Thin-Film Deposition

- -

Catalyst: A substance that **accelerates a reaction**, but **undergoes no net chemical changes**.

Homogeneous Catalyst: **A catalyst in the same phase** as the reaction mixture, e.g., the decomposition of hydrogen peroxide in aqueous solution catalyzed by iodide ion.

(page 955)

Heterogeneous Catalyst: A catalyst in a different phase from the reaction mixture, e.g., hydrogenation of ethene (C_2H_4) to ethane (C_2H_6), a gas phase reaction, in the presence of **a solid catalyst such as palladium, platinum, or nickel**.

Surface Characteristics of Silicon (001)
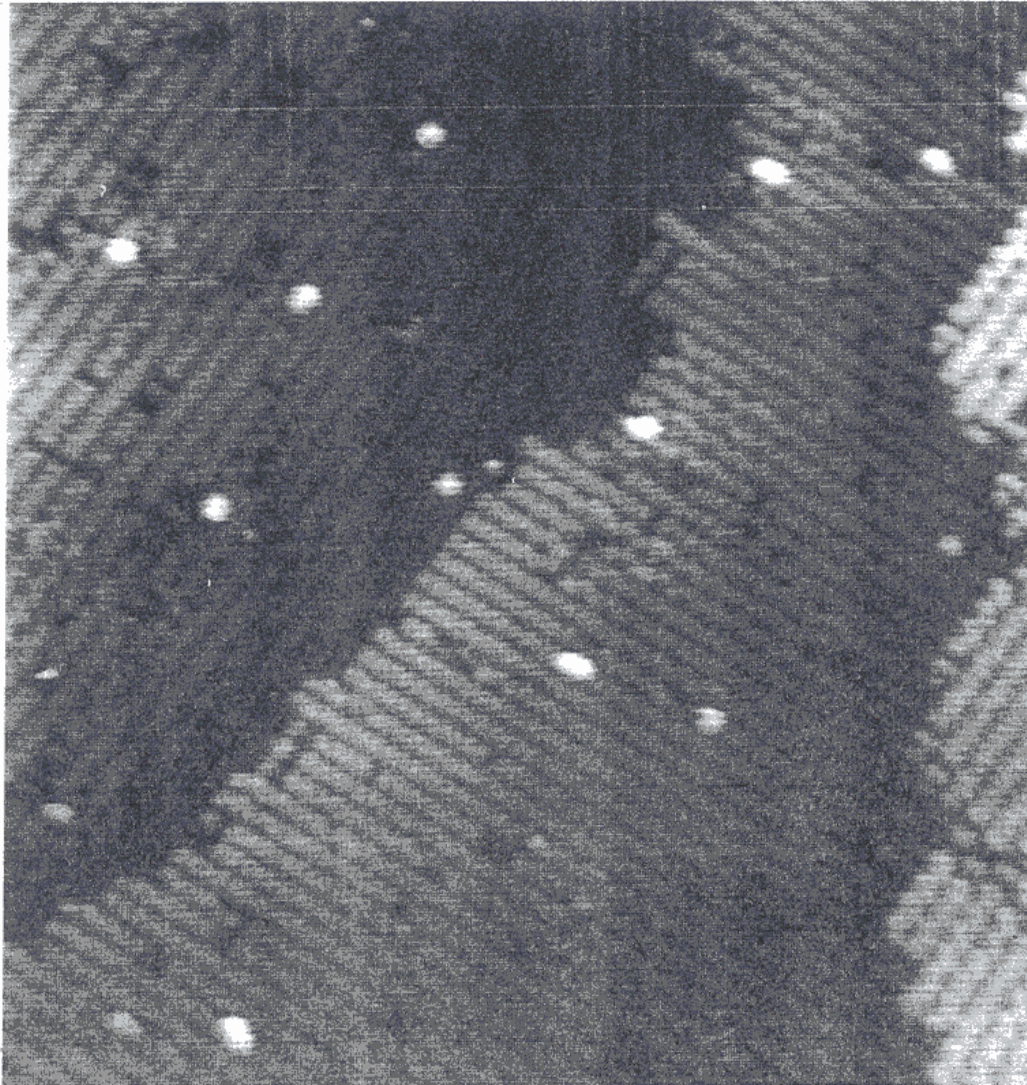
Terrace, Step, and Kink

FIGURE 1. A SCANNING tunneling microscope image of a silicon (001) surface after the deposition of a small amount of Si at room temperature. The image shows two single-layer steps (the jagged interfaces) separating three terraces. Because of the tetrahedral bonding configuration in the silicon lattice, dimer row directions are orthogonal on terraces joined by a single-layer step. The area pictured is 30 × 30 nm.

~Fig. 22A.1
~Fig. 22A.2 Terrace
~Fig. 22A.4 STM
~Fig. 22A.5 STM
~Fig. 22A.6 AFM

22A.2. Physisorption and Chemisorption

Physisorption: - **van der Waals interactions** between the adsorbate and
the substrate
- the enthalpy of physisorption $\approx -20\ kJ/mol$

Chemisorption: - the molecules (or atoms) stick to the surface by
forming a chemical bond

- the enthalpy of chemisorption $\Delta H < 0$

- $\Delta S < 0$ (due to the reduction of freedom of adsorbate)

$$\approx -200\ kJ/mol$$

- -

(skip)

Assumptions
1. Adsorption cannot proceed beyond monolayer coverage.
2. All sites are equivalent and the surface is uniform.
3. The ability of a molecule to adsorb at a given site is independent
of the occupation of neighboring sites.

Types of Adsorption Modes
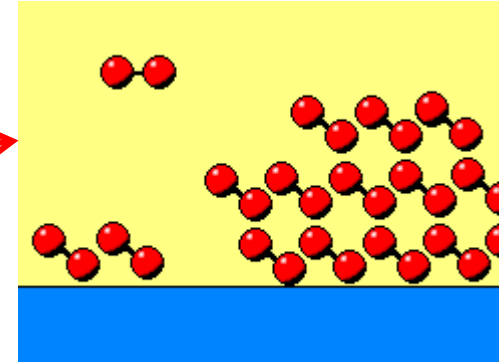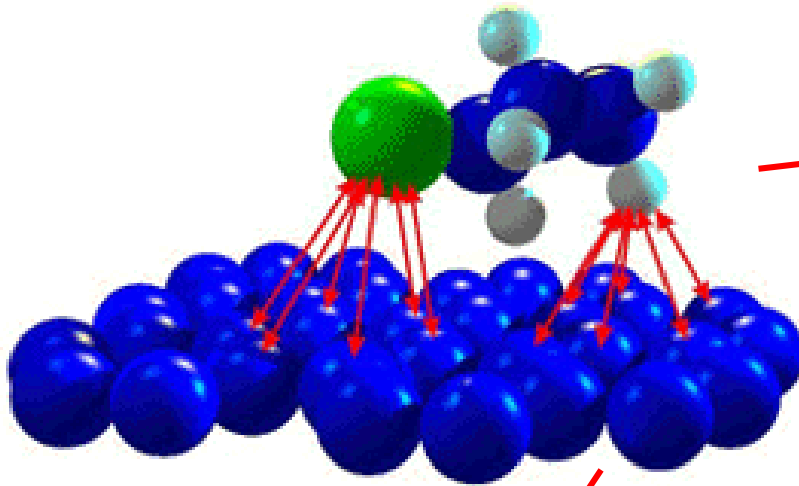
Physical Adsorption or

Physisorption

Bonding between molecules and surface is by **weak van der Waals forces**.
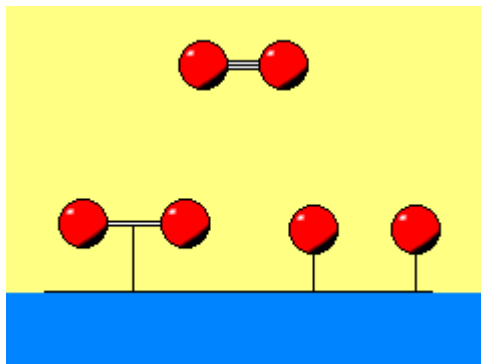
Chemical bond is formed between molecules and surface.

