CH 302 – Unit 3 Review 3

FUNDAMENTALS OF KINETICS, INORGANIC (???)

BY THE WAY, CHECK OUT OPEN STAX:

HTTP://CNX.ORG/CONTENTS/HAVXKYVS@9.422:HHZ1SPHC@3/INTRODUCTION

Introduction to Kinetics

There are four types of kinetics questions types that we have discussed in this class:

1. Overall rate of a reaction (think stoichiometry): If you can measure the rate of formation for a product, you can use stoichiometry to determine the rates for all other products and reactants

2. Rate Laws: The rate law is a fundamental equation used to calculate the rate of a reaction from the rate constant, k, and the concentrations of the reactants raised to the power of their "order". The overall reaction order is the sum of the orders of the reactants. **We will focus on this topic today for mechanisms.**

3. Empirical Rate Law: Because the order of reactants are not necessarily based on stoichiometry, you must run an experiment to measure this value based on the initial rate of reaction at different starting concentrations

4. Integrated Rate Law: Knowing the order of a reaction, you can determine the rate or concentrations of a reactant at any given point in time (calculus is necessary here because if the rate is dependent on concentration, the rate is changes as the reaction proceeds)

Work well for initial rates

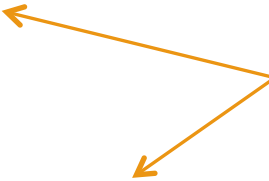Takes into account the fact that the rate can change over time

The Four Factors that Affect Rates

1. Nature of reactants/ Availability of the molecules
   ◦ Larger surface area = faster rate
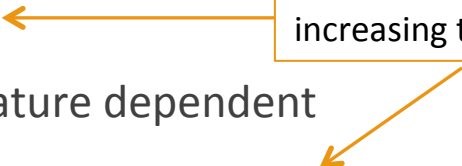   ◦ Ex: this is the reason why we chew our food (mechanical digestion)

2. Concentration (and pressure)
   ◦ Higher concentration, higher rate **if your reaction is first order or higher**
   ◦ Increases the rate based on the fact that the rate law is concentration dependent

3. Temperature
   ◦ Higher temperature, higher rate **always** (in this class)
   ◦ Increases the rate based on the fact that the **rate constant** in temperature dependent

4. Catalysts
   ◦ Catalysts decrease the **activation energy**, which increases the rate based on the Arrhenius Equation
   ◦ The activation energy is decreased by modifying the substrate orientation
   ◦ Increases the rate based on the fact that the rate constant is proportional to the **negative activation energy**

Increase the rate without changing the rate constant

Increase the rate by increasing the rate constant

Integrated Rate Laws

- **First Order: general formula, slope-intercept formula, half life**

$rate = k[A]$

$$\ln\frac{[A]_0}{[A]} = kt$$

$$\ln[A] = -kt + \ln[A]_0$$

$$\frac{\ln(2)}{k} = t_{1/2}$$

- **0th Order: general formula, slope-intercept formula, half life**

$rate = k$

$$[A]_0 - [A] = kt$$

$$[A] = -kt + [A]_0$$

$$\frac{[A]_0}{2k} = t_{1/2}$$

- **2nd Order: general formula, slope-intercept formula, half life**
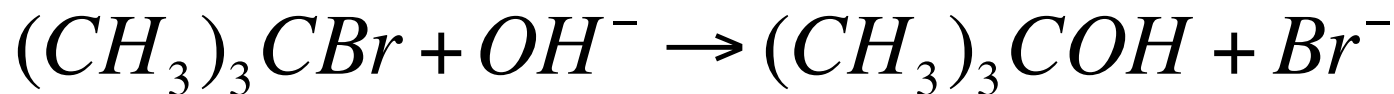
$rate = k[A]^2$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

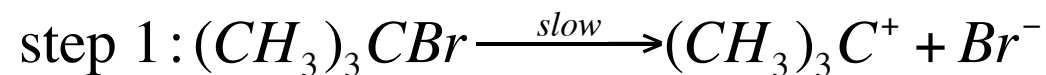$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$\frac{1}{k[A]_0} = t_{1/2}$$

Reaction Mechanisms: Elementary Steps

- At first we said that we cannot simply look at an overall equation and use stoichiometry to determine the rate law.

- However, we can determine the rate law if we can determine **the elementary steps**, or the steps that make up the overall reaction. **If you identify the correct elementary step, you will use stoichiometry to determine the rate law.**

- Most elementary steps are "fast." The elementary step we use to determine the rate law is the one labeled as "slow" or "rate limiting."

