



BITS, PILANI – K. K. BIRLA GOA CAMPUS

KINETICS & REACTOR DESIGN

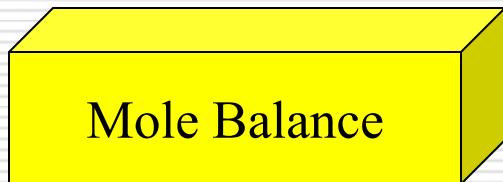
Chapter 4

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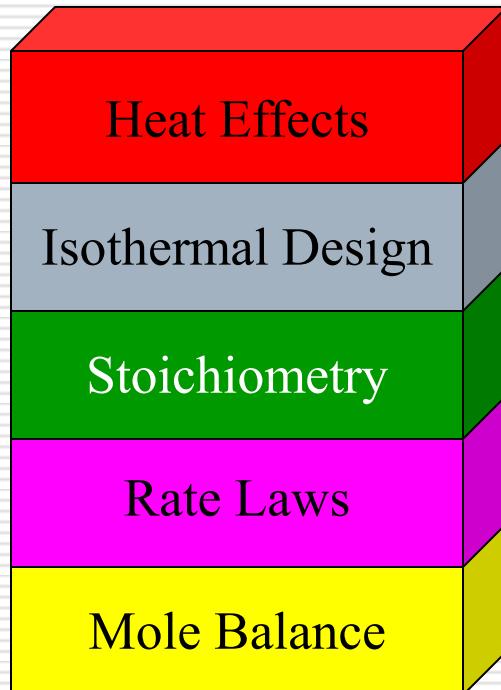


Time to put the Jigsaw together!!!

After this chapter you will be able to use the information from the previous 3 chapters together to arrive at a logical structure for design of reactors



Isothermal reactor design



Solve Reactor Engineering problems
via reasoning and not memorizing!!!

Just plugging formulas is risky

PART 1: Mole balances in terms of X

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)



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

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

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

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

$$V = V_0$$

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

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

$$V = V_0$$

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

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

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

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

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

From mole balance

From rate law

From stoichiometry

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

$$= \frac{kC_A}{F_{A0}}$$

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

$$\frac{dX}{dV} = \frac{k}{V_0 (1 + \varepsilon X)} Y \frac{T_0}{T}, \text{ where } Y = \frac{P}{P_0}$$

(A)

Integrating for the case of constant temperature and pressure gives

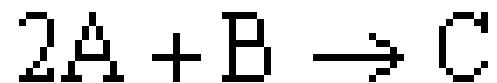
$$V = \frac{V_0}{k} \left[(1 + \varepsilon) \ln \frac{1}{1 - X} - \varepsilon X \right]$$

(B)

Algorithm for isothermal reactors.

Elementary Gas Phase reactions in various reactors (CSTR)

The elementary gas phase reaction takes place in a CSTR at constant temperature (500 K) and constant pressure (16.4 atm). The feed is equal molar in A and B.



Elementary Gas Phase reactions in various reactors (CSTR)

Mole balance

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

Rate Law

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

Stoichiometry

$$C_A = C_{A0} \frac{(1-X)}{(1-0.5X)}$$

DERIVE THE LAST
TWO



$$C_B = C_{A0}$$

Elementary Gas Phase reactions in various reactors (CSTR)

$$C_{A0} = \frac{y_{A0}P_0}{RT_0} = \frac{(0.5)(16.4 \text{ atm})}{\left(\frac{0.082 \text{ atm} \cdot \text{m}^3}{\text{kmol} \cdot \text{K}}\right)(500 \text{ K})} = 0.2 \frac{\text{kmol}}{\text{m}^3} = 0.2 \frac{\text{mol}}{\text{dm}^3}$$

$$-r_A = \left(0.08 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}} \right) \frac{(1-X)^2}{(1-0.5X)^2}$$

$$-r_A = k C_A^2 C_B = k C_{A0}^3 \frac{(1-X)^2}{(1-0.5X)^2}$$

$$V = \frac{F_{A0}X}{-r_A} = \frac{(5 \text{ mol/s})(0.9)[1-0.5(0.9)]^2}{\left(0.8 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}\right)(1-0.9)^2}$$

$$-r_A = \left(10 \frac{\text{dm}^6}{\text{mol}^2 \cdot \text{s}} \right) \left(0.2 \frac{\text{mol}}{\text{dm}^3} \right)^3 \frac{(1-X)^2}{(1-0.5X)^2}$$

$$V = 1701 \text{ dm}^3$$

Elementary Gas Phase reactions in various reactors (PFR)

Mole balance

$$V = F_{A0} \int_0^X \frac{dX}{-r_A}$$



Rate Law

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

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

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

$$v = v_o \left(1 - \frac{1}{2} X \right)$$

$$C_B = \frac{F_{A0}}{v} = \frac{F_{A0} \left(1 - \frac{X}{2} \right)}{v_o \left(1 - \frac{1}{2} X \right)} = C_{A0}$$

$$C_B = C_{A0}$$

Stoichiometry

Gas phase, isothermal ($T = T_0$), no pressure drop ($P = P_0$), $C_{A0} = C_{B0}$, $v = v_o(1 + \epsilon X)$

Elementary Gas Phase reactions in various reactors (PFR)

$$-r_A = kC_{A0}^3 \frac{(1-X)^2}{(1+\epsilon X)^2}$$

$$V = \frac{F_{A0}}{kC_{A0}^3} \int \frac{(1+\epsilon X)^2}{(1-X)^2} dX$$

$$V = \frac{F_{A0}}{kC_{A0}^3} \left[2\epsilon(1+\epsilon) \ln(1-X) + \epsilon^2 X + (\epsilon+1)^2 \frac{X}{1-X} \right]$$

$$V=227 \text{ dm}^3$$

$C_{A0}=0.2$, $v=v_o=25 \text{ dm}^3/\text{s}$,
 $k=10 \text{ dm}^6/\text{mol}^2 \text{ s}$, $\epsilon=-0.5$,
 $X=0.9$

$$V = \frac{\left(\frac{5 \text{ mol}}{\text{s}}\right)}{\left(10 \frac{\text{dm}^6}{\text{mol}^2 \cdot \text{s}}\right) \left(0.2 \frac{\text{mol}}{\text{dm}^3}\right)^3} = \left[2 \left(-\frac{1}{2}\right) \left(1 - \frac{1}{2}\right) \ln(1-0.9) + \left(-\frac{1}{2}\right)^2 (0.9) + \left(-\frac{1}{2} + 1\right)^2 \frac{0.9}{1-0.9} \right]$$

$$V = 6.25 \text{ dm}^3 [1.15 + 0.23 + 2.25] = 226.9 \text{ dm}^3$$

Elementary Gas Phase reactions in various reactors (Batch Reactor)

Mole balance

$$t = N_{A0} \int_0^X \frac{dX}{-r_A V} = C_{A0} \int_0^X \frac{dX}{-r_A}$$

Rate Law

$$-r_A = k C_A^2 C_B \quad C_A = \frac{N_A}{V_0} = \frac{N_{A0}}{V_0} (1 - X)$$

Stoichiometry

$$C_B = \frac{N_{A0}}{V_0} \left(\Theta_B - \frac{1}{2} X \right) = C_{A0} \left(1 - \frac{X}{2} \right)$$

$$P = \frac{N_T}{N_{T0}} P_0 = \frac{C_T}{C_{T0}} P_0$$

Elementary Gas Phase reactions in various reactors (Batch Reactors)

$$-r_A = k C_{A0}^3 (1-X)^2 \left(1 - \frac{X}{2}\right)$$

$$t = \frac{1}{k C_{A0}^2} \int_0^X \frac{dX}{(1-X)^2 \left(1 - \frac{X}{2}\right)}$$

$$C_{A0} = 0.2, k = 10 \text{ dm}^6/\text{mol}^2 \text{ s} \quad t = 41 \text{ sec}$$

$$P = \frac{N_T}{N_{T0}} P_0 = \frac{C_T}{C_{T0}} P_0$$

$$\begin{aligned} P &= \frac{N_T}{N_{T0}} P_0 = \frac{(N_{A0} + N_{B0} + \delta N_{A0} X) P_0}{N_{T0}} \\ &= (1 + \gamma_{A0} \delta X) P_0 \\ &= \left(1 + \left(\frac{1}{2}\right) \left(\frac{-1}{2}\right) (0.9)\right) 16.4 \\ &= 12.7 \text{ atm} \end{aligned}$$

Practice makes perfect!!!

The liquid phase reaction



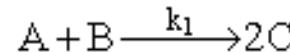
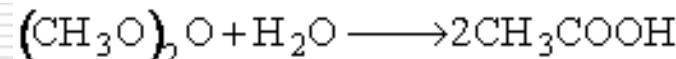
is carried out isothermally in a CSTR. Pure A enters at a volumetric flow rate of $25 \text{ dm}^3/\text{s}$ and at a concentration of 0.2 mol/dm^3 .

What CSTR volume is necessary to achieve a 90 % conversion when $k = 10 \text{ dm}^3/(\text{mol*s})$?
(1125 dm³)

What is the space time? **(45 secs)**

Practice makes perfect!!!

The hydrolysis of acetic anhydride is to be carried out at 25 °C. The water and acetic anhydride are mixed immediately before entering the reactor where the entering steam is 7.8 wt % acetic anhydride (1M) and 92.2 wt % water (51.2M). The volumetric feed rate of liquid in 0.0033 dm³/s.



$$k' = 1.97 \times 10^{-4} \text{ dm}^3/\text{mol s} @ 25^\circ\text{C} \text{ with } E = 12,000 \text{ cal/mol}$$

- (a) What conversion can be achieved in a 1 dm³ CSTR at 25°C?
- (b) What conversion can be achieved in a 0.311 dm³ PFR?
- (c) What time is required to achieve 80% conversion in a batch reactor?

Practice makes perfect!!!

Example: Determine X_e for a PFR with no pressure drop, $P = P_0$. Given that the system is gas phase and isothermal, determine the reactor volume when $X = 0.8 X_e$.

Reaction	Additional Information
$2A \rightleftharpoons B$	$C_{A0} = 0.2 \text{ mol/dm}^3$
	$k = 2 \text{ dm}^3/\text{mol}\cdot\text{min}$
	$K_C = 100 \text{ dm}^3/\text{mol}$
	$F_{A0} = 5 \text{ mol/min}$

Practice makes perfect!!!

- The following reaction takes place in a CSTR:



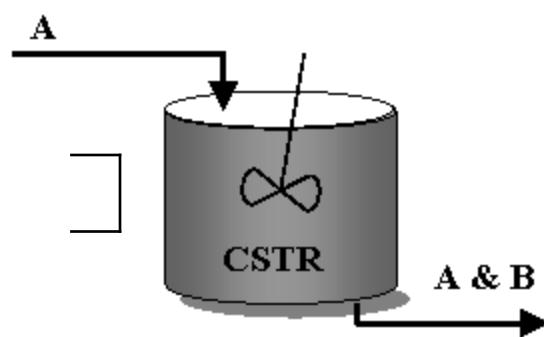
Pure A is fed to the reactor under the following conditions:

$$F_{T_0} = 40 \text{ mol/min}$$
$$C_{Ao} = 2 \text{ mol/dm}^3$$

$$V = 500 \text{ dm}^3$$

and

$$k = 0.1/\text{min}$$



Rate Law: $-r_A = kC_A$
What is the conversion in the CSTR?

Practice makes perfect!!!

