Essentials of Chemical Reaction Engineering I Webinar
Wednesday, March 9, 2011

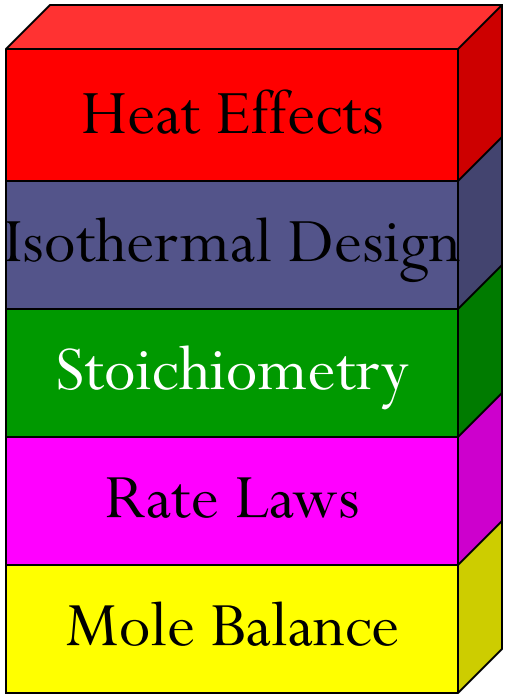
- Algorithm for Single Reactions with Conversion for
  - Batch Reactors (BR)
  - Continuous Stirred Tank Reactor (CSTR)
  - Plug Flow Reactors (PFR)
- Example: Problem from Professional Engineers Registration Exam

Pressure drop in Pack Bed Reactors (PBRs), the algorithm for multiple reactions and heat effects will be covered in a later lecture.

An expanded version of the power point slides can be found at **http://www.umich.edu/~essen/**

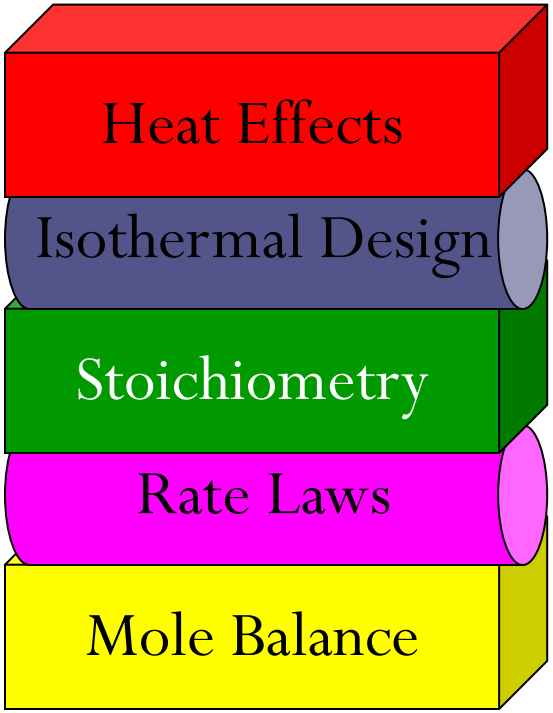
Separations

These topics do not build upon one another


Heat Effects
Isothermal Design
Stoichiometry
Rate Laws
Mole Balance

Mole Balance

Rate Laws


Heat Effects
Isothermal Design
Stoichiometry
Rate Laws
Mole Balance

Let's Begin CRE

- **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.

Reaction Rate

- The reaction rate is the rate at which the number of moles of a species looses its chemical identity per unit volume.
- The identity of a chemical species is determined by the *kind*, *number*, and *configuration* of that species' atoms.
- The rate of a reaction (*mol/dm^3/s*) can be expressed as :
  - The rate of Disappearance of the limiting reactant A: $\mathbf{-r_A}$

    or as
  - The rate of Formation (Generation) of product: $\mathbf{r_P}$

Reaction Rate: The Convention

Consider the isomerization

$$\mathbf{A \rightarrow B}$$

$-r_A$ = the rate of a disappearance of species A per unit volume (+10 mol/dm^3/s)

r_A = the rate of formation of species A per unit volume (–10 mol/dm^3/s)

r_B = the rate of formation of species B per unit volume (+10 mol/dm^3/s)

Reaction Rate

- For a gas-solid catalytic reaction, we refer to $-r_A'$, as the rate of disappearance of species A per unit mass of catalyst. (mol/gcat/s)

NOTE: (dC_A/dt) is **not** the definition of the rate of reaction

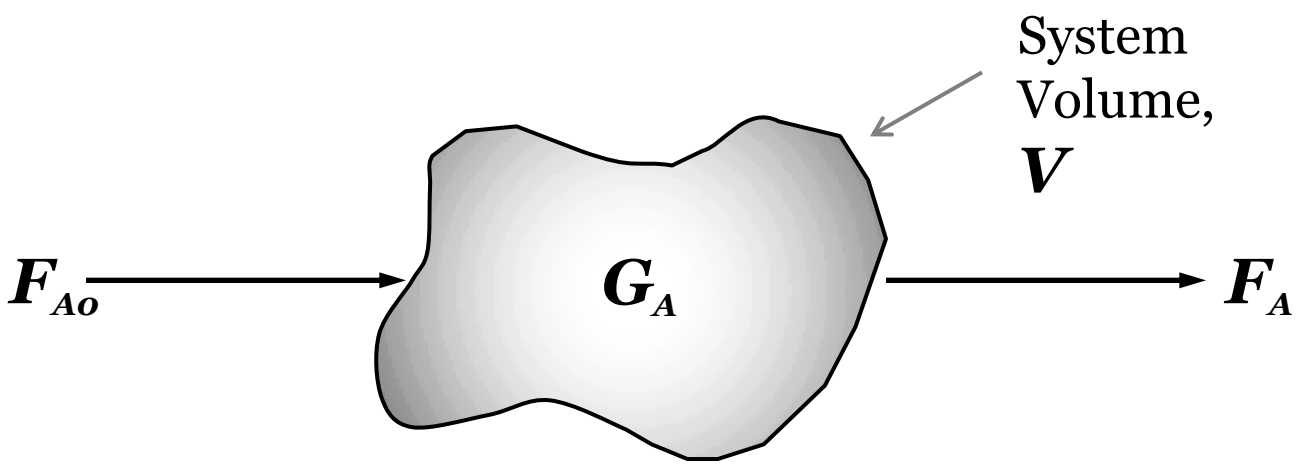
Reaction Rate

Consider species j:

1. r_j is the rate of formation of species j per unit volume [e.g. mol/dm^{3}s]
2. r_j is a function of concentration, temperature, pressure, and the type of catalyst (if any)
3. r_j is independent of the type of reaction system (batch, plug flow, etc.)
4. r_j is an algebraic equation, not a differential equation

(e.g. = $-r_A = kC_A$ or $-r_A = kC_A^2$)

General Mole Balance



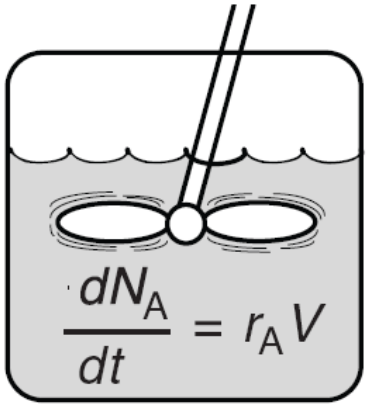
General Mole Balance on System Volume V

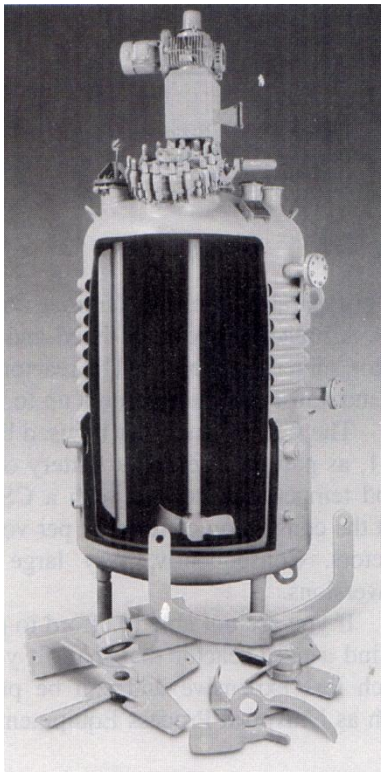
$$In - Out + Generation = Accumulation$$

