

Kinetics

UNIT 2: KINETICS OUTCOMES

All important vocabulary is in Italics and bold.

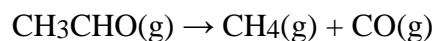
- Formulate an operational definition of **reaction rate**.
Include: examples of chemical reactions that occur at different rates.
- Identify **variables** used to monitor reaction rates (i.e. change per unit time, x/t).
Examples: pressure, temperature, pH, conductivity, color.
- Perform a lab to measure the average and instantaneous rate of a chemical reaction.
- Compare the rate of formation of a product to the rate of disappearance of a reactant given experimental rate data and reaction stoichiometry.
- Perform a lab to identify factors that affect the rate of a chemical reaction.
Include: nature of reactants, surface area, concentration, pressure, volume, temperature, and presence of a catalyst.
- Use the **Collision Theory** to explain the rate of chemical reactions. *Include: Activation energy*
- Draw potential energy diagrams for endothermic and exothermic reactions.
*Include: relative rates, effect of a catalyst, heat of reaction (**enthalpy**)*
- Describe qualitatively the relationship between factors which affect the rate of chemical reactions and the relative rate of a reaction using the *Collision Theory*.
- Explain the concept of a **reaction mechanism**.
Include: rate determining step, potential energy diagrams
- Determine the **rate law** and order of a chemical reaction from experimental data.
Include: various reaction orders, rate versus concentration graphs.
- Explain the scientific process connecting a chemical reaction to its experimental rate law, and to the prediction of an appropriate reaction mechanism.
Include: connecting the rate law to the RDS

Additional KEY Terms

Transition state	Elementary reaction
Bimolecular	Reaction intermediate

Part A

1. The decomposition of acetaldehyde to methane and carbon dioxide occurs according to the following equation:



The results of an experiment are given below:

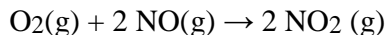
Time (s)	[CH ₃ CHO] (mol/L)
42	0.00667
73	0.00626
1050	0.00586
1900	0.00505
2420	0.00464
3100	0.00423
3840	0.00383
4800	0.00342
6650	0.00282
840	0.00241

- a. What is the rate of decomposition of acetaldehyde between 42 s and 105 s?

- b. What is the rate of decomposition in the interval 190 s to 480 s?

Part B – Hand in Project.

The formation of nitrogen dioxide from nitrogen dioxide and oxygen gas was studied. The balanced equation for the reaction is:



Below is the measured concentration of the three gases at various time intervals. Construct a well labeled graph (labeled axis with units, a title, etc.) to represent this data. Plot gas concentration on the Y-axis and time on the X-axis.

Purpose: To understand the connection between a balanced chemical equation, calculated rate data and graphical information of the reaction.

Time (min)	Concentration (mol/L)		
	O ₂	NO	NO ₂
0.0	0.000343	0.000514	0.000000
2.0	0.000317	0.000461	0.000053
4.0	0.000289	0.000406	0.000108
6.0	0.000271	0.000368	0.000146
10.0	0.000242	0.000311	0.000204
16.0	0.000216	0.000259	0.000256
26.0	0.000189	0.000206	0.000308
41.0	0.000167	0.000162	0.000353
51.0	0.000158	0.000143	0.000372
61.0	0.000150	0.000127	0.000387
71.0	0.000144	0.000116	0.000399

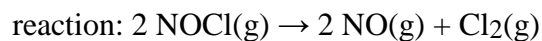
1. What is the average rate of nitrogen oxide, nitrogen dioxide, and oxygen over the entire 71 minute interval? Determine the average rate for each.
2. Find the instantaneous rates of consumption of NO and of formation of NO₂ at 4 minutes and 41 minutes into the experiment.

NOTE: Instantaneous rates are determined by drawing a tangent line to the curve at the point of interest and determining the slope of the tangent line using *2 point - rise/run calculations* (**rise** – [], **run** – **time**)

Conclusion: How does your calculated rate data compare to the slope of each curve seen on the graph compared to each other. How does the data compare to the balanced equation for this reaction?

