Unit 4: How Chemical Change Occurs
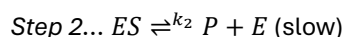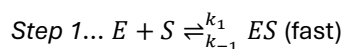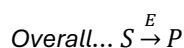
IMPORTANT EQUATIONS:

Relation between concentrations and rates...

$$rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t} = \frac{1}{e}\frac{\Delta[E]}{\Delta t}$$

Units for k...

Overall reaction order	Units of k
Zeroth	$M \cdot s^{-1}$
First	s^{-1}
Second	$M^{-1} \cdot s^{-1}$

Michaelis Menten mechanism...

$$\text{Overall... } S \xrightarrow{E} P$$

$$\text{Step 1... } E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \text{ (fast)}$$

$$\text{Step 2... } ES \overset{k_2}{\rightleftharpoons} P + E \text{ (slow)}$$

$$rate = k_2[ES]$$

Michaelis Menten constant...

$$K_M = \frac{k_{-1} + k_2}{k_1} \Longrightarrow rate = \frac{[E]_{total}[S]}{K_M + [S]} \Longrightarrow rate = k_2[E]_{total}$$

Integrated rate laws...

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

Flooding...

$$\frac{k_{obs,1}}{k_{obs,2}} = \frac{k[A]_1^m}{k[A]_2^m} = \left(\frac{[A]_1}{[A]_2}\right)^m$$

Half-life...

Zeroth order	First order	Second order
$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

EXAM: Monday, November 18th
5:45PM – 7:00PM @ PSYCH 105

SUBMICROSCOPIC MODELS OF CHEMICAL CHANGE

Reaction mechanisms...

Reaction mechanisms	step=by-step sequences of simple reactions by which an overall reaction occurs
Elementary reaction	a chemical reaction that has only a single transition state
Unimolecular elementary reaction	the rearrangement of a single reactant molecule to produce one or more product molecules
Bimolecular elementary reaction	the collision and reaction of two molecules or atoms in an elementary reaction
Trimolecular elementary reaction	the simultaneous collision of three atoms or molecules
Reaction intermediate	an atom or molecule that is a product in an earlier step and reacts away in a later step of a reaction mechanism

Terms pertaining to Gibbs free energy...

Exergonic	Gibbs free energy of the products is larger than that of the reactants
Endergonic	Gibbs free energy of the reactants is larger than that of the products

MEASURING REACTION RATES

Factors affecting reaction rates…

Catalyst	a substance that increases the rate of reaction by producing an alternate reaction pathway but is not consumed by the reaction

➔ The greater the $[catalyst]$, the more it will speed up the reaction

➔ If a reaction occurs on a surface, $\uparrow surface\ area, \uparrow rate$

Reaction rates…

➔ Instantaneous rate of reaction may be determined by…
- o If concentration changes can be measured at *very* short time intervals, then average rate a reasonably good approximation for initial rate
- o If we plot reactant concentration vs. time, initial rate at time t is given by the *negative* slope of a straight line that is tangent to the curve

➔ Reaction rates on $aA + bB \rightarrow dD + eE$…

➔ Given by $1\ mol\ A\ \left(\frac{b\ mol\ B}{a\ mol\ A}\right) = moles\ of\ B \Rightarrow \frac{b}{a}\Delta[A] = \Delta[B]$

$$rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t} = \frac{1}{e}\frac{\Delta[E]}{\Delta t}$$

Effects of concentration…

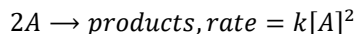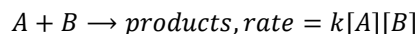| *Rate laws*	mathematical expressions that relate the rate of a chemical reaction to the concentration of reactants

➔ For any reactant…

$$rate = k[A]^m[B]^n \ldots = k\prod[reactant]^{stoic\ coeff}$$

➔ The overall order of the reaction is given by the sum of each individual orders

➔ Rate laws must be determined experimentally and are not reliably when predicted by reaction stoichiometry

