

UWO **CHEM 1302**

Fall 2024, Chapter 15 Notes



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15. Reaction Rates and Rate Laws

15.1 Introduction to Kinetics

15.1.1

Introduction to Kinetics

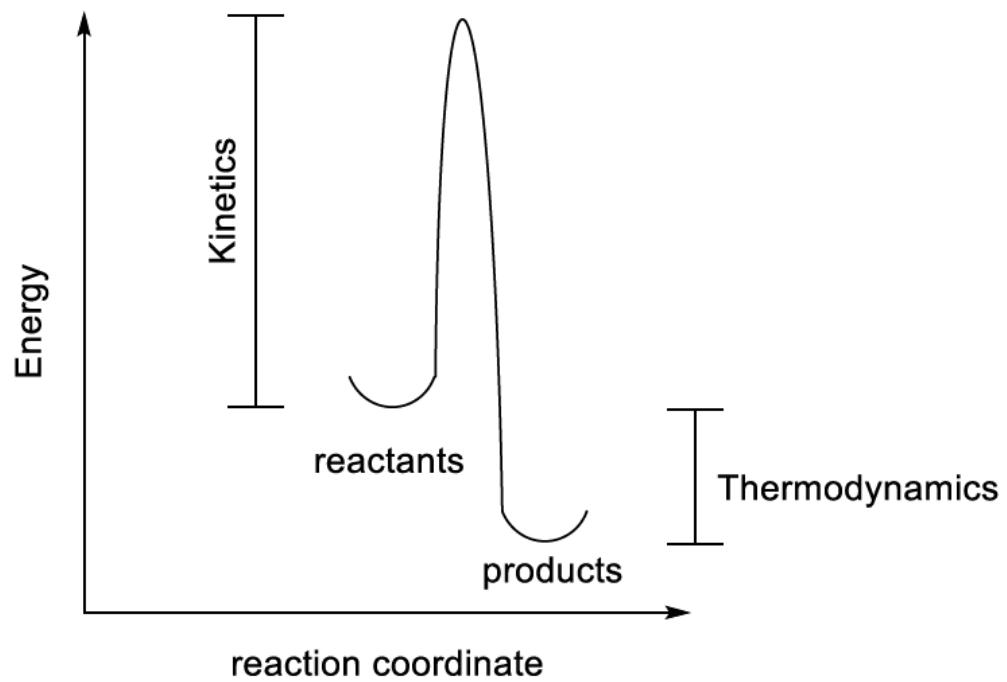
Kinetics: The study of the rates of chemical reactions

- While thermodynamics can tell us which reactions are possible (spontaneous or nonspontaneous) it cannot give us any information about how long the reaction will take.
- The most famous example of this is diamonds.



$$\Delta G < 0$$

- So if the reaction from diamond to graphite is spontaneous why do diamonds last forever?
- The rate of this reaction is so slow, that the Sun will become a red giant and consume the earth before any diamonds spontaneously change phase to graphite.

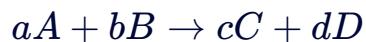


15.2 Rate of Reaction

15.2.1

Reaction Rates

- The reaction rate is a measure of the change in concentration of a reactant or product over time!
 - ex. In physics we know velocity= $\Delta d/t$, in chemistry, a reaction rate= $\Delta []/t$
 - The units of rate would be **M/s** where M=mol/L
- A general form of a **reaction rate** is shown below:



$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

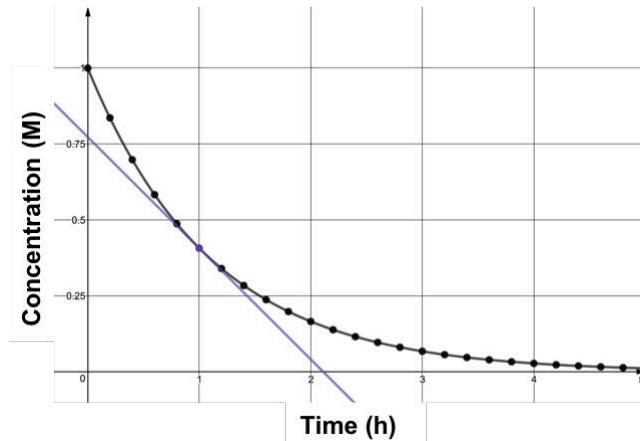
- As the reaction proceeds are we getting more/less of the reactant? _____ More/less of the product?
 - The **- sign** indicates that the concentration of reactants are decreasing (losing reactants as the reaction proceeds)
 - The **+ sign** indicates that the concentration of products is increasing (gaining product as the reaction proceeds)
-
- ****Rates must be determined through experimentation.**

Measuring Reaction Rates

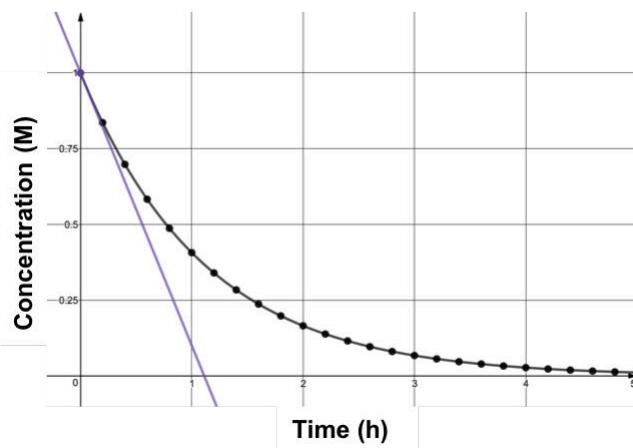
- Consider the reaction: $A \rightarrow B$
- The reaction rate can be measured using **any** substance in the reaction. **Reaction rate units are always M/s** (M stands for concentration, mol/L)

$$\text{Rate} = -\frac{\Delta [A]}{\Delta t} = \frac{\Delta B}{\Delta t}$$

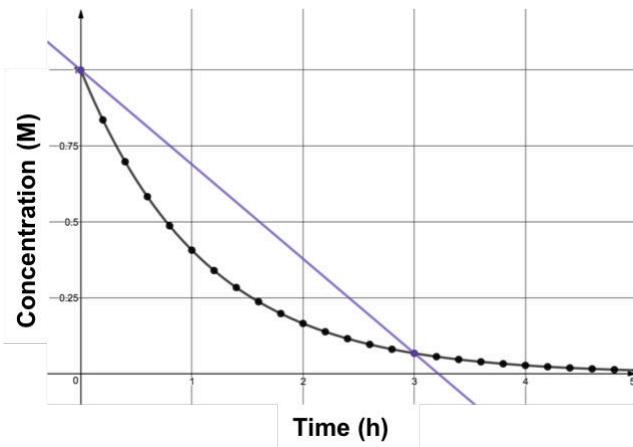
- Instantaneous rate:** the rate of reaction **at an instance in time** (the slope of the tangent line to a point in a concentration vs time graph)



- Initial rate** – instantaneous rate of a chemical reaction at $t = 0$, immediately after the reaction has begun



- **Average rate:** the rate of reaction **over a period of time** (the slope of the line connecting 2 points in a concentration vs time graph)



15.2.3

Practice: Rates of Reaction

If N_2 is consumed at 2 M/s, what is the rate of production of NH_3 and rate of consumption of H_2 in the reaction?



Rate of production of NH_3 (ans in M/s)

Rate of consumption of H_2 (ans in M/s)

15.2.4

In the following reaction the average rate of formation of NO(g) is 1.12 mol/Ls . If 2 minutes passes, what is the concentration of $\text{O}_2(\text{g})$ that is consumed?



1.4 M/s

$1.68 \times 10^2 \text{ M}$

$2.7 \times 10^2 \text{ M}$

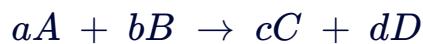
2.8 M/s

15.3 The Rate Law

15.3.1

Rate Laws

- We can use initial reaction rates (using initial concentrations of reactants) to get an expression of the reaction rate called the **rate law**.



