

Chemistry 105b
Dr. Jessica Parr
Lecture #3
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Kinetics/Chapter 13 Continued

Half-Life: the time required for half of the initial concentration of a reactant to react

1st half-life: 100% → 50%

2nd half-life: 50% → 25%

And so on...

The half-life may or may not be the same value for the each of the half-life's, depending on reaction rate/order/mechanism

Rate Law – a relationship between the rate of a reaction and the concentration of the reactants (also called the differential rate law)

Differential rate law: Rate = k[A]ⁿ

k = rate constant

n = reaction order, how the rate depends on concentration

We will find the reaction order for each reactant

The overall order is the sum of all the orders of each reactant

- The order of a reaction can only be determined by experiment
- Method of Initial Rates – compare instantaneous rates measured at the start of a reaction under different concentration conditions to determine the rate law for the reaction

Compare initial rates with different concentrations

1st Order – double concentration = double rate
triple concentration = triple rate
and so forth...

2nd Order – double concentration = quadruple rate
triple concentration = 9x rate
and so forth...

Consider the reaction: $aA + bB \rightarrow cC + dD$

$$-1/a (\Delta[A]/ \Delta t) = -1/b(\Delta[B]/ \Delta t) = 1/c(\Delta[C]/ \Delta t) = 1/d (\Delta[D]/ \Delta t)$$

Rate constant value can vary depending on which reactant or product is monitored
Units for rate should be amount/time (M/s)

0 order: k has units M/s

1st Order: k has units s⁻¹

2nd Order: k has units M⁻¹s⁻¹

The units for k are to balance out the concentration value to the correct units (1st Order is M, 2nd order is M²)

Ex. Initial rate data are listed in the table below for the reaction. Find the rate law
 $\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$

Experiment	$[\text{NH}_4^+]$	$[\text{NO}_2^-]$	Initial Rate
1	0.24	0.10	7.2×10^{-6}
2	0.12	0.10	3.6×10^{-6}
3	0.12	0.15	5.4×10^{-6}

$$\text{Rate} = k[\text{NH}_4^+]^m[\text{NO}_2^-]^n$$

Compare rate of experiment 2 to 1: The concentration of $[\text{NH}_4^+]$ is double while $[\text{NO}_2^-]$ remains constant, and the initial rate is doubled.

$$2 \times [\text{NH}_4^+] = 2 \times \text{Initial rate} = 1^{\text{st}} \text{ Order}$$

Compare rate of experiment 2 to 3, The concentration of $[\text{NO}_2^-]$ is multiplied by 1.5 as is the initial rate, while $[\text{NH}_4^+]$ remains constant

$$1.5 \times [\text{NO}_2^-] = 1.5 \times \text{Initial rate} = 1^{\text{st}} \text{ Order}$$

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

What is the value of the rate constant?

$$7.2 \times 10^{-6} \text{ M/s} = k(0.24\text{M})(0.10\text{M})$$

$$k = 3.0 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$$

$$\text{Rate} = 3.0 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}[\text{NH}_4^+][\text{NO}_2^-]$$