Lecture # 16 CHE331A

Introduction and Design equations for Ideal reactors

(BR, CSTR, PFR, PBR)

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

Collection and Analysis of Data

Design of Isothermal Reactors for Multiple Reactions

Nonelementary Homogeneous Reactions

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Reactions do not necessarily follow zero, first or second order rate laws

- Previously, simple power law models were used to the rate laws

$$-r_A = kC_A^{\alpha} C_B^{\beta}$$

- Large number of reactions exist that have non-integer values or follow more involved forms of the rate law

- Examples:
    - $CH_3CHO \rightarrow CH_4 + CO$ rate law: $-r_{CH3CHO} = kC_{CH3CHO}^{3/2}$
    - $H_2 + Br_2 \rightarrow 2HBr$ rate law: $r_{HBr} = k_1 \frac{C_{H2}C_{Br2}^{3/2}}{C_{HBr}+k_2C_{Br2}}$

Rate laws that do not follow integer orders usually have several elementary steps

- The number of elementary steps involve at least one *active intermediate*
- *Active intermediate* is
  - A short lived molecule present in small amounts that reacts as fast as it is formed
  - Formed by **collision** with other molecules $A + M \rightarrow A^{*} + M$
  - Formed when the translational K.E is transferred during collision into the internal energies, particularly vibrational, leading to bond rupture, rearrangement and decomposition
  - Not formed just due to molecules moving at high velocity

Theory of *Active Intermediates* suggests that the intermediate does not react instantaneously

- Since the Active Intermediate reacts as fast as it can be formed

$$r_{A^*} = 0$$

- This is referred to as the Pseudo-Steady-State Hypothesis (PSSH)
- Thus, if the active intermediate is involved in several reactions

$$r_{A^*} = \sum_{i=1}^{n} r_{iA^*} = 0 \quad where\ n\ is\ the\ number\ of\ reactions$$

- *Active intermediate* include free radicals, ionic intermediates, and enzyme-substrate complex

Gas-phase decomposition of azomethane (AZO) to ethane and nitrogen as an example

$$(CH_3)_2N_2 \rightarrow C_2H_6 + N_2$$

- Order changes from 1st order to 2nd order when pressure is reduced
  - $r_{C2H6} \propto C_{AZO}$ → at pressures greater than 1 atm (high conc of AZO)
  - $r_{C2H6} \propto C_{AZO}^2$ → at low pressures (below 50 mm Hg, low conc)
- Change in order explained by following elementary reaction steps
  - $(CH_3)_2N_2 + (CH_3)_2N_2 \xrightarrow{k_{1AZO*}} (CH_3)_2N_2 + [(CH_3)_2N_2]^*$
  - $[(CH_3)_2N_2]^* + (CH_3)_2N_2 \xrightarrow{k_{2AZO*}} (CH_3)_2N_2 + (CH_3)_2N_2$
  - $[(CH_3)_2N_2]^* \xrightarrow{k_{3AZO*}} C_2H_6 + N_2$

Rate laws for AZO decomposition in terms of the elementary steps is difficult to implement

- The rate laws are:
  - $(CH_3)_2N_2 + (CH_3)_2N_2 \xrightarrow{k_{1AZO*}} (CH_3)_2N_2 + [(CH_3)_2N_2]^* \quad r_{1AZO^*} = k_{1AZO*}C_{AZO}^2$
  - $[(CH_3)_2N_2]^* + (CH_3)_2N_2 \xrightarrow{k_{2AZO*}} (CH_3)_2N_2 + (CH_3)_2N_2 \quad r_{2AZO^*} = -k_{2AZO*}C_{AZO}C_{AZO*}$
  - $[(CH_3)_2N_2]^* \xrightarrow{k_{3AZO*}} C_2H_6 + N_2 \quad r_{3AZO^*} = -k_{3AZO*}C_{AZO*}$
- The rate of formation of C_2H_6 can be given by: $r_{C2H6} = k_{3AZO*}C_{AZO*}$
- These rate laws require the conc of the *active intermediate*
- We can apply *PSSH* to obtain rate laws in terms of measurable concentrations

Pseudo-Steady-State-Hypothesis (PSSH) can help in developing useful Rate Laws

- $\boldsymbol{r_{AZO^*}} = \sum_{i=1}^{3} r_{i,AZO^*} = r_{1AZO^*} + r_{2AZO^*} + r_{3AZO^*} = 0$
- $\boldsymbol{r_{AZO^*}} = k_{1AZO*} C_{AZO}^2 - k_{2AZO*} C_{AZO} C_{AZO*} - k_{3AZO*} C_{AZO*} = 0$
- Thus, $C_{AZO*} = \frac{k_1 C_{AZO}^2}{k_2 C_{AZO} + k_3}$, substituting into $r_{C2H6} = k_{3AZO*} C_{AZO*}$

$$r_{C2H6} = \frac{k_1 k_3 C_{AZO}^2}{k_2 C_{AZO} + k_3} \quad using \rightarrow k_i's$$

- At low AZO concentrations $\quad k_2 C_{AZO} \ll k_3 \quad r_{C2H6} = k_1 C_{AZO}^2$
- At high AZO concentrations $\quad k_2 C_{AZO} \gg k_3 \quad r_{C2H6} = \frac{k_1 k_3}{k_2} C_{AZO} = k C_{AZO}$
- Thus, the change in “apparent” order is observed and the rate law is consistent