

Announcements

- A 3-h open book exam on December 12, 2013
Monday 9:10 – 12:00 am
- November 14 & 21: Chapter 25 (Atkins/Paula)
Processes at solid surfaces
- November 21 & 28: Chapter 20 (Atkins/Paula)
The solid state
- December 5:
Single molecule spectroscopic methods

Atkins / Paula

《 *Physical Chemistry, 8th Edition* 》

Chapter 25.

Processes at solid surfaces

The growth and structure of solid surfaces

25.1 Surface growth

25.2 Surface composition

The extent of adsorption

25.3 Physisorption and chemisorption

25.4 Adsorption isotherms

25.5 The rates of surface processes

Heterogeneous catalysis

25.6 Mechanisms of heterogeneous catalysis

25.7 Catalytic activity at surfaces

Processes at electrodes

25.8 The electrode-solution interface

25.9 The rate of charge transfer

25.10 Voltammetry

25.11 Electrolysis

25.12 Working galvanic cells

25.13 Corrosion

Chapter 25: Processes at Solid Surfaces

THE GROWTH AND STRUCTURE OF SOLID SURFACES

- **adsorption**, the attachment of particles to a surface .
- **adsorbate**, the substance adsorbed.
- **adsorbent (or substrate)**, the substance on which another substance is adsorbed.
- **desorption**, the detachment of an adsorbed substance.

25.1 Surface growth

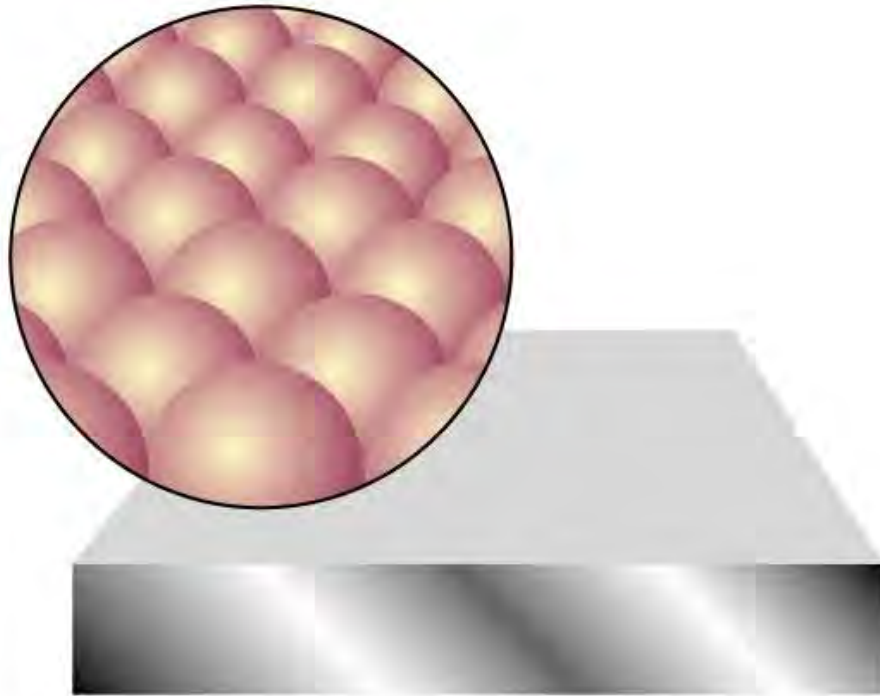


Fig. 25.1 A schematic diagram of the flat surface of a solid. This primitive model is largely supported by scanning tunnelling microscope images (see *Impact I9.1*).

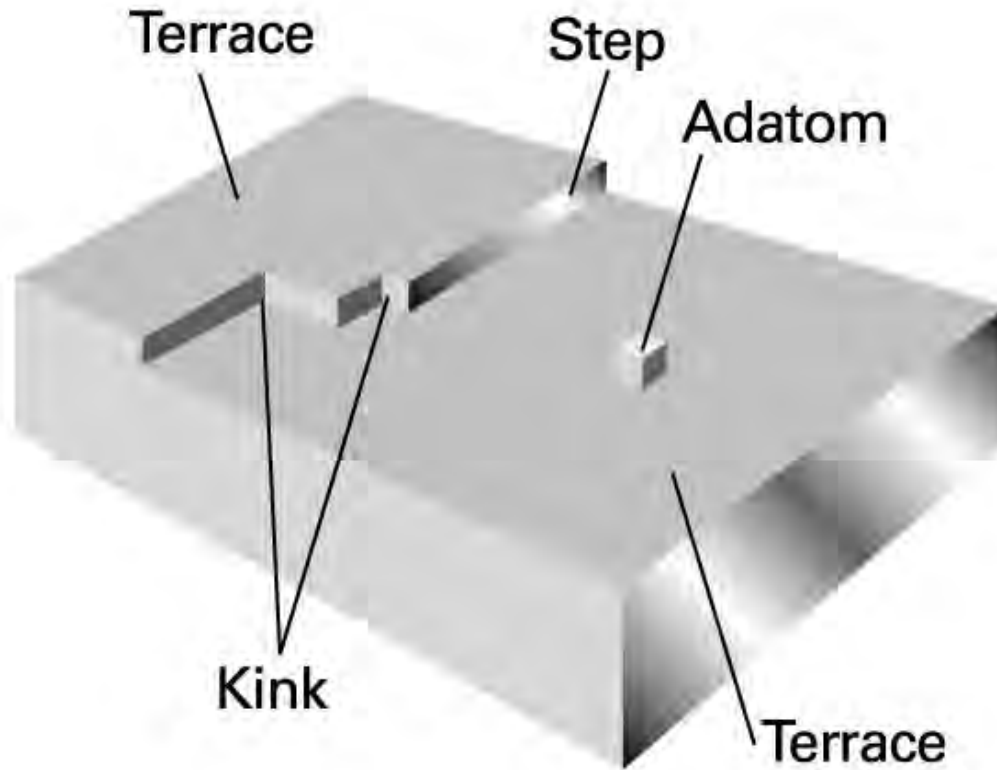


Fig. 25.2 Some of the kinds of defects that may occur on otherwise perfect terraces. Defects play an important role in surface growth and catalysis.

Chapter 25: Processes at Solid Surfaces

25.1 Surface growth

- step**, a discontinuity between two otherwise flat layers.
- terrace**, a flat region of a surface.
- dislocation**, a discontinuity in the regularity of the lattice.
- screw dislocation**, a defect in which the unit cells now form a continuous spiral around the end of the cut.
- screw axis**, the axis of a screw dislocation.

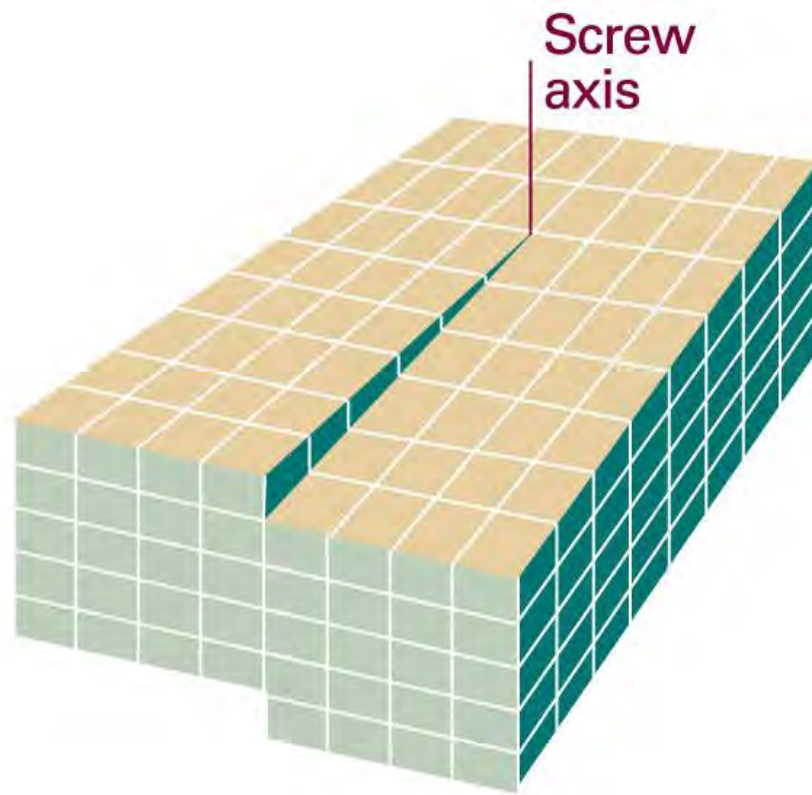


Fig. 25.3 A screw dislocation occurs where one region of the crystal is pushed up through one or more unit cells relative to another region. The cut extends to the screw axis. As atoms lie along the step the dislocation rotates round the screw axis and is not annihilated.

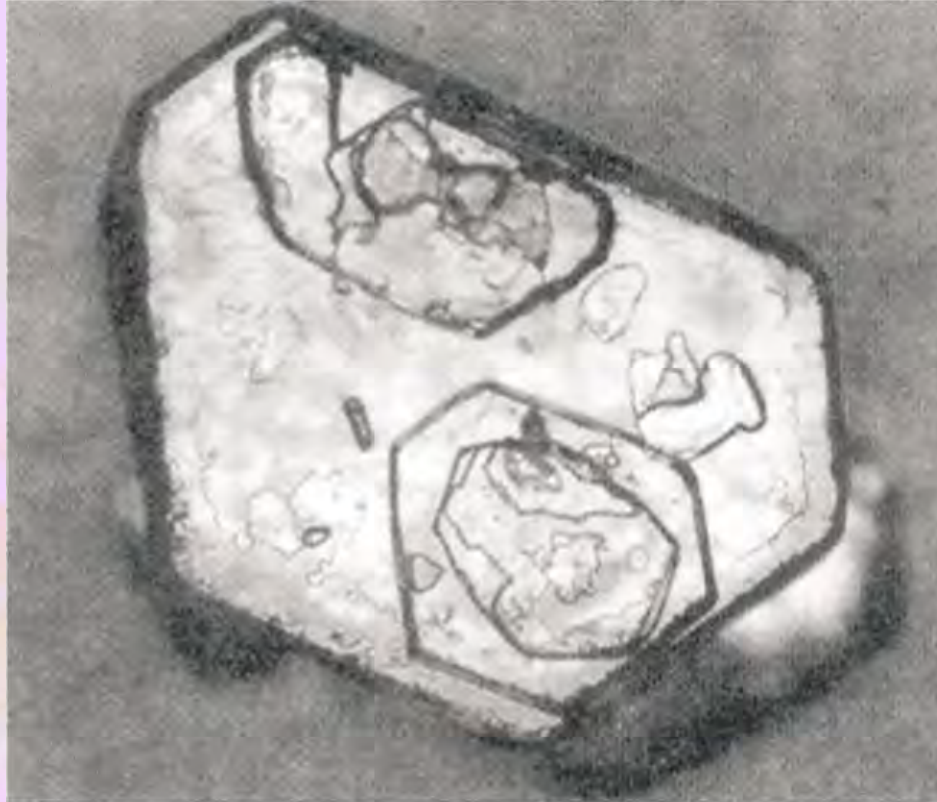


Fig. 25.4 The spiral growth pattern is sometimes concealed because the terraces are subsequently completed by further deposition. This accounts for the appearance of this cadmium iodide crystal. (H.M. Rosenberg, *The solid state*. Clarendon Press, Oxford (1978).)

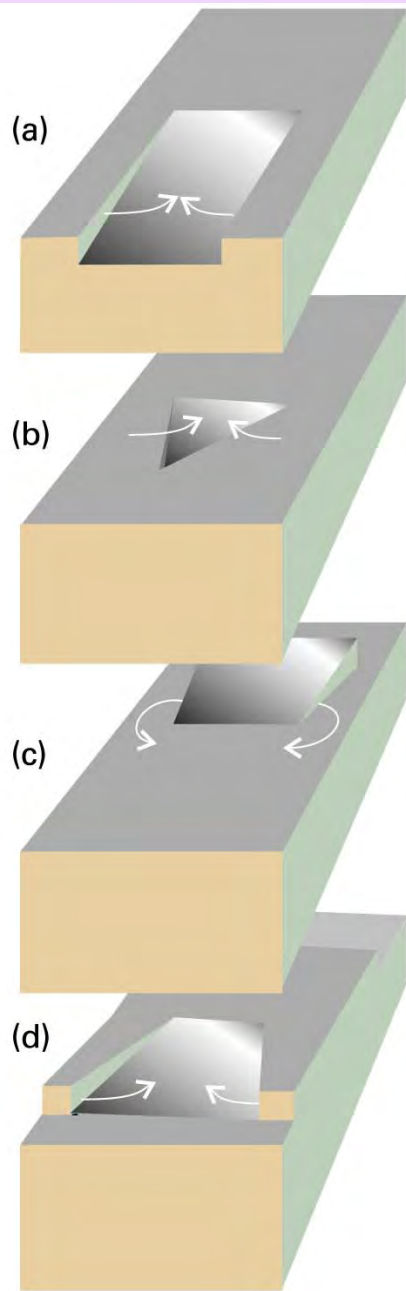


Fig. 25.5 Counter-rotating screw dislocations on the same surface lead to the formation of terraces. Four stages of one cycle of growth are shown here. Subsequent deposition can complete each terrace.

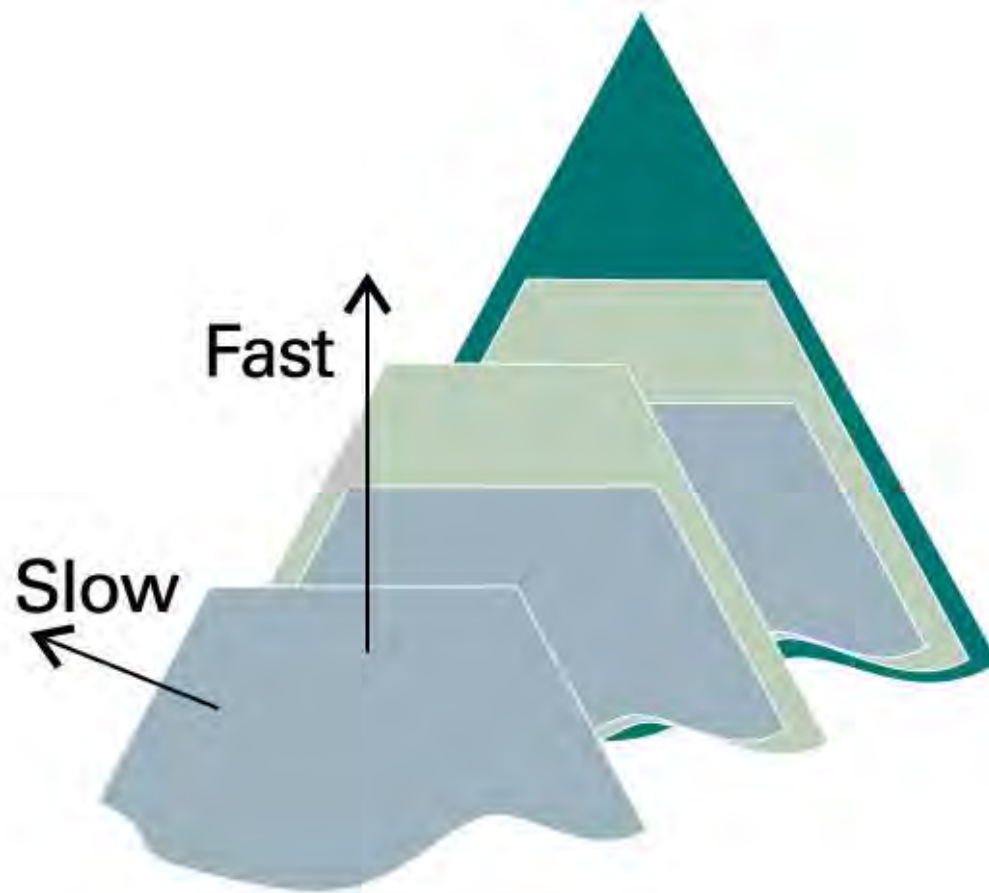


Fig. 25.6 The slower-growing faces of a crystal dominate its final external appearance. Three successive stages of the growth are shown.

