12.1 Chemical kinetics is the study of the rates of chemical reactions. The **instantaneous rate** of a reaction is the tangent to the concentration-versus-time graph for the reaction. The **initial rate** is the rate at the start of the reaction.

12.2 The **rate law** is the relation between the rate and the concentrations of substances present in the reaction mixture. The rate is reported in terms of the **rate constant** of the reaction; and reactions are classified by their **order**, the power to which the concentrations of the reactants (and products) are raised in the rate law. The rate law must be determined experimentally and cannot be deduced from the stoichiometry of the chemical equation for the reaction. Once the **integrated rate law**, the expression for the concentration in terms of the time, is known, it may be used to predict the concentration at any stage of the reaction. The **half-life** is the time taken for the concentration of a substance to fall to half its initial value. The half-life of a first-order reaction is independent of the initial concentration.

12.3 The rate of a reaction is affected by the surface area of the reactants, the presence of catalysts, the temperature, and (in most cases) the concentrations of the substances in the reaction mixture. The temperature-dependence of the rate constant is expressed by the **Arrhenius equation** and the two **Arrhenius parameters**, the **frequency factor** and the **activation energy**. Their role is explained by **collision theory**, in which A is proportional to the frequency of collisions and the relative orientation of the reactants during the encounter and E_a is the minimum energy needed for reaction. This theory is generalized by the **activated complex theory** in which it is proposed that an **activated complex**, an energeti-cally excited combination of reactant molecules, is formed and that the reactants must cross an **activation barrier**, an energy barrier to reaction, to form products.

12.4 A **catalyst**, a substance that speeds a reaction but is not itself consumed, may be either **homogeneous** (if it is in the same phase as the reactants) or **heterogeneous** (if it is in a different phase). Catalysts act by providing a path with a lower activation energy. **Enzymes** are biological catalysts.

12.5 A **reaction mechanism** consists of a sequence of **elementary reactions**, or reaction steps involving individual molecules. Elementary reactions can be classified according to their **molecularity**, the number of molecules taking part. **Unimolecular reactions**, in which a single molecule forms a product, obey first-order kinetics. **Bimolecular reactions**, elementary reactions between two molecules, obey second-order kinetics. A proposed mechanism must agree with the experimental rate law. The rate law implied by a mechanism is found by identifying the **rate-determining step**, the slowest step, and finding an expression for the concentration of any **reaction intermediates**, species that are produced and consumed in the reaction and taking part in it but are not present as initial reactants or final products.

12.6 Chain reactions are a class of reactions in which one intermediate reacts to produce another. In **radical chain reactions**, the intermediates, or **chain carriers**, are radicals. These reactions may include characteristic **initiation**, **propagation**, **retardation**, **inhibition**, and **termination** steps. Chain **branching**, in which more than one radical is produced in an elementary step, may lead to an explosion.

CLASSIFIED EXERCISES

Reaction Rates

12.1 (a) The rate of formation of O_2 is 1.5×10^{-3} mol/(L·s) in the reaction $2O_3(g) \rightarrow 3O_2(g)$. What is the rate of decomposition of ozone? (b) The rate of formation of the dichromate ions is 0.14 mol/(L·s) in the reaction $2CrO_4^{2-}(aq) + 2H^+(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$. What is the rate of reaction of the chromate ion in the reaction?

12.2 (a) Nitrogen dioxide decomposes at the rate of 6.5×10^{-3} mol/(L·s) by the reaction $2NO_2(g) \rightarrow N_2O_2(g) + O_2(g)$. Determine the rate of formation of O_2. (b) Manganate ions, MnO_4^{2-}, form permanganate ions and manganese(IV) oxide in an acidic solution at a rate of 2.0 mol/(L·min): $3MnO_4^{2-}(aq) + 4H^+(aq) \rightarrow$ $2MnO_4^-(aq) + MnO_2(l) + 2H_2O(l)$. What is the rate of formation of permanganate ions? What is the rate of reaction of $H^+(aq)$?

Instantaneous Reaction Rate

12.3 The decomposition of gaseous dinitrogen pentoxide in the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ gives the following data at 298 K.

Time, h	$[N_2O_5]$, mol/L
0	2.50×10^{-3}
1.11	1.88×10^{-3}
2.22	1.64×10^{-3}
3.33	1.43×10^{-3}
4.44	1.25×10^{-3}

temperature. (a) Write the rate law for the reaction. (b) Determine the half-life for the reaction. (c) If a 14.0-g sample of SO_2Cl_2 is sealed in a 2500-L reaction vessel and heated to the specified temperature, what mass will remain after 1.5 h?

