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.

Lecture 6 – Tuesday 1/29/2013

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

Review of Blocks 1, 2 and 3
Examples : Undergraduate Reactor Experiments
CSTR
PFR
BR

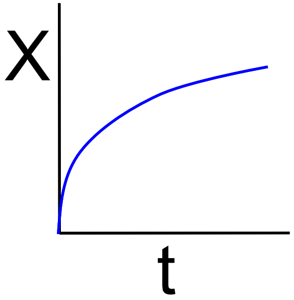
Gas Phase Reaction with Change in the Total Number of Moles

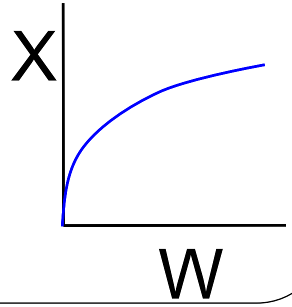
Review Lecture 2

Building Block 1: Mole Balances

in terms of conversion, X

Reactor	**Differential**	**Algebraic**	**Integral**
Batch	$N_{A0}\frac{dX}{dt}=-r_AV$		$t=N_{A0}\int_0^X\frac{dX}{-r_AV}$
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	$F_{A0}\frac{dX}{dW}=-r'_A$		$W=F_{A0}\int_0^X\frac{dX}{-r'_A}$





Review Lecture 3

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 $= \alpha + \beta$

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

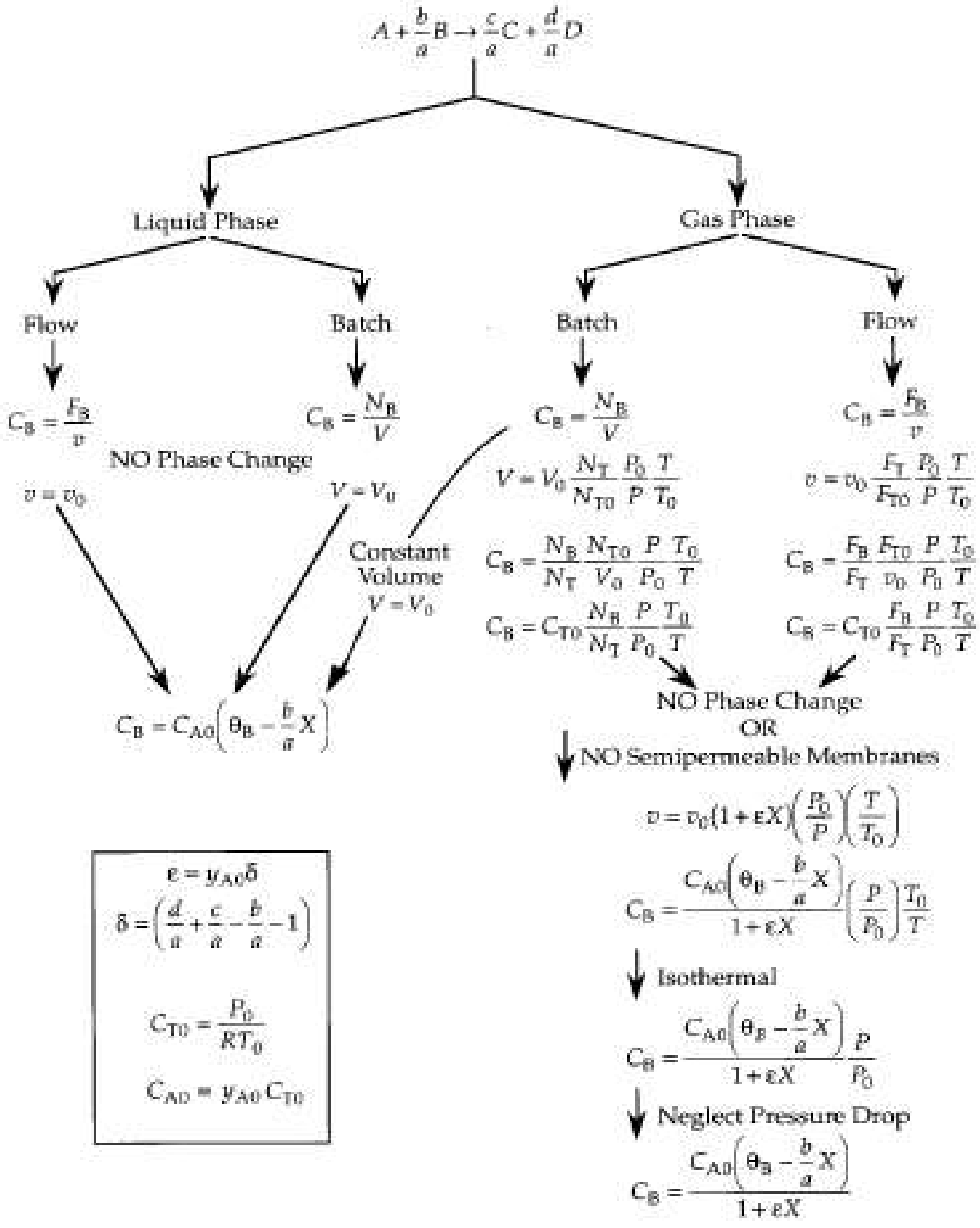
A reactor follows an elementary rate law if the reaction orders just happens to agree with the stoichiometric coefficients for the reaction as written.

