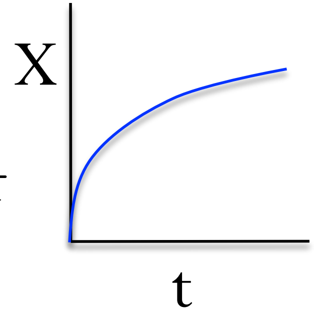
Lecture 6

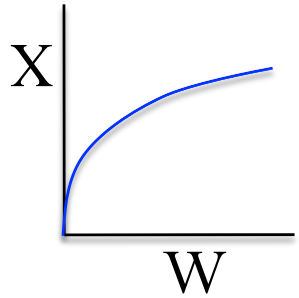
Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Previous Lectures

Reactor Mole Balances in terms of conversion

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		$V = \dfrac{F_{A0}X}{-r_A}$	
PFR	$F_{A0}\dfrac{dX}{dV} = -r_A$		$V = F_{A0}\displaystyle\int_0^X \frac{dX}{-r_A}$
PBR	$F_{A0}\dfrac{dX}{dW} = -r_A'$		$W = F_{A0}\displaystyle\int_0^X \frac{dX}{-r_A'}$





Previous Lectures

Rate Laws - Power Law Model

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

α order in A

β order in B

Overall Rection Order = $\alpha + \beta$

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

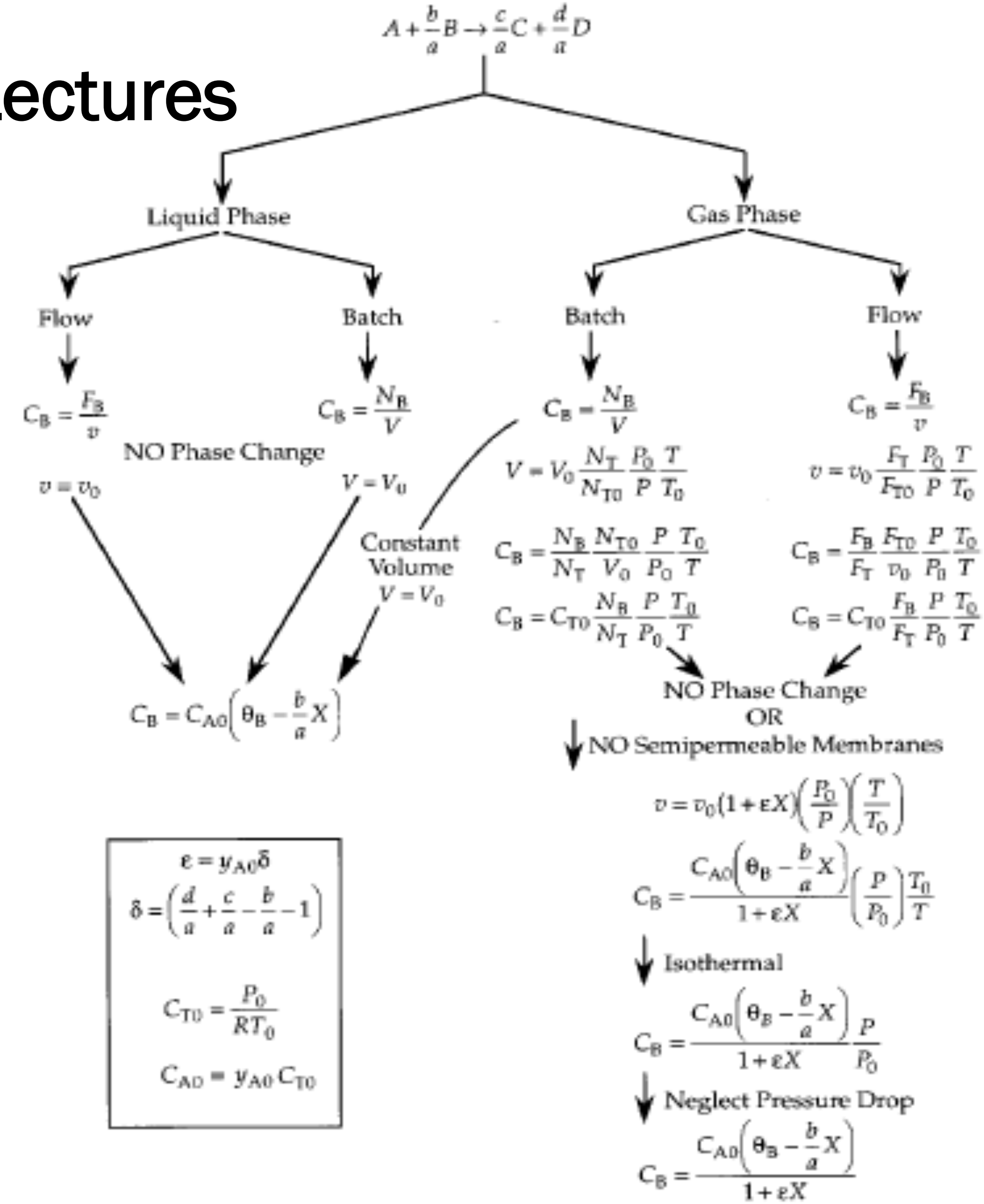
A reactor follows an elementary rate law if the reaction orders just happens to agree with the stoichiometric coefficients for the reaction as written.