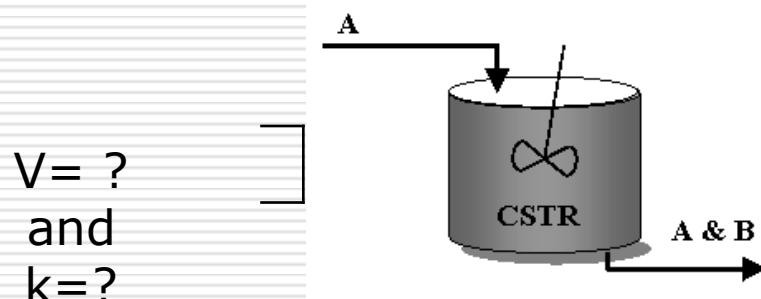
The following reaction takes place in a CSTR:



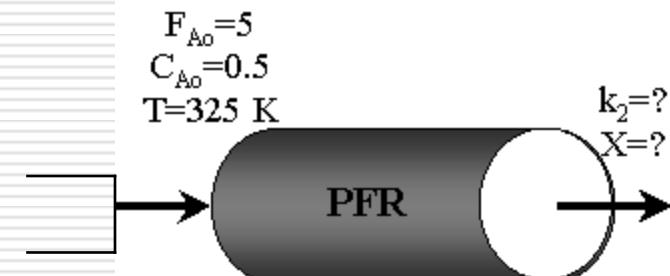
Pure A is fed to the reactor under the following conditions:

$$\begin{aligned} F_{A_0} &= 10 \text{ mol/min} \\ C_{A_0} &= 2 \text{ mol/dm}^3 \\ \text{At } T &= 350 \text{ K} \end{aligned}$$

Rate Law: $-r_A = kC_A$
The activation energy:
 $E = 20 \text{ kcal/mol}$



$$X = 0.75$$



Practice makes perfect!!!

The zero order reaction



is carried out in a CSTR and in a PFR. For an entering volumetric flowrate of $10 \text{ dm}^3/\text{s}$ at a concentration of $.5 \text{ mol/dm}^3$, what is the space time for each reactor to achieve 90% conversion.

Additional Information: $k_A = 0.01 \text{ mol/dm}^3\cdot\text{s}$

Zero order reaction in CSTR / PFR

Mole balance

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

$$V = \frac{\left(\frac{0.5 \text{ mol}}{\text{dm}^3}\right) \left(\frac{10 \text{ dm}^3}{\text{s}}\right) 0.9}{\frac{0.01 \text{ mol}}{\text{dm}^3 \times \text{s}}} = 450 \text{ dm}^3$$

Rate Law

$$-r_A = k_A$$

$$\tau = \frac{V}{v_0} = \frac{450 \text{ dm}^3}{\frac{10 \text{ dm}^3}{\text{s}}} = 45 \text{ s}$$

Stoichiometry

$$V = \frac{C_{A0} v_o X}{k_A}$$

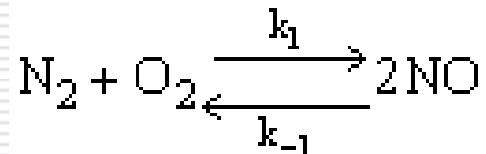
$$V = \frac{F_{A0} X}{k_A}$$

Zero order
reaction in CSTR
/ PFR

PFR: DIY

Final Problem

The following reaction follows an elementary rate law



Initially 77% N_2 , 15% O_2 , 8% inert are fed to a batch reactor where 80% of the equilibrium conversion ($X_e = 0.02$) is reached in 151 s. What is the specific reaction rate constant k_1 ?

Additional Information

$$X_e = 0.02, V = 0.4 \text{ dm}^3, K_C = 0.01, P = 20 \text{ atm}, T = 2700 \text{ K}$$

Scale up of liquid phase Batch reactor data

- Helps meet moving from lab scale (microplant) to real time reactors
- Analysis of batch scale data helps evaluate k
- Once k is known full scale batch reactor can be designed

Understanding Batch reactor times

$$t = N_{A0} \int_0^X \frac{dx}{-r_A V}$$

$$-r_A = kC_A^2$$

$$t = \frac{1}{kC_{A0}} \left[\frac{X}{1-X} \right]$$

Reaction time t_r	First order k (sec $^{-1}$)	Second order kC_{A0} (sec $^{-1}$)
Hours	10^{-4}	10^{-3}
Minutes	10^{-2}	10^{-1}
Seconds	1	10
Milliseconds	1000	10,000

For 1st Order

$$t = (1/k) \ln (X / 1 - X)$$

$$t = t_f + t_e + t_r + t_c$$

$$(1.5 - 3), (0.2 - 2.0), \\ \text{varies}, (0.5 - 1.0)$$

Slight Shift in approach!



GETTING TOUGH

Pressure Drop in Reactors

- ❑ In liquid phase reactions, the concentration of reactants is insignificantly affected by large changes in total pressure (TP)
- ❑ Effect of pressure can be neglected
- ❑ Important in gas phase reactions

Neglect ΔP



Include ΔP

Pressure Drop in Reactors

- Gas phase reactions occur in PFR or PBR

$$C_B = \frac{F_B}{v} = \frac{F_{A0} \left(\Theta_B - \frac{b}{a} x \right)}{v_0 (1 + \epsilon x)} \frac{T_0}{T} \frac{P}{P_0} = C_{A0} \frac{\left(\Theta_B - \frac{b}{a} x \right)}{(1 + \epsilon x)} \frac{T_0}{T} \frac{P}{P_0}$$

OBJECTIVE: Find ratio P/P_0 as a function of volume V or catalyst weight W to account for pressure drop

*** Differential form of the mole balance or design equation is used

Pressure Drop in PBR (STEP 1)

$(dX/dW) = F_1(X, P)$

Consider a second order irreversible gas phase reaction
that occurs isothermally in a PBR

$$A \rightarrow B \longrightarrow F_{AO} \frac{dX}{dW} = -r'_A \longrightarrow -r'_A = kC_A^2$$

$$C_A = \frac{F_A}{v} = C_{AO} \frac{(1-X)}{(1+\varepsilon X)} \frac{P}{P_0} \frac{T_0}{T} \longrightarrow -r_A = kC_A^2 = k \left(\frac{C_{AO}(1-X)}{(1+\varepsilon X)} \frac{P}{P_o} \right)^2$$

$$\frac{dX}{dW} = \frac{-r'_A}{F_{AO}} = k \frac{C_{AO}^2 (1-X)^2}{F_{AO} (1+\varepsilon X)^2} \left(\frac{P}{P_o} \right)^2 \longrightarrow \frac{dX}{dW} = k \frac{C_{AO}^2}{F_{AO}} \frac{(1-X)^2}{(1+\varepsilon X)^2} \left(\frac{P}{P_o} \right)^2$$

Pressure Drop in PBR (STEP 2)

$(dP/dW) = F_2(X, P)$

Need to find (P/P_0) as a function of W (or V if you have a PFR)

Ergun Equation

$$\frac{dP}{dz} = \frac{-G}{\rho g_c D_p} \left(\frac{1-\phi}{\phi^3} \right) \left[\underbrace{\frac{150(1-\phi)\mu}{D_p}}_{\text{laminar}} + \underbrace{1.75G}_{\text{turbulent}} \right]$$

ϕ = Porosity = void fraction = volume of void / total volume

$G = \rho u$ = superficial mass velocity (kg / m².s)

U = Superficial velocity = volumetric flow / superficial area (m/s)

Pressure Drop in PBR (STEP 2)

$(dP/dW) = F_2(X, P)$

From Continuity
Equation

$$\dot{m} = \dot{m}_0 \rightarrow \rho u = \rho_0 u_0 \rightarrow \rho = \frac{\rho_0 u_0}{u}$$

$$u = u_0 \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}} \rightarrow \rho = \frac{\rho_0 u_0}{u_0} \frac{P}{P_0} \frac{T_0}{T} \frac{F_{T0}}{F_T} \rightarrow \rho = \rho_0 \frac{P}{P_0} \frac{T_0}{T} \frac{F_{T0}}{F_T}$$

$$\frac{dP}{dz} = \frac{-G}{\rho_0 g_c D_p} \left(\frac{1-\phi}{\phi^3} \right) \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right] \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

$$dP / dz = \beta_o (P_0/P) (T/T_0)(F_T/F_{T0}) \rightarrow \beta_o = \frac{G}{\rho_0 g_c D_p} \left(\frac{1-\phi}{\phi^3} \right) \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right]$$

z is not our interest, W is!!!

Pressure Drop in PBR (STEP 2)

Get P in terms of W and not z!

CATALYST WEIGHT

**Bulk density is
mass of catalyst
per unit volume of
reactor bed**

$$W = z A_c \rho_b = z A_c (1 - \phi) \rho_c \rightarrow A$$

ρ_b = bulk density

ρ_c = solid catalyst density

ϕ = porosity (a.k.a., void fraction)

$$\frac{dP}{dz} = -\beta_0 \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}} \rightarrow$$

$$\frac{dP}{dz} = \frac{dP}{dz} \frac{A_c (1 - \phi) \rho_c}{A_c (1 - \phi) \rho_c}$$

$$\frac{dP}{dz} = \frac{dP}{d[z A_c (1 - \phi) \rho_c]} [A_c (1 - \phi) \rho_c]$$

$$\frac{dP}{dz} = \frac{dP}{dW} A_c (1 - \phi) \rho_c \rightarrow$$

$$\frac{dP}{dW} = \frac{dP}{dz} \frac{1}{A_c (1 - \phi) \rho_c}$$

$$\frac{dP}{dW} = \frac{-\beta_0}{A_c (1 - \phi) \rho_c} \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

Pressure Drop in PBR (STEP 2)

Get P in terms of W and not z!

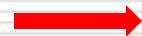
$$\frac{dP}{dW} = \frac{-\beta_0}{A_c(1-\phi)p_c} \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$



$$\frac{dP}{dW} = -\frac{\alpha}{2} \left(\frac{P_0}{P} \right) \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

$$\alpha = \frac{2\beta_0}{A_c(1-\phi)p_c} \frac{1}{P_0}$$

$$\frac{d\left(\frac{P}{P_0}\right)}{dW} = -\frac{\alpha}{2} \left(\frac{P}{P_0} \right) \frac{T}{T_0} \frac{F_T}{F_{T0}}$$



$$\frac{dy}{dW} = -\frac{\alpha}{2y} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

$$\left(y = \frac{P}{P_0} \right)$$



More suited for multiple reactions or for pressure drop in membrane reactors

For single reactions use Ergun equation

Pressure Drop in PBR (STEP 2)

Single Reactions

$$\frac{dP}{dW} = -\frac{\alpha}{2} \left(\frac{P_0}{P/P_0} \right) \frac{T}{T_0} \frac{F_T}{F_{T0}} \quad \longrightarrow \quad F_T = F_{T0} + F_{A0} \delta X = F_{T0} \left(1 + \frac{F_{A0} \delta X}{F_{T0}} \right)$$

$$F_T = F_{T0} (1 + y_{A0} \delta X) = F_{T0} (1 + \varepsilon X) \quad \longrightarrow \quad \frac{F_T}{F_{T0}} = (1 + \varepsilon X)$$

$$\frac{dP}{dW} = -\frac{\alpha}{2} \left(\frac{P_0}{P/P_0} \right) \frac{T}{T_0} (1 + \varepsilon X) \quad \longrightarrow \quad \frac{d(P/P_0)}{dW} = -\frac{\alpha}{2} \frac{1}{(P/P_0)} \frac{T}{T_0} (1 + \varepsilon X)$$

$$\boxed{\frac{dy}{dW} = -\frac{\alpha}{2y} \frac{T}{T_0} (1 + \varepsilon X)} \quad \longrightarrow \quad \boxed{\frac{dy}{dW} = -\frac{\alpha}{2y} (1 + \varepsilon X)}$$

Pressure Drop in PBR (FINALLY!)

$$\frac{dX}{dW} = f(X, P) \text{ and } \frac{dP}{dW} = f(X, P) \text{ or } \frac{dy}{dW} = f(y, X)$$

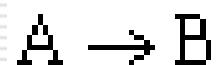


WHEW!!!!

