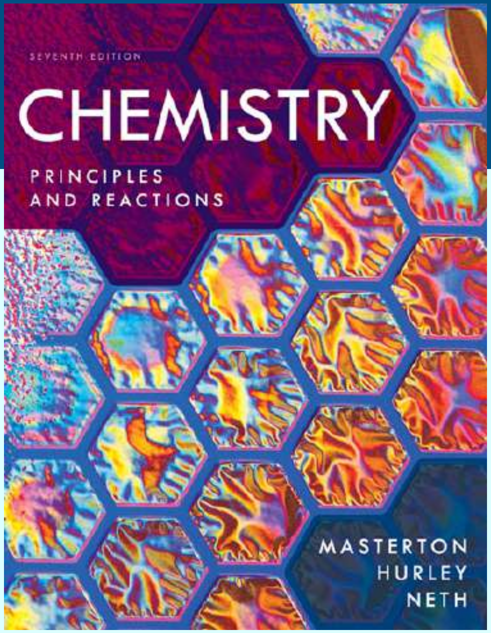

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Chapter 11
Rate of Reaction

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Outline

1. Meaning of reaction rate
2. Reaction rate and concentration
3. Reactant concentration and time
4. Models for reaction rate
5. Reaction rate and temperature
6. Catalysis
7. Reaction mechanisms

Thermochemistry

- We have looked at the energy involved in a chemical reaction
  - Chapter 8
    - Some reactions evolve heat (exothermic)
    - Some reactions absorb heat (endothermic)
  - In order for a chemical reaction to be ***feasible***, it must occur at a ***reasonable rate***

Factors that Influence the Rate of Reaction

- Concentration of reactants
- Process by which the reaction takes place
- Temperature
- Presence of a catalyst
- Reaction mechanism

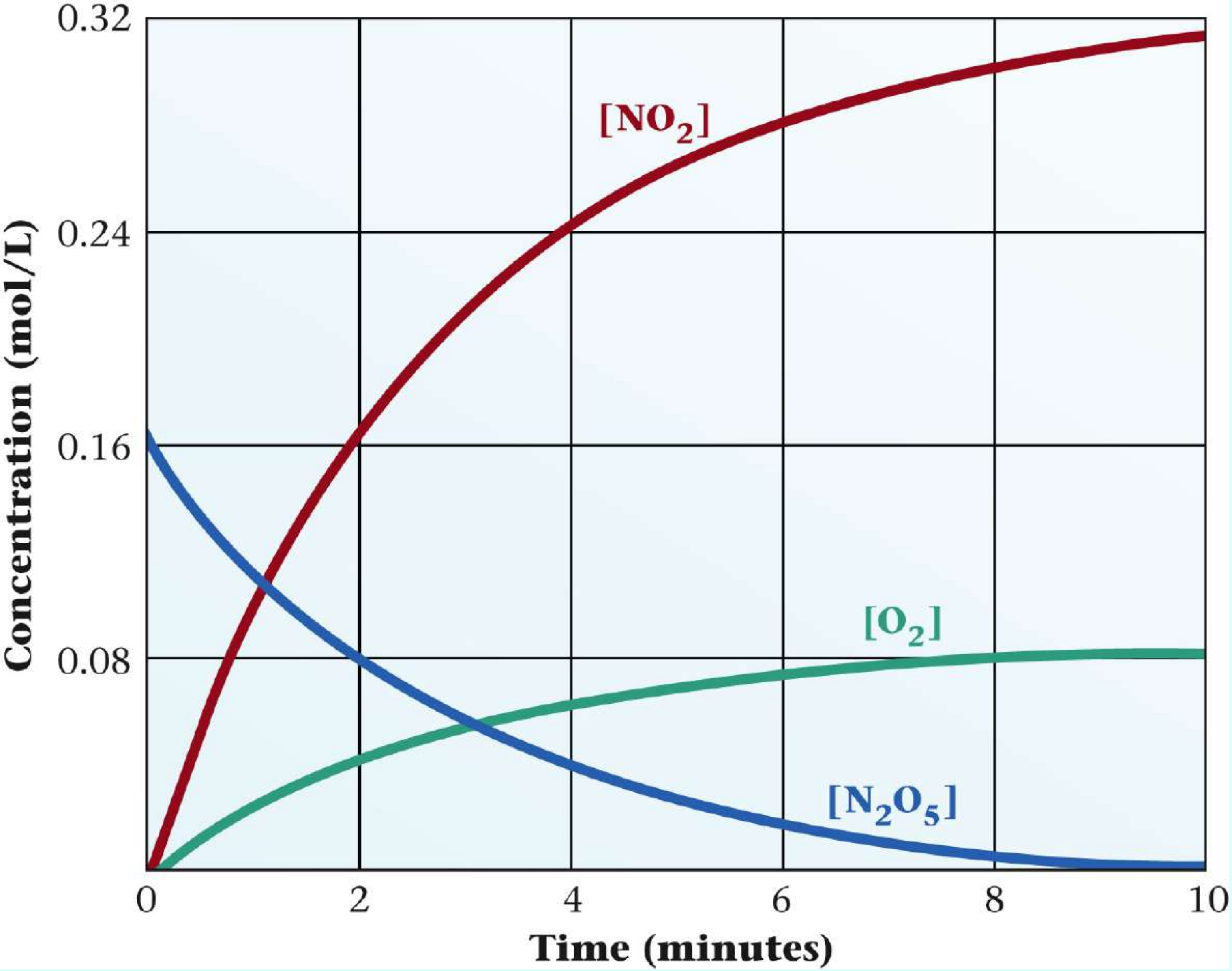
Meaning of Reaction Rate

- N_2O_5 (g) → $2NO_2$ (g) + ½O_2 (g)
  - What happens to the concentrations with time?
    - $[N_2O_5]$ decreases
    - $[NO_2]$ and $[O_2]$ increase
  - Mathematically, we can express the changes as

$$-\Delta[N_2O_5] = \frac{\Delta[NO_2]}{2} = \frac{\Delta[O_2]}{\frac{1}{2}}$$

$$\text{rate} = -\frac{\Delta[N_2O_5]}{\Delta t} = \frac{\Delta[NO_2]}{2\Delta t} = \frac{\Delta[O_2]}{\frac{1}{2}\Delta t}$$

Figure 11.1

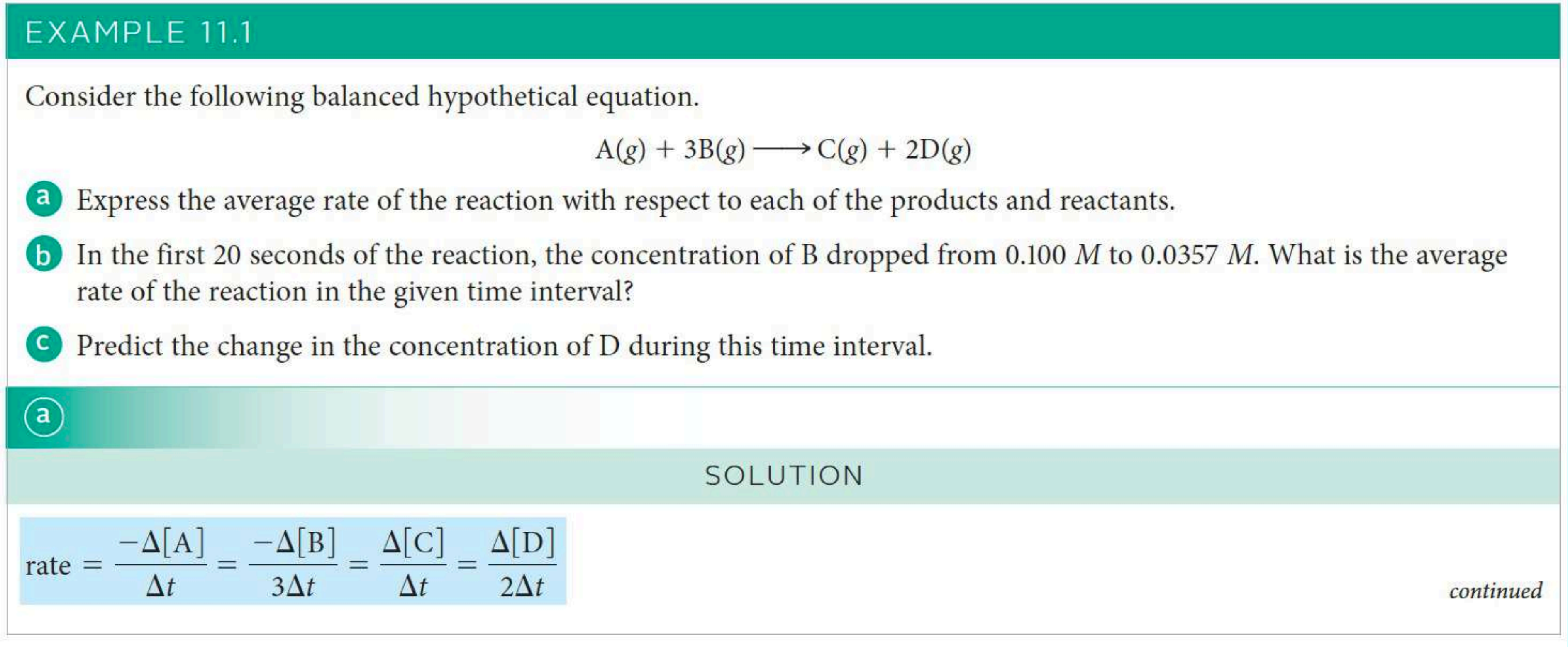

0.32
0.24
0.16
0.08
Concentration (mol/L)
0
2
4
6
8
10
Time (minutes)
[NO$_2$]
[O$_2$]
[N$_2$O$_5$]

General Form of the Rate Relationship

- For a reaction where aA + bB → cC + dD

$$rate = \frac{-\Delta[A]}{a\Delta t} = \frac{-\Delta[B]}{b\Delta t} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{d\Delta t}$$

Example 11.1



EXAMPLE 11.1

Consider the following balanced hypothetical equation.

$$A(g) + 3B(g) \longrightarrow C(g) + 2D(g)$$

ⓐ Express the average rate of the reaction with respect to each of the products and reactants.

ⓑ In the first 20 seconds of the reaction, the concentration of B dropped from 0.100 *M* to 0.0357 *M*. What is the average rate of the reaction in the given time interval?

ⓒ Predict the change in the concentration of D during this time interval.

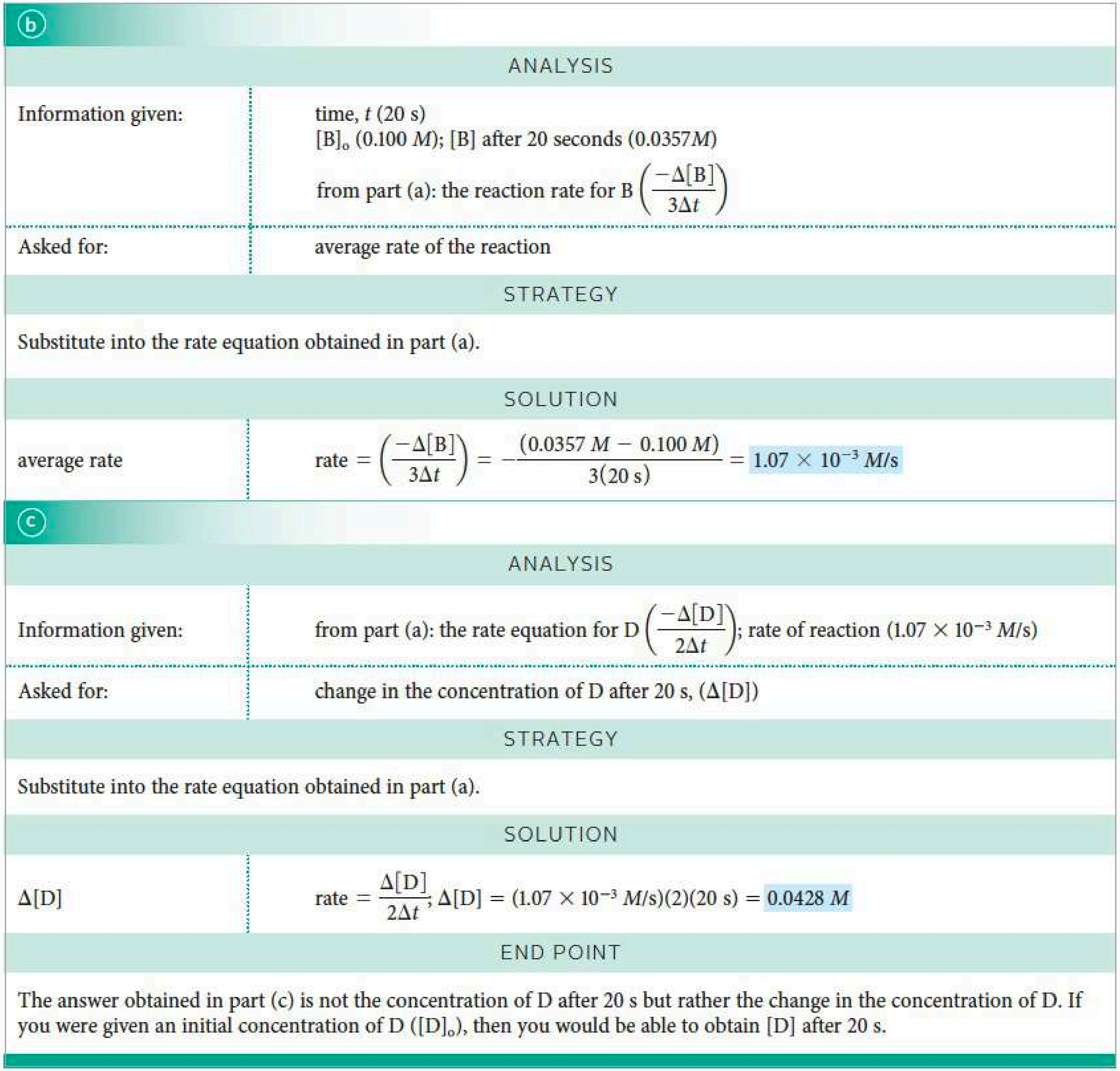
ⓐ

SOLUTION

$$\text{rate} = \frac{-\Delta[A]}{\Delta t} = \frac{-\Delta[B]}{3\Delta t} = \frac{\Delta[C]}{\Delta t} = \frac{\Delta[D]}{2\Delta t}$$

continued

Example 11.1 (Cont'd)



ⓑ

ANALYSIS

Information given:	time, t (20 s) $[B]_o$ (0.100 M); [B] after 20 seconds (0.0357M) from part (a): the reaction rate for B $\left(\frac{-\Delta[B]}{3\Delta t}\right)$
Asked for:	average rate of the reaction

STRATEGY

Substitute into the rate equation obtained in part (a).

SOLUTION

average rate

$$\text{rate} = \left(\frac{-\Delta[B]}{3\Delta t}\right) = -\frac{(0.0357\ M - 0.100\ M)}{3(20\ s)} = 1.07 \times 10^{-3}\ M/s$$

ⓒ

ANALYSIS

Information given:	from part (a): the rate equation for D $\left(\frac{-\Delta[D]}{2\Delta t}\right)$; rate of reaction ($1.07 \times 10^{-3}$ M/s)
Asked for:	change in the concentration of D after 20 s, (Δ[D])

STRATEGY

Substitute into the rate equation obtained in part (a).

SOLUTION

Δ[D]

$$\text{rate} = \frac{\Delta[D]}{2\Delta t};\ \Delta[D] = (1.07 \times 10^{-3}\ M/s)(2)(20\ s) = 0.0428\ M$$

END POINT

The answer obtained in part (c) is not the concentration of D after 20 s but rather the change in the concentration of D. If you were given an initial concentration of D ($[D]_o$), then you would be able to obtain [D] after 20 s.

Formation of Ammonia

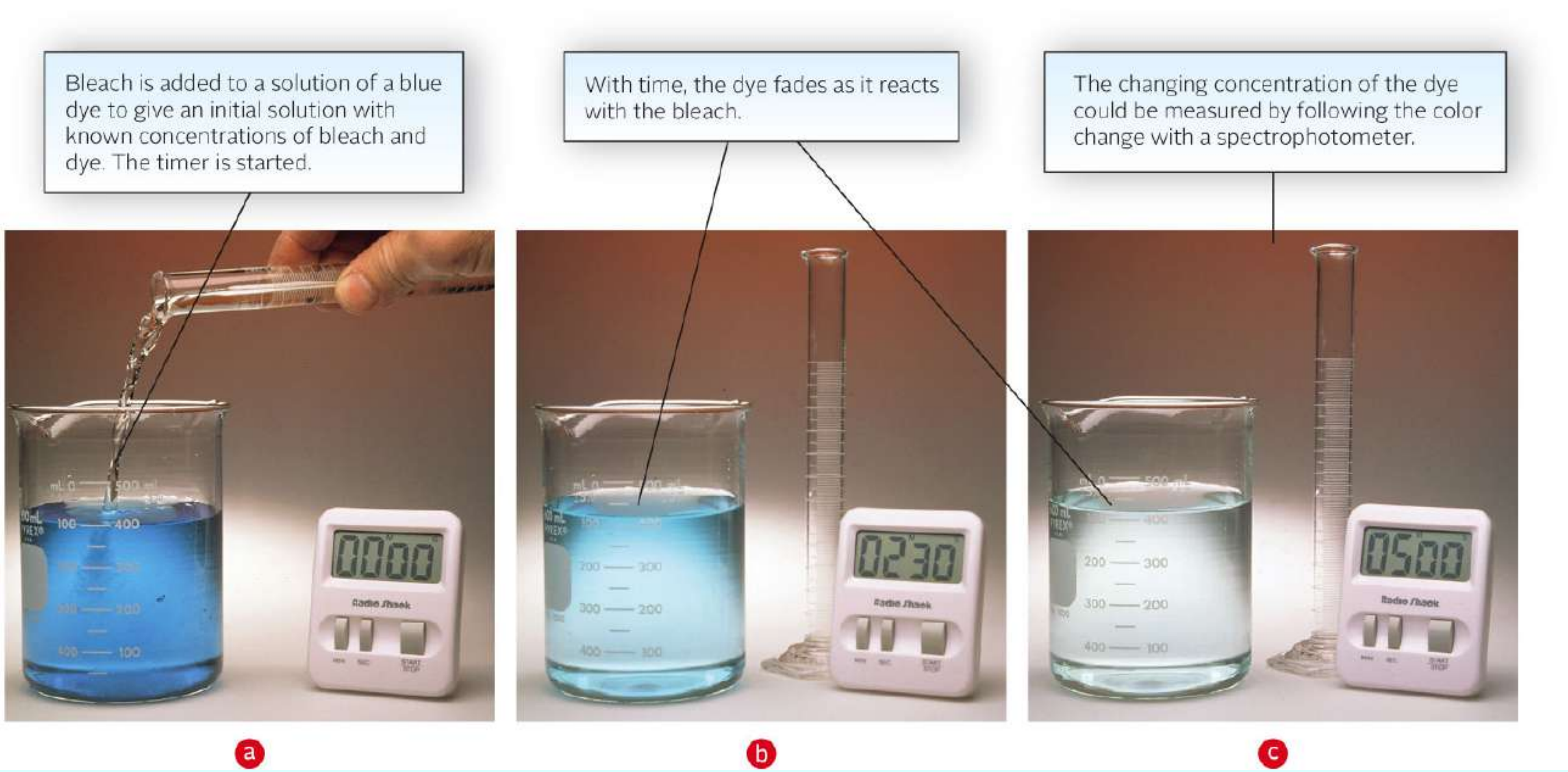
- $N_2\ (g) + 3H_2\ (g) \rightarrow 2NH_3\ (g)$

$$\text{rate} = \frac{-\Delta[N_2]}{\Delta t} = \frac{-\Delta[H_2]}{3\Delta t} = \frac{\Delta[NH_3]}{2\Delta t}$$

- If the N_2 is disappearing at 0.10 mol/L-min, the H_2 is disappearing at the rate of 0.30 mol/L-min and ammonia is appearing at a rate of 0.20 mol/L-min

Rate Measurements

- In order to measure a rate, something observable must change
- Color change:
  - $N_2O_5\ (g) \rightarrow 2NO_2\ (g) + \frac{1}{2}O_2\ (g)$

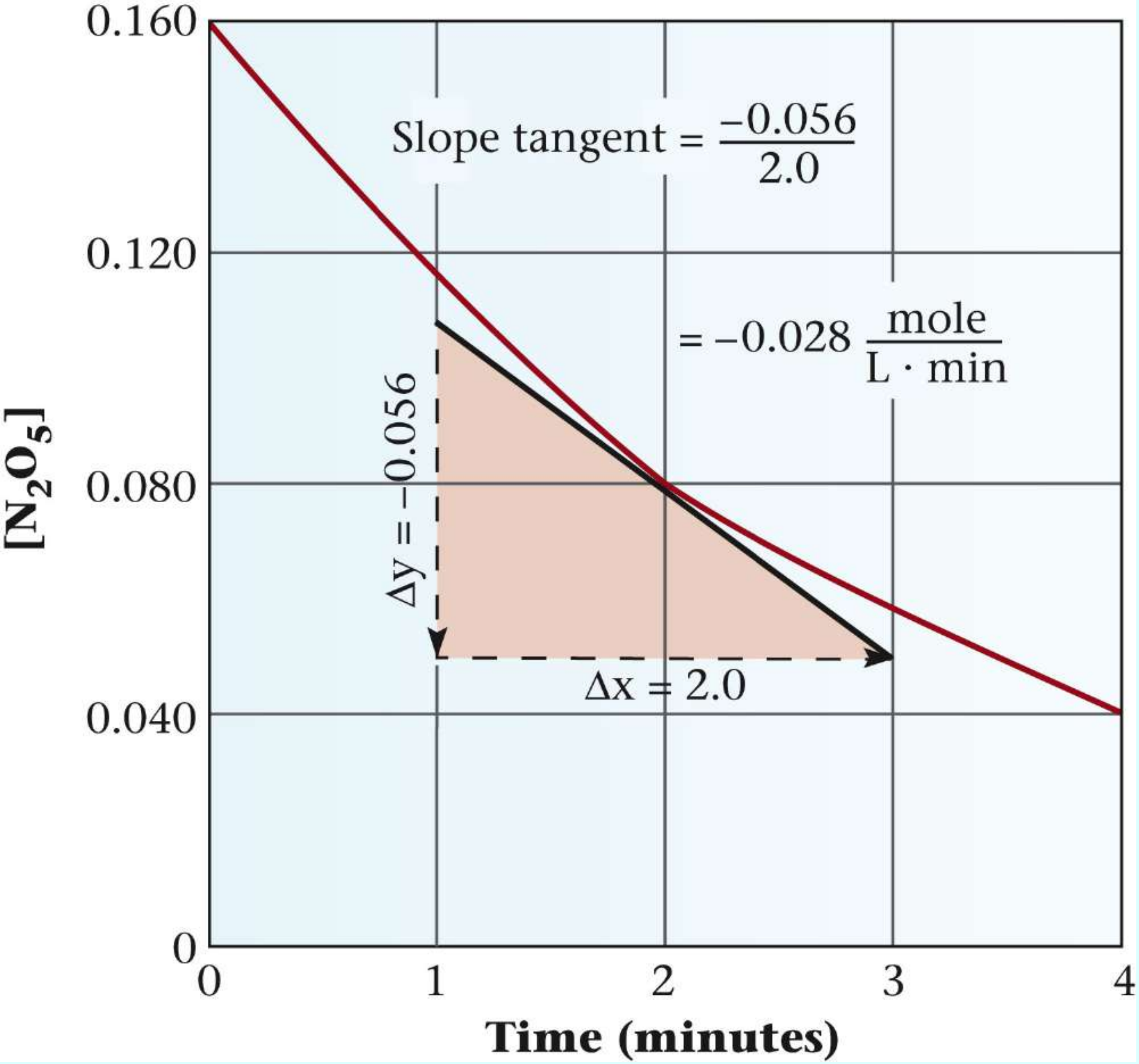


Bleach is added to a solution of a blue dye to give an initial solution with known concentrations of bleach and dye. The timer is started.

