

# CHE 1302

## Basic Principles of Modern Chemistry II

### Week 4

Hello and welcome to the weekly resources for Chemistry 1302! This resource covers topics typically taught by professors during the 4<sup>th</sup> week of classes.

On our website, <https://baylor.edu/tutoring>, you'll find the following links:

"Online Study Guide Resources" – If you don't see the topics you're learning right now, click here to find the weekly resources for the rest of the semester!

"How to Participate in Group Tutoring" - See if there is a Chemistry 1302 group tutoring session being hosted this semester – these are weekly question/answer sessions taught by our master tutors!

You can also view tutoring times for your course or schedule a private 30-minute appointment! Check out the website to learn more. You can also give us a call at (254)710-4135, or drop in. Our hours are Monday-Thursday 9 am – 8 pm on class days.

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**KEY WORDS:** Rate Laws, Method of Initial Rates, Integrated Rate Law, Catalysis

### TOPIC OF THE WEEK:

## Rate Laws & Method of Initial Rates

A rate law relates the **initial rate** (see Week 3) of a chemical reaction to **reactant concentrations** at the beginning of the reaction.

For the reaction:  $aA + bB \rightarrow cC$ ,

$$\text{Rate} = k[A]^m[B]^n$$

k = rate constant; different for each reaction

[A], [B] = initial concentrations of reactants (how much reactant is being put into the reaction)

m,n = reaction orders. What sort of **effect** does the **concentration of each substrate** have on the **reaction rate**? This is best determined experimentally.

- If you were to double the starting concentration of [A], and keep everything else the same, what would happen to the rate?
- In some reactions, the rate would double, too. In this case, the reaction would be said to be "first order with respect to [A]."

- In some reactions, the rate would quadruple. These reactions would be “second order with respect to [A]”
- In some reactions, the rate would be multiplied by 8. These reactions would be “third order with respect
- Here’s how you can solve for reaction order (**and determine rate equations!**):
- “The **method of initial rates**”
  - Find two experiments where everything but [A] (or everything but [B]) stayed the same. Let’s say that, in this case, everything but [A] stays the same, and [A] doubles.
  - Before doubling:  $rate_1 = k[A]^m * [B]^n$
  - After doubling, if everything but [A] stays the same,  $rate_2 = k[2A]^m * [B]^n$
  - If you were to divide these two equations by each other,  $\frac{rate_1}{rate_2} = \frac{k[B]^n}{k[B]^n} * \frac{[A]^m}{[2A]^m}$
  - Since k, [B], and n are constant between reactions:  $\frac{rate_1}{rate_2} = 1 * \left(\frac{1}{2}\right)^m$
  - The initial and final rates can be measured – these values will be given in a problem. Then, all you have to do is solve for m.
  - This process can be repeated for n. If concentration, rather than doubling, is cut in half, substitute [A]/2 into the second equation; if it triples, [3A], etc.

**Overall order of reaction = m + n**

NOTE: Unlike when solving for equilibrium constant, the m and n values are NOT derived from the coefficients in the balanced chemical equation! The orders of reaction must be determined by experiment.

Here is a ~2min video explaining this concept: <https://www.youtube.com/watch?v=6bsAf4Vn-ml>

Things that affect reaction rate:

Increasing temperature	Increases reaction rate
Adding catalysts (see Highlight 3)	Increases reaction rate
Increasing initial reactant concentrations	Increases reaction rate
Increasing surface area	Increases reaction rate
Adding inhibitors	Decreases reaction rate

## Highlight 1: Integrated Rate Law Equations

Suppose that you were to **graph the rate of a reaction over time**. (Recall the definition of reaction rate – a change in concentration over time.) What would you get if you found the **area under the curve**? In other words, what would you get if you multiplied *reaction rate at a certain point in time, y \* that point in time, x*? Well, according to the definition of reaction rate, that’s the same as  $\frac{\text{change in concentration}}{\text{time}} * \text{time}$ , which is just **change in concentration**.

“Integrate” means “find the area under the curve.” If the graph of reaction rate is a straight line, that’s easy enough, but what if it’s more complicated than that? The **integrated rate law** is **an equation, based on the rate equation, that can be used to calculate the area under the curve, or change in concentration.**

If you’ve taken calc, look through these derivations of the integrated rate equations – it may be easier than trying to memorize them. If you haven’t taken calc, just know the highlighted items!

**Zero (overall) order:** Rate=k

1. Rewrite “rate” as a derivative
  - a. *Keep in mind: the derivative is negative because A is a reactant (reactant concentration goes down as a reaction progresses)*
  - b.  $-\frac{d[A]}{dt} = k$
2. Integrate both sides
  - a.  $[A] = -kt + c$ , where  $c = [A]$  when  $t = 0$
  - b.  $[A]$  when  $t = 0$  is also known as  $[A]_0$ :  $[A]_t = -kt + [A]_0$

**First order:** Rate=k[A]

1. Rewrite rate as a derivative
  - a.  $-\frac{d[A]}{dt} = k[A]$
2. Separate variables:
  - a.  $\frac{1}{[A]} * d[A] = kdt$
3. Integrate:
  - a.  $\ln[A]_t = -kt + \ln[A]_0$
  - b. Notice: If you were to graph  $\ln[A]_t$  vs  $t$ , the line would be in  $y=mx+b$  format, which means that it is a straight line. (This is one way to test for first order reactions!) If you calculate the slope of the line, it’ll be equal to  $-k$ . The y-intercept will be equal to  $\ln[A]_0$ .