25.2 Surface composition

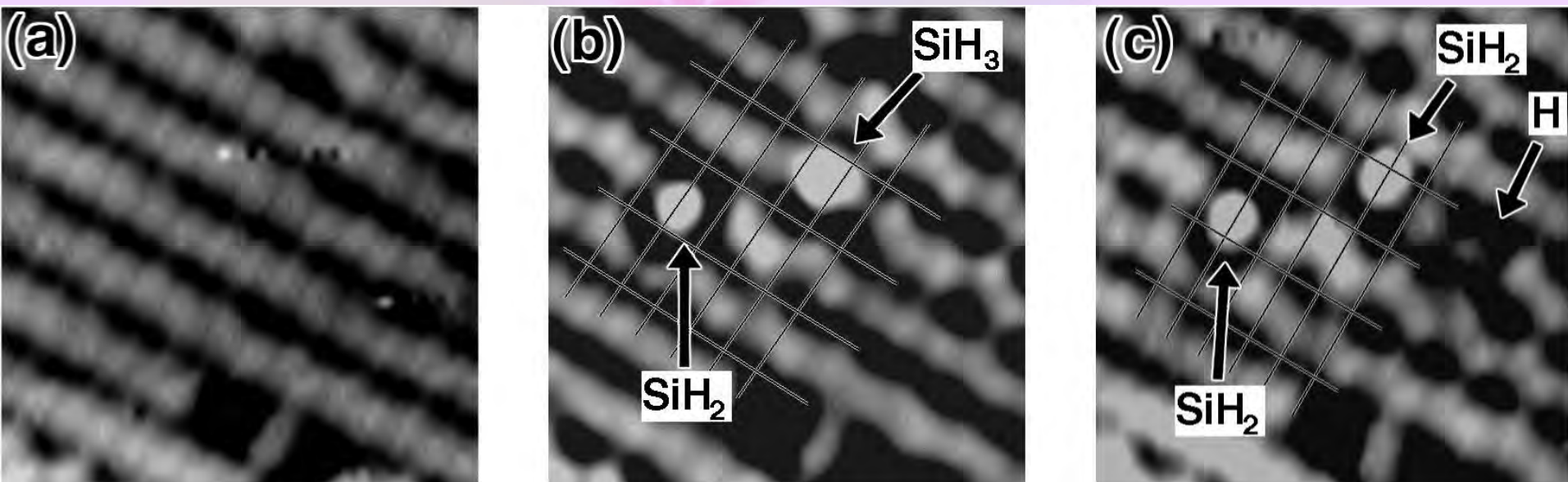


Fig. 25.7 Visualization by STM of the reaction $\text{SiH}_3 \rightarrow \text{SiH}_2 + \text{H}$ on a $4.7 \text{ nm} \times 4.7 \text{ nm}$ area of a Si(001) surface. (a) The Si(001) surface before exposure to $\text{Si}_2\text{H}_6(\text{g})$. (b) Adsorbed Si_2H_6 dissociates into $\text{SiH}_2(\text{surface})$, on the left of the image, and $\text{SiH}_3(\text{surface})$, on the right. (c) After 8 min, $\text{SiH}_3(\text{surface})$ dissociates to $\text{SiH}_2(\text{surface})$ and $\text{H}(\text{surface})$. (Reproduced with permission from Y. Wang, M.J. Bronikowski, and R.J. Hamers, *Surface Science* **64**, 311 (1994).)

Surface characterization tools:

1. Electron microscopy (*Impact I8.1*)
2. Scanning probe microscopy (*Impact I9.1*)
3. **Ionization techniques**
4. **Vibrational spectroscopy**
5. **Electron spectroscopy**
6. **Surface-extended X-ray absorption fine structure spectroscopy**
7. **Low-energy electron diffraction**
8. **Molecular beam techniques**

Chapter 25: Processes at Solid Surfaces

25.2 Surface composition

- ultrahigh vacuum (UHV)**, pressures lower than about 10^{-7} Pa.
- escape depth**, the maximum depth from which ejected electrons come.
- photoemission spectroscopy**, photoelectron spectroscopy applied to surfaces.
- secondary-ion mass spectrometry (SIMS)**, a technique in which a surface is ionized by bombardment with other ions and the secondary ions that emerge from the surface are detected by a mass spectrometer.

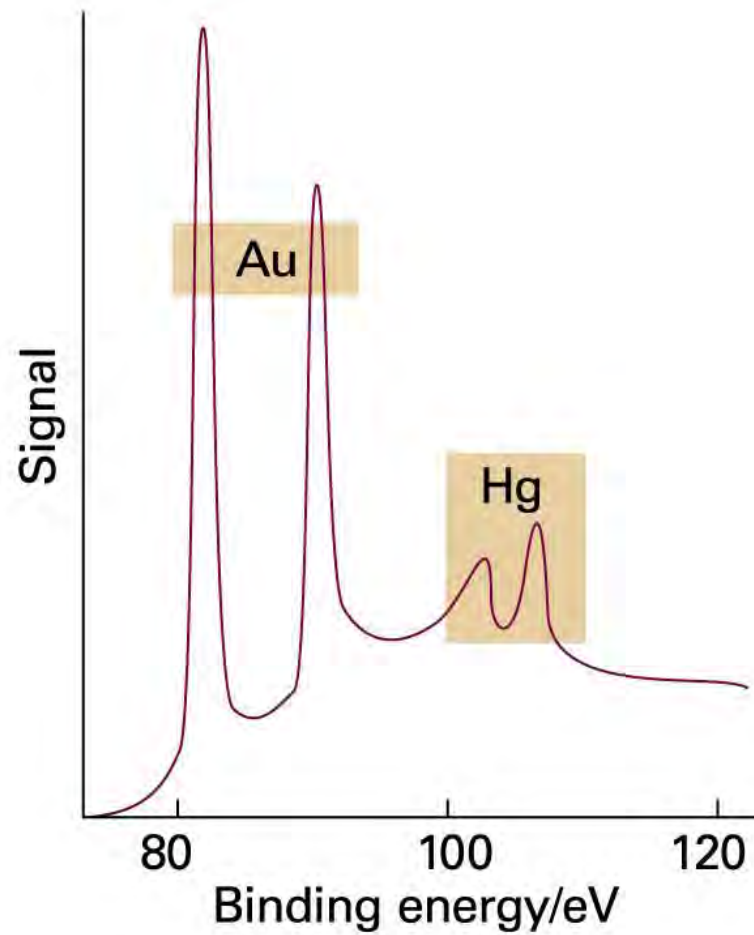


Fig. 25.8 The X-ray photoelectron emission spectrum of a sample of gold contaminated with a surface layer of mercury. (M.W. Roberts and C.S. McKee, *Chemistry of the metal–gas interface*, Oxford (1978).)

Chapter 25: Processes at Solid Surfaces

25.2 Surface composition (cont..)

- **reflection–absorption infrared spectroscopy (RAIRS)**, a technique for obtaining the infrared absorption spectrum of the adsorbate.
- **surface-enhanced Raman scattering (SERS)**, strong enhancement of the Raman spectrum of the adsorbate.
- **electron energy loss spectroscopy (EELS or HREELS)**, a technique in which the energy loss suffered by a beam of electrons is monitored when they are reflected from a surface.
- **Auger electron spectroscopy (AES)**, spectroscopy based on the Auger effect.

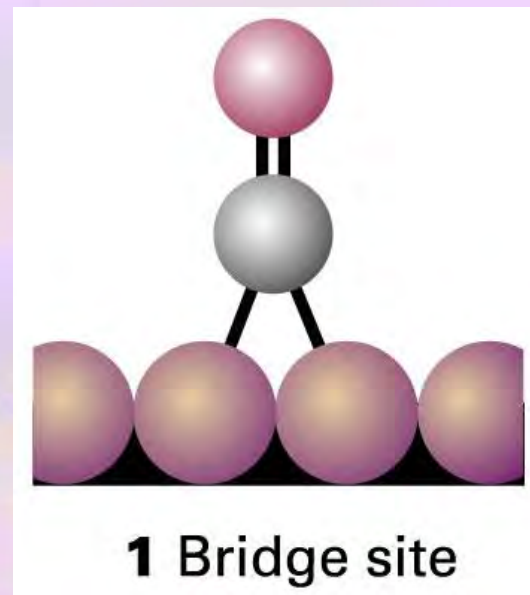
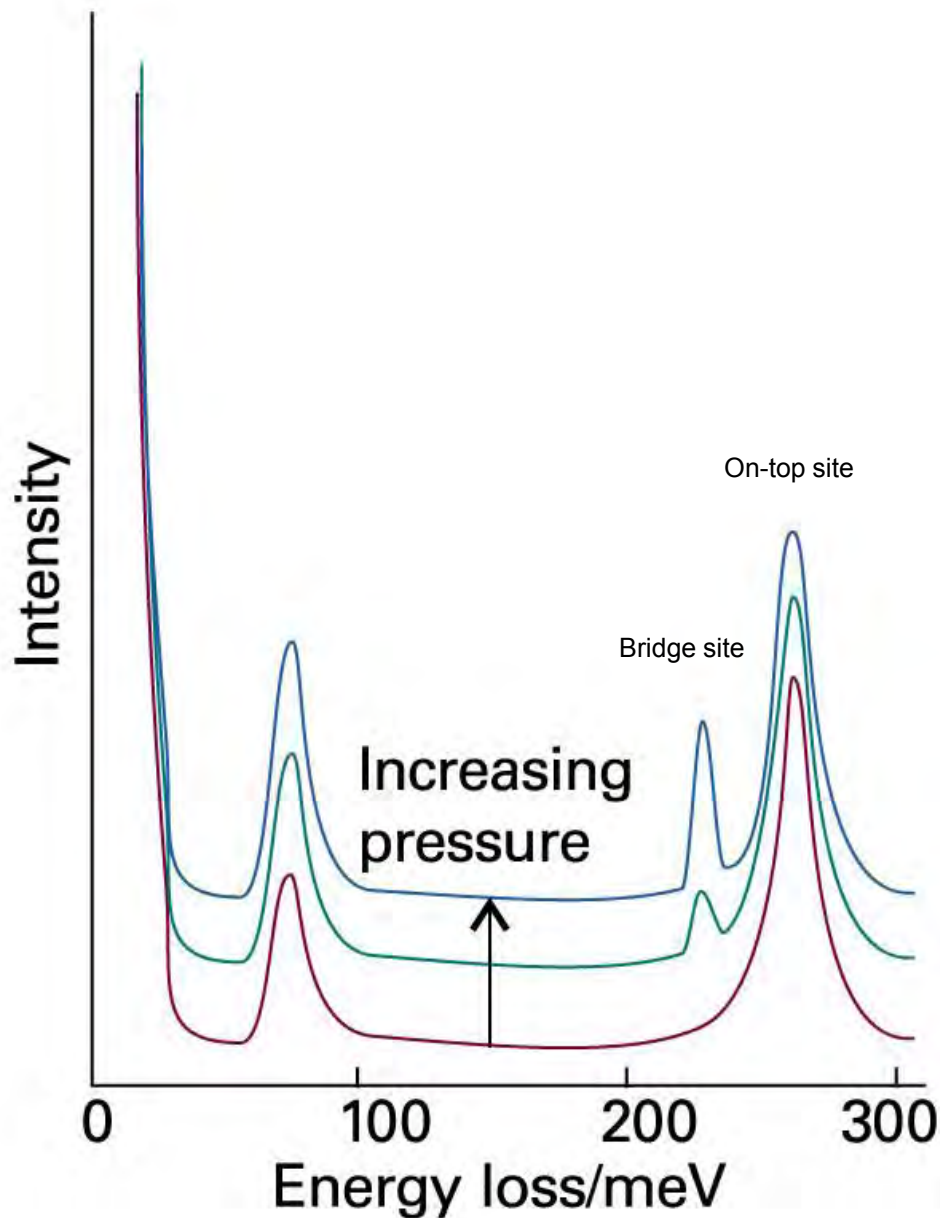


Fig. 25.9 The electron energy loss spectrum of CO adsorbed on Pt(111). The results for three different pressures are shown, and the growth of the additional peak at about 200 meV (1600 cm^{-1}) should be noted. (Based on spectra provided by Professor H. Ibach.)

Chapter 25: Processes at Solid Surfaces

25.2 Surface composition (cont..)

- **Auger effect**, the emission of a second electron after high energy radiation has expelled another.
- **X-ray fluorescence**, the generation of fluorescence by the Auger effect.
- **scanning Auger electron microscopy (SAM)**, a technique for mapping the spatial variation over a surface.
- **surface-extended X-ray absorption fine structure spectroscopy (SEXAFS)**, spectroscopy that makes use of the oscillations in X-ray absorbance observed on the high-frequency side of an absorption edge.

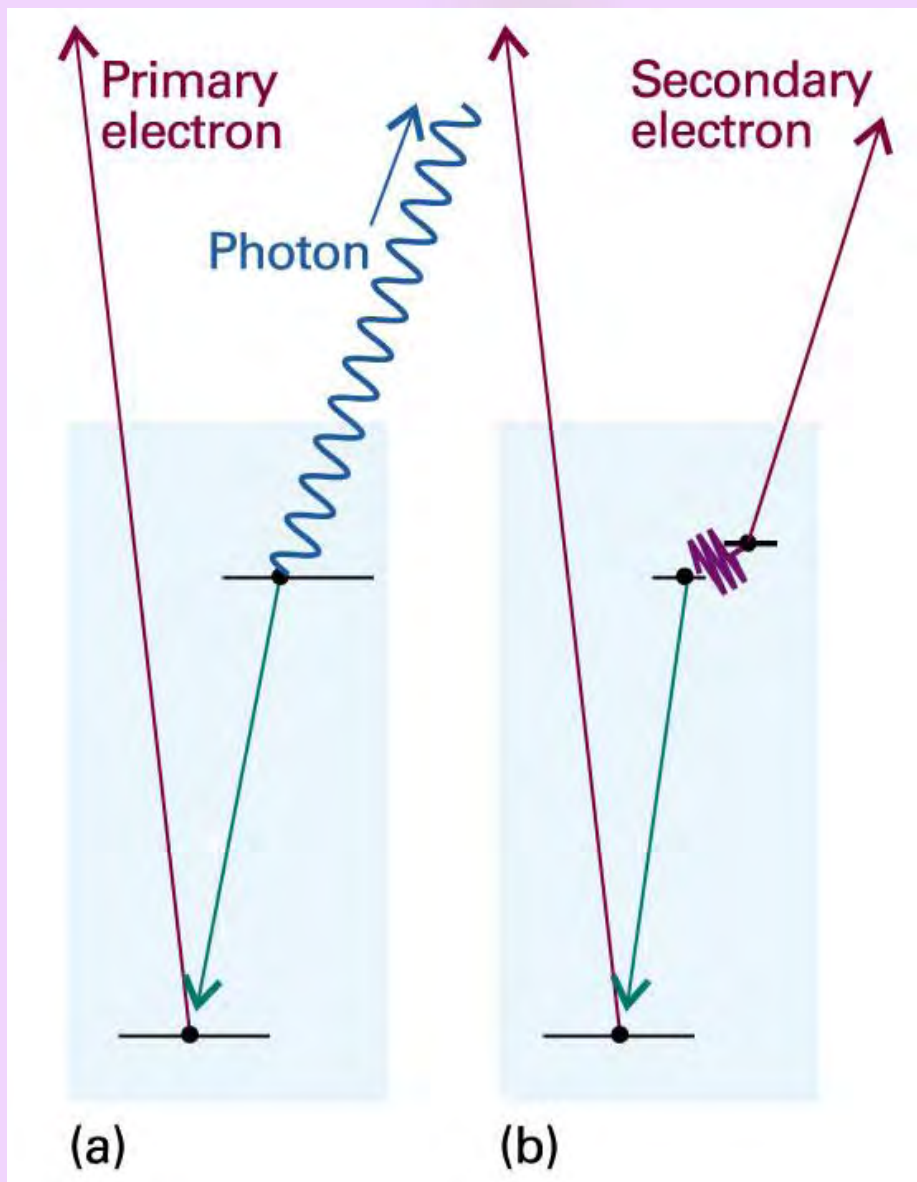


Fig. 25.10 When an electron is expelled from a solid (a) an electron of higher energy may fall into the vacated orbital and emit an X-ray photon to produce X-ray fluorescence. Alternatively, (b) the electron falling into the orbital may give up its energy to another electron, which is ejected in the Auger effect.

