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$_{collisions}$ $\uparrow \rightarrow$ 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 = $\frac{\Delta [\text{concentration}]}{\Delta t}$ is just the slope on a graph of Concentration versus Time

**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 = $M/\text{time}$)

For products, 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 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 → B, the data below was collected.

- What is the initial rate of reaction of A?
- What is the average rate of reaction of A between 20 and 40 sec?
- What is the average rate of reaction of A at 50 sec?

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

**Answer 1:**

- a. Choose the value at time = 0.0 and the very next data point.
  
  \[ \text{rate} = \frac{-\Delta[A]}{\Delta t} = \frac{-(0.905 - 1.000)}{(10.0 - 0.0)} = \frac{-(-0.0950)}{0.00950} = 0.00950 \text{ M/s} \]

- b. Choose the 2 data points given in the question.
  
  \[ \text{rate} = \frac{-\Delta[A]}{\Delta t} = \frac{-(0.670 - 0.819)}{(40.0 - 20.0)} = \frac{-(-0.1495)}{0.00745} = 0.00745 \text{ M/s} \]

- c. Choose 2 data points closest that bracket the point of interest.
  
  \[ \text{rate} = \frac{-\Delta[A]}{\Delta t} = \frac{-(0.549 - 0.670)}{(60.0 - 40.0)} = \frac{-(-0.1210)}{0.00605} = 0.00605 \text{ M/s} \]

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

Relating the consumption of one reactant to the consumption of another reactant, to the formation of a product, or to the overall reaction rate involves using the **inverse of the stoichiometric coefficients placed in front of the rate of that chemical.** For the reaction: $2A + B \rightarrow 3C$ the relative rates are written:

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

\[
\text{rate}_\text{rxn} = \frac{1}{2} \text{(rate A)} = \frac{1}{3} \text{(rate B)} = \frac{1}{3} \text{(rate C)} 
\]

**Example 2:** For the reaction $2A + B \rightarrow 3C$, 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:**

\[
\frac{1}{3} \text{(rate C)} = \frac{1}{2} \text{(rate A)} \rightarrow \frac{1}{3} \text{(rate C)} = \frac{1}{2} \text{(rate A)} \rightarrow (3) \frac{1}{3} \text{(rate C)} = (3) \frac{1}{2} \text{(rate A)} \rightarrow \text{rate C} = \frac{3}{2} \left(3.5 \times 10^{-2}\right) = 5.25 \times 10^{-2} \text{ M/hr} 
\]

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

**Answer 3:**

\[
\text{rate}_\text{rxn} = \frac{1}{2} \text{(rate A)} = \frac{1}{2} \left(3.5 \times 10^{-2}\right) = 1.75 \times 10^{-2} \text{ M/hr} 
\]

(note: the rate of reaction is used in the rate law; see below. The only time the rate of reaction is not the same as the rate of a reactant is if the reactant has a coefficient other than 1 in front of it.)

**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: $\text{Rate} = k[A]^n[B]^m$; $n, m, \text{ and } k \text{ are determined experimentally}$

$n$ 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., $\frac{1}{2}$) and other values (e.g., -1)

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

**Example 4:** Determine the units of k for a second order reaction.

**Answer 4:** 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, hr, etc.); Rate is always $\frac{M}{s}$ and for $[A]$ use M; this yields: $M = k \text{M}^2$

Solve for $k$: $M = k \text{M}^2$; $\frac{M}{s} \left(\frac{1}{\text{M}^2}\right) = k \text{ M}^{-1} \left(\frac{1}{\text{M}^2}\right)$; $\frac{M}{s} \left(\frac{1}{\text{M}^2}\right) = k \text{M}^{-1} \left(\frac{1}{\text{M}^2}\right)$; $k = \left(\frac{1}{\text{M}s}\right)$ 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: \[
\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[A]^n[B]^m[C]^l}{k[A]^2[B]^2[C]^2}
\]

