Topics for Midterm Exam

Lecture Note #1 (Introduction)
Definition of surface/interface, dispersion
Lecture Note #2
Flux, UHV
fcc, bcc, hcp
Miller index, lattice constant, surface atom density
Bimetallic, oxides, carbon
Wood's notation and matrix notation
Relaxation, reconstrcution
Lecture Note #3
X-ray, X-ray absorption spectroscopy
XPS, AES, UPS, HREELS
Diffraction: X-ray, SAED, LEED
Lecture Note #4
Physisorption vs. chemisorption
Non-dissociative adsorption
Dissociative adsorption
Sticking coefficient
Non-activated & activated adsorption
Reaction mechanism
Homeworks#1-3, last 2 Midterm Exams

Lecture Note #5 (Fall, 2022)

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)

Reading: Kolasinski, ch.4

Thermodynamics of ad/desorption (4.1)

Binding energies and activation barriers

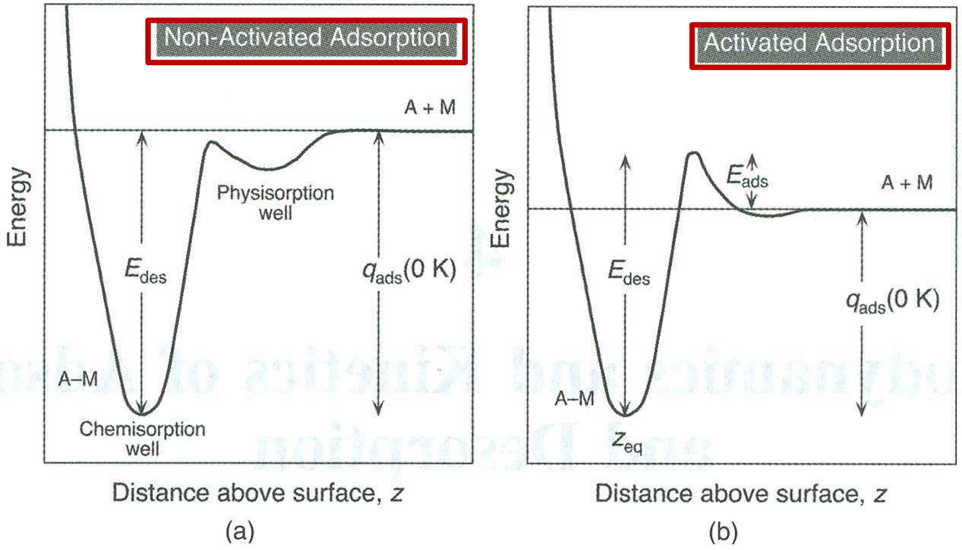


Figure 4.1 *One-dimensional potential energy curves for molecular adsorption: (a) nonactivated adsorption; (b) activated adsorption.* E_{ads}, E_{des}, *adsorption activation energy and desorption activation energy, respectively;* q_{ads}, *heat released by adsorption;* z_{eq}, *adsorbate-surface bond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

- In non-dissociative, non-activated adsorption, $E_{ads} = 0$ (ads activation E)

Adsorption bond binding energy (bond strength) $\varepsilon(\text{M-A}) = E_{des}$

$\varepsilon(\text{M-A}) = q_{ads}$ (heat released by adsorption)

- For activated adsorption, $E_{ads} > 0$

$E_{des} = E_{ads} + \varepsilon(\text{M-A})$,

$\varepsilon(\text{M-A}) = q_{ads} = E_{des} - E_{ads}$

- In dissociative adsorption, the intramolecular adsorbate bond with dissociation energy ε(A-A) is also broken,

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

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

Adsorption of a diatomic molecule A_2

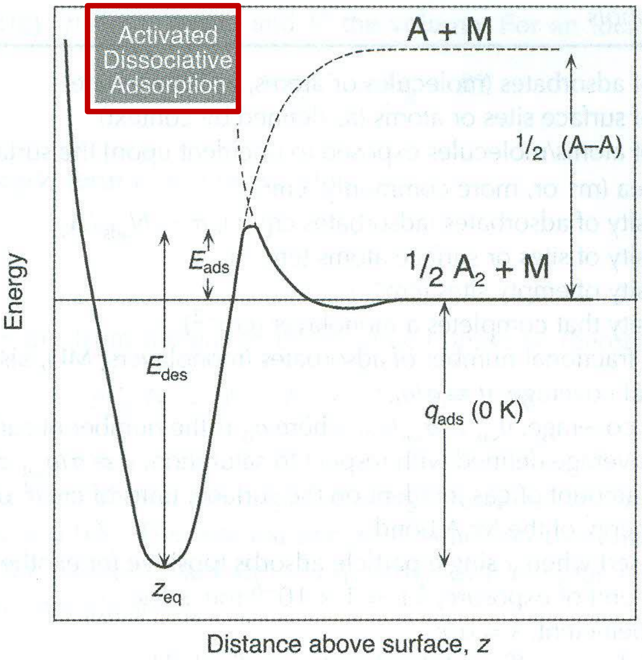


Figure 4.2 *Activated dissociative adsorption.* E_{ads}, E_{des}, *adsorption activation energy and desorption activation energy, respectively;* q_{ads}, *heat released by adsorption;* z_{eq}, *adsorbate-surface bond length.*

Thermodynamic quantities

- Gibbs (free) energy, G, $\Delta G < 0$ (spontaneous process)
  $\Delta G = \Delta H - T\Delta S$

- Adsorption (e.g. chemisorption) → usually exothermic process → $\Delta S < 0$ (gas in 2D), $\Delta G < 0$ (constant T & P, free energy↓, spontaneous) → $\Delta G = \Delta H - T\Delta S$ → $\Delta H < 0$ (exothermic) (or $\Delta_{ads}H < 0$)

- Temperature↓ → Adsorption↑

- exception: dissociate adsorbates & high translational mobility on the surface ($\Delta S > 0$). Repulsion between adsorbates by coverage↑ → less exothermic

  e.g., H_2 on glass: endothermic, $H_2(g) \rightarrow 2H$ (glass), $\Delta S > 0 \rightarrow \Delta H > 0$

Table 4.1 *Definition of symbols.*

N_{ads}	Number of adsorbates (molecules or atoms, as appropriate)
N_0	Number of surface sites or atoms (as defined by context)
N_{exp}	Number of atoms/molecules exposed to (incident upon) the surface
A_s	Surface area (m^2 or cm^2)
σ	Absolute coverage of adsorbates (adsorbates per unit area), $\sigma = N_{\mathrm{ads}}/A_s$
σ_0	Absolute coverage of sites or surface atoms
σ_*	Absolute coverage of empty sites
σ_{sat}	Absolute coverage that completes a monolayer
σ°	Absolute coverage of the standard state (standard state coverage)
θ	Fractional coverage, fraction of sites or surface atoms covered by adsorbates (monolayers, ML), $\theta \equiv \sigma/\sigma_0$
θ_{sat}	Saturation coverage, $\theta_{\mathrm{sat}} \equiv \sigma_{\mathrm{sat}}/\sigma_0$, where σ_0 is the number of surface atoms
ε	Exposure, amount of gas incident on the surface per unit area or Langmuir
$\varepsilon(\mathrm{M{-}A})$	Binding energy of the M–A bond, heat released when a single particle adsorbs
q_{ads}	Heat released when a finite number of particle adsorbs (positive for exothermic adsorption, usually in molar units such as $\mathrm{kJ\ mol^{-1}}$)
L	Langmuir, unit of exposure, $1\ \mathrm{L} = 1 \times 10^{-6}\ \mathrm{Torr} \times 1\ \mathrm{s}$
s	Sticking coefficient, $s = \sigma/\varepsilon$
	Integral sticking coefficient: total coverage divided by exposure, meaningful only if s is constant or as $\theta \to 0$ ML
	Instantaneous or differential sticking coefficient at coverage $\theta : s(\theta) = \mathrm{d}N_{\mathrm{ads}}/\mathrm{d}N_{\mathrm{exp}} = \mathrm{d}\sigma/\mathrm{d}\varepsilon$, evaluated at a specific value of θ
s_0	Initial sticking coefficient, sticking coefficient as $\theta \to 0$ 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

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

- In Fig. 4.1, 4.2 → 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))

- $-q_{ads} = U_a - U_g$ and $q_c = RT$ (g_c: heat of compression from gas(finite volume) into adsorbed layer(volume = 0))

c.f. heat of adsorption(q_{ads}): a positive quantity for exothermic adsorption
adsorption enthalpy($\Delta_{ads}H$): a negative quantity for exothermic adsorption

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

$$\boxed{-\Delta_{\mathrm{ads}}H(\theta) = q_{\mathrm{ads}}(\theta) + q_{\mathrm{c}}(\theta) = q_{\mathrm{st}}(\theta)} \tag{4.1.14}$$

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

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

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

where p is the equilibrium pressure that maintains a coverage θ 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 θ_{f}. The integral adsorption enthalpy is related to the heat of adsorption by

$$\Delta_{\mathrm{ads}}H_{\mathrm{int}} = \frac{\int_0^{\theta_{\mathrm{f}}} -q_{\mathrm{ads}}(\theta)\,\mathrm{d}\theta}{\int_0^{\theta_{\mathrm{f}}}\mathrm{d}\theta}. \tag{4.1.16}$$