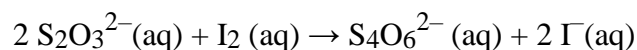
ANSWER THE FOLLOWING QUESTIONS ON STOICHIOMETRY AND RATE OF REACTION:

1. If NOCl(g) is decomposing at a rate of $1.1 \times 10^{-8} \text{ mol/L/min}$ in the following



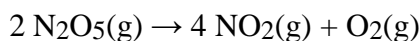
- What is the rate of formation of NO(g) ?
- What is the rate of formation of $\text{Cl}_2\text{(g)}$?

2. Thiosulfate ion is oxidized by iodine according to the following reaction:

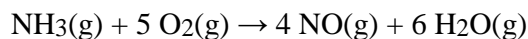


If, in a certain experiment, 0.0080 mol of $\text{S}_2\text{O}_3^{2-}$ is consumed in 1.0 L of solution each second, What is the rate of consumption of I_2 ? At what rates are $\text{S}_4\text{O}_6^{2-}$ and I^- produced in this solution?

3. If the decomposition of N_2O_5 gas occurs at a rate of $0.20 \text{ molL}^{-1}\text{s}^{-1}$, what would be the rate of formation of NO_2 gas and O_2 gas if the equation for the reaction is



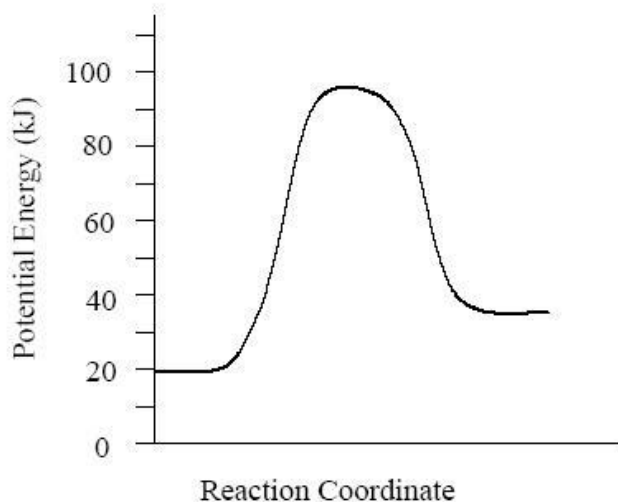
4. If ammonia gas, NH_3 , reacts at a rate of 0.090 mol/Ls according to the reaction 4



- at what rate does oxygen gas react under the same conditions?
- what is the rate of formation of water?
- what is the rate of production of nitrogen monoxide?

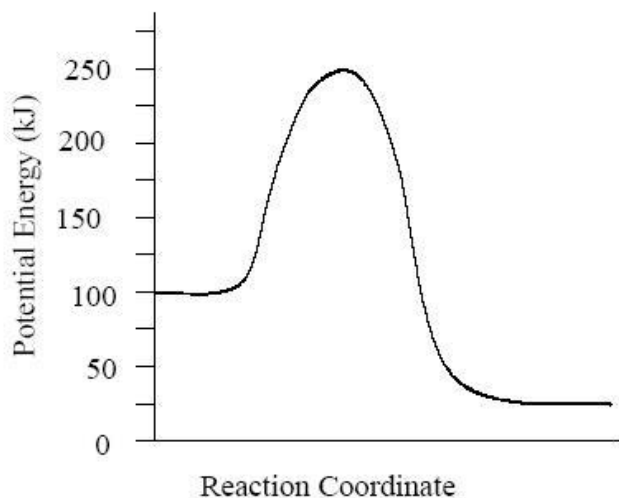
Collision Theory Worksheet

1.



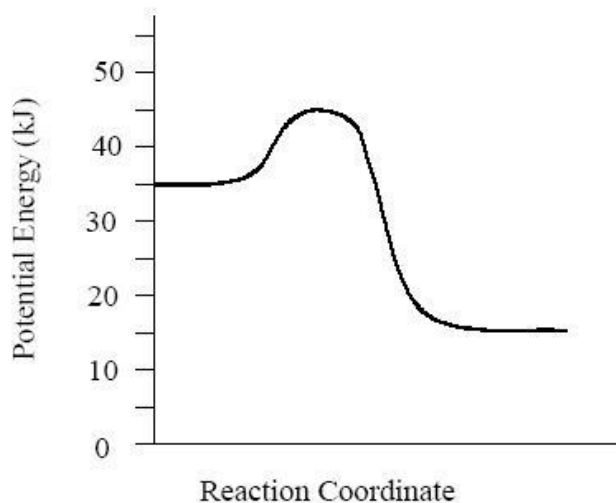
- What is the activation energy of the reaction shown by the diagram to the left?
- What is the enthalpy change for this reaction?
- Is this reaction endothermic or exothermic?

