18

CHAPTER

# CHEMICAL KINETICS

**18.1** Rates of Chemical Reactions

**18.2** Rate Laws

**18.3** Reaction Mechanisms

**18.4** Reaction Mechanisms and Rate

**18.5** Effect of Temperature on Reaction Rates

**18.6** Molecular Theories of Elementary Reactions

**18.7** Reactions in Solution

**18.8** Catalysis

# Thermodynamics

Equilibrium

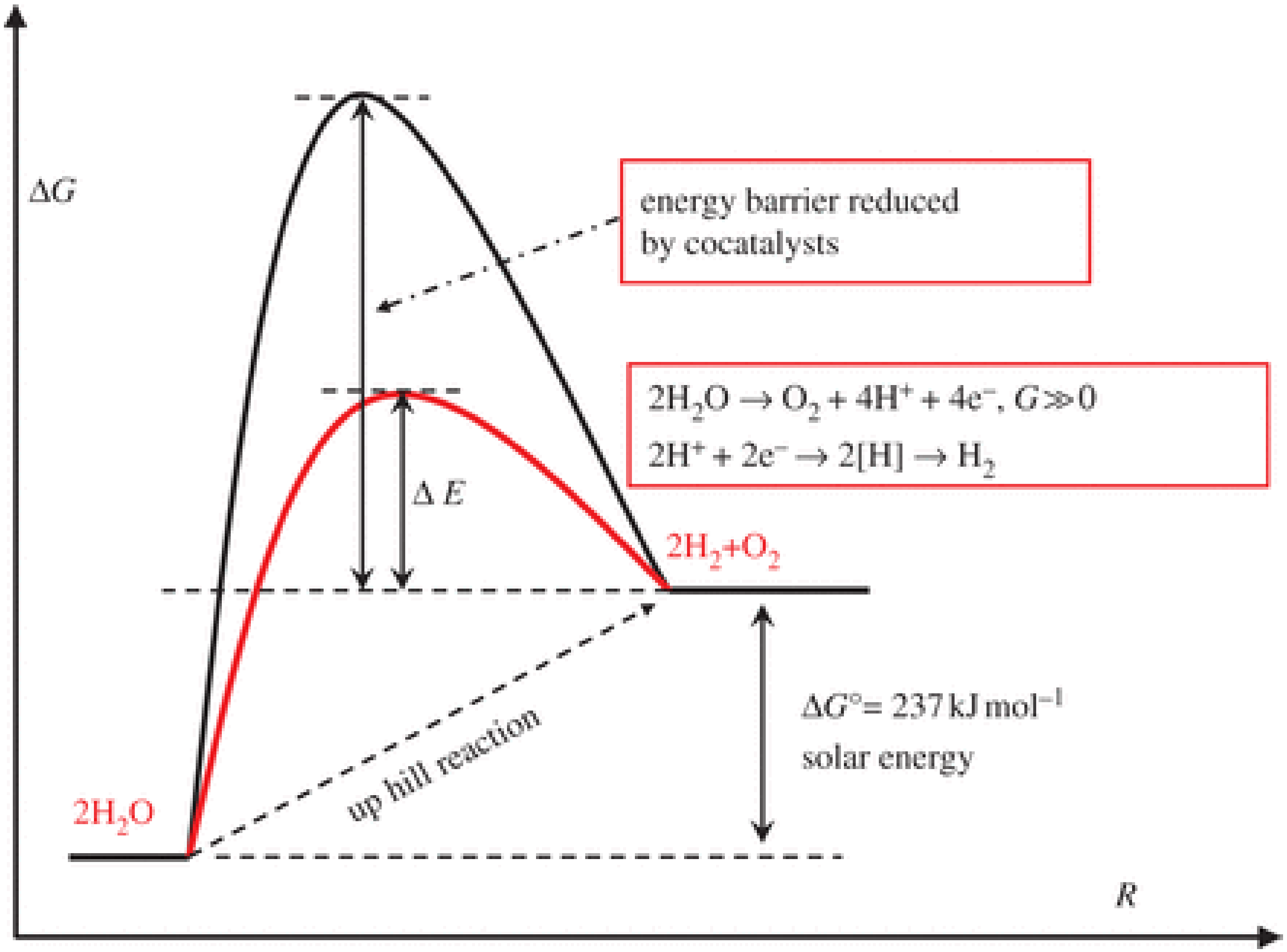
t = infinite

# Kinetics

Reaction rate

t = finite

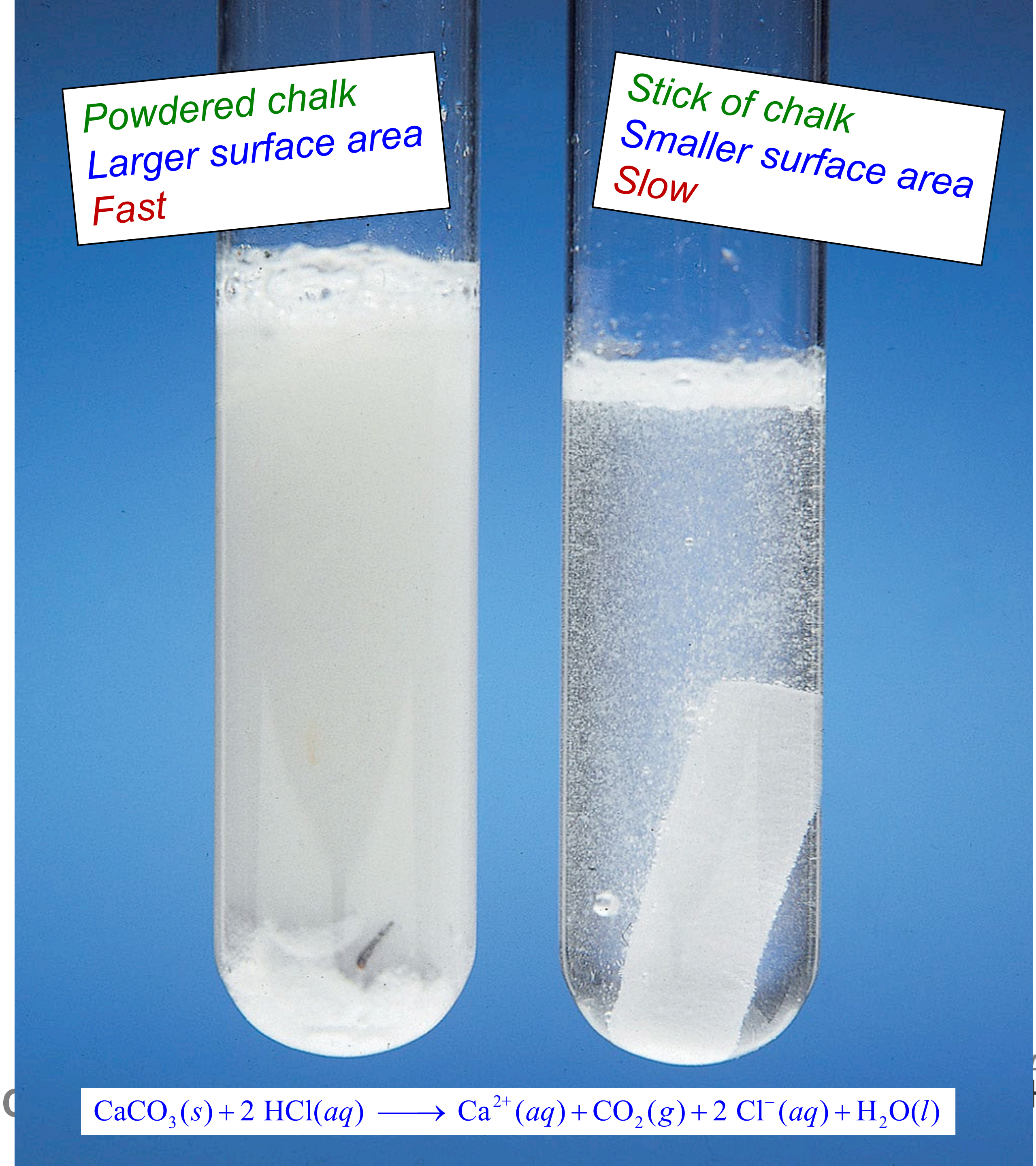
# Water Splitting



energy barrier reduced
by cocatalysts

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-, G \gg 0$
$2H^+ + 2e^- \rightarrow 2[H] \rightarrow H_2$

$\Delta G° = 237\ \mathrm{kJ\ mol^{-1}}$
solar energy



Powdered chalk
Larger surface area
Fast

Stick of chalk
Smaller surface area
Slow

$$CaCO_3(s) + 2\ HCl(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + 2\ Cl^-(aq) + H_2O(l)$$

# 18.1 RATES OF CHEMICAL REACTIONS

- **Rate depends on *concentration***

**Fig. 18.1** Zn + $H_2SO_4$ (*dilute*) Zn + $H_2SO_4$ (*conc*)

- **Rate also depends on *physical forms***

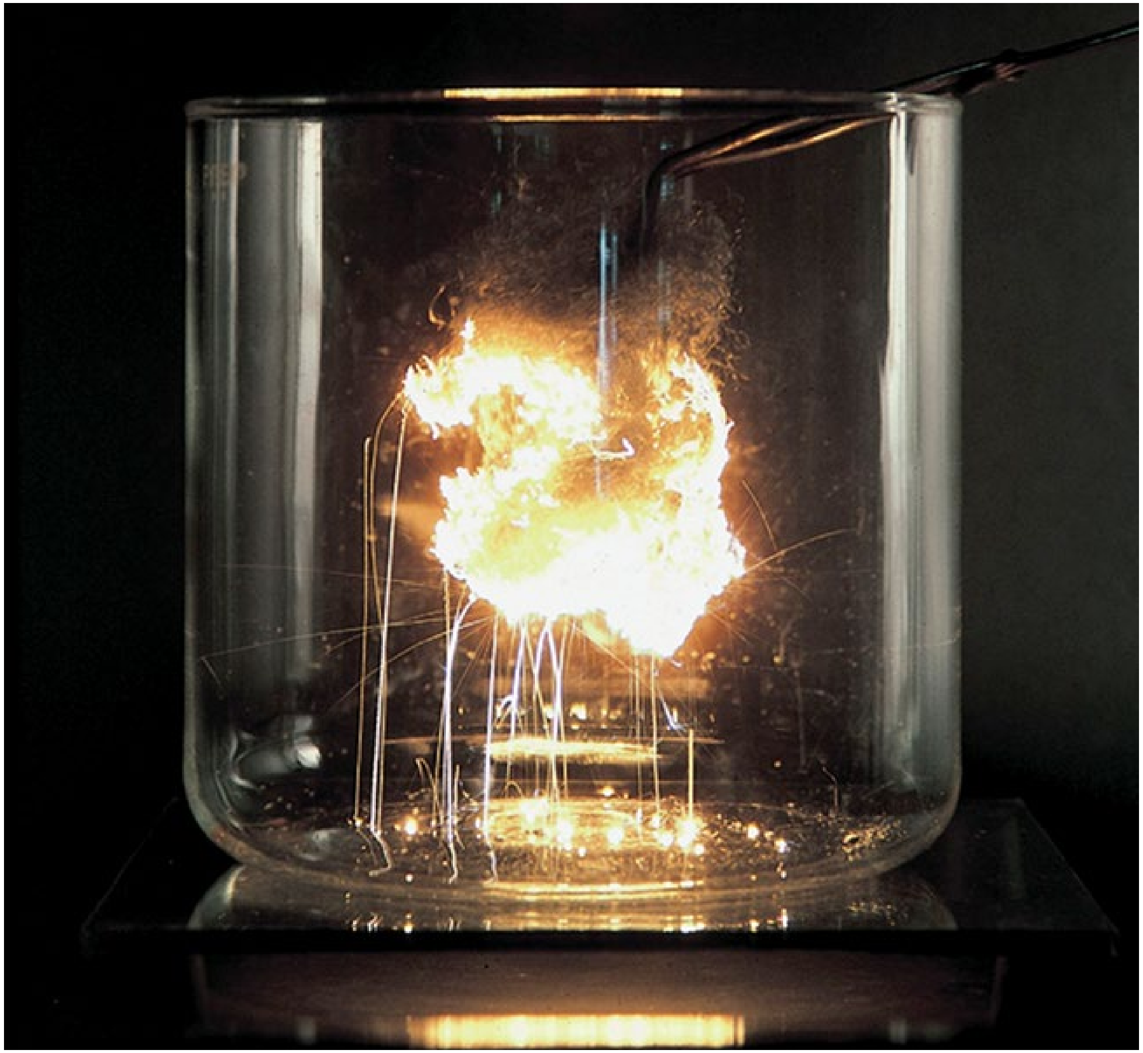


**Fig. 18.2** Steel wool burning in $O_2$

# ◆ Measuring Reaction rates

- **Quenching Method** ~ for slow reactions

  Rapid cooling at low temperature, chemical analysis

- **Absorption Spectroscopy**

  Real time measurement of amount of absorbed light by a reactant at a particular wavelength

  ~ Proportional to concentration

- **Average rate**

  Change in concentration / change in time ~ $\Delta[A]/\Delta t$

  Depends on the selected time interval

$$\text{Average reaction rate} = \frac{\text{Change in concentration}}{\text{Change in time}}$$

**Ex.** $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

**Average rate** $= \dfrac{\Delta[\mathrm{NO}]}{\Delta t} = \dfrac{[\mathrm{NO}]_\mathrm{f} - [\mathrm{NO}]_\mathrm{i}}{t_\mathrm{f} - t_\mathrm{i}}$

$$\text{average rate}\Big|_{0\mathrm{s}}^{50\mathrm{s}} = \frac{\Delta[\mathrm{NO}]}{\Delta t} = \frac{(0.0160 - 0)\ \mathrm{mol\ L^{-1}}}{(50-0)\ \mathrm{s}} = 3.2\times10^{-4}\ \mathrm{mol\ L^{-1}s^{-1}}$$

$$\text{average rate}\Big|_{50\mathrm{s}}^{100\mathrm{s}} = \frac{\Delta[\mathrm{NO}]}{\Delta t} = \frac{(0.0249 - 0.0160)\ \mathrm{mol\ L^{-1}}}{(100-50)\ \mathrm{s}} = 1.6\times10^{-4}\ \mathrm{mol\ L^{-1}s^{-1}}$$

→ Average rate depends on the time interval chosen

- **Instantaneous rate** $= d[\mathrm{A}]/dt$

$$\text{instantaneous rate} = \lim_{\Delta t \to 0} \frac{[\mathrm{NO}]_{t+\Delta t} - [\mathrm{NO}]_t}{\Delta t} = \frac{d[\mathrm{NO}]}{dt}$$

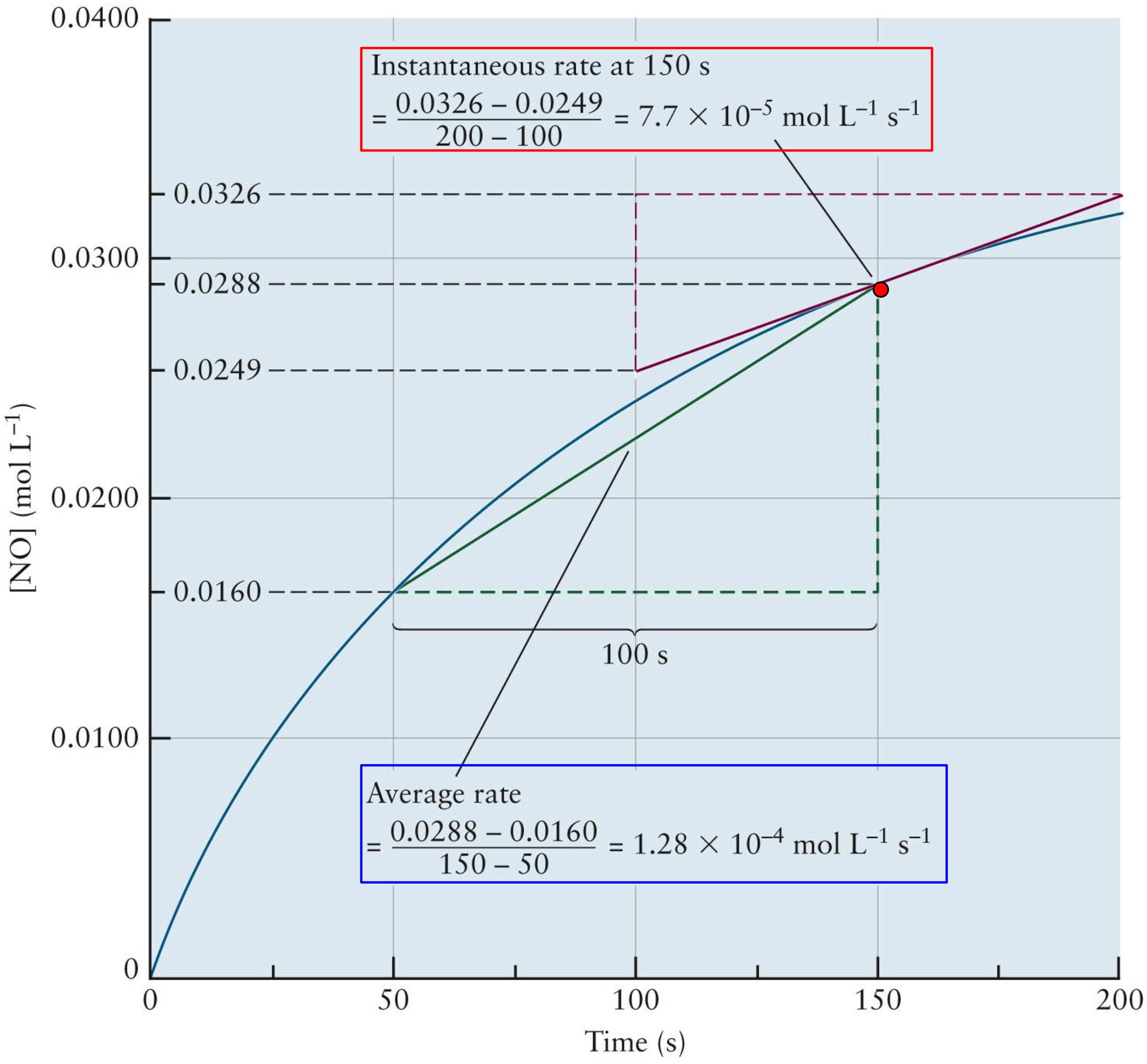
$$\text{(instantaneous) rate} = -\frac{d[\mathrm{NO_2}]}{dt} = -\frac{d[\mathrm{CO}]}{dt} = \frac{d[\mathrm{NO}]}{dt} = \frac{d[\mathrm{CO_2}]}{dt}$$