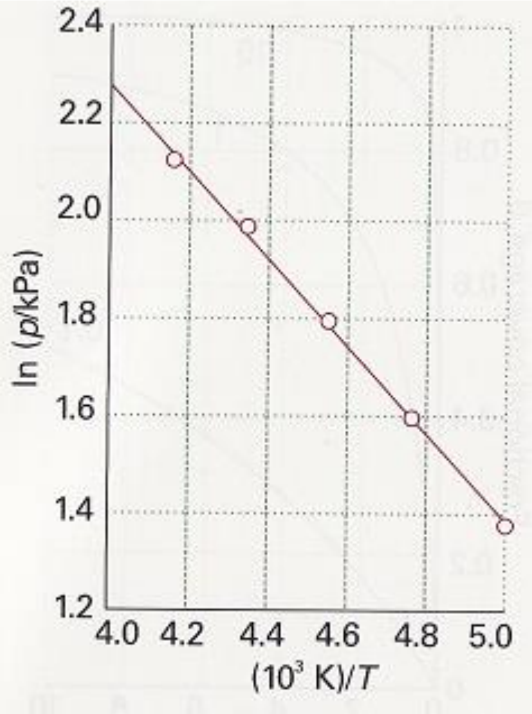
Isosteric enthalpy(heat) of adsorption

- $dG = Vdp - SdT$, and $d(\Delta G) = \Delta V dp - \Delta S dT$ for any change
- At equilibrium, $\Delta V dp - \Delta S dT = 0$.
- $\Delta V = V_{ad} - V_g \sim -nRT/p$
- $(\partial p / \partial T)_\theta = \Delta S / \Delta V = -(\Delta H/T)/(nRT/p) = -p\,\Delta H/nRT^2$ at constant θ
- $d \ln p = (\Delta H_{ad}/R)\, d(1/T) \rightarrow$ slope of ($\ln p$) – ($1/T$) plot gives $\Delta H_{ad}/R$

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

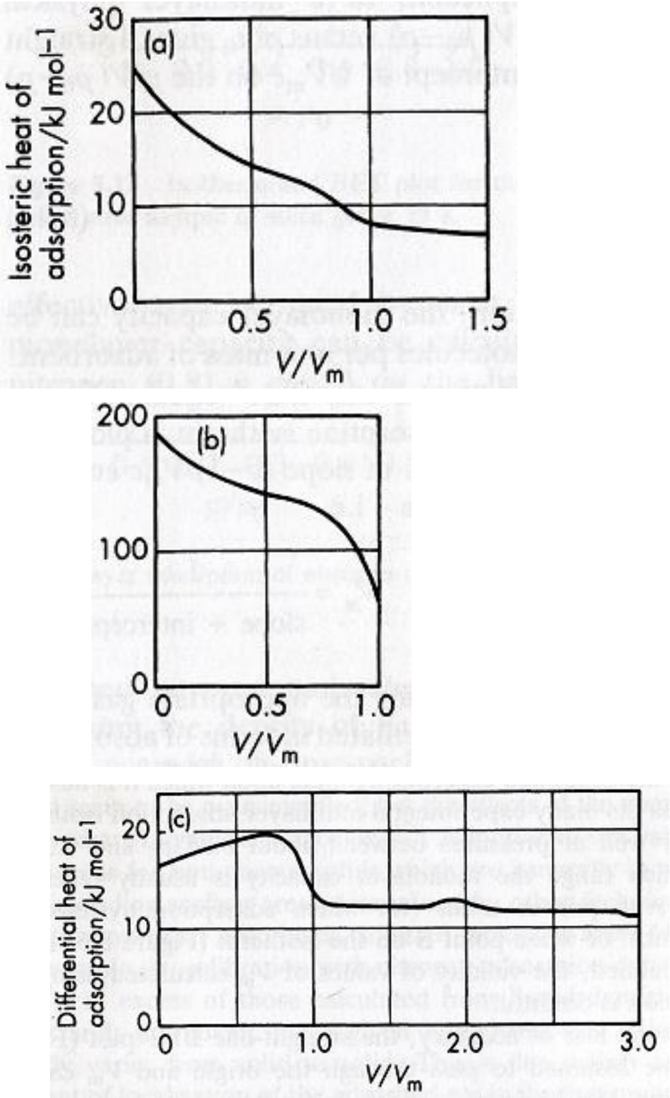
cf. isoteric: constant adsorption
isoteric enthalpy: standard enthalpy of adsorption at fixed coverage

Isosteric enthalpy(heat) of adsorption



CO on charcoal

$\Delta H_{ad} = -7.52$ 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

Heat of adsorption(q_{ads}) vs. coverage(θ)

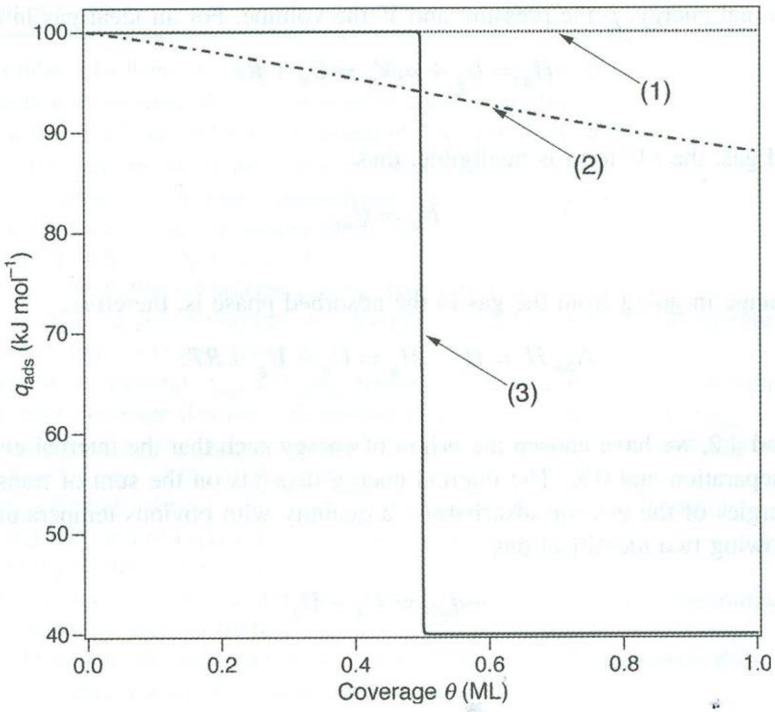


Figure 4.3 *Three different behaviours of the heat of adsorption, q_{ads}, as a function of coverage, θ. Case (1): the surface is composed of one and only one type of non-interacting site. Case (2): q_{ads} decreases linearly with θ. Case 3: the surface is composed of two types of sites with different 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 → q_{ads} is constant, $\Delta_{ads}H_{int} = -q_{ads}$
- Case (3): surface has two independent adsorption sites with different characteristic adsorption energies that fill sequentially → step-like behavior

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

Kinetics of adsorption (4.5)

Langmuir model assumes that

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

$A(g) + * \rightarrow A(ad)$: <u>non-dissociative</u>

*: 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,

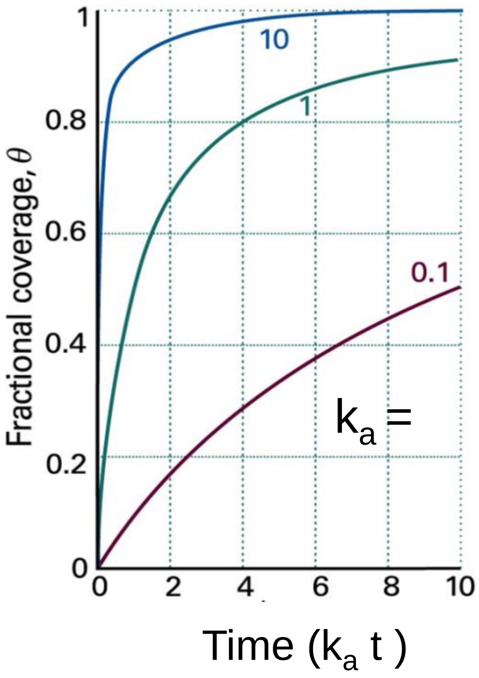
flux $Z_w = p/\sqrt{(2\pi m k_B T)}$, $(1-\theta)$: vacant site

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

cf. consider adsorption may be activated, rate,

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

$$\boxed{\theta(t) = 1-\exp(-k_a t)}$$



A_2 + * → 2A(ad) : dissociative

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

$k_a = 2 Z_w s_0/p$ (or $k_a \rightarrow k_a p$)

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

$$\boxed{\theta(t) = k_a t / (1 + k_a t)}$$

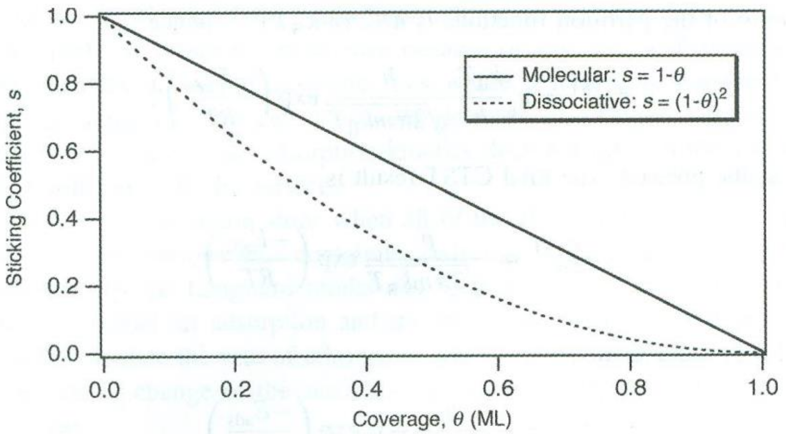


Figure 4.6 *Langmuir models (molecular and dissociative) of the sticking coefficient, s, as a function of coverage, θ.*

cf. consider adsorption may be activated, rate,

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

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

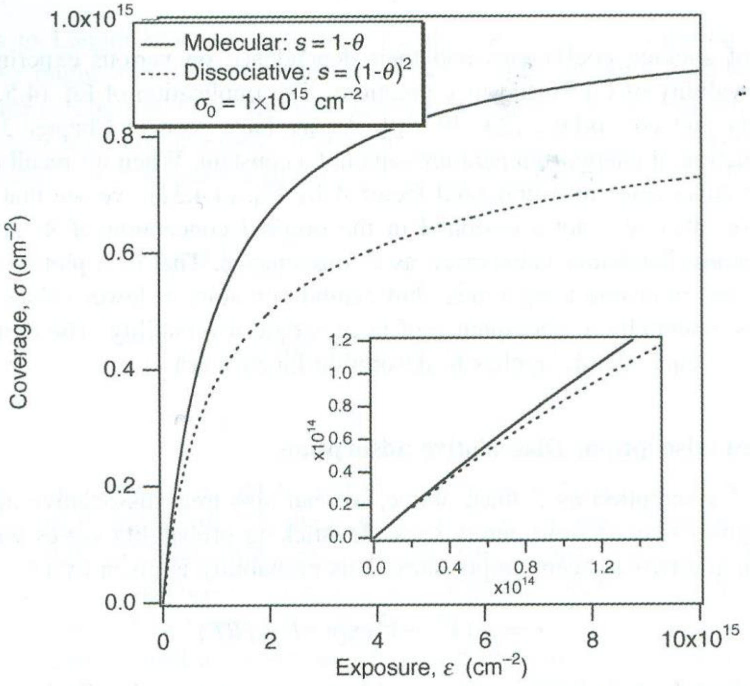


Figure 4.7 *Langmuir models (molecular and dissociative) of coverage, σ, as a function of exposure, ε.*