➔ It is possible to determine the order of an elementary reaction solely by looking at the reaction equation
- o This is true for all, but *only*, elementary reaction
- o Unimolecular elementary reaction: first order

$$A \longrightarrow products, rate = k[A]$$
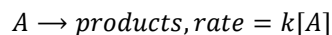
- o Bimolecular elementary reaction: second order

$$A + B \longrightarrow products, rate = k[A][B]$$

$$2A \longrightarrow products, rate = k[A]^2$$

Overall reaction order	*Units of k*
Zeroth	$M \cdot s^{-1}$
First	s^{-1}
Second	$M^{-1} \cdot s^{-1}$

Initial rates…

➔ Select two sets of data where all concentrations but one are the same and set up a ratio for the two rate laws

Unit 2 | Structures & Properties

MULTISTEP REACTIONS

Multistep reactions…

➔ Valid mechanism for a multistep reaction has these characteristics…
  o Should consist of a series of unimolecular and bimolecular elementary reaction steps that are plausible based on our knowledge of chemical bonding and interactions between molecules
    ▪ If a step has a 3 reactant species ➔ *extremely* unlikely to be a an elementary step
    ▪ If a reaction step involvers breaking a very strong bond, its unlikely to have a small enough activation energy fast enough t make the mechanism work
  o Sum of reaction steps should agree with the overall balanced reaction
  o Mechanisms must agree with experimentally observed values

Rate-determining step	slowest step in the mechanism

Equilibrium approximation…

➔ When the rate-determining step is not the first step, the rate law of the overall reaction can still be approximated as the rate law of the rate-determining step
➔ Cannot just express rate-determining step; its necessary to express relative steps as well

Intro to catalysts…

Catalyst	increases the rate of reaction by altering the mechanism

➔ Allows reaction to proceed via a pathway with a lower E_a than for the uncatalyzed mechanism
➔ Catalyzed reaction must involve at least two steps (can be more than two)
  o One where the catalyst interacts with a reactant to form an intermediate substance
  o One where the intermediate reacts to regenerate the original catalyst and form products
➔ The catalyst is *not* consumed by the reaction

Autocatalytic	when a product catalyzes a reaction

  o Autocatalytic reactions can be dangerous because the reaction can speed up significantly as a product is formed
➔ Since reactants and products included in both reactions are exactly the same, they are the same at the same energies (reaction coordinate diagram) ➔ a catalyst has no effect on the relative energies of the reactants and products

$$k_{catalyzed} > k_{uncatalyzed}$$

Types of catalysts (to be cont.)…

Homogenous catalyst	present in the same phase as the reactants

CATALYSTS

Heterogeneous catalysts...

Heterogeneous catalysts	present in different phase from the reaction

➜ Heterogeneous catalyst reactions have *at least* four steps in the reaction mechanism...
- (1) Absorption of the reactants onto the surface of the catalyst
- (2) Activation of the absorbed reactants
- (3) Reaction of the absorbed reactants
- (4) Diffusion of the products from the surface into the gas/liquid phase

➜ Used in the Haber-Bosch process
- o Used to increase the rate of reaction and allow opportunities at reasonable temperatures
- o Takes advantage of boiling points

Enzymes...

Enzymes	biological catalysts; significantly accelerates reactions
Substrates	the reactants with which the enzyme connects in an enzyme-catalyzed reaction

➜ Enzymes interactions with substrate molecules are often partially/entirely noncovalent
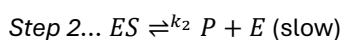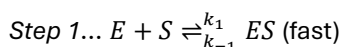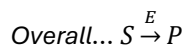- o Interacts through hydrogen bonding, ionic attraction, and/or dipole-dipole moment

Active site	only part of the large enzyme molecule interacts with a substance

➜ Induced-fit model...
- o As a substrate interacts with an enzyme, the substrate is distorted (atoms are shifted, bonds are stretched) to a structure closer to the transition state of the reaction. This lowers the energy of the transition state accelerating the reaction
- o Only molecules with correct functional groups in correct configurations are able to be induced to fit the active site of the enzyme

Enzyme kinetics and the Michaelis Menten mechanism...

