Kinetics
Chem1B, General Chemistry II

Learning Outcomes: By the end of this chapter you should be able to:

(1) Predict the effect of physical state, concentration, temperature, a catalyst, molecular orientation, and kinetic energy on the rate of a reaction.
(2) Use the given rate law for a reaction to solve for any variable in the equation (rate, rate constant, order, or concentration).
(3) Use the method of initial rates to determine the order (0th, 1st, or 2nd) of reaction for any reactant and determine the value for the rate constant.
(4) Use graphs of time versus concentration to determine whether a reaction is 0th, 1st, or 2nd order and use their integrated rate laws.
(5) Calculate the half-life for a 0th, 1st, or 2nd order reaction.
(6) Use all versions of the Arrhenius Equation to solve for its values.
(7) Use a complete mechanism to determine the overall rate law for a reaction.
(8) Label a reaction coordinate diagram for single or multistep reactions.

Equations and Constants

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

$$t_{1/2} = \frac{-\ln(0.5)}{k} \approx \frac{0.693}{k}$$
$$t_{1/2} = \frac{1}{k[A]_0}$$
$$k = Ae^{-EA/RT} \text{ or } \ln(k) = -\frac{E_a}{RT} + \ln(A)$$

R = universal gas constant, 8.314 J/mol K or 0.08206 L*atm/mol*K

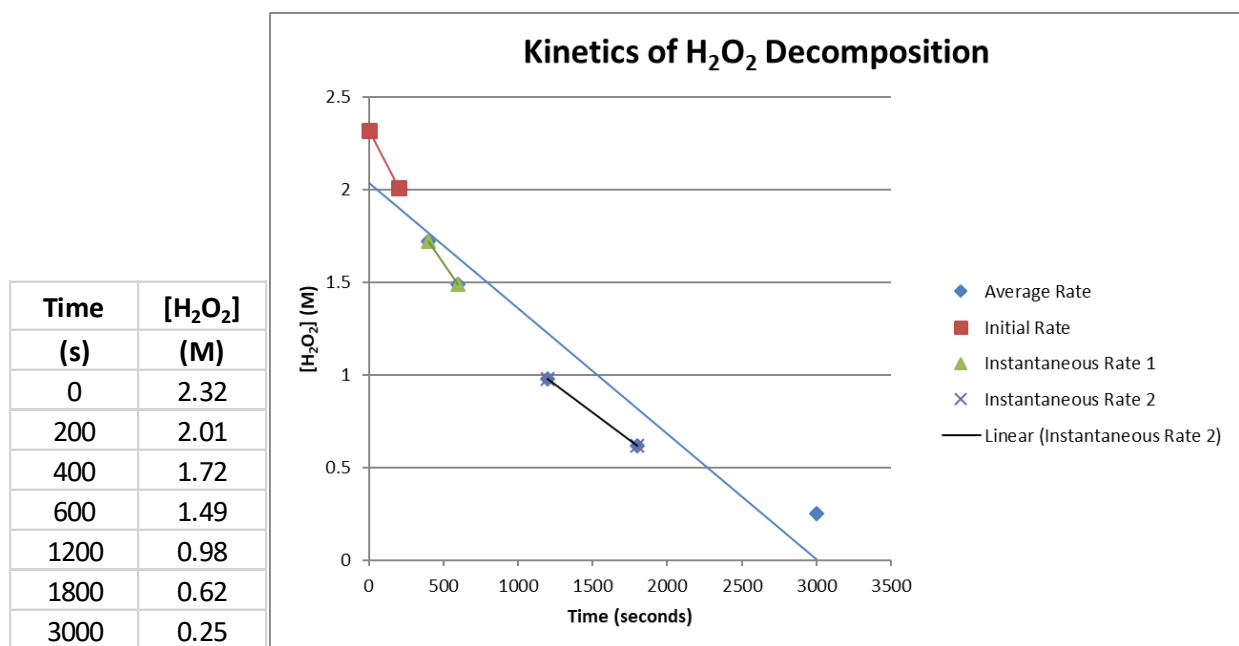$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

(1) Introduction to Kinetics
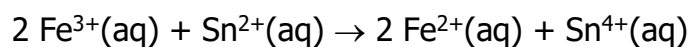
Kinetics studies how fast reactions progress

- How do we define rate?

