

### Rate Laws

$-r_A = k C_A^\alpha C_B^\beta$      $\alpha$  order in A  
 $\beta$  order in B  
 Overall Reaction Order =  $\alpha + \beta$

- Power Law Model
- $k$  is the specific reaction rate (constant) and is given by the Arrhenius Equation:

$$k = A e^{-E/RT}$$

Where:  
 E = activation energy (cal/mol)  
 R = gas constant (cal/mol\*K)  
 T = temperature (K)  
 A = frequency factor

$T \rightarrow \infty \quad k \rightarrow A \quad A \approx 10^{13}$   
 $T \rightarrow 0 \quad k \rightarrow 0$

### Stoichiometric Tables

$$A + \frac{b}{a} B \rightarrow \frac{c}{a} C + \frac{d}{a} D$$

Using stoichiometry, we set up all of our equations with the amount of reactant A as our basis.

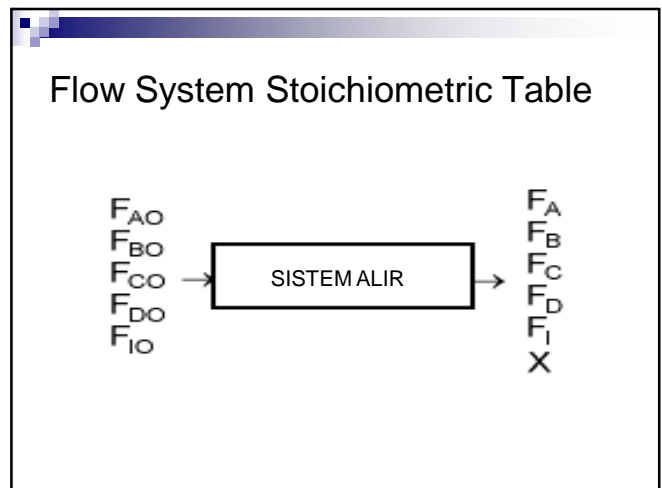
### Batch System Stoichiometric Table

Species	Symbol	Initial	Change	Remaining
A	A	$N_{A0}$	$-N_{A0}X$	$N_A = N_{A0}(1-X)$
B	B	$N_{B0} = N_{A0}\Theta_B$	$-\frac{b}{a}N_{A0}X$	$N_B = N_{A0}\left(\Theta_B - \frac{b}{a}X\right)$
C	C	$N_{C0} = N_{A0}\Theta_C$	$+\frac{c}{a}N_{A0}X$	$N_C = N_{A0}\left(\Theta_C + \frac{c}{a}X\right)$
D	D	$N_{D0} = N_{A0}\Theta_D$	$+\frac{d}{a}N_{A0}X$	$N_D = N_{A0}\left(\Theta_D + \frac{d}{a}X\right)$
Inert	I	$N_I = N_{A0}\Theta_I$	-----	$N_I = N_{A0}\Theta_I$
		$N_{T0}$		$N_T = N_{T0} + \delta N_{A0}X$

Where:  $\Theta_i = \frac{N_{i0}}{N_{A0}} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$  and  $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

**Concentration -- Batch System:**  $C_A = \frac{N_A}{V}$

**Constant Volume Batch:**  
 $V = V_0$   
 $C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)$   
 $C_B = \frac{N_B}{V} = \frac{N_{A0}}{V_0}\left(\Theta_B - \frac{b}{a}X\right) = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$   
 etc.



Species	Symbol	Reactor Feed	Change	Reactor Effluent
A	A	$F_{A0}$	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	B	$F_{B0} = F_{A0}\Theta_B$	$-\frac{b}{a}F_{A0}X$	$F_B = F_{A0}\left(\Theta_B - \frac{b}{a}X\right)$
C	C	$F_{C0} = F_{A0}\Theta_C$	$+\frac{c}{a}F_{A0}X$	$F_C = F_{A0}\left(\Theta_C + \frac{c}{a}X\right)$
D	D	$F_{D0} = F_{A0}\Theta_D$	$+\frac{d}{a}F_{A0}X$	$F_D = F_{A0}\left(\Theta_D + \frac{d}{a}X\right)$
Inert	I	$F_{I0} = F_{A0}\Theta_I$	-----	$F_I = F_{A0}\Theta_I$
		$F_{T0}$		$F_T = F_{T0} + \delta F_{A0}X$

Where:  $\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}u_0}{C_{A0}u_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$  and  $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

■ Concentration -- Flow System:

$$C_A = \frac{F_A}{v}$$

■ Liquid Phase Flow System:

$$v = v_0$$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0} = C_{A0}(1-X)$$

$$C_B = \frac{F_B}{v} = \frac{F_{A0}}{v_0} \left( \Theta_B - \frac{b}{a}X \right) = C_{A0} \left( \Theta_B - \frac{b}{a}X \right)$$

etc.

■ Gas Phase Flow System:

□ From the compressibility factor equation of state:  $v = v_0 \left( \frac{F_T}{F_{T0}} \right) \frac{T_0 P_0}{T P}$

□ The total molar flowrate is:  $F_T = F_{T0} + F_{A0}\delta X$

$$v = v_0 \left( 1 + y_{A0}\delta X \right) \frac{T_0 P_0}{T P}$$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0(1+\epsilon X)} \frac{T_0 P_0}{T P} = C_{A0} \frac{(1-X)}{(1+\epsilon X)} \frac{T_0 P_0}{T P}$$

$$C_B = \frac{F_B}{v} = \frac{F_{A0} \left( \Theta_B - \frac{b}{a}X \right)}{v_0(1+\epsilon X)} \frac{T_0 P_0}{T P} = C_{A0} \frac{\left( \Theta_B - \frac{b}{a}X \right)}{(1+\epsilon X)} \frac{T_0 P_0}{T P}$$

etc.

Algorithm for Isothermal Reactor Design

**Example:** The elementary gas phase reaction  $2A + B \rightarrow C$  takes place in a CSTR at constant temperature (500 K) and constant pressure (16.4 atm). The feed is equal molar in A and B.

**Mole Balance**  $v = \frac{F_{A0}X}{-r_A}$

**Rate Law**  $-r_A = kC_A^2 C_B$

For a gas phase system:  $C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0(1+\epsilon X) \frac{P_0}{P} \frac{T}{T_0}}$

If the conditions are isothermal ( $T = T_0$ ) and isobaric ( $P = P_0$ ):

$$C_A = C_{A0} \frac{(1-X)}{(1+\epsilon X)}$$

And if the feed is equal molar, then:

$$\epsilon = y_{A0}\delta = 0.5 \left( \frac{1}{2} - \frac{1}{2} - 1 \right) = -0.5$$

■ This leaves us with  $C_A$  as a function of conversion alone:

$$C_A = C_{A0} \frac{(1-X)}{(1-0.5X)}$$

■ Similarly for  $C_B$ :

$$C_B = C_{A0} \frac{\left( \Theta_B - \frac{1}{2}X \right)}{(1+\epsilon X)} = C_{A0} \frac{(1-0.5X)}{(1-0.5X)} = C_{A0}$$

[Why do you suppose  $C_B$  is a constant, when B is being consumed?]

$$C_{A0} = \frac{y_{A0}P_0}{RT_0} = \frac{(0.5)(16.4 \text{ atm})}{\left( \frac{0.082 \text{ atm} \cdot \text{m}^3}{\text{kmol} \cdot \text{K}} \right) (500 \text{ K})} = 0.2 \frac{\text{kmol}}{\text{m}^3} = 0.2 \frac{\text{mol}}{\text{dm}^3}$$

**Combine**

$$-r_A = kC_A^2C_B = kC_{A0}^3 \frac{(1-X)^2}{(1-0.5X)^2}$$

$$-r_A = \left(10 \frac{\text{dm}^6}{\text{mol}^2 \cdot \text{s}}\right) \left(0.2 \frac{\text{mol}}{\text{dm}^3}\right)^3 \frac{(1-X)^2}{(1-0.5X)^2}$$

$$-r_A = \left(0.08 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}\right) \frac{(1-X)^2}{(1-0.5X)^2}$$

**Evaluate**

$$V = \frac{F_{A0}X}{-r_A} = \frac{(5 \text{ mol/s})(0.9)[1-0.5(0.9)]^2}{\left(0.08 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}\right)(1-0.9)^2}$$

V = 1701 dm<sup>3</sup>

**Example:** The elementary liquid phase reaction

$$2A \rightarrow B$$

is carried out isothermally in a CSTR. Pure A enters at a volumetric flow rate of 25 dm<sup>3</sup>/s and at a concentration of 0.2 mol/dm<sup>3</sup>. What CSTR volume is necessary to achieve a 90% conversion when k = 10 dm<sup>3</sup>/(mol\*s)?

**Mole Balance**  $V = \frac{F_{A0}X}{-r_A}$

**Rate Law**  $-r_A = kC_A^2$

**Stoichiometry** liquid phase (v = v<sub>0</sub>)  $F_{A0} = v_0 C_{A0}$   
 $F_A = v C_A = v_0 C_A$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0}$$

$$C_A = C_{A0}(1-X)$$

**Combine**

$$V = \frac{v_0 C_{A0} X}{kC_{A0}^2(1-X)^2} = \frac{v_0 X}{kC_{A0}(1-X)^2}$$

**Evaluate**, at X = 0.9,

$$V = \frac{25 \frac{\text{dm}^3}{\text{s}} (0.90)}{\left(10 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}}\right) \left(0.2 \frac{\text{mol}}{\text{dm}^3}\right) (1-0.9)^2}$$

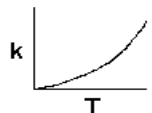
V = 1125 dm<sup>3</sup>

**Space Time**

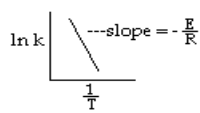
$$\tau = \frac{V}{v_0} = \frac{1125 \text{ dm}^3}{25 \frac{\text{dm}^3}{\text{s}}} = 45 \text{ s}$$

### Arrhenius Equation

1.)  $k = Ae^{-E/RT}$



2.)  $\ln k = \ln A - \frac{E}{R} \left(\frac{1}{T}\right)$



$k(T_2) = k(T_1) \exp \left[ \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right]$

