Name ________________________________Chem 163 Section: ______ Team Number: ______

ALE 2. Rate Laws: Expressing and Quantifying the Rate of Reaction

(Reference: 16.3 *Silberberg 5th edition*)

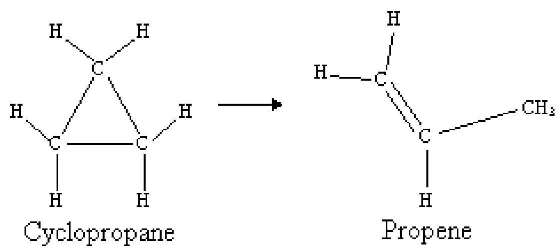
How are concentrations of reactants related to the rate of a reaction?

The Model: First-Order versus Second-Order Reactions

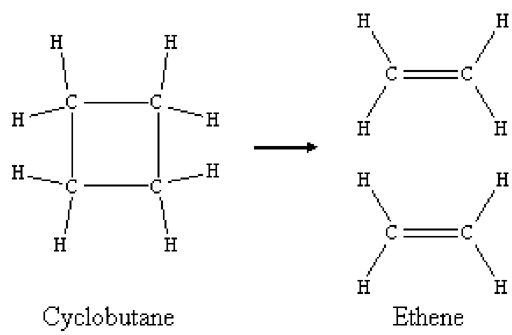
Suppose we are interested in the decomposition reaction of compound "A":

$$\textbf{A} \rightarrow \textbf{Product(s)}$$

It is possible that the decomposition is an **isomerization reaction** (Recall that isomers are compounds having the same formula, but different structures.), such as the isomerization of cyclopropane into propene:



It is also possible that the decomposition is a **dissociation reaction**, such as the fragmentation of cyclobutane into ethene:



If the rate of the reaction is dependent on the concentration of the reactant raised to the first power, then the reaction is said to be "**first order**", and its **rate law** is:

$$\textbf{rate} = \boldsymbol{k}\,\textbf{[A]} \qquad \textbf{(1)}$$

where ***k*** is the **rate constant** of the first-order reaction. In a **first-order reaction**, a reactant molecule simply undergoes simultaneous bond breakage/formation. Therefore, the rate of the first-order reaction is simply dependent on the concentration of the reacting species.

If the rate of the reaction is dependent on the concentration of the reactant raised to the second power, then the reaction is said to be "**second order**", and its rate law is:

$$\textbf{rate} = \boldsymbol{k}\,\textbf{[A]}^2 \qquad (2)$$

where ***k*** is the rate constant of the second-order reaction. In a **second-order reaction**, two molecules collide with each other. *<u>The reaction rate is dependent on the number of collisions that take place per unit time</u>*. If we double the concentration of the reacting species (A), not only have we doubled the number of *colliding* molecules, but we've also doubled the number of molecules that are being *collided with*. Therefore, there is a four-fold increase in the rate of the reaction. If we triple the concentration of the reacting species, not only have we tripled the number of *colliding* molecules, but we've also tripled the number of molecules that are being *collided with*. Therefore, there is a nine-fold increase in the rate of the reaction. Thus we see in a second-order reaction that if we multiply the concentration by a factor of x, the rate gets multiplied by a factor of x^2.

Key Questions

1. What are the units of:
   a. [A] (where A stands for the formula of some reactant)?
   b. the rate of a reaction?
   c. the rate constant of a first-order reaction? *Hint*: Use eq **1** and dimensional analysis using your answers to parts (a) and (b). <u>*Show your work below*</u>.
   d. the rate constant of a second-order reaction? *Hint*: Use eq **2** and dimensional analysis using your answers to parts (a) and (b). <u>*Show your work below*</u>

2. Consider the following reaction that is first order with respect to A and first order with respect to B:

$$\mathbf{A + B \rightarrow Products}$$

   a. By what factor would the reaction rate increase if [A] were doubled but [B] remains unchanged?_____
   b. By what factor would the reaction rate increase if [B] were tripled but [A] remains unchanged? ______
   c. Write the rate law for the reaction: ____
   d. By what factor would the reaction rate increase if [A] were tripled and [B] were doubled? __________

