CH 302 – Unit 4 Exam Review

FUNDAMENTALS OF KINETICS, ~~NUCLEAR~~, INORGANIC*

*DR. B ONLY

Exam Breakdown

Dr. B → 20 Q's, 6 inorganic + 14 kinetics (2 nuclear)

Dr. McCord → 25 Q's, 25 kinetics (2 nuclear)

Nuclear → Radioactive decay = 1st order

$t_{1/2}$ → stability

Preparing for Exam 4: Kinetics

1. Do the work:
   - Do the **Sapling**, Canvas EP, and Quest worksheets TWICE; make an outline for the conceptual material and deriving the graphs from your memorized equations
2. Understand the material quantitatively, visually (graphically), and conceptually:
   - The "macro-view" of this unit revolves around making calculations using experimental setups.
   - The "micro-view" of this unit revolves around understanding the molecular interactions: collision theory, transition-state theory, mechanisms, molecularity
3. Reflect on your answer to see if it makes sense:
   - k and t are always positive
   - $[A]_0$ is always greater than [A]
   - A reactant's rate is negative; a product's rate is positive (unless the vocabulary takes care of the sign for you)

Introduction to Kinetics

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

1. Relative rates 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.
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

These work well for initial rates

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)

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. How much your rate changes as a factor of concentration is based on the order of that reactant.
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

$$\text{rate} = k[A][B] \qquad A + B \rightarrow C$$

This is one example where stoichiometry DOES matter

This is one example where stoichiometry DOES matter

Relative Rates of a Reaction

The fundamental rate of a reaction can be described by the rate of change of any reactant or product of the reaction.

1. **Coefficients play an important role**
   - A coefficient in front of a species means it is going that number times the overall reaction rate
   - Nitrogen dioxide (NO_2) is going 4x the overall rate
2. **The rate of change for different species can be interconverted**
   - N_2O_5 is going half the rate of NO_2
3. **The rate of change for reactants and products are always opposite in sign**
   - The overall rate of N_2O_5 is negative, NO_2 and O_2 are positive
   - The rate of CONSUMPTION or DISAPPEARANCE of N_2O_5 is a magnitude (+ value)).

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

$$\text{rate} = \frac{-\Delta[N_2O_5]}{2\,\Delta t} = \frac{\Delta[NO_2]}{4\,\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

$$\text{rate } N_2O_5 = 2 \times \text{overall rate}$$

Warning: Units

$\frac{1}{M\cdot s}\ (\cancel{x}M)(\cancel{x}M)$

Introduction to Rate Laws

$$aA + bB \rightarrow cC + dD$$

$$rate = \underline{k[A]^x[B]^y}$$

Rate of reaction in the units of M/s

Rate constant (measured value). Units depend on the order of reaction; must cancel units of $[A]^x$, $[B]^y$ to get rate = M/s

x = order of A
y = order of B
x + y = overall order of the reaction
Order is usually positive integers, but can be fractional or negative in rare cases

What is the order? You have to use experimental data to figure it out.

Introduction to Rate Laws

$$aA + bB \longrightarrow cC + dD$$

$$rate = k[A]^x[B]^y$$

0th Order:

$$rate = k \qquad k = M/s$$

First Order:

$$rate = k[A] \text{ or } rate = k[B] \qquad k = 1/s$$

Second Order:

$$rate = k[A][B] \text{ or } rate = k[A]^2 \text{ or } rate = k[B]^2 \qquad k = 1/Ms$$

Overall Reaction Order, rate constant

Order can be applied to the total reaction:

- The order of the reaction is the sum of the exponents in the rate law.
- Our units of *k* are dependent on the order of the total reaction:
  - 0^{th} order: $k = Ms^{-1}$
  - 1^{st} order: $k = s^{-1}$
  - 2^{nd} order: $k = M^{-1}s^{-1}$
  - 3^{rd} order: $k = M^{-2}s^{-1}$
  - n^{th} order: $k = M^{-(n-1)}s^{-1}$

These are all based on the fact that the rate must be in Ms^{-1}, and you are cancelling out the concentration terms on the rate law

A few ways we can give the reaction order (these are all first-order, think about how they would be different for other orders)

- "A reaction is first order…"
- The slope of ln[A] vs t gives a straight line with a slope equal to -0.05
- The rate constant for a reaction is $0.05\ s^{-1}$
- "For the radioactive decay of…"
- "The substrate A has a half-life that is independent of concentration…"
- The concentration of [A] is 1.5 mM and the concentration of [B] is 200mM

Method of Initial Rates

What is the rate law for the reaction

$$A + B + C \rightarrow D$$

if the following data were collected?

