**Nuggets:** Factors affecting rate; What is a Rate; Average Rate; Initial Rate; Instantaneous Rate; Relative Rates; Rate Law; Rate Constant and Units; Evaluating Rate Laws: 1. Initial Rates Method, 2. Description

**FACTORS THAT AFFECT RATE:** To increase rate:
1. **Concentration** $\uparrow \rightarrow$ #collisions $\uparrow \rightarrow$ reaction rate $\uparrow$
2. **Temperature** $\uparrow \rightarrow$ KE $\uparrow \rightarrow$ $E_{\text{collisions}}$ $\uparrow \rightarrow$ more molecules have $E > E_a$ (i.e., have sufficient energy; $E_a$ = activation energy) $\rightarrow$ reaction rate $\uparrow$ (note: $k$, rate constant, also changes as $T$ changes)
3. **Catalyst** $\rightarrow E_a$ (activation energy) is lowered; more molecules have $E > E_a$; (i.e., have sufficient energy) $\rightarrow$ reaction rate $\uparrow$ (Note: both forward and reverse reaction rates $\uparrow$)
4. **Physical state** (particle size; heterogeneous rxns) $\rightarrow$ particle size (solids) $\downarrow \rightarrow$ #collisions $\uparrow$ since there is more surface area for greater contact $\rightarrow$ reaction rate $\uparrow$

**RATES** – defined as a change in concentration over a change in time; Rate $=$ $\frac{\Delta [\ ]}{\Delta t}$

$\Delta [\ ]/\Delta t$ is just the slope on a graph of Concentration versus Time

**By convention, rates are defined as positive.** Since $\Delta [\ ]/\Delta t$ has a negative value for reactants (reactant concentrations $\downarrow \Rightarrow$ negative value/slope), a **negative sign is added to yield a positive value.**

Rate $=$ $-\frac{\Delta[A]}{\Delta t}$ where $A$ is a reactant, $A \rightarrow B$ (rate units = $M/\text{time}$)

When products are used, **no negative sign is added as the rate will yield a positive value** (product concentration $\uparrow \Rightarrow$ positive value for slope);

Rate $=$ $\frac{\Delta[B]}{\Delta t}$ where $B$ is a product, $A \rightarrow B$ (rate units = $M/\text{time}$)

- **AVERAGE** rate is over a finite time: Determined by using the 2 closest times that bracket the time of interest and their corresponding concentrations;

  Average Rate $=$ $-\frac{\Delta[A]}{\Delta t} = -\left(\frac{[A]_{t_2} - [A]_{t_1}}{t_2 - t_1}\right)$;

- **INITIAL** rate is the rate from $\text{time} = 0$ to the next time data point;

  Initial Rate $=$ $-\frac{\Delta[A]}{\Delta t} = -\left(\frac{[A]_{t_2} - [A]_{t_1}}{t_2 - t_1}\right)$ where $t_1 = 0$;

- **INSTANTANEOUS** rate is the rate at an instant in time (see last page of Help Sheet to estimate instantaneous rate)
Average and Initial Rates (continued)

**Example 1:** For the reaction: \( A \rightarrow B \), the data below was collected.

a. What is the initial rate of reaction of \( A \)?
b. What is the average rate of reaction of \( A \) between 20 and 40 sec?
c. What is the average rate of reaction of \( A \) at 50 sec?

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>([A]) (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.000</td>
</tr>
<tr>
<td>10.0</td>
<td>0.905</td>
</tr>
<tr>
<td>20.0</td>
<td>0.819</td>
</tr>
<tr>
<td>30.0</td>
<td>0.741</td>
</tr>
<tr>
<td>40.0</td>
<td>0.670</td>
</tr>
<tr>
<td>50.0</td>
<td>0.607</td>
</tr>
<tr>
<td>60.0</td>
<td>0.549</td>
</tr>
</tbody>
</table>

**Answer 1:**

a. Choose the value at time \( t = 0 \) and the very next data point.

\[
\text{rate} = \frac{\Delta[A]}{\Delta t} = \frac{(0.905 - 1.000)}{(10.0 - 0.0)} = \frac{(-0.0950)}{0} = 0.0950 \text{M/s}
\]

b. Choose the 2 data points given in the question.

\[
\text{rate} = \frac{\Delta[A]}{\Delta t} = \frac{(0.670 - 0.819)}{(40.0 - 20.0)} = \frac{(-0.1495)}{20.0} = 0.00745 \text{M/s}
\]

c. Choose 2 data points closest that bracket the point of interest.

\[
\text{rate} = \frac{\Delta[A]}{\Delta t} = \frac{(0.549 - 0.670)}{(60.0 - 40.0)} = \frac{(-0.121)}{20.0} = 0.00605 \text{M/s}
\]

