

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 1/22/2013

- 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

Review Lecture 2

Reactor Mole Balances Summary

in terms of conversion, X

Reactor

Differential

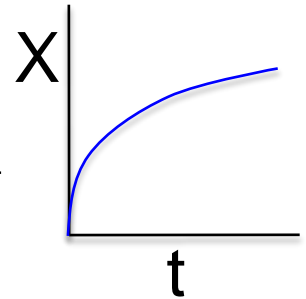
Algebraic

Integral

Batch

$$N_{A0} \frac{dX}{dt} = -r_A V$$

$$t = N_{A0} \int_0^X \frac{dX}{-r_A V}$$



CSTR

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

PFR

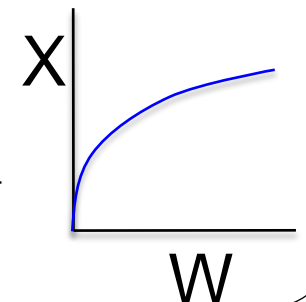
$$F_{A0} \frac{dX}{dV} = -r_A$$

$$V = F_{A0} \int_0^X \frac{dX}{-r_A}$$

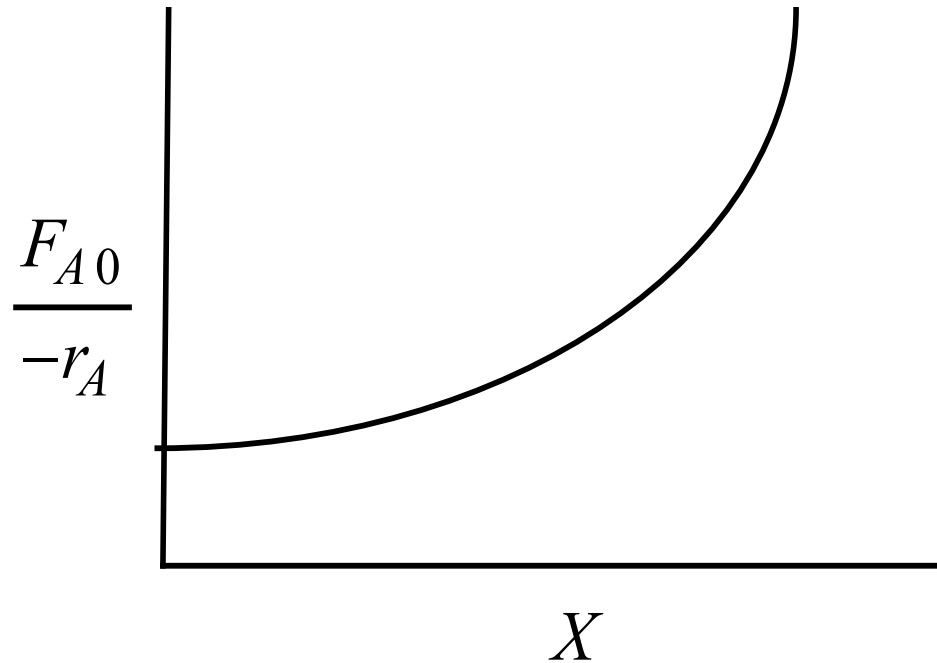
PBR

$$F_{A0} \frac{dX}{dW} = -r'_A$$

$$W = F_{A0} \int_0^X \frac{dX}{-r'_A}$$

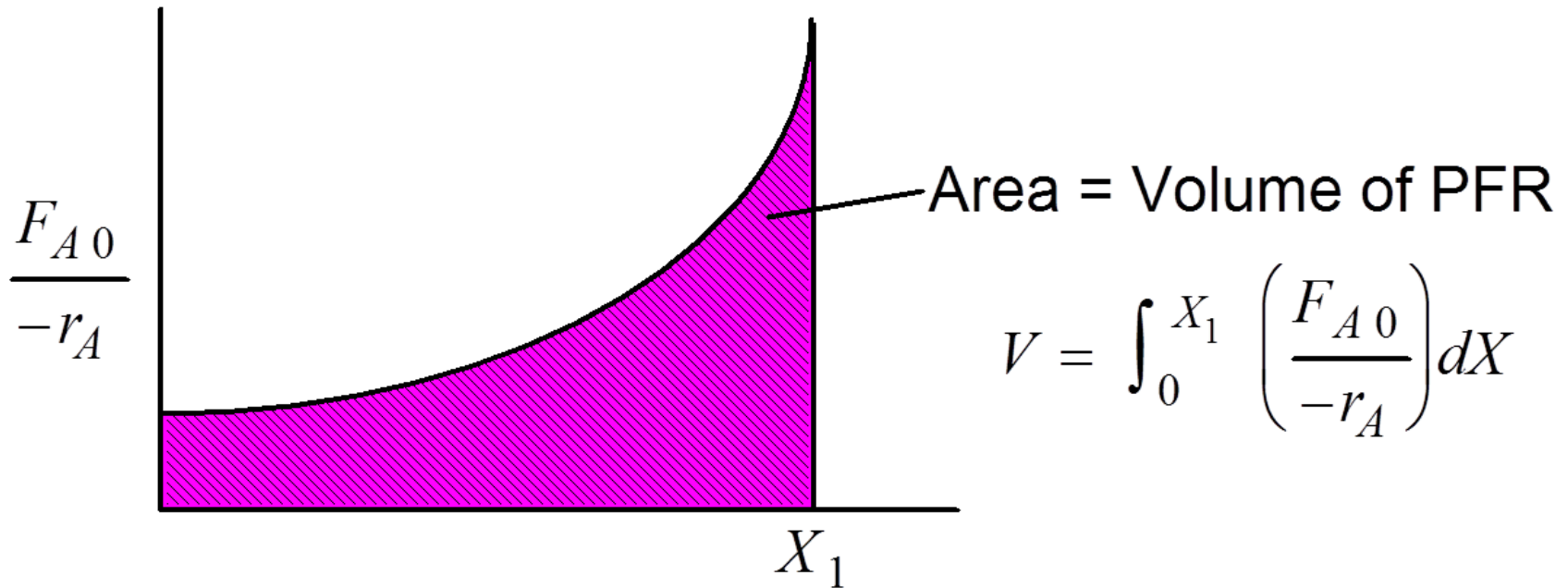