- **initial rate** ~ instantaneous rate at the beginning of reaction

In general,

$$a\ \mathrm{A} + b\ \mathrm{B} \longrightarrow c\ \mathrm{C} + d\ \mathrm{D}$$

$$\boxed{\text{rate} = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = -\frac{1}{b}\frac{d[\mathrm{B}]}{dt} = \frac{1}{c}\frac{d[\mathrm{C}]}{dt} = \frac{1}{d}\frac{d[\mathrm{D}]}{dt}}$$



Instantaneous rate at 150 s

$$= \frac{0.0326 - 0.0249}{200 - 100} = 7.7 \times 10^{-5}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

Average rate

$$= \frac{0.0288 - 0.0160}{150 - 50} = 1.28 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

instantaneous rate

$$= \frac{d[\text{NO}]}{dt}$$

$$\text{average rate} = \frac{\Delta[\text{NO}]}{\Delta t} = \frac{[\text{NO}]_\text{f} - [\text{NO}]_\text{i}}{t_\text{f} - t_\text{i}}$$

**Fig. 18.3** Time dependence of the concentration of NO in the reaction,

$$\text{NO}_2(g) + \text{CO}(g) \longrightarrow \text{NO}(g) + \text{CO}_2(g)$$

# 18.2 RATE LAWS

## ◆ Order of reaction

### ➢ *Rate Law*

~ Concentration dependence of rate

In general, $aA + bB \longrightarrow \text{products}$

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = k[A]^n[B]^m$$

*k*: rate constant (or rate coefficient)

*n*: reaction order with respect to A

*m*: reaction order w.r.t. B

*n* + *m*: overall reaction order

**Ex.** $N_2O_5\ (g) \rightarrow 2\ NO_2\ (g) + ½\ O_2\ (g)$

rate law: rate = $k\ [N_2O_5]$

1st order reaction

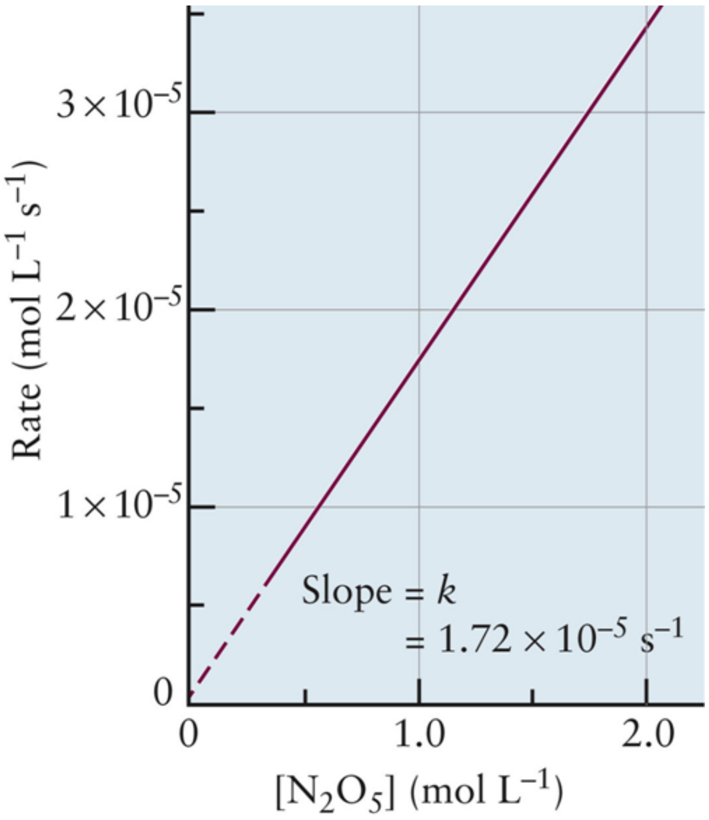
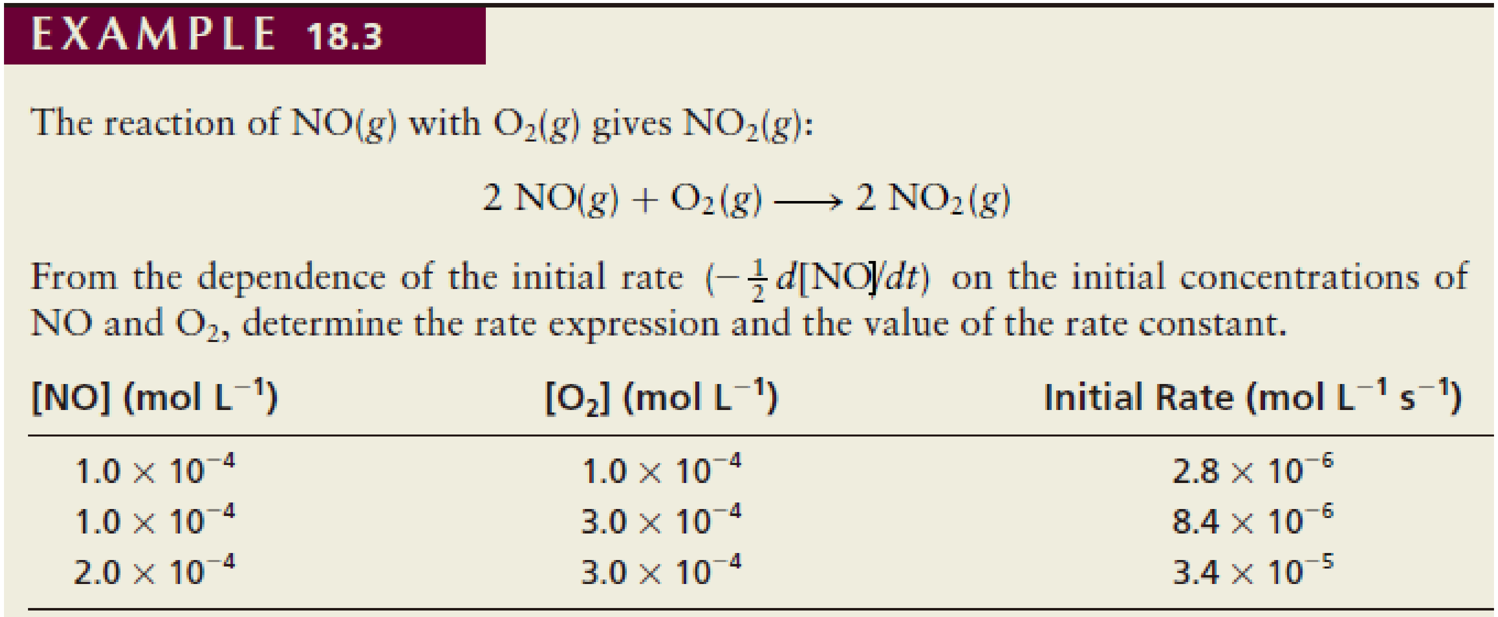


**Fig. 18.4** Rate of decomposition of $N_2O_5$ at 25°C is proportional to its concentration.



## EXAMPLE 18.3

The reaction of $NO(g)$ with $O_2(g)$ gives $NO_2(g)$:

$$2\ \mathrm{NO}(g) + \mathrm{O_2}(g) \longrightarrow 2\ \mathrm{NO_2}(g)$$

From the dependence of the initial rate $(-\frac{1}{2}\,d[\mathrm{NO}]/dt)$ on the initial concentrations of NO and $O_2$, determine the rate expression and the value of the rate constant.

| [NO] (mol $L^{-1}$) | [$O_2$] (mol $L^{-1}$) | Initial Rate (mol $L^{-1}$ $s^{-1}$) |
|---|---|---|
| $1.0 \times 10^{-4}$ | $1.0 \times 10^{-4}$ | $2.8 \times 10^{-6}$ |
| $1.0 \times 10^{-4}$ | $3.0 \times 10^{-4}$ | $8.4 \times 10^{-6}$ |
| $2.0 \times 10^{-4}$ | $3.0 \times 10^{-4}$ | $3.4 \times 10^{-5}$ |

$$\text{rate} = k[\mathrm{O_2}][\mathrm{NO}]^2$$ ← from the experiment

$$2.8 \times 10^{-6}\ \mathrm{mol\ L^{-1}\ s^{-1}} = k(1.0 \times 10^{-4}\ \mathrm{mol\ L^{-1}})(1.0 \times 10^{-4}\ \mathrm{mol\ L^{-1}})^2$$

$$k = 2.8 \times 10^{6}\ \mathrm{L^2\ mol^{-2}\ s^{-1}}$$

# ◆ Integrated Rate Laws

## ➢ First-Order Reactions: A → products

$$\text{rate} = -\frac{d[\text{A}]}{dt} = k[\text{A}] \quad \rightarrow \quad \text{rate} = -\frac{dc}{dt} = kc$$

$$\int_{c_0}^{c} \frac{1}{c}\, dc = -k\int_0^t dt \quad \rightarrow \quad \ln c - \ln c_0 = -kt$$

$$\boxed{\ln\frac{c}{c_0} = -kt \qquad \text{or} \qquad c = c_0 e^{-kt}}$$

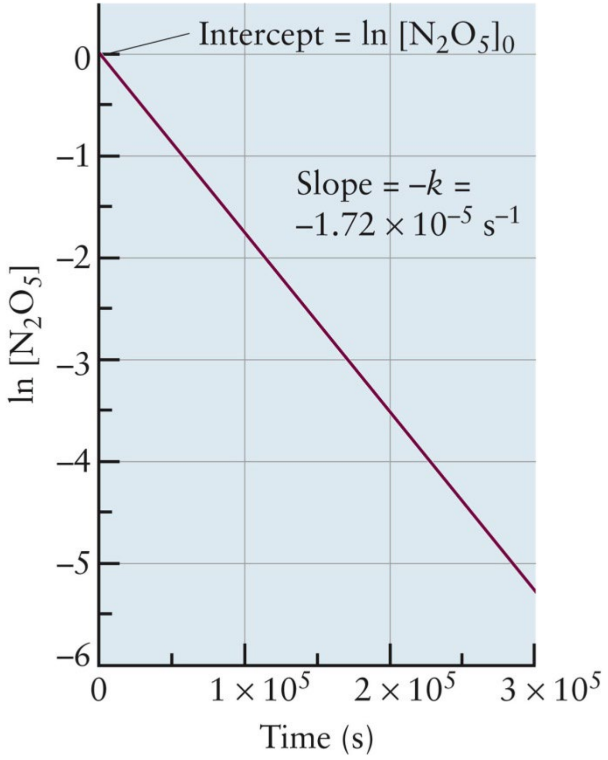
❖ **Half-life ($t_{1/2}$):** At $t_{1/2}$, $c = c_0/2$ .

$$-kt_{1/2} = \ln\left[\frac{c}{c_0}\right] = \ln\left[\frac{c_0/2}{c_0}\right] = -\ln 2$$

$$\boxed{t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k}}$$

→ independent of $c_0$

**Ex.** $N_2O_5\ (g) \rightarrow 2\ NO_2\ (g) + ½\ O_2\ (g)$ rate = $k\ [N_2O_5]$



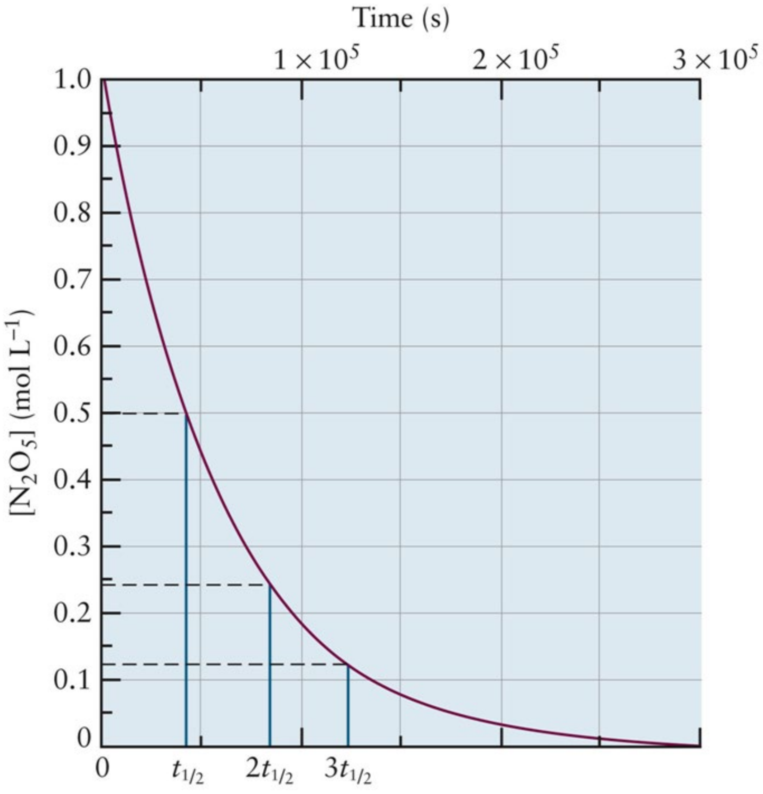


**Fig. 18.5** Decomposition of $N_2O_5$ in a 1st order reaction gives a straight line with negative slope in a plot of $\ln[N_2O_5]$ vs. time.

**Fig. 18.6** The same data as in Fig. 18.5 plotted in a $[N_2O_5]$ vs. time. The half-life, $t_{1/2}$, is the time it takes for the concentration to be reduced to half its initial value.

## ➢ Second-Order Reactions: A + A → products

$$[A] = c \quad \rightarrow \quad \text{rate} = -\frac{1}{2}\frac{dc}{dt} = kc^2$$

$$\int_{c_0}^{c} \frac{1}{c^2}\,dc = -2k\int_0^t dt \qquad \boxed{\frac{1}{c} = \frac{1}{c_0} + 2kt}$$

### ❖ Half-life ($t_{1/2}$)

$$\frac{1}{c_0/2} = \frac{1}{c_0} + 2kt_{1/2} \qquad \boxed{t_{1/2} = \frac{1}{2kc_0}}$$

**Ex.** $2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$

$$\text{rate} = -\frac{1}{2}\frac{d[NO_2]}{dt} = k[NO_2]^2$$

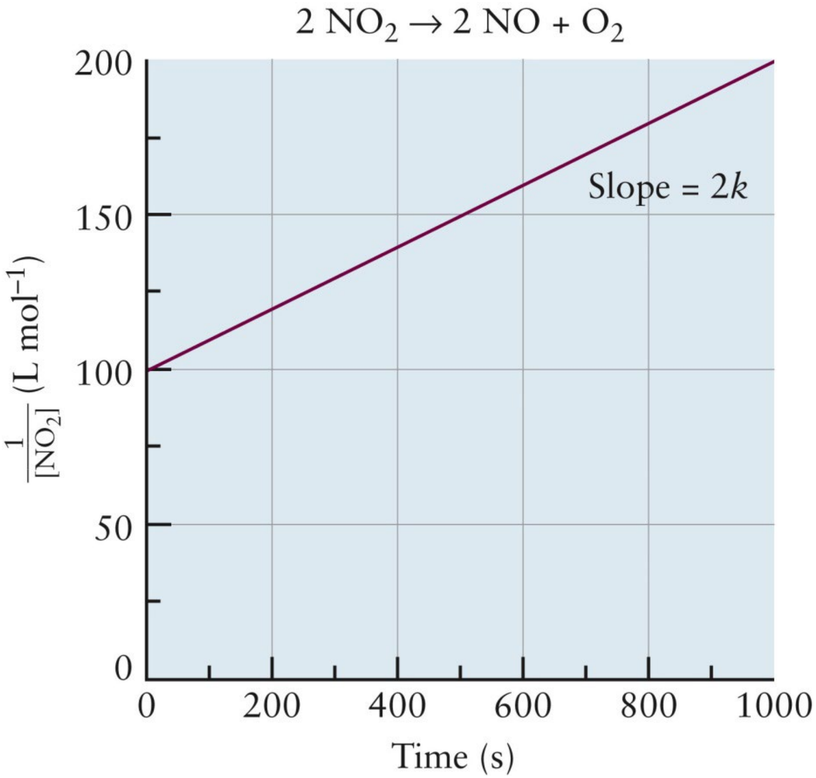


**Fig. 18.7** Decomposition of $NO_2$ in a 2nd order reaction gives a straight line with positive slope in a plot of $[NO_2]^{-1}$ vs. time.