Dissociative Langmuir adsorption with lateral interaction

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

Interaction energy w

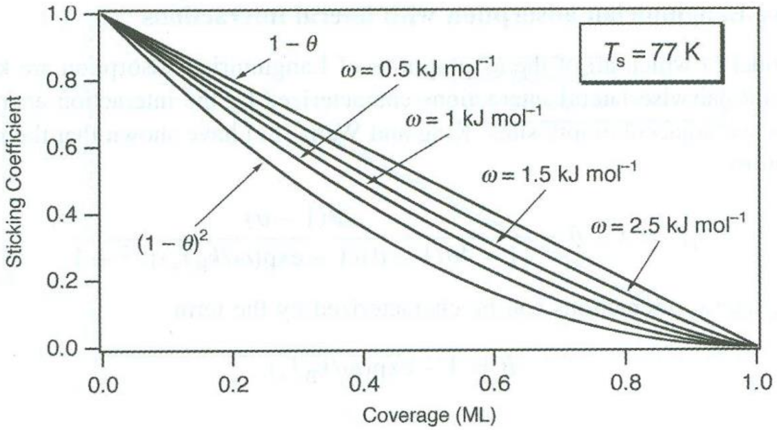


Figure 4.8 *The effect of lateral interactions on the dissociative sticking coefficient as a function of interaction strength, ω, and coverage θ at a fixed surface temperature $T_s = 77$ K.*

- For large repulsive interactions, w << 0
  dissociative adsorption → minimum 2 sites needed

$$s = s_0(1- 2\theta) \qquad \text{for } \theta < 0.5$$
$$s = 0 \qquad \text{for } \theta \geq 0.5$$

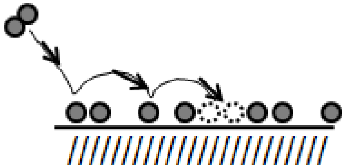
- For large attractive interactions, w >> 1
  same as non-dissociative adsorption
  (the adsorbate coalesce into close-packed islands)

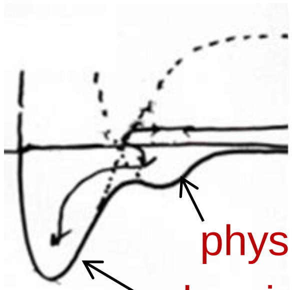
$$s = s_0(1- \theta) \qquad \text{for } \theta < 0.5$$

- 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↑: re-evaporation of the precursor state





physisorption well

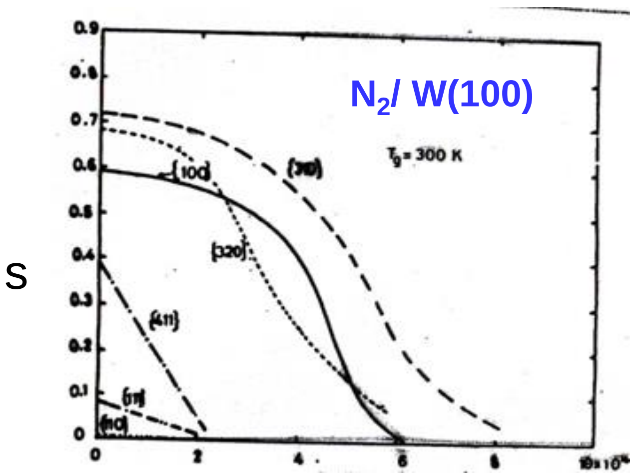
chemisorption well

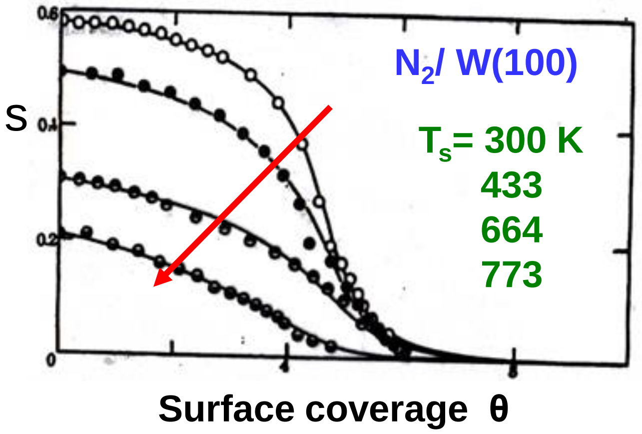
$N_2(g) \leftrightarrow N_2(ad) \rightarrow 2\,N(ad)$

- 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 ; **$\tau = \tau_0 \exp(-E_d/RT)$**

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

$N_2\,(g) \rightarrow 2\,N_{ad}$





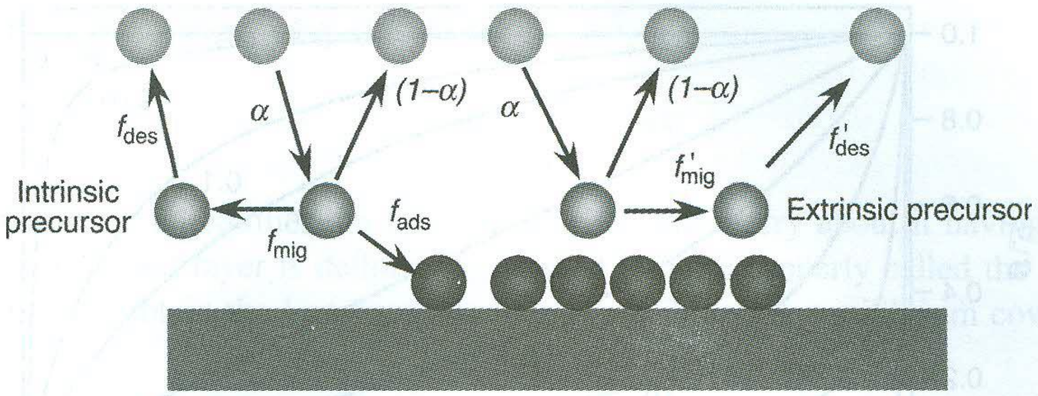


Figure 4.10 *The Kisliuk model of precursor mediated adsorption. Incident molecules trap into intrinsic or extrinsic precursors. Thereafter, sticking becomes a competitive process between desorption out of the precursor and transfer into the stable chemisorbed state.* α *is the probability to enter into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

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

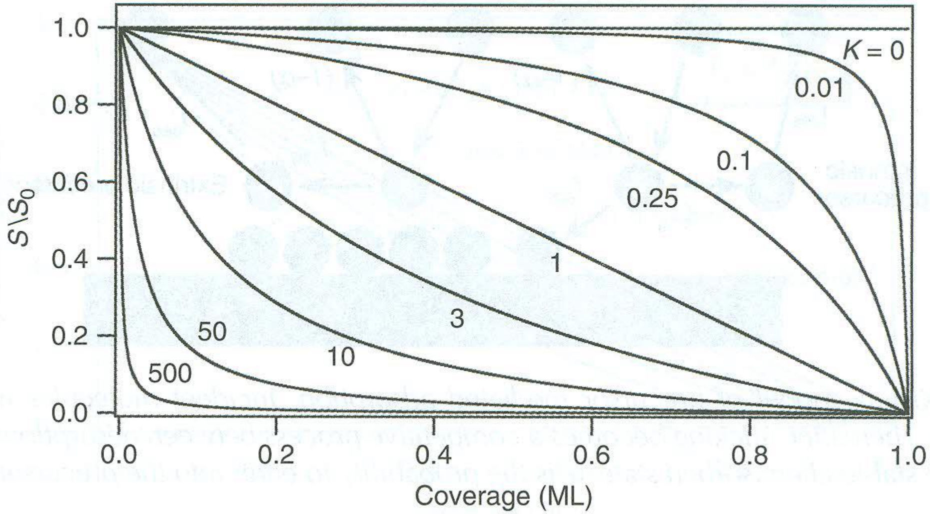


Figure 4.11 *The change of sticking coefficient, s, with coverage for precursor mediated adsorption is characterized by the parameter* K. *For* K = 0, *the sticking coefficient is constant, whereas for* K = 1 *it drops linearly with coverage as in Langmuirian adsorption. Large values of* K *decrease*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

Adsorption isotherms from kinetics (4.6)

Adsorption-desorption equilibrium

$$A(g) + * \leftrightarrow A(ad)$$

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

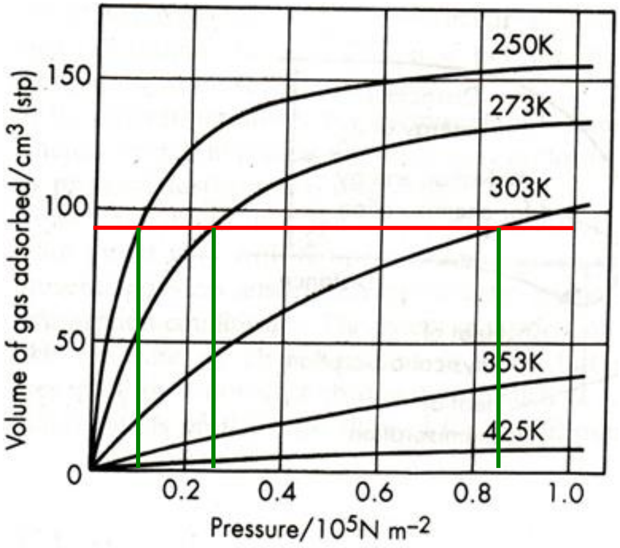
- The desorption rate constant
  $k_d = k_d^0 \exp(-E_d/RT)$