**Second order:** Rate=k[A]^2

1. Rewrite rate as a derivative:
  - a.  $-\frac{d[A]}{dt} = k[A]^2$
2. Separate variables
  - a.  $\frac{d[A]}{[A]^2} = -kdt$
3. Integrate both sides
  - a.  $-\frac{1}{[A]} + c = -kt$ , where  $c$  is  $[A]$  at  $t = 0$
  - b.  $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$
  - c.  $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

The table below summarizes key elements of the zero, first and second order reactions. Half-life will be discussed in the next section!

	Zero Order	First Order	Second Order
<b>Differential Rate Law</b>	Rate $(-\frac{d[A]}{dt}) = k$	Rate $(-\frac{d[A]}{dt}) = k[A]$	Rate $(-\frac{d[A]}{dt}) = k[A]^2$
<b>Integrated Rate Law</b>	$[A]_t = -kt + [A]_0$	$\ln[A]_t = -kt + \ln[A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
<b>Variables for Straight line plot</b>	$[A]_t$ versus $t$	$\ln [A]_t$ versus $t$	$\frac{1}{[A]_t}$ versus $t$
<b>Relationship btw Rate constant and slope of line plot</b>	Slope = -k	Slope = -k	Slope = k
<b>Half-Life</b>	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Graph from CHE 1302 Resource Spring 2021

To approach a "straight-line" problem:

Often, you will be given a straight-line graph and asked to (1) determine reaction order, (2) determine  $k$ , or (3) determine  $[A]_0$ . Here are some steps to follow:

1. What are the axes? Ex: Let's say the y-axis is labeled  $\ln[A]_t$ , and the x-axis is labeled  $t$
2. Compare them to the integrated rate law equations: Find an integrated rate law equation that uses these terms. **First order**
3. Replace each term with "x" or "y"  $y = -kx + [A]_0$
4. Now, you have an equation in  $y = mx + b$  format. You can figure out  $k$  and  $[A]_0$  by comparing them to the slope and y-intercept of the graph.  $m = -k$ ,  $b = [A]_0$

## Highlight 2: Half Life

Half life is the amount of **time** that it takes to get from the **initial concentration** to **half the initial concentration**. In other words, it is  $t$  when  $[A]_t = 0.5[A]_0$

Half life formulas are something that can either be memorized or derived from the integrated rate laws. To derive from the integrated rate laws, plug in  $0.5[A]_0$  for  $[A]_t$  and simplify:

**Zero order:**

The timescale in which there is a 50% reduction in the initial population is referred to as half-life. Half-life is denoted by the symbol ' $t_{1/2}$ '.

From the integral form, we have the following equation

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

Replacing  $t$  with half-life  $t_{1/2}$  we get:

$$\frac{1}{2}[A] = [A]_0 - kt_{1/2}$$

Therefore,  $t_{1/2}$  can be written as:

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

And,

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

[Zero Order Reaction - Definition, Derivation, Graph, Examples \(byjus.com\)](#)

### First order:

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

Substituting  $[A]_{0/2}$  for  $[A]$  and  $t_{1/2}$  for  $t$  (to indicate a half-life) into Equation 4.5.1 gives

$$\ln \frac{[A]_0}{[A]_{0/2}} = \ln 2 = kt_{1/2}$$

Substituting  $\ln 2 \approx 0.693$  into the equation results in the expression for the half-life of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k}$$

### [4.5: First Order Reaction Half-Life - Chemistry LibreTexts](#)

### Second order:

**Step 2:** Using the concentration-time equation for a second-order reaction we can solve for half-life. We know that at the half-life time  $t_{1/2}$ , the concentration of the reactant will be half as much as the initial concentration. Therefore, we can set  $[A]$  equal to  $[A_0]/2$ . Now we have the following equation and can solve for  $t_{1/2}$ .

$$\frac{1}{[A_0]/2} = \frac{1}{[A_0]} + kt_{1/2}$$

$$\frac{1}{[A_0]/2} - \frac{1}{[A_0]} = kt_{1/2}$$

$$\frac{1}{[A_0]} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{[A_0]k}$$

[How to Calculate Half-life of a Second-order Reaction | Chemistry | Study.com](#)

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## Highlight 3: Catalysis

A **catalyst** increases the rate of a reaction without being consumed. It changes the mechanism of the reaction by providing an alternative pathway with lower activation energy.

There are two types:

1. **Homogenous** (catalyst is soluble in reaction; includes **enzyme**—see below)
2. **Heterogeneous** (catalyst has different phase from reacting system, typically a solid)

The most common type of catalyst we encounter in chemistry is the **enzyme**, which is a **biological homogeneous catalyst**. Enzymes are extremely selective and usually catalyze one specific reaction, but no others.

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## Check Your Learning

1. For the reaction  $A + 2B \rightarrow C + 2D$  What are the values of  $m$  and  $n$  in the rate law,  $rate = k[A]^m * [B]^n$ , given the data in the table below?
2. The first order rate constant  $k$  for a particular reaction is  $6.8 \times 10^{-4} \text{ s}^{-1}$ . If the initial concentration of a reactant is  $1.35 \text{ M}$ , what will its concentration be after  $1420 \text{ s}$ ? (hint: use the first order integrated law!)

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## Things You May Struggle With

1. Don't try to figure the order of a reaction using the stoichiometry of an overall reaction.  $M$  and  $n$  are not related to the coefficients in the reaction equation.
2. Average rates are the changes in concentration over the entire reaction, while instantaneous rates are the changes in concentration at specific points in the reaction. Know the difference between these!
3. Be careful about units for rate constants. Use units for concentration and time in the rate laws, and then continue to keep track of the units when solving for  $k$ .

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That's all this week! Please reach out if you have any questions and don't forget to visit the Tutoring Center website for further information at [www.baylor.edu/tutoring](http://www.baylor.edu/tutoring). Answers to Check Your Learning are below.

1.  $m = 2, n = 0$
2.  $0.51 \text{ M}$