Concentrations:

$$C_A = C_{T0} \frac{F_A}{F_T} \tag{E4-8.6}$$

$$C_B = C_{T0} \frac{F_B}{F_T} \tag{E4-8.7}$$

$$C_C = C_{T0} \frac{F_C}{F_T} \tag{E4-8.8}$$

$$F_T = F_A + F_B + F_C \tag{E4-8.9}$$

Relative rates:

$$\frac{r_A}{-1} = \frac{r_B}{1} = \frac{r_C}{1}$$
$$r_B = -r_A \tag{E4-8.10}$$
$$r_C = r_A$$

5. **Combining and summarizing:**

Summary of equations describing flow and reaction in a membrane reactor

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

$$\frac{dF_B}{dV} = -r_A - k_C C_{T0} \left(\frac{F_B}{F_T} \right)$$

$$\frac{dF_C}{dV} = -r_A$$

$$-r_A = kC_{T0} \left[\left(\frac{F_A}{F_T} \right) - \frac{C_{T0}}{K_C} \left(\frac{F_B}{F_T} \right) \left(\frac{F_C}{F_T} \right) \right]$$

$$F_T = F_A + F_B + F_C$$

6. **Parameter evaluation:**

$$C_{T0} = \frac{P_0}{RT_0} = \frac{830.6 \text{ kPa}}{8.314 \text{ k Pa} \cdot \text{dm}^3/(\text{mol} \cdot \text{K}) \, (500 \text{ K})} = 0.2 \, \frac{\text{mol}}{\text{dm}^3}$$

$$k = 0.7 \text{ min}^{-1}, \, K_C = 0.05 \text{ mol/dm}^3, \, k_C = 0.2 \text{ min}^{-1}$$
$$F_{A0} = 10 \text{ mol/min}$$
$$F_{B0} = F_{C0} = 0$$

7. **Numerical solution.** Equations (E4-8.1) through (E4-8.10) were solved using Polymath and MATLAB, another ODE solver. The profiles of the molar flow rates are shown here. Table E4-8.1 shows the Polymath programs,

and Figure E4-8.1 shows the results of the numerical solution of the initial (entering) conditions.

$$V = 0: \quad F_A = F_{A0}, \quad F_B = 0, \quad F_C = 0$$

TABLE E4-8.1 POLYMATH PROGRAM

ODE REPORT (RKF45)

Differential equations as entered by the user
[1] d(Fa)/d(V) = ra
[2] d(Fb)/d(V) = -ra-kc*Cto*(Fb/Ft)
[3] d(Fc)/d(V) = -ra

Explicit equations as entered by the user
[1] kc = 0.2
[2] Cto = 0.2
[3] Ft = Fa+Fb+Fc
[4] k = 0.7
[5] Kc = 0.05
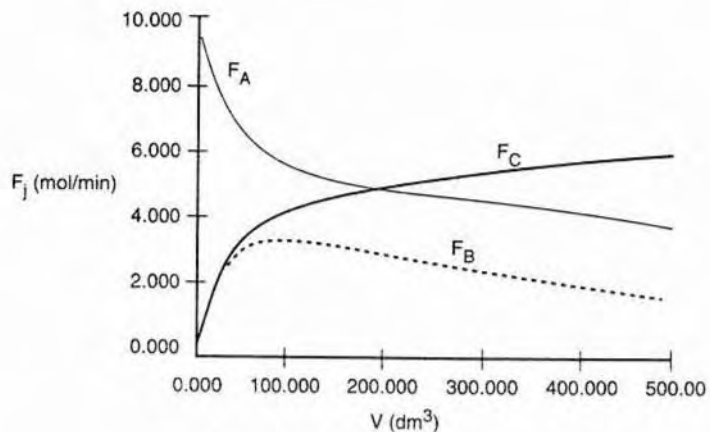[6] ra = -k*Cto*((Fa/Ft)-Cto/Kc*(Fb/Ft)*(Fc/Ft))


Figure E4-8.1   Polymath solution.

(c) From Figure E4-8.1 we see the exit molar flow rate of A is 4 mol/min. for which the corresponding conversion is

$$X = \frac{F_{A0} - F_A}{F_{A0}} = \frac{10 - 4}{10} = 0.6$$

Use of Membrane Reactors to Enhance Selectivity.   In addition to species leaving the membrane reactor, species can also be fed to the reactor through the membrane. For example, for the reaction

$$A + B \rightarrow C + D$$
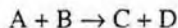
A could be fed only to the entrance, and B could be fed only through the membrane as shown here.
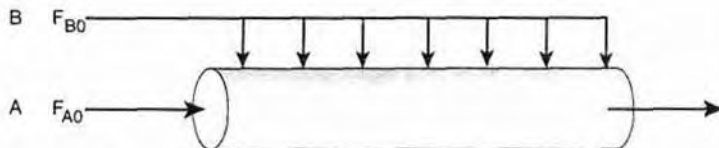
As we will see in Chapter 6, this arrangement is often used to improve selectivity when multiple reactions take place. Here B is usually fed uniformly through the membrane along the length of the reactor. The balance on B is

$$\frac{dF_B}{dV} = r_B + R_B \tag{4-44}$$

where $R_B = F_{B0}/V_t$ with F_{B0} the molar feed rate of B through sides and V_t the total reactor volume. The feed rate of B can be controlled by controlling the pressure drop across the reactor membrane.[11]

4.10 Unsteady-State Operation of Stirred Reactors

In this chapter, we have already discussed the unsteady operation of one type of reactor, the batch reactor. In this section, we discuss two other aspects of unsteady operation: startup of a CSTR and semibatch reactors. First, the startup of a CSTR is examined to determine the time necessary to reach steady-state operation [see Figure 4-14(a)], and then semibatch reactors are discussed. In each of these cases, we are interested in predicting the concentration and conversion as a function of time. Closed-form analytical solutions to the differential equations arising from the mole balance of these reaction types can be obtained only for zero- and first-order reactions. ODE solvers must be used for other reaction orders.
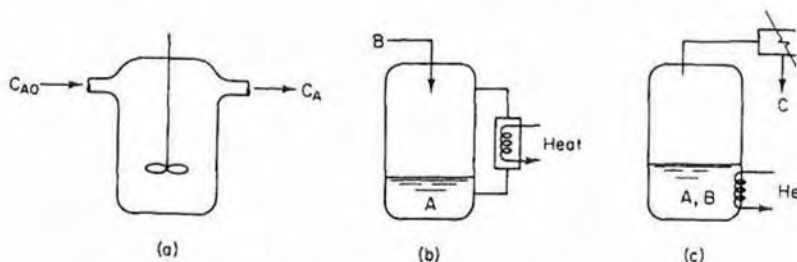
---

[11] The velocity of B through the membrane, U_B, is given by Darcy's law

$$U_B = K(P_s - P_r)$$

where K is the membrane permeability and P_s is the shell-side pressure and P_r the reactor side pressure.

$$F_{B0} = \frac{R_B}{C_{B0} a U_B} V_t = R_B V_t$$

where, as before, a is the membrane surface area per unit volume. C_{B0} is the entering concentration of B, and V_t is the total reactor volume.