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

Previous Lectures



Previous Lectures

Le Catalìste Flambé

344 Champs Elysées

Menu à 220FF

Appetizer	**Mole Balance**
Pate de Canard (supplément 15FF)	***Batch Reactor***
Coquilles Saint-Jacques	***CSTR***
Potage Crème de Cresson	***PFR/PBR***
Escargots à La Bourguignonne (supplement 15FF)	***Semibatch Reactor***
Entrée	**Rate Law**
Cassoulet	***Power Law (e.g.)***
Ragnons de Veau	***1st Order***
Coq au Vin	***2nd Order***
Boeuf à la provençale	***Non-Integer Order***
(Tous nos plats sont garnis)	
Dessert	**Stoichiometry**
Brie ou Crème Anglaise	***Gas or Liquid***
	Combine
1/2 bouteille de vin blanc ou vin rouge	***Mix together and digest with 1/2 bouteille of POLYMATH***

Service Compris

Previous Lectures

Choices

1. MOLE BALANCES

PFR	CSTR	BATCH
$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$	$V = \frac{F_{A0}X}{-r_A}$	$\frac{dX}{dt} = \frac{-r_A V}{N_{A0}}$

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

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

LIQUID Constant flow rate	IDEAL GAS Variable flow rate	IDEAL GAS Variable volume	LIQUID OR GAS 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

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

Today's lecture

- Block 1: Mole Balances
- Block 2: Rate Laws
- Block 3: Stoichiometry
- **Block 4: Combine**

Today's lecture

- Examples:

Liquid Phase ChE 460 Laboratory Experiment

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

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

Entering

Volumetric flow rate	$v_0 = 0.0033\ dm^3/s$
Acetic Anhydride	7.8% (1M)
Water	92.2% (51.2M)
Elementary with k'	$1.95x10^{-4}\ dm^3/(mol.s)$

Case I	CSTR	$V = 1dm^3$
Case II	PFR	$V = 0.311\ dm^3$

Today's lecture

- 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 $k = 0.29\ dm^3/(mol.s)$

Case I PFR with $v_0 = 10$ dm3/s

Find space time, τ with $X = 0.9$

Find reactor volume, V for $X = 0.9$

Case II Batch constant volume

Find the time, t, necessary to achieve 90% conversion. Compare τ and t.

Lecture 6

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 (Chapter 2 plots)

   B. Numerical (Quadrature Formulas Chapter 2 and appendices)

   C. Analytical (Integral Tables in Appendix)

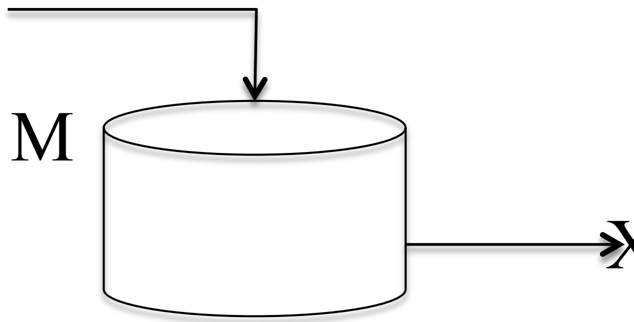
   D. Software Packages (Appendix- Polymath)

CSTR Laboratory Experiment

Example: $CH_3CO_2 + H_20 \rightarrow 2CH_3OOH$

$C_{A0} = 1M$

$C_{B0} = 51.2\ M$



$X = ?$

$$V = 1\ dm^3$$

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

$A + B \rightarrow 2C$

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

CSTR Laboratory Experiment

1) Rate Law:

$$-r_A = k_A C_A C_B$$

1) 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	$2F_{A0}X$	$F_C=2F_{A0}X$

