INTRODUCTION TO KINETICS

Name

SECTION

1. List four factors that affect the rate of a chemical reaction. For each, provide a brief statement describing how it affects the speed of a chemical reaction.

- 2. a. Define the term *reaction rate*.
 - b. For the following chemical reaction

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

write a rate expression in terms of

- i. the change in concentration of $\mathrm{N_2O_5}$ with time;
- ii. the change in concentration of NO_2 with time;
- iii. the change in concentration of O_2 with time;

- iv. write a statement that compares the rate of appearance of NO₂ to the rate of appearance of O₂;
- v. write a mathematical equation that equates the rates of the reactants and products in the reaction to each other.
- 3. In the plot below, three lines, labeled A, B, and C are shown. Identify (use the letter) which line best represents the *average rate*, *instantaneous rate*, and *initial rate* for the chemical reaction.



RATES OF REACTION

Name

Section

1. a. Given the following data

Time (min)	Exp. #1 [NO ₂] (M)	Exp. #2 [NO ₂] (M)							
0	0.350	1.05							
2	0.289	0.583							
4	0.245	0.324							
8	0.190	0.0999							
16	0.130	0.0095							
24	0.090	0.0009							
40	0.062								

for the reaction $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

The data for Exp. #1 is plotted below. Determine the average rate of the reaction between 8 and 24 min., the instantaneous rate of the reaction at 8 minutes, and the initial rate of the reaction.



b. The data for Exp. #2 is plotted below. Determine the average rate of the reaction between 8 and 24 minutes, the instantaneous rate of the reaction at 8 minutes, and the initial rate of the reaction.



- c. By what factor did the initial concentration change in going from Exp. #1 to Exp. #2?
- d. By what factor did the initial rate change in going from Exp. #1 to Exp. #2?
- e. Write an equation which describes how the initial rate of the reaction depends on the initial concentration.

METHOD OF INITIAL RATES

Name

Section

- 1. Define the terms *rate expression* and *rate law* for a chemical reaction.
- 2. Write the general rate law for the following reaction

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

Identify the rate constant in the rate law. What are the exponents in the rate law called?

3. What experimental data is needed to determine the order of a chemical reaction?

4. a. Consider the reaction

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

and the following initial rate data.

Experiment Number	P _{NO} (mmHg)	P _{H₂} (mmHg)	Initial Rate $\left(\frac{mmHg}{s}\right)$							
1	400	150	0.66							
2	400	300	1.34							
3	150	400	0.25							
4	300	400	1.03							

i. Determine the reaction order for NO and H_2 .

ii. Determine the overall order of the reaction.

iii. Write the specific rate law for the reaction.

iv. Determine the rate constant for the reaction (include units).

b. The following initial rate data were collected for the reaction at 100 °C.

$$2\mathrm{NO}_2(g) + \mathrm{F}_2(g) \to 2\mathrm{NO}_2\mathrm{F}(g)$$

Exp.	[NO ₂]	[F ₂]	Initial Rate (M/sec)
1	0.0482 M	0.0318 M	$1.90 imes 10^{-3}$
2	0.0120 M	0.0315 M	$4.69 imes 10^{-4}$
3	0.0480 M	0.127 M	$7.57 imes 10^{-3}$

i. Determine the reaction order for NO_2 and F_2 .

ii. Determine the overall order of the reaction.

iii. Write the specific rate law for the reaction.

INTEGRATED RATE LAW PART I

Name

Section

1. The reaction: $A(g) \rightarrow$ products

follows simple first order kinetics. When the initial concentration of A is 0.500 M, the initial rate of the reaction is determined to be 4.20×10^{-3} M s⁻¹. If the initial concentration of A is tripled, what would be the new initial rate of the reaction?

2. Write the integrated rate law for a reaction that follows simple first order kinetics.

3. The decomposition of H_2O_2 to H_2O follows first order kinetics with a rate constant of 0.0410 min⁻¹ at a particular temperature.

$$H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

Calculate the $[H_2O_2]$ after 10 minutes, if $[H_2O_2]_0$ is 0.200 M.

4. The decomposition of N_2O_5 to O_2 and NO_2 follows first order kinetics. If a sample at 25 °C with the initial concentration of N_2O_5 of 1.25×10^{-3} M falls to 1.02×10^{-3} M in 100 minutes, calculate the rate constant for the reaction.

5. Describe how a plot of *ln* [concentration] versus time can provide the rate constant for a reaction that follows simple first order kinetics.

6. Using the following data, establish that the decomposition N_2O_5 according to the reaction,

$$2N_2O_5(g) \rightarrow 2NO_2(g) + O_2(g)$$

follows first order kinetics. Determine the rate constant for the reaction.

Time (sec)	[N ₂ O ₅] (M)
0	$1.50 imes 10^{-3}$
2000	$1.40 imes 10^{-3}$
5000	$1.27 imes 10^{-3}$
7000	$1.18 imes 10^{-3}$
11000	1.03×10^{-3}
15000	$9.00 imes 10^{-4}$

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HALF-LIFE

Name

Section

1. a. For the reaction:

 $A(g) \rightarrow \text{products}$

when the $[A]_0 = 0.400$ M, what will the concentration of A be after one half-life?

b. What additional information would you need to determine the concentration of the products in the reaction after one half-life?

2. Beginning with the general form of the integrated rate law for a reaction that follows simple first order kinetics, derive the mathematical equation for the half-life of the reaction.

3. The decomposition of H_2O_2 to H_2O and O_2 follows first order kinetics with a rate constant of 0.0410 min⁻¹ at a particular temperature.

$$\mathrm{H}_{2}\mathrm{O}_{2}(l) \rightarrow 2\mathrm{H}_{2}\mathrm{O}(l) + \mathrm{O}_{2}(g)$$

How long would it take for half of the $\rm H_2O_2$ to decompose?

