Lecture 4

Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Lecture 4 – Tuesday

- Block 1
  - **Mole Balances**
  - Size CSTRs and PFRs given $-r_A = f(X)$
- Block 2
  - **Rate Laws**
  - Reaction Orders
  - Arrhenius Equation
- Block 3
  - **Stoichiometry**
  - Stoichiometric Table
  - Definitions of Concentration
  - Calculate the Equilibrium Conversion, X_e

Reactor Mole Balances Summary
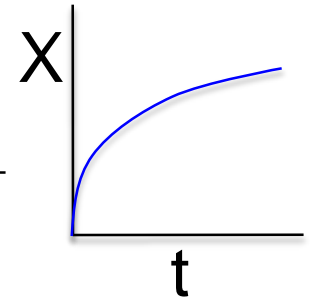
in terms of conversion, X

Reactor	Differential	Algebraic	Integral
Batch	$N_{A0}\dfrac{dX}{dt} = -r_A V$		$t = N_{A0}\displaystyle\int_0^X \dfrac{dX}{-r_A V}$
CSTR		$V = \dfrac{F_{A0}X}{-r_A}$	
PFR	$F_{A0}\dfrac{dX}{dV} = -r_A$		$V = F_{A0}\displaystyle\int_0^X \dfrac{dX}{-r_A}$
PBR	$F_{A0}\dfrac{dX}{dW} = -r_A'$		$W = F_{A0}\displaystyle\int_0^X \dfrac{dX}{-r_A'}$

