Chapter 14: Chemical Kinetics

1. Which one of the following units would *not* be an acceptable way to express reaction rate?
A) M/s B) $M \cdot min^{-1}$ C) $L \cdot mol^{-1} \cdot s^{-1}$ D) $mol \cdot L^{-1} \cdot s^{-1}$ E) mmHg/min

3. For the reaction $BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$ at a particular time, $-\Delta[BrO_3^-]/\Delta t = 1.5 \times 10^{-2}$ M/s. What is $-\Delta[Br^-]/\Delta t$ at the same instant?
A) 13 M/s
B) 7.5×10^{-2} M/s
C) 1.5×10^{-2} M/s
D) 3.0×10^{-3} M/s
E) 330 M/s

5. For the reaction $C_6H_{14}(g) \rightarrow C_6H_6(g) + 4H_2(g)$, $\Delta P(H_2)/\Delta t$ was found to be 2.5×10^{-2} atm/s, where $\Delta P(H_2)$ is the change in pressure of hydrogen. Determine $\Delta P(C_6H_{14})/\Delta t$ for this reaction at the same time.
A) 2.5×10^{-2} atm/s
B) -6.2×10^{-3} atm/s
C) -2.5×10^{-2} atm/s
D) 0.10 atm/s
E) 6.2×10^{-3} atm/s

7. For the overall chemical reaction shown below, which one of the following statements can be rightly assumed?
$2H_2S(g) + O_2(g) \rightarrow 2S(s) + 2H_2O(l)$
A) The reaction is third-order overall.
B) The reaction is second-order overall.
C) The rate law is, rate = $k[H_2S]^2[O_2]$.
D) The rate law is, rate = $k[H_2S][O_2]$.
E) The rate law cannot be determined from the information given.

9. For the hypothetical reaction $A + 3B \rightarrow 2C$, the rate should be expressed as
A) rate = $\Delta[A]/\Delta t$.
B) rate = $-\Delta[C]/\Delta t$.
C) rate = $-3\,\Delta[B]/\Delta t$.
D) rate = $^1/_2\,\Delta[C]/\Delta t$.
E) rate = $^1/_3\,\Delta[B]/\Delta t$.

11. The reaction $A + 2B \rightarrow$ products was found to have the rate law, rate = $k[A][B]^2$. Predict by what factor the rate of reaction will increase when the concentration of A is doubled and the concentration of B is also doubled.
A) 2 B) 4 C) 6 D) 8 E) 9

13. Appropriate units for a first-order rate constant are
A) M/s. B) 1/M·s. C) 1/s. D) $1/M^2$·s.

15. A rate constant will have the units mol $\cdot L^{-1} \cdot s^{-1}$ when the reaction is overall
A) zero order.
B) first order.
C) second order.
D) third order.
E) fourth order.

17. Chlorine dioxide reacts in basic water to form chlorite and chlorate according to the following chemical equation:

$$2ClO_2(aq) + 2OH^-(aq) \rightarrow ClO_2^-(aq) + ClO_3^-(aq) + H_2O(l)$$

A kinetic study of this reaction under a certain set of conditions yielded the data below.

Exp	$[ClO_2]$ (M)	$[OH^-]$ (M)	$-\Delta[ClO_2]/\Delta t$ (M/s)
1	0.0500	0.100	5.75×10^{-2}
2	0.100	0.100	2.30×10^{-1}
3	0.100	0.0500	1.15×10^{-1}

A) rate = $k[ClO_2][OH^-]$
B) rate = $k[ClO_2]^2[OH^-]$
C) rate = $k[ClO_2][OH^-]^2$
D) rate = $k[ClO_2]^2[OH^-]^2$
E) rate = $k[ClO_2]^4[OH^-]$

19. Use the following data to determine the rate law for the reaction shown below.
$2NO + H_2 \rightarrow N_2O + H_2O$

Expt. #	$[NO]_0$	$[H_2]_0$	Initial rate
1	0.021	0.065	1.46 M/min
2	0.021	0.260	1.46 M/min
3	0.042	0.065	5.84 M/min

A) rate = $k[NO]$
B) rate = $k[NO]^2$
C) rate = $k[NO][H_2]$
D) rate = $k[NO]^2[H_2]$
E) rate = $k[NO]^2[H_2]^2$

