

# Lecture # 18 CHE331A

Introduction & Design  
equations for IDEAL  
reactors  
(BR, CSTR, PFR, PBR)

Basic Concepts in  
Chemical kinetics &  
Design/Analysis of  
Isothermal Reactors

Collection & Analysis  
of Data; Isothermal  
Reactor Design for  
Multiple Reactions

**Nonelementary  
Homogeneous  
Reactions: *Active  
intermediates, PSSH  
and Chain Reactions***

**Nonelementary  
Homogeneous  
Reactions:  
Reactions involving  
Enzymes**



# Enzymes are bio-catalysts

- ▶ High-molecular weight protein or protein-like material
- ▶ Present in small quantities (usually) and are not consumed in the reaction
- ▶ Act on substrate (reactants) to chemically transform them at much faster rates than when not present → greater than  $10^3$  times faster
- ▶ Provide an alternate pathway, which lowers the activation energy
  - Formation of *Active Intermediate*
- ▶ They are very specific – catalyze one type of reaction
  - Undesirable products are less



# Enzymes are produced by living organisms

## ► Work under mild conditions

- pH 4 to 9 and temperatures 23 to 71 °C
- Extreme temps or pH environments → enzymes are denatured

## ► Named in terms of the reaction they catalyze

- Urease decomposes urea
- Exception:  $\alpha$ -amylase catalyzes starch → 1<sup>st</sup> step in HFCS production

## ► 6 classes of enzymes:

Enzyme	Reaction	Enzyme	Reaction
<b>Oxidoreductase</b>	$AH_2 + B + E \rightarrow A + BH_2 + E$	<b>Transferases</b>	$AB + C + E \rightarrow AC + B + E$
<b>Hydrolases</b>	$AB + H_2O + E \rightarrow AH + BOH + E$	<b>Isomerases</b>	$A + E \rightarrow isoA + E$
<b>Lyases</b>	$AB + E \rightarrow A + B + E$	<b>Ligases</b>	$A + B + E \rightarrow AB + E$

# Formation of Enzyme-Substrate complex is key to enzymatic reactions

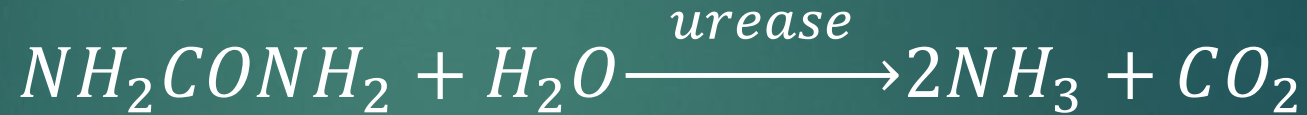
- ▶ Form enzyme-substrate complex by Lock-and-key or induced-fit models
  - Used to explain specific action of enzyme
- ▶ Interactions that stabilize the enzyme-substrate complex are hydrogen bonding, and hydrophobic, ionic and London van der Waals forces
- ▶ Lock-and-Key model was preferred due to the stereospecific effects of one enzyme acting on one substrate
- ▶ Induced-fit model is useful since it better explains the transformation of the substrate to form the products



# Mechanism of enzymatic reactions and the formation of active intermediates

- ▶ Example: Artificial kidney (Levine & LaCourse) to remove uric acid and creatinine

- ▶ Scheme proposed using urease enzyme to convert urea from the bloodstream



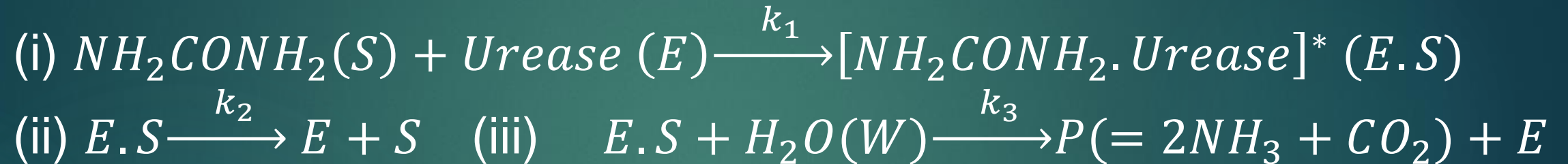
- ▶ Reaction mechanism proposed:

- Urease (E) reacts with urea (S) forming enzyme-substrate (E.S)
- The E.S complex can decomposes back to the urea(S) and urease (E)
- The E.S can also react with water (W) to give products ( $P = 2NH_3 + CO_2$ )



# Enzymatic action helps in the decomposition of Urea

## ► Reaction steps:



► The net rate of substrate disappearance and product formation can be determined by previous developments for multiple reactions (here 3)

$$\text{► } -r_S = \sum r_{i,S} = k_1 C_E C_S - k_2 C_{E.S} \qquad r_P = \sum r_{i,P} = k_3 C_{E.S} C_W$$

► These rate laws are not very useful since they require finding  $C_{E.S}$

- Put  $C_{E.S}$  in measurable quantities using PSSH





# Applying *PSSH* for this enzymatic reaction

- ▶ Need to determine  $C_{E.S}$  since  $-r_S = k_1 C_E C_S - k_2 C_{E.S}$  could also find  $r_P$
- ▶ Active intermediate formed is E.S and we can apply *PSSH*
- ▶  $r_{E.S} = \sum r_{i,E.S} = k_1 C_E C_S - k_2 C_{E.S} - k_3 C_W C_{E.S} = 0$
- ▶ Thus,  $C_{E.S} = \frac{k_1 C_E C_S}{k_2 + k_3 C_W} \Rightarrow -r_S = k_1 C_E C_S - k_2 \frac{k_1 C_E C_S}{k_2 + k_3 C_W}$   
$$-r_S = \frac{k_1 k_3 C_E C_S C_W}{k_2 + k_3 C_W}$$
- ▶ Still can not use the rate law since  $C_E$  is still not measurable
- ▶ Some E binds with S to form E.S,  $C_{E.S}$ , and some are free as E,  $C_E$
- ▶ Total E concentration ( $C_{E_t}$ ) is measurable and is a constant



# Since the enzyme is assumed not to deactivate (denature) $C_{E_t}$ is a constant

► Balance can be carried out for the enzyme amount, which is a constant

►  $C_{E_t} = C_E + C_{E.S}$       and       $C_{E_t} = C_E + \frac{k_1 C_E C_S}{k_2 + k_3 C_W}$

► Thus,  $C_E = \frac{C_{E_t}(k_2 + k_3 C_W)}{k_1 C_S + k_2 + k_3 C_W}$       Substituting into  $-r_S = \frac{k_1 k_3 C_E C_S C_W}{k_2 + k_3 C_W}$

$$-r_S = \frac{k_1 k_3 C_{E_t} C_S C_W}{k_1 C_S + k_2 + k_3 C_W}$$

► Water is in excess  $\Rightarrow k_{cat} = k_3 C_W$       Further,  $K_M = \frac{k_{cat} + k_2}{k_1}$

$$-r_S = \frac{k_{cat} C_{E_t} C_S}{C_S + K_M}$$

