# Chapter 23 Catalysis

**Catalyst:** a substance that accelerates a reaction but undergoes no net chemical change

**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

**Heterogeneous catalyst:** a catalyst in a different phase from the reaction mixture, e.g., hydrogenation of ethene to ethane, a gas phase reaction, in the presence of a solid catalyst such as palladium, platinum

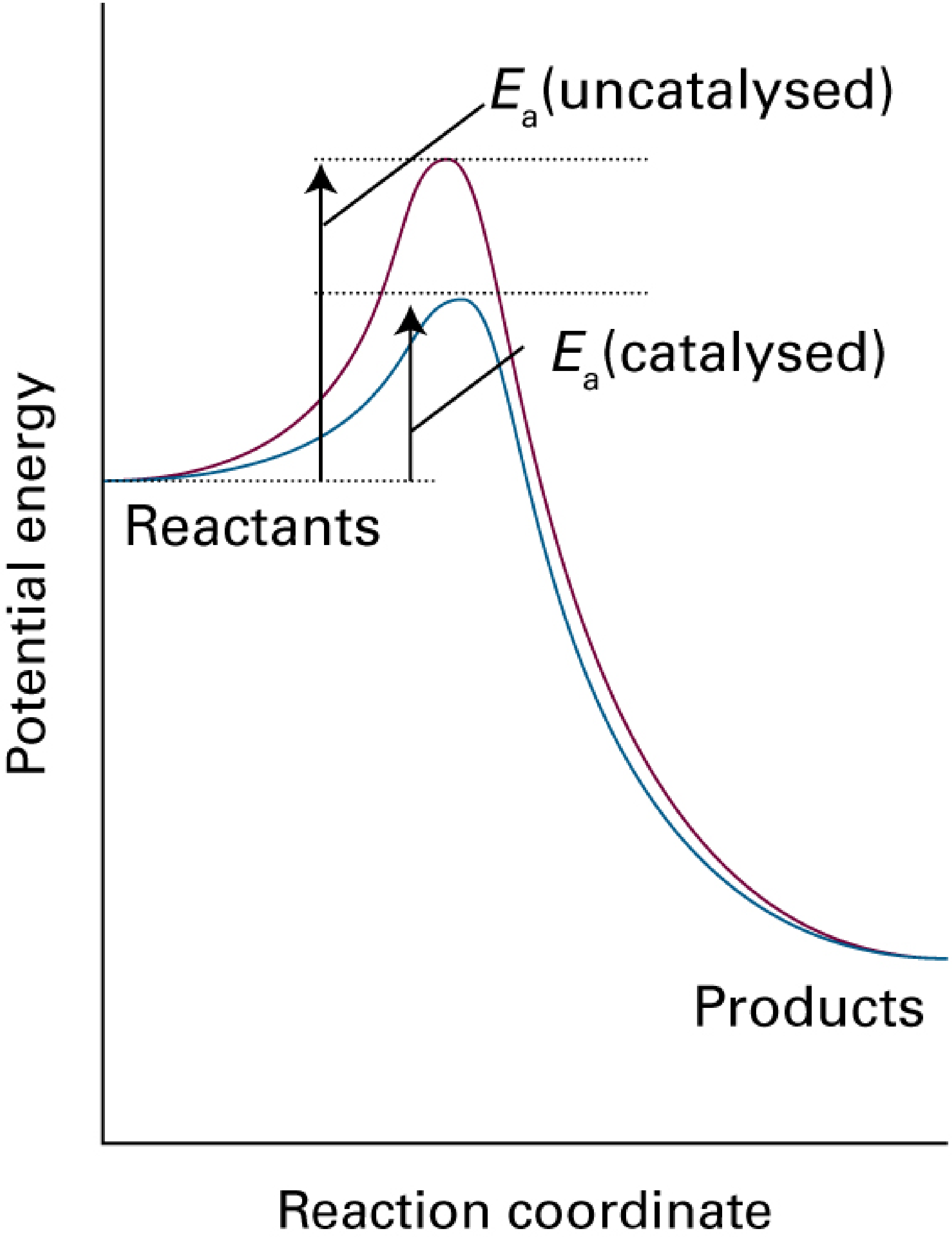


**Figure 23.1**
A catalyst provides a different path with a lower activation energy. The result is an increase in the rate of formation of products.

# Homogeneous Catalysis

- Features of homogeneous catalysis

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

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

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

The rate constant increases by a factor of 2000.

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

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

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

where the activity of $H_2O$ is set to 1.

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:

$$\frac{d[\mathrm{O_2}]}{dt} = k_\mathrm{r}[\mathrm{H_2O_2}]\left[\mathrm{H_3O^+}\right]\left[\mathrm{I^-}\right]$$

where $k_\mathrm{r} = k_\mathrm{a}K$.