12.30 Ethane, C_2H_6, forms $\cdot CH_3$ radicals at 700°C in a first-order reaction, for which $k = 1.98$ h^{-1}. (a) What is the half-life for the reaction? (b) Calculate the time needed for the amount of ethane to fall from 1.15×10^{-3} to 2.35×10^{-4} mol in a 500-mL reaction vessel at 700°C. (c) How much of a 6.88-mg sample of ethane in a 500-mL reaction vessel at 700°C will remain after 45 min?

12.31 A substance of chemical formula A_2 forms B in the first-order reaction $A_2 \rightarrow 2B$, in which the concentration of A_2 falls to 20% of its original concentration in 120 s. (a) What is the rate constant for the reaction? (b) Determine the time in which the concentration of A_2 falls to 10% of its original concentration.

12.32 For the first-order reaction $A_3 \rightarrow 3B_2 + C$, when $[A_3]_0 = 0.015$ mol/L the concentration of B_2 increases to 0.020 mol/L in 3.0 min. (a) What is the rate constant for the reaction? (b) How much more time would be needed for the concentration of B_2 to increase to 0.040 mol/L?

12.33 The following data were collected for the reaction $C_2H_6(g) \rightarrow 2 \cdot CH_3(g)$ at 700°C:

Time, s	0	1000	2000	3000	4000
$[C_2H_6]$, mmol/L	1.59	0.92	0.53	0.31	0.18

(a) Plot the data to confirm that the reaction is first order. (b) From the graph, determine the reaction rate constant.

12.34 The following data were collected for the reaction $2HI(g) \rightarrow H_2(g) + I_2(g)$ at 580 K.

Time, min	0	16.7	33.3	50.0	66.7
[HI], mmol/L	300	120	61	41	31

(a) Plot the data to confirm that the rate law is rate $= k[HI]^2$. (b) From the graph, determine the reaction rate constant.

12.35 The following data were obtained on the reaction $2A \rightarrow B$:

Time, s	0	5	10	15	20
[A], mmol/L	100	14.1	7.8	5.3	4.0

(a) Plot the data to determine the order of the reaction. (b) Determine the rate constant.

12.36 The following data were obtained on the reaction $2A_2 \rightarrow B$:

Time, s	0	100	200	300	400
$[A_2]$, mmol/L	250	143	81	45	25

(a) Plot the data to determine the order of the reaction. (b) Determine the rate constant.

Temperature Dependence of Reaction Rates

12.37 (a) Calculate the activation energy for the conversion of cyclopropane to propene from an Arrhenius plot of the following data:

T, K	750	800	850	900
k, s^{-1}	1.8×10^{-4}	2.7×10^{-3}	3.0×10^{-2}	0.26

(b) What is the value of the reaction rate constant at 600°C?

12.38 (a) Determine the activation energy for $C_2H_5I(g) \rightarrow C_2H_4(g) + HI(g)$ from an Arrhenius plot of the following data:

T, K	660	680	720	760
k, s^{-1}	7.2×10^{-4}	2.2×10^{-3}	1.7×10^{-2}	0.11

(b) What is the value of the reaction rate constant at 400°C?

12.39 The rate constant of the first-order reaction $2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$ is 0.38 s^{-1} at 1000 K and 0.87 s^{-1} at 1030 K. What is the activation energy of the reaction?

12.40 The rate constant of the second-order reaction $2HI(g) \rightarrow H_2(g) + I_2(g)$ at 575 K is 2.4×10^{-6} L/(mol·s); and at 630 K, it is 6.0×10^{-5} L/(mol·s). Calculate the activation energy of the reaction.

12.41 The rate constant of the reaction $O(g) + N_2(g) \rightarrow NO(g) + N(g)$, which occurs in the atmosphere, is 9.7×10^{10} L/(mol·s) at 800°C. The activation energy of the reaction is 315 kJ/mol. Determine the reaction rate constant at 700°C.

12.42 The rate constant of the reaction between CO_2 and OH^- in aqueous solution, to give the HCO_3^- ion is 1.5×10^{10} L/(mol·s) at 25°C. What is the reaction rate constant at blood temperature (37°C), given that the activation energy for the reaction is 38 kJ/mol?