21. At 25°C the rate constant for the first-order decomposition of a pesticide solution is 6.40×10^{-3} min^{-1}. If the starting concentration of pesticide is 0.0314 M, what concentration will remain after 62.0 min at 25°C?
A) 1.14×10^{-1} M
B) 47.4 M
C) –8.72.0 M
D) 2.11×10^{-2} M
E) 2.68×10^{-2} M

23. The following initial rate data apply to the reaction below.
$F_2(g) + 2Cl_2O(g) \rightarrow 2FClO_2(g) + Cl_2(g)$

Expt. #	$[F_2]$ (M)	$[Cl_2O]$ (M)	Initial rate
1	0.05	0.010	5.0×10^{-4}
2	0.05	0.040	2.0×10^{-3}
3	0.10	0.010	1.0×10^{-3}

Which of the following is the rate law (rate equation) for this reaction?
A) rate = $k[F_2]^2[Cl_2O]^4$
B) rate = $k[F_2]^2[Cl_2O]$
C) rate = $k[F_2][Cl_2O]$
D) rate = $k[F_2][Cl_2O]^2$
E) rate = $k[F_2]^2[Cl_2O]^2$

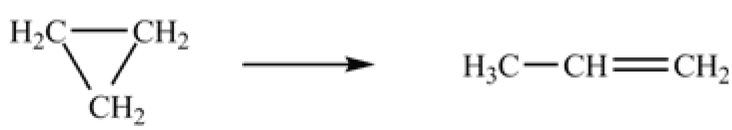
25. A first-order reaction has a rate constant of $3.00 \times 10^{-3}\ s^{-1}$. The time required for the reaction to be 75.0% complete is
A) 95.8 s. B) 462 s. C) 231 s. D) 201 s. E) 41.7 s.

27. Ammonium ion (NH_4^+) reacts with nitrite ion (NO_2^-) to yield nitrogen gas and liquid water. The following initial rates of reaction have been measured for the given reactant concentrations.

Expt. #	$[NH_4^+]$	$[NO_2^-]$	Initial rate (M/hr)
1	0.010	0.020	0.020
2	0.015	0.020	0.030
3	0.030	0.010	0.015

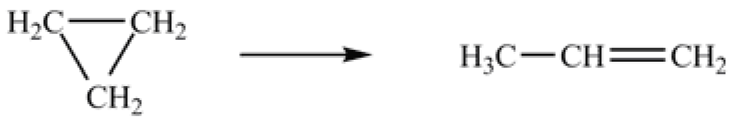
Which of the following is the rate law (rate equation) for this reaction?
A) rate = $k\ [NH_4^+]\ [NO_2^-]^4$
B) rate = $k\ [NH_4^+]\ [NO_2^-]$
C) rate = $k\ [NH_4^+]\ [NO_2^-]^2$
D) rate = $k\ [NH_4^+]^2\ [NO_2^-]$
E) rate = $k\ [NH_4^+]^{1/2}\ [NO_2^-]^{1/4}$

29. The isomerization of cyclopropane to form propene is a first-order reaction.



At 760 K, 15% of a sample of cyclopropane changes to propene in 6.8 min. What is the half-life of cyclopropane at 760 K?
A) 3.4×10^{-2} min B) 2.5 min C) 23 min D) 29 min E) 230 min

31. The isomerization of cyclopropane to propene follows first-order kinetics.



At 700 K, the rate constant for this reaction is 6.2×10^{-4} min^{-1}. How many minutes are required for 10.0% of a sample of cyclopropane to isomerize to propene?
A) 16,100 min B) 170 min C) 3,710 min D) 1.43×10^{-3} min E) 1,120 min

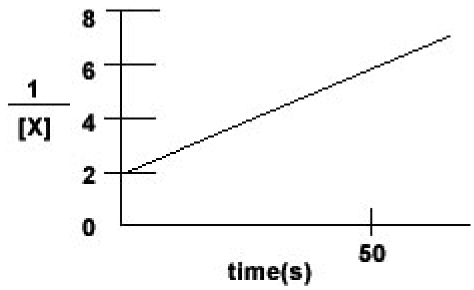
33. A city's water supply is contaminated with a toxin at a concentration of 0.63 mg/L. Fortunately, this toxin decomposes to a safe mixture of products by first-order kinetics with a rate constant of 0.27 day^{-1}. How long will it take for half of the toxin to decompose?
A) 0.17 days B) 0.27 days C) 0.38 days D) 2.3 days E) 2.6 days

35. A first-order reaction has a rate constant of 7.5×10^{-3}/s. The time required for the reaction to be 60% complete is
A) 3.8×10^{-3} s. B) 6.9×10^{-3} s. C) 68 s. D) 120 s. E) 130 s.