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

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

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

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

# 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.

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

(ES): active combination of the enzyme and substrate

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

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

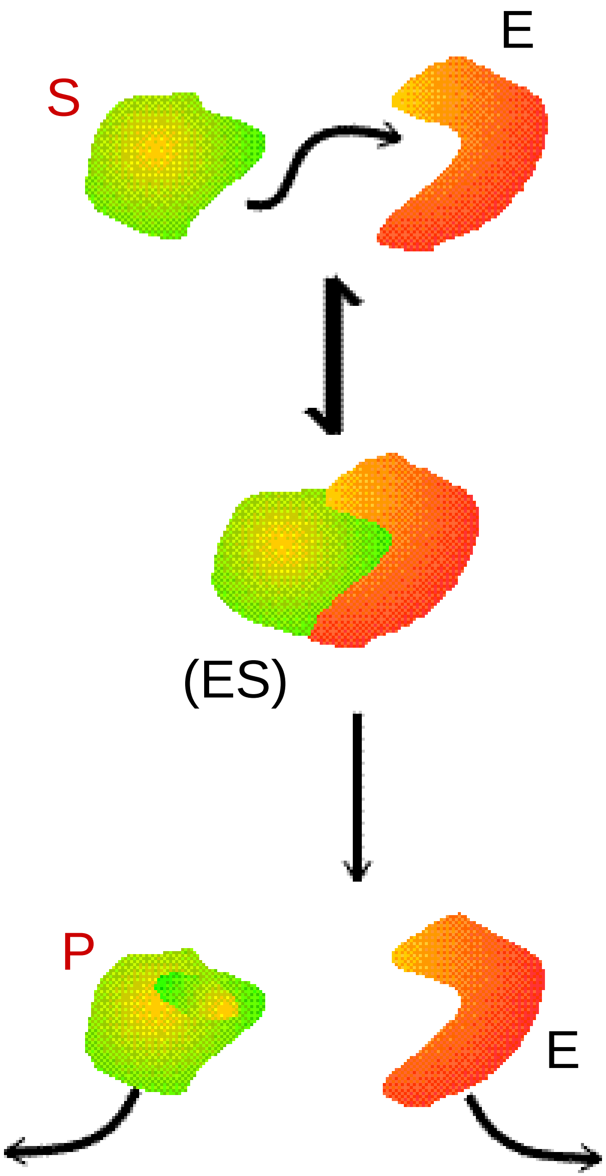


**Figure 23.2**
The basis of the Michaelis-Menten mechanism of enzyme action. Only a fragment of the large enzyme molecule E is shown.

# The steady-state approximation

$$k_a[\mathrm{E}][\mathrm{S}] - k_a^{'}[(\mathrm{ES})] - k_b[(\mathrm{ES})] \approx 0$$

$$\therefore [(\mathrm{ES})] \approx \frac{k_a[\mathrm{E}][\mathrm{S}]}{k_b + k_a^{'}}$$

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

Since only a little enzyme is added,

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

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

$$\Downarrow$$

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

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

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

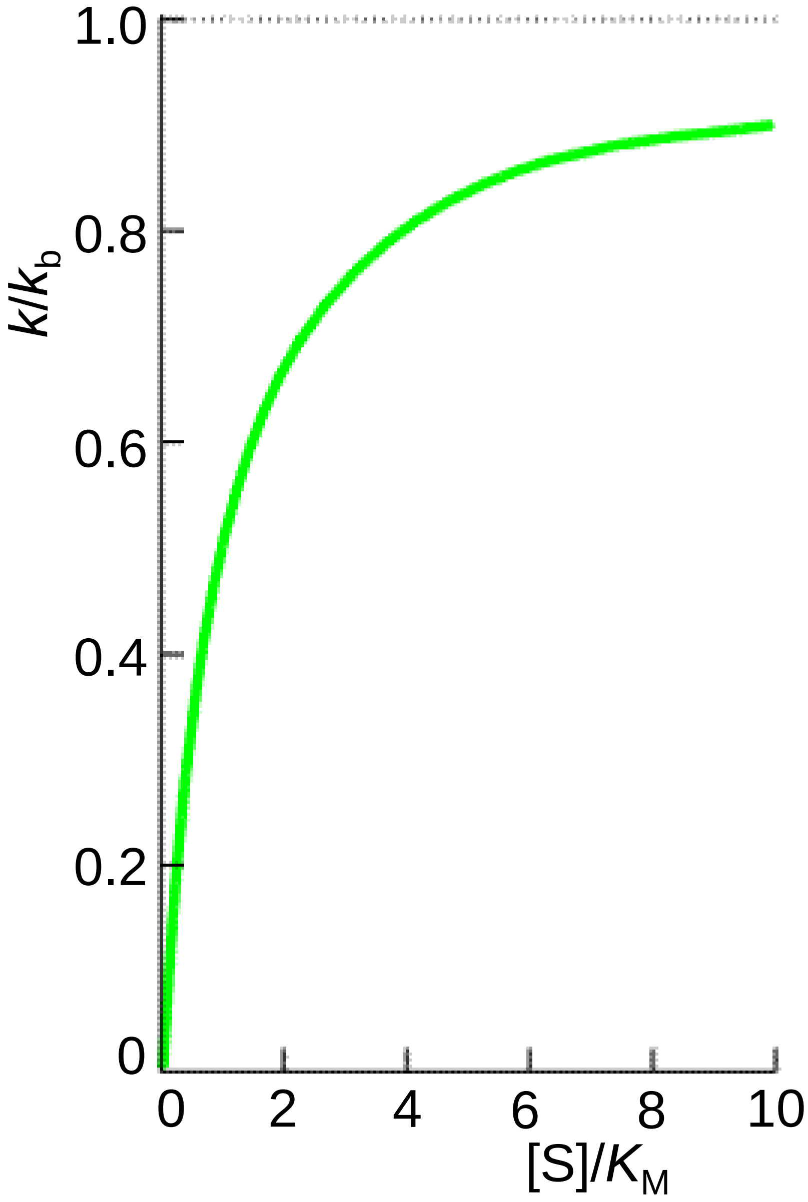
$$\therefore \frac{d[\mathrm{P}]}{dt} \approx \frac{k_a k_b[\mathrm{E}]_0[\mathrm{S}]}{k_b + k_a^{'} + k_a[\mathrm{S}]} = \frac{k_b[\mathrm{E}]_0[\mathrm{S}]}{k_M + [\mathrm{S}]}$$

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.