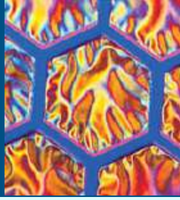
With time, the dye fades as it reacts with the bleach.

The changing concentration of the dye could be measured by following the color change with a spectrophotometer.

Figure 11.2 – Instantaneous Rate



Rate Measurements, (Cont'd)



- $N_2O_5\ (g) \rightarrow 2NO_2\ (g) + \tfrac{1}{2}O_2\ (g)$
- The rate of a reaction can be determined by measuring
  - Absorption of visible light by the NO_2 that forms
    - NO_2 is reddish-brown
    - N_2O_5 is colorless
  - The change in pressure that results from the increase in the number of moles of gas
    - 1 mol reactant → 2.5 mol product

Instantaneous Rate

- The instantaneous rate of a reaction is determined by calculating the slope of the line tangent to the concentration-time curve at the desired time

Reaction Rate and Concentration

- Rate is directly related to reactant concentration
- Consider H_2O_2
  - H_2O_2 (l) → H_2O (g) + ½O_2 (g)
  - When pure, decomposition is fast and explosive
  - When dilute, such as drugstore peroxide, the reaction is much slower and the solution is stable for months

Oxygen Concentration and Rate of Combustion

Steel wool in the flame reacts with atmospheric oxygen.

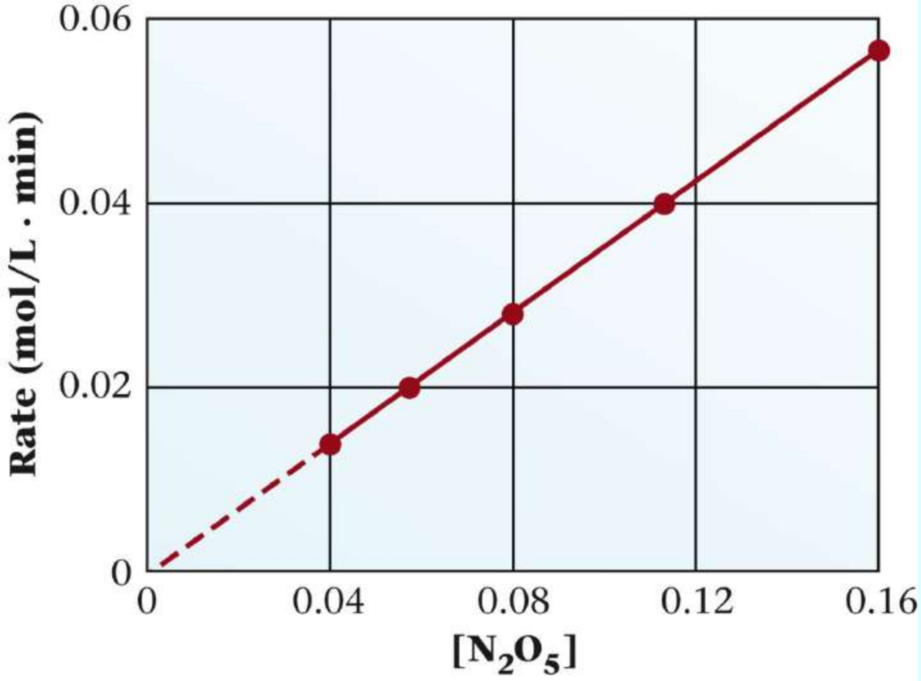
In a stream of pure oxygen, the steel wool reacts much faster.

Rate and Collision

- Reactions occur when two particles of reactant collide with each other
  - The larger the concentration of reactant, the more likely molecules will collide
  - Rate depends on concentration

Rate Expression and Rate Constant (Fig. 11.3)

- Plotting the rate vs. the concentration for the decomposition of N_2O_5 gives a straight line

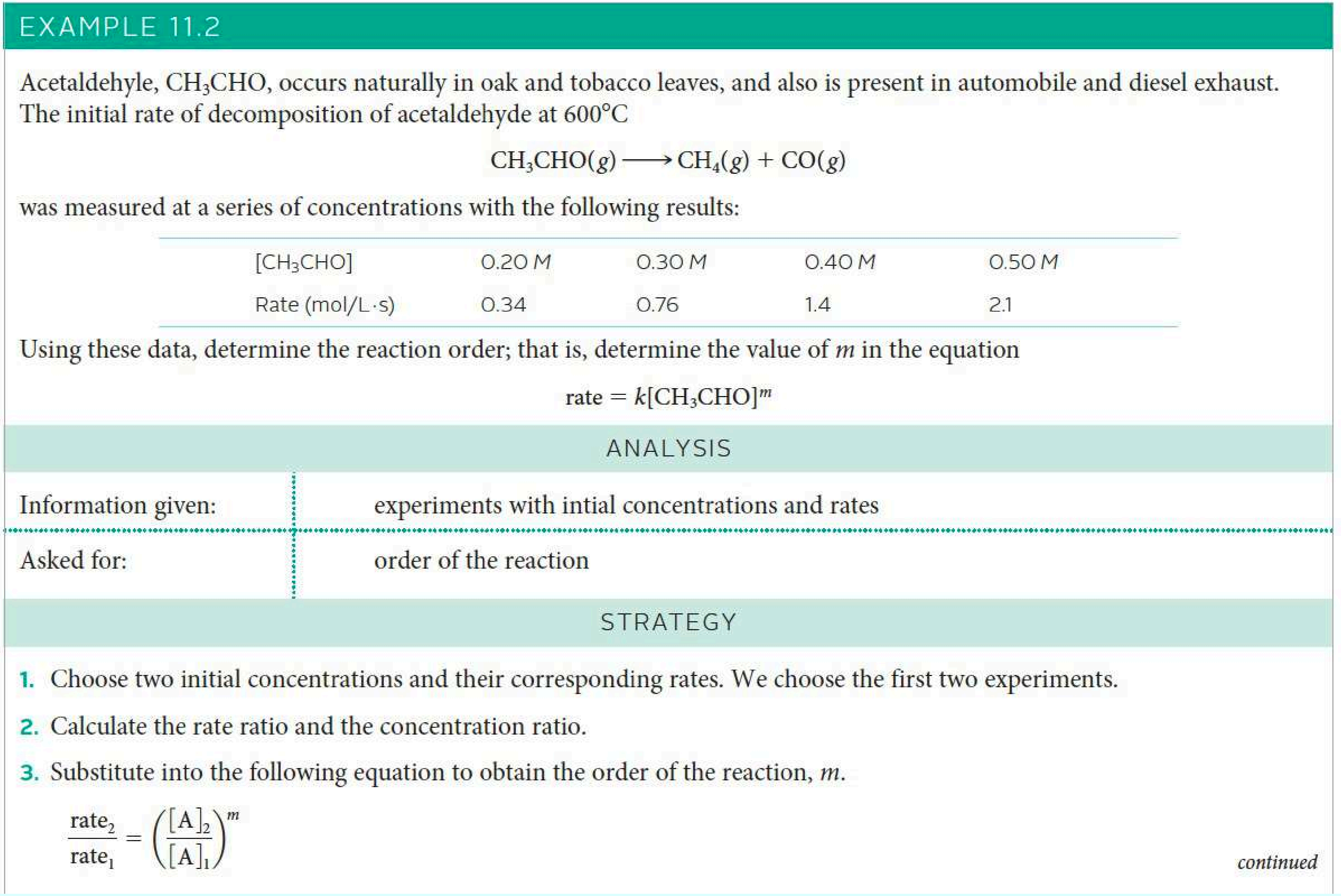


- The equation for the reaction is
  - Rate = $k[N_2O_5]$

Order and Determination of Order of Reaction

- Experiment must be done to determine the dependence of the rate of a reaction on the concentration of reactant
- In general, for
  - A → products
  - Rate = $k[A]^m$
  - m is the order of the reaction
  - m must be determined experimentally

Example 11.2



EXAMPLE 11.2

Acetaldehyle, CH_3CHO, occurs naturally in oak and tobacco leaves, and also is present in automobile and diesel exhaust. The initial rate of decomposition of acetaldehyde at 600°C

$$CH_3CHO(g) \longrightarrow CH_4(g) + CO(g)$$

was measured at a series of concentrations with the following results:

$[CH_3CHO]$	0.20 *M*	0.30 *M*	0.40 *M*	0.50 *M*
Rate (mol/L·s)	0.34	0.76	1.4	2.1

Using these data, determine the reaction order; that is, determine the value of *m* in the equation

$$\text{rate} = k[CH_3CHO]^m$$

ANALYSIS

Information given:	experiments with intial concentrations and rates
Asked for:	order of the reaction

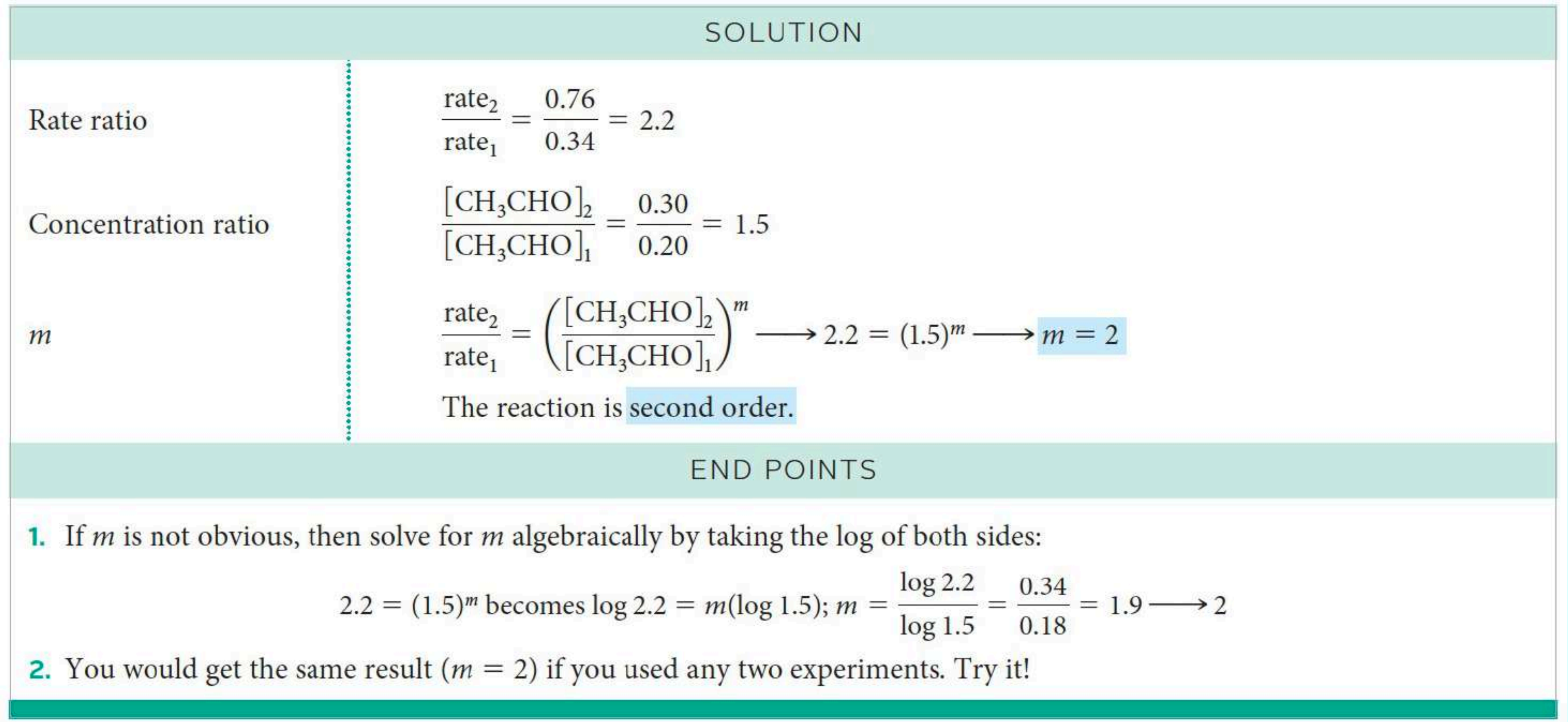
STRATEGY

1. Choose two initial concentrations and their corresponding rates. We choose the first two experiments.
2. Calculate the rate ratio and the concentration ratio.
3. Substitute into the following equation to obtain the order of the reaction, *m*.

$$\frac{\text{rate}_2}{\text{rate}_1} = \left(\frac{[A]_2}{[A]_1}\right)^m$$

continued

Example 11.2, (Cont’d)



SOLUTION

Rate ratio	$\frac{\text{rate}_2}{\text{rate}_1} = \frac{0.76}{0.34} = 2.2$
Concentration ratio	$\frac{[\mathrm{CH_3CHO}]_2}{[\mathrm{CH_3CHO}]_1} = \frac{0.30}{0.20} = 1.5$
m	$\frac{\text{rate}_2}{\text{rate}_1} = \left(\frac{[\mathrm{CH_3CHO}]_2}{[\mathrm{CH_3CHO}]_1}\right)^m \longrightarrow 2.2 = (1.5)^m \longrightarrow m = 2$ The reaction is second order.

END POINTS

1. If m is not obvious, then solve for m algebraically by taking the log of both sides:

$$2.2 = (1.5)^m \text{ becomes } \log 2.2 = m(\log 1.5);\ m = \frac{\log 2.2}{\log 1.5} = \frac{0.34}{0.18} = 1.9 \longrightarrow 2$$

2. You would get the same result ($m = 2$) if you used any two experiments. Try it!

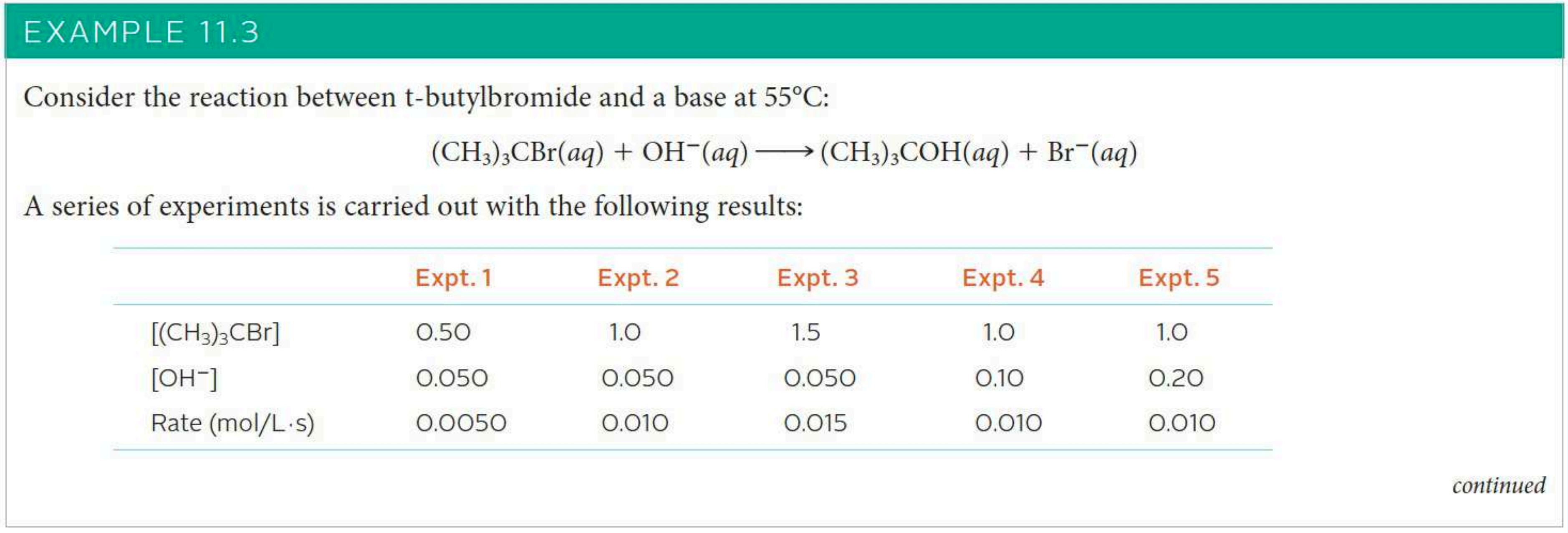
Calculating k

- Once the order of the reaction is known, the rate constant is easy to calculate
  - Use the rate and concentration data to solve for the rate constant
  - Units
    - Rate is always in mol/L-time
    - If the reaction is first order, the rate constant will have units of 1/time
    - The units of the rate constant tell the order of the reaction if they are given

Order of Reaction with Multiple Reactants

- aA + bB → products
- Rate = $k[A]^m[B]^n$
- There are three orders:
  - The order with respect to A
  - The order with respect to B
  - The overall order (m+n)
- The orders can be determined the same way they are for single reactants

Example 11.3



EXAMPLE 11.3

Consider the reaction between t-butylbromide and a base at 55°C:

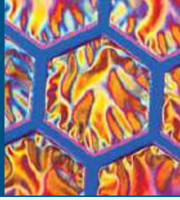
$$(CH_3)_3CBr(aq) + OH^-(aq) \longrightarrow (CH_3)_3COH(aq) + Br^-(aq)$$

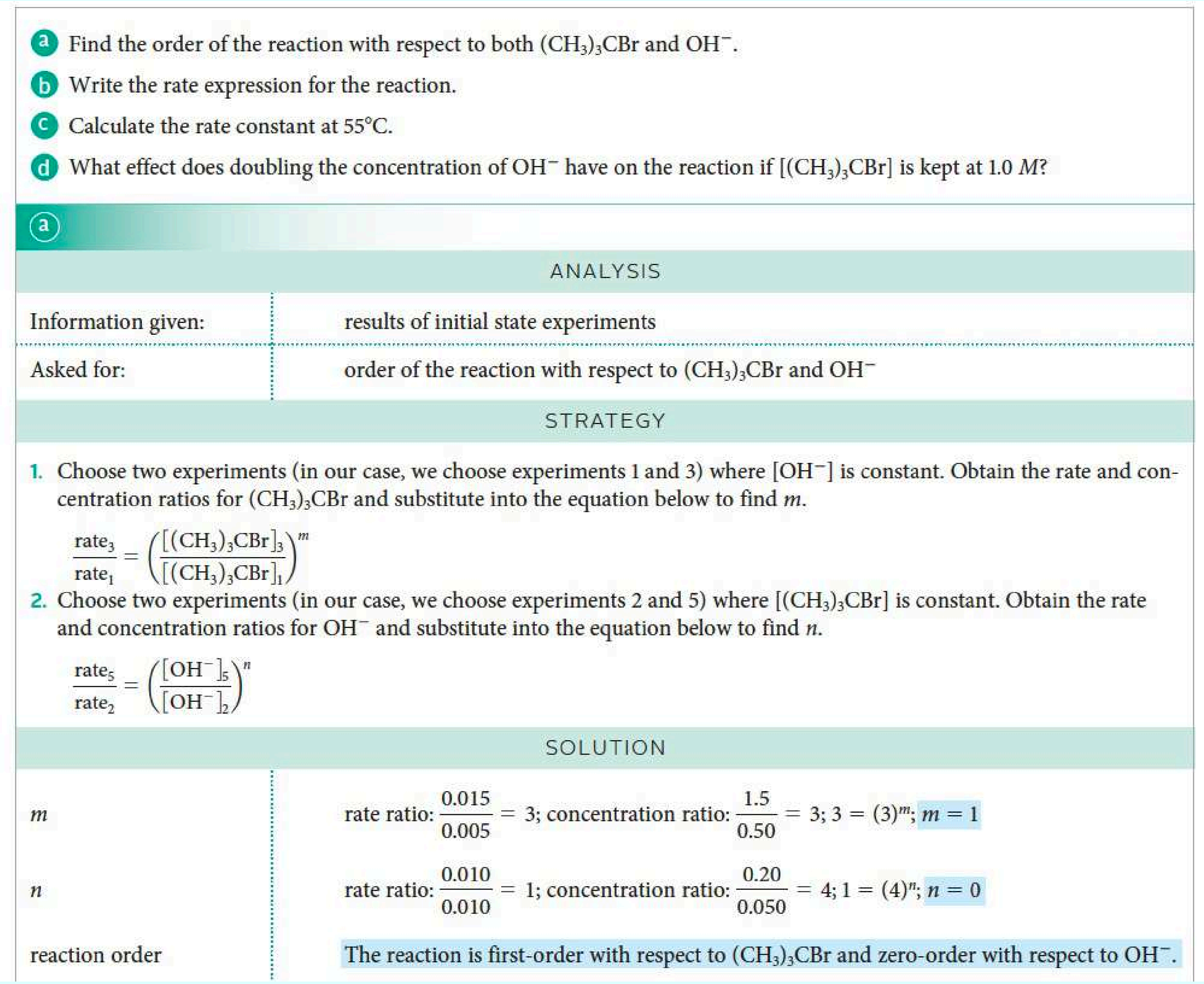
A series of experiments is carried out with the following results:

	Expt. 1	Expt. 2	Expt. 3	Expt. 4	Expt. 5
$[(CH_3)_3CBr]$	0.50	1.0	1.5	1.0	1.0
$[OH^-]$	0.050	0.050	0.050	0.10	0.20
Rate (mol/L·s)	0.0050	0.010	0.015	0.010	0.010

continued

Example 11.3, (Cont'd)





ⓐ Find the order of the reaction with respect to both $(CH_3)_3CBr$ and OH^-.

ⓑ Write the rate expression for the reaction.

ⓒ Calculate the rate constant at 55°C.

ⓓ What effect does doubling the concentration of OH^- have on the reaction if $[(CH_3)_3CBr]$ is kept at 1.0 *M*?