Figure 4-14 Semibatch reactors. (a) Reactor startup, (b) semibatch with cooling, and (c) reactive distillation. [Excerpted by special permission from *Chem. Eng.*, *63*(10) 211 (Oct. 1956). Copyright © 1956 by McGraw-Hill, Inc., New York, NY 10020.]

There are two basic types of semibatch operations. In one type, one the reactants in the reaction

$$A + B \rightarrow C + D$$

(e.g., B) is slowly fed to a reactor containing the other reactant (e.g., A), wh has already been charged to a reactor such as that shown in Figure 4-14 This type of reactor is generally used when unwanted side reactions occu high concentrations of B (Chapter 6) or when the reaction is highly exother (Chapter 8). In some reactions, the reactant B is a gas and is bubbled conti ously through liquid reactant A. Examples of reactions used in this type semibatch reactor operation include *ammonolysis*, *chlorination*, and *hydroly* The other type of semibatch reactor is reactive distillation and is shown sc matically in Figure 4-14(c). Here reactants A and B are charged simu neously and one of the products is vaporized and withdrawn continuou Removal of one of the products in this manner (e.g., C) shifts the equilibri toward the right, increasing the final conversion above that which would achieved had C not been removed. In addition, removal of one of the produ further concentrates the reactant, thereby producing an increased rate of re tion and decreased processing time. This type of reaction operation is cal *reactive distillation*. Examples of reactions carried out in this type of reac include *acetylation reactions* and *esterification reactions* in which water removed.

An expanded version of this section can be found on the CD-ROM.

4.10.1 Startup of a CSTR

Summary Notes

The startup of a fixed volume CSTR under isothermal conditions is rare, bu does occur occasionally. We can, however, carry out an analysis to estimate time necessary to reach steady-state operation. For the case when the reactor well mixed and as a result there are no spatial variations in r_A, we begin w the general mole balance equation applied to Figure 4-14(a):

$$F_{A0} - F_A + r_A V = \frac{dN_A}{dt} \tag{4-45}$$

Conversion does not have any meaning in startup because one cannot separate the moles reacted from the moles accumulated in the CSTR. Consequently, we *must* use concentration rather than conversion as our variable in the balance equation. For liquid-phase ($v = v_0$) reactions with constant overflow ($V = V_0$), using $\tau = V_0/v_0$, we can transform Equation (4-45) to

$$C_{A0} - C_A + r_A \tau = \tau \frac{dC_A}{dt} \tag{4-46}$$

First-order reaction

For a first-order reaction ($-r_A = kC_A$) Equation (4-46) then becomes

$$\frac{dC_A}{dt} + \frac{1 + \tau k}{\tau} C_A = \frac{C_{A0}}{\tau}$$

which, for the initial conditions $C_A = C_{A0}$ at $t = 0$ solves to

$$C_A = \frac{C_{A0}}{1 + \tau k} \left\{ 1 - exp\left[-(1 + \tau k)\frac{t}{\tau} \right] \right\} \tag{4-47}$$

Letting t_s be the time necessary to reach 99% of the steady-state concentration, C_{AS}:

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

Rearranging Equation (4-47) for $C_A = 0.99 C_{AS}$ yields

$$t_s = 4.6 \frac{\tau}{1 + \tau k} \tag{4-48}$$

For slow reactions with small k ($1 \gg \tau k$):

$$\boxed{t_s = 4.6\ \tau} \tag{4-49}$$

For rapid reactions with large k ($\tau k \gg 1$):

Time to reach steady state in an isothermal CSTR

$$\boxed{t_s = \frac{4.6}{k}} \tag{4-50}$$

For most first-order systems, steady state is achieved in three to four space times.

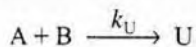### 4.10.2 Semibatch Reactors

Motivation

One of the best reasons to use semibatch reactors is to enhance selectivity in liquid-phase reactions. For example, consider the following two simultaneous reactions. One reaction produces the desired product D

$$A + B \xrightarrow{k_D} D$$
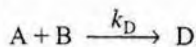
with the rate law

$$r_D = kC_A^2 C_B$$

and the other produces an undesired product U

$$A + B \xrightarrow{k_U} U$$

with the rate law

$$r_U = k_U C_A C_B^2$$

The instantaneous selectivity $S_{D/U}$ is the ratio of the relative rates

We want $S_{D/U}$ as large as possible.

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_D C_A^2 C_B}{k_U C_A C_B^2} = \frac{k_D}{k_U} \frac{C_A}{C_B}$$

and guides us how to produce the most of our desired product and least of our undesired product (see Section 6.1). We see from the instantaneous selectivity that we can increase the formation of D and decrease the formation of U by keeping the concentration of A high and the concentration of B low. This result can be achieved through the use of the semibatch reactor, which is charged with Pure A and to which B is fed slowly to A in the vat.

Of the two types of semibatch reactors, we focus attention primarily on the one with constant molar feed. A schematic diagram of this semibatch reactor is shown in Figure 4-15. We shall consider the elementary liquid-phase reaction
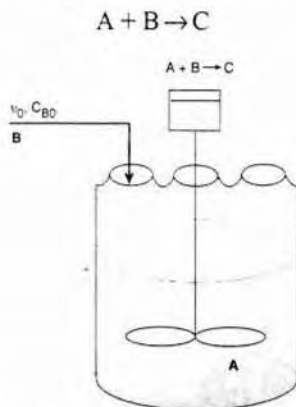
$$A + B \rightarrow C$$

Figure 4-15 Semibatch reactor.

in which reactant B is slowly added to a well-mixed vat containing reactant A.

A mole balance on species A yields

$$\begin{bmatrix} \text{Rate} \\ \text{in} \end{bmatrix} - \begin{bmatrix} \text{Rate} \\ \text{out} \end{bmatrix} + \begin{bmatrix} \text{Rate of} \\ \text{generation} \end{bmatrix} = \begin{bmatrix} \text{Rate of} \\ \text{accumulation} \end{bmatrix} \quad (4\text{-}51)$$

$$\overbrace{0} \quad - \quad \overbrace{0} \quad + \quad \overbrace{r_A V(t)} \quad = \quad \overbrace{\frac{dN_A}{dt}}$$

Three variables can be used to formulate and solve semibatch reactor problems: the concentrations, C_j, the number of moles, N_j, and the conversion, X.

