

Chapter 20. Chemical Kinetics

Concentrations of Reactants and Products = *function* $\alpha, \beta, \gamma, \dots$ (time)

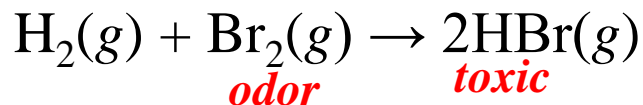
The methods of monitoring the concentrations

1. Pressure change



- The pressure of the system increases during the course of reaction.
- Inappropriate for the reactions that leave the overall pressure unchanged, and for reactions in solution.

2. Spectroscopy



By monitoring the intensity of **absorption** of light $h\nu$ by the bromine, the progress of the reaction can be monitored.

3. Polarimetry

When the optical activity of a mixture changes in the course of reaction, it can be monitored by measuring the **angle of optical rotation**.

4. Electrochemical Methods

When a reaction changes the **number or nature of ions** present in a solution, its course may be followed by monitoring the **electrical conductivity or pH** of the solution.

5. Characterization Methods

mass spectroscopy *charge/mass*

emission spectroscopy *h ν , electron, ion*

nuclear-magnetic resonance

Raman spectroscopy *h ν*

infra-red absorption **x-ray absorption** *h ν*

x-ray diffraction *h ν*

etc.

Methods of applying these analytical techniques

1. **Real-Time Analysis**: the composition of the system is analyzed while the reaction is in progress.
 2. **Quenching**: the reaction is frozen after it has been allowed to proceed for a certain time, and then the composition is analyzed by any suitable techniques.
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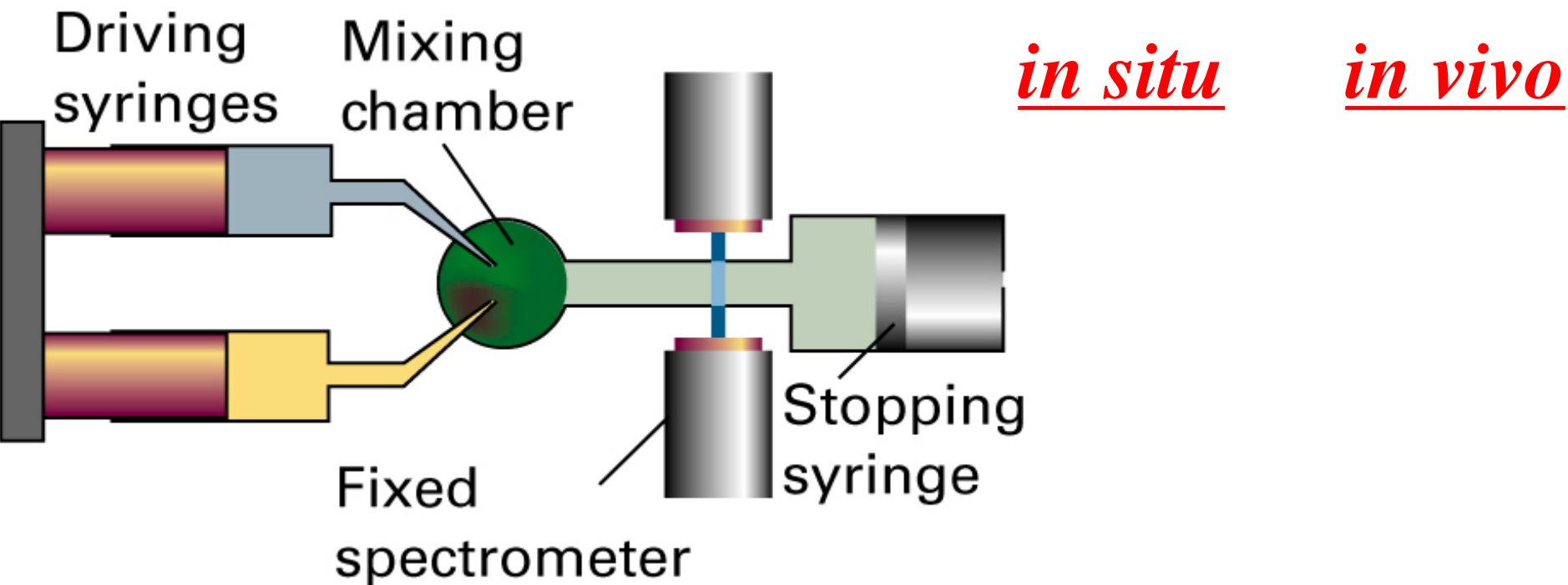
The Rates of Reactions



where [A], [B], [P]: the concentrations of the species, A, B, and P.

The rate of reaction

$$\frac{d[P]}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$



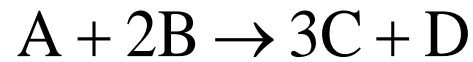
$$\underline{P(t), T(t), V(t), C_{\alpha}(t), C_{\beta}(t), C_{\gamma}(t), \dots}$$

Figure 20A.2. *Real-Time Analysis*

In the stopped-flow technique, the reagents are driven quickly into the mixing chamber by the driving syringes, and then the time dependence of the concentrations is monitored.

Steady State

Quenching



$$\underline{v = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = \frac{d[D]}{dt}}$$

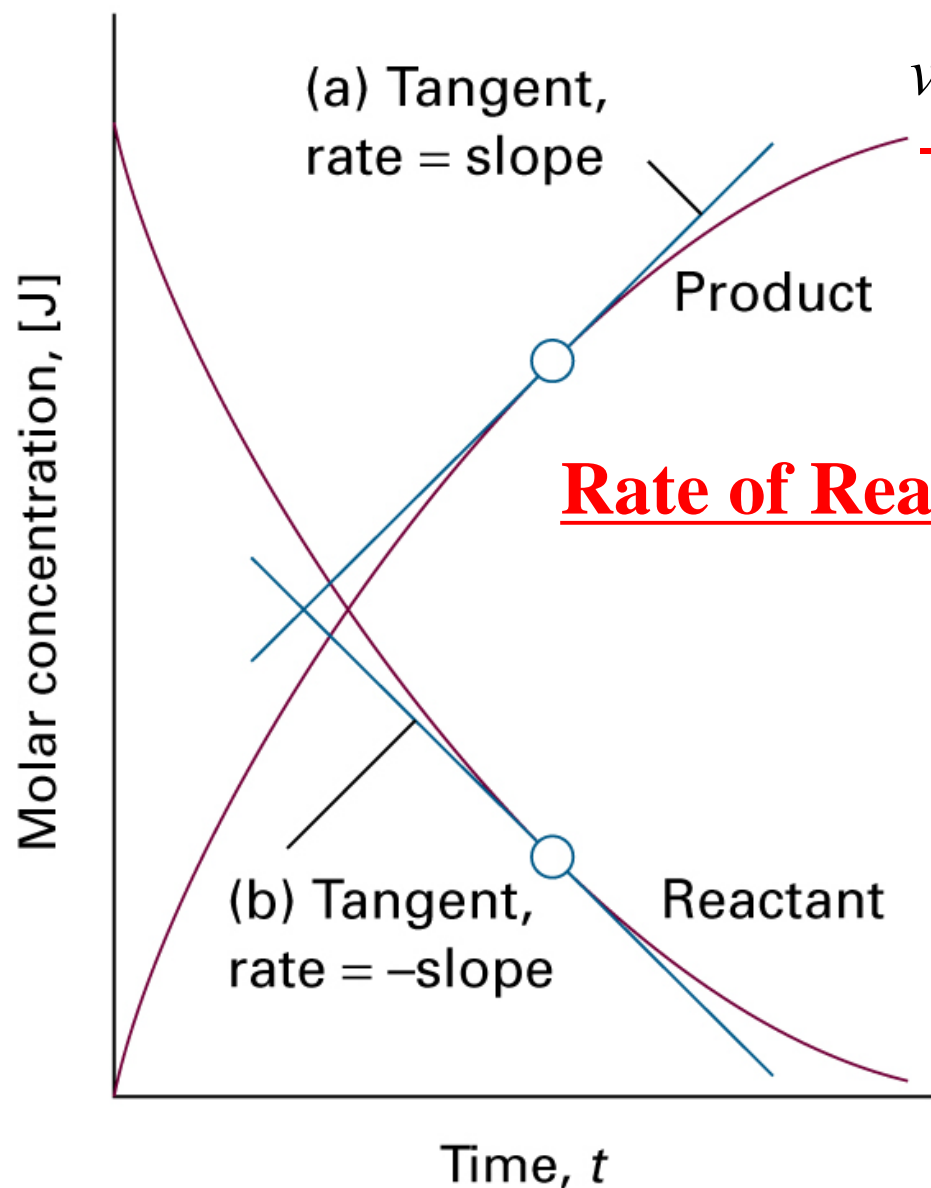


Figure 20A.3

The definition of (instantaneous) rate as the slope of the tangent drawn to the curve showing the variation of concentration with time. For negative slopes, the sign is changed when reporting the rate, so all **reaction rates** are positive.

20A.2(c). Determination of the Rate Law

A direct method for determining the rate law from the raw kinetic data giving the concentration as a function of time is from the measurement of slopes.*

The reaction between A and B: $A + B \rightarrow P$ (Product)

$$v = -\frac{d[A]}{dt} = k[A]^a[B]^b = \frac{d[P]}{dt}$$

Reaction Rate
Reaction Order

$$-\left(\frac{d[A]}{dt}\right) = k[A]^a[B]^b$$

$$\log\left\{-\left(\frac{d[A(t)]}{dt}\right)\right\} = \log k + a \log[A(t)] + b \log[B(t)]$$

A plot of the rate against various concentrations of A and B gives the orders a and b from the slopes, and $\log k$ from the intercept.

* Only when the rate constant k is independent of concentration.



$$v = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

The ambiguity in the definition of Reaction Rate is avoided if

we define the rate of reaction v as

$$v = \frac{1}{\nu_J} \frac{d[J]}{dt} \tag{20A.3b}$$

where ν_J is the stoichiometric constant of substance J .