ⓐ

ANALYSIS

Information given:	results of initial state experiments
Asked for:	order of the reaction with respect to $(CH_3)_3CBr$ and OH^-

STRATEGY

1. Choose two experiments (in our case, we choose experiments 1 and 3) where $[OH^-]$ is constant. Obtain the rate and concentration ratios for $(CH_3)_3CBr$ and substitute into the equation below to find *m*.

$$\frac{\text{rate}_3}{\text{rate}_1} = \left(\frac{[(CH_3)_3CBr]_3}{[(CH_3)_3CBr]_1}\right)^m$$

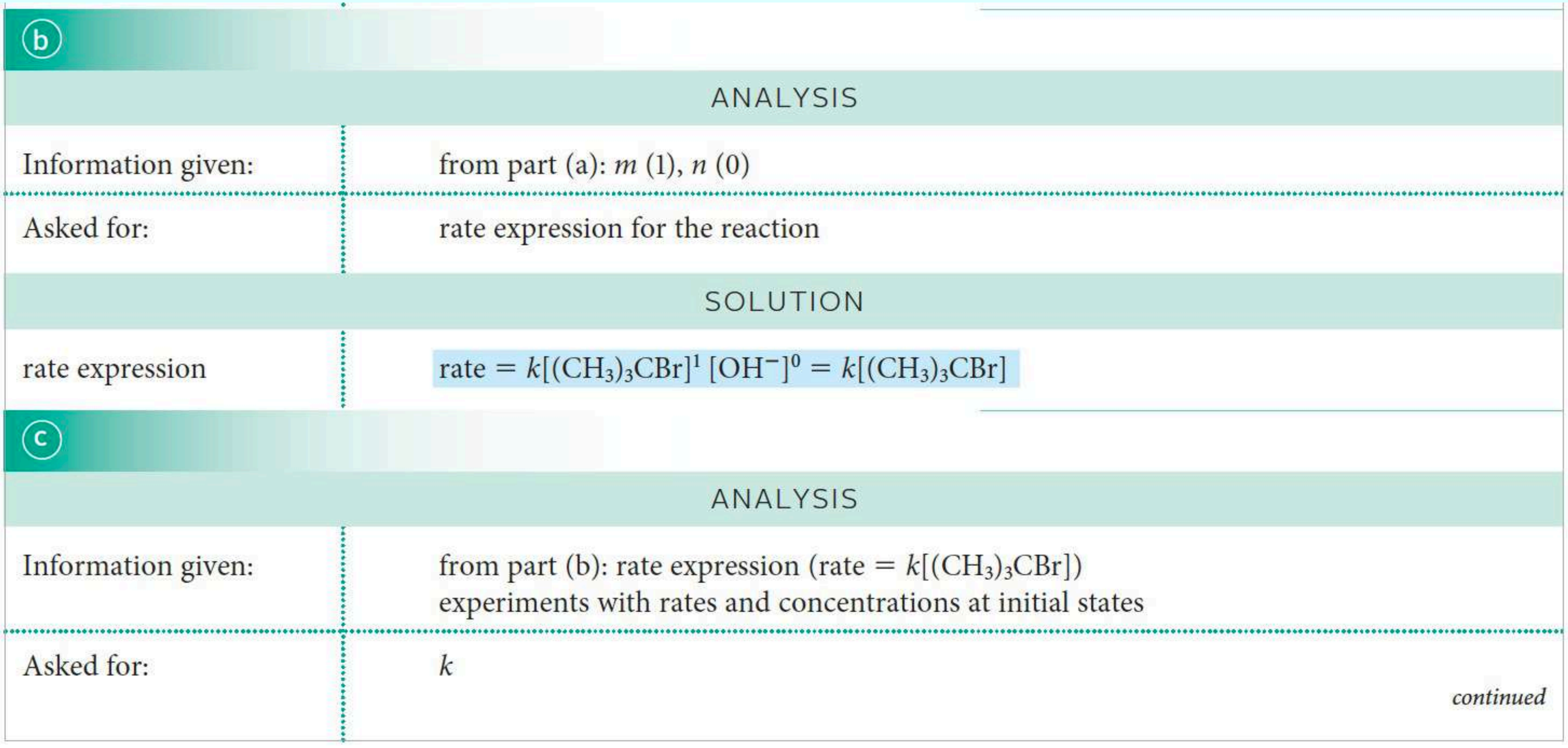
2. Choose two experiments (in our case, we choose experiments 2 and 5) where $[(CH_3)_3CBr]$ is constant. Obtain the rate and concentration ratios for OH^- and substitute into the equation below to find *n*.

$$\frac{\text{rate}_5}{\text{rate}_2} = \left(\frac{[OH^-]_5}{[OH^-]_2}\right)^n$$

SOLUTION

m	rate ratio: $\frac{0.015}{0.005} = 3$; concentration ratio: $\frac{1.5}{0.50} = 3$; $3 = (3)^m$; $m = 1$
n	rate ratio: $\frac{0.010}{0.010} = 1$; concentration ratio: $\frac{0.20}{0.050} = 4$; $1 = (4)^n$; $n = 0$
reaction order	The reaction is first-order with respect to $(CH_3)_3CBr$ and zero-order with respect to OH^-.

Example 11.3, (Cont’d)



ⓑ

ANALYSIS

Information given:	from part (a): *m* (1), *n* (0)
Asked for:	rate expression for the reaction

SOLUTION

rate expression	$\text{rate} = k[(CH_3)_3CBr]^1\,[OH^-]^0 = k[(CH_3)_3CBr]$

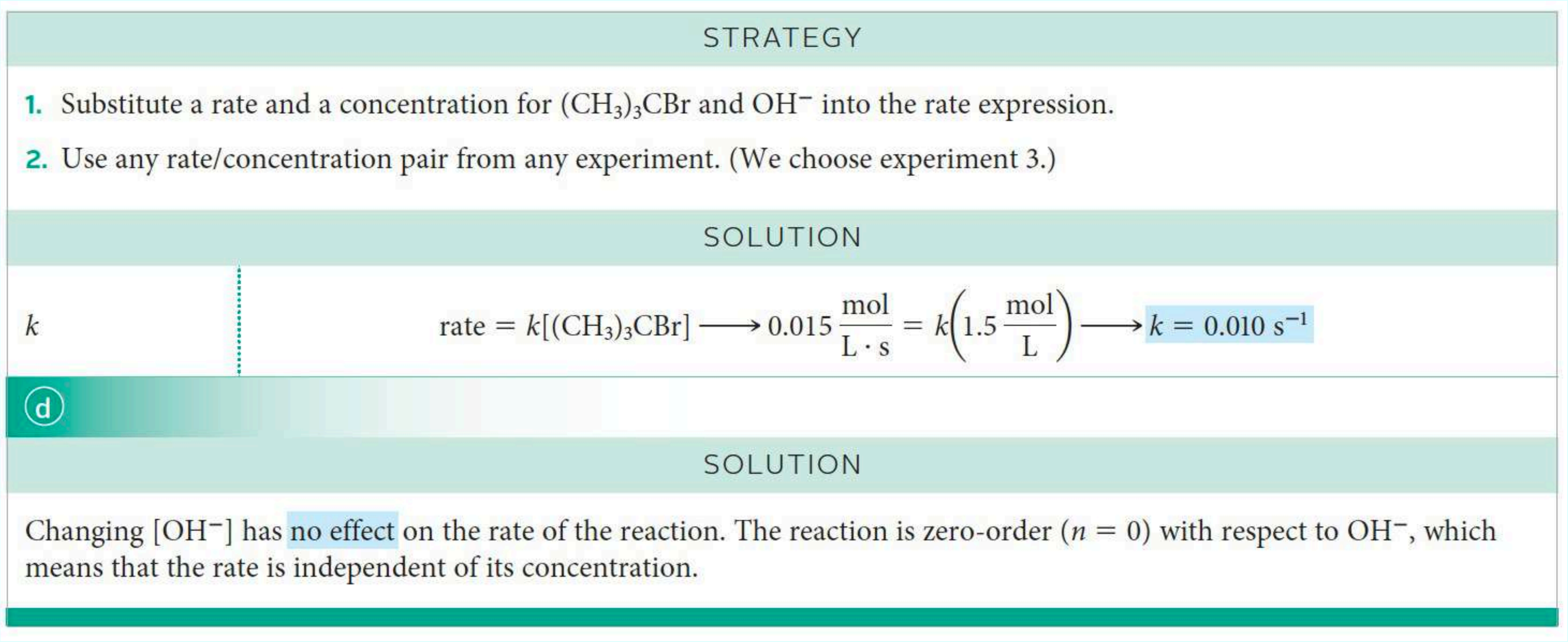
ⓒ

ANALYSIS

Information given:	from part (b): rate expression ($\text{rate} = k[(CH_3)_3CBr]$) experiments with rates and concentrations at initial states
Asked for:	k

continued

Example 11.3, (Cont'd)



STRATEGY

1. Substitute a rate and a concentration for $(CH_3)_3CBr$ and OH^- into the rate expression.
2. Use any rate/concentration pair from any experiment. (We choose experiment 3.)

SOLUTION

k

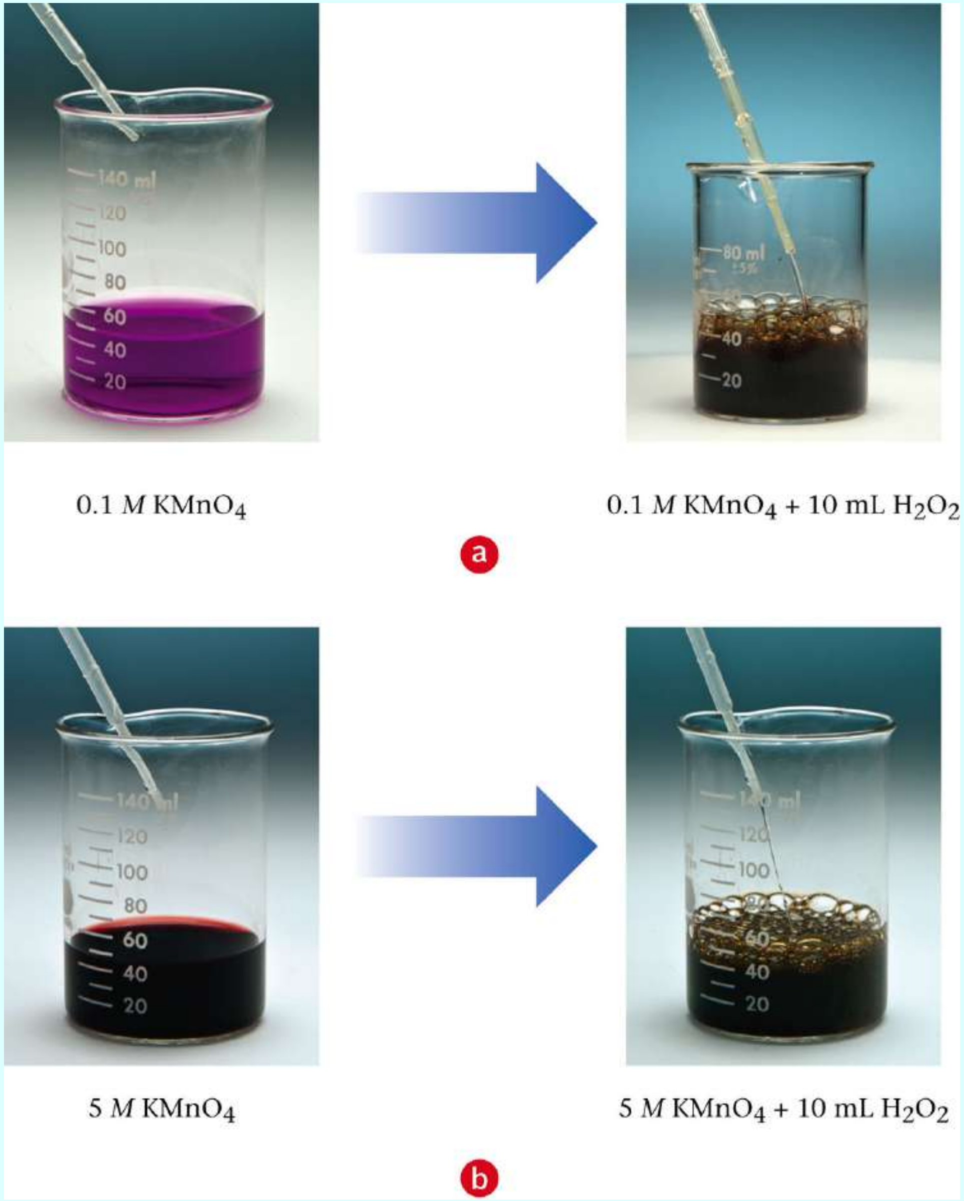
$$\text{rate} = k[(CH_3)_3CBr] \longrightarrow 0.015\,\frac{\text{mol}}{\text{L}\cdot\text{s}} = k\left(1.5\,\frac{\text{mol}}{\text{L}}\right) \longrightarrow k = 0.010\ \text{s}^{-1}$$

ⓓ

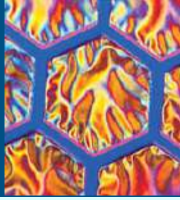
SOLUTION

Changing $[OH^-]$ has no effect on the rate of the reaction. The reaction is zero-order ($n = 0$) with respect to OH^-, which means that the rate is independent of its concentration.

Rate and Concentration



Reaction Concentration and Time



- The rate expression can be integrated (using calculus) to produce a concentration-time relationship
  - The relationship depends on the order of the reaction
  - A new term, the half-life, will also result

First-Order Reactions

- For A → products, the relationship is

$$\ln\frac{[A]_0}{[A]} = kt$$

- k is the rate constant
- t is time

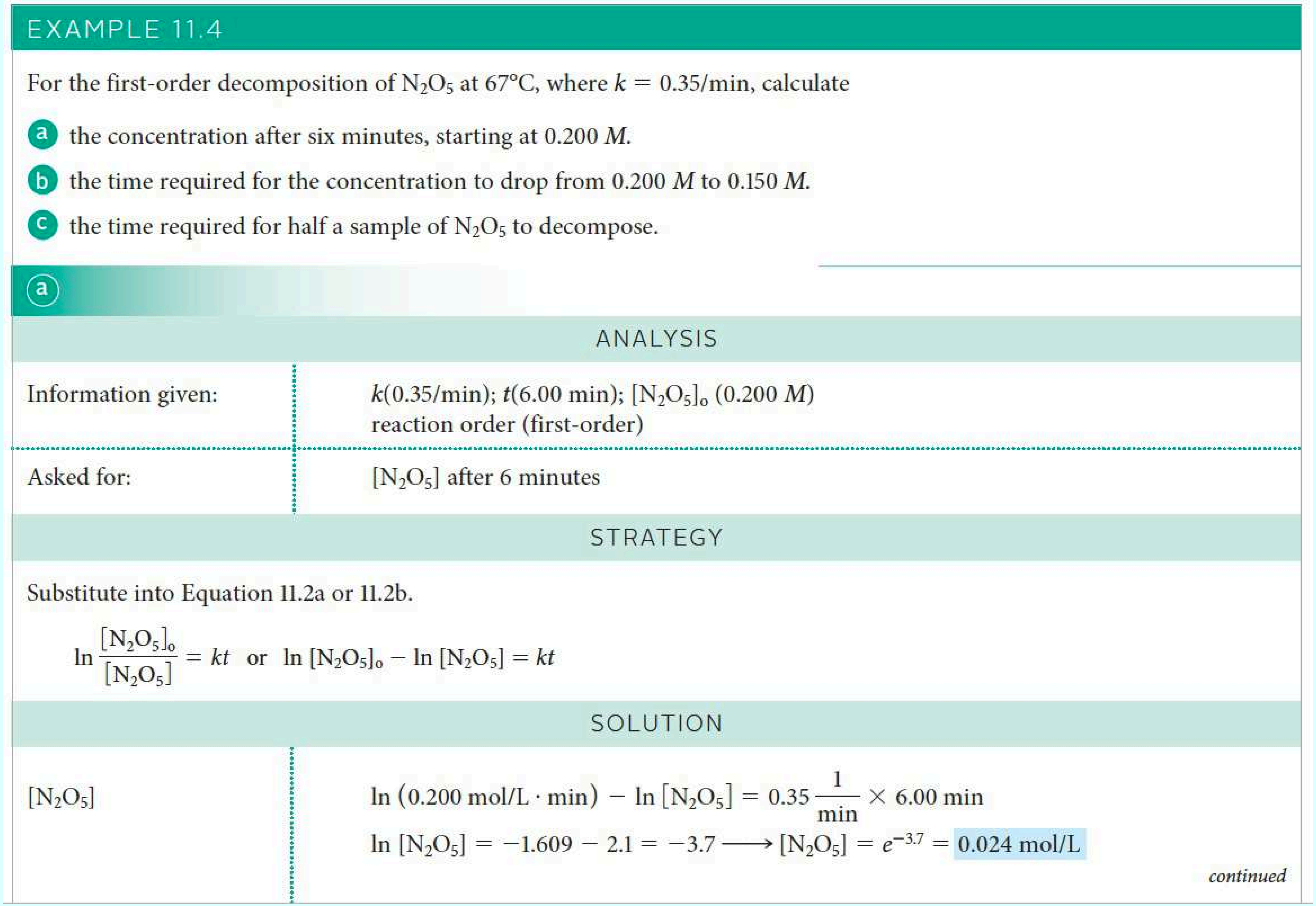
Graphical Interpretation of the First-Order Relationship

- We can put the first-order relationship into the form

$$\ln[A] = \ln[A]_0 - kt$$

- Where, using y = mx + b,
  - ln[A] is plotted on the y axis
  - t is plotted on the x axis
  - The slope of the line is –k
  - The y-intercept is $\ln[A]_0$

Example 11.4



EXAMPLE 11.4

For the first-order decomposition of N_2O_5 at 67°C, where $k = 0.35/\text{min}$, calculate

- ⓐ the concentration after six minutes, starting at 0.200 M.
- ⓑ the time required for the concentration to drop from 0.200 M to 0.150 M.
- ⓒ the time required for half a sample of N_2O_5 to decompose.

ⓐ

ANALYSIS

Information given:	$k(0.35/\text{min})$; $t(6.00\ \text{min})$; $[N_2O_5]_o\ (0.200\ M)$ reaction order (first-order)
Asked for:	$[N_2O_5]$ after 6 minutes

STRATEGY

Substitute into Equation 11.2a or 11.2b.

$$\ln\frac{[N_2O_5]_o}{[N_2O_5]} = kt \quad \text{or} \quad \ln\,[N_2O_5]_o - \ln\,[N_2O_5] = kt$$

SOLUTION

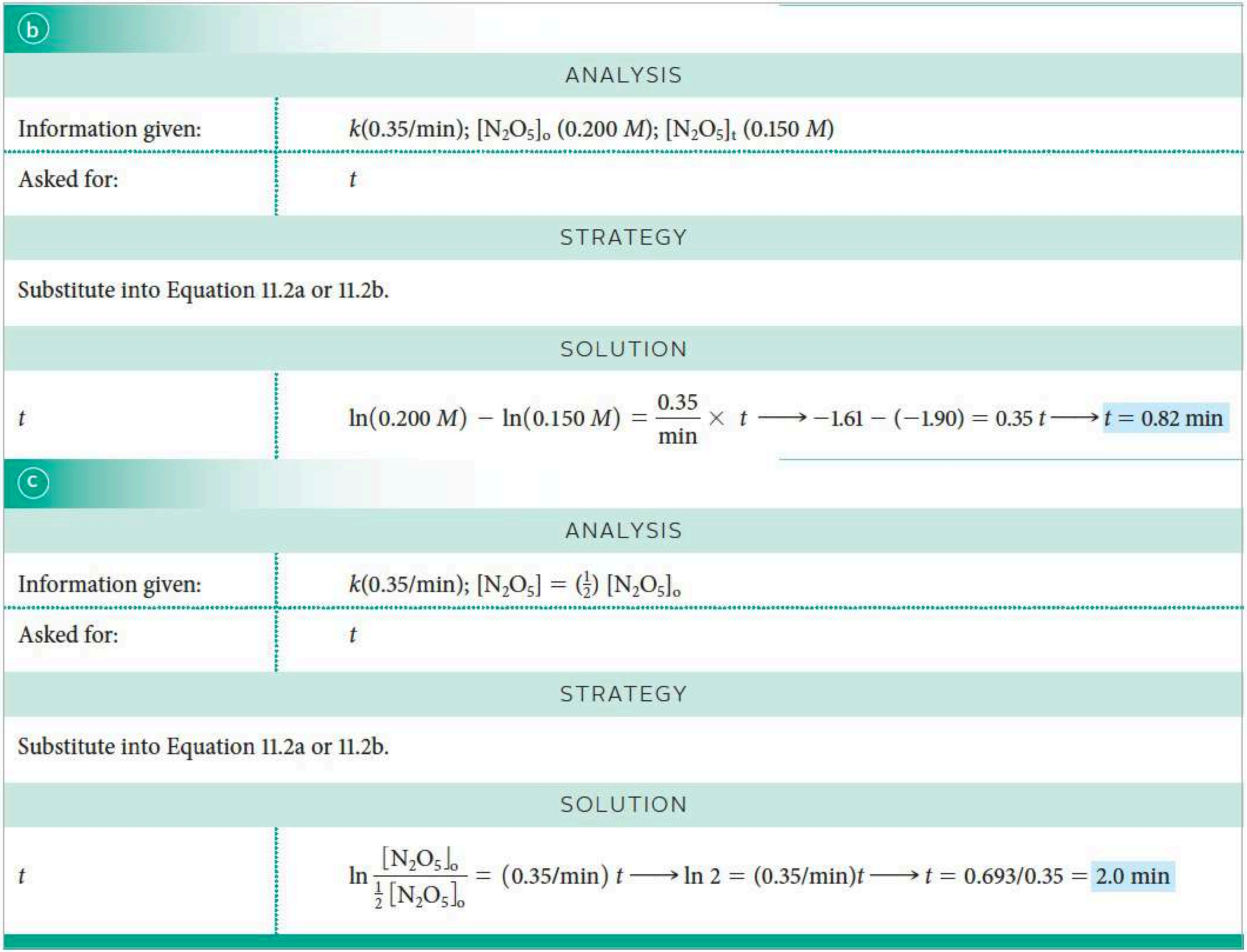
$[N_2O_5]$

$$\ln\left(0.200\ \text{mol/L}\cdot\text{min}\right) - \ln\left[N_2O_5\right] = 0.35\frac{1}{\text{min}} \times 6.00\ \text{min}$$

$$\ln\,[N_2O_5] = -1.609 - 2.1 = -3.7 \longrightarrow [N_2O_5] = e^{-3.7} = 0.024\ \text{mol/L}$$

continued

Example 11.4, (Cont’d)



ⓑ

ANALYSIS

Information given:	k(0.35/min); $[N_2O_5]_o$ (0.200 M); $[N_2O_5]_t$ (0.150 M)
Asked for:	t

STRATEGY

Substitute into Equation 11.2a or 11.2b.

SOLUTION

t	$\ln(0.200\,M) - \ln(0.150\,M) = \frac{0.35}{\text{min}} \times t \longrightarrow -1.61 - (-1.90) = 0.35\,t \longrightarrow t = 0.82\text{ min}$

ⓒ

ANALYSIS

Information given:	k(0.35/min); $[N_2O_5] = (\frac{1}{2})\,[N_2O_5]_o$
Asked for:	t

STRATEGY

Substitute into Equation 11.2a or 11.2b.