The Model: Overall Rate Orders

For the generic chemical reaction: $\boldsymbol{a}\,\mathbf{A} + \boldsymbol{b}\,\mathbf{B} \rightarrow \boldsymbol{d}\,\mathbf{D} + \boldsymbol{e}\,\mathbf{E}$

the rate law is: $\mathbf{rate} = \boldsymbol{k}\,\mathbf{[A]}^{x}\,\mathbf{[B]}^{y}$

where ***k*** is the rate constant, ***x*** is the order with respect to A, and ***y*** is the order with respect to B. The **overall order** of the reaction is $x + y$.

Key Questions

3. For each reaction and its corresponding rate law, indicate what the order is with respect to each reactant and the overall order of each reactant

	Reaction	Rate Law	Order with respect to		Overall Reaction Order
a.	$2\ NO_2 + F_2 \rightarrow 2\ NO_2F$	rate = $k\,[NO_2][F_2]$	NO_2 :	F_2:	
b.	$2\ NO + O_2 \rightarrow 2\ NO_2$	rate = $k\,[O_2][NO]^2$	NO :	O_2 :	
c.	$NO + N_2O_5 \rightarrow 3\ NO_2$	rate = $k\,[N_2O_5]$	NO :	N_2O_5 :	

4. True or False (circle your choice): There is a one-to-one relationship between the stoichiometric coefficient of a reactant and the order with respect to that reactant in the rate law. *Explain your answer*.

The Model: Determination of Rate Orders

So at this point, one may ask the question: "If stoichiometric coefficients do not determine the orders, then how are rate laws determined?" A very common way of determining the order with respect to a reactant in the rate law is the **Method of Initial Rates**. The standard strategy to employ is to perform the same reaction several times but at the same temperature. In each of the trials, the concentration of *one* of the reactants is changed while the concentrations of any other reactants are held constant. Any observed change in the initial rate of the reaction is, therefore, due to the change in concentration of that one reactant. The initial rate of the one trial serves as a "reference" to which the other trials' initial rates are compared. By determining the ratio of the initial rates of two trials in which [A] is different (but the concentration of any other reactant is the same), the order with respect to A may be determined.

$[A]_1$ = molar concentration of A in trial 1 $[A]_2$ = molar concentration of A in trial 2

$Rate_1$ = initial rate of reaction in trial 1 $rate_2$ = initial rate of reaction in trial 2

x = order with respect to A

$$\frac{Rate_2}{Rate_1} = \left(\frac{[A]_2}{[A]_1}\right)^x$$

Key Questions

5. Fill in the blanks in the following table. Be able to show your work and/or explain how you arrived at your answers.

	Factor by which [A] is changed in going from trial 1 to 2	Factor by which initial rate of reaction changes in going from trial 1 to 2	**x** (order with respect to A)
a.	[A] is doubled	rate doubles	
b.	[A] is halved	rate remains constant	
c.	[A] is tripled	rate increases by factor of 9	
d.		rate triples	1
e.	[A] is halved		2

Exercise

6. The oxidation of thallium(I) to thallium(III) by cerium(IV) is catalyzed by manganese(II). The kinetics of the aqueous reaction was observed several times at the same temperature:

$$\mathbf{2\,Ce^{4+}(\mathit{aq}) + Tl^{+}(\mathit{aq}) \xrightarrow{Mn^{2+}} 2\,Ce^{3+}(\mathit{aq}) + Tl^{3+}(\mathit{aq})}$$