Levenspiel Plots

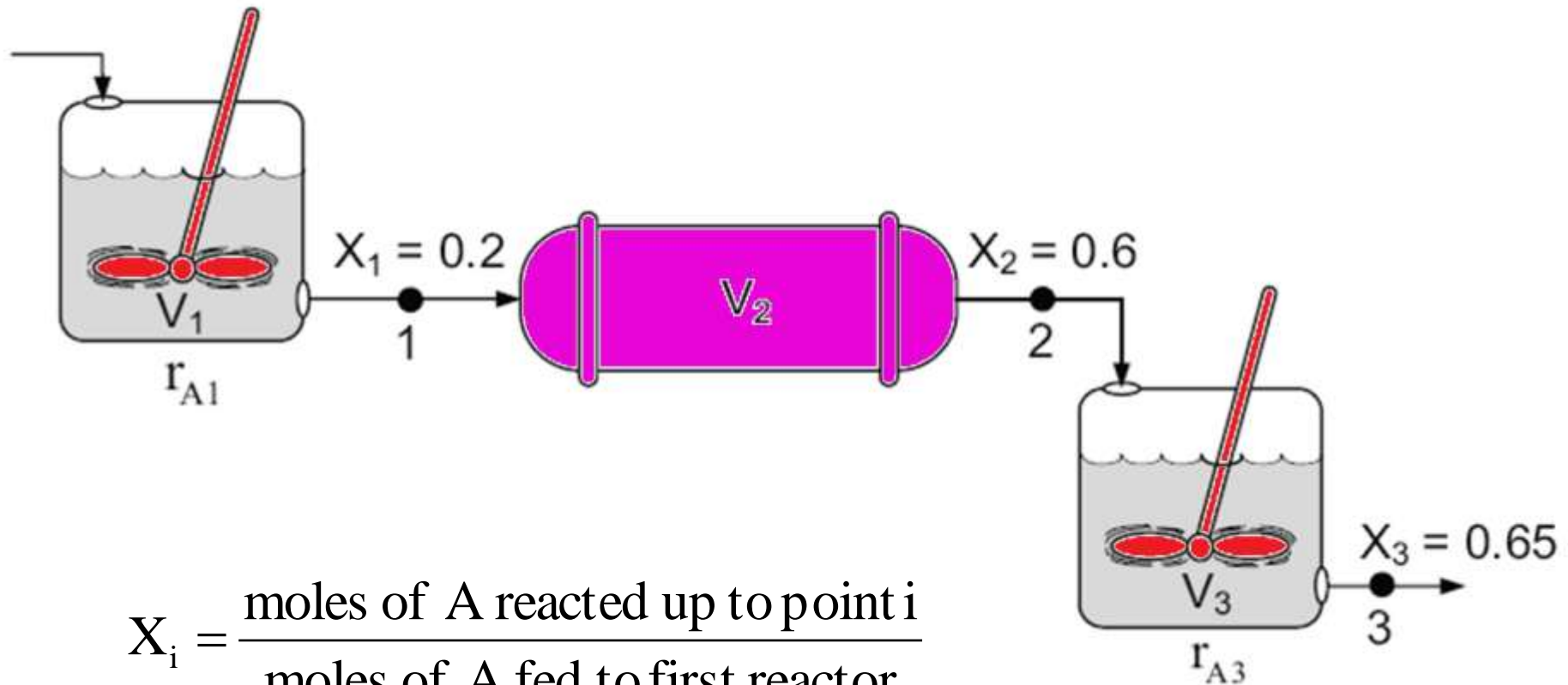


Review Lecture 2

PFR



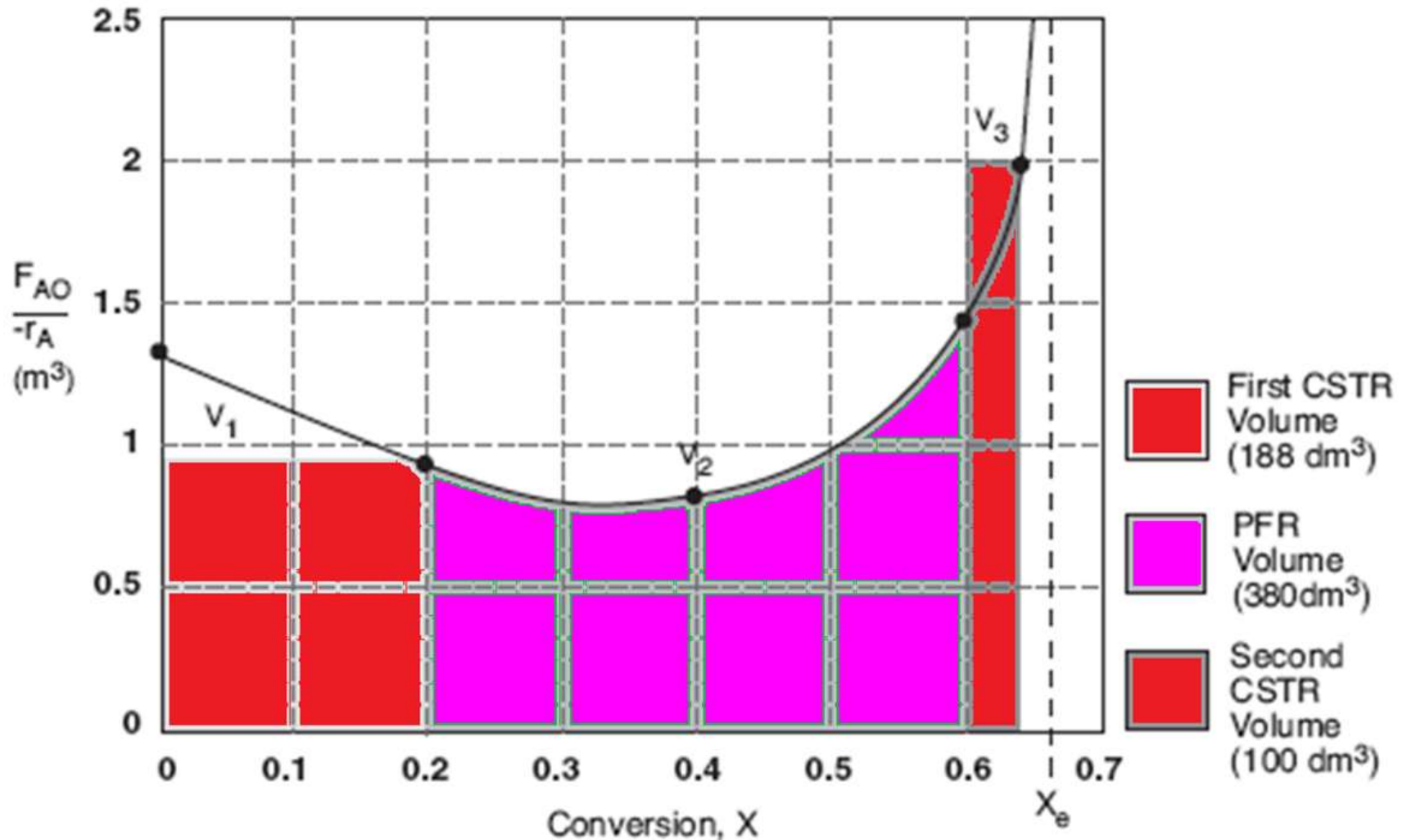
Reactors in Series



$$X_i = \frac{\text{moles of A reacted up to point i}}{\text{moles of A fed to first reactor}}$$

Only valid if there are no side streams

Reactors in Series



Review Lecture 2

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:

$$-r_A = k C_A^\alpha C_B^\beta$$

α order in A
 β order in B



$$\text{Overall Reaction Order} = \alpha + \beta$$

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

Review Lecture 3

Arrhenius Equation

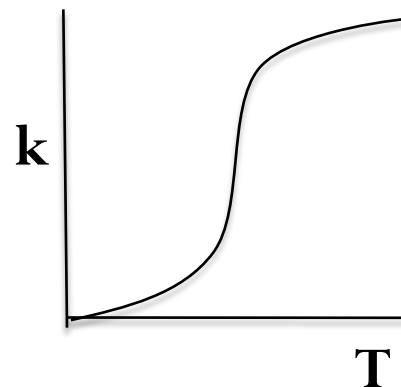
$$k = Ae^{-E/RT}$$

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)

