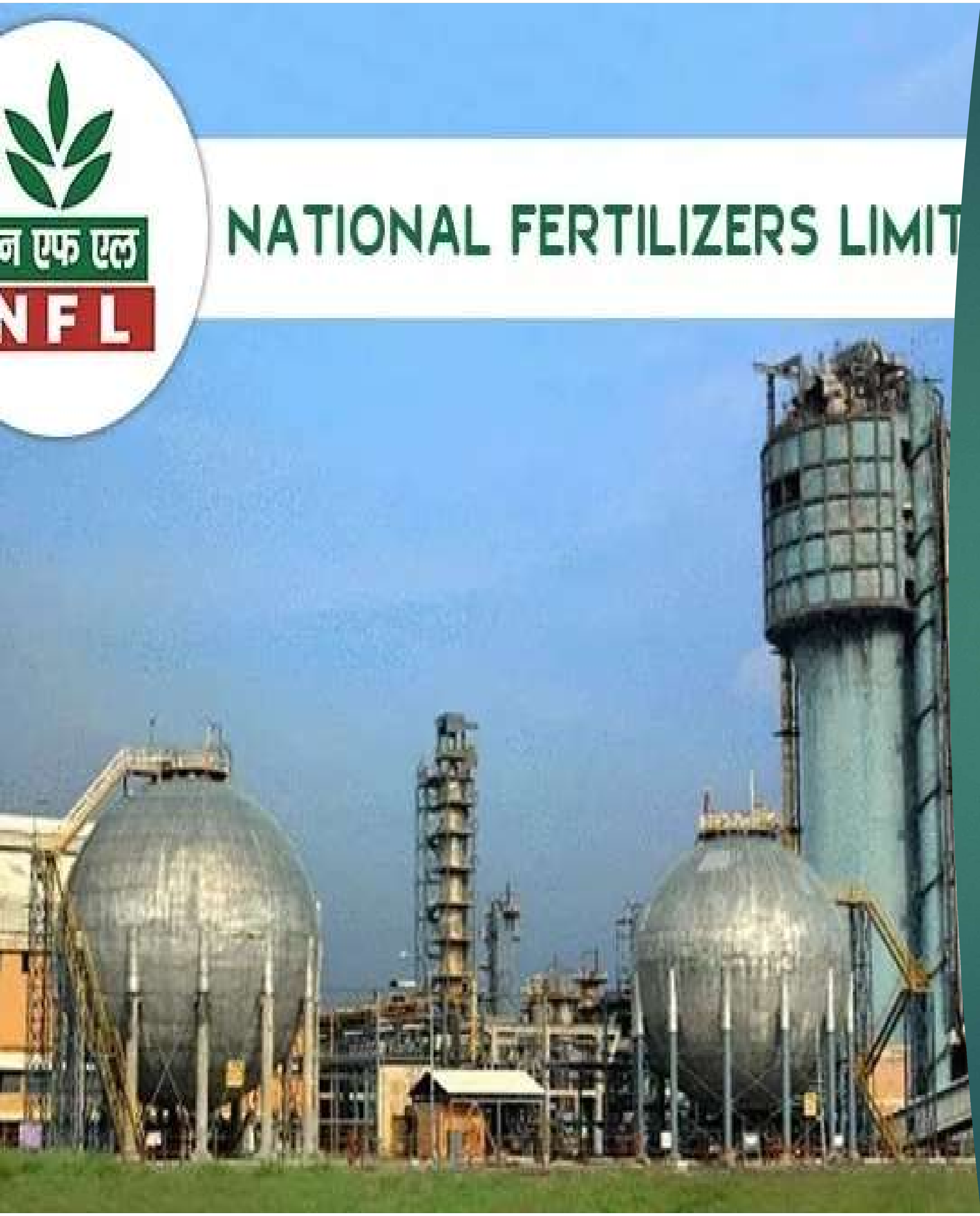

Lecture # 5.2 CHE331A

- **Rate as a function of conversion**
- **Developed stoichiometric table for single reaction**
- **Determined the relationship between concentration versus conversion for constant volume systems**
- **Need to determine concentration vs. conversion for variable volume system**

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In gas phase reactions with change in total number of moles $\dot{v}$ changes with residence time

- For gas-phase systems we can use the following equation of state:

  In general, for Batch: $PV = ZN_TRT$ or for Flow: $P\dot{v} = ZF_TRT$

- Above equation of state is also valid for the initial state/inlet

  For Batch: $P_0V_0 = Z_0N_{T0}RT_0$ or for Flow: $P_0\dot{v}_0 = Z_0F_{T0}RT_0$

- Thus, $V = V_0\left(\frac{P_0}{P}\right)\frac{T}{T_0}\left(\frac{Z}{Z_0}\right)\frac{N_T}{N_{T0}}$ OR $\dot{v} = \dot{v}_0\left(\frac{P_0}{P}\right)\frac{T}{T_0}\left(\frac{Z}{Z_0}\right)\frac{F_T}{F_{T0}}$