**FINALLY WE HAVE
SOMETHING**

**TWO COUPLED FIRST
ORDER DIFFERENTIAL
EQUATIONS SOLVED
ANALYTICALLY OR BY
COMPUTER**

ANALYTICAL SOLUTION



$$-r_A = kC_A^2$$

$$\frac{dy}{dW} = -\frac{\alpha}{2y}(1 + \varepsilon X)$$

IF $T = T_0$ AND $\varepsilon = 0$



$$y = (1 - \alpha W)^{1/2}$$



Never use this form when $\varepsilon \neq 0$ or for non-isothermal reactions

$$y = P / P_o = [1 - (2\beta_o z / P_o)]^{1/2} \quad \Delta P = f(z)$$

Where does this end?

For $\varepsilon = 0$ $C_A = C_{A0} (1 - X) y = C_{A0} (1 - X)(1 - \alpha W)^{1/2}$

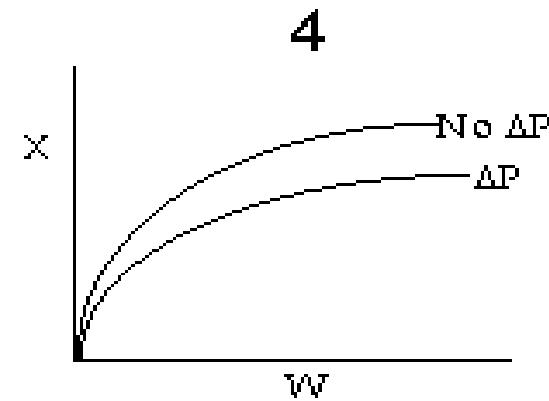
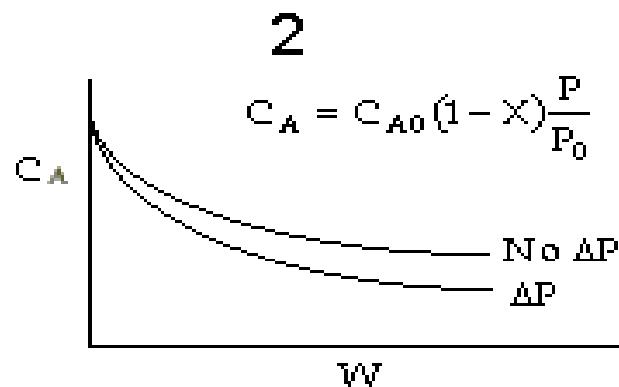
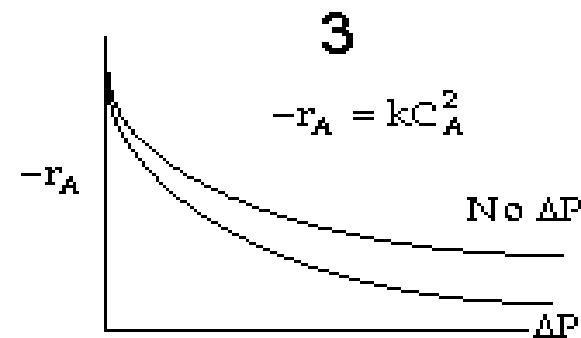
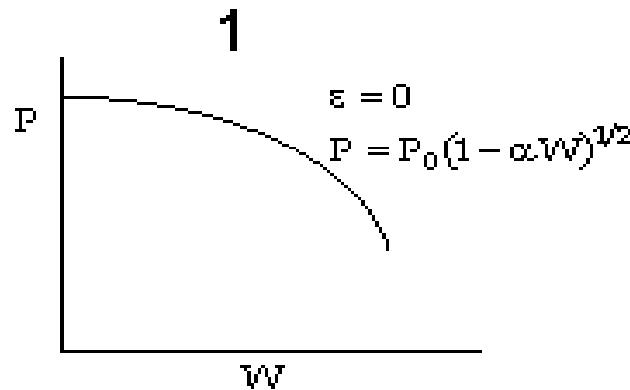
$$-\dot{r}_A = kC_A^2 = kC_{A0}^2 (1 - X)^2 (1 - \alpha W) \rightarrow F_{A0} \frac{dX}{dW} = -\dot{r}_A$$

$$\frac{dX}{dW} = \frac{kC_{A0}^2}{F_{A0}} (1 - X)^2 (1 - \alpha W) \rightarrow \left[\frac{1}{(1 - X)^2} \right] dX = \left[\frac{kC_{A0}^2}{F_{A0}} (1 - \alpha W) \right] dW$$

$$\int_0^X \left[\frac{1}{(1 - X)^2} \right] dX = \frac{kC_{A0}^2}{F_{A0}} \int_0^W (1 - \alpha W) dW \rightarrow \frac{X}{1 - X} = \frac{kC_{A0}^2}{F_{A0}} \left[W - \frac{\alpha W^2}{2} \right]$$

We can now solve for X given W, or for W given X

What does all this imply?



Calculating pressure drop (TB problem)

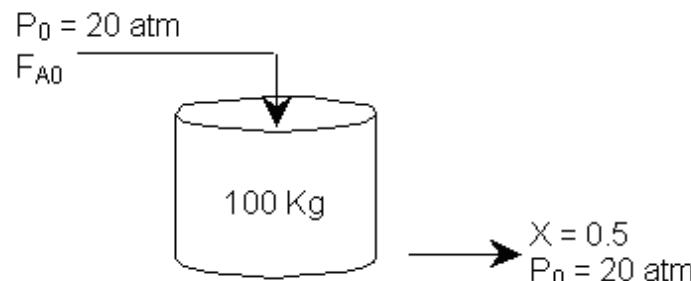
Plot the pressure drop in a 60 ft length of 1 and 1/2" Schedule 40 pipe packed with catalyst pellets 1/4" in diameter. There is a 104.4 lb_m/hr of gas flowing through the bed. The temperature is constant along the length of the pipe at 260 °C. The void fraction is 45 %and properties of gas are the same of air at this temperature. The entering pressure is 10 atm

$$y = P / P_o = [1 - (2\beta_o z / P_o)]$$

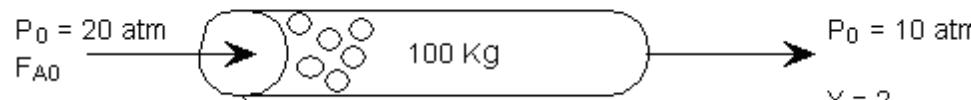
$$\beta_o = \frac{G}{P_0 g_c D_p} \left(\frac{1-\phi}{\phi^3} \right) \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right]$$

Calculating pressure drop (Let us try this)

The elementary isomerization $A \rightarrow B$ is carried out at 20 atm in a fluidized CSTR containing 100 kg of catalyst where 50% conversion is achieved



It is proposed to replace the CSTR with a packed bed reactor. The entering pressure was 20 atm and the exit pressure was found to be 10 atm.



What would be the conversion if No pressure drop?

$$\frac{dX}{dW} = -\frac{r_A'}{F_{A0}} = \frac{kC_{A0}}{F_{A0}}(1-X)_y \rightarrow \frac{dX}{dW} = \frac{kC_{A0}}{F_{A0}}(1-X)$$

$$\frac{dX}{1-X} = \frac{kC_{A0}}{F_{A0}} dW \rightarrow \ln \frac{1}{1-X} = \frac{kC_{A0}}{F_{A0}} W = \left(\frac{1}{100\text{kg}}\right)(100\text{kg}) = 1$$

$$\begin{aligned} \ln(1-X) &= -1 \\ 1-X &= e^{-1} \end{aligned} \rightarrow \boxed{X = 1 - e^{-1} = 0.632}$$

**What information can you obtain from the CSTR?
Recollect the kV problem related to CSTR / PFR.**

What would be the conversion in the PBR with pressure drop?

$$\frac{dX}{dW} = \frac{-r'_A}{F_{A0}} = \frac{-r'_A}{C_{A0}v_0} \quad -r'_A = kC_A \quad \rightarrow \quad \frac{dX}{dW} = -\frac{r'_A}{F_{A0}} = \frac{kC_{A0}}{F_{A0}}(1-X)y$$

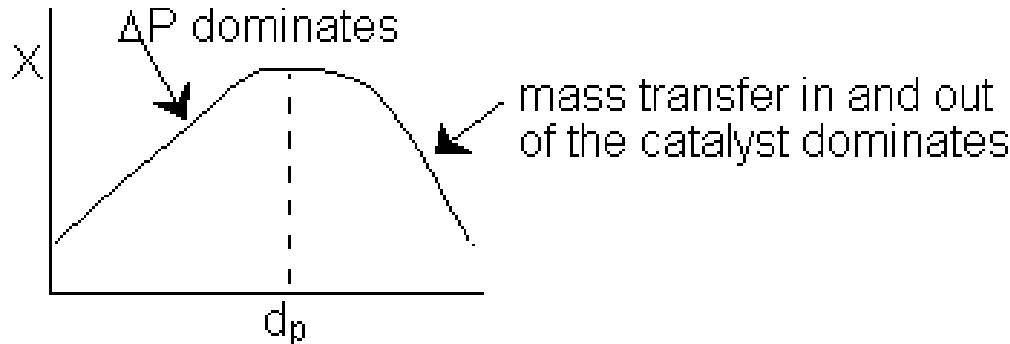
$$\frac{dX}{1-X} = \left(\frac{kC_{A0}}{F_{A0}} \right) (1-\alpha W)^{1/2} dW \quad \rightarrow \quad \ln \frac{1}{1-X} = \frac{kC_{A0}}{F_{A0}} \left[\frac{2}{3\alpha} \left[1 - (1-\alpha W)^{3/2} \right] \right]$$

NOTE $y = (1-\alpha W)^{1/2}$, $y^3 = (1-\alpha W)^{3/2}$

X = 0.54

How do you calculate the pressure drop parameter?

Plot the conversion as a function of particle diameter assume everything else is unchanged.



Suppose you could choose another pipe diameter to hold the same amount of catalyst. Would you choose a larger or smaller pipe diameter, or would you use the current pipe diameter? Explain.

As the particle diameter decreases, the pressure drop increases, so the concentration decreases as does the reaction rate. Consequently when the reaction rate is small the conversion will be small. As the particle size increases the pressure drop decreases and conversion increases. As the particle size increases the pressure drop decreases and the concentration increases. however, for large particles, it takes a long time for the reactants to diffuse in and out of the catalyst particle.