- At equilibrium, $d\theta/dt = 0$,

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

where $K = k_a / k_d$: equilibrium constant

NH$_3$/ charcoal



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

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

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

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

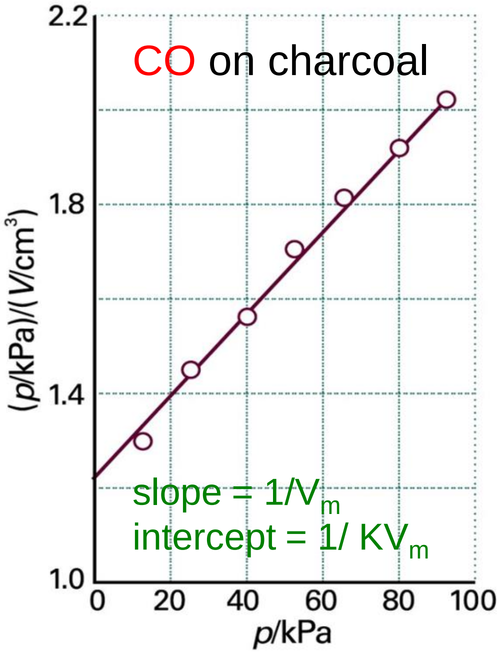
$\theta = V/V_m$ measured as a volume change,
 where V is the volume of gas adsorbed
 and V_m is the saturation volume (corresponding to complete coverage)

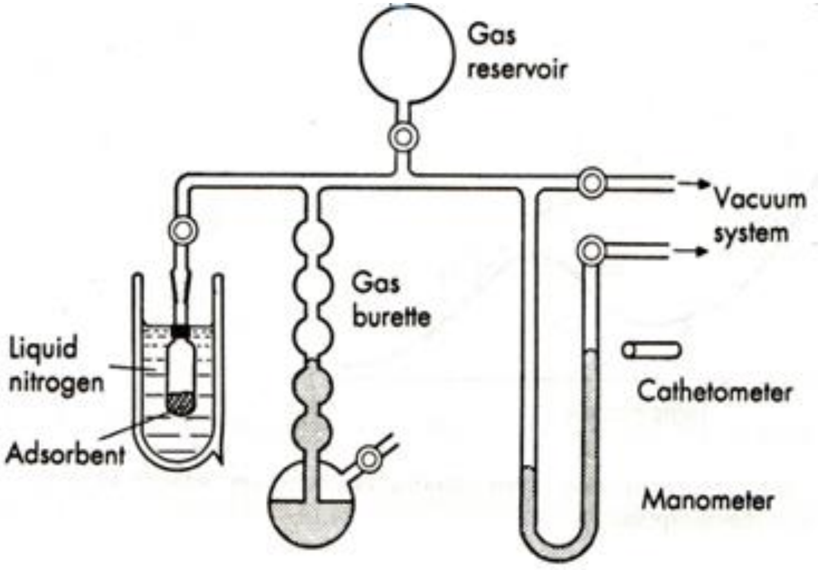
$V/ V_m = Kp /(1+Kp)$,

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

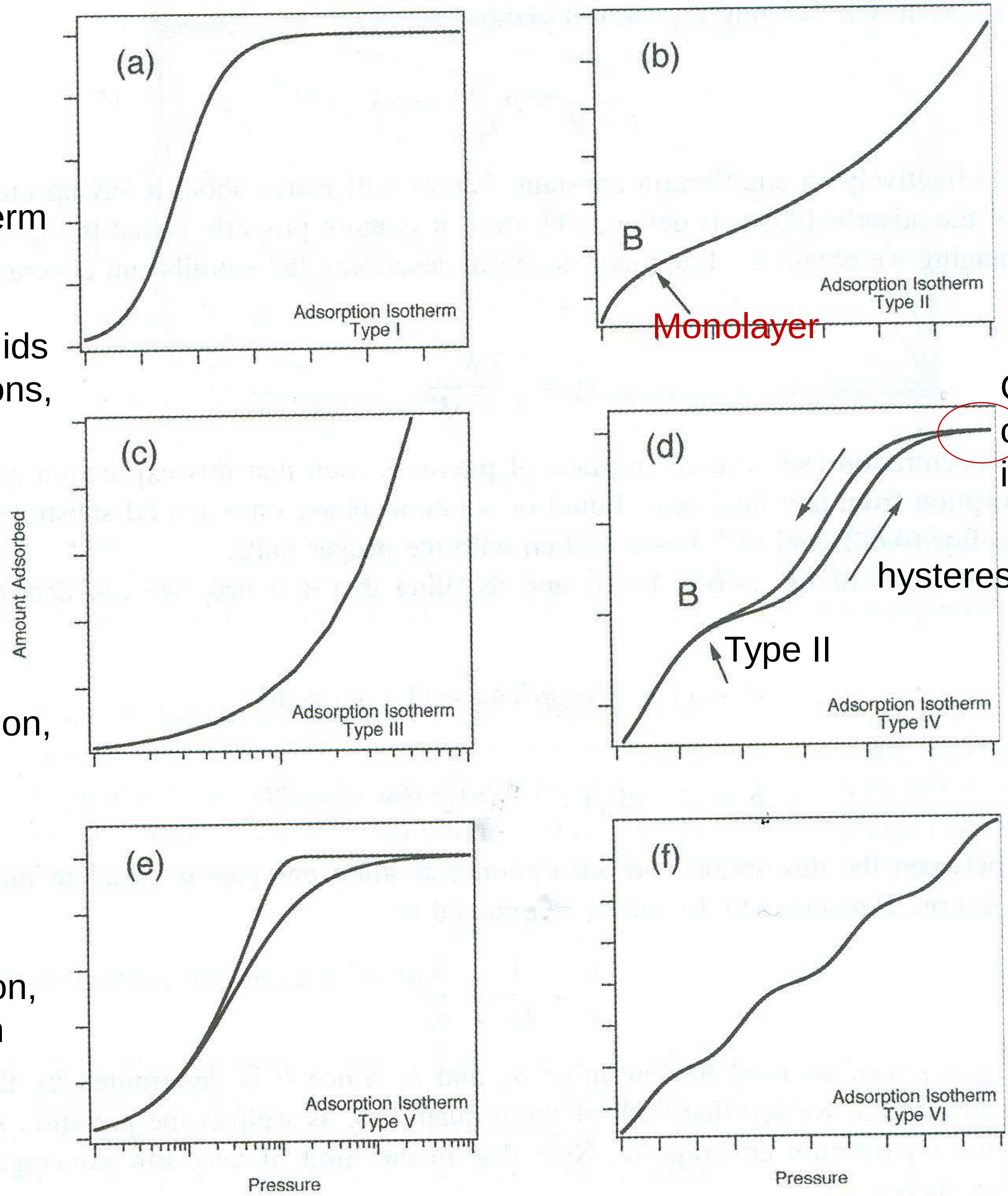
p/V vs. p plot gives a straight line

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





Classifications of adsorption isotherms



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

Monolayer

Monolayer adsorption + multilayer condensation, non-porous solids

Not common, multilayer

Capillary condensation in mesoporous

hysteresis

Type II

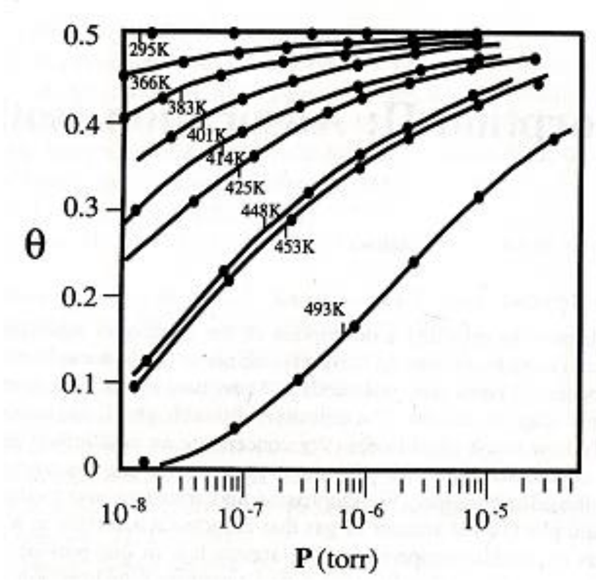
Mesoporous industrial adsorbents

Not common, type III with porous adsorbents

Stepwise multilayer adsorption on a uniform non-porous surface

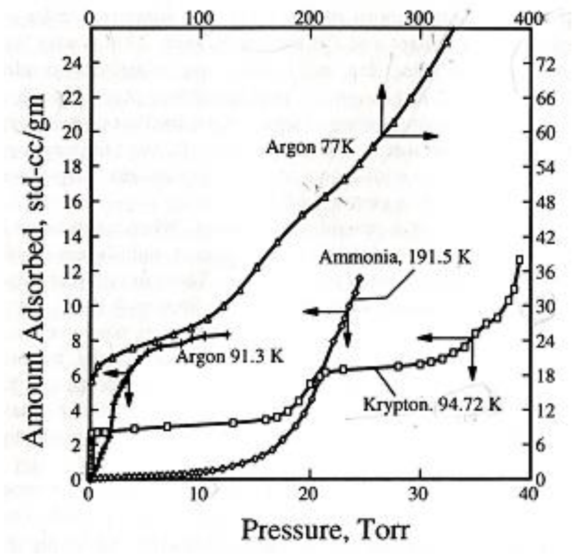
Figure 4.12 *The six types of physisorption isotherms in which coverage (either relative coverage θ or absolute coverage σ) is plotted against pressure, p, of a gaseous adsorbing species (or concentration, c, of a species dissolved in a liquid solution). The coverage is often expressed as specific coverage,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