Exp	$[A]_0$	$[B]_0$	~~$[C]_0$~~	Initial Rate
✓ 1	0.4	1.2	~~0.7~~	2.32×10^{-3}
2	1.3	1.2	~~0.9~~	7.54×10^{-3}
3	0.4	4.1	~~0.3~~	9.25×10^{-2}
4	1.3	1.2	~~0.2~~	7.54×10^{-3}

$$\boxed{\frac{Rate_2}{Rate_1} = \frac{k[A]_2^x[B_2]_2^y\cancel{[C]_2^z}}{k[A]_1^x[B_2]_1^y\cancel{[C]_1^z}}}$$

1) $2 \rightarrow 4$

$C = 0$ order

2) $1 \rightarrow 2$

$$\frac{0.00754}{0.00232} = \left(\frac{1.3}{0.4}\right)^x$$

$$3.25 = 3.25^x$$

$$x = 1$$

3) $1 \rightarrow 3$

$$\frac{0.0925}{0.00232} = \left(\frac{4.1}{1.2}\right)^y$$

$$y = 3$$

$$rate = k[A][B]^3$$

$$2.32 \times 10^{-3} = k(0.4)(1.2)^3$$

$$k = 3.63 \times 10^{-3}$$

$$rate = 3.63 \times 10^{-3}[A][B]^3$$

Integrated Rate Laws

$\rightarrow \Delta t$

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

$rate = k[A]$

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

$y = mx + b$

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

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

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

$rate = k$

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

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

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

- **2^{nd} Order: general formula, slope-intercept formula, half life**

$rate = k[A]^2$

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

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

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

Applying Integrated Rate Laws

The integrated rate laws can be written to yield straight lines on the curves. The main difference between them is the axes:

- All graphs have time as the x axis
- 0th order: y-axis is **concentration**
- 1st order: y-axis is the **natural log of the concentration**
- 2nd order: y-axis is the **inverse of the concentration**

The other difference is the slope

- 0th and 1st order have a negative slope (**slope = -k**)
- 2nd order has a positive slope (**slope = k**)

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

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

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

$t_{1/2}$ for first order (nuclear) $\propto$ stability

Half-Lives of Integrated Rate Laws

- First Order Half-Life: Independent of concentration

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

$[A]_0 \downarrow$, $t_{1/2}$ does not change

- 0th Order Half-Life: Directly related to concentration

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

$[A]_0 \downarrow$, $t_{1/2}$ goes down

- 2nd Order Half-Life: Inversely related to concentration

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

$[A]_0 \downarrow$, $t_{1/2}$ goes up

Warning 2: units, time must match rate law & answer

Nuclear Rate of Decay: Half-Life

- The rate at which an unstable isotope decays is measured by its half-life. Half-life is defined as the amount of time it takes for ½ of your material to decay. Remember: Half-life correlates with stability

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

- Radioactive decay follows first order kinetics. This means the rate of decay is dependent on the amount of the decaying material.

$$[A] = [A]_0 e^{-kt} \qquad \ln\frac{[A]_0}{[A]} = kt$$

First-Order Radioactive Decay

1. Easy: How long will it take for 256 grams of Pu-241 to decay into 16 grams? The half-life of Pu-241 is 14.4 years.

$$256 \xrightarrow[1]{} 128 \xrightarrow[2]{} 64 \xrightarrow[3]{} 32 \xrightarrow[4]{} 16$$

$$4 \times 14.4 = 57.6 \text{ years}$$

2. Challenging: How long will it take for 43,453 grams of Pu-241 to decay into 6,378 grams? The half-life of Pu-241 is 14.4 years.

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

$$\frac{\ln(2)}{t_{1/2}} = k \approx 0.048$$

$$\ln \frac{43,453}{6378} / k = t = 39.9y$$

Conceptual Note: Integrated Rate Laws

- Integrated rate laws take into account **a single reactant** that has 0th order, 1st order, or 2nd order kinetics. These equations fail when:
  - The reaction has any significant backward rate
  - The reaction is at equilibrium (backwards rate equals the forward rate)
  - When the overall rate depends on the concentration of another reactant
    - We get around this by setting up Pseudo-first Order conditions:

$$\underline{rate = k[\overset{\uparrow}{A}][B]}$$

$$K' = K\,[\text{constant}]$$

  - We can "mimic" first order conditions by using disproportionate starting conditions. Suppose we start with 2M A and 0.005 M B. We get a new expression with a new "k" value that is equal to the product of the original k and the relatively consistent concentration [A]:

$$rate = \boxed{k \cdot 2} \cdot [B] = \boxed{k'}[B] \rightarrow \ln \frac{[B]_0}{[B]} = Kt$$

This is the other example where stoichiometry DOES matter

Fundamentals of Mechanisms

We can propose a mechanism that dictates the kinetics of the reaction. The mechanism explains what is actually going on and helps us define the following terms:

1. **Rate-limiting step:** the slow step of a mechanism; dictates the rate of the reaction and activation energy
2. **Molecularity:** the number of species involved in the rate-limiting step
    - Unimolecular: the rate-limiting step involves a single species changing (breaking apart, dissolving, decomposing, etc.) into products; the rate law for this step is first order
    - Bimolecular: the rate-limiting step involves the collision of 2 species ; the rate law for this step is second order
    - Note: we do not often propose elementary steps that are termolecular and beyond. This is because it is very improbable for 3 species to collide with the correct energy / orientation
3. **The Overall Rate Law:** the rate law properly expressed in terms of only reactants
    - If the rate-limiting step involves an intermediate, you will need to substitute to in to express your rate in terms of only the reactants of the overall reaction

big

$$\rightarrow K = \frac{[Cl]^2}{[Cl_2]} = \frac{k_1}{k_{-1}} = \frac{K_{forward}}{k_{reverse}}$$

$$\text{rate} = k'[H_2][Cl_2]$$

Mechanisms: Example

Consider the following reaction mechanism for the formation of hydrochloric acid.

Overall : $H_2 + Cl_2 \rightarrow 2HCl$

$Cl_2 \rightleftharpoons 2Cl$ k_1 (fast, eq.)

$Cl + H_2 \rightleftharpoons H_2Cl$ k_2 (fast, eq.)

$H_2Cl + Cl \longrightarrow 2HCl$ k_3 (slow)

Here are the three layers of difficulty:

I) Identify the rate limiting step and the molecularity of this elementary step

II) Write the rate law for this reaction

III) What is the equilibrium constant for steps one and two with respect to their rate constants?

