CHEM 116 Rates of Reaction

FSG is cancelled today (Oct 14) in order to keep both FSG sections at the same pace (since there was no school yesterday) Lecture 12 Prof. Sevian



Today's agenda

- Graphing concentration data to determine reaction rates (ch. 14)
 - Initial rate of change vs. average rate of change
 - Concentration vs. time for one reactant that is measured
 - Concentration vs. time for other reactants and for products
 - Determining the order of a reaction from concentration vs. time data
- Tables of initial reaction rates to determine the order of reaction for different species involved in a reaction

Kinetics: Key terms

What makes kinetics difficult is that there are a lot of new ideas and new vocabulary all introduced at the same time. Becoming familiar with the vocabulary will help immensely.

Rate law Concentration Catalyst Overall order of reaction Order with respect to a particular reactant Rate constant Half-life Collision model Activated complex/transition state Activation energy Arrhenius equation Reaction mechanism Elementary step in reaction mechanism Rate-determining step Molecularity of a step Equilibrium

Kinetics

• The study of how quickly (or slowly) reactions occur

Using chemistry in the world:

- How do you produce chemicals?
 - What kinds of chemical reactions are there?
- What properties do materials have and why do they have those properties?
- How much of a given chemical can you produce? How can you control it?
 - Stoichiometry
 - How fast do reactions occur?
 - How much energy does it take to make a reaction occur, or how much energy does a reaction give off?
 - How pure can you make the chemical? (Are there competing reactions?)
 - Scaling up reactions to useful proportions
- How dangerous are specific chemicals?
 - LD50 of the desired products
 - Are there any byproducts or left over reactants? Are these dangerous?

What is rate of a reaction?

• Comparison: What is rate of travel? How fast you travel.

rate of travel (speed) = $\frac{\text{distance traveled}}{\text{time of travel}} = \frac{\Delta d}{\Delta t} = \frac{d_2 - d_1}{t_2 - t_1}$

- Rate of a reaction is how fast the reaction happens
- Measured mathematically as

rate of reaction (*rate*) = $\frac{\text{change of chemical concentration}}{\text{time elapsed}} = \frac{\Delta[A]}{\Delta t} = \frac{[A]_2 - [A]_1}{t_2 - t_1}$

• What if you couldn't measure reactant concentration but you could measure how much product is created?

The class did four different experiments

Control (same for everyone): 1 tablet Alka-Seltzer in 100 mL of room temperature water

- You Sent a member of your group to get a set of materials, noted the Group #
- · Set contained: 2 cups, water, Alka-Seltzer tablets
- · You measured time in seconds (digital watch or second hand on clock in front)

A) 2 tablets instead of 1	B) Higher temperature
Groups 1, 2, 3 and 4	Groups 5, 6, 7 and 8
Same control	Same control
 Experiment: 2 tablets instead of 1 tablet 	 Experiment: 1 tablet A-S in 100 mL of very warm water
C) Powdered tablet	D) Twice as much water
Groups 9, 10, 11 and 12	Groups 13, 14, 15 and 16
Same control	Same control
• Experiment: 1 crushed A-S tablet in same amount of room temp water	• Experiment: 1 tablet A-S in 200 mL (twice as much water as the control)

Results of Alka-Seltzer Experiments

In one Alka-Seltzer tablet, there are 1916 mg of the limiting reagent, sodium bicarbonate (f.w. 84.0). Thus the average rate of the reaction was calculated as the change in reactant molarity (from M of reactant present at the start, down to zero M at the end) divided by the time for the reaction to reach apparent completion (in seconds).

Expt #	Control	A) 2x	B) warm	C)	D)
1	55	58	1120	ciusiieu	241120
2	00	00			
2	80	88			
3	62	67			
4	56	66			
5			29		
6	60		30		
7	52		37		
8			40		
9	67			20	
10	60			40	
11	64			53	
12	69				60
13	51				47
14	46				23
15	62				57
16	50				48
Average time (s)	59.6	69.8	34.0	37.7	47.0
mg of lim reagent	1916	3832	1916	1916	1916
mmol lim reagent	22.8	45.6	45.6	45.6	45.6
mL water	100	100	100	100	200
Initial concen (M)	0.228	0.456	0.228	0.228	0.114
Avg Rate (M/s)	0.0038	0.0065	0.0067	0.0061	0.0024
Rate = (change in molarity of limiting reactant that reacted) /					

(average time for the reaction to reach apparent completion)

Extra credit assignment (due at beginning of class (2:00) on Tues Oct 14)

- Make a table like the following and fill it out
- In the Results column, explain in words what the results were and how they compare
 to the control
- Your answers in the "Why I think that happened" column do not need to be correct, but they do need to be what you think.

