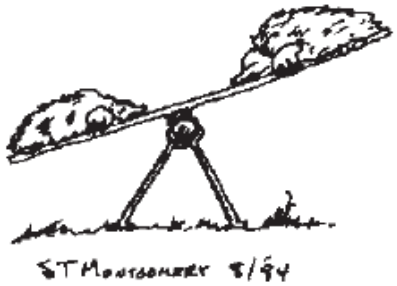
# Lecture 1

**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 1

- Introduction
- Definitions
- General Mole Balance Equation
  - Batch (BR)
  - Continuously Stirred Tank Reactor (CSTR)
  - Plug Flow Reactor (PFR)
  - Packed Bed Reactor (PBR)



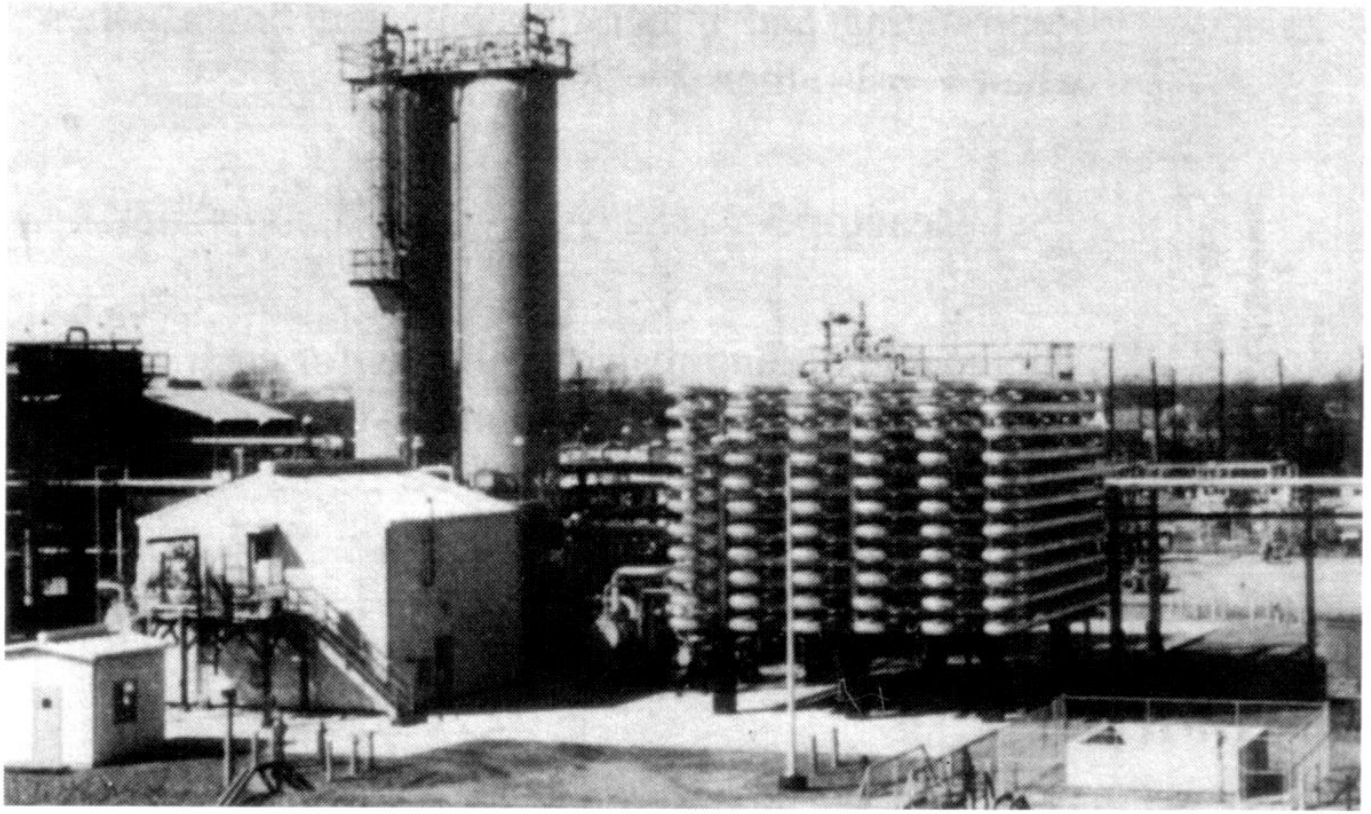
# Chemical Reaction Engineering

- *Chemical reaction engineering* is at the heart of virtually every chemical process. It separates the chemical engineer from other engineers.

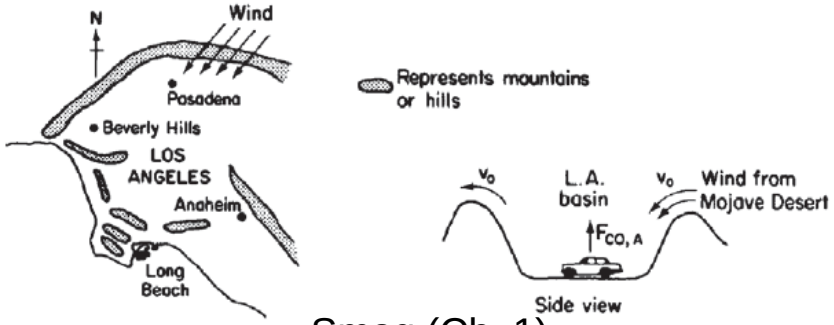
**Industries that Draw Heavily on Chemical Reaction Engineering (CRE) are:**

CPI (Chemical Process Industries)

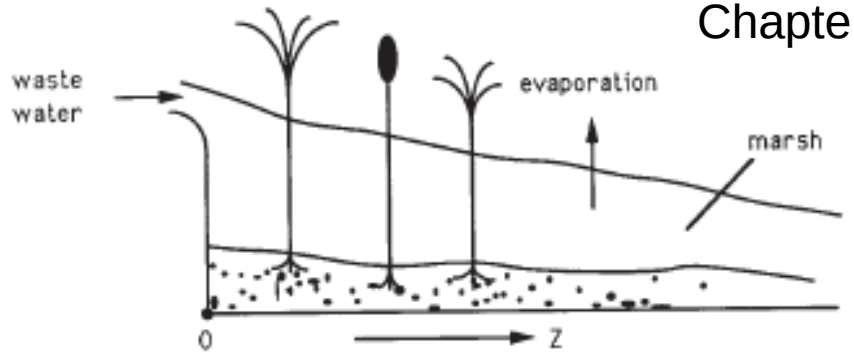
Examples like Dow, DuPont, Amoco, Chevron



Dimersol G (an organometallic catalyst) unit (two CSTRs and one tubular reactor in series) to dimerize propylene into isohexanes. Institut Français du Pétrole process. [Photo courtesy of Editions Technip (Institut Français du Pétrole).]

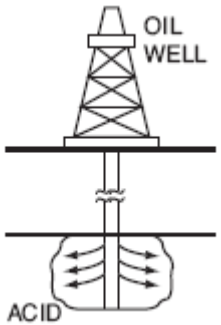



Smog (Ch. 1)




Wetlands (Ch. 7 DVD-ROM)

Hippo Digestion (Ch. 2)




Oil Recovery (Ch. 7)

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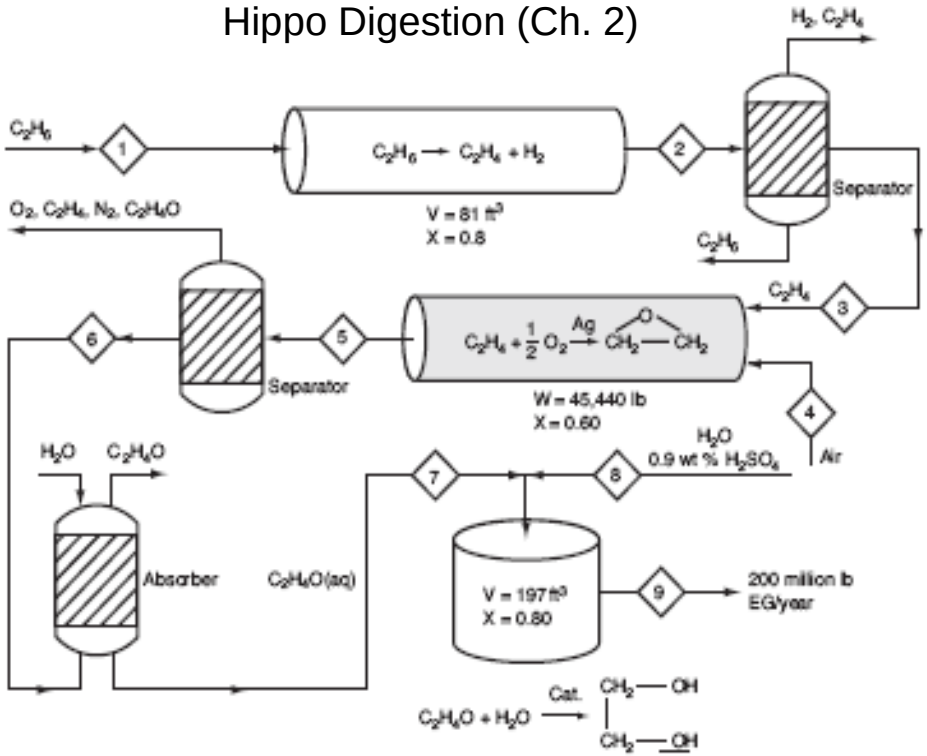
Pharmacokinetics of Cobra Bites Multiple Reactions in a Batch (Body) Reactor

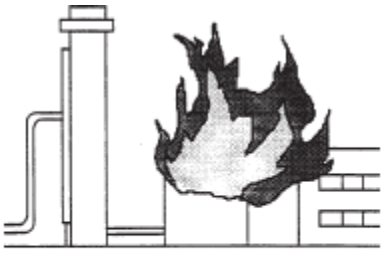
Cobra Bites (Ch. 8 DVD-ROM)




Chemical Plant for Ethylene Glycol (Ch. 5)


Effective Lubricant Design Scavenging Free Radicals

Lubricant Design (Ch. 9)



Nitroanaline Plant Explosion Exothermic Reactions That Run Away

Plant Safety (Ch. 11,12,13)

# Materials on the Web and CD-ROM

http://www.umich.edu/~elements/6e

# 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.

# Chemical Identity

- A chemical species is said to have reacted when it has lost its chemical identity.
- The identity of a chemical species is determined by the *kind*, *number*, and *configuration* of that species' atoms.