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

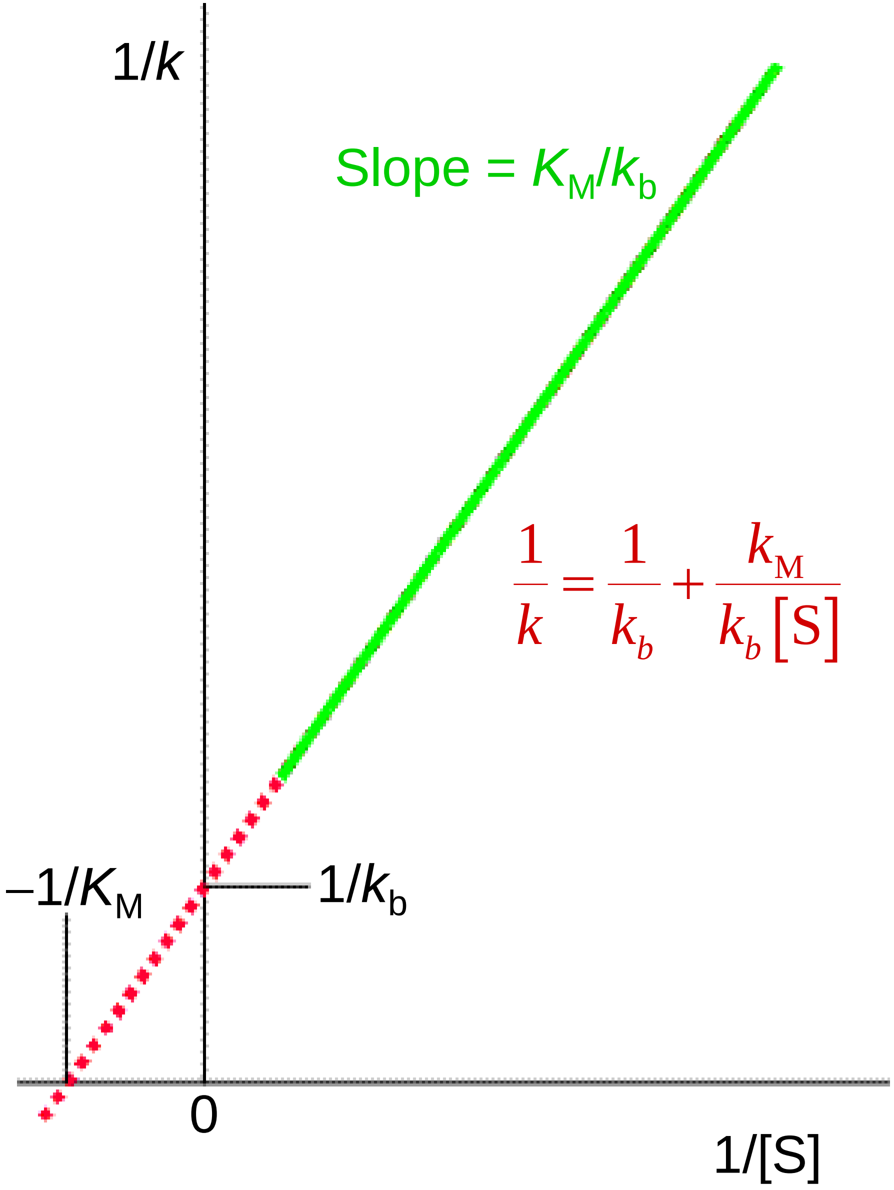
$$\frac{1}{k} = \frac{1}{k_b} + \frac{k_M}{k_b[\mathrm{S}]}$$



$$\frac{d[\mathrm{P}]}{dt} = \frac{k_b[\mathrm{E}]_0[\mathrm{S}]}{k_\mathrm{M}+[\mathrm{S}]} \cong k_1[\mathrm{E}]_0$$

$$k = \frac{k_b[\mathrm{S}]}{k_\mathrm{M}+[\mathrm{S}]} \qquad \frac{k}{k_b} = \frac{[\mathrm{S}]/k_\mathrm{M}}{1+[\mathrm{S}]/k_\mathrm{M}}$$

**Figure 23.3**
The variation of the effective rate constant *k* with substrate concentration according to the Michaelis-Menten mechanism.



$$\frac{d[\mathrm{P}]}{dt} = \frac{k_b[\mathrm{E}]_0[\mathrm{S}]}{k_\mathrm{M}+[\mathrm{S}]} \cong k_1[\mathrm{E}]_0$$

$$k = \frac{k_b[\mathrm{S}]}{k_\mathrm{M}+[\mathrm{S}]} \qquad \frac{k}{k_b} = \frac{[\mathrm{S}]/k_\mathrm{M}}{1+[\mathrm{S}]/k_\mathrm{M}}$$

$$\frac{1}{k} = \frac{1}{k_b} + \frac{k_\mathrm{M}}{k_\mathrm{b}[\mathrm{S}]}$$

**Figure 23.4**
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.

# Heterogeneous Catalysis

## Adsorption

The fractional coverage $\theta$: 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

$V_\infty$: the volume of adsorbate corresponding to complete monolayer coverage.

