14.0: Prelude

Log Review

14.0.1. Solve the equation for A.

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

14.0.2. Solve the equation for A_0.

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

14.0.3. Solve the equation for k.

$$A = A_0 e^{-kt}$$

14.0.4. Solve the equation for E_a.

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

14.0.5. Solve the equation for T.

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

14.0.6. Solve the equation for $t_{1/2}$.

$$A = A_0\left(\frac{1}{2}\right)^{\frac{t}{t_{1/2}}}$$

14.1: Rates of Chemical Reactions

Reaction Rates

14.1.1. In the reaction $2NO_2 \rightarrow 2NO + O_2$ at 300^0C, the concentration of NO_2 decreased from 0.0150 M to 0.0115M in 100s. What is the rate of disappearance of NO_2?

14.1.2. In the same reaction above, what is the rate of appearance of O_2?

14.1.3. For the reaction in Q1, the disappearance of NO_2 (g) was monitored as the following

Time (s)	$[NO_2](mol/l)$
0.0	0.124
10.0	0.110
20.0	0.088
30.0	0.073
40.0	0.054

What is the average rate of disappearance of NO_2 between 10.0 and 30.0 seconds?

14.1.4. Use the data in Q 14.1.3 to determine the relative rate of the reaction between 10.0 and 30.0 seconds.

14.1.5. Which of the following has the fastest appearance or disappearance rate?
C_3H_8 (g) + $5O_2$ (g) $\rightarrow$ $3CO_2$ (g) +$4H_2O$(l)

14.3: Effect of Concentration on Reaction Rate

Rate Equation and the Order of a Reaction

14.3.1. The reaction 2A+3B$\rightarrow$products is second order in A and first order in B. What is the rate?

14.3.2. In a reaction of third order in A, increasing the concentration of A by a factor of 4 will cause what kind of change in reaction rate?

14.3.3. For the reaction 2A+3B$\rightarrow$ C + 2D

Experiment	[A](M)	[B](M)	initial rate(M/s)
1	0.012	0.035	0.10
2	0.024	0.070	0.80
3	0.024	0.035	0.10

What is the order of reaction with respect to A?

14.3.4. What is the order of reaction with respect to B?

14.3.5. What is the order of overall reaction?

14.3.6. What is the rate constant for the reaction?

14.4: Integrated Rate Law

Chemical Kinetics & Half-Life

14.4.1. For the first order reaction A + B $\rightarrow$ C, the initial concentration of A is 0.26M, how long it must take for the concentration of A to reduce to 0.176M? k=0.33min^{-1}

14.4.2. If the initial concentration of the reactant of a first order reaction is 0.135M, what is the concentration after 1.5s. k=0.75s^{-1}

14.4.3. The rate constant for a second-order reaction is 0.26M^{-1}s^{-1}, if the initial concentration of reactant is 0.26M, how long it must take for the concentration to drop to 0.13M?

14.4.4. What is the rate constant of a first order reaction that has a half-life of 144s?

14.4.5. A reaction is in first order of the reactant A. A solution initially has 0.120M of A is found to have 0.015M after 54 min. What is the half-life?

Zero-Order Integrated Rate Problems

Figure 14.1: Consider the zero-order reaction for the following problems:

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

14.4.6. The rate of a zero-order-reaction is dependent on which of the followings:

a. Reactant
b. Product
c. Both
d. Neither

14.4.7. What is the rate constant if it takes 60 second for a 0.50 M of the ammonia gas to decompose to 0.25M?

14.4.8. How long does it take for 0.50M of the ammonia gas to decompose to 0.10M?

14.4.9. How long does it take for the reactant in question 3 to decompose to 25%?

14.4.10. How long does it take for 25% of the reactant in question 3 to be consumed?

14.4.11. What is $[NH_3]$ of a 0.80M $[NH_3]$ solution after 3 minutes?

14.4.12. Calculate the initial $[NH_3]$ if $[NH_3]$ =0.005M after 10 minutes?

First Order Rate Problems

Figure 14.2: Consider the first-order reaction for the following problems:

$$Br_2 \rightarrow 2Br$$

14.4.13. What is the rate constant if it takes 60 second for a 0.50 M mixture to decompose to 0.25M?

14.4.14. How long does it take for the reaction in question 14.4.3 to decompose to 0.10M?

14.4.15. How long does it take for the reactant in question 14.4.3 to decompose to 15%?

14.4.16. How long does it take for 15% of the reactant in question 14.4.3 to be consumed?

14.4.17. What is $[Br_2]$ of a 0.80M $[Br_2]$ solution after 3 minutes?

14.4.18. Calculate the initial $[Br_2]$ if $[Br_2]$ =0.005M after 10 minutes?

Second-Order Rate Problems

Consider the second-order reaction for the following problems:

$$2NOBr\ (g) \rightarrow 2NO\ (g) + Br_2\ (g)$$

14.4.19. What is the rate constant if it takes 75 seconds for a 0.90M mixture to decompose to 0.25M?

14.4.20. How long does it take for the reaction in Q 14.4.19 to decompose to 0.10M?

14.4.21. How long does it take for the reactant in Q 14.4.19 to decompose to 25%?

14.4.22. How long does it take for 25% of the reactant in Q 14.4.19 to be consumed?

14.4.23. What is [NOBr] of a .85M [NOBr]solution after 3 minutes?

14.4.24. Calculate the initial [NOBr] if [NOBr]=0.0080M after 15 minutes.

General Integrated Rate Problems

14.4.25. What is the rate constant of a zero-order reaction if it takes 87 seconds for a concentration of 0.32500M to decompose to 0.00387M?

14.4.26. A compound of 0.0452M has a rate constant of 4.95×10^{-5} M/s and decays to 0.0042M. How long did this process take?

14.4.27. After 35 seconds, only 0.029M of the mixture is left. Find the concentration of the initial mixture at a rate of $0.68 M^{-1}s^{-1}$.

14.4.28. For a first-order reaction, in 4 minutes a solution went from 0.0800M to 0.0060M. What is the rate constant for the reaction?

14.4.29. Beginning with 0.5046M of a substance that has a rate constant of $0.085s^{-1}$. How much for the substance is left after 25 seconds?

14.4.30. With a rate constant of $.019M^{-1}s^{-1}$, how long does it take a chemical to go from 0.0400M to 0.0020M?

14.5: Microscopic View of Reaction Rates

Two-State Arrhenius Equation

Figure 14.3: Consider the Arrhenius two state equation for the following problems:

$$\frac{k_1}{k_2} = \frac{Ae^{-E_a/RT_1}}{Ae^{-E_a/RT_2}}$$

14.5.1. Solve for k_1 from the equation above:

14.5.2. Solve for k_2 from the equation above:

14.5.3. Solve for E_a from the equation above:

14.5.4. Solve for R from the equation above:

14.5.5. Solve for T_1 from the equation above:

14.5.6. Solve for T_2 from the equation above:

Arrhenius Equation Problems

14.5.7. A first-order reaction has a rate constant of $4.4x10^{-3}s^{-1}$ at 350K and a rate constant of $9.8x10^{-2}s^{-1}$ at 580K. What is the activation energy?

14.5.8. A reaction with activation energy of 120kJ/mol has a rate constant of $0.25s^{-1}$ at 310K. What will be the temperature for the rate constant to be doubled?

14.5.9. The rate constant of a reaction increases by a factor of 10.0 when the temperature increases from 300K to 330K. What is the activation energy of the reaction?

14.5.10. The rate constant for a reaction is $1.5 \times 10^{-4} M^{-1}s^{-1}$ at 100^0C, and $1.2 \times 10^{-3} M^{-1}s^{-1}$ at 150^0C. What is the energy of activation?