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

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

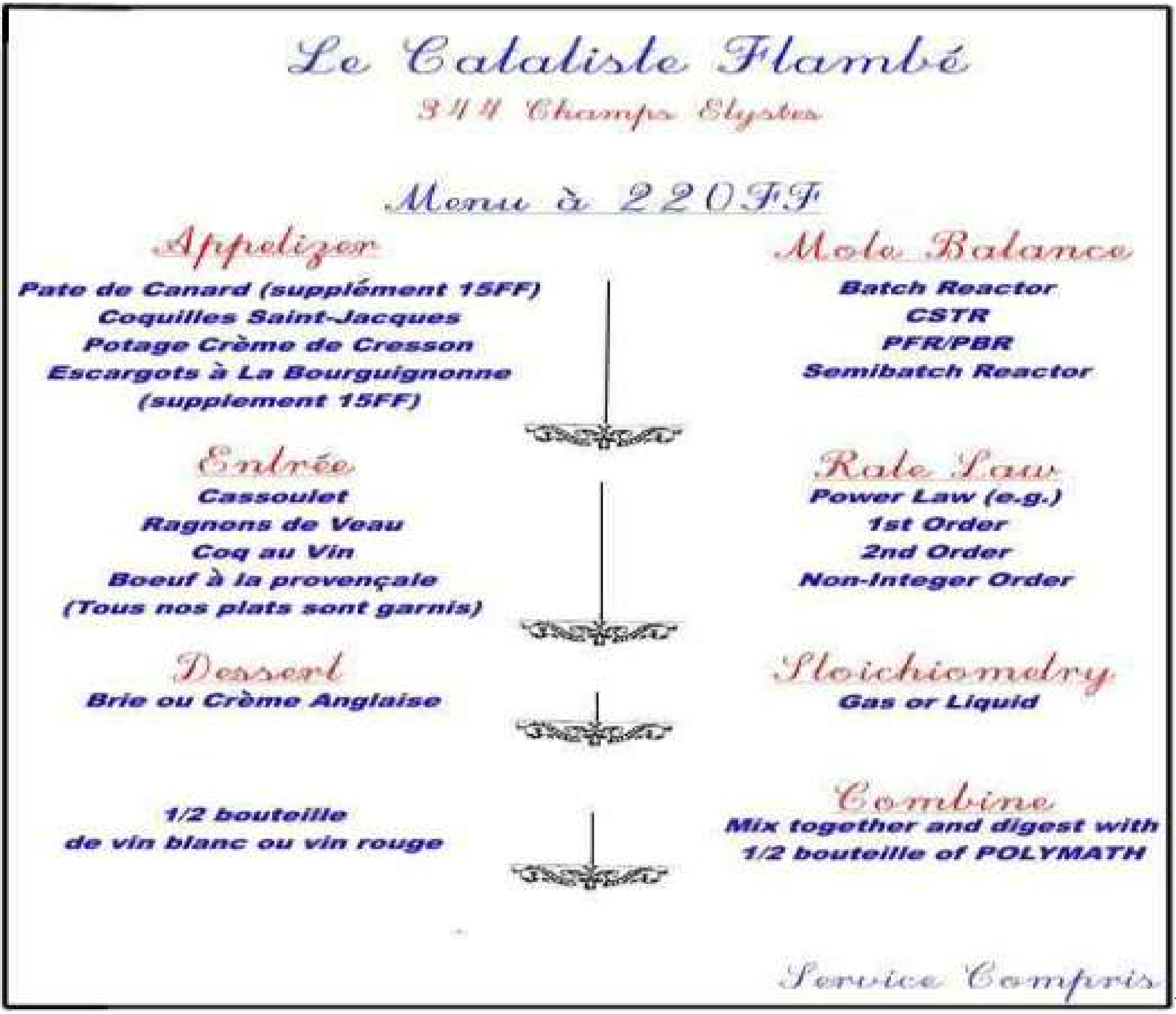
2nd order in A, 1st order in B, overall third order