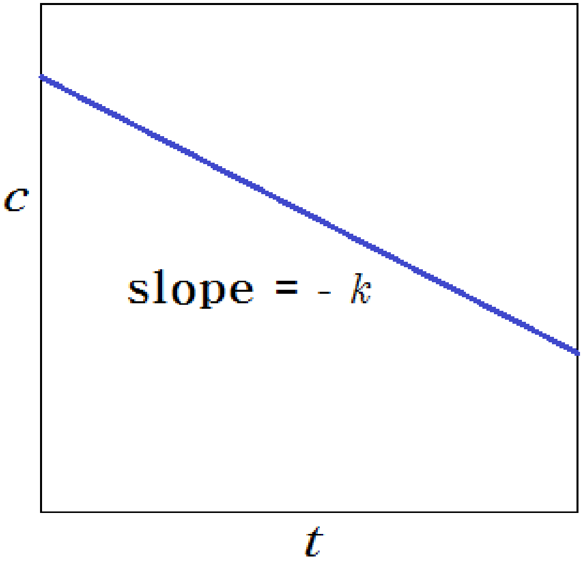
## ➢ Zeroth-Order Reactions: A + A → products

On solid surface ~ rate depends on desorption rate of *product* !

$$\text{rate} = \frac{dc}{dt} = -kc^0 = -k$$

$$\int_{c_0}^{c} dc = -k\int_0^t dt$$

$$\boxed{\therefore\ c = c_0 - kt}$$



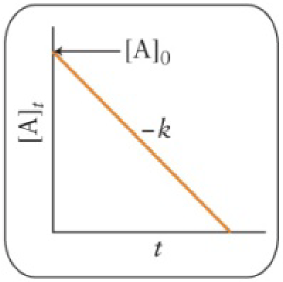
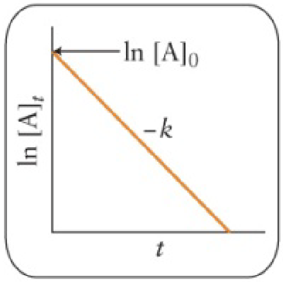
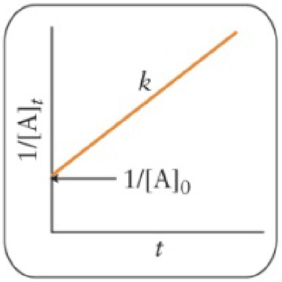
❖ **Half-life** ($t_{1/2}$)

$$c_0/2 = c_0 - kt_{1/2}$$

$$\boxed{t_{1/2} = \frac{c_0}{2k}}$$

**Ex.** $N_2O(g) \rightarrow N_2(g) + \frac{1}{2} O_2(g)$ on the surface of hot Pt

# TABLE 14.2 Rate Law Summary

| | Order of reaction | | |
|---|---|---|---|
| | 0 | 1 | 2 |
| Rate law | Rate = $k$ | Rate = $k[A]$ | Rate = $k[A]^2$ |
| Integrated rate law | $[A]_t = -kt + [A]_0$ | $[A]_t = [A]_0 e^{-kt}$ | $[A]_t = \frac{[A]_0}{1 + [A]_0 kt}$<br>$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$ |
| Plot to determine order |  |  |  |
| Slope of the line plotted | $-k$ | $-k$ | $k$ |
| Half-life | $t_{1/2} = \frac{[A]_0}{2k}$<br>(not used) | $t_{1/2} = \frac{\ln 2}{k} \approx \frac{0.693}{k}$ | $t_{1/2} = \frac{1}{k[A]_0}$<br>(not used) |

# 18.3 REACTION MECHANISMS

## ◆ Elementary Reactions

**Order of reaction = Molecularity**

- Unimolecular Reaction, (1st-order): A → products

  Ex) $N_2O_5^*(g) \rightarrow NO_2(g) + NO_3(g)$, rate = $k\,[N_2O_5^*]$

- Bimolecular Reaction, (2nd-order): A + A (or B) → products

  Ex) $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$, rate = $k\,[NO][O_3]$

- Termolecular Reaction, (3rd-order): A + B + C → products

  Ex) $I(g) + I(g) + Ar(g) \rightarrow I_2(g) + Ar(g)$, rate = $k\,[I]^2[Ar]$

# ◆ Reaction Mechanisms

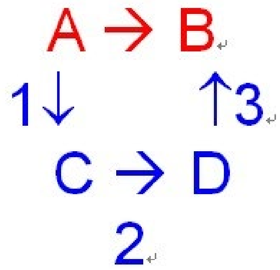
- Decomposition of overall reaction into a sequence of elementary reactions

Overall reaction: A → B

Elementary reaction 1: A → C

Elementary reaction 2: C → D

Elementary reaction 3: D → B



$$\begin{tikzcd} A \arrow[r] \arrow[d, "1"'] & B \\ C \arrow[r, "2"'] & D \arrow[u, "3"'] \end{tikzcd}$$

Overall reaction = Sum of elementary reactions:

Intermediates: C, D

❖ Rate-determining step: Slowest step in the mechanism

# ◆ Kinetics and Chemical Equilibrium

$$a\mathrm{A} + b\mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} c\mathrm{C} + d\mathrm{D}$$

If both forward & backward reactions are elementary reactions,

Forward rate = $k_1[A]^a[B]^b$

Backward rate = $k_{-1}[C]^c[D]^d$

## ◆ Principle of detailed balance

At equilibrium, forward rate = backward rate.

$$k_1\,([\mathrm{A}]_{\mathrm{eq}})^a([\mathrm{B}]_{\mathrm{eq}})^b = k_{-1}([\mathrm{C}]_{\mathrm{eq}})^c([\mathrm{D}]_{\mathrm{eq}})^d$$

## ◆ Mass action law

$$\frac{k_1}{k_{-1}} = \frac{([\mathrm{C}]_{\mathrm{eq}})^c([\mathrm{D}]_{\mathrm{eq}})^d}{([\mathrm{A}]_{\mathrm{eq}})^a([\mathrm{B}]_{\mathrm{eq}})^b} = K_{\mathrm{eq}}$$

# 18.4 REACTION MECHANISMS AND RATE

- **When the reaction-determining step is the first one…**

Ex. $2\,NO_2(g) + F_2(g) \rightarrow 2\,NO_2F(g)$, rate = $k_{obs}[NO_2][F_2]$

Reaction mechanism:

$$NO_2(g) + F_2(g) \xrightarrow{k_1} NO_2F(g) + F(g) \qquad \text{(slow)}$$

$$NO_2(g) + F(g) \xrightarrow{k_2} NO_2F(g) \qquad \text{(fast)}$$

$$\text{rate} = k_1[NO_2][F_2] \qquad \therefore\ k_{obs} = k_1$$

- **When the reaction-determining step is one or more fast steps…**

→ reaction order > 2

Ex. $2\ NO + O_2 \rightarrow 2\ NO_2$, rate = $k_{obs}[NO]^2[O_2]$

Reaction mechanism

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \qquad \text{(fast equilibrium)}$$

$$N_2O_2 + O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2\ NO_2 \qquad \text{(slow)}$$

$$\text{rate} = k_2K_1[NO]^2[O_2] \qquad \therefore\ k_{obs} = k_2K_1$$

## ❖ Fractional Order (?)

Overall reaction: $H_2 + Br_2 \rightarrow 2\,HBr$

rate = $k_{obs}[H_2][Br_2]^{1/2}$ ← determined by experiment

Reaction mechanism:

$$Br_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Br + Br + M \qquad \text{(fast)}$$

$$Br + H_2 \xrightarrow{k_2} HBr + H \qquad \text{(slow)}$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br \qquad \text{(fast)}$$

$$\text{rate} = k_2[Br][H_2]$$

$$[Br]^2/[Br_2] = K_1 = k_1 / k_{-1} \rightarrow [Br] = (K_1)^{1/2}[Br_2]^{1/2}$$

$$\boxed{\text{rate} = k_2(K_1)^{1/2}[H_2][Br_2]^{1/2}}$$

## ➢ Looks alike but different type of reaction

Overall reaction: $H_2 + I_2 \rightarrow 2\,HI$

rate = $k_{obs}[H_2][I_2]$ ← determined by experiment

Reaction mechanism (Sullivan):

$I_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} I + I + M$ (fast) $K_1 = [I]^2/[I_2]$

$I + I + H_2 \xrightarrow{k_2} 2\,HI$ (slow)

$\boxed{\text{rate} = [H_2][I]^2 = k_2K_1[H_2][I_2]}$

*cf.* $\boxed{\text{rate} = k_2(K_1)^{1/2}[H_2][Br_2]^{1/2}}$

# ◆ The Steady-State Approximation

## ❖ Lindemann's mechanism

$$N_2O_5(g) + M(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} N_2O_5^*(g) + M(g)$$

$$N_2O_5^*(g) \xrightarrow{k_2} NO_3(g) + NO_2(g)$$

Subsequent steps to form $O_2$ and $NO_2$ from $NO_3$ occur rapidly and do not affect the measured rate:

$$NO_3(g) + NO_2(g) \xrightarrow{k_3} NO(g) + NO_2(g) + O_2(g) \qquad \text{(fast)}$$

$$NO_3(g) + NO(g) \xrightarrow{k_4} 2\,NO_2(g) \qquad \text{(fast)}$$

Net rate of change of $[N_2O_5^*]$:

~ the steady-state concentration of $[N_2O_5^*]$ is unchanged throughout most of the course of the reaction

$$\frac{d[N_2O_5^*]}{dt} = 0 = k_1[N_2O_5][M] - k_{-1}[N_2O_5^*][M] - k_2[N_2O_5^*]$$

$$[\mathrm{N_2O_5^*}] = \frac{k_1[\mathrm{N_2O_5}][\mathrm{M}]}{k_2 + k_{-1}[\mathrm{M}]}$$

The rate of the overall reaction: $N_2O_5 \rightarrow 2\ NO_2 + (1/2)\ O_2$

$$\boxed{\mathrm{rate} = \frac{1}{2}\frac{d[\mathrm{NO_2}]}{dt} = k_2[\mathrm{N_2O_5^*}] = \frac{k_1 k_2[\mathrm{N_2O_5}][\mathrm{M}]}{k_2 + k_{-1}[\mathrm{M}]}}$$

~ Two limiting cases

i) Low pressure ($k_2 >> k_{-1}[M]$)

rate $\approx k_1[N_2O_5][M]$ ← 2nd-order reaction

ii) High pressure ( $k_2 << k_{-1}$ [M] )

$[N_2O_5]$ ← 1st-order reaction

## ◆ Chain Reactions

~ Photochemical reactions, Free radicals, *A*-bomb

$$CH_4(g) + F_2(g) \longrightarrow CH_3F(g) + HF(g)$$

Initiation: $CH_4 + F_2 \longrightarrow CH_3 + HF + F$

Propagation: $CH_3 + F_2 \longrightarrow CH_3F + F$

Propagation: $CH_4 + F \longrightarrow CH_3 + HF$

Termination: $CH_3 + F + M \longrightarrow CH_3F + M$

Branching Chain Reactions:

$$H(g) + O_2(g) \longrightarrow OH(g) + O(g)$$

$$O(g) + H_2(g) \longrightarrow OH(g) + H(g)$$

# 18.5 EFFECT OF TEMPERATURE ON REACTION RATES

## ◆ Gas-Phase Reaction Rate Constants

### ❖ Arrhenius Law (1889)

$$\boxed{k = Ae^{-E_a/RT}} \rightarrow \boxed{\ln k = \ln A - \frac{E_a}{RT}}$$

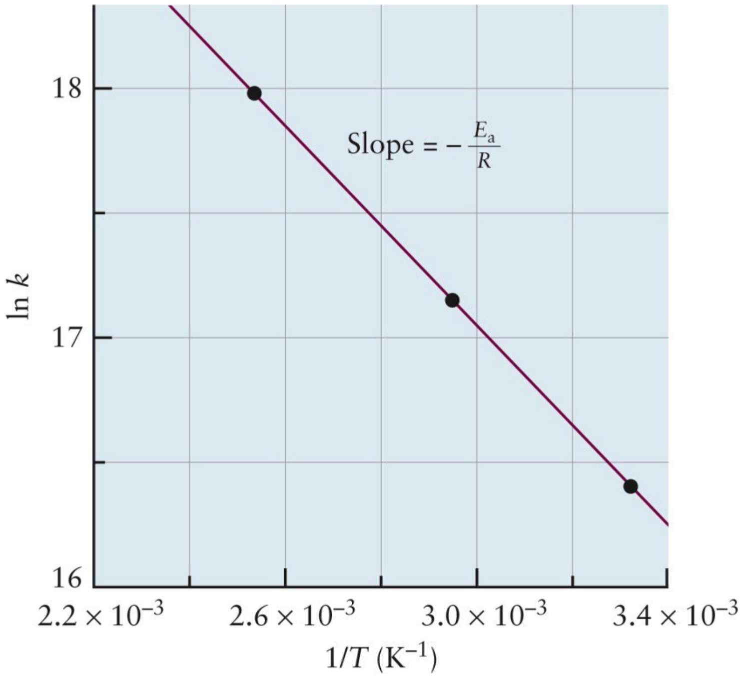


**Fig.18.9** An Arrhenius plot of ln *k* vs. 1/*T*. An extrapolation to 1/*T* = 0 gives the constant ln *A* from the intercept of this line.

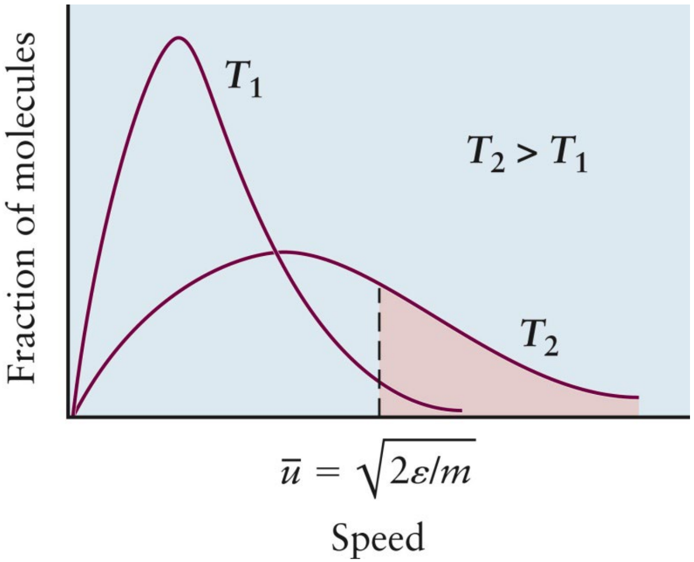


**Fig.18.10** The temperature dependence of the Maxwell-Boltzmann distribution of molecular energy plotted against the average speed, $\bar{u}$.