# Chemical Identity

- A chemical species is said to have reacted when it has lost its chemical identity.
- There are three ways for a species to loose its identity:

1. **Decomposition** $CH_3CH_3 \rightarrow H_2 + H_2C{=}CH_2$
2. **Combination** $N_2 + O_2 \rightarrow 2\ NO$
3. **Isomerization** $C_2H_5CH{=}CH_2 \rightarrow CH_2{=}C(CH_3)_2$

# Reaction Rate

- The reaction rate is the rate at which a species looses its chemical identity per unit volume.

- The rate of a reaction (mol/dm$^3$/s) can be expressed as either:
  - The rate of Disappearance of reactant: $-\mathbf{r_A}$

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

# Reaction Rate

Consider the isomerization

$$A \rightarrow B$$

**$r_A$ = the rate of formation of species A per unit volume**

**$-r_A$ = the rate of a disappearance of species A per unit volume**

**$r_B$ = the rate of formation of species B per unit volume**

# Reaction Rate

EXAMPLE: **A→B**

If Species B is being formed at a rate of 0.2 moles per decimeter cubed per second, i.e.,

**$r_B$ = 0.2 mole/dm$^3$/s**

**Then A is disappearing at the same rate:**

**$-r_A$= 0.2 mole/dm$^3$/s**

**The rate of formation (generation of A) is:**

**$r_A$= -0.2 mole/dm$^3$/s**

# Reaction Rate

- For a catalytic reaction we refer to $-r_A'$ , which is the rate of disappearance of species A on a per mass of catalyst basis. (mol/gcat/s)

**NOTE**: $dC_A/dt$ is not the rate of reaction

# Reaction Rate

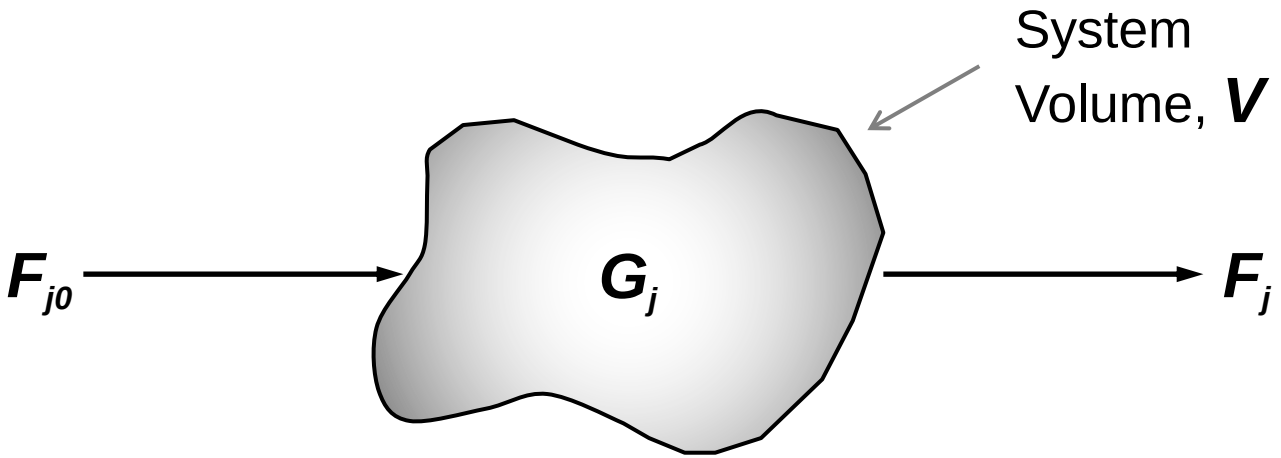
Consider species j:

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

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


# Building Block 1:

# General Mole Balances




$$\begin{bmatrix}\text{Molar Flow}\\ \text{Rate of}\\ \text{Species } j \text{ in}\end{bmatrix} - \begin{bmatrix}\text{Molar Flow}\\ \text{Rate of}\\ \text{Species } j \text{ out}\end{bmatrix} + \begin{bmatrix}\text{Molar Rate}\\ \text{Generation}\\ \text{of Species } j\end{bmatrix} = \begin{bmatrix}\text{Molar Rate}\\ \text{Accumulation}\\ \text{of Species } j\end{bmatrix}$$

$$F_{j0} - F_j + G_j = \frac{dN_j}{dt}$$

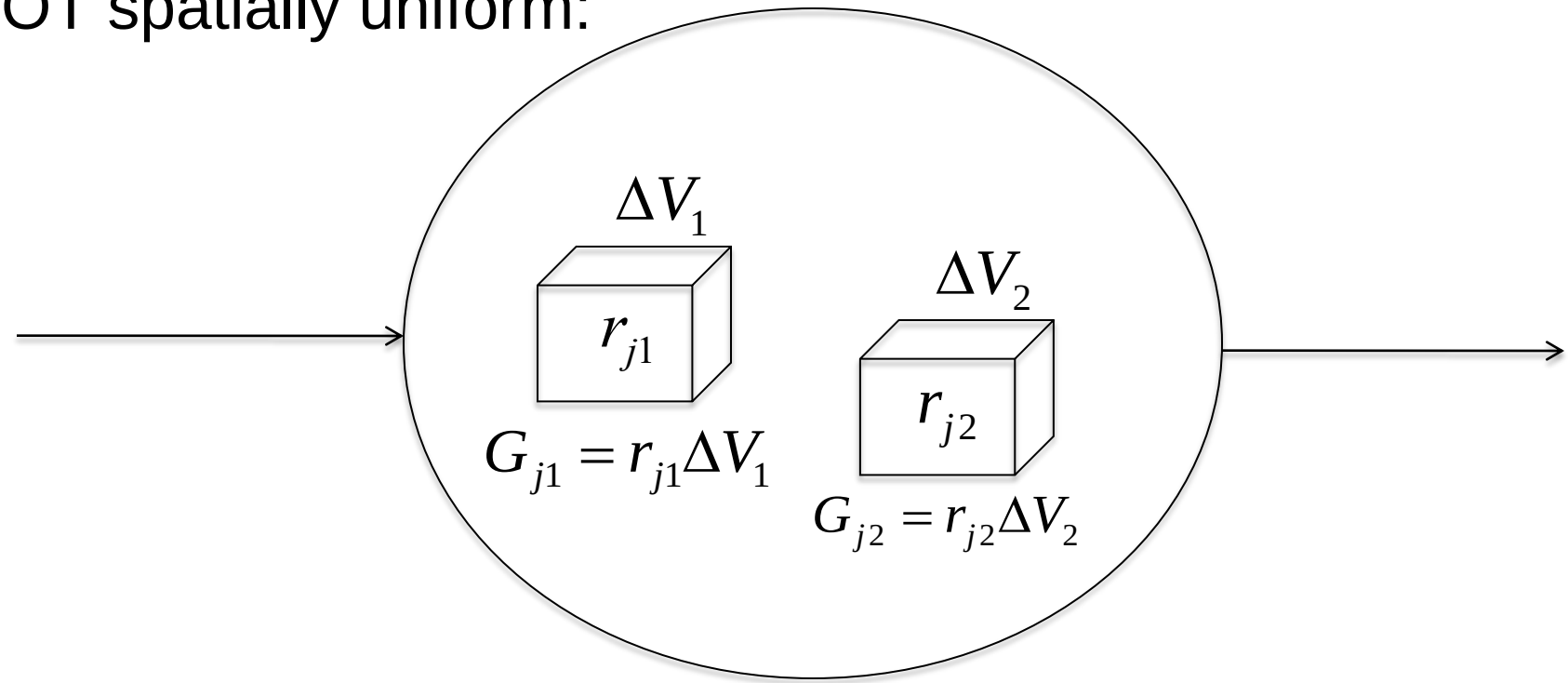
$$\left(\frac{\text{mole}}{\text{time}}\right) - \left(\frac{\text{mole}}{\text{time}}\right) + \left(\frac{\text{mole}}{\text{time}}\right) = \left(\frac{\text{mole}}{\text{time}}\right)$$


# Building Block 1:
# General Mole Balances

If spatially uniform:

$$G_j = r_j V$$

If NOT spatially uniform:




# Building Block 1:

# General Mole Balances

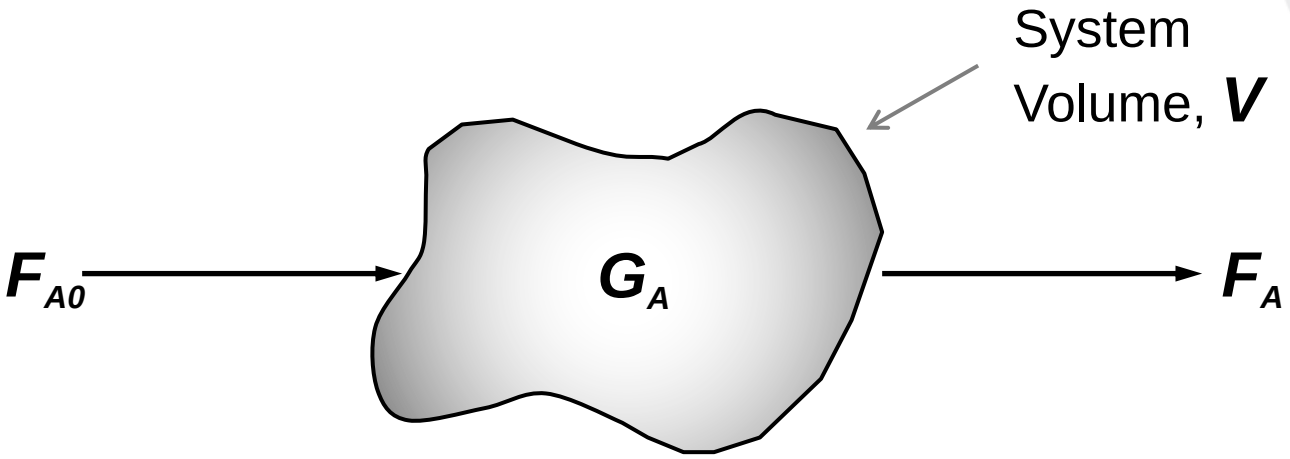
$$G_j = \sum_{i=1}^{n} r_{ji} \Delta V_i$$