$$F_{A0} - F_A + \int r_A dV = \frac{dN_A}{dt}$$

Batch Reactor Mole Balance

Batch





$$F_{A0} - F_A + \int r_A dV = \frac{dN_A}{dt}$$

$$F_{A0} = F_A = 0$$

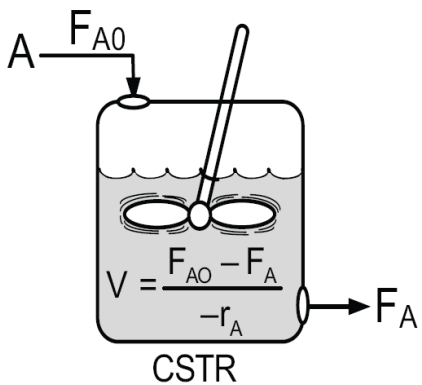
Well Mixed $\int r_A dV = r_A V$

$$\boxed{\frac{dN_A}{dt} = r_A V}$$

CSTR Mole Balance

$$F_{A0} - F_A + \int r_A dV = \frac{dN_A}{dt}$$

CSTR



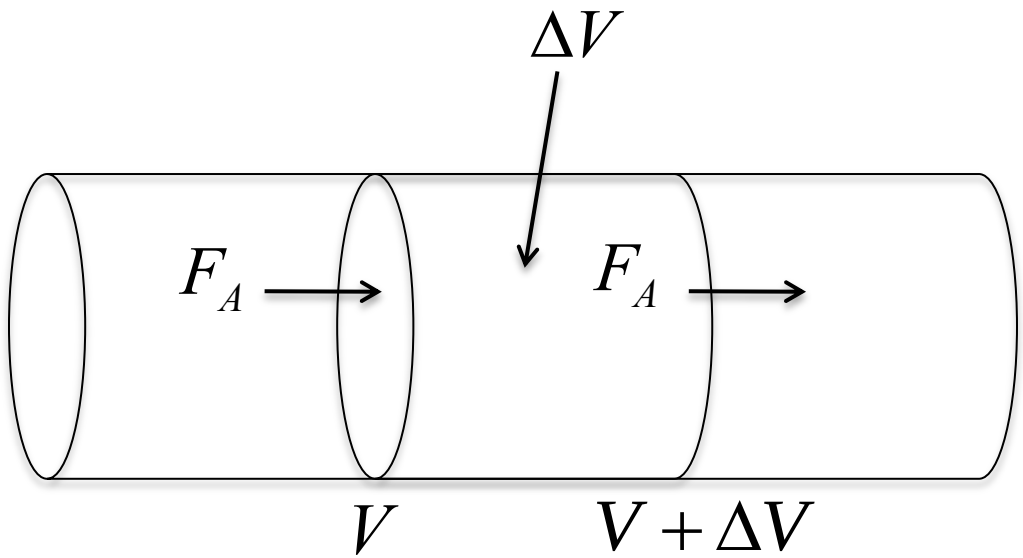
Steady State: $\frac{dN_A}{dt} = 0$

Well Mixed: $\int r_A dV = r_A V$

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

CSTR volume necessary to reduce the molar flow rate from F_{A0} to F_A.

Plug Flow Reactor Mole Balance



$$\begin{bmatrix} \text{In} \\ \text{at V} \end{bmatrix} - \begin{bmatrix} \text{Out} \\ \text{at V} + \Delta\text{V} \end{bmatrix} + \begin{bmatrix} \text{Generation} \\ \text{in } \Delta\text{V} \end{bmatrix} = 0$$

$$F_A\big|_V - F_A\big|_{V+\Delta V} + r_A \Delta V = 0$$

Plug Flow Reactor Mole Balance

Rearrange and take limit as $\Delta V \rightarrow 0$

$$\lim_{\Delta V \rightarrow 0} \frac{F_A\big|_{V+\Delta V} - F_A\big|_V}{\Delta V} = r_A$$

$$\boxed{\frac{dF_A}{dV} = r_A}$$

The integral form is: $$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$$

This is the volume necessary to reduce the entering molar flow rate (mol/s) from F_{A0} to the exit molar flow rate of F_A.

Packed Bed Reactor Mole Balance Analogous to PFR

Rearrange:

$$\frac{dF_A}{dW} = r'_A$$

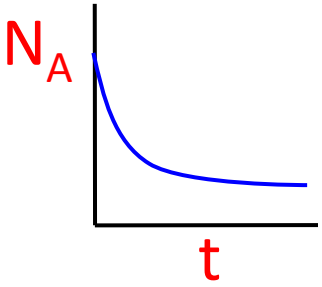
The integral form to find the catalyst weight is:

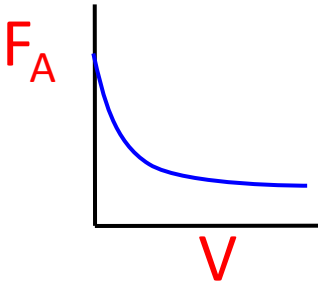
$$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A}$$

PBR catalyst weight necessary to reduce the entering molar flow rate F_{A0} to a molar flow rate F_A.

Reactor Mole Balance Summary

Reactor	Differential	Algebraic	Integral
Batch	$\frac{dN_A}{dt} = r_A V$		$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A V}$
CSTR		$V = \frac{F_{A0} - F_A}{-r_A}$	
PFR	$\frac{dF_A}{dV} = r_A$		$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$





Conversion X

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

Choose *limiting reactant* A as basis of calculation

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

$$X = \frac{\text{moles A reacted}}{\text{moles A fed}}$$

Batch

$$\begin{bmatrix}\text{Moles A}\\ \text{remaining}\end{bmatrix} = \begin{bmatrix}\text{Moles A}\\ \text{initially}\end{bmatrix} - \begin{bmatrix}\text{Moles A}\\ \text{reacted}\end{bmatrix}$$

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

$$dN_A = 0 - N_{A0}dX$$

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

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

$$t = 0 \quad X = 0$$
$$t = t \quad X = X$$

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

CSTR

$$\begin{bmatrix}\text{Moles A}\\ \text{leaving}\end{bmatrix} = \begin{bmatrix}\text{Moles A}\\ \text{entering}\end{bmatrix} - \begin{bmatrix}\text{Moles A}\\ \text{reacted}\end{bmatrix}$$

$$F_A = F_{A0} - F_{A0}X$$

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

$$V = \frac{F_{A0} - \left(F_{A0} - F_{A0}X\right)}{-r_A}$$

$$\boxed{V = \left(\frac{F_{A0}}{-r_A}\right)_{exit} X}$$

CSTR volume necessary to achieve conversion X.

PFR

$$\frac{dF_A}{dV} = r_A$$

$$F_A = F_{A0} - F_{A0}X$$

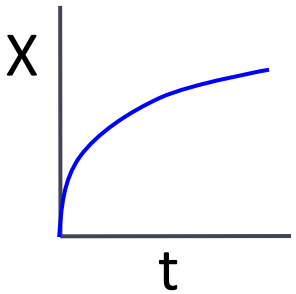
$$dF_A = 0 - F_{A0}dX$$

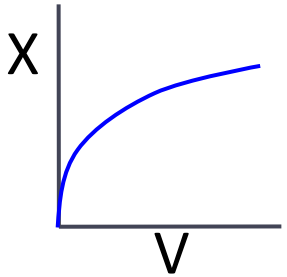
$$V = 0 \quad X = 0$$
$$V = V \quad X = X$$

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

Reactor Mole Balances in terms of conversion:Summary

Reactor	Differential	Algebraic	Integral
Batch	$N_{A0}\dfrac{dX}{dt} = -r_A V$		$t = N_{A0}\displaystyle\int_0^X \frac{dX}{-r_A V}$
CSTR		$V = \left(\dfrac{F_{A0}}{-r_A}\right)_{exit} X$	
PFR	$F_{A0}\dfrac{dX}{dV} = -r_A$		$V = \displaystyle\int_0^X \frac{F_{A0}}{-r_A} dX$
PBR	$F_{A0}\dfrac{dX}{dW} = -r'_A$		$W = \displaystyle\int_0^X \frac{F_{A0}}{-r'_A} dX$