	Results of this experiment in class	Why I think that happened
A) Two tablets instead of one		
B) Warm water instead of room temp water		
C) Tablet crushed first before adding to water		
D) Twice as much water used		

Alka-Seltzer: Bicarbonate + acid solution

NaHCO₃ (aq) + Citric acid (aq) \rightarrow Na - citrate (aq) + H₂O (l) + CO₂ (g)

in the Alka-Seltzer	in the Alka-Seltzer		
What did you v	ary in the experiment (compared to the control)?		
Amount of NaHCO ₃ (Alka-Seltzer) and amount of citric acid doubled \rightarrow Higher initial reactant concentration			
Temperature rai	sed \rightarrow all chemicals have higher KE		
Powdered tablet \rightarrow Increased surface area for reaction to occur			
Volume of water	$$ increased \rightarrow Lower initial reactant concentration		

Did the rate of the reaction change? Why?

rate of reaction (*rate*) = $\frac{\text{change of chemical concentration}}{\text{time elapsed}} = \frac{\Delta[A]}{\Delta t} = \frac{[A]_2 - [A]_1}{t_2 - t_1}$

Compare 2 tablets vs. 1 tablet "Back of the envelope" calculation

 Two tablets in 100 mL water Took about 70 sec for reaction to be complete

$$rate (2 tablets) = \frac{\Delta conc}{\Delta t} = \frac{\begin{pmatrix} (2 tablets - 0 tablet) \\ 0.100 L \end{pmatrix}}{70 s} = \begin{pmatrix} 20 \\ 70 \end{pmatrix} \frac{tablet}{L \cdot s} = 0.29 \frac{tablet}{L \cdot s}$$

• One tablet in 100 mL water (control) Took about 60 sec for reaction to be complete

$$rate (1 tablet) = \frac{\Delta conc}{\Delta t} = \frac{\left(\frac{1 tablet - 0 tablet}{0.100 L}\right)}{60 s} = \left(\frac{10}{60}\right) \frac{tablet}{L \cdot s} = 0.17 \frac{tablet}{L \cdot s}$$



2 tablets (higher conc) vs. 1 tablet (control)

2 tablets (higher conc) vs. 1 tablet (control) vs. twice as much water (lower conc.)



Average vs. instantaneous rxn rate



Note that the same comparison exists with initial rate as with

Average vs. initial rxn rate

average rate





The rate of a reaction changes over time because reactants get used up

Comparing concentrations of chemicals in a reaction



Example: Reaction rates and stoichiometry

Similar to Practice Exercise, p. 582

Compare the rates of appearance or disappearance of each chemical in the decomposition of NOCI.

$$2 \operatorname{NOCl}(g) \to 2 \operatorname{NO}(g) + \operatorname{Cl}_2(g)$$

If the initial rate of disappearance of NOCI is 4.20×10^{-4} mol/(L⁻h), what is the initial rate of appearance of Cl₂?

What we're after in kinetics

- We want to be able to understand and predict how much reactants remain (or products get formed) in a certain amount of time
- Change with time is rate
- Rate means calculus must be used, so we need to be careful which rate we are talking about
- We will use instantaneous rate at the start of a reaction (initial rate)
- Several factors affect the rate of a reaction
 - Initial concentration
 - Temperature
 - Amount of reactant exposed (surface area)
 - Presence of a catalyst
- A theory (equations) that predicts kinetics must explain these