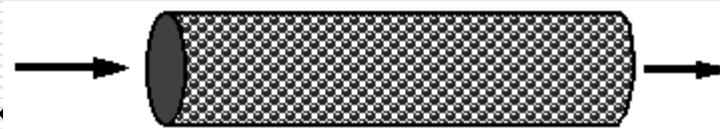
Practice (DIY)

What is the conversion of the PFR?



$$W = 500\text{kg}$$

$$k = 0.1111 \text{ dm}^3 \text{ s}^{-1}$$



$$X = ?$$

$$F_{A0} = 10 \text{ mol/s}$$

$$C_{A0} = 1 \text{ mol/dm}^3$$

$$\frac{dX}{dW} = \frac{-r'_A}{F_{A0}}$$

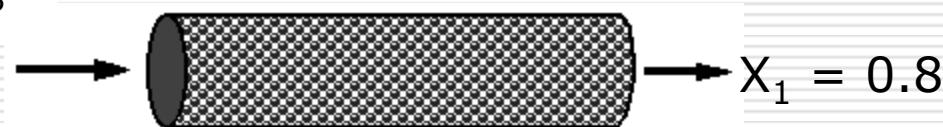
$$0.96$$

Practice (DIY)



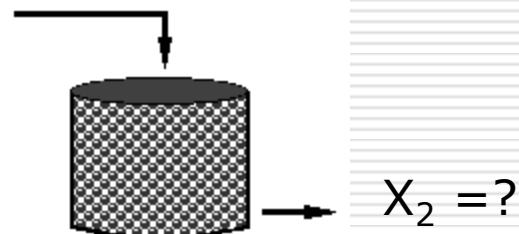
$$F_{A0} = 10 \text{ mol/s}$$

$$C_{A0} = 0.1 \text{ mol/dm}^3$$



$$W_2 = W_1$$
$$T = 350 \text{ K}$$

$$W_1 = ?$$
$$T = 325 \text{ K}; E = 2500 \text{ cal}$$



$$\mathbf{X = 0.66}$$

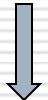
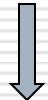
Solution

$$-r' A = \frac{-r_A}{\rho_B}$$

$$2 \ln \frac{1}{1-X} - X = \frac{k C_{A_0}}{F_{A_0}} W$$

$$k_2 = k_1 \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]$$

$$V = \frac{F_{A_0} X}{-r_A} \quad W = \frac{F_{A_0} X \rho_B}{-r_A}$$

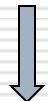
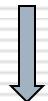


$$r' A = k_2 C_A$$

$$W k_1 = \frac{F_{A_0}}{C_{A_0}} \left[2 \ln \frac{1}{1-X} - X \right]$$

$$W k_2 = W k_1 \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right]$$

$$W = \frac{F_{A_0} X}{-r' A}$$



$$W k_1 = \frac{10}{0.1} \left[2 \ln \frac{1}{1-0.8} - 0.8 \right]$$

$$W k_2 = (242) \exp \left[\frac{2500}{1.987} \left(\frac{1}{325} - \frac{1}{350} \right) \right]$$

$$W = \frac{F_{A_0} X (1+X)}{k_2 C_{A_0} (1-X)}$$

$$= 242 \frac{\text{dm}^3}{\text{sec}}$$

$$= 319 \frac{\text{dm}^3}{\text{sec}}$$

$$W k_2 = \frac{F_{A_0} X (1+X)}{C_{A_0} (1-X)}$$

$$319 = \frac{(10)X(1+X)}{(0.1)(1-X)} \quad \mathbf{X = 0.66}$$



Space time and reactor design

In Chapter 2, we derived the following design equation for a CSTR:

$$V = \frac{F_{A0}X}{(-r_A)_{\text{exit}}} \quad (2-13)$$

which gives the volume V necessary to achieve a conversion X . As we saw in Chapter 2, the space time, τ , is a characteristic time of a reactor. To obtain the space time, τ , as a function of conversion we first substitute for $F_{A0} = v_0C_{A0}$ in Equation (2-13)

$$V = \frac{v_0C_{A0}X}{-r_A} \quad (4-6)$$

and then divide by v_0 to obtain the space time, τ , to achieve a conversion X in a CSTR

$$\tau = \frac{V}{v_0} = \frac{C_{A0}X}{-r_A} \quad (4-7)$$

This equation applies to a single CSTR or to the first reactor of CSTRs connected in series.

4.3.1 A Single CSTR

Let's consider a first-order irreversible reaction for which the rate law is

$$-r_A = kC_A$$

For liquid-phase reactions, there is no volume change during the course of the reaction, so we can use Equation (3-29) to relate concentration and conversion,

$$C_A = C_{A0}(1 - X) \quad (3-29)$$

We can combine mole balance Equation (4-7), the rate law and concentration, Equation (3-29) to obtain

$$\tau = \frac{1}{k} \left(\frac{X}{1 - X} \right)$$

Rearranging

$$X = \frac{\tau k}{1 + \tau k} \quad (4-8)$$

We could also combine Equations (3-29) and (4-8) to find the exit reactor concentration of A, C_A ,

$$C_A = \frac{C_{A0}}{1 + \tau k} \quad (4-10)$$

For a first-order reaction, the product τk is often referred to as the **Damköhler number**, Da , which is a dimensionless number that can give a quick estimate of the degree of conversion that can be achieved in continuous flow reactors. The Damköhler number is the ratio of the rate of reaction to the rate of convective transport of A at the entrance to the reactor.

$$Da = \frac{-r_{A0}V}{F_{A0}} = \frac{\text{Rate of reaction at entrance}}{\text{Entering flow rate of A}} = \frac{\text{"A reaction rate"}}{\text{"A convection rate"}}$$

The Damköhler number for a first-order irreversible reaction is

$$Da = \frac{-r_{A0}V}{F_{A0}} = \frac{kC_{A0}V}{v_0 C_{A0}} = \tau k$$

For a second-order irreversible reaction, the Damköhler number is

$$Da = \frac{-r_{A0}V}{F_{A0}} = \frac{kC_{A0}^2 V}{v_0 C_{A0}} = \tau k C_{A0}$$

Damkohler's number

It is important to know what values of Damkohler number, Da give high and low conversion in continuous flow reactors.

Equation for the 1st order liquid phase reaction in a CSTR can also be written in the Terms of Damkohler number

$$X = \frac{Da}{1 + Da}$$

if $Da < 0.1$, then $X < 0.1$

if $Da > 10$, then $X > 0.9$

CSTR in series

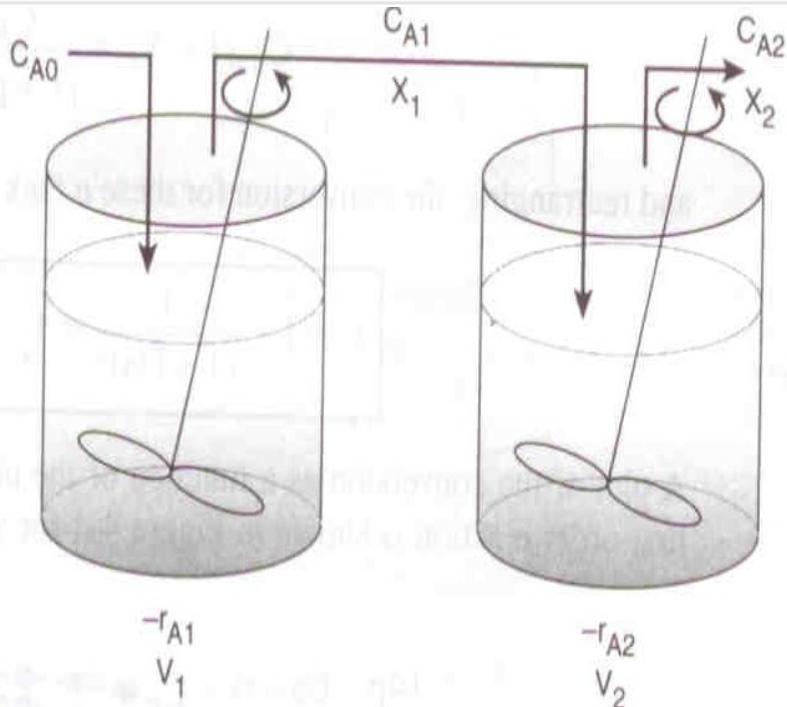
A first order reaction with no change in the volumetric flow rate is to be carried out in two CSTRs placed in series:

The effluent concentration of reactant A from the first CSTR can be found using Equation (4-9)

$$C_{A1} = \frac{C_{A0}}{1 + \tau_1 k_1}$$

with $\tau_1 = V_1/v_0$. From a mole balance on reactor 2,

$$V_2 = \frac{F_{A1} - F_{A2}}{-r_{A2}} = \frac{v_0(C_{A1} - C_{A2})}{k_2 C_{A2}}$$



Solving for C_{A2} , the concentration exiting the second reactor, we obtain

$$C_{A2} = \frac{C_{A1}}{1 + \tau_2 k_2} = \frac{C_{A0}}{(1 + \tau_2 k_2)(1 + \tau_1 k_1)}$$

If both reactors are of equal size ($\tau_1 = \tau_2 = \tau$) and operate at the same temperature ($k_1 = k_2 = k$), then

$$C_{A2} = \frac{C_{A0}}{(1 + \tau k)^2}$$

If instead of two CSTRs in series we had n equal-sized CSTRs connected in series ($\tau_1 = \tau_2 = \dots = \tau_n = \tau_i = (V_i/v_0)$) operating at the same temperature ($k_1 = k_2 = \dots = k_n = k$), the concentration leaving the last reactor would be

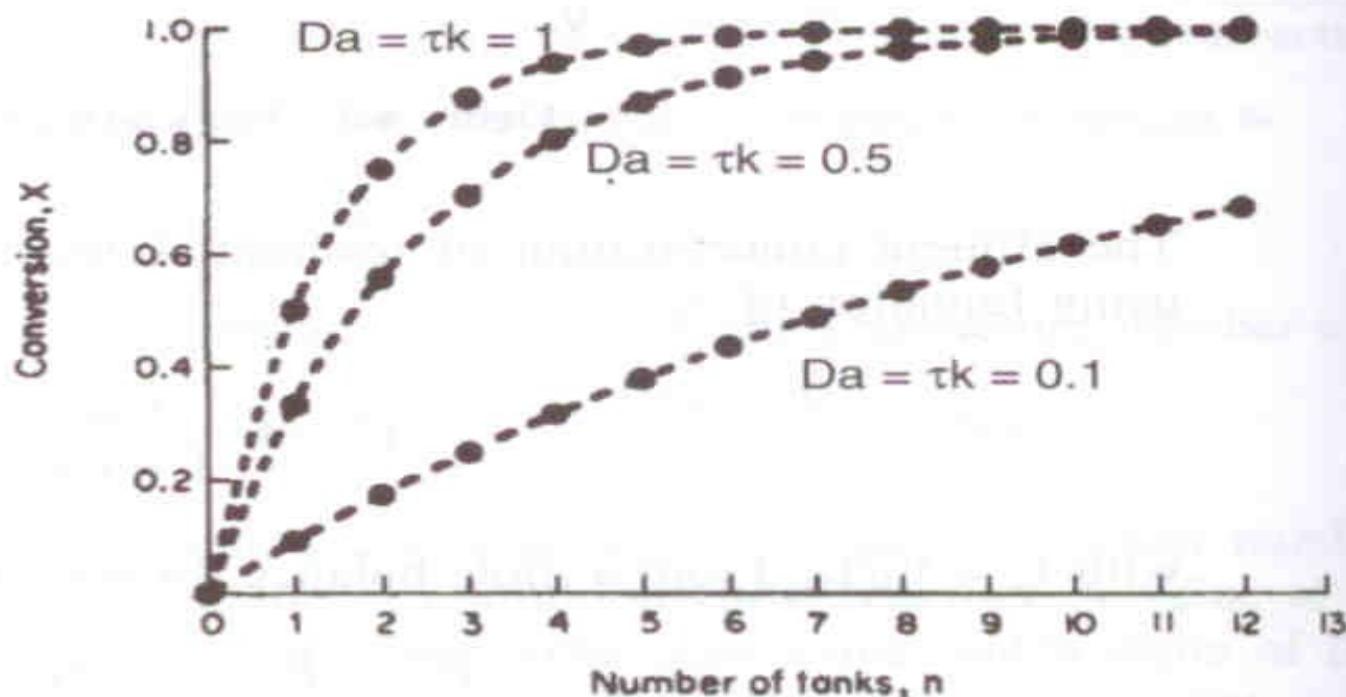
$$C_{An} = \frac{C_{A0}}{(1 + \tau k)^n} = \frac{C_{A0}}{(1 + Da)^n} \quad (4-10)$$

