Guide to Chapter 12. Chemical Kinetics

We will spend five lecture days on this chapter. During the first class meeting we will focus on what is kinetics and how do we understand reaction rates, rate laws, rate constants, and similar vocabulary. Keeping the vocabulary straight is critical. Next we will learn how to analyze experimental data of two types: initial concentration/rates and then time/concentration studies. For both, we will use the following vocabulary: reaction order, first, second and zeroth order reactions, and half-life. After we are comfortable with reaction rate laws and how they are determined, we will then tie these mathematical expressions to step-by-step chemical processes called the reaction mechanism. Finally, we will explore how catalysts work and how temperature affects reaction rates.

Read the introductory paragraph to Chapter 12.

Read Section 12.1 Reaction Rates.

Learning Objective 1: Determine the rate of a chemical reaction given concentration (y) vs. time (x) data. Use this data to determine the initial rate, average rate, and instantaneous rate. Hint: Review how to determine the slope of a straight line plot.

Learning Objective 2: Know the units of reaction rate

Learning Objective 3: Given the reaction rate based on a certain reactant or product, determine the relative reaction rate in terms of any other species in the reaction.

Do Problems 1 and 2 at the end of the section.

Do the following end-of-chapter problems: 30, 34, 36, 38

Problem Club Question A. Use seconds as the time component in the following three questions:
What are the units for rate?
What are the units for the rate constant in the expression rate = k[A]?  
What are the units for the rate constant in the expression rate = k[A]^2?

Answer: a. moles L^{-1} s^{-1}  
b. s^{-1}  
c. L mol^{-1} s^{-1}

Problem Club Question B. For the reaction:  O_3 + NO  \rightarrow  O_2 + NO_2 at 310^0 K, the rate expression is: rate = k[O_3][NO] and k = 3.0 \times 10^6 L mol^{-1} s^{-1}. Given that [O_3] = 2.0 \times 10^{-6} M and [NO] = 1.4 \times 10^{-6} M at some point in the reaction, calculate the rate at that point - give units!

Answer: rate = 8.4 \times 10^{-6} mol L^{-1} s^{-1}

Problem Club Question C. For the reaction: 2 O_3  \rightarrow  3 O_2, it was found that the rate of disappearance of O_3 was 2.4 \times 10^{-7} mol/L s. Calculate the rate of appearance of oxygen molecules, O_2.

Answer: 3.6 \times 10^{-7} mol L^{-1} s^{-1}

Read Section 12.2 Rate laws and reaction order

Learning Objective 4: Determine the reaction order from a given rate law.

Learning Objective 5: Given the rate law for a reaction, the rate constant and the reactant concentration(s), calculate the rate of the reaction.

Learning Objective 6: Given the rate law for a reaction, the reaction rate and the reactant concentrations, determine the rate constant, k.

Learning Objective 7: Determine the units for the rate constant, k.

Do Problem 3 at the end of Section 12.2.

Do the following end-of-chapter problems: 22, 40, 42, 44
Problem Club Question D. A reaction and its rate expression are given below. When \([C_4H_6] = 2.0 \text{ mol/L}\), the rate is 0.106 mol/L s. What is the rate when \([C_4H_6] = 4.0 \text{ mol/L}\)? Hint: Use the rate expression, the rate (0.106 mol/L s) and the corresponding concentration (2.0 M) to solve for the rate constant. Next use the rate constant and the new concentration, 4 M, to solve for the new rate.

\[2 \text{C}_4\text{H}_6 \rightarrow \text{C}_8\text{H}_{12} \quad \text{rate} = k[\text{C}_4\text{H}_6]^2\]

Answer: \(0.424 \text{ mol/L s}\)

Problem Club Question E. The oxidation of ammonia produces nitrogen and water as shown below. If the rate of formation of \(N_2\) is 0.70 M/s, determine the rates at which \(NH_3\) and \(O_2\) are consumed.

\[4 \text{NH}_3 + 3 \text{O}_2 \rightarrow 2 \text{N}_2 + 6 \text{H}_2\text{O}\]

Answer: \(\Delta [\text{NH}_3] = 1.4 \text{ mol/L s}; \Delta [\text{O}_2] = 1.05 \text{ mol/L s}\)

Problem Club Question F. What is the reaction order for the rate law: \(\text{rate} = k[A]^2\)?

Answer: second

Problem Club Question G. The decomposition of NOCl is second order in NOCl. When \([\text{NOCl}]_0 = 0.30 \text{ M}\), the rate is \(3.60 \times 10^{-9} \text{ M/s}\). Calculate \(k\).