- **Collision theory** states that the reaction rate is proportional to the number of successful collisions divided by time. **Therefore, it should make sense that the rate law can be determined by the slowest elementary step.**

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

Mechanism:

$$\text{step } 1 : (CH_3)_3CBr \xrightarrow{\quad slow \quad} (CH_3)_3C^+ + Br^-$$

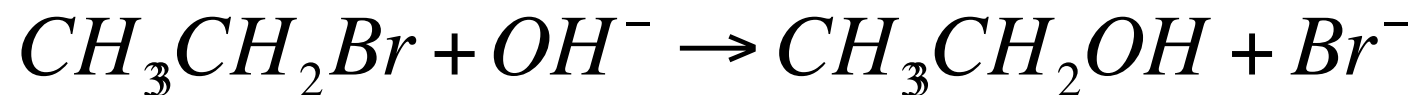$$\text{step } 2 : (CH_3)_3C^+ + OH^- \xrightarrow{\quad fast \quad} (CH_3)_3COH$$

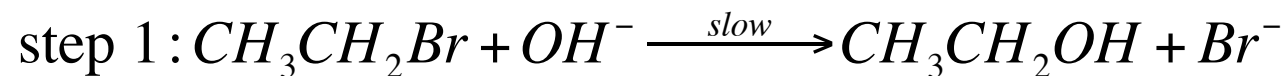$$\text{rate} = k_1 \, [(CH_3)_3CBr]$$

The rate of this reaction depends only on step 1. This elementary step involves a tert-butyl bromide decomposing in solution to form bromide and a carbocation. Because it involves only one reactant, we call this a unimolecular elementary step.

Reaction Mechanisms: Elementary Steps

$$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$$

Mechanism:

$$\text{step } 1: CH_3CH_2Br + OH^- \xrightarrow{\quad slow \quad} CH_3CH_2OH + Br^-$$

$$\text{rate} = k_1[CH_3CH_2Br][OH^-]$$

Observe the difference with this reaction. There is only one step so it is easy to determine the rate-limiting step, but this reaction is bimolecular. This means that the rate depends on the collision of 2 molecules.

Reaction Coordinate Diagrams

Be able to identify/explain the following on a graph:

1. The number of steps
   ◦ The number of "humps" on a diagram; each representing a high energy transition state
2. The number of intermediates
   ◦ The number of valleys between humps
3. The transition states
   ◦ High energy, transient states
   ◦ Always represent a higher energy state than the previously existing intermediate/reactant
4. Rate-limiting step (slow step vs. fast step)
   ◦ The hump with the greatest change in energy (not always the highest energy maxima on the diagram)
5. Activation Energy of the reaction
   ◦ The energy difference between the reactant/intermediate and the transition state of the rate-limiting step
6. The overall change in enthalpy
   ◦ The energy difference between the reactants and the products (think thermodynamic state functions)

Reaction Coordinate Diagrams
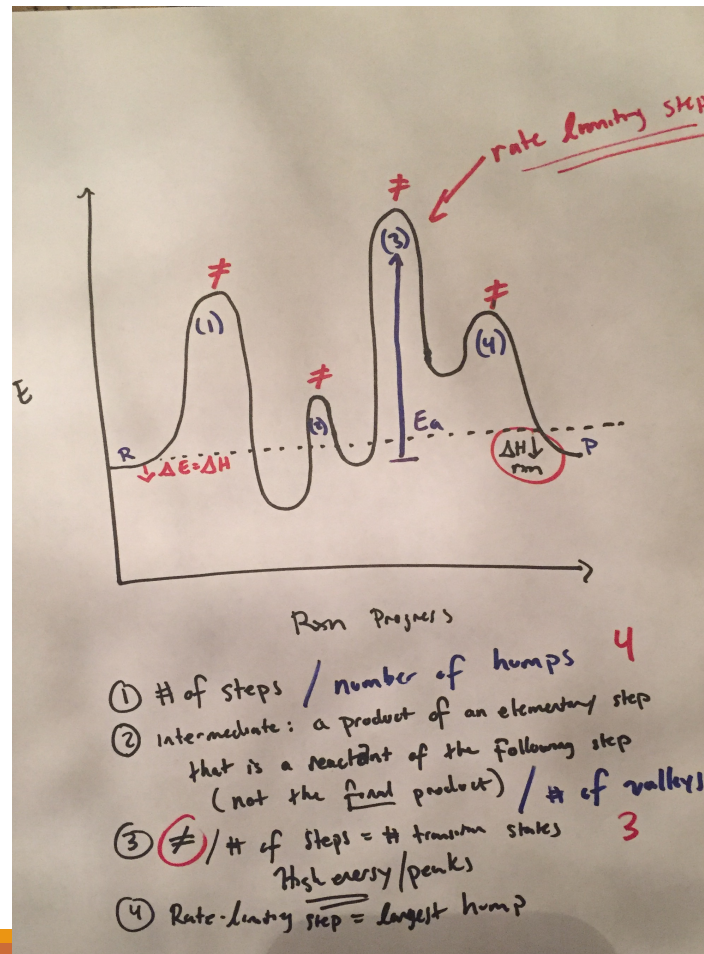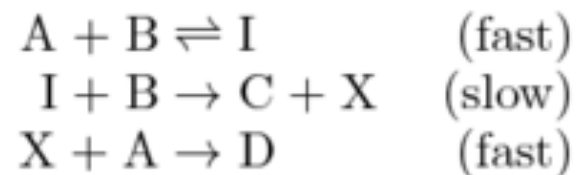
Mechanisms: Hard Example