12.43 Draw a reaction profile for an endothermic reaction. Label the activation energy, E_a, for the forward reaction and the enthalpy of reaction, ΔH. Mark the location of the activated complex. What is the relation of the activation energies of the reverse reaction, E_a', to that of the forward reaction?

12.44 The activation energy for a certain reaction is 125 kJ/mol and its enthalpy of reaction is -30 kJ/mol.

Draw a reaction profile for the reaction. Indicate the location of the activated complex. What is the activation energy, E'_a, of the reverse reaction?
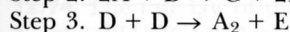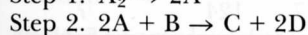
Catalysis

12.45 The contribution to the destruction of the ozone layer caused by high flying aircraft has been attributed to the following mechanism:

Step 1. $O_3 + NO \rightarrow NO_2 + O_2$
Step 2. $NO_2 + O \rightarrow NO + O_2$
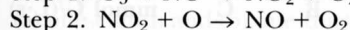
(a) What is the catalyst in the reaction? (b) What is the reaction intermediate?

12.46 A reaction was believed to occur by the following mechanism.

Step 1. $A_2 \rightarrow 2A$
Step 2. $2A + B \rightarrow C + 2D$
Step 3. $D + D \rightarrow A_2 + E$

(a) What is the overall reaction? (b) What is the catalyst in the reaction? (c) Which species are the reaction intermediates?

12.47 The presence of a catalyst reduces the activation energy of a certain reaction from 100 to 50 kJ/mol. By what factor does the rate of the reaction increase at 400 K, all other factors being equal?

12.48 The presence of a catalyst reduces the activation energy of a certain reaction from 88 to 62 kJ/mol. By what factor does the rate of the reaction increase at 300 K, all other factors being equal?

12.49 A reaction rate increases by a factor of 1000 in the presence of a catalyst at 25°C. The activation energy of the original pathway is 98 kJ/mol. What is the activation energy of the new pathway, all other factors being equal?
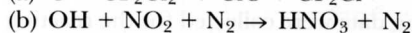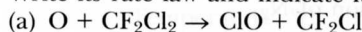
12.50 A reaction rate increases by a factor of 500 in the presence of a catalyst at 37°C. The activation energy of the original pathway is 106 kJ/mol. What is the activation energy of the new pathway, all other factors being equal?

Reaction Mechanisms

12.51 Each of the following steps is an elementary reaction. Write its rate law and indicate its molecularity:
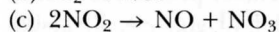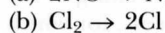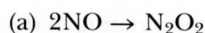
(a) $2NO \rightarrow N_2O_2$
(b) $Cl_2 \rightarrow 2Cl$
(c) $2NO_2 \rightarrow NO + NO_3$
(d) Which of these reactions might be radical chain initiating?

12.52 Each of the following is an elementary reaction. Write its rate law and indicate its molecularity:
(a) $O + CF_2Cl_2 \rightarrow ClO + CF_2Cl$
(b) $OH + NO_2 + N_2 \rightarrow HNO_3 + N_2$
(c) $ClO^- + H_2O \rightarrow HClO + OH^-$
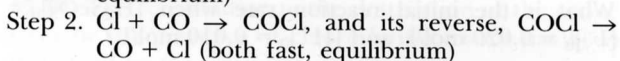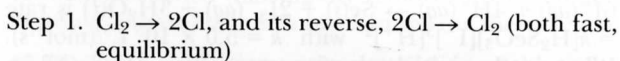(d) Which of these reactions might be radical chain propagating?

12.53 Write the overall reaction for the mechanism proposed below and identify the reaction intermediates:

Step 1. $ICl + H_2 \rightarrow HI + HCl$
Step 2. $HI + ICl \rightarrow HCl + I_2$

12.54 Write the overall reaction for the mechanism proposed below and identify the reaction intermediates:

Step 1. $Cl_2 \rightarrow 2Cl$
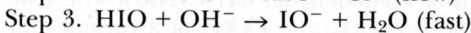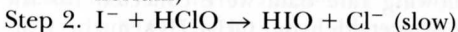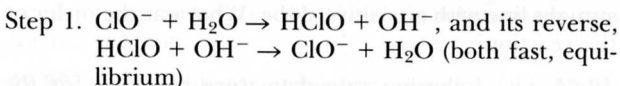Step 2. $Cl + CO \rightarrow COCl$
Step 3. $COCl + Cl_2 \rightarrow COCl_2 + Cl$
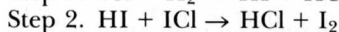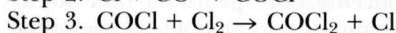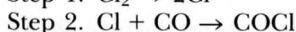
12.55 The production of phosgene, $COCl_2$, from carbon monoxide and chlorine is believed to take place by the following mechanism:

Step 1. $Cl_2 \rightarrow 2Cl$, and its reverse, $2Cl \rightarrow Cl_2$ (both fast, equilibrium)
Step 2. $Cl + CO \rightarrow COCl$, and its reverse, $COCl \rightarrow CO + Cl$ (both fast, equilibrium)
Step 3. $COCl + Cl_2 \rightarrow COCl_2 + Cl$ (slow)
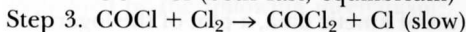
Write the rate law implied by this mechanism.

12.56 The mechanism proposed for the oxidation of iodide ion by the hypochlorite ion in aqueous solution is as follows:

Step 1. $ClO^- + H_2O \rightarrow HClO + OH^-$, and its reverse, $HClO + OH^- \rightarrow ClO^- + H_2O$ (both fast, equilibrium)
Step 2. $I^- + HClO \rightarrow HIO + Cl^-$ (slow)
Step 3. $HIO + OH^- \rightarrow IO^- + H_2O$ (fast)

Write the rate law implied by this mechanism.

UNCLASSIFIED EXERCISES

12.57 (a) The rate of formation of Cl^- in the reaction $3ClO^-(aq) \rightarrow Cl^-(aq) + ClO_3^-(aq)$, is 3.6 mol/(L·min). What is the rate of reaction of ClO^-? (b) In the Haber process for the industrial production of ammonia, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, the rate of ammonia production is 2.7×10^{-3} mol/(L·s). What is the rate of reaction of H_2?

12.58 Indicate two ways of expressing the reaction rate for each of the following reactions, using, in each case, the concentration of the species in bold print. Assume that the concentrations are in moles per liter and that time is expressed in seconds.
(a) $4\textbf{NH}_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g)$
(b) $\textbf{CH}_3\textbf{CHO}(g) \rightarrow \textbf{CH}_4(g) + CO(g)$
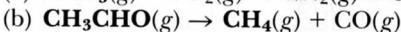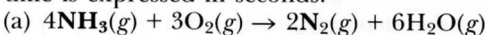
11.47 (a) 100.3°C (b) 81°C

11.49 168 g/mol

11.51 (a) −0.19°C (b) −0.82°C (c) −0.17°C

11.53 (a) −3.8°C (b) 1.63 (c) 0.208 moles of the electrolyte

11.55 182 g/mol

11.57 (a) 1.84 (b) 0.318 m (c) 92.0%

11.59 (a) 0.24 atm (b) 48.2 atm (c) 0.72 atm

11.61 (a) 15.0 atm (b) 16 atm (c) 48 atm or 5×10^1 atm

11.63 (a) 1.2 atm; 12.4 m (or 12 m, 2 sf) (b) 0.048 atm; 0.49 m (c) 8.2×10^{-5} atm; 8.6×10^{-4} m

11.65 3.3×10^3 g/mol

11.67 54 Torr

Unclassified Exercises

11.69 (a) 40% (b) 6.9 mol/L

11.71 (a) 5.56 m (b) 0.91 (c) 4.6 mol/L

11.73 (a) 4.98×10^{-1} mol/L (b) 17.37 Torr (c) 100.3°C

11.75 (a) If the partial pressure of CO_2 in the air above the solution is increased, the equilibrium will shift to the left, and more CO_2 will dissolve. (b) If the total pressure of the gas is increased by addition of nitrogen, no change in the equilibrium will occur, the partial pressure of CO_2 is unchanged, and the solubility is unchanged.

11.77 −51 kJ

11.79 1.3×10^2 g/mol

11.81 (a) $C_9H_{13}O_3N$ (b) 1.8×10^2 g/mol (c) $C_9H_{13}O_3N$

11.83 (a) $CO(NH_2)_2$ (b) $CO(NH_2)_2$ (c) $CO(NH_2)_2$ (d) 1.2 atm

11.85 7 atm (1 sf)

11.87 2.5×10^5 g/mol (2 sf)

11.89 (a) 11 Torr (b) 76 Torr

11.91 83%

Case Questions

1. (a) 1×10^{13} (b) 9×10^{-10} g

3. 50%

5. 3.4×10^{-2} g

CHAPTER 12

Classified Exercises

12.1 (a) 1.0×10^{-3} (mol O_3/L·s) (b) 0.28 (mol CrO_4^{2-}/L·s)