**RELATIVE RATES – comparing rates of reactants and products using stoichiometry**

Relating the consumption of one reactant to the consumption of another reactant or to the formation of a product. The inverse of the stoichiometric coefficient are placed in front of the rate of that chemical. For the reaction: \( 2A + B \rightarrow 3C \) the relative rates are written:

\[
\frac{1}{\text{coeff}_A} (\text{rate A}) = \frac{1}{\text{coeff}_B} (\text{rate B}) = \frac{1}{\text{coeff}_C} (\text{rate C}); \text{ substituting the coefficients and rates } \rightarrow \\
\frac{1}{2} (\text{rate A}) = \frac{1}{1} (\text{rate B}) = \frac{1}{3} (\text{rate C})
\]

**Example 2:** For the reaction, \( 3A \rightarrow B + 2C \), what is the rate of formation of \( C \) if the rate of disappearance of \( A \) is \( 3.5 \times 10^{-2} \text{M/hr} \)?

**Answer 2:** \( \frac{1}{3} (\text{rate A}) = \frac{1}{2} (\text{rate C}) \rightarrow \frac{1}{3} (3.5 \times 10^{-2}) = \frac{1}{2} (\text{rate C}) \rightarrow (2) \frac{1}{3} (3.5 \times 10^{-2}) = (2) \frac{1}{2} (\text{rate C}) \rightarrow \text{rate C} = \frac{2}{3} (3.5 \times 10^{-2}) = 2.3 \times 10^{-2} \text{M/hr}

**RATE LAW:** rate as a function of concentration; the rate law is written:

\[
\text{Rate} = k[^{\text{reactant}_1} \text{unknown exponent}_1][^{\text{reactant}_2} \text{unknown exponent}_2] \quad \text{where } k \text{ is the rate constant;}
\]

Using \( 2A + B \rightarrow 3C \), the rate law is: \( \text{Rate} = k[A]^n[B]^m \); \( n, m, k \) are determined experimentally \( n \) is the order of reactant \( 1 \); \( m \) is the order for reactant \( 2 \); and \( n + m = \text{reaction order} \)

Common exponent values (i.e., orders) are 0 (zero order), 1 (first order), and 2 (second order) but orders can also be fractions (e.g., \( 1/2 \)) and other values (e.g., -1)

**UNITS of \( k \):** units vary depending on the order of the reaction

**Example 3:** Determine the units of \( k \) for a second order reaction.

**Answer 3:** Start by writing a general rate law for a second order reaction: \( \text{Rate} = k[A]^2 \)

Substitute units (note: time units can be s, min, hrs, etc.); Rate is always \( \frac{M}{s} \) and for \([A]\) use \( \frac{M}{s} = k \text{M}^2 \)

Solve for: \( \frac{M}{s} = k \text{M}^2 \rightarrow \frac{M}{s} = k \text{M}^2 \rightarrow \frac{1}{M^2} = k \text{M}^2 \rightarrow \frac{M}{s} = k \text{M}^2 \rightarrow \frac{1}{M^2} = k \text{M}^2 \); \( k = \frac{1}{M^2} \) also written as: \( k = \text{M}^{-1} \text{s}^{-1} \)

**DIFFERENT METHODS TO DETERMINE RATE LAW (i.e., find the order(s) and \( k \))**

I. Initial rates method (see below: this Help Sheet)

II. Description (see below: this Help Sheet)

III. Integrated Rate Laws – Graphs (see Help Sheet #7)

IV. Half-life, \( 1/2 \): [\( A \)] versus time – Graphs (see Help Sheet #7)

V. Rate versus Concentration – Graphs (see Help Sheet #7)

VI. Mechanisms (see Help Sheet #8)
I. Initial rates method

1. Set up rate ratio from 2 experimental sets of data: 

\[
\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[A]^a_1[B]^b_1[C]^c_1}{k[A]^a_2[B]^b_2[C]^c_2}
\]

choose experiments so only 1 chemical concentration changes and all the other chemicals are constant

2. Cross out k and other chemicals with constant concentrations; solve for exponent of the one remaining chemical whose concentration is changing

3. Repeat for other chemicals/exponents until all exponents (i.e., orders) are evaluated

4. Choose any set of experimental data, plug in values with now known exponents (orders) and solve for k

Example 4: Determine the orders and k, and write the rate law for 2A + B \rightarrow 3C using the data provided:

<table>
<thead>
<tr>
<th>Exp</th>
<th>[A], M</th>
<th>[B], M</th>
<th>initial rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.10</td>
<td>2.0 x 10^{-2}</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.20</td>
<td>8.0 x 10^{-2}</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.10</td>
<td>4.0 x 10^{-2}</td>
</tr>
</tbody>
</table>