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

The techniques for measuring $d\theta/dt$ are flow methods, in which the sample itself acts as a pump because adsorption removes particles from the gas.

# Physisorption and Chemisorption

**Physisorption:** – van der Waals interaction 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 $\approx -200\ kJ/mol$

– usu., $\Delta H<0$, $\Delta S<0$ (due to the reduction of translational freedom of adsorbate)

## 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.

The dynamic equilibrium

$$\mathrm{A}(g)+\mathrm{M}(\text{surface}) \underset{k_d}{\overset{k_a}{\rightleftarrows}} \mathrm{AM}(\text{surface})$$

The rate of adsorption

$$\frac{d\theta}{dt}=k_a pN\left(1-\theta\right)$$

$p$ : the partial pressure of A

$N$ : the total number of adsorption sites

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

The rate of desorption

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

At equilibrium, there is no net change.

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

$$\therefore \theta=\frac{Kp}{1+Kp} \qquad K=\frac{k_a}{k_d}$$

Langmuir isotherm

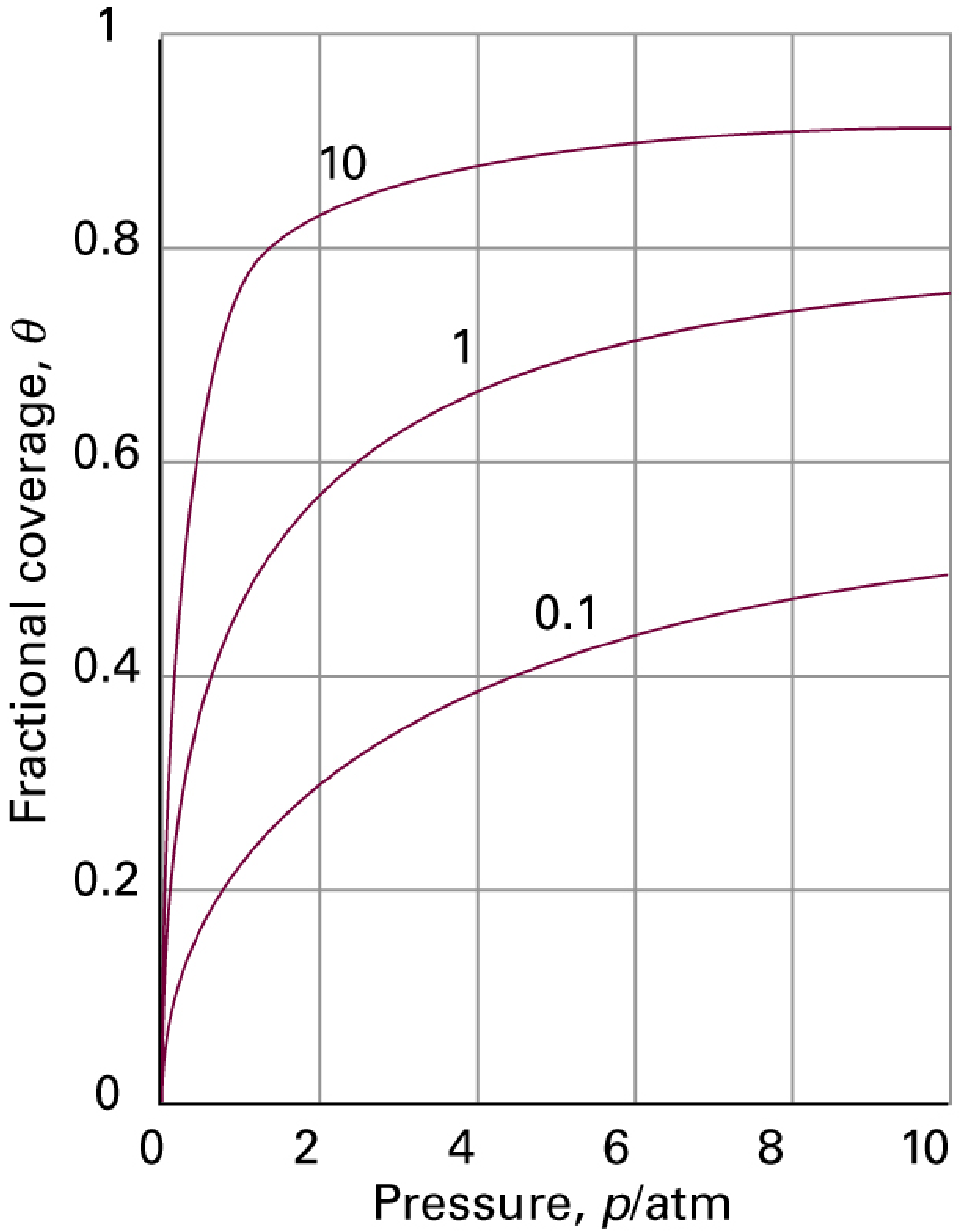


**Figure 23.5**
The Langmuir isotherm for non-dissociative adsorption for different values of *K*.

## 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

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

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

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 $V_\infty = 111\ \text{cm}^3$. The intercept at $p$=0 is 1.20, so

$$K = \frac{1}{(111\ \text{cm}^3)\times(1.20\ \text{kPa cm}^{-3})} = 7.51\times10^{-3}\ \text{kPa}^{-1}$$