Examples of adsorption isotherms

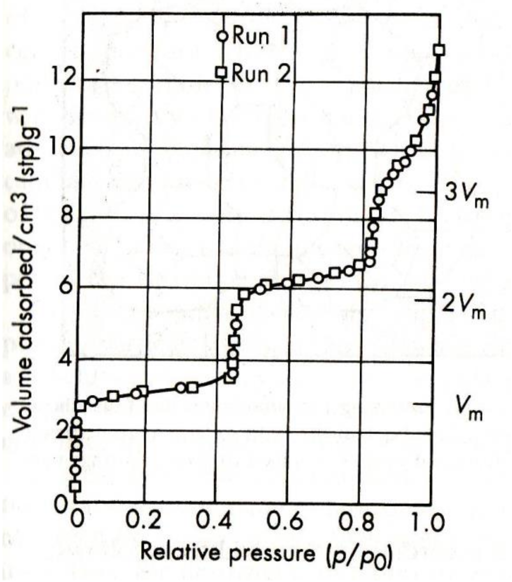


CO/Pd(111)

temp↑ → Langmuir isotherm



Ar, NH_3 /carbon black



Kr /carbon black

Stepwise isotherms→ uniform solid surface (each layer → complete monolayer

* carbon black graphitized at 3000 K

Langmuir adsorption isotherm

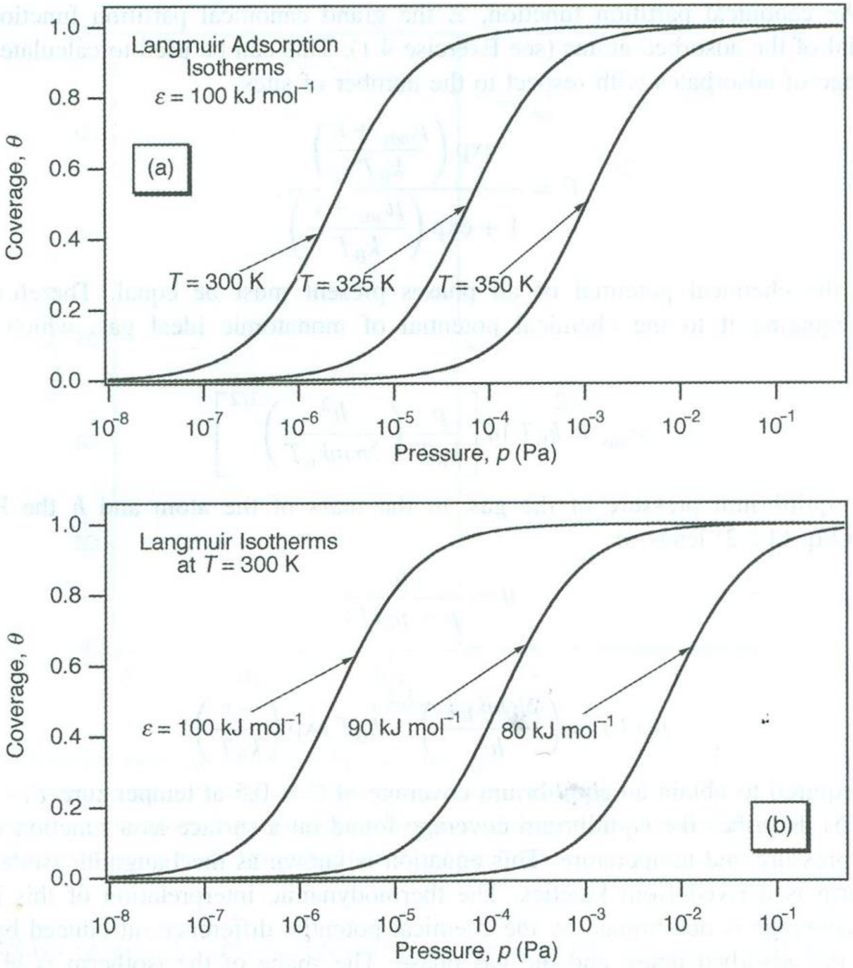


Figure 4.4 *Langmuir isotherms exhibit a dependence on the temperature and binding energy. (a) Constant heat of adsorption for various temperatures T. (b) Constant temperature for various adsorption energies ε.*

Other isotherms:
Freundlich adsorption isotherm

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

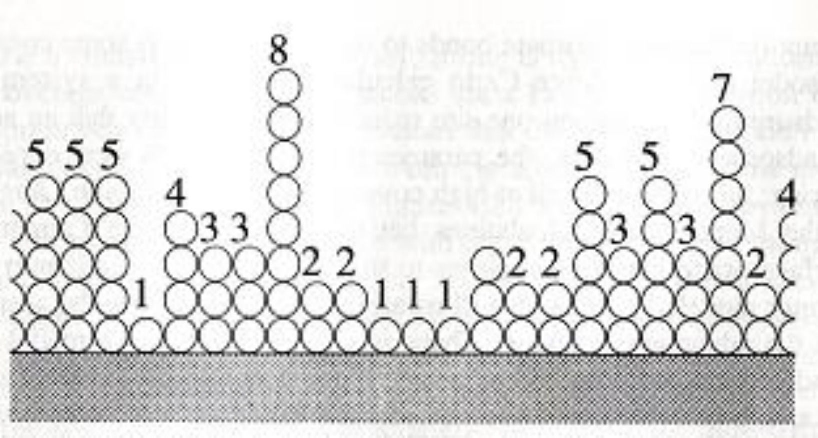
Log $V = \log k + (1/n)\ln p$

Multilayer physisorption

BET isotherm: Brunnauer, Emmett, Teller

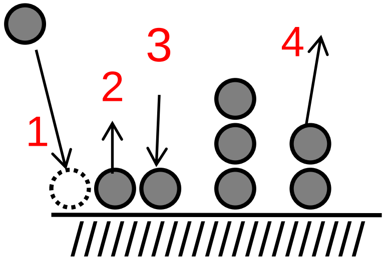
- Langmuir adsorption extended to allow multilayer adsorption
- Equilibrium maintained between the adjacent layers
- $\Delta H^o_{\mathbf{des}}$ for the first layer and $\Delta H^o_{\mathbf{vap}}$ ($=\Delta H_L$) for the multilayers
- used for surface area measurements

$$
\begin{aligned}
M(g) + \ * \quad & \leftrightarrow M_1(ad) \\
M(g) + M_1(ad) \quad & \leftrightarrow M_2(ad) \\
\ldots. & \\
M(g) + M_{n-1}(ad) & \leftrightarrow M_n(ad)
\end{aligned}
$$



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
- $k'_a = Z_w s'_0$, $k'_d = \nu' \exp(-\Delta H_{vap}/RT)$ for the 2nd layer and beyond.

ΔH_{des} : 1st layer

ΔH_{vap} : multilayer

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

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

....

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

(1) $\theta_0 + \theta_1 + \ldots + \theta_n\ (n \to \infty) = 1$

$\to \theta_0 + cK'p\,[1 + Kp + (K'p)^2 + (K'p)^3 + \cdots]\,\theta_0 = 1 \to \theta_0\,[1 + cK'p/(1 - K'p)] = 1$

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

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

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

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, $k'_a\,p_0\,(\theta_0 + \theta_1 + \ldots + \theta_n) = k'_d\,(\theta_0 + \theta_1 + \ldots + \theta_n) \to k'_a\,p_0 = k'_d \to$
  $K' = 1/p_0$ 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, $[p_0 + (c-1)p]/c\,p_0\,V_m = p/V(p_0 - p) \to$

$$\boxed{\mathbf{p/[V(p_0 - p)]} = 1/cV_m + [(c-1)/cV_m]\,\mathbf{(p/p_0)};\quad y = a + bx\ \text{type}}$$

BET equation

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

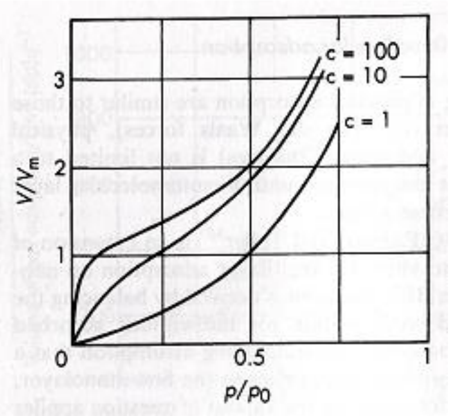
$$\frac{p}{V(p_0-p)}=\frac{1}{V_m c}+\frac{(c-1)}{V_m c}\frac{p}{p_0}$$

Intercept = $1/cV_m$

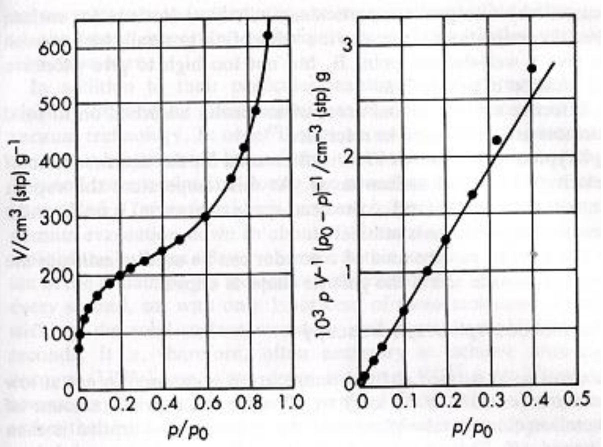
$$V_m=\frac{1}{\text{slope}+\text{intercept}}$$

V_m = monolayer capacity, p_0 : saturation vapor pressure

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



N_2/ silica gel @ 77 K



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

BET surface area, $A = n_m N_A a_m$

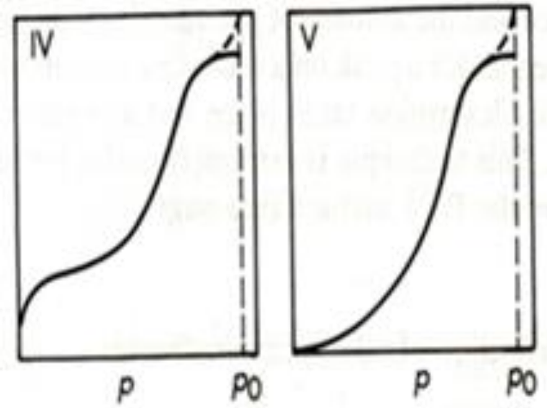
a_m: cross sectional area (N_2 (at 77K) = 0.162 nm^2)

