

CH302 Unit 3 Review 2

KINETIC PROBLEM TYPES, MECHANISMS

Introduction to Kinetics

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

1. **Relative rates of a reaction (stoichiometric rates):** 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
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)
5. **Mechanisms:** Using the known steps of a reaction to determine the overall rate law

} Initial rates

} any time frame

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

$T \uparrow, k \uparrow, t \downarrow$

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

4. Catalysts

$\downarrow E_a \quad \uparrow k$

- 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

$$\text{rate} = k[A]$$

\uparrow \uparrow

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

Increase the rate by increasing the rate constant

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

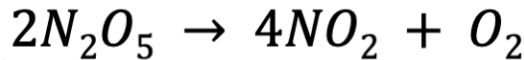
2. The rate of change for different species can be interconverted

- 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

Question: If N_2O_5 is consumed at an initial rate equal to 4.6 M/s, what is the overall rate of the reaction?

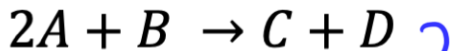


$\checkmark 4 \times \text{rate of rxn} = \text{rate of NO}_2$

$$\text{Rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t}$$

$\text{Rate of rxn} = \frac{1}{2} \text{rate of N}_2\text{O}_5$
 $2.3 \text{ M/s} = \frac{1}{2} \times 4.6 \text{ M/s}$

Introduction to Rate Laws



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

x = order of A

y = order of B

$x + y$ = order of rxn

$$\text{units of } k = \frac{1}{M^{\text{order}-1} \text{ s}}$$

if $x = 2$
 $y = 1$

order = 3

$$k = \frac{1}{M^2 \text{ s}}$$

or
 $M^{-2} \text{ s}^{-1}$

Rate Law Question

For the given reaction:



We carry out two experiments at the same temperature, but in the second experiment the initial concentration of NO is doubled while the initial concentration of O₂ is halved. The initial rate in the second experiment will be how many times that of the first?

$$\begin{array}{c} k[\text{NO}]^2 [\text{O}_2] \\ \downarrow \quad \quad \downarrow \\ (\times 2)^2 (\times 0.5) \\ \times \frac{4}{2} \\ \boxed{\times 2} \end{array}$$

$$\text{Rate} = .00232 = k(0.4)(1.2)^2$$

$$k = 3.36 \times 10^{-3} \frac{1}{M^3 s}$$

Method of Initial Rates

What is the rate law for the reaction



if the following data were collected?

$$\text{Rate} = k[A]^x[B]^y$$

Exp	[A] ₀	[B] ₀	[C] ₀	Initial Rate
1	0.4	1.2	0.3	2.32×10^{-3}
2	1.3	1.2	0.3	7.54×10^{-3}
3	0.4	4.1	0.3	9.25×10^{-2}
4	1.3	1.2	0.3	7.54×10^{-3}

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[A]_2^x[B]_2^y[C]_2^z}{k[A]_1^x[B]_1^y[C]_1^z}$$

Trial 2
Trial 1

$$\frac{.00754}{.00232} = \left(\frac{1.3}{0.4}\right)^x$$

$$3.25 = 3.25^x \quad x = 1$$

Trial 3
Trial 1

$$\frac{.0925}{.00232} = \left(\frac{4.1}{1.2}\right)^y$$

$$39.86 = 3.42^y$$

$$\log(39.86) = y \times \log(3.42)$$

$$y = 3$$

Integrated Rate Law Equations

	0 Order	1 st Order	2 nd Order
Rate Law	rate = k	rate = k[A]	rate = k[A] ²
Integrated Rate Law	$[A] = [A]_0 - kt$	$\ln[A] = \ln [A]_0 - kt$ $\ln\left(\frac{[A]_0}{[A]}\right) = kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Half Life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

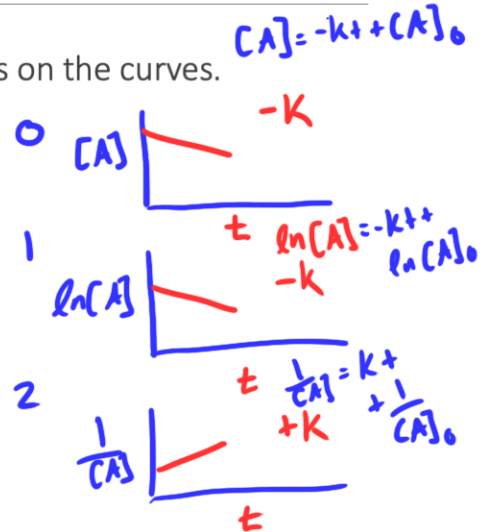
Applying Integrated Rate Laws – Straight Line Slope

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**)



Half-Lives of Integrated Rate Laws

- First Order Half-Life: Independent of concentration

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

$[A] \uparrow \downarrow$ $t_{1/2}$ constant

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

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

$[A] \uparrow$ $t_{1/2} \uparrow$

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

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

$[A] \uparrow$ $t_{1/2} \downarrow$

Example: 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.

$$256 \text{ g} \xrightarrow{1} 128 \text{ g} \xrightarrow{2} 64 \text{ g} \xrightarrow{3} 32 \text{ g} \xrightarrow{4} 16 \text{ g}$$

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

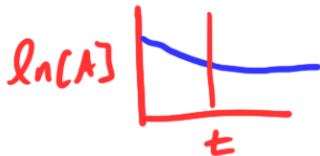
2. Challenging: How long will it take for 43,453 grams of Pu-241 to decay into 6,378 grams? The half-life of Pu-241 is 14.4 years.

$$\ln \frac{[A]_0}{[A]} = kt$$
$$\frac{\ln(2)}{k} = t_{1/2}$$

OR $\boxed{\frac{\ln(2)}{t_{1/2}} = k} = 0.048 \text{ y}^{-1}$

$$\ln \frac{43,453}{6,378} / 0.048 = \underline{39.9 \text{ years}}$$

Pseudo First Order



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

$$\text{rate} = k[A][B]$$

$$[A] = 0.01 \text{ M}$$
$$[B] = 5 \text{ M}$$

1st
order
effectively

$$\left\{ \begin{array}{l} \text{rate} = k'[A] \\ k' = k[B] = k(5 \text{ M}) \end{array} \right.$$

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

Mechanisms: Example

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



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?

$$\checkmark \text{Rate} = k' [\text{Cl}_2] [\text{H}_2]$$

$$1) \text{rate} = k_3 [\text{H}_2\text{Cl}] [\text{Cl}]$$

$$k_2 [\text{Cl}] [\text{H}_2] = k_{-2} [\text{H}_2\text{Cl}]$$

$$2) [\text{H}_2\text{Cl}] = \frac{k_2}{k_{-2}} [\text{Cl}] [\text{H}_2]$$

$$\text{rate} = \frac{k_3 k_2}{k_{-2}} [\text{Cl}]^2 [\text{H}_2]$$

$$k_1 [\text{Cl}_2] = k_{-1} [\text{Cl}]^2$$

$$[\text{Cl}]^2 = \frac{k_1}{k_{-1}} [\text{Cl}_2]$$

$$\text{rate} = \frac{k_3 k_2 k_1}{k_{-2} k_{-1}} [\text{Cl}_2] [\text{H}_2]$$