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

WIZE CONCEPT

It's important to be able to recognize the rate law!

- The rate law only includes reactants/products: _____
- ***k* is the rate constant**

WATCH OUT!

We use x and y here because **x and y are NOT the coefficients in the balanced equation!**

$$\text{overall reaction order} = x + y$$

The reaction order can't be determined from the overall balanced equation

a) We could determine the reaction order from experimental data

OR

b) We could determine the reaction order from a reaction mechanism (that shows elementary steps)

- We will take a look at both of these ways to figure out the order of the reaction next!

15.3.2

Determine the order of each reactant and the overall order for the following rate laws.

1. $v = k[\text{NO}][\text{C}]^2$

2. $v = k[\text{O}_3]^1$

3. $v = k[\text{O}_2]^{1/2}[\text{CH}_4]$

4. $v = k$

2.

3.

4.

Determining the Rate Law from Experimental Data

The reaction order can't be determined from the overall balanced equation

a) We could determine the reaction order from experimental data

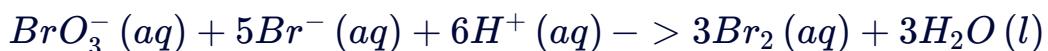
OR

b) We could determine the reaction order from a reaction mechanism (that shows elementary steps)



This method of finding the rate law is found on tests quite often!

Part 1: Use the rate data provided to determine an experimental rate law for the following reaction:



Trial	[BrO ₃ ⁻] (M)	[Br ⁻] (M)	[H ⁺] (M)	Initial Rate (M/s)
1	0.1	0.1	0.1	8.0x10 ⁻⁴
2	0.2	0.1	0.1	1.6x10 ⁻³
3	0.2	0.2	0.1	3.2x10 ⁻³
4	0.1	0.1	0.2	3.2x10 ⁻³

1) We'll write the general rate law expression:

2) Let's figure out what x would be (exponent for BrO_3^-):

(it doesn't matter which exponent we choose to solve for first!)

3) Let's figure out what y would be (exponent for Br^-):

4) Let's figure out what z would be (exponent for H^+):

5) Finally, we can write out the completed rate law:

Part 2: What is the overall reaction order?

Part 3: What is the rate constant?

To find k we can just substitute data in directly from the table with the experimental data.
We need the **completed rate law** and we can **choose any trial** to take #s from (choose the trial with the lowest numbers for easier calculations!)

Here we'll use trial 1:

According trial 1, rate= 8.0×10^{-14} , $[\text{BrO}_3^-] = 0.1\text{M}$, $[\text{Br}^-] = 0.1\text{M}$, $[\text{H}^+] = 0.1\text{M}$

Now rearrange to solve for k (the rate constant)!

What about the units for k?

Recall rate has units: _____

And concentration has units: _____

Part 4: If we were asked to solve for the rate but were given k and the reactant concentrations for a trial, how would we do that?

Shortcut to Find Units of k Quicker

For 0th order: k has units $M \text{ s}^{-1}$

For 1st order: k has units s^{-1}

For 2nd order: k has units $M^{-1} \text{ s}^{-1}$

Recognize a pattern?

What would the units for k be for a 3rd order reaction?

In summary, units of k will be: $M^{1-n} \text{ s}^{-1}$

Low yield:

What if the answer options don't have M but instead have moles and L?

What would the units be for a 2nd order reaction for example?

Well $M = \text{mol/L}$

So for a 2nd order reaction, we know the units would be $M^{-1} \text{ s}^{-1}$

This is the same as writing: $\frac{1}{M \text{ s}}$

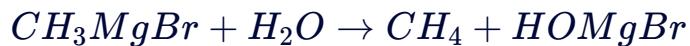
Now let's substitute M for mol/L:

$$\frac{1L}{\text{mol(s)}}$$

Which could be written as: $\text{Lmol}^{-1} \text{s}^{-1}$

15.3.5

Use the rate data provided to determine an experimental rate law for the following reaction. Solve for the rate constant, k, as well.