4.10.3 Writing the Semibatch Reactor Equations in Terms of Concentrations

Recalling that the number of moles of A, N_A, is just the product of concentration of A, C_A, and the volume, V, we can rewrite Equation (4-51) as

$$r_A V = \frac{d(C_A V)}{dt} = V\frac{dC_A}{dt} + C_A\frac{dV}{dt} \quad (4\text{-}52)$$

We note that since the reactor is being filled, the volume, V, varies with time. The reactor volume at any time t can be found from an **overall mass balance** of all species:

Overall mass
balance

$$\begin{bmatrix} \text{Rate} \\ \text{in} \end{bmatrix} - \begin{bmatrix} \text{Rate} \\ \text{out} \end{bmatrix} + \begin{bmatrix} \text{Rate of} \\ \text{generation} \end{bmatrix} = \begin{bmatrix} \text{Rate of} \\ \text{accumulation} \end{bmatrix} \quad (4\text{-}53)$$

$$\overbrace{\rho_0 v_0} \quad - \quad \overbrace{0} \quad + \quad \overbrace{0} \quad = \quad \overbrace{\frac{d(\rho V)}{dt}}$$

For a constant-density system, $\rho_0 = \rho$, and

$$\frac{dV}{dt} = v_0 \quad (4\text{-}54)$$

with the initial condition $V = V_0$ at $t = 0$, integrating for the case of constant volumetric flow rate v_0 yields

Semibatch
reactor
volume as a
function of time

$$\boxed{V = V_0 + v_0 t} \quad (4\text{-}55)$$

Substituting Equation (4-54) into the right-hand side of Equation (4-52) and rearranging gives us

$$-v_0 C_A + V r_A = \frac{V dC_A}{dt}$$

The **balance on A** [i.e., Equation (4-52)] can be rewritten as

Mole balance on A

$$\frac{dC_A}{dt} = r_A - \frac{v_0}{V}C_A$$

(4-5

A **mole balance on B** that is fed to the reactor at a rate F_{B0} is

In	+	Out	+	Generation	=	Accumulation
$\overbrace{F_{B0}}$	−	$\overbrace{0}$	+	$\overbrace{r_B V}$	=	$\dfrac{dN_B}{dt}$

Rearranging

$$\frac{dN_B}{dt} = r_B V + F_{B0}$$

(4-5

$$\frac{dVC_B}{dt} = \frac{dV}{dt}C_B + \frac{VdC_B}{dt} = r_B V + F_{B0}$$

Substituting Equation (4-55) in terms of V and differentiating, the mole ba ance on B becomes

Mole balance on B

$$\frac{dC_B}{dt} = r_B + \frac{v_0(C_{B0} - C_B)}{V}$$

(4-5

At time $t = 0$, the initial concentration of B in the vat is zero, $C_{Bi} = 0$. The conce tration of B in the feed is C_{B0}. If the reaction order is other than zero- or first-ord or if the reaction is nonisothermal, we must use numerical techniques to determi the conversion as a function of time. Equations (4-56) and (4-58) are easily solv with an ODE solver.

Example 4–9 Isothermal Semibatch Reactor with Second-Order Reaction

The production of methyl bromide is an irreversible liquid-phase reaction that fc lows an elementary rate law. The reaction

$$CNBr + CH_3NH_2 \rightarrow CH_3Br + NCNH_2$$
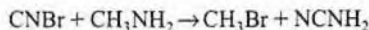
is carried out isothermally in a semibatch reactor. An aqueous solution of meth amine (B) at a concentration of 0.025 mol/dm³ is to be fed at a rate of 0.05 dm to an aqueous solution of bromine cyanide (A) contained in a glass-lined reactc The initial volume of fluid in a vat is to be 5 dm³ with a bromine cyanide conce tration of 0.05 mol/dm³. The specific reaction rate constant is

$$k = 2.2 \text{ dm}^3/\text{s} \cdot \text{mol}$$

Solve for the concentrations of bromine cyanide and methyl bromide and the rate reaction as a function of time.

Solution

Symbolically, we write the reaction as

$$A + B \rightarrow C + D$$

The reaction is elementary; therefore, the rate law is

Rate Law

$$\boxed{-r_A = kC_A C_B}$$

(E4-9.1)

Substituting the rate law in Equations (4-56) and (4-58) gives

Combined mole balances and rate laws on A, B, C, and D

$$\boxed{\frac{dC_A}{dt} = -kC_A C_B - \frac{v_0}{V}C_A}$$

(E4-9.2)

Polymath will combine for you. Thank you, Polymath!

$$\boxed{\frac{dC_B}{dt} = -kC_A C_B + \frac{v_0}{V}(C_{B0} - C_B)}$$

(E4-9.3)

$$\boxed{V = V_0 + v_0 t}$$

(E4-9.4)

Similarly for C and D we have

$$\frac{dN_C}{dt} = r_C V = -r_A V$$

(E4-9.5)

$$\frac{dN_C}{dt} = \frac{d(C_C V)}{dt} = V\frac{dC_C}{dt} + C_C\frac{dV}{dt} = V\frac{dC_C}{dt} + v_0 C_C$$

(E4-9.6)

Then

$$\boxed{\frac{dC_C}{dt} = kC_A C_B - \frac{v_0 C_C}{V}}$$

(E4-9.7)

and

$$\boxed{\frac{dC_D}{dt} = kC_A C_B - \frac{v_0 C_D}{V}}$$

(E4-9.8)

We could also calculate the conversion of A.

$$X = \frac{N_{A0} - N_A}{N_{A0}}$$

(E4-9.9)

$$\boxed{X = \frac{C_{A0}V_0 - C_A V}{C_{A0}V_0}}$$

(E4-9.10)

The initial conditions are $t = 0$: $C_{A0} = 0.05$ mol/dm³, $C_B = C_{C.} = C_D = 0$, and $V_0 = 5$ dm³.

Equations (E4-9.2) through (E4-9.10) are easily solved with the aid of an ODE solver such as Polymath (Table E4-9.1).