Michaelis Menten mechanism	a two-step reaction that applies to many enzyme-catalyzed reaction

➜ An enzyme E combines with a substrate S to from an enzyme substrate complex ES, which then separates to give the product P and *regenerate* the enzyme

$$Overall... \ S \xrightarrow{E} P$$

$$Step \ 1... \ E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \ (fast)$$

$$Step \ 2... \ ES \overset{k_2}{\rightleftharpoons} P + E \ (slow)$$

$$rate = k_2[ES]$$

Steady-state approximate	once the reactive intermediate ES forms, its concentration remains approximately constant through the course of the reaction

➜ The Michaelis Menten constant K_M is given by...

$$K_M = \frac{k_{-1} + k_2}{k_1} \Longrightarrow rate = \frac{[E]_{total}[S]}{K_M + [S]} \Longrightarrow rate = k_2[E]_{total}$$

Unit 2 | Structures & Properties

Relating to $[S]$ vs. $rate$ graphs...

➔ If $[S]$ is very low
  ○ First order in $[S]$

$$[S] \ll K_M$$

$$[S] + K_M \approx K_M$$

$$rate = \frac{k_2}{K_M}[S][E]_{total}$$

➔ If $[S]$ is very high
  ○ Zeroth order in $[S]$
  ○ $[S]$ is constant

$$[S] \gg K_M$$

$$[S] + K_M \approx [S]$$

$$rate = k_2[E]_{total}$$

➔ If $[S] = K_M$

$$rate = \frac{k_2[S][E]_{total}}{2[S]}$$

$$rate = \frac{1}{2}k_2[E]_{total} = \frac{1}{2}V_{max}$$

Enzyme denaturation and inhibitors...

Denaturation	process in which proteins lose their quaternary, tertiary, and secondary structure
Inhibitor	interacts with enzyme to decrease the enzymes catalytic efficiency
Irreversible inhibition	covalently binds to the enzymes active site producing a permanent loss in catalytic efficiency
Reversible inhibition	forms a noncovalent complex with the enzyme resulting in a temporary decrease in catalytic efficiency

➔ Reducing concentration returns catalytic efficiency to normal

Types of reversible inhibition...

Competitive inhibition	the substrate and inhibitor compete for the same active site on the enzyme

➔ Substrate cannot bind to a enzyme-inhibitor EI complex
➔ Concentration of enzyme available to from ES is lower and enzyme-catalyzed reaction is lower

Uncompetitive inhibition	the inhibitor binds to the ES complex, but not the active site forming ESI complex

➔ Formation of enzyme-substrate-inhibitor ESI complex decreases catalytic efficiency because it reduce the concentration of ES, which reduces the rate of rate-limiting step

Noncompetitive inhibition	the inhibitor binds to both the enzyme itself and the ES complex at the active site

➔ Forms inactive ESI complex and reduces concentration of ES

PREDICTING TIMING OF CHEMICAL/PHYSICAL PREOCESSES

Intro to integrated rate law...

Integrated rate law	relates the concentration of a reactant or product to the elapsed time of the reaction

➔ For $A \rightarrow products \Rightarrow \int_{[A]_0}^{[A]_t} \frac{1}{[A]^m} d[A] = -kt : m = reaction\ order$

Applications of integrated rate laws...

➔ For each reaction order $m = \{0,1,2\}$, notice how they take form $y = mx + b$

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

Flooding method...

Flooding	running a reaction that involves two or more reactants with a large excess of all but on reactant
Pseudo-order	order obtained under flooding conditions and is not necessarily the overall order of the reaction

➔ For $A + B \rightarrow products$
  (1) Make $[A]_0 \gg [B]_0$
    o $[A]_0$ is essentially constant
    o $rate = k[A]^m[B]^n$ becomes $rate \approx k_{obs}[B]^n : slope = \pm k_{obs}$
  (2) Run at a different high $[A]_0$ to find m, k

$$\frac{k_{obs,1}}{k_{obs,2}} = \frac{k[A]_1^m}{k[A]_2^m} = \left(\frac{[A]_1}{[A]_2}\right)^m$$

Half-life...

Zeroth order	First order	Second order
$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$