Take limit

$$G_j = \sum_{i=1}^{n} r_{ji} \Delta V_i \quad \lim_{\Delta V \to 0 \;\; n \to \infty} = \int r_j dV$$


# Building Block 1:

# General Mole Balances



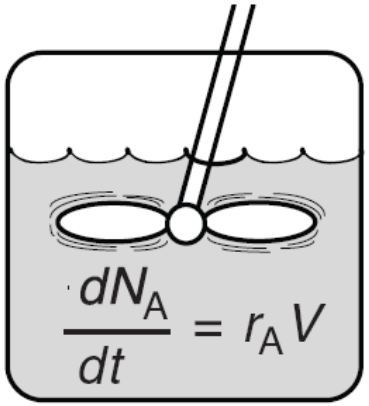

General Mole Balance on System Volume V

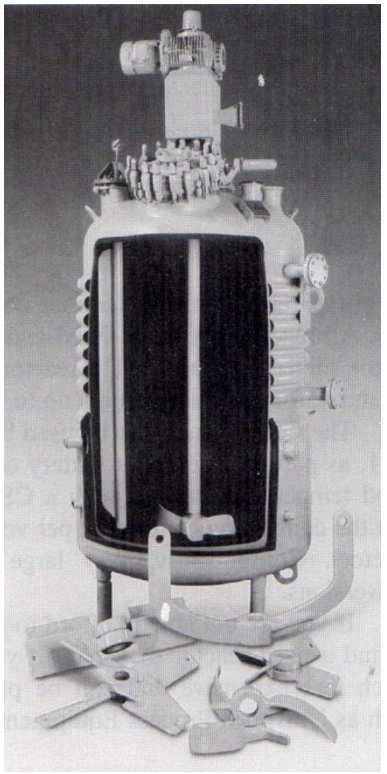
$$In - Out + Generation = Accumulation$$

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

# Batch Reactor - Mole Balances

## Batch



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

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

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

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

# Batch Reactor - Mole Balances

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

when $t = 0 \quad N_A = N_{A0}$

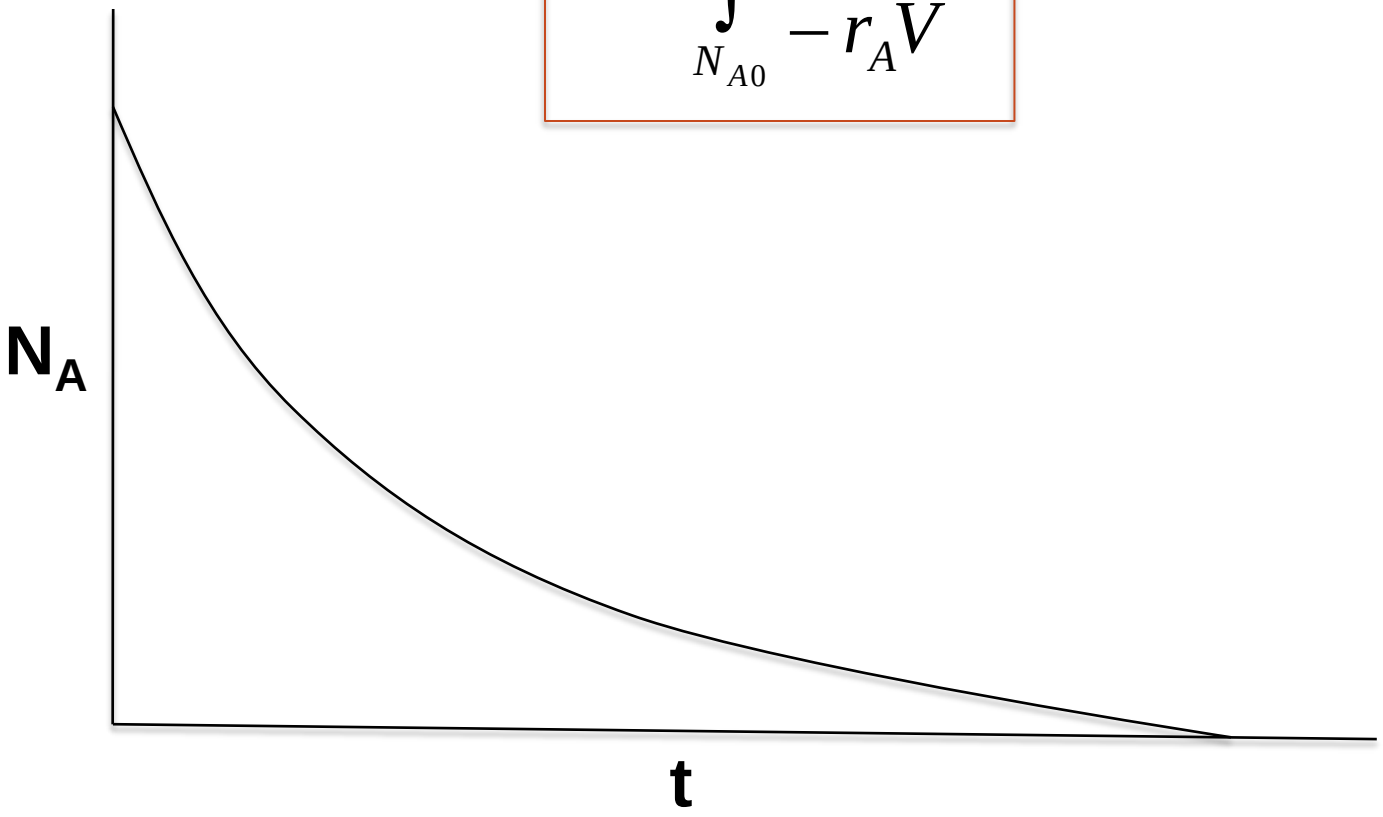
$t = t \quad N_A = N_A$

$$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{-r_A V}$$

Time necessary to reduce the number of moles of A from $N_{A0}$ to $N_A$.

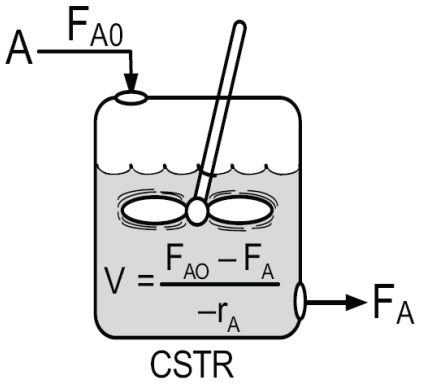
# Batch Reactor - Mole Balances

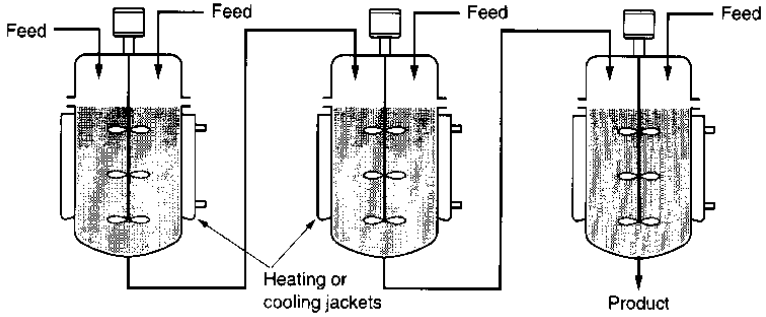
$$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{-r_A V}$$



