PEARSON

Chapter Summary and Review

Key Learning Outcomes

CHAPTER OBJECTIVES	ASSESSMENT
Express Reaction Rates (14.3)	• Example 14.1 For Practice 14.1 Exercises 27, 28, 29, 30, 31, 32, 33, 34, 35, 36
Determine the Order, Rate Law, and Rate Constant of a Reaction (14.4)	• Example 14.2 For Practice 14.2 Exercises 43, 44, 45, 46
Use Graphical Analysis of Reaction Data to Determine Reaction Order and Rate Constants (14.5)	• Examples 14.3, 14.5 For Practice 14.3, 14.5 Exercises 49, 50, 51, 52, 53, 54
Determine the Concentration of a Reactant at a Given Time (14.5)	• Example 14.4 For Practice 14.4 Exercises 53, 54, 55, 56
Work with the Half-Life of a Reaction (14.5)	• Example 14.6 For Practice 14.6 Exercises 55, 56, 57, 58
Use the Arrhenius Equation to Determine Kinetic Parameters (14.6)	• Examples 14.7, 14.8 For Practice 14.7, 14.8 Exercises 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72
Determine whether a Reaction Mechanism Is Valid (14.7)	• Example 14.9 For Practice 14.9 Exercises 75, 76, 77, 78

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Key Terms

Section 14.4

rate law
rate constant (k)
reaction order (n)
overall order

Section 14.5

integrated rate law 🔲
half-life $(t_{1/2})$ 🔲

Section 14.6

Arrhenius equation 🔲
activation energy (E_a) 🔲
frequency factor (A) 🔲
activated complex (transition state) 🔲
exponential factor 🔲
Arrhenius plot 🔲
collision model 🔲
orientation factor 🔲
collision frequency 🔲

Section 14.7

reaction mechanism 🔲
elementary step 🔲
reaction intermediate 🔲
molecularity 🔲
unimolecular 🔲
bimolecular 🔲
termolecular 🔲
rate-determining step 🔲

Section 14.8

catalyst 🔲
homogeneous catalysis 🔲
heterogeneous catalysis 🔲
hydrogenation 🔲
enzyme 🔲
active site 🔲
substrate 🔲

Key Concepts

Reaction Rates (14.1–14.3)

- The rate of a chemical reaction is a measure of how fast a reaction occurs. The rate reflects the change in the concentration of a reactant or product per unit time and is usually reported in units of M/s.
- Reaction rates generally depend on the concentration of the reactants, the temperature at which the reaction occurs, and the structure of the reactants.

Reaction Rate Laws and Orders (14.4)

- The rate of a first-order reaction is directly proportional to the concentration of the reactant, the rate of a second-order reaction is proportional to the square of the concentration of the reactant, and the rate of a zero-order reaction is independent of the concentration of the reactant.
- For a reaction with more than one reactant, the order with respect to each reactant is, in general, independent of the order with respect to other reactants. The rate law shows the relationship between the rate and the concentrations of each reactant and must be determined experimentally.

Integrated Rate Laws and Half-Life (14.5)

- The rate law for a reaction describes the relationship between the rate of the reaction and the concentrations of the reactants.
- The integrated rate law of a reaction describes the relationship between the concentrations of reactants and

- The integrated rate law for a reaction describes the relationship between the concentration of a reactant and time.
- The integrated rate law for a zero-order reaction shows that the concentration of the reactant varies linearly with time. For a first-order reaction, the *natural log* of the concentration of the reactant varies linearly with time, and for a second-order reaction, the *inverse* of the concentration of the reactant varies linearly with time.
- The half-life of a reaction can be derived from the integrated rate law and represents the time required for the concentration of a reactant to fall to one-half of its initial value. The half-life of a first-order reaction is *independent* of initial concentration of the reactant. The half-life of a zero-order or second-order reaction *depends* on the initial concentration of reactant.