- In the previous examples, our rate limiting step was the first step. If this is the case, your rate law is very easy to determine.

- However, a rate law must always be written in terms of the species that show up in the overall reaction. **In other words, intermediates cannot be written in the rate law**.

- We will need to do a few additional steps for an example where the slow step is not the first step.

Consider the multistep reaction that has the overall reaction
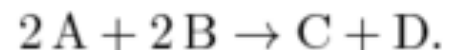
$$2\,A + 2\,B \rightarrow C + D.$$

What is the rate law expression that would correspond to the following proposed mechanism?

$$A + B \rightleftharpoons I \qquad \text{(fast)}$$
$$I + B \rightarrow C + X \qquad \text{(slow)}$$
$$X + A \rightarrow D \qquad \text{(fast)}$$

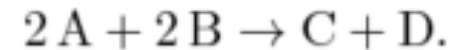# Mechanisms: Hard Example

Consider the multistep reaction that has the overall reaction

$$2\,A + 2\,B \rightarrow C + D.$$

What is the rate law expression that would correspond to the following proposed mechanism?

$$
\begin{array}{lr}
A + B \rightleftharpoons I & (\text{fast}) \\
I + B \rightarrow C + X & (\text{slow}) \\
X + A \rightarrow D & (\text{fast})
\end{array}
$$

$$2A + 2B \longrightarrow C + D$$

$$K_1[A][B] = k_{-1}[I]$$

STEP	Reaction
1, k_1	$A + B \rightleftharpoons I$ fast, @eq
2, k_2	$I + B \rightarrow C + X$ slow
3, k_3	$X + A \rightarrow D$

$$\text{rate} = k_2\,[I][B]$$

$\downarrow$ sub

$$K_1[A][B] = k_{-1}[I]$$

$$\rightarrow [I] = \left(\frac{K_1}{k_{-1}}\right)[A][B]$$

$$\text{rate} = \frac{k_2 \cdot k_1}{k_{-1}}\,[A][B]^2$$

$\downarrow$

$$\text{rate} = k^-\,[A][B]^2$$
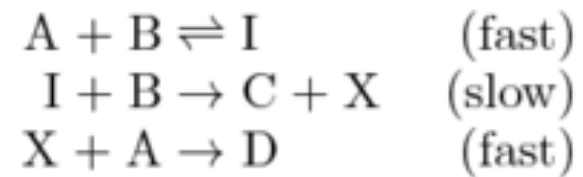
Mechanisms: Harder Example

- This problem shows that it can be trickier. In this case you are forced to include an intermediate in the rate law. It will have a negative order. This is OK.

Consider the reaction mechanism

Step	Reaction
1	$C_2H_4 + BrF \longrightarrow C_2H_4F + Br$
2	$C_2H_4F + BrF \longrightarrow C_2H_4F_2 + Br$
3	$Br + Br \longrightarrow Br_2$
overall	$C_2H_4 + 2\,BrF \longrightarrow C_2H_4F_2 + Br_2$

What is the rate law if step 2 is the rate-determining step?