37. Benzoyl chloride, C_6H_5COCl, reacts with water to form benzoic acid, C_6H_5COOH, and hydrochloric acid. This first-order reaction is 25% complete after 26 s. How much longer would one have to wait in order to obtain 99% conversion of benzoyl chloride to benzoic acid?
A) 393 s B) 419 s C) 183 s D) 293 s E) 209 s

39. A certain reaction A $\rightarrow$ *products* is second order in A. If this reaction is 85% complete in 12 minutes, how long would it take for the reaction to be 15% complete?
A) 110 s B) 27 s C) 62 s D) 130 s E) 22 s

41. For the reaction $X + Y \rightarrow Z$, the reaction rate is found to depend only upon the concentration of X. A plot of 1/X verses time gives a straight line.



What is the rate law for this reaction?
A) rate = k [X] B) rate = k $[X]^2$ C) rate = k [X][Y] D) rate = k $[X]^2[Y]$

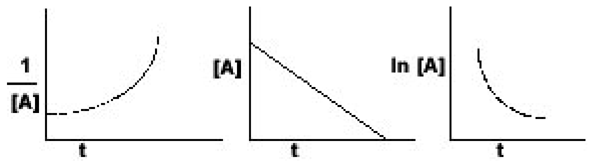
43. The thermal decomposition of acetaldehyde, $CH_3CHO \rightarrow CH_4 + CO$, is a second-order reaction. The following data were obtained at 518°C.

time, s	Pressure CH_3CHO, mmHg
0	364
42	330
105	290
720	132

Calculate the rate constant for the decomposition of acetaldehyde from the above data.
A) 2.2×10^{-3}/s
B) 0.70 mmHg/s
C) 2.2×10^{-3}/mmHg·s
D) 6.7×10^{-6}/mmHg·s
E) 5.2×10^{-5}/mmHg·s

45. For the chemical reaction $A \rightarrow B + C$, a plot of $[A]_t$ versus time is found to give a straight line with a negative slope. What is the order of reaction with respect to A?
A) zeroth
B) first
C) second
D) third
E) Such a plot cannot reveal the order of the reaction.

47. The graphs below all refer to the same reaction. What is the order of this reaction?



A) zeroth order B) first order C) second order D) unable to predict

49. For a second order reaction, the half-life is equal to
A) $t_{1/2} = 0.693/k$.
B) $t_{1/2} = k/0.693$.
C) $t_{1/2} = 1/k[A]_o$.
D) $t_{1/2} = k$.
E) $t_{1/2} = [A]_o/2k$.

51. The Arrhenius equation is $k = Ae^{-Ea/RT}$. The slope of a plot of ln k vs. 1/T is equal to
A) –k. B) k. C) E_a. D) $-E_a/R$. E) A.

53. The activation energy for the reaction $CH_3CO \rightarrow CH_3 + CO$ is 71 kJ/mol. How many times greater is the rate constant for this reaction at 170°C than at 150°C?
A) 0.40 B) 1.1 C) 2.5 D) 4.0 E) 5.0

55. At 25°C, by what factor is the reaction rate increased by a catalyst that reduces the activation energy of the reaction by 1.00 kJ/mol?
A) 1.63 B) 123 C) 1.04 D) 1.50 E) 2.53

57. The activation energy for the following reaction is 60. kJ/mol.
$Sn^{2+} + 2Co^{3+} \rightarrow Sn^{4+} + 2Co^{2+}$
By what factor (how many times) will the rate constant increase when the temperature is raised from 10°C to 28°C?
A) 1.002 B) 4.6 C) 5.6 D) 2.8 E) 696

59. The isomerization of methyl isocyanide, $CH_3NC \rightarrow CH_3CN$, follows first-order kinetics. The half-lives were found to be 161 min at 199°C and 12.5 min at 230°C. Calculate the activation energy for this reaction.
A) 6.17×10^{-3} kJ/mol
B) 31.4 kJ/mol
C) 78.2 kJ/mol
D) 124 kJ/mol
E) 163 kJ/mol