12.3 (a) 2.5×10^{-4} mol/L·h at 1.11 h; 2.0×10^{-4} mol/L·h at 2.22 h; 1.8×10^{-4} mol/L·h at 3.33 h

(b)
Time, h	$\Delta [N_2O_5]$, 10^{-4} mol/L·h
0	2.5
1.11	2.3
2.22	2.0
3.33	1.8
4.44	1.6

(a) and (c)

Concentrations vs. time
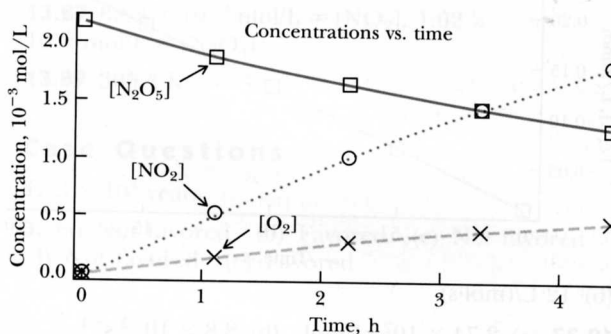
12.5 (a) (mol A/L·s) (b) s^{-1} (c) $L \cdot mol^{-1} \cdot s^{-1}$

12.7 9.6×10^{-5} mol N_2O_5/L·s

12.9 (a) 2.4×10^{-5} mol/L·s (b) The rate is doubled also.

12.11 (a) $k[X]^2[Y]^{1/2}$ (b) $k[A][B][C]^{1/2}$

12.13 (a) First order in SO_2, zero order in O_2, negative one-half order in SO_3, one-half order overall (b) Second order in A, negative second order in B, zero order in C, zero order in products, zero order overall

12.15 $k[CH_3Br][OH^-]$

12.17 (a) Reaction is second order in A_2, first order in B_3; overall order = 3 (b) $k[A_2]_0^2[B_3]_0$ (c) 1.2×10^2 $L^2 \cdot mol^{-2} \cdot s^{-1}$ (d) 0.85 mol/L·s

12.19 (a) and (b) Rate = $k[NO_2]_0[O_3]_0$; the reaction is first order in each reactant, second order overall (c) 4.3×10^7 $L \cdot mol^{-1} \cdot s^{-1}$ (d) 5.1 mol/L·s

12.21 (a) 6.93×10^{-4} s^{-1} (b) 7.6×10^{-3} s^{-1}

12.23 (a) 5.2 h (b) 1.79×10^{-2} mol/L (c) 126 min

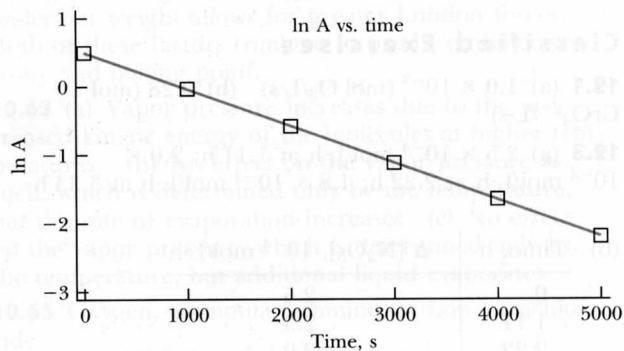**12.25** (a) 7.6×10^2 s (b) 1.5×10^2 s (c) 2.0×10^2 s

12.27 (a) 40 L/mol·s (b) 1.9×10^{-3} $L \cdot mol^{-1} \cdot s^{-1}$

12.29 (a) $k[SO_2Cl_2]$ (b) 247 min (c) 10.9 g

12.31 (a) 1.3×10^{-2} s^{-1} (b) 172 s

12.33 (a)

ln A vs. time

(b) 5.5×10^{-4} s^{-1}

12.35 (a)

1/[A] vs. time
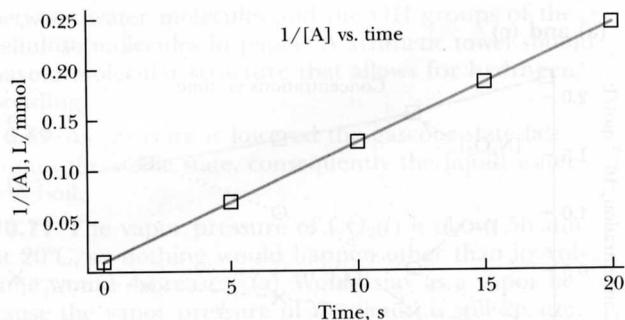
(b) 12 L/(mol·s)