20B.1. The First-Order Reactions



$$\underline{-\frac{d[A]}{dt} = k_1[A]}$$

$$-\frac{d[A]}{[A]} = k_1 dt$$

$$\int_{[A]_0}^{[A]_t} \left(-\frac{d[A]}{[A]} \right) = \int_0^t k_1 dt$$

$$-(\ln[A]_t - \ln[A]_0) = k_1 t$$

$$\ln \frac{[A]_t}{[A]_0} = -k_1 t$$

$$\underline{\therefore [A]_t = [A]_0 \exp(-k_1 t)}$$

k_1 = rate constant = independent of concentration ₇

$$[A]_t = [A]_0 \exp(-k_1 t) \quad \text{First-Order Reactions}$$

The concentration of A falls **exponentially** with time with a rate determined by k_1 .

20B.2. The Second-Order Reactions



$$\underline{-\frac{d[A]}{dt} = k_2 [A]^2}$$

$$\int_{[A]_0}^{[A]_t} \left(-\frac{d[A]}{[A]^2} \right) = \int_0^t k_2 dt$$

$$\therefore \frac{1}{[A]_t} - \frac{1}{[A]_0} = k_2 t$$

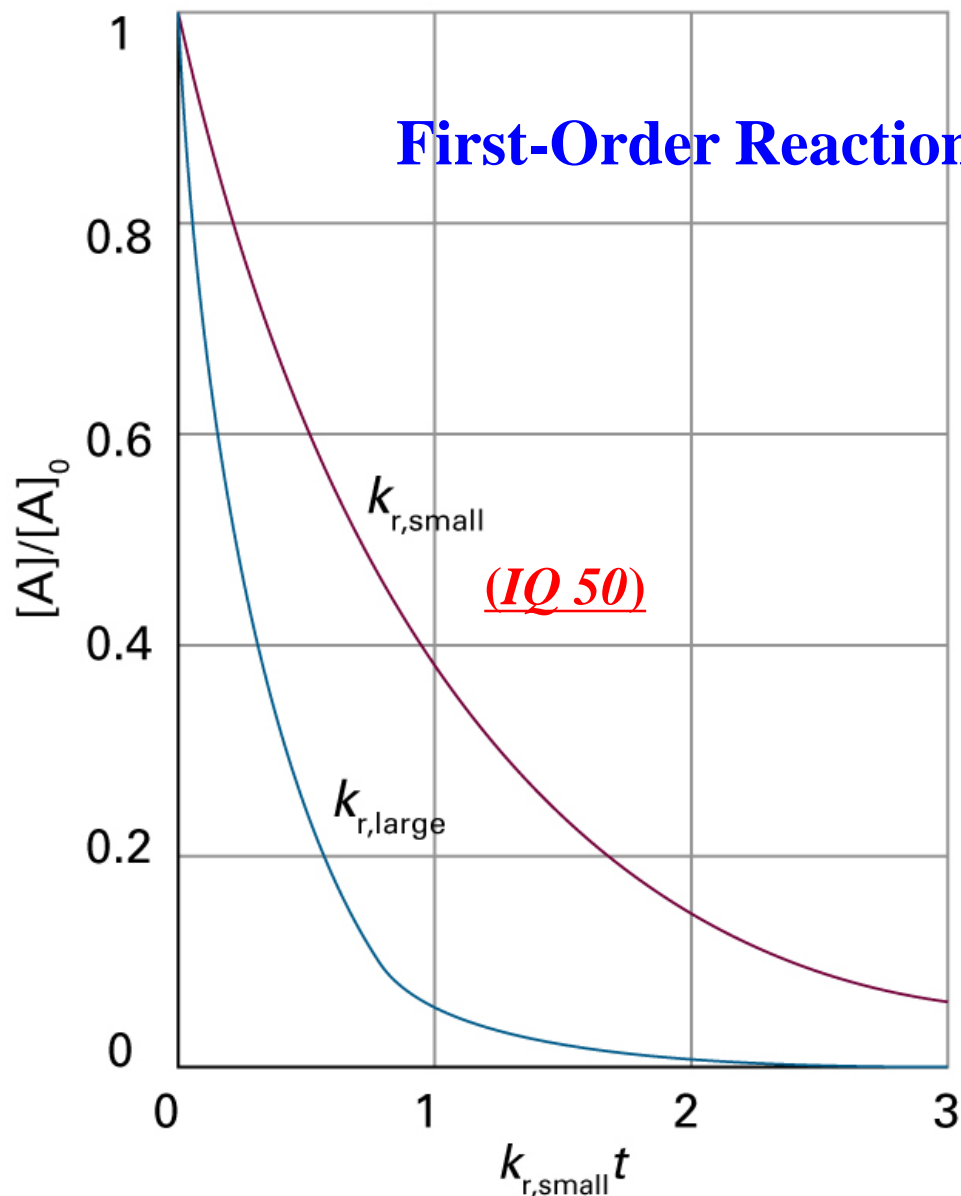
$$[A]_t = \frac{[A]_0}{1 + k_2 t [A]_0}$$

When $\frac{1}{[A]_t}$ is plotted against t , a straight line should be obtained and

the slope is second-order rate coefficient k_2 .



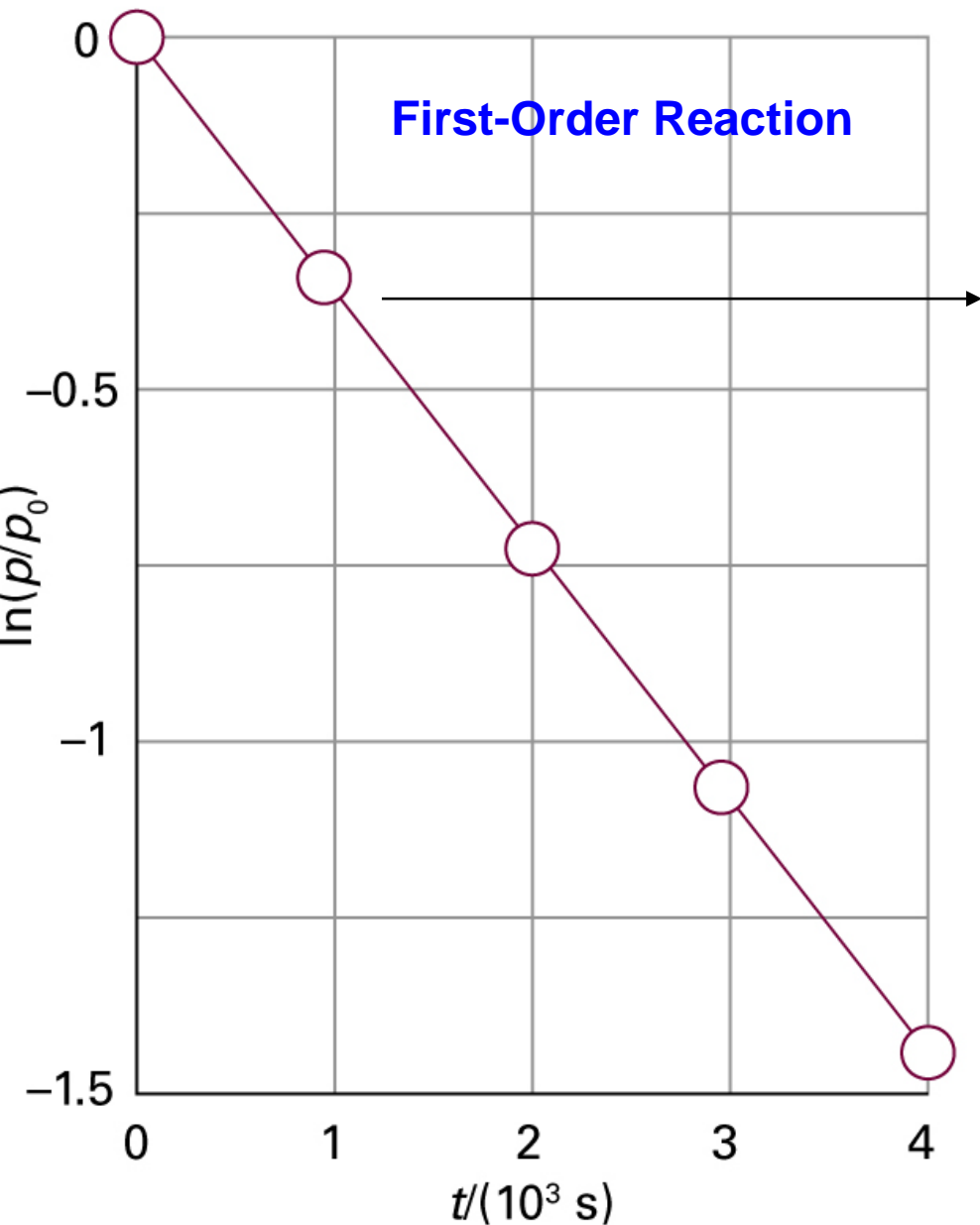
$$[A]_t = [A]_0 \exp(-k_1 t)$$



log [A] vs. time

Figure 20B.1

The **exponential decay** of the reactant in a first-order reaction. The larger the rate constant, the more rapid the decay: here $k_{large} = 3k_{small}$.



$$[A]_t = [A]_0 \exp(-k_1 t)$$

$$= [A]_0 \exp(-t / \tau)$$

k_1
 = First-Order Rate Constant

$\tau = \frac{1}{k_1}$ = Time Constant
 = Lifetime
 = Relaxation Time

Figure 20B.2

The determination of the rate constant of a first-order reaction: a straight line is obtained when **ln [A]** (or, as here, **ln p**) is plotted **against t**, and the slope gives **k**.



