

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 – Thursday 1/10/2013

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



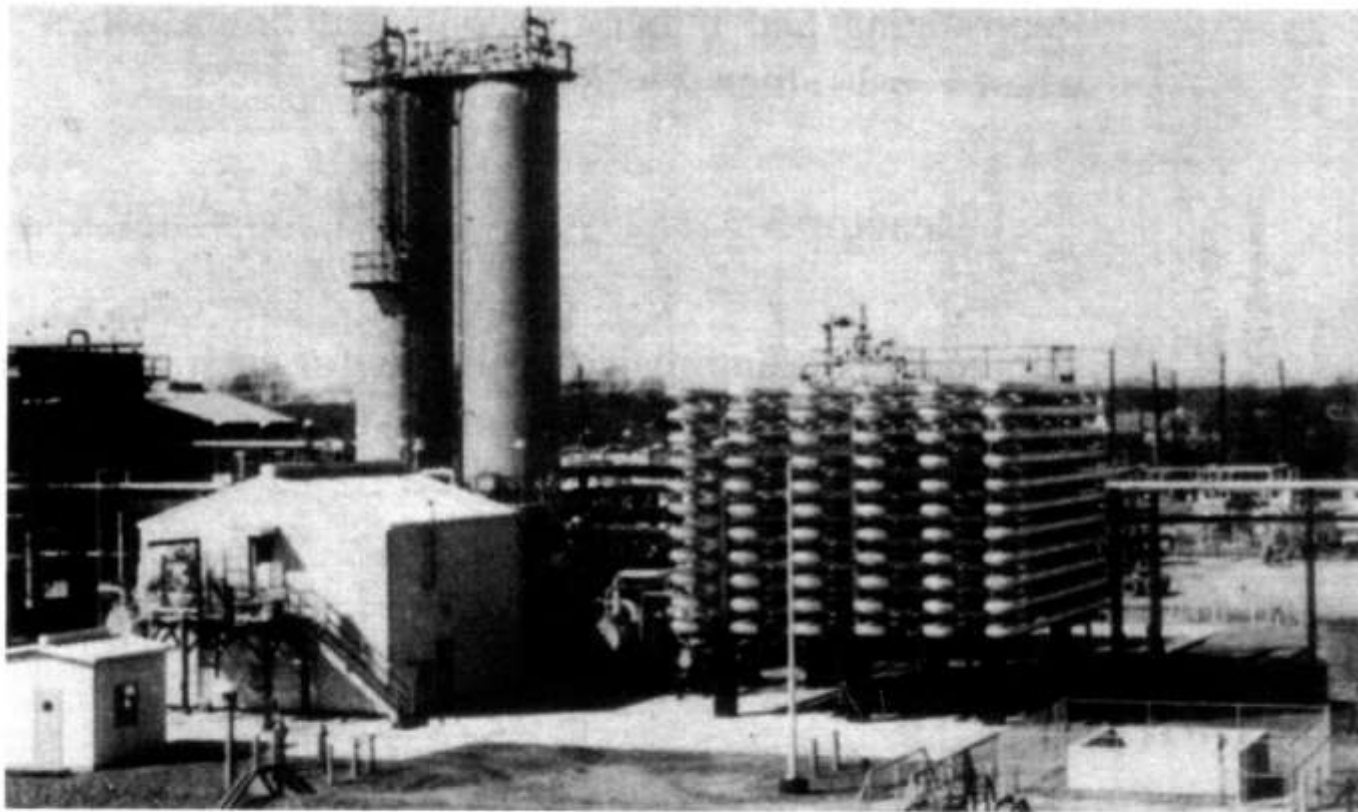
Chemical Reaction Engineering

- *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)

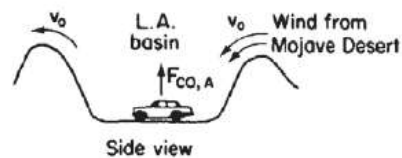
Examples like Dow, DuPont, Amoco, Chevron



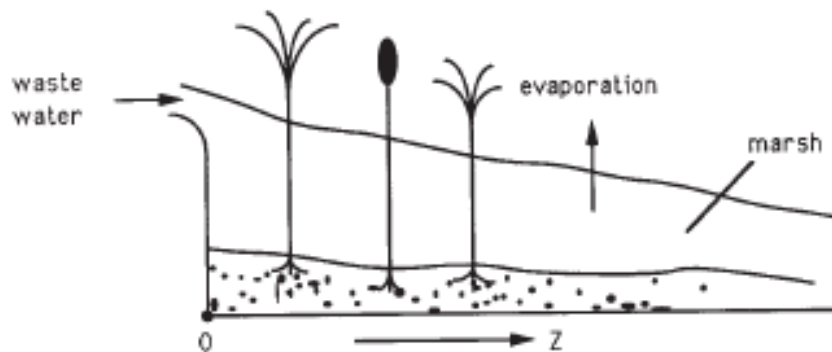
Dimersol G (an organometallic catalyst) unit (two CSTRs and one tubular reactor in series) to dimerize propylene into isohexanes. Institut Français du Pétrole process. [Photo courtesy of Editions Technip (Institut Français du Pétrole).]



Represents mountains or hills



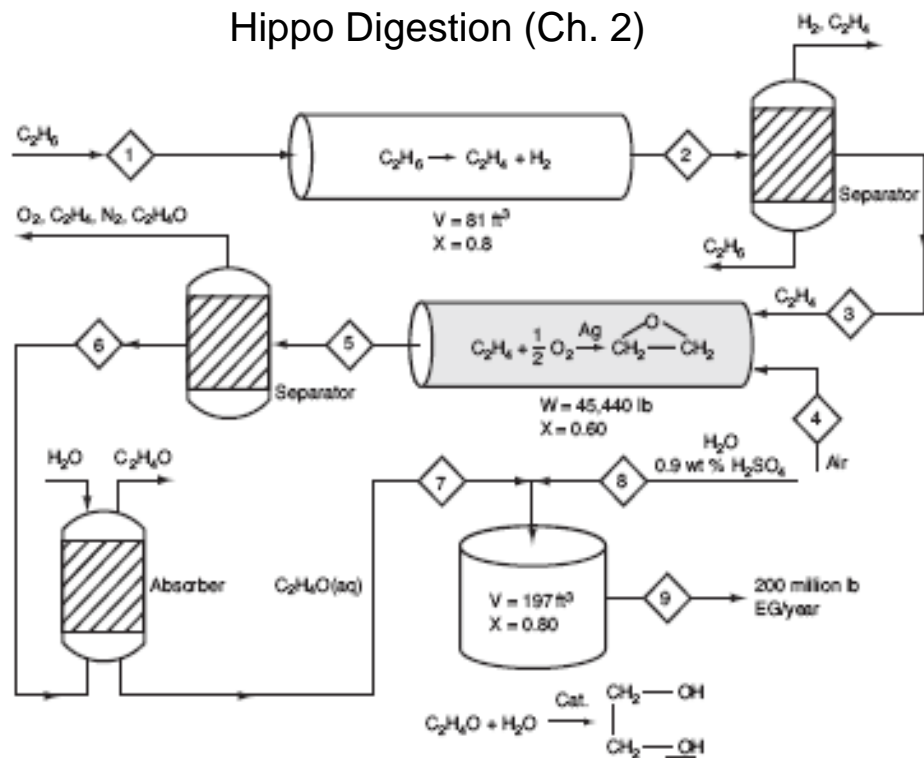
Smog (Ch. 1)



Wetlands (Ch. 7 DVD-ROM)



Hippo Digestion (Ch. 2)



Chemical Plant for Ethylene Glycol (Ch. 5)



Oil Recovery (Ch. 7)



Lu

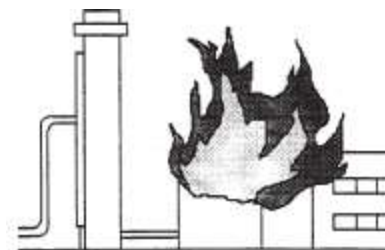
Pharmacokinetics of Cobra Bites
Multiple Reactions in a Batch (Body) Reactor

Cobra Bites (Ch. 8 DVD-ROM)



Effective Lubricant Design Scavenging Free Radicals

Lubricant Design (Ch. 9)



Nitroaniline Plant Explosion
Exothermic Reactions That Run Away

Plant Safety (Ch. 11,12,13)

Materials on the Web and CD-ROM

<http://www.umich.edu/~essen/>

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.

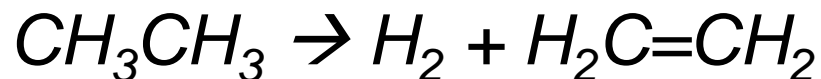
Chemical Identity

- 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.