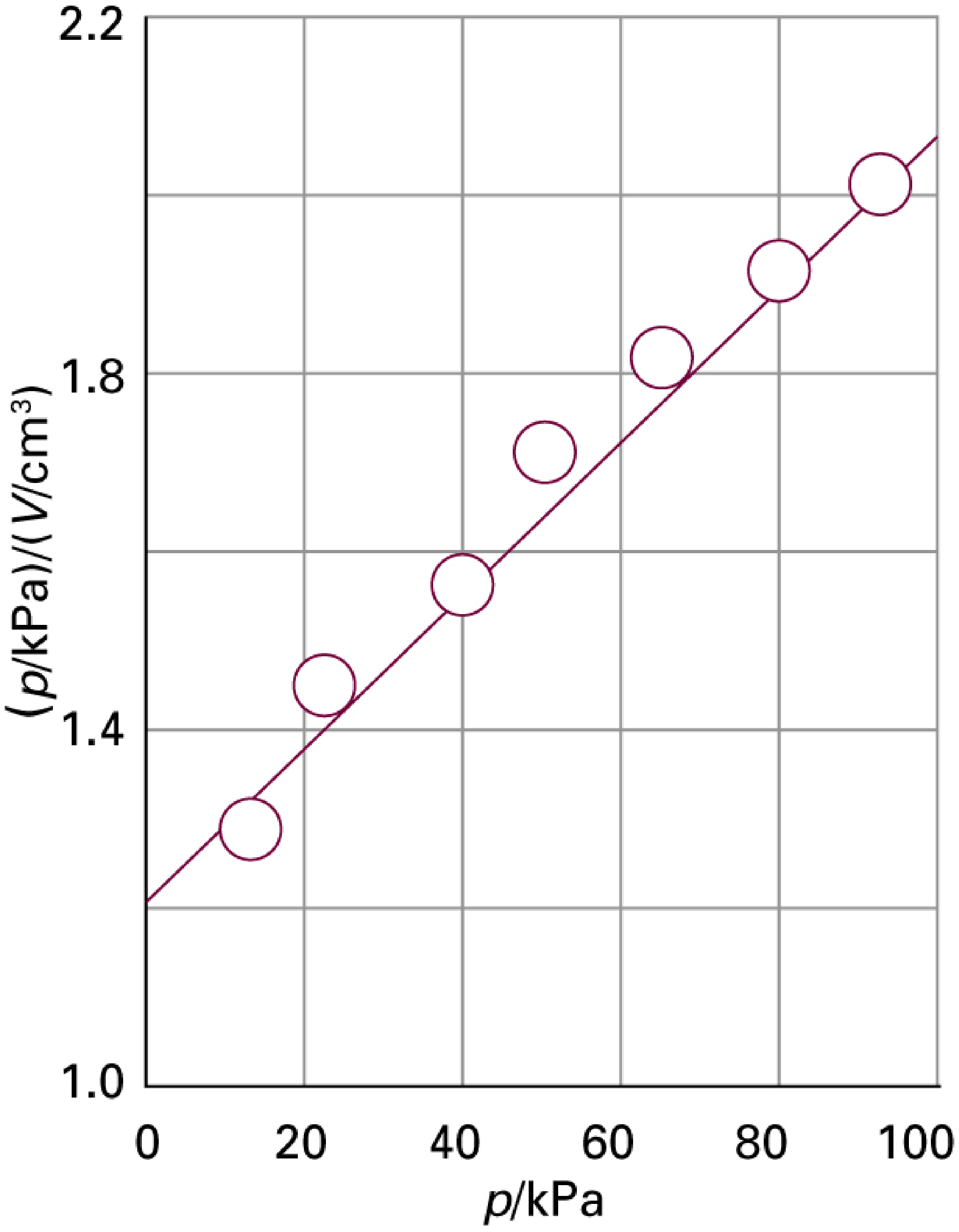


**Figure 23.6**
The plot of the data in Example. As illustrated here, the Langmuir isotherm predicts that a straight line should be obtained when $p/V$ is plotted against $p$.