14.5.11. For the reaction in Q 14.5.10, what would the rate constant (in $M^{-1}s^{-1}$) be at 200^0C?

14.6: Reaction Mechanisms

14.6.1. What is the intermediate reactant in the mechanism for the decomposition of ozone?

$$\text{step 1 } O_3(g) \rightarrow O_2(g) + O(g)$$
$$\underline{\text{step 2 } O_3(g) + O(g) \rightarrow 2O_2(g)}$$
$$total \quad 2O_3(g) \rightarrow 3O_2(g)$$

14.6.2. In the previous reaction, what is the molecularity for each step?

14.6.3. For the same reaction, what is the rate equation for step 2?

14.6.4. What is the rate determining step in the following mechanism?

$$\text{(1) fast } 2NO(g) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$$
$$\underline{\text{(2) slow } N_2O_2(g) + O_2(g) \xrightarrow{k_3} 2NO_2(g)}$$
$$overall: 2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

14.6.5. What is the rate equation for question 14.6.4?

14.6.6. What is the rate determining step in the following mechanism?

$$\text{(1) slow } H_2 + ICl \rightarrow HI + HCl$$
$$\underline{\text{(2) fast } HI + ICl \rightarrow I_2 + HCl}$$
$$overall: H_2 + 2ICl \rightarrow I_2 + 2HCl$$

14.6.7. What is the rate equation for question 14.6.6?

General Questions

14.1. Which of the following is not a valid unit for a reaction rate?

a. g/s
b. M/s
c. mol/hr
d. mol/L
e. mol/L-hr

14.2. In the following reaction, [NO_2] drops from 0.0150 to 0.00975 M in 100s at 300°C. What is the rate of disappearance of NO_2 for this period?

$$2NO_2 \rightarrow 2NO + O_2$$

14.3. In the following reaction, [N_2O_5] drops from 0.0300 to 0.0195 M in 300s at 300°C. What is the rate of appearance of O_2 for this period?

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

14.4. What is the rate law of the following reaction if it is first order in A and second order in D?

$$2A + 3D \rightarrow products$$

14.5. For the following reaction, the reaction rate increased by a factor of 9 when the concentration of B was tripled. What is the order in B?

$$A + B \rightarrow P$$

14.6. A reaction was found to be third order in A. By increasing the concentration of A by a factor of 3 will cause the reaction rate to _____.

a. decrease by a factor of the cube root of 3
b. increase by a factor of 27
c. increase by a factor of 9
d. remain constant
e. triple

14.7. Use the information below to answer the following questions:

a. Determine the order of the reaction in reactant A.
b. Determine the order of the reaction in reactant B.
c. Determine the overall order of the reaction.
d. Determine the rate constant for the reaction.

$$A + B \rightarrow P$$

Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.273	0.763	2.83
2	0.273	1.526	2.83
3	0.819	0.763	25.47

14.8. What is the rate law for the given data below for the following reaction?

$$yY + zZ \rightarrow products$$

Experiment Number	[Y](M)	[Z](M)	Initial Rate (M/s)
1	0.200	0.200	8.0×10^{-5}
2	0.400	0.200	3.2×10^{-4}
3	0.200	0.400	1.6×10^{-4}

14.9. What is the rate law that corresponds to the following reaction?

$$2A + B \rightarrow C$$

Experiment Number	[A](M)	[B](M)	Initial Rate (M/s)
1	0.023	0.033	0.188
2	0.045	0.066	0.750
3	0.090	0.066	0.750
4	0.090	0.990	1.688

Figure 14.4: Use the following table of experimental data to answer the questions below.

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

Experiment Number	[ClO_2](M)	[OH^-](M)	Initial Rate (M/s)
1	0.090	0.045	3.720E-02
2	0.030	0.045	4.140E-03
3	0.030	0.135	1.242E-02

14.10. What is the order of the reaction with respect to ClO_2?

14.11. What is the order of the reaction with respect to OH^-?

14.12. What is the order of the reaction overall?

14.13. What is the value of the rate constant for the reaction?

14.14. What are the units of the rate constant for the reaction?

14.15. What is the overall order of a reaction, if the rate constant is $1.3*10^{-4}$ $M^{-1}s^{-1}$ at 100°C and $1.4*10^{-3}$ $M^{-1}s^{-1}$ at 150°C?