Answer: \(4.0 \times 10^{-8} \text{ L/mol s}\)

Problem Club Question H. (ACS-Style) Answer: B

Problem Club Question I. (ACS-Style) Answer: B

Problem Club Question J. (ACS-Style) Answer: B

Read Section 12.3 Experimental determination of a rate law.

Learning Objective 8: Given initial rate/initial concentration data

a. Write the rate law for a given reaction.
b. Determine the order with respect to each reactant.
c. Determine the overall reaction order.
d. Calculate the rate constant, \(k\), (using proper units).
e. Determine the rate of reaction given the concentration of the reactant(s).

Do Problems 4 - 6 at the end of the section.

Do the following end-of-chapter problems: 46, 48

Problem Club Question K. Consider the following data for the reaction of \(A \rightarrow P\) in order to determine the rate expression using the Initial Concentration Initial Rate Method

<table>
<thead>
<tr>
<th>Initial ([A])</th>
<th>Initial Rate, (\Delta[P]/\Delta t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.012 \text{ mol/L hr}</td>
</tr>
<tr>
<td>2.0</td>
<td>0.024</td>
</tr>
<tr>
<td>3.0</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Answer: \(\text{rate} = k[A]\)

Problem Club Question L. Consider the following data for the reaction \(A + B \rightarrow P\) in order to determine the rate expression using the Initial Concentration Initial Rate Method

<table>
<thead>
<tr>
<th>Initial ([A])</th>
<th>Initial ([B])</th>
<th>Initial Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>0.012</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>0.024</td>
</tr>
<tr>
<td>3.0</td>
<td>1.0</td>
<td>0.035</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>0.096</td>
</tr>
<tr>
<td>1.0</td>
<td>2.0</td>
<td>0.048</td>
</tr>
</tbody>
</table>

Answer: \(\text{rate} = k[A][B]^2\)
Problem Club Question M. Consider the reaction: \( 2 \text{NO} + 2 \text{H}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O} \) and the following data in order to determine the rate expression for the reaction.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Initial [NO]</th>
<th>Initial [H(_2)]</th>
<th>Initial Rate (mol/L s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>1.00</td>
<td>(3.5 \times 10^{-5})</td>
</tr>
<tr>
<td>2</td>
<td>1.20</td>
<td>1.20</td>
<td>(5.0 \times 10^{-5})</td>
</tr>
<tr>
<td>3</td>
<td>0.80</td>
<td>0.80</td>
<td>(1.8 \times 10^{-5})</td>
</tr>
<tr>
<td>4</td>
<td>1.00</td>
<td>2.00</td>
<td>(7.0 \times 10^{-5})</td>
</tr>
<tr>
<td>5</td>
<td>2.00</td>
<td>1.00</td>
<td>(1.4 \times 10^{-4})</td>
</tr>
</tbody>
</table>

Answer: rate = k[NO]\(^2\)[H\(_2\)]

Problem Club Question N. (ACS-Style) Answer: A

Problem Club Question O. (ACS-Style) Answer: D

Problem Club Question P. (ACS-Style Answer: D

Read Sections 12.4 - 12.7. These four sections are perhaps the most important sections in the chapter in terms of evaluating experimental data to determine the rate law. They are combined here because they will be presented all together in lecture. Individual section titles: Section 12.4. Integrated rate law for a first order reaction; Section 12.5. Half-life of a first-order reaction; Section 12.6. Second-order reactions; and Section 12.7. Zeroth-order reactions.

Learning Objective 9: Use concentration(y) vs. time(x) data to determine the reaction order (zero, first, or second) with respect to a single reactant

Learning Objective 10: After establishing the rate law (previous objective), determine the value of the rate constant, k (with proper units)

Learning Objective 11: Having established the rate law, and given the concentration of the reagent, determine the reaction rate.

Learning Objective 12: Using the integrated rate law equations (handout) and knowing the reaction order determine the following values:
   a. rate constant, k
   b. reaction time for a given percent completion of a reaction.
   c. the concentration of a reactant after a given period of time.
   d. The time it takes for a given change in the concentration of the reactant.
   e. half-life

Learning Objective 13: Given graphical representations of concentration vs. time, select the graph that corresponds to the correct reaction order.

Do Problems 7 - 11 embedded within these sections.