CSTR Laboratory Experiment

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

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

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

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

CSTR Laboratory Experiment

$$-r_A = \underbrace{k'C_{B0}}_{k} C_{A0}(1-X) = kC_{A0}(1-X)$$

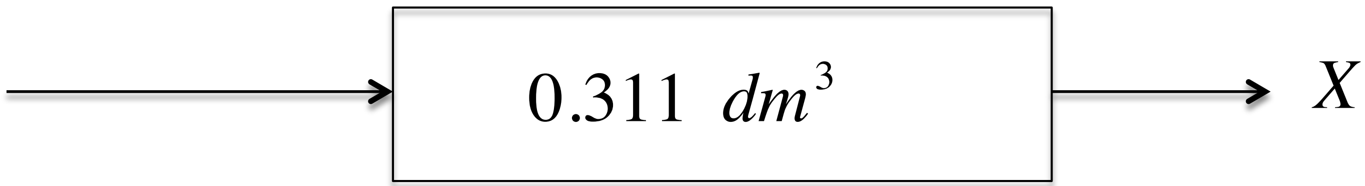
$$V = \frac{\upsilon_0 k C_{A0} X}{C_{A0}(1-X)} \Rightarrow \frac{V}{\upsilon_0} = \frac{kX}{(1-X)} \Rightarrow \tau = \frac{V}{\upsilon_0} = \frac{kX}{(1-X)}$$

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

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

PFR Laboratory Experiment

$A + B \rightarrow 2C$



1) Mole Balance:

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

2) Rate Law:

$$-r_A = kC_A C_B$$

3) Stoichiometry:

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

$$C_B \cong C_{B0}$$

PFR Laboratory Experiment

4) Combine: $-r_A = k'C_{B0}C_{A0}(1-X) = kC_{A0}(1-X)$

$$\frac{dX}{dV} = \frac{kC_{A0}(1-X)}{C_{A0}\upsilon_0}$$

$$\frac{dX}{(1-X)} = \frac{k}{\upsilon_0}dV = kd\tau$$

$$\ln\frac{1}{1-X} = k\tau$$

$$X = 1 - e^{-k\tau}$$

$$\tau = 94\ \text{sec} \qquad k = 0.01\ s^{-1}$$

$$\boxed{X = 0.61}$$

Example (Gas Flow, PFR)

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

$2A \rightarrow 2B + C$

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

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

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

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

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

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

4) Combine:

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

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

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

Example (Gas Flow, PFR)

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

$$\varepsilon = y_{A0}\delta = (1)\left(\frac{1}{2}\right) = \frac{1}{2}$$

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

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

$$V = V_0\tau = 2940\,\mathrm{L}$$

Gas Phase 2A → 2B + C

Example Constant Volume (Batch)

1) Mole Balance:

$$\frac{dX}{dt} = \frac{-r_A V_0}{N_{A0}} = \frac{-r_A}{N_{A0}/V_0} = \frac{-r_A}{C_{A0}}$$

2) Rate Law:

$$-r_A = kC_A^2$$

3) Stoich: Gas

$$V = V_0 \qquad \upsilon = \upsilon_0 \qquad \tau = \frac{V}{\upsilon}$$

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

$$-r_A = kC_{A0}^2(1-X)^2$$

Example Constant Volume (Batch)

4) Combine:

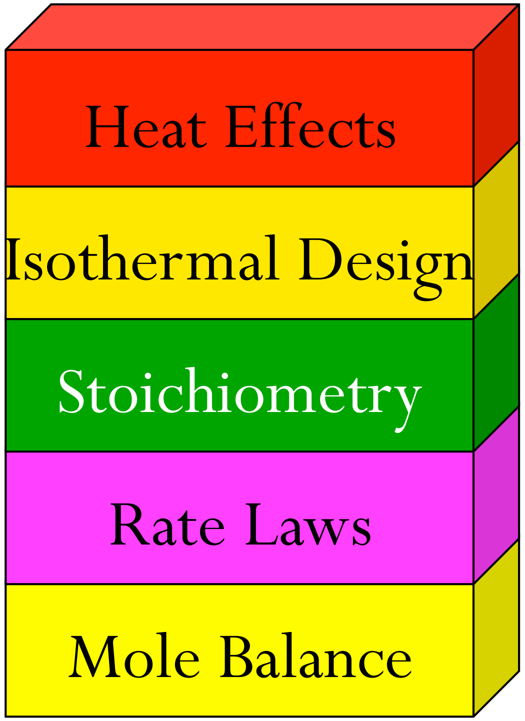
$$\frac{dX}{dt} = \frac{kC_{A0}^2(1-X)^2}{C_{A0}} = kC_{A0}(1-X)^2$$

$$\frac{dX}{d\tau} = kC_{A0}(1-X)^2$$

$$\frac{dX}{(1-X)^2} = kC_{A0}dt$$

$$\frac{1}{1-X} = kC_{A0}t$$

$$\boxed{t = 155\text{ sec}}$$


Heat Effects
Isothermal Design
Stoichiometry
Rate Laws
Mole Balance

End of Lecture 6