CH 302 – Unit 4 Review 1

FUNDAMENTALS OF KINETICS

BY THE WAY, CHECK OUT OPEN STAX FOR THOROUGH KINETICS INFO:

HTTPS://GOO.GL/6J7SMX

Solving Kinetics Problems

1. Identify the type of problem: Relative rates, rate law, integrated rate law, etc.
2. Write the equation that you will use to solve for your final answer
3. Solve the problem
    - Reflect on your answer to see if it makes sense

→ k, t always (+)

Introduction to Kinetics

There are four types of kinetics questions types 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
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)

These 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

Increase the rate without changing the rate constant

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 by increasing the rate constant

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. A few important notes:

1. Coefficients play an important role: if *b* = 3, the rate of consumption for B is 3 times the overall reaction rate; if *d* = 4, the rate of formation for D is 4 times the overall reaction rate
2. The rate of change for different species can be interconverted: based on the information above, we can say that the rate of formation for D is 4/3 the rate of consumption of B
3. The rate of change for reactants and products are always opposite in sign

$$\overset{1}{\cancel{a}}A + \overset{3}{\cancel{b}}B \rightarrow \overset{2}{\cancel{c}}C + \overset{4}{\cancel{d}}D$$

$$\underline{rate} = \frac{-\Delta[A]}{a\Delta t} = \boxed{\frac{-\Delta[B]}{\overset{3}{\cancel{b}}\Delta t}} = \frac{+\Delta[C]}{\overset{2}{\cancel{c}}\Delta t} = \frac{+\Delta[D]}{\overset{4}{\cancel{d}}\Delta t}$$

rxn rate ×3 = -rate B

rxn rate ×4 = rate D

$$\frac{-\overset{4}{\cancel{d}}\Delta[B]}{\overset{3}{\cancel{b}}\Delta t} = \frac{\Delta[D]}{\Delta t}$$

Overall Rate of a Reaction - Example

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

1. Write an expression that represents the overall rate of the reaction in terms of each of the reactants and products
2. Write the rate of formation of ammonia (NH_3) in terms of hydrogen (H_2).
3. Suppose the initial rate of formation of ammonia is 0.6M/s. Write the overall initial rate of the reaction.

$$\text{Rate} = \frac{-\Delta[N_2]}{\Delta t} = \underbrace{\frac{-\Delta[H_2]}{3\Delta t} = \frac{\Delta[NH_3]}{2\Delta t}}$$

$$\frac{-2\Delta[H_2]}{3\Delta t} = \frac{\Delta[NH_3]}{\Delta t}$$

$$\text{rxn rate} \frac{\times 2}{\cancel{2}} = \frac{0.6}{2} = 0.3\ M/s$$

Rate of a Reaction - Example

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

1. Write an expression that represents the overall rate of the reaction in terms of each of the reactants and products
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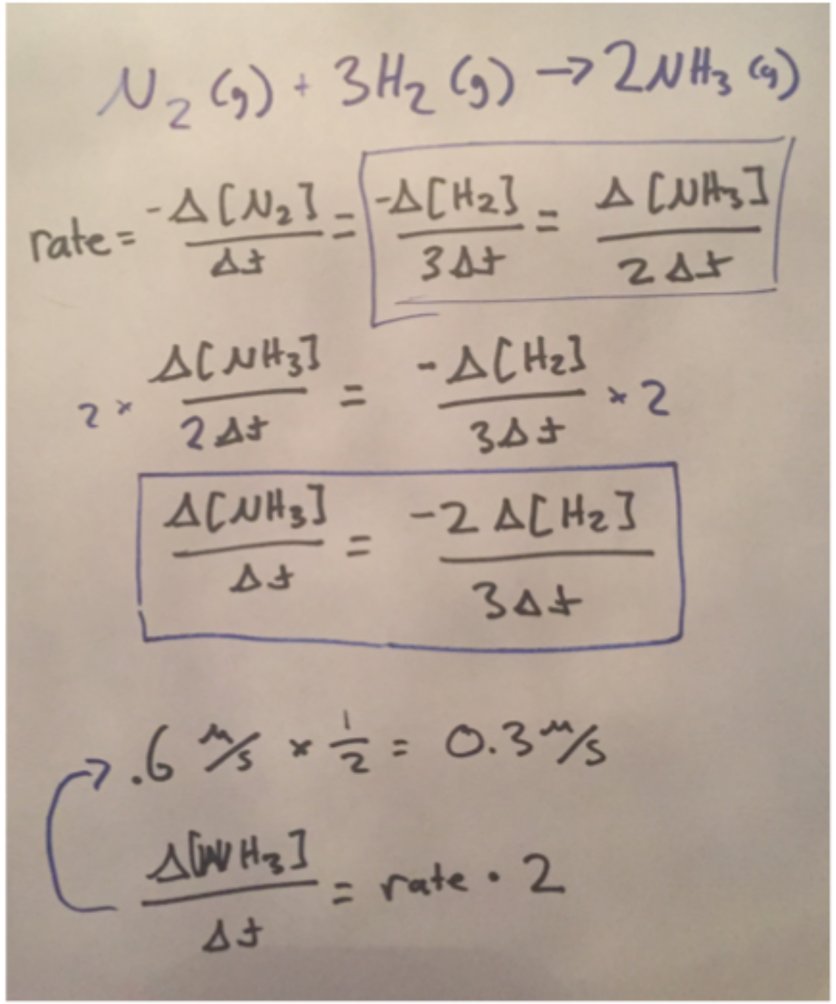


$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

$$\text{rate} = \frac{-\Delta[N_2]}{\Delta t} = \boxed{\frac{-\Delta[H_2]}{3\Delta t} = \frac{\Delta[NH_3]}{2\Delta t}}$$

$$2 \times \frac{\Delta[NH_3]}{2\Delta t} = \frac{-\Delta[H_2]}{3\Delta t} \times 2$$

$$\boxed{\frac{\Delta[NH_3]}{\Delta t} = \frac{-2\Delta[H_2]}{3\Delta t}}$$

$$.6\ m/s \times \frac{1}{2} = 0.3\ m/s$$

$$\frac{\Delta[NH_3]}{\Delta t} = \text{rate} \cdot 2$$

Introduction to Rate Laws

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

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

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

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

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

0th Order:

$rate = k$, $k = M/s$

First Order:

$rate = k[A]$ OR $k[B]$, $k = \frac{1}{s}$

Second Order:

$rate = k[A]^2$ OR $[B]^2$ OR $[A][B]$, $k = \frac{1}{M \cdot s}$

$$\frac{Rate_2}{Rate_1} = \frac{\cancel{k}\,[C_5H_{10}]^x\,\cancel{[Br_2]^y}}{\cancel{k}\,[C_5H_{10}]^x\,\cancel{[Br_2]^y}}$$

Empirical Rate Laws

Consider the bromination of pentene:

$$2C_5H_{10} + Br_2 \rightarrow 2C_5H_{11}Br$$

Start with the rate law:

$$rate = k\,[C_5H_{10}]^{\boxed{x} \rightarrow =1}[Br_2]^{\boxed{y} \rightarrow =1}$$

Then use the data to solve for x, y, and k.

Trial #	$[C_5H_{10}]$	$[Br_2]$	Rate
1	2M	2M	10M/s
2	4M	2M	20M/s
3	4M	4M	40M/s

$\times 2$

$\times 2^x$

$\times 2$

$\times 2^y$

$$rate = k\,[C_5H_{10}][Br_2]$$

$$10 = k(2)(2) \quad , K = 2.5$$

Empirical Rate Laws: solution

Trial #	$[C_5H_{10}]$	$[Br_2]$	Rate
1	2M	2M	10M/s
2	4M	2M	20M/s
3	4M	4M	40M/s

Between trials 1, 2: we doubled the concentration of pentene and the rate doubled. No change was made to bromine.

Between trials 2, 3: we doubled the concentration of bromine and the rate doubled. No change was made in pentene. This is indicative of a reaction that is first order in bromine.

Now that we know the order of the reaction, we can set up our equation: rate = $k[C_5H_{10}]^1[Br_2]^1$. The reaction is second order overall.