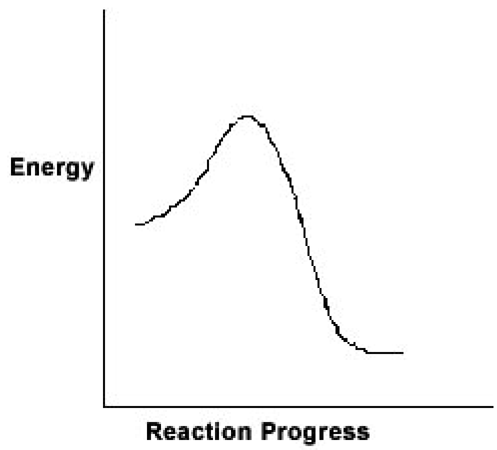
61. The reaction $C_4H_{10} \rightarrow C_2H_6 + C_2H_4$ has an activation energy (E_a) of 350 kJ/mol, and the E_a of the reverse reaction is 260 kJ/mol. Estimate ΔH, in kJ/mol, for the reaction as written above.

A) –90 kJ/mol
B) +90 kJ/mol
C) 350 kJ/mol
D) –610 kJ/mol
E) +610 kJ/mol

63. Given that E_a for a certain biological reaction is 48 kJ/mol and that the rate constant is $2.5 \times 10^{-2}\ s^{-1}$ at 15°C, what is the rate constant at 37°C?

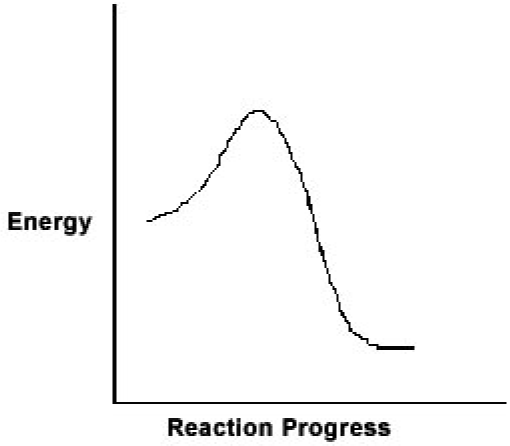
A) $2.7 \times 10^{-2}\ s^{-1}$
B) $2.5 \times 10^{-1}\ s^{-1}$
C) $1.0 \times 10^{-1}\ s^{-1}$
D) $6.0 \times 10^{-3}\ s^{-1}$
E) $1.1\ s^{-1}$

65. For the chemical reaction system described by the diagram below, which statement is true?



A) The forward reaction is endothermic.
B) The activation energy for the forward reaction is greater than the activation energy for the reverse reaction.
C) At equilibrium, the activation energy for the forward reaction is equal to the activation energy for the reverse reaction.
D) The activation energy for the reverse reaction is greater than the activation energy for the forward reaction.
E) The reverse reaction is exothermic.

67. For the chemical reaction system described by the diagram below, which statement is true?



If the E_a for the forward reaction is 25 kJ/mol and the enthalpy of reaction is –95 kJ/mol, what is E_a for the reverse reaction?
A) 120 kJ/mol B) 70 kJ/mol C) 95 kJ/mol D) 25 kJ/mol E) –70 kJ/mol

69. When the concentrations of reactant molecules are increased, the rate of reaction increases. The best explanation for this phenomenon is that as the reactant concentration increases,
A) the average kinetic energy of molecules increases.
B) the frequency of molecular collisions increases.
C) the rate constant increases.
D) the activation energy increases.
E) the order of reaction increases.

71. The rate law for the reaction $H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$ is rate = $k[H_2O_2][I^-]$. The following mechanism has been suggested.
$H_2O_2 + I^- \rightarrow HOI + OH^-$ *slow*
$OH^- + H^+ \rightarrow H_2O$ *fast*
$HOI + H^+ + I^- \rightarrow I_2 + H_2O$ *fast*
Identify all intermediates included in this mechanism.
A) H^+ and I^-
B) H^+ and HOI
C) HOI and OH^-
D) H^+ only
E) H_2O and OH^-