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 the 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 5: Determine the orders and k, and write the rate law for \( A + B \rightarrow C \) 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 \times 10^{-2}</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.20</td>
<td>8.0 \times 10^{-2}</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.10</td>
<td>4.0 \times 10^{-2}</td>
</tr>
</tbody>
</table>

Answer 5: 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 (Experiments 1 and 3 denoted as 1, or Experiments 1 and 2 denoted as 2)

\[
\frac{\text{rate}_3}{\text{rate}_1} = \frac{k[A]^n[B]^m}{k[A]^2[B]^2}, \text{ cancel k’s and insert #’s: } \frac{4.0 \times 10^{-2}}{2.0 \times 10^{-2}} = \frac{[0.20]^n(0.10)^m}{[0.10]^2(0.10)^m} ;
\]

\[
2 = \left( \frac{0.20}{0.10} \right)^n \left( \frac{0.10}{0.10} \right)^m = 2^n \times 1^m ; \quad 2 = 2^n ; \quad n = 1
\]

(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.)

2. Repeat for m with Experiments 1 and 2:

\[
\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[A]^n[B]^m}{k[A]^2[B]^2} ; \quad \frac{8.0 \times 10^{-2}}{2.0 \times 10^{-2}} = \frac{[0.10]^n(0.20)^m}{[0.10]^2(0.10)^m} ;
\]

\[
4 = \left( \frac{0.10}{0.10} \right)^n \left( \frac{0.20}{0.10} \right)^m = 1^n \times 2^m ; \quad 4 = 2^m ; \quad m = 2
\]

2. Rate law: Rate = \( k[A]^1[B]^2 \)

3. Solve for k: Plug in values from any exp (I chose Experiment 1) and solve for k; \( 2.0 \times 10^{-2} = k(0.10)^1(0.10)^2 \); solve for k; \( k = 20 \text{M}^{-2} \text{s}^{-1} \)
II. Description (not always classified as a “method” to solve the rate law but very important for understanding)

Example 6: 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 6: 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
\[
\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[A]^n[B]^m}{k[A]^n[B]^m} = \left(\frac{[A]}{[A]}\right)^n ;
\]

Let rate_2 and [A]_2 = 1, and change rate_1 and [A]_1 to match the information provided in I and solve: \(\frac{4}{1} = \left(\frac{2}{1}\right)^n ; 4 = 2^n ; n = 2\)

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

Let rate_2 and [B]_2 = 1, and change the rate_1 and [B]_1 to match the information provided in II and solve: \(\frac{1}{1} = \left(\frac{2}{1}\right)^m ; 1 = 2^m ; m = 0\)

3. Rate = k[A]^2[B]^0; Rate = k[A]^2

1. Assume the following reaction occurs as follows: 2NO_2(g) → 2NO(g) + 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 NO_2?
b. What is the average rate of consumption of NO_2 between 50sec and 150sec?
c. What is the concentration of NO_2 at 150sec?
d. What is the average rate of consumption of NO_2 at 150sec?
e. What is the concentration of NO_2 at 350sec?
f. What is the average rate of consumption of NO_2 at 350sec?
g. Explain why the rate of consumption of NO_2 is dropping.

2. For the reaction N_2(g) + 3H_2(g) → 2NH_3(g), the rate of consumption of N_2 is 6.0 \times 10^{-2}M/min.
a. What is the rate of consumption for H_2?
b. What is the rate of formation for NH_3?

c. What is the rate of consumption for H_2?

3. If the rate of appearance of O_2 is 3.25 \times 10^{-5}M/min, what is the rate of disappearance of O_3?
   \[2O_3(g) \rightarrow 3O_2(g)\]
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, \(\text{AB} \rightarrow \text{A} + \text{B}\), 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 as: \(\text{rate} = k[\text{AB}]^2\)
   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 \([\text{AB}] = 0.35\text{M}\) what would the rate of reaction be?

![Graph with [AB] versus time](image)

6. A general reaction written as \(\text{A} + \text{B} \rightarrow \text{AB}\) is studied and yields the following data:

<table>
<thead>
<tr>
<th>Exp.</th>
<th>([\text{A}]_0)</th>
<th>([\text{B}]_0)</th>
<th>Rate_{rxn} (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 \(\text{A}\) and \(\text{B}\)?
   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 \(\text{B}\) doubles.