2.



- What is the activation energy of the reaction in the diagram to the left?
- What is the enthalpy change for this reaction?
- Is this reaction endothermic or exothermic?
- What would be the activation energy of the reverse reaction?

3.



- What is the activation energy of the diagram to the left?
- What is the enthalpy change for this reaction?
- Is this reaction endothermic or exothermic?
- What would be the activation energy of the reverse reaction?

Questions:

1. Describe how the activation energy of a reaction affects the overall rate of the chemical reaction.
2. What is the activated complex or transition state and how is it related to reaction rates? Label the position of the activated complex in each of the diagrams above.
3. Use your knowledge of collision theory and activation energy to explain why gasoline can mix with air and not ignite while sitting alone, but explodes in the cylinder of an engine or ignites when it is touched by a flame.
4. Does every collision between reactant particles produce a reaction? Explain.
5. Explain why the enthalpy change for an exothermic reaction is negative, even though the container gets warmer.

ANSWER THE FOLLOWING QUESTIONS ON FACTORS THAT AFFECT RATE:

1. In general, what effect does an increase in the concentration of the reactants have on the rate of the reaction? (explain using the collision theory)
2. How do changes each of the following factors affect the rate of a chemical reaction? Use diagrams to clarify your explanations.
 - a. Temperature
 - b. particle size
 - c. pressure
3. How does a catalyst influence the rate of a reaction? How do catalysts make this possible? Illustrate your answer with a specific example. Draw a diagram.
4. Which equation of the following pairs of equations would occur the fastest at under the same conditions? Explain your answers.
 - a. i) $\text{Zn}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \rightarrow \text{ZnS}(\text{s})$
ii) $\text{Zn}(\text{s}) + \text{S}(\text{s}) \rightarrow \text{ZnS}(\text{s})$
 - b. i) $2 \text{H}_2\text{O}_2(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
ii) $\text{Cu}(\text{s}) + 2 \text{AgNO}_3(\text{aq}) \rightarrow 2 \text{Ag}^+(\text{aq}) + \text{Cu}(\text{NO}_3)_2(\text{aq})$
 - c. i) $\text{Pb}(\text{NO}_3)_2(\text{aq}) + 2 \text{KI}(\text{aq}) \rightarrow \text{PbI}_2(\text{aq}) + 2 \text{KNO}_3(\text{aq})$
ii) $\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{g})$
 - d. i) $2 \text{Fe}(\text{s}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{Fe}_2\text{O}_3(\text{s})$
ii) $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$

CATALYSTS AND LIFE

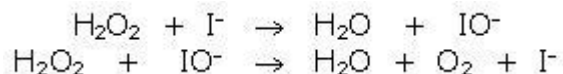
Do some research on the internet and find these answers:

1. Define the following terms:
 - a. Catalyst
 - b. Enzyme
2. What is a catalytic converter designed to do?
3. List, in words, the reactions that take place inside a catalytic converter:
4. List three functions of enzymes in the human body:
5. Your saliva has a special enzyme called *amylase*, what reaction involves this enzyme?
6. Why does one large piece of bread take longer to digest than several small pieces?
7. Parents often tell their children to chew their food. Explain in scientific terms, why this is a good idea?

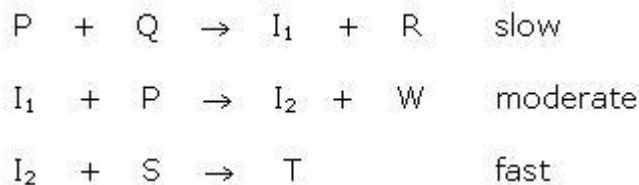
ANSWER THE FOLLOWING QUESTIONS ON RATE MECHANICS:

1. Using what you know of the Collision Theory, explain why the reaction $2A + B \rightarrow C$ would be unlikely to occur in one step?

