~ 50 nm
- Maropores: width > 50 nm

Hysteresis loop in physisorption



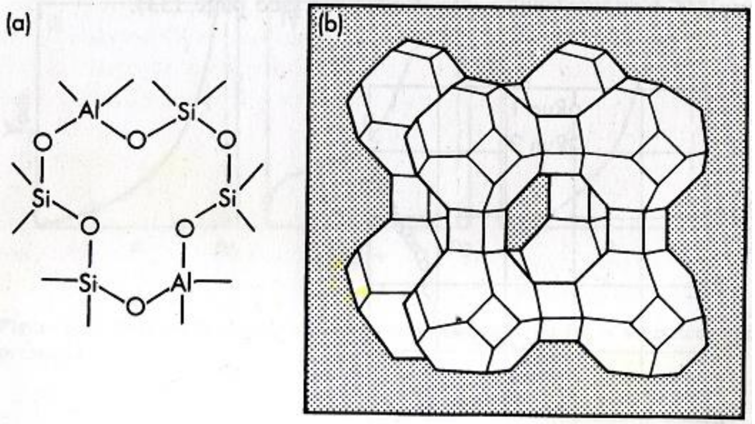
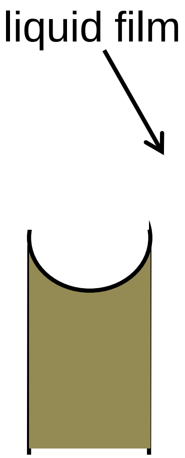


Figure 5.7 Zeolite structure. (a) 6-ring containing two aluminium and four silicon tetrahedral centres. (b) Zeolite A structure. Each of the eight sodalite units depicted contains 24 aluminium or silicon tetrahedral centres arranged to give six 4-rings plus eight 6-rings

Capillary Condensation



- Kelvin equation: $RT \ln p_r/p_0 = 2\gamma M/\rho r = 2\gamma V_m/r$ for a convex liquid-vapor interface
- For a liquid film inside a pore of radius r, which has a concave interface

  $RT \ln p_r/p_0 = -2\gamma V_m \cos\theta/r$