SOLUTION

t	$\ln\frac{[N_2O_5]_o}{\frac{1}{2}[N_2O_5]_o} = (0.35/\text{min})\,t \longrightarrow \ln 2 = (0.35/\text{min})t \longrightarrow t = 0.693/0.35 = 2.0\text{ min}$

The Half Life

- The ***half life*** of a reaction is the time it takes for ***half the initial concentration of reactant to react***
- For a first order reaction, at the half life, $[A] = 1/2[A]_0$ so

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

- Notice that for a first order reaction, the half life is independent of the starting concentration of reactant

Applications of First Order Kinetics

- Radioactive decay is a first-order process
- If X_0 is the initial amount of radioactive element,

$$\ln \frac{X_0}{X} = kt$$

Table 11.1

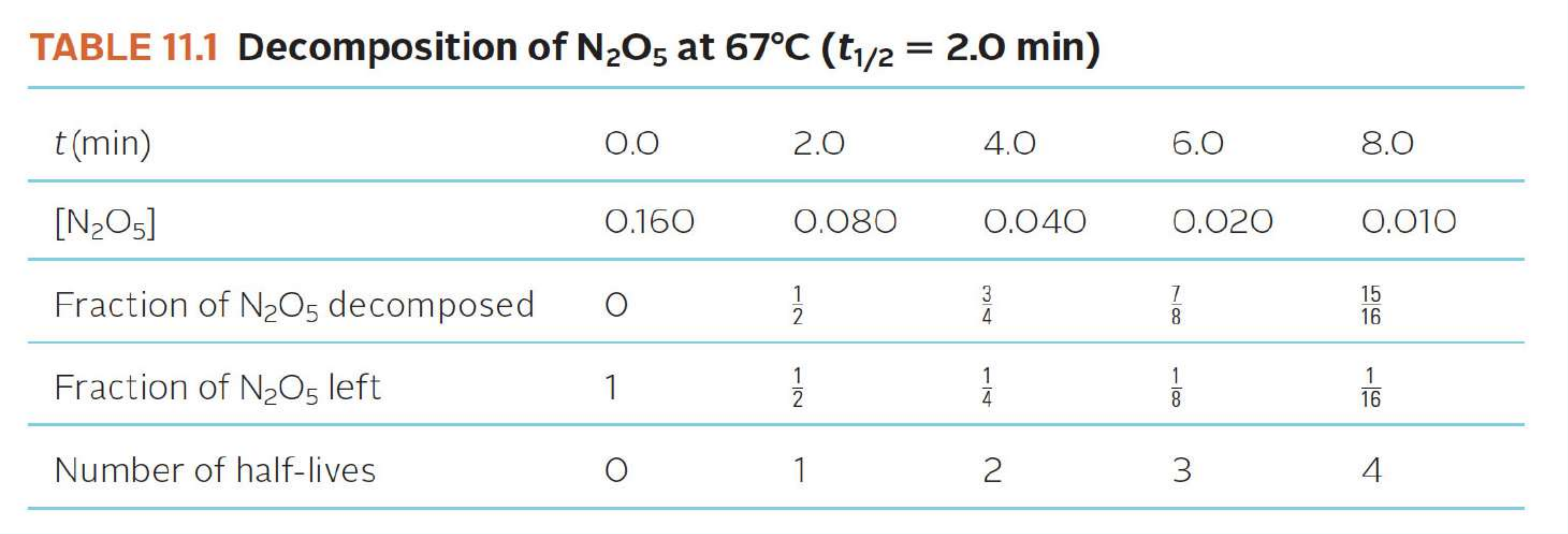
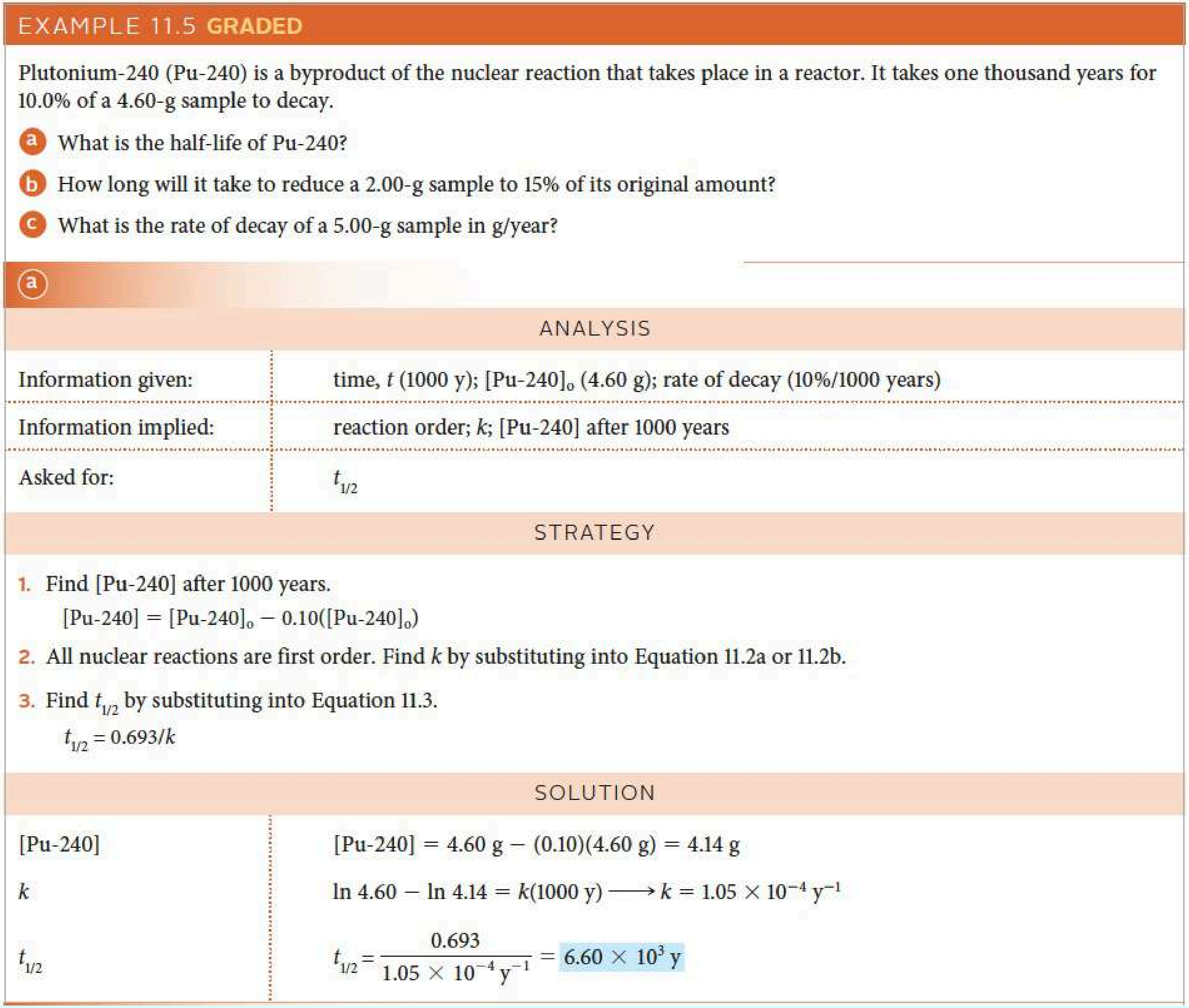


TABLE 11.1 **Decomposition of N_2O_5 at 67°C ($t_{1/2} = 2.0$ min)**

t (min)	0.0	2.0	4.0	6.0	8.0
$[N_2O_5]$	0.160	0.080	0.040	0.020	0.010
Fraction of N_2O_5 decomposed	0	$\frac{1}{2}$	$\frac{3}{4}$	$\frac{7}{8}$	$\frac{15}{16}$
Fraction of N_2O_5 left	1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$
Number of half-lives	0	1	2	3	4

Example 11.5



EXAMPLE 11.5 GRADED

Plutonium-240 (Pu-240) is a byproduct of the nuclear reaction that takes place in a reactor. It takes one thousand years for 10.0% of a 4.60-g sample to decay.

ⓐ What is the half-life of Pu-240?

ⓑ How long will it take to reduce a 2.00-g sample to 15% of its original amount?

ⓒ What is the rate of decay of a 5.00-g sample in g/year?

ⓐ

ANALYSIS

Information given:	time, t (1000 y); $[\text{Pu-240}]_o$ (4.60 g); rate of decay (10%/1000 years)
Information implied:	reaction order; k; [Pu-240] after 1000 years
Asked for:	$t_{1/2}$

STRATEGY

1. Find [Pu-240] after 1000 years.

   $[\text{Pu-240}] = [\text{Pu-240}]_o - 0.10([\text{Pu-240}]_o)$

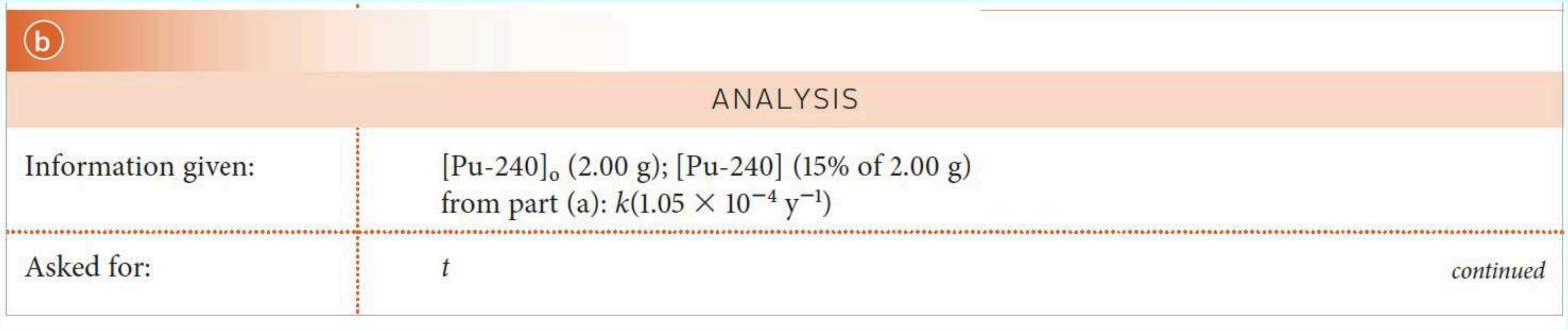
2. All nuclear reactions are first order. Find k by substituting into Equation 11.2a or 11.2b.
3. Find $t_{1/2}$ by substituting into Equation 11.3.

   $t_{1/2} = 0.693/k$

SOLUTION

[Pu-240]	$[\text{Pu-240}] = 4.60\text{ g} - (0.10)(4.60\text{ g}) = 4.14\text{ g}$
k	$\ln 4.60 - \ln 4.14 = k(1000\text{ y}) \longrightarrow k = 1.05 \times 10^{-4}\text{ y}^{-1}$
$t_{1/2}$	$t_{1/2} = \dfrac{0.693}{1.05 \times 10^{-4}\text{ y}^{-1}} = 6.60 \times 10^3\text{ y}$

Example 11.5, (Cont'd)

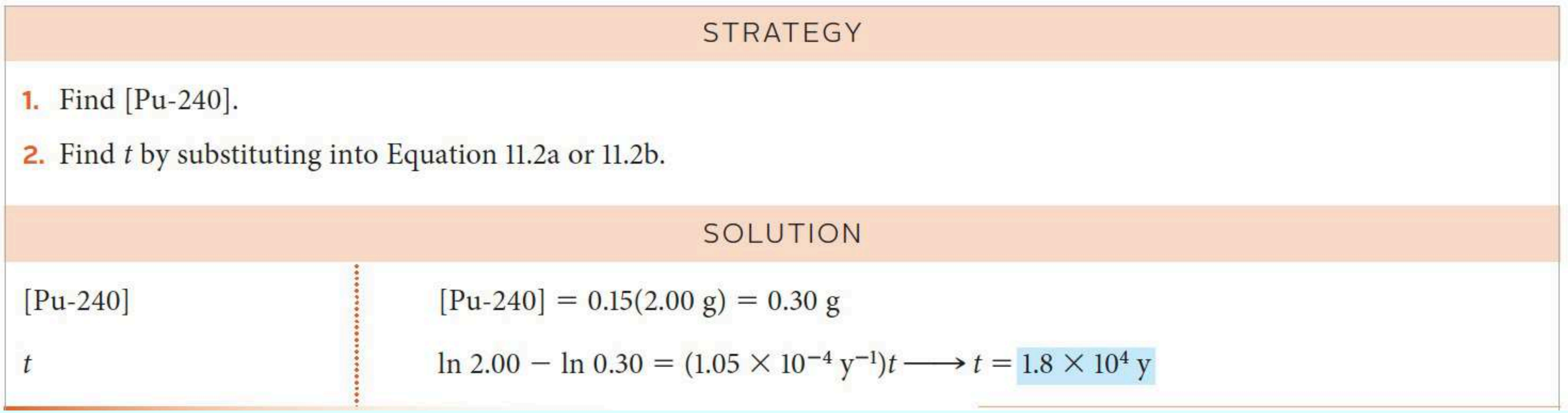


ⓑ

ANALYSIS

Information given:	[Pu-240]$_o$ (2.00 g); [Pu-240] (15% of 2.00 g) from part (a): $k(1.05 \times 10^{-4}\ \mathrm{y}^{-1})$
Asked for:	t

continued



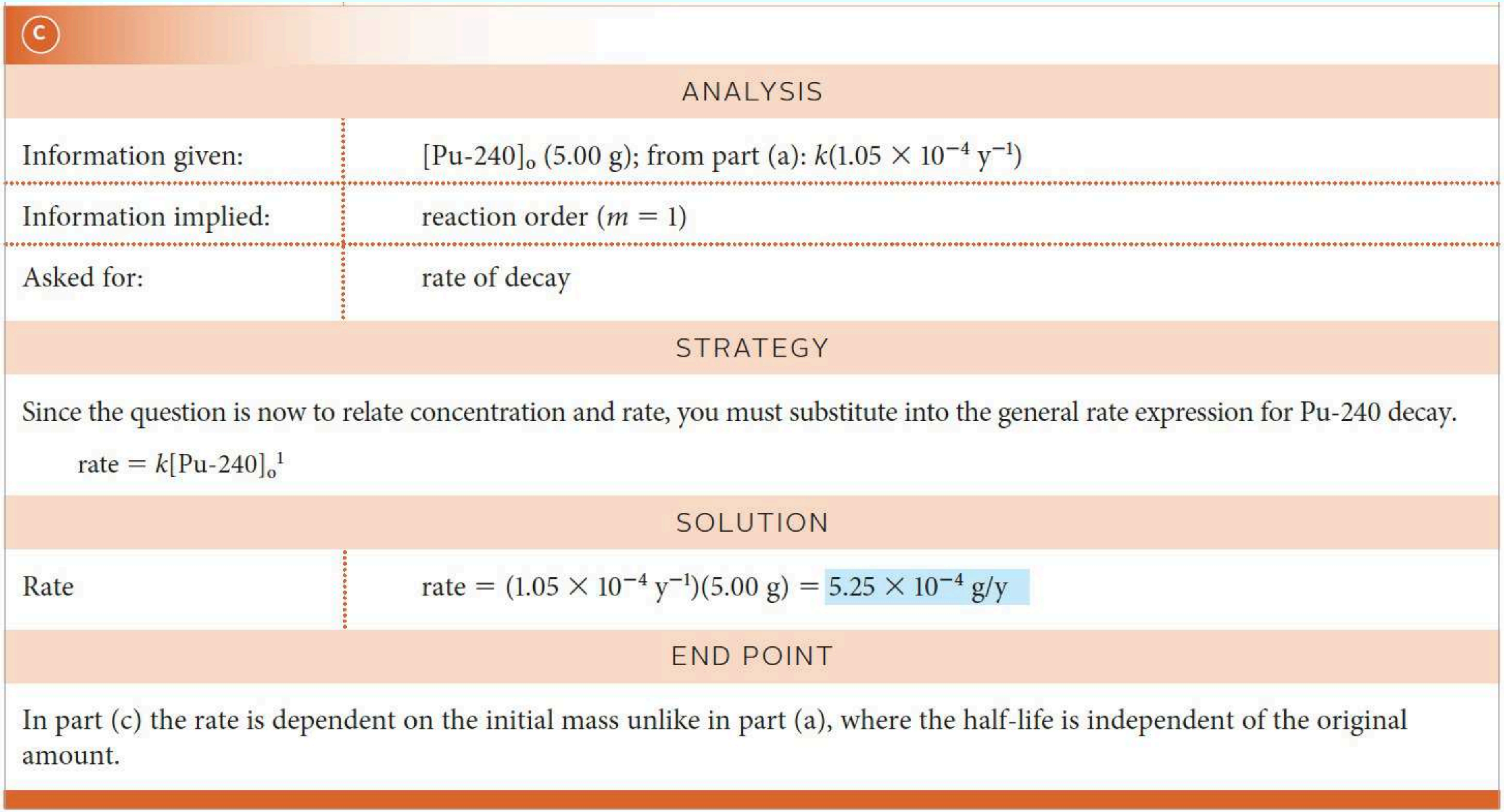
STRATEGY

1. Find [Pu-240].
2. Find t by substituting into Equation 11.2a or 11.2b.

SOLUTION

[Pu-240]	[Pu-240] = 0.15(2.00 g) = 0.30 g
t	$\ln 2.00 - \ln 0.30 = (1.05 \times 10^{-4}\ \mathrm{y}^{-1})t \longrightarrow t = 1.8 \times 10^{4}\ \mathrm{y}$

Example 11.5, (Cont'd)



ⓒ

ANALYSIS

Information given:	$[\text{Pu-240}]_o$ (5.00 g); from part (a): $k(1.05 \times 10^{-4}\ \text{y}^{-1})$
Information implied:	reaction order ($m = 1$)
Asked for:	rate of decay

STRATEGY

Since the question is now to relate concentration and rate, you must substitute into the general rate expression for Pu-240 decay.

$$\text{rate} = k[\text{Pu-240}]_o^{\,1}$$

SOLUTION

Rate	$\text{rate} = (1.05 \times 10^{-4}\ \text{y}^{-1})(5.00\ \text{g}) = 5.25 \times 10^{-4}\ \text{g/y}$

END POINT

In part (c) the rate is dependent on the initial mass unlike in part (a), where the half-life is independent of the original amount.

Zero Order Reactions

- For a zero order reaction A → products

$$\text{Rate} = k[A]^0 = k$$

$$[A] = [A]_0 - kt$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

$$\text{linear} : [A] \text{ vs. } t$$

- Note that the ***half life of a zero order reaction does depend on the initial concentration*** of reactant

Decomposition of HI

- The decomposition of HI over a solid surface is one example of a zero order reaction
- $HI\ (g) \xrightarrow{Au} \frac{1}{2}\ H_2\ (g) + \frac{1}{2}\ I_2\ (g)$

Second-Order Reactions

- For A→ products, Rate = k$[A]^2$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

$$linear : \frac{1}{[A]} vs.t$$

Table 11.2

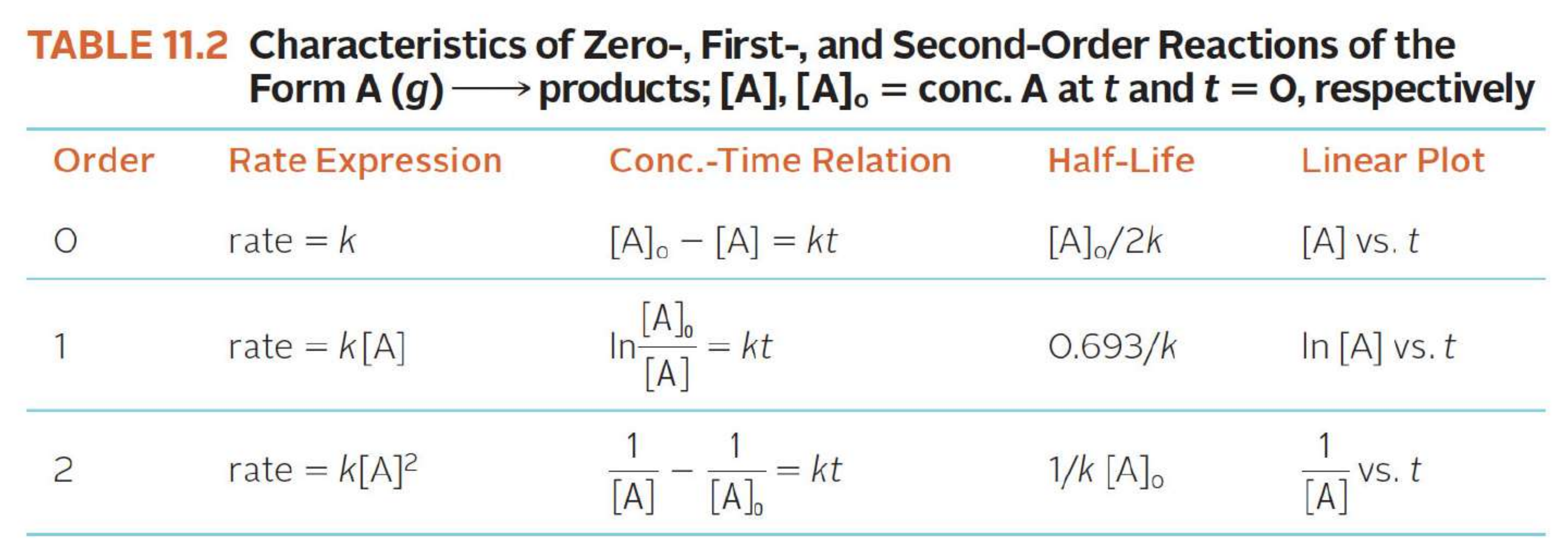
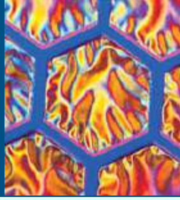


TABLE 11.2 **Characteristics of Zero-, First-, and Second-Order Reactions of the Form A (*g*) $\longrightarrow$ products; [A], $[A]_o$ = conc. A at *t* and *t* = 0, respectively**

Order	Rate Expression	Conc.-Time Relation	Half-Life	Linear Plot
0	rate = k	$[A]_o - [A] = kt$	$[A]_o/2k$	[A] vs. t
1	rate = $k[A]$	$\ln\frac{[A]_o}{[A]} = kt$	$0.693/k$	ln [A] vs. t
2	rate = $k[A]^2$	$\frac{1}{[A]} - \frac{1}{[A]_o} = kt$	$1/k\,[A]_o$	$\frac{1}{[A]}$ vs. t

Example 11.6



EXAMPLE 11.6

The following data were obtained for the gas-phase decomposition of hydrogen iodide:

Time (h)	0	2	4	6
[HI]	1.00	0.50	0.33	0.25

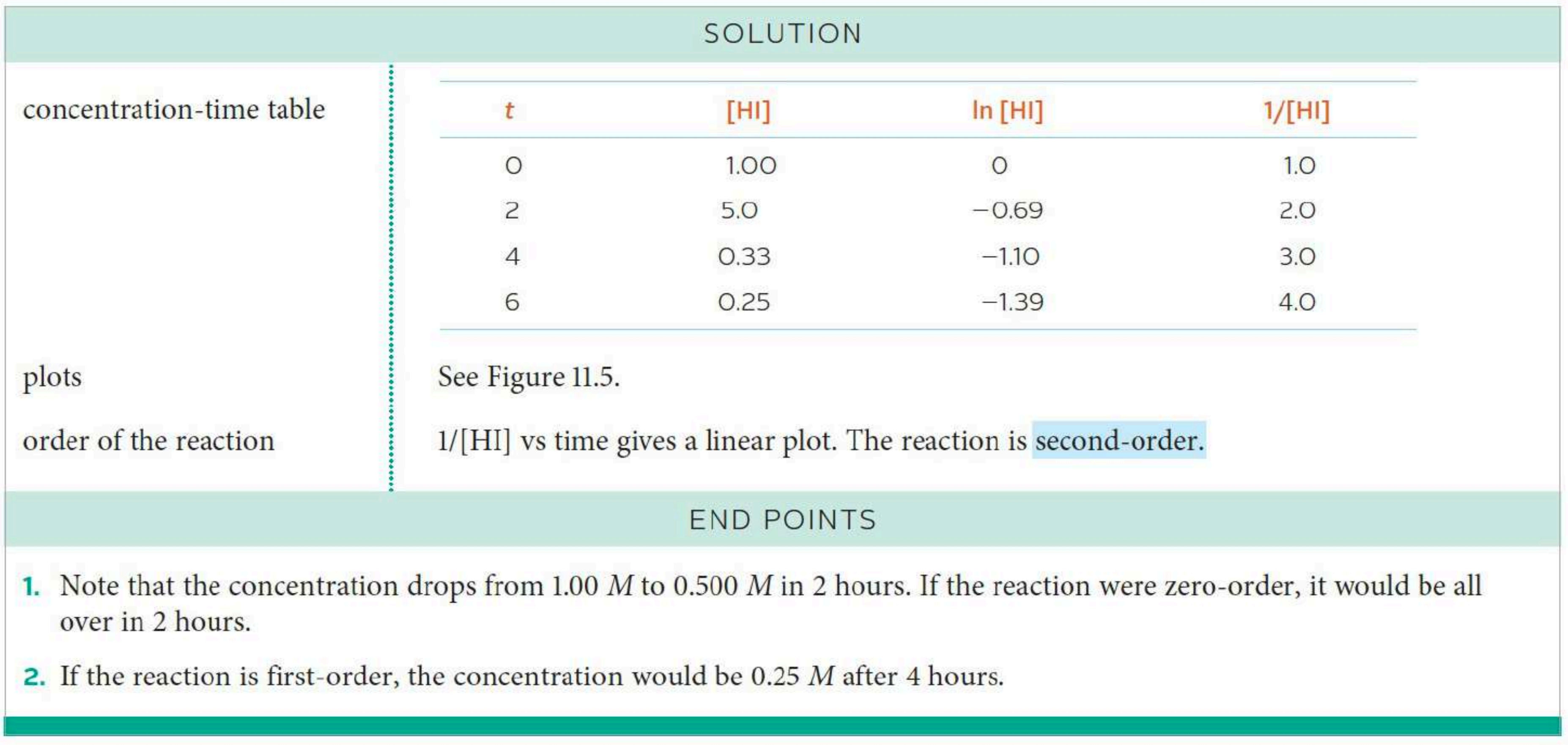
Is this reaction zero-, first-, or second-order in HI?