Levenspiel Plots

Reactor Sizing

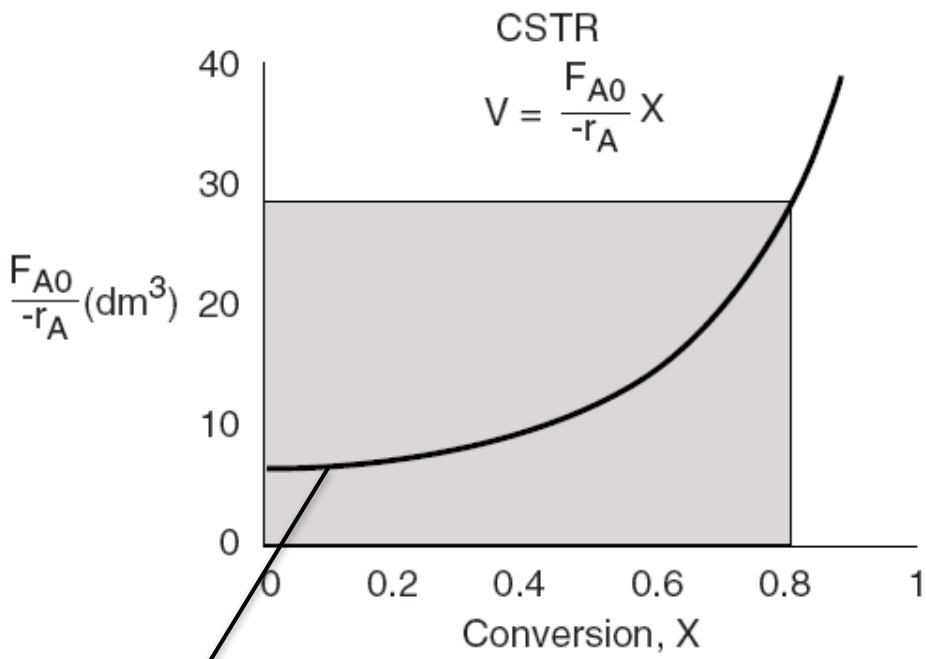
$$V = \int_0^X \frac{F_{A0}}{-r_A} dX \qquad V = \left(\frac{F_{A0}}{-r_A}\right)_{exit} X$$

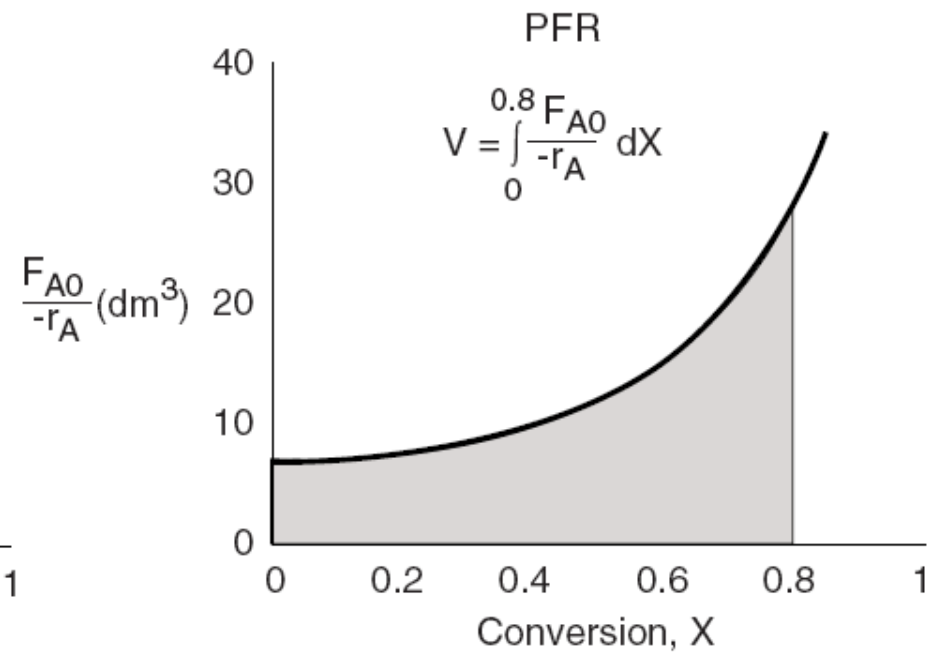
Just suppose we were given $-r_A$ as a function of conversion, $-r_A = f(X)$, then we could size any CSTR or PFR at the same conditions by constructing a Levenspiel plot of $(F_{A0}/-r_A)$ as a function of X i.e.,

$$\frac{F_{A0}}{-r_A} = g(X)$$

The volume of a CSTR and the volume of a PFR can be represented as the shaded areas in the Levenspiel Plots shown as:

Levenspiel Plots





$$\frac{F_{A0}}{-r_A} = g(X)$$

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 $-r_A = f(X)$

Reaction Engineering

These topics build upon one another

Rate Laws - Power Law Model

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

α order in A

β order in B

Overall Rection Order $= \alpha + \beta$

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

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

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 3rd order

Non Elementary Rate Laws

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

If $-r_A = k_A C_A^2$

- Second Order in A
- Zero Order in B
- Overall Second Order

Reversible Reaction

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

Elementary

$$-r_A = k_A C_A^2 C_B - k_{-A} C_C^3$$

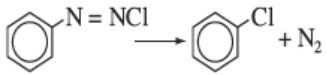
$$= k_A \left[C_A^2 C_B - \frac{C_C^3}{k_A / k_{-A}} \right]$$

$$= k_A \left[C_A^2 C_B - \frac{C_C^3}{K_e} \right]$$

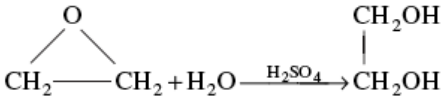
Table 3-1 Example of Reaction Rate Laws

A. First-Order Rate Laws

(1) $C_2H_6 \longrightarrow C_2H_4 + H_2$ $\qquad -r_A = kC_{C_2H_6}$

(2) 

$\qquad -r_A = kC_{\phi N=NCl}$

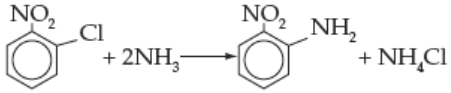
(3) 

$\qquad -r_A = kC_{CH_2OCH_2}$

(4) $CH_3COCH_3 \longrightarrow CH_2CO + CH_4$ $\qquad -r_A = kC_{CH_3COCH_3}$

(5) $nC_4H_{10} \rightleftharpoons iC_4H_{10}$ $\qquad -r_n = k[C_{nC_4} - C_{iC_4}/K_C]$

B. Second-Order Rate Laws

(1) 

$\qquad -r_A = k_{ONCB}C_{ONCB}C_{NH_3}$ †

(2) $CNBr + CH_3NH_2 \longrightarrow CH_3Br + NCNH_2$ $\qquad -r_A = kC_{CNBr}C_{CH_3NH_2}$

(3)

$$\underset{A}{CH_3COOC_2H_5} + \underset{B}{C_4H_9OH} \rightleftharpoons \underset{C}{CH_3COOC_4H_9} + \underset{D}{C_2H_5OH}$$

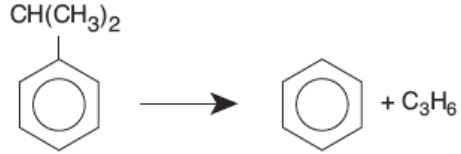
$\qquad -r_A = k[C_AC_B - C_CC_D/K_C]$

C. Nonelementary Rate Laws

(1) Homogeneous

$CH_3CHO \longrightarrow CH_4 + CO$ $\qquad -r_{CH_3CHO} = kC^{3/2}_{CH_3CHO}$

(2) Heterogeneous



Cumene (C) ⟶ Benzene (B) + Propylene (P)

$$-r_C = \frac{k[P_C - P_BP_P/K_P]}{1 + K_BP_B + K_CP_C}$$

Arrhenius Equation

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

E = Activation energy (cal/mol)