- What units is rate usually in?

There are **six** main factors that affect (speed up/slow down) the rate of a reaction.

- What are they?

- Briefly describe *how* and *why* each affects reaction rate.

(2) Rate Laws

The **rate** of a reaction can be calculated for any given reactant or product.

- What is the key difference between the rate of reaction for a reactant versus a product?

- In your own words, describe *initial rate, instantaneous rate,* and *average rate*. How are they the same? How are they different?

Stoichiometric coefficients must be included when calculating rate.

- In your own words, describe how to account for stoichiometry in reaction rates.

Kinetics of H_2O_2 Decomposition

Time	[H_2O_2]
(s)	(M)
0	2.32
200	2.01
400	1.72
600	1.49
1200	0.98
1800	0.62
3000	0.25

Legend:
- ◆ Average Rate
- ■ Initial Rate
- ▲ Instantaneous Rate 1
- ✕ Instantaneous Rate 2
- — Linear (Instantaneous Rate 2)

y-axis: [H_2O_2] (M)
x-axis: Time (seconds)

Ex. 1) The following data was collected from the reaction:

$$2\ Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow 2\ Fe^{2+}(aq) + Sn^{4+}(aq)$$

Time (s)	0	30	60
[Fe^{3+}]	0.100	0.050	0.025

a.) Find the average rage for [Fe^{3+}].

b.) Assuming the rate in (a) is constant, calculate [Fe^{3+}] at t = 75 sec.

c.) Find the average rate of $[Fe^{2+}]$.

d.) Find the average rate of $[Sn^{4+}]$.

Rate laws are equations used to express the speed of a particular reaction.

- Write the generic form of a rate law for a reaction. Define each term.

- What are three orders of reaction we will be discussing?

Ex. 2: For A → products, use the following data to answer the questions.

[A]	2.50	0.833
Rate (M/s)	0.625	0.0692

a.) Determine the order of the reaction with respect to A.

b.) Find the rate constant, including units.

(3) The Method of Initial Rates

The **method of initial rates** varies the concentration of reactants and measures their initial rates over a series of experiments.

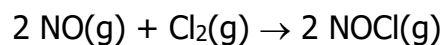Ex. 3) The following data was collected from the reaction:

$$2\ HgCl_2 + C_2O_4^{2-} \rightarrow 2\ Cl^- + 2\ CO_2 + Hg_2Cl_2$$

Exp.	$[HgCl_2]$	$[C_2O_4^{2-}]$	Rate
1	0.105	0.15	1.8×10^{-5}
2	0.105	0.30	7.1×10^{-5}
3	0.052	0.30	3.5×10^{-5}

a.) Determine the rate law.

b.) Calculate k, including units.

Ex. 4) The following data was collected from the reaction:

$$2 \text{ NO(g)} + \text{Cl}_2\text{(g)} \rightarrow 2 \text{ NOCl(g)}$$

Exp.	$[NO]$	$[Cl_2]$	Rate
1	0.0125	0.0255	2.27×10^{-5}
2	0.0125	0.0510	4.55×10^{-5}
3	0.0250	0.0255	9.08×10^{-5}

a.) Determine the rate law.

b.) Find the value of k, including units, from Experiment 2.

