

Totally Epic AP Chem Review: Rate Laws

The Rate of a Chemical Reaction: defined as change in concentration of a reactant or product per unit time.

$$\text{Rate} = \frac{\Delta[\text{Reactant}]}{\Delta\text{time}} \text{ OR } \frac{\Delta[\text{Product}]}{\Delta\text{time}}$$

Rate Unit: M/time, M time⁻¹, mol/(L · time), or mol L⁻¹ time⁻¹ (Hint: these are all the Same thing!!)

As time goes on, the rate of a reaction slows down because concentration of the reactants decreases.

Reaction Rate and Stoichiometry: In most reactions, the coefficients of the balanced equation are not all the same.

To be consistent, the change in the concentration of each substance is multiplied by 1/coefficient.

Given the reaction: $A + 3 B \rightarrow 2 C$

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{1}{3} \frac{\Delta[B]}{\Delta t} = \frac{1}{2} \frac{\Delta[C]}{\Delta t}$$

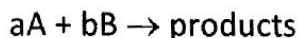
Four Factors Affecting Reaction Rate: MEMORIZE THESE!!!!

1. Increasing the Surface area of a solid reactant can increase the rate by increasing the number of collisions between the reactant particles.
2. Catalysts increase the rate by lowering the activation energy of a reaction.
3. Increasing the temperature results in a faster reaction: heat 'em up, speed 'em up!
 → The rate constant is temperature dependent and a rise in temperature will increase the rate constant!
4. Increasing concentration of reactants increases the number of reactants colliding with each other, thus yielding more product.

The Rate Law: the mathematical relationship between rate of the reaction and the concentrations of the reactants

→ The rate law **must** be determined experimentally!

For the reaction

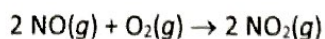


The rate law would have the form

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

1. The exponent on each reactant, n and m , are called the orders with respect to that reactant.
2. k is called the rate constant: a larger k means a faster reaction!
3. n and m are NOT necessarily the stoichiometric coefficients of A and B.
4. $n + m = p$, the overall rate order (or the order of the reaction).
rxn

Example



the experimentally determined rate law is $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$.

The reaction is said to be:

2nd order with respect to NO,
1st order with respect to O₂,
3rd order overall.

Overall Reaction Order

A. Zero order reaction rate: rate of reaction is independent of the concentration of the reactant(s).

B. First order reaction rate: rate of reaction is directly proportional to concentration of one of the reactants.

→ Radioactive decay is a very common example of a first-order process. They have a constant half-life.

$$k = \frac{0.693}{\text{half-life}} \quad \left. \vphantom{\frac{0.693}{\text{half-life}}} \right\} \text{ on F.C!}$$

$\frac{1}{2}$ life independent of [reactants]!

C. Second order reaction rate: the rate of the reaction is directly proportional to the square of the concentration of one of the reactants.

How to Determine Orders

1. Order must be determined experimentally!

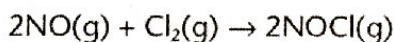
2. In reaction with multiple reactants, changing the concentration of 1 reactant will affect the overall rate of the reaction.

a. Change the initial concentration of 1 reactant at a time, while holding the initial concentration of the other reactants constant!

b. Conduct multiple trials with changing concentrations of each reactant and measure the rate each time to determine the effect of each change.

Strategy #1: Chart-tabulous! Compare trials in which the concentration of one of the reactants stays the same to determine how changing the concentration of a single reactant affects the rate of reaction.

For example, for the following reaction, this data was collected.



Trial	[NO] mol/L	[Cl ₂] mol/L	Rate
1	0.200	0.200	1.20×10^{-6}
2	0.400	0.200	4.80×10^{-6}
3	0.200	0.400	2.40×10^{-6}
4	0.400	0.400	9.6×10^{-6}

Handwritten annotations: Trial 1 to 2: [NO] 2x, [Cl₂] c, Rate 4x. Trial 1 to 3: [NO] c, [Cl₂] 2x, Rate 2x.

a) Comparing Trial 1 and Trial 2:

→ The concentration of NO doubled, while the concentration of Cl₂ remains constant, and the reaction rate increases by a factor of 4.

Therefore, the rate of reaction with respect to NO is 2nd order ($2^2 = 4$).

b) Comparing Trial 1 and Trial 3:

→ The concentration of NO remains constant, while the concentration of Cl₂ doubled, and the reaction rate increases by a factor of 2.

Therefore, the rate of reaction with respect to Cl₂ is 1st order ($2^1 = 2$).

c) Thus, the rate law for the reaction is: $\text{rate} = k [\text{NO}]^2 [\text{Cl}_2]$

You can use the same method for gaseous reactions with pressure!

→ P is directly proportional to concentration.

Strategy #2: Go straight! Different orders require different plots to generate straight lines.

To create the needed graphs, set time as your x-axis, and graph three different y-axes (in alphabetical order!)