$$C_{A0}(1 - X) = \frac{C_{A0}}{(1 + Da)^n}$$

and rearranging, the conversion for these n tank reactors in series will be

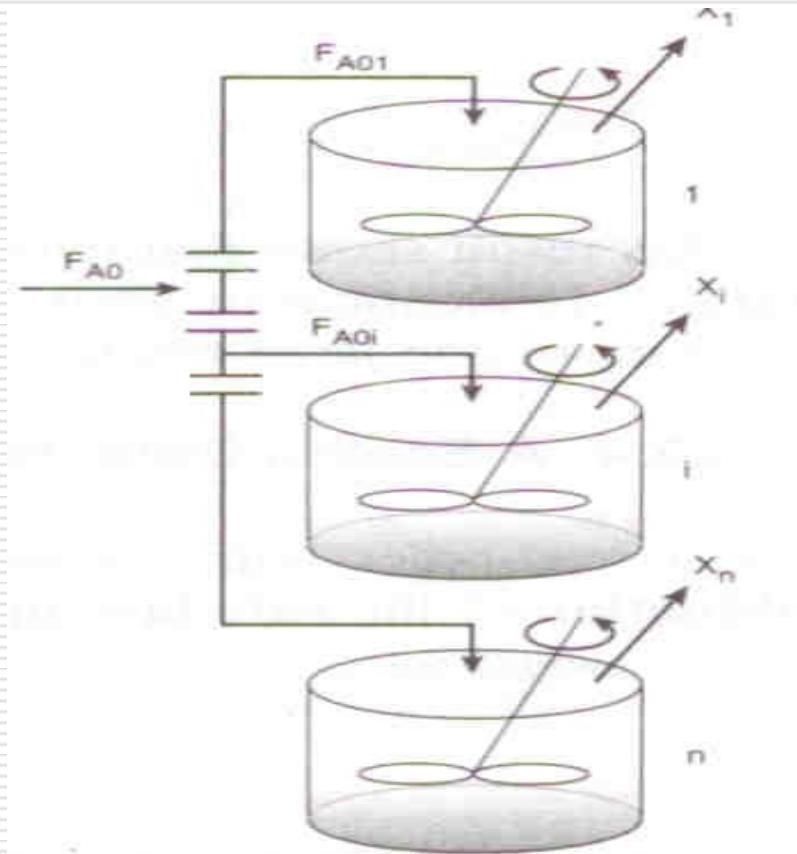
$$X = 1 - \frac{1}{(1 + Da)^n} \equiv 1 - \frac{1}{(1 + \tau k)^n}$$

A plot of the conversion as a function of the number of reactors in series for first-order reaction is shown in Figure 4-4 for various values of the Damköhler



CSTR's in parallel

We now consider the case in which equal sized reactors are placed in parallel rather than in series, and the feed is distributed equally among each of the reactors



$$V_i = F_{A0i} \left(\frac{X_i}{-r_{Ai}} \right) \quad (4-12)$$

Since the reactors are of equal size, operate at the same temperature, and have identical feed rates, the conversion will be the same for each reactor:

$$X_1 = X_2 = \dots = X_n = X$$

as will be the rate of reaction in each reactor

$$-r_{A1} = -r_{A2} = \dots = -r_{An} = -r_A$$

The volume of each individual reactor, V_i , is related to the total volume, V , of all the reactors by the equation

$$V_i = \frac{V}{n}$$

A similar relationship exists for the total molar flow rate, which is equally divided:

$$F_{A0i} = \frac{F_{A0}}{n}$$

Substituting these values into Equation (4-12) yields

$$\frac{V}{n} = \frac{F_{A0}}{n} \left(\frac{X_i}{-r_{Ai}} \right)$$

$$V = \frac{F_{A0}X_i}{-r_{Ai}} = \frac{F_{A0}X}{-r_A} \quad (4-1)$$

This result shows that the conversion achieved in any one of the reactors in parallel is identical to what would be achieved if the reactant were fed one stream to one large reactor of volume V !

4.3.4 A Second-Order Reaction in a CSTR

For a second-order liquid-phase reaction being carried out in a CSTR, **combination of the rate law and the design equation** yields

$$V = \frac{F_{A0}X}{-r_A} = \frac{F_{A0}X}{kC_A^2} \quad (4-2)$$

Using our stoichiometric table for constant density $v = v_0$, $C_A = C_{A0}(1 - X)$, and $F_{A0}X = v_0 C_{A0}X$, then

$$V = \frac{v_0 C_{A0}X}{kC_{A0}^2(1 - X)^2}$$

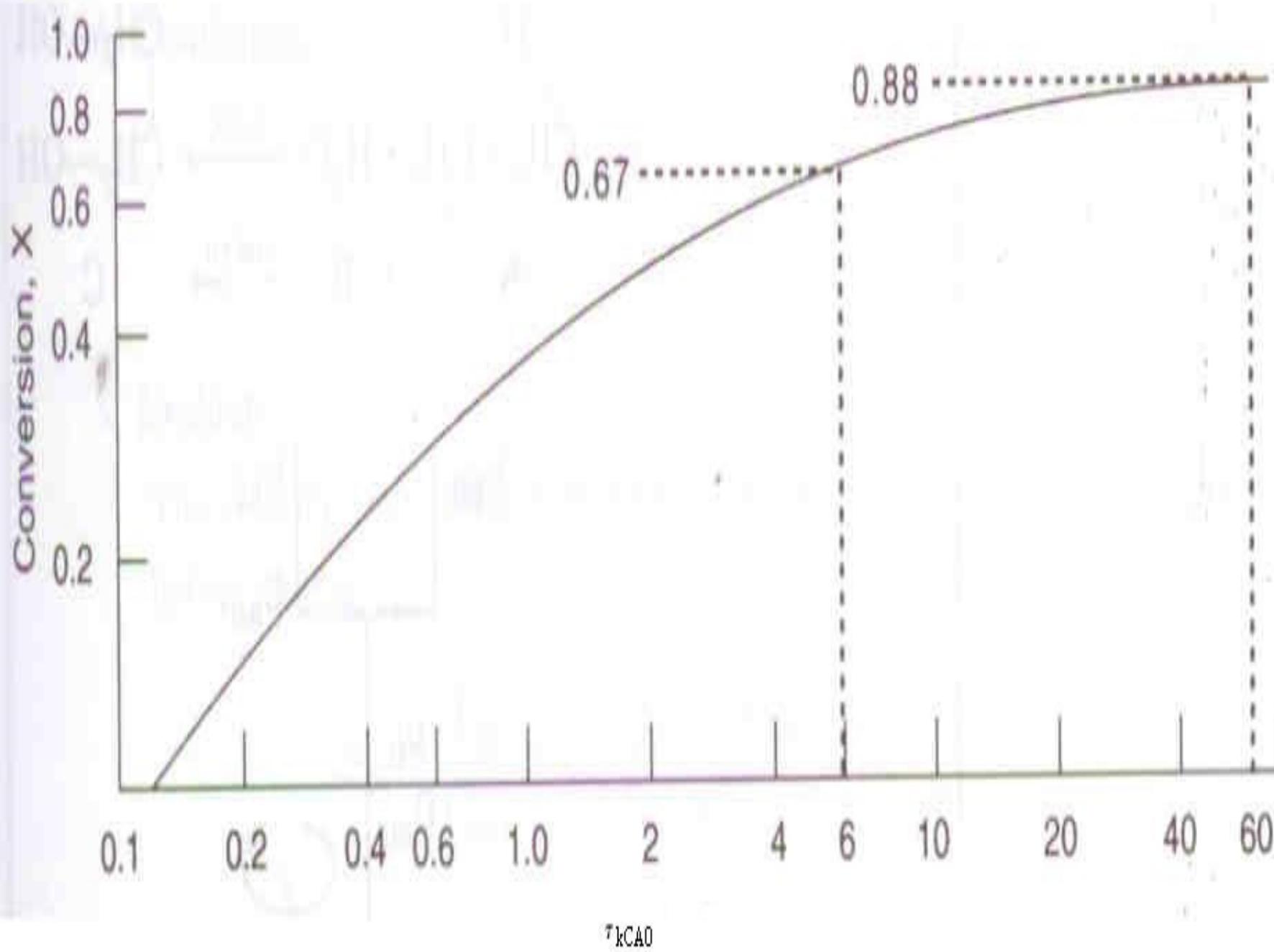
Dividing by v_0 ,

$$\tau = \frac{V}{v_0} = \frac{X}{kC_{A0}(1 - X)^2} \quad (4-3)$$

We solve Equation (4-15) for the conversion X :

$$\begin{aligned} X &= \frac{(1 + 2\tau kC_{A0}) - \sqrt{(1 + 2\tau kC_{A0})^2 - (2\tau kC_{A0})^2}}{2\tau kC_{A0}} \\ &= \frac{(1 + 2\tau kC_{A0}) - \sqrt{1 + 4\tau kC_{A0}}}{2\tau kC_{A0}} \end{aligned} \quad (4-4)$$

$$X = \frac{(1 + 2Da) - \sqrt{1 + 4Da}}{2Da}$$



Example 4-2 Producing 200 Million Pounds per Year in a CSTR

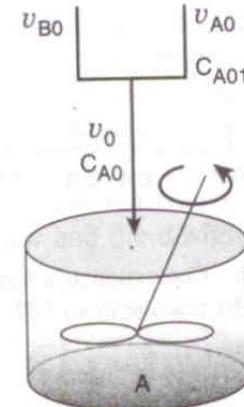
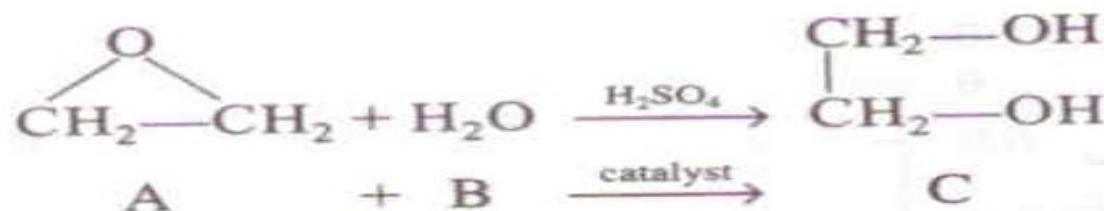
Close to 12.2 billion metric tons of ethylene glycol (EG) were produced in 2000, which ranked it the twenty-sixth most produced chemical in the nation that year on a total pound basis. About one-half of the ethylene glycol is used for *antifreeze* while the other half is used in the manufacture of polyesters. In the polyester category, 88% was used for fibers and 12% for the manufacture of bottles and films. The 2004 selling price for ethylene glycol was \$0.28 per pound.

It is desired to produce 200 million pounds per year of EG. The reactor is to be operated isothermally. A 1 lb mol/ft³ solution of ethylene oxide (EO) in water is fed to the reactor (shown in Figure E4-2.1) together with an equal volumetric solution of water containing 0.9 wt % of the catalyst H₂SO₄. The specific reaction rate constant is 0.311 min⁻¹, as determined in Example 4-1. Practical guidelines for reactor scale-up were recently given by Mukesh¹ and by Warsteel².

- If 80% conversion is to be achieved, determine the necessary CSTR volume.
- If two 800-gal reactors were arranged in parallel, what is the corresponding conversion?
- If two 800-gal reactors were arranged in series, what is the corresponding conversion?

Solution

Assumption: Ethylene glycol (EG) is the only reaction product formed.