The Effect of Temperature on Reaction Rate (14.6)

- The rate constant of a reaction generally depends on temperature and can be expressed by the Arrhenius equation, which consists of a frequency factor and an exponential factor.
- The frequency factor represents the number of times that the reactants approach the activation barrier per unit time. The exponential factor is the fraction of approaches that are successful in surmounting the activation barrier and forming products.
- The exponential factor depends on both the temperature and the activation energy, a barrier that the reactants must overcome to become products. The exponential factor increases with increasing temperature but decreases with increasing activation energy.
- We can determine the frequency factor and activation energy for a reaction by measuring the rate constant at different temperatures and constructing an Arrhenius plot.
- For reactions in the gas phase, Arrhenius behavior can be described with the collision model. In this model, reactions occur as a result of sufficiently energetic collisions. The colliding molecules must be oriented in such a way that the reaction can occur. The frequency factor contains two terms: p, which represents the fraction of collisions that have the proper orientation, and z, which represents the number of collisions per unit time.

Reaction Mechanisms (14.7)

- Most chemical reactions occur in several steps. The series of individual steps by which a reaction occurs is the reaction mechanism.
- In order for a proposed reaction mechanism to be valid, it must fulfill two conditions: (a) the steps must sum to the overall reaction, and (b) the mechanism must predict the experimentally observed rate law.
- For mechanisms with a slow initial step, we derive the rate law from the slow step.
- For mechanisms with a fast initial step, we first write the rate law based on the slow step but then assume that the fast steps reach equilibrium, so we can write concentrations of intermediates in terms of the reactants.

Catalysis (14.8)

- A catalyst is a substance that increases the rate of a chemical reaction by providing an alternative mechanism that has a lower activation energy for the rate-determining step.
- Catalysts can be homogeneous or heterogeneous. A homogeneous catalyst exists in the same phase as the reactants and forms a homogeneous mixture with them. A heterogeneous catalyst generally exists in a different phase than the reactants.
- Enzymes are biological catalysts capable of increasing the rate of specific biochemical reactions by many orders of magnitude.

Key Equations and Relationships

The Rate of Reaction (14.3⬚)

For a reaction $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$, the rate is defined as

$$\text{rate} = -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\text{B}]}{\Delta t} = +\frac{1}{c}\frac{\Delta[\text{C}]}{\Delta t} = +\frac{1}{d}\frac{\Delta[\text{D}]}{\Delta t}$$

The Rate Law (14.4⬚)

$$\begin{aligned}
\text{rate} &= k[A]^n & \text{(single reactant)} \\
\text{rate} &= k[A]^m[\text{B}]^n & \text{(Multiple reactant)}
\end{aligned}$$

Integrated Rate Laws and Half-Life (14.5 ▢)

Reaction Order	Integrated Rate Law	Units of k	Half-Life Expression
0	$[A]_t = -kt + [A]_0$	$M \cdot s^{-1}$	$t_{1/2} = \dfrac{[A]_0}{2k}$
1	$\ln[A]_t = -kt + \ln[A]_0$	s^{-1}	$t_{1/2} = \dfrac{0.693}{k}$
2	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	$M^{-1} \cdot s^{-1}$	$t_{1/2} = \dfrac{1}{k[A]_0}$

Arrhenius Equation (14.6 ▢)

$$\begin{aligned}
k &= Ae^{-E_a/RT} \\
\ln k &= \frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A & \text{(linearized form)} \\
\ln \frac{k_2}{k_1} &= \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) & \text{(two-point form)} \\
k &= pze^{-E_a/RT} & \text{(collision theory)}
\end{aligned}$$

Rate Laws for Elementary Steps (14.7 ▢)

Elementary Step	Molecularity	Rate Law
A ⟶ products	1	rate = $k[A]$
A + A ⟶ products	2	rate = $k[A]^2$
A + B ⟶ products	2	rate = $k[A][B]$
A + A + A ⟶ products	3 (rare)	rate = $k[A]^3$
A + A + B ⟶ products	3 (rare)	rate = $k[A]^2[B]$
A + B + C ⟶ products	3 (rare)	rate = $k[A][B][C]$