Chemical Adsorption or

Chemisorption

Dr. K. L. Yeung (Hong Kong Univ.)
http://teaching.ust.hk/~ceng511/notes/

22B. Adsorption & Desorption

The fractional coverage θ : the extent of surface coverage

$$\theta = \frac{\text{number of adsorption sites occupied}}{\text{number of adsorption sites available}}$$

$$\theta = \frac{V}{V_{\infty}}$$

V : the volume of adsorbate adsorbed

V_{∞} : the volume of adsorbate corresponding to

complete monolayer coverage

$\dfrac{d\theta}{dt}$: the rate of adsorption

(22B.1a)

22B. The Dynamic Equilibrium

$$A(gas\ or\ liquid) + M(surface) \underset{k_d}{\overset{k_a}{\rightleftarrows}} AM(surface)$$

MBE
Sputter Deposition
CVD
Spin Coating

The rate of <u>adsorption</u>

$$\frac{d\theta}{dt} = k_a p N(1-\theta) \quad \textbf{(22B.1a)}$$

p : the partial pressure of A

N : the total number of adsorption sites

$N(1-\theta)$: the number of vacant sites

The rate of <u>desorption</u>

$$-\frac{d\theta}{dt} = k_d N\theta \qquad \textbf{(22B.1b)}$$

At equilibrium, there is no net change. **(skip---)**

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

$$\therefore \theta = \frac{K\ p}{1 + K\ p} \qquad K = \frac{k_a}{k_d} \qquad \text{Langmuir isotherm} \qquad \textbf{(22.B2)}$$
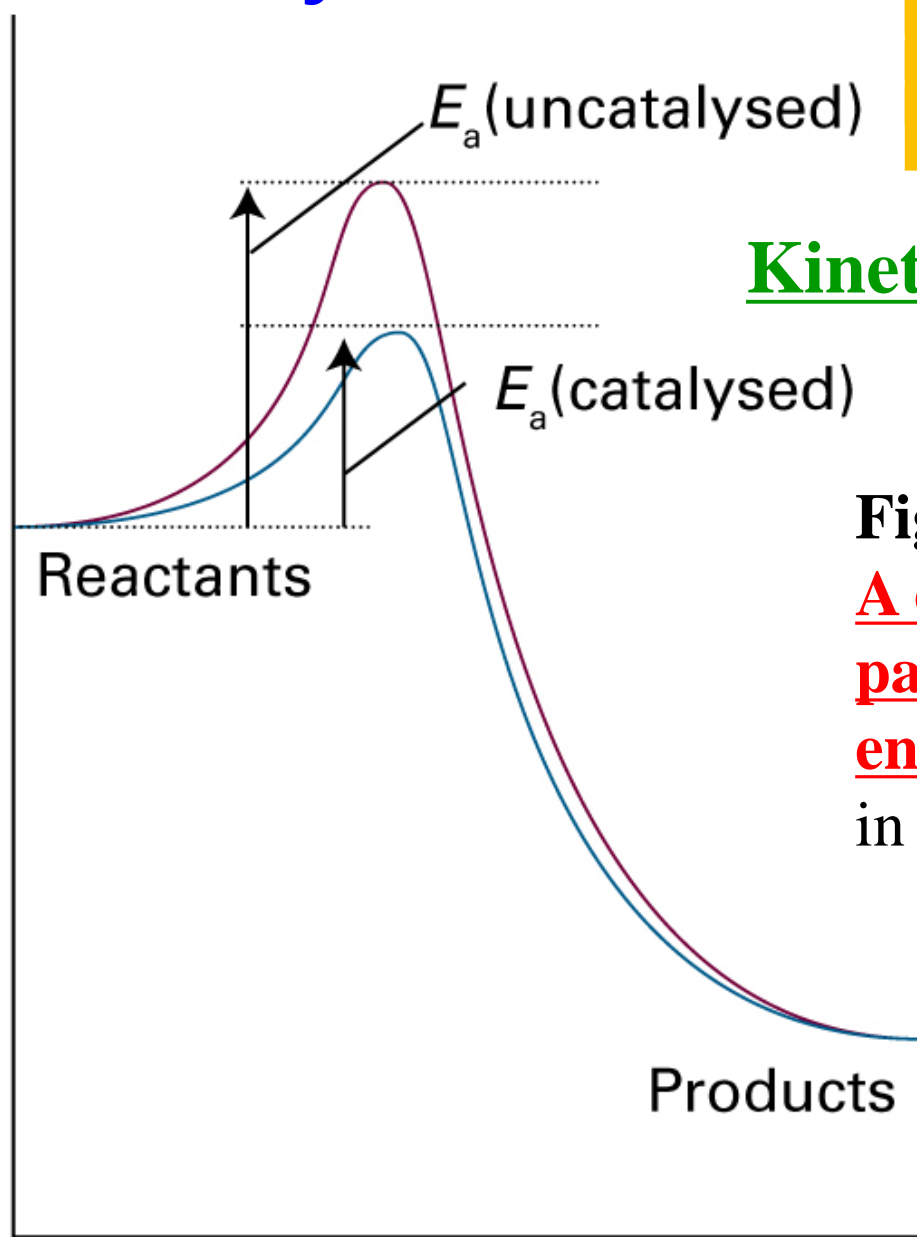
22C. Catalysis

$$H_2 \leftrightarrow 2H^+ + 2e \quad (0.000 \text{ V vs. NHE})$$
$$Li \leftrightarrow Li^+ + e \quad (-3.045 \text{ V vs. NHE})$$
$$Au \leftrightarrow Au^+ + e \quad (1.830 \text{ V vs. NHE})$$

Normal Hydrogen Electrode

G

Kinetics or Thermodynamics

E_a(uncatalysed)

E_a(catalysed)

