

# Enzymes

## Features

- Catalysts – increase rate of rxn (forward and reverse)
- Lowers **activation energy**
- Do **NOT** change:
  - ⇒ equilibrium constant
  - ⇒ free energy  $\Delta G$
  - ⇒ enthalpy  $\Delta H$
- Recycled in reaction (appear in products + reactants)
- Sensitive to **pH** and **temperature**
- Enzyme specificity for substrates

### Cofactors + Coenzymes

purpose: to improve enzymatic function

**Cofactors:** inorganic molecules, metals ions ( $Zn^{+2}$ ,  $Cu^{+2}$ ,  $Fe^{3+}$ )

**Coenzymes:** small, organic, vitamin derivatives ( $NAD^+$ ,  $FAD$ , coenzyme A)

- **Apoenzymes**
- **Holoenzymes**
- **Prosthetic groups**

## Six Classification

### MNEMONIC

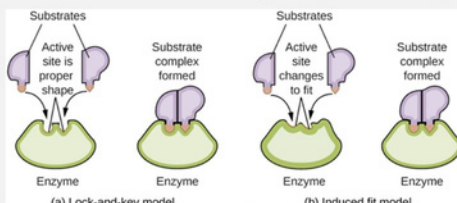
Main Enzymes – LIL' HOT:

Ligase  
Isomerase  
Lyase  
Hydrolase  
Oxidoreductase  
Transferase

1. **Ligase** – join, use ATP (i.e. DNA Ligase)
2. **Isomerase** – rearrangement, isomers (constitutional and stereoisomers)
3. **Lyase** – cleavage **w/ out  $H_2O$**
4. **Hydrolase** – cleavage **with  $H_2O$**
5. **Oxidoreductase** – redox, transfer  $e^-$
6. **Transferase** – transfer of functional group, include **kinases** (transfer  $P_i$  from ATP)

## Enzyme Activity

- Enzyme-substrate binding
  - **Lock and key theory** (specificity)
  - **Induced fit model** (accepted theory)



(a) Lock-and-key model (b) Induced fit model  
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↓  $K_m = \uparrow$  **affinity**  
 ▪ Enzyme activity *independent* of  $[S]$   
 ↑  $K_m = \downarrow$  **affinity** (more substrate needed)  
 ▪ Enzyme activity *highly dependent* on  $[S]$

## Enzyme Kinetics

- ↑ Substrate concentration  $[S] = \uparrow$  Reaction rate  $[V]$  until reaching  $V_{max}$  (**saturation**).

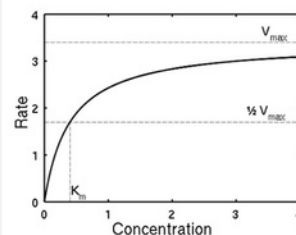
### Michaelis-Menten equation

$$v = \frac{V_{max} [S]}{K_m + [S]}$$

At  $1/2 v_{max}$ ,  $[S] = K_m$

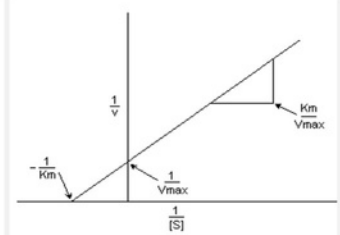
- **catalytic efficiency** =  $k_{cat}/K_m$

### Michaelis-Menten



https://commons.wikimedia.org/wiki/File:Michaelis-Menten\_saturation\_curve\_of\_an\_enzyme\_reaction\_LARGE.svg

### Lineweaver-Burk



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## Enzyme Regulation

### Feedback inhibition

negative feedback



**positive feedback:** amplifies response to stimulus (i.e. childbirth)

### Reversible inhibition

### Irreversible inhibition

- **Allosteric**
- **Phosphorylation**
- **Zymogens**

	Competitive	Noncompetitive	Mixed	Uncompetitive
<b>Binding Site</b>	Active Site	Allosteric Site	Allosteric Site	Allosteric Site
<b>Impact on <math>K_m</math></b>	Increases	Unchanged	Increases or Decreases	Decreases
<b>Impact on <math>V_{max}</math></b>	Unchanged	Decreases	Decreases	Decreases