TABLE E4-9.1 POLYMATH PROGRAM

ODE REPORT (RKF45)

Differential equations as entered by the user
[1] d(Ca)/d(t) = -k*Ca*Cb-vo*Ca/V
[2] d(Cb)/d(t) = -k*Ca*Cb+vo*(Cbo-Cb)/V
[3] d(Cc)/d(t) = k*Ca*Cb-vo*Cc/V
[4] d(Cd)/d(t) = k*Ca*Cb-vo*Cd/V

Explicit equations as entered by the user
[1] k = 2.2
[2] vo = 0.05
[3] Cbo = 0.025
[4] Vo = 5
[5] Cao = 0.05
[6] rate = k*Ca*Cb
[7] V = Vo+vo*t
[8] X = (Cao*Vo-Ca*V)/(Cao*Vo)

Living Example Problem

The concentrations of bromine cyanide (A) and methyl amine are shown as a function of time in Figure E4-9.1, and the rate is shown in Figure E4-9.2.
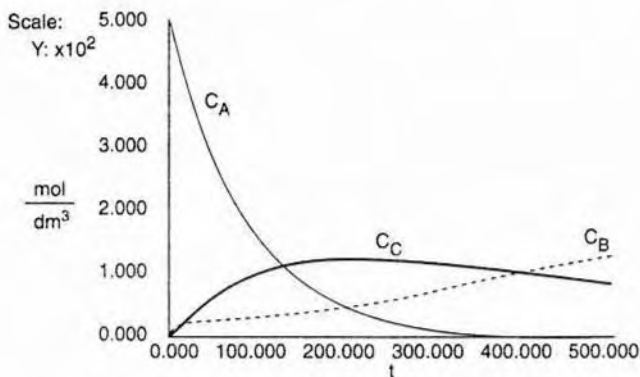
Why does the concentration of CH_3Br (C) go through a maximum wrt time?

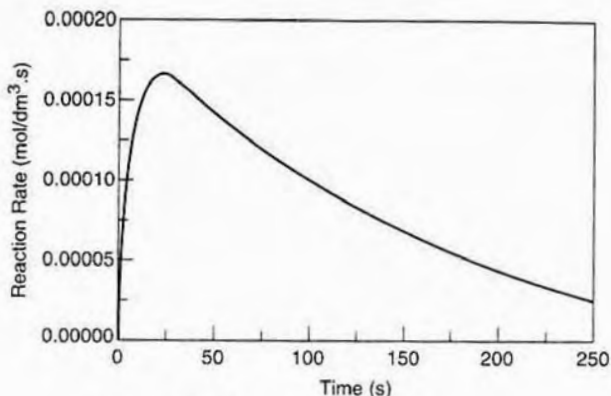**Figure E4-9.1**   Polymath output: Concentration–time trajectories.

Figure E4-9.2   Reaction rate–time trajectory.

4.10.4 Writing the Semibatch Reactor Equations in Terms of Conversion

Consider the reaction

$$A + B \rightleftharpoons C + D$$

in which B is fed to a vat containing only A initially. The reaction is first-order in A and first-order in B. The number of moles of A remaining at any time, t, is

The limiting reactant is the one in the vat.

$$
\begin{bmatrix} \text{Number of moles} \\ \text{of A in the vat} \\ \text{at time } t \end{bmatrix}
=
\begin{bmatrix} \text{Number of moles} \\ \text{of A in the vat} \\ \text{initially} \end{bmatrix}
-
\begin{bmatrix} \text{Number of moles} \\ \text{of A reacted up} \\ \text{to time } t \end{bmatrix}
\qquad (4\text{-}59)
$$

$$\overbrace{N_A} \qquad = \qquad \overbrace{N_{A0}} \qquad - \qquad \overbrace{N_{A0}X}$$

where X is the moles of A reacted per mole of A initially in the vat. Similarly, for species B,

$$
\begin{bmatrix} \text{Number of} \\ \text{moles of B in} \\ \text{the vat at time } t \end{bmatrix}
=
\begin{bmatrix} \text{Number of} \\ \text{moles of B in} \\ \text{the vat initially} \end{bmatrix}
+
\begin{bmatrix} \text{Number of} \\ \text{moles of B} \\ \text{added to the vat} \end{bmatrix}
-
\begin{bmatrix} \text{Number of moles} \\ \text{of B reacted} \\ \text{up to time } t \end{bmatrix}
\qquad (4\text{-}60)
$$

$$\overbrace{N_B} \qquad = \qquad \overbrace{N_{Bi}} \qquad + \qquad \overbrace{\int_0^t F_{B0}\, dt} \qquad - \qquad \overbrace{N_{A0}X}$$

For a constant molar feed rate and no B initially in the vat,

$$N_B = F_{B0}t - N_{A0}X \qquad (4\text{-}$$

A **mole balance** on species A gives

$$r_A V = \frac{dN_A}{dt} = -N_{A0}\frac{dX}{dt} \qquad (4\text{-}$$

The number of moles of C and D can be taken directly from the stoichiome table; for example,

$$N_C = N_{Ci} + N_{A0}X \qquad (4\text{-}$$

For a reversible second-order reaction $A + B \rightleftharpoons C + D$ for which rate law is

$$-r_A = k\left(C_A C_B - \frac{C_C C_D}{K_C}\right) \qquad (4\text{-}$$

Recalling Equation (4-55), the **concentrations of A, B, C, and D are**

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0 + v_0 t} \qquad C_C = \frac{N_{A0}X}{V_0 + v_0 t}$$

$$C_B = \frac{N_B}{V} = \frac{N_{Bi} + F_{B0}t - N_{A0}X}{V_0 + v_0 t} \qquad C_D = \frac{N_{A0}X}{V_0 + v_0 t} \qquad (4\text{-}$$

Combining equations (4-62), (4-64), and (4-65), substituting for the concent tions, and dividing by N_{A0}, we obtain

$$\boxed{\frac{dX}{dt} = \frac{k[(1-X)(N_{Bi} + F_{B0}t - N_{A0}X) - (N_{A0}X^2/K_C)]}{V_0 + v_0 t}} \qquad (4\text{-}$$

Equation (4-66) needs to be solved numerically to determine the conversion a function of time.

The third variable, in addition to concentration and conversion, we c use to analyze semibatch reactors is number of mole N_A, N_B, etc. This meth is discussed in the Summary Notes on the CD-ROM.

Summary Notes

Equilibrium Conversion.   For reversible reactions carried out in a semibat reactor, the maximum attainable conversion (i.e., the equilibrium conversic will change as the reaction proceeds because more reactant is continuous added to the reactor. This addition shifts the equilibrium continually to t right toward more product.