7. The following reaction, \(\text{CO} + \text{Cl}_2 \rightarrow \text{COCl} + \text{Cl}\) was studied by the method of initial rates.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>([\text{CO}]_0)</th>
<th>([\text{Cl}_2]_0)</th>
<th>Rate_{rxn} (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 \(\text{CO}\) and \(\text{Cl}_2\)?
   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. (This is the harder version of an initial rates method question.) The reaction of NO with H$_2$ was followed and the data collected shown below.

\[ 2\text{NO}(g) + \text{H}_2(g) \rightarrow \text{N}_2\text{O}(g) + \text{H}_2\text{O}(g) \]

<table>
<thead>
<tr>
<th>Exp.</th>
<th>[NO]</th>
<th>[H$_2$]</th>
<th>Rate$_{rxn}$ (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.50 x 10$^{-4}$ M</td>
<td>2.00 x 10$^{-4}$ M</td>
<td>1.26 x 10$^{-9}$</td>
</tr>
<tr>
<td>2</td>
<td>4.50 x 10$^{-4}$ M</td>
<td>2.00 x 10$^{-4}$ M</td>
<td>1.13 x 10$^{-8}$</td>
</tr>
<tr>
<td>3</td>
<td>3.00 x 10$^{-4}$ M</td>
<td>6.00 x 10$^{-4}$ M</td>
<td>1.51 x 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, A + B + C → D

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 M, B = 2.0 M, and C = 5.0 M and the rate is 1.0 x 10$^{-4}$ 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. When the concentration of A is 0.010M the rate of consumption of A is 1.0 x 10$^{-2}$ M/min. What is the value of the rate constant? Include units.
c. When the concentration of A is 0.010M 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?
d. When the concentration of A is increased to 0.050M, 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. When the concentration of A is 0.15M the rate of reaction is 3.7 x 10$^{-3}$ M/min, what is the value of the rate constant? Include units.
c. When the concentration of A is 0.50M what is the rate of consumption of A?
d. What is the rate of production of B at this time?

12. The following reaction, 2NO + Cl$_2$ → 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 Cl$_2$ was doubled, the rate doubled.

a. What is the order of NO?
b. What is the order of Cl$_2$?
c. What is the rate law?
d. When [NO] = 0.050M and [Cl$_2$] = 0.12M, the rate was 1.5 x 10$^{-2}$. What is the rate constant?
13. a. A reaction was run: \( B + C \rightarrow BC \). When \([B] = 2.0\text{M}\) and \([C] = 0.0100\text{M}\), the following graph of \([C]\) versus time was experimentally determined. Using the graph below, estimate the initial rate of reaction. 

![Graph of[C] versus Time](image)

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

**ANSWERS**

1. a. \( 4.2 \times 10^{-5} \text{M/s} \)

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

b. \( 2.4 \times 10^{-5} \text{M/s} \)

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

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

d. \( 1.7 \times 10^{-5} \text{M/s} \)

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

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

f. \( 0.70 \times 10^{-5} \text{M/s} \)

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

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

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

\[ \frac{1}{3} \text{(rate H}_2) = \frac{1}{3} \text{(rate H}_3) ; \text{rate H}_2 = 3(6.0 \times 10^{-2}) = 1.8 \times 10^{-1} \text{M/min}\]

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

\[ \frac{1}{2} \text{(rate N}_2) = \frac{1}{2} \text{(rate NH}_3) ; \text{rate NH}_3 = 2(6.0 \times 10^{-2}) = 1.2 \times 10^{-1} \text{M/min}\]

3. rate of appearance \( \text{O}_3 = 2.17 \times 10^{-5} \text{M/min} \)

\[ \frac{1}{3} \text{(rate O}_3) = \frac{1}{3} \text{(rate O}_2) ; \text{rate O}_3 = \frac{2}{3}(3.25 \times 10^{-5}) = 2.17 \times 10^{-5} \text{M/s}\]