$A$: Pre-exponential factor

~ Collision frequency, Spatial conformation

$E_a$: Activation energy

~ Effective collision intensity for reaction to occur

~ A threshold energy for reaction

$\exp(-E_a/RT)$

~ Fraction of molecules exceeding the critical energy $E_a$

- Rate constant at $T_1$ vs. rate constant at $T_2$

$\ln k_1 = \ln A - E_a/RT_1$ , $\ln k_2 = \ln A - E_a/RT_2$

$$\boxed{\ln k_1 - \ln k_2 = \ln \frac{k_1}{k_2} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

# The Reaction Coordinate and the Activated Complex

- Reaction coordinate (or path)

  ~ Along which reactants feel the lowest possible potential energy

$$A + B \rightleftarrows [AB]^{*} \longrightarrow \text{products}$$

$[AB]^{*}$: Activated Complex (or Transition State)

  ~ Unstable complex at the *saddle point*

- Energy profile along the reaction coordinate for the reaction

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

- $\Delta U = E_{a,f} - E_{a,r}$: Change in internal energy of the chemical reaction

  ~ Thermodynamic quantity obtained from calorimetric measurements

- $E_{a,f}$, $E_{a,r}$: Activation energies for the forward and reverse reactions

  ~ Obtained from temperature dependence of rate constants

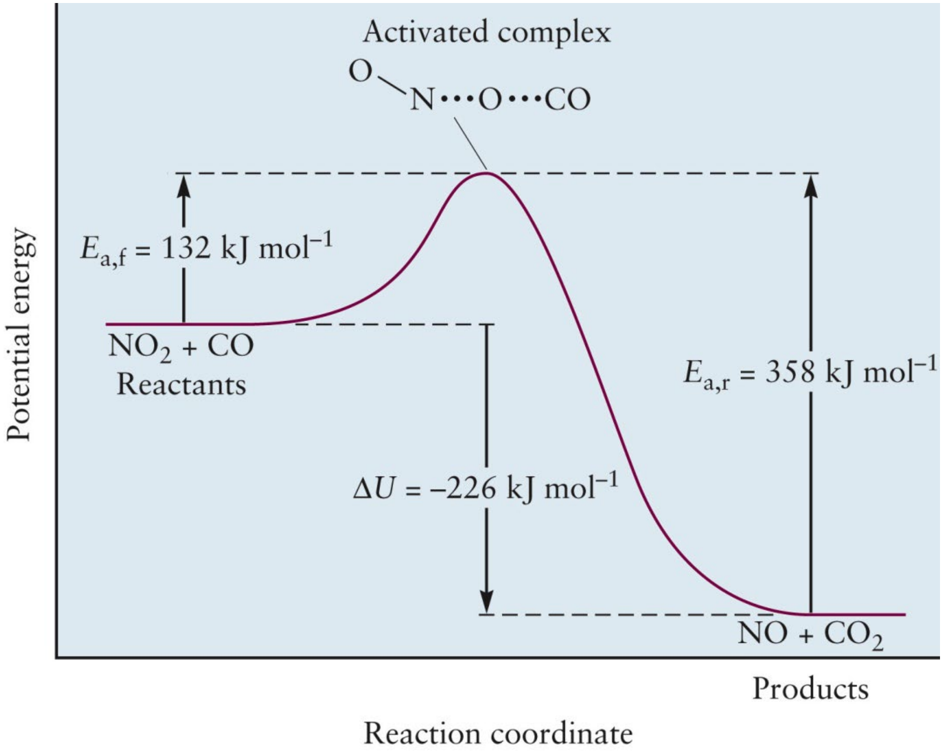


**Fig. 18.11** The energy profile along the reaction coordinate for the reaction:

$$NO_2 + CO \rightarrow NO + CO_2$$

- $E_a > 0$ always for elementary reactions
  - → There is always some energy barrier to surmount.
  - → Rates of elementary reactions increase with increasing temperature
- *"Negative activation energy"* possible for overall reactions
  - → rates of overall reactions decrease with increasing temperature

**Ex)** $2\,NO + O_2 \rightarrow 2\,NO_2$, rate = $k_{obs}[NO]^2[O_2]$

Reaction mechanism:

$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ (fast equilibrium)

$N_2O_2 + O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2\,NO_2$ (slow)

rate = $k_2K_1[NO]^2[O_2]$ $\therefore$ $k_{obs} = k_2K_1$

$k_2$ is for elementary reaction → increases with increasing $T$

$K_1$ is an equilibrium constant

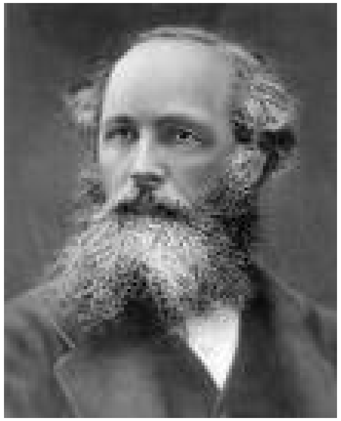
→ Could decrease with increasing $T$ for exothermic reaction!

# Maxwell-Boltzmann distribution of speed

$$\frac{\Delta N}{N} = f(v)\Delta v \quad \text{with} \quad f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

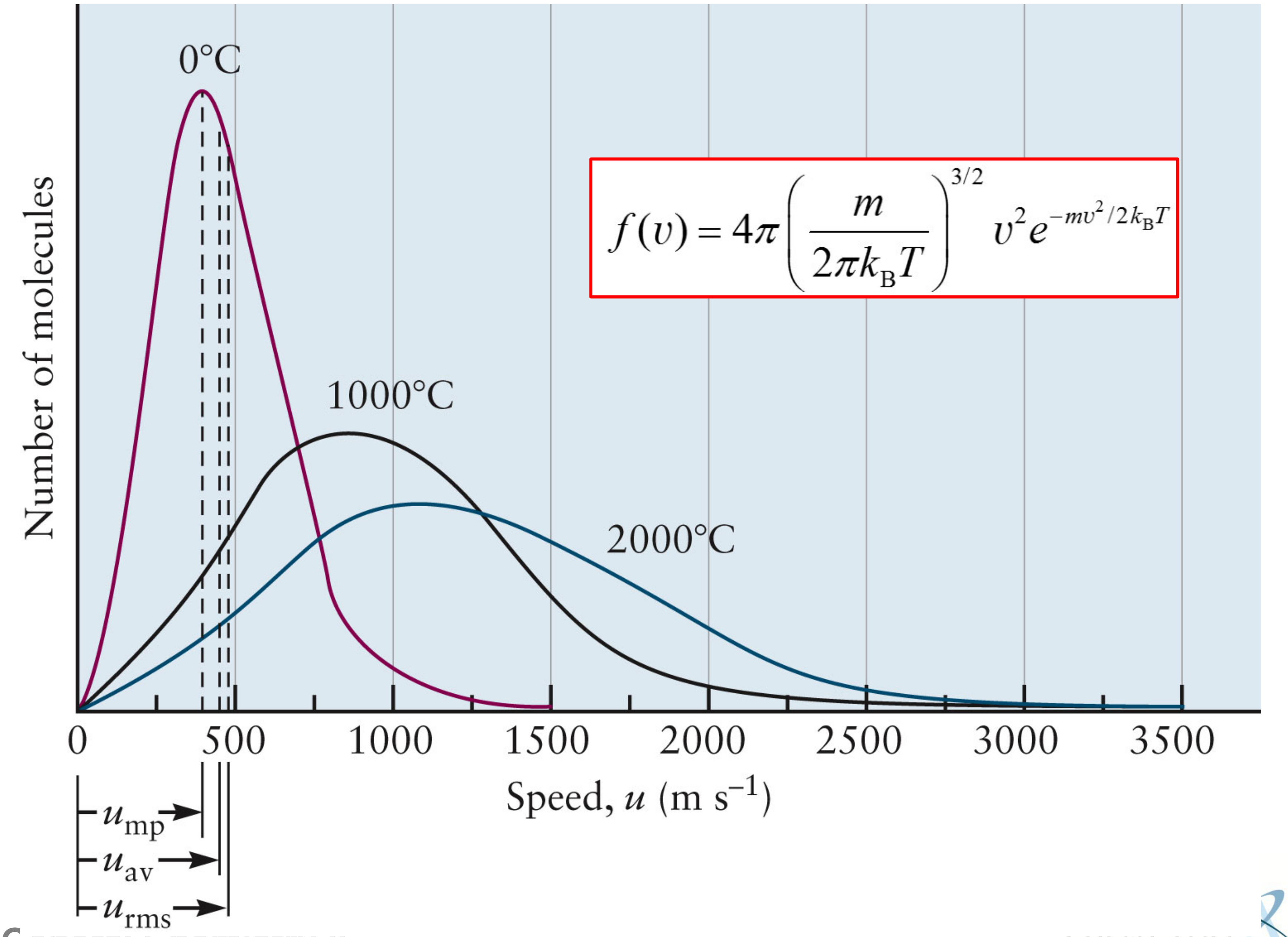
$$\boxed{or \;\; f(v) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_B T}}$$

Boltzmann constant: $k_B = R / N_\mathrm{A} = 1.38066 \times 10^{-23}\ \mathrm{J \cdot K^{-1}}$



James Clerk Maxwell
(Scotland, 1831-1879)

Ludwig Eduard Boltzmann
(Austria, 1844-1906)



$$f(v) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_B T}$$

(1) Most probable speed:

$$v_{mp} = \sqrt{\frac{2k_BT}{m}} = \sqrt{\frac{2RT}{M}} \qquad \left[\frac{df(v)}{dv} = 0\right]_{v=v_{mp}}$$

(2) Average speed:

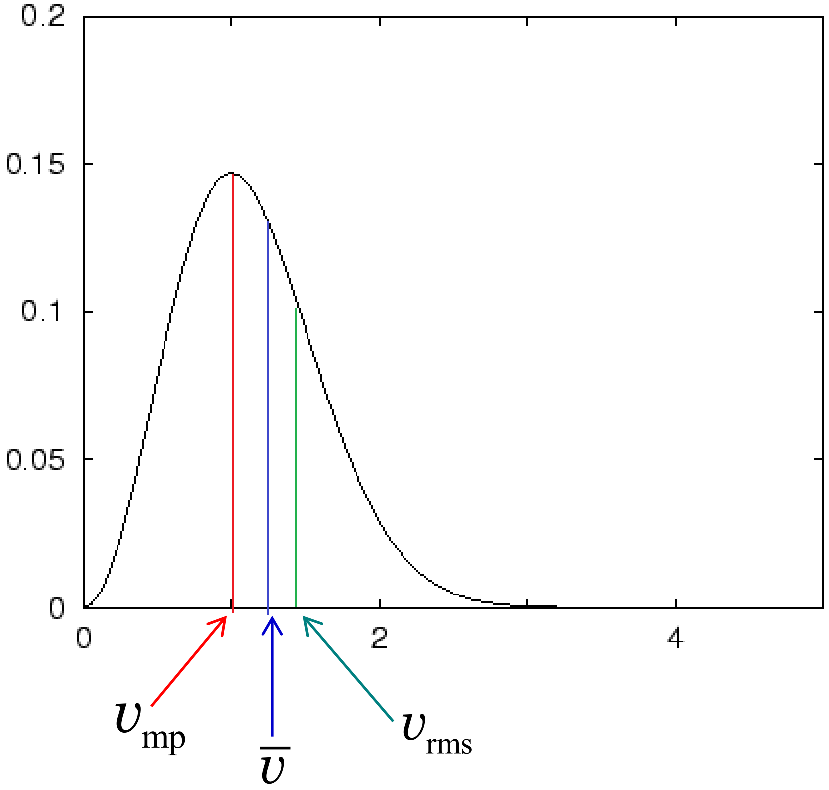
$$\bar{v} = \int_0^\infty vf(v)dv = \sqrt{\frac{8k_BT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

(3) Mean square speed:

$$\overline{v^2} = \int_0^\infty v^2 f(v)dv = \frac{3k_BT}{m} = \frac{3RT}{M}$$

(4) Root-mean-square speed:

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3RT}{M}}$$



$$\boldsymbol{v_{mp} < \bar{v} < v_{rms} = 1.000 : 1.128 : 1.225}$$

# 18.6 MOLECULAR THEORIES OF ELEMENTARY REACTIONS

## ■ Collision Theory

- Rate of collisions between a particular A molecule with other A molecules in a gas:

$$Z_1 = \sqrt{2}\,\frac{N_A}{V}\pi d^2\bar{u} = 4\frac{N_A}{V}d^2\sqrt{\frac{\pi RT}{M}} \qquad (9.26)$$

$$Z_1 = \sqrt{2}\,\frac{N_A}{V}\pi d^2\bar{u} = 4\sigma_c\sqrt{\frac{k_B T}{\pi m}}\left(\frac{N_A}{V}\right) \qquad (18.7)$$

$$= 5\times10^9\ \text{s}^{-1} \quad (\text{for } N_2 \text{ at 1 atm and 298 K})$$

# ◆ Molecule-Molecule Collisions

- Collision cylinder: Cross section, $A = \pi d^2$

Volume : $V_{\text{cyl}} = A \times l = \pi d^2 \times \bar{u} \times 1\ \text{s}$

Collision rate $= Z_1 = \dfrac{n}{V} V_{\text{cyl}} = \sqrt{2}\,\dfrac{N}{V}\pi d^2 \bar{u}$

$$\boxed{Z_1 = 4\frac{N}{V} d^2 \sqrt{\frac{\pi R T}{M}}}$$

An average molecule sweeps out a cylinder of volume $\pi d^2 \bar{u}$ in 1 second. It will collide with any molecules whose centers lie within the cylinder.

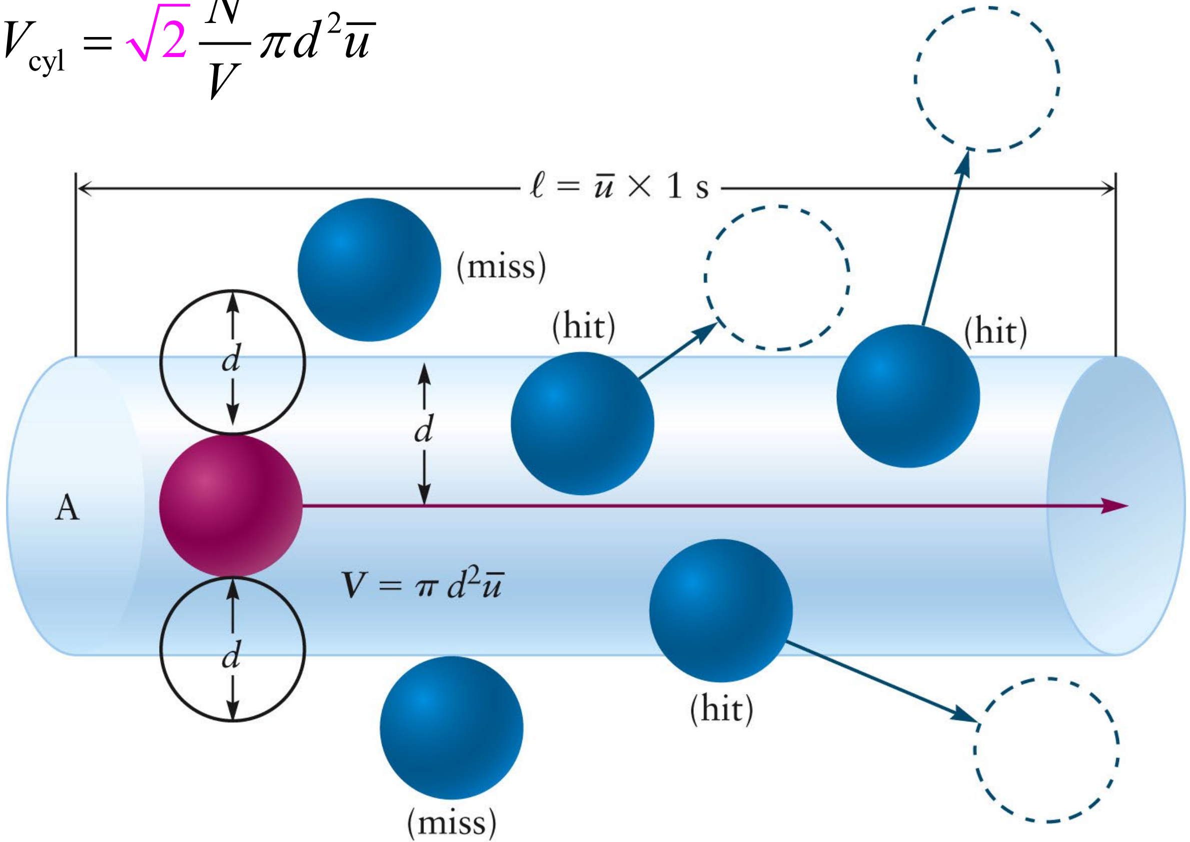


**Fig. 9.20.** Collision cylinder

❖ Collision cross section, $\sigma_c = \pi d^2$ : ← hard sphere cross section

~ Geometric cross section of a sphere that represents the “size” of a molecule

➢ Total rate of collisions between A molecules with B molecules in a gas per unit volume:

$$Z_{\mathrm{AB}} = \sigma_c \sqrt{\frac{8k_{\mathrm{B}}T}{\pi\mu}} \left(\frac{N_{\mathrm{A}}}{V}\right)\left(\frac{N_{\mathrm{B}}}{V}\right)$$

Reduced mass,
$\mu = m_{\mathrm{A}} m_{\mathrm{B}} / (m_{\mathrm{A}} + m_{\mathrm{B}})$

## ◆ Derivation of an expression for the bimolecular rate constant $k_{AB}$

$$Z_{\mathrm{AB}} = \sigma_c \sqrt{\frac{8k_{\mathrm{B}}T}{\pi\mu}}\left(\frac{N_{\mathrm{A}}}{V}\right)\left(\frac{N_{\mathrm{B}}}{V}\right)$$

Reduced mass,
$\mu = m_{\mathrm{A}}m_{\mathrm{B}}/(m_{\mathrm{A}} + m_{\mathrm{B}})$

1) Macroscopic second-order rate law: Rate = $k_r (N_A/V)(N_B/V) = Z_{AB}$

→ $k_{\mathrm{r}} = \sigma_{\mathrm{r}}\overline{u}$ ($\sigma_r$ : reaction cross section)

2) Defining an energy-dependent reaction cross section, $\sigma_r(\varepsilon)$, to account for the fact that only those collisions that meet a specific energy criterion will lead to the reaction.

$$\mathrm{Rate} = k_{\mathrm{r}}\left(\frac{N_{\mathrm{A}}}{V}\right)\left(\frac{N_{\mathrm{B}}}{V}\right) = \sigma_{\mathrm{r}}(\varepsilon)\overline{u}\left(\frac{N_{\mathrm{A}}}{V}\right)\left(\frac{N_{\mathrm{B}}}{V}\right) = \sigma_{\mathrm{r}}(\varepsilon)\left(\frac{2\varepsilon}{\mu}\right)^{1/2}\left(\frac{N_{\mathrm{A}}}{V}\right)\left(\frac{N_{\mathrm{B}}}{V}\right)$$

3) Find the threshold energy for reaction and determine the functional dependence of $\sigma_r(\varepsilon)$ on $\varepsilon$.