bimolecular

order = 2

$$\text{rate} = K_3[H_2Cl][Cl]$$

$$\frac{K_2[Cl][H_2]}{k_{-2}} = \cancel{k_{-2}}[H_2Cl]$$

$$\text{rate} = \frac{k_3 k_2}{k_{-2}}[H_2][Cl]^2$$

$$\frac{K_1[Cl_2]}{k_{-1}} = \cancel{k_{-1}}[Cl]^2$$

$$\text{rate} = \frac{k_3 k_2 k_1}{k_{-2} k_{-1}}[H_2][Cl_2]$$

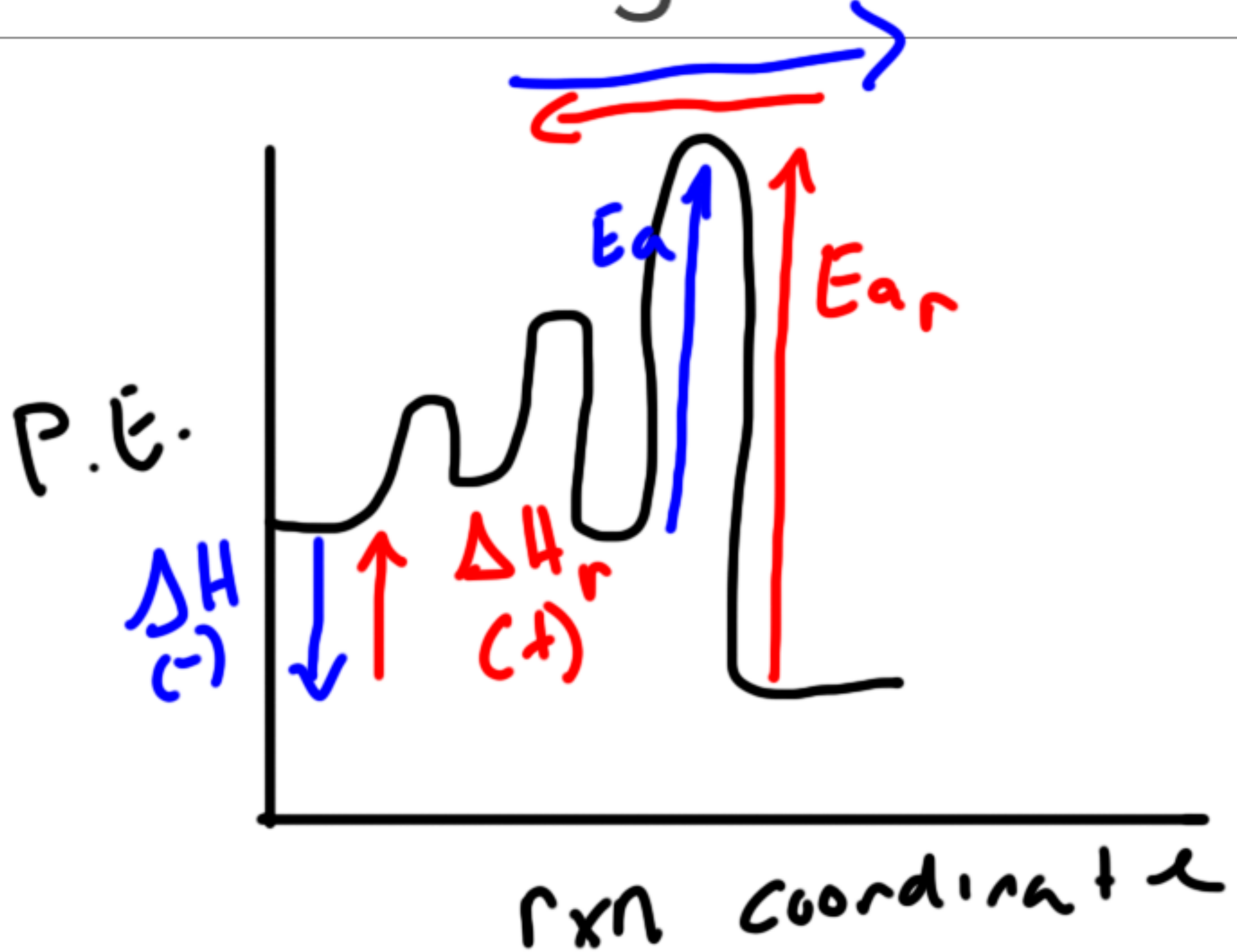
Reaction Coordinate Diagrams

Consider the following reaction mechanism for the formation of hydrochloric acid.

Overall : $H_2 + Cl_2 \rightarrow 2HCl$

$Cl_2 \rightleftharpoons 2Cl$ k_1 (fast, eq.)
$Cl + H_2 \rightleftharpoons H_2Cl$ k_2 (fast, eq.)
$H_2Cl + Cl \longrightarrow 2HCl$ k_3 (slow)

Suppose this reaction is exothermic

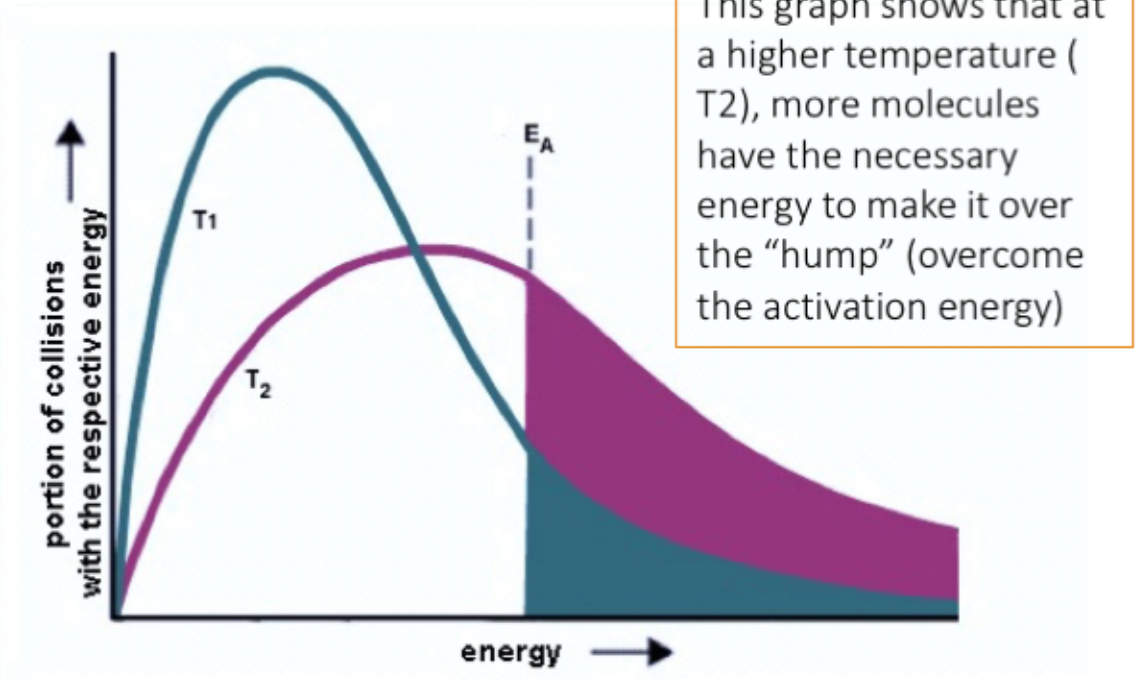


Collision Theory: Activation Energy

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)

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

$T\uparrow \quad k\uparrow$ (little) $\quad \text{rate}\uparrow \quad t_{1/2}\downarrow \quad // \quad E_a\downarrow \quad k\uparrow \quad \text{rate}\uparrow$

Kinetics: 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.**

$$✓ \quad \ln\left(\frac{k_2}{k_1}\right) = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \rightarrow \ln\left(\frac{t_1}{t_2}\right)$$

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**
- Enzymes are biological catalysts
- Unlike temperature, changing the activation energy will have no effect on the equilibrium properties of the products and the reactants.

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