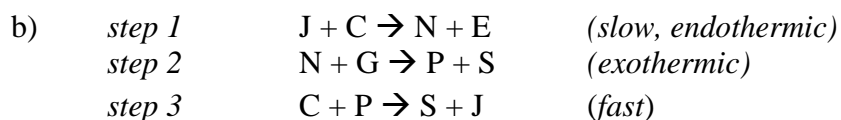
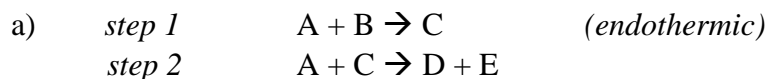
2. Given the following reaction mechanism:

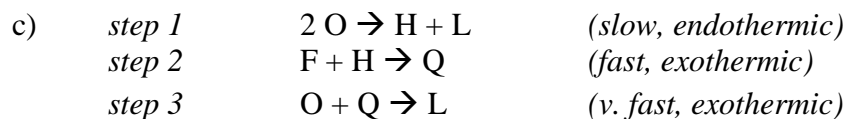


- a) Write the balanced net reaction.
b) Identify the reaction intermediate(s).
c) Identify the catalyst(s)
3. Examine the following reaction mechanism:

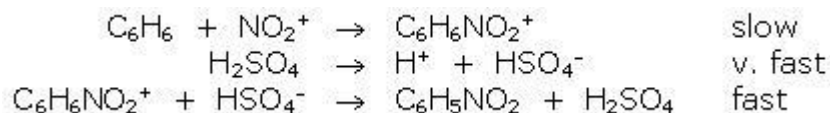


- a) Write out the net reaction.
b) Increasing $[\text{P}]$, increases the rate of the net reaction.
Increasing $[\text{Q}]$, increases the rate of the net reaction. Increasing $[\text{S}]$, has no effect of the rate.
Explain why this is possible.
4. Given the following elementary steps, determine the overall reaction mechanism, highlight any intermediates or catalysts, and draw a possible Potential Energy diagram of the overall reaction (assuming overall reaction is exothermic).



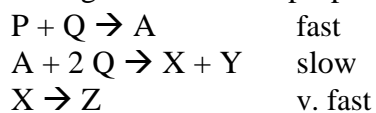


5. A proposed mechanism for the preparation of the poisonous liquid nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) is



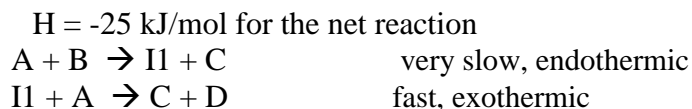
- What is the RDS? Why?
- What is the net reaction?
- Without H_2SO_4 this is a very slow reaction. Explain
- Draw a PE diagram to represent this reaction.

6. The following mechanism is proposed for a reaction:



- What would happen to the rate as the concentration of Q was increased?
- Write the net reaction.
- What is the RDS? Why?
- Why might step 2 be slower?

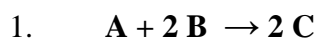
7. Draw the 'reaction progress' (reaction coordinate) diagram to illustrate the following reaction mechanism. Write the net reaction for the mechanism.



Rate Law Practice

Instructions:

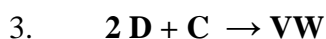
Given the overall reaction stoichiometry, and the experimentally determined initial rate data, write the rate law and determine the value of k for each.



[A] mol/L	[B] mol/L	Rate (mol/Lmin)
1.0	1.0	0.50
2.0	1.0	4.0
2.0	2.0	8.0



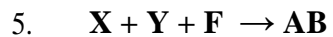
[M] mol/L	[N] mol/L	Rate (molL ⁻¹ min ⁻¹)
0.50	1.0	0.48
0.50	2.0	0.96
2.5	1.0	2.40



[D] mol/L	[C] mol/L	Rate (mol/Lmin)
0.25	0.75	2.2
0.50	0.75	2.2
0.25	1.50	8.8



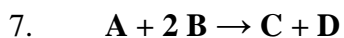
[A] mol/L	[B] mol/L	[C] mol/L	Rate (mol/Lmin)
1.0	2.0	0.50	0.35
2.0	2.0	0.50	1.40
2.0	1.0	0.50	1.40
1.0	2.0	1.0	0.70



[X] mol/L	[Y] mol/L	[F] mol/L	Rate (mol/Lmin)
0.45	0.20	0.55	0.66
1.35	0.20	0.55	5.94
0.45	0.60	0.55	1.98
0.45	0.60	1.10	1.98



Trial	[A] _i mol/L	[B] _i mol/L	Initial Rate (molL ⁻¹ s ⁻¹)
1	0.25	0.060	0.041
2	0.75	0.060	0.12
3	0.50	0.12	0.16