14.16. For a zero-order reaction, a plot of _____ versus _____ is linear.

a. $1/[A], t$
b. $\ln[A]_t$, $1/t$
c. $\ln[A]_t$, t
d. $[A], t$
e. $t, 1/[A]$

14.17. For a first-order reaction, a plot of _____ versus _____ is linear.

a. $1/[A], t$
b. $\ln[A]_t$, $1/t$
c. $\ln[A]_t$, t
d. $[A], t$
e. $t, 1/[A]$

14.18. For a second-order reaction, a plot of _____ versus _____ is linear.

a. $1/[A], t$
b. $\ln[A]_t$, $1/t$
c. $\ln[A]_t$, t
d. $[A], t$
e. $t, 1/[A]$

14.19. Determine the rate constant ($M^{-1}s^{-1}$) by using integrated rate law for the following reaction. The reaction follows second-order kinetics, and $[NO_2]$ drops from 0.0200 to 0.0130 M in 200s at 300°C.

$$2NO_2 \rightarrow 2NO + O_2$$

14.20. The reaction below is a first-order reaction. At 230.3°C, k = $6.29*10^{-4}$ s^{-1}. If $[CH_3\text{-}N{\equiv}C]_0$ is 0.00100 M, what is $[CH_3\text{-}N{\equiv}C]$ in M after $1.000*10^3$ s?

$$CH_3 - N \equiv C \rightarrow CH_3 - C \equiv N$$

Chapter 14: Rates of Chemical Reactions

14.21. If a first-order reaction has a rate constant of 0.33 min^{-1}, what is the time for the reactant concentration to decrease from 0.13 M to 0.088M?

14.22. Why does the rate of reaction increase, when the temperature of the reaction increases?

a. activation energy is lowered
b. reactant molecules collide less frequently
c. reactant molecules collide less frequently and with greater energy per collision
d. reactant molecules collide with greater energy per collision
e. reactant molecules collide more frequently with less energy per collision

14.23. What do reaction rates depend on?

a. collision energy
b. collision frequency
c. collision orientation
d. all of these
e. none of these

14.24. What is the species that exists at the maximum on the potential energy profile of a reaction?

a. activated complex
b. activation energy
c. atomic state
d. enthalpy of reaction
e. product

14.25. What is the activation energy (kJ) of a reaction whose rate constant increases by a factor of 10.0 when the temperature is increased from 303K to 333K?

14.26. The rate constant for a reaction is $1.3*10^{-4}$ $M^{-1}s^{-1}$ at 100°C, and $1.1*10^{-3}$ at 150°C. What is the energy of activation (in kJ/mol) for this reaction?

14.27. What is a plausible mechanism for the following reaction?

$$A + 2B \rightarrow C + D \quad rate = k[A]^2$$

a. step 1: A + A → E + D (slow)
   step 2: E + 2B → C + A (fast)
b. step 1: A + B → E + C (slow)
   step 2: E + B → D (fast)
c. step 1: A + A → E + D (slow)
   step 2: E + 2B → C + A (fast)
d. step 1: A + A + B → E + C (slow)
   step 2: E + C → D + F (fast)
   step 3: F → C (fast)
e. None of these mechanisms is plausible for this reaction

14.28. What is the intermediate reactant in the following reaction mechanism?

$$A + B \rightarrow C + D$$

$$B + D \rightarrow X$$

14.29. What is the molecularity and rate law for the following reaction?

$$NO_3 + CO \rightarrow NO_2 + CO_2$$

14.30. Which of the following will lower the activation energy for a reaction?

a. adding a suitable catalyst
b. increasing the concentration of reactants
c. raising the temperature of the reaction
d. all the above
e. none of the above

14.31. What type of catalyst is used in automotive catalytic converters?

a. enzymes
b. heterogenous
c. homogenous
d. noble gas
e. nonmetal oxides