Run	$[CH_3MgBr]_0$	$[H_2O]_0$	initial rate
1	1.0 M	1.0 M	0.0045
2	2.0 M	1.0 M	0.0091
3	2.0 M	2.0 M	0.0183

rate=k[H₂O] where k is 0.009/Ms

rate=k[CH₃MgBr][H₂O] where k is 0.009/Ms

rate=k[CH₃MgBr][H₂O] where k is 0.0045/Ms

rate=k[CH₃MgBr][H₂O]² where k is 0.0045/Ms

15.3.6

The following data was gathered for the reaction:



Initial [A] (M)	Initial [B] (M)	Initial [D] (M)	Initial Rate (M/s)
1.0	1.0	1.0	3.5×10^{-2}
0.5	0.5	1.0	4.4×10^{-3}
2.0	1.0	1.0	7.0×10^{-2}
0.5	0.5	2.0	4.4×10^{-3}
1.0	2.0	1.0	1.4×10^{-1}

Find the rate law exponents and the rate constant for this reaction. Report your exponents as integers and your rate constant as a decimal to two significant figures without units in the answer field.

$$v = k[A]^x[B]^y[D]^z$$

x

y

z

k

15.3.7

The reaction $A + 2B \rightarrow$ products was found to follow the rate law: $\text{rate} = k[A]^2[B]$. Predict by what factor the rate of reaction will increase when the concentration of A is doubled, the concentration of B is tripled, and the temperature remains constant.

5

6

12

18

none of these

15.3.8

Suppose a gas-phase reaction has the rate law, $\text{rate} = k[\text{A}][\text{B}]^2$. Which of the following could be the units for the rate constant, k ?

$\text{M}\cdot\text{s}^{-1}$



$\text{mol}^{-2}\cdot\text{s}^{-1}$



$\text{L}^2\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$



$\text{L}^{-2}\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$

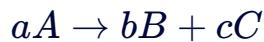


15.4 Integrated rate Laws

15.4.1

Integrated rate Laws

- gives [] of reactants and products at any time after the start of the reaction
- By integrating general rate equations we can obtain integrated rate laws. These laws allow us to predict the concentration of a species over the entire course of a reaction.
- The general form of the 0th, 1st, and 2nd order integrated rate laws are on your formula sheet and are also shown below. These equations are applied to a system which depends on the concentration of one species [A].
- Note your formula sheet has assumed that a = 1. Be very careful that if a does not equal 1 you remember to include it.



$$[A] = [A]_0 - kt \quad 0^{th}$$

$$\ln [A] = \ln [A]_0 - kt \quad 1st \text{ (linear form)}$$

$$[A] = [A]_0 e^{-kt} \quad 1st \text{ (exponential form)}$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \quad 2nd$$

[A] is the concentration of a species at time, t.

[A]₀ is the initial concentration.

t is time in seconds!

- In order to determine if a reaction is 0th 1st or 2nd order in a substrate, scientists can plot [A] vs t
 - in 0 order: [A] decreases in a linear fashion as t increases, slope=-ak (show how!)

-
- in 1st order: $[A]$ decays exponentially with t , larger k will result in _____ (slower/faster) decay, and _____ (shorter/longer) half life (see half life equation for 1st order to help: 1st order: $t_{1/2}=\ln 2/ak$)
 - but if you plot $\ln[A]$ vs t you will get a linear decline in $[A]$ as t increases (this is how you can confirm it is 1st order!)
 - this linear plot also has slope= $-ak$
 - for 2nd order: if we plot $1/[A]$ vs t we get a straight line with slope= ak

15.4.2

For each of the above integrated rate laws determine what will need to be plotted in order to obtain a straight line graph. What is the significance of the slope and y intercept? Remember that a straight line has the formula $y = mx + b$

0th order:

1st order:

2nd order:

15.4.3

N_2O_4 decomposes to NO_2 in a first order process with a rate constant of 0.0007 s^{-1} . How long will it take for 75% of a sample of N_2O_4 to decompose?