We can use any trial to solve for k. For example: 10M/s = k(2M)(2M), k = (10M/s)/ $(2M)^2$, $k = 2.5M^{-1}S^{-1}$

Important: trials 1, 3 don't make for a great comparison at the beginning because both reagents have different concentrations. It's difficult to determine which reagent is causing the rate to change

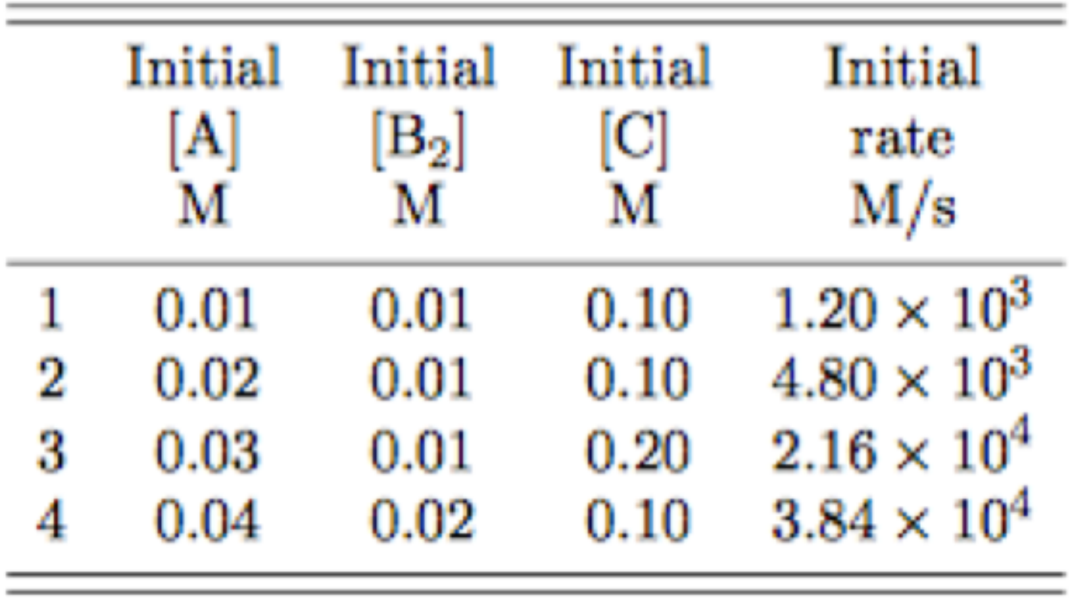
$1.44 = 1.22^x \Rightarrow \log(1.44)$
$= x \cdot \log(1.22)$

Exam Question (do on your own)

For the reaction:

$$A + B_2 + 2C \rightarrow D,$$

You run an experiment to determine the initial rates of the reaction under 4 different starting conditions. Write the complete rate law for the reaction. What is the value of k?



	Initial [A] M	Initial [B_2] M	Initial [C] M	Initial rate M/s
1	0.01	0.01	0.10	1.20×10^3
2	0.02	0.01	0.10	4.80×10^3
3	0.03	0.01	0.20	2.16×10^4
4	0.04	0.02	0.10	3.84×10^4

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

Exam Question

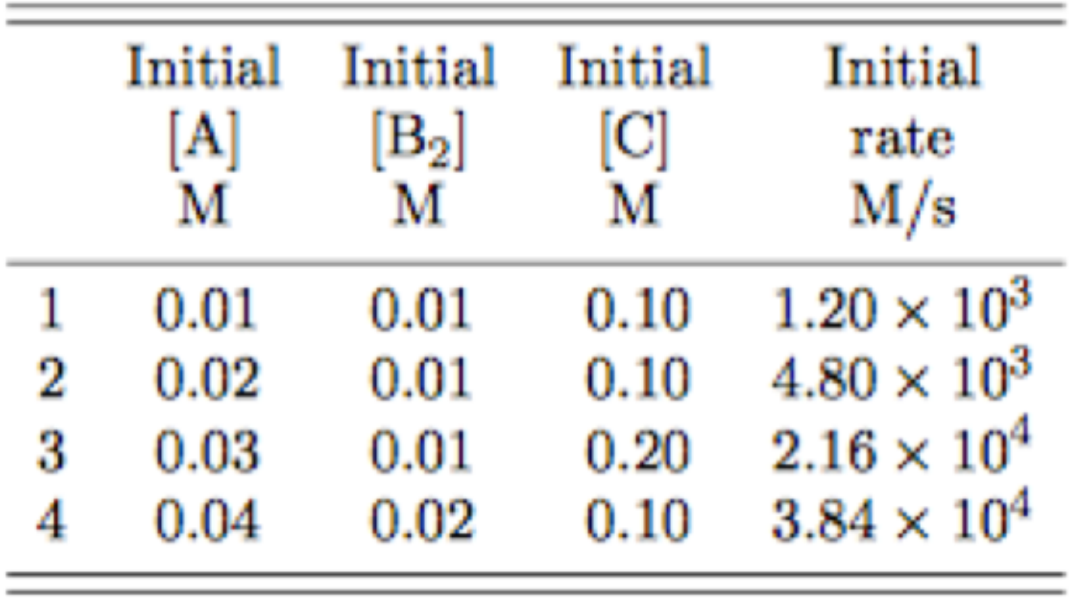
For the reaction:

$A + B_2 + 2C \rightarrow D$,

You run an experiment to determine the initial rates of the reaction under 4 different starting conditions. Write the complete rate law for the reaction. What is the value of k?

Rate = $1.2 \times 10^{10}[A]^2[B_2][C]$

(units of *k* omitted)



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

Integrated Rate Laws

$y = mx + b$

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

$rate = k[A]$

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

independent on [A]

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

$rate = k$

$$[A]_0 - [A] = kt \qquad [A] = -kt + [A]_0 \qquad \frac{[A]_0}{2k} = t_{1/2}$$

directly dependent on [A]

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

$rate = k[A]^2$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \qquad \frac{1}{[A]} = +kt + \frac{1}{[A]_0} \qquad \frac{1}{k[A]_0} = t_{1/2}$$

inversely dependent

First Order: Visual

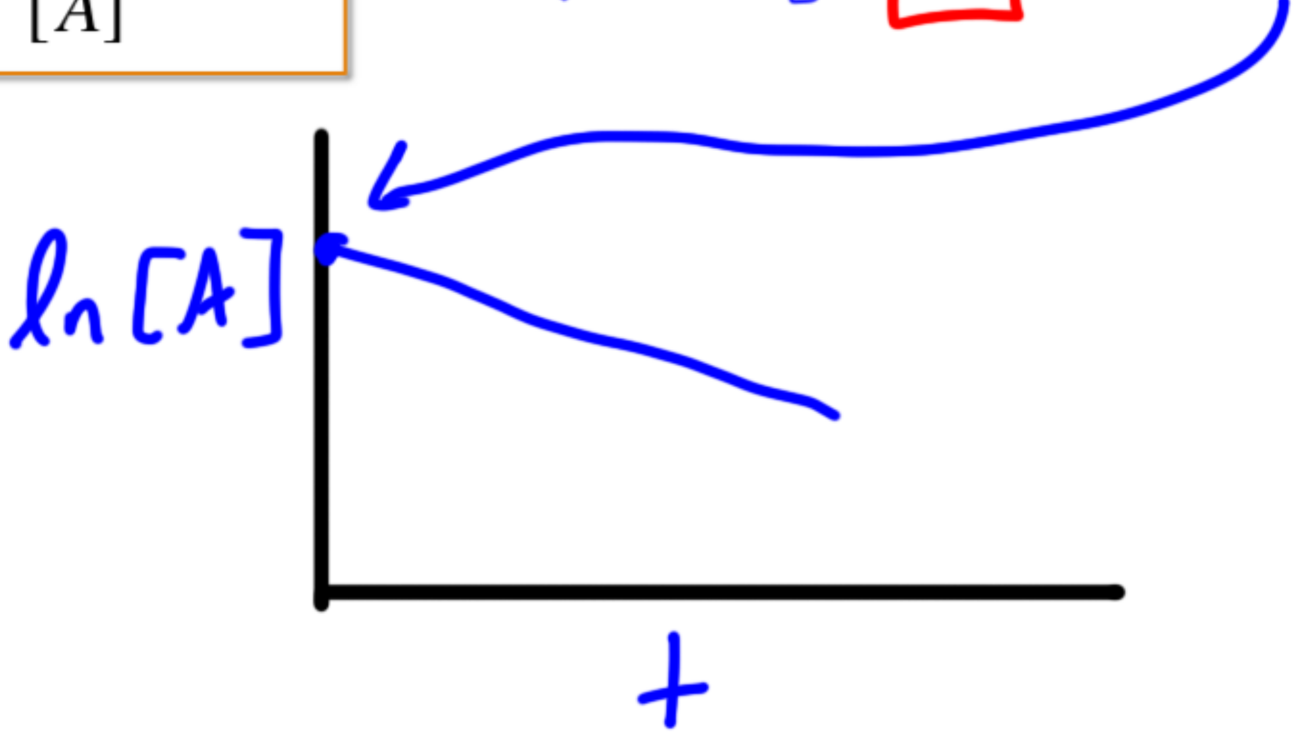
First Order: general formula, slope-intercept formula, half life