The specified Ethylene Glycol (EG) production rate in lb mol/min is

$$F_C = 2 \times 10^8 \frac{\text{lb}}{\text{yr}} \times \frac{1 \text{ yr}}{365 \text{ days}} \times \frac{1 \text{ day}}{24 \text{ h}} \times \frac{1 \text{ h}}{60 \text{ min}} \times \frac{1 \text{ lb mol}}{62 \text{ lb}} = 6.137 \frac{\text{lb mol}}{\text{min}}$$

From the reaction stoichiometry

$$F_C = F_{A0} X$$

we find the required molar flow rate of ethylene oxide to be

$$F_{A0} = \frac{F_C}{X} = \frac{6.137}{0.8} = 7.67 \frac{\text{lb mol}}{\text{min}} \quad (58.0 \text{ g mol/s})$$

(a) We now calculate the single CSTR volume to achieve 80% conversion using the CRE algorithm.

1. Design equation:

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

2. Rate law:

$$-r_A = kC_A$$

3. Stoichiometry. Liquid phase ($v = v_0$):

$$C_A = \frac{F_A}{v_0} = \frac{F_{A0}(1 - X)}{v_0} = C_{A0}(1 - X)$$

4. Combining:

$$V = \frac{F_{A0} X}{kC_{A0}(1 - X)} = \frac{v_0 X}{k(1 - X)} \quad (\text{E4-2.4})$$

5. Evaluate:

The entering volumetric flow rate of stream A, with $C_{A01} = 1 \text{ lb mol/ft}^3$ before mixing, is

$$v_{A0} = \frac{F_{A0}}{C_{A01}} = \frac{7.67 \text{ lb mol/min}}{1 \text{ lb mol/ft}^3} = 7.67 \frac{\text{ft}^3}{\text{min}}$$

From the problem statement $v_{B0} = v_{A0}$

$$F_{B0} = v_{B0} C_{B01} = \left(7.67 \frac{\text{ft}^3}{\text{min}}\right) \cdot \left(62.4 \frac{\text{lb}}{\text{ft}^3} \times \frac{1 \text{ lb mol}}{18 \text{ lb}}\right) = 26.6 \frac{\text{lb mol}}{\text{min}}$$

The total entering volumetric flow rate of liquid is

$$\overbrace{v_0 = v_{A0} + v_{B0}}^{15.34 \frac{\text{ft}^3}{\text{min}}} \quad (7.24 \text{ dm}^3/\text{s})$$

Substituting in Equation (E4-2.4), recalling that $k = 0.311 \text{ min}^{-1}$, yields

$$\begin{aligned} V &= \frac{v_0 X}{k(1 - X)} = 15.34 \frac{\text{ft}^3}{\text{min}} \frac{0.8}{(0.311 \text{ min}^{-1})(1 - 0.8)} = 197.3 \text{ ft}^3 \\ &= 1480 \text{ gal (5.6 m}^3\text{)} \end{aligned}$$

A tank 5 ft in diameter and approximately 10 ft tall is necessary to achieve 80% conversion.

(b) CSTRs in parallel. For two 800-gal CSTRs arranged in parallel (as shown in Figure E4-2.2) with $7.67 \text{ ft}^3/\text{min}$ ($v_0/2$) fed to each reactor, the conversion achieved can be calculated by rearranging Equation (E4-2.4)

$$\frac{V}{v_0} k = \tau k = \frac{X}{1 - X}$$

to obtain

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

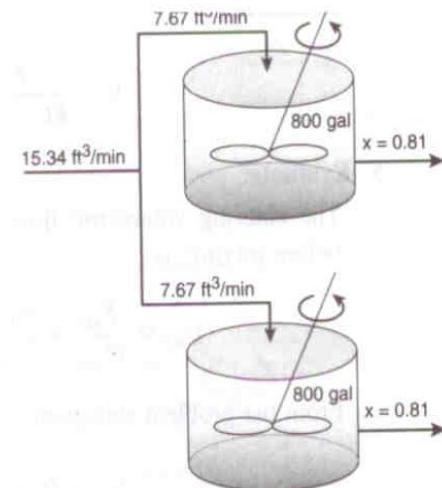
where

$$\tau = \frac{V}{v_0/2} = \left(800 \text{ gal} \times \frac{1 \text{ ft}^3}{7.48 \text{ gal}} \right) \times \frac{1}{7.67 \text{ ft}^3/\text{min}} = 13.94 \text{ min}$$

The *Damköhler number* is

$$Da = \tau k = 13.94 \text{ min} \times \frac{0.311}{\text{min}} = 4.34$$

$$X = \frac{Da}{1 + Da} = \frac{4.34}{1 + 4.34} = 0.81$$



The conversion exiting each of the CSTRs in parallel is 81%.

(c) CSTRs in series. If the 800-gal reactors are arranged in series, the conversion in the first reactor [cf. Equation (E4-2.5)] is

$$X_1 = \frac{\tau_1 k}{1 + \tau_1 k} \quad (E4-2.5)$$

where

$$\tau = \frac{V_1}{v_{01}} = \left(800 \text{ gal} \times \frac{1 \text{ ft}^3}{7.48 \text{ gal}} \right) \times \frac{1}{15.34 \text{ ft}^3/\text{min}} = 6.97 \text{ min}$$

where

$$\tau = \frac{V_1}{v_{01}} = \left(800 \text{ gal} \times \frac{1 \text{ ft}^3}{7.48 \text{ gal}} \right) \times \frac{1}{15.34 \text{ ft}^3/\text{min}} = 6.97 \text{ min}$$

The Damköhler number is

$$Da_1 = \tau_1 k = 6.97 \text{ min} \times \frac{0.311}{\text{min}} = 2.167$$

$$X_1 = \frac{2.167}{1 + 2.167} = \frac{2.167}{3.167} = 0.684$$

To calculate the conversion exiting the second reactor, we recall that $V_1 = V_2 = V$ and $v_{01} = v_{02} = v_0$; then

$$\tau_1 = \tau_2 = \tau$$

A mole balance on the second reactor is

In	-	Out	+	Generation	= 0
$\overbrace{F_{A1}}$	-	$\overbrace{F_{A2}}$	+	$\overbrace{r_{A2}V}$	= 0

Basing the conversion on the total number of moles reacted up to a point, mole of A fed to the first reactor,

$$F_{A1} = F_{A0} (1 - X_1) \quad \text{and} \quad F_{A2} = F_{A0} (1 - X_2)$$

Rearranging

$$V = \frac{F_{A1} - F_{A2}}{-r_{A2}} = F_{A0} \frac{X_2 - X_1}{-r_{A2}}$$

$$-r_{A2} = kC_{A2} = k \frac{F_{A2}}{v_0} = \frac{kF_{A0}(1 - X_2)}{v_0} = kC_{A0}(1 - X_2)$$

Combining the mole balance on the second reactor [cf. Equation (2-24)] with the rate law, we obtain

$$V = \frac{F_{A0}(X_2 - X_1)}{-r_{A2}} = \frac{C_{A0}v_0(X_2 - X_1)}{kC_{A0}(1 - X_2)} = \frac{v_0}{k} \left(\frac{X_2 - X_1}{1 - X_2} \right) \quad (\text{E4-2.7})$$

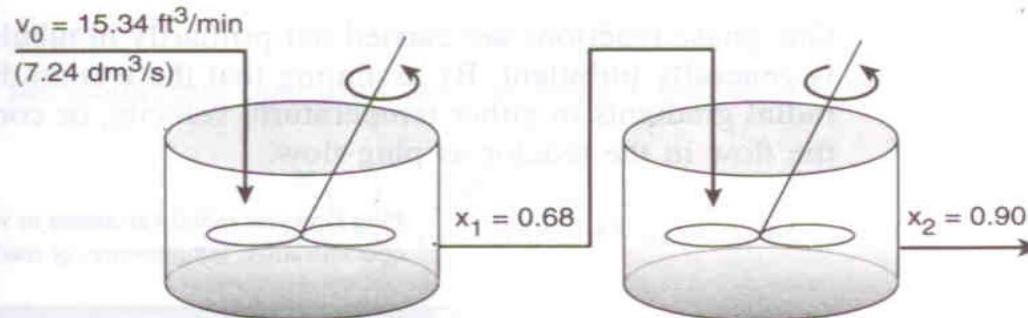
Solving for the conversion exiting the second reactor yields

$$X_2 = \frac{X_1 + Da}{1 + Da} = \frac{X_1 + \tau k}{1 + \tau k} = \frac{0.684 + 2.167}{1 + 2.167} = 0.90$$

The same result could have been obtained from Equation (4-11):

$$X_2 = 1 - \frac{1}{(1 + \tau k)^n} = 1 - \frac{1}{(1 + 2.167)^2} = 0.90$$

Two hundred million pounds of EG per year can be produced using two 800-gal (3.0-m³) reactors in series.



4.4 Tubular Reactors

Gas-phase reactions are carried out primarily in tubular reactors where the flow is generally turbulent. By assuming that there is no dispersion and there are no radial gradients in either temperature, velocity, or concentration, we can model the flow in the reactor as plug-flow.

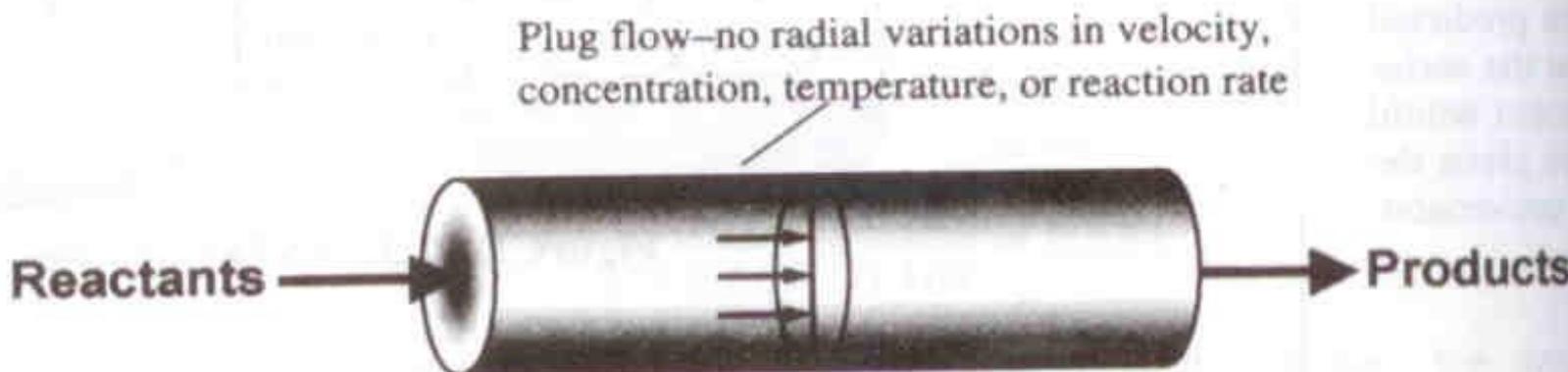


Figure 1-9 (Revisited) Tubular reactor.

Laminar reactors are discussed in Chapter 13 and dispersion effects in Chapter 14. The *differential form* of the PFR design equation

$$F_{A0} \frac{dX}{dV} = -r_A \quad (2-15)$$

must be used when there is a pressure drop in the reactor or heat exchange between the PFR and the surroundings. In the absence of pressure drop or heat exchange, the integral form of the *plug-flow design equation* is used,

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} \quad (2-16)$$

As an example, consider the reaction



for which the rate law is

$$-r_A = kC_A^2$$

We shall first consider the reaction to take place as a liquid-phase reaction and then to take place as a gas-phase reaction.

Liquid Phase $v = v_0$

The combined PFR mole balance and rate law is

$$\frac{dX}{dV} = \frac{kC_A^2}{F_{A0}}$$

If the reaction is carried out in the liquid phase, the concentration of A is

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

and for the isothermal operation, we can bring k outside the integral

$$V = \frac{F_{A0}}{kC_{A0}^2} \int_0^X \frac{dX}{(1 - X)^2} = \frac{v_0}{kC_{A0}} \left(\frac{X}{1 - X} \right)$$

This equation gives the reactor volume to achieve a conversion X . Dividing by v_0 ($\tau = V/v_0$) and solving for conversion, we find

$$X = \frac{\tau k C_{A0}}{1 + \tau k C_{A0}} = \frac{Da_2}{1 + Da_2}$$

where Da_2 is the Damköhler number for a second-order reaction.