Potential energy

Reactants

Products

Reaction coordinate

Figure 22C.1
A catalyst provides a different path with a lower activation enthalpy. The result is an increase in the rate of formation of products.
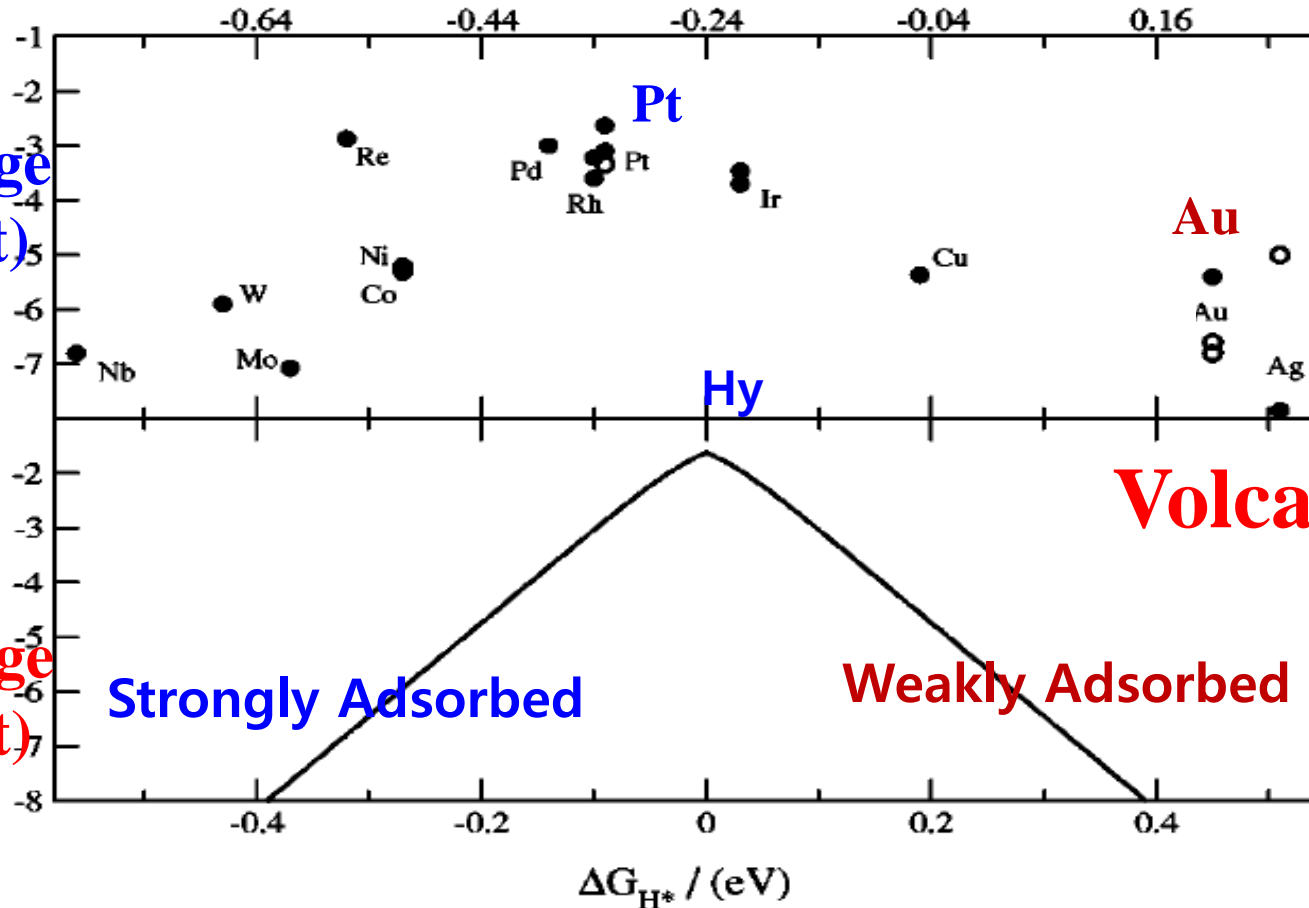
Catalyst: Altered Activation Barrier

Hydrogen chemisorption energy

~Fig. 22C.2

Log (Exchange Current)

T = 300 K

Pt

Au

Hy

Volcano Curve

Log (Exchange Current)

Strongly Adsorbed

Weakly Adsorbed

Free energy for hydrogen adsorption

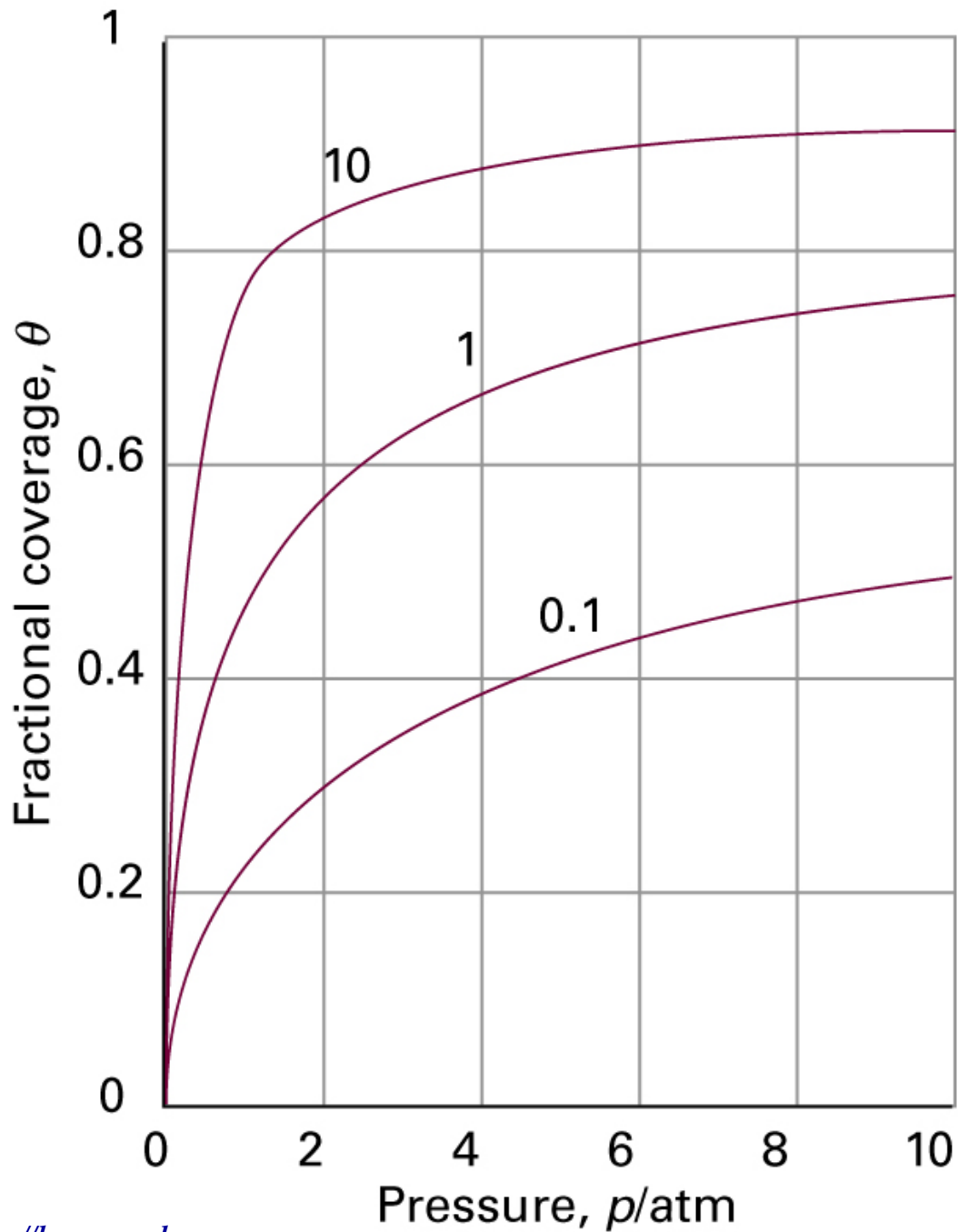*U. Stimming, J. Electrochem. Soc. (2005).*

Figure 22B.2
The Langmuir isotherm for non-dissociative adsorption for different values of K.

Example 1

The data given below are the adsorption of CO on charcoal at 273 K. Confirm that they fit the Langmuir isotherm, and find the constant K and the volume corresponding to complete coverage. In each case V has been corrected to 1.00 atm (101.325 kPa).

p/kPa	13.3	26.7	40.0	53.3	66.7	80.0	93.3
V/cm^3	10.2	18.6	25.5	31.5	36.9	41.6	46.1

