Lecture # 17 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* and *PSSH*

Nonelementary Homogeneous Reactions: Chain Reactions & the case of Ethane Cracking

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Application of PSSH to Chain Reactions

- **Reaction steps during chain reactions are more complex and more than one *active intermediate* is formed**
- **Chain reactions occur in several steps:**
  - Initiation – Formation of active intermediate
  - Propagation or chain transfer – reaction of the active intermediate with reactant or product to form another active intermediate
  - Termination – deactivation of the active intermediate to form product
- **Example:** thermal cracking of ethane to form ethylene, methane, butane and hydrogen

The elementary reaction steps for thermal cracking of ethane

- Initiation: (i) $C_2H_6 \xrightarrow{k_1} 2CH_3^{\cdot}$ $\qquad r_{1,C2H6} = -k_1 C_{C2H6}$
- Propagation: (ii) $CH_3^{\cdot} + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5^{\cdot}$ $\qquad r_{2,C2H6} = -k_2 C_{CH3*} C_{C2H6}$

  (iii) $C_2H_5^{\cdot} \xrightarrow{k_3} C_2H_4 + H^{\cdot}$ $\qquad r_{3,C2H4} = k_3 C_{C2H5*}$

  (iv) $H^{\cdot} + C_2H_6 \xrightarrow{k_4} C_2H_5^{\cdot} + H_2$ $\qquad r_{4,C2H6} = -k_4 C_{H*} C_{C2H6}$
- Termination: (v) $2C_2H_5^{\cdot} \xrightarrow{k_{5C2H5*}} C_4H_{10}$ $\qquad r_{5,C2H5*} = -k_5 C_{C2H5*}^2$
- Derive the rate law for ethylene formation in measurable quantities using ***PSSH***

Applying *PSSH* for the active intermediates

- $\boldsymbol{r_{C2H4}} = \sum_{i=1}^{n} r_{i,C2H4} = r_{3,C2H4} = k_3 C_{C2H5*}$ only in reaction (iii)!
  - Need to find C_{C2H5*} in terms of measurable quantities

- Apply *PSSH* for C_{C2H5*}: $\boldsymbol{r_{C2H5*}} = \sum_{i=1}^{5} r_{i,C2H5*} = 0$

$$\boldsymbol{r_{C2H5*}} = r_{1,C2H5*} + r_{2,C2H5*} + r_{3,C2H5*} + r_{4,C2H5*} + r_{5,C2H5*} = 0$$

- Using Stoichiometry since $r_{i,C2H5*}$ *is not necessary given*

$r_{1,C2H5*} = 0$ since not involved in reaction (i) $r_{2,C2H5*} = -r_{2,C2H6}$

$r_{3,C2H5*} = -r_{3,C2H4}$ $r_{4,C2H5*} = -r_{4,C2H6}$ $r_{5,C2H5*}$ $given\ (= -k_5 C_{C2H5*}^2)$

- Thus, $\boldsymbol{r_{C2H5*}} = 0 - r_{2,C2H6} - r_{3,C2H4} - r_{4,C2H6} + r_{5,C2H5*} = 0$

Applying *PSSH* to the other *active intermediates*

- $\boldsymbol{r_{C2H4}} = r_{3,C2H4} = k_3 C_{C2H5*}$
- $-r_{2,C2H6} - r_{3,C2H4} - r_{4,C2H6} + r_{5,C2H5*} = 0$ with $r_{5,C2H5*} = -k_5 C^2_{C2H5*}$ (A)

$-r_{2,C2H6} = k_2 C_{CH3*} C_{C2H6}$; $-r_{3,C2H4} = -k_3 C_{C2H5*}$; $-r_{4,C2H6} = k_4 C_{H*} C_{C2H6}$

- Determine C_{CH3*} and C_{H*} using *PSSH* $\rightarrow$ $\boldsymbol{r_j} = \sum_{i=1}^{n} r_{i,j} = 0$
- $\boldsymbol{r_{CH3*}} = r_{1,CH3*} + r_{2,CH3*} = -2r_{1,C2H6} + r_{2,C2H6} = 0$ (B)

  From (B) $-2r_{1,C2H6} = r_{2,C2H6}$ $\Rightarrow$ $2k_1 C_{C2H6} = k_2 C_{CH3*} C_{C2H6}$
- $\boldsymbol{r_{H*}} = r_{3,H*} + r_{4,H*} = r_{3,C2H4} + r_{4,C2H6} = 0$ (C)

  Substituting (C) into (A) we have: $r_{2,C2H6} = r_{5,C2H5*}$

Rate of ethylene formation can be determined after applying *PSSH* to the three intermediates

- $\boldsymbol{r_{C2H4}} = r_{3,C2H4} = k_3 C_{C2H5*}$ Require C_{C2H5*} Apply PSSH for C_{i*}
- From PSSH of C_{CH3*}: $-2r_{1,C2H6} = r_{2,C2H6}$

$$\Rightarrow\ 2k_1 C_{C2H6} = k_2 C_{CH3*} C_{C2H6} \quad \Rightarrow \quad C_{CH3*} = \frac{2k_1}{k_2}$$

- From PSSH of C_{H*} *and* C_{C2H5*}: $r_{2,C2H6} = r_{5,C2H5*}$

$$\Rightarrow -k_2 C_{CH3*} C_{C2H6} = -k_5 C_{C2H5*}^2 \quad \Rightarrow \quad C_{C2H5*} = \left\{\frac{2k_1}{k_5} C_{C2H6}\right\}^{1/2}$$

- And, $\boldsymbol{r_{C2H4}} = k_3 C_{C2H5*} = k_3 \left\{\frac{2k_1}{k_5} C_{C2H6}\right\}^{1/2}$

$$\boldsymbol{r_{C2H4}} = k_3 \left\{\frac{2k_1}{k_5}\right\}^{1/2} C_{C2H6}{}^{1/2}$$

Rate of Ethane disappearance can also be determined

$$\boldsymbol{r_{C2H6}} = \sum_{i=1}^{n} r_{i,C2H6} = r_{1,C2H6} + r_{2,C2H6} + r_{4,C2H6}$$

- $r_{1,C2H6} = -k_1 C_{C2H6}$; $\quad r_{2,C2H6} = -k_2 C_{CH3*} C_{C2H6}$; $\quad r_{4,C2H6} = -k_4 C_{H*} C_{C2H6}$
- Need C_{H*} in terms of measurables: $\boldsymbol{r_{H*}} = r_{3,H*} + r_{4,H*} = r_{3,C2H4} + r_{4,C2H6} = 0$
- $-r_{3,C2H4} = -k_3 C_{C2H5*} = k_3 \left\{\frac{2k_1}{k_5}\right\}^{1/2} C_{C2H6}{}^{1/2}$ and $-r_{4,C2H6} = k_4 C_{H*} C_{C2H6}$

$$C_{H*} = \frac{k_3}{k_4}\left\{\frac{2k_1}{k_5}\right\}^{1/2} C_{C2H6}{}^{-1/2}$$

- $\boldsymbol{r_{C2H6}} = r_{1,C2H6} + r_{2,C2H6} + r_{4,C2H6} = -k_1 C_{C2H6} - k_2 C_{CH3*} C_{C2H6} - k_4 C_{H*} C_{C2H6}$

$$-r_{C2H6} = 3k_1 C_{C2H6} + k_3\left\{\frac{2k_1}{k_5}\right\}^{1/2} C_{C2H6}{}^{1/2}$$

Design equation for a constant volume Batch Reactor for a full numerical solution

- Mole/Species balance equations can be written for each species
- For species 'i': $\frac{dN_i}{dt} = r_i . V$ $\rightarrow$ $\frac{dC_i}{dt} = r_i$ for 8 species, 8 ODEs

1 – C_2H_6; 2 – CH_3*; 3 – CH_4; 4 – C_2H_5*; 5 – C_2H_4; 6 – H*; 7 – H_2; 8 – C_4H_{10}

- For example: $\frac{dC_1}{dt} = -k_1C_1 - k_2C_1C_2 - k_4C_1C_6$ & $\frac{dC_2}{dt} = 2k_1C_1 - k_2C_1C_2$
- For rate constants k_1 to k_5 and $C_{1,0}$ given we can determine the evolution of the 8 species (including active intermediates) with time
- This has been done for Ethane cracking in example 7-2 part (b)