STRATEGY

1. Prepare a table listing [HI], ln[HI], and 1/[HI] as a function of time from the experimental data given.
2. Make a plot of each concentration-time relationship.
3. See Table 11.2 for the order of the reaction based on the linear plot that you obtain.

continued

Example 11.6, (Cont’d)



SOLUTION

concentration-time table

t	[HI]	ln [HI]	1/[HI]
0	1.00	0	1.0
2	5.0	−0.69	2.0
4	0.33	−1.10	3.0
6	0.25	−1.39	4.0

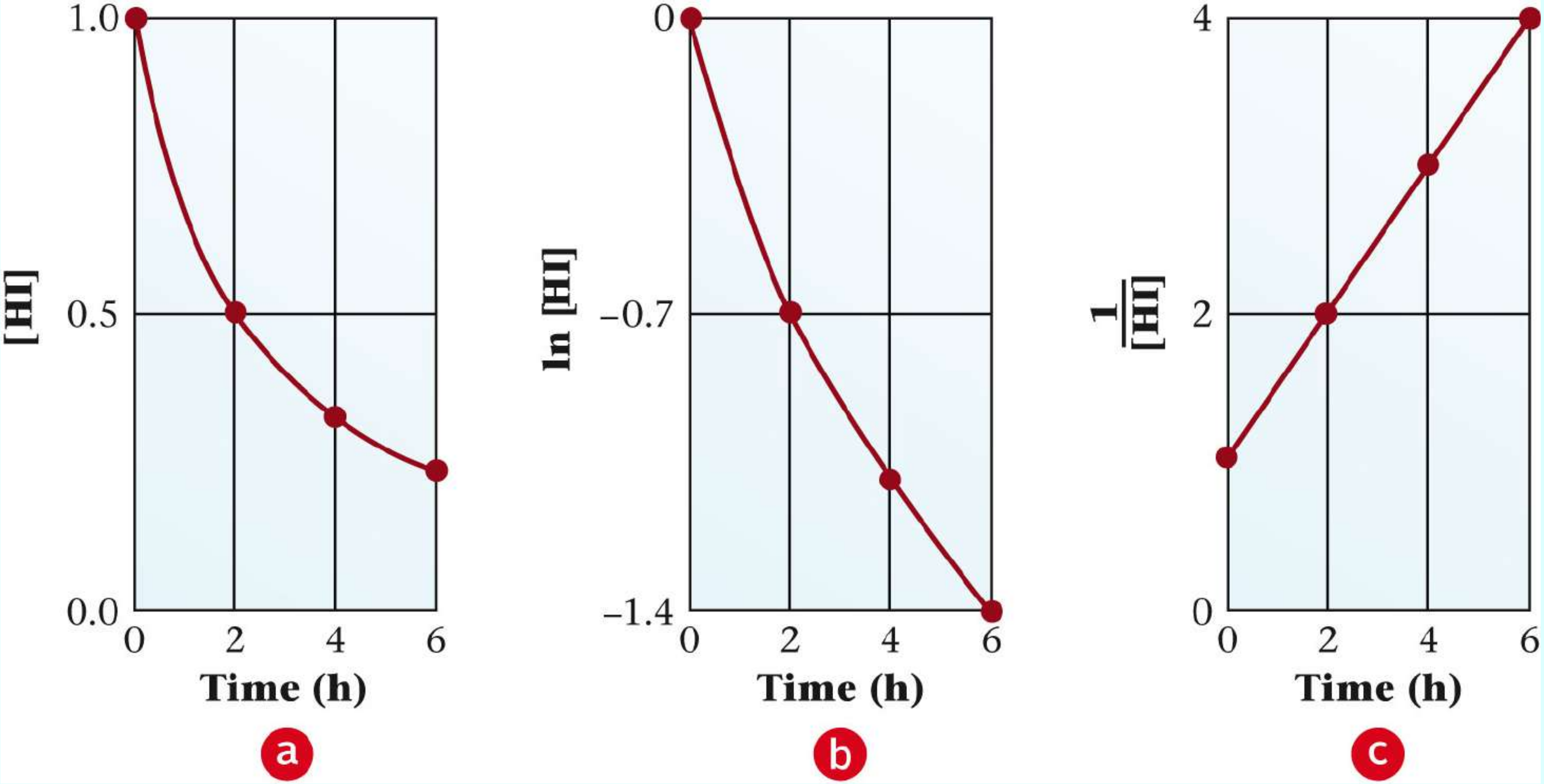
plots: See Figure 11.5.

order of the reaction: 1/[HI] vs time gives a linear plot. The reaction is second-order.

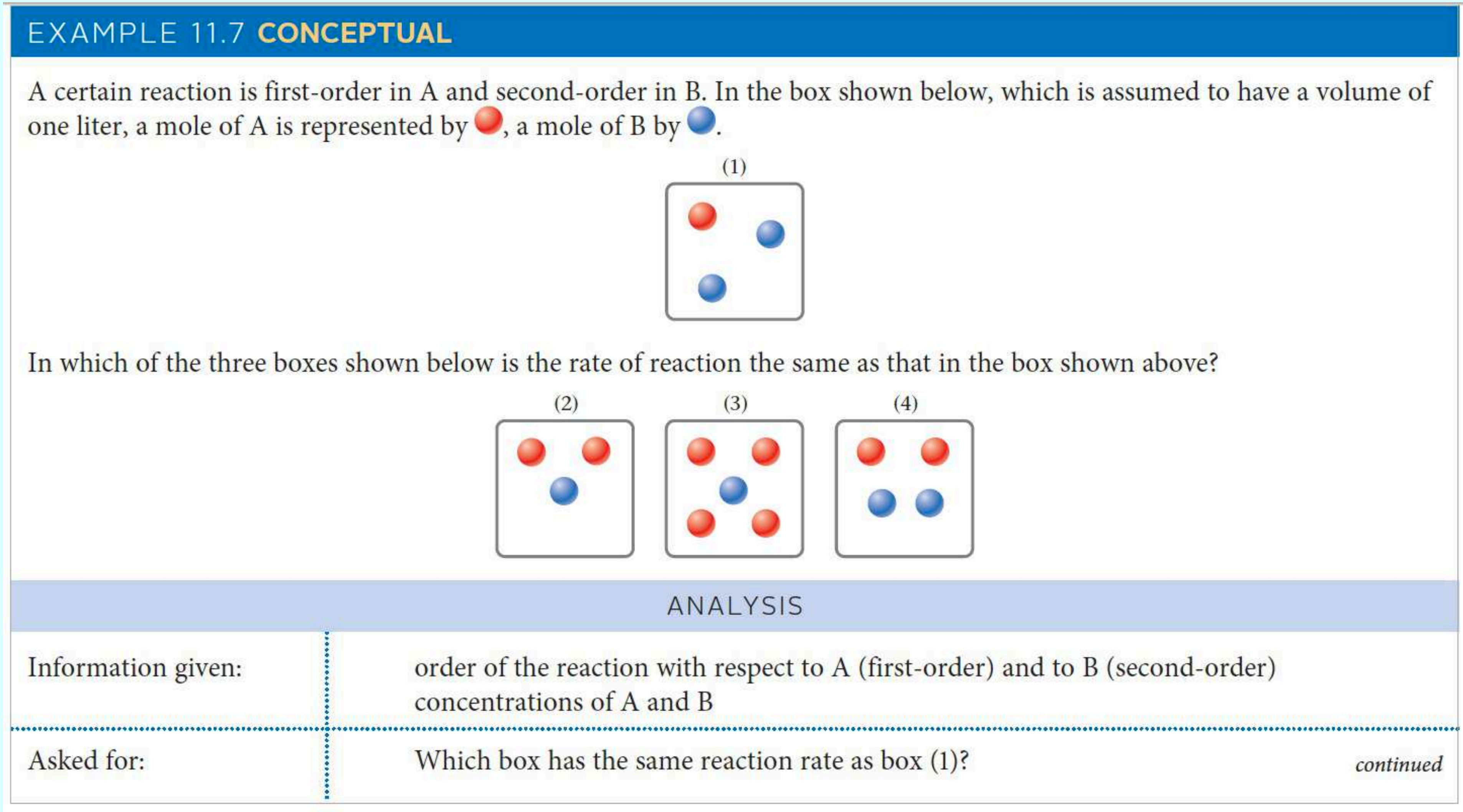
END POINTS

1. Note that the concentration drops from 1.00 *M* to 0.500 *M* in 2 hours. If the reaction were zero-order, it would be all over in 2 hours.
2. If the reaction is first-order, the concentration would be 0.25 *M* after 4 hours.

Figure 11.5


1.0
0.5
0.0
[HI]
0
2
4
6
Time (h)
a
0
−0.7
−1.4
ln [HI]
0
2
4
6
Time (h)
b
4
2
0
1/[HI]
0
2
4
6
Time (h)
c

Example 11.7



EXAMPLE 11.7 CONCEPTUAL

A certain reaction is first-order in A and second-order in B. In the box shown below, which is assumed to have a volume of one liter, a mole of A is represented by 🔴, a mole of B by 🔵.

(1)

In which of the three boxes shown below is the rate of reaction the same as that in the box shown above?

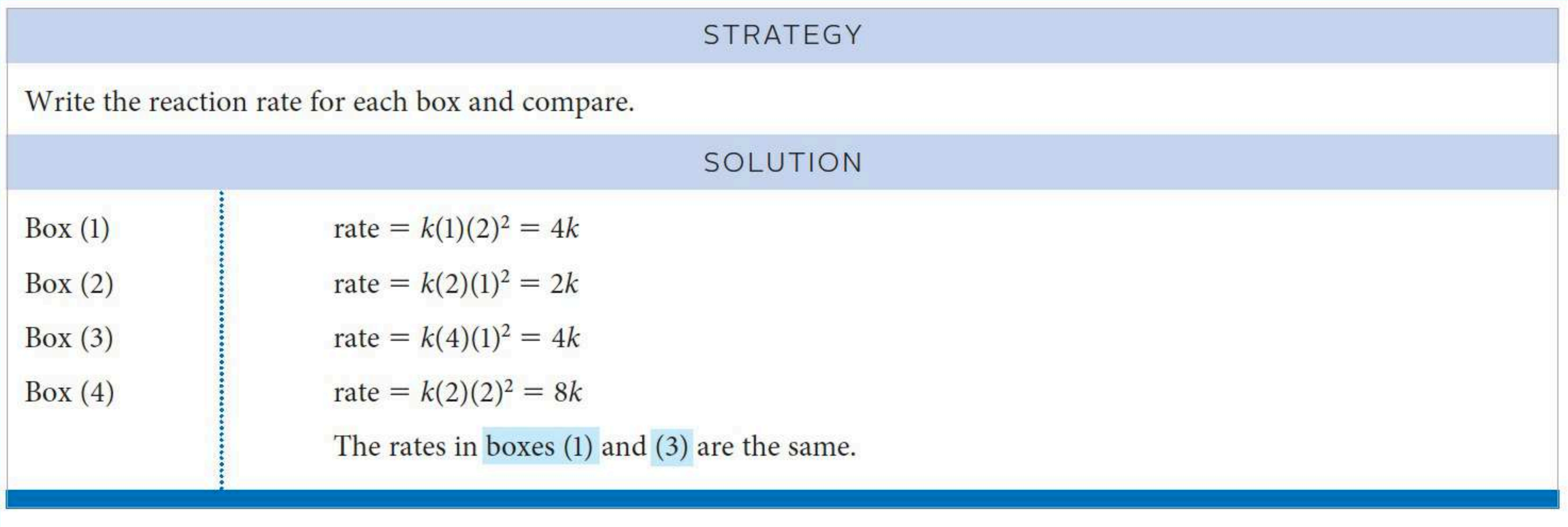
(2) (3) (4)

ANALYSIS

Information given:	order of the reaction with respect to A (first-order) and to B (second-order) concentrations of A and B
Asked for:	Which box has the same reaction rate as box (1)?

continued

Example 11.7, (Cont'd)



STRATEGY

Write the reaction rate for each box and compare.

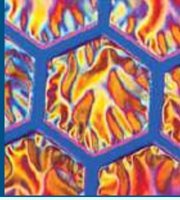
SOLUTION

Box (1)	rate $= k(1)(2)^2 = 4k$
Box (2)	rate $= k(2)(1)^2 = 2k$
Box (3)	rate $= k(4)(1)^2 = 4k$
Box (4)	rate $= k(2)(2)^2 = 8k$
	The rates in boxes (1) and (3) are the same.

Modeling Reaction Rates

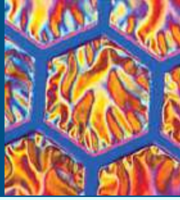
- Two basic models of reaction rates
  1. Collision Model
  2. Transition State Model

Collision Model: Activation Energies



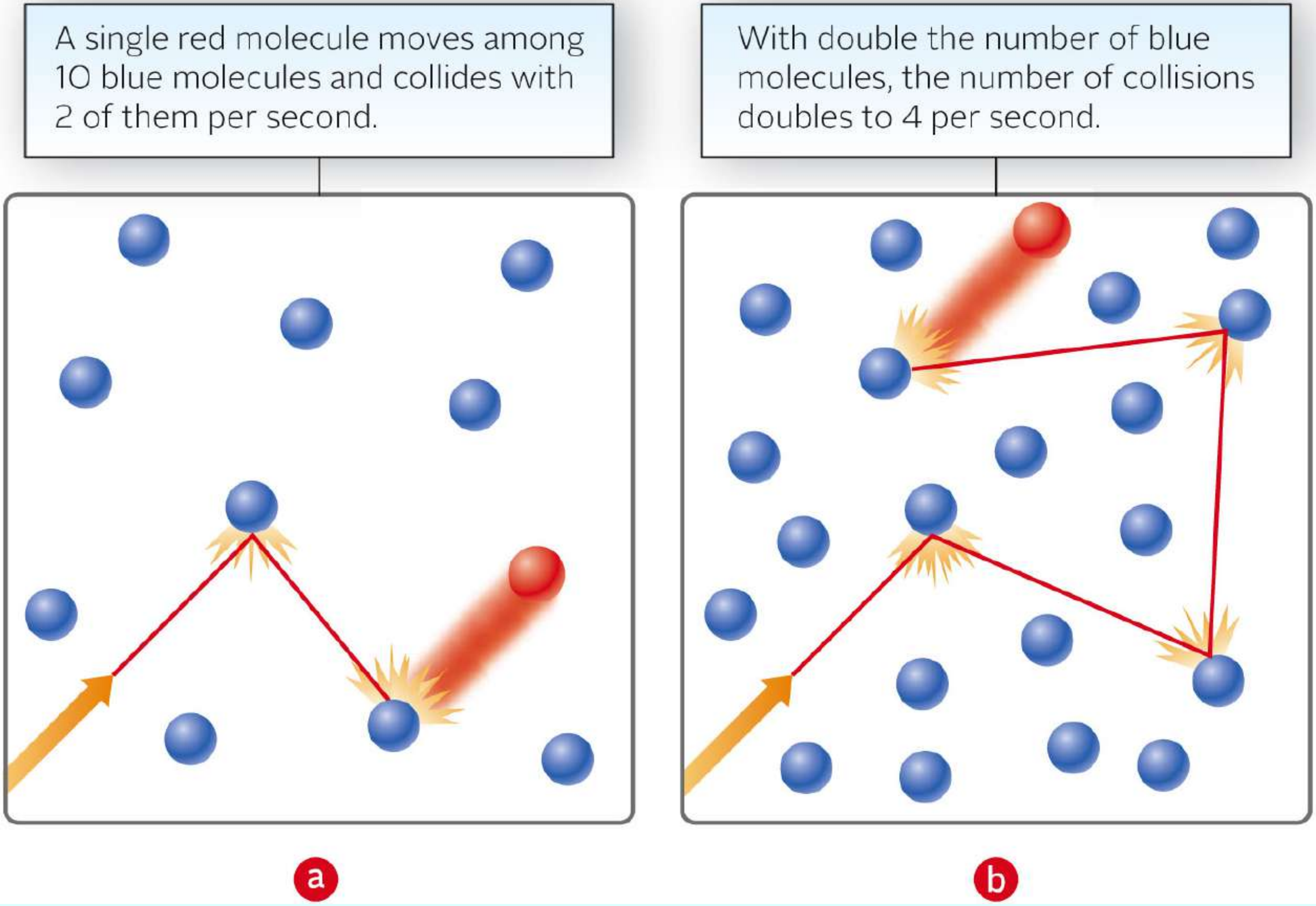
- $CO\ (g) + NO_2\ (g) \rightarrow CO_2\ (g) + NO\ (g)$
- Reaction takes place directly between CO and NO_2
  - Doubling [CO] doubles the rate
  - Doubling $[NO_2]$ doubles the rate
- Experimentally, the rate expression is
  - $\text{Rate} = k[CO][NO_2]$
- From kinetic theory, every CO molecule should collide with 10^9 molecules of NO_2 in one second
  - Reaction should be over in a fraction of a second
  - In reality the half life is about 10 sec, so not every collision leads to a reaction

Collisions, Effective and Ineffective



- Why does every collision not lead to a reaction?
  - Molecules have to be oriented properly (sterics)
  - Kinetic energy of collision may not be high enough to overcome repulsions of electrons in molecules
    - For every reaction, there is a minimum energy which the molecules must possess to react
    - This energy is the ***activation energy***

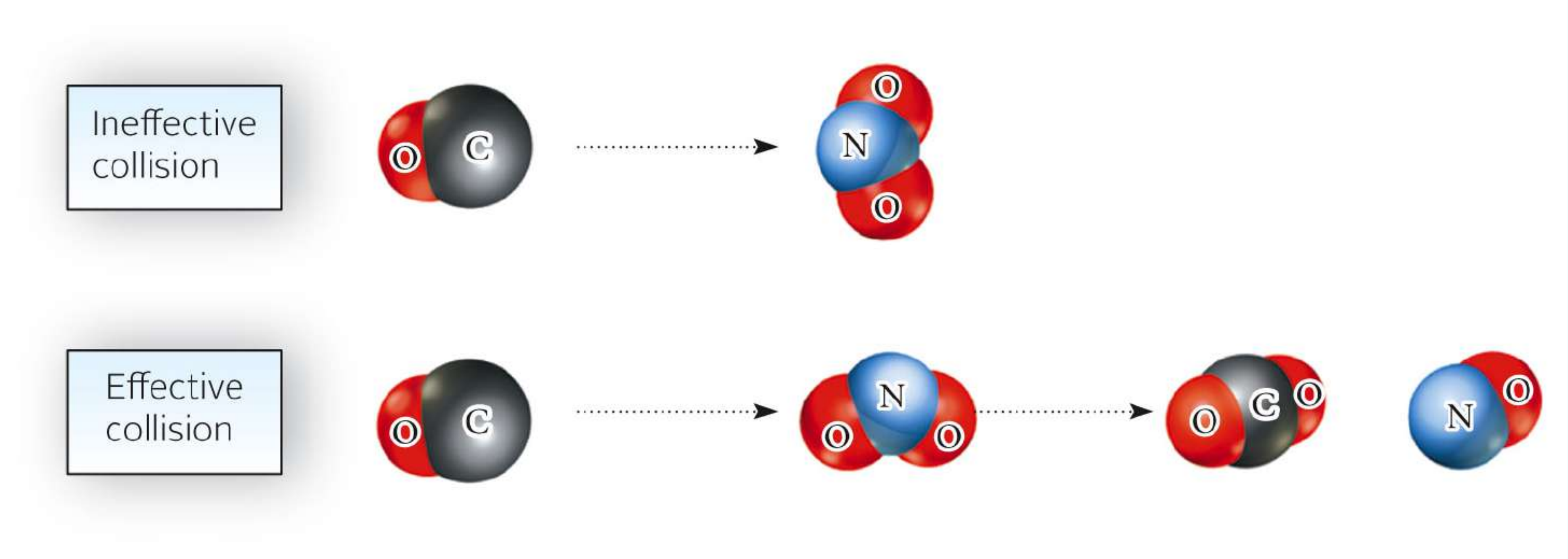
Figure 11.6



A single red molecule moves among 10 blue molecules and collides with 2 of them per second.

With double the number of blue molecules, the number of collisions doubles to 4 per second.