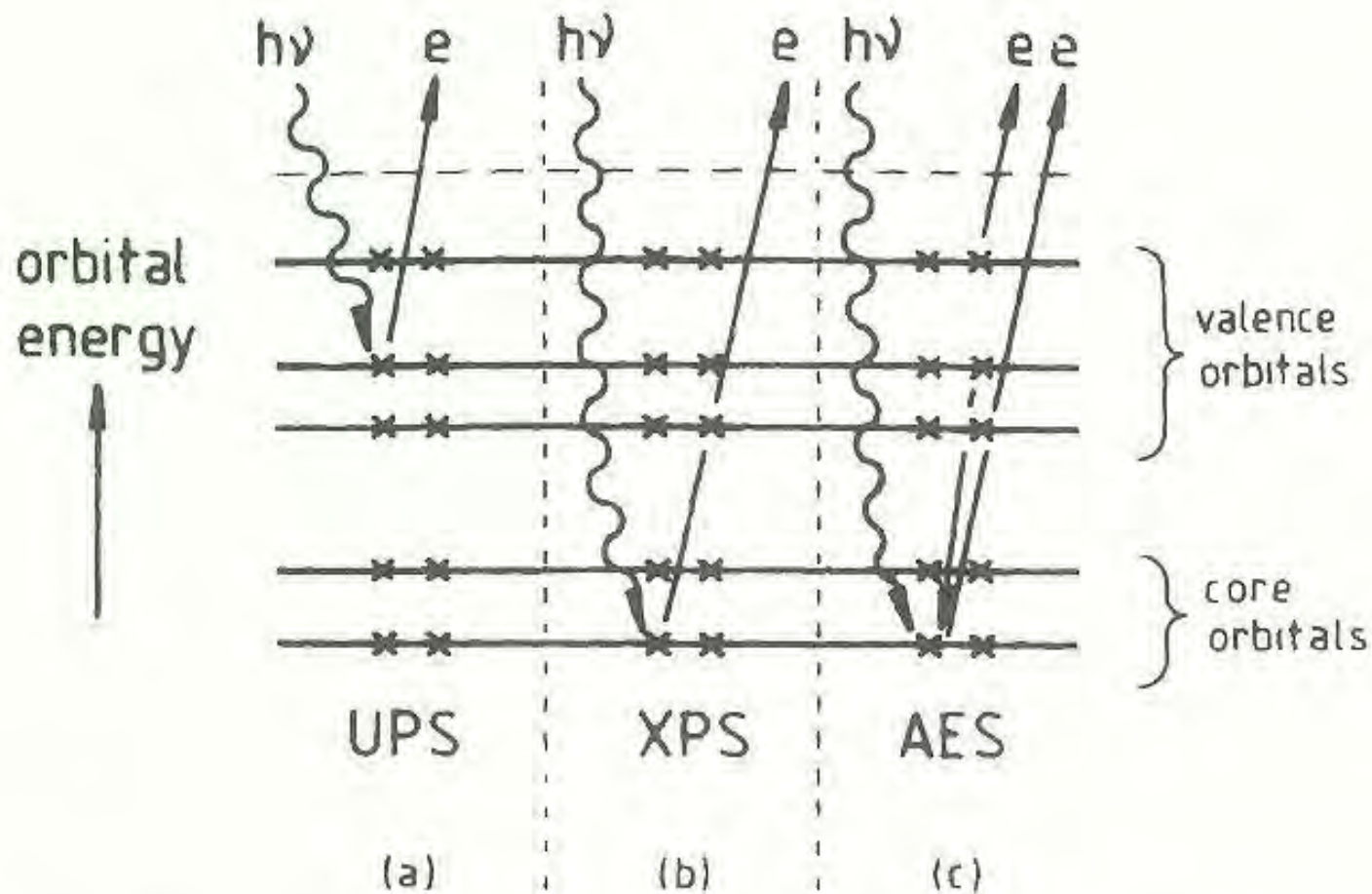


Figure 8.1 Processes occurring in (a) ultraviolet photoelectron spectroscopy (UPS), (b) X-ray photoelectron spectroscopy (XPS), (c) Auger electron spectroscopy (AES)

Chapter 25: Processes at Solid Surfaces

25.2 Surface composition (cont..)

- **reconstruction**, modification of the substrate surface layers in response to adsorbates.
- **low-energy electron diffraction (LEED)**, electron diffraction by surfaces.
- **molecular beam scattering (MBS)**, the scattering of a beam of adsorbate molecules by a surface.

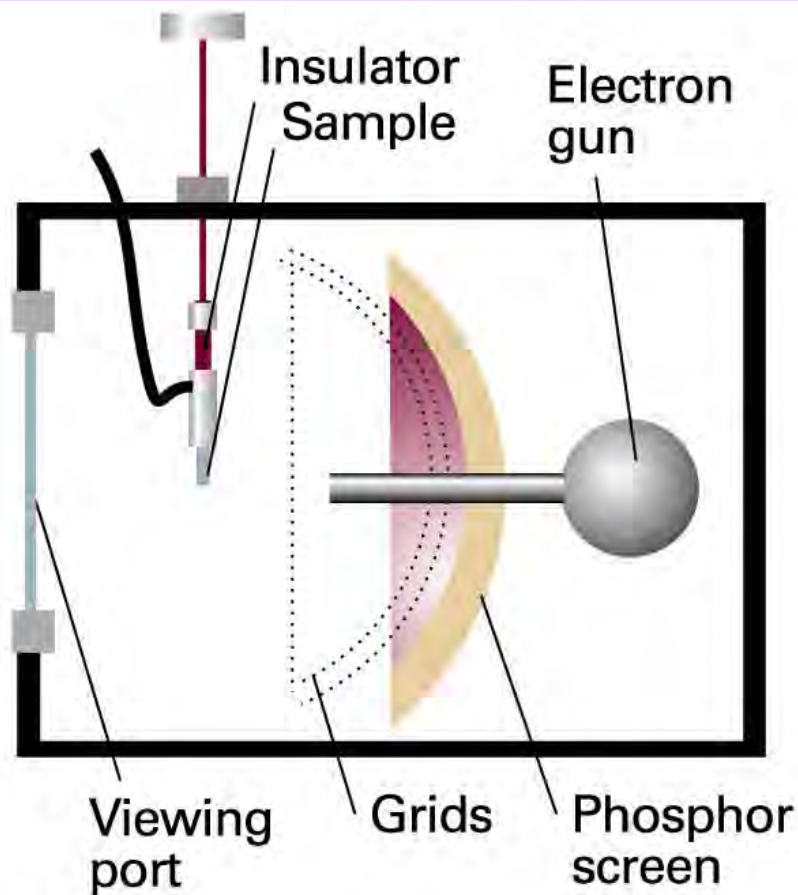


Fig. 25.11 A schematic diagram of the apparatus used for a LEED experiment. The electrons diffracted by the surface layers are detected by the fluorescence they cause on the phosphor screen.

LEED

Electron energy:
10-200 eV

Wavelength:
100-400 pm

The de Broglie
wavelength:

$$\lambda = h/p$$

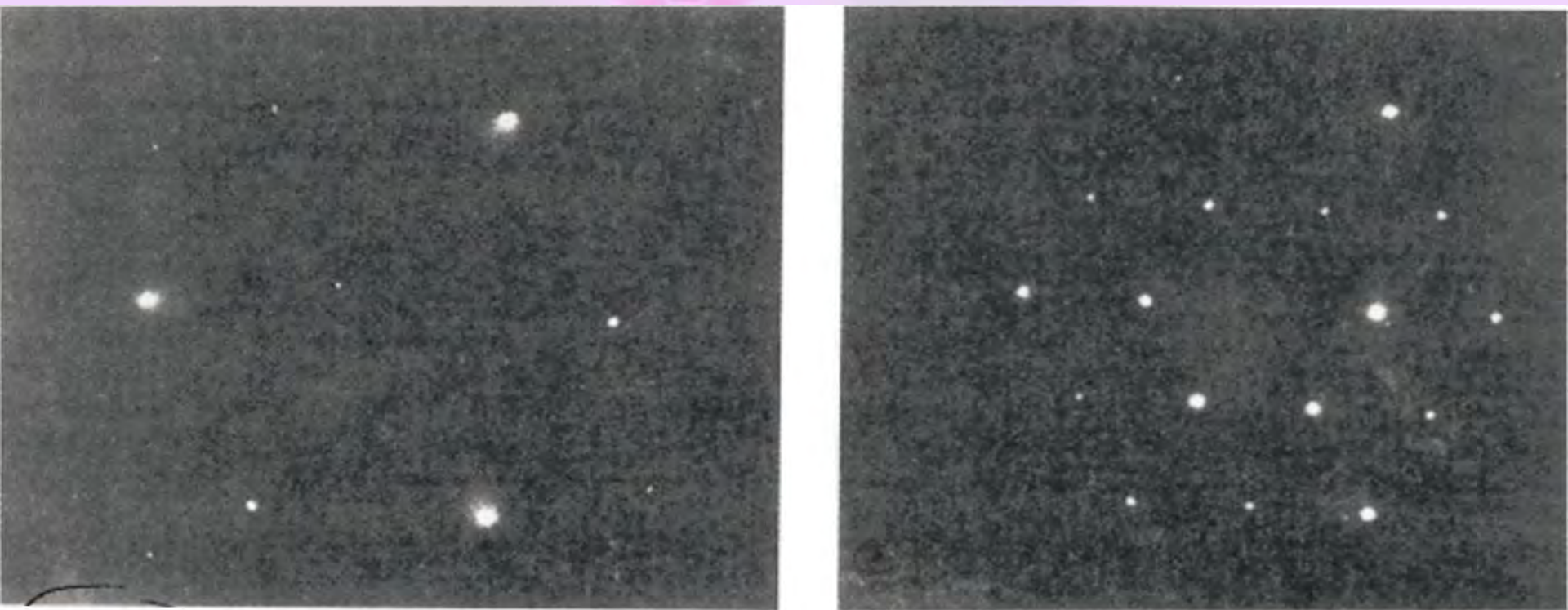


Fig. 25.12 LEED photographs of (a) a clean platinum surface and (b) after its exposure to propyne, $\text{CH}_3\text{C}\equiv\text{CH}$. (Photographs provided by Professor G.A. Somorjai.)

The results of LEED experiments show that the surface of a crystal rarely has exactly the same for as a slice through the bulk.

As a general rule, it is found that metal surfaces are simply truncations of the bulk lattice, but the distance between the top layer of atoms and the one below is contracted by ~5%.

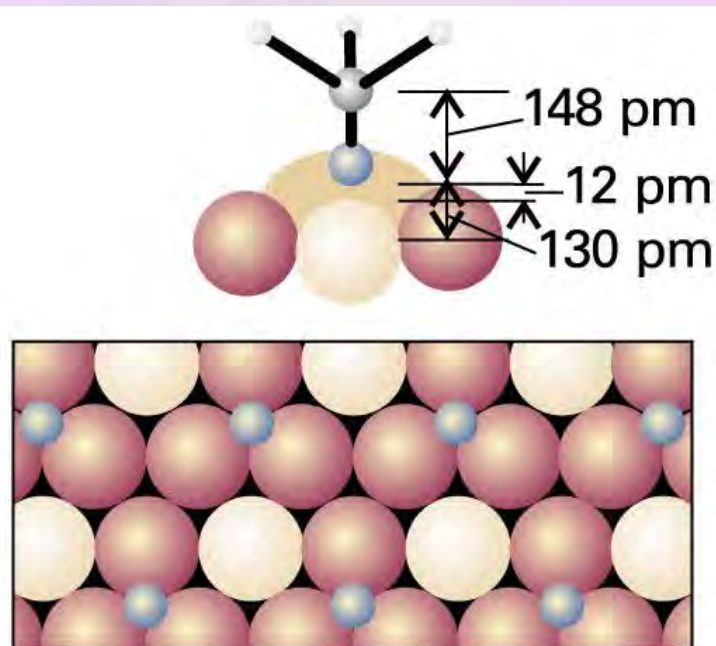
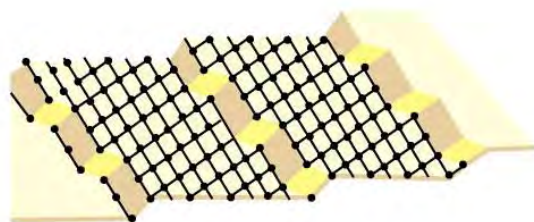
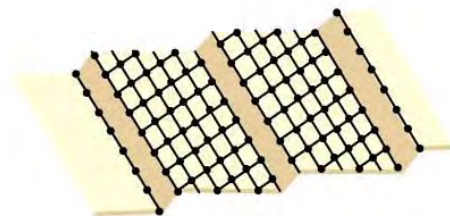
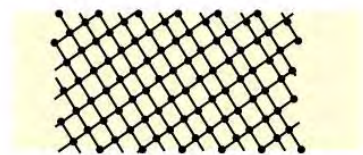


Fig. 25.13 The structure of a surface close to the point of attachment of $\text{CH}_3\text{C}-$ to the (110) surface of rhodium at 300 K and the changes in positions of the metal atoms that accompany chemisorption.



The interpretation of LEED data is much more complicated than the interpretation of bulk X-ray data.