4) Using the Maxwell-Boltzmann distribution, $f(\varepsilon)$, integrating the energy-dependent reaction probability over all possible relative kinetic energies weighted by that distribution.

$$\text{Total rate} = \left( \int_0^\infty \sigma_r(\varepsilon) \left( \frac{2\varepsilon}{\mu} \right)^{1/2} f(\varepsilon) d\varepsilon \right) \left( \frac{N_A}{V} \right) \left( \frac{N_B}{V} \right)$$

Rate constant: $$k_r = \int_0^\infty \sigma_r(\varepsilon) \left( \frac{2\varepsilon}{\mu} \right)^{1/2} f(\varepsilon) d\varepsilon \qquad (18.9)$$

Maxwell-Boltzmann distribution:

$$f(u) = 4\pi\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} u^2 \exp(-mu^2/2k_\mathrm{B}T) \qquad (18.10)$$

Substitutions: $\varepsilon = \mu u^2/2, \quad u^2 = 2\varepsilon/\mu, \quad du = d\varepsilon/(2\mu\varepsilon)^{1/2}$

Relate $f(u)du$ to $f(\varepsilon)d\varepsilon$:

$$f(u)du = 4\pi\left(\frac{\mu}{2\pi k_\mathrm{B}T}\right)^{3/2} \frac{2\varepsilon}{\mu} \exp(-\varepsilon/k_\mathrm{B}T) \frac{d\varepsilon}{(2\mu\varepsilon)^{1/2}}$$

$$= 2\pi\left(\frac{\mu}{\pi k_\mathrm{B}T}\right)^{3/2} \varepsilon^{1/2} \exp(-\varepsilon/k_\mathrm{B}T)d\varepsilon = f(\varepsilon)d\varepsilon$$

$$\therefore \quad k_\mathrm{r} = 2\pi\left(\frac{1}{\pi k_\mathrm{B}T}\right)^{3/2} \int_0^\infty \sigma_\mathrm{r}(\varepsilon)\left(\frac{2\varepsilon}{\mu}\right)^{1/2} \varepsilon^{1/2} \exp(-\varepsilon/k_\mathrm{B}T)d\varepsilon$$

$$= \left(\frac{8}{\pi\mu k_\mathrm{B}T}\right)^{1/2}\left(\frac{1}{k_\mathrm{B}T}\right)\int_0^\infty \varepsilon\sigma_\mathrm{r}(\varepsilon)\exp(-\varepsilon/k_\mathrm{B}T)d\varepsilon \qquad (18.11)$$

- Assert that only the relative velocity directed along the line of centers, $v_{AB}$, is effective in activating reaction.

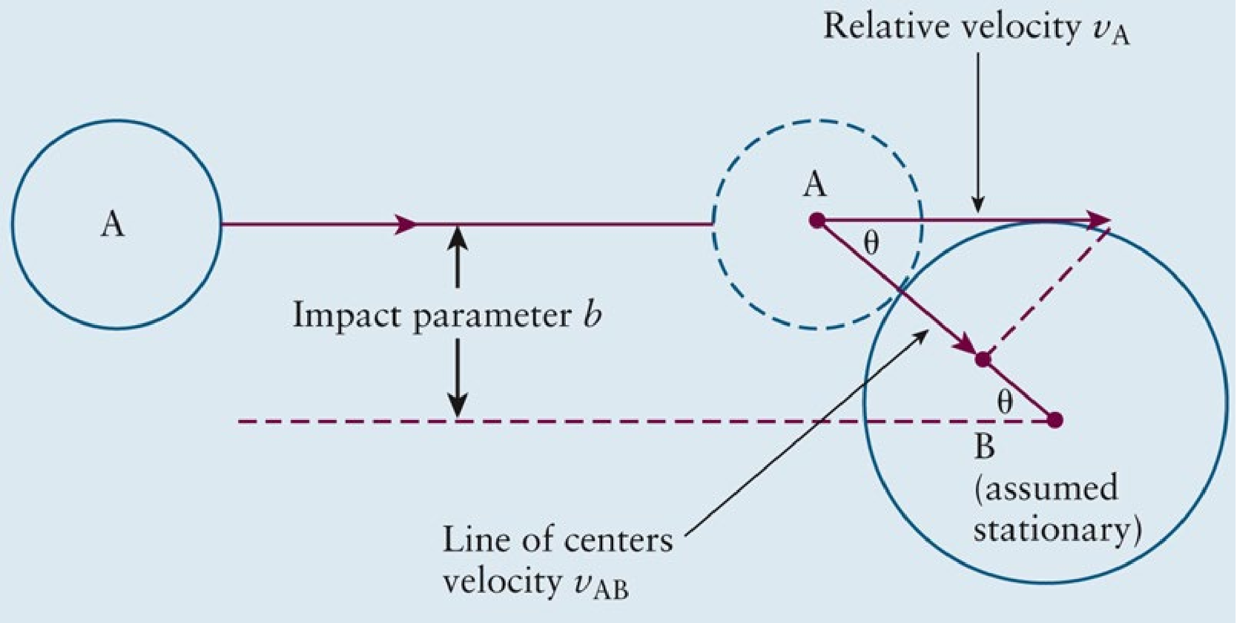
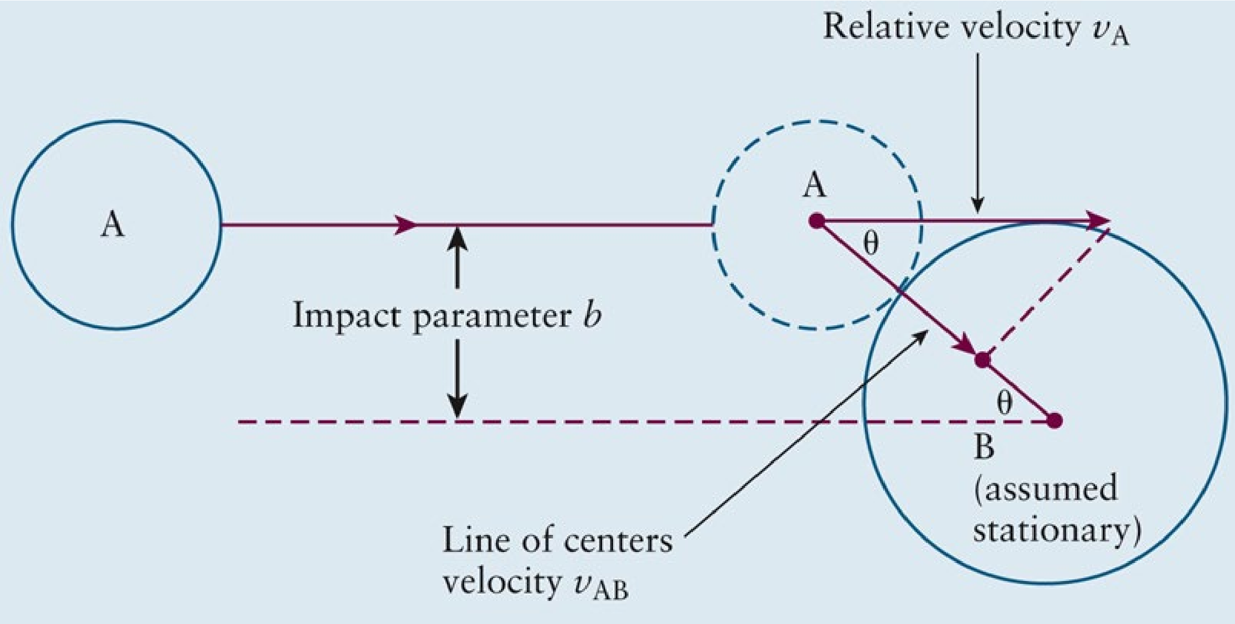


**Fig. 18.13** Impact parameter *b*

- Velocity of A relative to B, $v_A$
- Distance between centers of A and B in contact, *d*
- Impact parameter, *b*: ~ Distance between parallel lines passing through the centers of A and B



- Component of the velocity directed along the line of centers, $v_{AB}$

$$v_{AB} = v_A \cos\theta \quad \text{and} \quad \sin\theta = b/d$$

$$\sin^2\theta + \cos^2\theta = 1 \quad \rightarrow \quad \cos\theta = [(d^2 - b^2)/d^2]^{1/2}$$

$$v_{AB} = v_A [(d^2 - b^2)/d^2]^{1/2}$$

$$\varepsilon = \tfrac{1}{2}\mu v^2 \qquad \therefore \quad \varepsilon_{AB} = \varepsilon_A (d^2 - b^2)/d^2 \qquad (18.12)$$

Impact parameter and reaction

Head-on collision, $b = 0$ (probability of reaction = 1)

No reaction as $b$ increases (probability of reaction = 0)

The largest value of $b$ for reaction to occur, $b_0$

$$b_0^2 = \left(1 - \frac{\varepsilon_\mathrm{a}}{\varepsilon}\right) d^2$$

$\varepsilon_\mathrm{a}$ : Energy associated with $b_0$

~ Specific energy that corresponds to the largest impact parameter that leads to reaction.

~ Smaller values of $\varepsilon_\mathrm{a}$ do not lead to reaction

Multiply both sides by π and identify $\sigma_r(\varepsilon) = \pi b_0^2$ and $\sigma_c = \pi d^2$ :

$$\boxed{\sigma_r(\varepsilon) = \sigma_c\left(1 - \frac{\varepsilon_a}{\varepsilon}\right)} \qquad (18.13)$$

- $\sigma_r(\varepsilon) < 0$ for all values of $\varepsilon < \varepsilon_a$

  → Physically unacceptable

- $\sigma_r(\varepsilon) = 0$ for $\varepsilon = \varepsilon_a$

- $\sigma_r(\varepsilon) > 0$ for all values of $\varepsilon > \varepsilon_a$

  Saturation at $\sigma_r(\varepsilon) = \sigma_c(= \pi d^2)$

  → Every collision leads to reaction!

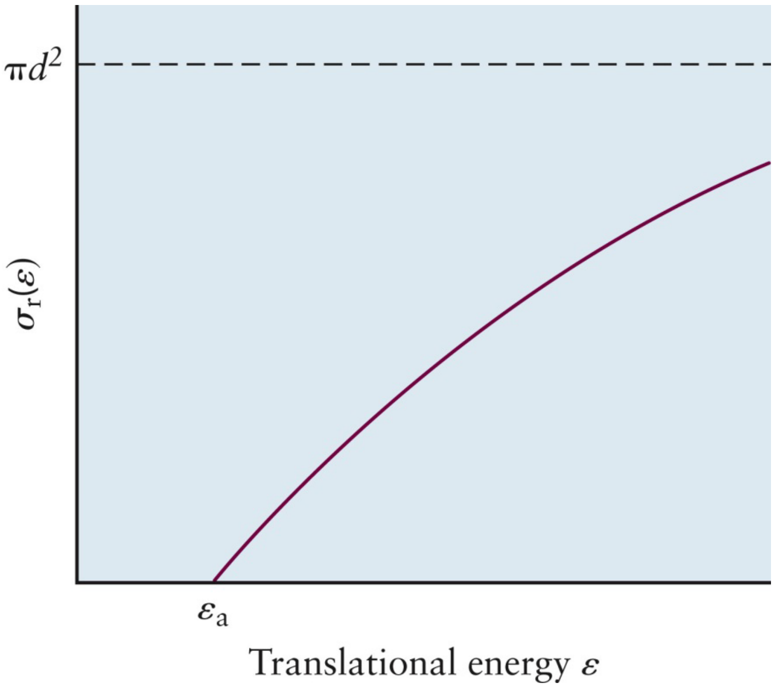


**Fig. 18.14** Reactive cross section $\sigma_r(\varepsilon)$ vs. relative translational energy ε.

$$k_\mathrm{r} = \left(\frac{8}{\pi\mu k_\mathrm{B}T}\right)^{1/2}\left(\frac{1}{k_\mathrm{B}T}\right)\int_0^\infty \varepsilon\sigma_\mathrm{r}(\varepsilon)\exp(-\varepsilon/k_\mathrm{B}T)d\varepsilon \qquad (18.11)$$

$$\sigma_\mathrm{r}(\varepsilon) = \sigma_\mathrm{c}\left(1-\frac{\varepsilon_\mathrm{a}}{\varepsilon}\right) \qquad (18.13)$$

$$\int_0^\infty \varepsilon\sigma_\mathrm{r}(\varepsilon)\exp(-\varepsilon/k_\mathrm{B}T)d\varepsilon = \sigma_\mathrm{c}\int_0^\infty \varepsilon\left(1-\frac{\varepsilon_\mathrm{a}}{\varepsilon}\right)\exp(-\varepsilon/k_\mathrm{B}T)d\varepsilon$$

$$= (k_\mathrm{B}T)^2\sigma_\mathrm{c}\exp(-\varepsilon_\mathrm{a}/k_\mathrm{B}T)$$

$$\therefore \quad k_\mathrm{r} = \left(\frac{8}{\pi\mu k_\mathrm{B}T}\right)^{1/2}\left(\frac{1}{k_\mathrm{B}T}\right)(k_\mathrm{B}T)^2\sigma_\mathrm{c}\exp(-\varepsilon_\mathrm{a}/k_\mathrm{B}T)$$

$$= \sigma_\mathrm{c}\left(\frac{8k_\mathrm{B}T}{\pi\mu}\right)^{1/2}\exp(-\varepsilon_\mathrm{a}/k_\mathrm{B}T) = A\left(\sqrt{T}\right)\exp(-E_\mathrm{a}/RT) \qquad (18.14)$$

→ Temperature dependent rate constant in terms of molecular parameters

## ❖ Steric factor, *P*

~ Orientation of reacting molecules affects the pre-exponential factor

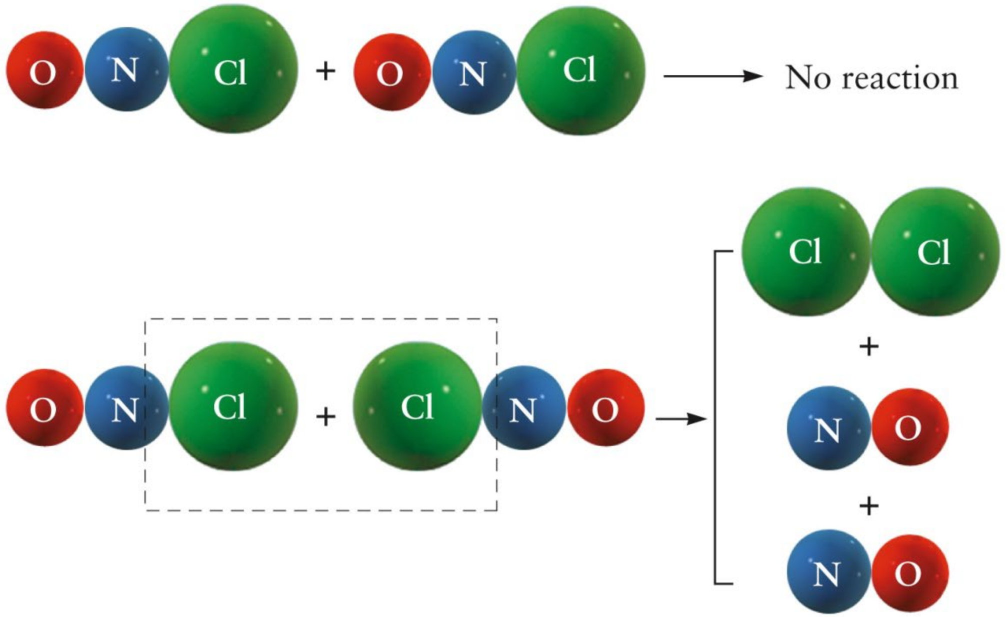


**TABLE 18.1**

**Steric Factors for Gas-Phase Reactions**

| Reaction | Steric Factor *P* |
|---|---|
| $2\ NOCl \rightarrow 2\ NO + Cl_2$ | 0.16 |
| $2\ NO_2 \rightarrow 2\ NO + O_2$ | $5.0 \times 10^{-2}$ |
| $2\ ClO \rightarrow Cl_2 + O_2$ | $2.5 \times 10^{-3}$ |
| $H_2 + C_2H_4 \rightarrow C_2H_6$ | $1.7 \times 10^{-6}$ |
| $K + Br_2 \rightarrow KBr + Br$ | 4.8 |

Adapted from P. W. Atkins and J. de Paula, *Physical Chemistry*, 9th ed. New York: W. H. Freeman, 2010, Table 22.1, p. 942.