Building Block 3:
Stoichiometry



Review Lecture 5

Building Block 4: Combine



Le Cataliste Flambé
344 Champs Elysées

Menu à 220FF

Appetizer

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

Mole Balance

Batch Reactor
CSTR
PFR/PBR
Semibatch Reactor

Entrée

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

Rate Law

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

Dessert

Brie ou Crème Anglaise

Stoichiometry

Gas or Liquid

1/2 bouteille
de vin blanc ou vin rouge

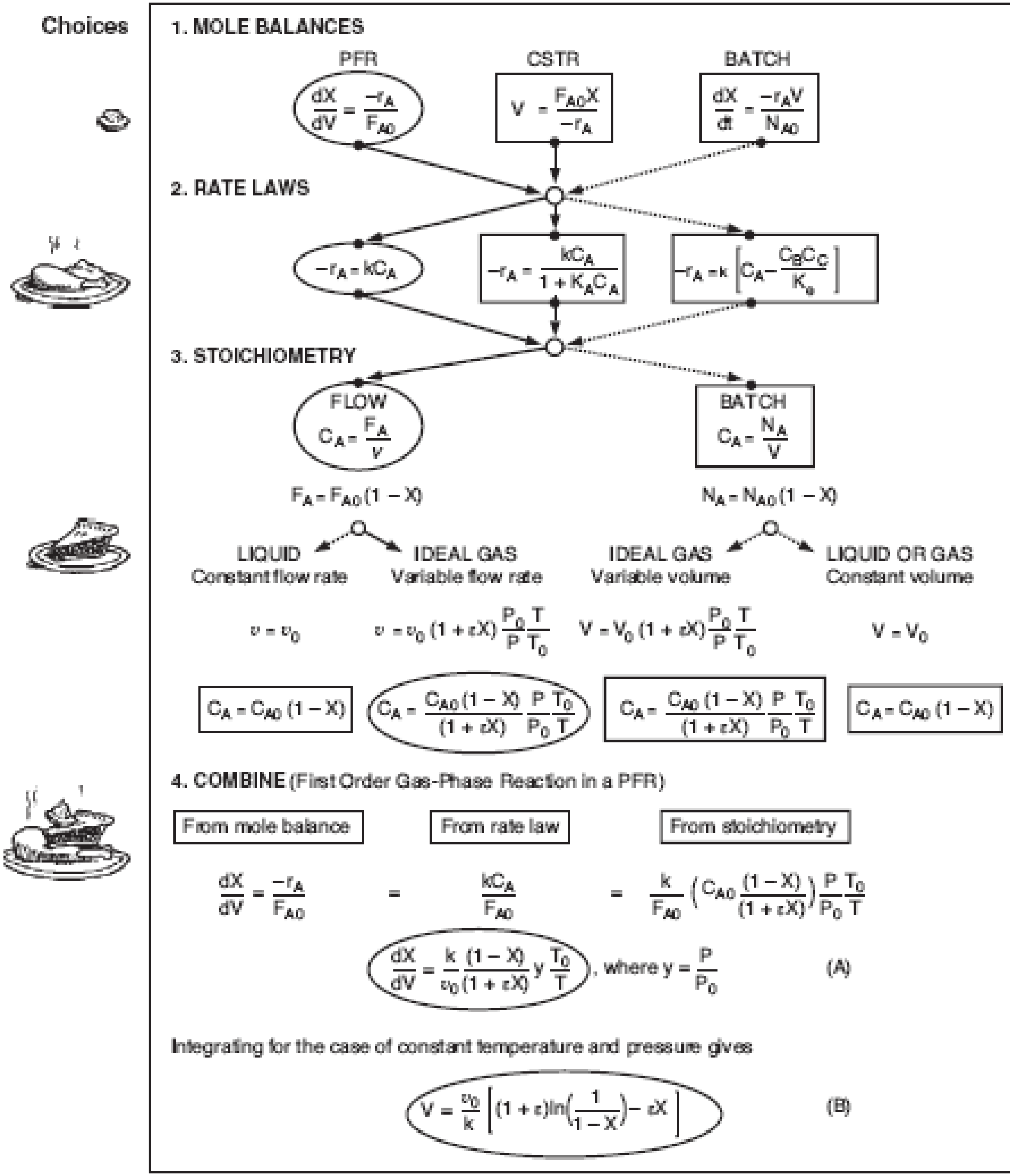
Combine

Mix together and digest with
1/2 bouteille of POLYMATH

Service Compris

Review Lecture 5

Building Block 4: Combine



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 $C_A = \frac{F_A}{\upsilon}$

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

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

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

LIQUID
Constant flow rate

$\upsilon = \upsilon_0$

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

IDEAL GAS
Variable flow rate

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

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

IDEAL GAS
Variable volume

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

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

LIQUID OR GAS
Constant volume

$V = V_0$

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

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

From mole balance | From rate law | From stoichiometry

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

$$\frac{dX}{dV} = \frac{k}{\upsilon_0}\frac{(1 - X)}{(1 + \varepsilon X)}\, y \,\frac{T_0}{T}, \text{ where } y = \frac{P}{P_0} \qquad \text{(A)}$$