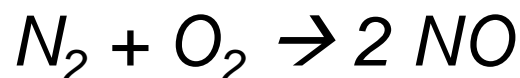
Chemical Identity

- 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



2. Combination



3. Isomerization



Reaction Rate

- The reaction rate is the rate at which a species loses its chemical identity per unit volume.
- The rate of a reaction ($\text{mol/dm}^3/\text{s}$) 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



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

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

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

Reaction Rate

EXAMPLE: $A \rightarrow B$

If Species B is being formed at a rate of 0.2 moles per decimeter cubed per second, i.e.,
 $r_B = 0.2 \text{ mole/dm}^3/\text{s}$

Then A is disappearing at the same rate:

$$-r_A = 0.2 \text{ mole/dm}^3/\text{s}$$

The rate of formation (generation of A) is:

$$r_A = -0.2 \text{ mole/dm}^3/\text{s}$$

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

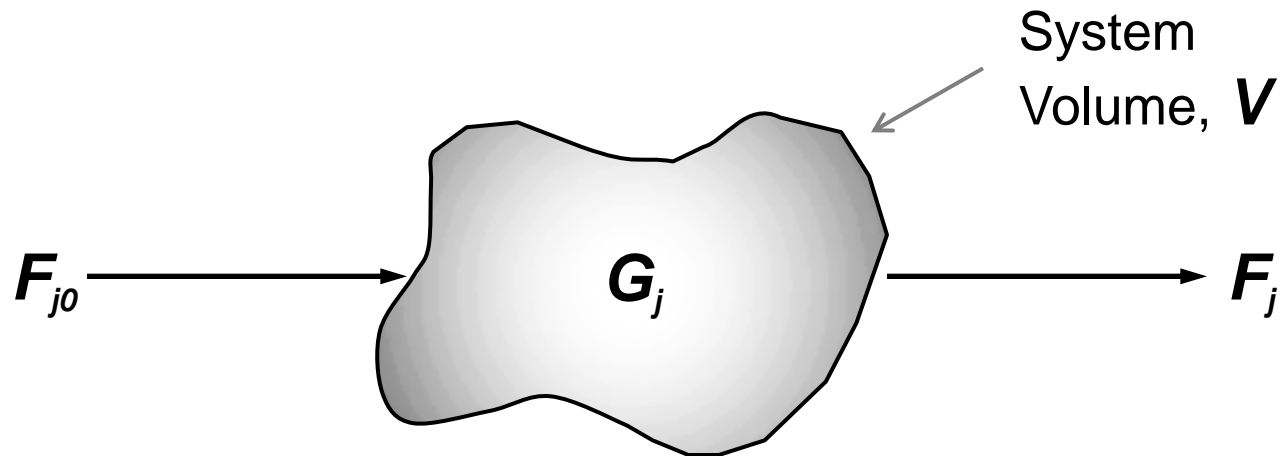
Reaction Rate

Consider species j:

1. r_j is the rate of formation of species j per unit volume [e.g. mol/dm³s]
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 $-r_A = kC_A^2$)

Building Block 1:

General Mole Balances



$$\left[\begin{array}{c} \text{Molar Flow} \\ \text{Rate of} \\ \text{Species } j \text{ in} \end{array} \right] - \left[\begin{array}{c} \text{Molar Flow} \\ \text{Rate of} \\ \text{Species } j \text{ out} \end{array} \right] + \left[\begin{array}{c} \text{Molar Rate} \\ \text{Generation} \\ \text{of Species } j \end{array} \right] = \left[\begin{array}{c} \text{Molar Rate} \\ \text{Accumulation} \\ \text{of Species } j \end{array} \right]$$

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

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

Building Block 1:

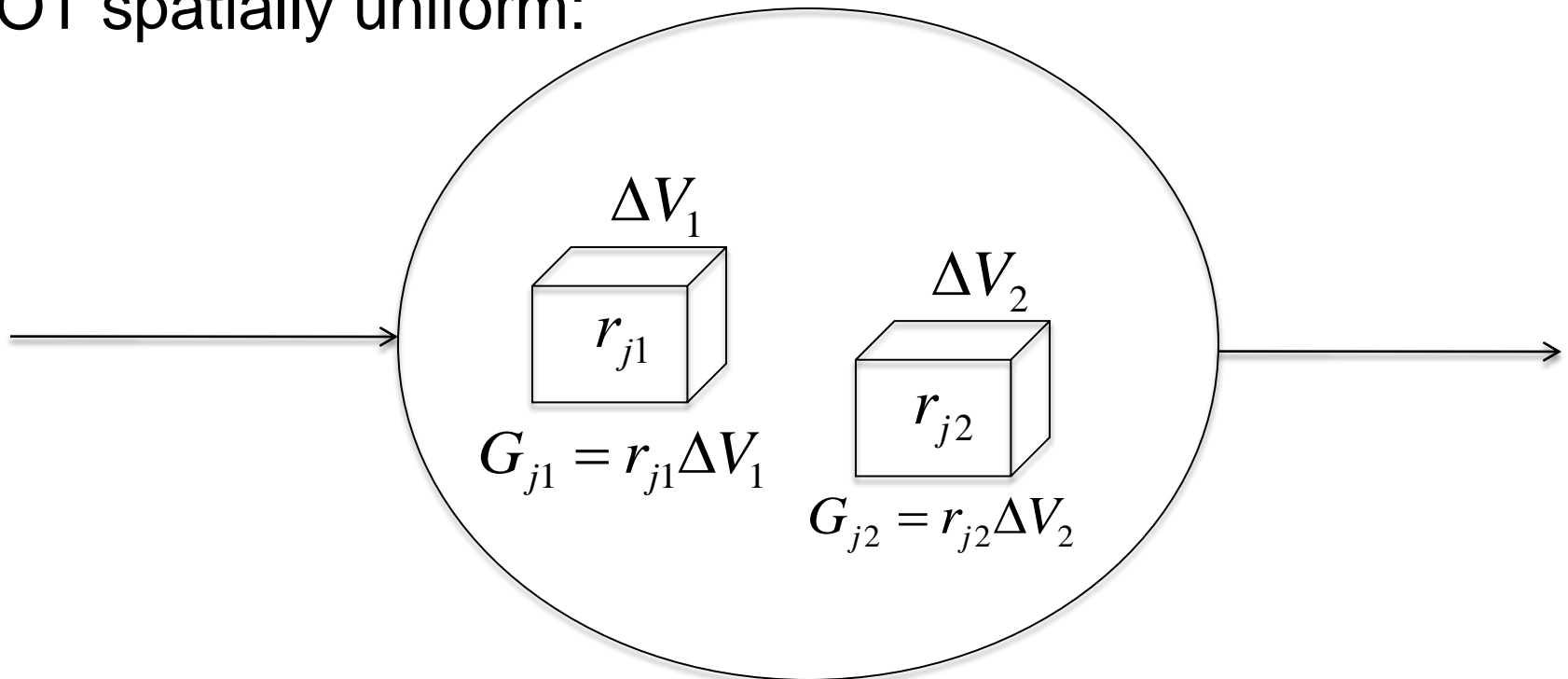
General Mole Balances



If spatially uniform:

$$G_j = r_j V$$

If NOT spatially uniform:



Building Block 1:

General Mole Balances



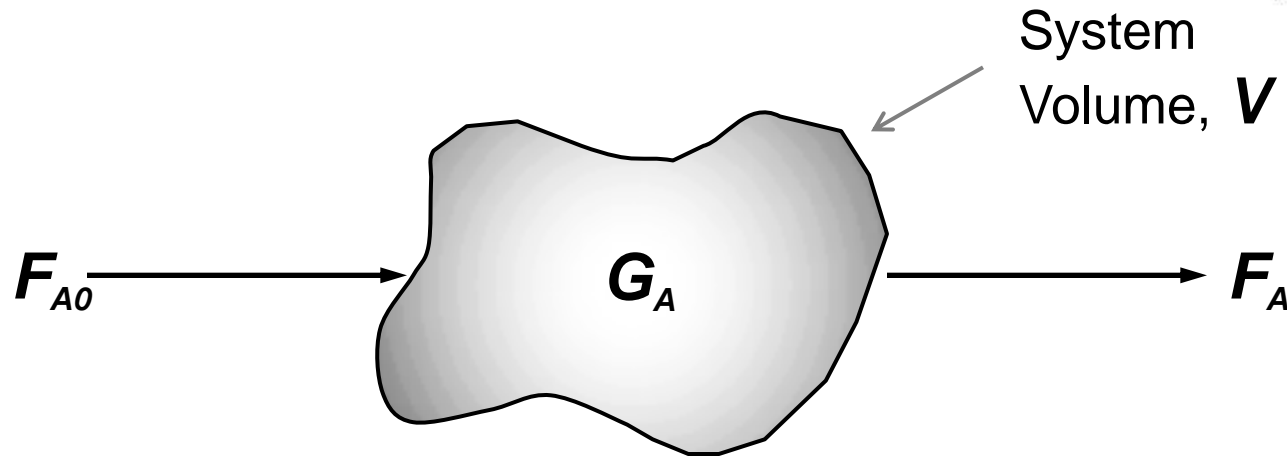
$$G_j = \sum_{i=1}^n r_{ji} \Delta V_i$$

Take limit

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

Building Block 1:

General Mole Balances



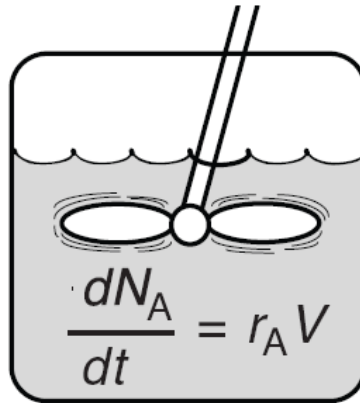
General Mole Balance on System Volume V

$$In - Out + Generation = Accumulation$$

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

Batch Reactor - Mole Balances

Batch



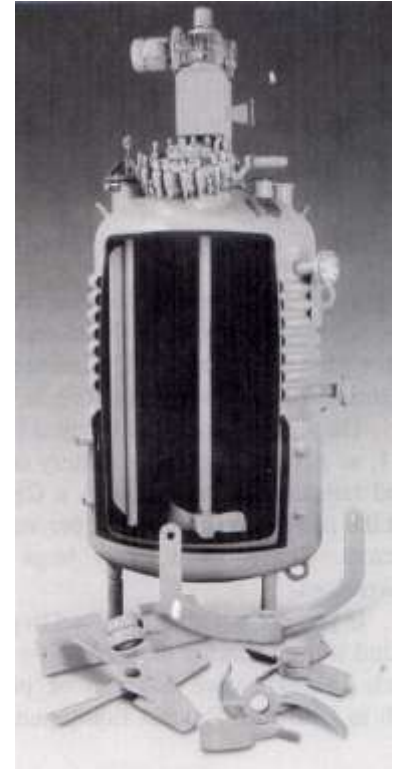
$$F_{A0} - F_A + \int r_A dV = \frac{dN_A}{dt}$$

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

Well-Mixed

$$\int r_A dV = r_A V$$

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



Batch Reactor - Mole Balances

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

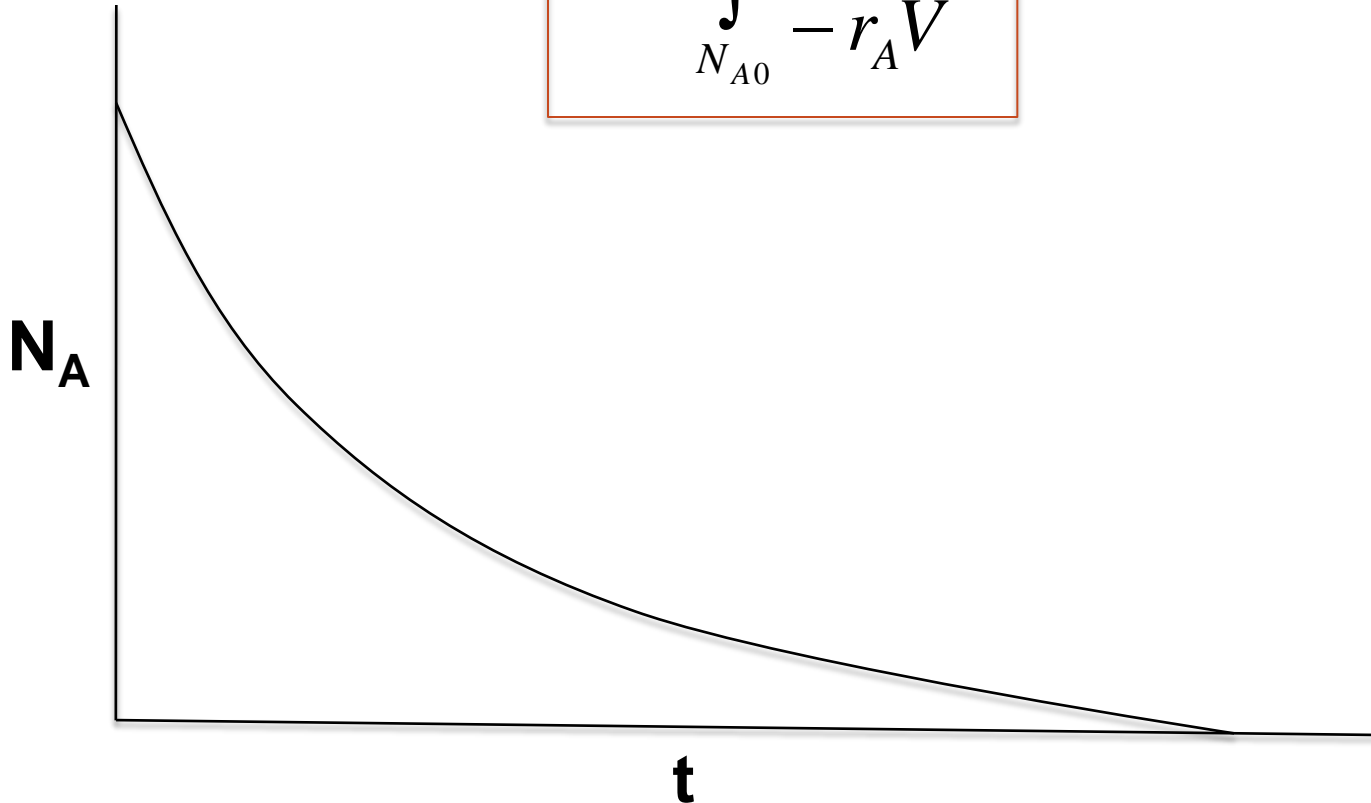
when $t = 0 \quad N_A = N_{A0}$
 $t = t \quad N_A = N_A$

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

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

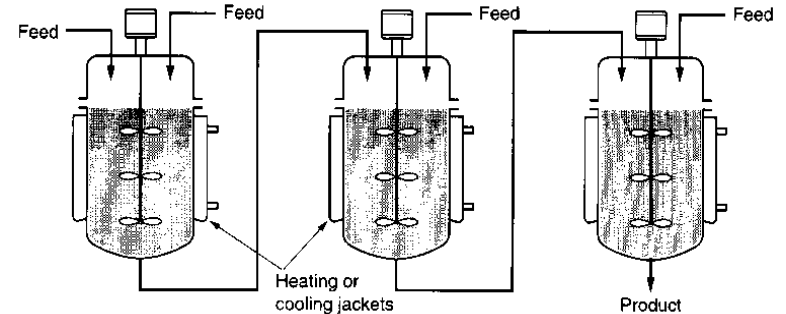
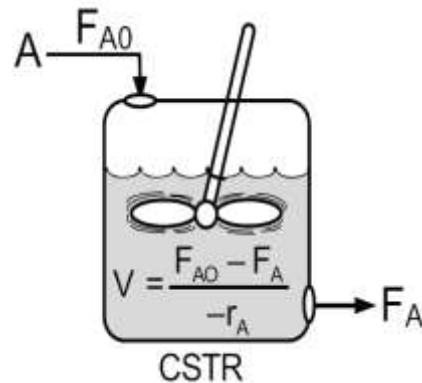
Batch Reactor - Mole Balances