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. $1.2 \times 10^{-2}$ M/s (use the graph and use 2 data points: one at time = 0 and a second time that is close to zero; 
rate $= \frac{-\Delta [AB]}{\Delta t} = \frac{-(1.00 - 0.88)}{(0.0 - 10.0)} = 1.2 \times 10^{-2}$ M/s ;

could also use the rate after ~20 seconds: rate $= \frac{-\Delta [AB]}{\Delta t} = \frac{-(1.00 - 0.76)}{(0.0 - 20.0)} = 1.2 \times 10^{-2}$ M/s }

b. $k = 1.2 \times 10^{-2}$ M$^{-1}$s$^{-1}$ (use: rate $= k[AB]^2$ and the initial rate information; $1.2 \times 10^{-2} = k(1.00)^2; k = 1.2 \times 10^{-2}$ M$^{-1}$s$^{-1}$;)

c. rate would quadruple (from the rate law given rate $= k[AB]^2$: since the order of A is 2 and rate $\propto [A]^2 \rightarrow$ rate $= (2)^2 = 4$
where the [AB] = 2 represents doubling the concentration)

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

6. a. rate $= k[A]^n[B]^m$

b. rate law $= k[A]^2$ (for [A]: Exps 2 over 1: 
rate$_2$ $= \frac{k[A]^n[B]^m}{k[A]^n[B]^m}; 1.6 \times 10^{-4} = \frac{k(0.20)^n(0.10)^m}{k(0.10)(0.10)^m};$

$\frac{1.6 \times 10^{-4}}{4.0 \times 10^{-5}} = \left( \frac{k}{k} \right) \left( \frac{0.20}{0.10} \right) \frac{n}{m}; (4) = (1)(2)^n(1)^m; 4 = 2^n, n = 2;

for [B]: Exps 3 over 1: 
rate$_3$ $= \frac{k[A]^n[B]^m}{k[A]^n[B]^m}; 4.0 \times 10^{-5} = \frac{k(0.10)^2(0.20)^m}{k(0.10)^2(0.10)^m}; 4.0 \times 10^{-5} = \left( \frac{k}{k} \right) \left( \frac{0.10}{0.10} \right)^2 \frac{2}{0.20};$

$(1) = (1)(1)^2(2)^m; 1 = 2^m, m = 0$

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

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

e. no change; not part of the rate law

7. a. rate $= k[CO][Cl_2]^m$

b. rate $= k[CO][Cl_2]^2$ (For [CO]: Exps 2 over 1: 
rate$_2$ $= \frac{k[CO]^n[Cl_2]^m}{k[CO]^n[Cl_2]^m}; 1.32 \times 10^{-2} = \frac{k(0.02)^n(0.01)^m}{k(0.01)^n(0.01)^m};$

$\frac{1.32 \times 10^{-2}}{6.60 \times 10^{-3}} = \left( \frac{k}{k} \right) \left( \frac{0.02}{0.01} \right)^n \left( \frac{0.01}{0.01} \right)^m; (2) = (1)(2)^n(1)^m; 2 = 2^n, n = 1;

For [Cl$_2$]: Exps 3 over 1: 
rate$_3$ $= \frac{k[CO]^n[Cl_2]^m}{k[CO]^n[Cl_2]^m}; 2.64 \times 10^{-2} = \frac{k(0.01)^1(0.02)^m}{k(0.01)^1(0.01)^m}; 2.64 \times 10^{-2} = \left( \frac{k}{k} \right) \left( \frac{0.01}{0.01} \right)^1 \left( \frac{0.02}{0.01} \right)^m;