Solution

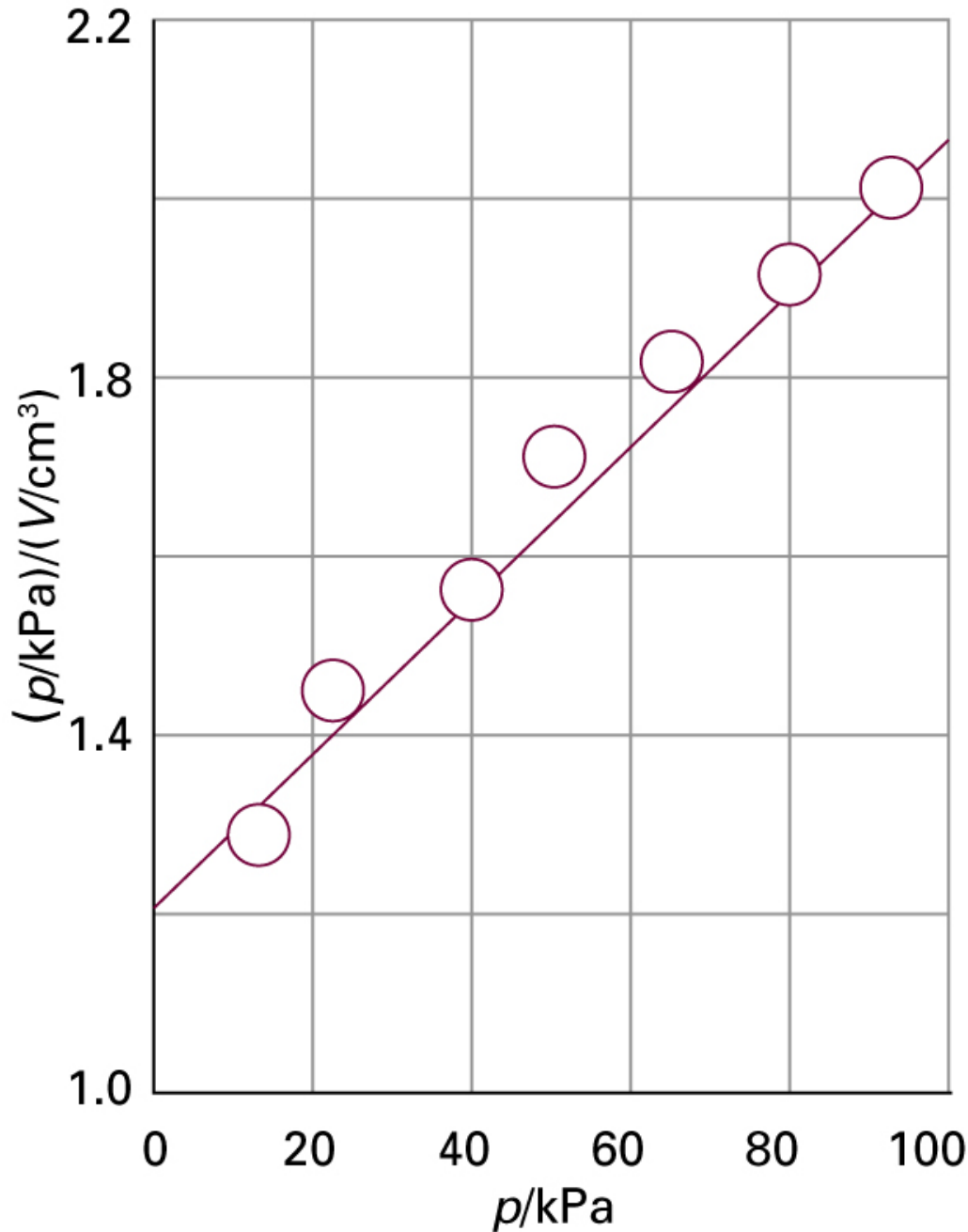$$Kp\theta + \theta = Kp \quad \text{with} \quad \theta = V/V_\infty$$

$$\frac{p}{V} = \frac{p}{V_\infty} + \frac{1}{KV_\infty}$$

Hence, a plot of p/V against p should give a straight line of slope $1/V_\infty$ and intercept $1/KV_\infty$.

p/kPa	13.3	26.7	40.0	53.3	66.7	80.0	93.3
$(p$/kPa$)/(V$/cm$^3)$	1.30	1.44	1.57	1.69	1.81	1.92	2.02

The slope is 0.00900 and so $V_\infty = 111$ cm^3. The intercept at $p=0$ is 1.20, so

$$K = \frac{1}{(111 \text{ cm}^3) \times (1.20 \text{ kPa cm}^{-3})} = 7.51 \times 10^{-3} \text{ kPa}^{-1}$$

Figure 22B.1
The plot of the data in Example. As illustrated here, the Langmuir isotherm predicts that a straight line should be obtained when p/V is plotted against p.

The rate of adsorption for adsorption with dissociation is proportional to the pressure and to the probability that both atoms will find sites, which is proportional to the square of the number of vacant sites,

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

The rate of desorption

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

At equilibrium

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

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

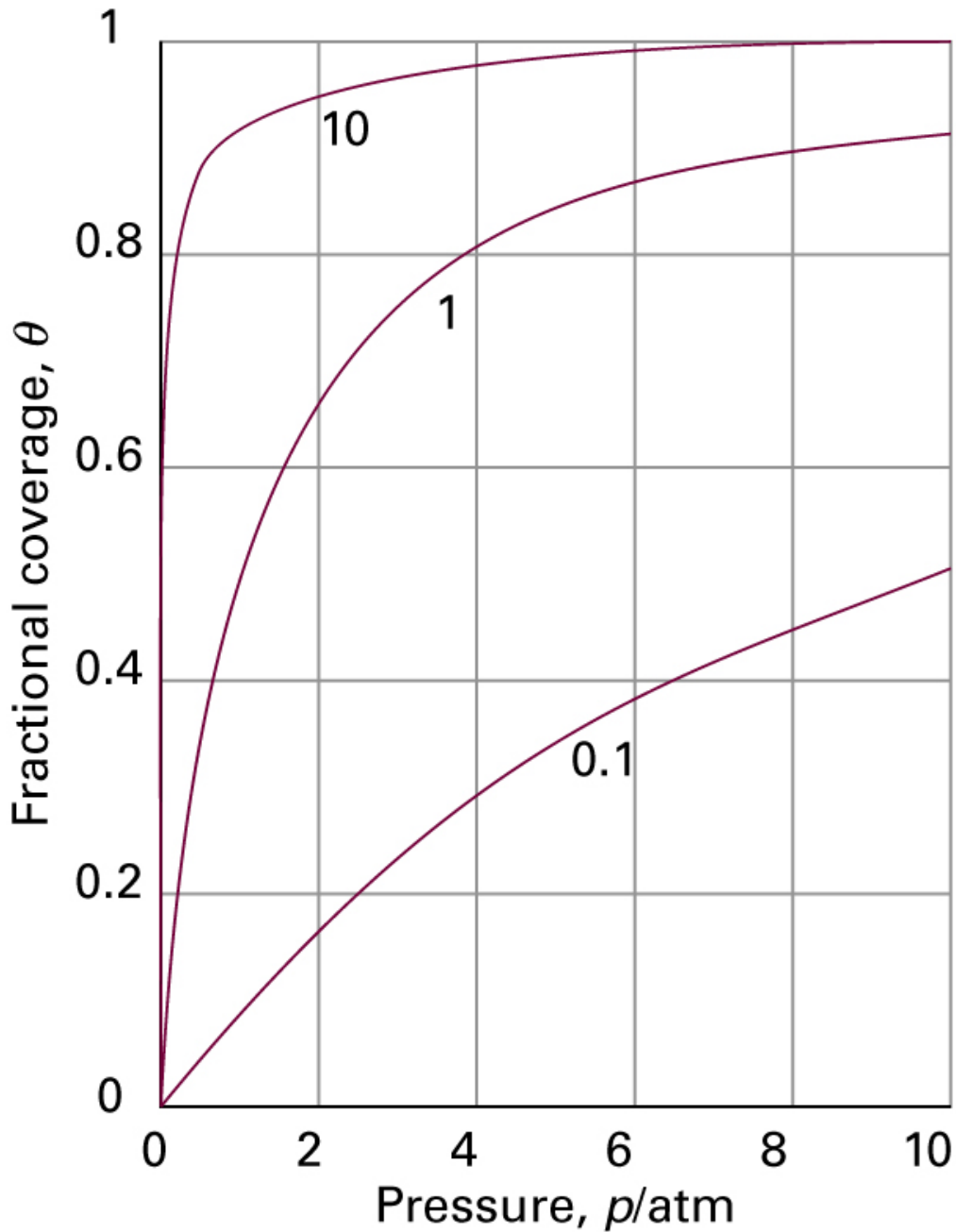Langmuir isotherm for adsorption with dissociation

Figure 22B.3
The Langmuir isotherm for dissociative adsorption,
$X_2(g) \rightarrow 2X(\text{surface})$
for different values of K.