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 = ∞: BET isotherm



Classifications of adsorption isotherms

Brunner classification

Type I: Langmuir adsorption

Type II: monolayer + multilayer

Type III: multilayer adsorption

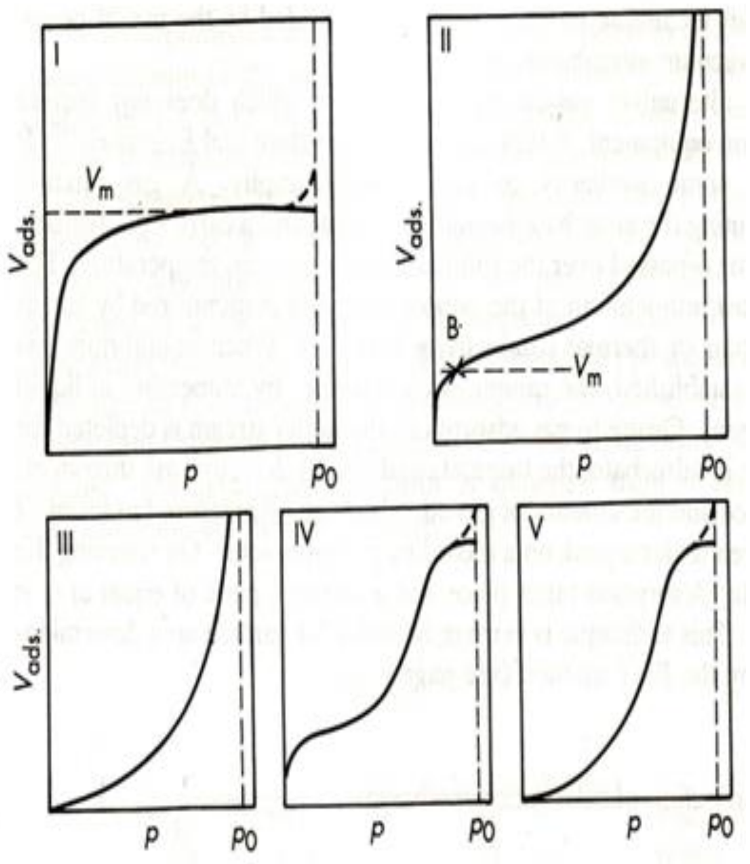
Type IV: Type II on porous solids

Type V: Type III on a porous adsorbent

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

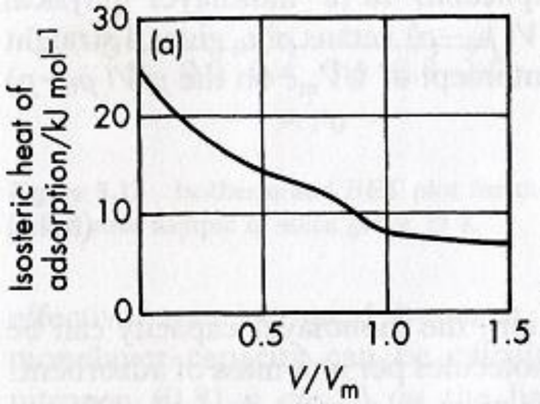
Physical adsorption

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

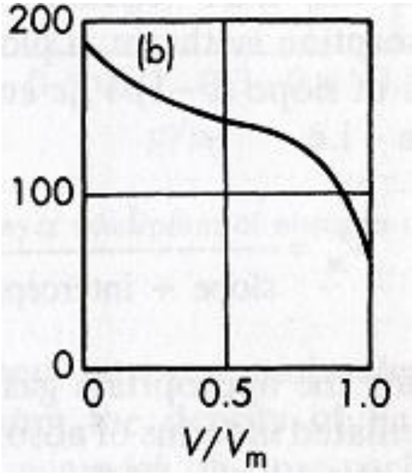


p_0 = saturation vapor pressure

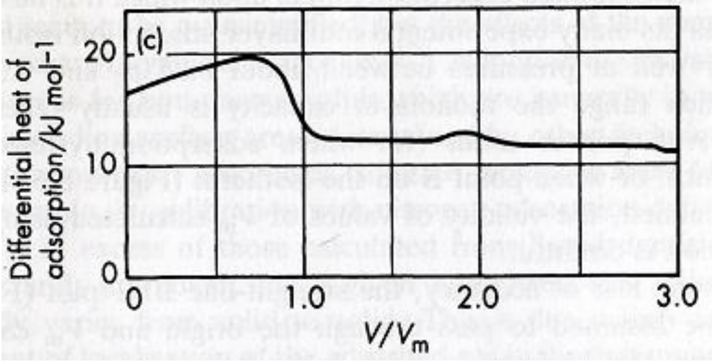
Isosteric enthalpy(heat) of adsorption



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



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



Up to 1 ML → interaction between adsorbates → more exothermic

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

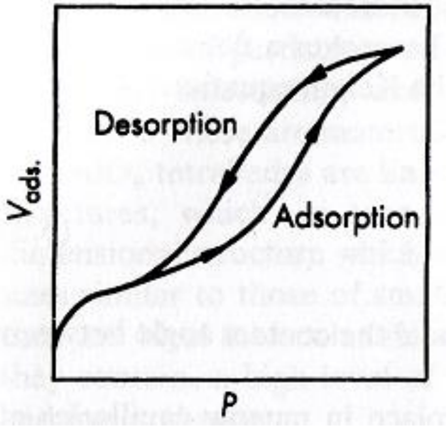
Representative example: Zeolites

- Natural or synthetic materials
- SiO_4 and 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

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

Hysteresis loop
in physisorption



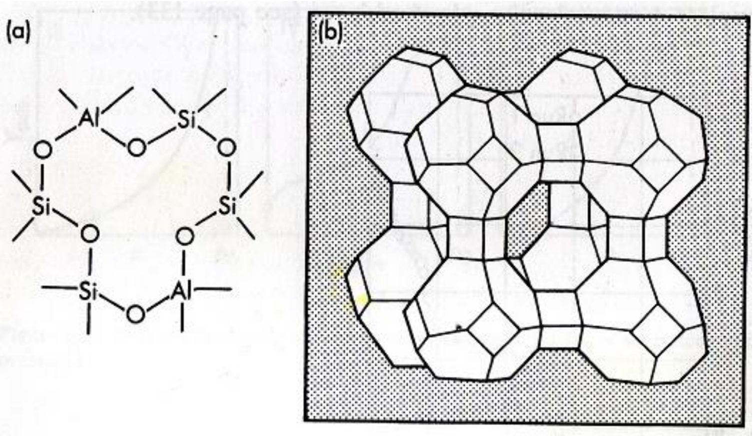


Figure 5.7 Zeolite structure. (a) 6-ring containing two aluminium and four silicon tetrahedral centres. (b) Zeolite A structure. Each of the eight sodalite units depicted contains 24 aluminium or silicon tetrahedral centres arranged to give six 4-rings plus eight 6-rings

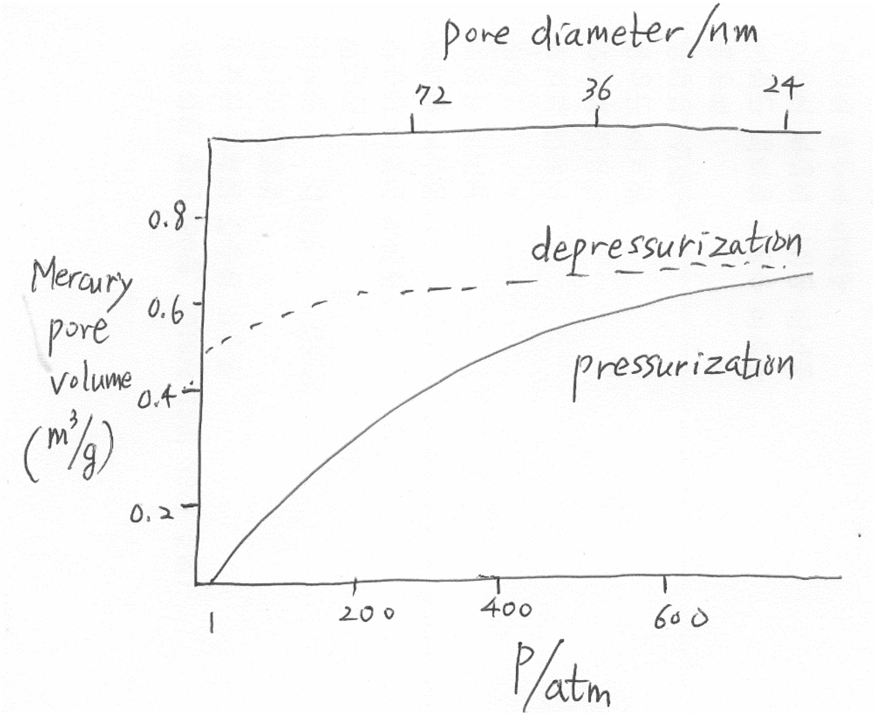
Pore size distribution: Mercury intrusion porosimetry

- Volume of mercury (contact angle ~140°) into pores as a function of pressure

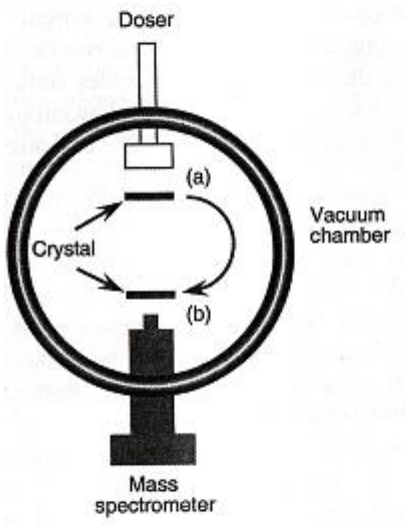
- Pore size distribution,

$$\boxed{p = 2\gamma\cos\theta/r}$$

$r > 2\gamma\cos\theta/p$ → filling pores, $p\uparrow$ → filling in smaller r pores → volume↑