If the reaction $A + B \rightleftharpoons C + D$ were allowed to reach equilibrium after feeding species B for a time t, the equilibrium conversion could be calculated as follows at equilibrium [see Appendix C]:
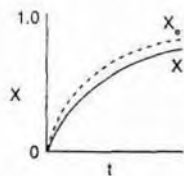
$$K_C = \frac{C_{Ce}C_{De}}{C_{Ae}C_{Be}} = \frac{\left(\dfrac{N_{Ce}}{V}\right)\left(\dfrac{N_{De}}{V}\right)}{\left(\dfrac{N_{Ae}}{V}\right)\left(\dfrac{N_{Be}}{V}\right)}$$

$$= \frac{N_{Ce}N_{De}}{N_{Ae}N_{Be}}$$

(4-67)

The relationship between conversion and number of moles of each species is the same as shown in Table 3-1 except for species B, for which the number of moles is given by Equation (4-61). Thus

$$K_C = \frac{(N_{A0}X_e)(N_{A0}X_e)}{N_{A0}(1 - X_e)(F_{B0}t - N_{A0}X_e)}$$

$$= \frac{N_{A0}X_e^2}{(1 - X_e)(F_{B0}t - N_{A0}X_e)}$$

(4-68)

Rearranging yields

$$t = \frac{N_{A0}}{K_C F_{B0}}\left(K_C X_e + \frac{X_e^2}{1 - X_e}\right)$$

(4-69)

or

Equilibrium
conversion
in a semibatch
reactor

$$X_e = \frac{K_C\left(1 + \dfrac{F_{B0}t}{N_{A0}}\right) - \sqrt{\left[K_C\left(1 + \dfrac{F_{B0}t}{N_{A0}}\right)\right]^2 - 4(K_C - 1)K_C\dfrac{tF_{B0}}{N_{A0}}}}{2(K_C - 1)}$$

(4-70)

Reactive distillation is used with thermodynamically limited reversible liquid-phase reactions and is particularly attractive when one of the products has a lower boiling point than the reactants. For reversible reactions of this type,

$$A(\ell) + B(\ell) \rightleftharpoons C(\ell) + D(g, \ell)$$
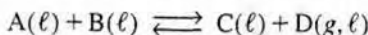
the equilibrium lies far to the left, and little product is formed. However, if one or more of the product (e.g., D) is removed by vaporization, as shown in Figure 4-16,
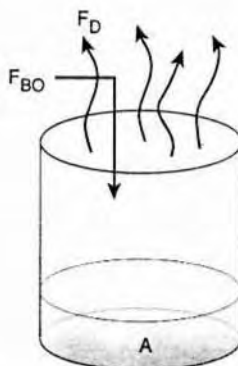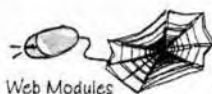
Figure 4-16 Reactive distillation with B fed to a vat containing A and D vaporizing.

Web Modules

the reaction will continue toward completion. The equilibrium constraint is removed, and more product will be formed. The fundamentals of reactive distillation are given on the CD-ROM web module.

4.11 The Practical Side

Summary Notes

The material presented in this chapter has been for isothermal ideal reactors. We will build on the concepts developed in this chapter when we discuss nonideal reactors in Chapters 13 and 14. A number of practical guidelines for the operation of chemical reactors have been presented over the years, and tables and some of these descriptions are summarized and presented on the CD-ROM and web. The articles are listed in Table 4-7.

TABLE 4-7 LITERATURE THAT GIVE PRACTICAL GUIDELINES FOR
REACTOR OPERATION

D. Mukesh, *Chem. Eng.*, 46 (January 2002). S. Dutta and R. Gualy, *CEP*, 37 (October 2000); *C&EN*, 8 (January 10, 2000). S. Jayakumar, R. G. Squires, G. V. Reklaitis, P. K. Andersen, and L. R. Partin, *Chem. Eng. Educ.*, 136 (Spring 1993). R. W. Cusack, *Chem. Eng.*, 88 (February 2000). A. Bakker, A. H. Haidari, and E. M. Marshall, *CEP*, 30 (December 2001). P. Trambouze, *CEP*, 23 (February 1990). G. Scholwsky and B. Loftus-Koch, *Chem. Eng.*, 96 (February 2000). J. H. Worstell, *CEP*, 55 (June 2000). J. H. Worstell, *CEP*, 68 (March 2001). S. Dutta and R. Gualy, *Chem. Eng.*, 72 (June 2000). A. Abu-Khalaf, *Chem. Eng. Educ.*, 48 (Winter 1994).

- For example, Mukesh gives relationships between the CSTR tank diameter, T, impeller size diameter, D, tank height, H, and the liquid level, ℓ. To scale up a pilot plant (1) to a full scale plant (2), the following guidelines are given

$$\frac{D_2}{D_1} = \frac{T_2}{T_1} = \frac{\ell_2}{\ell_1} = \frac{H_2}{H_1} = R$$

And the rotational speed, N_2, is

$$N_2 = N_1 R^{-n}$$

where values of n for different pumping capacities and Froude numbers are given in Mukesh's article.

Closure. This chapter presents the heart of chemical reaction engineering for isothermal reactors. After completing this chapter, the reader should be able to apply the algorithm building blocks

Evaluate
Combine
Stoichiometry
Rate Law
Mole Balance
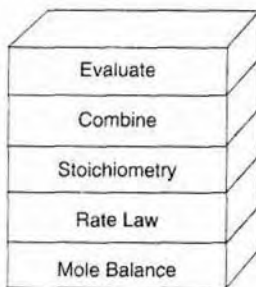
to any of the reactors discussed in this chapter: batch reactor, CSTR, PFR, PBF, membrane reactor, and semibatch reactor. The reader should be able to account for pressure drop and describe the effects of the system variables such as particle size on the conversion and explain why there is an optimum in the conversion when the catalyst particle size is varied. The reader should be able to use either conversions (Part 1) or concentration and molar flow rates (Part 2) to solve chemical reaction engineering problems. Finally, after completing this chapter, the reader should be able to work the California Professional Engineering Exam Problems in approximately 30 minutes [cf. P4-11$_B$ through P4-15$_B$] and to diagnose and troubleshoot malfunctioning reactors [cf. P4-8$_B$].

