# 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

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

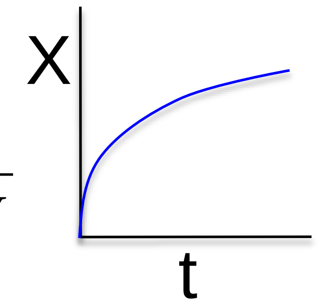
**Review of Blocks 1, 2 and 3**
**Examples : Undergraduate Reactor Experiments**
**CSTR**
**PFR**
**BR**
**Gas Phase Reaction with Change in the Total Number of Moles**

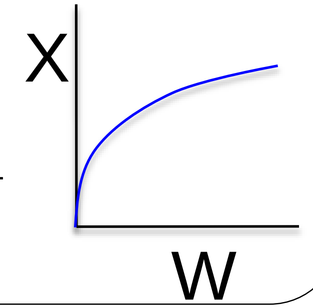
Review Lecture 2

# Building Block 1: Mole Balances

in terms of conversion, X

| Reactor | Differential | Algebraic | Integral |
|---|---|---|---|
| Batch | $N_{A0}\dfrac{dX}{dt} = -r_A V$ | | $t = N_{A0}\displaystyle\int_0^X \dfrac{dX}{-r_A V}$ |
| 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 | $F_{A0}\dfrac{dX}{dW} = -r'_A$ | | $W = F_{A0}\displaystyle\int_0^X \dfrac{dX}{-r'_A}$ |