73. The rate law for the reaction $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$ is rate = $k[NO_2][O_3]$. Which one of the following mechanisms is consistent with this rate law?
   A) $NO_2 + NO_2 \rightarrow N_2O_4$ (*fast*)
   $N_2O_4 + O_3 \rightarrow N_2O_5 + O_2$ (*slow*)
   B) $NO_2 + O_3 \rightarrow NO_5$ (*fast*)
   $NO_5 + NO_5 \rightarrow N_2O_5 + {}^5/_2O_2$ (*slow*)
   C) $NO_2 + O_3 \rightarrow NO_3 + O_2$ (*slow*)
   $NO_3 + NO_2 \rightarrow N_2O_5$ (*fast*)
   D) $NO_2 + NO_2 \rightarrow N_2O_2 + O_2$ (*slow*)
   $N_2O_2 + O_3 \rightarrow N_2O_5$ (*fast*)

75. The gas phase reaction of nitrogen dioxide and carbon monoxide was found by experiment to be second-order with respect to NO_2, and zeroth-order with respect to CO below 25°C.
   $NO_2 + CO \rightarrow NO + CO_2$
   Which one of the following mechanisms is consistent with the observed reaction order?
   A) $NO_2 + 2CO \rightarrow N + 2CO_2$ *fast*
   $N + NO_2 \rightarrow 2NO$ *slow*
   B) $NO_2 + 2CO \rightarrow N + 2CO_2$ *slow*
   $N + NO_2 \rightarrow 2NO$ *fast*
   C) $NO_2 + NO_2 \rightarrow NO_3 + NO$ *fast*
   $NO_3 + CO \rightarrow NO_2 + CO_2$ *slow*
   D) $NO_2 + NO_2 \rightarrow NO_3 + NO$ *slow*
   $NO_3 + CO \rightarrow NO_2 + CO_2$ *fast*

77. Complete the following statement: A catalyst
   A) increases the activation energy.
   B) alters the reaction mechanism.
   C) increases the average kinetic energy of the reactants.
   D) increases the concentration of reactants.
   E) increases the collision frequency of reactant molecules.

79. The activation energy of a certain uncatalyzed reaction is 64 kJ/mol. In the presence of a catalyst, the E_a is 55 kJ/mol. How many times faster is the catalyzed than the uncatalyzed reaction at 400°C? Assume that the frequency factor remains the same.
   A) 5.0 times B) 1.16 times C) 15 times D) 2.0 times E) 0.2 times

81. Peroxodisulfate ion can oxidize iodide ions to iodine according to the balanced equation
$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$.
The reaction is catalyzed by certain chemical species. Identify the catalyst in the following mechanism:
step 1: $Fe^{3+} + 2I^- \rightarrow Fe^{2+} + I_2$
step 2: $S_2O_8^{2-} + Fe^{2+} \rightarrow 2SO_4^{2-} + Fe^{3+}$
A) Fe^{3+} B) I^- C) $S_2O_8^{2-}$ D) Fe^{2+} E) SO_4^{2-}

83. For the reaction whose rate law is rate = k[X], a plot of which of the following is a straight line?
A) [X] versus time
B) ln [X] versus time
C) 1/[X] versus time
D) [X] versus 1/time
E) ln [X] versus 1/time

85. At a particular temperature the first-order gas-phase reaction $2N_2O_5 \rightarrow 2N_2O_4 + O_2$ has a half-life for the disappearance of dinitrogen pentoxide of 3240 s. If 1.00 atm of N_2O_5 is introduced into an evacuated 5.00 L flask, what will be the total pressure of the gases in the flask after 1.50 hours?
A) 0.685 atm B) 1.00 atm C) 0.315 atm D) 1.68 atm E) 1.34 atm

87. When acetaldehyde at a pressure of 364 mmHg is introduced into an evacuated 500. mL flask at 518°C, the half-life for the second-order decomposition process, $CH_3CHO \rightarrow CH_4 + CO$, is 410. s. What will the total pressure in the flask be after 1.00 hour?
A) 327 mmHg B) 654 mmHg C) 37 mmHg D) 691 mmHg E) 728 mmHg

89. The first-order decomposition of phosphene to phosphorus and hydrogen $4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$ has a half-life of 35.0 s at 680°C. Starting with 520 mmHg of pure phosphene in an 8.00-L flask at 680°C, how long will it take for the total pressure in the flask to rise to 1.000 atm?
A) 628 s B) 33.4 s C) 51.2 s D) 111 s E) 48.3 s