**Fig. 18.15** The steric effect on the reaction probability.

# ■ Transition State Theory

~ Activated Complex Theory

~ Gas and solution phase reactions

~ Formation of an activated complex (intermediate product) while passing through the transition state along the reaction coordinate

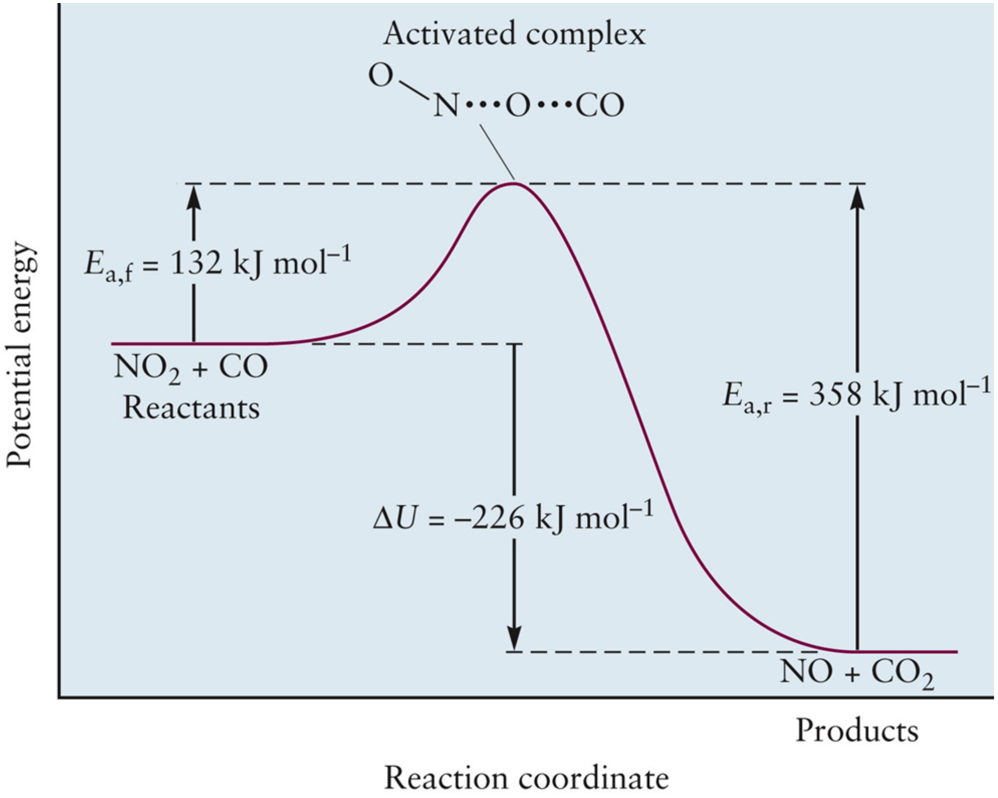


**Fig. 18.11** The energy profile along the reaction coordinate for the reaction:

$NO_2 + CO \rightarrow NO + CO_2$

## ❖ Eyring formula for the rate constant:

$$\boxed{k_r = \kappa \frac{k_B T}{h} K^{\dagger}}$$

$\kappa$ : Transmission coefficient

~ Measures the probability that the system will proceed through the transition state

$k_B T/h$: Rate at which the activated complex dissociates to form products

~ $5 \times 10^{12}$ $s^{-1}$ at 300 K

$K^{\dagger}$ : Equilibrium constant involving the activated complex

## ✧ Thermodynamic formulation of transition state theory

Substitute $\exp(-\Delta G^{\dagger}/RT)$ for $K^{\dagger}$

$$k_{\mathrm{r}} = \kappa\frac{k_{\mathrm{B}}T}{h}\exp(-\Delta G^{\dagger}/RT) = \kappa\frac{k_{\mathrm{B}}T}{h}\exp(-\Delta H^{\dagger}/RT)\exp(\Delta S^{\dagger}/R)$$

Compare to the Arrhenius equation:

$$k_{\mathrm{r}} = A\exp(-E_{\mathrm{a}}/RT)$$

$$\boxed{A \Leftrightarrow \kappa\frac{k_{\mathrm{B}}T}{h} \qquad E_{\mathrm{a}} \Leftrightarrow \Delta G^{\dagger} = \Delta H^{\dagger} - T\Delta S^{\dagger}}$$

# ◆ Isotope Effects in Chemical Kinetics

## ❖ Kinetic isotope effect:

~ Isotopic substitution affects the rates of chemical reactions.

~ Primary effect for the isotope involved in a bond

Secondary effect for the isotope involved in an adjacent bond

~ Assume that zero-point energies of the relevant vibration are identical for both isotopes in the activated complex

~ Zero-point energy of the heavier isotope is less than that of the lighter one in the reactants producing an increase in activation energies and a decrease in reaction rates.

C–H bond: $k_H(T)$, $E_{a,H} = E - \frac{1}{2}h\nu_{CH}$ ($E_{vib,CH} = h\nu_{CH}$ = 36 kJ mol$^{-1}$ )

C–D bond: $k_D(T)$, $E_{a,D} = E - \frac{1}{2}h\nu_{CD}$ ($E_{vib,CD} = h\nu_{CD}$ = 25 kJ mol$^{-1}$ )

$$\frac{k_{\mathrm{H}}(T)}{k_{\mathrm{D}}(T)}=\frac{A\exp(-E_{\mathrm{a,H}}/RT)}{A\exp(-E_{\mathrm{a,D}}/RT)}=\frac{\exp[(-E+\frac{1}{2}h\nu_{\mathrm{CH}}/RT)}{\exp[(-E+\frac{1}{2}h\nu_{\mathrm{CD}}/RT)}$$

$$=\exp\left[\tfrac{1}{2}\left(h\nu_{\mathrm{CH}}-h\nu_{\mathrm{CD}}\right)\ /RT\right]=8.33 \text{ at } 300\text{ K}$$

*E*: Energy difference between PE min of reactants and PE max of ACT

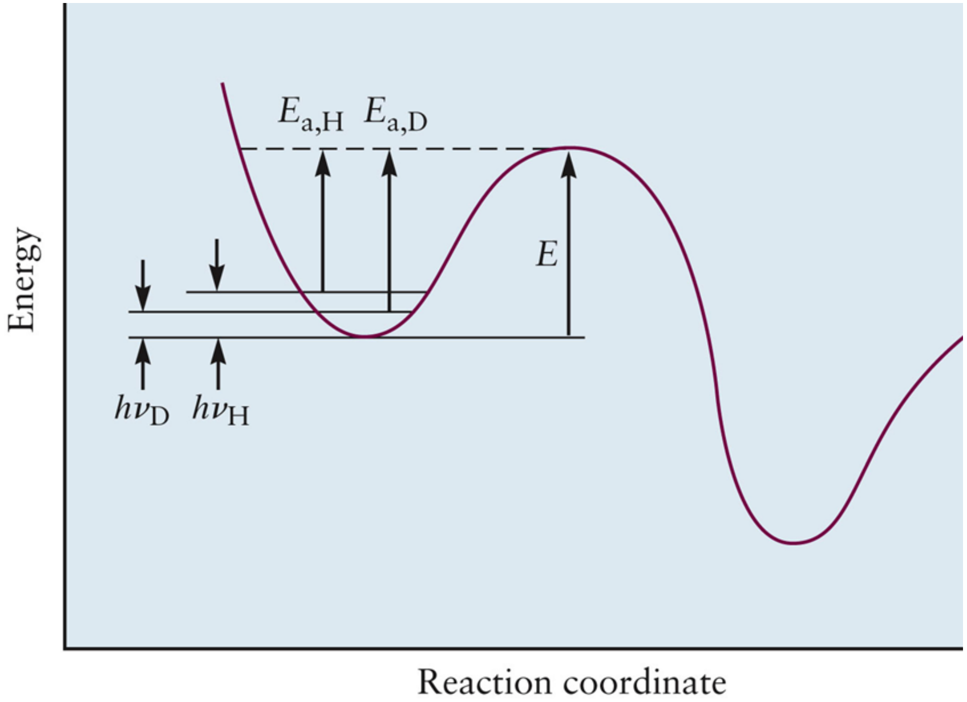
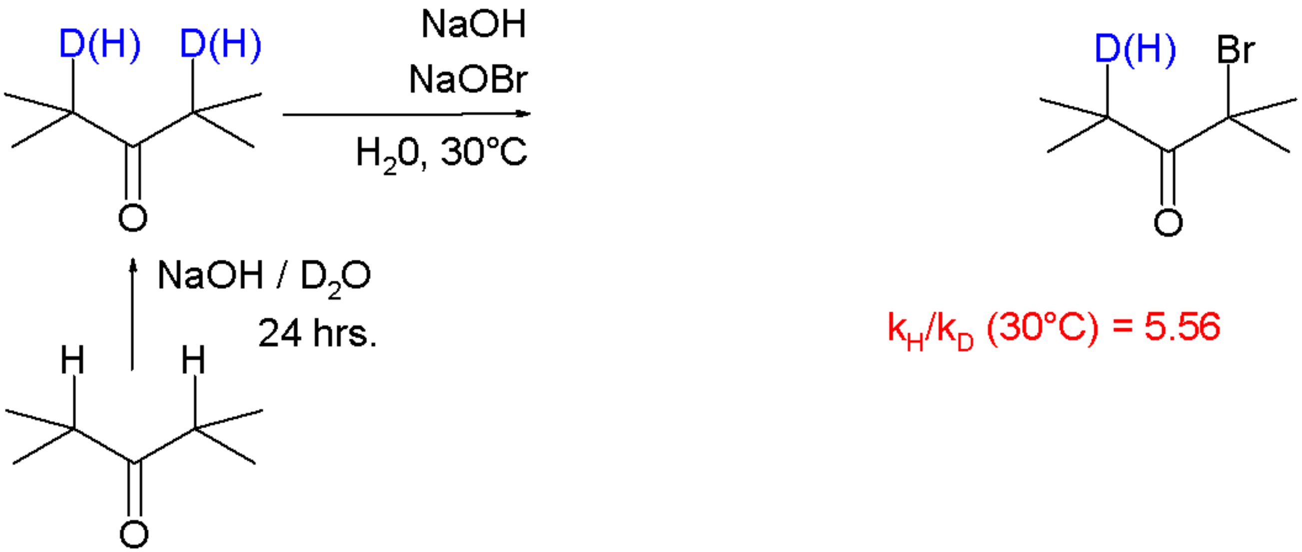


**Fig. 18.16** Energy profile along a C–H bond reaction coordinate showing the origin of the primary kinetic isotope effect. The zero-point vibrational energy of the C–D bond is less than that of the C–H bond, which leads to an increase in the activation energy $E_a$ for reactions that involve breaking C–D bonds.

# Primary Isotope Effect



$k_H/k_D$ (30°C) = 5.56

# Secondary Isotope Effect

$$\frac{k_H}{k_D} = 1.22$$

# ◆ Molecular Beams

- ~ Gas-phase reactions, large and expensive instrument
- ~ Two molecular beams cross in a vacuum chamber
- ~ Molecular beam of narrow range of velocity selected by velocity selector (Fig. 9.13)
- ~ Excite or fracture product molecules by laser gun
- ~ Study vibrational and rotational states of product molecules

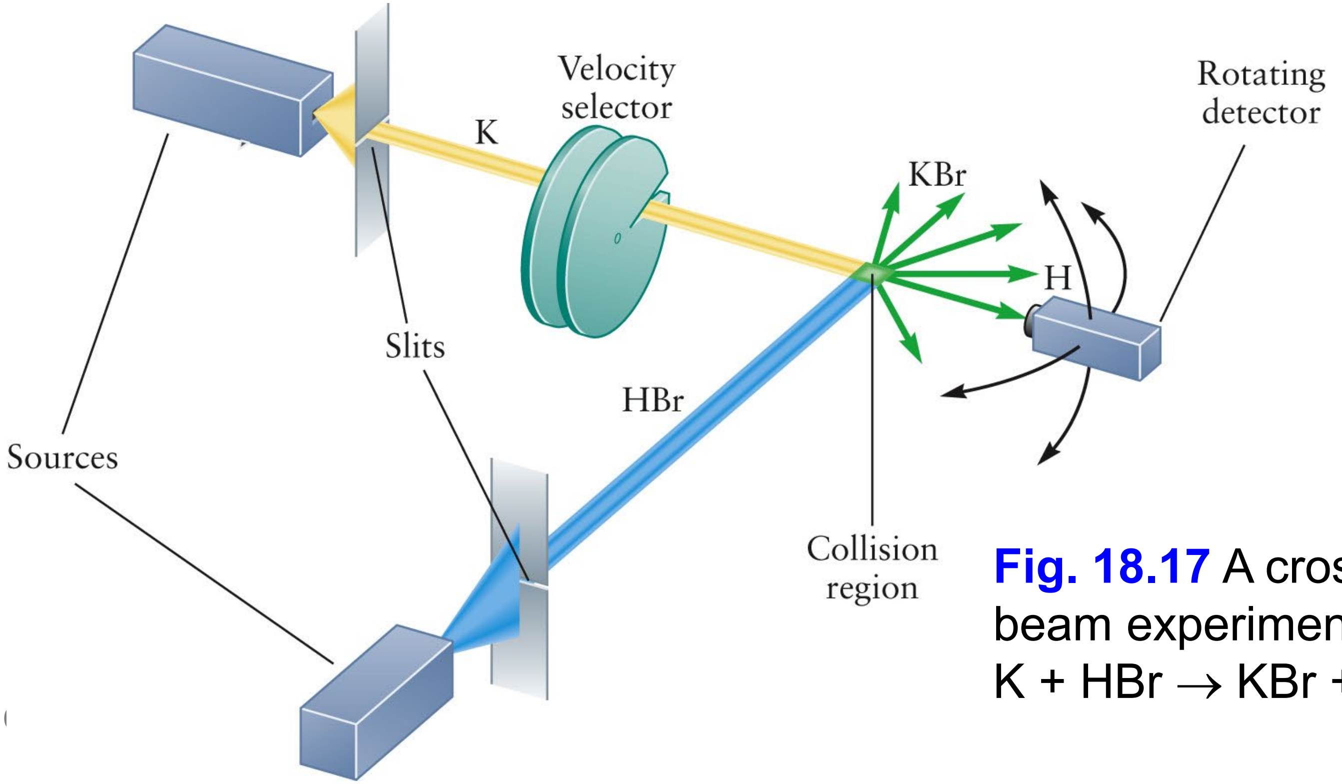


**Fig. 18.17** A crossed molecular beam experiment for the reaction K + HBr → KBr + H.

# **18.7** REACTIONS IN SOLUTION

"Cage" effect: reactant surrounded by solvent molecules

- **Two-step sequence reaction:**

$$\mathrm{A}+\mathrm{B}\ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}\ \mathrm{AB},\quad \mathrm{AB}\ \xrightarrow{k_2}\ \text{products}\qquad \text{Rate}=k_2[\mathrm{AB}]$$

$$\frac{d[\mathrm{AB}]}{dt}=k_1[\mathrm{A}][\mathrm{B}]-k_{-1}[\mathrm{AB}]-k_2[\mathrm{AB}]=0\ \rightarrow\ [\mathrm{AB}]=\frac{k_1[\mathrm{A}][\mathrm{B}]}{k_{-1}+k_2}$$

$$\text{Rate}=k_2[\mathrm{AB}]=\frac{k_1k_2[\mathrm{A}][\mathrm{B}]}{k_{-1}+k_2}$$

(1) Activation-energy-controlled reaction

$$k_2 < k_{-1}, \qquad \text{Rate} = \frac{k_1 k_2}{k_{-1}}[\text{A}][\text{B}] = k_2 K_1 [\text{A}][\text{B}]$$

~ Slow second step implies a large activation energy

(2) Diffusion-controlled reaction

$$k_2 >> k_{-1}, \quad \text{Rate} = k_1[\text{A}][\text{B}]$$

~ $k_1$ is limited by the rate at which the reactants encounter one another by diffusion

# ◆ Diffusion

## ❖ Einstein's theory of Brownian motion (1905)

$$\overline{(\Delta r)^2} = 6Dt \qquad D : \text{diffusion coefficient}$$

$\Delta r$ : diffusive displacement (actually, root mean square value)

## ❖ Smoluchowski's model (1916) for diffusion-controlled reactions

Diffusion-controlled rate constant:

$$k_{\mathrm{d}} = 4\pi R^{*} D N_{\mathrm{A}}$$

where $R^* = r_A + r_B$ and $D = D_A + D_B$.