Do the following end-of-chapter problems: 24, 26, 50, 52, 54, 56, 58, 60, 62, 64

Problem Club Question Q. The reaction \( \text{CCl}_3\text{CO}_2\text{H(aq)} \rightarrow \text{CO}_2 + \text{CHCl}_3 \) was found to proceed at 70\(^\circ\)C according to the following data:

<table>
<thead>
<tr>
<th>time, h</th>
<th>[CCl(_3)CO(_2)H]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.1000</td>
</tr>
<tr>
<td>1.00</td>
<td>0.0940</td>
</tr>
<tr>
<td>2.00</td>
<td>0.0884</td>
</tr>
<tr>
<td>3.00</td>
<td>0.0831</td>
</tr>
<tr>
<td>4.00</td>
<td>0.0782</td>
</tr>
</tbody>
</table>

a. Determine the order of the reaction
b. Determine the value of the rate constant
c. Determine the concentration of \( \text{CCl}_3\text{CO}_2 \) after 5.00 hours and 10.00 hours

d. How long would it take for the concentration of \( \text{CCl}_3\text{CO}_2\text{H} \) to drop from 0.10000 mol/L down to 0.09000 mol/L?

e. How long would it take for the reaction to become 95% complete? Hint: Make the final concentration equal to 5% of the initial concentration because 95% of it is gone.

Answer: 4.

Problem Club Question R. The reaction: \( A \rightarrow \text{products} \) was found to proceed according to the data that follows.

<table>
<thead>
<tr>
<th>t, min</th>
<th>[CCl(_3\text{CO}_2\text{H}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.1000</td>
</tr>
<tr>
<td>1.00</td>
<td>0.0900</td>
</tr>
<tr>
<td>2.00</td>
<td>0.0800</td>
</tr>
<tr>
<td>3.00</td>
<td>0.0700</td>
</tr>
</tbody>
</table>

a. What is the rate expression and the order of the reaction?
b. Determine the value of the rate constant
c. What is the half life?
d. Determine the concentration of \( A \) after 2.40 minutes and 5.00 minutes.
e. How long would it take for the concentration of \( A \) to drop from 0.10000 mol/L down to 0.02000 mol/L?
f. How long would it take for the reaction to become 98% complete?

Answer: a. rate = \( k \); zero

Problem Club Question S. At 25\(^\circ\)C, the reaction \( \text{I}^- + \text{ClO}^- \rightarrow \text{IO}^- + \text{Cl}^- \) proceeds according to the rate law: rate = \( k[\text{I}^-]^2 \) where \( k = 0.0606 \text{ L mol}^{-1}\text{s}^{-1} \). If a solution is initially 0.00350 M with respect to each reactant, what will be the concentration of each species present after 300 s? Hint: Use the time-conc equation for the appropriate order - also note that the rate only depends on the concentration of iodide.

Answer: both will be 0.00329 M

Problem Club Question T. What is the half life for a first order reaction if the rate constant, \( k = 2.05 \times 10^{-2} \text{ s}^{-1} \)?

Answer: 33.8 s

Problem Club Question U. Rate constants for several first order reactions are: 0.0410 \text{ s}^{-1}, 0.521 \text{ s}^{-1}, 0.0033 \text{ s}^{-1}, 1.83 \text{ s}^{-1}, and 2.00 \text{ s}^{-1}. The half life is shortest for the reaction with which \( k \) value?

Answer: 2.00 \text{ s}^{-1}

Problem Club Question V. At 500\(^\circ\)C, the decomposition of \( \text{XY}_4(g) \) to its elements yields these data below.

What is the concentration of \( \text{XY}_4 \) after 5 hours? Hint: Determine the rate expression first, then determine \( k \), finally solve for the concentration after 5 hrs.

<table>
<thead>
<tr>
<th>Time</th>
<th>[\text{XY}_4]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 hr</td>
<td>2.11</td>
</tr>
<tr>
<td>1 hr</td>
<td>1.79</td>
</tr>
<tr>
<td>2 hr</td>
<td>1.47</td>
</tr>
<tr>
<td>3 hr</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Answer: 0.51 M

Problem Club Question W. A reaction that is first order has a rate constant of 4.5 \text{ min}^{-1}. How long will it take for the concentration of reactant to change from 0.40 M to 0.05 M?

Answer: 0.46 min

Problem Club Question X. A second order reaction has an initial concentration of reactant equal to 0.02 M. If the rate constant is 10 \text{ M}^{-1}\text{s}^{-1}, calculate the time required to decrease the concentration to 0.005 M.

Answer: 15 s
Read Sections 12.8 Reaction Mechanisms and Section 12.9. Rate laws and reaction mechanisms

Learning Objective 14: Write the overall reaction from a given mechanism.

Learning Objective 15: Determine the "molecularity" of an elementary step in a given mechanism.

Learning Objective 16: Write the rate law for any elementary step in a given reaction mechanism.

Learning Objective 17: Given a reaction mechanism with two or more steps, identify the intermediate(s), if present.

Learning Objective 18: Derive the rate law from a given reaction mechanism.

Learning Objective 19: Determine which of several proposed mechanisms is consistent with a given rate law.