Figure 11.7


Ineffective collision
O
C
O
N
O
Effective collision
O
C
N
O
O
O
C
O
N
O

Quantitative Aspects of Collision Theory

- $k = pZf$
  - p is the steric factor, accounting for the fact that only certain orientations of molecules will lead to effective collision
  - Z is the collision frequency, the number of collisions per unit time at unit concentrations of reactants
  - f is the fraction of collision in which the energy of collision is equal to or greater than the activation energy

Collision Frequency Relationship

$$f = e^{\frac{-E_a}{RT}}$$

- E_a is the activation energy
- R is the gas constant in J/mol-K
- T is the Kelvin temperature

$$k = pZe^{\frac{-E_a}{RT}}$$

- This combined equation tells us that the larger the activation energy, the smaller the rate constant

Table 11.3

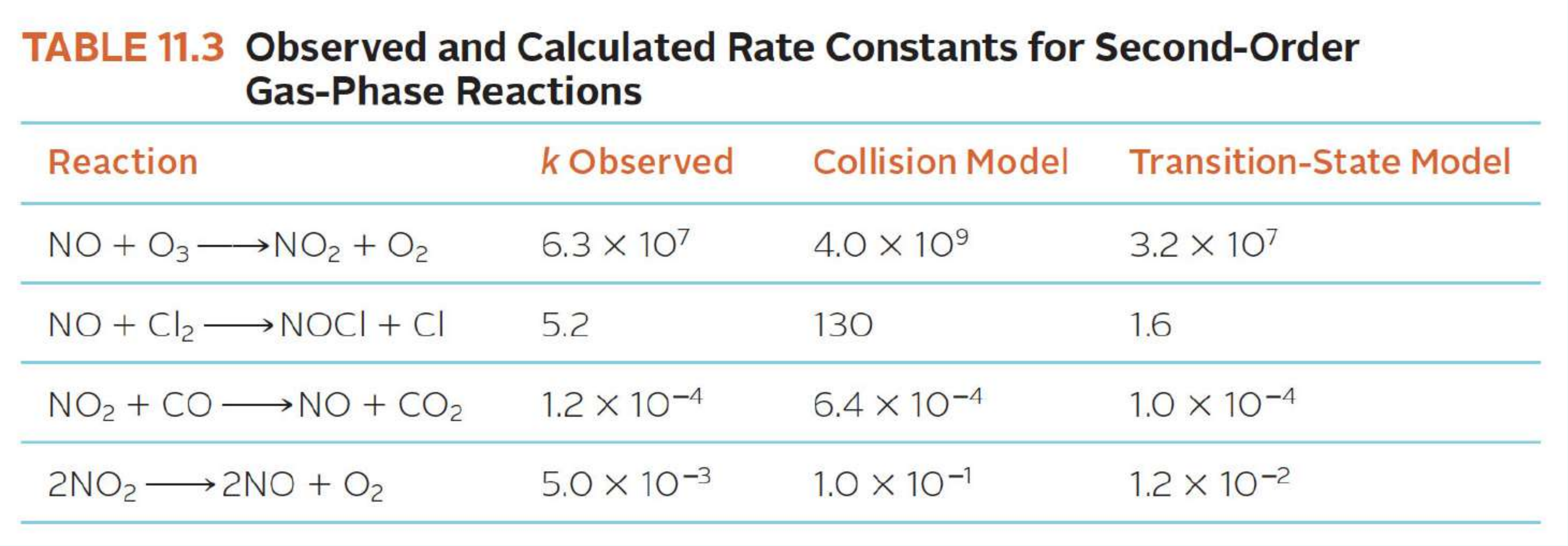


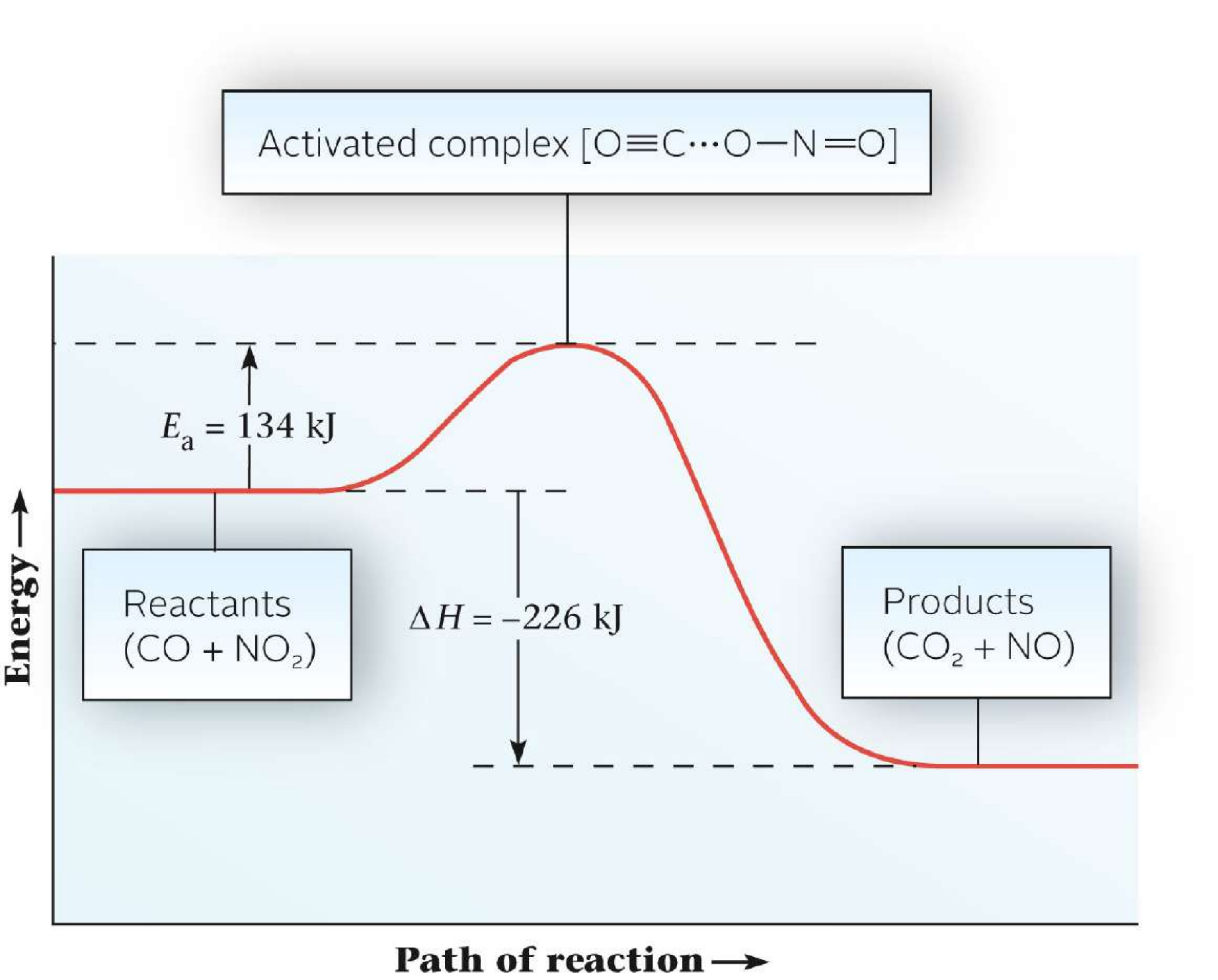
TABLE 11.3 Observed and Calculated Rate Constants for Second-Order Gas-Phase Reactions

Reaction	*k* Observed	Collision Model	Transition-State Model
$NO + O_3 \longrightarrow NO_2 + O_2$	6.3×10^{7}	4.0×10^{9}	3.2×10^{7}
$NO + Cl_2 \longrightarrow NOCl + Cl$	5.2	130	1.6
$NO_2 + CO \longrightarrow NO + CO_2$	1.2×10^{-4}	6.4×10^{-4}	1.0×10^{-4}
$2NO_2 \longrightarrow 2NO + O_2$	5.0×10^{-3}	1.0×10^{-1}	1.2×10^{-2}

Transition-State Model

- Consider the activation energy diagram for the CO-NO_2 reaction
  - In it, energy is plotted on the y-axis
  - Reaction path is plotted on the x-axis
- The reactants form an intermediate called an ***activated complex***
  - The state of the system at the activated complex is called a ***transition state***

Figure 11.8



Activated complex [O≡C···O—N=O]
E_a = 134 kJ
Reactants
($CO + NO_2$)
ΔH = −226 kJ
Products
($CO_2 + NO$)
Energy ⟶
Path of reaction ⟶

Understanding Activation Energy Diagrams

- Note the similarity of the diagram to the energy diagrams introduced in Chapter 8
  - An additional feature is the high-energy ***activated complex*** that forms upon collision
    - The activated complex is at low concentration, in equilibrium with reactant and product
    - The activated complex may proceed to form product, or fall back to reactant(s)
    - The activation energy is the difference in energy between reactant and activated complex
    - ΔH is the difference in energy between reactant and product, just as it was in Chapter 8

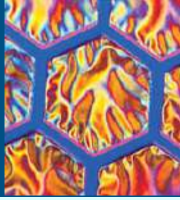
Transition States and Activated Complexes

- In this model, the rate of reaction is controlled by the rate at which the activated complex forms
- The transition state model is somewhat more accurate than the collision model, at least when p=1
- Transition state model explains why the activation energy is ordinarily much smaller than the bond enthalpies in the reactant molecules

Reaction Rate and Temperature

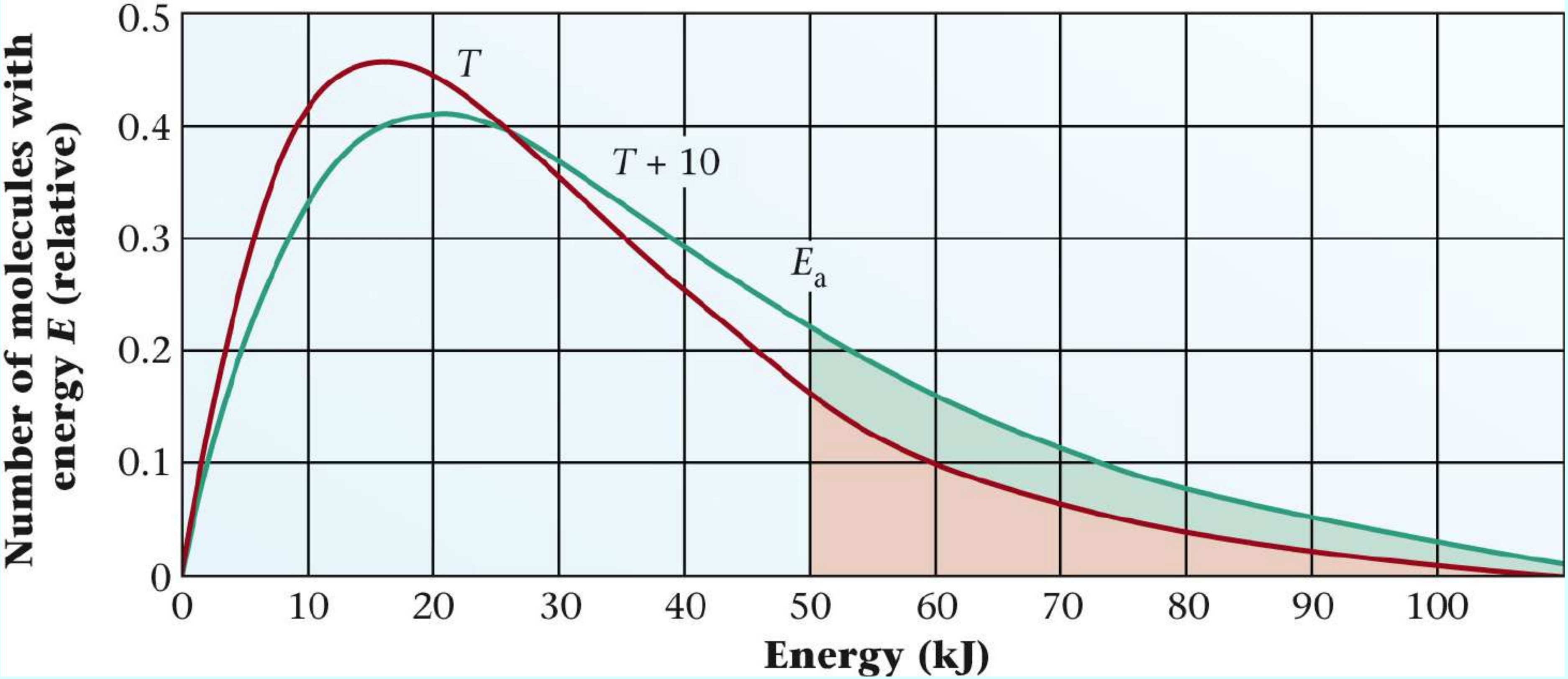
- Reaction rate ordinarily increases with temperature
  - To cook food more quickly, raise the oven temperature
  - To slow the reactions that lead to food spoilage, lower the temperature in the refrigerator or freezer
- Every 10 °C increase in temperature doubles the reaction rate
  - This rule is general and approximate!

Kinetic Theory Revisited



- Recall from kinetic theory of gases that the temperature is a measure of the average kinetic energy of molecules
  - Higher temperatures mean higher kinetic energies
  - The higher the temperature, the larger the fraction of molecules that possess the activation energy (or greater)
  - With a larger fraction of molecules possessing E_a, a larger fraction of effective collisions results

Figure 11.9

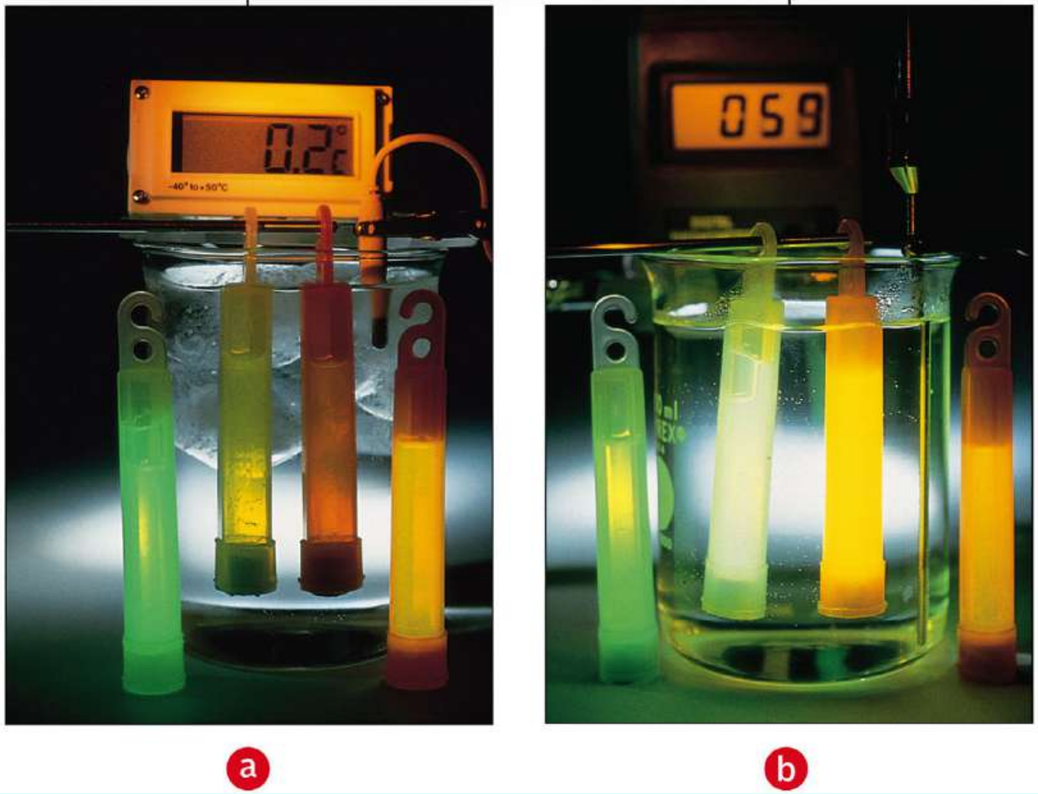


Number of molecules with energy E (relative)
0.5
0.4
0.3
0.2
0.1
0
T
T + 10
Ea
0
10
20
30
40
50
60
70
80
90
100
Energy (kJ)

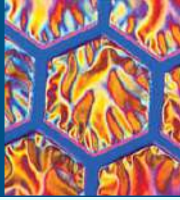
Temperature and Reaction Rate

The light sticks outside the beaker at room temperature are brighter than the two sticks cooled to 0.2°C because the reaction rate is larger at the higher temperature.

With the light sticks in the beaker heated well above room temperature, to 59°C, these sticks are now much brighter than those at room temperature.



Arrhenius Theory



- Recall from the collision model

$$k = pZe^{\frac{-E_a}{RT}}$$

- Combining p and z into a single term called the Arrhenius pre-exponential, A, results in

$$k = Ae^{\frac{-E_a}{RT}}$$

Graphical Interpretation of the Arrhenius Equation

- The Arrhenius equation can be put into y=mx+b form

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

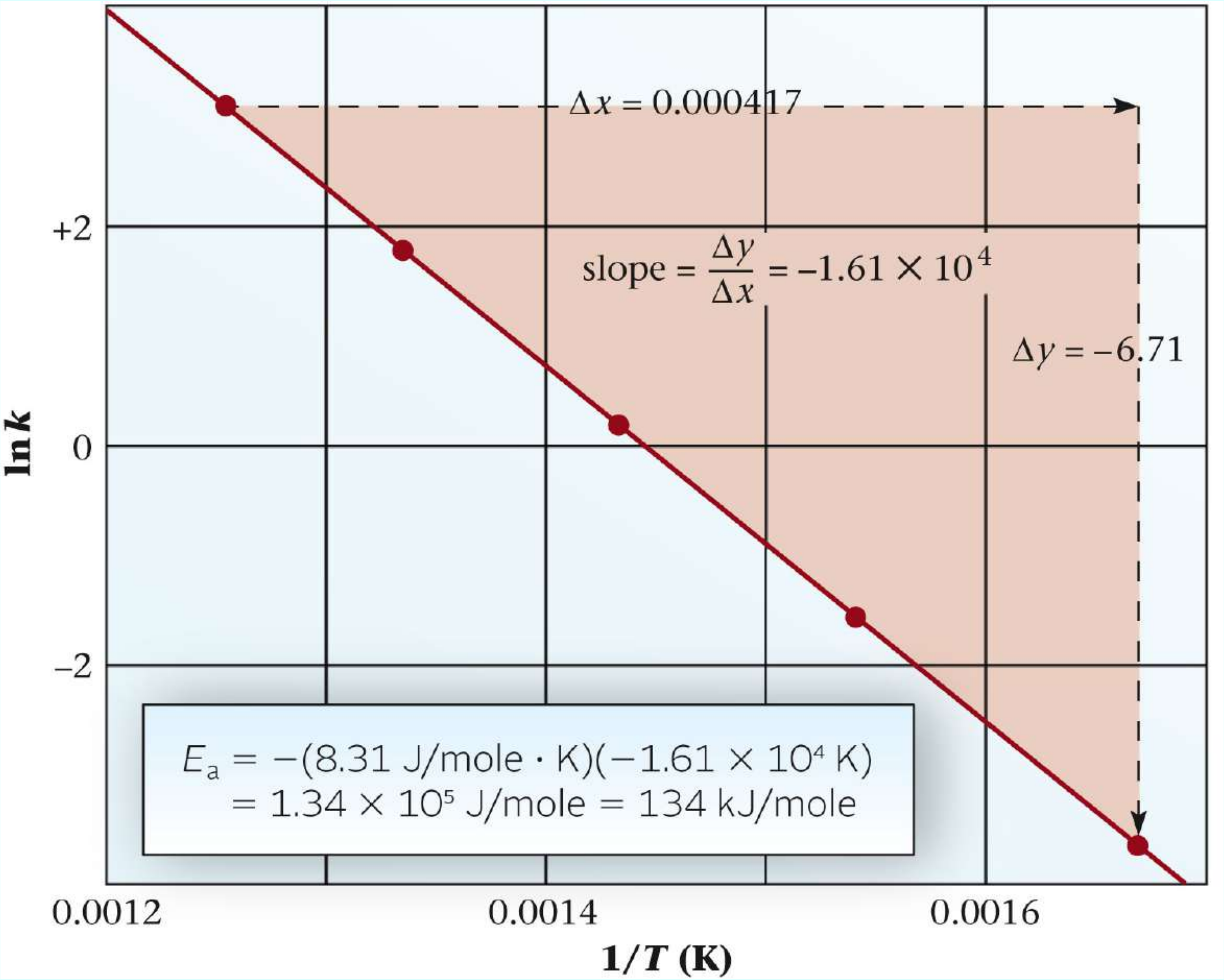
- A plot of ln(k) on the y-axis vs. 1/T on the x-axis yields
    - A slope equal to $-E_a/R$
    - A y-intercept equal to ln(A)
- ***By obtaining experimental data that allows the calculation of k at various temperatures, the activation energy can be determined***

Recall the Two-Point Vapor Pressure Equation

- Clausius-Clapeyron
  - Taking two temperatures and two vapor pressures, the ΔH_{vap} can be determined
  - The ***Arrhenius equation*** is similar in nature and can be used for two k values and two temperatures
    - E_a may then be calculated

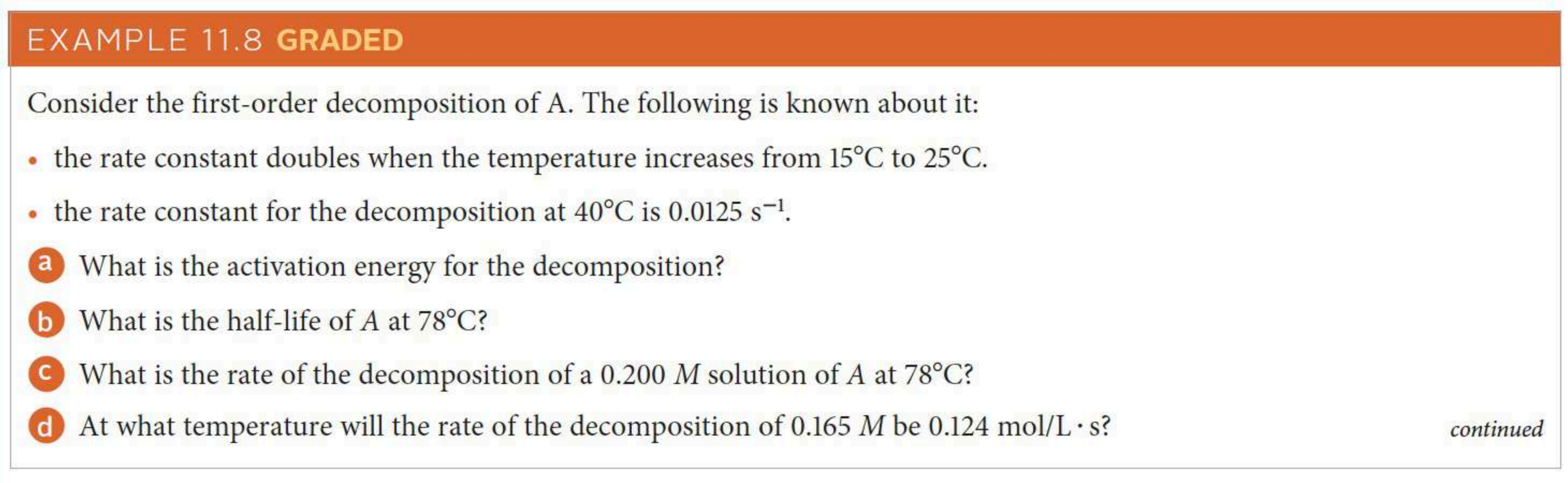
$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Figure 11.10



$$E_a = -(8.31\ \text{J/mole} \cdot \text{K})(-1.61 \times 10^4\ \text{K})$$
$$= 1.34 \times 10^5\ \text{J/mole} = 134\ \text{kJ/mole}$$

Example 11.8



EXAMPLE 11.8 **GRADED**

Consider the first-order decomposition of A. The following is known about it:

- the rate constant doubles when the temperature increases from 15°C to 25°C.
- the rate constant for the decomposition at 40°C is 0.0125 s^{-1}.

ⓐ What is the activation energy for the decomposition?