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



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

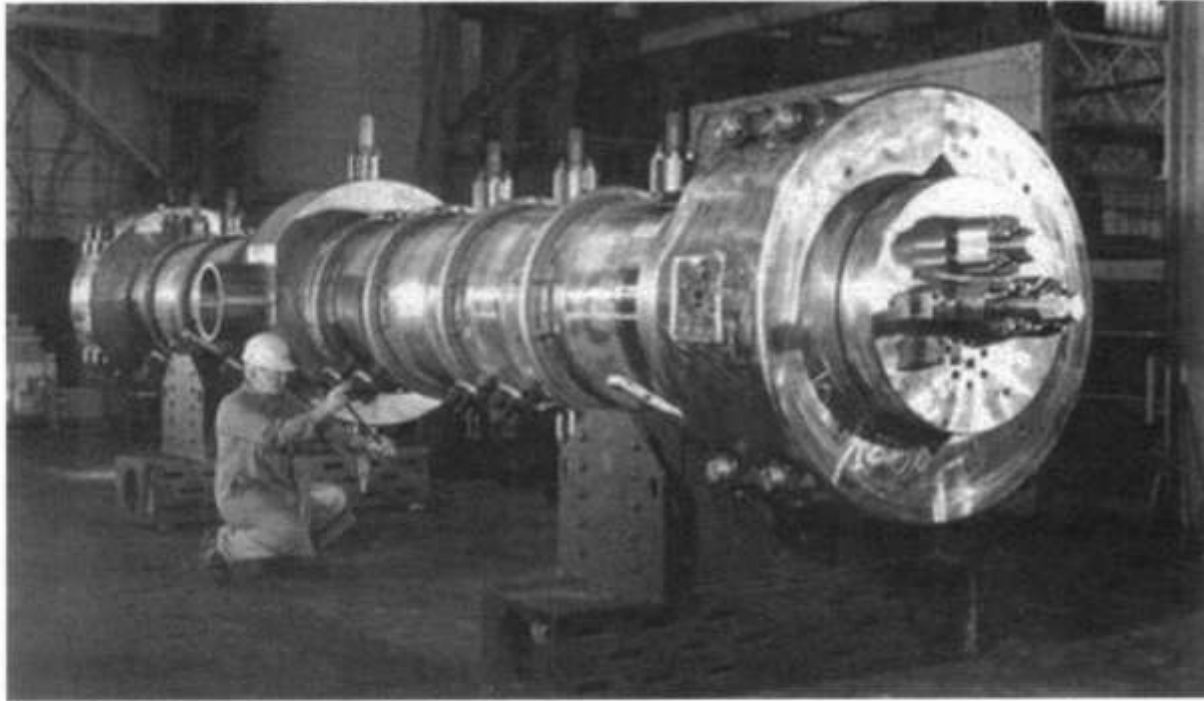
$$\int r_A dV = r_A V$$

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

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

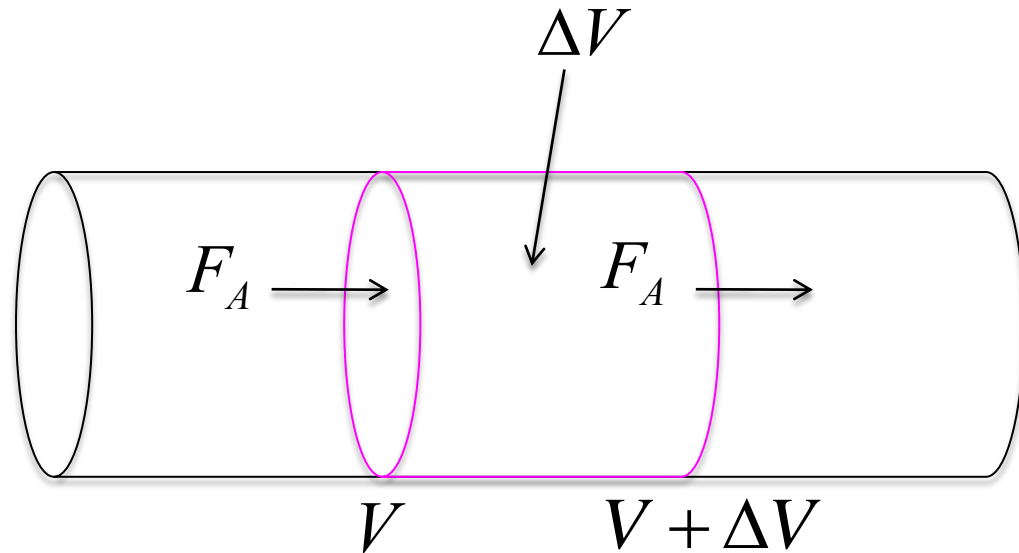
CSTR volume necessary to reduce the molar flow rate from F_{A0} to F_A .

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



$$\left[\begin{array}{c} \textit{In} \\ \textit{at } V \end{array} \right] - \left[\begin{array}{c} \textit{Out} \\ \textit{at } V + \Delta V \end{array} \right] + \left[\begin{array}{c} \textit{Generation} \\ \textit{in } \Delta V \end{array} \right] = 0$$

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

Plug Flow Reactor - Mole Balances

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

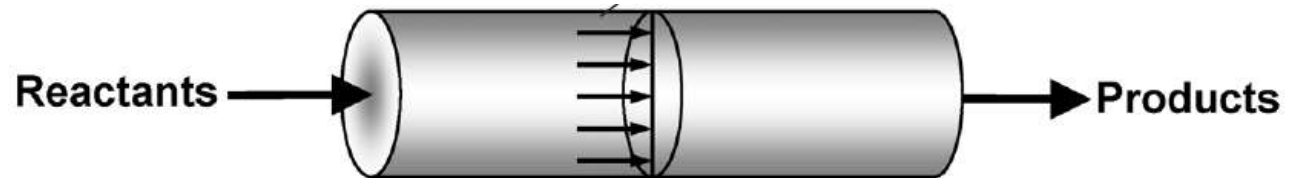
$$\lim_{\Delta V \rightarrow 0} \frac{F_A|_{V+\Delta V} - F_A|_V}{\Delta V} = r_A$$

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

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

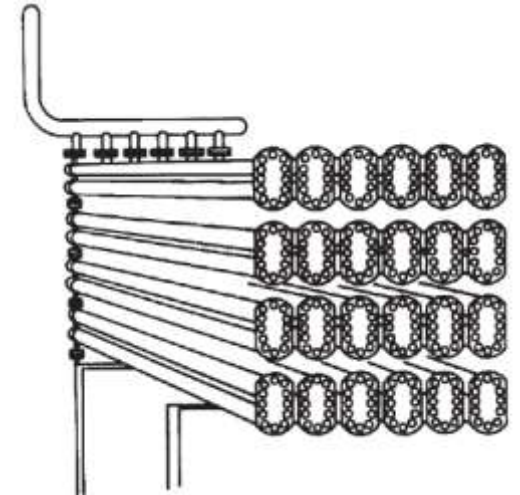


$$F_{A0} - F_A + \int r_A dV = \frac{dN_A}{dt}$$

Steady State

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

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



Alternative Derivation

Plug Flow Reactor - Mole Balances

Differentiate with respect to V

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

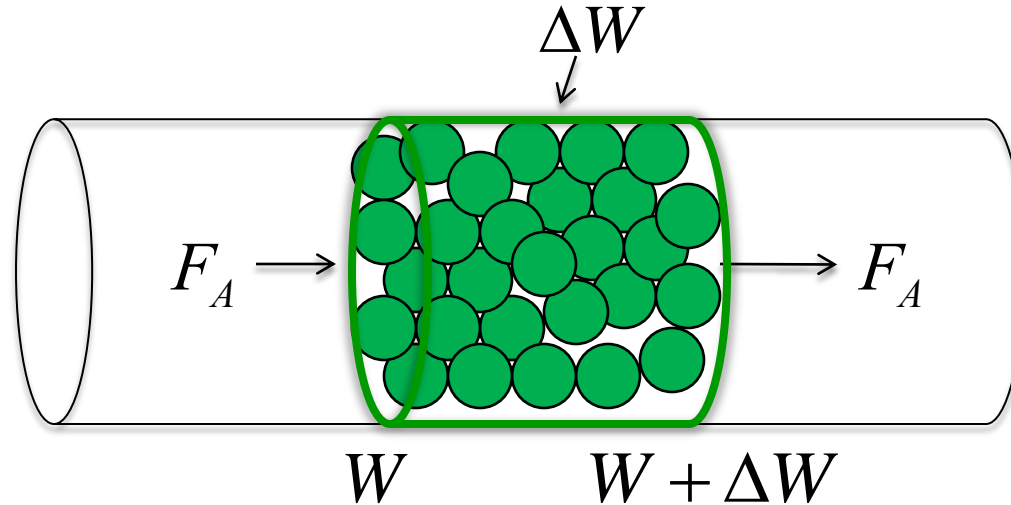
The integral form is:

$$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$$

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

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

Packed Bed Reactor - Mole Balances

Rearrange:

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

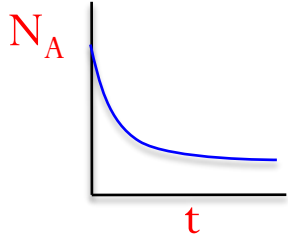
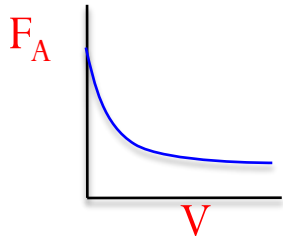
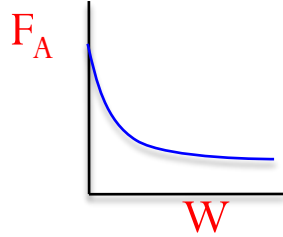
The integral form to find the catalyst weight is:

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

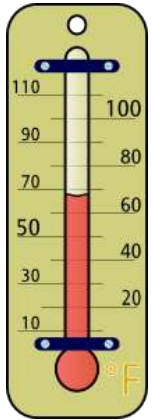
PBR catalyst weight necessary to reduce the entering molar flow rate F_{A0} to molar flow rate F_A .

Reactor Mole Balances Summary

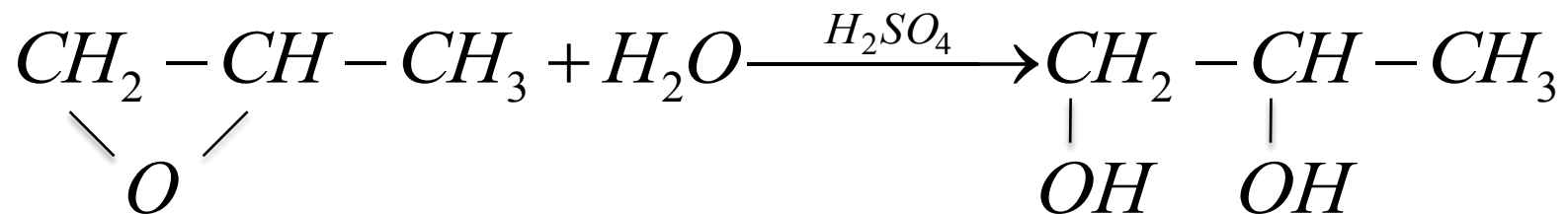
The GMBE applied to the four major reactor types
(and the general reaction $A \rightarrow B$)