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Levenspiel Plots

PFR

$$\frac{F_{A0}}{-r_A}$$

Area = Volume of PFR

$$V = \int_0^{X_1} \left(\frac{F_{A0}}{-r_A} \right) dX$$

X_1
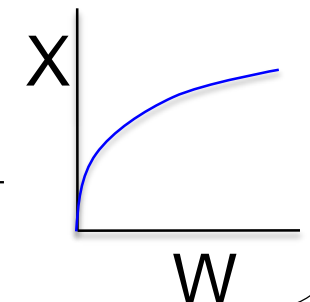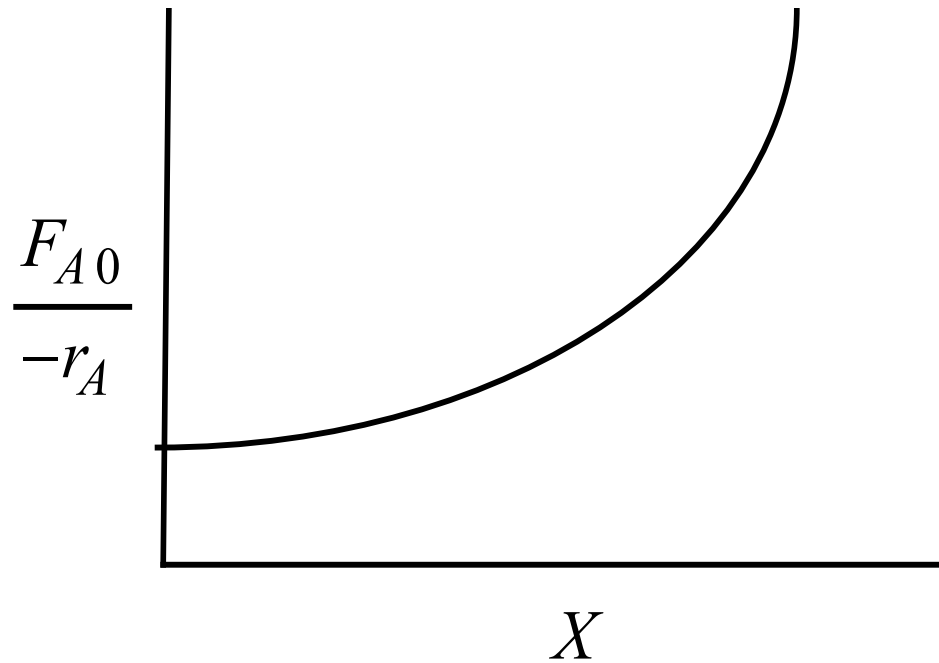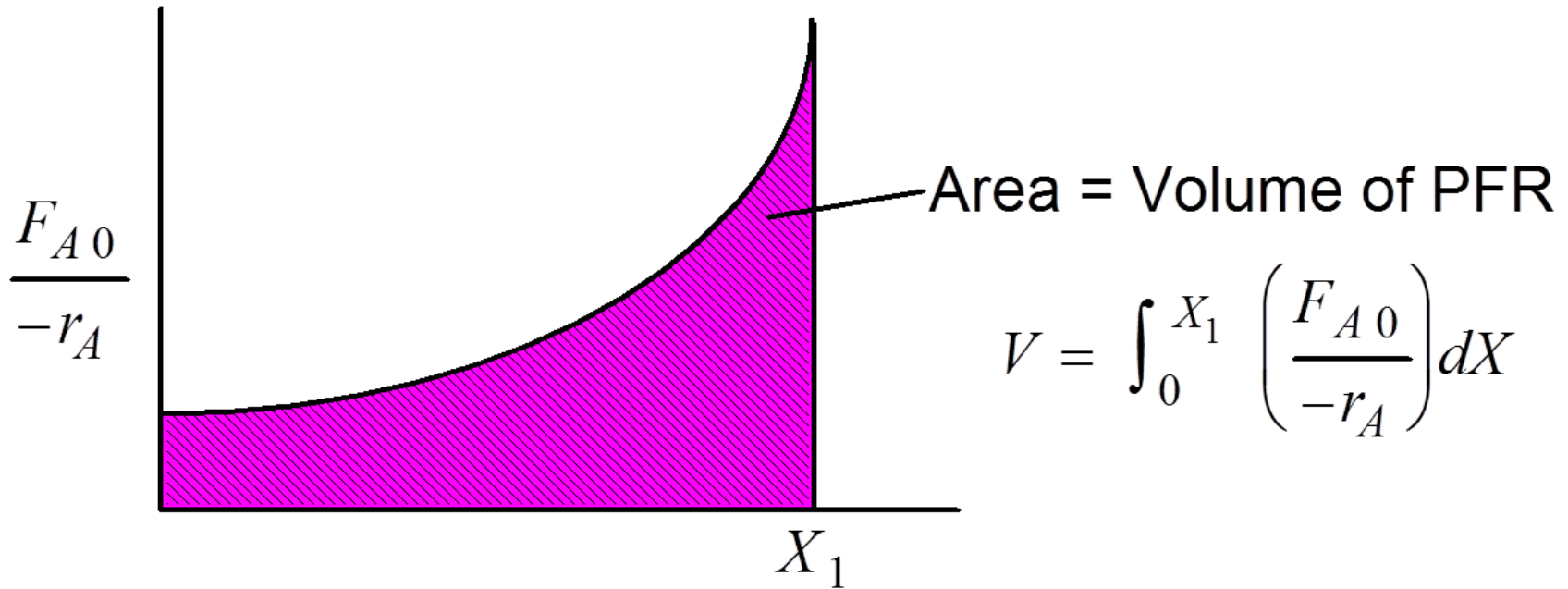
Reactors in Series