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,

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

The rate of desorption

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

At equilibrium

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

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

Langmuir isotherm for adsorption with dissociation

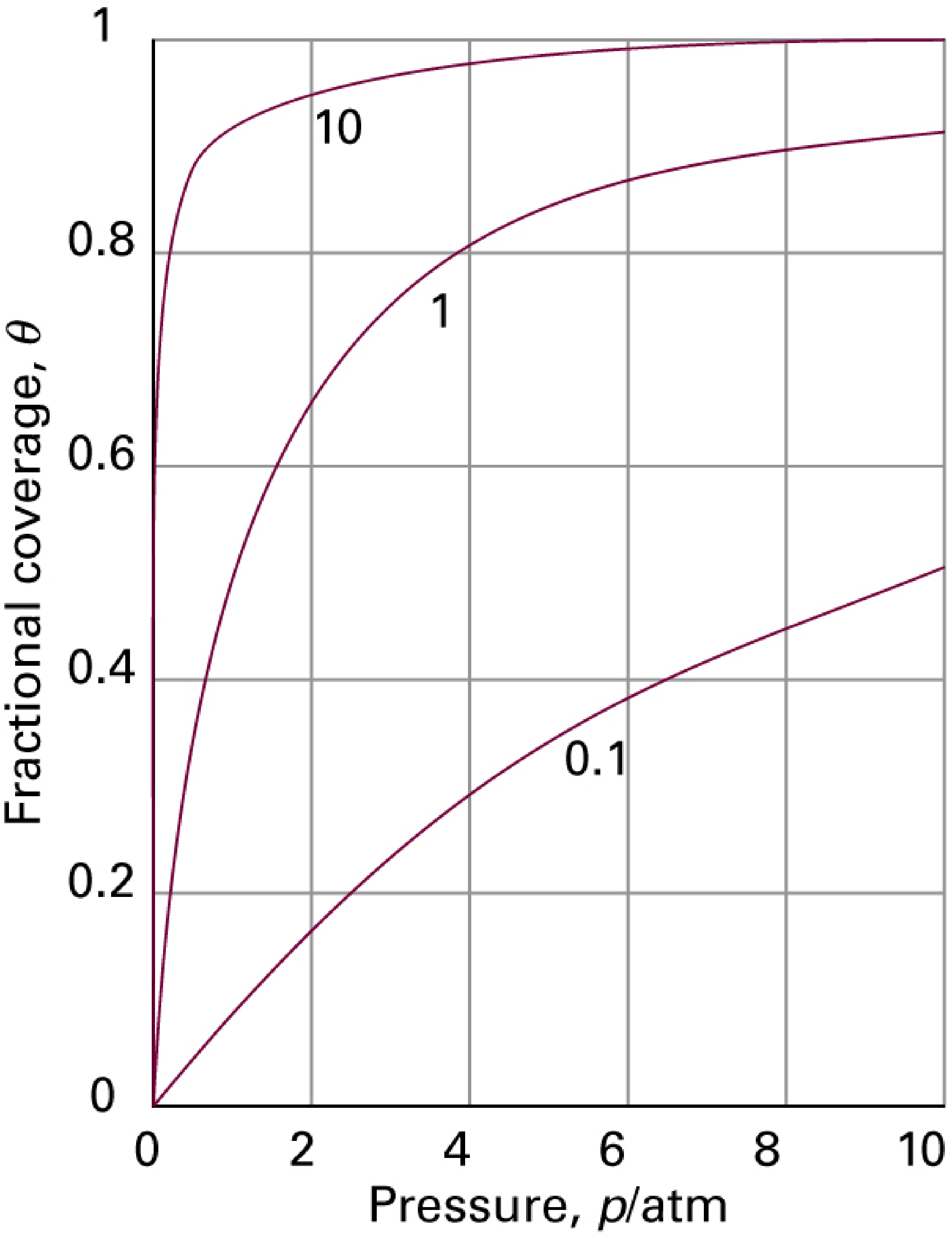


**Figure 23.7**
The Langmuir isotherm for dissociative adsorption,
$X_2(g) \rightarrow 2X(\text{surface})$
for different values of $K$.

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

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H^{\mathrm{o}}_{\mathrm{ads}}}{RT^2}$$

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 $\mathrm{cm}^3$ 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 $\theta$ is constant,