Trial	[A] _i mol/L	[B] _i mol/L	Initial Rate (molL ⁻¹ s ⁻¹)
1	0.0100	0.0240	1.45 x 10 ⁻⁴
2	0.0100	0.0120	7.25 x 10 ⁻⁵
3	0.0200	0.0480	5.80 x 10 ⁻⁴



Trial	[A] _i mol/L	[B] _i mol/L	Initial Rate (molL ⁻¹ h ⁻¹)
1	0.0012	0.042	3.6 x 10 ⁻²
2	0.00060	0.084	3.6 x 10 ⁻²
3	0.00060	0.021	9.0 x 10 ⁻³

9. The reaction $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$ is run in the presence of an excess of acid. The following data were obtained:

Trial	Initial [I ₂] (mol/L)	Initial [CH ₃ COCH ₃] (mol/L)	Initial Rate (mol/L s)
1	0.100	0.100	1.16 x 10 ⁻⁷
2	0.100	0.0500	5.79 x 10 ⁻⁸
3	0.500	0.0500	5.77 x 10 ⁻⁸

ANSWER KEY

1. k = 0.50 2. k = 0.96 3. k = 3.9 4. k = 0.70 5. k = 16 6. k = 2.7 7. k = 0.600 8. k = 710
9. k = 1.16 x 10⁻⁶

More Rate Law Practice

1. A *second-order* reaction initially proceeds at a rate of 0.500 mol/Ls . What will be the rate when half the starting material remains? When a quarter of the starting material remains?

2. The following experimental data was recorded for the *elementary* reaction $2\text{A} \rightarrow \text{B}$.

[A] (mol/L)	Rate (mol/L•s)
0.050	3.0×10^{-4}
0.10	1.2×10^{-3}
0.20	4.8×10^{-3}
x	6.5×10^{-2}

- Using the data given, determine the order of the reaction with respect to A?
- What is the overall order of reaction?
- Write the rate law for this reaction.
- Calculate k . (**0.12**)
- Calculate the concentration of A for trial 4. ($7.4 \times 10^{-1} \text{ mol/L}$)

3. The reaction



Was studied and the following data were obtained:

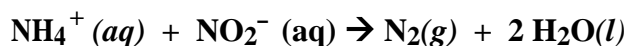
Trial	[I ⁻] (mol/L)	[OCl ⁻] (mol/L)	Initial Rate (mol/L•s)
1	0.12	0.18	7.91×10^{-2}
2	0.060	0.18	3.95×10^{-2}
3	0.24	0.090	7.91×10^{-2}
4	0.060	0.090	1.98×10^{-2}
5	0.085	0.105	X

- What is the rate law?
- Is this an elementary reaction? How do you know?
- What is the value of the rate constant? (**3.7**)
- What is the rate of trial 5? ($3.3 \times 10^{-2} \text{ mol/L}$)

4. The reaction: $A + B + C \rightarrow E + F + G$
 Was studied at 0°C and the following data was collected

Trial	[A] (mol/L)	[B] (mol/L)	[C] (mol/L)	Initial Rate (mol/L•s)
1	1.0	2.0	2.0	1.66
2	2.0	2.0	2.0	3.33
3	1.0	4.0	2.0	6.66
4	1.0	1.0	4.0	0.42

- a) Determine the rate law for this reaction and find the value of k . (**0.42**)
 b) What is the rate if $[A] = 1.5 \text{ mol/L}$, $[B] = 2.5 \text{ mol/L}$, $[C] = 0.25 \text{ mol/L}$?
 c) What is the stoichiometry of the reactants in the Rate Determining Step?
5. Ammonium ions and nitrate ions react in water to form nitrogen gas.