# 18.8 CATALYSIS

~ A substance that takes part in a chemical reaction and speeds up the rate but undergoes no permanent chemical change itself

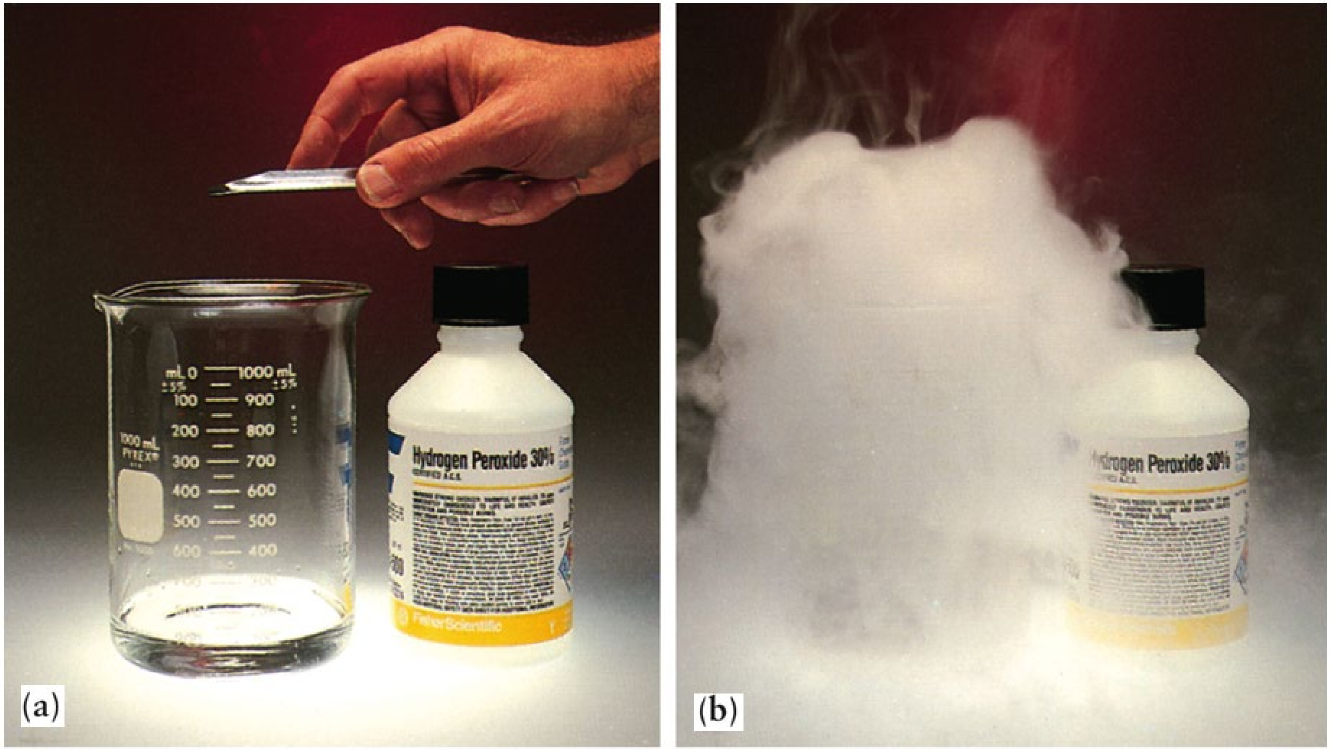


**Fig. 18.18** (a) Decomposition of $H_2O_2$ to $H_2O$ and $O_2$ catalyzed by a very small amount of transition metal oxide. (b) The water evolves as steam because of the heat given off in the reaction.

- Catalysts provide alternative pathways for reaction by lowering the activation energy $E_a$.

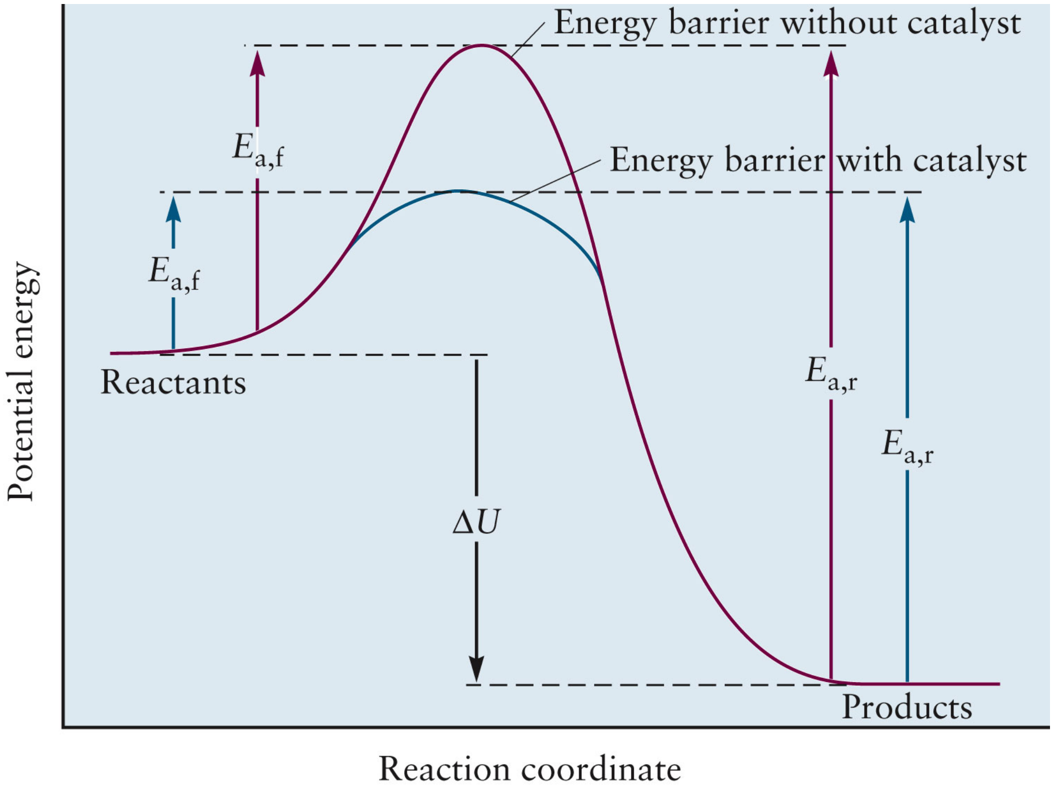


**Fig. 18.19** A catalyst speeds up the reaction by reducing the activation energy. Both the uncatalyzed (red) and catalyzed (blue) reaction coordinates are shown.

- **Homogeneous catalysis**

$$Tl^+(aq) + 2\,Ce^{4+}(aq) \xrightarrow{Ag^+(aq)} Tl^{3+}(aq) + 2\,Ce^{3+}(aq)$$

$$Ag^+ + Ce^{4+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Ag^{2+} + Ce^{3+} \quad \text{(fast)}$$

$$Tl^+ + Ag^{2+} \xrightarrow{k_2} Tl^{2+} + Ag^+ \quad \text{(slow)}$$

$$Tl^{2+} + Ce^{4+} \xrightarrow{k_3} Tl^{3+} + Ce^{3+} \quad \text{(fast)}$$

- **Heterogeneous catalysis**

Ex 1) $C_2H_4(g) + H_2(g) \xrightarrow{Pt(s)} C_2H_6(g)$

Ex 2) Catalytic converter to reduce the emission of pollutants in the exhaust streams of automobile engines

Oxidation: $CO, C_xH_y, O_2 \xrightarrow{*} CO_2, H_2O$

Reduction: $NO, NO_2 \xrightarrow{*} N_2, O_2$

*Pt and *Rh deposited on a fine honeycomb mesh of alumina ($Al_2O_3$)

Can be poisoned by Pb → unleaded fuel must be used

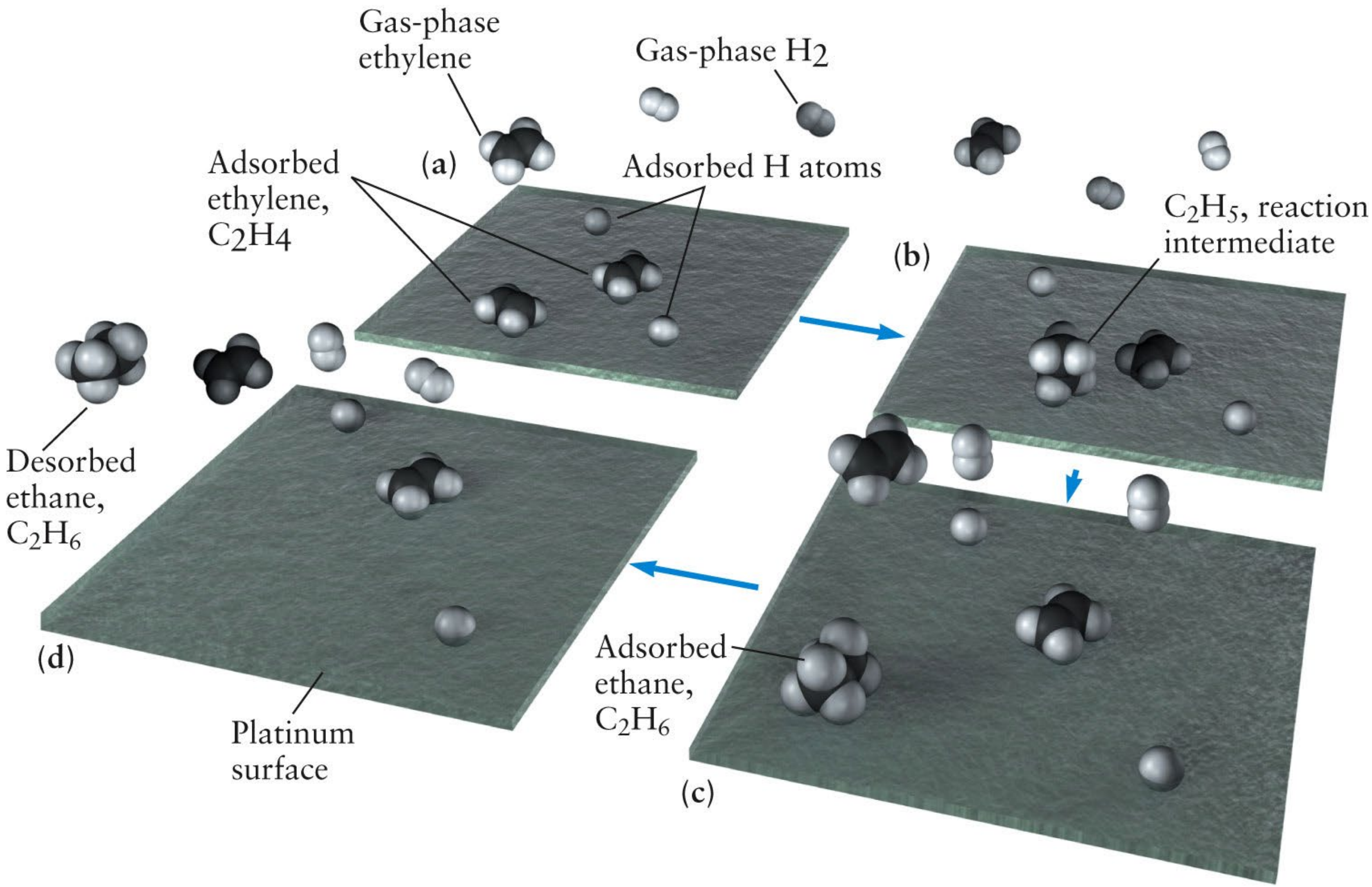


**Fig. 18.20** The reaction $H_2 + C_2H_4$ is catalyzed on the surface of platinum by promoting the dissociation of $H_2$ to H atoms, which can then add to $C_2H_4$ stepwise to give ethane.

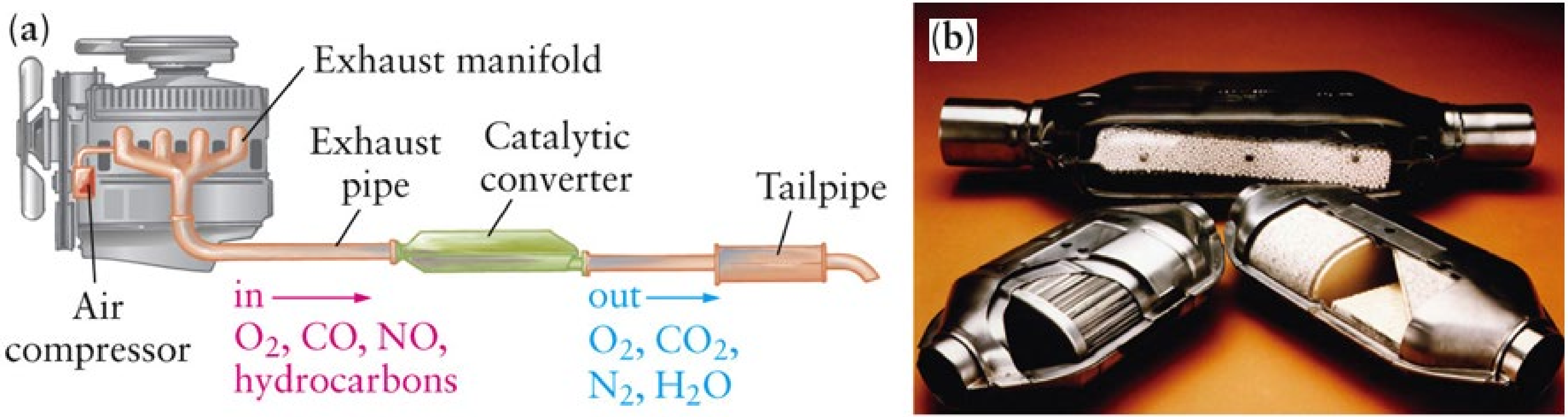


**Fig. 18.21** (a) A catalytic converter used to reduce car pollution and (b) its inside.

## ◆ Enzyme Catalysis

- **Enzyme:** A catalyst for a reaction in living organism with selectivity, a protein binding a substrate in a small region (*active site*)
- **Substrate**: A reactant in a biochemical reaction, a small organic molecule, a small region of much larger molecule such as a proton or a nucleic acid
- Glycolysis: Oxidation of glucose to $CO_2$ and $H_2O$ in a series of metabolic reactions
- Hydrolysis of urea catalyzed by the enzyme urease

$$H_3O^+(aq) + (NH_2)_2CO(aq) + H_2O(l) \xrightarrow{\text{Urease}} 2\ NH_4^+(aq) + HCO_3^-(aq)$$

# ◆ Enzyme Kinetics

## Classification of enzymes

1) Oxidoreductase – Redox reaction
2) Transferase – Functional group transfer reaction
3) Hydrolase – Hydrolysis reaction
4) Lyase – Addition to carbon-carbon double bond
5) Isomerase – isomerization reaction
6) Ligase – bond-forming reaction

- Many enzymes require **cofactors** to carry out their catalytic functions.

~ Metal ions

($Fe^{2+}/Fe^{3+}$ in cytochromes, catalyzing electron-transfer reactions)

~ Small organic molecules called coenzymes (ex. Vitamins)

# ◆ Michaelis-Menten mechanism

~ Well-known enzyme-catalyzed reaction model for reaction kinetics

$$\mathrm{E+S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{ES} \xrightarrow{k_2} \mathrm{E+P}$$

E: free enzyme, S: substrate, P: final product
ES: complex of substrate bound to the active site of enzyme

## ❖ Mass conservation

$[\mathrm{E_T}] = [\mathrm{E}] + [\mathrm{ES}]$ ,  $[\mathrm{E_T}]$: Total concentration of enzyme

## ❖ Steady-state approximation

$$\frac{d[\mathrm{ES}]}{dt} = -\frac{d[\mathrm{E}]}{dt} = 0 = k_1[\mathrm{E}][\mathrm{S}] - (k_{-1}+k_2)[\mathrm{ES}]$$

$$= k_1\big([\mathrm{E_T}]-[\mathrm{ES}]\big)[\mathrm{S}] - (k_{-1}+k_2)[\mathrm{ES}]$$

$$[\mathrm{ES}] = \frac{k_1[\mathrm{E_T}][\mathrm{S}]}{(k_{-1}+k_2)+k_1[\mathrm{S}]} = \frac{[\mathrm{E_T}][\mathrm{S}]}{K_\mathrm{m}+[\mathrm{S}]} \qquad K_\mathrm{m} = \frac{k_{-1}+k_2}{k_1}$$ : Michaelis constant

- Rate of formation of product

$$\boxed{\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}] = \frac{k_2[\mathrm{E_T}][\mathrm{S}]}{K_\mathrm{m} + [\mathrm{S}]}}$$

**Michaelis-Menten equation**

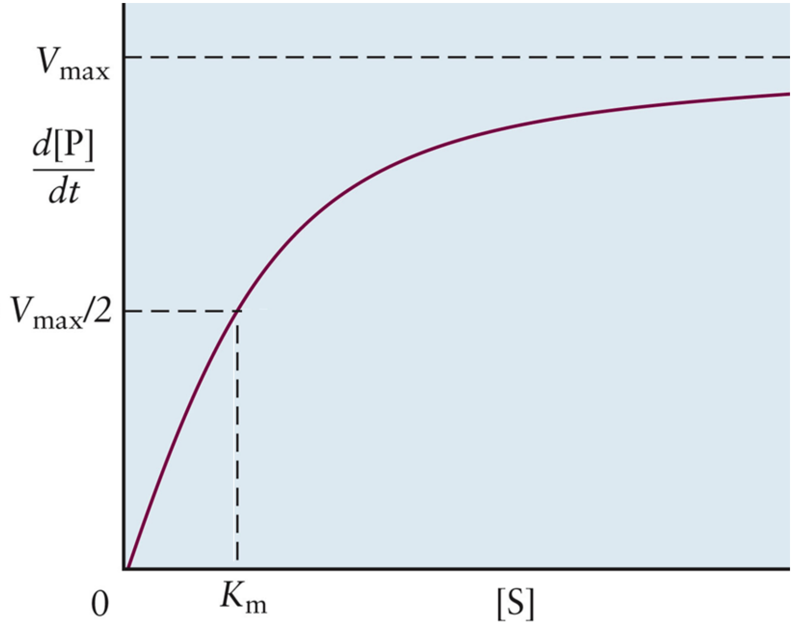


**Fig. 18.23** Michaelis-Menten plot of the dependence of the rate of an enzyme-catalyzed reaction on the concentration of the substrate, showing saturation behavior as [S] → ∞.