- Using the definition of δ (change in total moles per mol A reacted)

$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1,$ then $N_T = N_{T0} + \delta N_{A0}X$ OR $F_T = F_{T0} + \delta F_{A0}X$

The volume/volumetric flowrate can be further generalized

- $N_T = N_{T0} + \delta N_{A0} X$ OR $F_T = F_{T0} + \delta F_{A0} X$ can be presented as

$$\frac{N_T}{N_{T0}} = 1 + \varepsilon X \quad \text{OR} \quad \frac{F_T}{F_{T0}} = 1 + \varepsilon X$$

where $\epsilon = y_{A0}\delta$ and y_{A0} is the initial/inlet mol fraction of limiting reactant A

- Thus, $\boxed{V = V_0 \left(\frac{P_0}{P}\right) \frac{T}{T_0} \left(\frac{Z}{Z_0}\right) (1 + \varepsilon X)}$ OR $\boxed{\dot{v} = \dot{v}_0 \left(\frac{P_0}{P}\right) \frac{T}{T_0} \left(\frac{Z}{Z_0}\right) (1 + \varepsilon X)}$

- For gas-phase systems with compressibility factor not changing

$$V = V_0 \left(\frac{P_0}{P}\right) \frac{T}{T_0} (1 + \varepsilon X) \quad \text{OR} \quad \dot{v} = \dot{v}_0 \left(\frac{P_0}{P}\right) \frac{T}{T_0} (1 + \varepsilon X)$$

Concentrations in terms of conversion for variable volume systems

- For Batch systems: $V = V_0\left(\frac{P_0}{P}\right)\frac{T}{T_0}\left(\frac{Z}{Z_0}\right)(1+\varepsilon X)$
- And the Volume, Temp., Pressure and conversion are related
  - e.g., for constant volume system the pressure is related to temp. and conv.
- With $C_j = \frac{N_j}{V}$ also $C_T = \frac{N_T}{V} = \frac{P}{ZRT}$ and $C_{T0} = \frac{N_{T0}}{V_0} = \frac{P_0}{Z_0RT_0}$
- $C_j = \frac{N_j}{V} = \frac{N_{A0}[\theta_j + \left({}^{\mu_j}/_{a}\right)X]}{V} = \frac{N_{A0}[\theta_j + \left({}^{\mu_j}/_{a}\right)X]}{V_0\left(\frac{P_0}{P}\right)\frac{T}{T_0}\left(\frac{Z}{Z_0}\right)(1+\varepsilon X)} = C_{A0}\left(\frac{P}{P_0}\right)\frac{T_0}{T}\left(\frac{Z_0}{Z}\right)\frac{[\theta_j + \left({}^{\mu_j}/_{a}\right)X]}{(1+\varepsilon X)}$
- The same expression will be obtained for flow reactors

After determining the relationship between vol. & conv. then $-r_A = f(X)$ can be determined

- For a rate law $-r_A = k.C_A.C_B$ and after substituting for C_A and C_B

- For a constant volume system:

$$\boxed{-r_A = kC_{A0}^2(1-X).\left(\theta_B - \frac{b}{a}X\right) = f(X)}$$

- And for a variable volume system

$$\boxed{-r_A = k.C_{A0}^2.\frac{(1-X)\left(\theta_B - \frac{b}{a}X\right)}{(1+\varepsilon X)^2}\left(\frac{P}{P_0}\right)^2\left(\frac{T_0}{T}\right)^2\left(\frac{Z_0}{Z}\right)^2 = g(X)}$$

The rate law can be simplified further

- For equimolar amounts of A and B, $\theta_B = 1$, and $A + B \rightarrow products$
  - For constant vol. system: $-r_A = kC_{A0}^2.(1 - X)^2 \; = f_1(X)$
  - For variable vol. system: $-r_A = k.C_{A0}^2.\frac{(1-X)^2}{(1+\varepsilon X)^2}\left(\frac{P}{P_0}\right)^2\left(\frac{T_0}{T}\right)^2\left(\frac{Z_0}{Z}\right)^2 = g_1(X)$
  - With $P = P_0, T = T_0 \; and \; Z = Z_0$

$$-r_A = k.C_{A0}^2.\frac{(1 - X)^2}{(1 + \varepsilon X)^2}$$

- Thus, $\frac{1}{-r_A}$ versus X can be determined and, from Levenspiel plots the volume of the CSTR or PFR can be determined

Please go through Ex. 3.5, 4th Edition

Example 3.5

- A mixture of 28% SO_2 and 7.2% air is charged to a flow reactor where the total pressure is 1485 kPa (14.7 atm) and T = 227 ^oC. Make the Levenspiel plot from which the volume of isothermal flow reactors can be determined for various conversion.