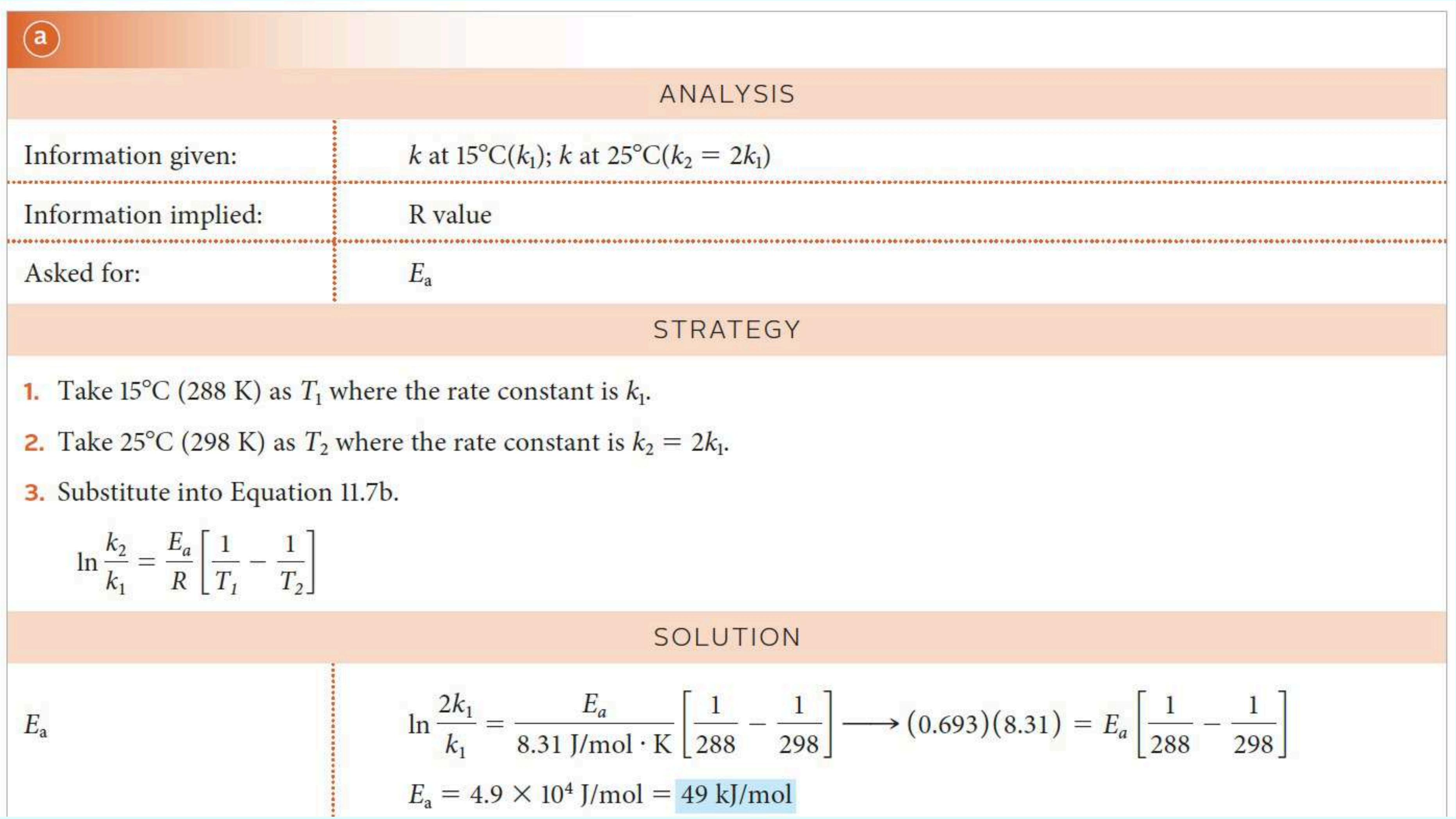
ⓑ What is the half-life of *A* at 78°C?

ⓒ What is the rate of the decomposition of a 0.200 *M* solution of *A* at 78°C?

ⓓ At what temperature will the rate of the decomposition of 0.165 *M* be 0.124 mol/L · s?

continued

Example 11.8, (Cont'd)



ⓐ

ANALYSIS

Information given:	k at 15°C(k_1); k at 25°C($k_2 = 2k_1$)
Information implied:	R value
Asked for:	E_a

STRATEGY

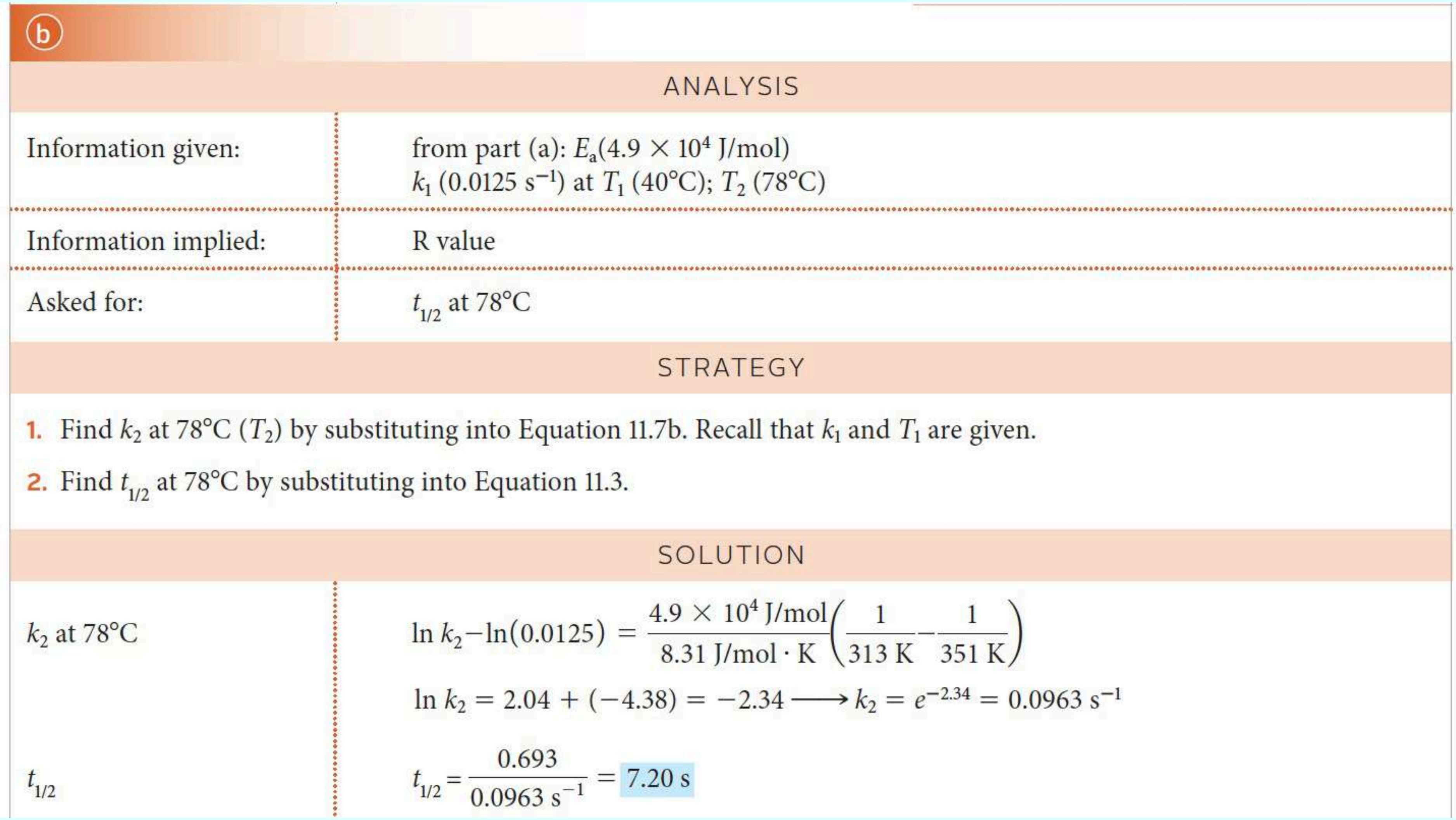
1. Take 15°C (288 K) as T_1 where the rate constant is k_1.
2. Take 25°C (298 K) as T_2 where the rate constant is $k_2 = 2k_1$.
3. Substitute into Equation 11.7b.

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

SOLUTION

E_a	$\ln\frac{2k_1}{k_1} = \frac{E_a}{8.31\ \text{J/mol}\cdot\text{K}}\left[\frac{1}{288} - \frac{1}{298}\right] \longrightarrow (0.693)(8.31) = E_a\left[\frac{1}{288} - \frac{1}{298}\right]$ $E_a = 4.9 \times 10^4$ J/mol = 49 kJ/mol

Example 11.8, (Cont’d)



ⓑ

ANALYSIS

Information given:	from part (a): $E_a (4.9 \times 10^4 \text{ J/mol})$ k_1 (0.0125 s^{-1}) at T_1 (40°C); T_2 (78°C)
Information implied:	R value
Asked for:	$t_{1/2}$ at 78°C

STRATEGY

1. Find k_2 at 78°C (T_2) by substituting into Equation 11.7b. Recall that k_1 and T_1 are given.
2. Find $t_{1/2}$ at 78°C by substituting into Equation 11.3.

SOLUTION

k_2 at 78°C

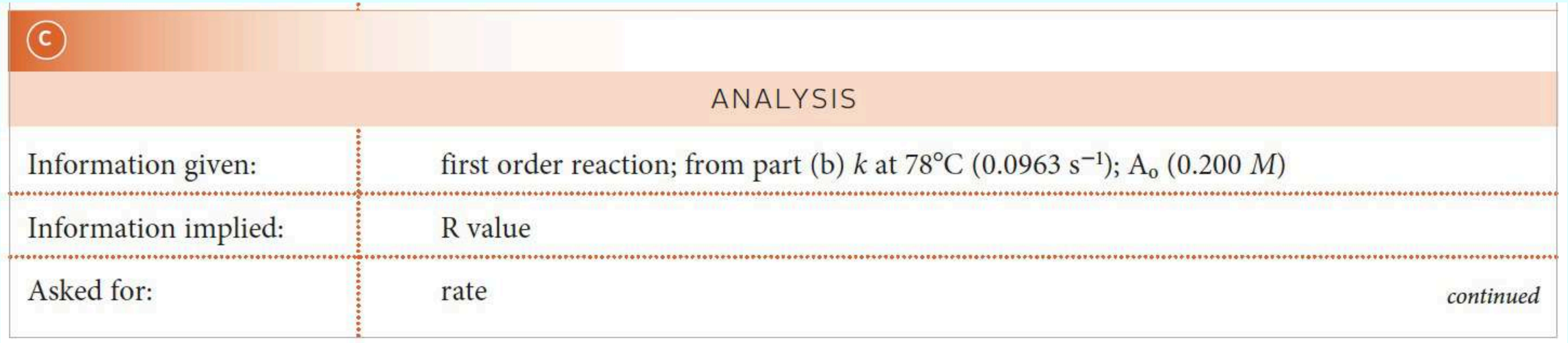
$$\ln k_2 - \ln(0.0125) = \frac{4.9 \times 10^4 \text{ J/mol}}{8.31 \text{ J/mol} \cdot \text{K}}\left(\frac{1}{313 \text{ K}} - \frac{1}{351 \text{ K}}\right)$$

$$\ln k_2 = 2.04 + (-4.38) = -2.34 \longrightarrow k_2 = e^{-2.34} = 0.0963 \text{ s}^{-1}$$

$t_{1/2}$

$$t_{1/2} = \frac{0.693}{0.0963 \text{ s}^{-1}} = 7.20 \text{ s}$$

Example 11.8, (Cont’d)

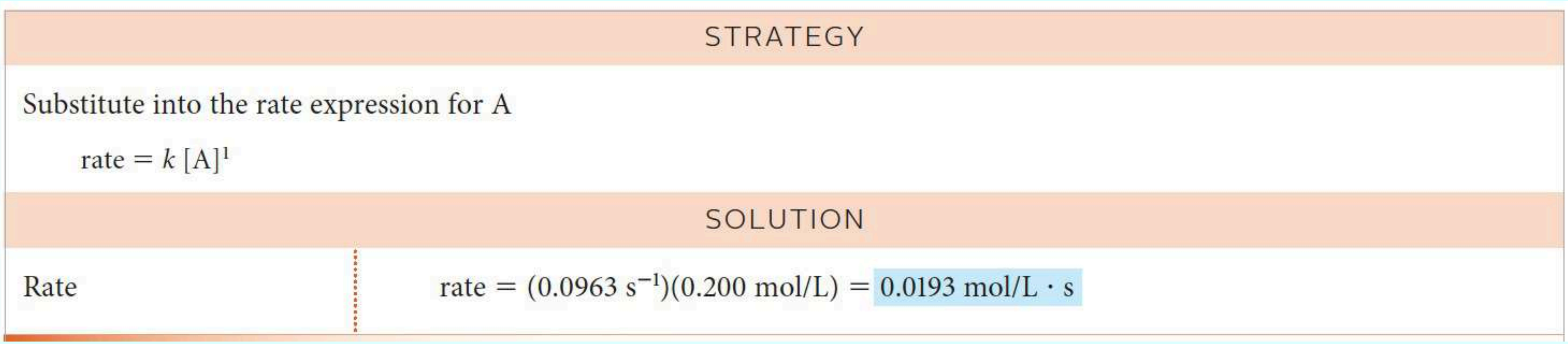


ⓒ

ANALYSIS

Information given:	first order reaction; from part (b) k at 78°C (0.0963 s^{-1}); A_o (0.200 M)
Information implied:	R value
Asked for:	rate

continued



STRATEGY

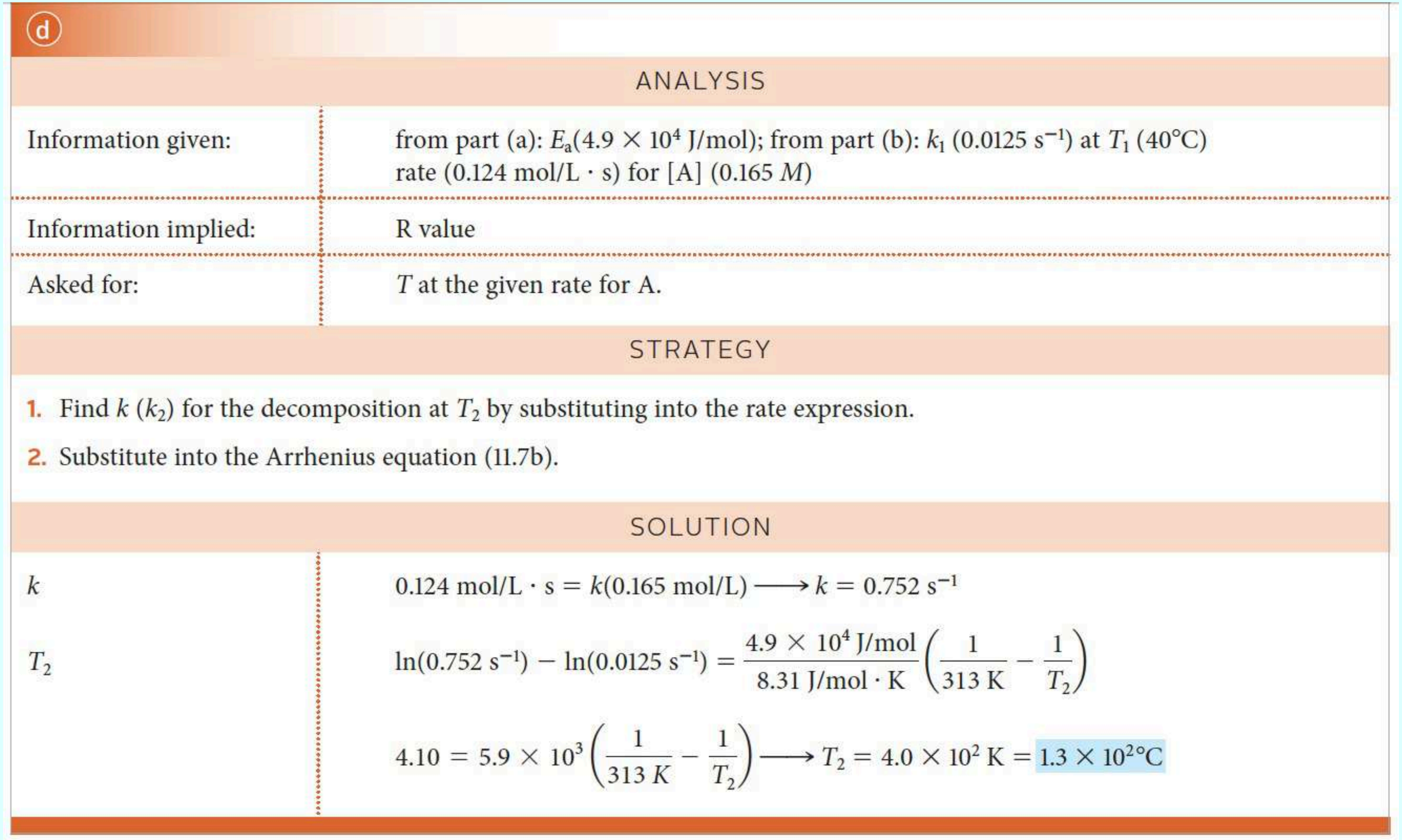
Substitute into the rate expression for A

$$\text{rate} = k\,[\text{A}]^1$$

SOLUTION

Rate	rate = $(0.0963\ \text{s}^{-1})(0.200\ \text{mol/L}) = 0.0193\ \text{mol/L} \cdot \text{s}$

Example 11.8, (Cont'd)



ⓓ

ANALYSIS

Information given:	from part (a): $E_a(4.9 \times 10^4$ J/mol); from part (b): k_1 (0.0125 s^{-1}) at T_1 (40°C) rate (0.124 mol/L · s) for [A] (0.165 *M*)
Information implied:	R value
Asked for:	*T* at the given rate for A.

STRATEGY

1. Find *k* (k_2) for the decomposition at T_2 by substituting into the rate expression.
2. Substitute into the Arrhenius equation (11.7b).

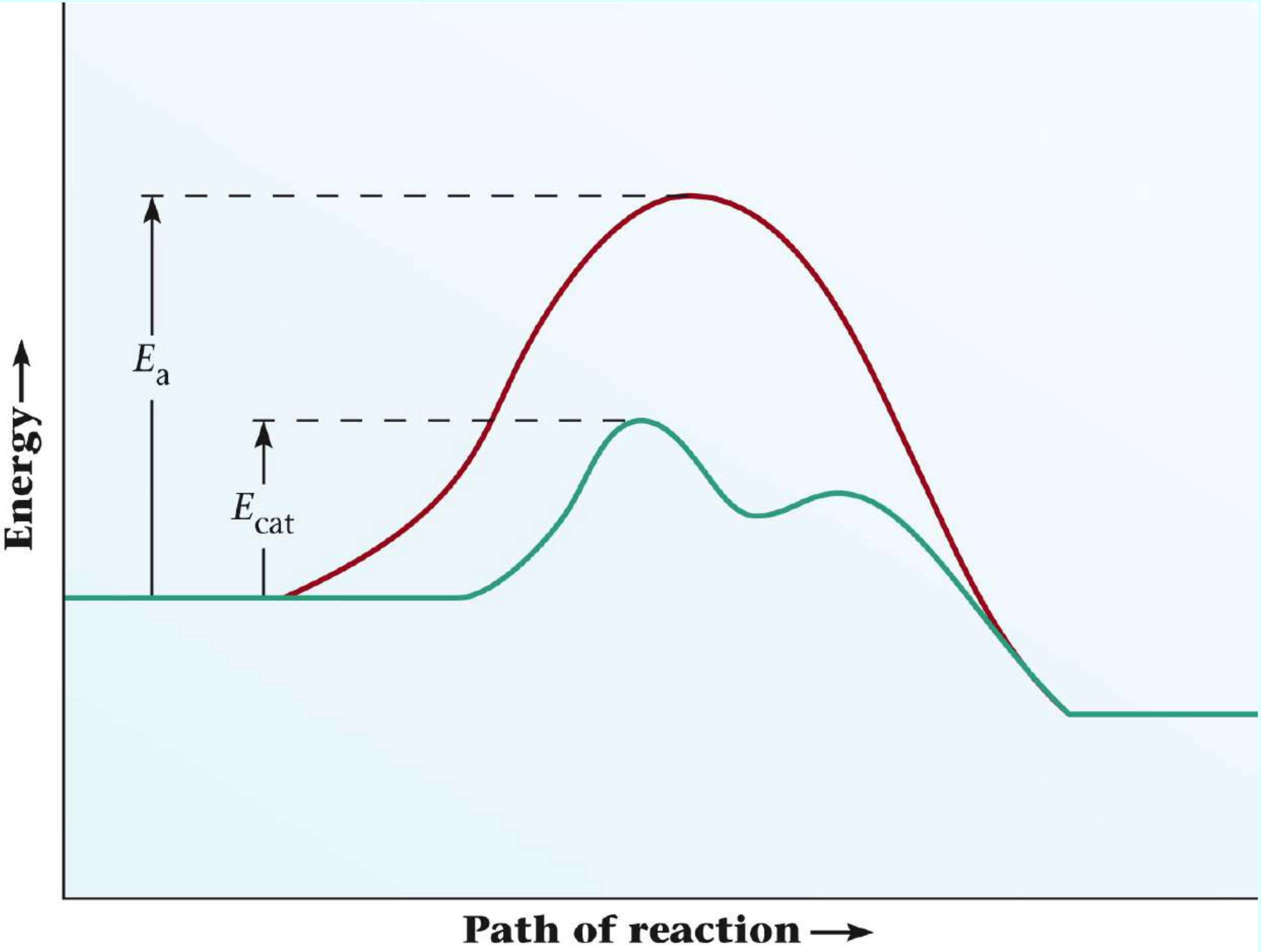
SOLUTION

k	$0.124 \text{ mol/L} \cdot \text{s} = k(0.165 \text{ mol/L}) \longrightarrow k = 0.752 \text{ s}^{-1}$
T_2	$\ln(0.752 \text{ s}^{-1}) - \ln(0.0125 \text{ s}^{-1}) = \dfrac{4.9 \times 10^4 \text{ J/mol}}{8.31 \text{ J/mol} \cdot \text{K}}\left(\dfrac{1}{313 \text{ K}} - \dfrac{1}{T_2}\right)$ $4.10 = 5.9 \times 10^3\left(\dfrac{1}{313\ K} - \dfrac{1}{T_2}\right) \longrightarrow T_2 = 4.0 \times 10^2 \text{ K} = 1.3 \times 10^2 \text{°C}$

Catalysis

- A ***catalyst*** is a ***substance that increases the rate*** of a reaction ***without being consumed*** by it
  - Catalysts act by introducing a lower-energy path by which the reaction can take place
  - An activated complex forms at lower energy than without the presence of the catalyst

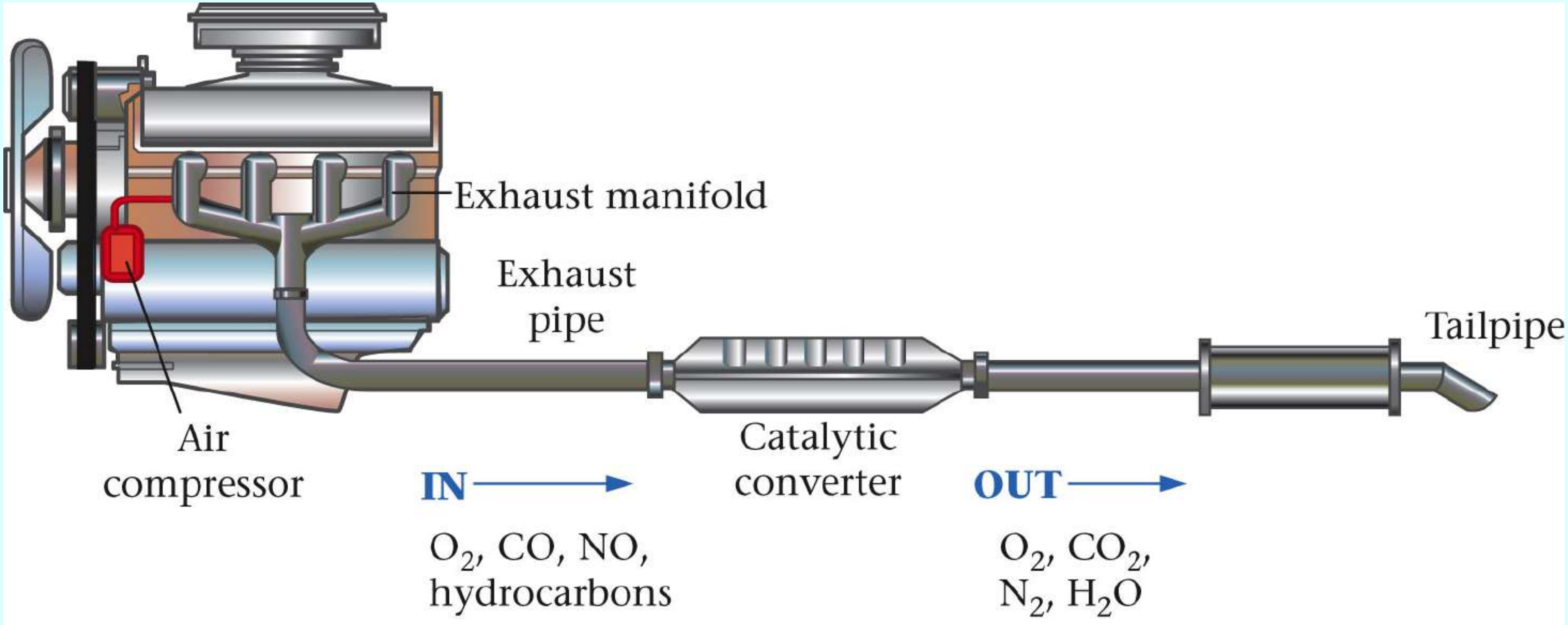
Figure 11.11 – Reaction Diagram



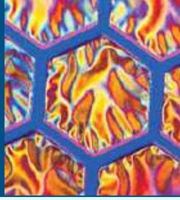
Heterogeneous Catalysis

- A ***heterogeneous catalyst is in a phase different from that of the reaction mixture***
  - Commonly a solid that is used for a gas or liquid phase reaction
  - Decomposition of N_2O on a gold surface
- Common heterogeneous catalyst: the ***catalytic converter***, which contains a metal such as Pt
  - Catalyzes the oxidation of CO to CO_2
  - Catalyzes the oxidation of unburned hydrocarbons to CO_2 and water