Rate law must be determined experimentally

Some reactions and their experimentally determined rate laws

$2 \operatorname{N}_2\operatorname{O}_5(g) \to 4 \operatorname{NO}_2(g) + \operatorname{O}_2(g)$	Rate = $k [N_2O_5]$	
$\mathrm{NO}\left(g\right) + \mathrm{N}_{2}\mathrm{O}_{5}\left(g\right) \rightarrow 3 \mathrm{NO}_{2}\left(g\right)$	Rate = $k [N_2O_5]$	
$2 \operatorname{NO}_{2}(g) + \operatorname{F}_{2}(g) \to 2 \operatorname{NO}_{2}\operatorname{F}(g)$	Rate = $k [NO_2] [F_2]$	
$2 \operatorname{NO} (g) + \operatorname{O}_2 (g) \to 2 \operatorname{NO}_2 (g)$	Rate = $k [NO]^2 [O_2]$	
$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$	Rate = $k [CH_3CHO]^{3/2}$	
Important: Order of rate determined by experiment may not match		

Important: Order of rate determined by experiment may not match stoichiometric coefficients

Key points about kinetics so far

- Study the vocabulary
- Reaction rate has weird units
- Be clear whether you are talking about average reaction rate or initial reaction rate
- The equations which we will study all talk about initial reaction rate, which is the instantaneous reaction rate measured at the beginning of a reaction (at t=0)
- Relating rates at which products appear (+) and reactants disappear (-) has to do with inverse stoichiometric coefficients
- Reaction rate depends on several factors: initial concentration, temperature, surface area of reactants exposed, presence of a catalyst

Order of reaction rate

Conclusion: Unless you have a zeroorder reaction rate, it is difficult to tell from the concentration vs. time graph what order the reaction rate is.



What does "order" mean?

•	Zero order		
	rate = <i>k</i> [A] ⁰	if you double [A] [A] ×2 if you triple A_[A] ×3	rate stays the same rate ×2 ⁰ = stays same rate ×3 ⁰ = stays same
•	First order		
	rate = k [A] ¹	if you double [A]	rate doubles
		[A]×2	rate×2 ¹
		if you triple A, [A]×3	rate×3 ¹
•	Second order		
	rate = k [A] ²	if you double [A]	rate quadruples
		[A]×2	rate×2 ² = rate×4
		if you triple A, [A]×3	rate×3 ² = rate×9

Two ways to figure out the dependence of the rate on concentration of chemicals in the reaction

1. Graph a version of concentration vs. time and examine mathematical shape of curve

Zero order
$$rate = k[A]^0$$

 $-\frac{d[A]}{dt} = k \rightarrow \int_{\text{when } t=0}^{\text{at time } t} d[A] = -\int_0^t k \, dt \rightarrow [A]_t = [A]_0 - k \, t$

First order $rate = k[A]^{1}$ $-\frac{d[A]}{dt} = k[A] \rightarrow \int_{\text{when } t=0}^{\text{at time } t} \frac{d[A]}{[A]} = -\int_{0}^{t} k \, dt \rightarrow \ln[A]_{t} = \ln[A]_{0} - k \, t$ Second order $rate = k[A]^{2}$ $-\frac{d[A]}{dt} = k[A]^{2} \rightarrow \int_{\text{when } t=0}^{\text{at time } t} \frac{d[A]}{[A]^{2}} = -\int_{0}^{t} k \, dt \rightarrow \frac{1}{[A]_{t}} = \frac{1}{[A]_{0}} - k \, t$

2. Measure initial rate at many different initial concentrations and compare



Method 2: Determining rate law by measuring initial rate at various concentrations

Example

Given the following measurements of initial rate of reaction under various conditions of initial concentrations of reactants, determine:

- the rate law
- the value of the rate law constant, k
- the units of k

	Initial Concentration (M)		Initial rate
Experiment	[NO]	[O ₂]	(M/s)
1	0.020	0.010	0.028
2	0.020	0.020	0.057
3	0.020	0.040	0.114
4	0.040	0.020	0.227
5	0.010	0.020	0.014

lodine clock reaction



And then, two things can happen:

• Tri-iodide gets reduced back to iodide ion by thiosulfate

• When the thiosulfate gets used up, tri-iodide reacts with starch to form blue starch-triiodide complex

 $I_{3}^{-} + starch \rightarrow blue complex$ Signal that all the tri-iodide is gone