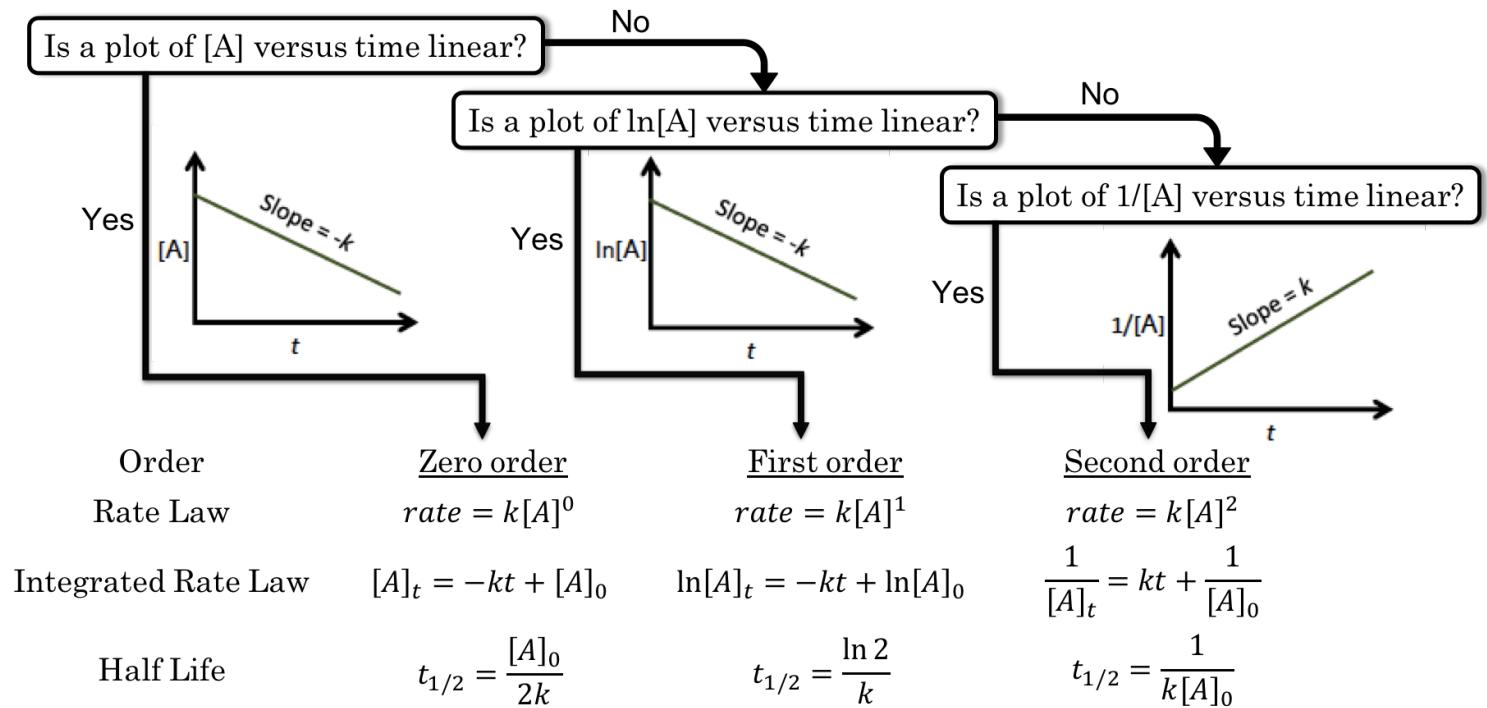
200 seconds

1200 seconds

33 minutes

60 minutes

15.4.4



15.4.5

First Order Reactions

- For first-order reactions, the differential rate law is:

$$\text{Rate} = k[A]^1 = k[A]$$

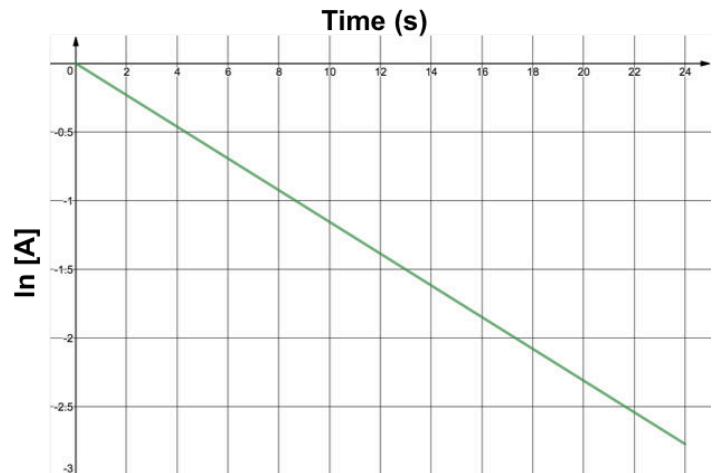
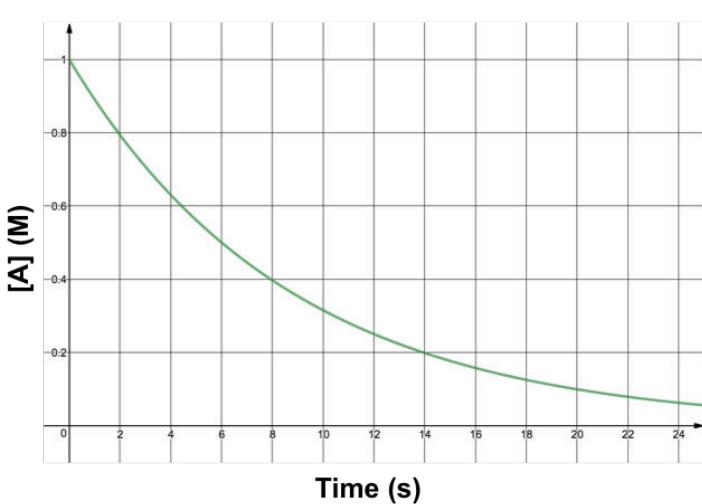
- The integrated rate law for a first-order reaction is:

$$[A] = [A]_0 e^{-kt}$$

- The integrated rate law can be rearranged to a standard linear equation format:

$$\begin{aligned}\ln[A] &= -kt + \ln[A]_0 \\ y &= mx + b\end{aligned}$$

- A plot of $\ln[A]$ versus t for a first-order reaction is a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$.