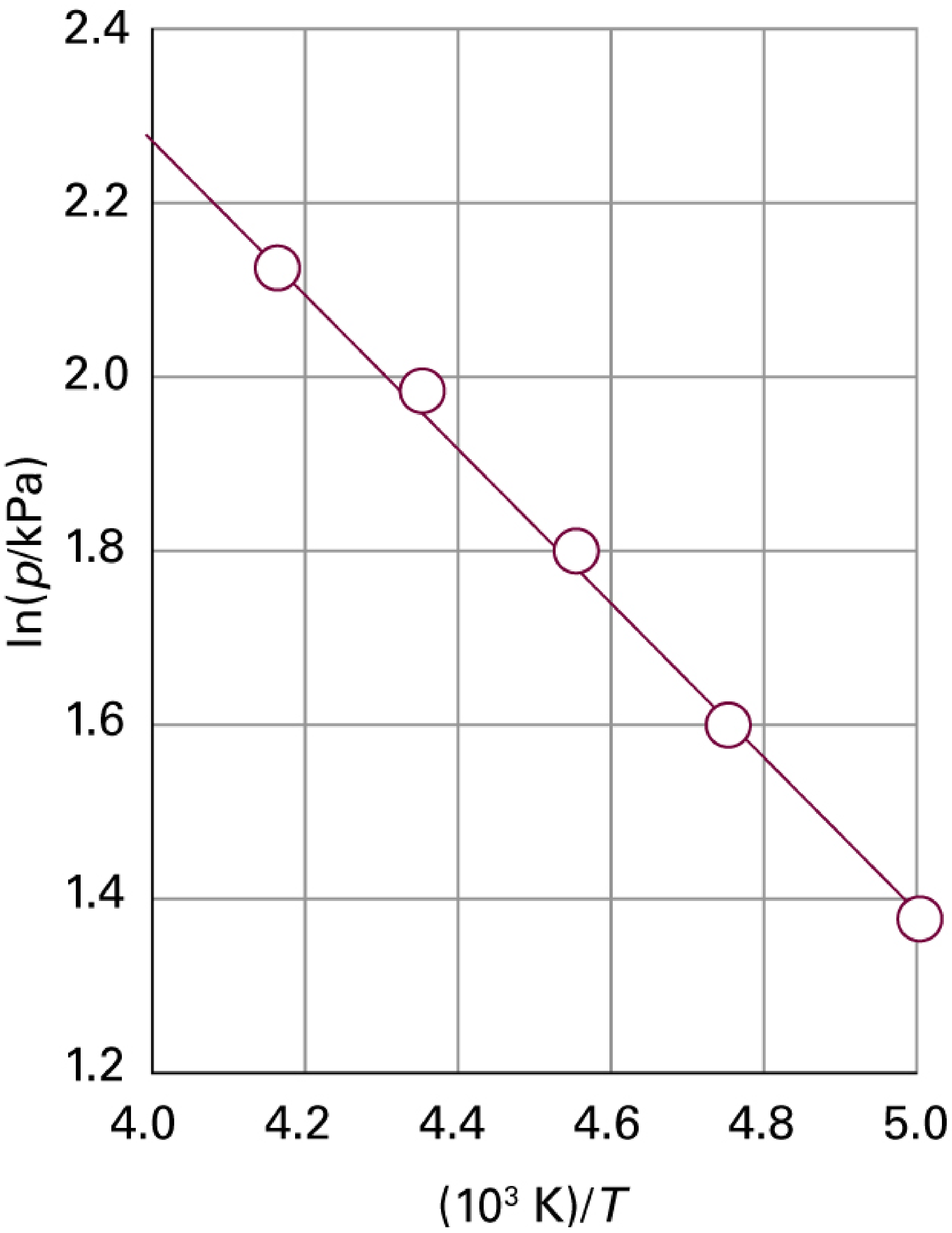
$$\ln K + \ln p = \text{constant}$$

$$\therefore \left(\frac{\partial \ln p}{\partial T}\right)_\theta = -\left(\frac{\partial \ln K}{\partial T}\right)_\theta = -\frac{\Delta H^\circ_{\text{ads}}}{RT_2}$$

With $d\left(1/T\right)/dT = -1/T^2$,

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

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



The slope is –0.904, so

$$\Delta H^{\circ}_{\mathrm{ads}} = -(0.904\times 10^{3}\ K)\times R$$
$$= -7.52\ \mathrm{kJ\,mol^{-1}}$$

**Figure 23.8**
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

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

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

$p^*$ : the vapor pressure above a layer adsorbate, resembling a pure bulk liquid

$V_{\mathrm{mon}}$ : the volume corresponding to monolayer coverage

$c$ : constant $\quad c = e^{\left(\Delta H^\circ_{\mathrm{des}} - \Delta H^\circ_{\mathrm{vap}}\right)/RT}$

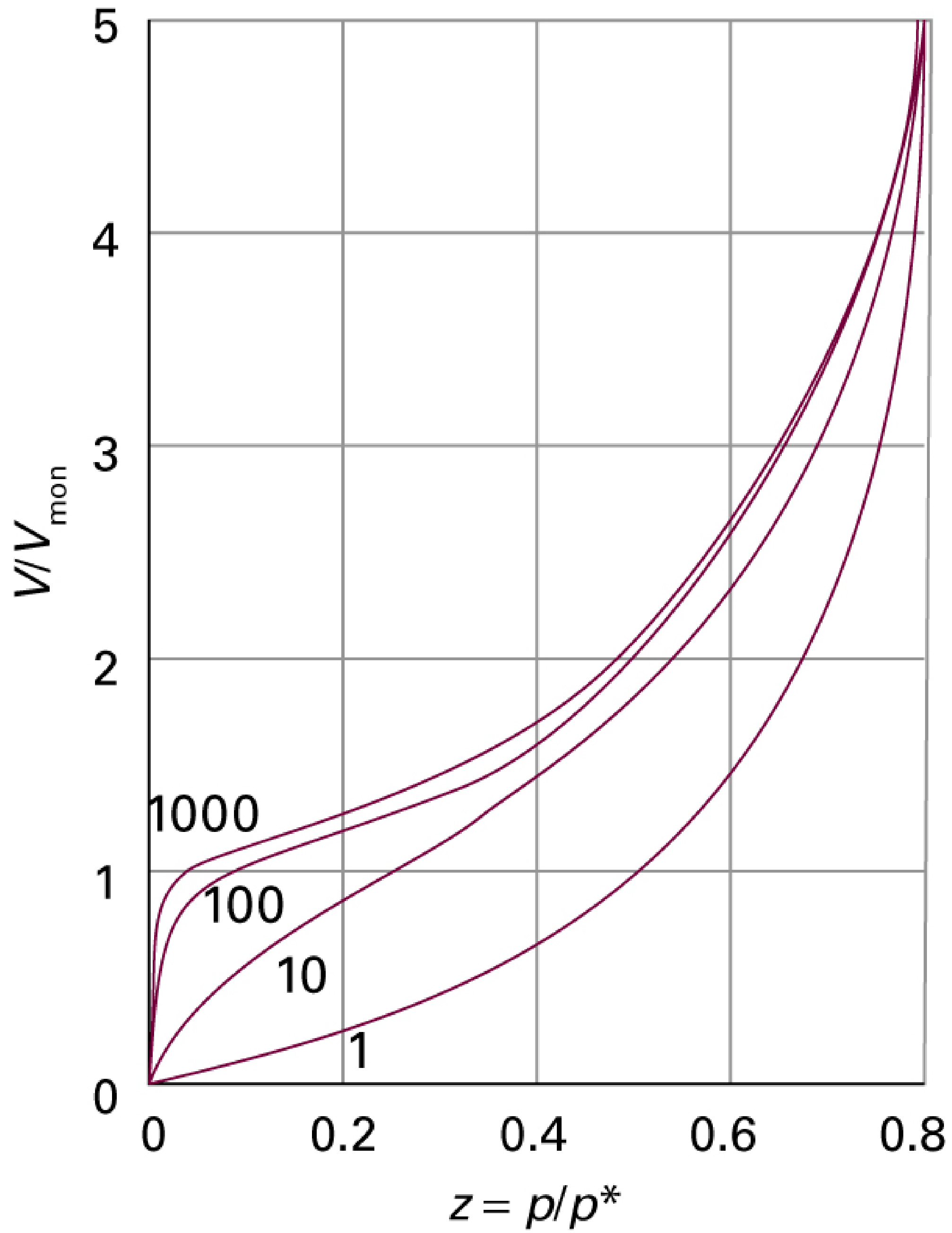


**Figure 23.9**

Plot of the BET isotherm for different values of *c* . The value of $V/V_{\mathrm{mon}}$ 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 $V_{\text{mon}}$ and $c$.