Second-Order Reaction

$$-\frac{d[A]}{dt} = k_2[A]^2$$

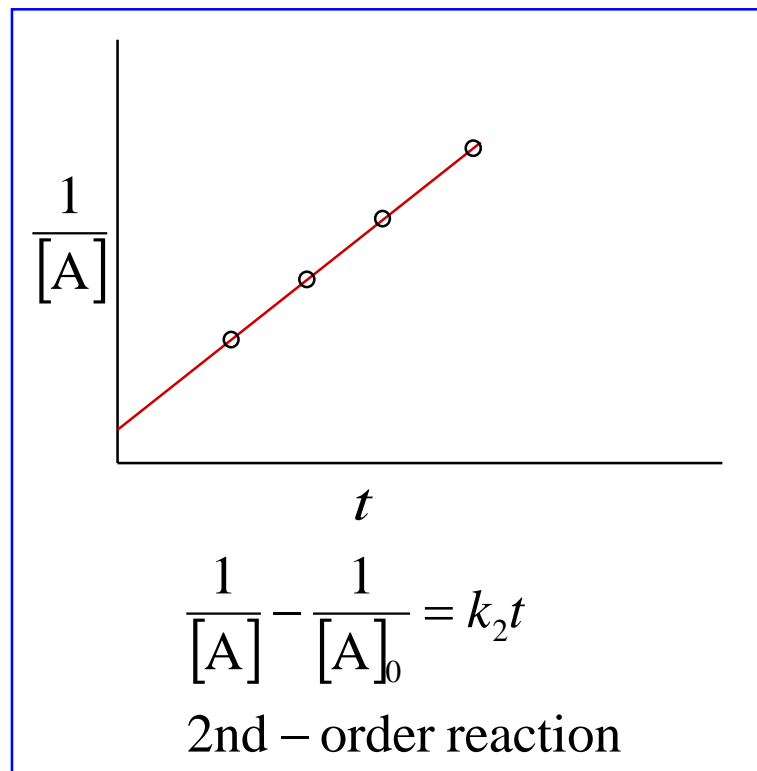
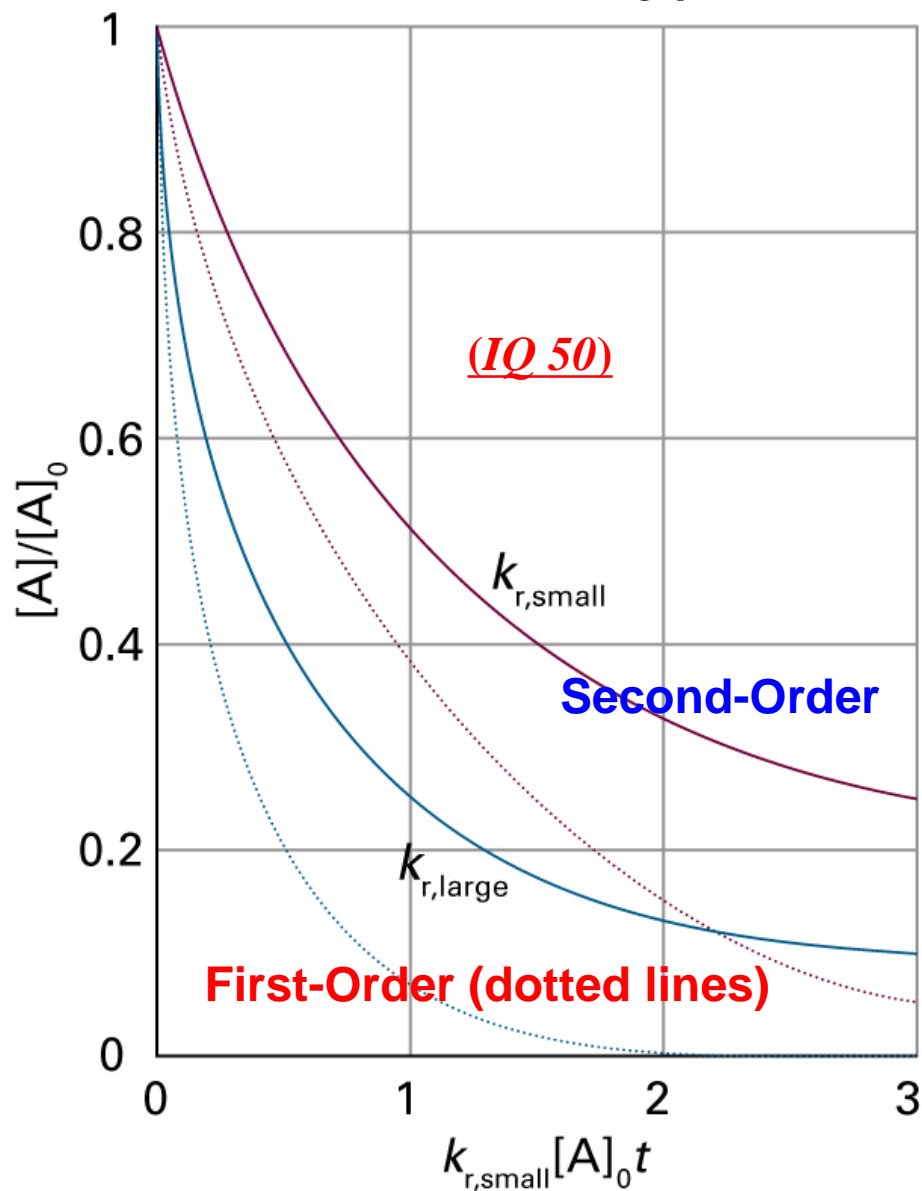


Figure 20B.3

The variation with time of the concentration of a reactant in a second-order reaction. The dotted line is the corresponding decay in a first-order reaction with the same initial rate. For this illustration, $k_{large} = 3k_{small}$.

* Only when the rate constant k is independent of concentration.

Table 20B.3 Integrated rate laws

Order	Reaction	Rate law*	$t_{1/2}$
0	$A \rightarrow P$	$v = k_r$ $k_r t = x$ for $0 \leq x \leq [A]_0$	$[A]_0/2k_r$
1	$A \rightarrow P$	$v = k_r[A]$ $k_r t = \ln \frac{[A]_0}{[A]_0 - x}$	$(\ln 2)/k_r$
2	$A \rightarrow P$	$v = k_r[A]^2$ $k_r t = \frac{x}{[A]_0([A]_0 - x)}$	$1/k_r[A]_0$
	$A + B \rightarrow P$	$v = k_r[A][B]$ $k_r t = \frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}$	
	$A + 2 B \rightarrow P$	$v = k_r[A][B]$ $k_r t = \frac{1}{[B]_0 - 2[A]_0} \ln \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	

* Only when the rate constant k is independent of concentration.

Order	Reaction	Rate law*	$t_{1/2}$
	A → P with autocatalysis	$v = k_r[A][P]$ $k_r t = \frac{1}{[A]_0 + [P]_0} \ln \frac{[A]_0([P]_0 + x)}{([A]_0 - x)[P]_0}$	
3	A + 2 B → P	$v = k_r[A][B]^2$ $k_r t = \frac{2x}{(2[A]_0 - [B]_0)([B]_0 - 2x)[B]_0} + \frac{1}{(2[A]_0 - [B]_0)^2} \ln \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
$n \geq 2$	A → P	$v = k_r[A]^n$ $k_r t = \frac{1}{n-1} \left\{ \frac{1}{([A]_0 - x)^{n-1}} - \frac{1}{[A]_0^{n-1}} \right\}$	$\frac{2^{n-1} - 1}{(n-1)k_r[A]_0^{n-1}}$

* $x = [P]$ and $v = dx/dt$.

20B.1. Half-Life and Time Constant

A simple indication of the rate of a chemical reaction is the time it takes for the concentration of a reagent to fall to half of its initial value: this is called **the half-life of the reaction**, and is denoted $t_{1/2}$.

First-Order Reaction:

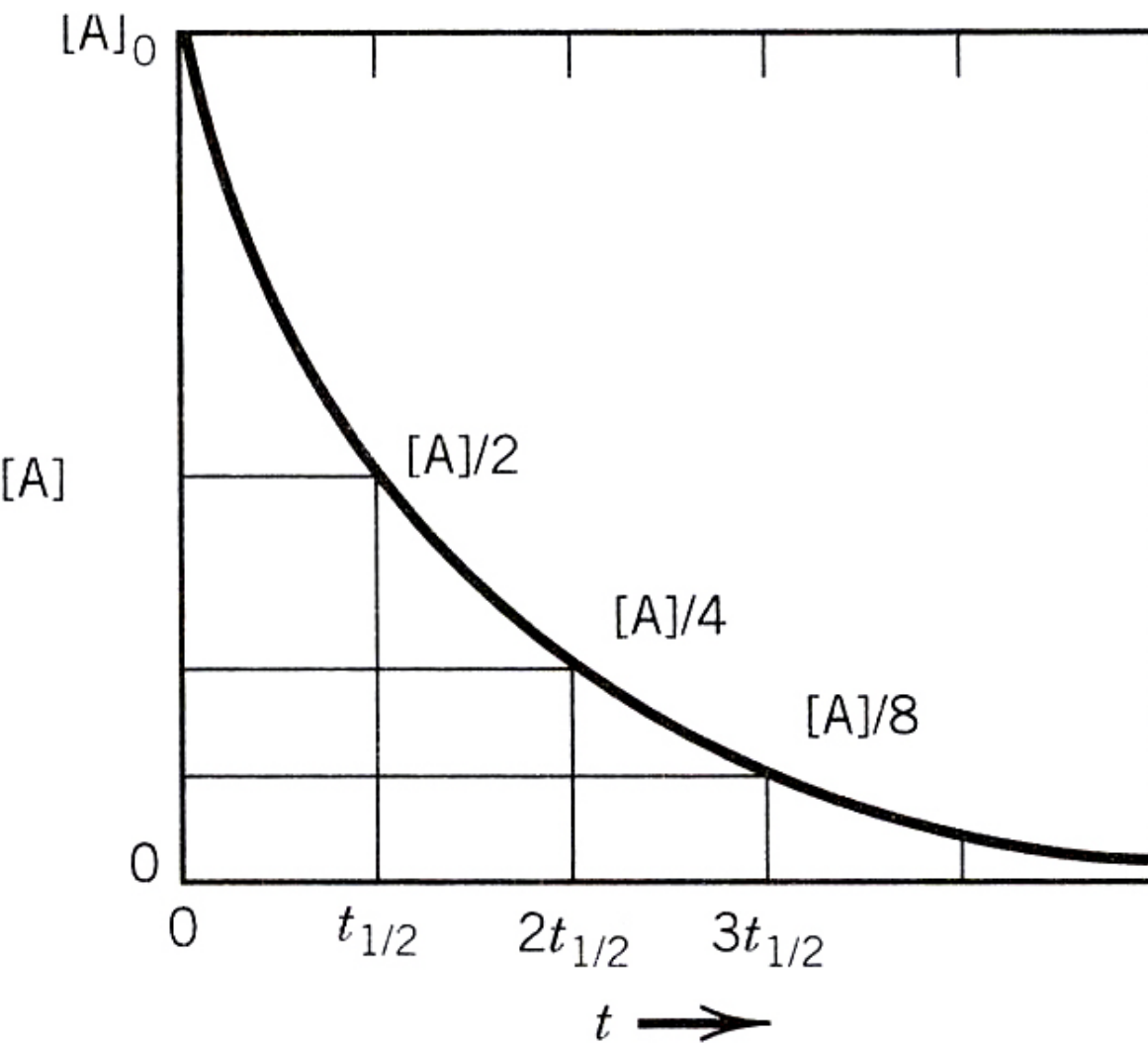
$$[A]_0 \rightarrow \frac{1}{2}[A]_0 \text{ at } t_{1/2}$$
$$-k_1 t_{1/2} = \ln \frac{\frac{1}{2}[A]_0}{[A]_0} = -\ln 2$$