# CSTR - Mole Balances

CSTR




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

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

# CSTR - Mole Balances

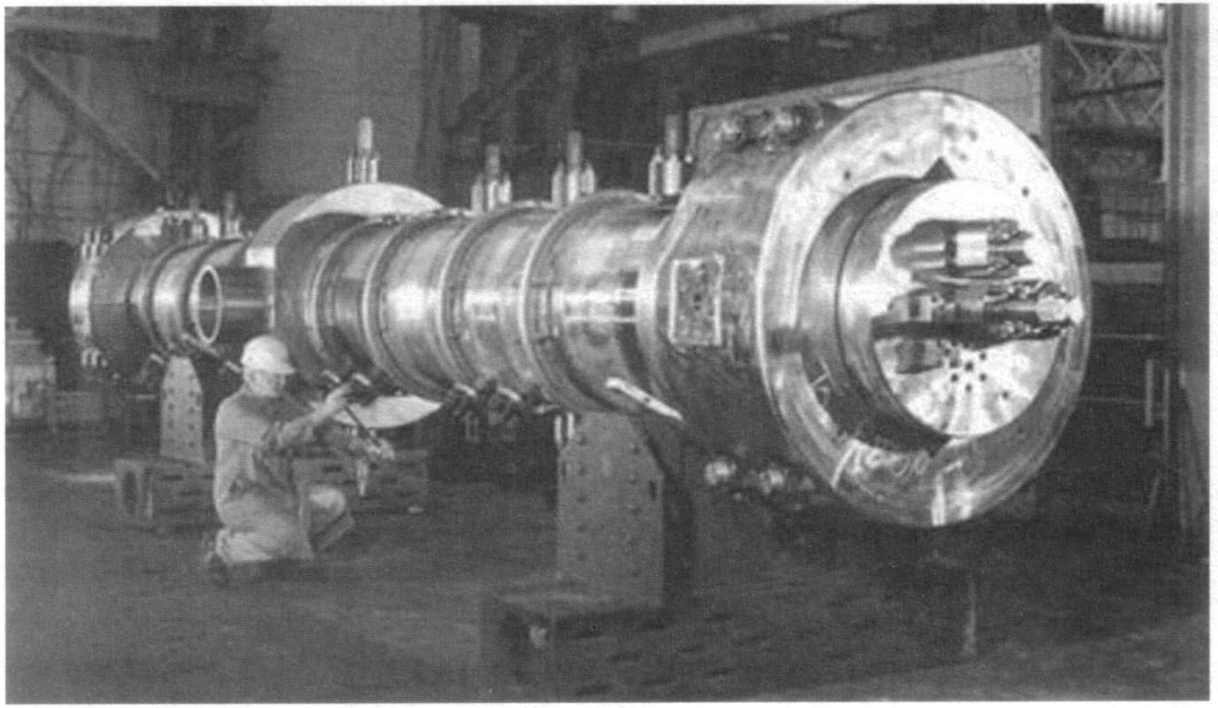
Well Mixed $$\int r_A dV = r_A V$$

$$F_{A0} - F_A + r_A V = 0$$

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

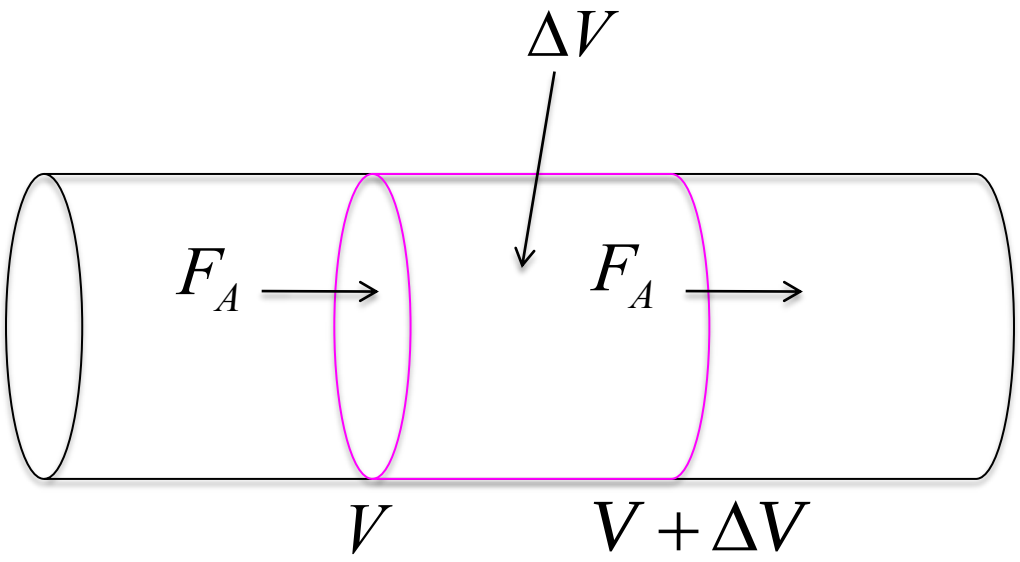
CSTR volume necessary to reduce the molar flow rate from $F_{A0}$ to $F_A$.

# Plug Flow Reactor - Mole Balances



Polyethylene reactor; this 16-in inner-diameter reactor is designed to operate at 35,000 psi and 600°F; in operation, this reactor is in a vertical configuration. Courtesy of Autoclave Engineers, Division of Snap-tite, Inc.

# Plug Flow Reactor - Mole Balances




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

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

# Plug Flow Reactor - Mole Balances

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

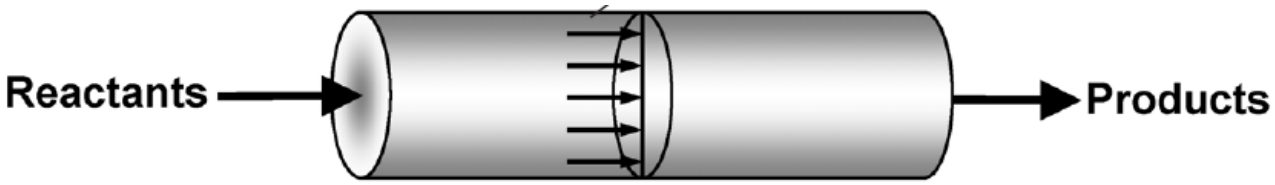
$$\lim_{\Delta V \rightarrow 0} \frac{F_A\big|_{V+\Delta V} - F_A\big|_V}{\Delta V} = r_A$$

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

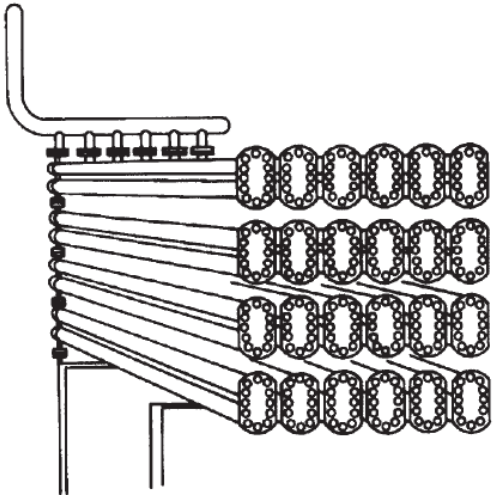
This is the volume necessary to reduce the entering molar flow rate (mol/s) from $F_{A0}$ to the exit molar flow rate of $F_A$.

# Plug Flow Reactor - Mole Balances

PFR




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



Steady State

$$\frac{dN_A}{dt} = 0$$

$$F_{A0} - F_A + \int r_A dV = 0$$

## Alternative Derivation

# Plug Flow Reactor - Mole Balances

Differientiate with respect to V

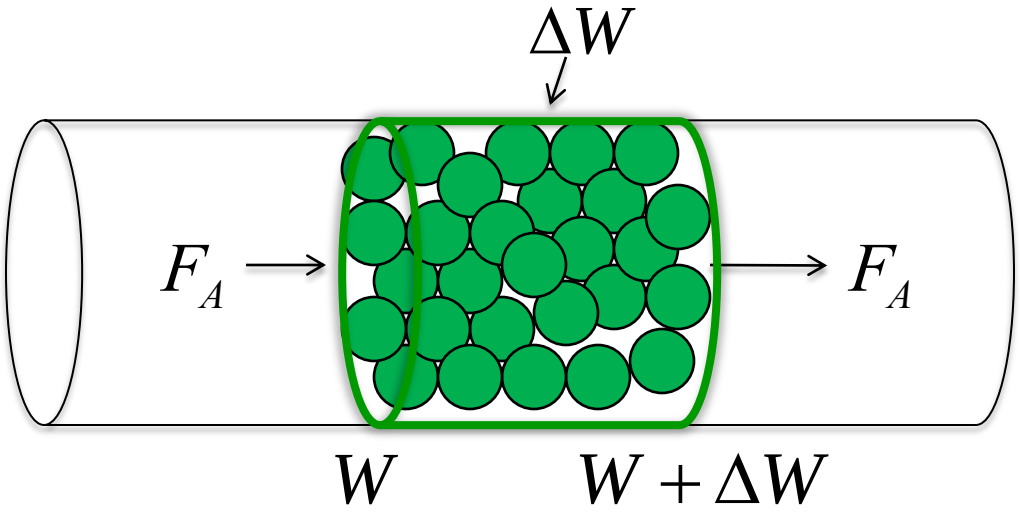
$$0 - \frac{dF_A}{dV} = -r_A \quad \Longrightarrow \quad \boxed{\frac{dF_A}{dV} = r_A}$$

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 Balances

PBR




$$F_A(W) - F_A(W+\Delta W) + r'_A \Delta W = \frac{dN_A}{dt}$$

Steady State

$$\frac{dN_A}{dt} = 0$$

$$\lim_{\Delta W \to 0} \frac{F_A\big|_{W+\Delta W} - F_A\big|_W}{\Delta W} = r'_A$$

# Packed Bed Reactor - Mole Balances

Rearrange:

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

The integral form to find the catalyst weight is:

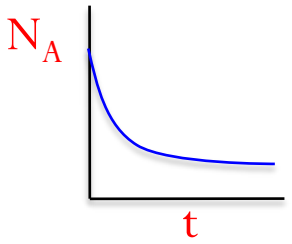
$$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A}$$

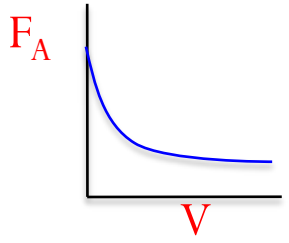
PBR catalyst weight necessary to reduce the entering molar flow rate $F_{A0}$ to molar flow rate $F_A$.

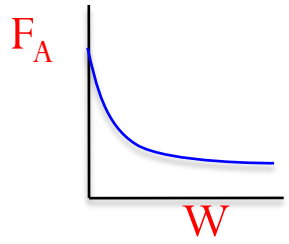
# Reactor Mole Balances Summary

The GMBE applied to the four major reactor types (and the general reaction A→B)

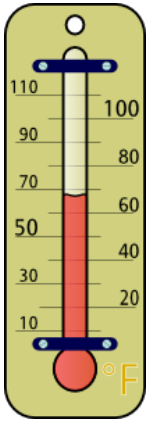
| Reactor | Differential | Algebraic | Integral |
|---|---|---|---|
| Batch | $\frac{dN_A}{dt} = r_A V$ | | $t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A V}$ |
| CSTR | | $V = \frac{F_{A0} - F_A}{-r_A}$ | |
| PFR | $\frac{dF_A}{dV} = r_A$ | | $V = \int_{F_{A0}}^{F_A} \frac{dF_A}{dr_A}$ |
| PBR | $\frac{dF_A}{dW} = r'_A$ | | $W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A}$ |