Answer 4: Start by writing the general rate law: Rate = k[A]^n[B]^m

1. Choose 2 experiments from the data in which only one chemical concentration changes (Exp 1 and 3; or Exp 1 and 2)

2. Solve for n (exponent for A) by choosing Exp 1 and Exp 3. Easier if the Exp with the larger rate (Exp 3) is placed on top.

\[
\frac{\text{rate}_3}{\text{rate}_1} = \frac{k[A]^n_3[B]^m_3}{k[A]^n_1[B]^m_1}; \text{ cancel k’s and insert } #’s: \frac{4.0 x 10^{-2}}{2.0 x 10^{-2}} = \frac{[0.20]^n[0.10]^m}{[0.10]^n[0.10]^m}; 2 = \left(\frac{0.20}{0.10}\right)^n \left(\frac{0.10}{0.10}\right)^m = 2^n 1^m; 2 = 2^n; n = 1
\]

(Note how B dropped out of the expression; this was because [B] was constant and the expression reduces from the 2 variables (n and m) to a single variable (n) which is now a solvable problem.)

3. Repeat for m with Exp 1 and Exp 2: 

\[
\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[A]^n_2[B]^m_2}{k[A]^n_1[B]^m_1}; \frac{8.0 x 10^{-2}}{2.0 x 10^{-2}} = \frac{[0.10]^n[0.20]^m}{[0.10]^n[0.10]^m}; 4 = \left(\frac{0.20}{0.10}\right)^n \left(\frac{0.10}{0.10}\right)^m = 1^n 2^m; 4 = 2^m; m = 2
\]

4. Rate law: Rate = k[A]^1[B]^2

5. Solve for k: Plug in values from any exp (I chose Exp 1) and solve for k; 2.0 x 10^{-2} = k(0.10)^1(0.10)^2; solve for k; k = 20 M^{-2} s^{-1}

II. Description (not all instructors classify this as a “method” to solve the rate law)

Example 5: Determine the rate law for 2A + B \rightarrow 3C given

I. When [A] doubles, the rate increases by 4

II. When [B] doubles, the rate is unchanged.

Answer 5: Start by writing the general rate law: Rate = k[A]^n[B]^m

1. From info I, [A] is changing and it is assumed that [B] is constant since no info was provided; set up rate ratio and [B] cancels since it is constant →

\[
\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[A]^n_1[B]^m_1}{k[A]^n_2[B]^m_2}; \text{ rate}_1 = \frac{k[A]^n_1}{k[A]^n_2}; \text{ rate}_2 = \left(\frac{[A]}{[A]}_2\right)^n
\]

Let rate_2 and [A]_2 = 1, and change rate_1 and [A]_1 to match the information provided in I and solve: 

\[
4 = \left(\frac{2}{1}\right)^n; 4 = 2^n; n = 2
\]

2. From info II, [B] is changing and it is assumed that [A] is constant since no info was provided; set up rate ratio and [A] cancels since it is constant →

\[
\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[A]^n_1[B]^m_1}{k[A]^n_2[B]^m_2}; \text{ rate}_1 = \frac{k[B]^m_1}{k[B]^m_2}; \text{ rate}_2 = \left(\frac{[B]}{[B]}_2\right)^m
\]

Let rate_2 and [B]_2 = 1, and change the rate_1 and [B]_1 to match the information provided in II and solve: 

\[
1 = \left(\frac{2}{1}\right)^m; 1 = 2^m; m = 0
\]

3. Rate = k[A]^2[B]^0; Rate = k[A]^2
1. Assume the following reaction occurs as follows: \(2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g)\)

<table>
<thead>
<tr>
<th>time (s)</th>
<th>[NO(_2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0100</td>
</tr>
<tr>
<td>50.0</td>
<td>0.0079</td>
</tr>
<tr>
<td>100.0</td>
<td>0.0065</td>
</tr>
<tr>
<td>150.0</td>
<td>0.0055</td>
</tr>
<tr>
<td>200.0</td>
<td>0.0048</td>
</tr>
<tr>
<td>250.0</td>
<td>0.0043</td>
</tr>
<tr>
<td>300.0</td>
<td>0.0038</td>
</tr>
<tr>
<td>350.0</td>
<td>0.0034</td>
</tr>
<tr>
<td>400.0</td>
<td>0.0031</td>
</tr>
</tbody>
</table>

a. What is the initial rate of consumption for \(\text{NO}_2\)?
b. What is the average rate of consumption of \(\text{NO}_2\) between 50sec and 150sec?
c. What is the concentration of \(\text{NO}_2\) at 150sec?
d. What is the average rate of consumption of \(\text{NO}_2\) at 150sec?
e. What is the concentration of \(\text{NO}_2\) at 350sec?
f. What is the average rate of consumption of \(\text{NO}_2\) at 350sec?
g. Explain why the rate of consumption of \(\text{NO}_2\) is dropping.