15.4.6

Second Order Reactions

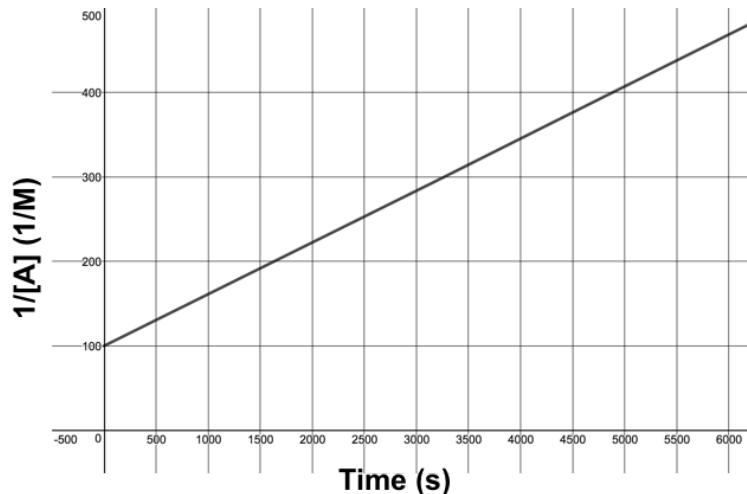
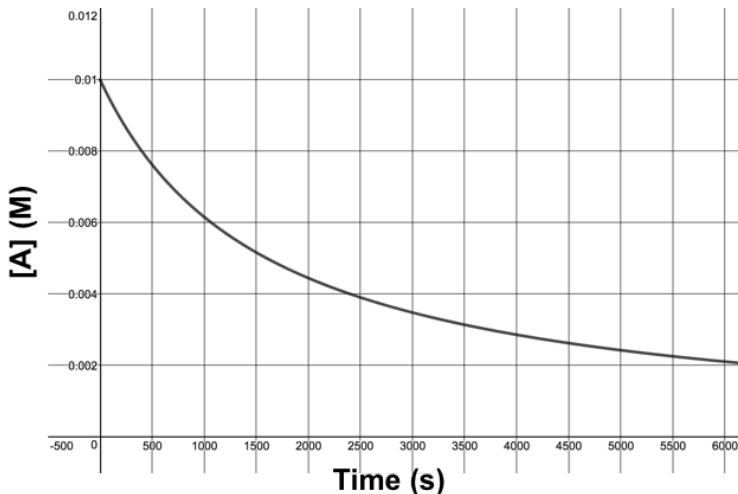
- For second-order reactions, the differential rate law is:

$$\text{Rate} = k[A]^2$$

- The integrated rate law for a second-order reaction has the form of the equation of a straight line:

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

- A plot of $1/[A]$ versus t for a second-order reaction is a straight line with a slope of k and an intercept of $1/[A]_0$.



15.5 Half-lives for Various Orders

15.5.1

Half Life for Various Orders

Another important concept in kinetics is half-life, $t_{1/2}$. This is the time it takes for the concentration of a reactant to be cut in half.

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

- Although it is fairly easy to derive the half-life equation from the integrated rate law we do not have to because it is given on the formula sheet and shown below.
- *If the stoichiometric coefficient of A, a, is not 1 we must include it with k in these equations just like the integrated rate laws!*

$$\begin{aligned}t_{1/2} &= \frac{[A]_0}{2k} && 0^{th} \\t_{1/2} &= \frac{\ln 2}{k} && 1^{st} \\t_{1/2} &= \frac{1}{k[A]_0} && 2^{nd}\end{aligned}$$

- we can see that for 1st order reactions, the half-life is independent of the initial concentration
- for radiocarbon dating, we also use first order kinetics, and can use another equation:

$$\frac{[At]}{[A_0]} = 0.5^{\frac{t}{t_{1/2}}}$$

[At]=concentration of substance at a particular time

[A₀]=initial concentration of substance

t=how much time has passed

t_{1/2}=half life

- note: if you use this equation, both t and t_{1/2} must have the same units!
- for 2nd order, t is inversely proportional to the initial concentration of the reactant
- and for the n order, t_{1/2} directly proportional to [A₀]¹⁻ⁿ

15.5.2

Americium-241 is a synthetic isotope made in nuclear reactors around the world. Chances are you have been in close proximity to this radioactive isotope thousands of time in your life because it is used in household smoke detectors. For a smoke detector to be functioning properly it needs more than 22mg of Americium-241. ^{241}Am is an alpha emitter whose decay obeys a first order rate-law (as do all nuclear decays) with a half-life of 432.6 years. If a typical smoke detector contains 25 mg of ^{241}Am , how long will the smoke detector last assuming the batteries are replaced regularly?

6 years

18 years

80 years

111 years

15.5.3

Americium-241 is a synthetic isotope made in nuclear reactors around the world. Chances are you have been in close proximity to this radioactive isotope thousands of time in your life because it is used in household smoke detectors. ^{241}Am is an alpha emitter whose decay obeys a first order rate-law (as do all nuclear decays) with a half-life of 432.6 years. What is the rate constant of its decay? How much ^{241}Am would remain of a 25mg sample if it were left for 300 years.

5.25 mg



12.98 mg



15.46 mg



24.11 mg