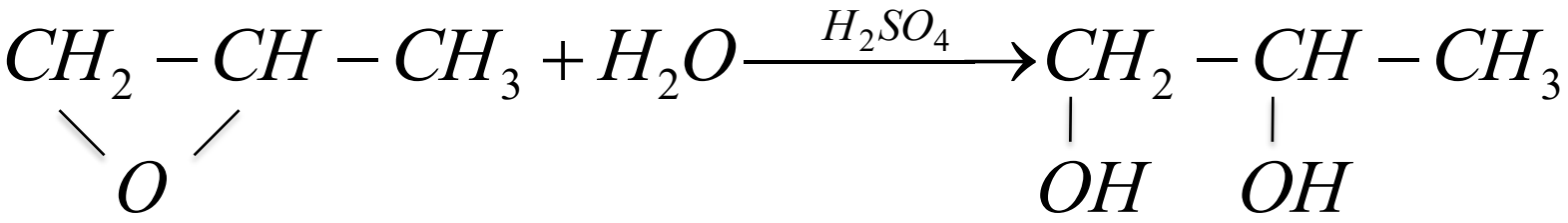



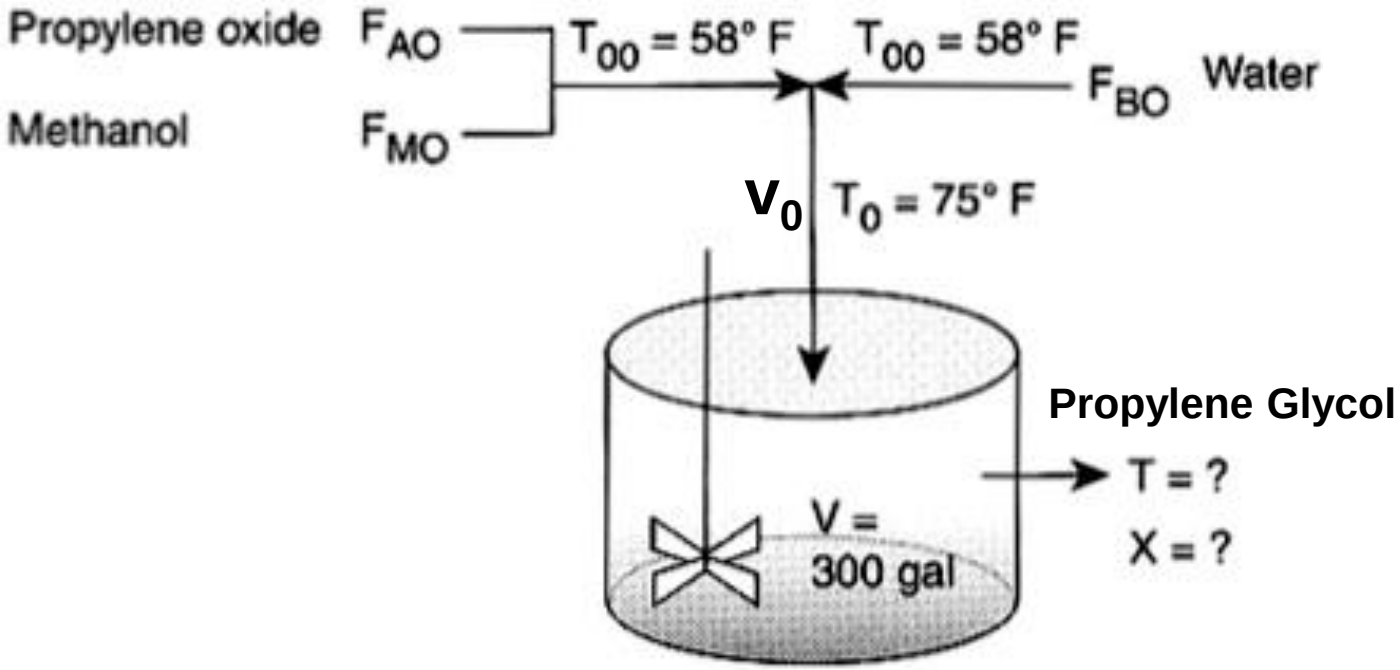
# Reactors with Heat Effects




- EXAMPLE: Production of Propylene Glycol in an Adiabatic CSTR

- Propylene glycol is produced by the hydrolysis of propylene oxide:






What are the exit conversion X and exit temperature T?

***Solution***

Let the reaction be represented by

$$A+B \rightarrow C$$

**1. Mole Balance and design equation:**

$$F_{A0} - F_A + r_A V = 0$$

The design equation in terms of $X$ is

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

**2. Rate Law:**

$$-r_A = kC_A$$

3. **Stoichiometry** (liquid phase, $v = v_0$):

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

4. **Combining** yields

$$V = \frac{F_{A0}X}{kC_{A0}(1-X)} = \frac{v_0X}{k(1-X)}$$

**Solving** for $X$ as a function of $T$ and recalling that $\tau = V/v_0$ gives

$$X_{MB} = \frac{\tau k}{1 + \tau k} = \frac{\tau A e^{-E/RT}}{1 + \tau A e^{-E/RT}}$$

This equation relates temperature and conversion through the **mole balance**.

Parameter Evaluation ($C_{A0}$, $\Theta_i$, $\tau$): The total liquid volumetric flow rate entering the reactor is

$$V = 300 \text{ gal} = 40.1 \text{ ft}^3$$

$$\tau = \frac{V}{v_0} = \frac{40.1 \text{ ft}^3}{326.3 \text{ ft}^3/\text{h}} = 0.123 \text{ h}$$

$$C_{A0} = \frac{F_{A0}}{v_0} = \frac{43.0 \text{ lb mol/h}}{326.3 \text{ ft}^3/\text{h}}$$

$$= 0.132 \text{ lb mol/ft}^3$$

For methanol: $\Theta_M = \dfrac{F_{M0}}{F_{A0}} = \dfrac{71.87 \text{ lb mol/h}}{43.0 \text{ lb mol/h}} = 1.67$

For water: $\Theta_B = \dfrac{F_{B0}}{F_{A0}} = \dfrac{802.8 \text{ lb mol/h}}{43.0 \text{ lb mol/h}} = 18.65$

Evaluate mole balance terms: The conversion calculated from the mole balance, $X_{MB}$, is found form Equation (E8-8.5).

$$X_{MB} = \frac{(2.084 \times 10^{12}) \exp(-16{,}306/T)}{1 + (2.084 \times 10^{12}) \exp(-16{,}306/T)}, \; T \text{ is in } ^\circ\text{R}$$

**5.** The **energy balance** for this adiabatic reaction in which there is negligible energy input provided by the stirrer is

$$X_{EB} = \frac{\Sigma\, \Theta_i C_{P_i}(T - T_{i0})}{-[\Delta H^{\circ}_{Rx}(T_R) + \Delta C_P(T - T_R)]}$$

## Evaluate energy balance terms

$$\Sigma\Theta_i C_{P_i} = C_{P_A} + \Theta_B C_{P_B} + \Theta_M C_{P_M}$$
$$= 35 + (18.65)(18) + (1.67)(19.5)$$

Substituting all the known quantities into the energy balance gives us

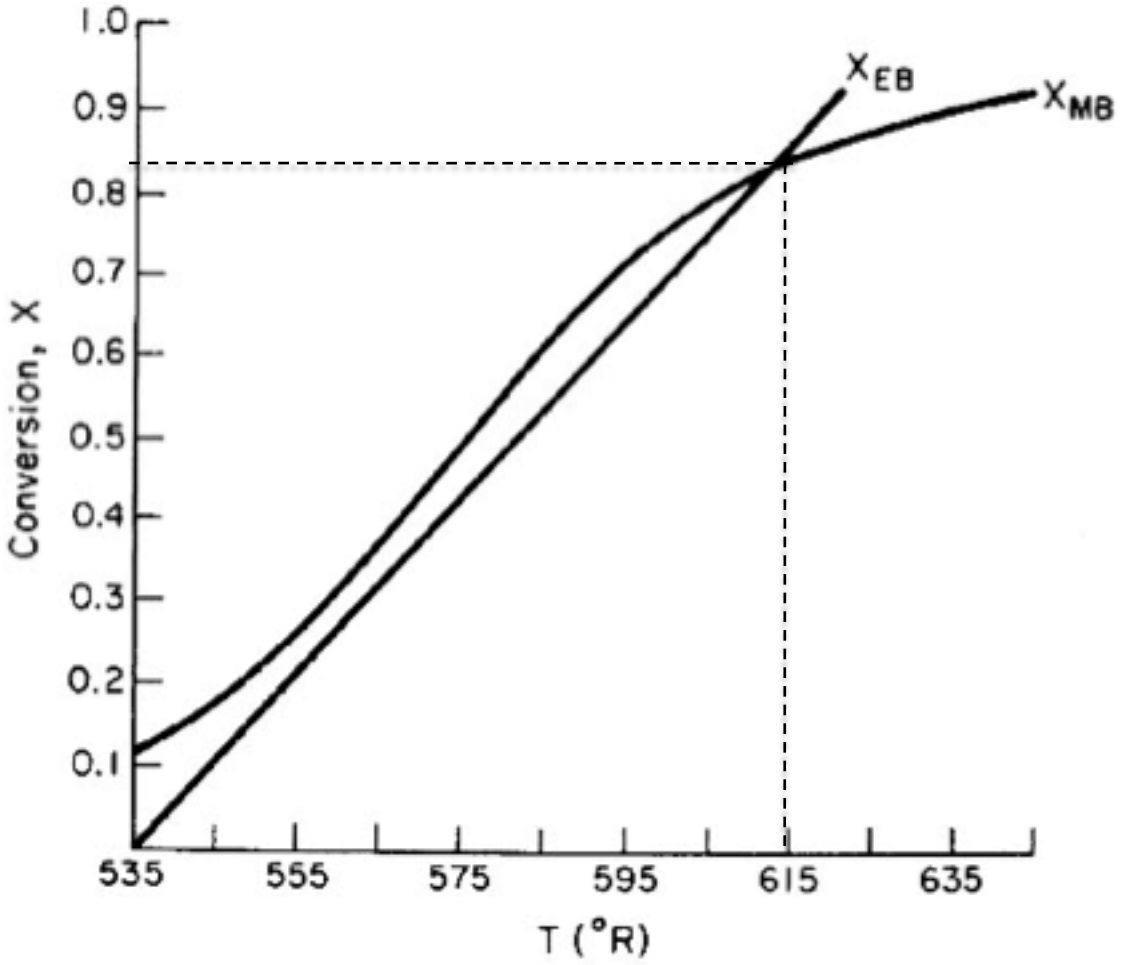
$$X_{EB} = \frac{(403.3 \text{ Btu/lb mol} \cdot °\text{F})(T - 535)°\text{F}}{-[-36{,}400 - 7(T - 528)] \text{ Btu/lb mol}}$$

$$X_{EB} = -\frac{\Sigma\ \Theta_i C_{P_i}(T - T_{i0})}{\Delta H^\circ_{Rx}(T_R) + \Delta C_P(T - T_R)}$$