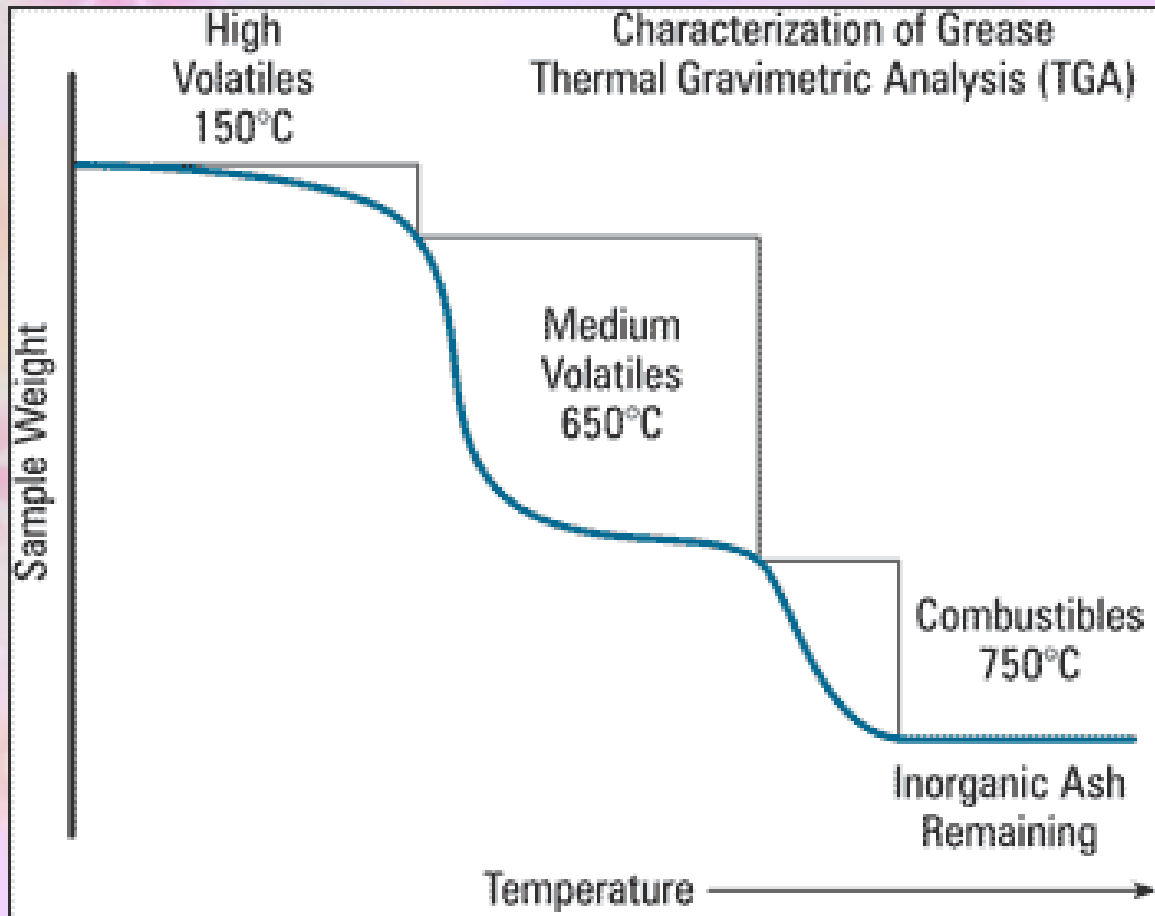
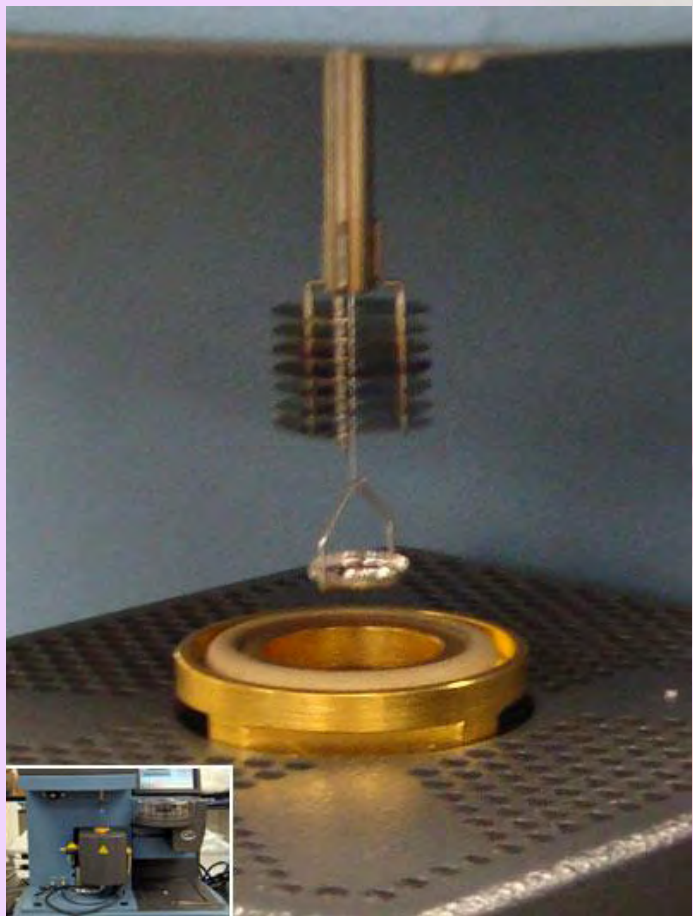
Fig. 25.14 LEED patterns may be used to assess the defect density of a surface. The photographs correspond to a platinum surface with (top) low defect density, (middle) regular steps separated by about six atoms, and (bottom) regular steps with kinks. (Photographs provided by Professor G.A. Samorjai.)

Chapter 25: Processes at Solid Surfaces

THE EXTENT OF ADSORPTION

- **fractional coverage**, θ , the fraction of adsorption sites occupied.
- **rate of adsorption**, the rate of change of fractional coverage; $d\theta/dt$.
- **flash desorption**, a technique in which a sample is suddenly heated and the resulting rise of pressure is interpreted in terms of the amount of adsorbate originally on the sample.
- **gravimetry**, the determination of fractional coverage by measurement of mass.
- **quartz crystal microbalance (QCM)**, the determination of mass that makes use of the modification of the crystal's vibrational frequency by an adsorbate.

Thermogravimetric Analysis (TGA)



Chapter 25: Processes at Solid Surfaces

25.3 Physisorption and chemisorption

- physisorption**, adsorption by van der Waals interaction between the adsorbate and the substrate.
- accommodation**, the process of losing energy resulting in adsorption .
- chemisorption**, adsorption by the formation of a chemical bond.

Table 25.1 Maximum observed enthalpies of physisorption, $\Delta_{\text{ad}}H^\ominus/(\text{kJ mol}^{-1})$

C_2H_2	-38	H_2	-84
C_2H_4	-34	H_2O	-59
CH_4	-21	N_2	-21
Cl_2	-36	NH_3	-38
CO	-25	O_2	-21
CO_2	-25		

Data: D.O. Haywood and B.M.W. Trapnell, *Chemisorption*. Butterworth (1964).

Hydrogen bond energy between H_2O molecules?

Chapter 25: Processes at Solid Surfaces

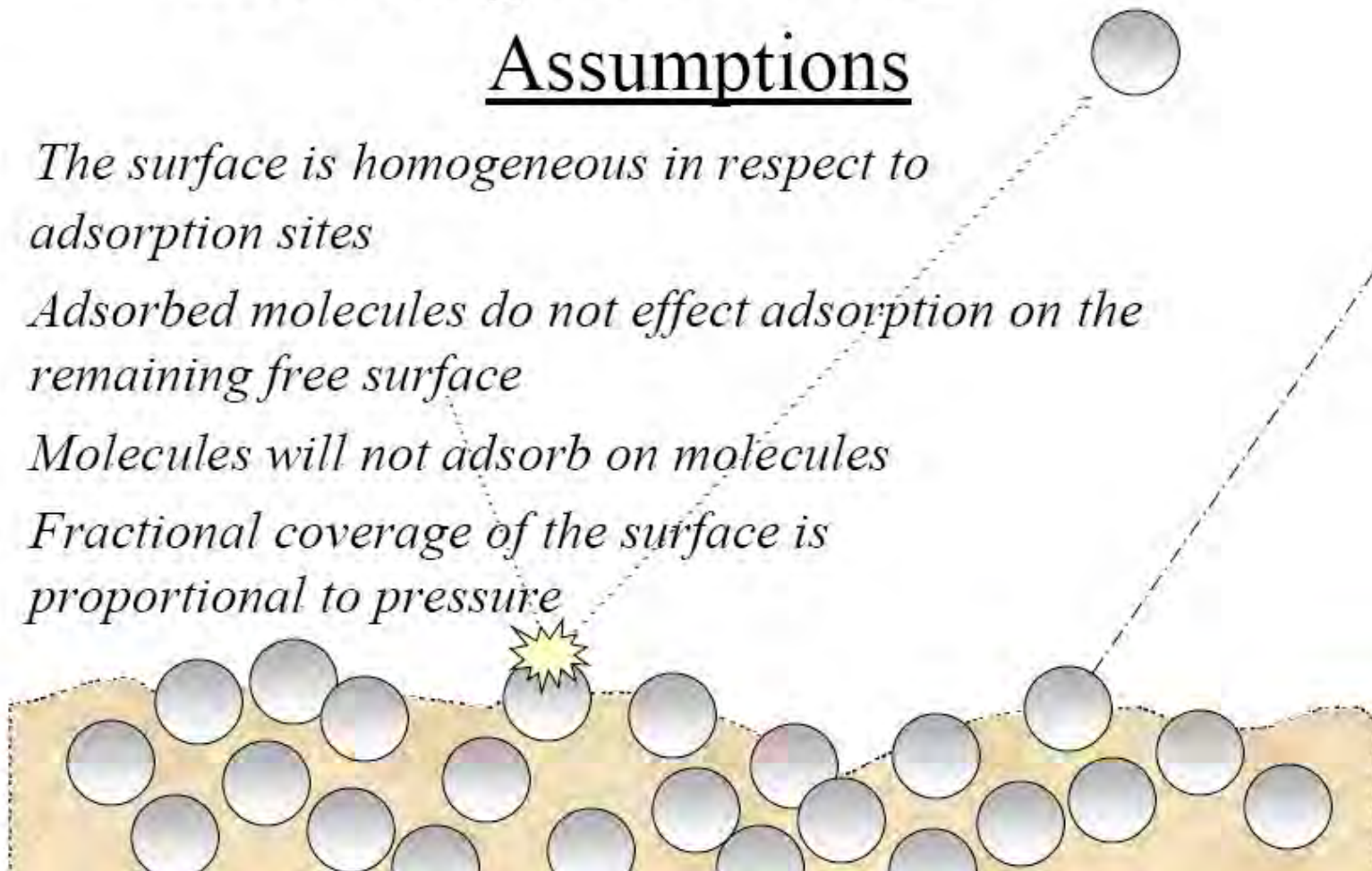
25.4 Adsorption isotherms

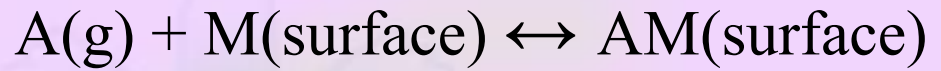
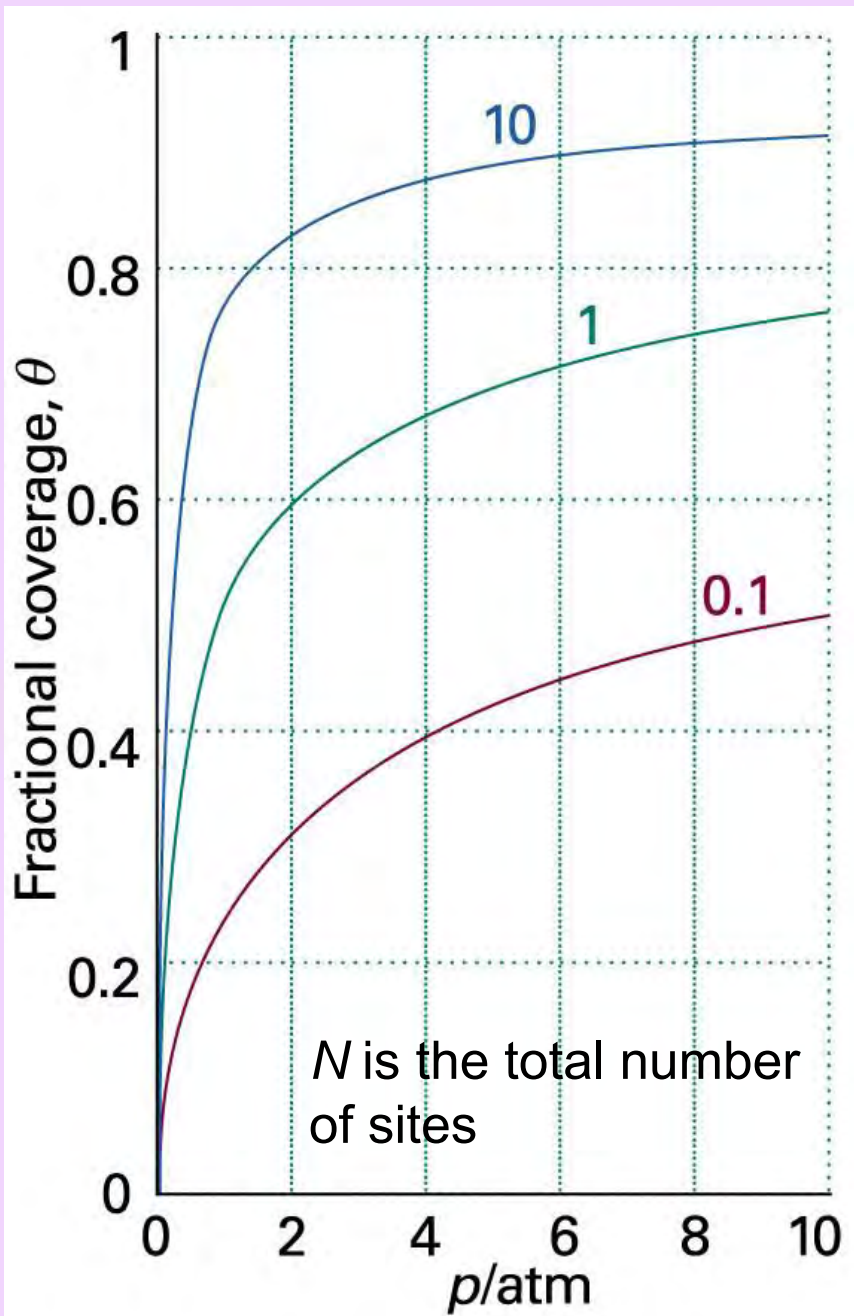
- **adsorption isotherm**, the relation between fractional coverage and partial pressure of a substrate.
- **Langmuir isotherm**, $\theta = Kp/(1 + Kp)$, $K = k_a/k_d$.
- **isosteric enthalpy of adsorption**, the standard enthalpy of adsorption at a fixed surface coverage; $\Delta_{ad}H^\circ = RT^2(\partial \ln K/\partial T)_\theta$.
- **BET isotherm**, $V/V_{mon} = cz/(1 - z)\{1 - (1 - c)z\}$, $z = p/p^*$.
- **Temkin isotherm**, $\theta = c_1 \ln(c_2p)$.
- **Freundlich isotherm**, $\theta = c_1p^{1/c_2}$.

The Langmuir Model

Assumptions

- *The surface is homogeneous in respect to adsorption sites*
- *Adsorbed molecules do not effect adsorption on the remaining free surface*
- *Molecules will not adsorb on molecules*
- *Fractional coverage of the surface is proportional to pressure*





Adsorption:

$$\frac{d\theta}{dt} = k_a p N (1 - \theta)$$

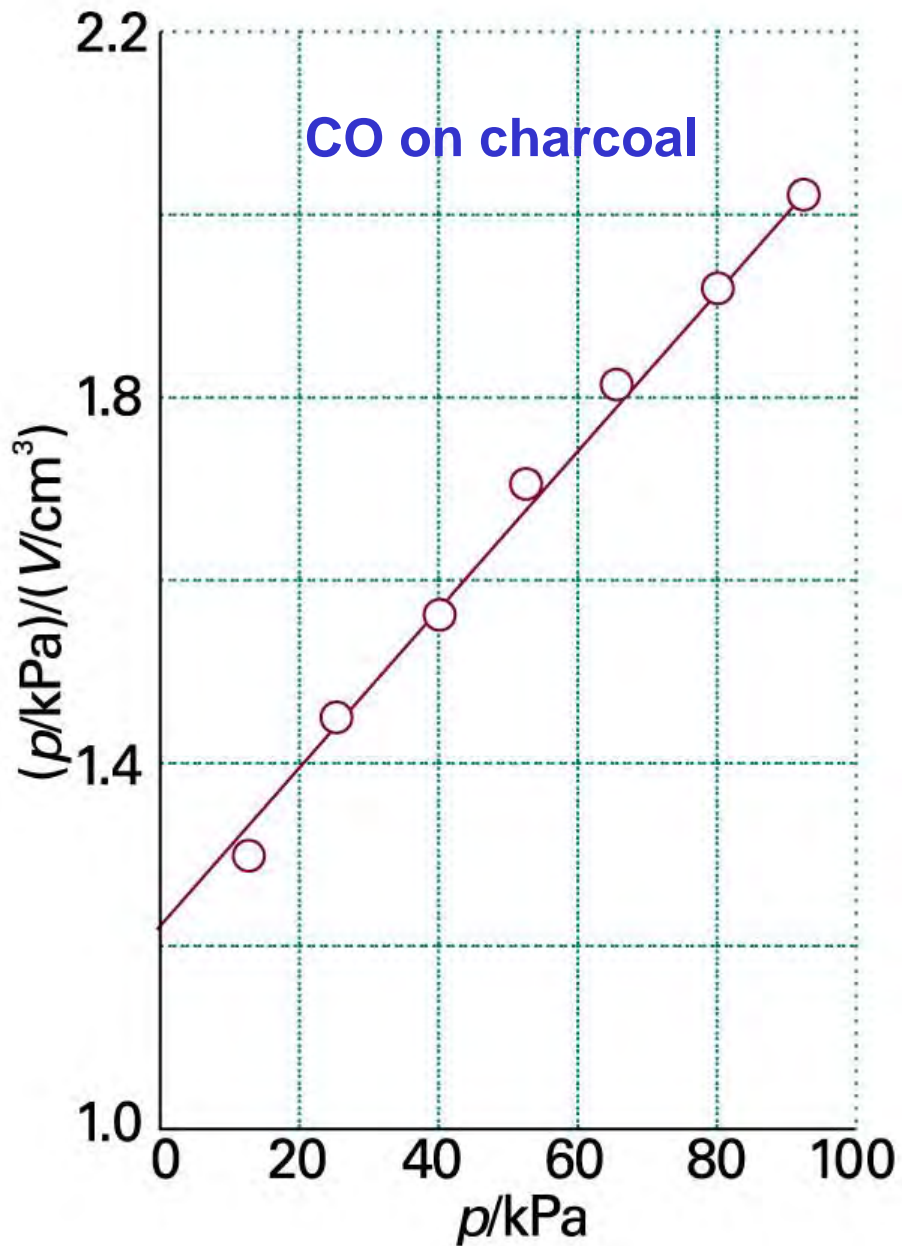
Desorption:

$$\frac{d\theta}{dt} = -k_d N \theta$$

$$K \equiv \frac{k_a}{k_d}$$

$$\therefore \theta = \frac{Kp}{1 + Kp}$$

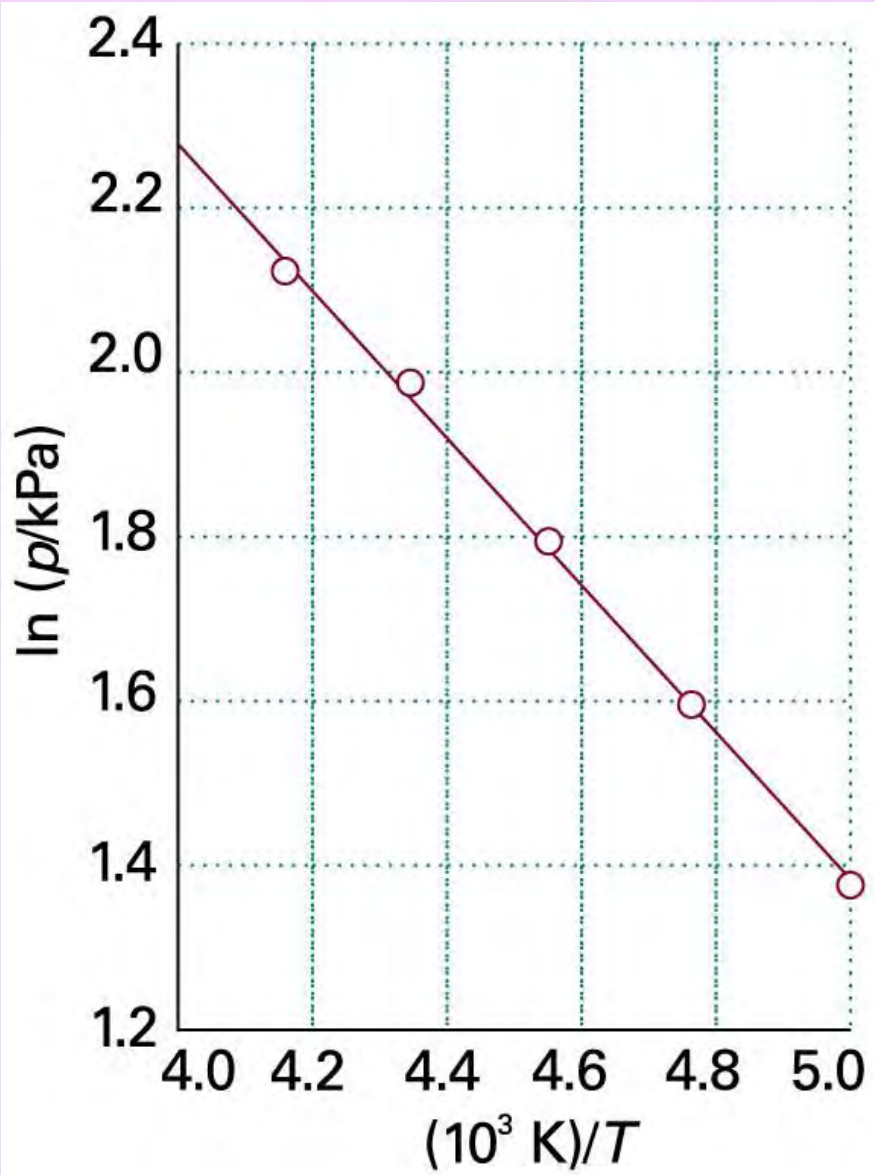
Fig. 25.17 The Langmuir isotherm for non-dissociative adsorption for different values of K .



$$\theta = \frac{V}{V_m} = \frac{Kp}{1 + Kp}$$

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

Fig. 25.15 The plot of the data in Example 25.1. As illustrated here, the Langmuir isotherm predicts that a straight line should be obtained when p/V is plotted against p .



At constant θ

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

$$\ln K + \ln p = \text{const.}$$

$$\left(\frac{\partial \ln p}{\partial T} \right)_{\theta} = - \left(\frac{\partial \ln K}{\partial T} \right) = - \frac{\Delta_{ad}H^{\circ}}{RT^2}$$

or

$$\left(\frac{\partial \ln p}{\partial (1/T)} \right)_{\theta} = \frac{\Delta_{ad}H^{\circ}}{R}$$

Fig. 25.18 The isosteric enthalpy of adsorption can be obtained from the slope of the plot of $\ln p$ against $1/T$, where p is the pressure needed to achieve the specified surface coverage. The data used are from Example 25.2.

The van 't Hoff equation

The equation that relates the change in temperature T to the change in the equilibrium constant K in chemical thermodynamics,

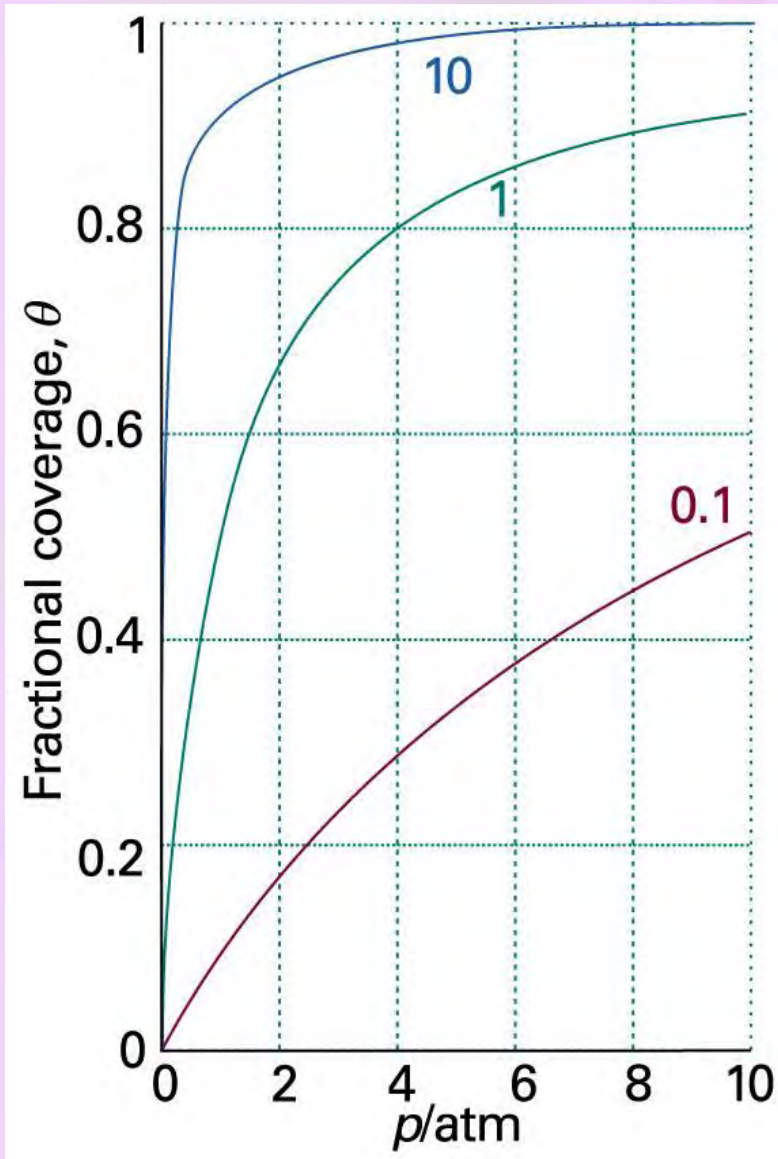
$$\Delta G^{\ominus} = -RT \ln K$$

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

$$\ln K = -\frac{\Delta H^{\ominus}}{RT} + \frac{\Delta S^{\ominus}}{R}$$

$$\frac{d \ln K}{dT} = \frac{\Delta H^{\ominus}}{RT^2}$$

Dissociative adsorption, $X_2(g) \rightarrow 2X(\text{surface})$



Adsorption

$$\frac{d\theta}{dt} = k_a p(1 - \theta)^2$$

Desorption

$$\frac{d\theta}{dt} = -k_d \theta^2$$

$$\therefore \theta = \frac{(Kp)^{1/2}}{1 + (Kp)^{1/2}}$$

Fig. 25.16 The Langmuir isotherm for dissociative adsorption, $X_2(g) \rightarrow 2X(\text{surface})$, for different values of K .

BET isotherm

(Brunauer, Emmett, Teller)

$$\frac{V}{V_{\text{mon}}} = \frac{cz}{(1-z)[1-(1-c)z]}$$

where

$$z = \frac{p}{p^*}$$

$$c = e^{(\Delta_{\text{des}}H^\circ - \Delta_{\text{vap}}H^\circ)/RT}$$

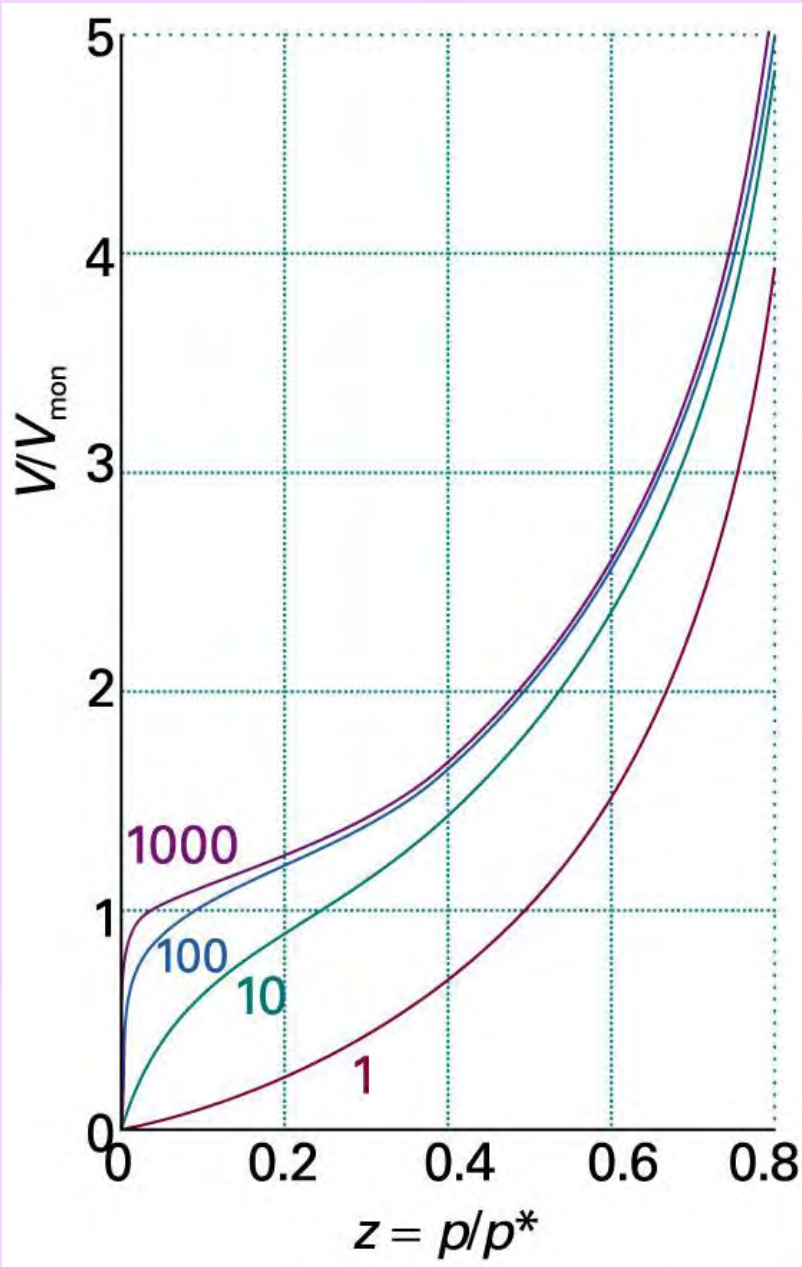


Fig. 25.19 Plots of the BET isotherm for different values of c . The value of V/V_{mon} rises indefinitely because the adsorbate may condense on the covered substrate surface.

- BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material.
- In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published an article about the BET theory *J. Am. Chem. Soc.*, 1938, **60**, 309 for the first time.
- “BET” consists of the first initials of their family names.



Edward Teller
(1/15/1908 – 9/9/2003)

Brunauer, Emmett and Teller model of adsorption in multi-molecular layers

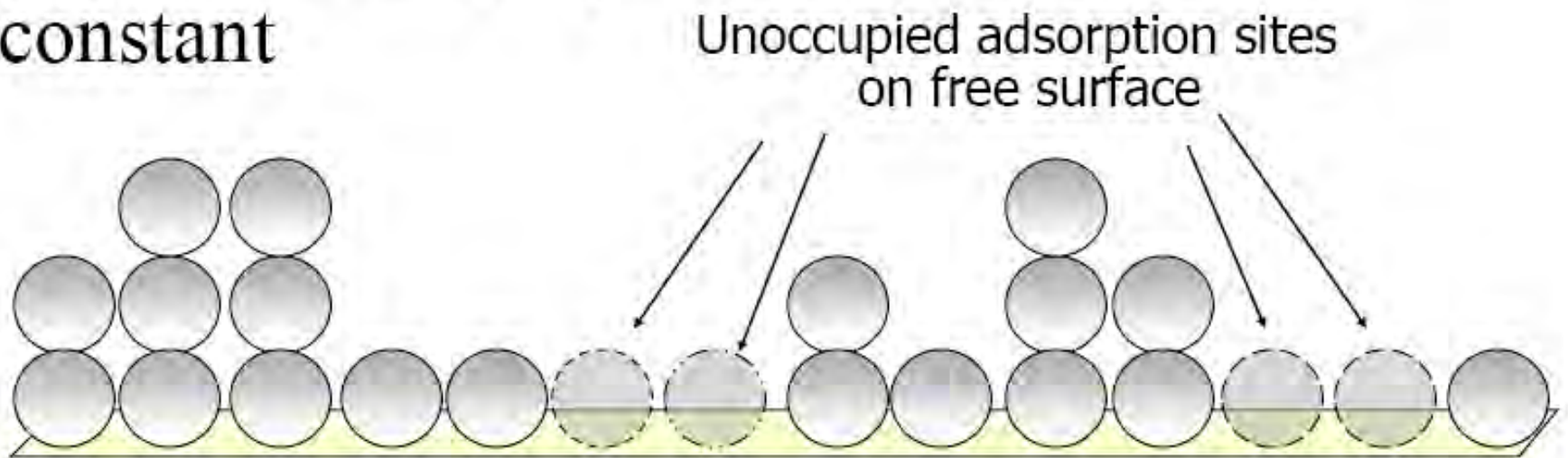
The Motivation

- *Evidence of multilayer adsorption existed*
- *Layer polarization theory inadequate*

The Model

- *B.E.T. theory would be generalization of Langmuir's theory*
- *Main difference would be allowing condensation on previously adsorbed molecules*

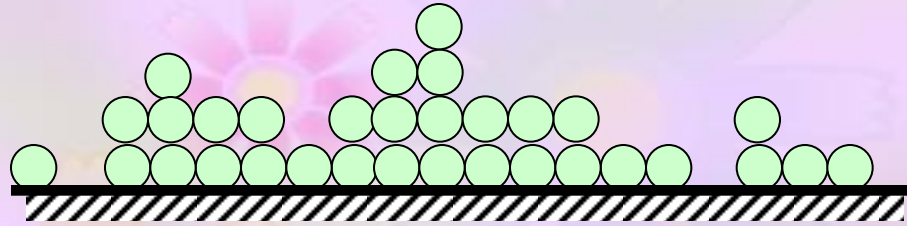
At equilibrium, layer distribution is constant



S_0 Free surface:	4 units
S_1 Surface occupied by single layer:	4 units
S_2 Surface occupied by double layer:	3 units
S_3 Surface occupied by triple layer:	<u>3 units</u>

Derivation of the BET isotherm

Consider a surface:



Definition:

$\theta_0, \theta_1, \dots, \theta_n$ = Surface area covered by 0, 1, ..., n layers of adsorbed molecules.