The isosteric standard enthalpy of adsorption: the standard enthalpy of adsorption at a fixed surface coverage

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H_{\text{ads}}^0}{RT^2}$$

the van't Hoff equation

Example 2:

The data below show the pressures needed for the volume of adsorption (corrected to 1.00 atm and 273 K) to be 10.0 cm³ using the same sample as in Example 1. Calculate the adsorption enthalpy at this surface coverage.

T/K	200	210	220	230	240	250
p/kPa	4.00	4.95	6.03	7.20	8.47	9.85

Solution:

The Langmuir isotherm can be rearranged to
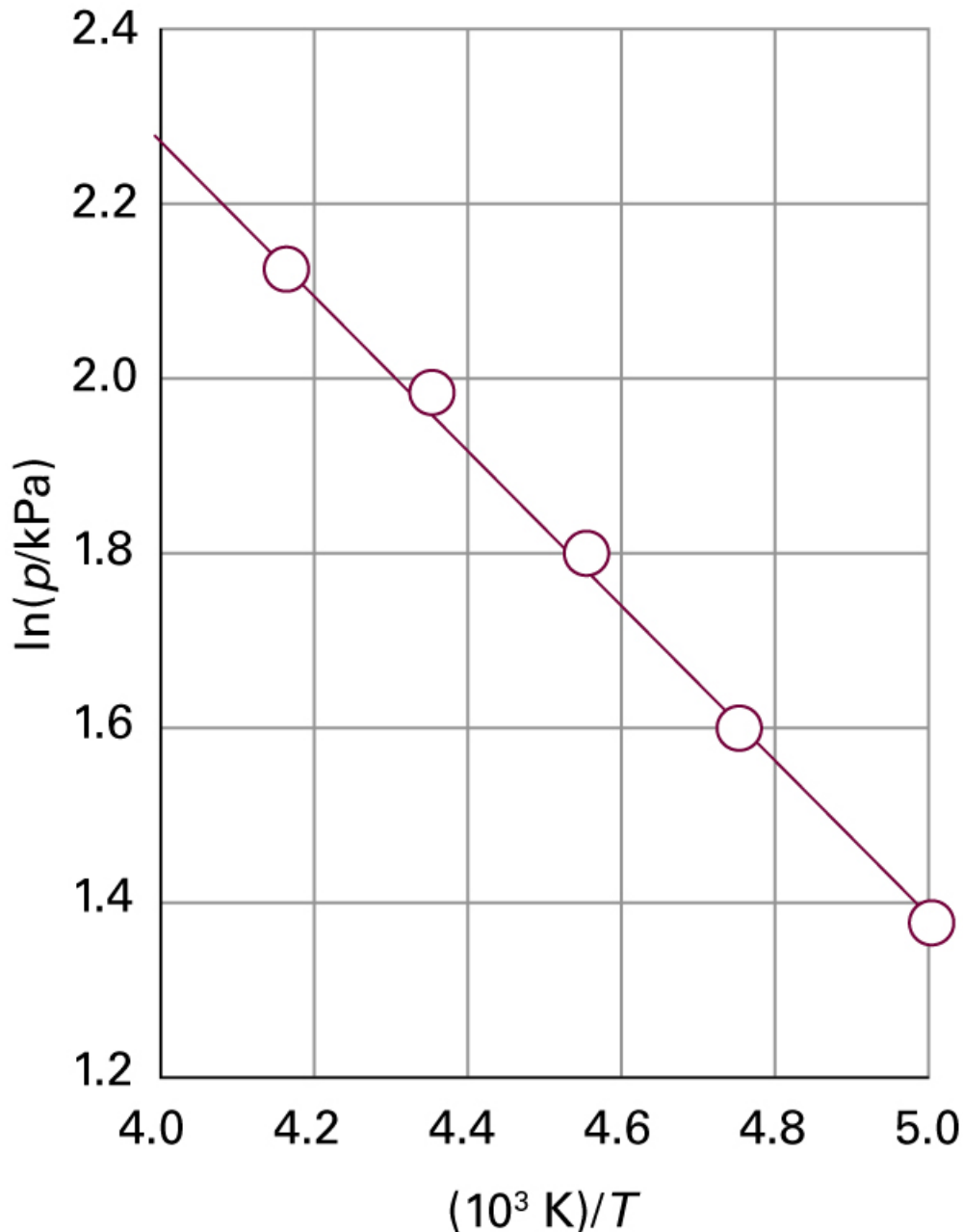
$$Kp = \frac{\theta}{1-\theta}$$

when θ is constant

$$\ln K + \ln p = \text{constant}$$

$$\therefore \left(\frac{\partial \ln p}{\partial T}\right)_\theta = -\left(\frac{\partial \ln K}{\partial T}\right)_\theta = -\frac{\Delta H^0_{\text{ads}}}{RT^2}$$

with $d(1/T)/dT = -1/T^2$,

$$\left(\frac{\partial \ln p}{\partial(1/T)}\right)_\theta = \frac{\Delta H^0_{\text{ads}}}{R}$$

Therefore, a plot of $\ln p$ against $1/T$ should be a straight line with the slope $\Delta H^0_{\text{ads}}/R$

The slope is −0.904, so

$$\Delta H^0_{\mathrm{ads}} = -\left(0.904 \times 10^3\, K\right) \times R$$

$$= -7.52 \,\mathrm{kJ\,mol^{-1}}$$

Figure 22B.4
The isoteric 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 coverage.

Isotherm with multilayer adsorption

BET isothem: Stephen Brunauer, Paul Emmett, Edward Teller

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

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

$p*$: the vapor pressure above a layer adsorbate,

resembling a pure bulk liquid

V_{mon} : the volume corresponding to monolayer coverage

c : constant $c = e^{\left(\Delta H_{des}^0 - \Delta H_{vap}^0\right)/RT}$
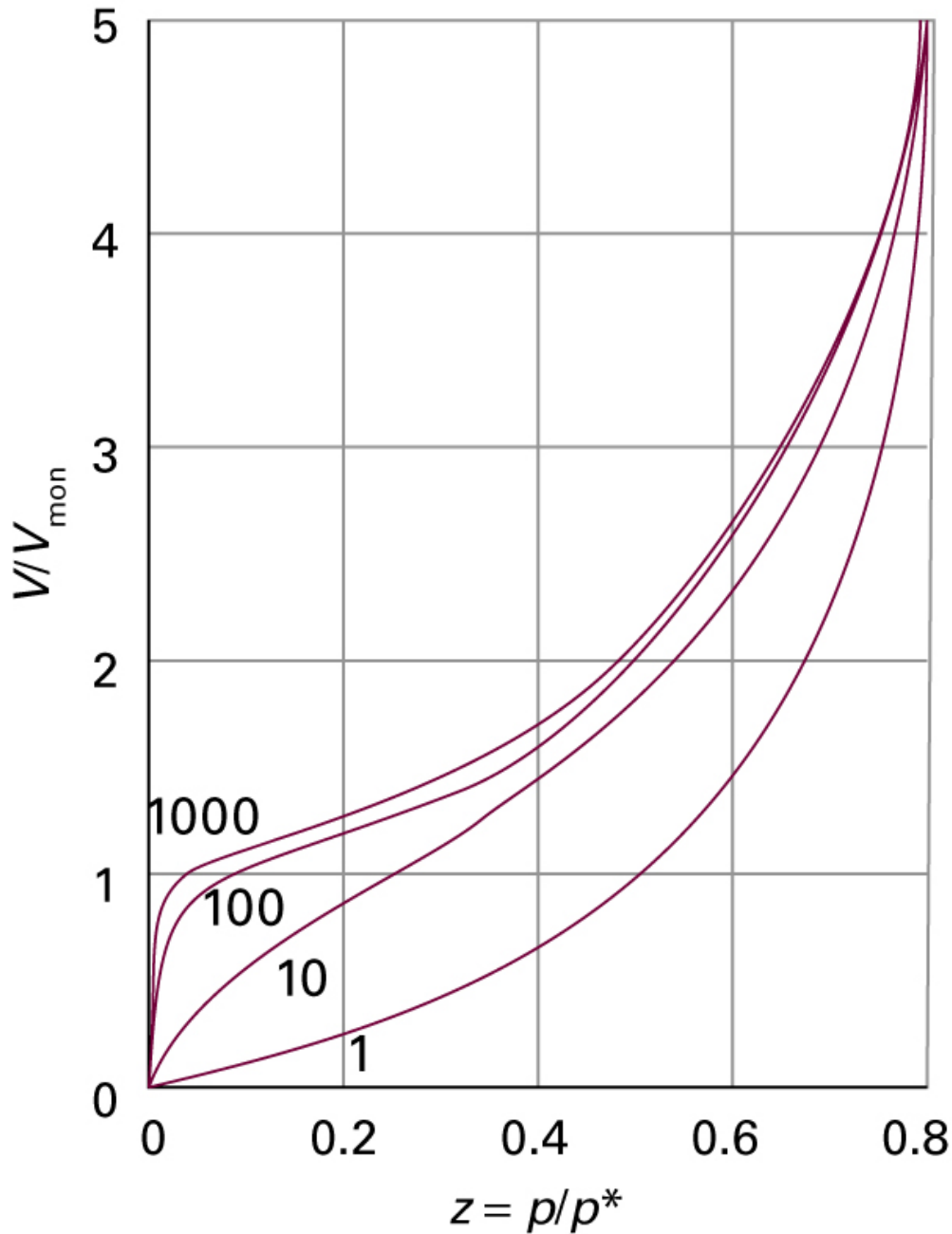
Figure 22B.5
Plot of the BET isotherm for different values of c. The value of V/V_{mon} rises indefinitely because the adsorbate may condense on the covered substrate surface.