$$\boxed{X_{EB} = \frac{403.3(T - 535)}{36{,}400 + 7(T - 528)}}$$

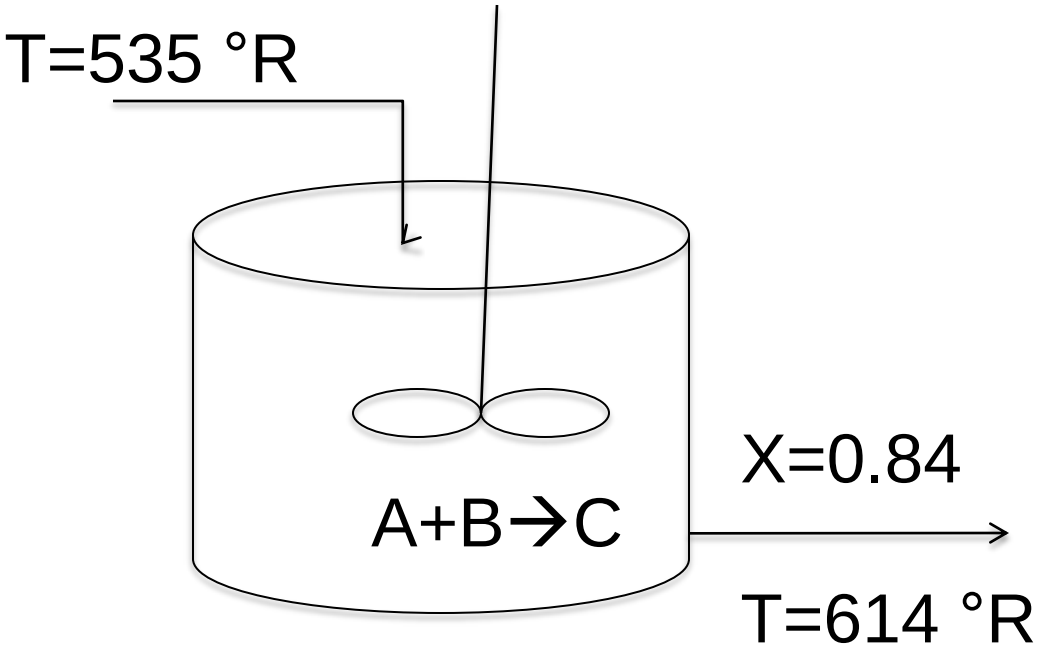
**7. Solving.**

| $T$ (°R) | $X_{MB}$ [Eq. (E8-8.10)] | $X_{EB}$ [Eq. (E8-8.12)] |
|---|---|---|
| 535 | 0.108 | 0.000 |
| 550 | 0.217 | 0.166 |
| 565 | 0.379 | 0.330 |
| 575 | 0.500 | 0.440 |
| 585 | 0.620 | 0.550 |
| 595 | 0.723 | 0.656 |
| 605 | 0.800 | 0.764 |
| 615 | 0.860 | 0.872 |
| 625 | 0.900 | 0.980 |


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Conversion, X
$X_{EB}$
$X_{MB}$
535
555
575
595
615
635
T (°R)

# Analysis

We have applied our CRE algorithm to calculate the Conversion (X=0.84) and Temperature (T=614 °R) in a 300 gallon CSTR operated adiabatically.



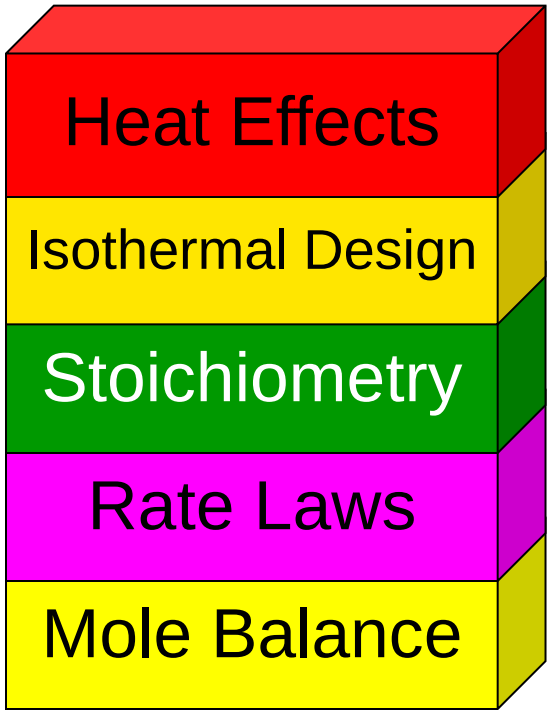
# Keeping Up

# Separations

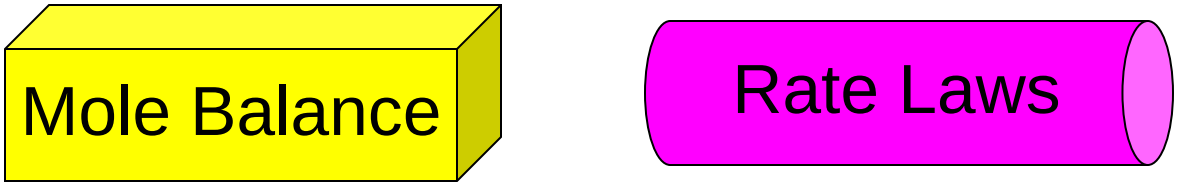

These topics do not build upon one another.

# Reaction Engineering

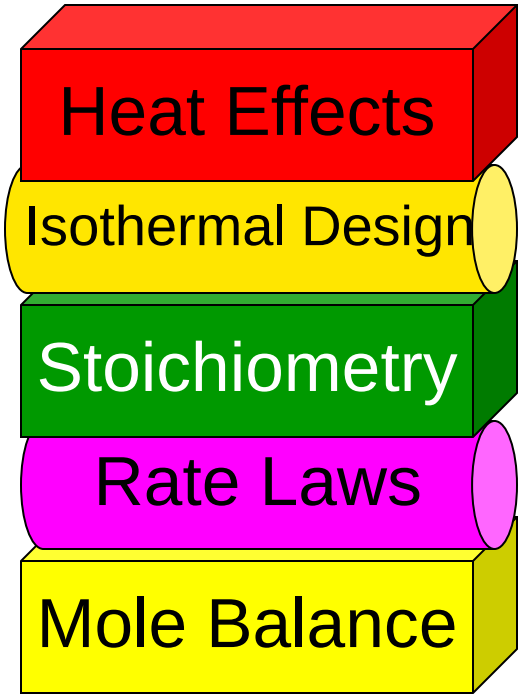

These topics build upon one another.




CRE Algorithm



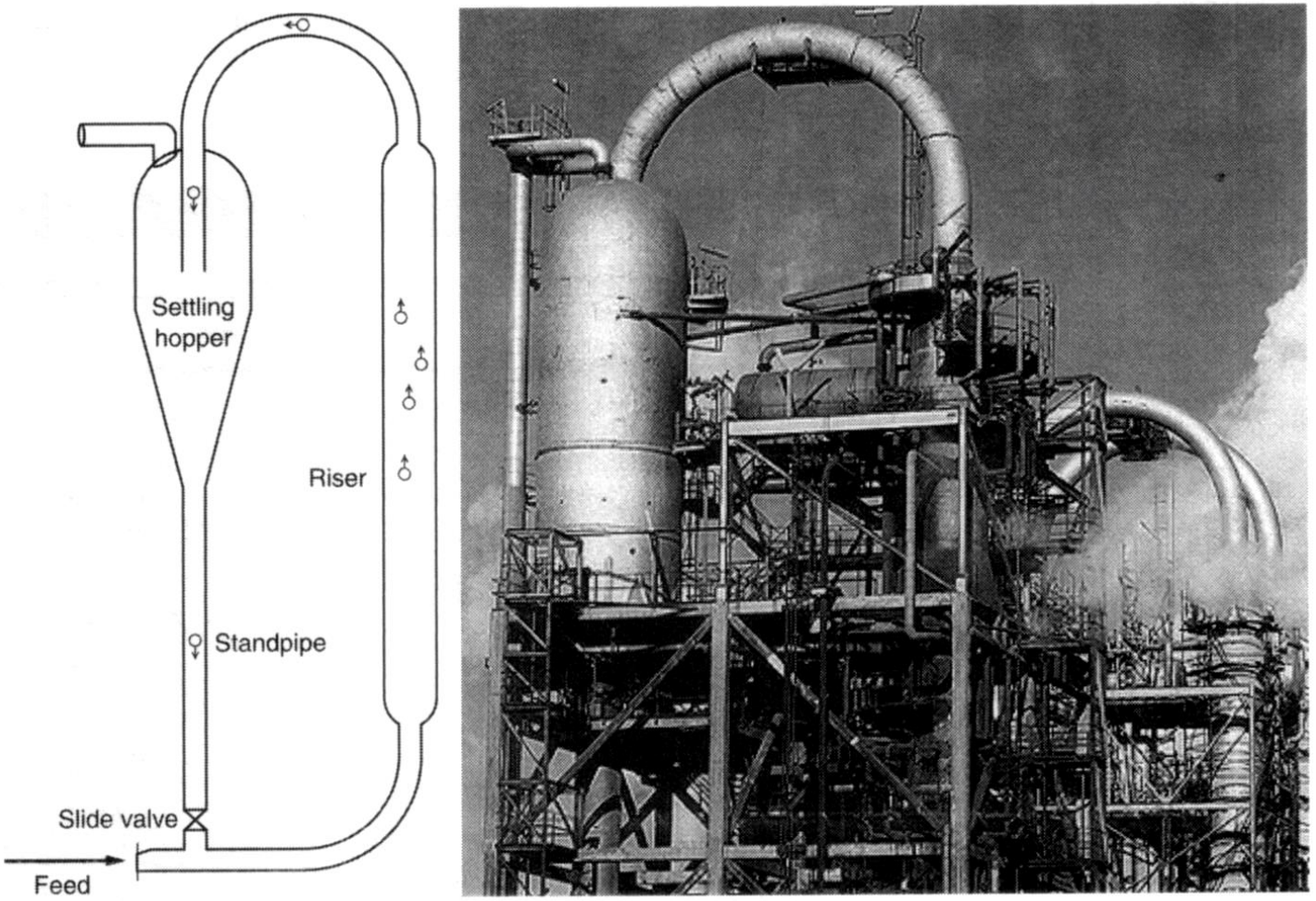

Be careful not to cut corners on any of the **CRE building blocks** while learning this material!




Otherwise, your Algorithm becomes unstable.