SUMMARY

1. Solution algorithm—**Conversion**
   a. **Design equations** (Batch, CSTR, PFR, PBR):

$$N_{A0} \frac{dX}{dt} = -r_A V, \quad V = \frac{F_{A0} X}{-r_A}, \quad F_{A0} \frac{dX}{dV} = -r_A, \quad F_{A0} \frac{dX}{dW} = -r_A' \quad (S4\text{-}1)$$

b. **Rate law**: For example,

$$-r_A = kC_A^2$$ (S4

c. **Stoichiometry**: $A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$

(1) *Gas phase*, $v = v_0(1 + \varepsilon X)\left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1 - X)}{v} = \frac{F_{A0}(1 - X)}{v_0(1 + \varepsilon X)}\left(\frac{P}{P_0}\right)\frac{T_0}{T} = C_{A0}\left(\frac{1 - X}{1 + \varepsilon X}\right)y\frac{T_0}{T}$$ (S4

$$\frac{dy}{dW} = -\frac{\alpha(1 + \varepsilon X)}{2y}\left(\frac{T}{T_0}\right)$$ (S4

For a packed bed

$$\alpha = \frac{2\beta_0}{A_c(1 - \phi)\rho_c P_0} \text{ and } \beta_0 = \frac{G(1 - \phi)}{\rho_0 g_c D_p \phi^3}\left[\frac{150(1 - \phi)\mu}{D_p} + 1.75G\right]$$

(2) *Liquid phase*: $v = v_0$ (S4

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

d. **Combining** for isothermal operation

Gas: $-r_A' = kC_{A0}^2\frac{(1 - X)^2}{(1 + \varepsilon X)^2}y^2$ (S4

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

e. Solution techniques:
   (1) Numerical integration—Simpson's rule (S4
   (2) Table of integrals
   (3) Software packages
       (a) Polymath
       (b) MATLAB

2. Solution algorithm—**Measures other than conversion**
   When using measures other than conversion for reactor design, the mole b
   ances are written for each species in the reacting mixture:

Mole balances

$$\frac{dF_A}{dV} = r_A, \quad \frac{dF_B}{dV} = r_B, \quad \frac{dF_C}{dV} = r_C, \quad \frac{dF_D}{dV} = r_D$$ (S4

The mole balances are then coupled through their relative rates of reaction. If

Rate law

$$-r_A = k C_A^\alpha C_B^\beta \tag{S4-9}$$

for $aA + bB \rightarrow cC + dD$, then

Stoichiometry

$$r_B = \frac{b}{a} r_A, \quad r_C = -\frac{c}{a} r_A, \quad r_D = -\frac{d}{a} r_A \tag{S4-10}$$

Concentration can also be expressed in terms of the number of moles (batch) and in molar flow rates (flow).

$$Gas: \quad C_A = C_{T0} \frac{F_A}{F_T} \frac{P}{P_0} \frac{T_0}{T} = C_{T0} \frac{F_A}{F_T} \frac{T_0}{T} y \tag{S4-11}$$

$$C_B = C_{T0} \frac{F_B}{F_T} \frac{T_0}{T} y \tag{S4-12}$$

$$F_T = F_A + F_B + F_C + F_D + F_I \tag{S4-13}$$

$$\frac{dy}{dW} = \frac{-\alpha}{2y} \left(\frac{F_T}{F_{T0}} \right) \left(\frac{T}{T_0} \right) \tag{S4-14}$$
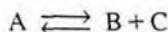
$$Liquid: \quad C_A = \frac{F_A}{v_0} \tag{S4-15}$$

Combine

3. An ODE solver (e.g., Polymath) will combine all the eqations for you.

   Variable density with $\varepsilon = 0$ or $\varepsilon X \ll 1$ and isothermal:

   IFF $\varepsilon = 0$

   $$\frac{P}{P_0} = (1 - \alpha W)^{1/2} \tag{S4-16}$$

4. For **membrane reactors** the mole balances for the reaction

   $$A \rightleftharpoons B + C$$

   when reactant A and product C do not diffuse out the membrane
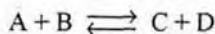
   $$\frac{dF_A}{dV} = r_A, \quad \frac{dF_B}{dV} = r_B - R_B, \quad \text{and} \quad \frac{dF_C}{dV} = r_C \tag{S4-17}$$

   with

   $$R_B = k_c C_B \tag{S4-18}$$

   and k_c is the overall mass transfer coefficient.

5. For **semibatch reactors**, reactant B is fed continuously to a vat initially containing only A:

   $$A + B \rightleftharpoons C + D$$

The combined mole balance, rate law, and stoichiometry in terms of conversion is

$$\frac{dX}{dt} = \frac{k[(1-X)(N_{Bi} + F_{B0}t - N_{A0}X) - (N_{A0}X^2/K_C)]}{V_0 + v_0 t} \tag{S4-19}$$

ODE SOLVER ALGORITHM

When using an ordinary differential equation (ODE) solver such as Polymath or MATLAB, it is usually easier to leave the mole balances, rate laws, and concentrations as separate equations rather than combining them into a single equation as we did to obtain an analytical solution. Writing the equations separately leaves it to the computer to combine them and produce a solution. The formulations for a packed-bed reactor with pressure drop and a semibatch reactor are given below for two elementary reactions carried out isothermally.

Gas Phase

$A + B \rightarrow 3C$
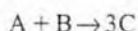
Packed-Bed Reactor

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

$$r_A = -kC_A C_B$$

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

$$C_B = C_{A0}\frac{\theta_B - X}{1+\varepsilon X}y$$

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

(where $y = P/P_0$)
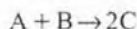
$k = 10.0$

$\alpha = 0.01$

$\varepsilon = 0.33$

$\theta_B = 2.0$

$C_{A0} = 0.01$

$F_{A0} = 15.0$

$W_{final} = 80$

Liquid Phase

$A + B \rightarrow 2C$

Semibatch Reactor

$$\frac{dC_A}{dt} = r_A - \frac{v_0 C_A}{V}$$

$$\frac{dC_B}{dt} = r_A + \frac{v_0(C_{B0} - C_B)}{V}$$

$$\frac{dC_C}{dt} = -2r_A - \frac{v_0 C_C}{V}$$

$$r_A = -kC_A C_B$$

$$V = V_0 + v_0 t$$

$k = 0.15$

$K_C = 4.0$

$V_0 = 10.0$

$v_0 = 0.1$

$C_{B0} = 0.1$
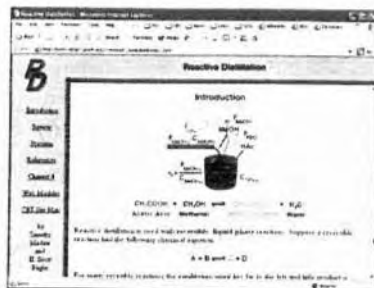
$C_{Ai} = 0.02$

$t_{final} = 200$

CD-ROM MATERIAL

• Learning Resources

Summary Notes

1. *Summary Notes*
2. *Web Modules*
   A. Wetlands   B. Reactive Distillation

Web Modules

3. *Interactive Computer Modules*
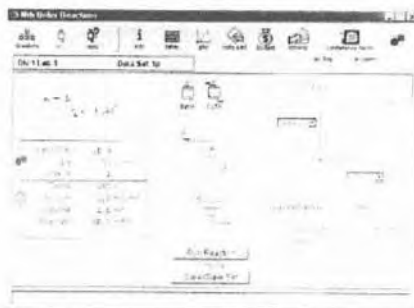   A. Murder Mystery   B. Tic-Tac

Interactive

Computer Modules

C. Reactor Lab Modules
   The following reactor Lab Modules have been developed by Professor
   Richard Herz in the Chemical Engineering Department at the University
   of California, San Diego. They are copyrighted by UCSD and Professor
   Hertz and are used here with their permission.

