

## Unit 4: How Chemical Change Occurs

## IMPORTANT EQUATIONS:

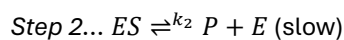
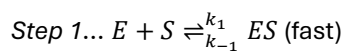
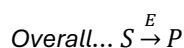
Relation between concentrations and rates...

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

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...



$$rate = k_2[ES]$$

Michaelis Menten constant...

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

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

## SUBMICROSCOPIC MODELS OF CHEMICAL CHANGE

Reaction mechanisms...

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

Terms pertaining to Gibbs free energy...

<i>Exergonic</i>	<u>Gibbs free energy of the products is larger than that of the reactants</u>
<i>Endergonic</i>	<u>Gibbs free energy of the reactants is larger than that of the products</u>

## MEASURING REACTION RATES

Factors affecting reaction rates...

<i>Catalyst</i>	a substance that increases the rate of reaction by producing an alternate reaction pathway but is not consumed by the reaction
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- 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...
  - If concentration changes can be measured at very short time intervals, then average rate a reasonably good approximation for initial rate
  - 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  $1 \text{ mol } A \left( \frac{b \text{ mol } B}{a \text{ mol } A} \right) = \text{moles of } B \Rightarrow \frac{b}{a} \Delta[A] = \Delta[B]$

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

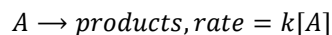
Effects of concentration...

<i>Rate laws</i>	mathematical expressions that relate the rate of a chemical reaction to the concentration of reactants
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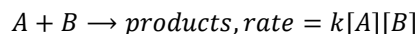
- For any reactant...

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

- 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
  - This is true for all, but *only*, elementary reaction
  - Unimolecular elementary reaction: first order



- Bimolecular elementary reaction: second order



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

## MULTISTEP REACTIONS

Multistep reactions...

- ➔ Valid mechanism for a multistep reaction has these characteristics...
  - 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 an elementary step
    - If a reaction step involves breaking a very strong bond, it's unlikely to have a small enough activation energy fast enough to make the mechanism work
  - Sum of reaction steps should agree with the overall balanced reaction
  - Mechanisms must agree with experimentally observed values

<i>Rate-determining step</i>	<u>slowest step in the mechanism</u>
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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; it's necessary to express relative steps as well

Intro to catalysts...

<i>Catalyst</i>	<u>increases the rate of reaction by altering the mechanism</u>
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- ➔ 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)
  - One where the catalyst interacts with a reactant to form an intermediate substance
  - One where the intermediate reacts to regenerate the original catalyst and form products
- ➔ The catalyst is *not* consumed by the reaction

<i>Autocatalytic</i>	<u>when a product catalyzes a reaction</u>
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- 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

$$k_{\text{catalyzed}} > k_{\text{uncatalyzed}}$$

Types of catalysts (to be cont.)...

<i>Homogenous catalyst</i>	<u>present in the same phase as the reactants</u>
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## CATALYSTS

Heterogeneous catalysts...

<i>Heterogeneous catalysts</i>	<u>present in different phase from the reaction</u>
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- 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
- Used to increase the rate of reaction and allow opportunities at reasonable temperatures
  - Takes advantage of boiling points

Enzymes...

<i>Enzymes</i>	<u>biological catalysts; significantly accelerates reactions</u>
<i>Substrates</i>	<u>the reactants with which the enzyme connects in an enzyme-catalyzed reaction</u>

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

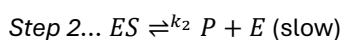
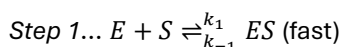
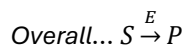
<i>Active site</i>	<u>only part of the large enzyme molecule interacts with a substance</u>
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- Induced-fit model...
- As a substrate interacts with an enzyme, the substrate is distorted (atoms are shifted, bonds are stretched) to a structure closer to the transition state of the reaction. This lowers the energy of the transition state accelerating the reaction
  - 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...

<i>Michaelis Menten mechanism</i>	<u>a two-step reaction that applies to many enzyme-catalyzed reaction</u>
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- An enzyme  $E$  combines with a substrate  $S$  to form an enzyme substrate complex  $ES$ , which then separates to give the product  $P$  and *regenerate* the enzyme



$$\text{rate} = k_2[ES]$$

<i>Steady-state approximate</i>	<u>once the reactive intermediate <math>ES</math> forms, its concentration remains approximately constant through the course of the reaction</u>
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- The Michaelis Menten constant  $K_M$  is given by...

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

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...

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

- Reducing concentration returns catalytic efficiency to normal

Types of reversible inhibition...

<i>Competitive inhibition</i>	<u>the substrate and inhibitor compete for the same active site on the enzyme</u>
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- Substrate cannot bind to a enzyme-inhibitor *EI* complex
- Concentration of enzyme available to form *ES* is lower and enzyme-catalyzed reaction is lower

<i>Uncompetitive inhibition</i>	<u>the inhibitor binds to the <i>ES</i> complex, but not the active site forming <i>ESI</i> complex</u>
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- Formation of enzyme-substrate-inhibitor *ESI* complex decreases catalytic efficiency because it reduces the concentration of *ES*, which reduces the rate of rate-limiting step

<i>Noncompetitive inhibition</i>	<u>the inhibitor binds to both the enzyme itself and the <i>ES</i> complex at the active site</u>
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- Forms inactive *ESI* complex and reduces concentration of *ES*

## PREDICTING TIMING OF CHEMICAL/PHYSICAL PROCESSES

Intro to integrated rate law...

<i>Integrated rate law</i>	relates the concentration of a reactant or product to the elapsed time of the reaction
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→ For  $A \rightarrow \text{products} \Rightarrow \int_{[A]_0}^{[A]_t} \frac{1}{[A]^m} d[A] = -kt$ ;  $m = \text{reaction order}$

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...

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

→ For  $A + B \rightarrow \text{products}$

(1) Make  $[A]_0 \gg [B]_0$

○  $[A]_0$  is essentially constant

○  $\text{rate} = k[A]^m[B]^n$  becomes  $\text{rate} \approx k_{\text{obs}}[B]^n$ ;  $\text{slope} = \pm k_{\text{obs}}$

(2) Run at a different high  $[A]_0$  to find  $m, k$

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

Half-life...

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