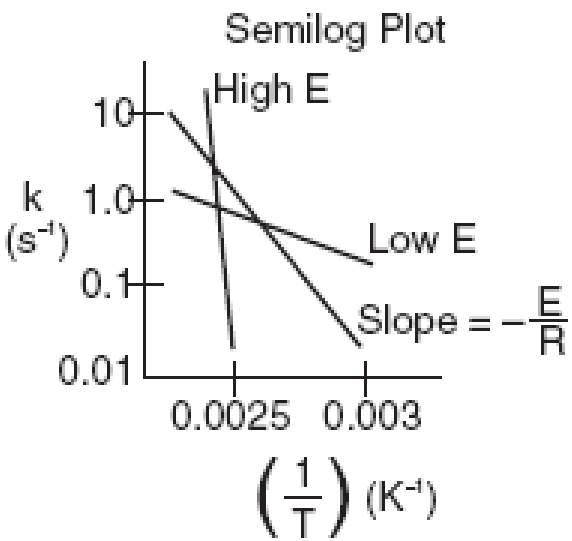
R = Gas constant (cal/mol*K)

T = Temperature (K)

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

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

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



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 $-r_A = f(X)$

Reaction Engineering

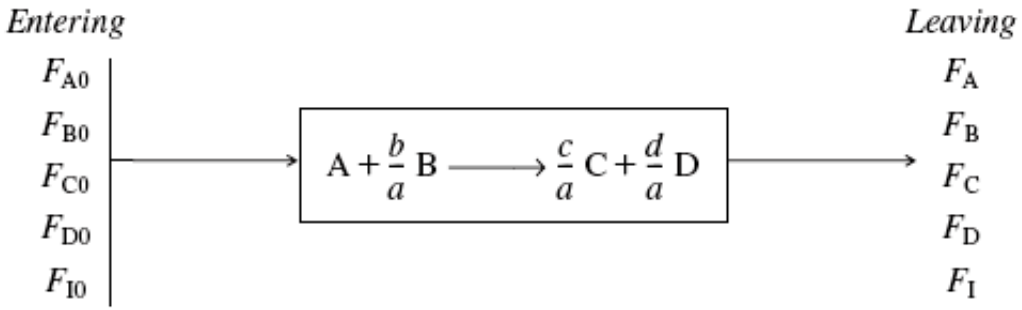
These topics build upon one another

We shall set up **<u>Stoichiometry Tables</u>** to express the concentration as a function of conversion then combine $C_i = f(X)$ with the appropriate rate law to obtain $-r_A = f(X)$.

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

A is the *Limiting Reactant*.

Flow System Stochiometric 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: $\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}\upsilon_0}{C_{A0}\upsilon_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$ and

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 = \frac{\text{Change in total number of moles}}{\text{Mole of A reacted}}$$

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

Liquid Phase Flow System: $\upsilon = \upsilon_0$

Liquid Systems

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0} = C_{A0}(1-X)$$

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

Equimolar feed: $\Theta_B = 1$

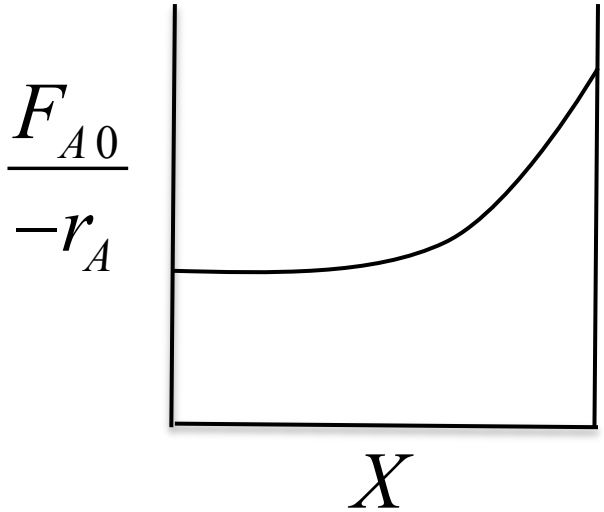
Stoichiometric feed: $\Theta_B = \frac{b}{a}$

Liquid Systems

If the rate of reaction were $-r_A = kC_A C_B$

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

This gives us $-r_A = f(X)$



For Gas Phase Flow Systems

Combining the compressibility factor equation of state with $Z = Z_0$

<u>Stoichiometry:</u>

$$C_T = \frac{P}{ZRT}$$

$$C_{T0} = \frac{P_0}{Z_0 R T_0}$$

$$C_T = \frac{F_T}{\upsilon}$$

$$C_{T0} = \frac{F_{T0}}{\upsilon_0}$$

$$\frac{C_T}{C_{T0}} = \frac{(F_T/\upsilon)}{(F_{T0}/\upsilon_0)} = \frac{(P/ZRT)}{(P_0/Z_0 R T_0)}$$

We obtain:

$$\boxed{\upsilon = \upsilon_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0}}$$

For Gas Phase Flow Systems: Conversion

$$\upsilon = \upsilon_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0}$$

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

Substituting F_T gives:

$$\upsilon = \upsilon_0 \left(\frac{F_{T0} + F_{A0}\delta X}{F_{T0}} \right) \frac{T}{T_0} \frac{P_0}{P}$$

$$\upsilon = \upsilon_0 \left(1 + \frac{F_{A0}}{F_{T0}} \delta X \right) \frac{T}{T_0} \frac{P_0}{P}$$

$$\upsilon = \upsilon_0 \left(1 + y_{A0}\delta X \right) \frac{T}{T_0} \frac{P_0}{P}$$

$$\boxed{\upsilon = \upsilon_0 \left(1 + \varepsilon X \right) \frac{T}{T_0} \frac{P_0}{P}}$$

For Gas Phase Flow Systems: Conversion

$$\boxed{\upsilon = \upsilon_0 (1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P}}$$

where

$$\varepsilon = \frac{F_{A0}}{F_{T0}} \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) = y_{A0} \delta$$

$$\boxed{\varepsilon = y_{A0} \delta}$$

$$\varepsilon = \frac{\text{change in total number of moles for complete conversion}}{\text{total number of moles fed to the reactor}}$$

For Gas Phase Flow Systems: Conversion

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

Gas Phase Flow System: $\upsilon = \upsilon_0 (1+\varepsilon X)\frac{T}{T_0}\frac{P_0}{P}$

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0 (1+\varepsilon X)\frac{T}{T_0}\frac{P_0}{P}} = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}\frac{T_0}{T}\frac{P}{P_0}$$

$$C_B = \frac{F_B}{\upsilon} = \frac{F_{A0}\left(\Theta_B - \frac{b}{a}X\right)}{\upsilon_0 (1+\varepsilon X)\frac{T}{T_0}\frac{P_0}{P}} = \frac{C_{A0}\left(\Theta_B - \frac{b}{a}X\right)}{(1+\varepsilon X)}\frac{T_0}{T}\frac{P}{P_0}$$

- If constant temperature and no pressure drop

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0(1+\varepsilon X)} = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}$$

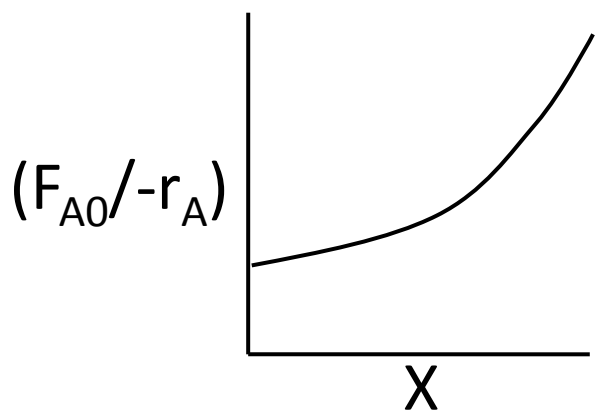
$$C_B = \frac{F_B}{\upsilon} = \frac{F_{A0}\left(\Theta_B - \frac{b}{a}X\right)}{\upsilon_0(1+\varepsilon X)} = \frac{C_{A0}\left(\Theta_B - \frac{b}{a}X\right)}{(1+\varepsilon X)}$$