Example 3:

The data below relate the adsorption of N_2 on rutile (TiO_2) at 75 K. Confirm that they fit a BET isotherm in the range of pressures reported, and determine V_{mon} and c.

p/kPa	0.160	1.87	6.11	11.67	17.02	21.92	27.29
V/mm³	601	720	822	935	1046	1146	1254

At 75 K, p^*=76.0 kPa. The volumes have been corrected to 1.00 atm and 273 K and refer to 1.00 g of substrate.

Solution:

The BET equation can be reorganized into

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

$(c-1)/cV_{mon}$ can be obtained from the slope of a plot of the expression on the left against z, and cV_{mon} can be found from the intercept at z=0. The results can then be combined to give c and V_{mon}.

p/kPa	0.160	1.87	6.11	11.67	17.02	21.92	27.29
10^3z	2.11	24.6	80.4	154	224	288	359
$10^4z/(1-z)(V/\text{mm}^3)$	0.035	0.350	1.06	1.95	2.76	3.53	4.47

When $10^4z/(1-z)$ is plotted against 10^3z, the intercept is 0.0398, so

$$\frac{1}{cV_{\text{mon}}} = 3.98 \times 10^{-6} \text{ mm}^{-3}$$

The slope of the line is 1.23×10^{-2}, so

$$\frac{c-1}{cV_{\text{mon}}} = \left(1.23 \times 10^{-2}\right) \times 10^3 \times 10^{-4} \text{ mm}^{-3} = 1.23 \times 10^{-3} \text{ mm}^{-3}$$

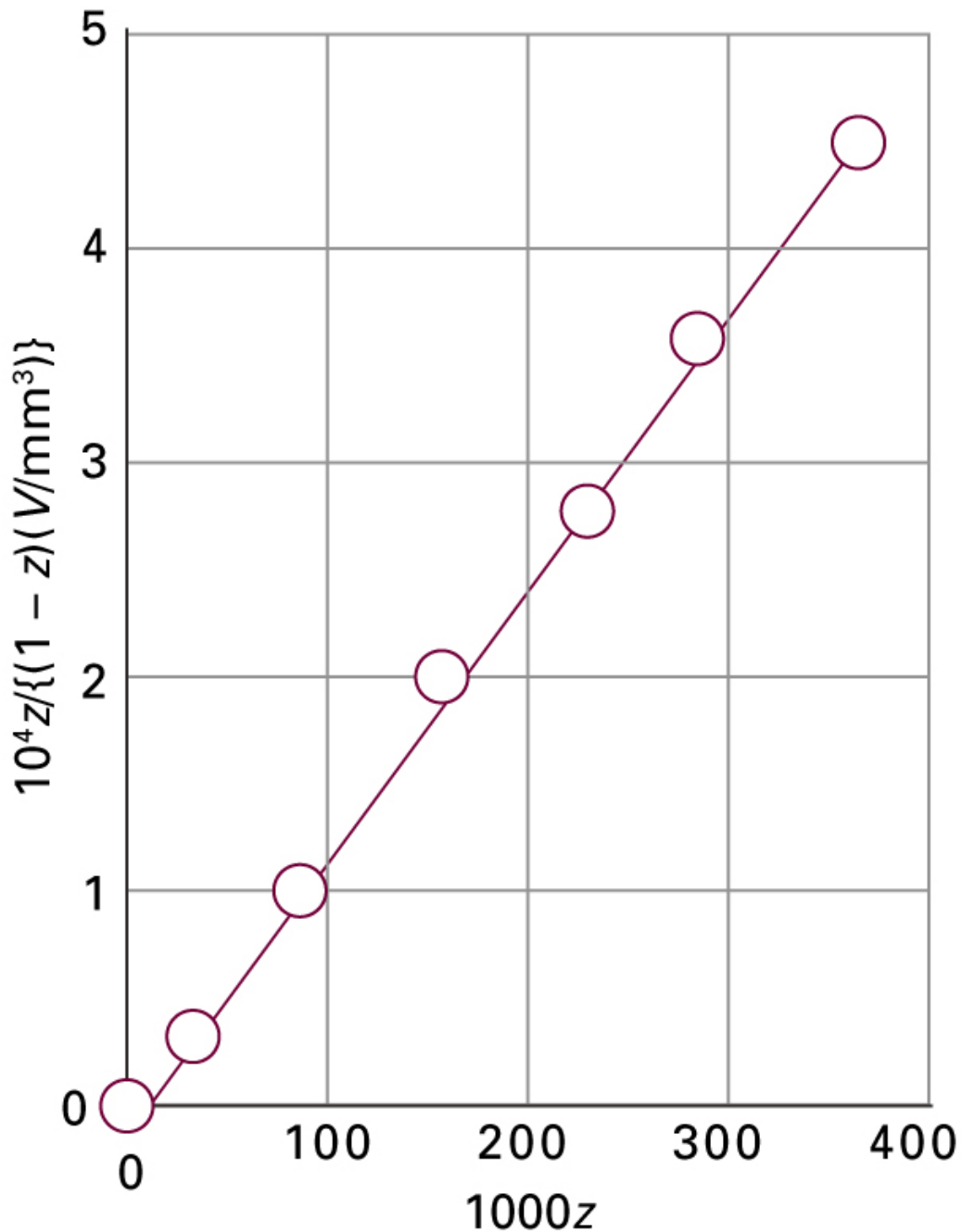$$\therefore c = 310 \text{ and } V_{\text{mon}} = 811 \text{ mm}^3$$

Figure 22B.6
The BET isotherm can be tested, and the parameters determined, by plotting $z/(1-z)V$ against $z=p/p^*$.

$$c \approx 1, \quad \text{the BET isotherm}$$

$$\frac{V}{V_{\text{mon}}} = \frac{1}{1-z}$$

Deviations from the Langmuir isotherm which assumes the independence and equivalence of the adsorption sites