Do Problems 12 - 14 embedded within these sections.

Do the following end-of-chapter problems: 66, 68, 70, 72, 74, 76

Problem Club Question BB. The reaction of CO\(_2\) with hydroxide ion in aqueous solution is postulated to occur according to the mechanism below. What is the rate law for the mechanism?

\[
\begin{align*}
\text{CO}_2(aq) + \text{OH}^- (aq) & \rightarrow \text{HCO}_3^-(aq) \quad \text{slow} \\
\text{HCO}_3^-(aq) + \text{OH}^- (aq) & \rightarrow \text{CO}_3^{2-}(aq) + \text{H}_2\text{O} \quad \text{fast}
\end{align*}
\]

Answer: rate = k [CO\(_2\)][OH\(^-\)]

Problem Club Question CC. The available kinetic data for the reaction 2 NO(g) + O\(_2\)(g) \rightarrow 2 NO\(_2\)(g) is consistent with the following reaction mechanism. Obtain the rate law for the reaction from the proposed mechanism. What is the role of NO\(_3\)?

\[
\begin{align*}
\text{NO}(g) + \text{O}_2(g) & \leftrightarrow \text{NO}_3(g) \quad \text{fast} \\
\text{NO}(g) + \text{NO}_3(g) & \rightarrow 2 \text{NO}_2(g) \quad \text{slow}
\end{align*}
\]

Answer: rate = k [NO]\(^2\)[O\(_2\)]; NO\(_3\) is intermediate

Problem Club Question DD. (ACS-Style) Answer: C

Problem Club Question EE. (ACS-Style) Answer: D

Problem Club Question FF. (ACS-Style) Answer: D

Read Section 12.10 and 12.11 on reaction rates and temperatures.

Learning Objective 20: List the factors that are important for a reaction going to completion according to the collision model.

Learning Objective 21: Interpret and identify the different parts of a potential energy profile diagram. Determine if the diagram is for an exothermic or endothermic reaction. The areas on the diagram to identify include: the reactant energy, product energy, the transition state, the energy of activation (forward), the energy of activation (reverse), and ΔH.

Learning Objective 22: Given known energies in an energy profile diagram, determine the missing energy.
Learning Objective 23: Describe how increasing the temperature can effect the rate of a chemical reaction.

Learning Objective 24: Use the Arrhenius equation to determine the energy of activation, $E_a$, for a reaction.

Do Problems 15 and 16 embedded within these sections.

Do the following end-of-chapter problems: 28, 78, 80, 82, 84, 86

Problem Club Question GG. For the given reaction rate law: $rate = k[A][B]^2$, which of the following will change the value of the rate constant, $k$?
A. doubling [A]  
B. doubling [B]  
C. removing some product  
D. decreasing the temperature  
E. more than one of the above.
Answer: D

Problem Club Question HH. A certain reaction has $E_a = 146 \text{ kJ/mol}$. If the specific rate constant is $4.25 \times 10^{-4} \text{ s}^{-1}$ at $25^\circ \text{C}$, what is the rate constant at $100^\circ \text{C}$?
Answer: $59 \text{ s}^{-1}$

Problem Club Question II. For a certain reaction, the activation energy is $62 \text{ kJ}$ and the enthalpy change is $-22 \text{ kJ}$. Sketch this energy profile and label both forward and reverse activation energies. What is $E_{act}$ for the reverse reaction?
Answer: $84 \text{ kJ}$

Problem Club Question JJ. (ACS-Style) Answer: A

Problem Club Question KK. (ACS-Style) Answer: E

Problem Club Question LL. (ACS-Style) Answer: B


Learning Objective 25: Describe the role of a catalyst and explain the difference between a homogeneous and a heterogeneous catalyst. Know how a catalyst affects a potential energy profile diagram.

Learning Objective 26: Given a reaction mechanism, identify the following: the catalyst (if present), the intermediate(s) (if present), and the rate-determining step.

Do Problem 17 embedded within these sections.

Do the following end-of-chapter problems: 88, 90, 92, 94

Problem Club Question MM. A catalyst:
A. decreases the activation energy.  
B. changes $\Delta H$ for the reaction.  
C. is chemically changed by the reaction  
D. changes the rate determining step  
E. decreases the value of the rate constant  
Answer: A

Problem Club Question NN. (ACS-Style) A catalyst will
(A) alter the pathway (mechanism) of a chemical reaction.  
(B) increase $\Delta H$ for the reaction.  
(C) decrease $\Delta H$ for the reaction.  
(D) decrease $E_a$ for the forward reaction only.  
Answer: A
Problem Club Question OO. (ACS-Style) Answer: C