c.) Which reaction will progress faster: 2 $HgCl_2$ + $C_2O_4^{2-}$ or 2 NO + Cl_2? Explain.
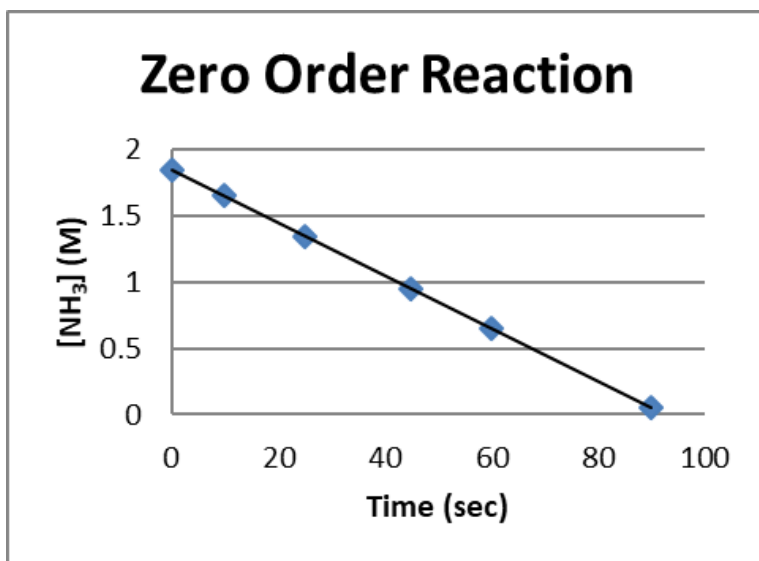
(4) Integrated Rate Laws

Zeroth, first, and second order rate laws can be **integrated** (linearized) to create straight-line graphs.

- Write the integrated rate laws for zeroth, first, and second order reactions. How are they the same? How are they different?

- Describe the graphs for zeroth, first, and second order reactions. What is on the y-axis? The x-axis? What in the integrated rate laws does the slope represent? The y-intercept? Using only graphs, how could you determine the order of the reaction? How could you use this in lab?

Zero Order Reaction

2 NH$_3$(g) --> N$_2$(g) + 3 H$_2$(g)
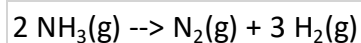
Time	[NH$_3$]	
(s)	(M)	
0	1.85	
10	1.65	
25	1.35	
45	0.95	
60	0.65	
90	0.05	

First Order Reaction

H$_2$O$_2$(aq) --> H$_2$O(l) + 1/2 O$_2$(g)
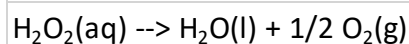
Time	[H$_2$O$_2$]	ln([H$_2$O$_2$])
(s)	(M)	
0	2.32	0.8415672
200	2.01	0.6981347
400	1.72	0.5423243
600	1.49	0.3987761
1200	0.98	-0.0202027
1800	0.62	-0.4780358
3000	0.25	-1.3862944

Second Order Reaction

2 NO$_2$(g) --> 2 NO(g) + O$_2$(g)
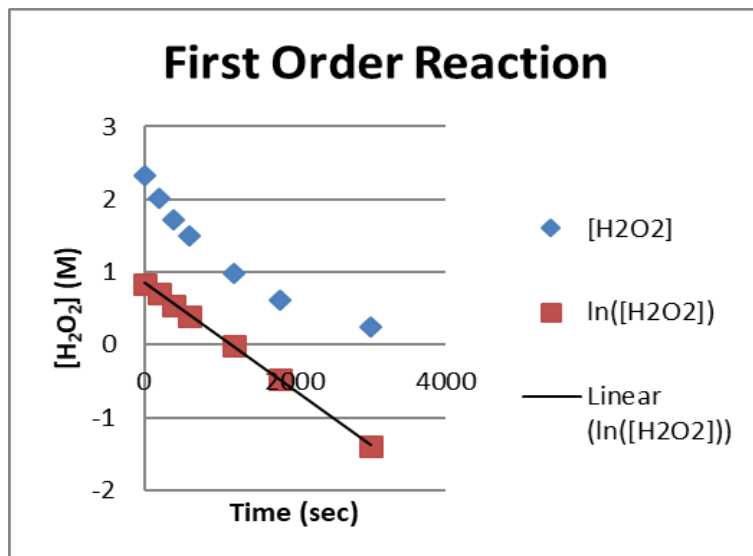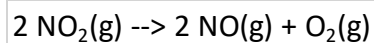
Time	[NO$_2$]	1/[NO$_2$]
(s)	(M)	
0	0.1	10
5	0.017	58.823529
10	0.009	111.11111
15	0.0062	161.29032
20	0.0047	212.76596