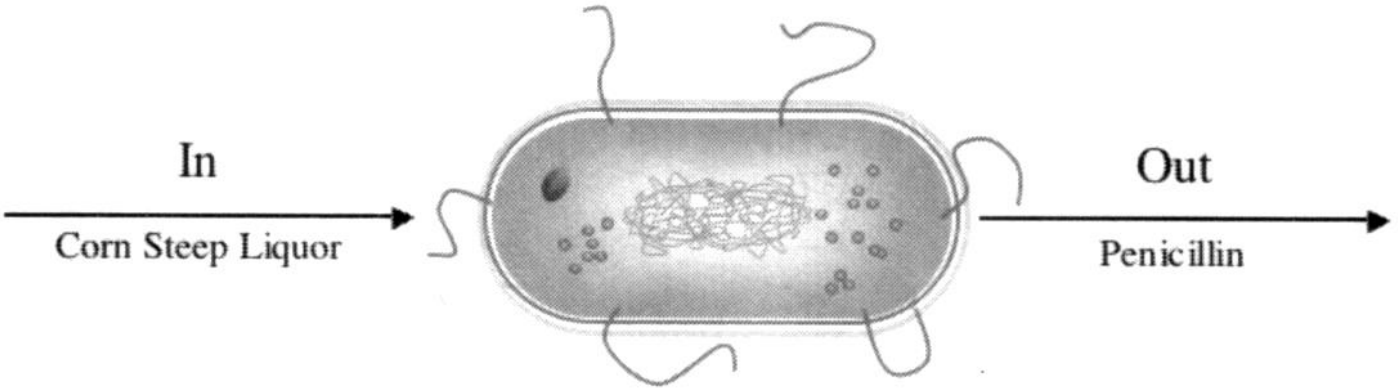
# End of Lecture 1

# Supplemental Slides
# Additional Applications of CRE



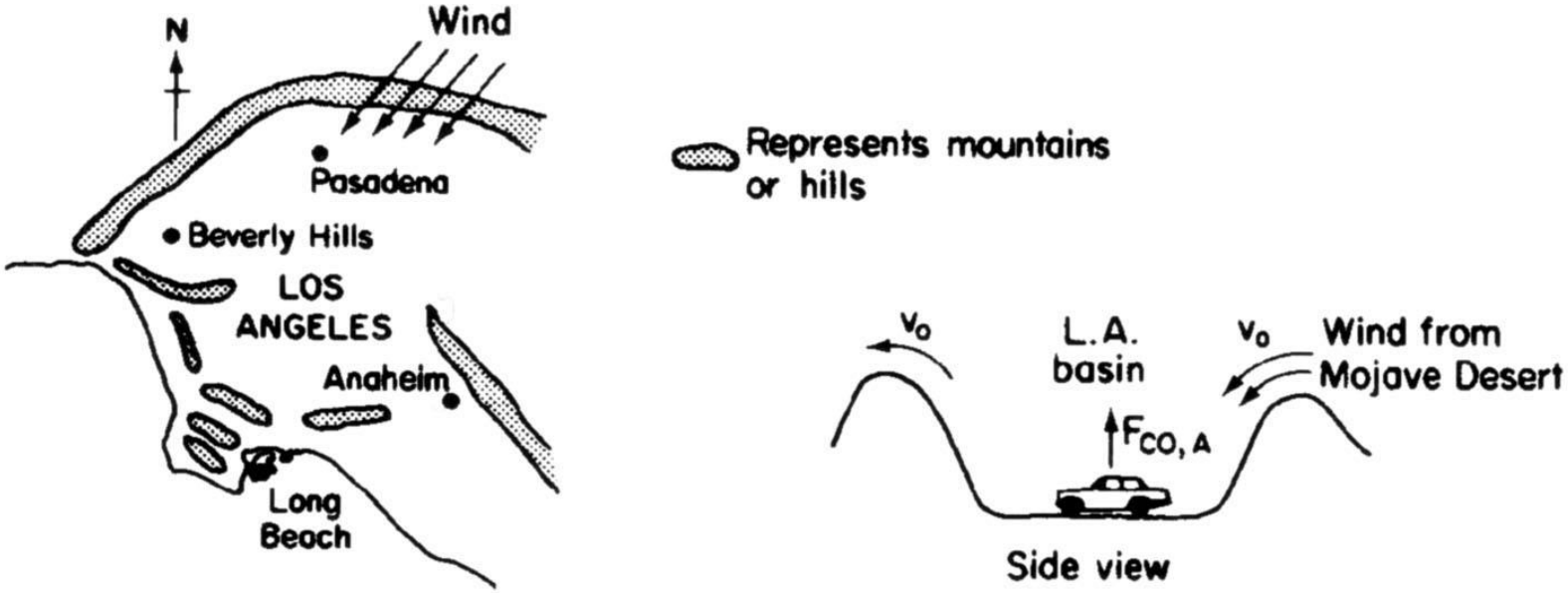

The reactor is 3.5 m in diameter and 38 m tall.
[Schematic and photo courtesy of Sasol/Sastech PT Limited.]

# Supplemental Slides
# Additional Applications of CRE




*Penicillium chrysogenum*

# Supplemental Slides
# Additional Applications of CRE




Schematic diagrams of the Los Angeles basin.

# Supplemental Slides
# Additional Applications of CRE

Hippo Digestion (Ch. 2)

# Supplemental Slides
# Additional Applications of CRE

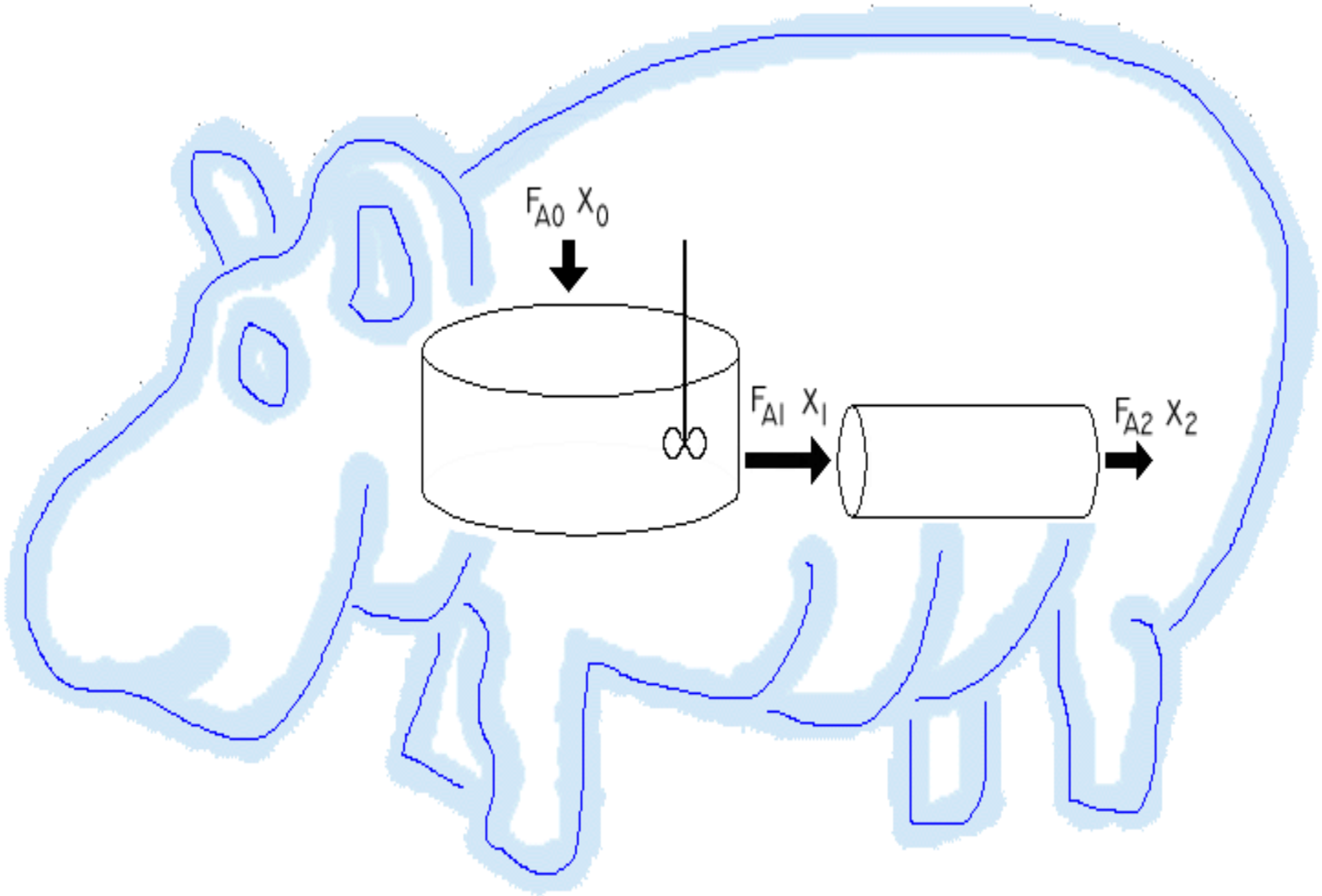
## Modeling the Digestive System of a Hippopotamus*

Matthew Robertson, Fredrik Persson, Brian Vicente, Professor H. Scott Fogler

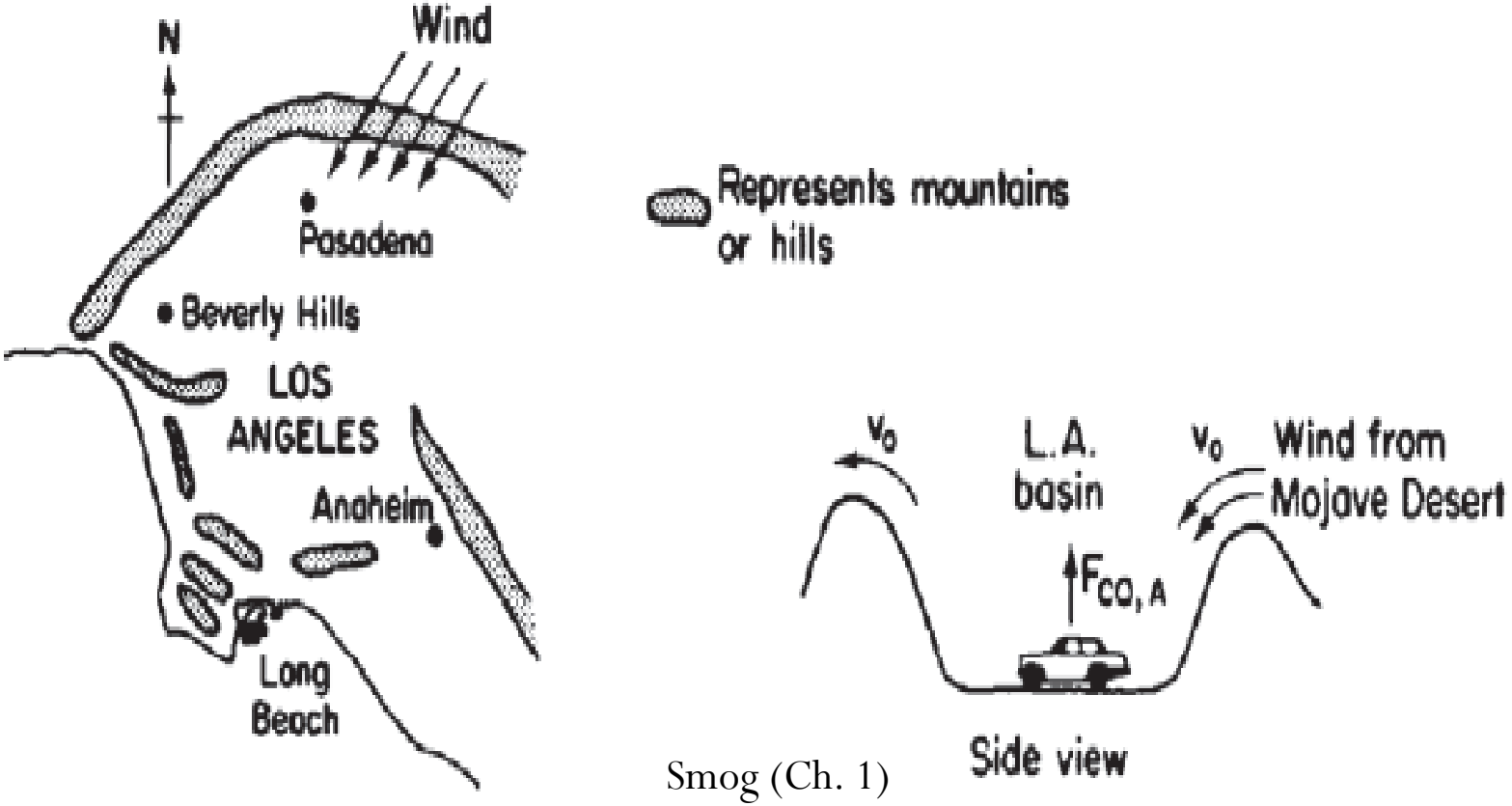
"Even hippo's like Chemical Reaction Engineering."

