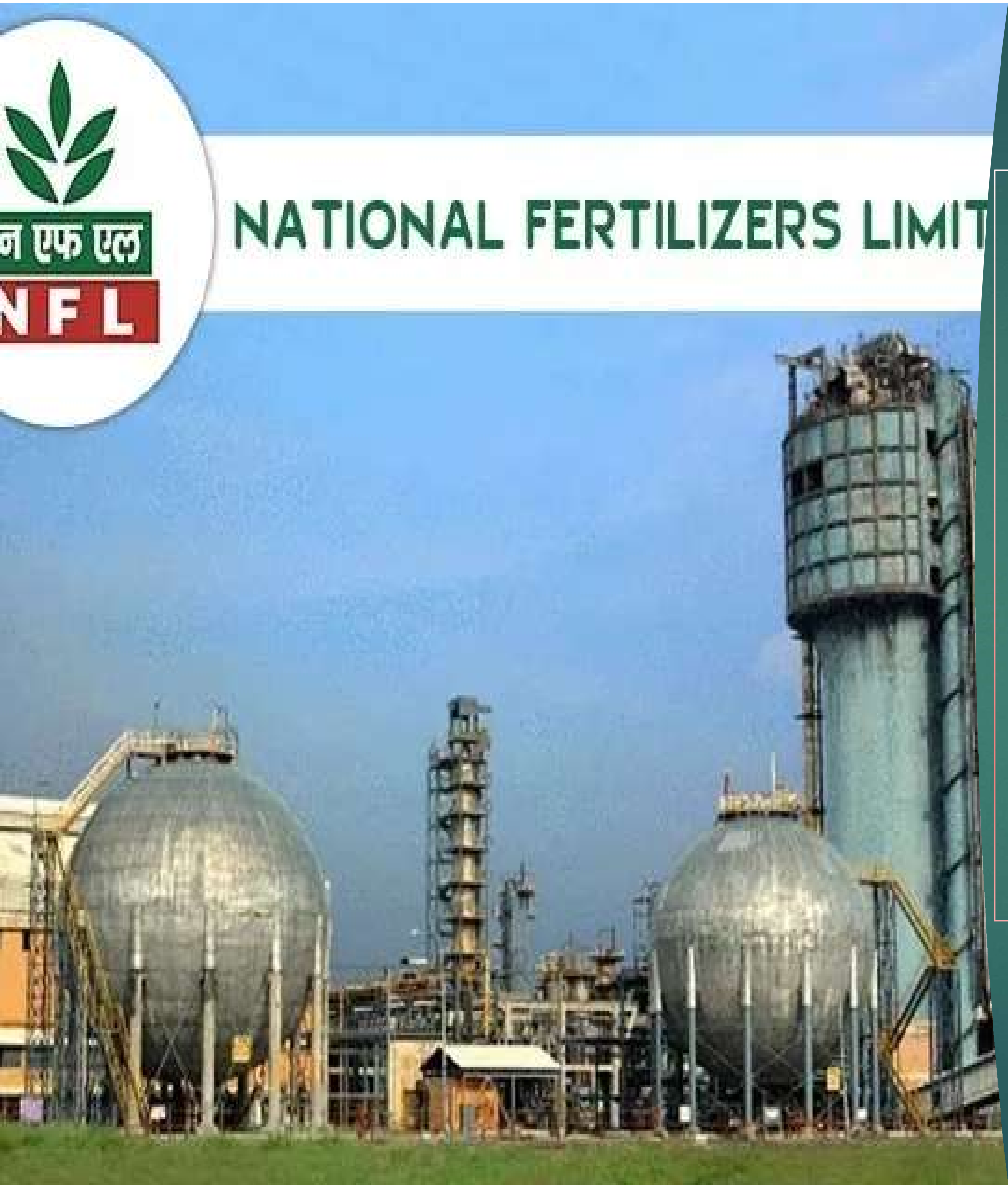


Lecture # 5.1 CHE331A

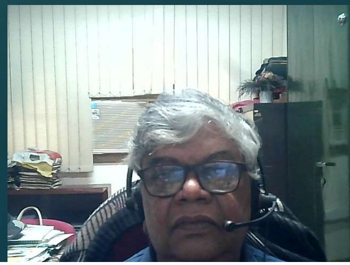
- Reaction rate is a function of concentration
- Some more about reactions
- Rate laws and the forms of reaction rates
- Rate constant, activation energy and

  Equilibrium constants
- Rate as a function of conversion
  - Performance equations

GOUTAM DEO

CHEMICAL ENGINEERING DEPARTMENT

IIT KANPUR



To use the design equation in terms of conversion we need to find $-r_A = g(X)$

- We have seen $-r_A = f(T, C_j)$, $\rightarrow$ we need to find out $C_j = h(X)$
- To determine this relationship the stoichiometry of the reaction is important
- For a reaction $A + \frac{b}{a}B \rightleftharpoons \frac{c}{a}C + \frac{d}{a}D$ we have $\frac{\Delta N_A}{-1} = \frac{\Delta N_B}{-{}^{b}/_{a}} = \frac{\Delta N_C}{{}^{c}/_{a}} = \frac{\Delta N_D}{{}^{c}/_{a}}$
- Number of moles of species A remaining after time ***t*** (BR) or volume ***V*** or ***W*** (flow reactors) is given by: $N_A = N_{A0}(1 - X)$ for BR and

  $F_A = F_{A0}(1 - X)$ for CSTR/PFR/PBR
- Based on the above the stoichiometry moles of the other species can be determined $\rightarrow$ best done by a stoichiometric table (single reaction)

The stoichiometry table for a batch system

Species	Initial (mol)	Change (mol)	Remaining (mol)
A	N_{A0}	$-(N_{A0}X)$	$N_A = N_{A0} - N_{A0}X$
B	N_{B0}	$-\frac{b}{a}(N_{A0}X)$	$N_B = N_{B0} - \frac{b}{a}N_{A0}X$
C	N_{C0}	$\frac{c}{a}(N_{A0}X)$	$N_C = N_{C0} + \frac{c}{a}N_{A0}X$
D	N_{D0}	$\frac{d}{a}(N_{A0}X)$	$N_D = N_{D0} + \frac{d}{a}N_{A0}X$
I (inerts)	N_{I0}	--	$N_I = N_{I0}$
Total =	N_{T0}		$N_T = N_{T0} + \delta N_{A0}X$

$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$ **is the change in number moles per mol A reacted**

- **Concentrations are given by** $\frac{N_i}{V}$

$$\frac{\Delta N_A}{-1} = \frac{\Delta N_B}{-{}^{b}/_{a}} = \frac{\Delta N_C}{{}^{c}/_{a}} = \frac{\Delta N_D}{{}^{c}/_{a}} = N_{A0}X$$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V}; \quad C_B = \frac{N_{B0}-({}^{b}/_{a})N_{A0}X}{V}$$

$$C_C = \frac{N_{C0}+({}^{c}/_{a})N_{A0}X}{V}; \quad C_D = \frac{N_{D0}+({}^{d}/_{a})N_{A0}X}{V}$$

- **Defining with respect to N_{A0}**

$$\theta_i = \frac{N_{io}}{N_{A0}} = \frac{C_{io}}{C_{A0}} = \frac{y_{io}}{y_{A0}}$$

$$C_A = \frac{N_{A0}(1-X)}{V}; \quad C_B = \frac{N_{A0}[\theta_B-({}^{b}/_{a})X]}{V}$$

$$C_C = \frac{N_{A0}[\theta_C+({}^{c}/_{a})X]}{V}; \quad C_D = \frac{N_{A0}[\theta_D+({}^{d}/_{a})X]}{V}$$

For flow systems a similar approach can be taken

- For flow systems: N_i is replaced by F_i and V by $\dot{v}$ in the stoichio. table
- Thus,

$$C_A = \frac{F_A}{\dot{v}} = \frac{F_{A0} - F_{A0}X}{\dot{v}}; \qquad C_B = \frac{F_{B0} - ({}^{b}/_{a})F_{A0}X}{\dot{v}}$$

$$C_C = \frac{F_{C0} + ({}^{c}/_{a})F_{A0}X}{\dot{v}}; \qquad C_D = \frac{F_{D0} + ({}^{d}/_{a})F_{A0}X}{\dot{v}}$$

Apply to:
$N_2 + 3H_2 = 2NH_3$

- **Defining with respect to F_{A0}:** $\theta_i = \frac{F_{io}}{F_{A0}} = \frac{C_{io}}{C_{A0}} = \frac{y_{io}}{y_{A0}}$

$$C_A = \frac{F_{A0}(1 - X)}{\dot{v}}; \qquad C_B = \frac{F_{A0}[\theta_B - ({}^{b}/_{a})X]}{\dot{v}}$$

$$C_C = \frac{F_{A0}[\theta_C + ({}^{c}/_{a})X]}{\dot{v}}; \qquad C_D = \frac{F_{A0}[\theta_D + ({}^{d}/_{a})X]}{\dot{v}}$$

- V *and* $\dot{v}$ may be function of X, $\rightarrow$ we now need to find $V(X)$ & $\dot{v}(X)$

For some cases the volume of the reacting system is a constant (const. volume systems)

- For liquid-phase reactions taking place in solution, the solvent usually dominates the system
  - Change in density is small/negligible, except for polymerization reactions
- For gas-phase reactions, constant volume occurs for
  - Sealed constant-volume vessel, with appropriate T and P measurements
  - Isothermal reaction with the number of moles of reactants is equal to the number of moles of products in the stoichiometric equation
- Thus, $V = V_0$ for batch systems OR $\dot{v} = \dot{v}_0$ for flow systems

$$C_i = \frac{N_{A0}[\theta_i + (\mu_i/a)X]}{V_0} \quad \text{OR} \quad C_i = \frac{F_{A0}[\theta_i + (\mu_i/a)X]}{\dot{v}_0} \qquad \frac{\mu_i}{a} \rightarrow \text{stoichio. coeffecient}$$

Constant volume systems can readily be used for determining $-r_A = f(X)$

- For $V = V_0$ for batch systems OR $\dot{v} = \dot{v}_0$ for flow systems, and a rate law given for A reacting with B as $-r_A = k.C_A.C_B$

- $C_i = \frac{N_{A0}[\theta_i + (\mu_i/a)X]}{V_0}$ OR $C_i = \frac{F_{A0}[\theta_i + (\mu_i/a)X]}{\dot{v}_0}$ $\rightarrow$ $\boxed{C_i = C_{A0}\,[\theta_i + (\mu_i/a)X]}$

- Then, $-r_A = kC_{A0}(1 - X).C_{A0}\left(\theta_B - \frac{b}{a}X\right)$

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

Reading Assignment: Ex 3-2 and 3-3 from Fogler, 4th Edition