For Gas Phase Flow Systems: Conversion

If $-r_A = kC_AC_B$, and Isothermal and isobaric

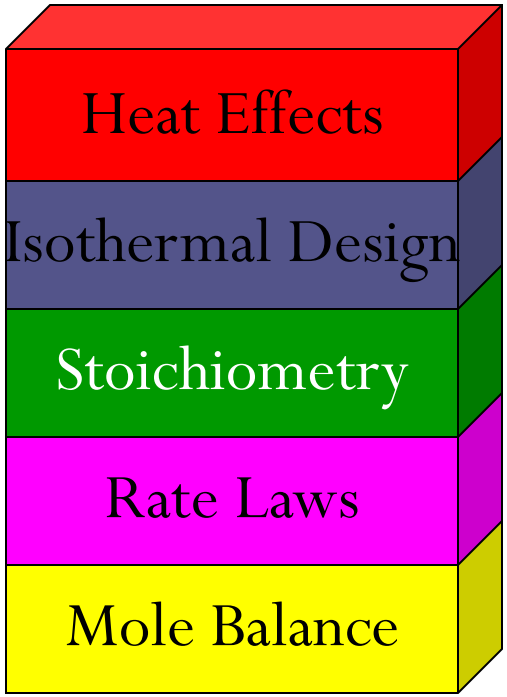
$$-r_A = k_A C_{A0}^2 \left[\frac{(1-X)}{(1+\varepsilon X)} \frac{\left(\Theta_B - \frac{b}{a}X\right)}{(1+\varepsilon X)} \right]$$

This gives us



Reaction Engineering

These topics build upon one another


Heat Effects
Isothermal Design
Stoichiometry
Rate Laws
Mole Balance

Le Cataliste Flambé

344 Champs Elystes

Menu à 220FF

Appetizer

Pate de Canard (supplément 15FF)
Coquilles Saint-Jacques
Potage Crème de Cresson
Escargots à La Bourguignonne
(supplement 15FF)

Entrée

Cassoulet
Ragnons de Veau
Coq au Vin
Boeuf à la provençale
(Tous nos plats sont garnis)

Dessert

Brie ou Crème Anglaise

1/2 bouteille
de vin blanc ou vin rouge

Mole Balance

Batch Reactor
CSTR
PFR/PBR
Semibatch Reactor

Rate Law

Power Law (e.g.)
1st Order
2nd Order
Non-Integer Order

Stoichiometry

Gas or Liquid

Combine

Mix together and digest with
1/2 bouteille of POLYMATH

Service Compris

Choices

1. MOLE BALANCES

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

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

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

2. RATE LAWS

$-r_A = kC_A$

$-r_A = \frac{kC_A}{1 + K_A C_A}$

$-r_A = k\left[C_A - \frac{C_B C_C}{K_e}\right]$

3. STOICHIOMETRY

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

BATCH: $C_A = \frac{N_A}{V}$

$F_A = F_{A0}(1 - X)$

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

LIQUID	IDEAL GAS	IDEAL GAS	LIQUID OR GAS
Constant flow rate	Variable flow rate	Variable volume	Constant volume
$v = v_0$	$v = v_0(1 + \varepsilon X)\frac{P_0}{P}\frac{T}{T_0}$	$V = V_0(1 + \varepsilon X)\frac{P_0}{P}\frac{T}{T_0}$	$V = V_0$
$C_A = C_{A0}(1 - X)$	$C_A = \frac{C_{A0}(1 - X)}{(1 + \varepsilon X)}\frac{P}{P_0}\frac{T_0}{T}$	$C_A = \frac{C_{A0}(1 - X)}{(1 + \varepsilon X)}\frac{P}{P_0}\frac{T_0}{T}$	$C_A = C_{A0}(1 - X)$

4. COMBINE (First Order Gas-Phase Reaction in a PFR)

From mole balance | From rate law | From stoichiometry

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = \frac{kC_A}{F_{A0}} = \frac{k}{F_{A0}}\left(C_{A0}\frac{(1 - X)}{(1 + \varepsilon X)}\right)\frac{P}{P_0}\frac{T_0}{T}$$

$$\frac{dX}{dV} = \frac{k}{v_0}\frac{(1 - X)}{(1 + \varepsilon X)}y\frac{T_0}{T}, \text{ where } y = \frac{P}{P_0} \qquad \text{(A)}$$

Integrating for the case of constant temperature and pressure gives

$$V = \frac{v_0}{k}\left[(1 + \varepsilon)\ln\left(\frac{1}{1 - X}\right) - \varepsilon X\right] \qquad \text{(B)}$$

Part 1: Mole Balances in Terms of Conversion

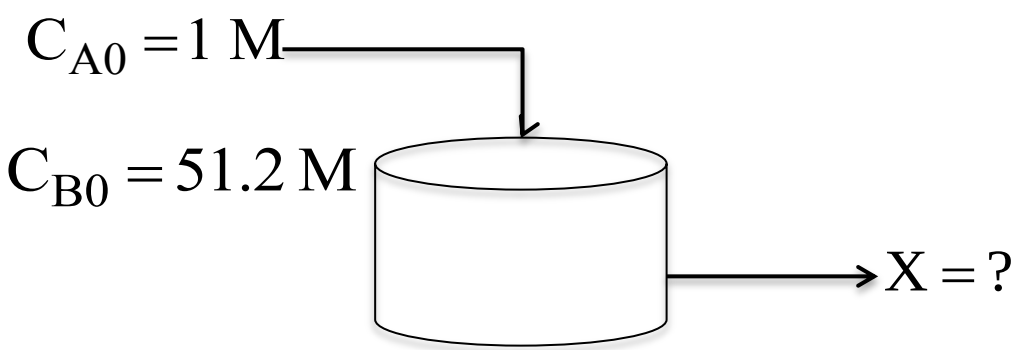
Algorithm for Isothermal Reactor Design

1. Mole Balance and Design Equation
2. Rate Law
3. Stoichiometry
4. Combine
5. Evaluate
   A. Graphically (Levenspiel plots)
   B. Numerical (Quadrature Formulas)
   C. Analytical (Integral Tables)
   D. Software Packages (Polymath)

CSTR Laboratory Experiment

Example: $(CH_2CO)_2O + H_2O \rightarrow 2CH_3COOH$

$$A + B \rightarrow 2C$$



$$V = 1\ dm^3$$

$$\upsilon_0 = 3.3 \cdot 10^{-3}\ \frac{dm^3}{s}$$

$$\tau = \frac{V}{\upsilon_0} = \frac{1\ dm^3}{3.3 \times 10^{-3}\ \frac{dm^3}{s}} = 303s$$

CSTR Laboratory Experiment

1) Mole Balance: CSTR: $$V = \frac{F_{A0}X}{-r_A}$$

2) Rate Law: $$-r_A = k_A C_A C_B$$

3) Stoichiometry:

A	F_{A0}	$-F_{A0}X$	$F_A=F_{A0}(1-X)$
B	$F_{A0}\Theta_B$	$-F_{A0}X$	$F_B=F_{A0}(\Theta_B-X)$
C	0	$2F_{A0}X$	$F_C=2F_{A0}X$

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0} = C_{A0}(1-X)$$

CSTR Laboratory Experiment

3) Stoichiometry (cont'd):

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0} = C_{A0}(1-X)$$

$$C_B = \frac{F_{A0}(\Theta_B - X)}{\upsilon_0} = C_{A0}(\Theta_B - X)$$

$$\Theta_B = \frac{51.2}{1} = 51.2$$

$$C_B = C_{A0}(51.2 - X) \approx C_{A0}(51.2) \approx C_{B0}$$

$$-r_A = \underbrace{k_A C_{B0}}_{k} C_{A0}(1-X) = kC_{A0}(1-X) \quad , \quad k = 0.01 \ \ s^{-1}$$