Gas Phase

For constant-temperature ($T = T_0$) and constant-pressure ($P = P_0$) *gas-phase reactions*, the concentration is expressed as a function of conversion:

$$C_A = \frac{F_A}{v} = \frac{F_A}{v_0(1 + \varepsilon X)} = \frac{F_{A0}(1 - X)}{v_0(1 + \varepsilon X)} = C_{A0} \frac{(1 - X)}{(1 + \varepsilon X)}$$

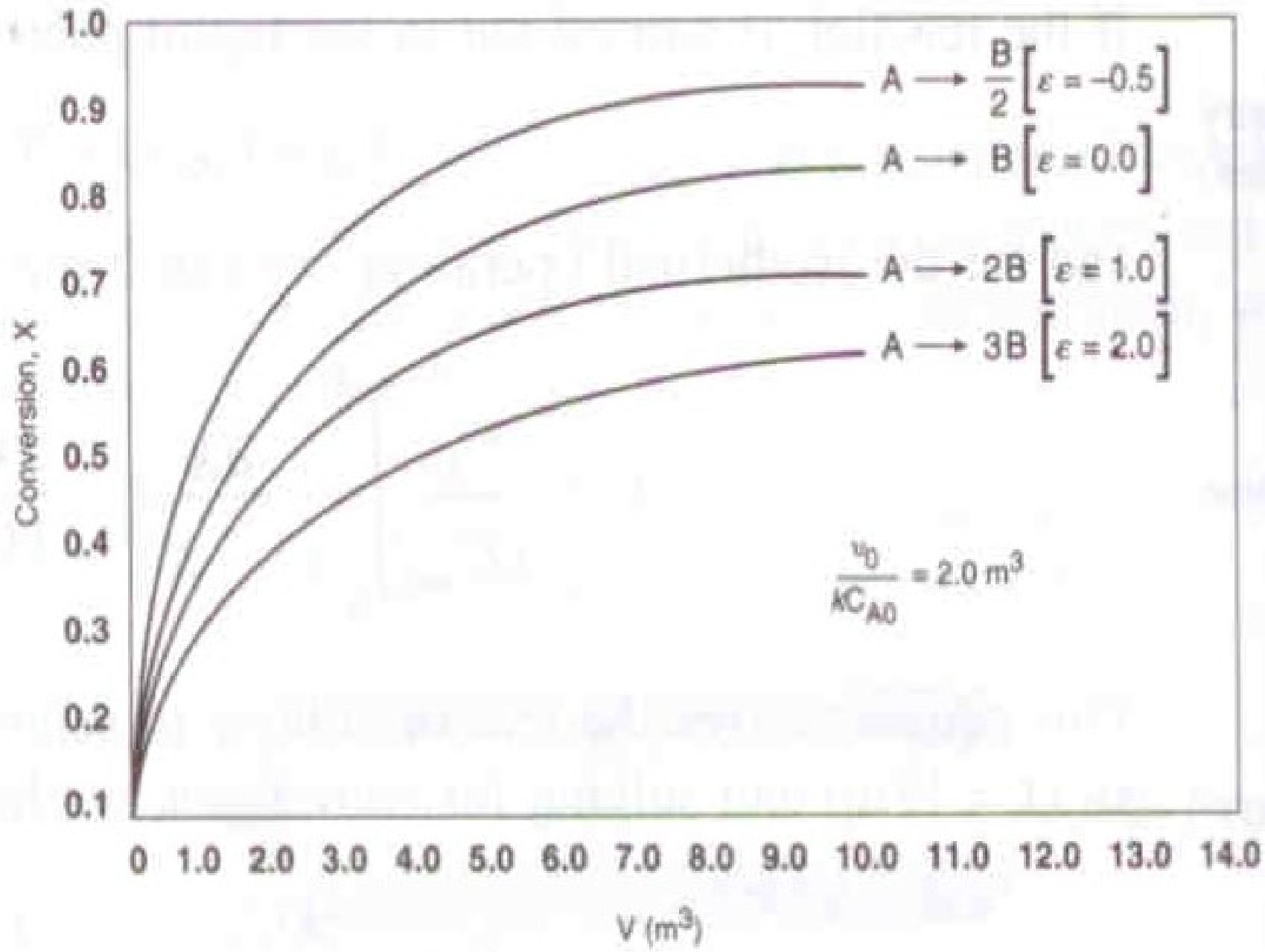
and then combining the PFR mole balance, rate law, and stoichiometry

$$V = F_{A0} \int_0^X \frac{(1 + \varepsilon X)^2}{k C_{A0}^2 (1 - X)^2} dX$$

The entering concentration C_{A0} can be taken outside the integral sign since it is not a function of conversion. Because the reaction is carried out isothermally, the specific reaction rate constant, k , can also be taken outside the integral sign.

$$V = \frac{F_{A0}}{k C_{A0}^2} \int_0^X \frac{(1 + \varepsilon X)^2}{(1 - X)^2} dX$$

$$V = \frac{v_0}{k C_{A0}} \left[2\varepsilon(1 + \varepsilon) \ln(1 - X) + \varepsilon^2 X + \frac{(1 + \varepsilon)^2 X}{1 - X} \right]$$



fluid moves through the reactor at a constant volumetric flow rate ($v = v_0$) as the conversion increases.

When there is a decrease in the number of moles ($\delta < 0$, $\epsilon < 0$) in the gas phase (e.g., $2A \rightarrow B$), the volumetric gas flow rate decreases as the conversion increases; for example,

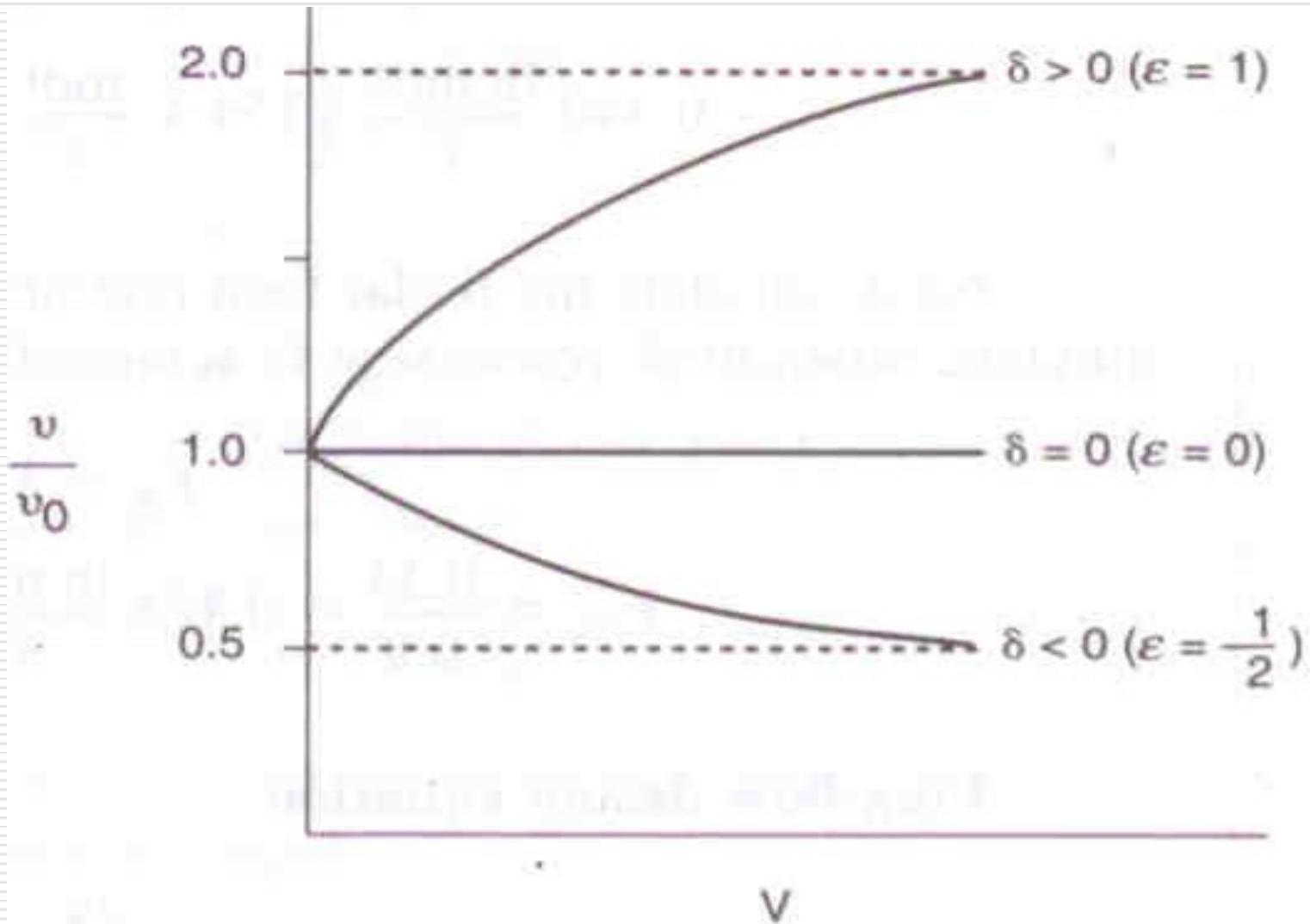
$$v = v_0(1 - 0.5X)$$

Consequently, the gas molecules will spend longer in the reactor than they would if the flow rate were constant, $v = v_0$. As a result, this longer residence time would result in a higher conversion than if the flow were constant at v_0 .

On the other hand, if there is an increase in the total number of moles ($\delta > 0$, $\epsilon > 0$) in the gas phase (e.g., $A \rightarrow 2B$), then the volumetric flow rate will increase as the conversion increases; for example,

$$v = v_0(1 + X)$$

and the molecules will spend less time in the reactor than they would if the volumetric flow rate were constant. As a result of this smaller residence time in the reactor the conversion will be less than what would result if the volumetric flow rate were constant at v_0 .



Change in gas-phase volumetric flow rate down the length of the reactor

Example 4-3 Producing 300 Million Pounds per Year of Ethylene in a Plug-Flow Reactor: Design of a Full-Scale Tubular Reactor

Ethylene ranks fourth in the United States in total pounds of chemicals produced each year, and it is the number one organic chemical produced each year. Over 50 billion pounds were produced in 2000, and it sold for \$0.27 per pound. Sixty-five percent of the ethylene produced is used in the manufacture of fabricated plastics,

Determine the PFR volume required to produce 300 million pounds of ethylene a year cracking a feed stream of pure ethane. The reaction is irreversible and follows a elementary rate law. We want to achieve 80% conversion of ethane operating the reactor isothermally at 1100 K at a pressure of 6 atm

Solution:



Let A = C₂H₆, B = C₂H₄, and C = H₂. In symbols,



The molar flow rate of ethylene exiting the reactor is

$$F_B = 300 \times 10^6 \frac{\text{lb}}{\text{year}} \times \frac{1 \text{ year}}{365 \text{ days}} \times \frac{1 \text{ day}}{24 \text{ h}} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{\text{lb mol}}{28 \text{ lb}}$$

$$= 0.340 \frac{\text{lb mol}}{\text{s}} \left(154.4 \frac{\text{mol}}{\text{s}} \right)$$

$$F_B = F_{A0} X$$

$$F_{A0} = \frac{0.34}{0.8} = 0.425 \frac{\text{lb mol}}{\text{s}} \quad (402 \times 10^6 \text{ lb/yr})$$

1. Plug-flow design equation:

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

Rearranging and integrating for the case of no pressure drop

2. Rate law:³

$$V = F_{A0} \int_0^X \frac{dX}{-r_A}$$

$$-r_A = kC_A \quad \text{with } k = 0.072 \text{ s}^{-1} \text{ at } 1000 \text{ K} \quad (\text{E4-3.2})$$

The activation energy is 82 kcal/g mol.