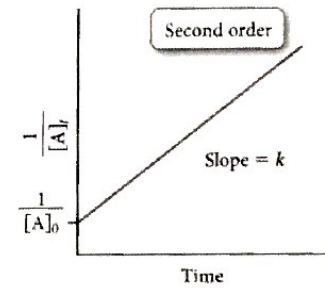
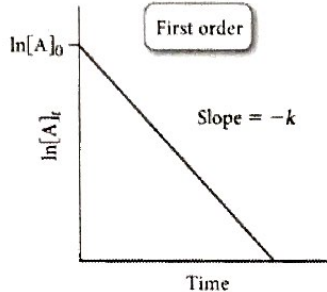
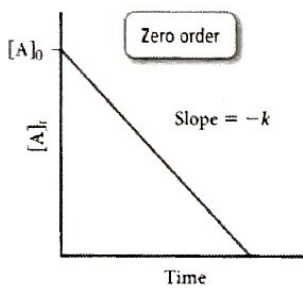
The graph which is **most linear** is the one you want!

Alpha Order!

M^{1-p}
time

Graph vs time	If this is most linear, the reaction is	Units of k
Concentration of the reactant, [A]	Zero order (k = - slope)	$M \cdot \text{sec}^{-1}$
Natural log of the concentration, $\ln[A]$	First order (k = - slope)	sec^{-1}
Reciprocal of the concentration, $1/[A]$	Second order (k = slope)	$M^{-1} \cdot \text{sec}^{-1}$

The graph which is **most linear** is the one you want!



Note: for each rate order, the **absolute value** of the slope equals the rate constant \rightarrow IF you pick the correct graph!

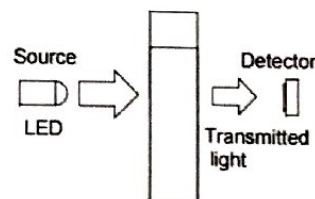
$$k = |\text{slope}|$$

Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	Rate = $k[A]^0$	$M \cdot s^{-1}$	$[A]_t = -kt + [A]_0$		$t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k} \frac{[A]_0}{2}$ not AP tested
1	Rate = $k[A]^1$	s^{-1}	$\ln[A]_t = -kt + \ln[A]_0$ $\ln \frac{[A]_t}{[A]_0} = -kt$		AP tested! $t_{1/2} = \frac{0.693}{k} = \frac{1}{k} (0.693)$ on F.C. \hat{U}
2	Rate = $k[A]^2$	$M^{-1} \cdot s^{-1}$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$		$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k} \frac{1}{[A]_0}$ not AP tested

Colorimetry: An Experimental Method to Measure Reaction Rate

Colorimetry: an experimental method to measure reaction rate by using a colorimeter (or spectrophotometer) to determine the concentration of solution by analyzing its color intensity.

- Light from an LED light source passes through a cuvette (tiny container) filled with a solution sample, as shown in the figure to the right.
- Some of the incoming light is absorbed by the solution. As a result, light of a lower intensity strikes a photodiode.
- The colorimeter is set to a wavelength the solution being studied absorbs the most, based on the color of the solution: of course, colorimetry only works if one of your reactants or products is colored. ☺



Beer's Law

$$A = abc \quad] \text{ on F.C.}$$

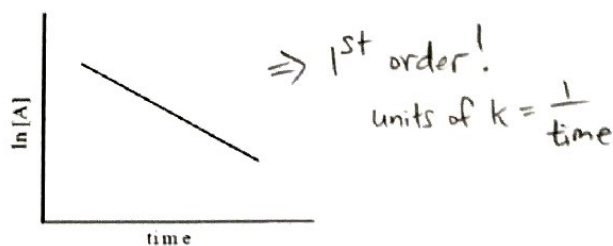
A: absorbance

a: molar absorptivity (a proportionality constant that's different for every solution)

b: path length (usually 1.00 cm)

c: concentration (measured in molarity)

- Beer's Law is important because it demonstrates that absorbance is directly proportional to concentration (providing the absorbing substance, wavelength, and path length are fixed).
- By measuring the change in absorbance over time, you can use Beer's law to convert absorbance to concentration.
- Graphing [reactant] vs. time, $\ln[\text{reactant}]$ vs. time, and $1/[\text{reactant}]$ vs. time will allow you to determine if the reaction being studied is zero, first, or second order with respect to that reactant:
 - If [reactant] vs. time is most linear, the reaction is 0th order with respect to that reactant.
 - If $\ln[\text{reactant}]$ vs. time is most linear, the reaction is 1st order with respect to that reactant.
 - If $1/[\text{reactant}]$ vs. time is most linear, the reaction is 2nd order with respect to that reactant.



1. Which of the following statements best describe this graph?

I. The graph represents a reactant that is second order.

II. The absolute value of the slope for the graph is equal to the rate constant, k .

III. The units for the rate constant, k will be $M^{-1} \text{time}^{-1}$

- a. I only **(b.)** II only c. I and II only d. II and III only e. I, II, and III