

CHEM 116

Solutions and Reaction Speed

October 10, 2006
Prof. Sevian



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Please sit with your groups today

We will be doing an exercise in groups today. It will minimize disruption and maximize work time if you sit with your group from the start of class today.



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Agenda

Finish properties of solutions that we can measure in the lab

1. Vapor pressure decrease
2. Boiling point elevation
3. Freezing point depression
4. Osmotic pressure existence
5. Increased solubility of gases (solute) in a liquid solvent when the pressure increases or temperature decreases

Kinetics: the study of how fast reactions occur

- What factors affect reaction rates?
- How do we measure reaction rates? How do reaction rates differ from one another?
 - Measure concentration vs. time and examine graph
 - Vary concentrations of one or another reactant
 - Finding order of reaction rate with respect to various reactants
 - Determining rate constant

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Key points from last lecture

- Colligative properties are properties of a solution compared to the pure solvent
- Colligative properties are caused by the presence of the solute
- When solute is present, the vapor pressure is lower, boiling point is elevated and freezing point is depressed (the liquid phase of a solution is extended at both ends over the pure solvent)
- Real solutions have van't Hoff factors that are larger when less solute is dissolved. This is because at lower concentrations, dissolved + and - solute particles cannot pair as easily.
- Because colligative properties depend on the concentration of solute dissolved in a solvent, colligative properties can be used to determine molecular weights of solutes

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

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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?

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What factors can affect the speed of a reaction?

- Everyone is comparing to the same control
React Alka-Seltzer in water at room temperature
How much time does it take to react?
What could we vary?

- Send one person from your group
Groups A-D: Exp1: 2 tablets instead of 1
Groups E-H: Exp2: higher temperature
Groups I-L: Exp3: powdered tablet
Groups M-P: Exp4: change volume of water



- Do the experiment (5 minutes)

- Report what you learned to the class

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Four Experiments, Each Repeated 4x

- Control:
 - Water
 - Alka-Seltzer tablet
 - Add Alka-Seltzer to water at same instant
- Experiment: keep all but one thing the same
Change one of the following:
 - Exp 1: Increase both sodium bicarbonate and citric acid concentrations by using 2 Alka-Seltzer tablets instead of one
 - Exp 2: Different temperature
 - Exp 3: Increase surface area
 - Exp 4: Decrease concentrations of reactants in solution

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What is rate of a reaction?

- What is rate of travel? How fast you travel.

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

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

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

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

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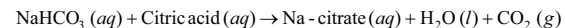
What factors can affect the speed of a reaction?

- Everyone compared to the same control
React 1 tablet of Alka-Seltzer in water at room temperature
How much time does it take for the reaction to appear to finish?
- We looked at how the reaction rate changed for four variations
Experiment 1: 2 tablets instead of 1
Experiment 2: higher temperature
Experiment 3: powdered tablet
Experiment 4: increase volume of water



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Alka-Seltzer: Bicarbonate + acid solution



↑
in the
Alka-Seltzer

↑
in the
Alka-Seltzer

What did you vary in the reaction?	What appeared to happen?
Amount of NaHCO ₃ (Alka-Seltzer) and amount of citric acid doubled	2 tablets took a little longer to react, but not twice as long
Temperature	Shorter time in hot water
Surface area for reaction to occur	Powdered tablet reacted faster
Volume of water	No appreciable difference (or maybe a little bit shorter rxn time)

Did the speed of the reaction change over time? Why?

What appeared to happen to the reaction rate

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

What did we vary in the reaction?	What happened?	How does the rate of the experiment compare to the rate of the control?
Amount of NaHCO ₃ and amount of citric acid (Alka-Seltzer) doubled	2 tablets took longer to react, but not 2x as long	Rate(2 tablets) ????? Rate (1 tablet)
Temperature	Shorter time in hot water	Rate(hot water) > Rate(cold water)
Surface area for reaction to occur	Powdered tablet reacted faster	Rate(powdered) > Rate(whole tablet)
Volume of water	No appreciable difference or maybe a little less time	Rate(more water) ??? Rate(less water)

Compare 2 tablets vs. 1 tablet

- Two tablets in 100 mL water
Took about one minute (60 sec) for reaction to be complete

$$\text{rate (2 tablets)} = \frac{\Delta \text{conc}}{\Delta t} = \frac{(2 \text{ tablets} - 0 \text{ tablet}) / 0.100 \text{ L}}{1 \text{ min}} = 20 \frac{\text{tablet}}{\text{L} \cdot \text{min}}$$

- One tablet in 100 mL water
Took about 3/4 minute (45 sec) for reaction to be complete

$$\text{rate (1 tablet)} = \frac{\Delta \text{conc}}{\Delta t} = \frac{(1 \text{ tablet} - 0 \text{ tablet}) / 0.100 \text{ L}}{0.75 \text{ min}} = 13.3 \frac{\text{tablet}}{\text{L} \cdot \text{min}}$$

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A discrepancy?

Rate = $k[A]^n$ (where the power n is some number)
So if [A] is larger, then rate should increase also

Why when we added more reactants (2 tablets is twice as much sodium bicarbonate and citric acid) did the reaction last for a little longer but not 2x as long?

Explanation in words:
We measured rate as

$$\text{rate of reaction (rate)} = \frac{\text{change of chemical concentration}}{\text{time elapsed}} = \frac{\Delta[A]}{\Delta t}$$

using ΔA = all of the reactants apparently reacted, and Δt = the entire time that it took. For rate to be the same, when ΔA is doubled, Δt must also double. So we expected 2 tablets to take twice as long as 1 tablet in the same amount of water.