$X_1 = 0.2$

$X_2 = 0.6$

$X_3 = 0.65$
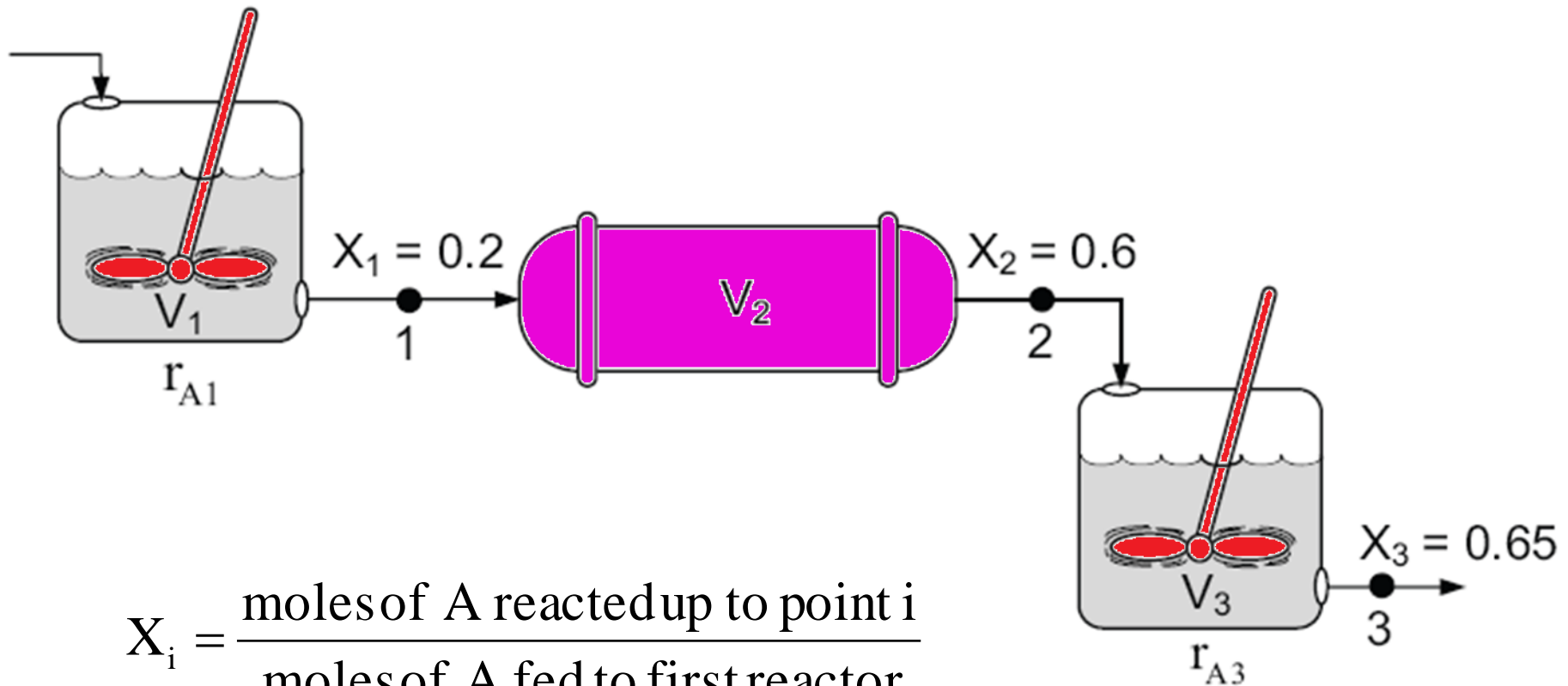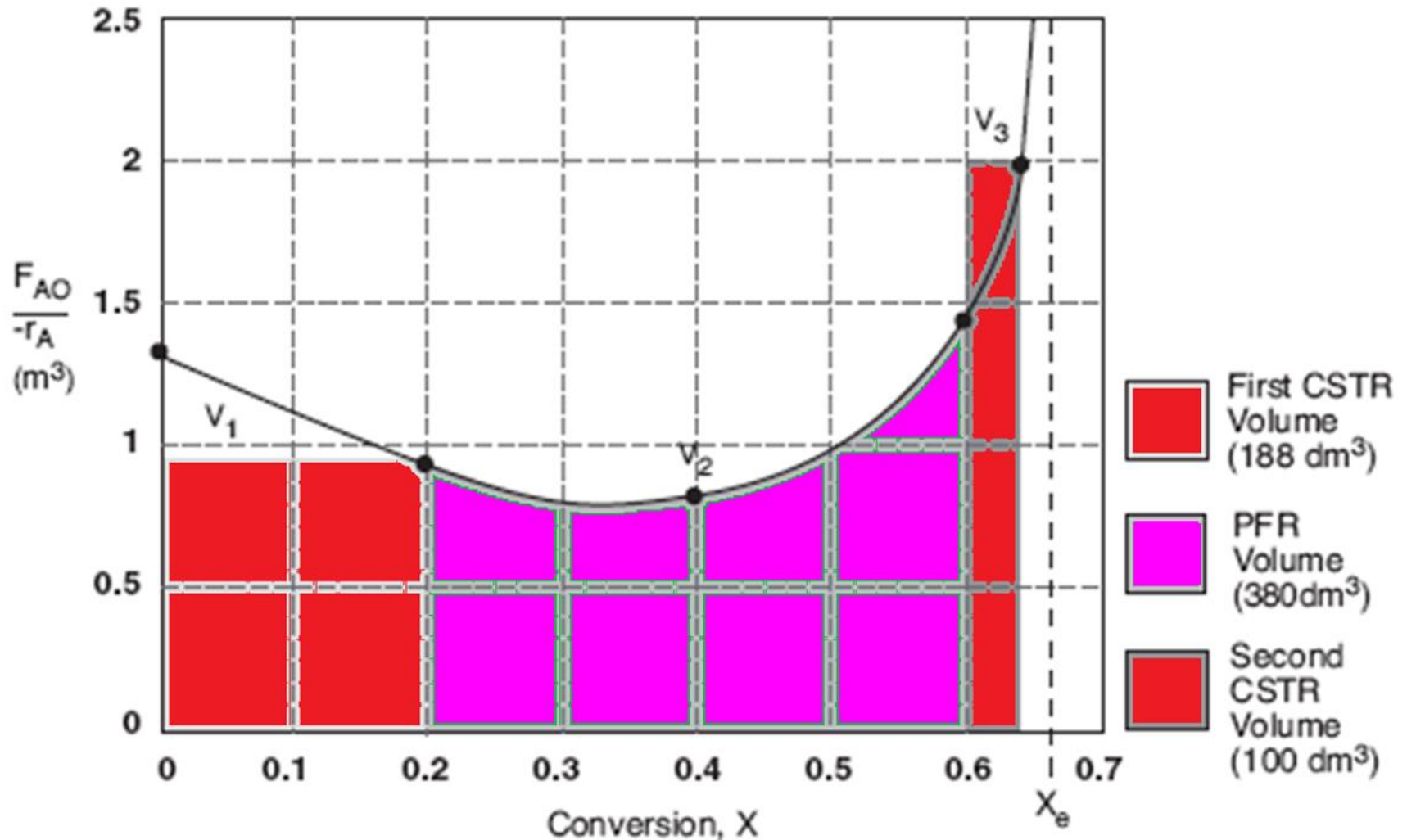
$$X_i = \frac{\text{moles of A reacted up to point i}}{\text{moles of A fed to first reactor}}$$
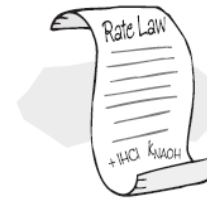
Only valid if there are no side streams