$$\therefore t_{1/2} = \frac{\ln 2}{k_1}$$

$$\tau = \frac{1}{k_1}$$

$$[A]_t = [A]_0 \exp(-k_1 t)$$
$$= [A]_0 \exp(-t / \tau)$$

- **Time Constant**
- **Lifetime**
- **Relaxation Time**



$$[A]_t = [A]_0 \exp(-k_1 t)$$

$$= [A]_0 \exp(-t / \tau)$$

$$t_{1/2} = \frac{\ln 2}{k_1}$$

For a first-order reaction, one-half of the reactant disappears in $t_{1/2}$ independent of the initial concentration.

20D. Temperature Dependence of Reaction Rates

In many experiments, the temperature dependence of the rate has been found to fit the expression proposed by **Arrhenius**:

$$k_r = A \exp\left(-\frac{E_a}{RT}\right)$$

Rate Constant

Activation Enthalpy
≈ Activation Energy

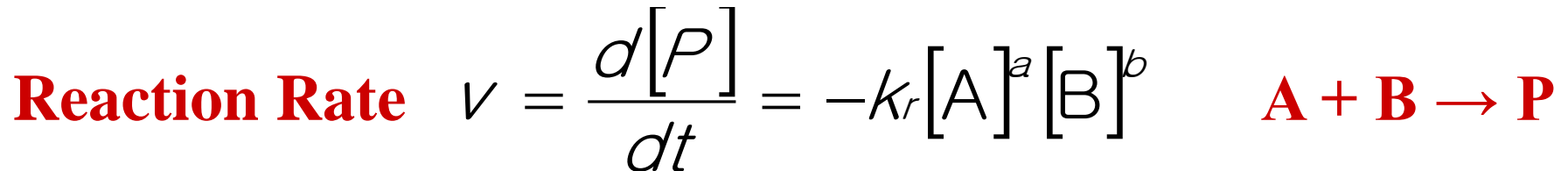
where A and E_a are

Pre-Exponential Factor: Independent of temperature

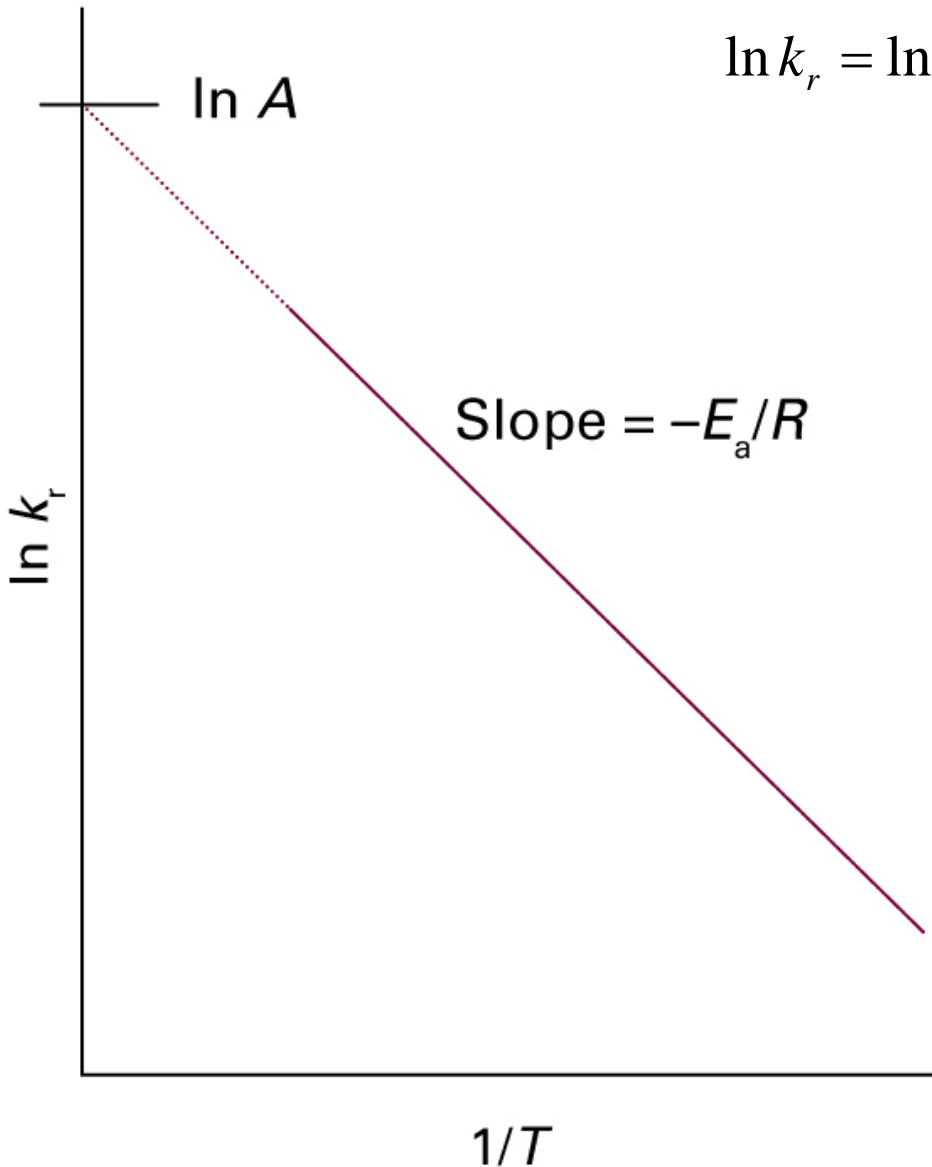
Activation Energy: Determined from a plot of $\ln k_r$ against $1/T$

Approximately independent of temperature

$$\ln k_r = \ln A - \frac{E_a}{RT}$$



Rate Constant: k_r



$$\ln k_r = \ln A - \frac{E_a}{RT}$$

Figure 20D.1

A plot of $\ln k$ against $1/T$ is a straight line when the reaction follows the behavior described by the

Arrhenius-Type
Temperature
Dependence.



$$\begin{aligned}\Delta G &= G_{\text{activated}} - G_{\text{reactant}} \\ &= \Delta H - T \Delta S \\ &= \Delta E - T \Delta S + P \Delta V\end{aligned}$$

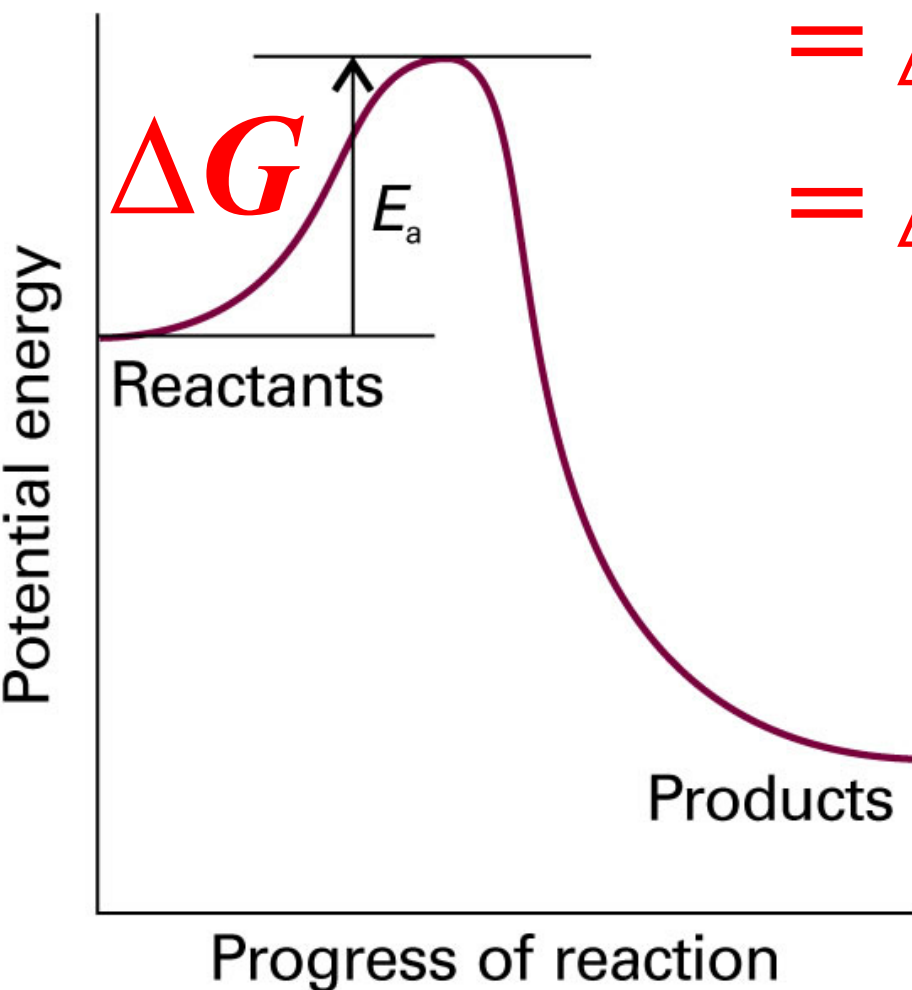
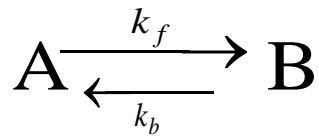


Figure 20D.3. A potential energy profile for an **exothermic (not always)** reaction. The height of the barrier between the reactants and products is the **activation energy (activation enthalpy)** of the reaction.