Experiment	$[Ce^{4+}]_{initial}$	$[Tl^{+}]_{initial}$	$[Mn^{2+}]$	Initial rate of formation of Tl^{3+} ($M\ s^{-1}$)
1	0.0050	0.0025	0.0010	2.0×10^{-4}
2	0.0050	0.0050	0.0010	2.0×10^{-4}
3	0.0100	0.0025	0.0010	4.0×10^{-4}
4	0.0050	0.0050	0.0030	6.0×10^{-4}

a. Determine the rate orders with respect to Ce^{4+}, to Tl^{+}, and to Mn^{2+} and *explain or show how you arrived at your answers*.
i. The order with respect to Ce^{4+} is ______________. *Work/Explanation*:

ii. The order with respect to Tl^{+} is ______________ . *Work/Explanation*:

ii. The order with respect to Mn^{2+} is ______________ . *Work/Explanation*:

b. Write the rate law for the reaction.

c. Calculate the value of the rate constant. *Show your work using correct units and sig. figs*. and *circle your answer*.

d. What would the initial rate of the formation of Tl^{3+} be if $[Ce^{4+}]_{initial}$ = 0.0100 *M*, $[Tl^{+}]_{initial}$ = 0.00500 *M*, and $[Mn^{2+}]$ = 0.00300 *M*? <u>*Show work using correct units and sig. figs.*</u> and <u>*circle your answer.*</u>

Model: Kinetics of a Unimolecular Reaction

Under certain conditions ozone in the atmosphere decomposes by dissociation ($O_3 \rightarrow O_2 + O$) with the kinetics given below. The data in the graph (fig. 1) and in table 1 are described by the three equations below.

Equations that describe the decomposition of ozone, O_3:

Equation 1. **reaction rate = - $\Delta[O_3]/\Delta t$**

Equation 2. rate law: **Rate = $\Delta[O_3]/\Delta t$ = - k $[O_3]$**

Equation 3. integrated rate law: **Ln $([O_3]/[O_3]_o)$ = - k t** Where: $[O_3]_o$ = conc. of O_3 @ t = 0

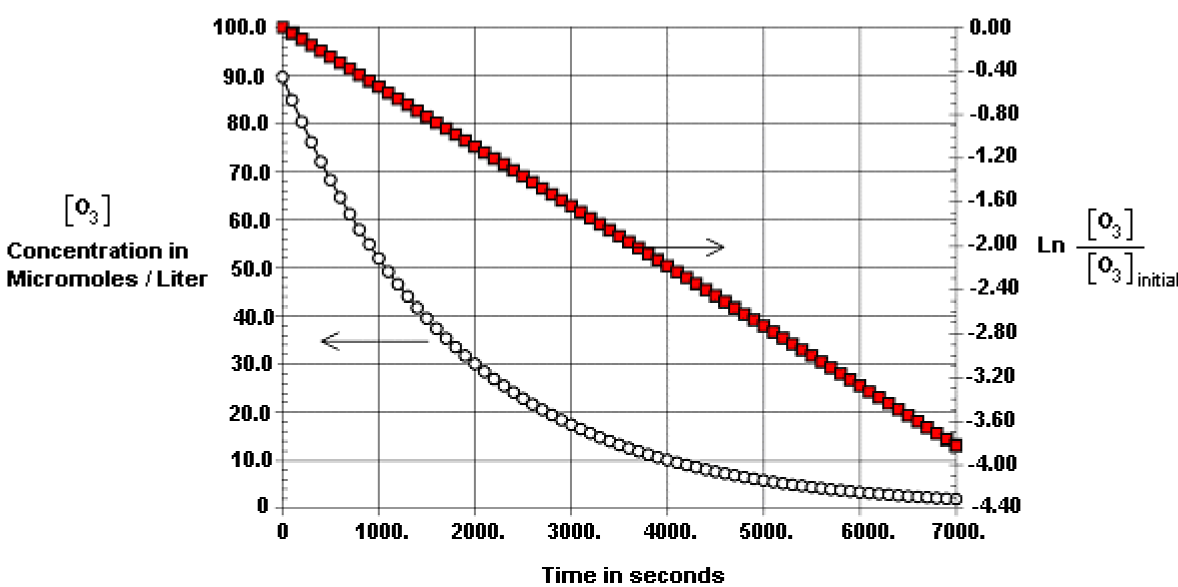


Figure 1. Data describing the decomposition of ozone. Note that the curved line refers to the left scale, and the straight line refers to the right scale.