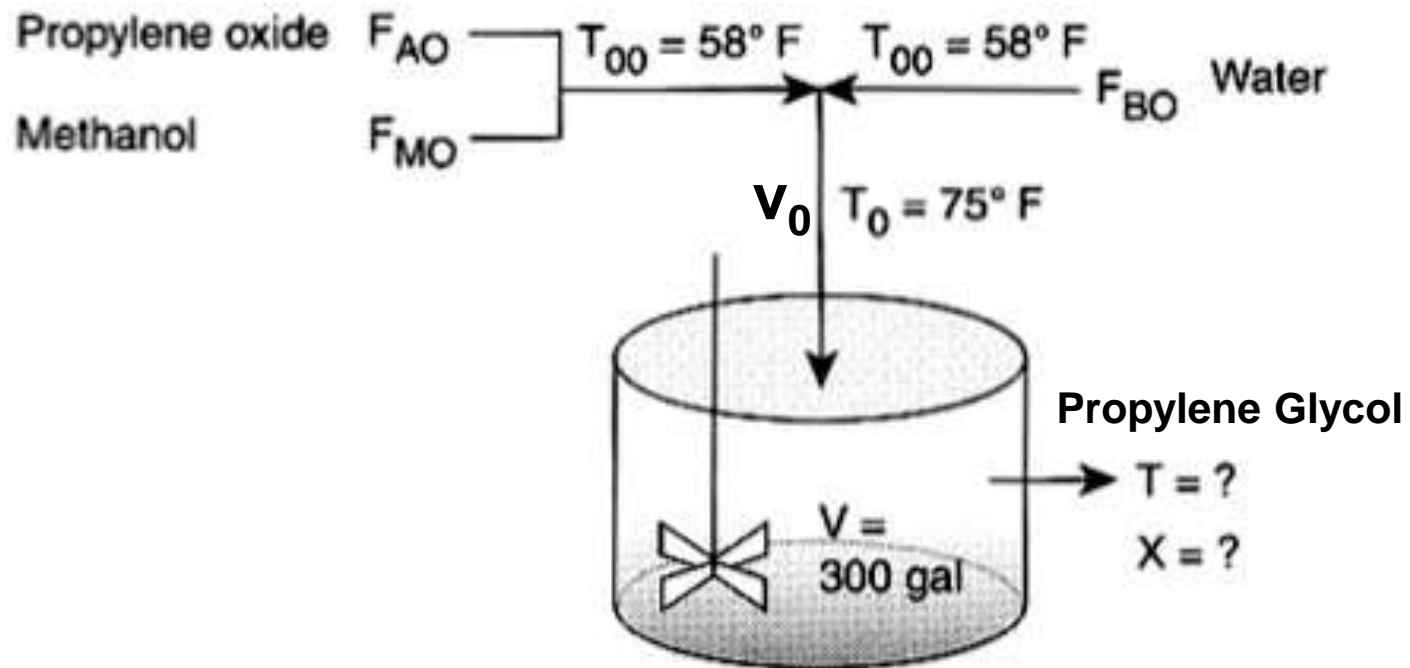
Reactor	Differential	Algebraic	Integral	
Batch	$\frac{dN_A}{dt} = r_A V$		$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A V}$	
CSTR		$V = \frac{F_{A0} - F_A}{-r_A}$		
PFR	$\frac{dF_A}{dV} = r_A$		$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{dr_A}$	
PBR	$\frac{dF_A}{dW} = r'_A$		$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A}$	

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



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**.

- b. *Stoichiometry* (C_{A0} , Θ_i , τ): 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: $\Theta_M = \frac{F_{M0}}{F_{A0}} = \frac{71.87 \text{ lb mol/h}}{43.0 \text{ lb mol/h}} = 1.67$

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

c. *Evaluate mole balance terms:* The conversion calculated from the mole balance, X_{MB} , is found from 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

$$X_{\text{EB}} = \frac{\sum \Theta_i C_{p_i} (T - T_{i0})}{-[\Delta H_{\text{Rx}}^{\circ}(T_R) + \Delta C_p (T - T_R)]}$$

d. Evaluate energy balance terms

$$\begin{aligned}\sum \Theta_i C_{P_i} &= C_{P_A} + \Theta_B C_{P_B} + \Theta_M C_{P_M} \\ &= 35 + (18.65)(18) + (1.67)(19.5)\end{aligned}$$

Substituting all the known quantities into the energy balance gives us

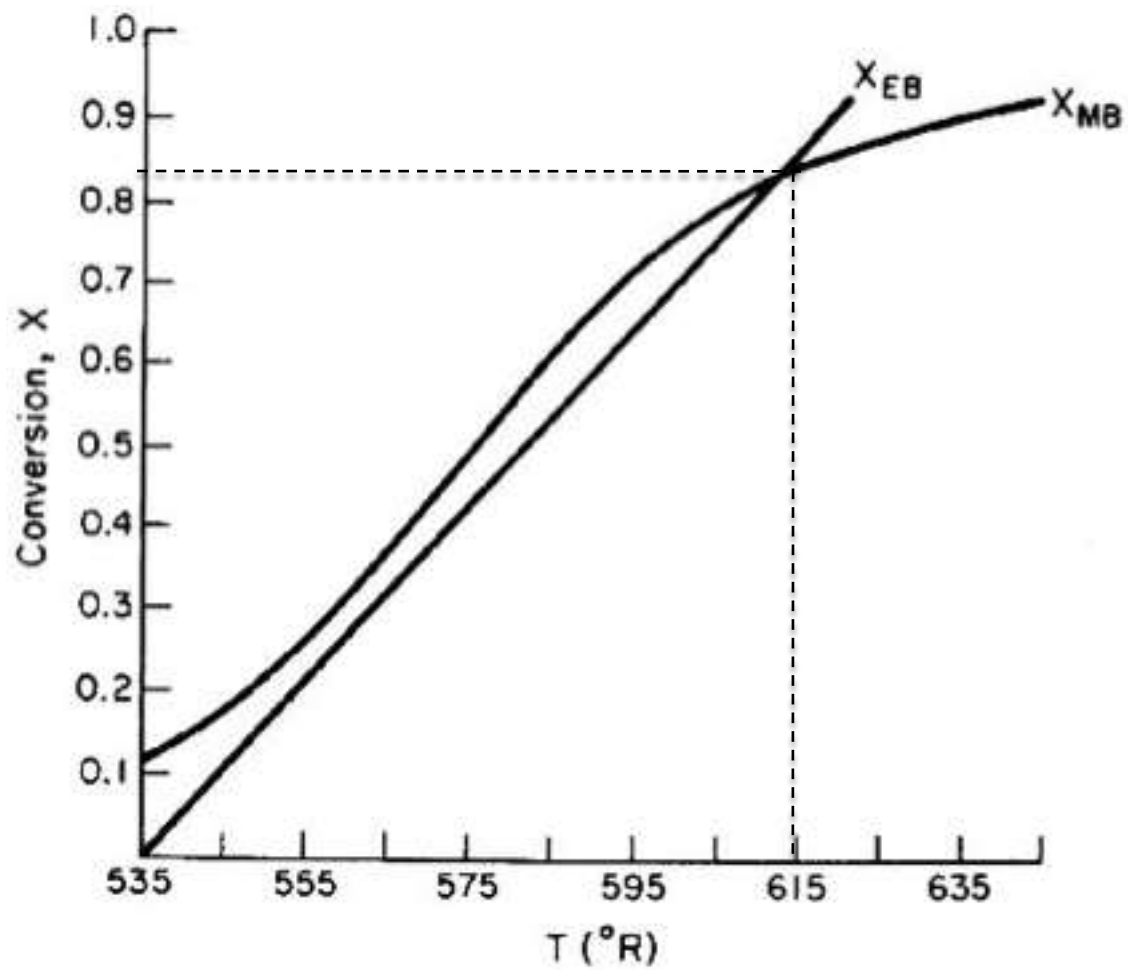
$$X_{EB} = \frac{(403.3 \text{ Btu/lb mol} \cdot ^\circ\text{F})(T - 535)^\circ\text{F}}{-[-36,400 - 7(T - 528)] \text{ Btu/lb mol}}$$

$$X_{EB} = -\frac{\sum \Theta_i C_{P_i} (T - T_{i0})}{\Delta H_{Rx}^\circ(T_R) + \Delta C_P (T - T_R)}$$

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

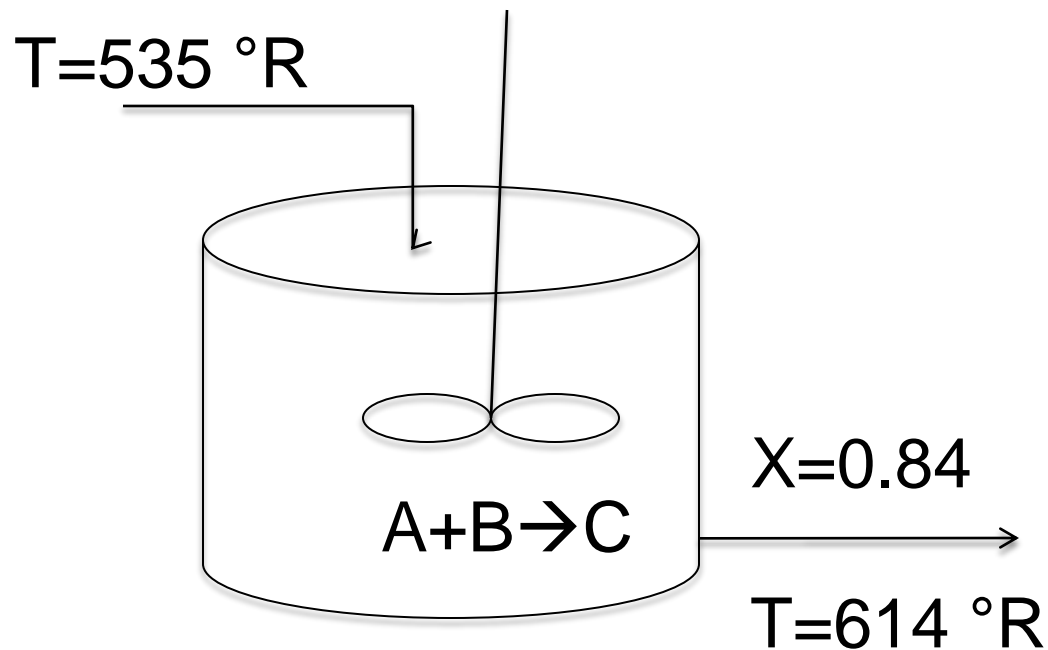
7. Solving.