- Maximum rate, $V_\mathrm{max} = k_2[\mathrm{E_T}]$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}] = \frac{V_\mathrm{max}[\mathrm{S}]}{K_\mathrm{m} + [\mathrm{S}]} \longrightarrow V_\mathrm{max} \text{ as [S] becomes very large}$$

- Determination of $K_m$:

$$K_\mathrm{m} = [S]\left[\left(\frac{V_\mathrm{max}}{d\mathrm{P}/dt}\right) - 1\right] \longrightarrow [S] \quad \text{when } d\mathrm{P}/dt = V_\mathrm{max}/2$$

- Turnover number, $k_\mathrm{cat}$

~ Number of substrate molecules converted into product per enzyme molecule per second

$$k_\mathrm{cat} \equiv k_2 = \frac{V_\mathrm{max}}{E_\mathrm{T}}$$

- Catalytic efficiency for low substrate concentration

When $k_2 >> k_{-1}[S]$,

$K_m = k_2/k_1$ ($\equiv k_\mathrm{cat}/k_1$) and the 1st step is rate-determining:

$$\frac{d[\mathrm{P}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] = \left(\frac{k_\mathrm{cat}}{K_\mathrm{m}}\right)[\mathrm{E}][\mathrm{S}]$$

Maximum rate of the 1st step is the rate of E-S encounter ← diffusion-limited

# ◆ Lineweaver-Burk equation

$$\frac{1}{d[\mathrm{P}]/dt} = \left(\frac{K_\mathrm{m}}{V_\mathrm{max}}\right)\left(\frac{1}{[\mathrm{S}]}\right) + \frac{1}{V_\mathrm{max}}$$

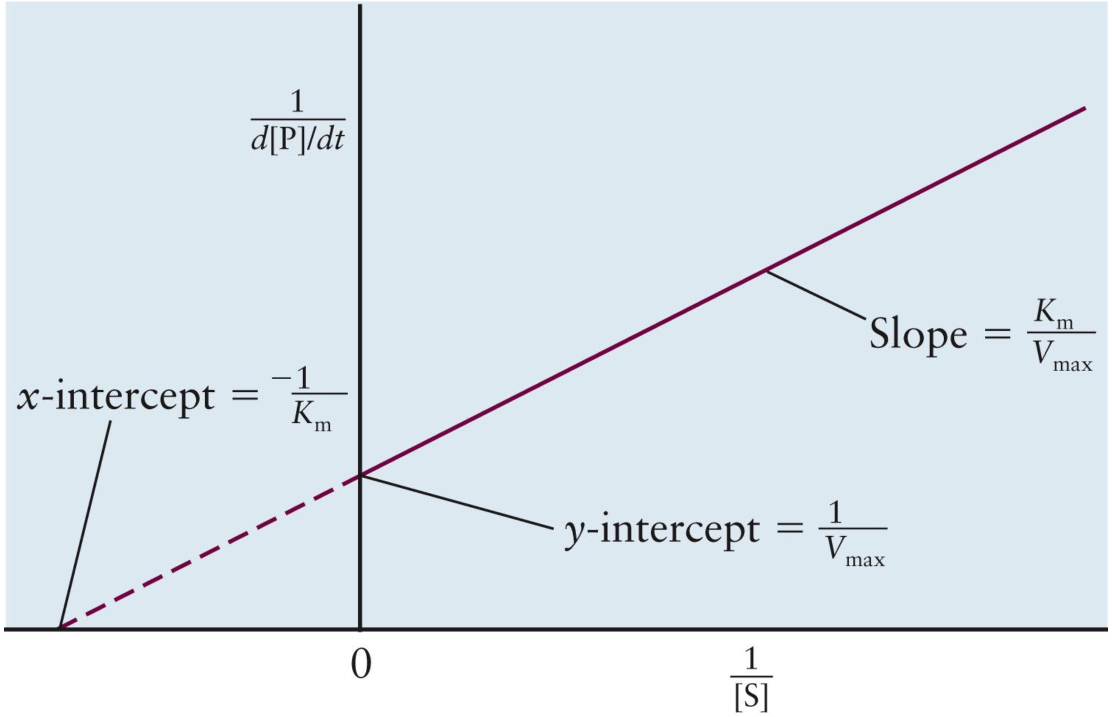


**Fig. 18.24** The Lineweaver-Burk linear plot used to determine parameters $K_\mathrm{m}$ and $V_\mathrm{max}$.

# ❖ Temperature dependence of enzyme-catalyzed reactions

~ Rate increases , doubled every 10 $^{o}$C

~ Fall off above 50-60 $^{o}$C due to unfolding and degrading of 3D structures of protein

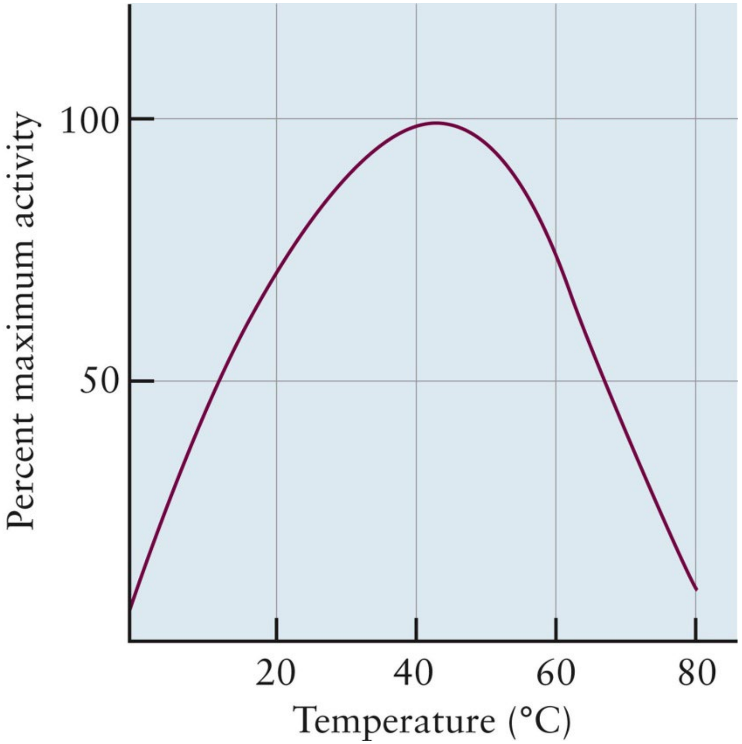


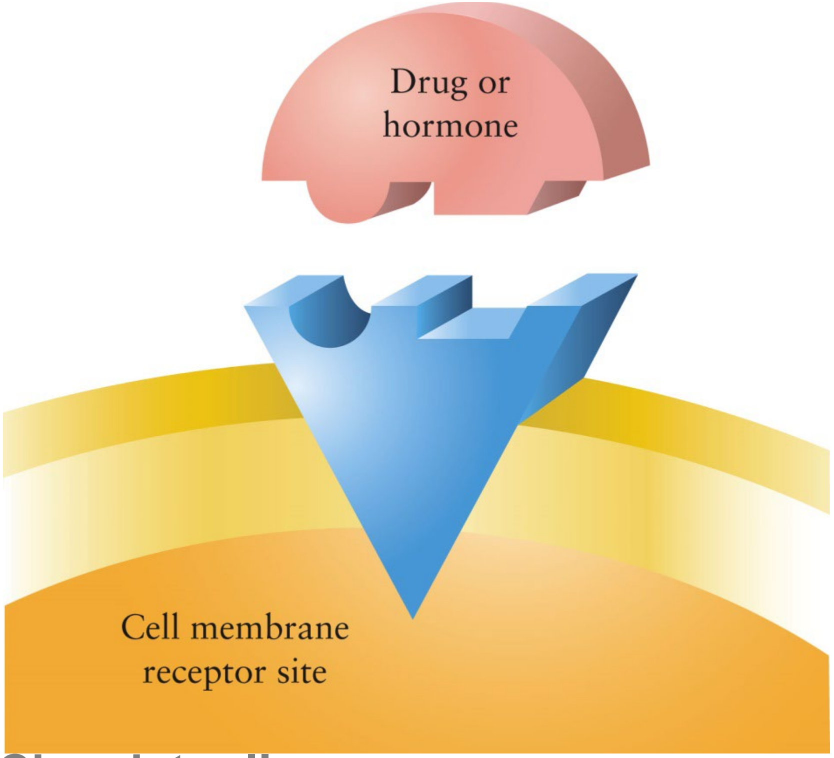
**Fig. 18.25** Plot of the activity of an enzyme vs. temperature. The increase in rate at low temperatures is described by the Arrhenius equation whereas the falloff in rate at higher temperatures is due to loss of structure necessary for function.

# ◆ Mechanisms of Enzyme-Catalyzed Reactions

~ High degree of specificity of enzyme-catalyzed reactions

## ❖ ‘Lock-and-key’ mechanism

Binding of substrates (the key) effected through molecular recognition by the active site of enzymes (the lock)



Lock and key mechanism

# ◆ Induced fit hypothesis

Binding of the substrate by the active site is cooperative.

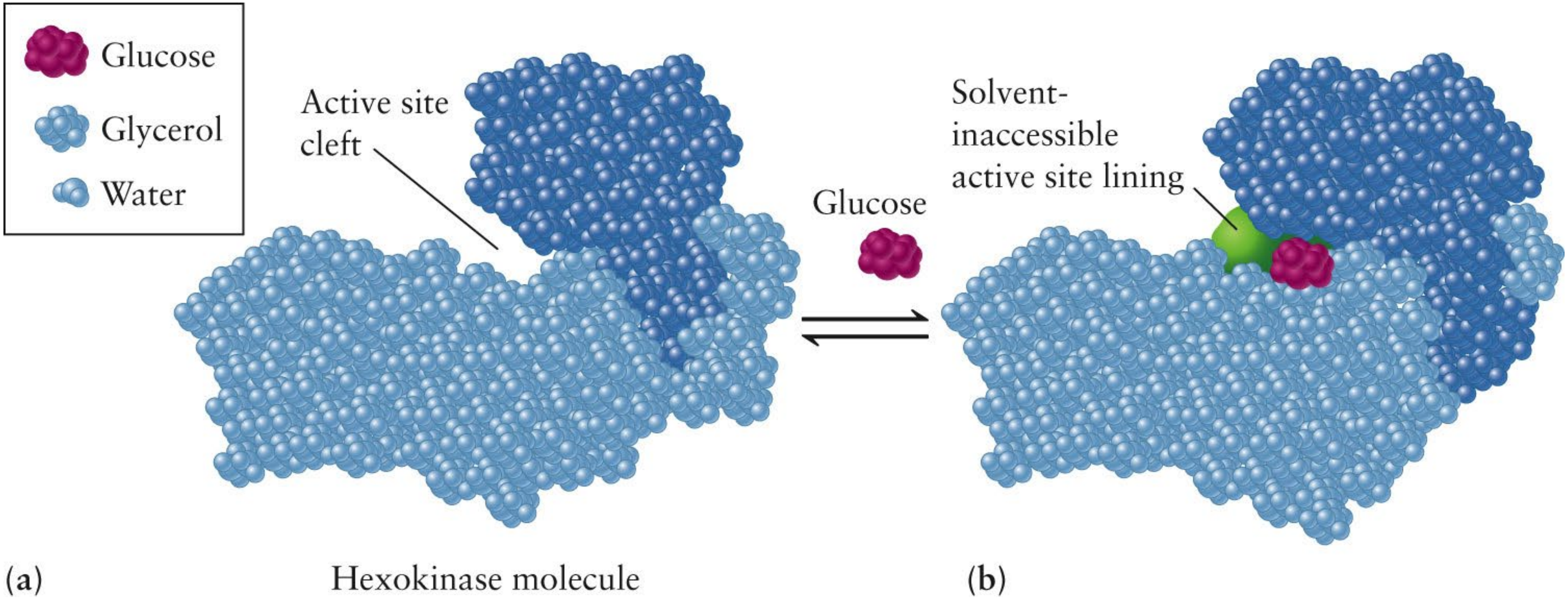
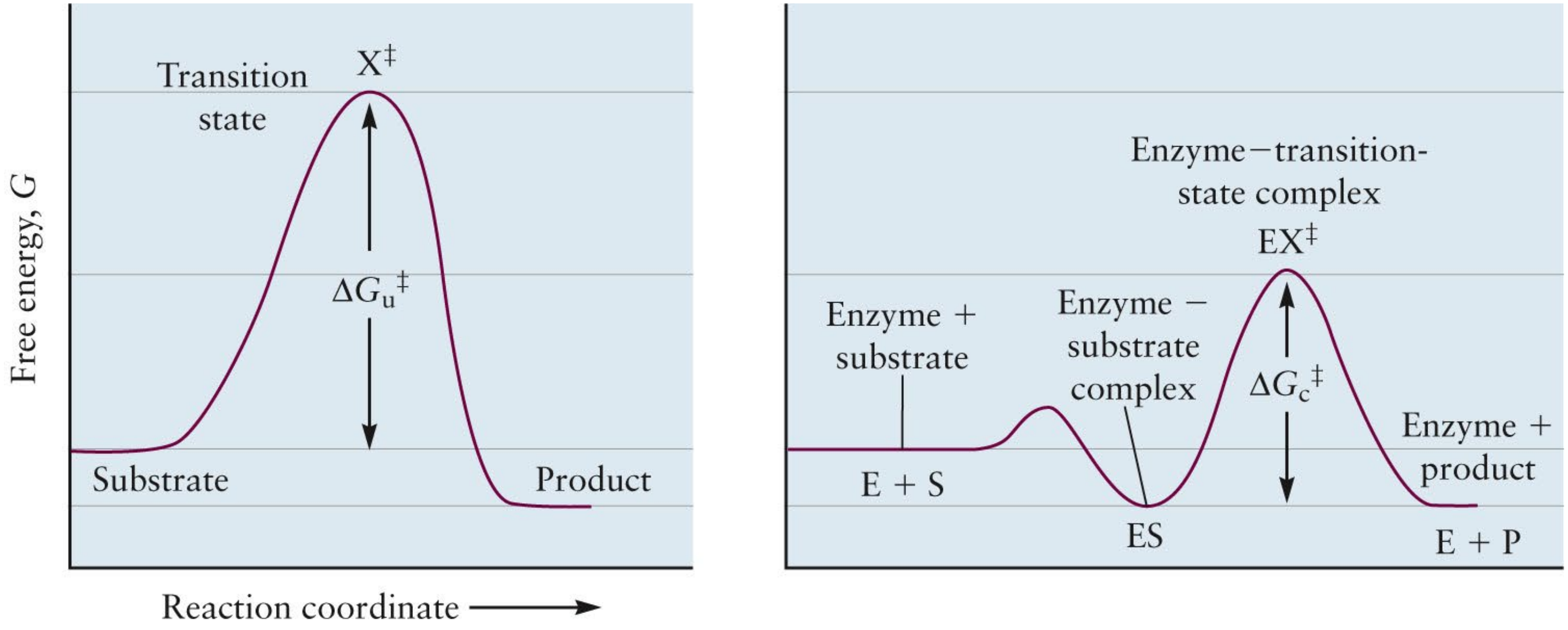


**Fig.18.26** The enzyme hexokinase showing (a) the active site before binding substrate and (b) binding of glucose accompanied by global structural changes that brings the two domains together and closes off the active site.

# ◆ Thermodynamics of enzyme-catalyzed reactions

~ Interplay between the destabilization of ES complex and the stabilization of the transition state EX$^\dagger$



(a) $S \rightleftharpoons X^\ddagger \rightarrow P$

(b) $E + S \rightleftharpoons ES \rightleftharpoons EX^\ddagger \rightarrow E + P$

**Fig. 18.27** (a) Free-energy profile for the uncatalyzed conversion of substrate to product. (b) Energy profile for the enzyme-catalyzed reaction that shows the preferential stabilization of the enzyme transition-state complex with respect to the enzyme substrate complex.