$rate = k[A]$

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

$$\ln[A] = \underbrace{-k}_{}t + \ln[A]_0$$

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



Zeroth Order: Visual

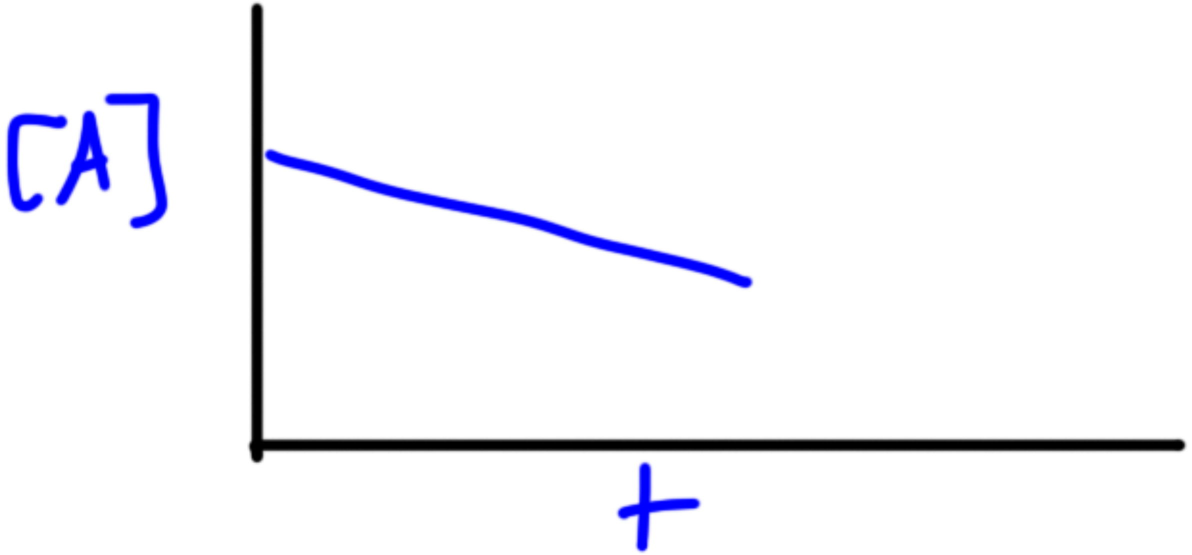
0^{th} Order: general formula, slope-intercept formula, half life

$rate = k$

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

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

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



Second Order: Visual

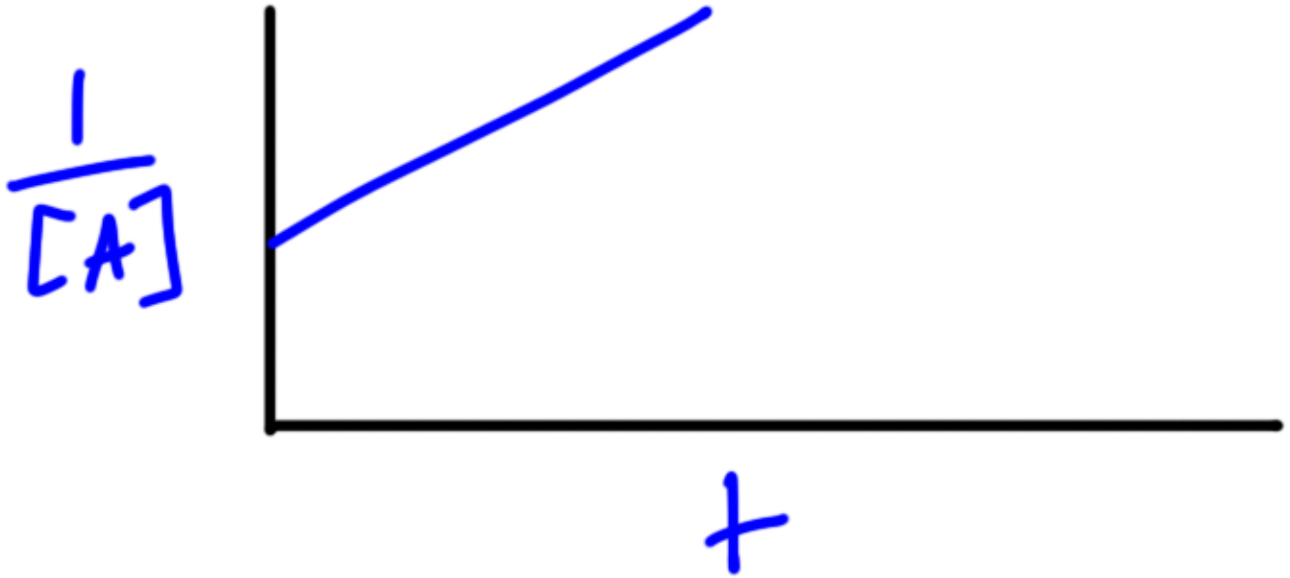
2nd Order: general formula, slope-intercept formula, half life

$rate = k[A]^2$

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

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

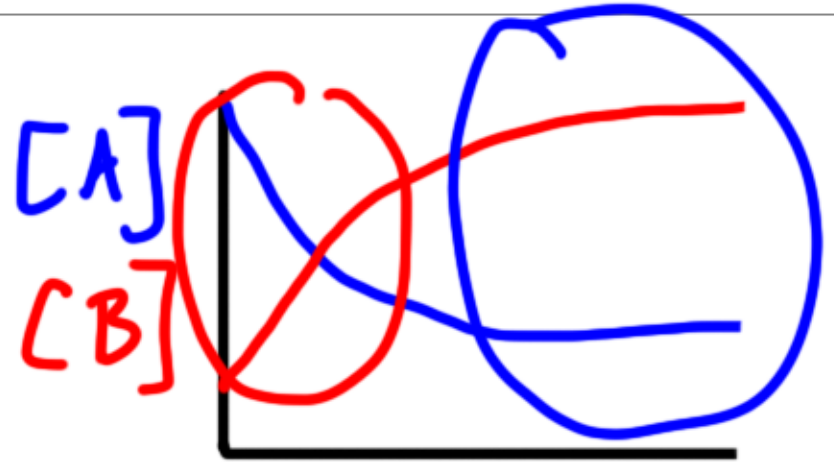
$$\frac{1}{k[A]_0} = t_{1/2}$$



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:

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 (we use “pseudo-first order” to get around this)



$$\text{rate} = K[A]^2$$

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

$$[A] = 0.0005\,M$$

$$[B] = 5\,M$$

$$\text{rate} = K'[A] \quad K' = k \cdot [B]$$

Exam Question

For the reaction below:

$$cyclobutane(g) \rightarrow 2\ ethylene(g)$$

at 800K, a plot of ln[cyclobutane] vs time (in seconds) gives a straight line with a slope of -1.6. Calculate the time (in seconds) needed for the concentration of cyclobutane to fall to 1/16 of its initial value.