Table 1. Data on Ozone Decomposition (half-life time = 1270 s)

Time (s)	**0**	**100.**	**900.**	**1000.**	**6900.**	**7000.**
O_3 concentration (x 10^{-6} M)	89.63	84.87	54.84	51.92	2.07	1.96
$\ln([O_3]/[O_3]_o)$	0.00	-0.0546	-0.4914	-0.5460	-3.767	-3.822

Key Questions

Please.... Neatly show your work with units and significant figures for all questions that involve a calculation and mark/label the graph where you obtained data points

7. Use figure 1 to determine how long it takes for ***half*** the ozone to decompose. What is the concentration of ozone after that time?

8. Use figure 1 to determine ***initial reaction rate*** of the ozone decomposition. Provide both the magnitude and the units.

9. Use figure 1 to determine the approximate rate of the reaction after 1.92 hours have passed.

10. Referring to figure 1, how does the rate of the reaction change with time? Why does the rate change with time?

11. The reaction is ___________ order of the reaction with respect to ozone.

12. Overall, the decomposition of ozone reaction is _____________ order.

13. If the concentration of ozone were doubled, the reaction rate would ________________________ .

14. What parameter in the integrated rate law determines the slope of the straight line in the graph?

15. Why does the concentration data, when plotted in the above graph with time on the x-axis, produce a curved line in one case and a straight line in the other?

16. How do you think an increase in temperature would affect the *rate constant* for the decomposition of ozone? Explain.

17. Draw lines on the graph in fig. 1 to mark the half-life time and the concentration at the half-life time and label this time with $t_{½}$ and the concentration with $C_{½}$.

18. Write the ***rate law*** (i.e. the differential rate law, equation 2) for the ozone decomposition reaction.

19. Write the ***integrated rate law*** (i.e. equation 3) for the ozone decomposition reaction.

20. Calculate the rate constant (use sig. figs. and units) for the ozone decomposition reaction from the slope of the straight line in fig. 1.

Exercises involving Rate Laws

21. Given the following rate law: Rate = k $[CHCl_3]$ $[Cl_2]^{1/2}$

    a. What is the reaction order with respect to chloroform, $CHCl_3$? ______order

    b. What is the reaction order with respect to chlorine? ______order

    c. What is the overall reaction order? ______order

    d. If the concentration of chloroform is cut in half, what will happen to the reaction rate? Give a quantitative response.

    e. If the concentration of chlorine is tripled, what will happen to the reaction rate? Give a quantitative response.

22. The rate of a reaction is expressed in terms of changes in concentration of reactants and products. Write the balanced chemical equation for the following the reaction described by the following mathematical equation: $\text{Rate} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$

23. Give the individual reaction orders for each substance and the overall reaction order for the following rate law: $\text{Rate} = k\frac{[O_3]^2}{[O_2]}$

Reaction Order for: a.) O_3 = _______ b.) O_2 = _______ c.) Overall reaction = _______

24. By what factor does the rate change for the rate in the previous problem change if…..

a. $[O_3]$ is doubled? _____________ c. $[O_2]$ is doubled? _____________

b. $[O_2]$ is halved? _____________ d. $[O_3]$ is halved? _____________

25. Find the rate law, calculate the rate constant and determine the overall reaction order for the reaction **$H_2 + I_2 \rightarrow 2\ HI$** from the following data at 450°C. Show/explain your work using correct units and sig. figs.

Experiment	**Initial Rate ($mol\ L^{-1}\ s^{-1}$)**	**Initial $[H_2]$ (mol/L)**	**Initial $[I_2]$ (mol/L)**
1	1.9×10^{-23}	0.0113	0.0011
2	1.1×10^{-22}	0.0220	0.0033
3	9.3×10^{-23}	0.0550	0.0011
4	1.9×10^{-22}	0.0220	0.0056