*From a problem suggested by **Professor Alice P. Gast**
["Animal Guts as Ideal Reactors", Chemical Engineering Education, Winter 1998, pp 24-29]

# Supplemental Slides
# Additional Applications of CRE

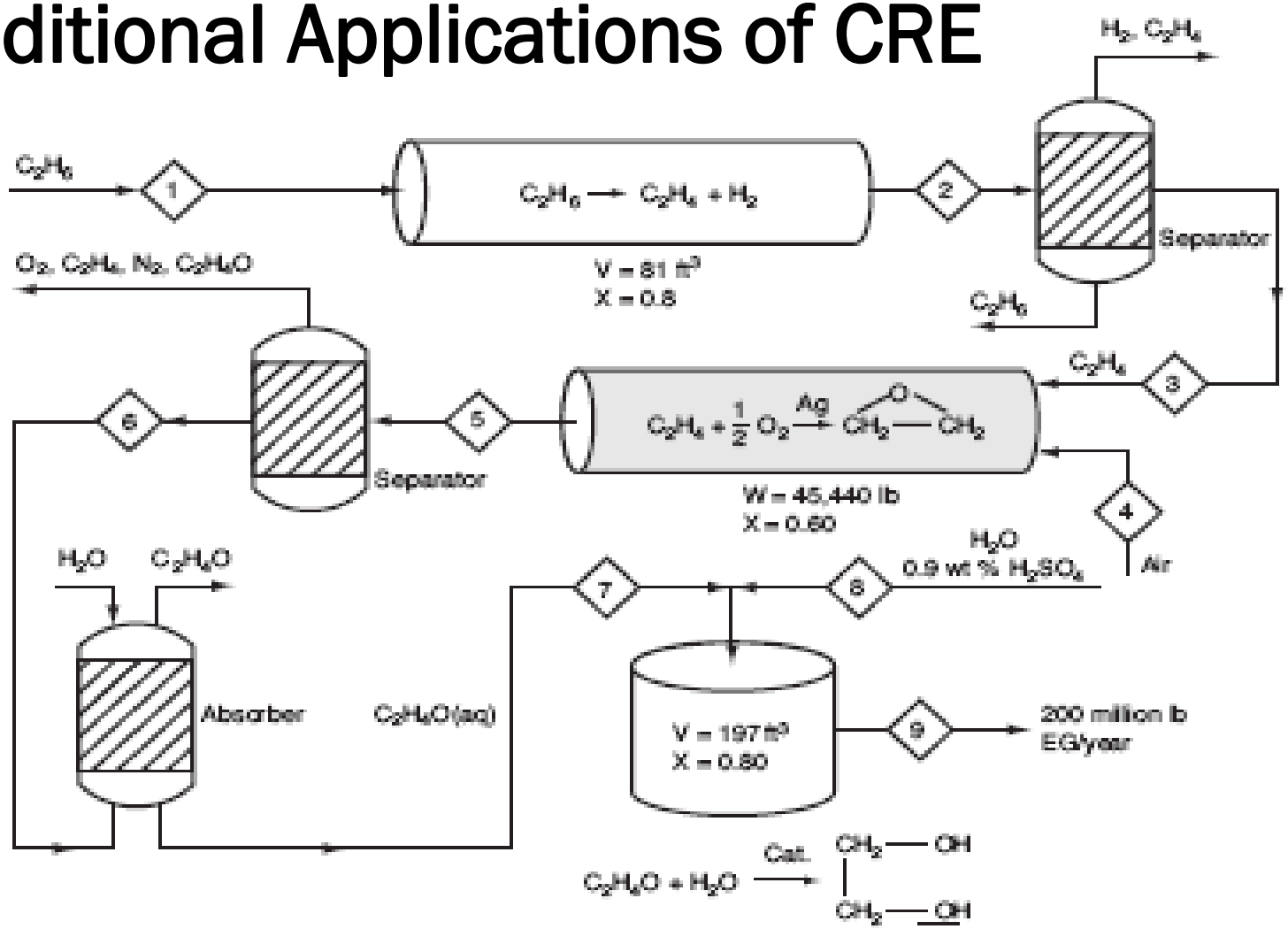


# Supplemental Slides
# Additional Applications of CRE



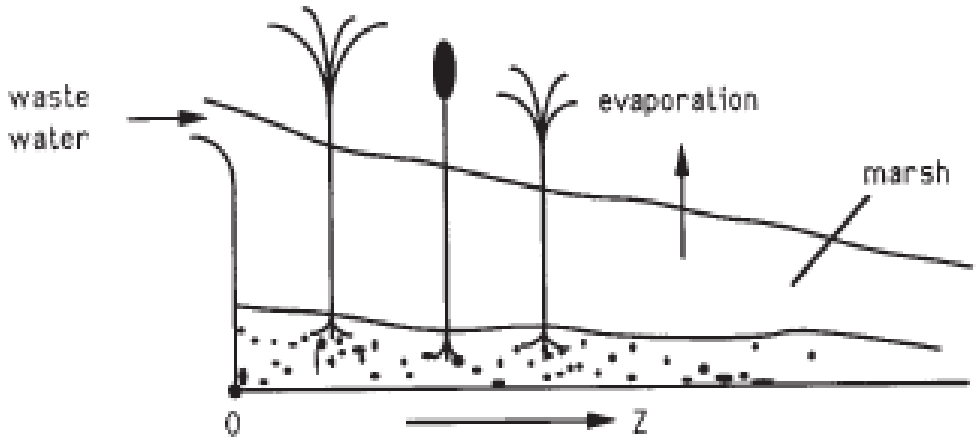

Smog (Ch. 1)

# Supplemental Slides
# Additional Applications of CRE

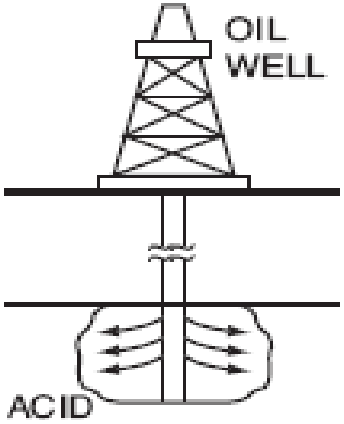



Chemical Plant for Ethylene Glycol (Ch. 5)

# Supplemental Slides
# Additional Applications of CRE




Wetlands (Ch. 7 DVD-ROM)




Oil Recovery (Ch. 7)

# Supplemental Slides
# Additional Applications of CRE

**Lu**

Pharmacokinetics
of Cobra Bites
Multiple Reactions
in a Batch
(Body) Reactor

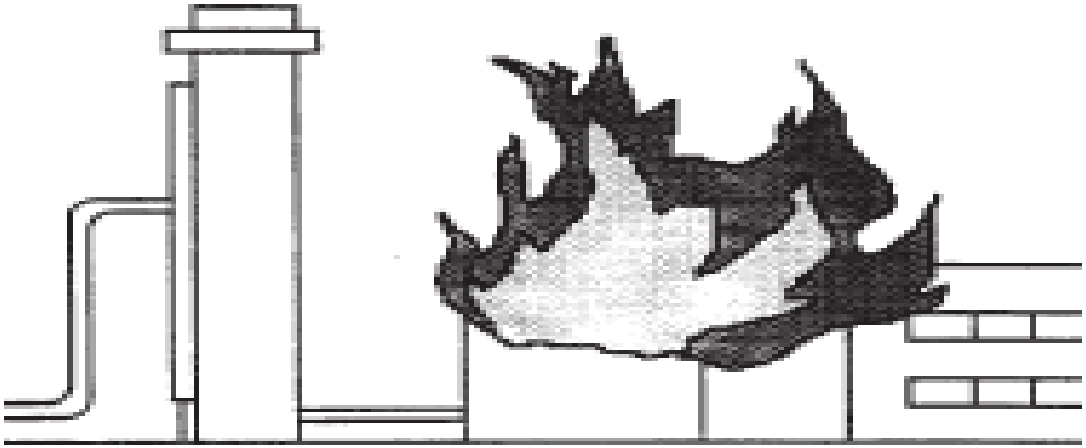
Cobra Bites
(Ch. 8 DVD-ROM)

# Supplemental Slides
# Additional Applications of CRE


Effective Lubricant Design Scavenging Free Radicals

Lubricant Design (Ch. 9)

# Supplemental Slides
# Additional Applications of CRE



Nitroanaline Plant Explosion
Exothermic Reactions That
Run Away

Plant Safety
(Ch. 11,12,13)