| $p$/kPa | 0.160 | 1.87 | 6.11 | 11.67 | 17.02 | 21.92 | 27.29 |
|---|---|---|---|---|---|---|---|
| $V$/mm$^3$ | 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

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

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

| $p$/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

$$\frac{1}{cV_{\text{mon}}} = 3.98\times10^{-6}\ \text{mm}^{-3}$$

The slope of the line is $1.23\times10^{-2}$, so

$$\frac{c-1}{cV_{\text{mon}}} = (1.23\times10^{-2})\times10^{3}\times10^{-4}\ \text{mm}^{-3} = 1.23\times10^{-3}\ \text{mm}^{-3}$$

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

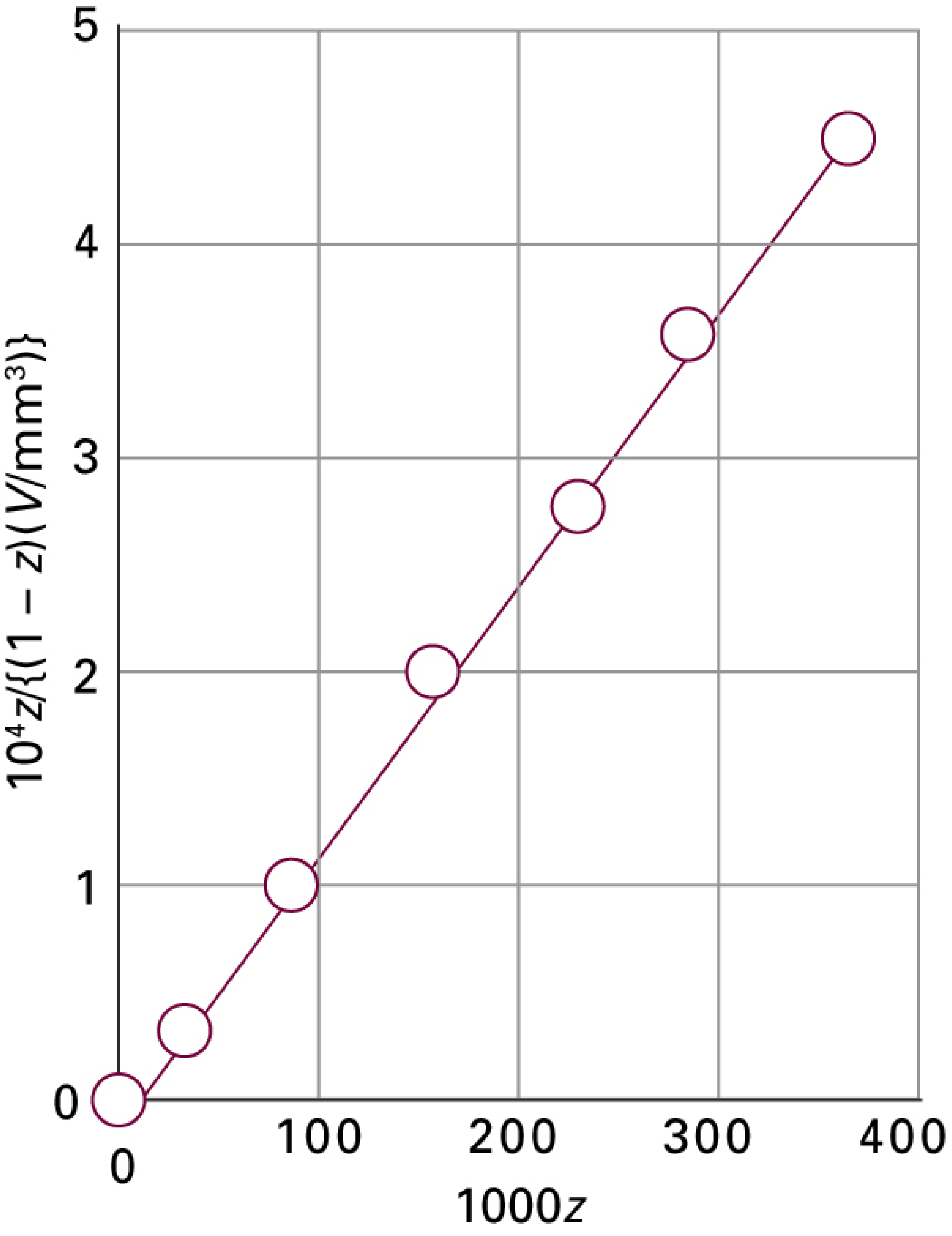


**Figure 23.10**
The BET isotherm can be tested, and the parameters determined, by plotting $z/(1-z)V$ against $z=p/p^*$.

$c \gg 1,$ 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

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