Integrated rate Law oops

1st order $\ln\frac{[A]_0}{[A]} = kt$

$k = 1.6\ \frac{1}{s}$

$\frac{\ln(16)}{1.6} = 1.6 \cdot t$

$t = 1.73\ s$

4 half-lives

$\frac{\ln(2)}{1.6} = 0.43$

$\times 4 = \boxed{1.73\ s}$

Relative Rate

Exam Question

The initial rate of formation of O_2 in the following reaction is 3.2M/s and the rate law is ~~rate = k[N_2O_5]~~.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

What is the initial rate of consumption of N_2O_5?

Rate $O_2 \times 2$ =

rate N_2O_5

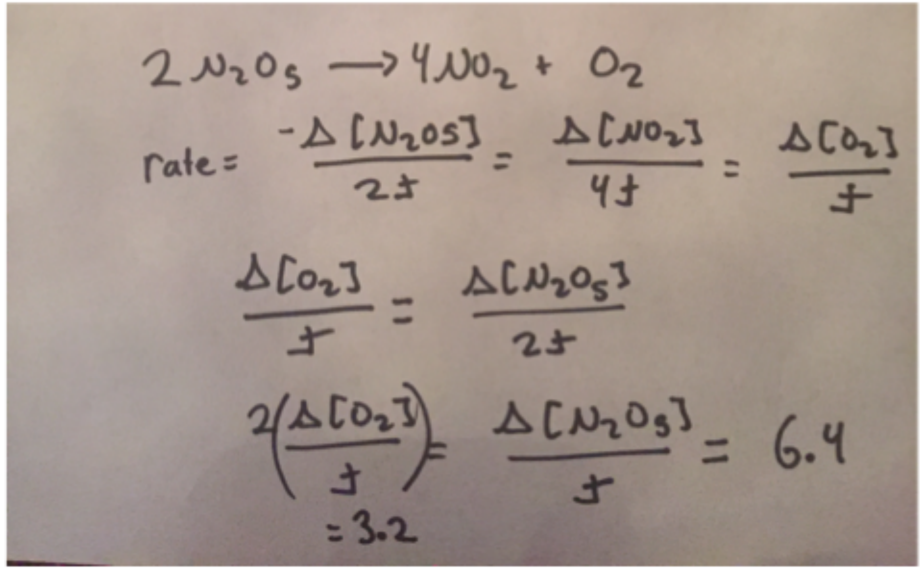
= 6.4 M/s

Exam Question

The initial rate of formation of O_2 in the following reaction is 3.2M/s.

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

What is the initial rate of consumption of N_2O_5?



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

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

$$\frac{\Delta[O_2]}{t} = \frac{\Delta[N_2O_5]}{2t}$$

$$2\underbrace{\left(\frac{\Delta[O_2]}{t}\right)}_{=3.2} = \frac{\Delta[N_2O_5]}{t} = 6.4$$

Exam Question

Integrated rate
2nd order

Consider the reaction:

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

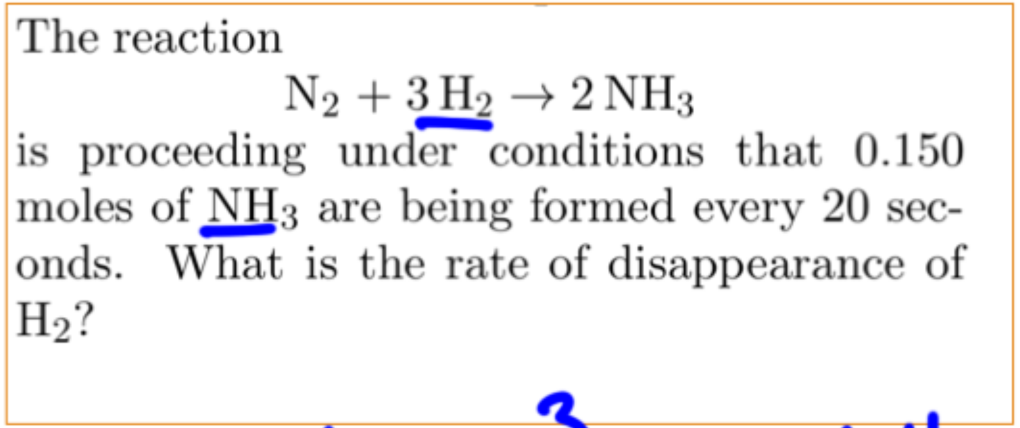
How long will it take for the concentration of NO_2 to decrease from 8.3M to 3.6M? Answer in minutes.

$k = 1 \times 10^{-3}\ M^{-1}S^{-1}$

$$\frac{\frac{1}{3.6} - \frac{1}{8.3}}{0.001} = t$$

$$= \underline{157s} = 2.62\ \text{min}$$

Exam Question



The reaction

$$N_2 + \underline{3\,H_2} \rightarrow 2\,NH_3$$

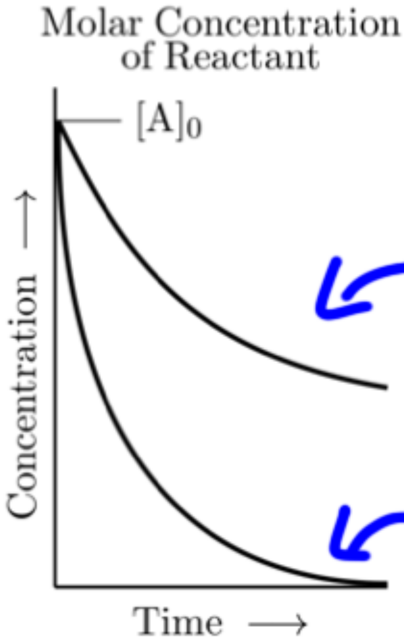
is proceeding under conditions that 0.150 moles of $\underline{NH}_3$ are being formed every 20 seconds. What is the rate of disappearance of H_2?

$$\text{Rate } H_2 = \frac{3}{2} \underbrace{\text{rate } NH_3}$$

$$1.1125 \times 10^{-2}\ \text{mol}/\text{s} = 1.5 \times (0.150/20\ \text{s})$$

Exam Question

Consider the concentration-time dependence graph for two first-order reactions.



Which reaction has the larger rate constant?

Longer half life?

Basic Rate Law

Exam Question

Consider the reaction

$$4\,\mathrm{Fe}^{2+}(\mathrm{aq}) + \mathrm{O}_2(\mathrm{aq}) + 2\,\mathrm{H}_2\mathrm{O}(\ell) \rightarrow 4\,\mathrm{Fe}^{3+}(\mathrm{aq}) + 4\,\mathrm{OH}^-(\mathrm{aq})$$

$$\text{rate} = k[\mathrm{Fe}^{2+}][\mathrm{OH}^-]^2[\mathrm{O}_2]\,.\,!$$

$1 + 2 + 1 = 4$

What is the overall order of the reaction and the order with respect to O_2?

1. 5 and 1

2. 7 and 1

3. 3 and 1

[✓ **4.** 4 and 1] **correct**

5. 4 and 2

This is the other example where stoichiometry DOES matter

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.