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20C.1. First-Order Reactions Approaching Equilibrium



- considering Backward Reaction

$$\frac{d[A]}{dt} = -k_f [A] + k_b [B] \quad (20C.2)$$

If the initial amount of A is $[A]_0$, and if initially there is no B present, then $[A] + [B] = [A]_0$ at all times:

$$\frac{d[A]}{dt} = -k_f [A] + k_b ([A]_0 - [A]) = -(k_f + k_b)[A] + k_b [A]_0$$

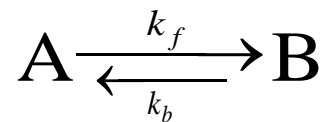
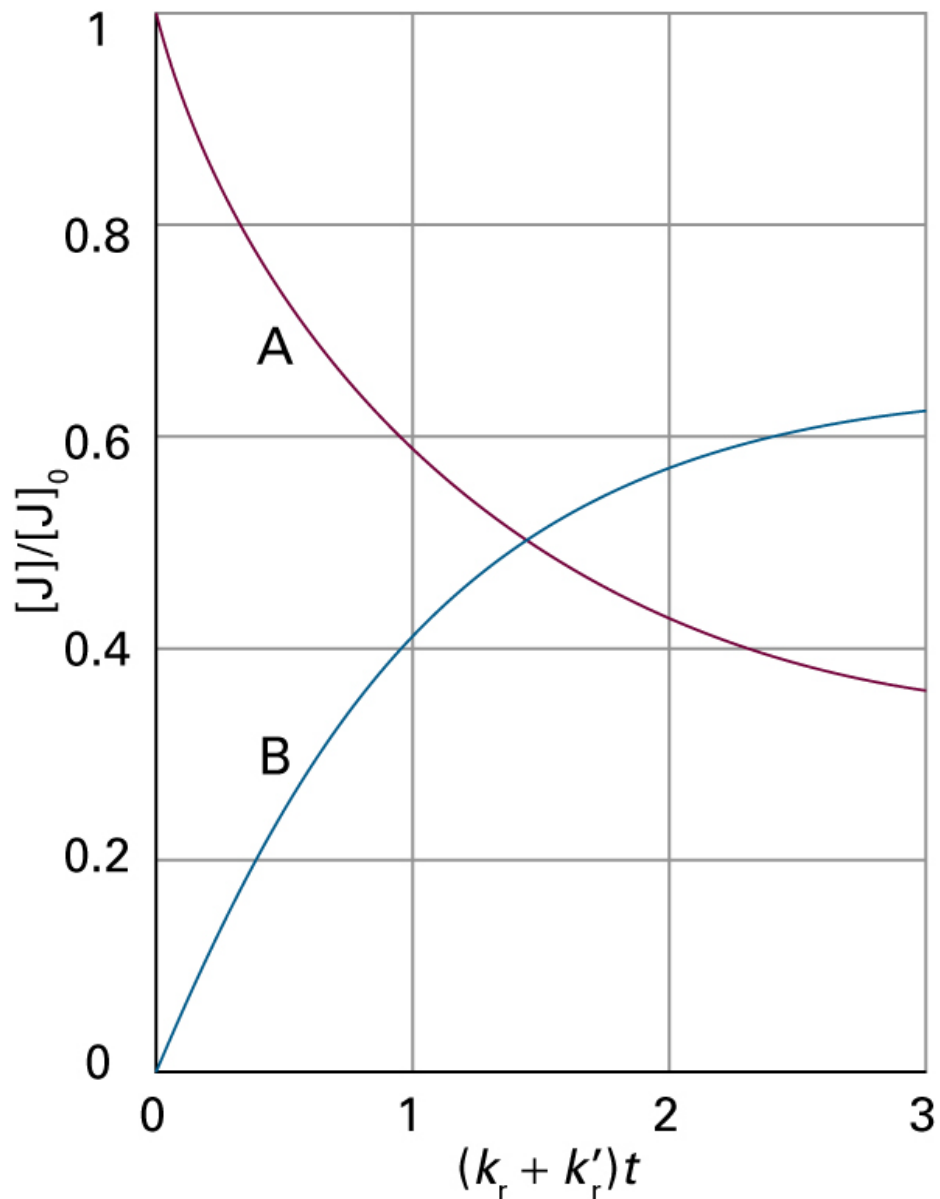
The solution of this first-order differential equation:

$$[A]_t = [A]_0 \left\{ \frac{k_b + k_f \exp[-(k_f + k_b)t]}{k_f + k_b} \right\} \quad (20C.4)$$

If $k_b = 0$ (no reverse reaction), the equation becomes

$$[A]_t = [A]_0 \exp(-k_f t)$$

ppt 20-7



$$[A] + [B] = [A]_0$$

Figure 20C.1

The approach of concentrations to their equilibrium values as predicted by the equation for a reaction $A \rightleftharpoons B$ that is first-order in each direction, and for which $k_f = 2k_b$.

$$[A]_t = [A]_0 \left\{ \frac{k_b + k_f \exp[-(k_f + k_b)t]}{k_f + k_b} \right\} \quad (20C.4)$$

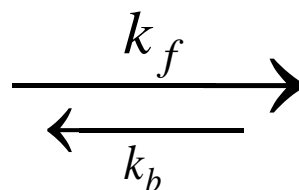
What is the final state of the system?

$$t \rightarrow \infty \quad [A]_\infty = \frac{k_b [A]_0}{k_f + k_b}, \quad [B]_\infty = [A]_0 - [A]_\infty = \frac{k_f [A]_0}{k_f + k_b} \quad [A] + [B] = [A]_0$$

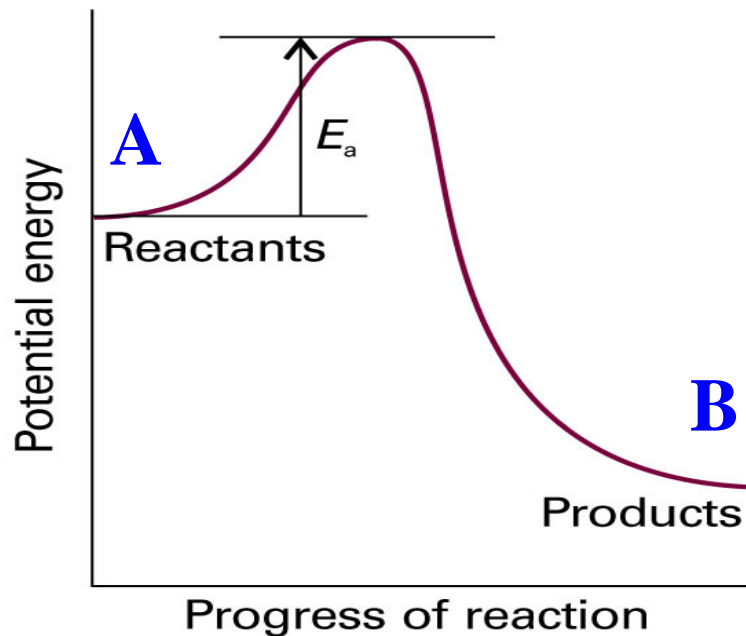
$$K = \frac{[B]_\infty}{[A]_\infty} = \frac{k_f}{k_b}$$

Equilibrium Constant

First-Order Reactions Approaching Equilibrium



(20C.6)



20C.2. Relaxation Method

The term **relaxation** denotes the return of a system to equilibrium. It is used in chemical kinetics to indicate that **an externally applied influence** has shifted the equilibrium position of a reaction, normally **suddenly**, and that the reaction is adjusting to the equilibrium composition characteristic of new conditions.



$$x = x_0 e^{-\frac{t}{\tau}}, \quad \frac{1}{\tau} = k_f + k_b \quad \text{at } T_2$$

where x_0 is the departure from equilibrium immediately after the temperature jump, and x is the departure from equilibrium at the new temperature after a time t .

$$\text{at } T_1 \quad [A]_t = [A]_b \left\{ \frac{k_b + k_f \exp[-(k_f + k_b)t]}{k_f + k_b} \right\}$$

$$k_f [A]_{eq} = k_b [B]_{eq} \quad \text{at } T_1 \quad \text{Equilibrium Constant } K = \frac{[B]_{\infty}}{[A]_{\infty}} = \frac{k_f}{k_b}$$

We write the deviation of $[A]$ from its new equilibrium value as x , so **at T_2**
 $[A] = [A]_{eq} + x$ and $[B] = [B]_{eq} - x$ **at T_2** . The concentration of A then changes as:

$$\begin{aligned} \frac{d[A]}{dt} &= -k_f [A] + k_b [B] \quad \text{at } T_2 && k_f(T_2) \quad k_b(T_2) \\ &= -k_f ([A]_{eq} + x) + k_b ([B]_{eq} - x) && \text{perturbation} \\ &\approx -(k_f + k_b)x \end{aligned}$$

Because of $d[A]/dt = dx/dt$,

$$\frac{dx}{dt} = -(k_f + k_b)x$$

$$\frac{dx}{x} = -(k_f + k_b)dt \Rightarrow \ln \frac{x}{x_0} = -(k_f + k_b)t$$

$$x = x_0 e^{-(k_f + k_b)t} = x_0 e^{-\frac{t}{\tau}}, \text{ where } \frac{1}{\tau} = k_f + k_b$$

Since $K \approx k_f/k_b$, its value may be combined with the relaxation-time measurement to find the individual k_f and k_b .