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

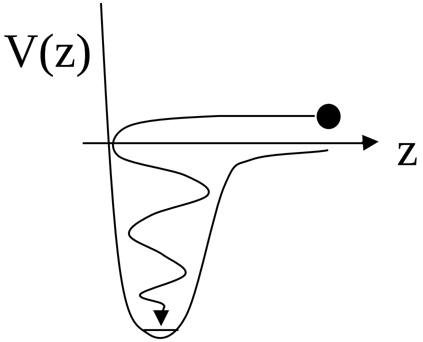
Desorption rate

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

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

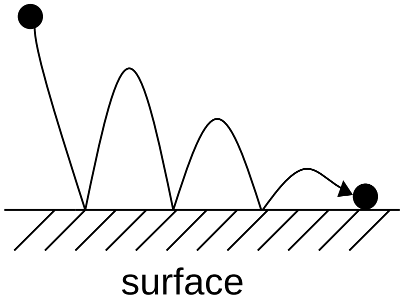
n = 1 : 1^{th}-order desorption : M(ad) → M(g)

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



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

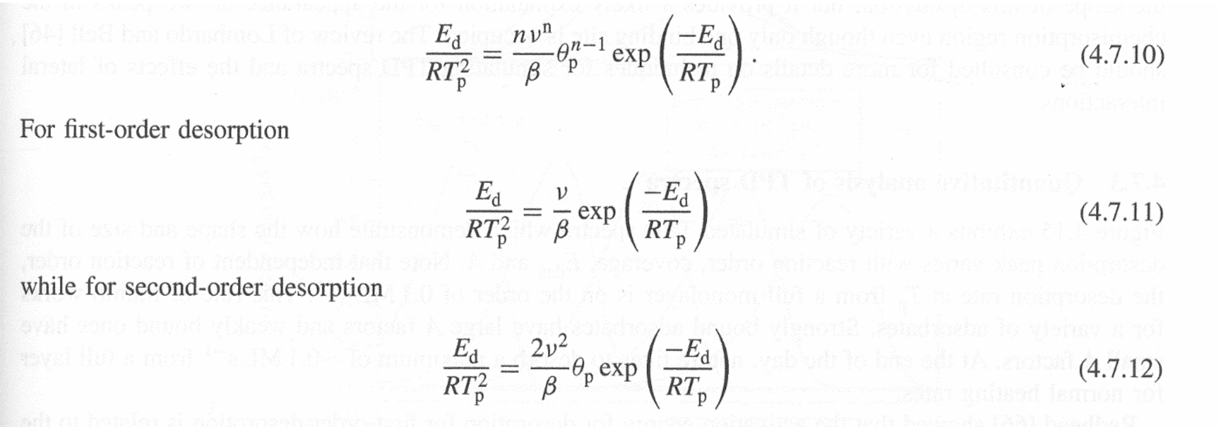
$T = T_0 (1+ \beta t)$, where the heating rate $\beta = 0.1\sim 10$ K/s



e.g. N(ad) + H(ad) → NH(ad) + H(ad) → NH_2(ad) + H(ad) → NH_3(ad) → NH_3(g)

desorption

Temperature programmed desorption (TPD) (4.7)



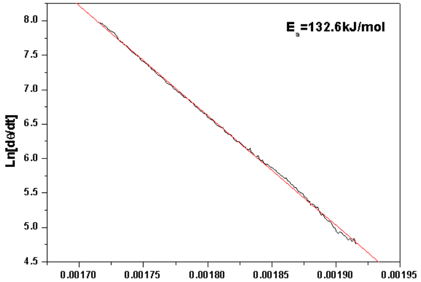
$$\frac{E_d}{RT_p^2} = \frac{n\nu^n}{\beta}\theta_p^{n-1}\exp\left(\frac{-E_d}{RT_p}\right). \qquad (4.7.10)$$

For first-order desorption

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

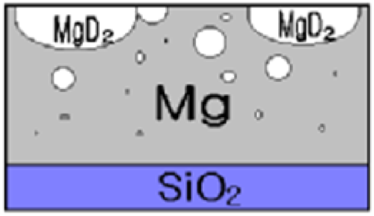
while for second-order desorption

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



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}



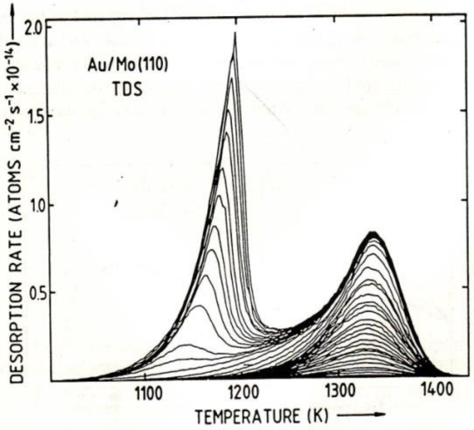
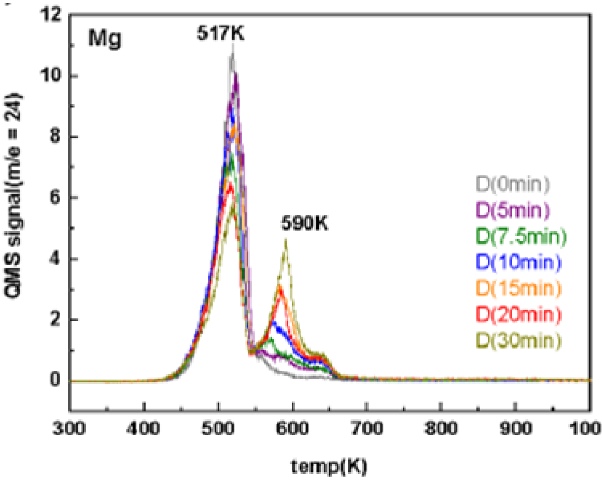
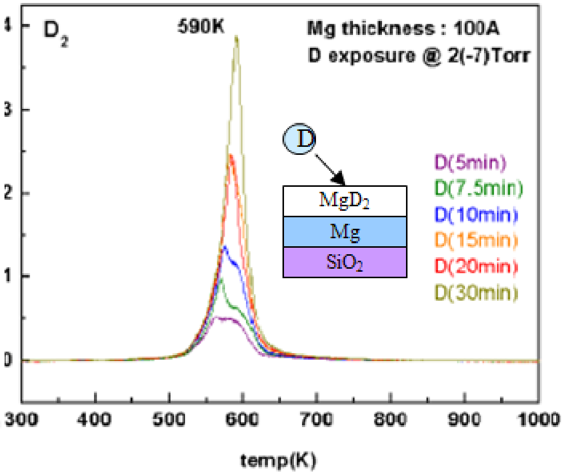


Figure 2 *Thermal desorption spectra of* Au *on* Mo(110) *in the coverage range from* 0 to 2 ML. *Heating rate* 5.2 K s^{-1}
(Reproduced with permission from *Surf. Sci.*, 1988, **195**, 207)





1^{st} –order desorption

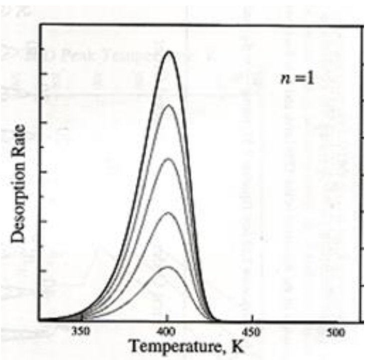
- The peak temperature is coverage-independent
- Asymmetric peak shape

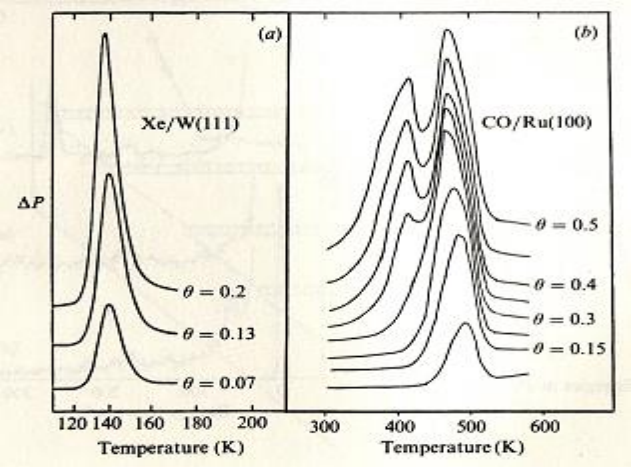
$$E_{des} = RT_p \left[\ln\left(\frac{AT_p}{\beta}\right) - 3.46 \right]$$

~ 31 kT_p

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

calculated

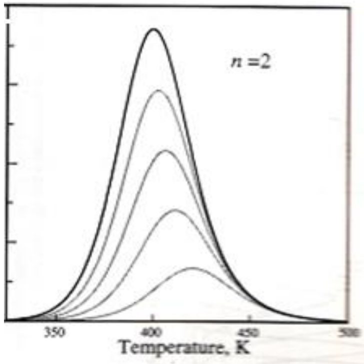


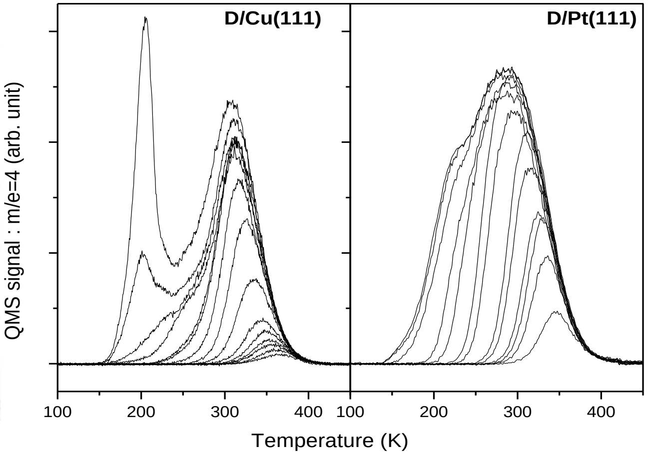


2^{nd} –order desorption

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

calculated





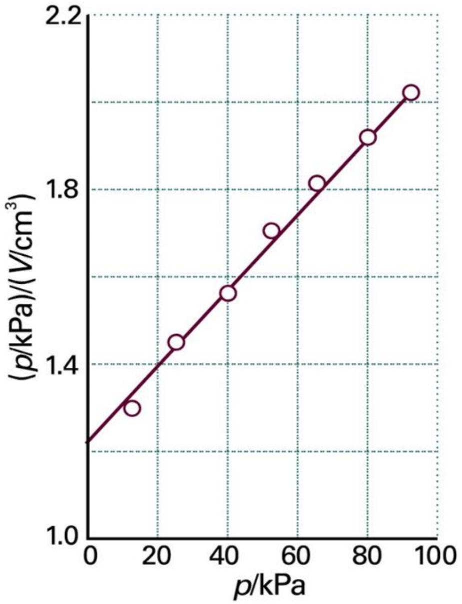
Summary

- 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).