Reactors in Series

Two steps to get $-r_A = f(X)$

Step 1: Rate Law $-r_A = g(C_i)$

Step 2: Stoichiometry $(C_i) = h(X)$

Step 3: Combine to get $-r_A = f(X)$

Building Block 2: Rate Laws

Power Law Model:

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

α order in A

β order in B

Overall Rection Order $= \alpha + \beta$

$$2A + B \rightarrow 3C$$

A reactor follows an elementary rate law if the reaction orders just happens to agree with the stoichiometric coefficients for the reaction as written.

e.g. If the above reaction follows an elementary rate law

$$-r_A = k_A C_A^2 C_B$$

2nd order in A, 1st order in B, overall third order

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Arrhenius Equation

$$k = Ae^{-E/RT}$$

$T \to \infty \quad k \to A$

$T \to 0 \quad k \to 0$

$A \approx 10^{13}$

E = Activation energy (cal/mol)

R = Gas constant (cal/mol*K)

T = Temperature (K)

A = Frequency factor (same units as rate constant k)

(units of A, and k, depend on overall reaction order)

$$\ln k_{\mathrm{A}} = \ln A - \frac{E}{R}\left(\frac{1}{T}\right)$$

Semilog Plot

High E

Low E

Slope = $-\dfrac{E}{R}$

$\left(\dfrac{1}{T}\right)$ (K⁻¹)