2. For the reaction \(\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)\), with the rate of consumption of \(\text{N}_2\) is \(6.0 \times 10^{-2}\)M/min.

a. What is the rate of consumption for \(\text{H}_2\)?
b. What is the rate of formation for \(\text{NH}_3\)?

3. If the rate of appearance of \(\text{O}_2\) is \(3.25 \times 10^{-5}\)M/min, what is the rate of disappearance of \(\text{O}_3\)?

\[2\text{O}_3(g) \rightarrow 3\text{O}_2(g)\]

4. The following reaction occurs with a Pt catalyst: \(\text{H}_2 + \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3-\text{CH}_3\)

How will the following change over time? (write I for increase, D for decrease, or NC for no change)

a. \([\text{H}_2]\)

b. \([\text{CH}_3-\text{CH}_3]\)

c. amount Pt
d. the rate constant, \(k\)

e. the order of the reaction

5. A reaction, \(\text{AB} \rightarrow A + B\), was studied and the data (concentration of \(\text{AB}\) versus time) was plotted on the graph shown. The rate law for the reaction was determined to be: rate = \(k[\text{AB}]^2\)

a. Using the graph, what was the initial rate of reaction?
b. Determine the rate constant \(k\).
c. If the concentration of \(\text{AB}\) was doubled, what would occur to the reaction rate?
d. If \([\text{AB}] = 0.35\)M what would the rate of reaction be?
6. A general reaction written as \( A + 2B \rightarrow C \) is studied and yields the following data:

<table>
<thead>
<tr>
<th>Exp.</th>
<th>([A]_0)</th>
<th>([B]_0)</th>
<th>Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10 M</td>
<td>0.10 M</td>
<td>4.0 ( \times ) 10^{-5}</td>
</tr>
<tr>
<td>2</td>
<td>0.20 M</td>
<td>0.10 M</td>
<td>1.6 ( \times ) 10^{-4}</td>
</tr>
<tr>
<td>3</td>
<td>0.10 M</td>
<td>0.20 M</td>
<td>4.0 ( \times ) 10^{-5}</td>
</tr>
</tbody>
</table>

a. Write the general form of the rate law from the reaction above.
b. From the data above, determine the orders in the rate law for A and B?
c. What is the value of k? Include units.
d. What is the order of the reaction?
e. What happens to the rate when the concentration of B doubles.

7. The following reaction, \( CO + Cl_2 \rightarrow COCl + Cl \) was studied by the method of initial rates.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>([CO]_0)</th>
<th>([Cl_2]_0)</th>
<th>Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00 ( \times ) 10^{-2} M</td>
<td>1.00 ( \times ) 10^{-2} M</td>
<td>6.60 ( \times ) 10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>2.00 ( \times ) 10^{-2} M</td>
<td>1.00 ( \times ) 10^{-2} M</td>
<td>1.32 ( \times ) 10^{-2}</td>
</tr>
<tr>
<td>3</td>
<td>1.00 ( \times ) 10^{-2} M</td>
<td>2.00 ( \times ) 10^{-2} M</td>
<td>2.64 ( \times ) 10^{-2}</td>
</tr>
</tbody>
</table>

a. Write the general form of the rate law from the reaction above.
b. Determine the orders in the rate law for CO and \( Cl_2 \)?
c. What is the value of k (include units)?
d. What is the order of the reaction?
e. If the concentrations of both reactants were doubled, what would be the change in rate of reaction?

8. The reaction of NO with \( H_2 \) was followed and the data collected shown below.

\[
2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)
\]

<table>
<thead>
<tr>
<th>Exp.</th>
<th>([NO])</th>
<th>([H_2])</th>
<th>Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.50 ( \times ) 10^{-4} M</td>
<td>2.00 ( \times ) 10^{-4} M</td>
<td>1.26 ( \times ) 10^{-9}</td>
</tr>
<tr>
<td>2</td>
<td>4.50 ( \times ) 10^{-4} M</td>
<td>2.00 ( \times ) 10^{-4} M</td>
<td>1.13 ( \times ) 10^{-8}</td>
</tr>
<tr>
<td>3</td>
<td>3.00 ( \times ) 10^{-4} M</td>
<td>6.00 ( \times ) 10^{-4} M</td>
<td>1.51 ( \times ) 10^{-8}</td>
</tr>
</tbody>
</table>

a. Write the general form of the rate law from the reaction above.
b. Determine the orders in the rate law for NO and \( H_2 \).
c. Determine the value of the rate constant; include units
d. What are the reaction orders with respect to each reactant?
e. What is the order of the reaction?  
f. If the concentration of NO was doubled and the concentration of \( H_2 \) cut in half, what would the change in rate of reaction be?