# Building Block 2: Rate Laws

## Power Law Model:

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

$\alpha$ order in A

$\beta$ 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

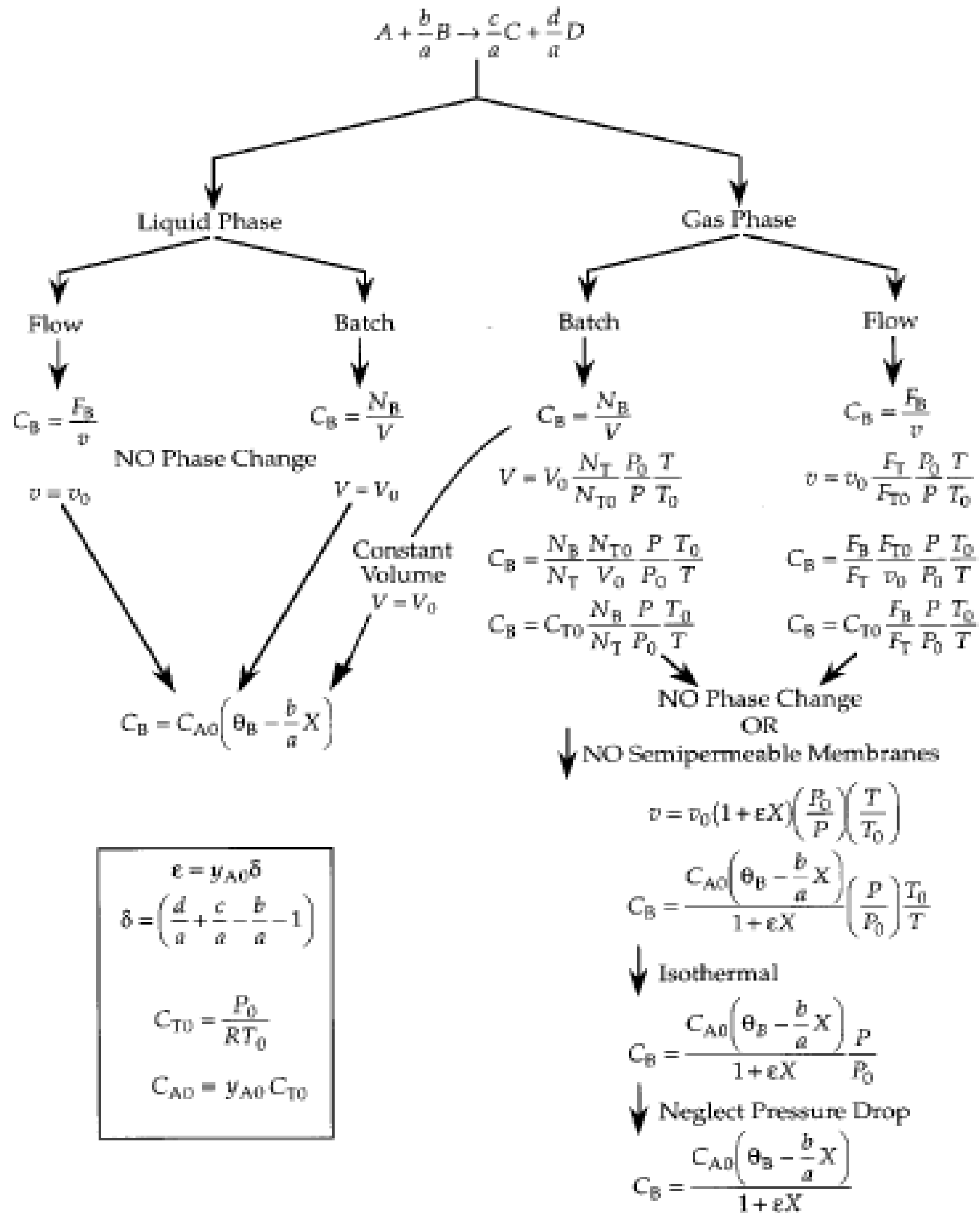
$$-r_A = k_A C_A^2 C_B$$

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

Review Lecture 4

# Building Block 3:

# Stoichiometry



# Building Block 4: Combine

## Le Catalyste Flambé

344 Champs Elysées

### Menu à 220FF

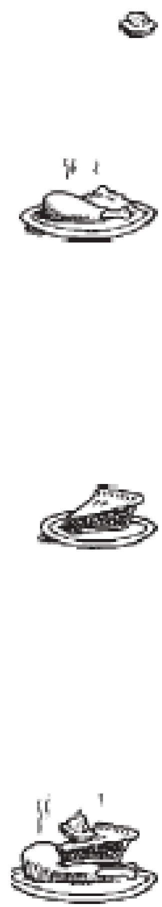
| | |
|---|---|
| **Appetizer** | **Mole Balance** |
| Pate de Canard (supplément 15FF)<br>Coquilles Saint-Jacques<br>Potage Crème de Cresson<br>Escargots à La Bourguignonne<br>(supplement 15FF) | Batch Reactor<br>CSTR<br>PFR/PBR<br>Semibatch Reactor |
| **Entrée** | **Rate Law** |
| Cassoulet<br>Ragnons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