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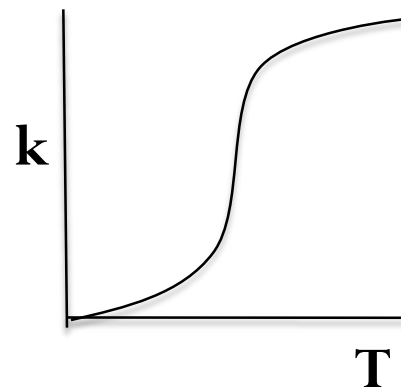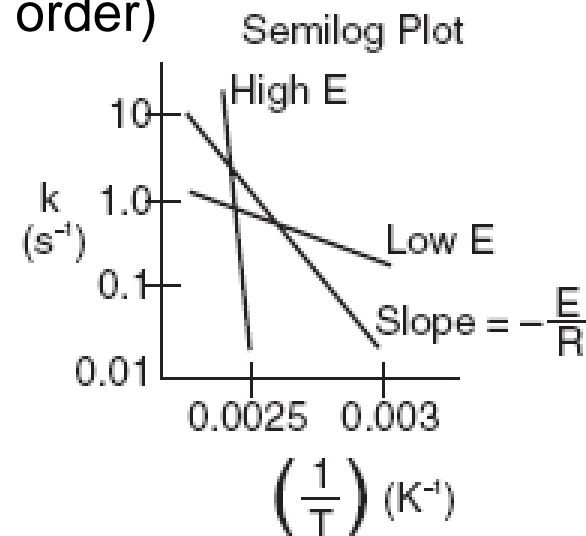
Reaction Engineering

Mole Balance

Rate Laws

Stoichiometry

These topics build upon one another

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Algorithm

How to find $-r_A = f(X)$

Step 1: Rate Law $\quad -r_A = g\left(C_i\right)$

Step 2: Stoichiometry $\quad \left(C_i\right) = h\left(X\right)$

Step 3: Combine to get $\quad -r_A = f\left(X\right)$

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Building Block 3: Stoichiometry

We shall set up Stoichiometry Tables using species A as our basis of calculation in the following reaction. We will use the stoichiometric tables to express the concentration as a function of conversion. We will combine C_i = f(X) with the appropriate rate law to obtain $-r_A$ = f(X).

$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D$$
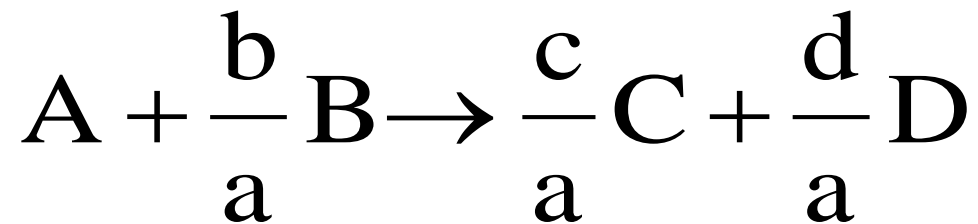
A is the limiting reactant.

Stoichiometry

$$N_A = N_{A0} - N_{A0}X$$

For every mole of A that reacts, **b/a** moles of B react. Therefore moles of B remaining:

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

Let $\Theta_B = N_{B0}/N_{A0}$

Then:

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

$$N_C = N_{C0} + \frac{c}{a}N_{A0}X = N_{A0}\left(\Theta_C + \frac{c}{a}X\right)$$

Batch System - Stoichiometry Table

Species	Symbol	Initial	Change	Remaining
A	A	N_{A0}	$-N_{A0}X$	$N_A = N_{A0}(1-X)$
B	B	$N_{B0} = N_{A0}\Theta_B$	$-b/aN_{A0}X$	$N_B = N_{A0}(\Theta_B - b/aX)$
C	C	$N_{C0} = N_{A0}\Theta_C$	$+c/aN_{A0}X$	$N_C = N_{A0}(\Theta_C + c/aX)$
D	D	$N_{D0} = N_{A0}\Theta_D$	$+d/aN_{A0}X$	$N_D = N_{A0}(\Theta_D + d/aX)$
Inert	I	$N_{I0} = N_{A0}\Theta_I$	----------	$N_I = N_{A0}\Theta_I$
		F_{T0}		$N_T = N_{T0} + \delta N_{A0}X$