The Temkin isotherm

$$\theta = c_1 \ln\left(c_2 p\right)$$

$$c_1, c_2 : \text{constants}$$

The Freundlich isotherm

$$\theta = c_1 p^{\frac{1}{c_2}}$$

22C. Homogeneous Catalysis
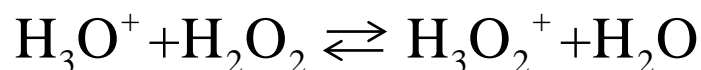
- Features of homogeneous catalysis

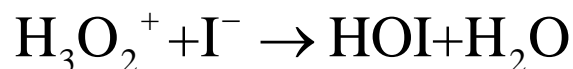$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

$E_a = 76 \text{ kJ mol}^{-1}$ in the absence of catalyst

$E_a = 57 \text{ kJ mol}^{-1}$ in the presence of iodide ion

The rate constant increases by a factor of 2000.
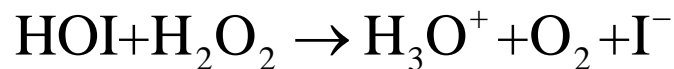
- - - - - - - - - -

$$H_3O^+ + H_2O_2 \rightleftarrows H_3O_2^+ + H_2O \qquad K = \frac{\left[H_3O_2^+\right]}{\left[H_2O_2\right]\left[H_3O^+\right]}$$

$$H_3O_2^+ + I^- \rightarrow HOI + H_2O \qquad v = k_a\left[H_3O_2^+\right]\left[I^-\right]$$

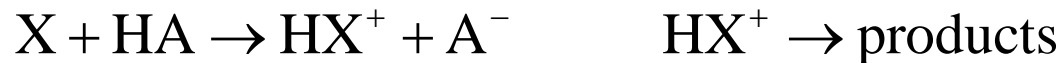$$HOI + H_2O_2 \rightarrow H_3O^+ + O_2 + I^- \qquad \text{(fast)}$$

The second step is rate-determining step, therefore we can obtain the rate law of the overall reaction by setting the overall rate equal to the rate of the second step:

$$\frac{d[O_2]}{dt} = k_r[H_2O_2][H_3O^+][I^-]$$

where $k_r = k_a K$.

In acid catalysis, the crucial step is the transfer of a proton to the substrate:

$$X + HA \rightarrow HX^+ + A^- \qquad HX^+ \rightarrow \text{products}$$

In base catalysis, a proton is transferred from the substrate to a base:

$$XH + B \rightarrow X^- + BH^+ \qquad X^- \rightarrow \text{products}$$
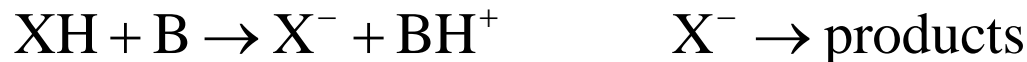
Enzymes

The Michaelis-Menten Mechanism $\mathrm{E + S \rightarrow P + E}$
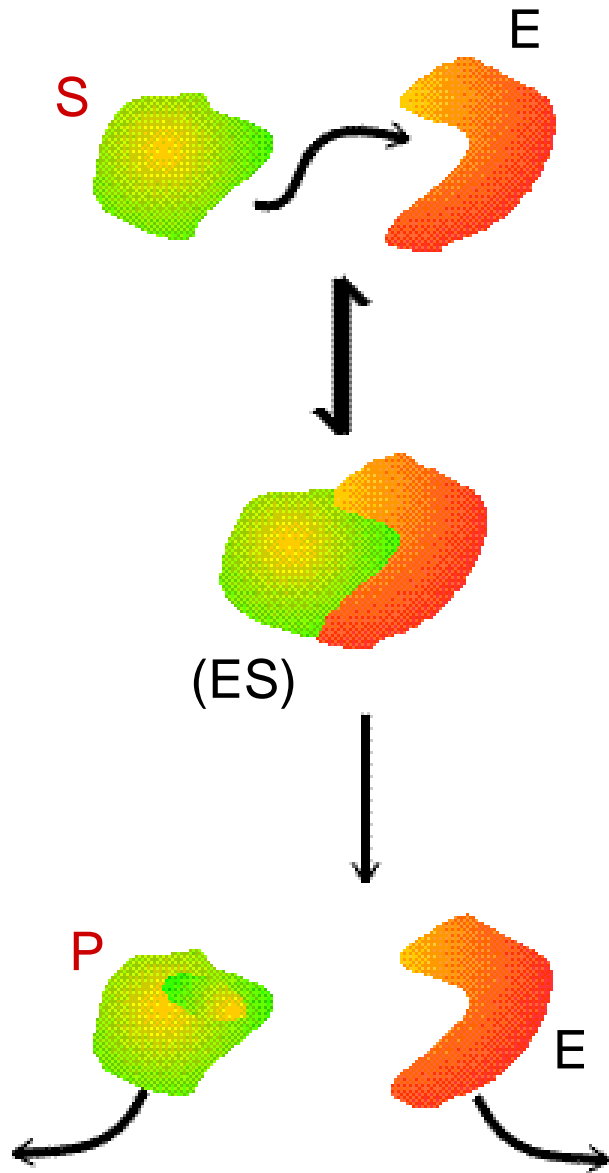
Experiments show that the rate of formation of the product depends on the concentration of the enzyme, and so although the net reaction is simply S→P, this must reflect an underlying mechanism with steps that involve the enzyme.

$$\mathrm{E + S} \underset{k'_a}{\overset{k_a}{\rightleftharpoons}} \mathrm{(ES)} \xrightarrow{k_b} \mathrm{P + E}$$

(ES): active combination of the enzyme and substrate

$$\frac{d[\mathrm{P}]}{dt} = k_b[(\mathrm{ES})]$$

$$\frac{d[(\mathrm{ES})]}{dt} = k_a[\mathrm{E}][\mathrm{S}] - k'_a[(\mathrm{ES})] - k_b[(\mathrm{ES})]$$

S

E

(ES)

P

E

Figure
The basis of the Michaelis-Menten mechanism of enzyme action. Only a fragment of the large enzyme molecule E is shown.

The steady-state approximation

$$k_a[\text{E}][\text{S}] - k'_a[(\text{ES})] - k_b[(\text{ES})] \approx 0$$

$$\therefore [(\text{ES})] \approx \frac{k_a[\text{E}][\text{S}]}{k_b + k'_a}$$

If $[\text{E}]_0$ is the total concentration of the enzyme, then $[\text{E}]+[(\text{ES})]=[\text{E}]_0$.

Since only a little enzyme is added,

$$[\text{S}] + [(\text{ES})] \approx [\text{S}]$$

$$\therefore [(\text{ES})] \approx \frac{k_a\{[\text{E}]_0 - [(\text{ES})]\}[\text{S}]}{k_b + k'_a}$$

$$\Downarrow$$

$$[(\text{ES})] \approx \frac{k_a[\text{E}]_0[\text{S}]}{k_b + k'_a + k_a[\text{S}]}$$

$$\frac{d[\mathrm{P}]}{dt} = k_b [(\mathrm{ES})]$$

$$[(\mathrm{ES})] \approx \frac{k_a [\mathrm{E}]_0 [\mathrm{S}]}{k_b + k'_a + k_a [\mathrm{S}]}$$

$$\therefore \frac{d[\mathrm{P}]}{dt} \approx \frac{k_a k_b [\mathrm{E}]_0 [\mathrm{S}]}{k_b + k'_a + k_a [\mathrm{S}]} = \frac{k_a [\mathrm{E}]_0 [\mathrm{S}]}{k_M + [\mathrm{S}]}$$

where $k_M = \dfrac{k_b + k'_a}{k_a}$ is the Michaelis constant

The rate of enzymolysis depends linearly on the amount of enzyme added, and also on the amount of substrate present.