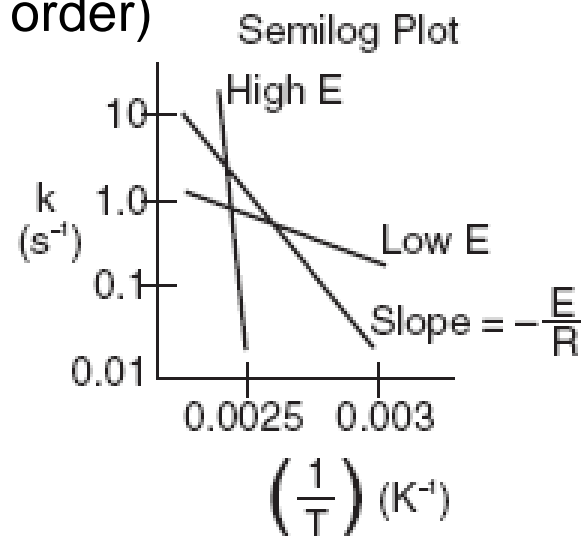


$$T \rightarrow \infty \quad k \rightarrow A$$

$$T \rightarrow 0 \quad k \rightarrow 0$$

$$A \approx 10^{13}$$

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



Reaction Engineering



Mole Balance



Rate Laws



Stoichiometry

These topics build upon one another

Review Lecture 3

Algorithm

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

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

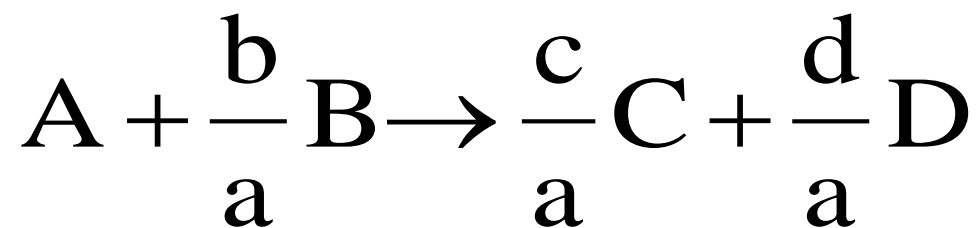


Step 2: Stoichiometry $(C_i) = h(X)$

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

Building Block 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 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:

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

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

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

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

Where: $\Theta_i = \frac{N_{i0}}{N_{A0}} = \frac{C_{i0}\nu_0}{C_{A0}\nu_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$ and $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

15 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

$$\text{Then } V = V_0$$

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

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

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: $\Theta_B = 1$

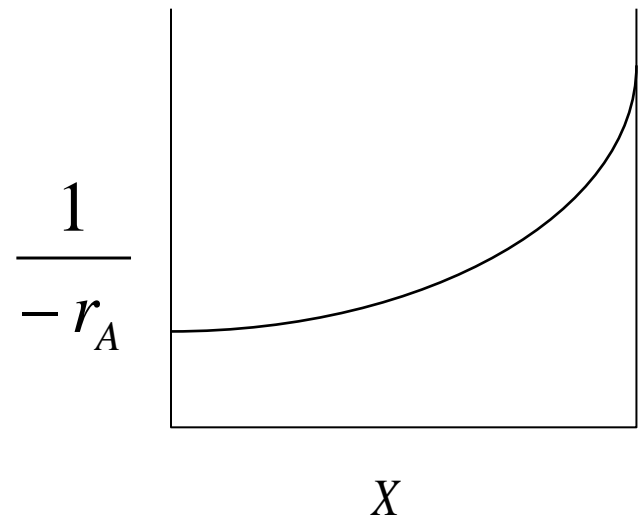
Stoichiometric feed: $\Theta_B = \frac{b}{a}$

Stoichiometry Constant Volume Batch

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

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

and we have $-r_A = f(X)$

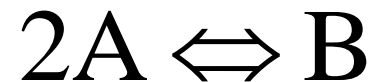


Batch Reactor - Example

Calculate the equilibrium conversion for gas phase reaction, X_e .

Consider the following elementary reaction with $K_C=20 \text{ dm}^3/\text{mol}$ and $C_{A0}=0.2 \text{ mol/dm}^3$.

Find X_e for both a batch reactor and a flow reactor.



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

Batch Reactor - Example

Calculate X_e $C_{A0} = 0.2 \text{ mol/dm}^3$

$$K_C = 20 \text{ dm}^3/\text{mol}$$

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

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

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

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

Batch Reactor - Example

<u>Symbol</u>	<u>Initial</u>	<u>Change</u>	<u>Remaining</u>
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: $-r_A=0$

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

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

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

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

Batch Reactor - Example

Solution:

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

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

Stoichiometry: $A \rightarrow B / 2$

Constant Volume: $V = V_0$

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

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

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

$$X_{eb} = 0.703$$

Flow System – Stoichiometry Table

Entering

F_{A0}

F_{B0}

F_{C0}

F_{D0}

F_{I0}

Leaving

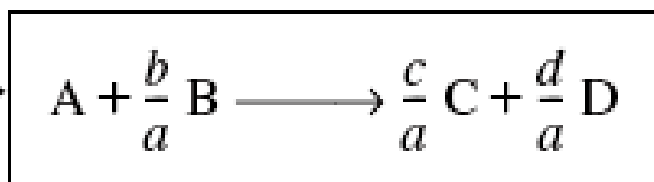
F_A

F_B

F_C

F_D

F_I



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

Where: $\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}\nu_0}{C_{A0}\nu_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$

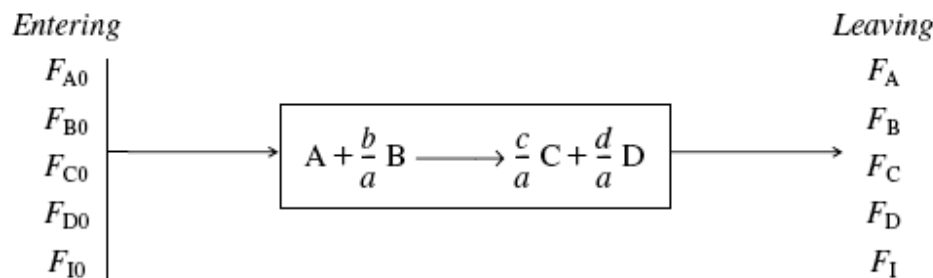
Flow System – Stoichiometry Table

<u>Species</u>	<u>Symbol</u>	<u>Reactor Feed</u>	<u>Change</u>	<u>Reactor Effluent</u>
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: $\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}v_0}{C_{A0}v_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$ and $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

Concentration – Flow System $C_A = \frac{F_A}{v}$

Flow System – Stoichiometry Table



<u>Species</u>	<u>Symbol</u>	<u>Reactor Feed</u>	<u>Change</u>	<u>Reactor Effluent</u>
A	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	B	$F_{B0} = F_{A0}\Theta_B$	$-b/a F_{A0}X$	$F_B = F_{A0}(\Theta_B - b/aX)$
C	C	$F_{C0} = F_{A0}\Theta_C$	$+c/a F_{A0}X$	$F_C = F_{A0}(\Theta_C + c/aX)$
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Inert	I	$F_{I0} = F_{A0}\Theta_I$	-----	$F_I = F_{A0}\Theta_I$
		<hr/> F_{T0}		<hr/> $F_T = F_{T0} + \delta F_{A0}X$

Where: $\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}v_0}{C_{A0}v_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$ and $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

Concentration – Flow System $C_A = \frac{F_A}{v}$

Stoichiometry

Concentration Flow System: $C_A = \frac{F_A}{v}$

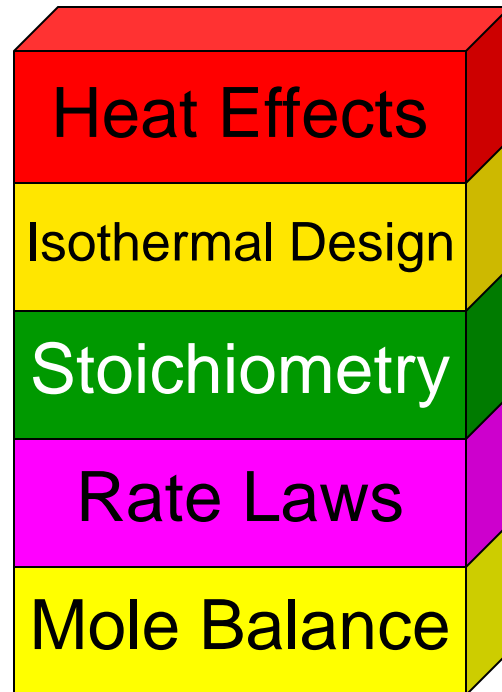
Liquid Phase Flow System: $v = v_0$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0} = C_{A0}(1-X) \quad \text{Flow Liquid Phase}$$

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

etc.

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



End of Lecture 4