Where: $\Theta_i = \dfrac{N_{i0}}{N_{A0}} = \dfrac{C_{i0}\upsilon_0}{C_{A0}\upsilon_0} = \dfrac{C_{i0}}{C_{A0}} = \dfrac{y_{i0}}{y_{A0}}$ and $\delta = \dfrac{d}{a} + \dfrac{c}{a} - \dfrac{b}{a} - 1$

δ = change in total number of mol per mol A reacted

Stoichiometry Constant Volume Batch

Note: **If** the reaction occurs in the liquid phase

or

if a gas phase reaction occurs in a rigid (e.g. steel) batch reactor

Then $V = V_0$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)$$

$$C_B = \frac{N_B}{V} = \frac{N_{A0}}{V_0}\left(\Theta_B - \frac{b}{a}X\right) = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

etc.

Stoichiometry Constant Volume Batch

Suppose $-r_A = k_A C_A^2 C_B$

Batch: $V = V_0$

$$-r_A = k_A C_{A0}{}^2 (1-X)^2 \left(\Theta_B - \frac{b}{a} X \right)$$

Equimolar feed: $\Theta_B = 1$

Stoichiometric feed: $\Theta_B = \dfrac{b}{a}$

Stoichiometry Constant Volume Batch

If $-r_A = k_A C_A^2 C_B$, then

$$-r_A = C_{A0}{}^3 (1-X)^2 \left(\Theta_B - \frac{b}{a} X \right)$$ Constant Volume Batch

and we have $-r_A = f(X)$
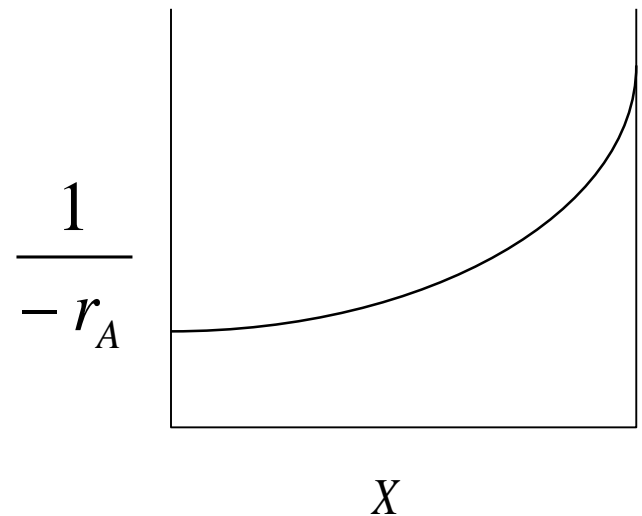
Batch Reactor - Example

Calculate the equilibrium conversion for gas phase reaction, X_e .

Consider the following elementary reaction with K_C=20 dm^3/mol and C_{A0}=0.2 mol/dm^3.
Find X_e for both a batch reactor and a flow reactor.

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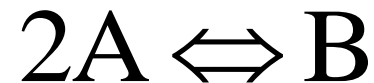
$$-r_A = k_A \left[C_A{}^2 - \frac{C_B}{K_C} \right]$$

Batch Reactor - Example

Calculate X_e

$$C_{A0} = 0.2 \, mol/dm^3$$

$$K_C = 20 \, dm^3/mol$$

Step 1: $\dfrac{dX}{dt} = \dfrac{-r_A V}{N_{A0}}$

Step 2: rate law: $\quad -r_A = k_A C_A^2 - k_B C_B$

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

$$K_C = \frac{k_A}{k_B}$$

Batch Reactor - Example

Symbol	Initial	Change	Remaining
A	N_{A0}	$-N_{A0}X$	$N_{A0}(1-X)$
B	0	$\frac{1}{2} N_{A0}X$	$N_{A0} X/2$

Totals: $N_{T0}=N_{A0}$ $N_T=N_{A0} -N_{A0} X/2$

@ equilibrium: $-r_A=0$

$$0 = C_{Ae}^2 - \frac{C_{Be}}{K_C}$$

$$K_e = \frac{C_{Be}}{C_{Ae}^2}$$

$$C_{Ae} = \frac{N_{Ae}}{V} = C_{A0}\left(1 - X_e\right)$$

$$C_{Be} = C_{A0}\frac{X_e}{2}$$

Batch Reactor - Example

Solution:

At equilibrium $\quad -r_A = 0 = k_A\left[C_{Ae}^{\,2} - \dfrac{C_{Be}}{K_C}\right]$ $\qquad K_C = \dfrac{C_{Be}}{C_{Ae}^2}$

Stoichiometry: $\qquad A \longrightarrow B/2$

Constant Volume: $\qquad V = V_o$

Batch

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

Batch Reactor - Example

$$K_e = \frac{C_{A0} \dfrac{X_e}{2}}{\left[C_{A0}\left(1 - X_e\right)\right]^2} = \frac{X_e}{2C_{A0}\left(1 - X_e\right)^2}$$

$$2K_e C_{A0} = \frac{X_e}{\left(1 - X_e\right)^2} = 2(20)(0.2) = 8$$

$$X_{eb} = 0.703$$

Flow System – Stoichiometry Table
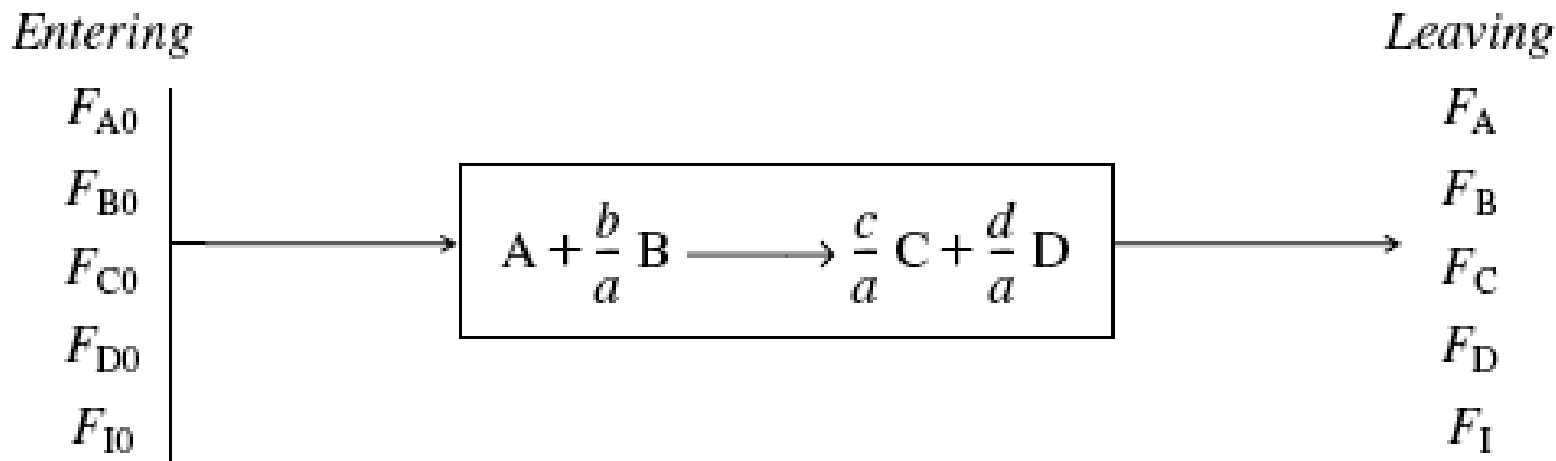
Entering | | Leaving

F_{A0} $\qquad\qquad\qquad\qquad$ F_A

F_{B0} $\qquad\qquad\qquad\qquad$ F_B

F_{C0} $\qquad A + \dfrac{b}{a}B \longrightarrow \dfrac{c}{a}C + \dfrac{d}{a}D \qquad$ F_C

F_{D0} $\qquad\qquad\qquad\qquad$ F_D

F_{I0} $\qquad\qquad\qquad\qquad$ F_I

Species	**Symbol**	**Reactor Feed**	**Change**	**Reactor Effluent**
A	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	B	$F_{B0} = F_{A0}\Theta_B$	$-b/aF_{A0}X$	$F_B = F_{A0}(\Theta_B - b/aX)$