$(4) = (1)(1)^1(2)^m; 4 = 2^m, m = 2$

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

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

e. an increase by a factor of 8 (rate $= (2)^1(2)^2 = 8$)
8. a. \( \text{rate} = k[\text{NO}]^n[\text{H}_2]^m \)

b. \( \text{rate} = k[\text{NO}]^2[\text{H}_2] \)  
   \{For [NO]: Exps 2 over 1, \}\n   \begin{align*}
   \frac{\text{rate}_2}{\text{rate}_1} &= \frac{k[\text{NO}]^n[\text{H}_2]^m}{k[\text{NO}]^n[\text{H}_2]^m} ; \\
   1.13 \times 10^{-8} &= k(4.50 \times 10^{-4})^n(2.00 \times 10^{-4})^m; \\
   \frac{1.13 \times 10^{-8}}{1.26 \times 10^{-9}} &= \left( \frac{k}{k} \right) \left( \frac{4.50 \times 10^{-4}}{1.50 \times 10^{-4}} \right)^n \left( \frac{2.00 \times 10^{-4}}{2.00 \times 10^{-4}} \right)^m; \\
   8.97 &= (3)^n(1)^m; 8.97 = 3^n; 9 = 3^n; n = 2;
   \end{align*}

For [H2]: Exps 3 over 1:
\begin{align*}
   \frac{\text{rate}_3}{\text{rate}_1} &= \frac{k[\text{NO}]^n[\text{H}_2]^m}{k[\text{NO}]^n[\text{H}_2]^m} ; \\
   1.51 \times 10^{-8} &= k(3.00 \times 10^{-4})^2(6.00 \times 10^{-4})^m; \\
   \frac{1.51 \times 10^{-8}}{1.26 \times 10^{-9}} &= \left( \frac{k}{k} \right) \left( \frac{3.00 \times 10^{-4}}{1.50 \times 10^{-4}} \right)^2 \left( \frac{6.00 \times 10^{-4}}{2.00 \times 10^{-4}} \right)^m; \\
   11.98 &= (2)^2(3)^m; 11.98 = (4)(3)^m; 2.99 = 3^m; 3 = 3^m; m = 1
\end{align*}

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 H2; second order with respect to NO

e. 3 \( [n + m = 2 + 1 = 3] \)
f. an increase by a factor of 2 \( \{\text{rate} = (2)^2(1/2)^1 = 2\} \)

9. a. \( \text{rate} = k[\text{A}]^a[\text{B}]^b[\text{C}]^2 = k[\text{A}]^a[\text{C}]^2 \)  
   \{for [A]: \}
   \begin{align*}
   \frac{\text{rate}_1}{\text{rate}_2} &= \frac{[\text{A}]^a}{[\text{A}]^a} ; \\
   3 &= \frac{(3)^a}{(1)^a} ; 3 = 3^a; a = 1;
   \end{align*}

   \begin{align*}
   \text{For [B]:} & \quad \frac{\text{rate}_1}{\text{rate}_2} = \frac{[\text{B}]^b}{[\text{B}]^b} ; \\
   1 &= \frac{(2)^b}{(1)^b} ; 1 = 2^b; b = 0;
   \end{align*}

   \begin{align*}
   \text{For [C]:} & \quad \frac{\text{rate}_1}{\text{rate}_2} = \frac{[\text{C}]^2}{[\text{C}]^2} ; \\
   9 &= \frac{(3)^c}{(1)^c} ; 9 = 3^c; c = 2
   \end{align*}

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

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

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

b. \( k = 1.0 \times 10^{2}\text{M}^{-1}\text{min}^{-1} \) \{\( 1.0 \times 10^{-2}\text{M}/\text{min} = k(0.010\text{M})^2 \); solve for \( k = 1.0 \times 10^{2}\text{min}^{-1} \) \}

c. \( 2.0 \times 10^{-2} \text{M}/\text{min} \) \{\( \frac{1}{2}\text{rate A} = \frac{1}{2}\text{rate B} \); \( \text{rate B} = \frac{2}{3}\text{rate A} \); \( \text{rate B} = 2(1.00 \times 10^{-2}) = 2.0 \times 10^{-2}\text{M}/\text{min} \) \}

d. \( 0.25 \text{M}/\text{min} \) \( \{\text{rate}_{\text{rxn}} = k[\text{A}]^2; \text{rate}_{\text{rxn}} = (1.0 \times 10^{2}) (0.050)^2 = 0.25\text{M}/\text{min}; \text{rate}_{\text{rxn}} = \frac{1}{1}\text{(rate A)} = \text{rate A} = 0.25 \text{M}/\text{min} \) \}