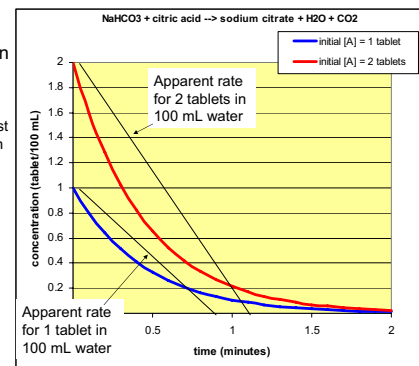
In our experiment in class, it took less than twice the time for 2 tablets to react, compared to the time for 1 tablet to react. So rate really is larger when $[A]_0$ is larger.

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Resolving an apparent discrepancy

Graphical explanation

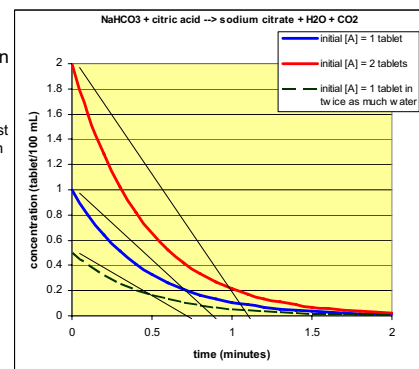
Say 0.2 tablet/100mL is the smallest concentration that your eye can tell there is still rxn happening



Resolving an apparent discrepancy

Graphical explanation

Say 0.2 tablet/100mL is the smallest concentration that your eye can tell there is still rxn happening



Average vs. instantaneous rxn rate

- Average rxn rate

$$\text{rate of reaction (rate)} = \frac{\text{(change of chemical concentration between beginning of rxn and end)}}{\text{total time elapsed}} = \frac{\Delta[A]}{\Delta t}$$

- Instantaneous rxn rate (tangent to curve)

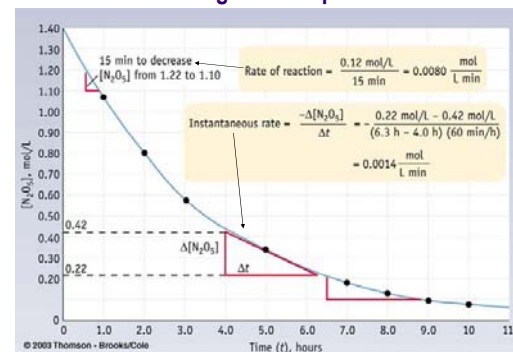
$$\text{rate of reaction (rate)} = \frac{\text{(change of chemical concentration over a short period of time)}}{\text{the short time elapsed}} = \frac{\Delta[A]}{\Delta t}$$

Usually in chemistry, we are interested in the instantaneous rxn rate at the very beginning (at $t = 0$)

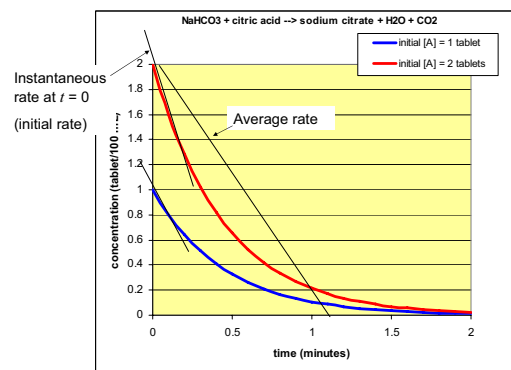
INITIAL REACTION RATE

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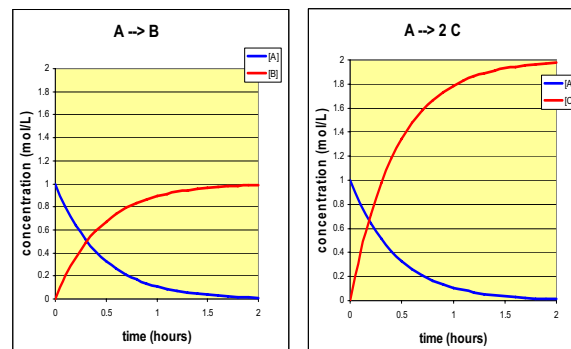
The rate of a reaction changes over time because reactants get used up



Average vs. instantaneous rxn rate



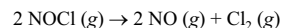
Comparing concentrations of chemicals in a reaction



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 NOCl.



If the initial rate of disappearance of NOCl is $4.20 \times 10^{-4} \text{ mol}/(\text{L}\cdot\text{h})$, what is the initial rate of appearance of Cl_2 ?

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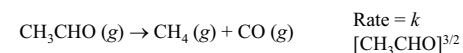
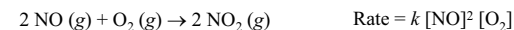
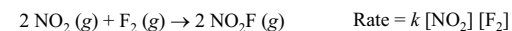
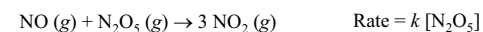
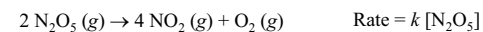
What we're after in kinetics

- 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

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Rate law must be determined experimentally

Some reactions and their *experimentally determined* rate laws



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

Key points about kinetics from today

- Study the vocabulary
- Reaction rate has weird units
- Be clear whether you are talking about average reaction rate or instantaneous reaction rate
- The equations which we will study all talk about instantaneous reaction rate, most easily measured at the beginning of a reaction (initial rate)
- 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

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