Where: $\quad \Theta_i = \dfrac{F_{i0}}{F_{A0}} = \dfrac{C_{i0}\upsilon_0}{C_{A0}\upsilon_0} = \dfrac{C_{i0}}{C_{A0}} = \dfrac{y_{i0}}{y_{A0}}$

Flow System – Stoichiometry Table

Species	Symbol	Reactor Feed	Change	Reactor Effluent
C	C	$F_{C0}=F_{A0}\Theta_C$	$+c/aF_{A0}X$	$F_C=F_{A0}(\Theta_C+c/aX)$
D	D	$F_{D0}=F_{A0}\Theta_D$	$+d/aF_{A0}X$	$F_D=F_{A0}(\Theta_D+d/aX)$
Inert	I	$F_{I0}={}_{A0}\Theta_I$	----------	$F_I=F_{A0}\Theta_I$
		F_{T0}		$F_T=F_{T0}+\delta F_{A0}X$

Where: $\quad \Theta_i = \dfrac{F_{i0}}{F_{A0}} = \dfrac{C_{i0}\upsilon_0}{C_{A0}\upsilon_0} = \dfrac{C_{i0}}{C_{A0}} = \dfrac{y_{i0}}{y_{A0}} \quad$ and $\quad \delta = \dfrac{d}{a} + \dfrac{c}{a} - \dfrac{b}{a} - 1$

Concentration – Flow System $\quad C_A = \dfrac{F_A}{\upsilon}$

Flow System – Stoichiometry Table

Species	Symbol	Reactor Feed	Change	Reactor Effluent
A	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	B	$F_{B0} = F_{A0}\Theta_B$	$-b/aF_{A0}X$	$F_B = F_{A0}(\Theta_B - b/aX)$
C	C	$F_{C0} = F_{A0}\Theta_C$	$+c/aF_{A0}X$	$F_C = F_{A0}(\Theta_C + c/aX)$
D	D	$F_{D0} = F_{A0}\Theta_D$	$+d/aF_{A0}X$	$F_D = F_{A0}(\Theta_D + d/aX)$
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: $\Theta_i = \dfrac{F_{i0}}{F_{A0}} = \dfrac{C_{i0}\upsilon_0}{C_{A0}\upsilon_0} = \dfrac{C_{i0}}{C_{A0}} = \dfrac{y_{i0}}{y_{A0}}$ and $\delta = \dfrac{d}{a} + \dfrac{c}{a} - \dfrac{b}{a} - 1$

Concentration – Flow System $C_A = \dfrac{F_A}{\upsilon}$

Stoichiometry

Concentration Flow System: $\quad C_A = \dfrac{F_A}{\upsilon}$
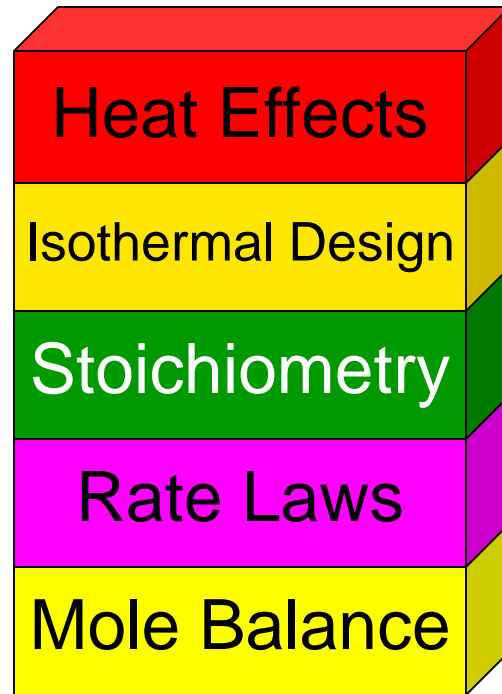
Liquid Phase Flow System: $\quad \upsilon = \upsilon_0$

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0} = C_{A0}(1-X) \quad \text{Flow Liquid Phase}$$

$$C_B = \frac{N_B}{\upsilon} = \frac{N_{A0}}{\upsilon_0}\left(\Theta_B - \frac{b}{a}X\right) = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

etc.

We will consider C_A and C_B for gas phase reactions in the next lecture

End of Lecture 4