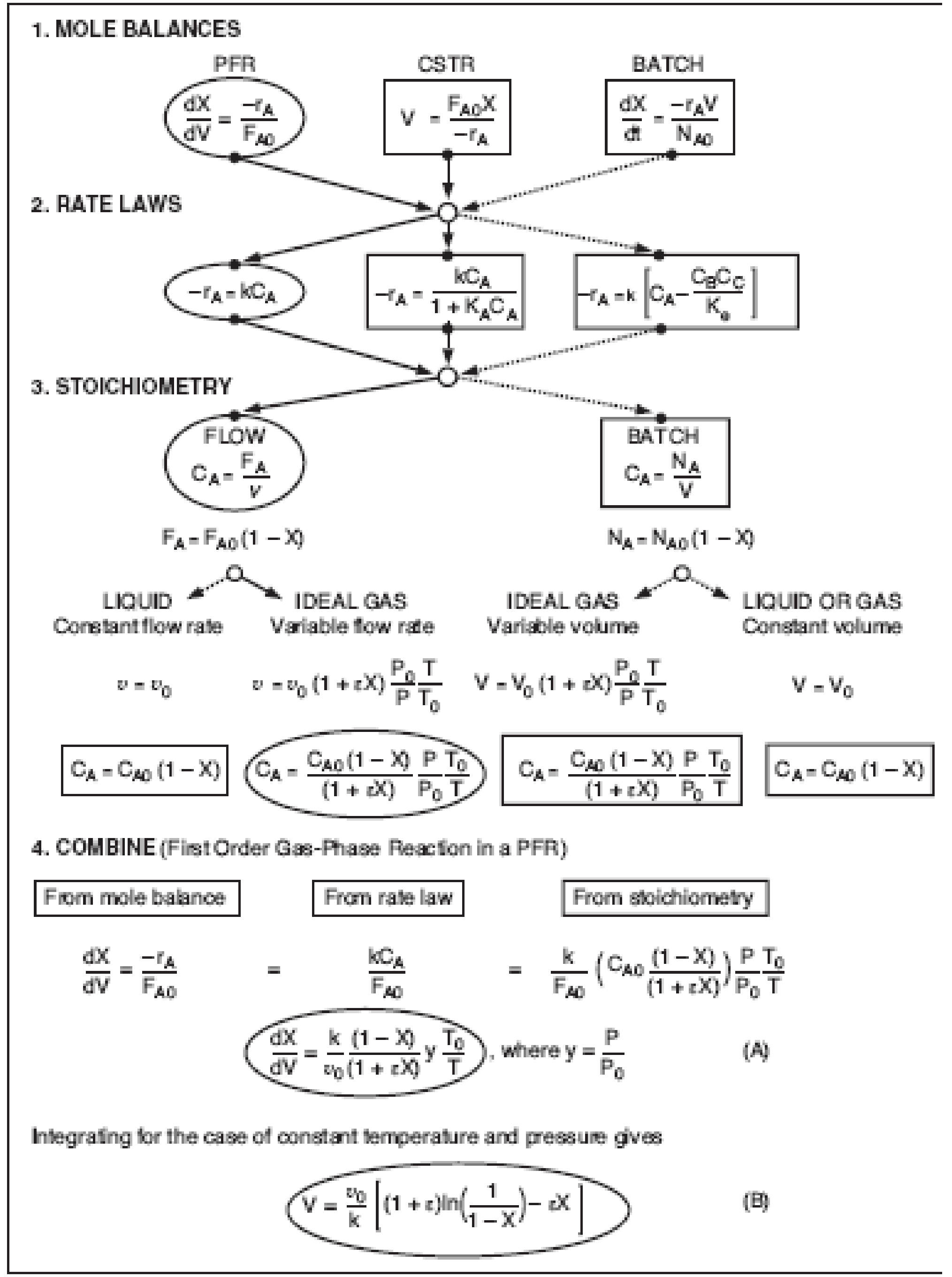
Service Compris

# Review Lecture 5

# Building Block 4: Combine

Choices





# 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' | | $1.95 \times 10^{-4}\ dm^3/(mol.s)$ |
| Case I | CSTR | $V = 1 dm^3$ |
| 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, $\tau$ 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 $\tau$ 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)

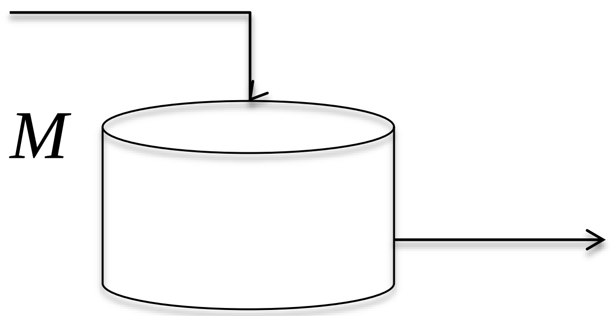
   D. Software Packages (Appendix- Polymath)

# 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 → 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

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

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

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

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

# PFR Laboratory Experiment

A + B → 2C

$$0.00324\frac{dm^3}{s} \longrightarrow \boxed{0.311\ dm^3} \longrightarrow X = ?$$

**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)

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

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

A → B + ½C

4) Combine:

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

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

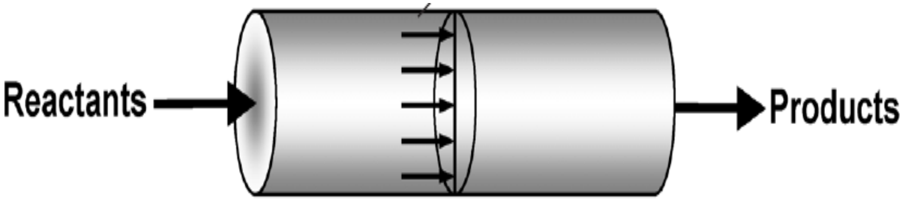
$$\Rightarrow \int_0^X \frac{\left(1 + \varepsilon X\right)^2}{\left(1 - X\right)^2} dX = \int_0^V \frac{kC_{A0}}{\upsilon_0} dV = \frac{kC_{A0}V}{\upsilon_0} = \overbrace{kC_{A0}\tau}^{Da}$$

# Gas Flow PFR Example

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

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

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




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

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

# 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)

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

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

# Constant Volume Batch Example

4) Combine:

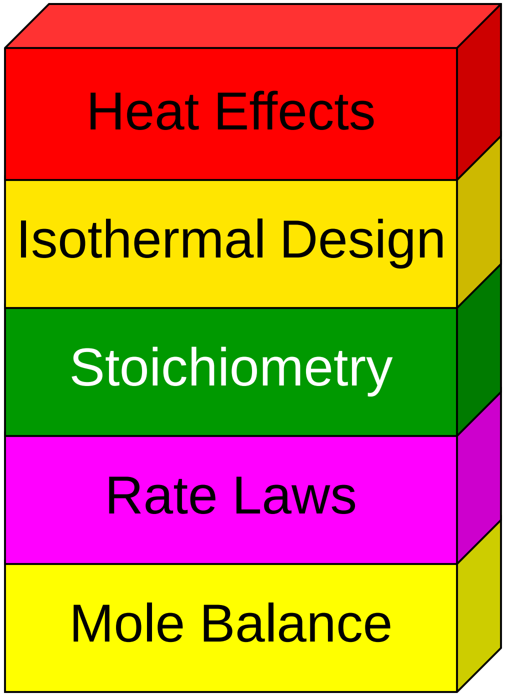
$$\frac{dX}{dt} = \frac{kC_{A0}^2(1-X)^2}{C_{A0}} = kC_{A0}(1-X)^2$$

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

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

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

$$\boxed{t = 155\,\mathrm{sec}}$$


Heat Effects
Isothermal Design
Stoichiometry
Rate Laws
Mole Balance

# End of Lecture 6