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

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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 then when not present $\rightarrow$ 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 ^{o}C
  - Extreme temps or pH environments → enzymes are denatured
- Named in terms of the reaction they catalyze
  - Urease decomposes urea
  - Exception: α-amylase catalyzes starch → 1st step in HFCS production
- 6 classes of enzymes:

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

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 $NH_2CONH_2 + H_2O \xrightarrow{urease} 2NH_3 + CO_2$

- 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:

(i) $NH_2CONH_2(S) + Urease\ (E) \xrightarrow{k_1} [NH_2CONH_2.Urease]^*\ (E.S)$

(ii) $E.S \xrightarrow{k_2} E + S$ (iii) $E.S + H_2O(W) \xrightarrow{k_3} P(= 2NH_3 + CO_2) + E$

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

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

- 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 $-\boldsymbol{r_S} = k_1 C_E C_S - k_2 C_{E.S}$ could also find $\boldsymbol{r_P}$
- Active intermediate formed is E.S and we can apply *PSSH*
- $\boldsymbol{r_{E.S}} = \sum r_{i,E.S} = k_1 C_E C_S - k_2 C_{E.S} - k_3 C_W C_{E.S} = 0$
- Thus, $C_{E.S} = \frac{k_1 C_E C_S}{k_2 + k_3 C_W}$ $\Rightarrow$ $-\boldsymbol{r_S} = k_1 C_E C_S - k_2 \frac{k_1 C_E C_S}{k_2 + k_3 C_W}$

$$-\boldsymbol{r_S} = \frac{k_1 k_3 C_E C_S C_W}{k_2 + k_3 C_W}$$

- 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 $-\boldsymbol{r_S} = \frac{k_1 k_3 C_E C_S C_W}{k_2 + k_3 C_W}$

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

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

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