Temperature Jumping Up

[A]
Concentration, [A]

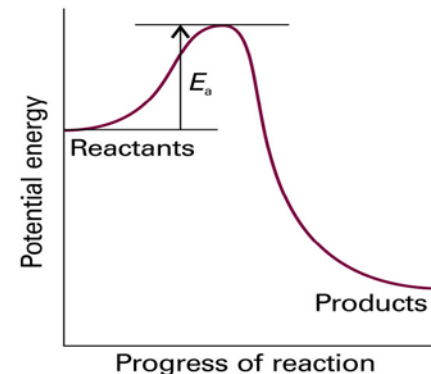
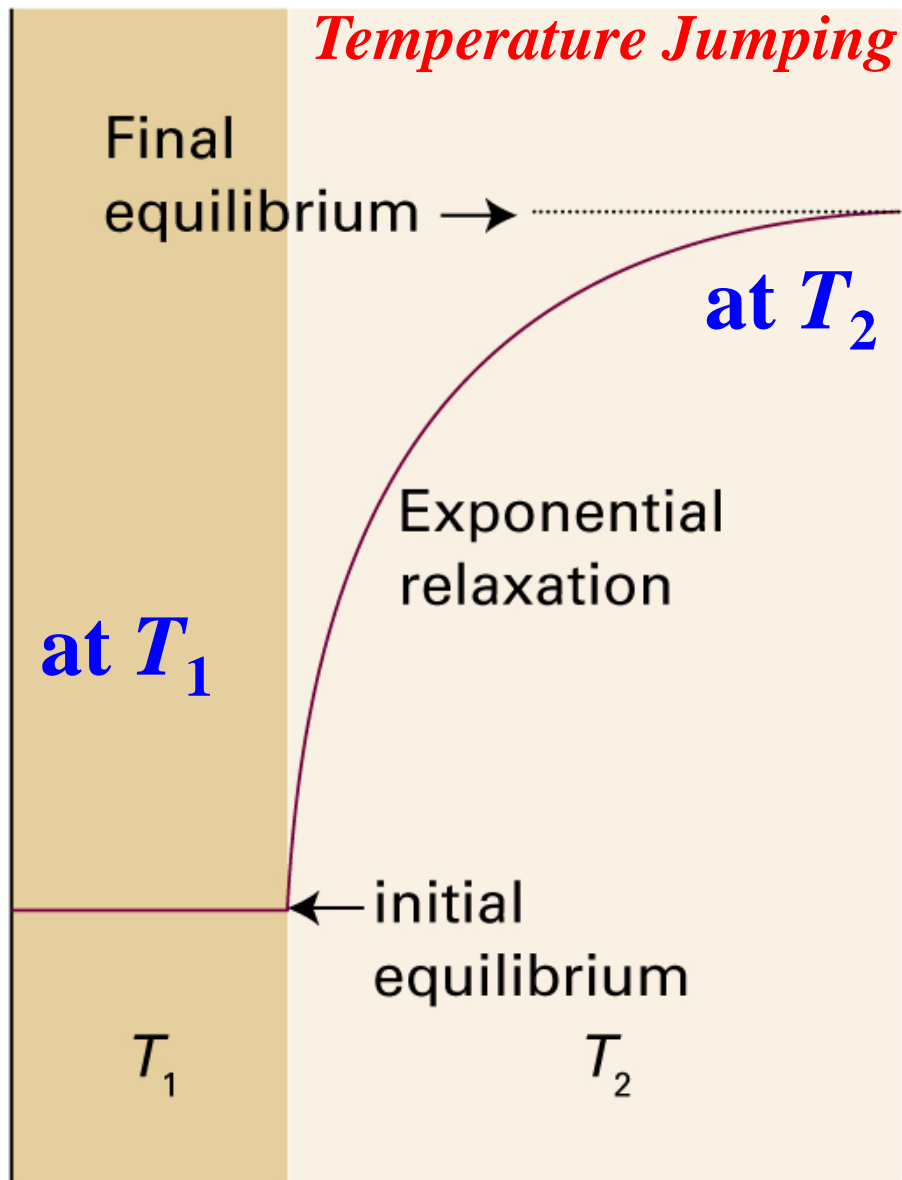


Figure 20C.2

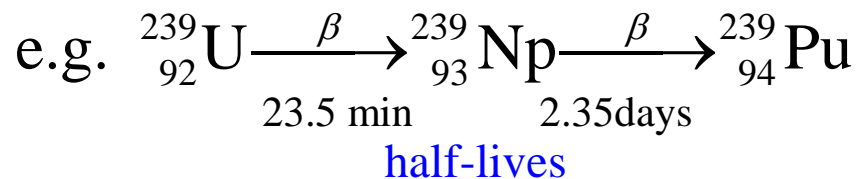
The relaxation to the new equilibrium composition

when a reaction initially at equilibrium at a temperature T_1 is subjected to a **sudden change** to temperature T_2 .

20E.2. Consecutive Reactions and the Steady State



(Assume no backward reaction)



$$\frac{d[A]}{dt} = -k_1[A], \quad \frac{d[B]}{dt} = k_1[A] - k_1'[B], \quad \frac{d[C]}{dt} = k_1'[B]$$

We suppose that only A is present initially, and that its concentration is then $[A]_0$.

$$[A]_t = [A]_0 \exp(-k_1 t) \quad (20E.4a)$$

If this result is inserted into the equation for B and the condition $[B]_0=0$ imposed, we arrived at

$$[B]_t = [A]_0 \left\{ \frac{k_1}{k_1' - k_1} \right\} \left(e^{-k_1 t} - e^{-k_1' t} \right) \quad (20E.4b)$$

$$[A]_t + [B]_t + [C]_t = [A]_0$$

$$[C]_t = [A]_0 - [A]_t - [B]_t = [A]_0 \left\{ 1 + \left(\frac{1}{k_1 - k_1'} \right) \right\} \left(k_1' e^{-k_1 t} - k_1 e^{-k_1' t} \right) \quad (20E.4c)$$

The solution for [B]



$$\frac{d[A]}{dt} = -k[A] \quad (1)$$

$$\frac{d[B]}{dt} = k_1[A] - k_1'[B] \quad (2)$$

$$\frac{d[C]}{dt} = k_1'[B] \quad (3)$$

$$[A] = [A]_0 \exp(-k_1 t) \quad (4)$$

(4) \rightarrow (2)

$$\frac{d[B]}{dt} = k_1[A]_0 \exp(-k_1 t) - k_1'[B] \quad (5)$$

$$\text{Let } Y = [B]e^{k_1't}$$

$$\frac{dY}{dt} = e^{k_1't} \frac{d[B]}{dt} + [B]k_1'e^{k_1't}$$

$$\therefore e^{-k_1't} \frac{dY}{dt} = \frac{d[B]}{dt} + k_1'[B] \quad (6)$$

Rearranging eq (5)

$$\frac{d[B]}{dt} + k_1'[B] = k_1[A]_0 \exp(-k_1t) \quad (7)$$

From eqs (6) and (7)

$$e^{-k_1't} \frac{dY}{dt} = k_1[A]_0 \exp(-k_1t)$$

$$\frac{dY}{dt} = k_1[A]_0 e^{(k_1'-k_1)t}$$

$$dY = k_1[A]_0 e^{(k_1'-k_1)t} dt$$

$$Y_t - Y_0 = \frac{k_1[A]_0}{k_1' - k_1} e^{(k_1'-k_1)t} - \frac{k_1[A]_0}{k_1' - k_1}$$

$$[B]e^{k_1't} - 0 = \frac{k_1[A]_0}{k_1' - k_1} e^{(k_1'-k_1)t} - \frac{k_1[A]_0}{k_1' - k_1}$$

$$[B] = \frac{k_1[A]_0}{k_1' - k_1} (e^{-k_1t} - e^{-k_1't})$$

(i) The three equations for [A], [B] and [C] indicate how to analyze a reaction scheme consisting of **two consecutive first-order reactions**.

(ii) **“Rate-Determining Step”** **{Bottle-Neck Effect}**

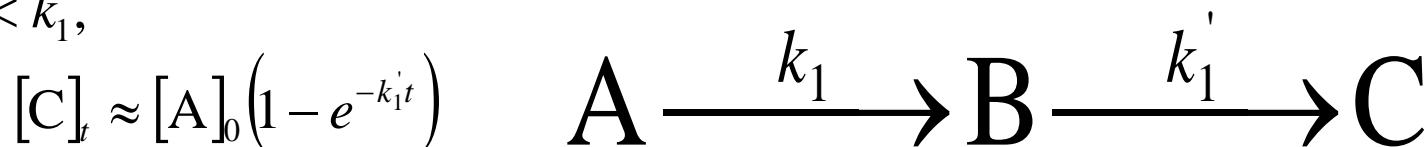
If $k_1' \gg k_1$, whenever B molecules is formed, it decays quickly into C.

Sec. 20E.4

$$[C]_t = [A]_0 \left\{ 1 + \left(\frac{1}{k_1 - k_1'} \right) \left(k_1' e^{-k_1 t} - k_1 e^{-k_1' t} \right) \right\} \quad \text{병목현상}$$
$$\cong [A]_0 \left\{ 1 + \left(\frac{k_1'}{k_1 - k_1'} \right) e^{-k_1 t} \right\} \approx [A]_0 (1 - e^{-k_1 t})$$

The formation of C depends only on the smaller rate coefficient, as anticipated. For this reason, the step with the slowest rate is called **the rate-determining step** of the reaction.