Integrating for the case of constant temperature and pressure gives

$$V = \frac{\upsilon_0}{k}\left[(1 + \varepsilon)\ln\left(\frac{1}{1 - X}\right) - \varepsilon X\right] \qquad \text{(B)}$$

Today’s lecture

- Example for Liquid Phase Undergraduate Laboratory Experiment

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

$$A + B \rightarrow 2C$$

Entering

Volumetric flow rate	$v_0 = 0.0033\ dm^3/s$
Acetic Anhydride	7.8% (1M)
Water	92.2% (51.2M)
Elementary with k’	$1.95\times10^{-4}\ dm^3/(mol.s)$

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

Today's lecture

- Example for 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.

Part 1: Mole Balances in terms of Conversion

Algorithm for Isothermal Reactor Design

1. **Mole Balances** and Design Equation
2. Rate Laws
3. Stoichiometry
4. Combine
5. Evaluate

    A. Graphically (Chapter 2 plots)

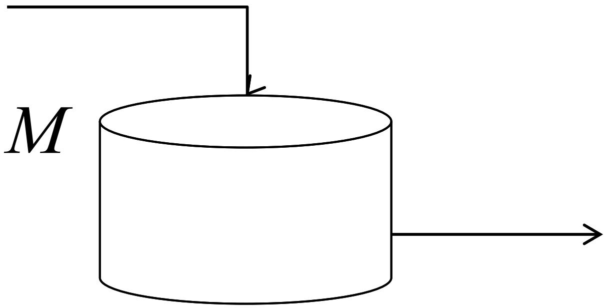
    B. Numerical (Quadrature Formulas Chapter 2 and appendices)

    C. Analytical (Integral Tables in Appendix)

    D. Software Packages (Appendix- Polymath)

CSTR Laboratory Experiment

Example: $CH_3CO_2 + H_20 \rightarrow 2CH_3OOH$



$C_{A0} = 1M$

$C_{B0} = 51.2\ M$

$X = ?$

$V = 1\ \ dm^3$

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

$A + B \rightarrow 2C$

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

CSTR Laboratory Experiment

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

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

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

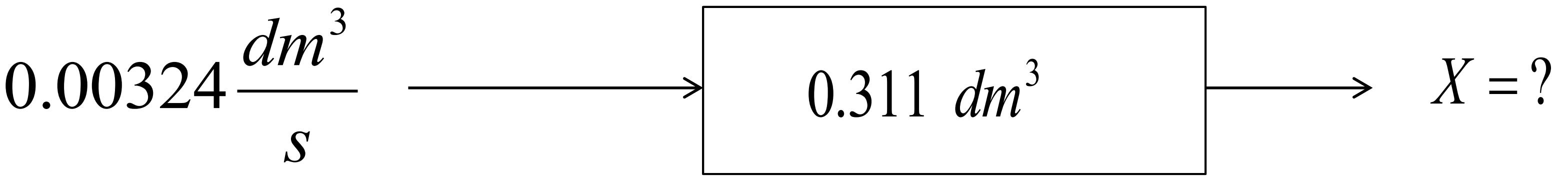
$$V = \frac{\upsilon_0 k C_{A0} X}{C_{A0}(1-X)} \Rightarrow \frac{V}{\upsilon_0} = \frac{kX}{(1-X)} \Rightarrow \tau = \frac{V}{\upsilon_0} = \frac{kX}{(1-X)}$$