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

- 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.**

Mechanism:

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

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

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

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

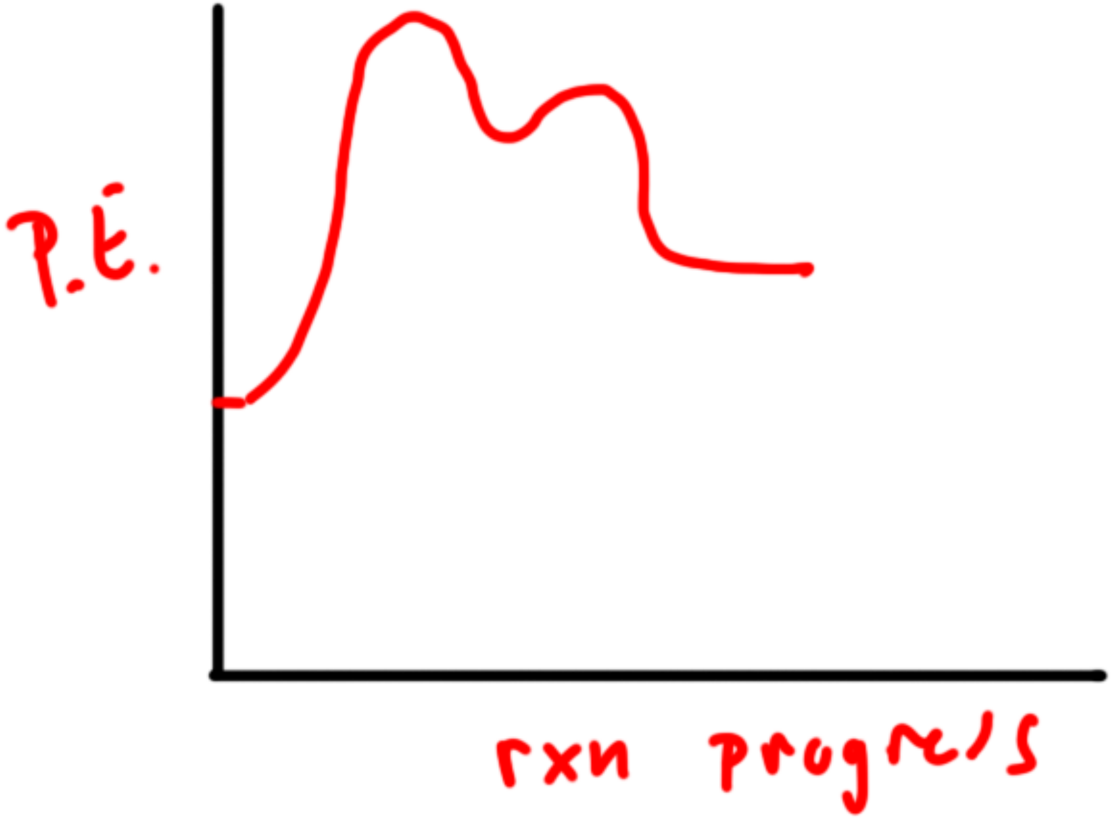
$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

Mechanism:

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

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

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



Reaction Mechanisms: Elementary Steps

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

Mechanism:

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

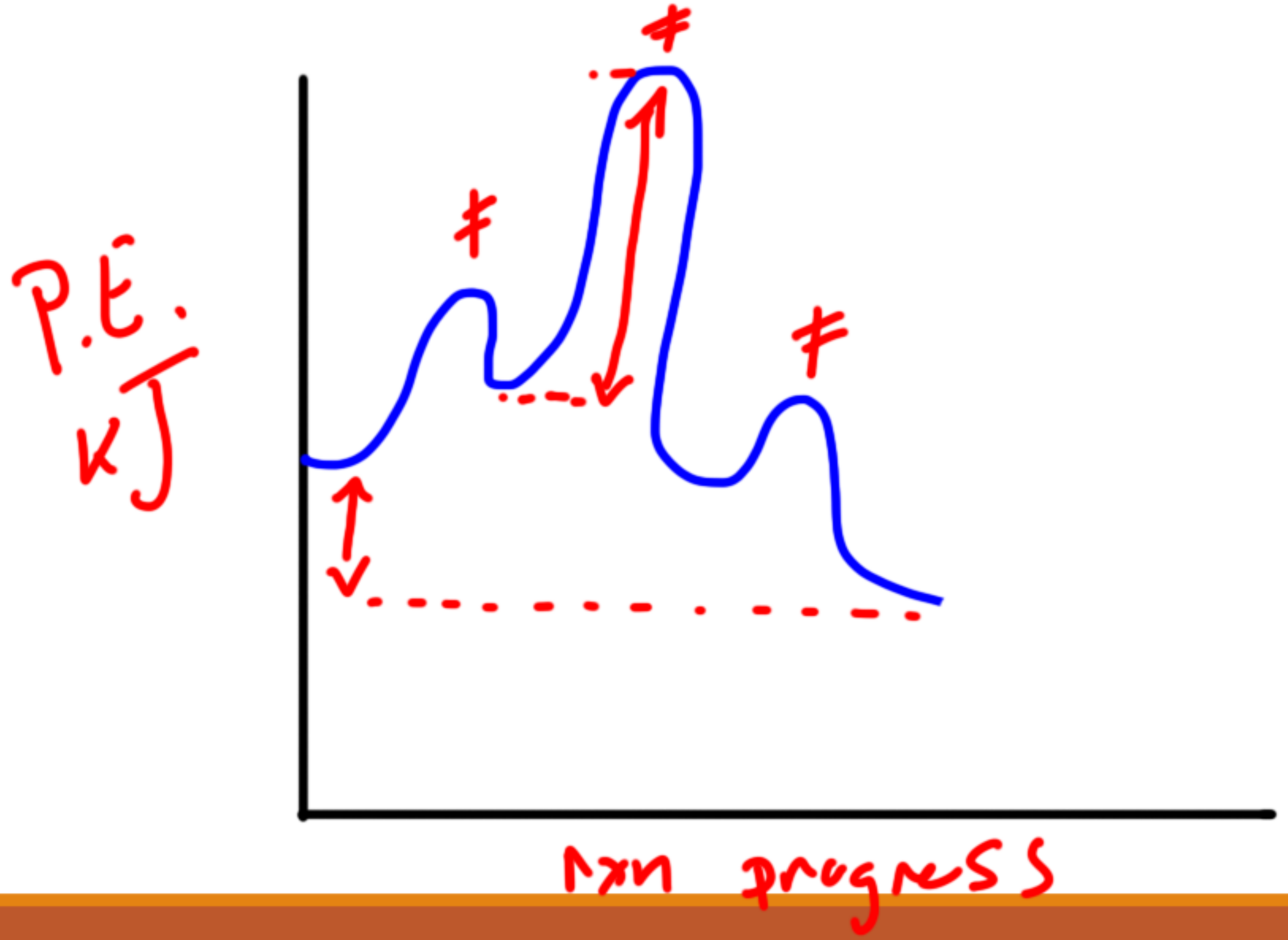
$$\text{rate} = \text{k}_1[CH_3CH_2Br][OH^-]$$

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

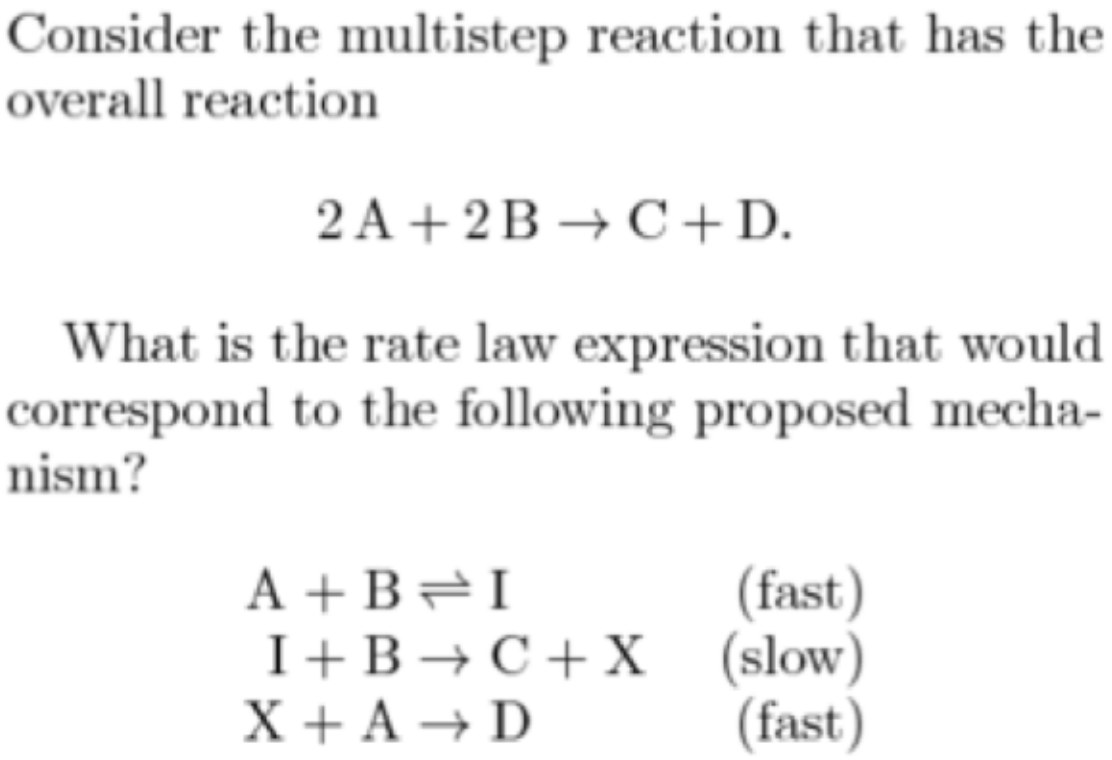
Be able to identify/explain the following on a graph:

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)



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.