Mechanisms: Harder Example
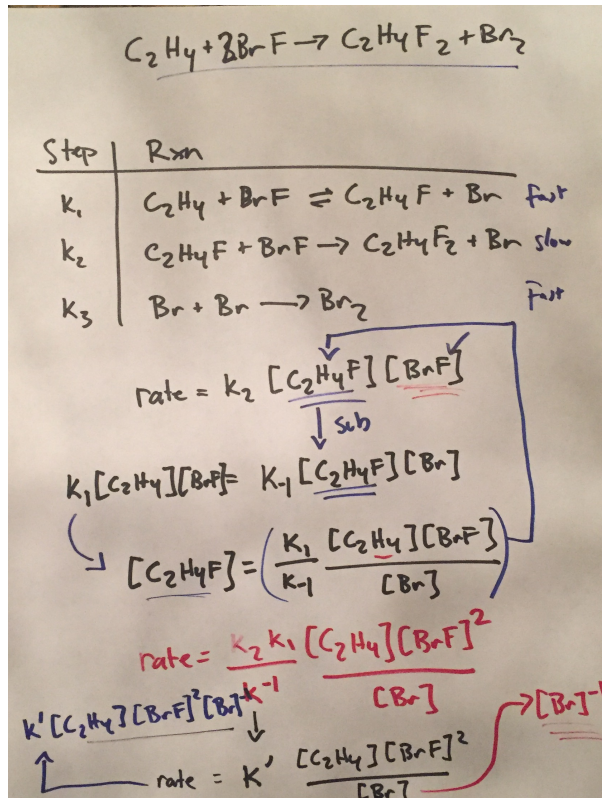
Consider the reaction mechanism

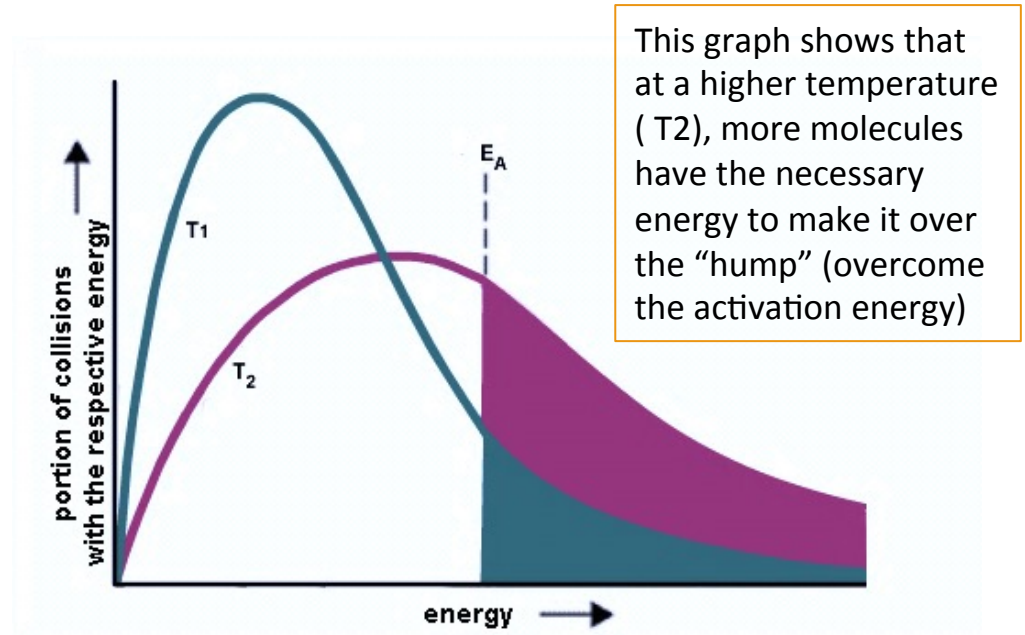| Step	Reaction
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What is the rate law if step 2 is the rate-determining step?

Collision Theory: Activation Energy

Earlier, I mentioned that **Collision Theory** states that the reaction rate is proportional to the number of successful collisions divided by time.

- We can define a "successful collision" as one that has sufficient energy to break or form the bonds in the elementary step.

- **The energy required for a successful elementary step is called the Activation Energy.**

- Remember: you can increase the probability of collisions by increasing the surface area or increasing the concentration.

- Taking it one step further, the Arrhenius Equation give us two very helpful ways of increasing the rate of a reaction:
  1. **You can increase the temperature**
  2. **You can add a catalyst (lower Ea)**

  Increase the rate constant

This graph shows that at a higher temperature (T2), more molecules have the necessary energy to make it over the "hump" (overcome the activation energy)

$$k = Ae^{\frac{-Ea}{RT}}$$

Collision Theory: Temperature and Catalysts

How does temperature affect the rate of reaction?

- By increasing the temperature, you are increasing the number of particles that have enough energy to collide successfully. In other words, **you are increasing the number of particles with the ability to overcome the activation energy.**

- **Based on the Arrhenius Equation, you will get a higher rate constant that will give you a faster rate of reaction.**

How does adding a catalyst affect the rate of reaction?

- Catalysts lower the activation energy **by stabilizing the transition state.**

- Like temperature, **this mathematically results in a higher rate constant**

- Catalysts are not consumed in the reaction. They will show up on the reactant and product side of the reaction mechanism

- Enzymes are biological catalysts

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$k = Ae^{\frac{-Ea}{RT}}$$