Ex. 5) For A → products, find [A] at t = 2.50 minutes for a second-order reaction when $[A]_0$ = 3.50 M and k = 0.0168 M^{-1} s^{-1}.

(5) Half-Life

The **half-life** is defined as the amount of time required for the initial concentration of reactant to decrease to half its original amount.

- Write the equations for the half-life of zeroth, first, and second order reactions. How are they the same? How are they different?

Ex. 6) The decomposition of H_2O_2 is **first-order**: 2 H_2O_2(aq) → O_2(g) + 2 H_2O(l)

a.) Calculate [H_2O_2] at t = 132 s if the initial concentration of H_2O_2 was 3.61 M and the rate constant (k) is 7.30 × 10^{-4} s^{-1}.

b.) Calculate the half-life ($t_{1/2}$) for the decomposition of H_2O_2, using the above value of k.

Ex. 7) Calculate the half-life of a second order reaction when $[A]_0 = 1.00$ M and $k = 0.002$ M^{-1} s^{-1}.

Ex. 8) For a second order reaction at t = 300 seconds, $[A]_t = 0.63$ M and $[A]_0 = 1.00$ M.

a.) Calculate k, including units.

b.) Determine the half-life ($t_{1/2}$) for the above reaction.

(6) The Arrhenius Equation

The **Arrhenius Equation** can be used for any order reaction and includes its dependence on temperature.

- Write all *three* forms of the Arrhenius Equation. Define each term. When would you use which?

Ex. 9) At 298 K, a first order reaction has a rate constant (k) of 3.46×10^{-5} s^{-1}. Calculate T when $t_{1/2}$ = 2 hrs. and the activation energy (E$_a$) is 106 kJ/mol.
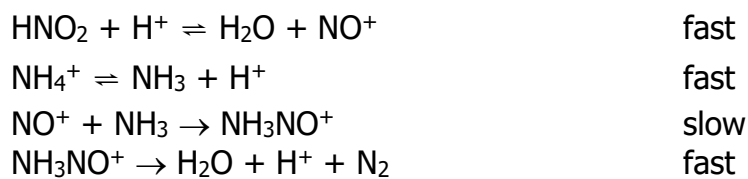
(7) Mechanisms

Mechanisms break reactions down into their single steps.

- What is molecularity? When can it be used to determine rate laws?

Ex. 10) Determine the rate law for: $2 NO + O_2 \rightarrow 2 NO_2$

$2 NO \rightleftharpoons N_2O_2$	fast
$N_2O_2 + O_2 \rightarrow 2 NO_2$	slow

Ex. 11) Determine the raw law for: $NH_4^+ + HNO_2 \rightarrow N_2 + 2 H_2O + H^+$

$HNO_2 + H^+ \rightleftharpoons H_2O + NO^+$	fast
$NH_4^+ \rightleftharpoons NH_3 + H^+$	fast
$NO^+ + NH_3 \rightarrow NH_3NO^+$	slow
$NH_3NO^+ \rightarrow H_2O + H^+ + N_2$	fast

(8) Reaction Coordinate Diagrams

Reaction Coordinate Diagrams graph the energy of a reaction (y-axis) against the reaction progress (x-axis).

Ex. 12) Draw two reaction coordinate diagrams for an exothermic, single-step reaction (1) with and (2) without a catalyst. Label all important features.

Ex. 13) Draw a reaction coordinate diagram for an endothermic, two-step reaction without a catalyst. Label all important features.