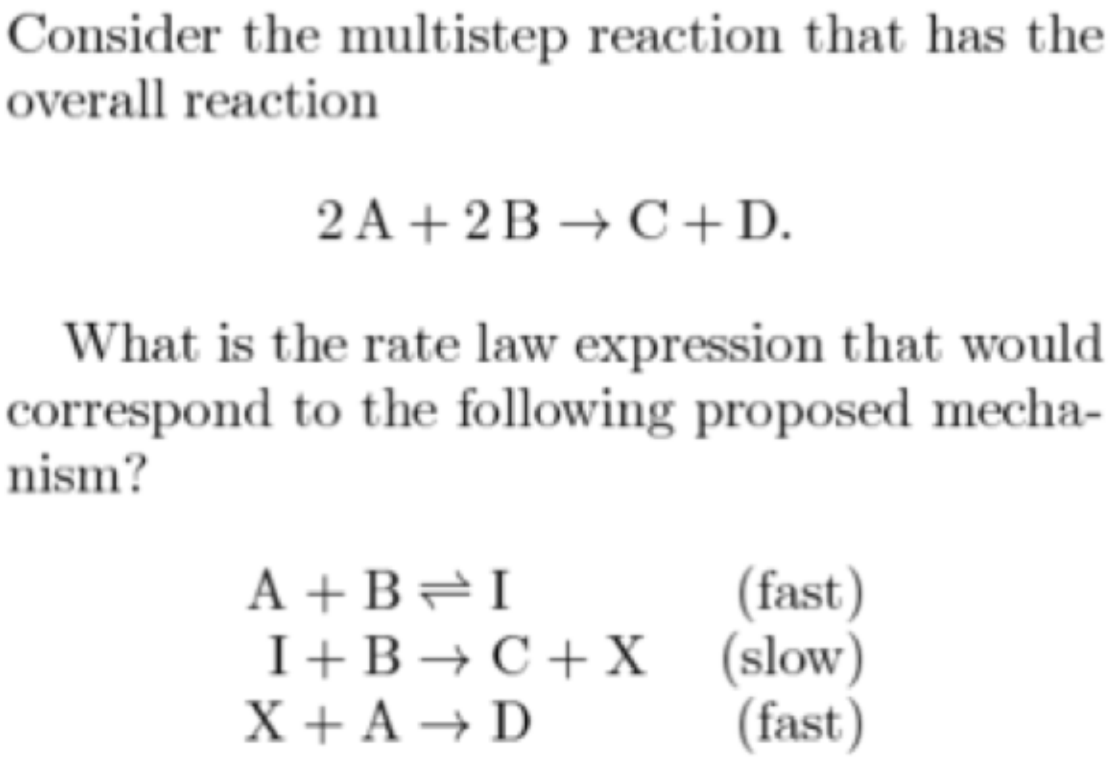
Consider the multistep reaction that has the overall reaction

$$2\,\mathrm{A} + 2\,\mathrm{B} \rightarrow \mathrm{C} + \mathrm{D}.$$

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

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

Mechanisms: Hard Example



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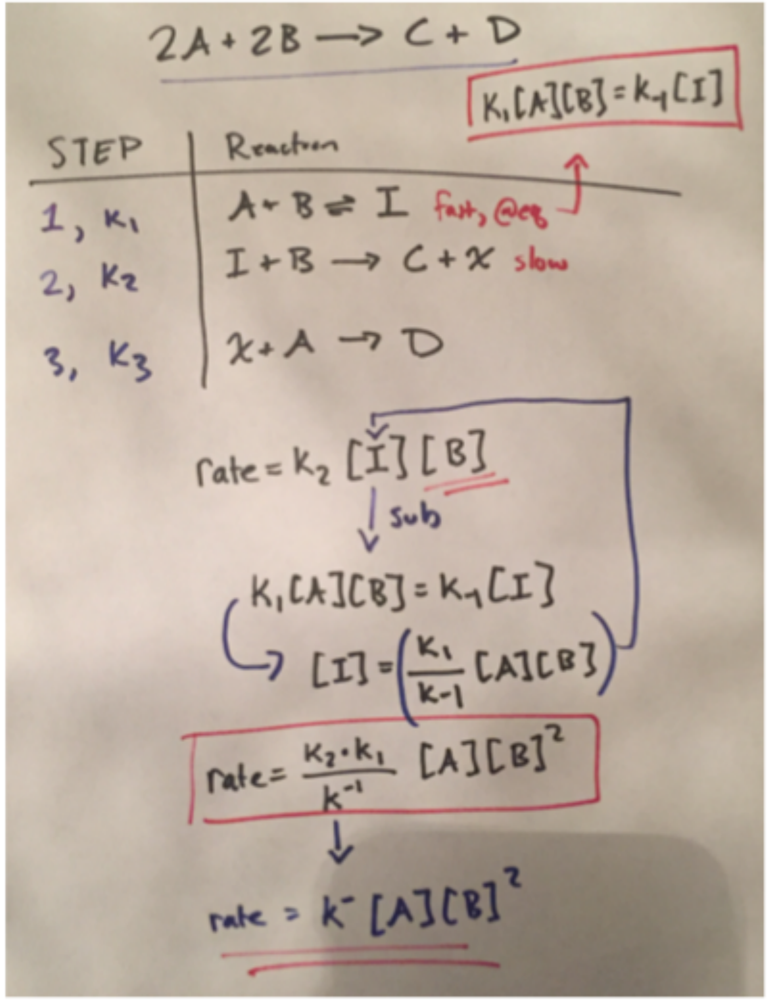
Mechanisms: Hard Example



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

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

STEP	Reaction
1, K_1	$A + B \rightleftharpoons I$ fast, @eq
2, K_2	$I + B \longrightarrow C + X$ slow
3, K_3	$X + A \longrightarrow D$