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

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

PFR Laboratory Experiment

A + B → 2C



$0.00324 \frac{dm^3}{s}$

$0.311\ dm^3$

$X = ?$

1) Mole Balance:

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

2) Rate Law:

$$-r_A = kC_AC_B$$

3) Stoichiometry:

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

$$C_B \cong C_{B0}$$

PFR Laboratory Experiment

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

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

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

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

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

$$\tau = \frac{V}{\upsilon_0} = \frac{0.311 dm^3}{0.00324\, dm^3 / \sec} = 96.0 \sec \qquad k = 0.01\, s^{-1}$$

$$\boxed{X = 0.61}$$

Gas Flow PFR Example

2 NOCl → 2 NO + Cl_2

2A → 2B + C

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

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

1) Mole Balance:

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

2) Rate Law:

$$-r_A = kC_A^2$$

Gas Flow PFR Example

3) Stoichiometry:
(Gas Flow)

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

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

A → B + ½C

4) Combine:

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

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

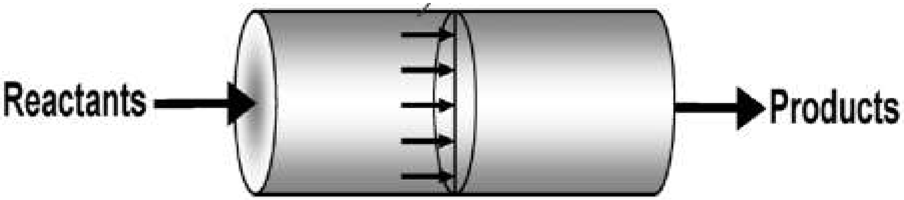
$$\Rightarrow \int_0^X \frac{(1 + \varepsilon X)^2}{(1 - X)^2} dX = \int_0^V \frac{kC_{A0}}{\upsilon_0} dV = \frac{kC_{A0} V}{\upsilon_0} = \overbrace{kC_{A0}\tau}^{Da}$$

Gas Flow PFR Example

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

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

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



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

$$\boxed{V = V_0\tau = 2940\ L}$$

Constant Volume Batch Example

Gas Phase 2A → 2B + C   t=?

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) Stoichiometry: $$V=V_0$$

(Gas Flow)

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

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

Constant Volume Batch Example

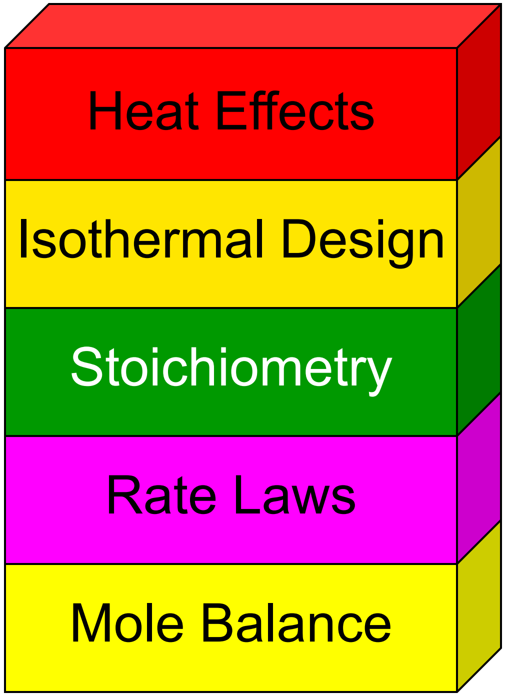
4) Combine: $$\frac{dX}{dt}=\frac{kC_{A0}^{2}(1-X)^{2}}{C_{A0}}=kC_{A0}(1-X)^{2}$$

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

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

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

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



Heat Effects

Isothermal Design

Stoichiometry

Rate Laws

Mole Balance

End of Lecture 6