9. For the following reaction, \( 2A + B + C \rightarrow 5D \)

a. Given the following information, write the rate law for the above reaction with the specific orders for A, B, and C:

   I. When the concentration of A is tripled the rate is tripled.
   II. When the concentration of B is double the rate is unchanged.
   III. When the concentration of C is tripled the rate is increased by a factor of 9.
b. If the initial concentrations are \( A = 1.0 \text{ M}, B = 2.0 \text{ M}, \) and \( C = 5.0 \text{ M} \) and the rate is \( 1.0 \times 10^{-4} \text{ M/s}, \) what is the rate constant for this reaction (include the proper units)?
c. If the concentration of A, B, and C are doubled, by what factor is the rate changed?
10. The reaction A → 2B + C is found to be second order with respect to the reactant, A.
   a. Given this information, write the rate law.
   b. What are the units of the rate constant, k?
   c. When the concentration of A is 0.01M the rate of consumption of A is 1.0 x 10⁻² M/min. What is the value of the rate constant?
   d. When the concentration of A is 0.01M the rate of consumption of A is 1.0 x 10⁻² M/min. What is the rate of production of B at this point in time?
   e. When the concentration of A is increased to 0.05M, what is the new rate of loss of A?

11. The reaction 3A → 2B is found to be first order with respect to the reactant, A.
   a. Write the rate law.
   b. What are the units of the rate constant?
   c. When the concentration of A is 0.15M the rate of consumption of A is 3.7 x 10⁻³ M/min, what is the value of the rate constant?
   d. When the concentration of A is 0.15M the rate of consumption of A is 3.7 x 10⁻³ M/min. What is the rate of production of B at this time?
   e. When the concentration of A is increased to 0.95M, what is the new rate of loss of A?

12. The following reaction, 2NO + Cl₂ → 2NOCl, was analyzed.
   It was found that when the concentration of NO was tripled the rate tripled. In another experiment, when the concentration of NO was cut in half and the concentration of Cl₂ was doubled, the rate doubled.
   a. What is the order of NO?
   b. What is the order of Cl₂?
   c. What is the overall rate law?
   d. When [NO] = 0.050M and [Cl₂] = 0.12M, the rate was 1.5 x 10⁻². What is the rate constant?

13. a. A reaction was run: B + C → BC. When [B] = 2.0M and [C] = 0.0100M, the following graph of [C] versus time was experimentally determined. Using the graph below, estimate the initial rate of reaction.

b. If the rate law was determined to be rate = k[B]²[C] and the reaction was run again with [B] = 4.0M and [C] = 0.0100M, what is the new initial rate of reaction?
ANSWERS

1. a. \(4.2 \times 10^{-5} \text{ M/s} \) \(\{\text{rate} = \frac{-\Delta \text{[NO}_2\text{]}}{\Delta t} = \frac{-(0.0100 - 0.0079)}{(0.0 - 50.0)} = 4.2 \times 10^{-5} \text{ M/s}\}\)

b. \(2.4 \times 10^{-5} \text{ M/s} \) \(\{\text{rate} = \frac{-\Delta \text{[NO}_2\text{]}}{\Delta t} = \frac{-(0.0079 - 0.0055)}{(50.0 - 150.0)} = 2.4 \times 10^{-5} \text{ M/s}\}\)

c. \(0.0055 \text{M} \) \(\{\text{read it off the table}\}\)

d. \(1.7 \times 10^{-5} \text{ M/s} \) \(\{\text{rate} = \frac{-\Delta \text{[NO}_2\text{]}}{\Delta t} = \frac{-(0.0065 - 0.0048)}{(100.0 - 200.0)} = 1.7 \times 10^{-5} \text{ M/s}\}\)

e. \(0.0034 \text{M} \) \(\{\text{read it off the table}\}\)

f. \(0.70 \times 10^{-5} \text{ M/s} \) \(\{\text{rate} = \frac{-\Delta \text{[NO}_2\text{]}}{\Delta t} = \frac{-(0.0038 - 0.0031)}{(300.0 - 400.0)} = 0.70 \times 10^{-5} \text{ M/s}\}\)

g. As the concentration of a chemical drops, its rate of reaction will also drop.