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



Analysis

We have applied our CRE algorithm to calculate the Conversion ($X=0.84$) and Temperature ($T=614\text{ }^{\circ}\text{R}$) in a 300 gallon **CSTR** operated adiabatically.



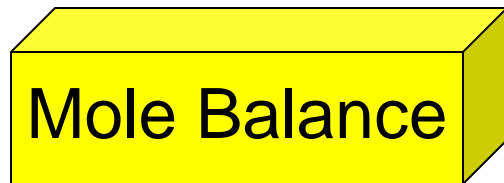
Keeping Up

Separations



These topics do not build upon one another.

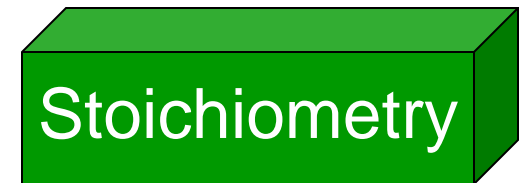
Reaction Engineering



Mole Balance

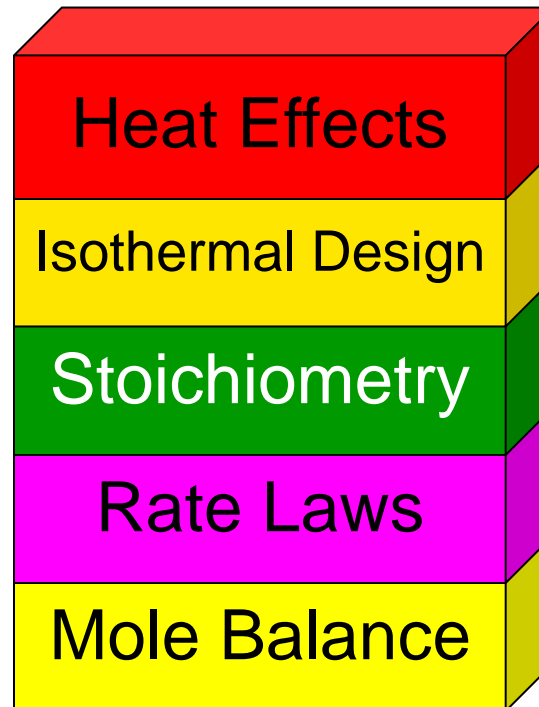


Rate Laws

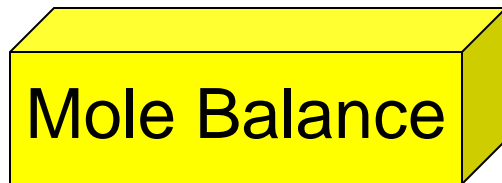


Stoichiometry

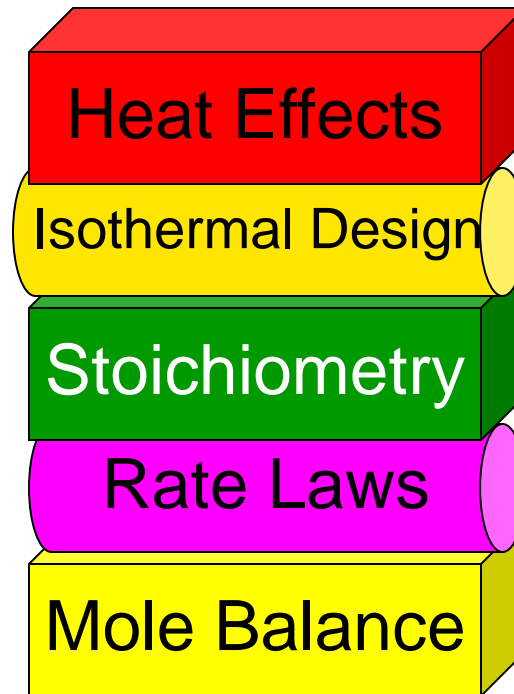
These topics build upon one another.



CRE Algorithm



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

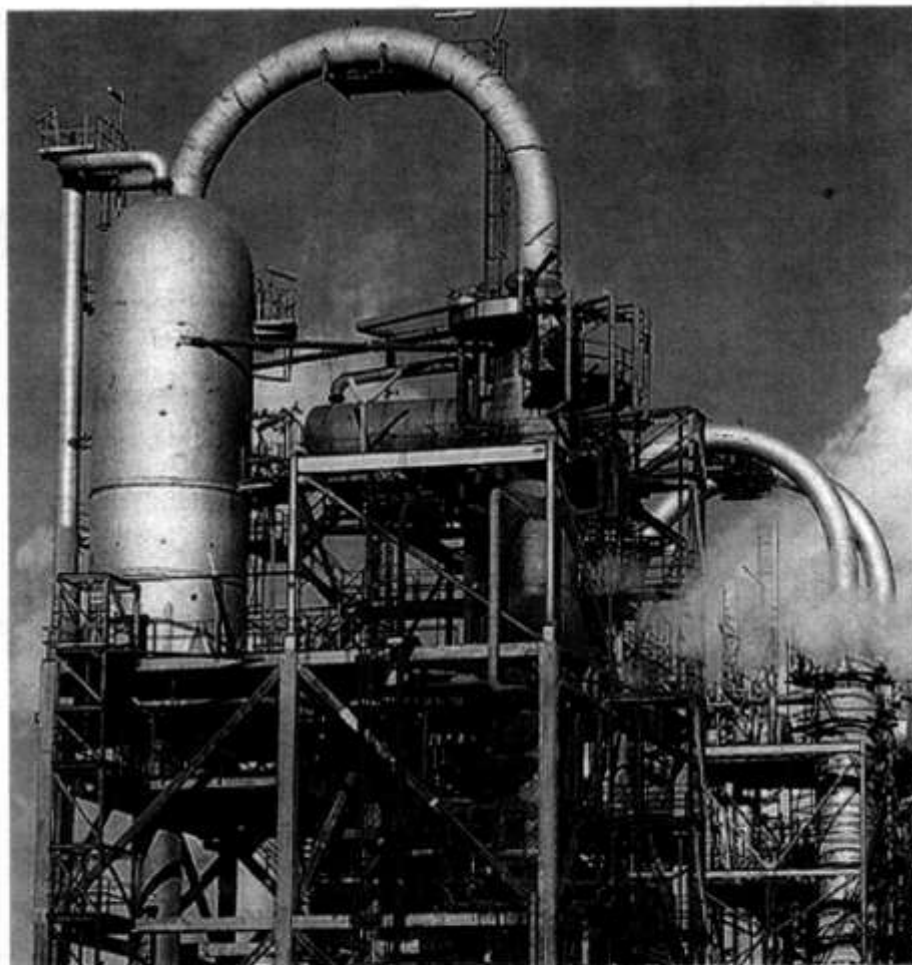
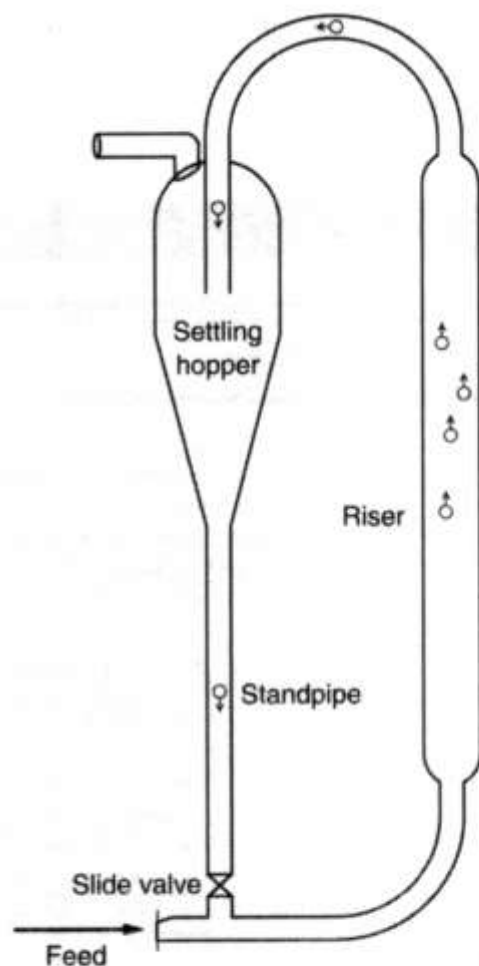


Otherwise, your Algorithm becomes unstable.