(Midterm Exam, 2019)

7. A graph for the adsorption of CO on charcoal is shown below. Prove this graph follows a Langmuir isotherm. Calculate the saturation volume of adsorbed CO on charcoal.



7.

$$KP\theta + \theta = Kp$$

With $\theta = V/V_m$, where V_m is the volume corresponding to complete coverage, this expression can be rearranged into

$$\frac{P}{V} = \frac{P}{V_m} + \frac{1}{KV_m}$$

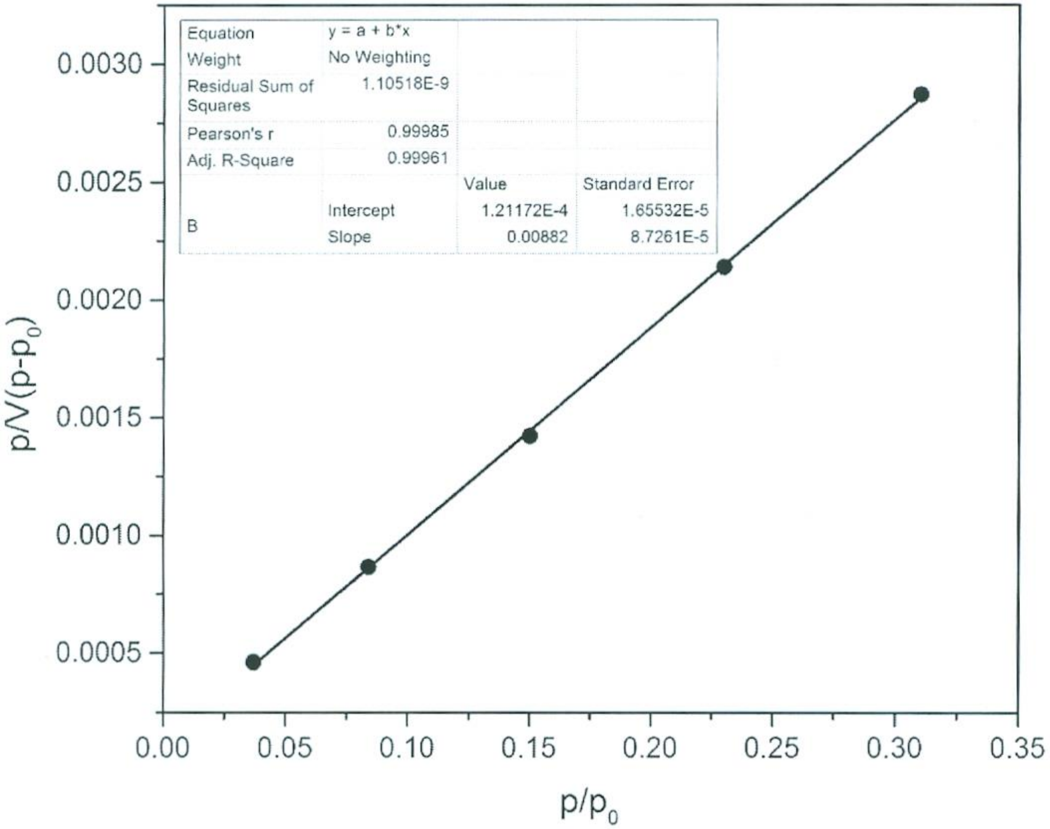
Hence, a plot of p/V against p should give a straight line of slope $1/V_m$ and intercept $1/KV_m$.

The slope is 0.00900, so **V_m=111 cm^3**

8. The data for the adsorption of N_2 on 0.92 g silica gel at 77 K are shown below.

Pressure/kPa	3.7	8.5	15.2	23.6	31.5	38.2	46.1	54.8
Volume/cm^3	82	106	124	142	157	173	196	227

The graph below is obtained from these data. Calculate the surface area of the alumina. (The area covered by one nitrogen molecule is 16.2×10^{-20} m^2. The saturation vapor pressure is 101.3 kPa.)



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1.10518E-9		
Pearson's r	0.99985		
Adj. R-Square	0.99961		
		Value	Standard Error
B	Intercept	1.21172E-4	1.65532E-5
	Slope	0.00882	8.7261E-5

8.

The linear relationship of the equation is maintained only in the range of $0.05 < p/p_0 < 0.35$

In our textbook, it is said that "V_m can be calculated on the basis of a single gas-adsorption measurement (usually with p/p_0 between 0.2 and 0.3). So, you have to choose data only in the range $0.05<p/p_0<0.35$ or $0.2<p/p_0<0.3$ when you linearized with this problem's data.

$$\therefore V_m = 111.8\ cm^3$$

$$S_{total} = \frac{V_m \cdot N_A \cdot s}{V}, S_{BET} = \frac{S_{total}}{a}$$

s : the adsorption cross section of the adsorbing species (the molecular area of nitrogen is 16.2×10^{-20} m^2)

V : molar volume (22.4 L=22,400 cm^3), a : the mass of the solid sample or adsorbent

$S_{total} = 486.9\ m^2$, $\therefore \boldsymbol{S_{BET} = 529.2\ m^2/g}$

(Midterm Exam, 2020)

7. The following results refer to the adsorption of nitrogen on a graphitized sample of carbon black, and give the ratio of the nitrogen pressures for temperature of 90 K and 77 K which are required to achieve a given amount of adsorption:

Amount of N_2 adsorbed (V/V_m)	0.4	0.8	1.2
p(90 K) / p(77 K)	14.3	17.4	7.8

Calculate an isosteric enthalpy of adsorption for each value of V/V_m and comment on the value obtained.

#7.

Amount of N_2 adsorbed (V/V_m)	0.4	0.8	1.2
$P(90K)$ / $P(77K)$	14.3	17.4	7.8
$\ln P$	2.66	2.86	2.05

Derivatization from Langmuir theory & Van't Hoff equation

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

$$\ln K + \ln P = \ln\left(\frac{\theta}{1-\theta}\right)$$

$$\left[\frac{\partial}{\partial T}\ln K\right]_\theta = -\left[\frac{\partial}{\partial T}\ln P\right]_\theta$$

$$\left[\ln\frac{P_1}{P_2}\right]_\theta = \frac{\Delta H^\circ_{ad}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\rightarrow \Delta H^\circ_{ad} = R\cdot\ln\frac{P_1}{P_2}\div\left(\frac{1}{T_1}-\frac{1}{T_2}\right), \quad \left(\begin{array}{l} R = 8.314\ J/K\cdot mol \\ T_1 = 90K \\ T_2 = 77K \end{array}\right.$$

1) $V/V_m = 0.4$; $\Delta H^\circ_{ad} = 8.314\times 2.66\div(1/90-1/77) = -11789\ J/mol = -11.8\ kJ/m$

2) $V/V_m = 0.8$; $\Delta H^\circ_{ad} = 8.314\times 2.86\div(1/90-1/77) = -12676\ J/mol = -12.7\ kJ/$

3) $V/V_m = 1.2$; $\Delta H^\circ_{ad} = 8.314\times 2.05\div(1/90-1/77) = -9085\ J/mol = -9.1\ kJ/$

Values reflect multilayer physical adsorption on fairly uniform solid surface

(Midterm Exam, 2020)

8. **(20 pts)** The designers of a new industrial plant wanted to use a catalyst code-named CR-1 in a step involving the fluorination of butadiene. As a first step in the investigation they determined the form of the adsorption isotherm. The volume of butadiene adsorbed per gram of CR-1 at 15 ℃ varied with pressure as given below. Is the Langmuir isotherm suitable at this pressure? Investigate whether the BET isotherm gives a better description of the adsorption of butadiene on CR-1. At 15 ℃, p*(butadiene) = 200 kPa. Find V_{mon} and c.

P/kPa	13.3	26.7	40.0	53.3	66.7	80.0
V/cm^3	17.9	33.0	47.0	60.8	75.3	91.3

#8

p /kPa	13.3	26.7	40.0	53.3	66.7	80.0
V /cm^3	17.9	33.0	47.0	60.8	75.3	91.3

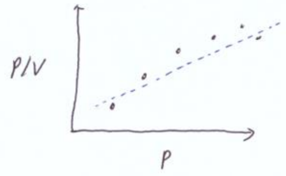
1) Langmuir isotherm equation : $\theta = \frac{Kp}{1+Kp}$ $\left(K = \frac{k_a}{k_d}\right)$

With $\theta = V/V_m$, $Kp\theta + \theta = Kp$ can be rearranged into $\frac{p}{V} = \frac{p}{V_m} + \frac{1}{KV_m}$

Hence, a plot of p/V against p should give a straight line

⇒

p / kPa	13.3	26.7	40.0	53.3	66.7	80.0
p/V	0.74	0.81	0.85	0.88	0.89	0.88



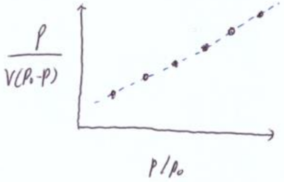
$y = 0.002x + 0.7481$, $R^2 = 0.7969$

2) BET equation : $\frac{p}{V(p_0-p)} = \frac{1}{V_m \cdot C} + \frac{(C-1)}{V_m \cdot C} \cdot \frac{p}{p_0}$ $<$ intercept $= \frac{1}{C \cdot V_m}$; $V_m = \frac{1}{\text{Slope} + \text{intercept}}$

$p_0 = 200$ kPa,

⇒

p/p_0	0.0665	0.134	0.200	0.267	0.334	0.400
$\frac{p}{V(p_0-p)}$	0.00398	0.00467	0.00532	0.00598	0.00665	0.00730



$y = 0.0099x + 0.0033$, $R^2=1$

linear relationship

$\therefore V_m = \frac{1}{0.0099 + 0.0033} = 75.8$ cm^3

$C = \frac{1}{V_m \cdot 0.0099} = 1.33$