INTEGRATED RATE LAW PART II

Name

Section

1. The reaction:

 $B(g) \rightarrow \text{products}$

follows simple second order kinetics. When the initial concentration of B is 0.500 M, the initial rate of the reaction is determined to be 8.40×10^{-3} M s⁻¹. When the initial concentration of B is tripled, what change would you expect to observe in the initial rate of the reaction?

2. Write the integrated rate law for a reaction that follows simple second order kinetics.

3. a. The decomposition of NOCl(g)

 $2NOCl(g) \rightarrow 2NO(g) + Cl_{,(g)}$

is a second order reaction with a rate constant of 0.0480 $M^{-1} \cdot \sec^{-1}$ at 200 °C. In an experiment at 200 °C, the initial concentration of NOCl was 0.400 M. What is the concentration of NOCl after 15.0 minutes have elapsed?

- b. How many minutes will it take for the concentration of NOCl(g) to drop to 0.150 M?
- 4. Derive a mathematical equation for the half-life for a reaction which follows simple second order kinetics.

5. The initial concentration of NOCl, described in 3a. above, is 0.400 M. Calculate the half-life for the decomposition reaction.

6. Describe how a plot of *ln* [concentration] versus time can provide the rate constant for a reaction which follows simple second order kinetics.

7. Using the following data, establish that the decomposition of NO_2 according to the reaction,

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

follows second order kinetics. Determine the rate constant for the reaction.

Time (sec)	[NO ₂] (M)
0	0.0100
25	0.0088
50	0.0079
75	0.0071
100	0.0065
150	0.0055
175	0.0051
200	0.0048
250	0.0042
300	0.0038



TEMPERATURE DEPENDENCE OF THE RATE CONSTANT

Name

1. a. The following rate data was obtained at different temperatures for the reaction

 $O_3(g) + NO(g) \rightarrow O_2(g) + NO_2(g)$

Temperature (K)	1/ _T	k (M ⁻¹ ·sec ⁻¹)	ln k
600		0.28	
650		0.22	
700		1.30	
750		6.00	
800		23.0	

Sketch the plot of ln k (y-axis) versus $\frac{1}{\text{temperature}}(x-\text{axis})$



Section

b. Write the Arrhenius equation and identify each term.

c. Define the term *activation energy*.

- d. Determine the activation energy using the plot you made in 1a.
- 2. a. At 300 $^{\circ}$ C the rate constant for the reaction

$$\overset{\text{CH}_2}{\underset{\text{CH}_2}{\longrightarrow}} \overset{\text{CH}_2}{\underset{\text{CH}_2}{\longrightarrow}} H_2\text{C=CH-CH}_3$$

is $2.41 \times 10^{-10} \text{ sec}^{-1}$. At 400 °C the rate constant is $1.16 \times 10^{-6} \text{ sec}^{-1}$. Calculate the activation energy for the reaction.

b. Estimate the rate of the rearrangement reaction at 800 °C.

c. If the activation energy for the decomposition of N_2O_5 is $1.0 \times 10^2 \frac{kJ}{mol}$, calculate the temperature change necessary to double the rate at room temperature.

3. Sketch the energy profile diagram for the exothermic reaction

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

and label the important features, including reactants, products, activated complex, the energy of activation, and the enthalpy of the reaction.

REACTION MECHANISMS

Name

Section

1. Given the chemical equation

$$R + BG \rightarrow RG + B$$

Describe the interaction between reactant particles that must occur to convert them to products. You may draw one or more pictures as part of your description.

2. Write the general differential form of the rate law for the reaction above.

3. The following table summarizes several experiments where the concentrations of R and BG were varied to determine the effect on the initial rate of the reaction.

Experiment Number	R (M)	BG (M)	Initial Rate $(\frac{M}{s})$						
1	0.240	0.125	$1.85 imes 10^{1}$						
2	0.480	0.124	$3.68 imes 10^{1}$						
3	0.479	0.249	$7.37 imes 10^{1}$						

Determine the rate law for the reaction.

4. How do the exponents in the rate law that was obtained in Question 3 compare to the coefficients in the balanced chemical equation in Question 1?

5. Define the term *reaction mechanism*.

6. a. Optional: Look at the simulation (http://introchem.chem.okstate.edu/DCICLA/K2GBM.htm) for the reaction:

$$2G + B \rightarrow G_2B$$

The rate law is known to be rate = $k[G]^2$. Suggest a possible mechanism for this reaction.

b. Why is B not part of the rate law? (Hint: do all of the steps in a mechanism contribute to the overall rate? Why or why not?)

7. The rate law for the following reaction

$$2\mathrm{NO}_2(g) + \mathrm{F}_2(g) \to 2\mathrm{NO}_2\mathrm{F}(g)$$

was experimentally determined to be

rate =
$$k[NO_2]^1[F_2]^1$$

Which of the following mechanisms is the most reasonable? Explain your reasoning for making the choice you did.

a.
$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

b. $NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g)$ (fast) $NO_2(g) + F(g) \rightarrow NO_2F(g)$ (slow)

c.
$$\operatorname{NO}_2(g) + \operatorname{F}_2(g) \to \operatorname{NO}_2\operatorname{F}(g) + \operatorname{F}(g)$$
 (slow)
 $\operatorname{NO}_2(g) + \operatorname{F}(g) \to \operatorname{NO}_2\operatorname{F}(g)$ (fast)

8. Suggest a mechanism for the reaction

$$CH_3NC(g) \rightarrow CH_3CN(g)$$

if the experimental rate law is rate = $k[CH_3NC]^1$.