End of Lecture 1

Supplemental Slides

Additional Applications of CRE

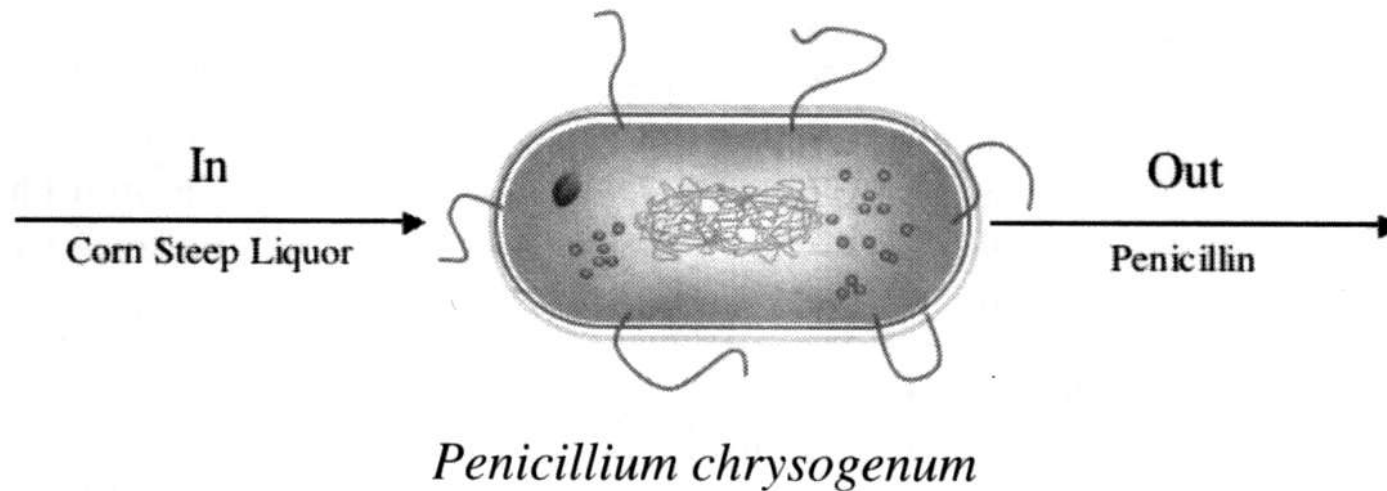


The reactor is 3.5 m in diameter and 38 m tall.

[Schematic and photo courtesy of Sasol/Sastech PT Limited.]

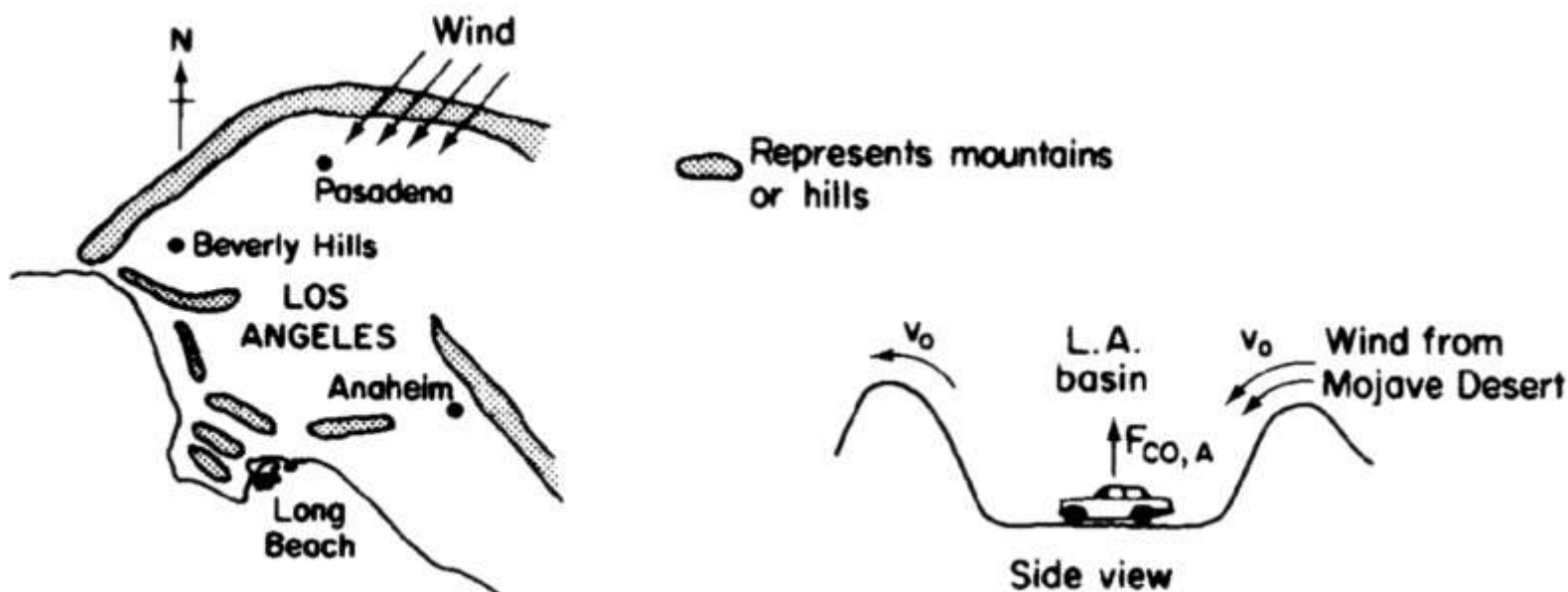
Supplemental Slides

Additional Applications of CRE



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^{*}

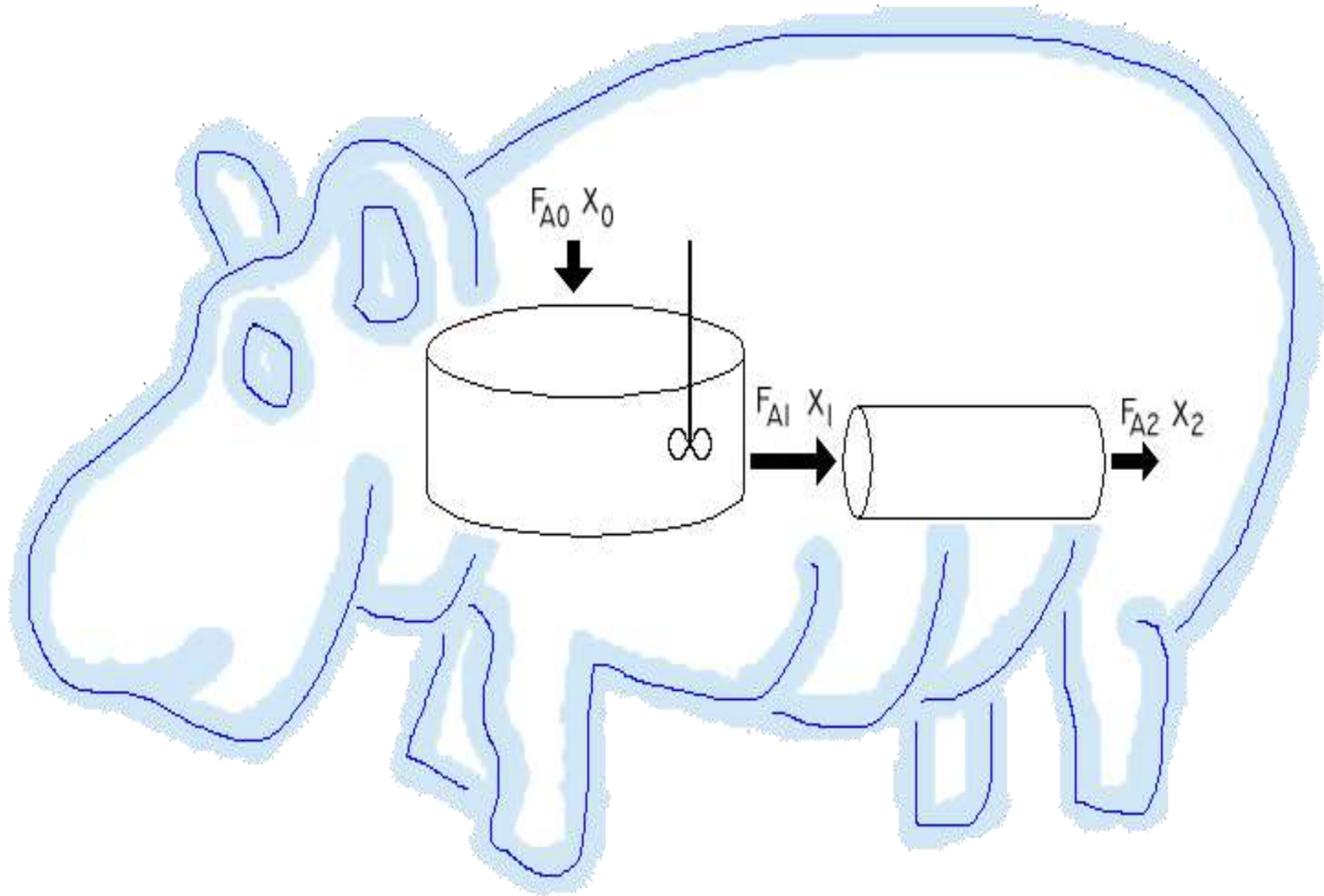
Matthew Robertson, Fredrik Persson, Brian Vicente, Professor H. Scott Fogler



"Even hippo's like Chemical Reaction Engineering."