11. a. \( \text{rate} = k[\text{A}]^1 \)

b. \( k = 0.025\text{min}^{-1} \) \{\( 3.7 \times 10^{-3}\text{M}/\text{min} = k(0.15\text{M}) \); solve for \( k = 0.0247\text{min}^{-1} \) \}

c. \( 0.0375\text{M}/\text{min} \) \{\( \frac{1}{3}\text{rate A} = \frac{1}{3}\text{rate B} \); \( \text{rate B} = \frac{2}{3}\text{rate A} \); \( \text{rate B} = 2(0.0375) = 0.075 \text{M}/\text{min} \) \}

d. \( 0.025\text{M}/\text{min} \) \{\( \frac{1}{3}\text{rate A} = \frac{1}{3}\text{rate B} \); \( \text{rate B} = \frac{2}{3}\text{rate A} \); \( \text{rate B} = 2(0.025) = 0.050\text{M}/\text{min} \) \}

12. a. \( \{\text{for [A]}: \}
   \begin{align*}
   \frac{\text{rate}_1}{\text{rate}_2} &= \frac{[\text{NO}]^n}{[\text{NO}]^n} ; \\
   3 &= \frac{(3)^n}{(1)^n} ; 3 = 3^n; n = 1
   \end{align*}

b. \( \{\text{rate}_1 = k[\text{NO}]^n[\text{Cl}_2]^m \); \( \frac{\text{rate}_1}{\text{rate}_2} = \frac{k[\text{NO}]^n[\text{Cl}_2]^m}{k[\text{NO}]^n[\text{Cl}_2]^m} ; \\
   2 &= \frac{(0.5)^1(2)^m}{(1)^1(1)^m} ; 2 = \left( \frac{0.5}{1} \right) \left( \frac{2}{1} \right)^m; (2) = (0.5)^1(2)^m; 4 = 2^m; m = 2 \)

c. \( \text{rate} = k[\text{NO}]^1[\text{Cl}_2]^2 \)

d. \( 21 \text{M}^{-2}\text{s}^{-1} \) \{\( 1.5 \times 10^{-2} = k(0.05)^1(0.12)^2 \); solve for \( k = 20.83 \) \}
13. a. 6.7 x 10^{-5} \text{M/s} \quad \{\text{take the point at } t = 0 \text{ and another point close to } t = 0; \text{ I choose } t = 3\text{sec; determine rate } = -\Delta C/\Delta t; \text{ rate } = -(0.0080 - 0.0010)/(3.0 - 0.0) = 6.7 \times 10^{-5} \text{M/s}\}

b. 2.7 \times 10^{-4} \text{M/s} \quad \{\text{by inspection, since B has an order of 2, when the } [B] \text{ is doubled the rate will increase by a factor of 4; in this case, } \text{rate}_{\text{new}} = \text{rate}_{\text{old}} \times 4 = (6.7 \times 10^{-5})(4) = 2.7 \times 10^{-4} \text{M/s}; \text{ another way would be to first calculate } k \text{ from the information given in part “a”: rate } = k[B]^2[C]; 6.7 \times 10^{-5} = k[2.0]^2[0.0100]; k = 1.7 \times 10^{-3}; \text{ for part “b” now solve for the new rate with the known } k \text{ and concentrations: rate } = k[B]^2[C]; \text{ rate } = (1.7 \times 10^{-3})(4.0)^2(0.0100) = 2.7 \times 10^{-4} \text{M/s}\}
ESTIMATING INSTANTANEOUS RATE

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 = \( -\Delta[A]/\Delta t \).

Rate = \( -\left( \frac{0.003 - 0.001}{42 - 44} \right) = \left( \frac{0.002}{-28} \right) = 7 \times 10^{-5} \text{ M/s} \)