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{E}]_0, \qquad k = \frac{k_b [\mathrm{S}]}{k_M + [\mathrm{S}]}$$

$$\frac{1}{k} = \frac{1}{k_b} + \frac{k_M}{k_b [\mathrm{S}]}$$
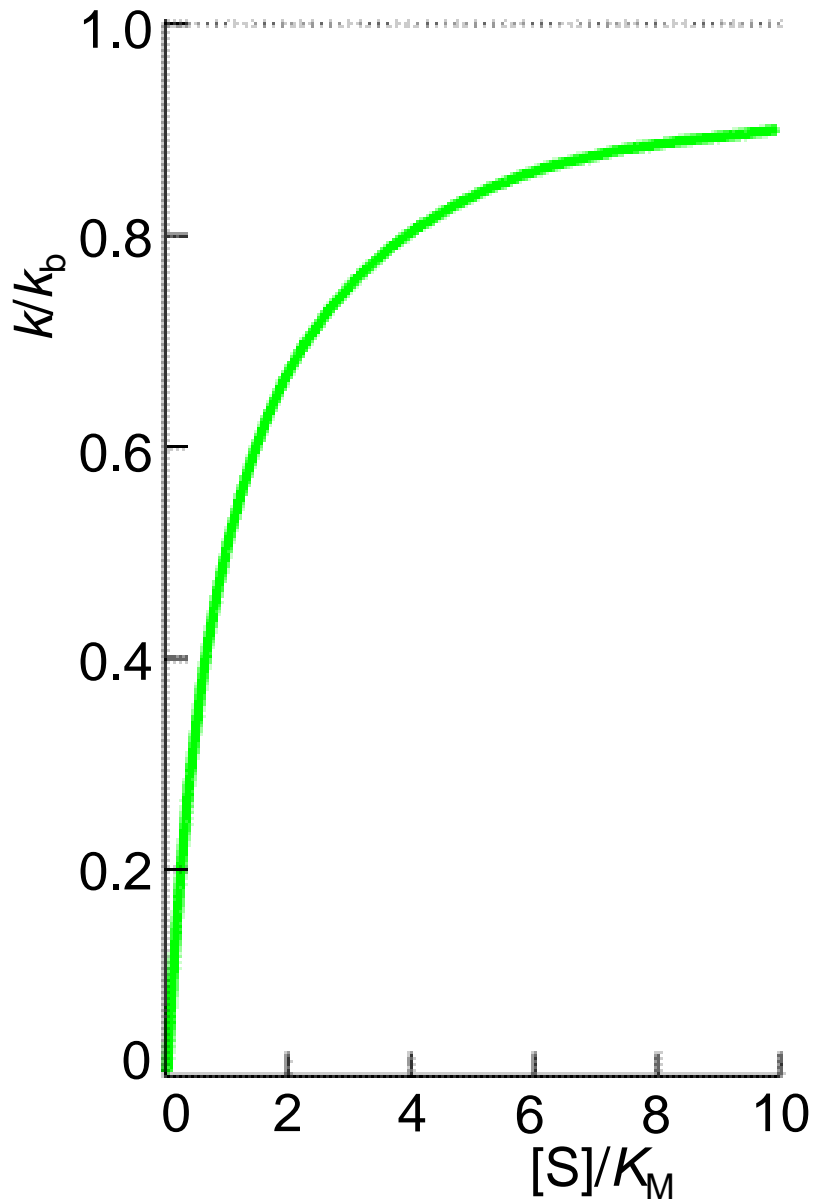
$$\frac{d[\text{P}]}{dt} = \frac{k_b [\text{E}]_0 [\text{S}]}{k_M + [\text{S}]} \cong k_1 [\text{E}]_0$$

$$k = \frac{k_b [\text{S}]}{k_M + [\text{S}]} \qquad \frac{k}{k_b} = \frac{[\text{S}]/k_M}{1 + [\text{S}]/k_M}$$

$$\frac{1}{k} = \frac{1}{k_b} + \frac{k_M}{k_b [\text{S}]}$$

Figure
The variation of the effective rate constant k with substrate concentration according to the Michaelis-Menten mechanism.
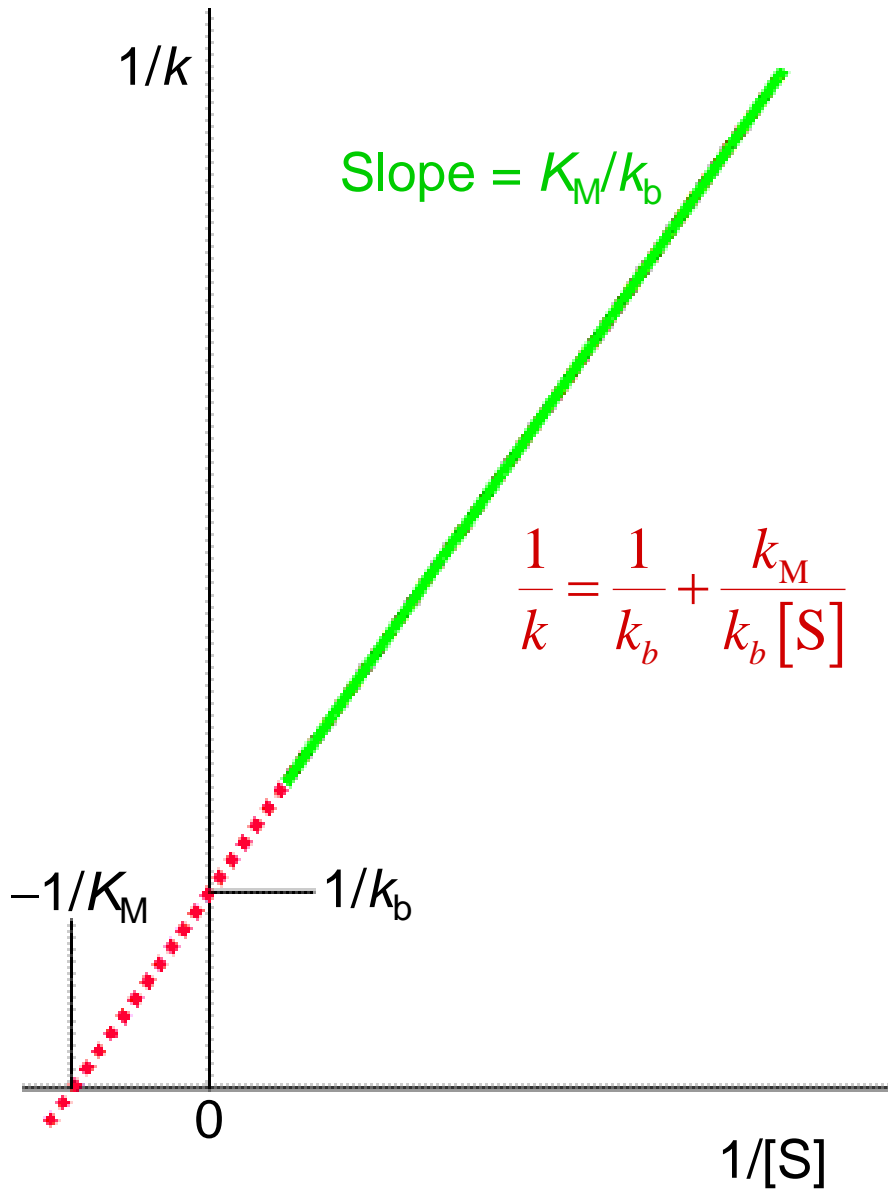
Figure
A Lineweaver-Burk plot for the analysis of an enzymolysis that proceeds by a Michaelis-Menten mechanism, and the significance of the intercepts and the slope.

Slope $= K_M/k_b$

$$\frac{1}{k} = \frac{1}{k_b} + \frac{k_M}{k_b\,[\text{S}]}$$

$1/k$

$-1/K_M$ $1/k_b$

0

$1/[\text{S}]$

Problems from Chap. 22

D 22A.2 (AFM / SEM / STM / TEM)

D 22C.2 (Fig. 22B.8, Fig. 22C.2, and ppt 22-8)

-171206(수) Final (2 p.m.)

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