Solved Problems

- **Living Example Problems**

Living Example Problem • **Professional Reference Shelf**

R4.1. *Spherical Packed-Bed Reactors*

When small catalyst pellets are required, the pressure drop can be significa One type of reactor that minimizes pressure drop and is also inexpensive build is the spherical reactor, shown here. In this reactor, called ultraformer, dehydrogenation reactions such as

$$\text{Paraffin} \longrightarrow \text{Aromatic} + 3H_2$$

are carried out.
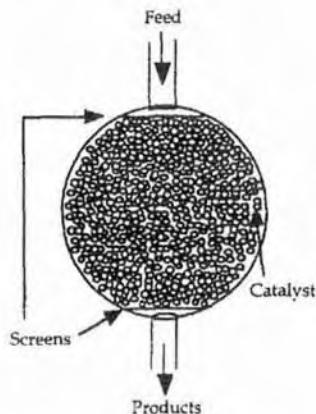
Spherical ultraformer reactor. (Courtesy of Amoco Petroleum Products.)
This reactor is one in a series of six used by Amoco for reforming petroleum naphtha. Photo by K. R. Renicker, Sr.

Analysis of a spherical reactor equation along with an example problem a carried out on the CD-ROM.

R4.2 *Recycle Reactors*

Recycle reactors are used (1) when conversion of unwanted (toxic) produ is required and they are recycled to extinction, (2) the reaction is autoca lytic or (3) it is necessary to maintain isothermal operation. To design recyc

Green engineering   reactors, one simply follows the procedure developed in this chapter and th adds a little additional bookkeeping.
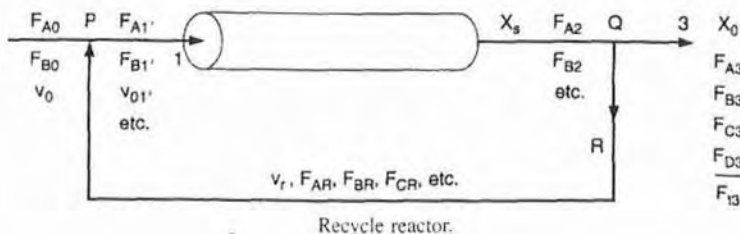
Recycle reactor.

As shown in the CD-ROM, two conversions are usually associated with recycle reactors: the overall conversion, X_0, and the conversion per pass, X_S.

R4.3. *Aerosol Reactors*

Aerosol reactors are used to synthesize nano-size particles. Owing to their size, shape, and high specific surface area, nanoparticles can be used in a number of applications such as in pigments in cosmetics, membranes, photocatalytic reactors, catalysts and ceramics, and catalytic reactors.

We use the production of aluminum particles as an example of an aerosol plug-flow reactor (APFR) operation. A stream of argon gas saturated with Al vapor is cooled.

Nanoparticles

Aerosol reactor and temperature profile.
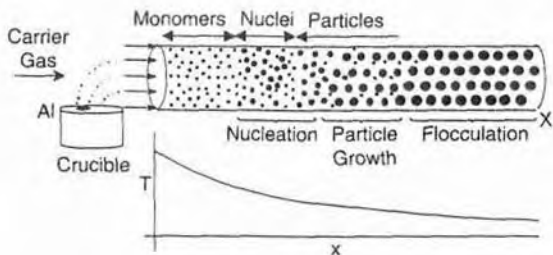
As the gas is cooled, it becomes supersaturated, leading to the nucleation of particles. This nucleation is a result of molecules colliding and agglomerating until a critical nucleus size is reached and a particle is formed. As these particles move down, the supersaturated gas molecules condense on the particles causing them to grow in size and then to flocculate. In the development on the CD-ROM, we will model the formation and growth of aluminum nanoparticles in an AFPR.

R4.4 *Critiquing Journal Articles*

After graduation, your textbooks will be, in part, the professional journals that you read. As you read the journals, it is important that you study them with a critical eye. You need to learn if the author's conclusion is supported by the data, if the article is new or novel, if it advances our understanding, and if the analysis is current. To develop this technique, one of the major assignments used in the graduate course in chemical reaction engineering at

the University of Michigan for the past 25 years has been an in-depth analysis and critique of a journal article related to the course material. Significant effort is made to ensure that a cursory or superficial review is not carried out. The CD-ROM gives an example and some guidelines about critiquing journal articles.

QUESTIONS AND PROBLEMS

The subscript to each of the problem numbers indicates the level of difficulty: A, least difficult; D, most difficult.

$$A = \bullet \quad B = \blacksquare \quad C = \blacklozenge \quad D = \blacklozenge\blacklozenge$$

Homework Problems

In each of the following questions and problems, rather than just drawing a box around your answer, write a sentence or two describing how you solved the problem, the assumptions you made, the reasonableness of your answer, what you learned, and any other facts that you want to include. You may wish to refer to W. Strunk and E. B. White, *The Elements of Style*, 4th ed. (New York: Macmillan, 2000) and Joseph M. Williams, *Style: Ten Lessons in Clarity & Grace*, 6th ed. (Glenview, Ill.: Scott, Foresman, 1999) to enhance the quality of your sentences. See the Preface for additional generic parts (x), (y), (z) to the home problems.

P4-1$_A$ Read through all the problems at the end of this chapter. Make up and solve an *original* problem based on the material in this chapter. (a) Use real data and reactions. (b) Make up a reaction and data. (c) Use an example from everyday life (e.g., making toast or cooking spaghetti). In preparing your original problem, first list the principles you want to get across and why the problem is important. Ask yourself how your example will be different from those in the text or lecture. Other things for you to consider when choosing a problem are relevance, interest, impact of the solution, time required to obtain a solution, and degree of difficulty. Look through some of the journals for data or to get some ideas for industrially important reactions or for novel applications of reaction engineering principles (the environment, food processing, etc.). At the end of the problem and solution describe the creative process used to generate the idea for the problem. (d) Write a question based on the material in this chapter that requires critical thinking. Explain why your question requires critical thinking. [*Hint:* See Preface, Section B.2] (e) Listen to the audios on the CD 🎧 Lecture Notes, pick one, and describe how you might explain it differently.