3. **Stoichiometry.** For isothermal operation and negligible pressure drop, the concentration of ethane is calculated as follows:

Gas phase, constant T and P :

$$v = \dot{v}_0 \frac{F_T}{F_{T0}} = v_0(1 + \epsilon X) :$$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0(1+\epsilon X)} = C_{A0} \left(\frac{1-X}{1+\epsilon X} \right) \quad (\text{E4-3.3})$$

$$C_C = \frac{C_{A0}X}{(1+\epsilon X)} \quad (\text{E4-3.4})$$

4. We now combine Equations (E4-3.1) through (E4-3.3) to obtain

$$\begin{aligned}V &= F_{A0} \int_0^X \frac{dX}{kC_{A0}(1-X)/(1+\varepsilon X)} = F_{A0} \int_0^X \frac{(1+\varepsilon X)dX}{kC_{A0}(1-X)} \\&= \frac{F_{A0}}{C_{A0}} \int_0^X \frac{(1+\varepsilon X)dX}{k(1-X)}\end{aligned}\quad (\text{E4-3.5})$$

5. Evaluate.

Since the reaction is carried out isothermally, we can take k outside the integral sign and use Appendix A.1 to carry out our integration.

$$V = \frac{F_{A0}}{kC_{A0}} \int_0^X \frac{(1+\varepsilon X)dX}{1-X} = \frac{F_{A0}}{kC_{A0}} \left[(1+\varepsilon) \ln \frac{1}{1-X} - \varepsilon X \right] \quad (\text{E4-3.6})$$

6. Parameter evaluation:

$$\begin{aligned}C_{A0} &= y_{A0} C_{T0} = \frac{y_{A0} P_0}{RT_0} = (1) \left(\frac{6 \text{ atm}}{(0.73 \text{ ft}^3 \cdot \text{atm/lb mol} \cdot {}^\circ\text{R}) \times (1980 {}^\circ\text{R})} \right) \\&= 0.00415 \frac{\text{lb mol}}{\text{ft}^3} \quad (0.066 \text{ mol/dm}^3)\end{aligned}$$

$$\varepsilon = y_{A0}\delta = (1)(1 + 1 - 1) = 1$$

Oops! The rate constant k is given at 1000 K, and we need to calculate k at reaction conditions, which is 1100 K.

$$-r_A = kC_A \quad \text{with } k = 0.072 \text{ s}^{-1} \text{ at } 1000 \text{ K} \quad (\text{E4-3.2})$$

The activation energy is 82 kcal/g mol.

3. **Stoichiometry.** For isothermal operation and negligible pressure drop, the concentration of ethane is calculated as follows:
Gas phase, constant T and P :

$$v = v_0 \frac{F_T}{F_{T_0}} = v_0(1 + \varepsilon X) :$$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = C_{A0} \left(\frac{1-X}{1+\varepsilon X} \right) \quad (\text{E4-3.3})$$

$$C_C = \frac{C_{A0}X}{(1+\varepsilon X)} \quad (\text{E4-3.4})$$

4. We now **combine** Equations (E4-3.1) through (E4-3.3) to obtain

$$\begin{aligned} V &= F_{A0} \int_0^X \frac{dX}{kC_{A0}(1-X)/(1+\varepsilon X)} = F_{A0} \int_0^X \frac{(1+\varepsilon X)dX}{kC_{A0}(1-X)} \\ &= \frac{F_{A0}}{C_{A0}} \int_0^X \frac{(1+\varepsilon X)dX}{k(1-X)} \end{aligned} \quad (\text{E4-3.5})$$

5. Evaluate.

Since the reaction is carried out isothermally, we can take k outside the integral sign and use Appendix A.1 to carry out our integration.

$$V = \frac{F_{A0}}{kC_{A0}} \int_0^X \frac{(1+\varepsilon X)dX}{1-X} = \frac{F_{A0}}{kC_{A0}} \left[(1+\varepsilon) \ln \frac{1}{1-X} - \varepsilon X \right] \quad (\text{E4-3.6})$$

6. Parameter evaluation:

$$\begin{aligned} C_{A0} &= y_{A0} C_{T0} = \frac{y_{A0} P_0}{RT_0} = (1) \left(\frac{6 \text{ atm}}{(0.73 \text{ ft}^3 \cdot \text{atm/lb mol} \cdot {}^\circ\text{R}) \times (1980 {}^\circ\text{R})} \right) \\ &= 0.00415 \frac{\text{lb mol}}{\text{ft}^3} \quad (0.066 \text{ mol/dm}^3) \end{aligned}$$

$$\varepsilon = y_{A0}\delta = (1)(1+1-1) = 1$$

Oops! The rate constant k is given at 1000 K, and we need to calculate k at reaction conditions, which is 1100 K.

$$\begin{aligned}
 k(T_2) &= k(T_1) \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] \\
 &= k(T_1) \exp \left[\frac{E}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \right] \\
 &= \frac{0.072}{\text{s}} \exp \left[\frac{82,000 \text{ cal/g mol}(1100 - 1000) \text{ K}}{1.987 \text{ cal/(g mol} \cdot \text{K})(1000 \text{ K})(1100 \text{ K})} \right] \\
 &= 3.07 \text{ s}^{-1}
 \end{aligned}$$

Substituting into Equation (E4-3.6) yields

$$\begin{aligned}
 V &= \frac{0.425 \text{ lb mol/s}}{(3.07/\text{s})(0.00415 \text{ lb mol/ft}^3)} \left[(1+1) \ln \frac{1}{1-X} - (1)X \right] \\
 &= 33.36 \text{ ft}^3 \left[2 \ln \left(\frac{1}{1-X} \right) - X \right]
 \end{aligned}$$

For $X = 0.8$,

$$\begin{aligned}
 V &= 33.36 \text{ ft}^3 \left[2 \ln \left(\frac{1}{1-0.8} \right) - 0.8 \right] \\
 &= 80.7 \text{ ft}^3 = (2280 \text{ dm}^3 = 2.28 \text{ m}^3)
 \end{aligned}$$

It was decided to use a bank of 2-in. schedule 80 pipes in parallel that are 40 ft in length. For pipe schedule 80, the cross-sectional area, A_C , is 0.0205 ft². The number of pipes necessary is

$$n = \frac{80.7 \text{ ft}^3}{(0.0205 \text{ ft}^2)(40 \text{ ft})} = 98.4 \quad (\text{E4-3.9})$$

To determine the concentrations and conversion profiles down the length of the reactor, z , we divide the volume Equation (E4-3.8) by the cross-sectional area, A_C ,

$$z = \frac{V}{A_C} \quad (\text{E4-3.10})$$

Equation (E4-3.9) was used along with $A_C = 0.0205 \text{ ft}^2$, and Equations (E4-3.8) and (E4-3.3) were used to obtain Figure E4-3.1. Using a bank of 100 pipes will give us the reactor volume necessary to make 300 million pounds per year of ethylene from ethane. The concentration and conversion profiles down any one of the pipes are shown in Figure E4-3.1.

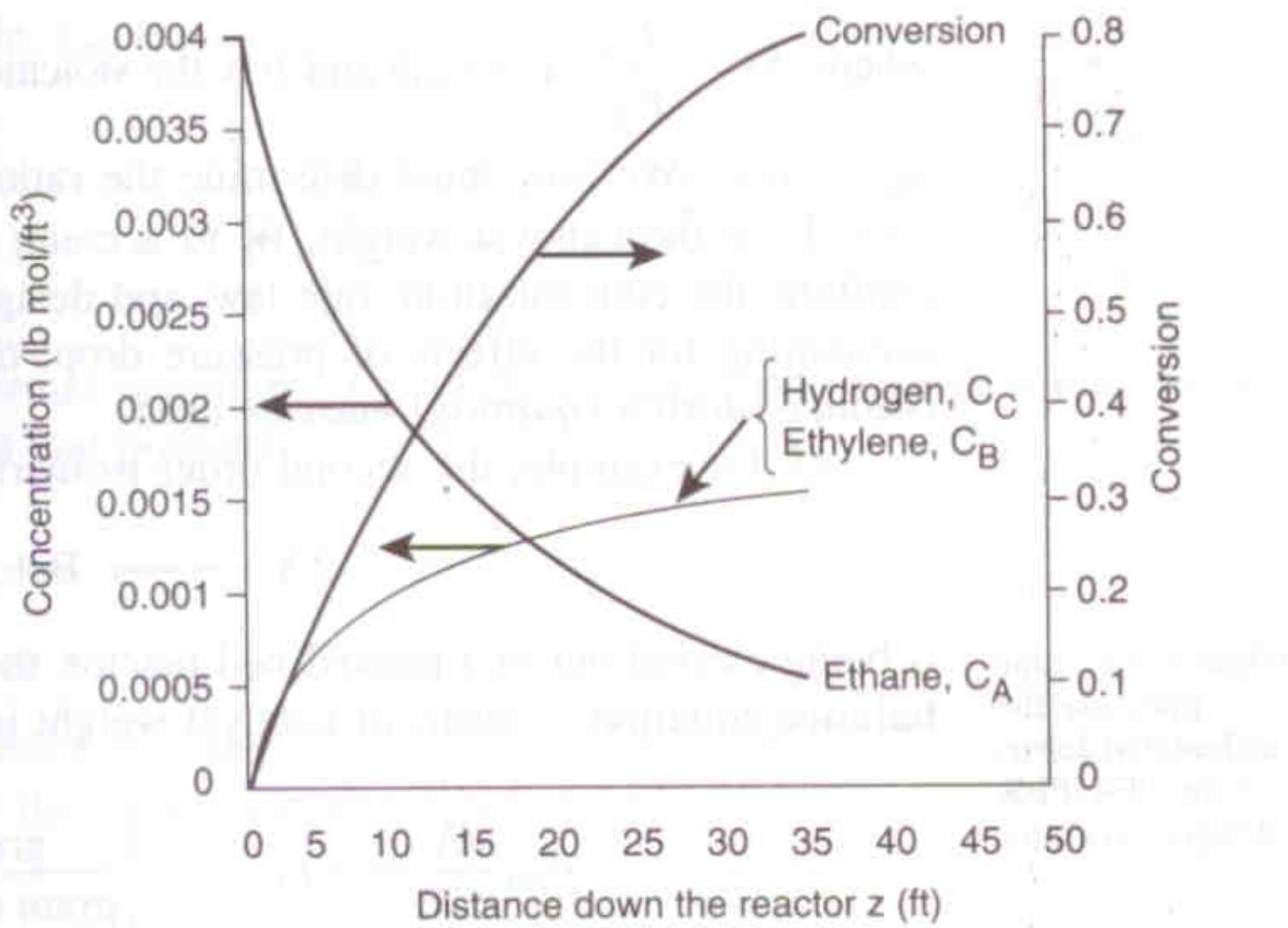


Figure E4-3.1 Conversion and concentration profiles.

Objective Assessment of Chapter

- ❑ Describe the CRE algorithm that allows the reader to solve chemical reaction engineering problems through logic rather than memorization
- ❑ Size batch reactors, semi-batch reactors, CSTRs, PFRs, PBRs, membrane reactors, and micro-reactors for isothermal operation given the rate law and feed conditions
- ❑ Account for the effects of pressure drop on conversion in packed bed tubular reactors

If you look upwards and see the stars, stop admiring them. Start thinking as to whether you have lost your roof!!!