The following experimental data was recorded:

$[\text{NO}_2^-]$ (mol/L)	$[\text{NH}_4^+]$ (mol/L)	Rate (mol/L•s)
0.0100	0.200	5.40×10^{-7}
0.0200	0.200	1.08×10^{-6}
0.0400	0.200	2.15×10^{-6}
0.200	0.0202	1.08×10^{-6}
0.200	0.0404	2.16×10^{-6}
0.200	0.0606	3.24×10^{-6}

- a) What is the order of the reaction with respect to NH_4^+ and NO_2^- ?
 b) What is the overall order of the reaction?
 c) Write the rate law for the reaction.
 d) Is this an elementary reaction?
 e) What is k for the reaction? (**2.70×10^{-4}**)
 f) What is the rate of reaction if $[\text{NO}_2^-]$ is 0.300 mol/L and $[\text{NH}_4^+]$ is 0.0200 mol/L ?
6. Assume the $\text{N}_2\text{O}(\text{g})$ and $\text{O}_2(\text{g})$ react according to the rate

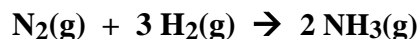
$$\text{law Rate} = k[\text{N}_2\text{O}] [\text{O}_2]$$

How does the rate change if:

- a) the concentration of O is doubled?
 b) the volume of the enclosing vessel is reduced by half?
 c) the temperature is decreased?
 d) what is the stoichiometry of the reactants in the Rate Determining Step?

More More Rate Law Practice

1. Write the rate law for the following *elementary* reaction:



- a) Determine the value of k , when $[\text{N}_2] = 0.50 \text{ mol/L}$ and $[\text{H}_2] = 1.5 \text{ mol/L}$ and NH_3 is produced at a rate of 2.5 mol/Ls .

2. For the *elementary* reaction $\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$

- a) Write the rate law.
b) Find k if HI is produced at a rate of $1.0 \times 10^{-4} \text{ mol/Lmin}$ when $[\text{H}_2] = 0.025 \text{ mol/L}$ and $[\text{I}_2] = 0.050 \text{ mol/L}$.
c) What is the rate of production of HI if the concentration of both reactants is 0.10 mol/L and the temperature is the same as in (b)?
d) How would the rate be affected if $[\text{H}_2]$ is doubled AND the $[\text{I}_2]$ is halved?

3. For the *single step* reaction $2 \text{A} \rightarrow \text{C}$

- a) Write the rate law.
b) Find k if C is produced at a rate of 1.0 mol/Lhr when 10.0 moles of A are in a 2.0 L container.
c) What would the rate of production of C be at the same temperature if 10.0 moles of A were placed in a 500.0 mL container?
d) If the concentration of A was reduced by 25% , by what percentage would the rate decrease?

4. For the *one step* reaction $\text{A}(\text{g}) + 2 \text{B}(\text{g}) \rightarrow \text{C}(\text{g})$

- a) What is the rate law?
b) How does the rate change if
c) $[\text{A}]$ is doubled?
d) $[\text{B}]$ is tripled?
e) The volume of the container is reduced to one-half?

5. Assume that $\text{NO}(\text{g})$ and $\text{H}_2(\text{g})$ react according to the rate law

$$\text{Rate} = k[\text{NO}]^2 [\text{H}_2]$$

How does the rate change if:

- the concentration of H_2 is doubled?
 - the volume of the enclosing vessel is reduced by half?
 - the temperature is increased?
6. Write the following for the reaction $\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$
- The rate expression for the reaction
 - The order of the reaction in each of the reagents
 - The overall order of the reaction
7. The rate constant for the reaction $\text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3$ is $14.5 \text{ L} / \text{mol}\cdot\text{sec}$. If the concentration of nitric acid is 0.050 M and the concentration of ammonia is 0.10 M , what will the rate of this reaction be?
8. When two compounds, A and B, are mixed together, they form compound C, by a reaction that's not well understood. Fortunately, the following rate information was experimentally determined, as shown below:

[A] (mol/L)	[B] (mol/L)	Rate (mol/L·sec)
0.050	0.050	4.0×10^{-3}
0.10	0.050	8.0×10^{-3}
0.050	0.10	1.6×10^{-2}

- Determine the rate expression for this reaction.

- Determine the rate constant for this reaction.

Kinetics Review

1. Explain the Collision Theory of reactions.
2. Does every collision between reacting particles lead to products?
What other factors are involved?
3. What is meant by the rate of reaction?
4. How does each of the following factors affect the rate of a chemical reaction?
 - a) temperature
 - b) concentration
 - c) particle surface area
 - d) inhibitor
 - e) catalyst
5. Which of these statements are true?
 - a) Increasing the temperature can speed up all chemical reactions.
 - b) Once a chemical reaction gets started, the colliding particles no longer have to “climb over” the activation energy barrier.
 - c) Enzymes are biological catalysts.
6. Consider the reaction: $2A + 1B \rightarrow 2C$
 - a) What is the rate of decomposition of B compared to A?
 - b) The rate of production of C compared to A?
7. In the reaction $A + B \rightarrow C$, we found the following rate data:

Trial	[A]	[B]	Initial rate
1	0.026	0.015	2.80×10^{-3}
2	0.026	0.030	5.60×10^{-3}
3	0.052	0.015	11.2×10^{-3}

Using this information, find the overall rate law for this reaction, find the order of the reaction for each reactant, and the overall reaction order.