CSTR Laboratory Experiment

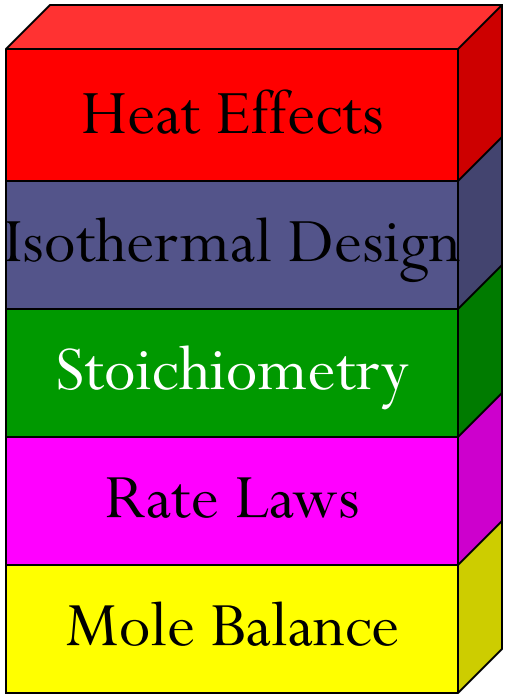
1) Mole Balance: CSTR: $V = \frac{F_{A0}X}{-r_A}$

$$V = \frac{\upsilon_0 C_{A0} X}{k C_{A0}(1-X)} \Rightarrow \frac{V}{\upsilon_0} = \frac{X}{k(1-X)} \Rightarrow \tau = \frac{V}{\upsilon_0} = \frac{X}{k(1-X)}$$

$$X = \frac{\tau k}{1+\tau k}$$

$$\tau k = (303s)\left(0.01\ s^{-1}\right) = 3.03$$

$$\boxed{X = \frac{3.03}{4.03} = 0.75}$$


Heat Effects
Isothermal Design
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General Guidelines for California Problems

Some hints:

1. Group unknown parameters/values on the same side of the equation

   <u>example</u>: [unknowns] = [knowns]

2. Look for a Case 1 and a Case 2 (usually two data points) to make intermediate calculations
3. Take ratios of Case 1 and Case 2 to cancel as many unknowns as possible
4. Carry all symbols to the end of the manipulation before evaluating, UNLESS THEY ARE ZERO

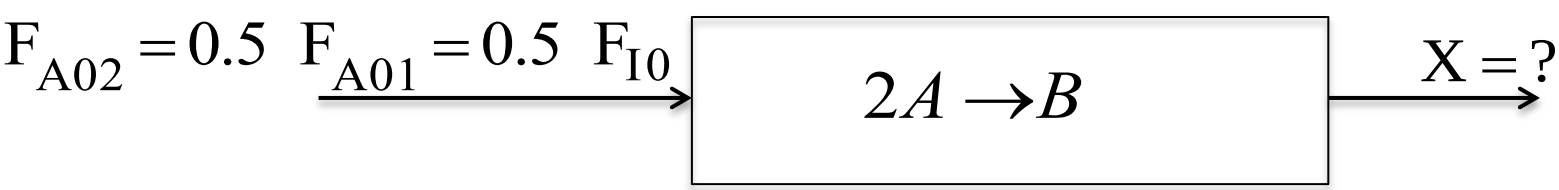
California Professional Engineers Exam is not curved, 75% or better to pass.

California Profession Engineers Exam

The irreversible elementary gas phase reaction takes place in an isothermal plug-flow reactor. Reactant A and a diluent I are fed in an equimolar ratio and the conversion of A is 80%.

If the molar feed rate of A is cut in half, what is the conversion of A assuming that the feed rate of I is left unchanged?

When $F_{A01} = F_{I0}$ then $X = 0.8$



Unknown: $V, k, T, P, C_{A0}, F_{A0}, F_{I0}, V_0$

Gas Phase PFR

Will the conversion increase or decrease?

INCREASE: Slower Volumetric Rate (Reactants spend more time in the reactor)

DECREASE: Concentration of Reactant Diluted

Gas Phase PFR

Assumptions:

$$T = T_0,\ P = P_0,\ V_1 = V_2,$$

$$k_1 = k_2,\ P_1 = P_2,\ C_{T01} = C_{T02}$$

1) Mole Balance:

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

2) Rate Law:

$$-r_A = kC_A^2$$

3) Stoichiometry: (gas phase) $T = T_0,\ P = P_0,\ \therefore \upsilon = \upsilon_0(1 + \varepsilon X)$

$$A \rightarrow \tfrac{1}{2} B$$

Gas Phase PFR

$$A \rightarrow \frac{1}{2}B$$

$$\delta = \frac{1}{2} - 1 = -\frac{1}{2}$$

$$\varepsilon_1 = y_{A01}\delta = \left(\frac{1}{2}\right)\left(-\frac{1}{2}\right) = -\frac{1}{4}$$

$$\varepsilon_2 = y_{A02}\delta = \left(\frac{1}{3}\right)\left(-\frac{1}{2}\right) = -\frac{1}{6}$$

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

Gas Phase PFR

4) Combine:

$$-r_A = kC_A^2 = -r_A = kC_{A0}^2\left(\frac{(1+X)}{(1+\varepsilon X)}\right)^2$$

$$\frac{dX}{dV} = \frac{kC_{A0}^2}{F_{A0}}\left(\frac{(1-X)}{(1+\varepsilon X)}\right)^2$$

$$V = \frac{F_{A0}}{kC_{A0}^2}\int_0^X\left(\frac{(1+\varepsilon X)}{(1-X)}\right)^2 dX$$

$$\frac{kC_{A0}^2 V}{F_{A0}} = 2\varepsilon(1+\varepsilon)\ln(1-X)+\varepsilon^2 X+(1+\varepsilon)^2\frac{X}{1-X}$$

Gas Phase PFR

Case 1: $\varepsilon_1 = -\frac{1}{4},\ X = 0.5$

$$\frac{VkC_{A01}^2}{F_{A01}} = 2\left(-\frac{1}{4}\right)\left(1-\frac{1}{4}\right)\ln(1-0.8) + \left(\frac{1}{4}\right)^2(0.8) + \left(1-\frac{1}{4}\right)^2\frac{0.8}{1-0.8} = 2.9$$

Case 2: $\varepsilon_2 = -\frac{1}{6},\ X_2 = ?$

$RHS(X_2)$

$$\frac{kC_{A02}^2V}{F_{A02}} = 2\varepsilon_2(1+\varepsilon_2)\ln(1-X_2) + \varepsilon_2^2X_2 + (1+\varepsilon_2)^2\frac{X_2}{1-X_2}$$

Take ratio of Case 2 to Case 1

$$\frac{\text{Case 2}}{\text{Case 1}} = \frac{\dfrac{kC_{A02}^2V}{F_{A02}}}{\dfrac{kC_{A01}^2V}{F_{A01}}} = \frac{2\varepsilon_2(1+\varepsilon_2)\ln(1-X_2) + \varepsilon_2^2X_2 + (1+\varepsilon_2)^2\dfrac{X_2}{1-X_2}}{2\varepsilon_1(1+\varepsilon_1)\ln(1-X_1) + \varepsilon_1^2X_1 + (1+\varepsilon_1)^2\dfrac{X_1}{1-X_1}}$$

Gas Phase PFR

Must make this assumption to keep pressure the same, $C_{T02}=C_{T01}$

$$\frac{\cancel{k}\left(\frac{C_{A02}^2}{F_{A02}}\right)\cancel{V}}{\cancel{k}\left(\frac{C_{A01}^2}{F_{A01}}\right)\cancel{V}} = \left(\frac{C_{A02}}{C_{A01}}\right)^2\left(\frac{F_{A01}}{F_{A02}}\right) = \left(\frac{y_{A02}}{y_{A01}}\frac{\cancel{C_{T02}}}{\cancel{C_{T01}}}\right)^2\left(\frac{F_{A01}}{F_{A02}}\right)$$

$$= \left(\frac{y_{A02}}{y_{A01}}\right)^2\left(\frac{F_{A01}}{F_{A02}}\right) = \frac{RHS(X_2)}{2.9}$$

$$y_{A01} = \frac{1}{2} \qquad y_{A02} = \frac{1}{3} \qquad \frac{F_{A02}}{F_{A01}} = \frac{1}{2}$$

$$\frac{RHS(X_2)}{2.9} = \left(\frac{2}{3}\right)^2\left(\frac{1}{\left(\cancel{1/2}\right)}\right) = \frac{8}{9}$$