Figure 11.12


Exhaust manifold
Exhaust pipe
Tailpipe
Air compressor
IN →
Catalytic converter
OUT →
O_2, CO, NO, hydrocarbons
O_2, CO_2, N_2, H_2O

The Catalytic Converter

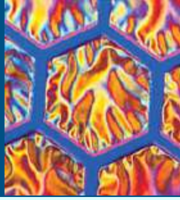


- The other component of a catalytic converter is a metal such as rhodium
  - Rh catalyzes the ***reduction*** of NO to nitrogen and oxygen
- The “magic” of the catalytic converter
  - By combining different metals, it is possible to carry out oxidation and reduction simultaneously, on different molecules, within the same catalytic converter

Homogeneous Catalysis

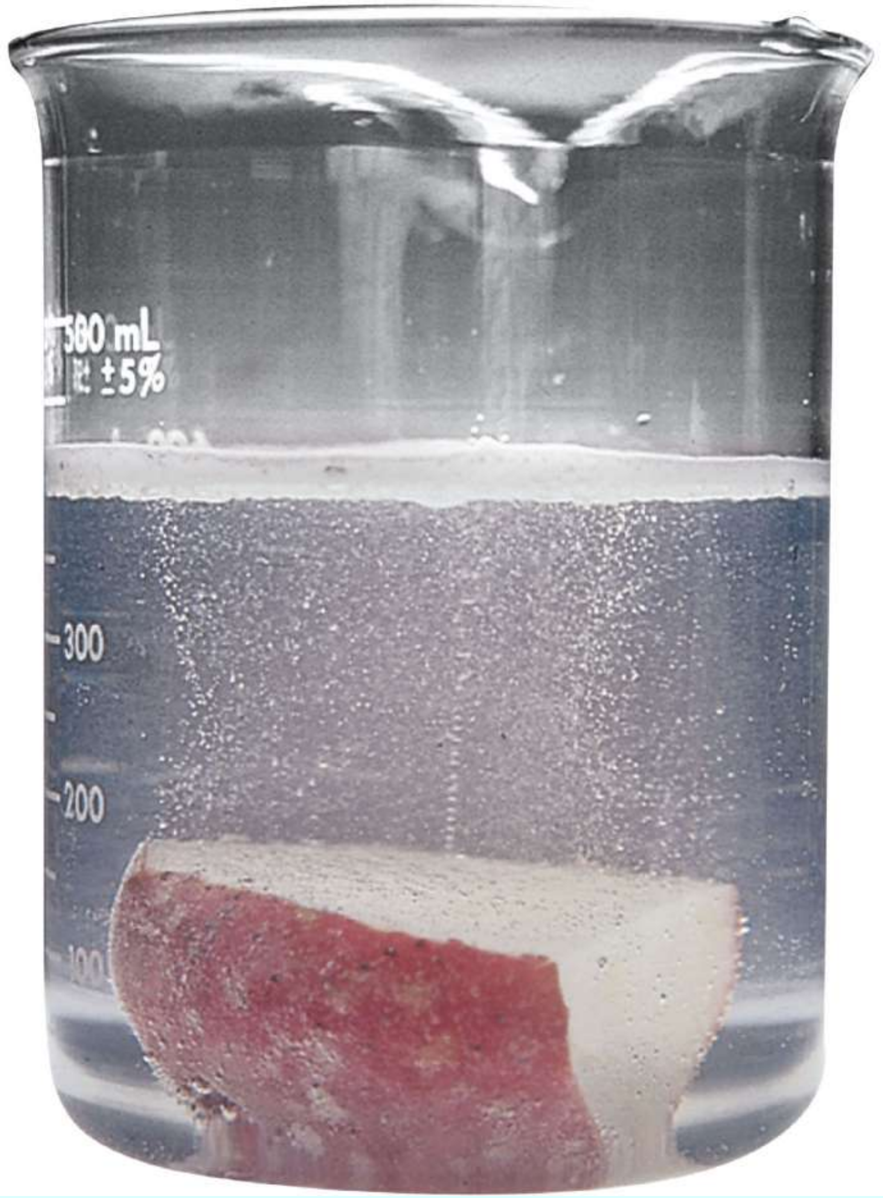
- Homogeneous catalysts are present in the same phase as the reactants
  - Example: decomposition of H_2O_2
    - $H_2O_2\ (aq) \rightarrow 2H_2O\ (l) + O_2\ (g)$
  - Reaction is slow without a catalyst
  - Reaction becomes rapid if NaI (aq) is added

Enzymes

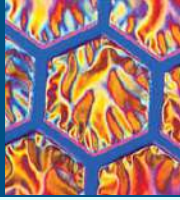


- Enzymes are biocatalysts
  - The same decomposition of hydrogen peroxide can be catalyzed by the enzyme called catalase
  - Enzymes can be very specific
    - One enzyme can be targeted to perform a very specific reaction
    - Maltose can be converted to glucose by maltase
  - Enzymes can speed up biological reactions by a factor of 10^{12} or greater

Figure 11.13

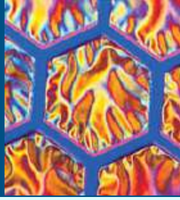


Reaction Mechanisms



- A reaction mechanism is a description of a path, usually a series of steps, by which a reaction takes place
- Earlier, we saw the reaction
  - $CO\ (g) + NO_2\ (g) \rightarrow CO_2\ (g) + NO\ (g)$
    - Takes place directly at high temperatures
    - Occurs as a series of steps at lower temperatures

The CO-NO_2 Reaction at Low Temperature



- At low temperature
    - $NO_2 (g) + NO_2 (g) \rightarrow NO_3 (g) + NO (g)$
    - $CO (g) + NO_3 (g) \rightarrow CO_2 (g) + NO_2 (g)$
- Overall, the sum of the steps is the same:
    - $CO (g) + NO_2 (g) \rightarrow CO_2 (g) + NO (g)$
- The ***nature of the rate expression*** and hence the ***reaction order depends on the mechanism by which the reaction takes place***

Elementary Steps

- The individual steps in a mechanism are called elementary steps
  - Almost always unimolecular, bimolecular or termolecular:
    - $A \rightarrow B + C$rate $= k[A]$
    - $A + B \rightarrow C + D$ rate $= k[A][B]$
    - $A + B + C \rightarrow D + E$rate $= k[A][B][C]$

Notes on Rate Expressions for Elementary Reactions

- Note that an elementary step implies that a reaction takes place exactly as written
  - This is different from an overall reaction, where the actual mechanism is unknown
- Therefore, ***the rate expression can be written directly from the elementary step equation***
  - This is ***only true for elementary steps***
  - ***For overall reactions, experiments must still be done to determine the rate expression***

Slow Steps

- In a mechanism, one step is often slower than the other (or others if more than two steps)
  - The ***slow step is rate-determining***
  - The rate of the slow step is the rate of the reaction

A Real-World Example

- Consider three people grading an examination
  - A spends 10 s grading question 1
  - B spends 15 s grading question 2
  - C takes 5 min to grade question 3
- The rate at which the exam is graded is

$$\frac{1\,\text{exam}}{10\text{s} + 15\text{s} + 300\text{s}} = 0.00308\,\frac{\text{exam}}{\text{s}}$$

- The rate at which grader C graded is

$$\frac{1\,\text{exam}}{300\text{s}} = 0.00333\,\frac{\text{exam}}{\text{s}}$$

- These numbers are approximately equal

Another Real-World Example

- On a two-lane highway, the slowest driver is the limiting factor in determining how fast cars following can proceed

Slow Steps

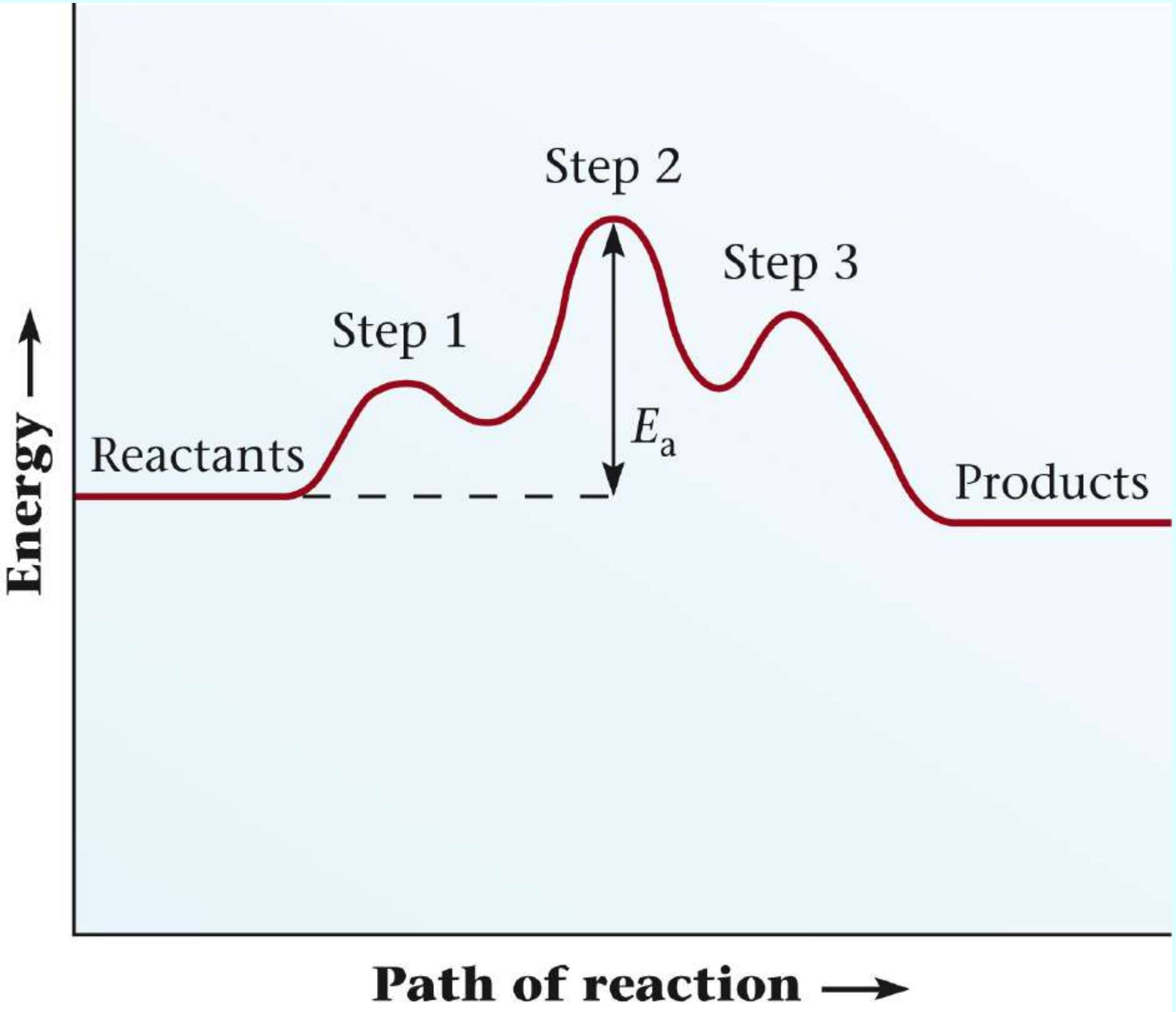
- Conclusions
    1. The overall rate of a reaction cannot exceed the rate of the slowest step
    2. If that step is by far the slowest, its rate will be approximately equal to that of the overall reaction
    3. The slowest step in a reaction will ordinarily be the one with the highest activation energy

Deducing a Rate Expression from a Proposed Mechanism

1. Find the slowest step and equate the rate of the overall reaction to the rate of that step
2. Find the rate expression for that slowest step

Figure 11.14

- In figure 11.14, clearly step 2 has the largest activation energy, so it is the slowest step



Deducing the Slower Step

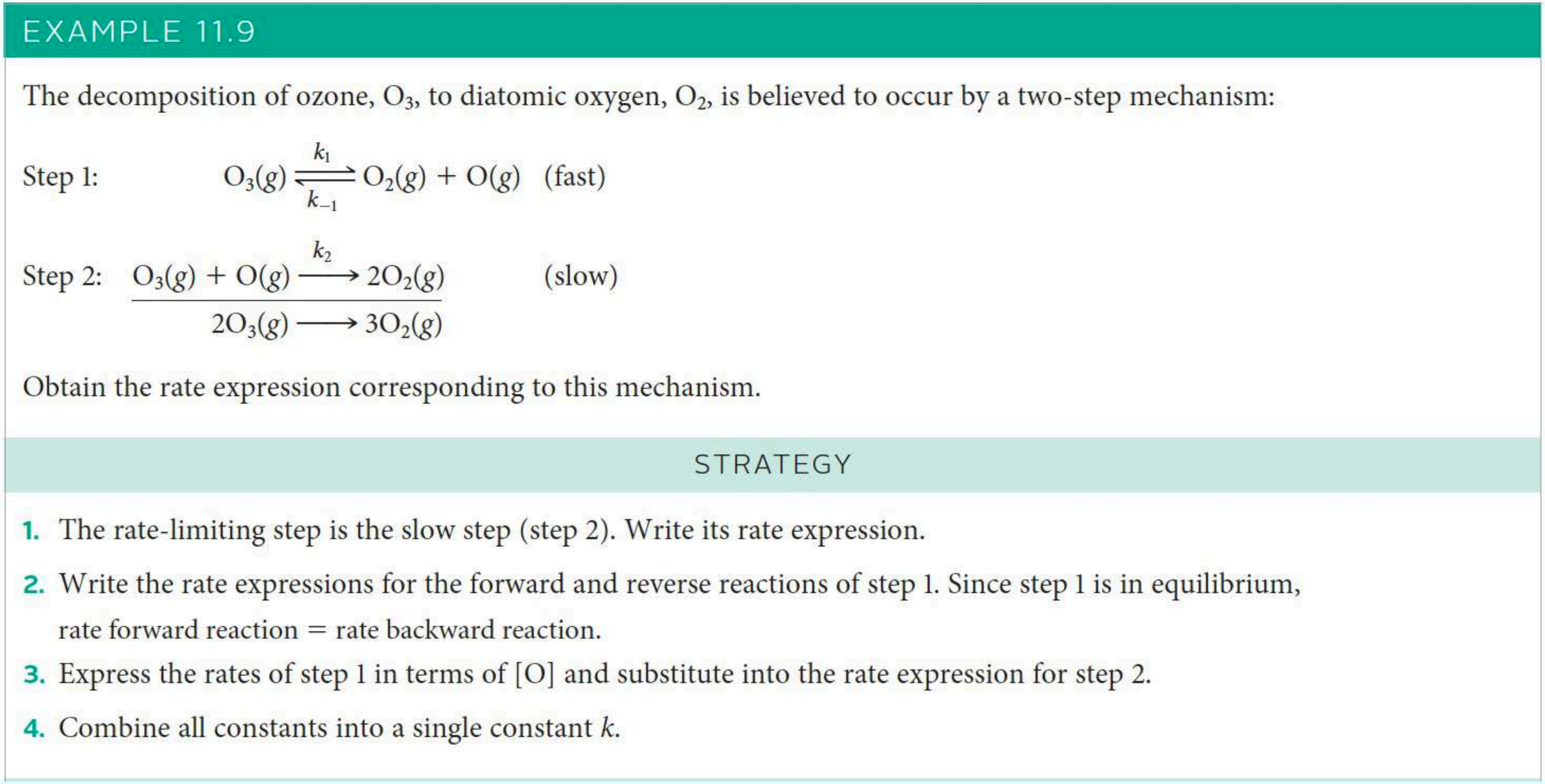
  - NO_2 (g) + NO_2 (g) $\rightarrow$ NO_3 (g) + NO (g) (slow)
  - CO (g) + NO_3 (g) $\rightarrow$ CO_2 (g) + NO_2 (g) (fast)
- Overall, the sum of the steps is the same:
  - CO (g) + NO_2 (g) $\rightarrow$ CO_2 (g) + NO (g)

  - Rate = $k[NO_2]^2$
  - Note that ***this rate expression is different*** from the one we saw at high temperature; in other words, ***the rate expression depends on the mechanism***

Reactive Intermediates

- Mechanisms often involve reactive intermediates
  - These are produced in one step and consumed in a subsequent step
  - These do not appear in overall reactions
  - Concentrations are too small to observe experimentally
  - The terms for such species are eliminated in the process of determining the rate expression

Example 11.9



EXAMPLE 11.9

The decomposition of ozone, O_3, to diatomic oxygen, O_2, is believed to occur by a two-step mechanism:

Step 1: $O_3(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2(g) + O(g)$ (fast)

Step 2: $O_3(g) + O(g) \xrightarrow{k_2} 2O_2(g)$ (slow)

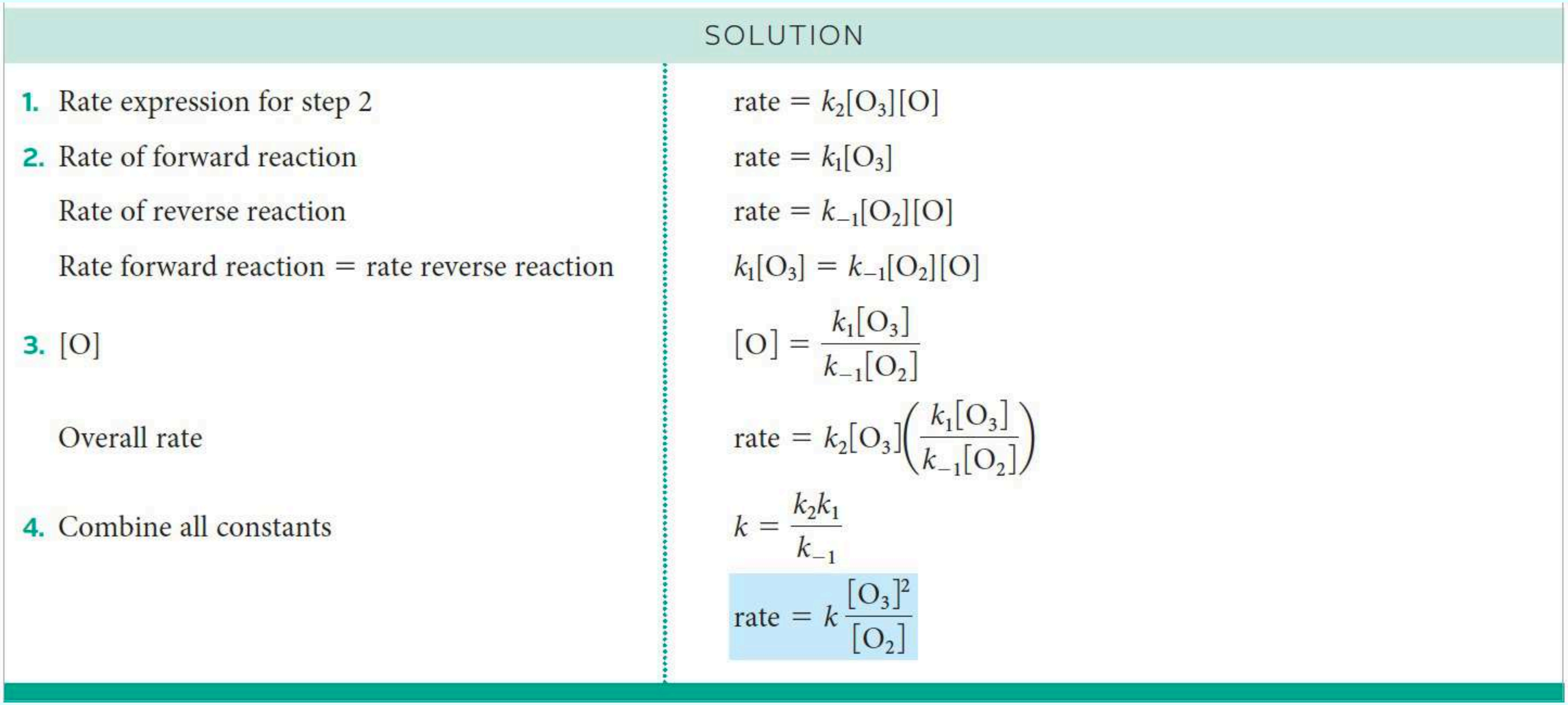
$$2O_3(g) \longrightarrow 3O_2(g)$$

Obtain the rate expression corresponding to this mechanism.

STRATEGY

1. The rate-limiting step is the slow step (step 2). Write its rate expression.
2. Write the rate expressions for the forward and reverse reactions of step 1. Since step 1 is in equilibrium, rate forward reaction = rate backward reaction.
3. Express the rates of step 1 in terms of [O] and substitute into the rate expression for step 2.
4. Combine all constants into a single constant k.

Example 11.9, (Cont’d)



SOLUTION	
1. Rate expression for step 2	rate = $k_2[O_3][O]$
2. Rate of forward reaction	rate = $k_1[O_3]$
Rate of reverse reaction	rate = $k_{-1}[O_2][O]$
Rate forward reaction = rate reverse reaction	$k_1[O_3] = k_{-1}[O_2][O]$
3. [O]	$[O] = \dfrac{k_1[O_3]}{k_{-1}[O_2]}$
Overall rate	$\text{rate} = k_2[O_3]\left(\dfrac{k_1[O_3]}{k_{-1}[O_2]}\right)$
4. Combine all constants	$k = \dfrac{k_2k_1}{k_{-1}}$
	$\text{rate} = k\dfrac{[O_3]^2}{[O_2]}$

Limitations on Mechanism Studies

- More than one mechanism is usually compatible with the data obtained from experiment
- It can be difficult to ascertain which mechanism is the true mechanism for a reaction

Key Concepts

1. Determine the reaction order from
    - Initial rate data
    - Concentration-time data
    - The reaction mechanism
2. Relate concentration and time for various orders of reaction
3. Use the Arrhenius equation to relate the rate constant to temperature