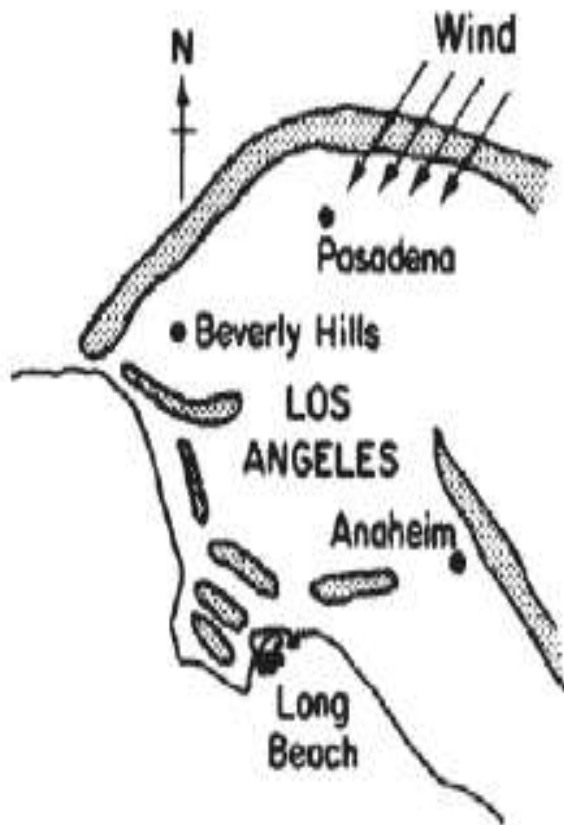
Supplemental Slides


Additional Applications of CRE

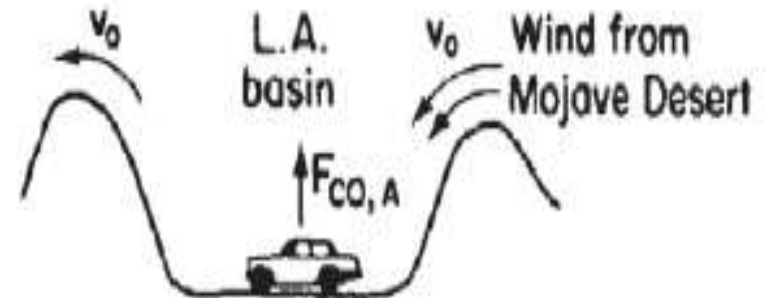


Supplemental Slides

Additional Applications of CRE



 Represents mountains or hills

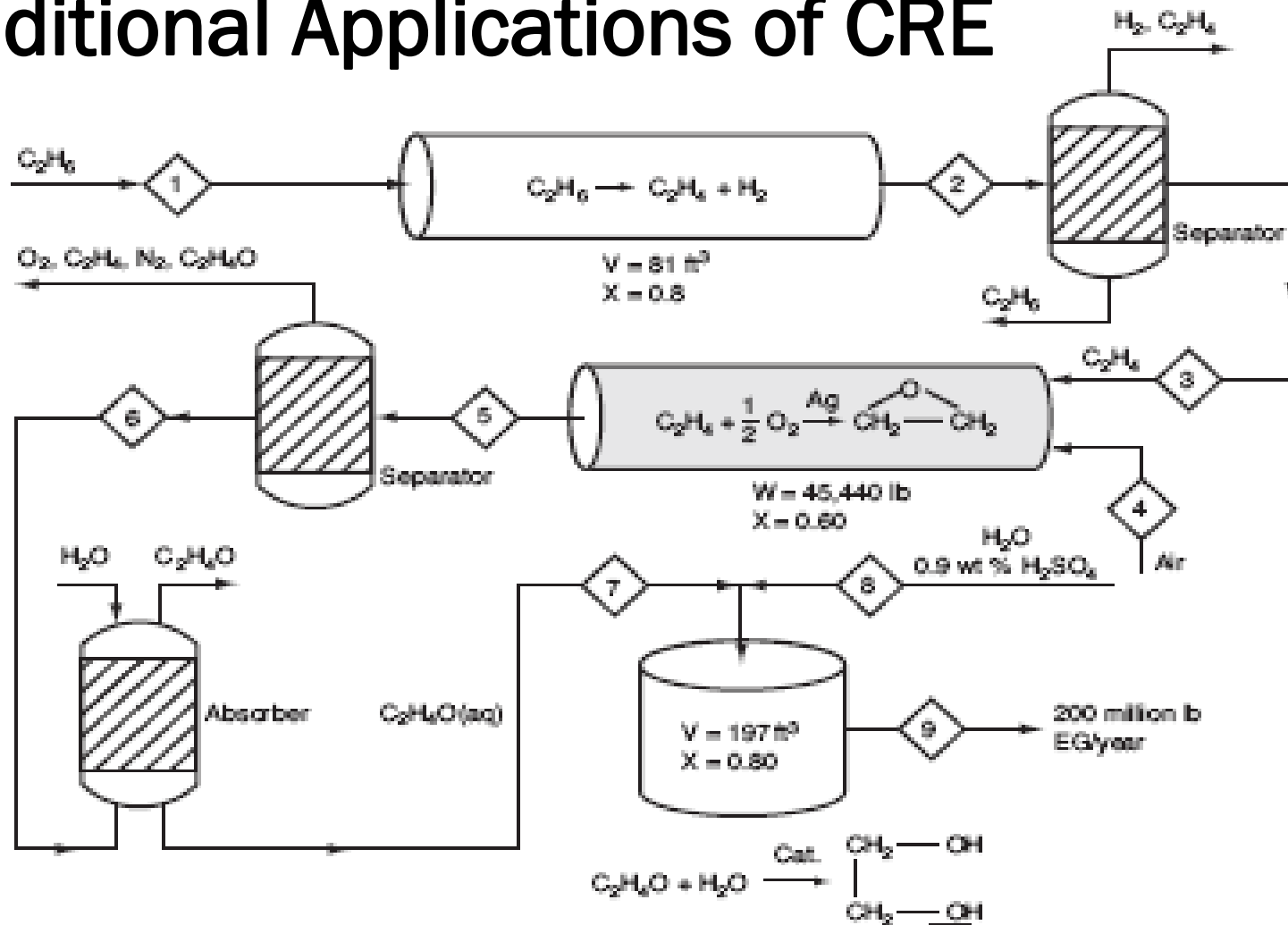


Smog (Ch. 1)

Side view

Supplemental Slides

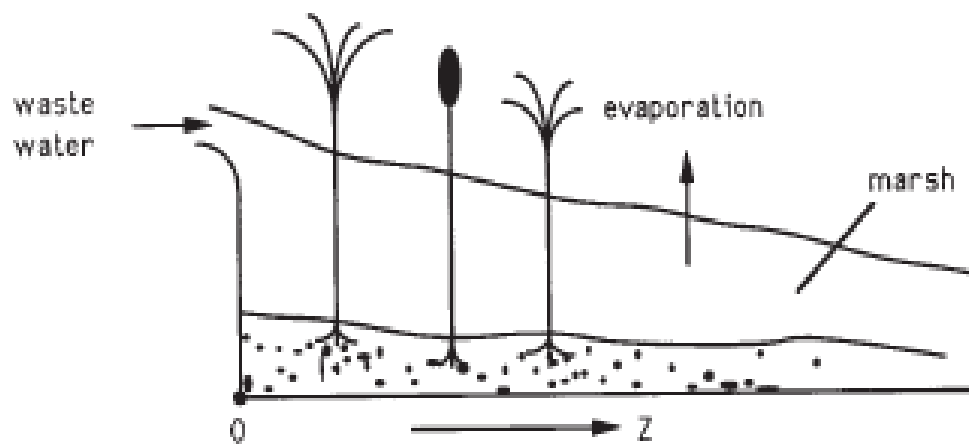
Additional Applications of CRE



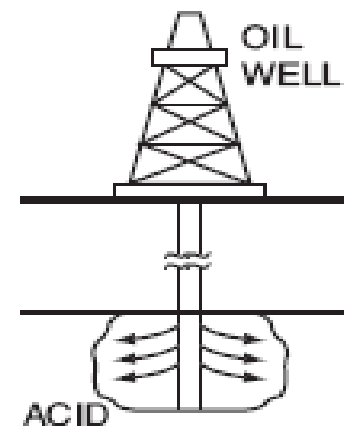
Chemical Plant for Ethylene Glycol (Ch. 5)

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

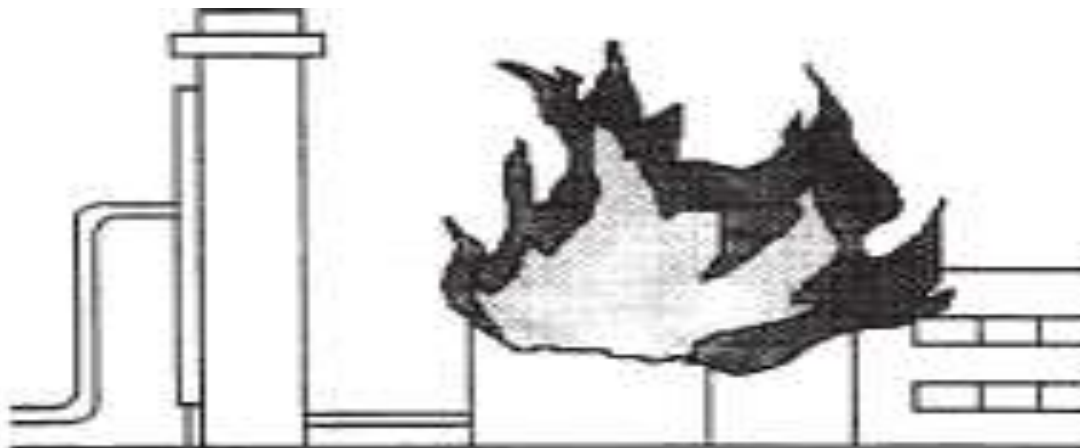


Effective Lubricant
Design Scavenging
Free Radicals

Lubricant Design (Ch. 9)

Supplemental Slides

Additional Applications of CRE



Nitroanaline Plant Explosion
Exothermic Reactions That
Run Away

Plant Safety
(Ch. 11,12,13)