At equilibrium, θ_0 must remain constant,

Rate of evaporation from 1st layer = Rate of condensation onto bare surface

$$k_{-1}\theta_1 = k_1 p \theta_0 \quad (\text{I})$$

Similarly at equilibrium, θ_1 must remain constant,

Rate of condensation onto bare surface + Rate of evaporation from the 2nd layer
= Rate of condensation on the 1st layer + Rate of evaporation from the 1st layer

$$k_1 p \theta_0 + k_{-2} \theta_2 = k_2 p \theta_1 + k_{-1} \theta_1 \quad (\text{II})$$

Substituting into (I) gives

$$k_{-2}\theta_2 = k_2 p \theta_1$$

Extending this argument to other layers,

$$k_{-i}\theta_i = k_i p \theta_{i-1} \tag{III}$$

Since the total surface area, $A = \sum_{i=0}^{\infty} \theta_i$

the total volume of gas molecules adsorbed on surface is $V = V_0 \sum_{i=0}^{\infty} i \theta_i$

where V_0 is the volume of gas adsorbed per unit area when the surface is covered with a complete layer. Defining V_m , the volume of gas adsorbed when the entire surface is covered with a complete monolayer, the average number of layers is then

$$\frac{V}{V_m} = \frac{V}{AV_0} = \frac{\sum_{i=0}^{\infty} i\theta_i}{\sum_{i=0}^{\infty} \theta_i}$$

(IV)

From eq. (III)

$$k_{-1}\theta_1 = k_1 p \theta_0 \longrightarrow \theta_1 = \left(\frac{k_1}{k_{-1}} p \right) \theta_0 \equiv y \theta_0$$

If we assume that the properties of the 1st, 2nd, ... layers are equivalent, then,

$$\frac{k_2}{k_{-2}} = \dots = \frac{k_i}{k_{-i}} = g$$

From eq. (III)

$$k_{-i}\theta_i = k_i p \theta_{i-1} \longrightarrow \theta_i = \left(\frac{k_i}{k_{-i}} p \right) \theta_{i-1} = (gp)^{i-1} \theta_1 \equiv z^{i-1} \theta_1$$

or

$$\theta_i = z^{i-1} y \theta_0 = (y/z) z^i \theta_0 \equiv cz^i \theta_0$$

(V)

Substituting (V) into (IV) yields

$$\frac{V}{V_m} = \frac{\sum_{i=0}^{\infty} i\theta_i}{\sum_{i=0}^{\infty} \theta_i} = \frac{\sum_{i=1}^{\infty} icz^i\theta_0}{\theta_0 + \sum_{i=1}^{\infty} cz^i\theta_0} = \frac{c \sum_{i=1}^{\infty} iz^i}{1 + c \sum_{i=1}^{\infty} z^i}$$

Mathematically, it is known

$$\sum_{i=1}^{\infty} x^i = x \sum_{i=0}^{\infty} x^i = \frac{x}{1-x}$$

also

$$\sum_{i=1}^{\infty} ix^i = x + 2x^2 + 3x^3 + \dots = x(1 + 2x + 3x^2 + 4x^3 + \dots)$$

$$= x \frac{d}{dx} \left(\sum_{i=1}^{\infty} x^i \right) = x \frac{d}{dx} \left(\frac{x}{1-x} \right) = \frac{x}{(1-x)^2}$$

Finally,

$$\frac{V}{V_m} = \frac{c \sum_{i=1}^{\infty} iz^i}{1 + c \sum_{i=1}^{\infty} z^i} = \frac{cz}{(1-z)^2} \frac{1}{1 + \frac{cz}{1-z}} = \frac{cz}{(1-z)(1-z+cz)}$$

or

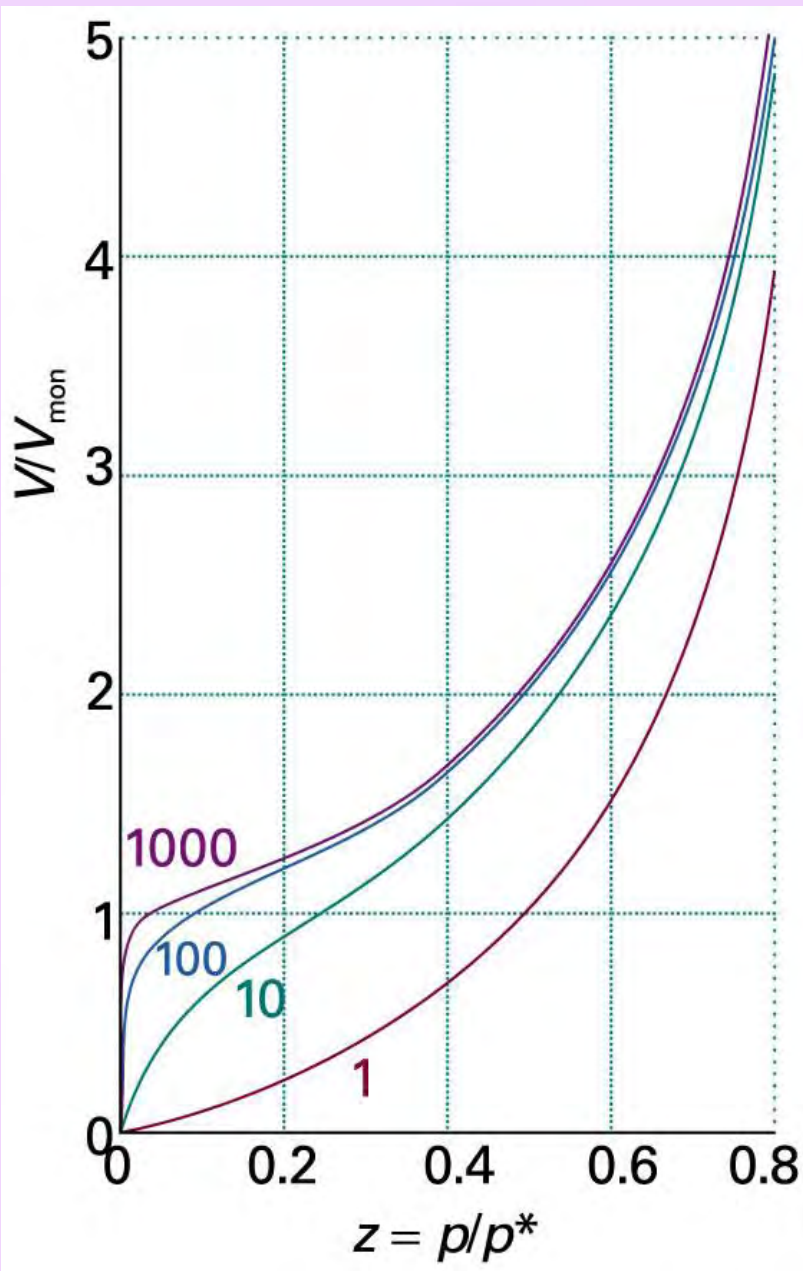
$$V = \frac{V_m cz}{(1-z)[1+(c-1)z]}$$

or

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

Note that at the saturation gas pressure, p^* , an infinite number of adsorbate layers must build up on the surface, i.e. $V \rightarrow \infty$. This is possible only when $z=1$. Since $z \equiv gp$, it means $gp^* = 1$ or $g = 1/p^*$. Alternatively,

$$V = \frac{V_m cz}{(1-z)[1+(c-1)z]} = \frac{V_m c(p/p^*)}{(1-(p/p^*))[1+(c-1)(p/p^*)]}$$

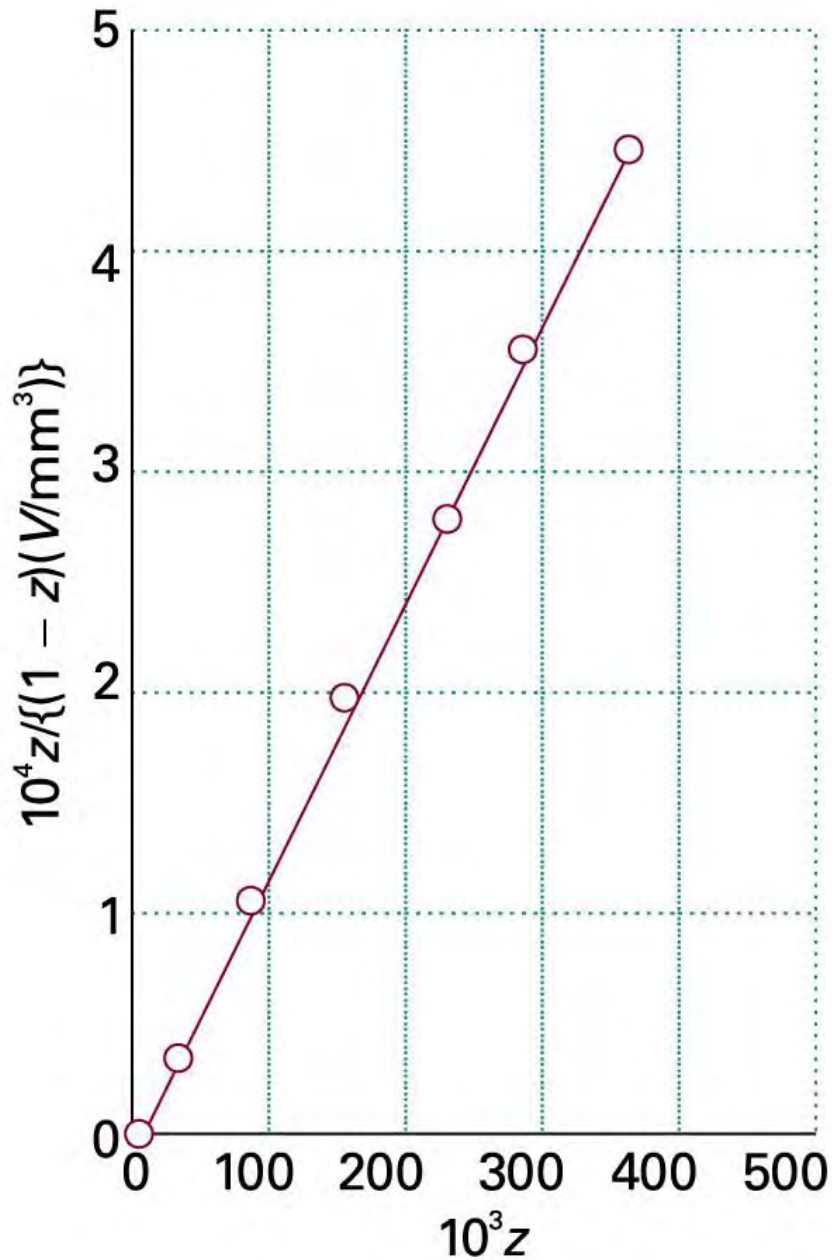


$$\frac{V}{V_m} = \frac{c(p/p^*)}{(1 - (p/p^*)) [1 + (c-1)(p/p^*)]}$$

What is c ?

Fig. 25.19 Plots of the BET isotherm for different values of c . The value of V/V_{mon} rises indefinitely because the adsorbate may condense on the covered substrate surface.

Interaction between adsorbates



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

$$c = \frac{y}{z} = \frac{(k_1/k_{-1})p}{(k_i/k_{-i})p} = \frac{K_{ad}}{K_{con}} = \frac{K_{vap}}{K_{des}}$$

$$c = e^{(\Delta_{des}H^\circ - \Delta_{vap}H^\circ)/RT}$$

Fig. 25.20 The BET isotherm can be tested, and the parameters determined, by plotting $z/(1-z)V$ against $z = p/p^*$. The data are from Example 25.3.

BET isomtherm is a generalized form of the Langmuir model

$$\frac{V}{V_m} = \frac{c(p/p^*)}{(1-(p/p^*))[1+(c-1)(p/p^*)]}$$

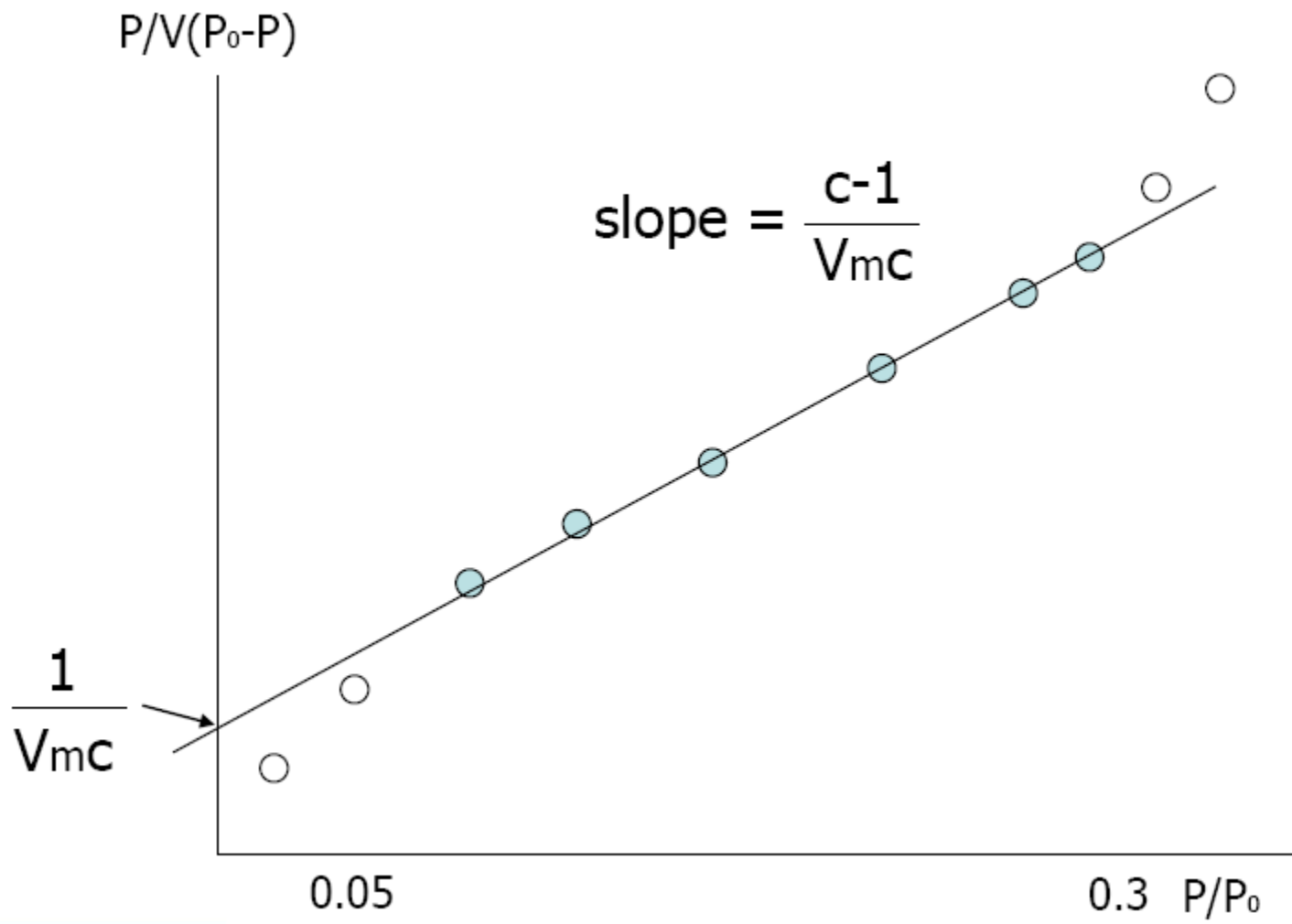
Assuming that the value of c is sufficiently large, then $c-1 \sim c$.