12.37 (a) 2.74×10^2 kJ/mol   (b) 8.8×10^{-2} s^{-1}

12.39 2.4×10^2 kJ/mol

12.41 2.9×10^9 L/mol·s

12.43 $E_a' = E_a - \Delta H$
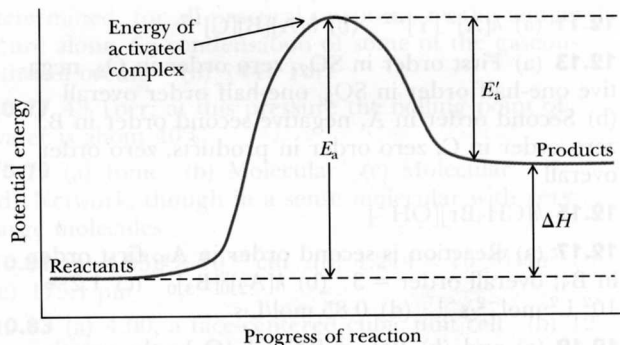
12.45 (a) NO   (b) NO$_2$

12.47 3.3×10^6

12.49 80.9 kJ/mol

12.51 (a) $k[NO]^2$, bimolecular   (b) $k[Cl_2]$, unimolecular   (c) $k[NO_2]^2$, bimolecular   (d) Because Cl and NO are radicals, (b) and (c)

12.53 2 ICl + H$_2$ → 2 HCl + I$_2$; HI is the only intermediate

12.55 $k[CO][Cl_2]^{3/2}$

Unclassified Exercises

12.57 (a) 5.4 mol ClO$^-$/L·min   (b) 4.05 mol H$_2$/L·s

12.59 (a) 1/3   (b) 2/3   (C) 2

12.61 8.0×10^{-6} mol/L·s

12.63 Second order

12.65 (a) A = 1, B = 2, C = 0; overall rate is 3
(b) $k[A]_0 [B]_0^2$ (c) 20 L^2/mol^2·s   (d) 2.9×10^{-9} mol, L·s

12.67 (a) 0.132 mol/L   (b) 39 min   (c) 34 min

12.69 (a) 0.0504 mg   (b) 0.106 atm

12.71 300 kJ/mol

12.73 (a) Bimolecular   (b) Unimolecular   (c) Termolecular

12.75 (a) NO   (b) NO$_2$

12.77 (a) 88 kJ/mol   (b) 2.3×10^{-2} L/mol·s

12.79 75 kJ/mol

12.81 (a) Cl   (b) ClO   (c) Cl, ClO, O   (d) Step 1 is initiating, step 2 is propagating   (e) Cl + Cl → Cl$_2$

12.83 Step 2: Cl + H$_2$ → HCl + H, step 3: H + Cl$_2$ → HCl + Cl, step 4: Cl + Cl → Cl$_2$, step 5: H + H → H$_2$, step 6: H + Cl → HCl

12.85

Time, min	Rate, mol/(L·min)
0	1.01×10^{-3}
5	6.07×10^{-4}
10	3.65×10^{-4}
15	2.2×10^{-4}
20	1.3×10^{-4}
30	4.8×10^{-4}
100	~0

Case Questions

1. (a) CH$_2$—CH$_2$OH(g)   (b) CH$_3$CH$_2$ · (g) + H$_2$O(g)

3. (a) NO$_2$(g) + · O · (g) → NO$_3$(g)   (b) NO$_2$(g) + NO$_3$(g) ⇌ N$_2$O$_5$(g)   (c) 2 HNO$_3$(aq)

CHAPTER 13

Classified Exercises

13.1 (a) [COCl][Cl]/[CO][Cl$_2$] (unitless)
(b) [HBr]^2/[H$_2$][Br$_2$] (unitless)   (c) [O$_2$]^3/[O$_3$]^2 (units; mol/L)

13.3 (a) 0.024 atm^2 (b) 6.4 atm

13.5 Case 1: 48.8; case 2: 48.9; case 3: 48.9

13.7 (a) 2.4×10^{-2} (b) 1.90

13.9 (a) 0.50   (b) No   (c) Products

13.11 (a) 6.94; 0.121   (b) Yes