2. a. rate consumption \(H_2 = 1.8 \times 10^{-1} \text{M/min} \) \(\{\frac{1}{3}(\text{rate} \text{H}_2) = \frac{1}{3}(\text{rate} \text{H}_2) \}\); rate \(H_2 = 3(6.0 \times 10^{-2}) = 1.8 \times 10^{-1} \text{M/min}\)

b. rate formation \(\text{NH}_3 = 1.2 \times 10^{-1} \text{ M/min} \) \(\{\frac{1}{2}(\text{rate} \text{NH}_3) = \frac{1}{2}(\text{rate} \text{NH}_3) \}\); rate \(\text{NH}_3 = 2(6.0 \times 10^{-2}) = 1.2 \times 10^{-1} \text{M/min}\)

3. rate of appearance \(\text{O}_3 = 2.17 \times 10^{-5} \text{ M/min} \) \(\{\frac{1}{2}(\text{rate} \text{O}_3) = \frac{1}{3}(\text{rate} \text{O}_3) \};\) rate \(\text{O}_3 = \frac{2}{3}(3.25 \times 10^{-5}) = 2.17 \times 10^{-5} \text{M/s}\)

4. a. \(D\) (reactants decrease)  b. \(I\) (products increase)  c. \(NC\) (catalysts are not consumed)  d. \(NC\) (k is not a function of time)  e. \(NC\) (order is not a function of time)

5. a. \(1.2 \times 10^{-2} \text{ M} \) \(\{\text{use the graph and use 2 data points: one at time = 0 and a second time that is close to zero; \}\}\)

\(\text{rate} = \frac{-\Delta \text{[AB]}}{\Delta t} = \frac{-(1.00 - 0.88)}{(0.0 - 10.0)} = 1.2 \times 10^{-2} \text{ M/s} \); \(\text{could also use the rate after ~20 seconds: \}\}\)

\(\text{rate} = \frac{-\Delta \text{[AB]}}{\Delta t} = \frac{-(1.00 - 0.76)}{(0.0 - 20.0)} = 1.2 \times 10^{-2} \text{ M/s}\}

b. \(k = 1.2 \times 10^{-2} \text{M}^{-1} \text{s}^{-1}\) \(\{\text{use: rate} = k[\text{AB}]^2; 1.2 \times 10^{-2} = k(1)^2; k = 1.2 \times 10^{-2} \text{M}^{-1} \text{s}^{-1}\}\)

c. rate would quadruple \(\{\text{since the order of A is 2, then rate} = k[\text{AB}]^2 \text{ and rate} = \text{[A]}^2 \rightarrow \text{rate} = (2)^2 = 4\}\)

d. rate \(= 1.5 \times 10^{-3} \text{ M/s}\) \(\{\text{rate} = k[\text{AB}]^2 \};\) rate \(= (1.2 \times 10^{-2})(0.35)^2 = 1.47 \times 10^{-3} \text{ M/s}\)

6. a. \(k[A]^n[B]^m\)

b. rate law \(= k[A]^2 \) \(\{\text{for [A]: Exp} 2 \text{ over 1:} \}\)

\(\frac{\text{rate}}{\text{rate}_1} = \frac{k[A]^2[B]^m}{k[A]^2[B]^m} ; \frac{1.6 \times 10^{-4}}{4.0 \times 10^{-5}} = \frac{k(0.20)^n(0.10)^m}{k(0.10)^n(0.10)^m} ; \frac{1.6 \times 10^{-4}}{4.0 \times 10^{-5}} \) \(\left(\frac{k}{k}\right) \left(\frac{0.20}{0.10}\right)^n \left(\frac{0.10}{0.10}\right)^m ; \left(4\right) = \left(1\right) \left(2\right)^n \left(1\right)^m ; n = 2^n \); \(n = 2\)

\(\text{for [B]: Exp} 3 \text{ over 1:} \) \(\frac{\text{rate}}{\text{rate}_1} = \frac{k[A]^n[B]^3}{k[A]^n[B]^3} ; \frac{4.0 \times 10^{-5}}{4.0 \times 10^{-5}} = \frac{k(0.10)^2(0.20)^m}{k(0.10)^2(0.10)^m} ; \frac{4.0 \times 10^{-5}}{4.0 \times 10^{-5}} \) \(\left(\frac{k}{k}\right) \left(\frac{0.10}{0.10}\right)^2 \left(\frac{0.20}{0.10}\right)^m ; \left(1\right) = \left(1\right) \left(2\right)^m ; m = 0\)

c. \(k = 4 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}\) \(\{\text{use any exp: Exp} 1: 4.0 \times 10^{-5} = k(0.10)^2(0.10)^0 ; k = 4 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}\}\)

d. \(n + m = 2 + 0 = 2\)

e. no change; not part of the rate law
7. a. rate = \(k[\text{CO}]^n[\text{Cl}_2]^m\)

b. rate = \(k[\text{CO}][\text{Cl}_2]^2\)  
   \{For [CO]: Exps 2 over 1: \(\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[\text{CO}]^{\text{n}}[\text{Cl}_2]^{\text{m}}}{k[\text{CO}]^{\text{1}}[\text{Cl}_2]^{\text{2}}}\); \(1.32 \times 10^{-2}/6.60 \times 10^{-3} = k(0.02)^{\text{n}}(0.01)^{\text{m}}/k(0.01)^{\text{n}}(0.01)^{\text{m}}\); \(1.32/6.60 = (k/0.02)^{n}(0.01)^{m}; (2) = (1)(2)^n(1)^m; 2 = 2^n; n = 1; \}