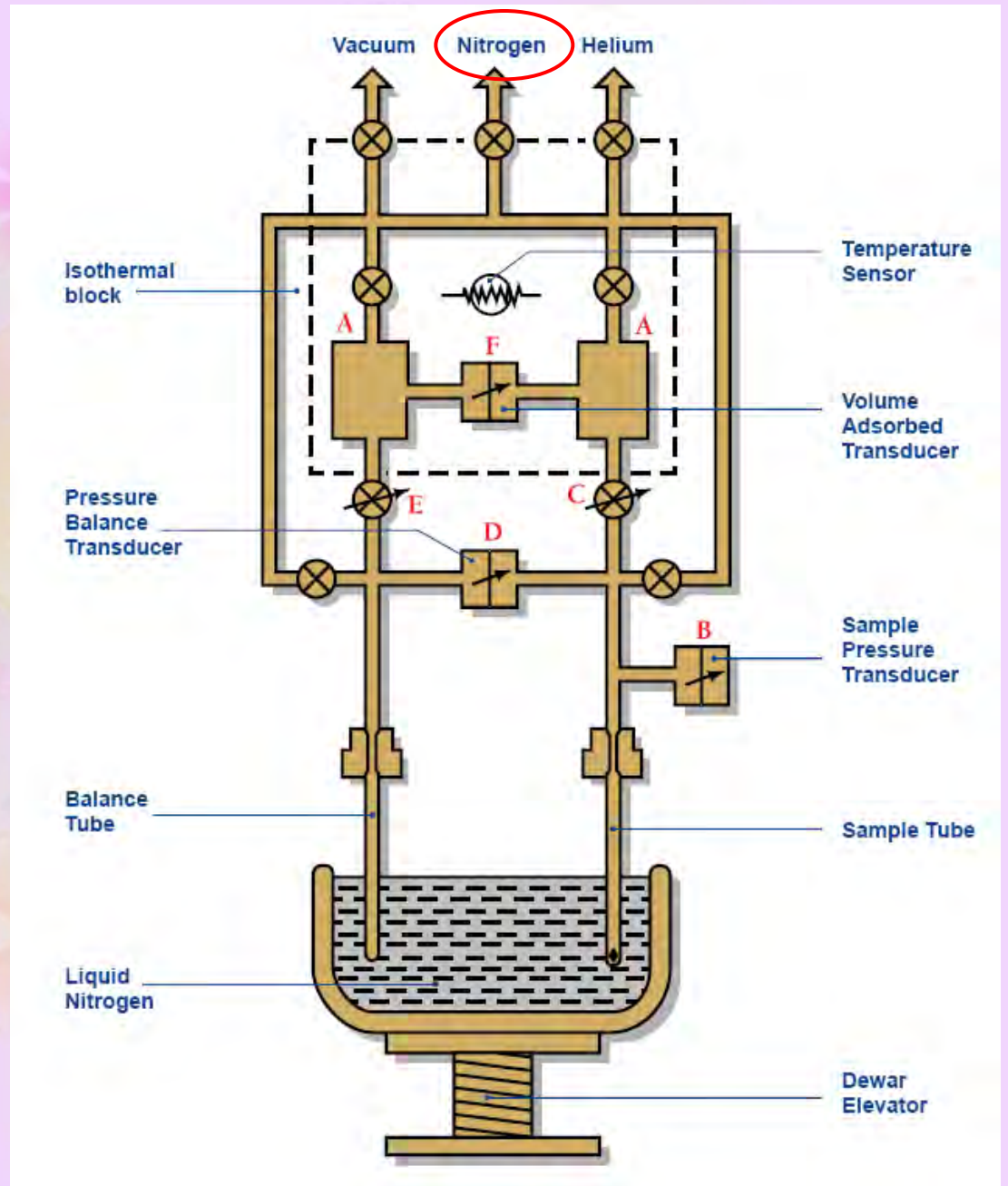
At $p/p^* \ll 1$, the above equation can be reduce to the Langmuir equation as

$$\frac{V}{V_m} = \frac{c(p/p^*)}{1+c(p/p^*)} = \frac{c^* p}{1+c^* p}$$

Application of Langmuir and BET models

- Plotting the linear form of BET or Langmuir equation allows determination of the monolayer volume V_m
- Knowing V_m allows the number of molecules to be calculated
- Multiplying the number of molecules by the surface area occupied by each molecule yields the total surface area of the sample

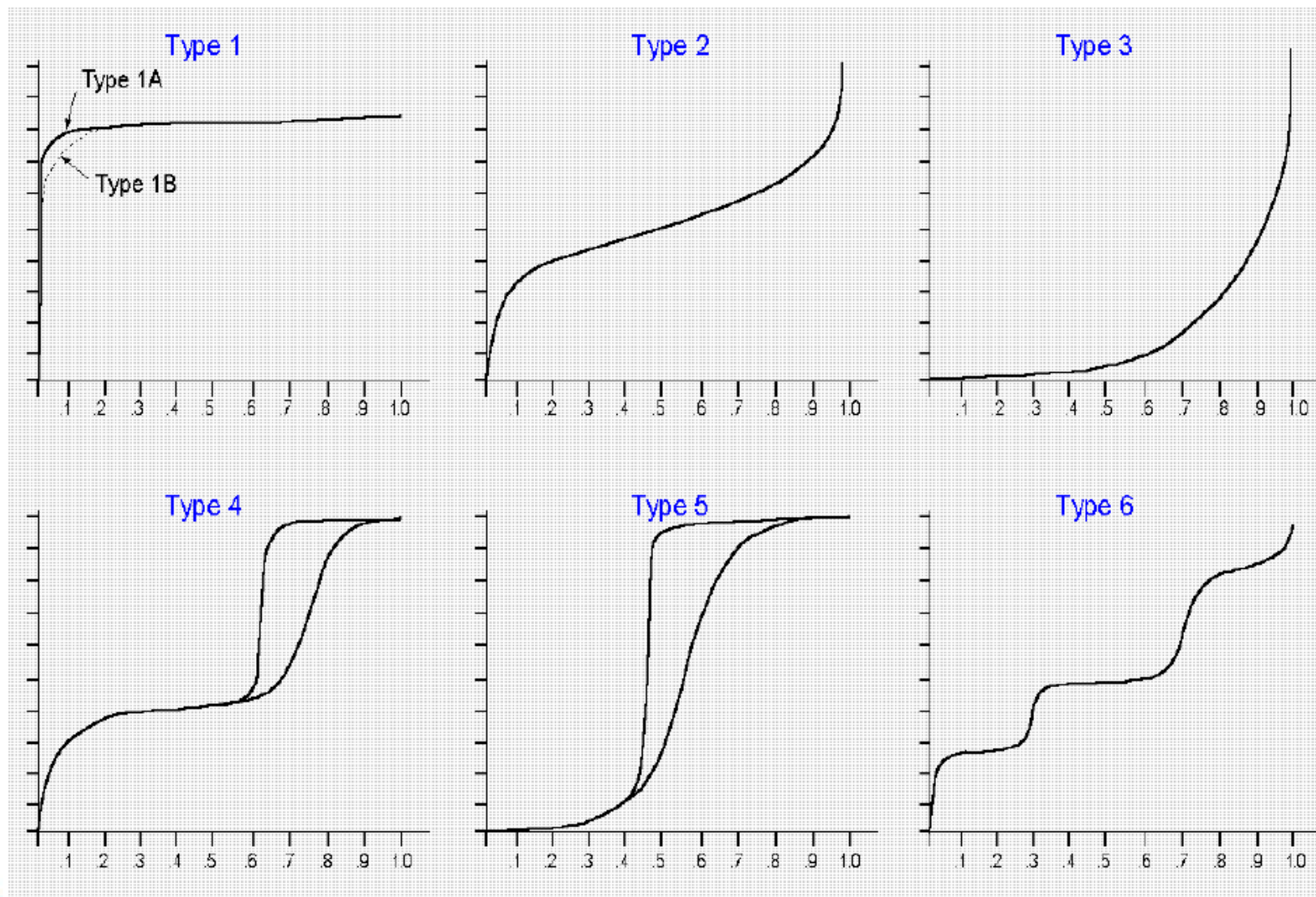




Thickness of adsorbed multi-molecular films

- BET and Langmuir equations are employed when the volume of the monolayer is of primary interest
- Neither model adequately reproduces the isotherm at higher degrees of coverage

General Types of Isotherms



Chapter 25: Processes at Solid Surfaces

25.5 The rates of surface processes

- **second harmonic generation (SHG)**, the process of generating radiation of twice the incident frequency (by a surface layer).
- **precursor state**, the initial state of an adsorbate molecule on a surface before it forms a chemical bond.
- **sticking probability**, s , the proportion of collisions with a surface that lead to adsorption; $s = (1 - \theta)s_0$.
- **half-life** for adsorption, $t_{1/2} = (\ln 2)/k_d$.

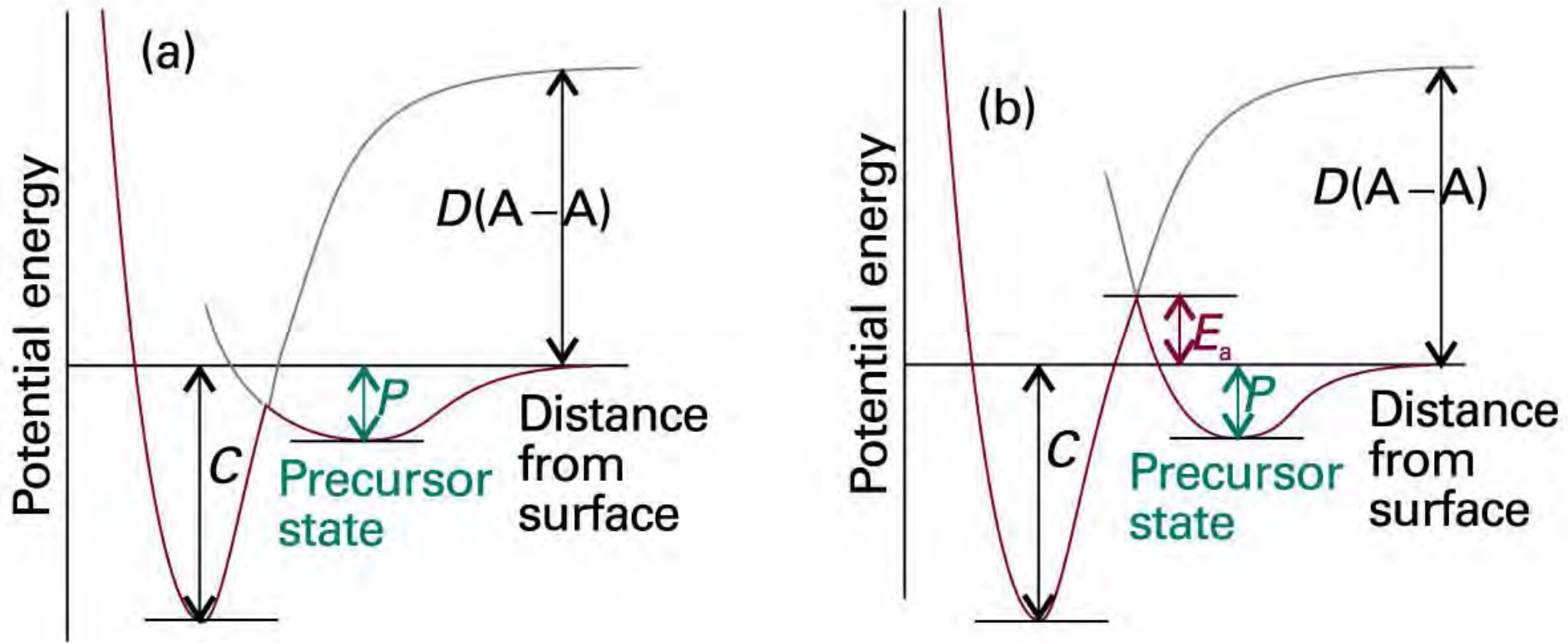
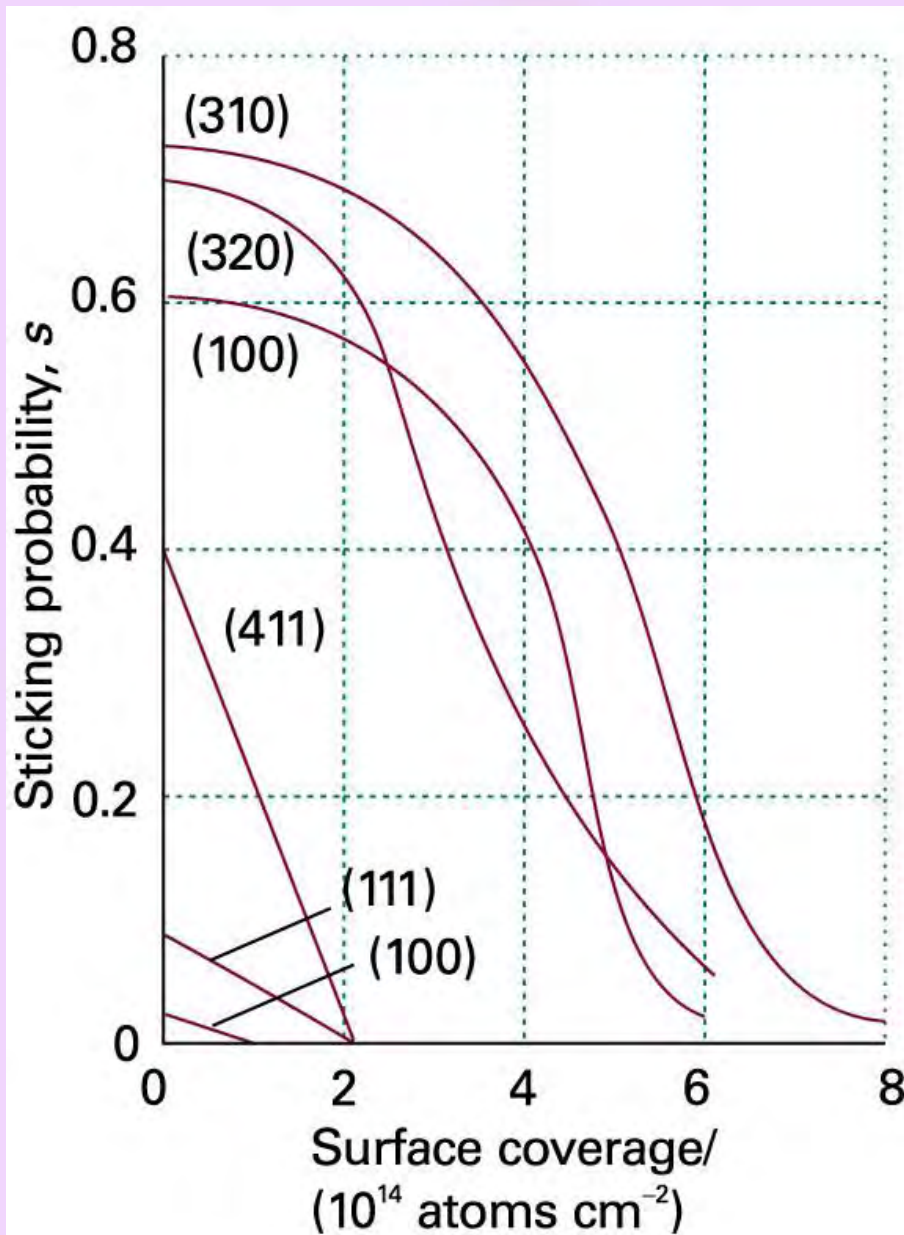


Fig. 25.21 The potential energy profiles for the dissociative chemisorption of an A₂ molecule. In each case, P is the enthalpy of (non-dissociative) physisorption and C that for chemisorption (at $T = 0$). The relative locations of the curves determines whether the chemisorption is (a) not activated or (b) activated.