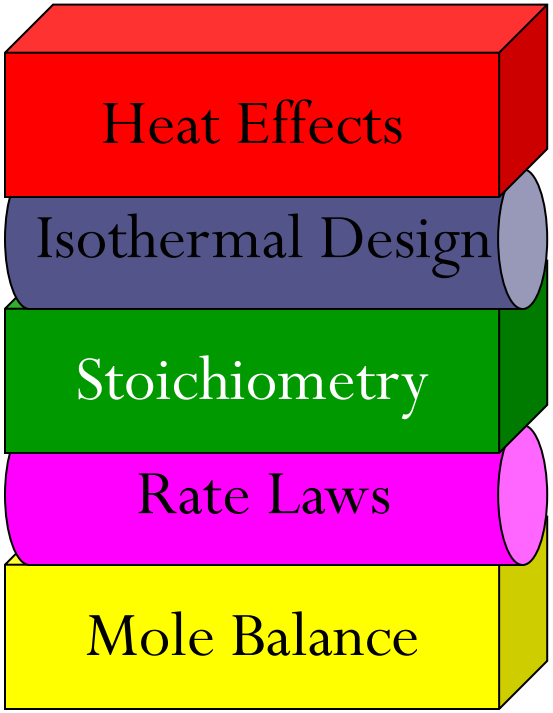
Gas Phase PFR

$$\left(\frac{8}{9}\right)(2.9) = 2.58 = \overbrace{2\varepsilon_2(1+\varepsilon_2)\ln(1-X_2) + \varepsilon_2^2 X_2 + (1+\varepsilon_2)^2 \frac{X_2}{1-X_2}}^{RHS(X_2)}$$

$$\varepsilon_2 = y_{A02}\delta = \frac{-1}{6}$$

$$2.58 = 2\left(-\frac{1}{6}\right)\left(1-\frac{1}{6}\right)\ln(1-X_2) + \left(-\frac{1}{6}\right)^2 X_2 + \left(1-\frac{1}{6}\right)^2 \frac{X_2}{1-X_2}$$

One equation and one unknown. Solve trial and error or with computer to find: **X=0.758**


Heat Effects
Isothermal Design
Stoichiometry
Rate Laws
Mole Balance

Please note: In the following material you will find one more example of a gas phase reaction with volume change and the algorithm for membrane reactors and multiple reactions.

For Gas Phase Flow Systems

$$C_A = \frac{F_A}{\upsilon} = \frac{F_A}{\upsilon_0\left(\frac{F_T}{F_0}\right)}\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right) = \frac{F_{T0}}{\upsilon_0}\left(\frac{F_A}{F_T}\right)\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$$

$$C_A = C_{T0}\left(\frac{F_A}{F_T}\right)\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$$

$$C_{T0} = \frac{F_{T0}}{\upsilon_0}$$

$$C_B = C_{T0}\left(\frac{F_B}{F_T}\right)\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$$

Why is there an Activation Energy?

For the reaction to occur, the reactants must overcome an energy barrier or activation energy E_A. The energy to overcome their barrier comes from the transfer to the kinetic energy from molecular collisions into internal energy (e.g. Vibrational Energy).

1. The molecules need energy to disort or stretch their bonds in order to break them and thus form new bonds
2. As the reacting molecules come close together they must overcome both stearic and electron repulsion forces in order to react.

– Examples:

Gas Phase : PFR and Batch Calculation

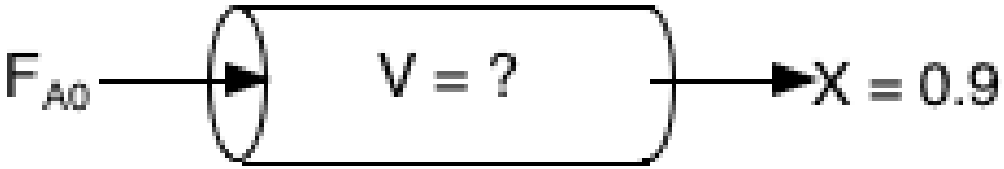
$$2NOCl \rightarrow 2NO + Cl_2$$

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

Pure NOCl fed with $C_{NOCl,0}$ = 0.2 mol/dm^3 follows an elementary rate law with k = 0.29 dm^3/mol•s)

PFR with v_0 = 10 dm^3/s

Find reactor volume, V and tau for X = 0.9



Example: Gas Flow PFR

$$2NOCl \rightarrow 2NO + Cl_2$$

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

$$\upsilon_0 = 10 \ \frac{dm^3}{s} \qquad k = 0.29 \frac{dm^3}{mol \cdot s} \qquad C_{A0} = 0.2 \frac{mol}{dm^3}$$

$$T = T_0 \qquad P = P_0 \qquad X = 0.9$$

1) Mole Balance:

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

2) Rate Law:

$$-r_A = kC_A^2$$

Example: Gas Flow PFR

3) Stoich: Gas $T = T_0,\ P = P_0 \therefore$

$$\upsilon = \upsilon_0(1+\varepsilon X)$$

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0(1+\varepsilon X)} = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}$$

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

4) Combine:

$$-r_A = kC_A^2 = \frac{kC_{A0}^2(1-X)^2}{(1+\varepsilon X)^2}$$

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = \frac{kC_{A0}^2(1-X)^2}{C_{A0}\upsilon_0(1+\varepsilon X)^2}$$

$$\Rightarrow \int_0^X \frac{(1+\varepsilon X)^2}{(1-X)^2}dX = \int_0^V \frac{kC_{A0}}{\upsilon_0}dV = \frac{kC_{A0}V}{\upsilon_0} = kC_{A0}\tau$$

Da

678

Example: Gas Flow PFR

$$kC_{A0}\tau = 2\varepsilon(1+\varepsilon)\ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon)^2 X}{1-X}$$

$$\mathrm{A} \rightarrow \mathrm{B} + \mathrm{C}/2$$

$$\varepsilon = y_{A0}\delta = (1)\left(\frac{1}{2} + 1 - 1\right) = \frac{1}{2} \quad , \quad X = 0.9$$

$$kC_{A0}\tau = 17.02$$

$$\tau = \frac{17.02}{kC_{A0}} = 294 \ \ \mathrm{sec}$$

$$V = \upsilon_0 \tau = 2940 \ \ dm^3$$

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

Liquid Phase

- **Flow**: $C_B = \frac{F_B}{v}$
- **Batch**: $C_B = \frac{N_B}{V}$

NO Phase Change

$v = v_0$ $\qquad$ $V = V_0$

Constant Volume $V = V_0$

$$C_B = C_{A0}\left(\theta_B - \frac{b}{a}X\right)$$

Gas Phase

- **Batch**: $C_B = \frac{N_B}{V}$

$$V = V_0 \frac{N_T}{N_{T0}} \frac{P_0}{P} \frac{T}{T_0}$$

$$C_B = \frac{N_B}{N_T} \frac{N_{T0}}{V_0} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_B = C_{T0} \frac{N_B}{N_T} \frac{P}{P_0} \frac{T_0}{T}$$

- **Flow**: $C_B = \frac{F_B}{v}$

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

$$C_B = \frac{F_B}{F_T} \frac{F_{T0}}{v_0} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_B = C_{T0} \frac{F_B}{F_T} \frac{P}{P_0} \frac{T_0}{T}$$

NO Phase Change
OR
NO Semipermeable Membranes

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

$$C_B = \frac{C_{A0}\left(\theta_B - \frac{b}{a}X\right)}{1 + \varepsilon X}\left(\frac{P}{P_0}\right)\frac{T_0}{T}$$

Isothermal

$$C_B = \frac{C_{A0}\left(\theta_B - \frac{b}{a}X\right)}{1 + \varepsilon X}\frac{P}{P_0}$$

Neglect Pressure Drop

$$C_B = \frac{C_{A0}\left(\theta_B - \frac{b}{a}X\right)}{1 + \varepsilon X}$$

$$\varepsilon = y_{A0}\delta$$

$$\delta = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)$$

$$C_{T0} = \frac{P_0}{RT_0}$$

$$C_{A0} = y_{A0} C_{T0}$$

$$A + 2B \rightleftharpoons C$$

Mole Balance

① Write mole balance on each species.†

$$\text{e.g.,}\quad \frac{dF_A}{dV} = r_A,\quad \frac{dF_B}{dV} = r_B,\quad \frac{dF_C}{dV} = r_C$$

Rate Law

② Write rate law in terms of concentration.

$$\text{e.g.,}\quad -r_A = k_A\left(C_A C_B^2 - \frac{C_C}{K_C}\right)$$

Relative Rates

③ Relate the rates of reaction of each species to one another.

$$\frac{-r_A}{1} = \frac{-r_B}{2} = \frac{r_C}{1}$$

$$\text{e.g.,}\quad r_B = 2r_A,\quad r_C = -r_A$$

Stoichiometry

④ **(a)** Write the concentrations in terms of molar flow rates for isothermal ***gas-phase*** reactions.

$$\text{e.g.,}\quad C_A = C_{T0}\frac{F_A}{F_T}\frac{P}{P_0},\quad C_B = C_{T0}\frac{F_B}{F_T}\frac{P}{P_0}$$

$$\text{with}\quad F_T = F_A + F_B + F_C$$

(b) For ***liquid-phase*** reactions, use concentration, e.g., C_A, C_B

Pressure Drop

⑤ Write the *gas-phase* pressure drop term in terms of molar flow rates.

$$\frac{dy}{dW} = -\frac{\alpha}{2y}\frac{F_T}{F_{T_0}},\quad \text{with}\quad y = \frac{P}{P_0}$$

Combine

⑥ Use an ODE solver or a nonlinear equation solver (e.g., Polymath) to combine Steps ① through ⑤ to solve for, for example, the profiles of molar flow rates, concentration, and pressure.