For [Cl2]: Exps 3 over 1: \(\frac{\text{rate}_3}{\text{rate}_1} = \frac{k[\text{Cl}_2]^{\text{3}}[\text{Cl}_2]^{\text{m}}}{k[\text{Cl}_2]^{\text{1}}[\text{Cl}_2]^{\text{1}}}\); \(2.64 \times 10^{-2}/6.60 \times 10^{-3} = k(0.01)^{\text{1}}(0.02)^{\text{m}}/k(0.01)^{\text{1}}(0.01)^{\text{1}}; 2.64/6.60 = (k/0.01)^{1}(0.02)^{m}; (4) = (1)(1)^{2}(2)^{m}; 4 = 2^{m}; m = 2\}

c. \(k = 6.60 \times 10^3 \text{ M}^{-2}\text{s}^{-1}\)  
   \{use any exp; exp 1: \(6.6 \times 10^{-3} = k(0.01)^{1}(0.01)^2; k = 6.6 \times 10^3 \text{ M}^{-2}\text{s}^{-1}\)}

d. \(n + m = 1 + 2 = 3\)

e. an increase by a factor of 8  
   \{rate = (2)^{1}(2)^{2} = 8\}

8. a. rate = \(k[\text{NO}]^n[\text{H}_2]^m\)

b. rate = \(k[\text{NO}][\text{H}_2]^2\)  
   \{For [NO]: Exps 2 over 1: \(\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[\text{NO}]^{\text{n}}[\text{H}_2]^{\text{2}}}{k[\text{NO}]^{\text{1}}[\text{H}_2]^{\text{2}}}\); \(1.13 \times 10^{-8}/1.26 \times 10^{-9} = k(4.5 \times 10^{-4})^{n}(2.0 \times 10^{-4})^{2}/k(1.5 \times 10^{-4})^{1}(2.0 \times 10^{-4})^{2}\); \(1.13/1.26 = (k/1.50)^1(4.5 \times 10^{-4})^{n}(2.0 \times 10^{-4})^{2}; (8.97) = (1)(3)^{n}(1)^{2}; 8.97 = 3^n; 9 = 3^n; n = 2; \}

For [H2]: Exps 3 over 1: \(\frac{\text{rate}_3}{\text{rate}_1} = \frac{k[\text{H}_2]^{\text{3}}[\text{H}_2]^{\text{m}}}{k[\text{H}_2]^{\text{1}}[\text{H}_2]^{\text{1}}}\); \(1.51 \times 10^{-8}/1.26 \times 10^{-9} = k(3.0 \times 10^{-4})^{3}(6.0 \times 10^{-4})^{2}/k(1.5 \times 10^{-4})^{2}(2.0 \times 10^{-4})^{2}\); \(1.51/1.26 = (k/1.50)^2(3.0 \times 10^{-4})^{3}; (11.98) = (1)(2)^{2}(3)^{3}; 11.98 = (4)(3)^{3}; 2.99 = 3^{m}; 3 = 3^{m}; m = 1\}

c. \(k = 280. \text{ M}^{-2}\text{s}^{-1}\)  
   \{use any exp; Exp 1: \(1.26 \times 10^{-9} = k(1.5 \times 10^{-4})^{2}(2 \times 10^{-4})^{1}; k = 280. \text{ M}^{-2}\text{s}^{-1}\)}

d. first order with respect to \(\text{H}_2\); second order with respect to \(\text{NO}\)

e. \(n + m = 2 + 1 = 3\)

f. an increase by a factor of 2  
   \{rate = (2)^{1/2} = 2\}

9. a. rate = \(k[\text{A}]^1[\text{B}]^0[\text{C}]^2 = k[\text{A}]^1[\text{C}]^2\)  
   \{for [A]: \(\frac{\text{rate}_1}{\text{rate}_2} = \frac{[\text{A}]^{\text{a}}}{[\text{A}]^{\text{2}}}\); \(3/1 = (3)^{\text{a}}/1^{\text{2}}; \) \(3 = 3^{\text{a}}; a = 1\); \}