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

sub

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

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

$\boxed{\text{rate} = \frac{K_2 \cdot k_1}{k^{-1}} [A][B]^2}$

$\text{rate} = k^{-}[A][B]^2$

Consider the multistep reaction that has the overall reaction

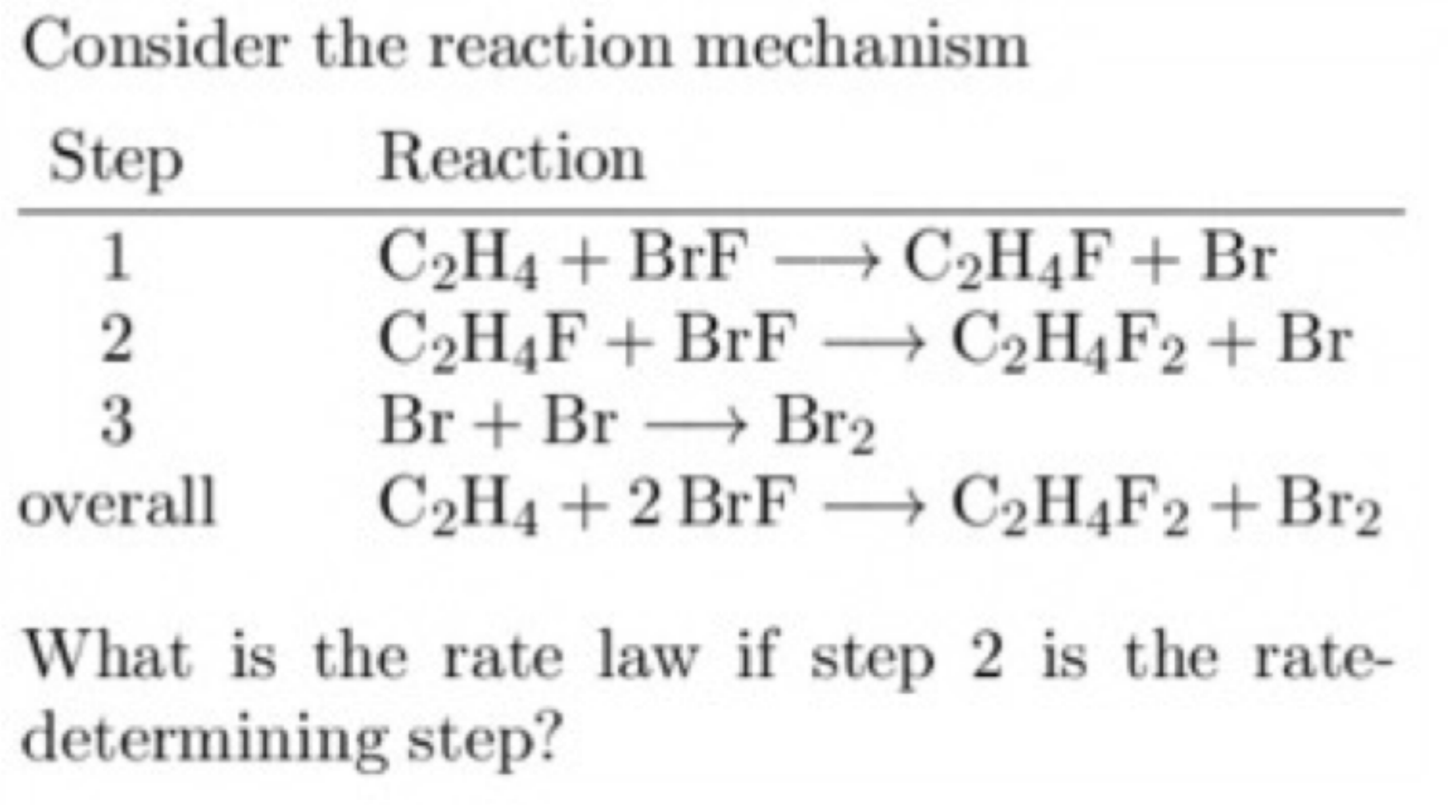
$$2\,A + 2\,B \rightarrow C + D.$$

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

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

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.

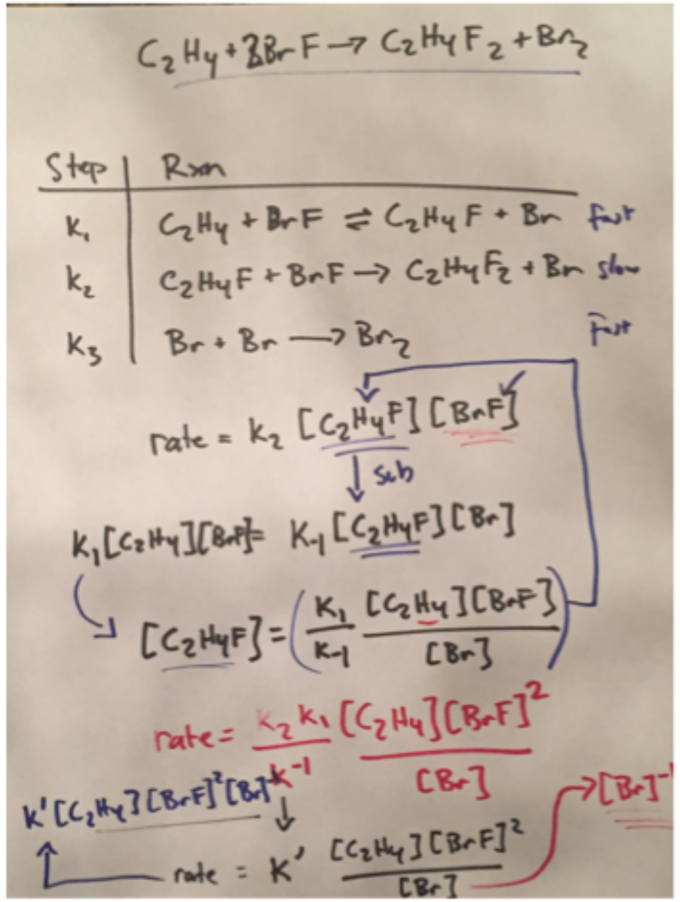


Consider the reaction mechanism

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



$C_2H_4 + 2BrF \rightarrow C_2H_4F_2 + Br_2$

Step	Rxn	
k_1	$C_2H_4 + BrF \rightleftharpoons C_2H_4F + Br$	fast
k_2	$C_2H_4F + BrF \rightarrow C_2H_4F_2 + Br$	slow
k_3	$Br + Br \rightarrow Br_2$	fast

$$\text{rate} = k_2 [C_2H_4F][BrF]$$

sub

$$k_1[C_2H_4][BrF] = k_{-1}[C_2H_4F][Br]$$

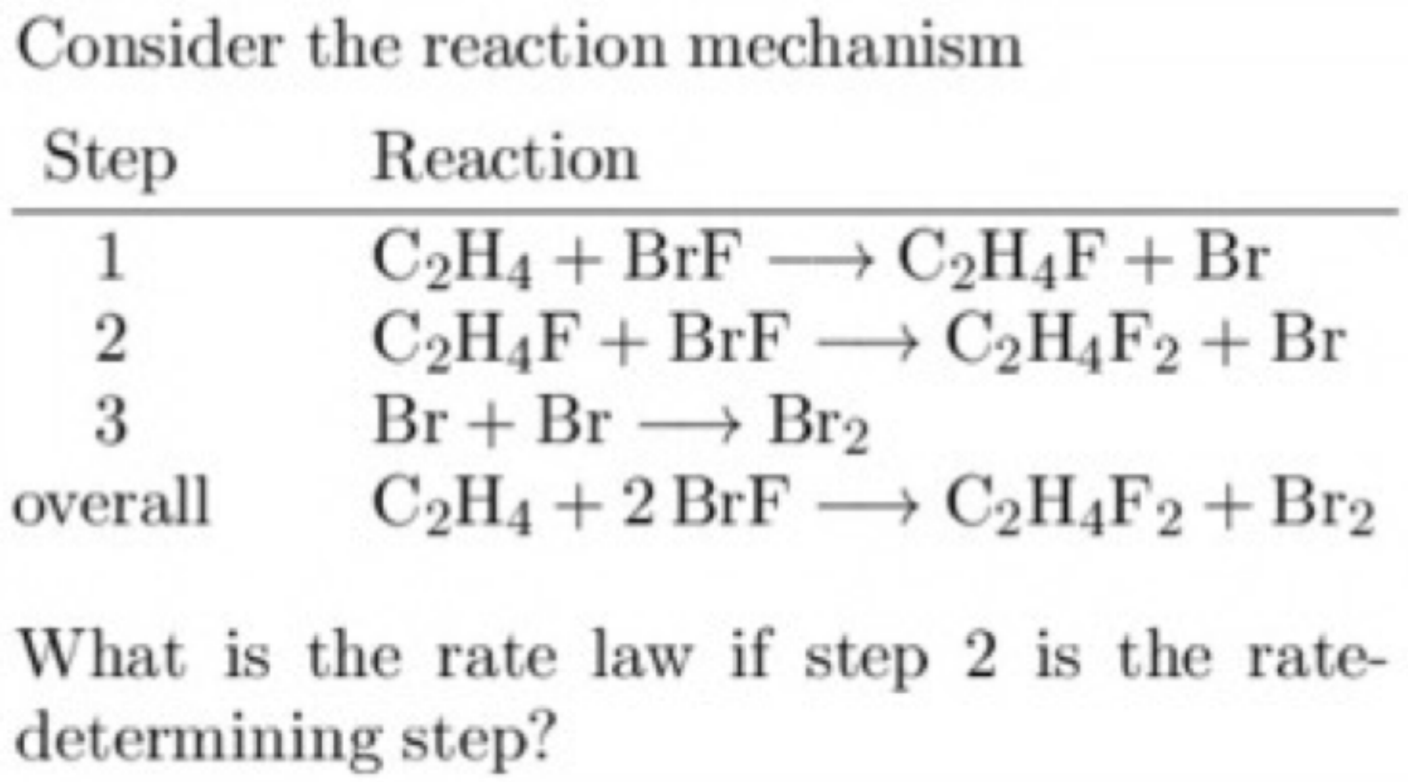
$$[C_2H_4F] = \left(\frac{k_1}{k_{-1}} \frac{[C_2H_4][BrF]}{[Br]}\right)$$