If $k_1' \ll k_1$,



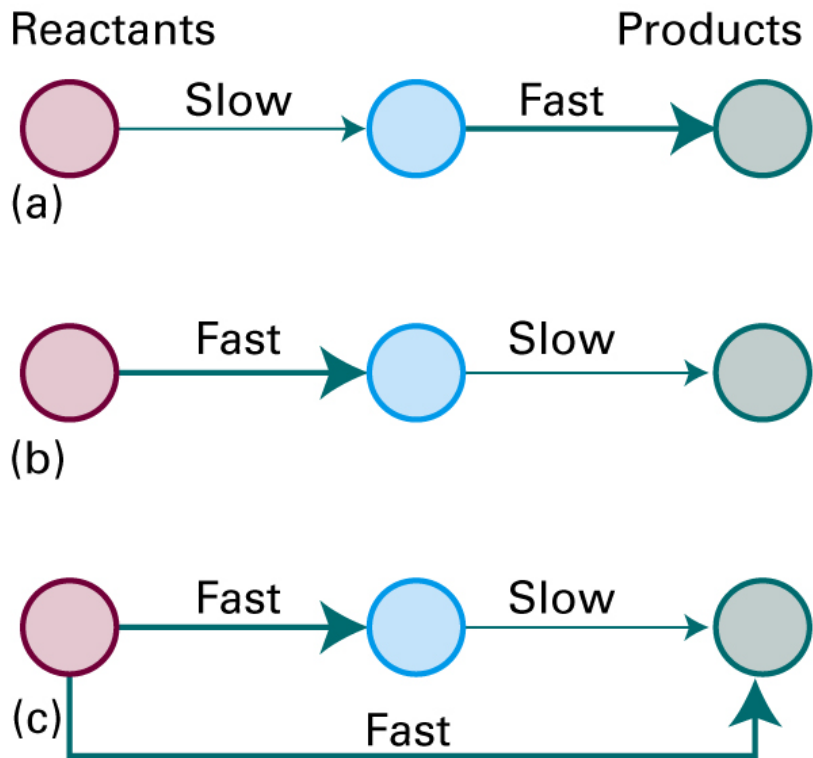
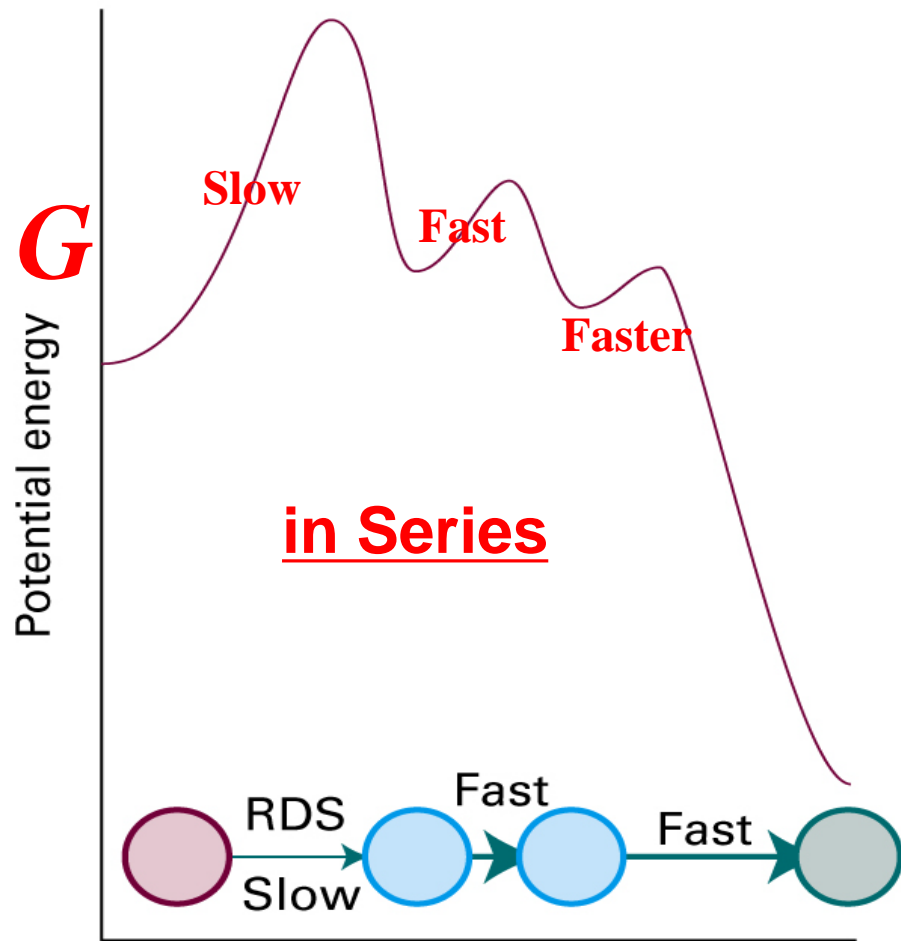


Figure 20E.4

- (a) The first step is rate determining.
- (b) The second step is rate-determining.
- (c) Although one step is slow, it is not rate-determining step because there is a **fast route that circumvents it**.

낙하산 인사



x-axis:

Progress of reaction

High (10^{23}) Dimensional Space

Figure 20E.5. Reaction profile for a mechanism in which the first step is rate-determining step.

20E.3. Steady-State Approximation

A couple of kinetic steps can induce
mathematical complexity.

The steady-state approximation assumes that during the major part of the reaction,

the concentrations of all reaction intermediates are approximately constant, and

the rates of changes of all reaction intermediates are negligibly small.

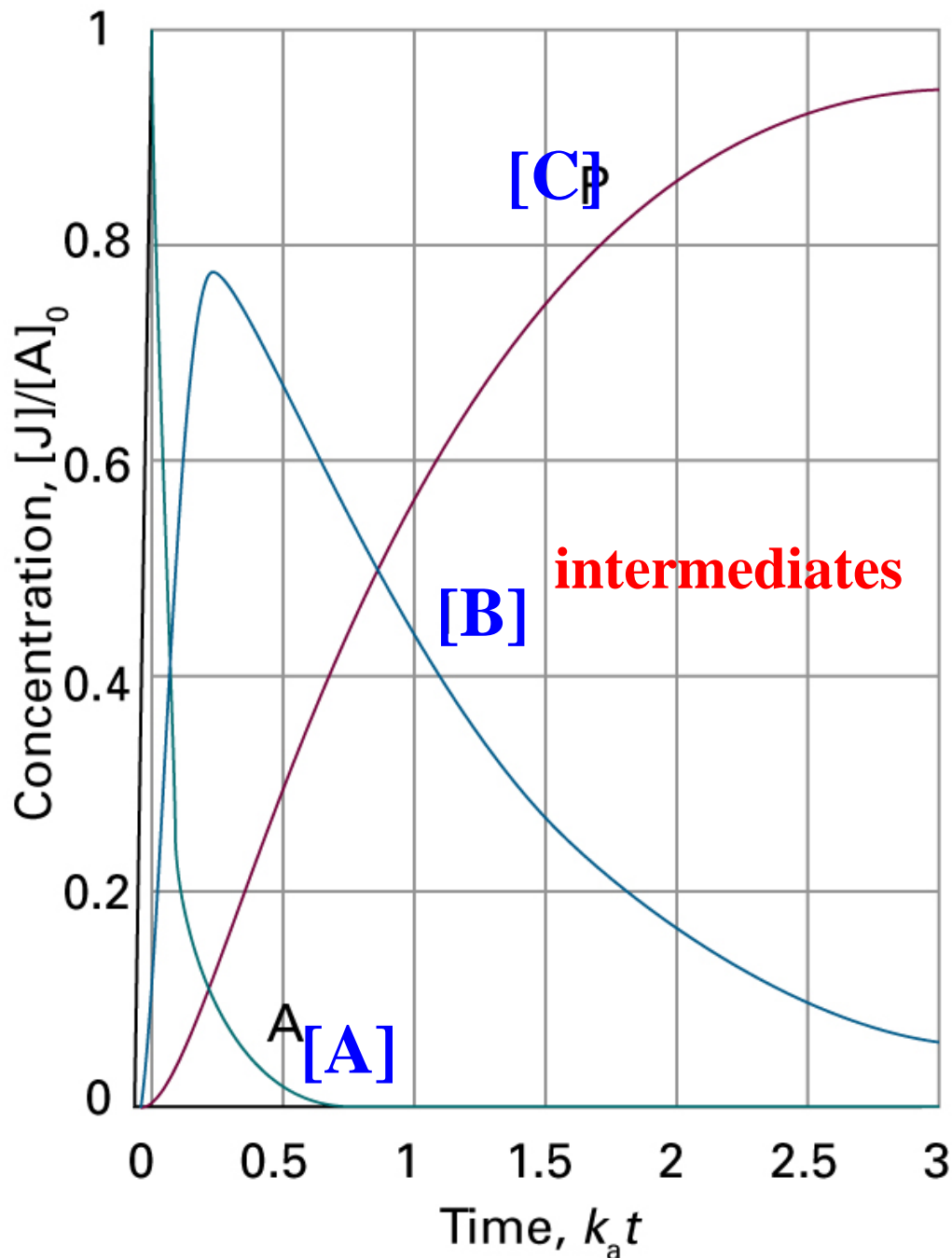


Figure 20E.1

The curves are plots with $k_1 = 10k_1'$. If the intermediate B is in fact the desired product, it is important to be able to predict when its concentration is greatest.

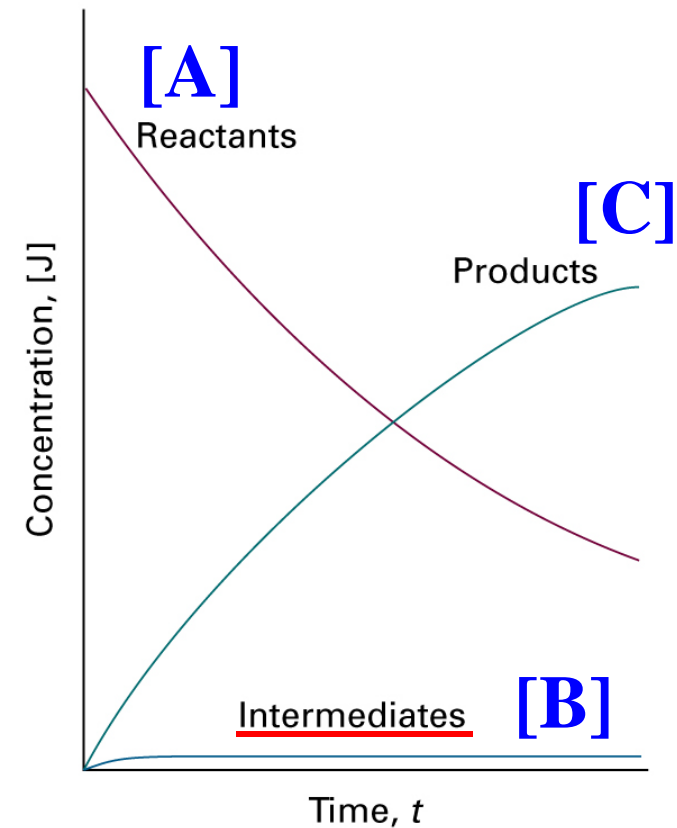
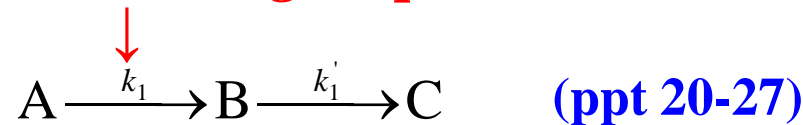


Fig. 20E.2

Steady-State Approximation

The concentrations of intermediates remain small and hardly change during most of the course of the reaction.