8. The reaction: $NO + O_3 \rightarrow NO_2 + O_2$ is first order for NO and second order over all. Write the rate law for this reaction.
9. Describe the factors that will affect the value of the specific rate constant, k .
10. Suggest a rate law for the following *elementary* reactions.
 - a) $A + 2B \rightarrow 3C + D$
 - b) $O_3 + O \rightarrow 2O_2$
 - c) $2NO_2 \rightarrow NO_3 + NO$

11. Given the mechanism:



- Give the net overall reaction.
- Suggest a rate law for the overall mechanism
- Draw a reaction coordinate diagram (Potential Energy diagram).

12. For the elementary, one-step reaction $2\text{C} + \text{D} \rightarrow \text{X} + \text{R}$ the following data was collected.

[C] (mol/L)	[D] (mol/L)	initial Rate (mol/L s)
0.2	0.1	3.0×10^{-2}
0.2	0.2	6.0×10^{-2}
0.4	0.2	2.4×10^{-1}

- Based on the reaction stoichiometry, what is the rate law?
- Use the experimental data to determine the rate law.
- What is the value for the rate constant, k ? (7.5)
- What is the overall order of this reaction?

13. For the elementary reaction $2\text{NO}_{(g)} + \text{Cl}_{2(g)} \rightarrow 2\text{NOCl}_{(g)}$,

- Suggest a rate law.
- What happens to the rate if [NO] doubles?
- What happens to the rate if [Cl₂] triples?
- What happens to the rate if the size of the container is halved?
- What happens to the rate if the size of the container is increased to 3 times its original size?

14. For the reaction $2\text{A} + \text{B} + 3\text{C} \rightarrow 2\text{D} + \text{E}$ the following rate data was collected

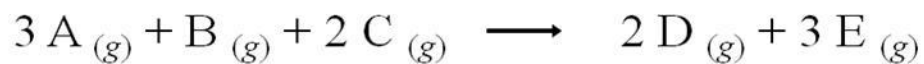
Trial	[A] (mol/L)	[B] (mol/L)	[C] (mol/L)	Rate (mol/L s)
1	0.10	0.20	0.10	4.20×10^{-5}
2	0.20	0.20	0.10	8.36×10^{-5}
3	0.30	0.20	0.10	1.27×10^{-4}
4	0.10	0.10	0.10	1.02×10^{-5}
5	0.60	0.40	0.30	1.01×10^{-3}
6	0.25	x	0.15	7.50×10^{-3}

- Using the data, calculate the rate law for this reaction.
- What is the overall order of reaction?
- Calculate the value of k . (0.011)
- What is the rate of reaction if [A] = 0.325 mol/L [B] = 0.285 mol/L and [C] = 0.155 mol/L?
- Find the missing [B] in trial 6.
- What is the stoichiometry of the reactants in the Rate Determining Step?

Trial Number	[H ₂ O ₂] (mol/L)	[HI] (mol/L)	Rate (mol/Ls)
1	0.10	0.10	0.0076
2	0.10	0.20	0.0152
3	0.20	0.10	0.0152



Trial	[A] (mol/L)	[B] (mol/L)	Initial Rate (mol/Ls)
1	0.10	0.20	2.0
2	0.30	0.20	18.0
3	0.20	0.40	16.0



Trial	[A] (mol/L)	[B] (mol/L)	[C] (mol/L)	Rate (mol/Ls)
1	0.10	0.10	0.10	0.20
2	0.20	0.10	0.10	0.40
3	0.20	0.20	0.10	1.60
4	0.20	0.10	0.20	0.40
5	0.50	0.40	0.25	?
6	?	0.60	0.50	6.00

- Write the rate law for this reaction.
- Calculate the value of the rate constant (k).
- Calculate the rate for Trial #5.
- Calculate the concentration of A in Trial #6.