$$\text{rate} = \frac{k_2 k_1}{k^{-1}} \frac{[C_2H_4][BrF]^2}{[Br]}$$

$$\text{rate} = k' \frac{[C_2H_4][BrF]^2}{[Br]}$$

$[Br]^{-1}$

$k'[C_2H_4][BrF]^2[Br]^{-1}$



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	$C_2H_4 + 2\,BrF \longrightarrow C_2H_4F_2 + Br_2$

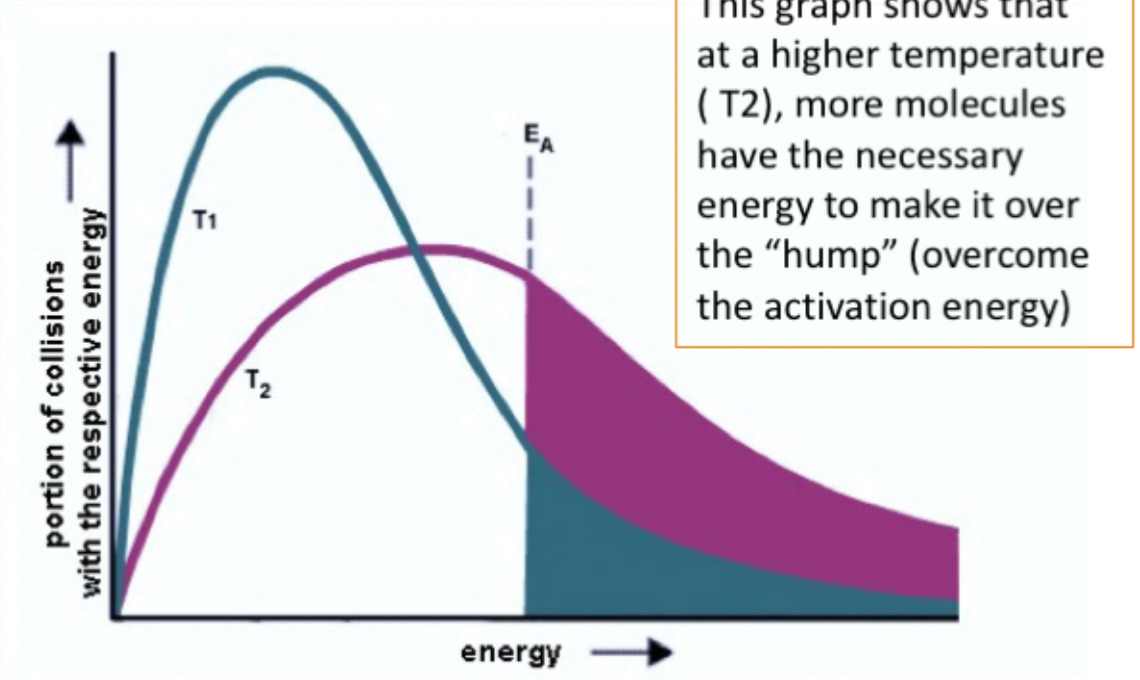
What is the rate law if step 2 is the rate-determining step?

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

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

$$\mathrm{k} = \mathrm{A}e^{\frac{-Ea}{RT}}$$

Fundamentals of Nuclear

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.**

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

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

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

Exam Questions

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.

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.

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Exam Review Slides

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**)

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

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

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

Half-Lives of Integrated Rate Laws

- First Order Half-Life: Independent of concentration

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

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

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

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

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

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:

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

  - We can "mimic" first order conditions by using disproportionate starting conditions. Suppose we start with 2M A and 0.05M 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]:

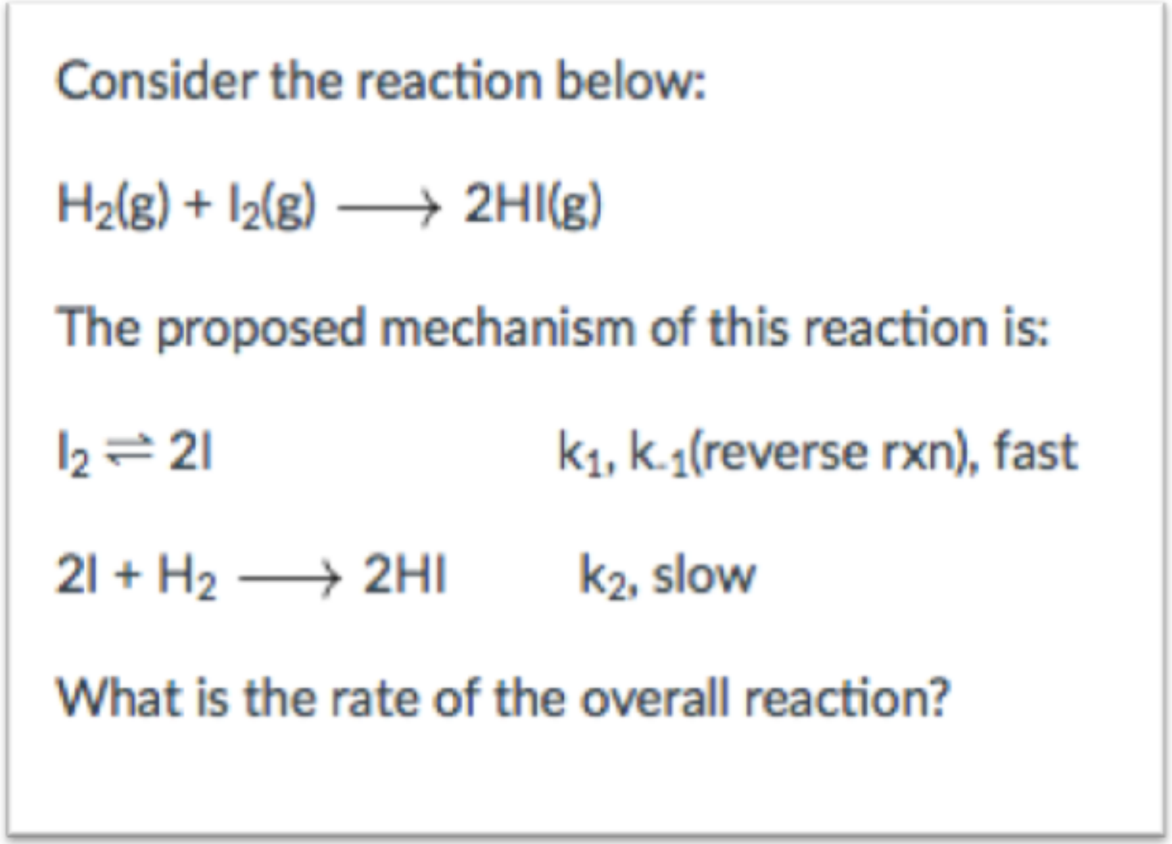
$$rate = k \cdot 2 \cdot [B] = k'[B]$$

Fundamentals of Mechanisms

We can propose a mechanism that dictates the kinetics of the reaction. This 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 mole of a single species ; 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 trimolecular 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 reaction below:

$H_2(g) + I_2(g) \longrightarrow 2HI(g)$

The proposed mechanism of this reaction is:

$I_2 \rightleftharpoons 2I$ k_1, k_{-1}(reverse rxn), fast

$2I + H_2 \longrightarrow 2HI$ k_2, slow

What is the rate of the overall reaction?