Rate-Limiting Step



$$[A] = [A]_0 e^{-k_1 t}, \quad [B] = \frac{k_1 [A]_0}{k_1' - k_1} (e^{-k_1 t} - e^{-k_1' t})$$

$$\frac{[B]}{[A]} = \frac{k_1}{k_1' - k_1} (1 - e^{(k_1 - k_1') t})$$

$$\text{If } k_1' \gg k_1, \quad \frac{[B]}{[A]} = \frac{k_1 (1 - e^{-k_1' t})}{k_1'}$$

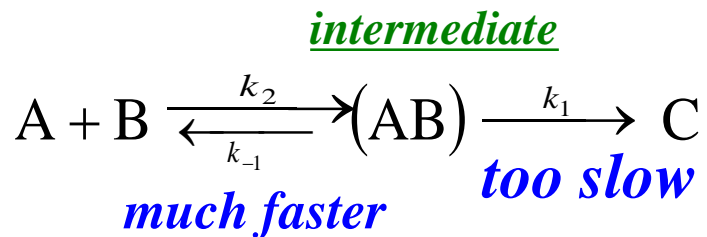
$$k_1' t \gg 1, \quad \frac{[B]}{[A]} = \frac{k_1}{k_1'}, \quad \therefore [B] = \frac{k_1}{k_1'} [A] \ll [A]$$

$$\frac{d[B]}{dt} = \frac{k_1}{k_1'} \frac{d[A]}{dt} \ll \frac{d[A]}{dt}$$

$$\therefore \frac{d[B]}{dt} \approx 0 \quad (20E.5)$$

20E.5. Pre-Equilibrium

The intermediate is in equilibrium with the reactants (approximately).



$$\frac{d[(\text{AB})]}{dt} = k_2[\text{A}][\text{B}] - k_{-1}[(\text{AB})]$$

Steady-state approximation

$$k_2[\text{A}][\text{B}] - k_{-1}[(\text{AB})] \approx 0$$

$$[(\text{AB})] = \frac{k_2}{k_{-1}}[\text{A}][\text{B}]$$

$$[(\text{AB})] = K[\text{A}][\text{B}]$$

$$\frac{d[\text{C}]}{dt} = k_1[\text{AB}] = k_1K[\text{A}][\text{B}]$$

$$K = \frac{[\text{Product}]}{[\text{Reactant}]} = \frac{[\text{B}]_{\infty}}{[\text{A}]_{\infty}} = \frac{k_f}{k_b}$$

(20E.12)

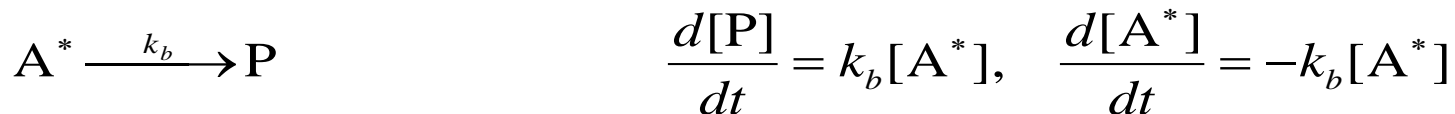
Therefore, the reaction has overall second-order kinetics.

Unimolecular Reactions

반응속도가 단일 반응물의 1차 반응으로 표시되는 반응.
그러나 실제로는 타 분자와의 충돌에 인한 에너지 이동을 포함한 복잡한 과정이며, 외견상 간단한 속도식으로 표시되는 경우가 많다.



Lindemann-Hinshelwood mechanism



If the unimolecular step is slow enough to be the rate-determining step,
the overall reaction will have the first-order kinetics (by steady-state).

$$\frac{d[\text{A}^*]}{dt} = k_a[\text{A}]^2 - k'_a[\text{A}^*][\text{A}] - k_b[\text{A}^*] \cong 0 \quad \therefore [\text{A}^*] = \frac{k_a[\text{A}]^2}{k_b + k'_a[\text{A}]}$$

$$\therefore \frac{d[\text{P}]}{dt} = k_b[\text{A}^*] = \frac{k_a k_b [\text{A}]^2}{k_b + k'_a [\text{A}]} \quad (*) \text{ (not first-order yet) } \quad (20F.4)$$

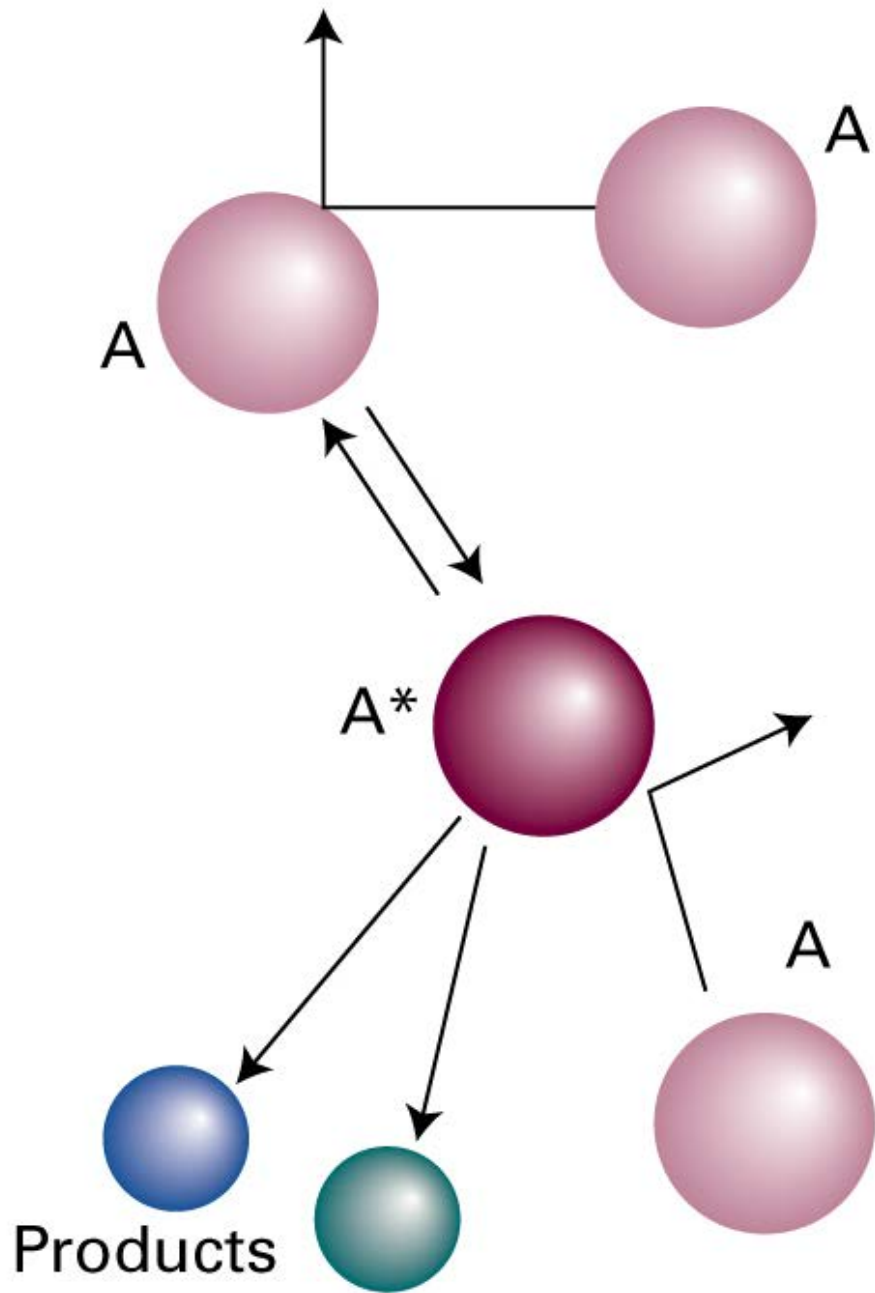


Figure 20F.1
Unimolecular Reactions.

The species A is excited by collision with A, and the excited A molecule (A^*) may either be deactivated by a collision with A, or go on to decay by a unimolecular process to form products.

$$\frac{d[\text{P}]}{dt} = \frac{k_a k_b [\text{A}]^2}{k_b + k'_a [\text{A}]} \quad (*)$$

If $k'_a [\text{A}^*][\text{A}] \gg k_b [\text{A}^*]$, or $k'_a [\text{A}] \gg k_b$, then $\frac{d[\text{P}]}{dt} = k[\text{A}]$, (20F.7)

where $k = \frac{k_a k_b}{k'_a}$

If $k'_a [\text{A}] \ll k_b$,

$$\therefore \frac{d[\text{P}]}{dt} = k_a [\text{A}]^2 \quad \text{from eq} (*)$$
(20F.6)

Lindemann-Hinshelwood mechanism:

As the concentration (and therefore the partial pressure) of A is reduced, the reaction should switch to overall second-order kinetics. The physical reason for the change of order is that at low pressures the rate-determining step is the bimolecular formation of A*.

Problems from Chap. 20

E 20A.2(b) 20A.5(b)

D 20B.2

E 20B.4(b)

P 20B.16

D 20D.2

P 20E.3