Sticking probability:

$$S = \frac{\text{rate of adsorption}}{\text{rate of collision}}$$

Fig. 25.22 The sticking probability of N_2 on various faces of a tungsten crystal and its dependence on surface coverage. Note the very low sticking probability for the (110) and (111) faces. (Data provided by Professor D.A. King.)

According to the kinetic model of gases, the rate of collision with a surface:

$$Z_w = \frac{p}{\sqrt{2\pi mkT}}$$

(25.1a)

where p is the pressure and m is the mass of the molecule.

- For air at 1 atm and 25 °C, the collision flux is $3 \times 10^{27} \text{ m}^{-2}\text{s}^{-1}$. Because 1 m² of metal surface consists of about 10^{19} atoms, each atom is struck about 10^8 times each second. If $S = 1$, it will take only 10 ns to form a monolayer.
- In UHV, where the pressure is 10^{-9} Pa (or 10^{-14} atm), the collision flux is reduced to $3 \times 10^{13} \text{ m}^{-2}\text{s}^{-1}$, meaning that each surface atom is hit once every $10^5 - 10^6$ s, or about once a day.

Chapter 25: Processes at Solid Surfaces

25.5 The rates of surface processes (cont..)

- **temperature-programmed desorption (TPD)**, the observation of a surge in desorption rate when the temperature is raised linearly.
- **thermal desorption spectroscopy (TDS)**, another name for temperature-programmed desorption.
- **field-ionization microscopy (FIM)**, a technique that portrays the electrical characteristics of a surface by using the ionization of noble gas atoms .

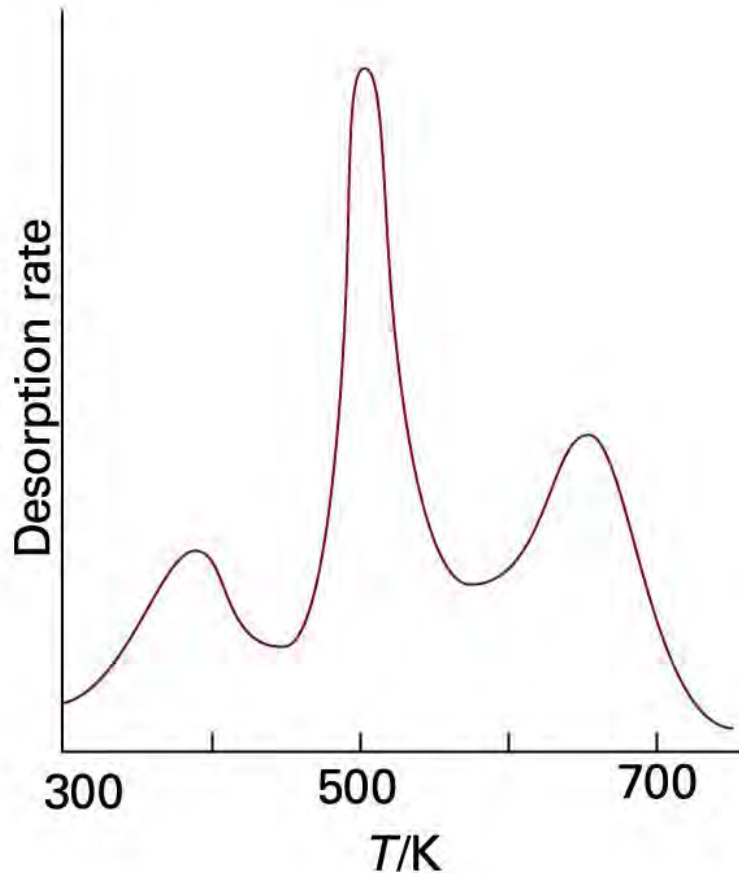


Fig. 25.23 The flash desorption spectrum of H₂ on the (100) face of tungsten. The three peaks indicate the presence of three sites with different adsorption enthalpies and therefore different desorption activation energies. (P.W. Tamm and L.D. Schmidt, *J. Chem. Phys.* **51**, 5352 (1969).)

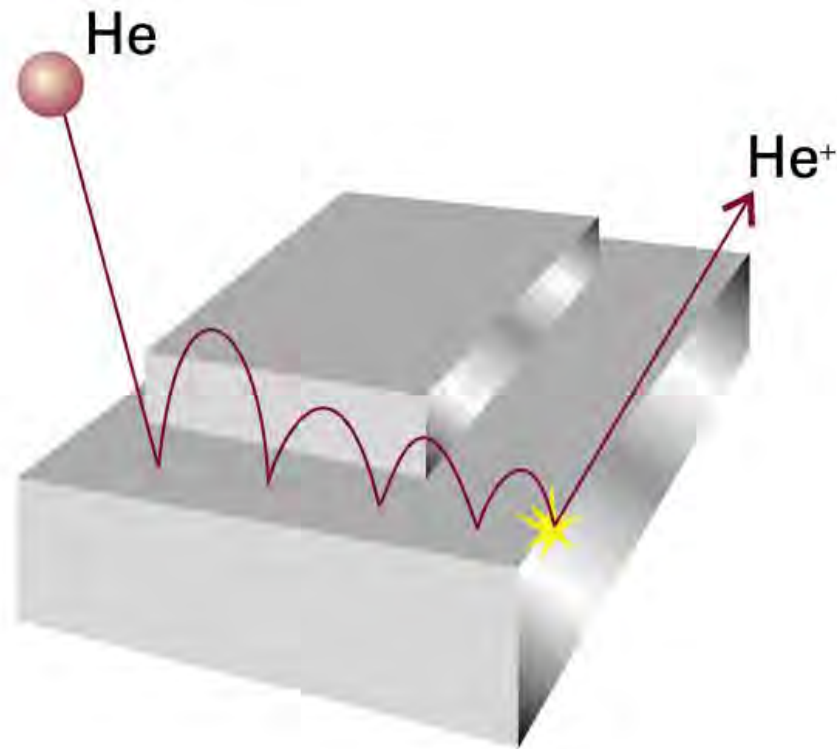


Fig. 25.24 The events leading to an FIM image of a surface. The He atom migrates across the surface until it is ionized at an exposed atom, when it is pulled off by the externally applied potential. (The bouncing motion is due to the intermolecular potential, not gravity!)

$$k_d = Ae^{-E_d / RT}$$

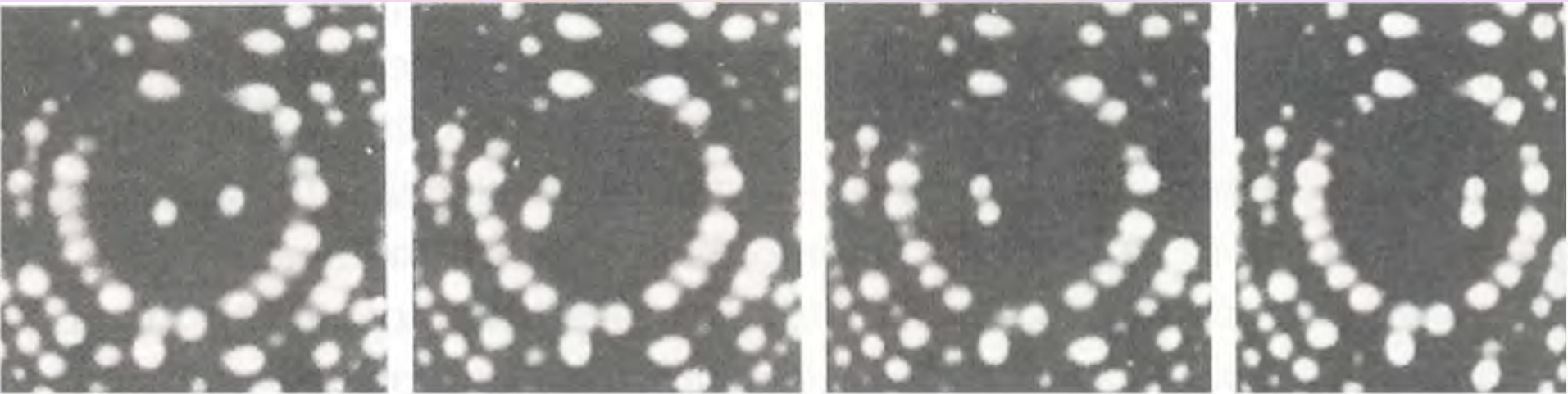


Fig. 25.25 FIM micrographs showing the migration of Re atoms on rhenium during 3 s intervals at 375 K. (Photographs provided by Professor G. Ehrlich.)

Chapter 25: Processes at Solid Surfaces

HETEROGENEOUS CATALYSIS

- **coadsorption**, the joint adsorption of two or more adsorbates.

25.6 Mechanisms of heterogeneous catalysis

- **shape-selective catalyst**, a solid with a pore size that can distinguish shapes and sizes at a molecular scale.
- **Langmuir–Hinshelwood mechanism**, a reaction that takes place by encounters between molecular fragments and atoms adsorbed on the surface: $v = kK_A K_B p_A p_B / (1 + K_A p_A + K_B p_B)^2$.
- **Eley–Rideal mechanism**, a reaction in which a gas-phase molecule collides with another molecule already adsorbed on the surface: $v = kK p_A p_B / (1 + K p_A)$.

Table 25.3 Activation energies of catalysed reactions

	Catalyst	$E_a / (\text{kJ mol}^{-1})$
$2 \text{HI} \rightarrow \text{H}_2 + \text{I}_2$	None	184
	Au(s)	105
	Pt(s)	59
$2 \text{NH}_3 \rightarrow \text{N}_2 + 3 \text{H}_2$	None	350
	W(s)	162
$2 \text{N}_2\text{O} \rightarrow 2 \text{N}_2 + \text{O}_2$	None	245
	Au(s)	121
	Pt(s)	134
$(\text{C}_2\text{H}_5)_2\text{O}$ pyrolysis	None	224
	$\text{I}_2(\text{g})$	144

Data: G.C. Bond, *Heterogeneous catalysis*. Clarendon Press, Oxford (1986).

Table 25.4 Chemisorption abilities*

	O ₂	C ₂ H ₂	C ₂ H ₄	CO	H ₂	CO ₂	N ₂
Ti, Cr, Mo, Fe	+	+	+	+	+	+	+
Ni, Co	+	+	+	+	+	+	-
Pd, Pt	+	+	+	+	+	-	-
Mn, Cu	+	+	+	+	±	-	-
Al, Au	+	+	+	+	-	-	-
Li, Na, K	+	+	-	-	-	-	-
Mg, Ag, Zn, Pb	+	-	-	-	-	-	-

* +, Strong chemisorption; ±, chemisorption; -, no chemisorption.

Unimolecular decomposition

- Rate is proportional to the surface coverage only
- $\text{PH}_3(\text{ad})$ on W

$$v = k\theta = \frac{kKp}{1 + Kp}$$

when $Kp \ll 1$

$$v = kKp$$

first-order decomposition

when $Kp \gg 1$

$$v = k$$

zeroth-order decomposition

Langmuir-Hinshelwood (LH) mechanism

– Reactions take place by encounters between molecular fragments and atoms adsorbed on the surface



$$v = k\theta_A\theta_B$$

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B}$$

$$\theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B}$$

$$v = \frac{kK_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2}$$

Eley-Rideal (ER) mechanism

- A surface-catalyzed reaction, a gas-phase molecule collides with another molecule already adsorbed on the surface
- Almost all thermal surface-catalyzed reactions are thought to take place by this mechanism
- $\mathbf{H(g) + D(ad) \rightarrow HD(g)}$



$$v = k\theta_A p_B$$

$$v = \frac{kKp_A p_B}{1 + Kp_A}$$

When $Kp_A \gg 1$, $v = kp_B$

the rate determining step is the collision of B with adsorbed fragments.

Table 25.5 Properties of catalysts

Catalyst	Function	Examples
Metals	Hydrogenation Dehydrogenation	Fe, Ni, Pt, Ag
Semiconducting oxides and sulfides	Oxidation Desulfurization	NiO, ZnO, MgO, Bi ₂ O ₃ /MoO ₃ , MoS ₂
Insulating oxides	Dehydration	Al ₂ O ₃ , SiO ₂ , MgO
Acids	Polymerization Isomerization Cracking Alkylation	H ₃ PO ₄ , H ₂ SO ₄ , SiO ₃ /Al ₂ O ₃ , zeolites

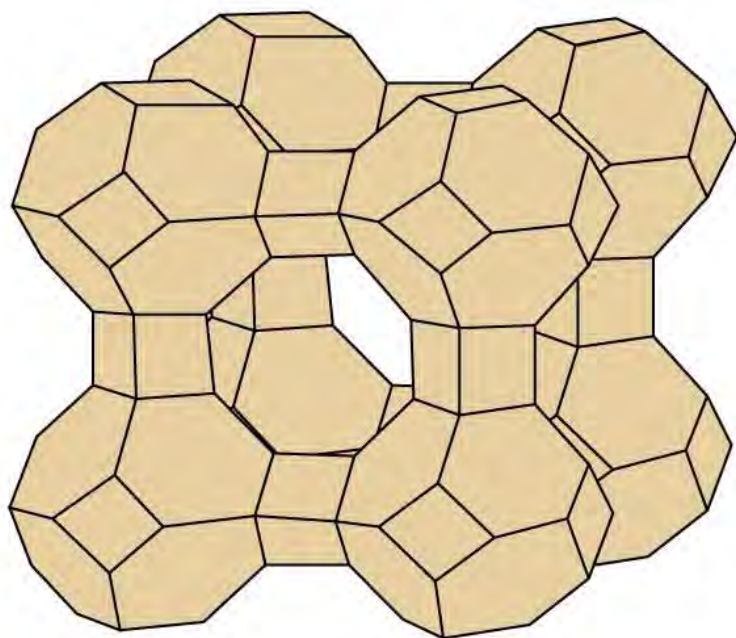
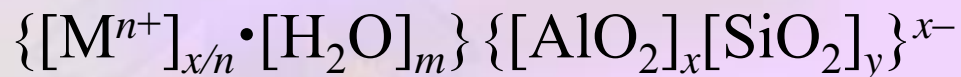
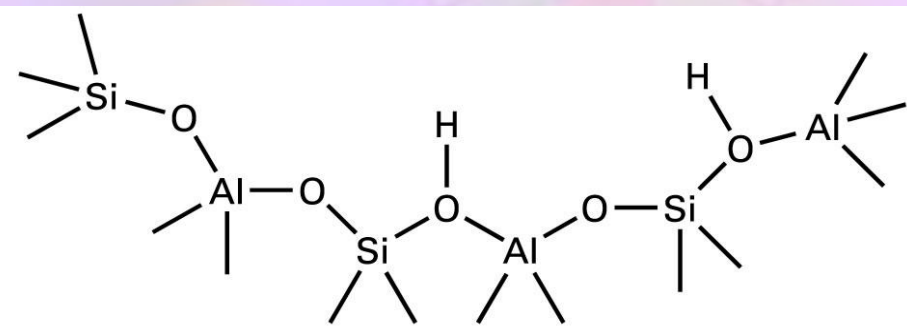


Fig. 25.29 A framework representation of the general layout of the Si, Al, and O atoms in a zeolite material. Each vertex corresponds to a Si or Al atom and each edge corresponds to the approximate location of a O atom. Note the large central pore, which can hold cations, water molecules, or other small molecules.

Zeolites are microporous aluminosilicates with the formula of



where M^{n+} cations and H_2O molecules bind inside the cavities or pores of the Al-O-Si framework.



Some zeolites for which $M=H^+$ are very strong acids and catalyse a variety of reactions, including the dehydration of methanol to form hydrocarbons such as gasoline and other fuels:

