Chemical Reaction Engineering

Lecture 2

General algorithm of Chemical Reaction Engineering

- Mole balance
- Rate laws
- Stoichiometry
- Energy balance

- Combine and Solve

Classification of reactions

- Phases involved:
  - **Homogeneous** reaction – reaction that occur in one phase
  - **Heterogeneous** reaction – reaction that involves more than one phase and usually occurs at the interface between the phases (e.g. heterogeneous catalysis)
- Equilibrium position
  - **Reversible** reaction – reaction that can proceed in either direction depending on the concentration of reagents and products
  - **Irreversible** reaction – reaction that at given conditions can be assumed to proceed in one direction only (i.e. reaction equilibrium involves much smaller concentration of the reagents)

Elementary reactions

- Kinetics of chemical reactions determined by the elementary reaction steps.
- **Molecularity** of an elementary reaction is the number of molecules coming together to react in one reaction step (e.g. **uni-molecular**, **bimolecular, termolecular**)
- Probability of meeting 3 molecules is very small, so uni-molecular and bimolecular reaction are the only two to consider

Elementary reactions

Uni-molecular: first order in the reactant

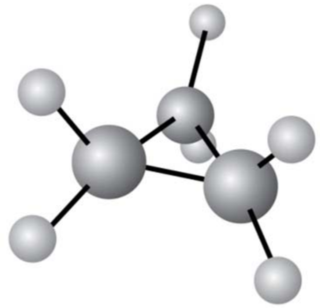
$$A \longrightarrow P \qquad \frac{d[A]}{dt} = -k[A]$$

Bimolecular: first order in the reactant

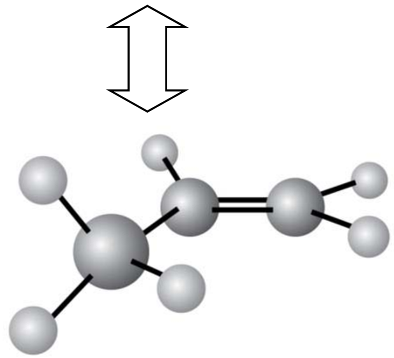
$$A + B \longrightarrow P \quad \frac{d[A]}{dt} = -k[A][B]$$

Proportional to collision rate

$$H + Br_2 \longrightarrow HBr + Br$$



1 Cyclopropane



2 Propene

! rate of disappearance of individual components can be calculated as:

$$v = \frac{1}{\nu_i}\frac{dn_i}{dt} = \frac{d\xi}{dt}$$

Relative Rates of Reaction

$$aA + bB \longrightarrow cC + dD$$

- if we are interested in species A we can use A as the basis of calculation and define the reaction rate with respect to A

$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D \qquad \frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

- Reaction rate is not a constant, it depends
  - on concentration of the reagents
  - on the temperature
  - on the total pressure in the reactions involving gas phase
  - ionic strength and solvent in liquid state
  - presence of a catalyst

$$-r_A = [k_A(T)][fn(C_A, C_B, \ldots)]$$

Rates of Reaction

$$-r_A = [k_A(T)][\,fn(C_A, C_B, \ldots)]$$

Arrhenius law

$$\boxed{k(T) = Ae^{-E/RT}}$$

algebraic function of concentrations

$$C_A{}^{\alpha} \cdot C_B{}^{\beta} \cdot \ldots$$

- reaction order: $n = \alpha + \beta + \ldots$
- reaction rate is found experimentally, data on frequency factor (A), activation energy (E) and the order of the reaction can be found in relevant handbooks.
- units of the reaction rate constant

$$[k] = \frac{(Concentration)^{1-n}}{time}$$

Non-Elementary Reaction rates

- The reaction rate dependence on the concentration and temperature will become more complicated when a reaction comprising **several elementary steps** is considered (incl. catalytic and reversible reactions)

Reversible reaction

- Let's consider a reaction of diphenyl formation

$$\underset{B}{2C_6H_6} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{D}{C_{12}H_{10}} + H_2$$

- rate of change for benzene

$$\frac{d[C_6H_6]}{dt} = r_B = -2k_1C_B{}^2 + 2k_{-1}C_DC_{H_2}$$

Equilibrium constant

$$\frac{d[C_6H_6]}{dt} = r_B = -2k_1 C_B{}^2 + 2k_{-1} C_D C_{H_2}$$

- noticing that the equilibrium constant: $K_C = k_1 / k_{-1}$

in terms of concentration

$$-r_B = 2k_1 \left(C_B{}^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

- reaction rates in terms of other reagents:

$$\frac{r_D}{1} = \frac{-r_B}{2} = k_1 \left(C_B{}^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

Few more facts of K

- From thermodynamics $$RT\ln K = -\Delta_r G^\theta$$

- for gases, K can be defined in terms of pressures or concentrations

$$K_p = \frac{p_C^{c/a}\, p_D^{d/a}}{p_A p_B^{b/a}} \qquad K_C = \frac{C_C^{c/a} C_D^{d/a}}{C_A C_B^{b/a}} = K_p (RT)^{-\delta}; \delta = \frac{c}{a} + \frac{d}{a} - \frac{b}{a} - 1$$

- temperature dependence:

$$\frac{d\ln K}{dT} = \frac{\Delta_r H(T)}{RT^2} \qquad \frac{d\ln K}{dT} = \frac{\Delta_r H^\theta(T_R) + \Delta c_p (T - T_R)}{RT^2}$$

$$K_p(T) = K_p(T_1)\exp\left[\frac{\Delta_r H^\theta(T)}{RT^2}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

Reaction rate

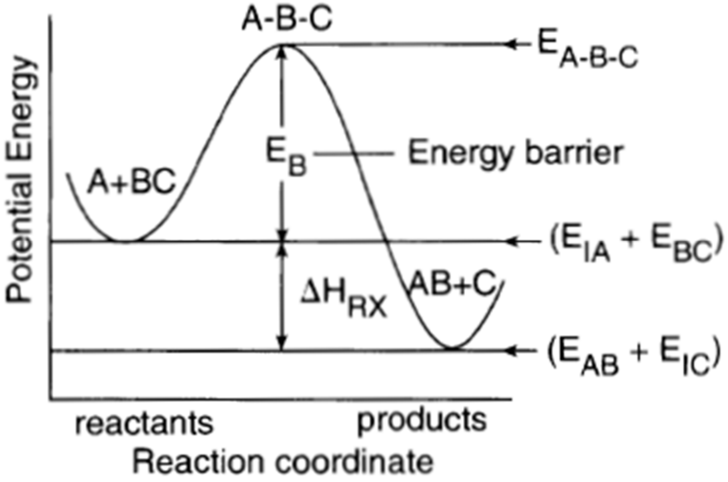
- Below, we will consider only the concentration and temperature dependence of the reaction rate

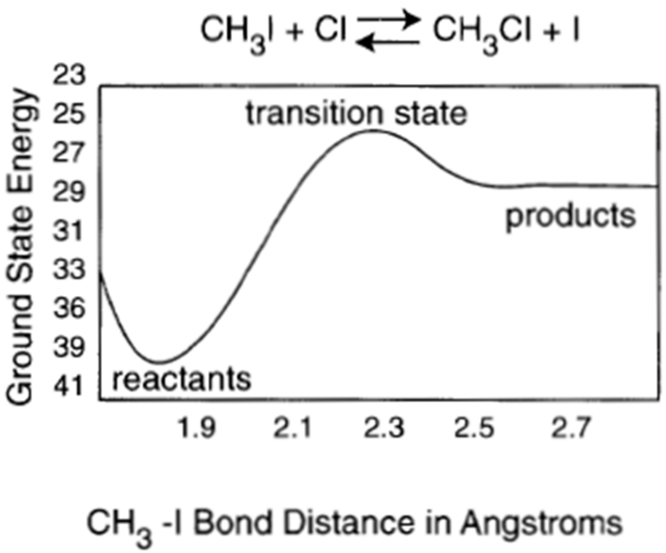
Dependence on the concentration can be calculated knowing reaction mechanism, as before

$$\frac{d[C_6H_6]}{dt} = r_B = -2k_1\left[C_B{}^2 + \frac{C_D C_{H_2}}{K_C}\right]$$

Temperature dependence:
Arrhenius equation

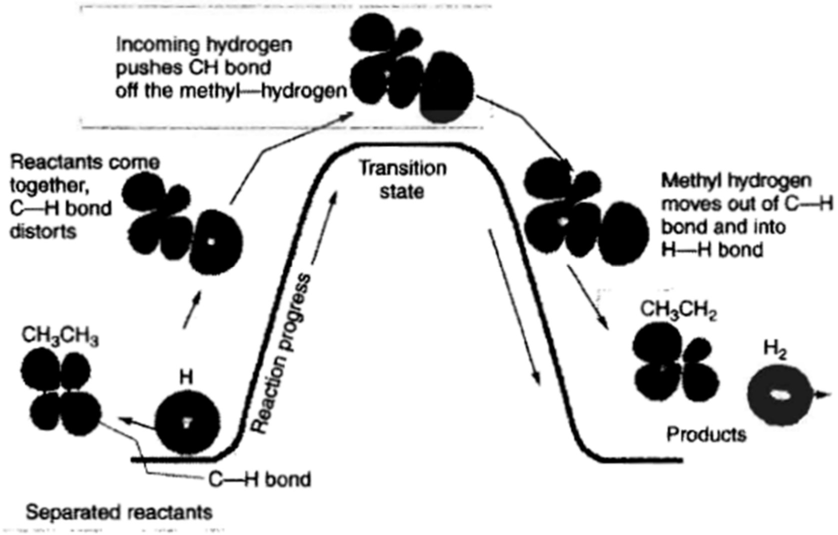
$$\boxed{k(T) = Ae^{-E/RT}}$$

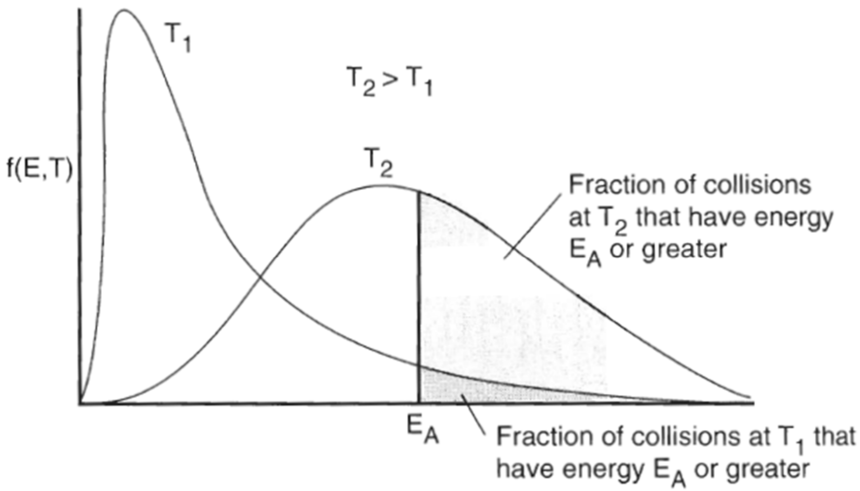




Reaction rate

- From the **collision theory**, only molecules with the energy higher than the activation energy can react:





- The usual “rule of thumb that the reaction rate doubles with every 10ºC is not always true:

$$k(T_1)/k(T_2) = e^{-E/R\cdot\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

Summary of the Reactor design equations

In the previous lecture we found design equations for various reactors:

	Differential Form	*Algebraic Form*	*Integral Form*
Batch	$N_{A0}\frac{dX}{dt} = -r_A V$		$t = N_{A0}\int_0^X \frac{dX}{-r_A V}$
CSTR		$V = \frac{F_{A0}(X_{out} - X_{in})}{(-r_A)_{out}}$	
PFR	$F_{A0}\frac{dX}{dV} = -r_A$		$V = F_{A0}\int_{X_{in}}^{X_{out}} \frac{dX}{-r_A}$
PBR	$F_{A0}\frac{dX}{dW} = -r'_A$		$W = F_{A0}\int_{X_{in}}^{X_{out}} \frac{dX}{-r'_A}$

To solve them we need to find disappearence rate as a function of conversion:

$$-r_A = g(X)$$

Relative Rates of Reaction

$$aA + bB \longrightarrow cC + dD$$

- if we are interested in species A we can define A as the basis of calculation

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

- conversion: $$X_A = \frac{\text{Moles of A reacted}}{\text{Moles of A fed}}$$

- Let's see how we can relate it to the reaction rate for various types of reactors.

Batch reactor

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

- conversion: $X_A = \dfrac{\text{Moles of A reacted}}{\text{Moles of A fed}}$

- number of moles A left after conversion:

$$N_A = N_{A0} - N_{A0}X = N_{A0}\left(1 - X\right)$$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}\left(1 - X\right)}{V}$$

- number of moles B left after conversion:

$$N_B = N_{B0} - N_{A0}\frac{b}{a}X$$

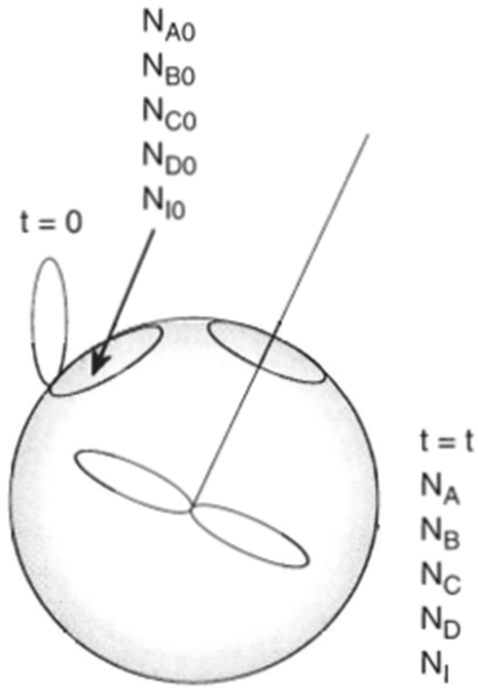
$$C_B = \frac{N_B}{V} = \frac{N_{B0} - \left(b/a\right)N_{A0}X}{V} = \frac{N_{A0}\left(\Theta_B - \left(b/a\right)X\right)}{V}$$

Batch reactors

- For every component in the reactor we can write after conversion X is achieved:

TABLE 3-3. STOICHIOMETRIC TABLE FOR A BATCH SYSTEM

Species	*Initially* (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}	—	$N_I = N_{I0}$
Totals	N_{T0}		$N_T = N_{T0} + \underbrace{\left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)}_{\delta} N_{A0}X$



δ - the total molar increase per mole of A reacted $N_T = N_{T0} + \delta \cdot N_{A0} \cdot X$

Batch reactor

- Now, if we know the **number of moles of every component** we can calculate **concentration** as a function of conversion.

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V}$$

$$C_B = \frac{N_B}{V} = \frac{N_{B0} - b/a\, N_{A0} X}{V} = \frac{N_{A0}(\Theta_B - (b/a)X)}{V}$$

$$C_C = \frac{N_C}{V} = \frac{N_{A0}(\Theta_C + (c/a)X)}{V}$$

$$C_D = \frac{N_D}{V} = \frac{N_{A0}(\Theta_D + (d/a)X)}{V}$$

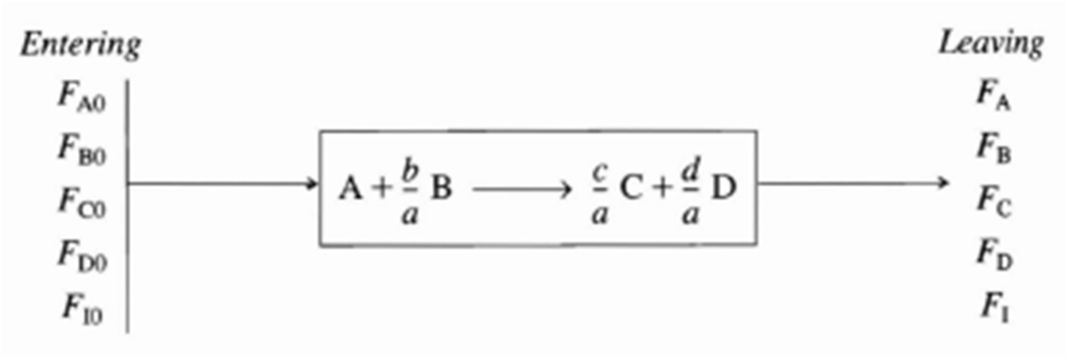
- However, generally V can be a function of X as well...
- In a constant volume reactor (e.g. batch reactor, liquid reactor):

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

$$C_B = C_{A0}(\Theta_B - (b/a)X), \quad \text{etc.}$$

Flow reactors

- Equations for flow reactors are the same with number of moles ***N*** changed for flow rate ***F*** [mol/s].



Flow reactors

- Stoichiometric table for a flow system

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

Flow reactors

- For a flow system a concentration at any point can be obtained from molar flow rate F and volumetric flow rate

$$C_A = \frac{F_A}{v} = \frac{moles/time}{liter/time}$$

- For reaction in liquids, the volume change is negligible (if no phase change occurred):

$$C_A = \frac{F_A}{v} = C_{A0}\left(1 - X\right) \qquad C_B = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

Reactions involving volume change

- In a gas phase reaction a molar flow rate might change as the reaction progresses

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

4 moles **2 moles**

- In a gas phase reaction a molar flow rate might change as the reaction progresses

Batch reactor with variable volume

- As such it would be a rare case (e.g. internal combustion engine), but a good model case:

$$PV = ZN_T RT$$

compressibility factor

- If we divide the gas equation at any moment in time by the one at moment zero:

$$V = V_0 \left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)\left(\frac{Z}{Z_0}\right)\left(\frac{N_T}{N_{T0}}\right)$$

$$\left(\frac{N_T}{N_{T0}}\right) = 1 + \left(\frac{N_{A0}}{N_{T0}}\right)\delta \cdot X = 1 + \varepsilon X$$

$$V = V_0 \left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)(1 + \varepsilon X)$$

function V=g(X)

Flow reactor with variable flow rate

- Using the gas equation we can derive the total concentration as:

total concentration: $C_T = \frac{F_T}{v} = \frac{P}{ZRT}$ at the entrance: $C_{T0} = \frac{F_{T0}}{v} = \frac{P_0}{Z_0 R T_0}$

total volume rate: $v = v_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{Z}{Z_0} \frac{T}{T_0}$

$$C_j = \frac{F_j}{v} = F_j \Big/ \left(v_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{Z}{Z_0} \frac{T}{T_0} \right) = C_{T0} \frac{F_j}{F_T} \frac{P}{P_0} \underbrace{\frac{Z_0}{Z}}_{=1} \frac{T_0}{T}$$

Flow reactor with variable flow rate

- In a gas phase reaction a molar flow rate might change as the reaction progresses

$$v = v_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{Z}{Z_0} \frac{T}{T_0}$$

$$F_T = F_T + F_{A0} \cdot \delta \cdot X$$

$$\Rightarrow$$

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

$$C_j = \frac{F_{A0}\left(\Theta_j + \nu_j X\right)}{v_0 \left(1 + \varepsilon X\right) \frac{P_0}{P} \frac{T}{T_0}}$$

Example 3.6 (p.118)

$$N_2O_4 \rightleftarrows 2NO_2$$

- For reaction above calculate
  - equilibrium conversion in a constant batch reactor;
  - equilibrium conversion in a flow reactor;
  - assuming the reaction is elementary, express the rate of the reaction
  - plot Levenspil plot and determine CSTR volume for 80% conversion
- assume the feed is pure N_2O_4 at 340K and 202.6kPa. Concentration equilibrium constant: K_C=0.1mol/l; k_A=0.5 min^{-1}.

Example

1. Batch reactor

TABLE E3-6.1. STOICHIOMETRIC TABLE

Species	Symbol	Initial	Change	Remaining
N_2O_4	A	N_{A0}	$-N_{A0}X$	$N_A = N_{A0}(1-X)$
NO_2	B	0	$+2N_{A0}X$	$N_B = 2N_{A0}X$
		$N_{T0} = N_{A0}$		$N_T = N_{T0} + N_{A0}X$

equilibrium conversion:

$$K_C = \frac{C_{Be}^2}{C_{Ae}} = \frac{4C_{A0}^2 X_e^2}{C_{A0}(1-X_e)} = \frac{4C_{A0}X_e^2}{1-X_e}$$

$$C_{A0} = \frac{y_{A0}P_0}{RT_0} = 0.071\text{mol/dm}^3.$$

$$\boxed{X_e = 0.44}$$

Example

2. Flow reactor

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

$$C_B = \frac{C_{A0}X}{1+\varepsilon X}$$

$$K_C = \frac{C_{Be}^{\ 2}}{C_{Ae}} = \frac{4C_{A0}^{\ 2}X_e^{\ 2}}{C_{A0}\left(1-X_e\right)} = \frac{4C_{A0}X_e^{\ 2}}{\left(1-X_e\right)\left(1+\varepsilon X_e\right)}$$

$$C_{A0} = \frac{y_{A0}P_0}{RT_0} = 0.071\,\mathrm{mol/dm^3}.$$

$$\boxed{X_e = 0.51}$$

Example

3. Rate laws

$$-r_A = k_A\left[C_A - \frac{C_B{}^2}{K_C}\right]$$

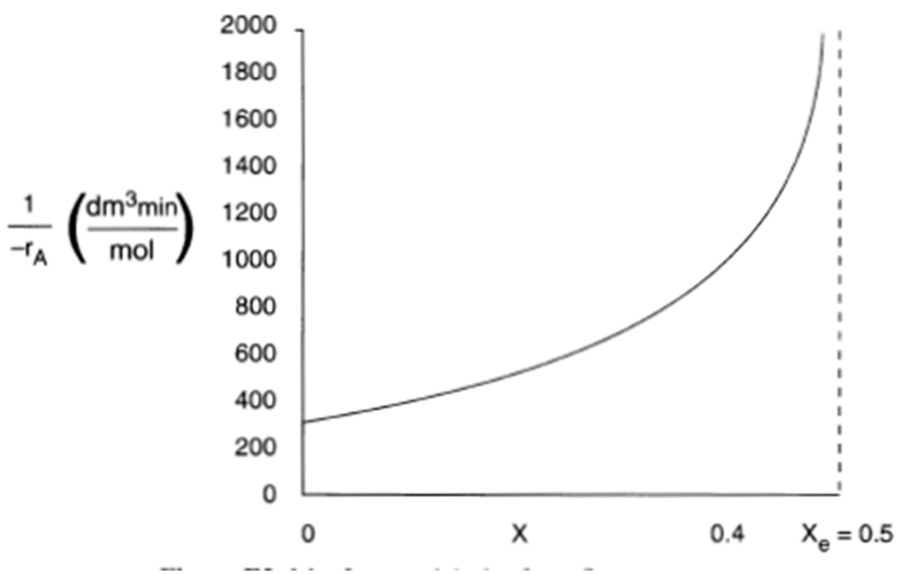
– Constant volume

$$-r_A = k_A\left[C_{A0}\left(1-X\right) - \frac{4C_{A0}{}^2X^2}{K_C}\right]$$

– Flow

$$-r_A = k_A\left[\frac{C_{A0}\left(1-X\right)}{1+\varepsilon X} - \frac{4C_{A0}{}^2X^2}{K_C\left(1+\varepsilon X\right)^2}\right]$$

– Levenspiel plot



Example

4. CSTR volume for X=0.4, feed of 3 mol/min

$$-r_A = k_A \left[C_{A0}\left(1 - X\right) - \frac{4C_{A0}{}^2 X^2}{K_C} \right]$$

– Constant volume

$$-r_A \big|_{X=0.4} = 7 \cdot 10^{-4}$$

$$V = \frac{F_{A0} X}{-r_A \big|_X} = 1714\,\mathrm{dm}^3$$

– PFR – in the next lecture ☺

Problems

- Class: P3-15
- Home: P3-7, P3-13