† For PBR, use $\frac{dF_A}{dW} = r_A,\ \frac{dF_B}{dW} = r_B,\ \frac{dF_C}{dW} = r_C$.

$$A + 2B \rightleftharpoons C$$

Mole Balance

① Write mole balance on each species.†

$$\text{e.g.,}\quad \frac{dF_A}{dV} = r_A,\quad \frac{dF_B}{dV} = r_B,\quad \frac{dF_C}{dV} = r_C$$

Rate Law

② Write rate law in terms of concentration.

$$\text{e.g.,}\quad -r_A = k_A\left(C_A C_B^2 - \frac{C_C}{K_C}\right)$$

Relative Rates

③ Relate the rates of reaction of each species to one another.

$$\frac{-r_A}{1} = \frac{-r_B}{2} = \frac{r_C}{1}$$

e.g., $r_B = 2r_A$, $r_C = -r_A$

Stoichiometry

④ (a) Write the concentrations in terms of molar flow rates for isothermal ($T = T_0$) *gas-phase* reactions.

$$\text{e.g.,}\quad C_A = C_{T0}\frac{F_A}{F_T}\frac{P}{P_0},\quad C_B = C_{T0}\frac{F_B}{F_T}\frac{P}{P_0}$$

with $F_T = F_A + F_B + F_C$

(b) For *liquid-phase* reactions, use concentration, e.g., C_A, C_B

Pressure Drop

⑤ Write the *gas-phase* pressure drop term in terms of molar flow rates.

$$\frac{dy}{dW} = -\frac{\alpha}{2y}\frac{F_T}{F_{T_0}}, \quad \text{with} \quad y = \frac{P}{P_0}$$

Combine

⑥ Use an ODE solver or a nonlinear equation solver (e.g., Polymath) to combine Steps ① through ⑤ to solve for, for example, the profiles of molar flow rates, concentration, and pressure.

† For a PBR, use $\frac{dF_A}{dW} = r_A$, $\frac{dF_B}{dW} = r_B$, and $\frac{dF_C}{dW} = r_C$.

Figure 6-1 Isothermal reaction design algorithm for mole balances.

Mole balance on every species

TABLE 8-1 MOLE BALANCES FOR MULTIPLE REACTIONS

General Mole Balance

$$\frac{dN_j}{dt} = F_{j0} - F_j + \int^V r_j dV$$

	Molar Quantities (Gas or Liquid)	Concentration (Liquid)
Batch		
	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A$
	$\frac{dN_B}{dt} = r_B V$	$\frac{dC_B}{dt} = r_B$
	$\vdots$	$\vdots$
PFR/PBR		
	$\frac{dF_A}{dV} = r_A$	$\frac{dC_A}{dV} = \frac{r_A}{v_0}$
	$\frac{dF_B}{dV} = r_B$	$\frac{dC_B}{dV} = \frac{r_B}{v_0}$
	$\vdots$	$\vdots$

TABLE 8-1 MOLE BALANCES FOR MULTIPLE REACTIONS (Cont'd)

CSTR	
$V = \dfrac{F_{A0} - F_A}{(-r_A)_{exit}}$	$V = \dfrac{v_0[C_{A0} - C_A]}{(-r_A)_{exit}}$
$V = \dfrac{F_{B0} - F_B}{(-r_B)_{exit}}$	$V = \dfrac{v_0[C_{B0} - C_B]}{(-r_B)_{exit}}$
$\vdots$	$\vdots$
Membrane: C diffuses out	
$\dfrac{dF_A}{dV} = r_A$	$\dfrac{dF_A}{dV} = r_A$
$\dfrac{dF_B}{dV} = r_B$	$\dfrac{dF_B}{dV} = r_B$
$\dfrac{dF_C}{dV} = r_C - R_C$	$\dfrac{dF_C}{dV} = r_C - R_C$
$\vdots$	$\vdots$
Semibatch B added to A	
$\dfrac{dN_A}{dt} = r_A V$	$\dfrac{dC_A}{dt} = r_A - \dfrac{v_0 C_A}{V}$
$\dfrac{dN_B}{dt} = F_{B0} + r_B V$	$\dfrac{dC_B}{dt} = r_B + \dfrac{v_0[C_{B0} - C_B]}{V}$
$\vdots$	$\vdots$

TABLE 8-2 MODIFICATION TO THE CRE ALGORITHM

Identify	1. Number Each and Every Reaction Separately
Mole Balance	2. Mole Balance on Each and Every Species
	3. *Rate Law* for Every Reaction

TABLE 8-2 MODIFICATION TO THE CRE ALGORITHM (Cont'd)

Rates

3. *Rate Law* for Every Reaction

e.g., $-r_{ij} = k_{ij} f\left(C_A, C_B, \ldots C_j\right)$

The subscript "*i*" refers to the reaction number and the subscript "*j*" refers to the species.

4. *Net Rates of Reaction* for Each Species, e.g., *j*

$$r_j = \sum_{i=1}^{N} r_{ij}$$

For N reactions, the net rate of formation of species A is:

$$r_A = \sum_{i=1}^{N} r_{iA} = r_{1A} + r_{2A} + \ldots$$

5. *Relative Rates* for every reaction

For a given reaction *i*: $a_i A + b_i B \rightarrow c_i C + d_i D$

$$\boxed{\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i}}$$

r_{ij}
- species
- reaction number

TABLE 8-2 MODIFICATION TO THE CRE ALGORITHM (Cont'd)

$$\boxed{\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i}}$$

The remaining steps to the algorithm in Table 6-2 remain unchanged, e.g.,

Stoichiometry

Gas Phase

$$C_j = C_{T0}\frac{F_j}{F_T}\frac{P}{P_0}\frac{T_0}{T}$$

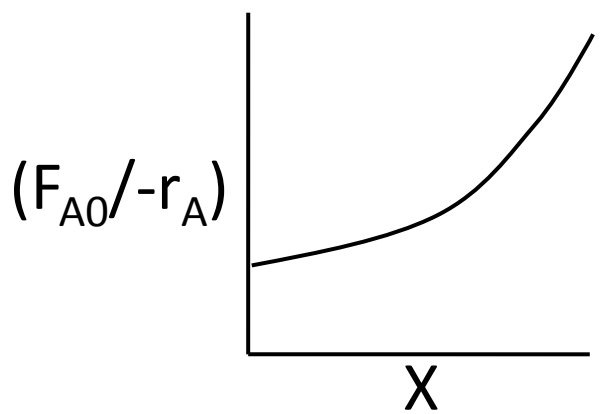
$$F_T = \sum_{j=1}^{n} F_j$$

Liquid Phase

$$C_j = \frac{F_j}{v_0}$$

For Gas Phase Flow Systems: Conversion

If $-r_A = kC_AC_B$

$$-r_A = k_A C_{A0}^2 \left[\frac{(1-X)}{(1+\varepsilon X)} \frac{\left(\Theta_B - \frac{b}{a}X\right)}{(1+\varepsilon X)} \left(\frac{P}{P_0} \frac{T_0}{T} \right)^2 \right]$$

This gives us