P4-2$_B$ **What if...** you were asked to explore the example problems in this chapter to learn the effects of varying the different parameters? This sensitivity analysis can be carried out by either downloading the examples from the web or by loading the programs from the CD-ROM supplied with the text. For each of the example problems you investigate, write a paragraph describing your findings.

Before solving the problems, state or sketch qualitatively the expected results or trends.

  (a) **What if** you were asked to give examples of the material in this book that are found in everyday life? What would you say?

  (b) **Example 4-1.** What would be the error in k if the batch reactor were only 80% filled with the same composition of reactants instead of being completely filled as in the example? What generalizations can you draw from this example?

(c) **Example 4-2.** How would your reactor volume change if you only needed 50% conversion to produce the 200 million pounds per year required? What generalizations can you draw from this example?

(d) **Example 4-3.** What would be the reactor volume for $X = 0.8$ if the pressure were increased by a factor of 10 assuming everything else remains the same? What generalizations can you draw from this example?

(e) **Example 4-4.** How would the pressure drop change if the particle diameter were reduced by 25%? What generalizations can you draw from this example?

(f) **Example 4-5.** What would be the conversion with and without pressure drop if the entering pressure were increased by a factor of 10? Would the optimum diameter change? If so, how? What would the conversion be if the reactor diameter were decreased by a factor of 2 for the same mass flow rate?

(g) **Example 4-6.** Load the *Living Example Problem 4-6* from the CD-ROM. How much would the catalyst weight change if the pressure was increased by a factor of 5 and the particle size decreased by a factor of 5? (Recall α is also a function of P_0)? Use plots and figures to describe what you find.

(h) **Example 4-7.** Load the *Living Example Problem 4-7* from the CD-ROM. How would the results change if the pressure were doubled and the temperature was decreased 20°C?

(i) **Example 4-8.** Load the *Living Example Problem 4-8* from the CD-ROM. Vary parameters (e.g., k_C), and ratios of parameters (k/k_C), ($k\tau C_{A0}/K_e$), etc., and write a paragraph describing what you find. What ratio of parameters has the greatest effect on the conversion $X = (F_{A0} - F_A)/F_{A0}$?

(j) **Example 4-9.** Load the *Living Example Problem 4-9* from the CD-ROM. The temperature is to be lowered by 35°C so that the reaction rate constant is now (1/10) its original value. (i) If the concentration of B is to be maintained at 0.01 mol/dm^3 or below, what is the maximum feed rate of B? (ii) How would your answer change if the concentration of A were tripled?

(k) **Web Module on Wetlands** from the CD-ROM. Load the *Polymath program* and vary a number of parameters such as rainfall, evaporation rate, atrazine concentration, and liquid flow rate, and write a paragraph describing what you find. This topic is a hot Ch.E. research area.

(l) **Web Module on Reactive Distillation** from the CD-ROM. Load the *Polymath program* and vary the parameters such as feed rate, and evaporation rate, and write a paragraph describing what you find.

(m) **Web Module on Aerosol Reactors** from the CD-ROM. Load the *Polymath program* and (1) vary the parameters such as cooling rate and flow rate, and describe their effect on each of the regimes nucleation, growth and flocculation. Write a paragraph describing what you find. (2) It is proposed to replace the carrier gas by helium

    (i) Compare your plots (He versus Ar) of the number of Al particles as a function of time. Explain the shape of the plots.

    (ii) How does the final value of d_p compare with that when the carrier gas was argon? Explain.

    (iii) Compare the time at which the rate of nucleation reaches a peak in the two cases [carrier gas = Ar and He]. Discuss the comparison.

<u>Data for a He molecule:</u> Mass = 6.64×10^{-27} kg, Volume = 1.33×10^{-29} Surface area = 2.72×10^{-19} m^2, Bulk density = 0.164 kg/m^3, at norr temperature ($25°C$) and pressure (1 atm).

(n) Vary some of the operating costs, conversions, and separations in Fig 4-10 to learn how the profit changes. Ethylene oxide, used to make e ylene glycol, sells for \$0.56/lb while ethylene glycol sells for \$0.38/ Is this a money-losing proposition? Explain.

(o) What should you do if some of the ethylene glycol splashed out of reactor onto your face and clothing? (*Hint*: Recall www.siri.org/.)

(p) What safety precautions should you take with the ethylene oxide forn tion discussed in Example 4-6? With the bromine cyanide discussed Example 4-9?

(q) **Load reactor lab** on to your computer and call up *D1 Isothermal Re tors*. Detailed instructions with screen shots are given in Chapter 4 of Summary Notes. (1) For **L1** Nth Order Reactions. Vary the parameters E, T for a batch, CSTR, and PFR. Write a paragraph discussing trends (e.g., first order versus second order) and describe what you fi (2) Next choose the "Quiz" on membrane at the top of the screen, a find the reaction order (3) and turn in your performance number.

Performance number: _____

(r) **The Work Self Tests on the Web.** Write a question for this problem t involves critical thinking and explaining why it involves critical thinkin See examples on the Web Summary Note for Chapter 4.

P4-3$_B$ Load the Interactive Computer Modules (ICM) from the CD-ROM. Run t modules and then record your performance number, which indicates yo mastery of the material. Your instructor has the key to decode your perfe mance number.

(a) ICM—Mystery Theater—A real "Who done it?", see *Pulp and Paper*, (January 1993) and also *Pulp and Paper*, 9 (July 1993). The outcome the murder trial is summarized in the December 1995 issue of *Pape maker*, page 12. You will use fundamental chemical engineering fro Sections 4.1 to 4.3 to identify the victim and the murderer.

Performance number: _____

(b) ICM—Tic Tac—Knowledge of all sections is necessary to pit your v against the computer adversary in playing a game of Tic-Tac-Toe.

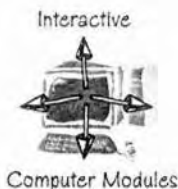Performance number: _____

P4-4$_A$ If it takes 11 minutes to cook spaghetti in Ann Arbor, Michigan, and 14 mi utes in Boulder, Colorado, how long would it take in Cuzco, Peru? Discu ways to make the spaghetti more tasty. If you prefer to make a creative sp ghetti dinner for family or friends rather than answering this question, tha OK, too; you'll get full credit—but **only if** you turn in your receipt and brir your instructor a taste. (*Ans. t* = 21 min)

P4-5$_A$ The liquid-phase reaction

$$A + B \longrightarrow C$$

follows an elementary rate law and is carried out isothermally in a flow sy tem. The concentrations of the A and B feed streams are 2 *M* before mixin The volumetric flow rate of each stream is 5 dm^3/min, and the enterin temperature is 300 K. The streams are mixed immediately before enterin