For [B]: \(\frac{\text{rate}_1}{\text{rate}_2} = \frac{[\text{B}]^{\text{b}}}{[\text{B}]^{\text{1}}}\); \(1 = (2)^{\text{b}}/(1)^{\text{1}}\); \(1 = 2^{\text{b}}; b = 0; \) For [C]: \(\frac{\text{rate}_1}{\text{rate}_2} = \frac{[\text{C}]^{\text{c}}}{[\text{C}]^{\text{1}}}\); \(9/1 = (3)^{\text{c}}/1^{\text{1}}\); \(9 = 3^{\text{c}}; c = 2\}

b. \(k = 4.0 \times 10^{-6} \text{ 1/M}^2\text{s}\)  
   \{1 \times 10^{-4} = k(1)^{1}(2)^{0}(5)^{2}\}

c. The rate increases by a factor of 8.  
   \{rate = (2)^{1}(2)^{0}(2)^{2} = 8\}

10. a. rate = \(k[\text{A}]^2\)

b. \(\frac{1}{\text{M} \times \text{time}}\)  
   \{rate = k[\text{A}]^2; \text{M/time} = k(\text{M}^2); \text{solve for } k; k = \frac{1}{\text{M} \times \text{time}}\}

c. \(k = 1.0 \times 10^2 \text{ M}^{-1}\text{min}^{-1}\)  
   \{1 \times 10^{-2} = k(0.01)^2; \text{solve for } k; k = 1.0 \times 10^2\}

d. \(2.0 \times 10^{-2}\text{M/min}\)  
   \{\(1/(\text{rate A}) = \frac{1}{2}(\text{rate B})\); \(\text{rate B} = \frac{2}{1}(\text{rate A})\); \(\text{rate B} = 2(1.00 \times 10^{-2}) = 2.0 \times 10^{-2}\text{M/min}\}\}

e. \(0.25\text{M/min}\)  
   \{rate = k[\text{A}]^2; \text{rate } = (100)(0.05)^2 = 0.25\text{M/min}\}
11. a. rate = k[A]  
   b. 1/min \{rate = k[A]; M/min = k(M); solve for k; k = 1/(min)\}  
   c. k = 0.025 min^{-1} \{3.7 \times 10^{-3} = k(0.15); solve for k; k = 0.0247\}  
   d. 0.0025 M/min \{rate = k[A]; rate = \frac{2}{3}(3.7 \times 10^{-3}) \text{ M/min}\}  
   e. 0.024 M/min \{rate = k[A]; rate = (0.025)(0.15) = 0.0238 M/min\}  

12. a. \frac{[\text{NO}]}{[\text{Cl}_2]}_1 = \frac{[\text{NO}]}{[\text{Cl}_2]}_2  
   \quad 3 = \frac{(3)^n}{(1)^n}; \quad 3 = \frac{(3)}{(1)}; \quad 3 = 3^n; \quad n = 1  
   b. \frac{[\text{NO}]}{[\text{Cl}_2]}_1 = \frac{[\text{NO}]}{[\text{Cl}_2]}_2  
   \quad 2 = \frac{(0.5)^m}{(1)^m}; \quad 2 = \left(\frac{0.5}{1}\right)^m; \quad (2) = (0.5)^m; \quad m = 2  
   c. rate = k[\text{NO}]^1[\text{Cl}_2]^2  
   d. 21 M^{-2}s^{-1} \{1.5 \times 10^{-2} = k(0.12)^2; solve for k; k = 20.83\}  

13. a. 6.7 \times 10^{-5} M/s \{\text{take the point at } t = 0 \text{ and another point close to } t = 0; \text{ I choose } t = 3 \text{ sec}; \text{ determine rate } = \frac{-\Delta[C]}{\Delta t}; \text{ rate } = -(0.0080 - 0.0010)/(3.0 - 0.0) = 6.7 \times 10^{-5} M/s\}  
   b. 2.7 \times 10^{-4} M/s \{\text{by inspection, since } B \text{ has an order of 2, when the } [B] \text{ is doubled the rate will increase by a factor of 4; in this case, } rate_{\text{new}} = rate_{\text{old}} \times 4 = (6.7 \times 10^{-5})(4) = 2.7 \times 10^{-4} M/s; \text{ another way would be to first calculate } k \text{ from the information given in part } \text{“a”: } rate = k[B]^2[C]; \text{ rate } = (6.7 \times 10^{-5})(4)^2(0.0100) = 2.7 \times 10^{-4} M/s\}
Question
Using the graph below approximate the instantaneous rate at 30 seconds for the reaction: \( A \rightarrow B \)

Answer
Step 1. Draw a line tangent to the point at 30 seconds.

Step 2: Choose 2 points on the tangent line and estimate their coordinates.

Step 3: Using the coordinates to determine the slope of the tangent line which will be an approximate instantaneous rate at 30 seconds; rate = \(-\Delta[A]/\Delta t\).

\[
\text{Rate} = \frac{(0.003 - 0.001)}{14 - 42} = \frac{0.002}{-28} = 7 \times 10^{-5} \text{M/s}
\]