

TABLE 3-2. DESIGN EQUATIONS

| | Differential Form | Algebraic Form | Integral Form |
|----------------------|---------------------------------------|---------------------------------------|---|
| Batch | $N_{A0} \frac{dX}{dt} = -r_A V$ (2-6) | | $t = N_{A0} \int_0^X \frac{dX}{-r_A V}$ (2-9) |
| The design equations | Backmix (CSTR) | $V = \frac{F_{A0} X}{-r_A}$ (2-13) | |
| | Tubular (PFR) | $F_{A0} \frac{dX}{dV} = -r_A$ (2-15) | $V = F_{A0} \int_0^X \frac{dX}{-r_A}$ (2-16) |
| | Packed bed (PBR) | $F_{A0} \frac{dX}{dW} = -r'_A$ (2-17) | $W = F_{A0} \int_0^X \frac{dX}{-r'_A}$ (2-18) |

With these additional relationships, one observes that if the rate law is given and the concentrations can be expressed as a function of conversion, *then in fact we have $-r_A$ as a function of X and this is all that is needed to evaluate the design equations.* One can use either the numerical techniques described in Chapter 2, or, as we shall see in Chapter 4, a table of integrals, and/or software programs (e.g., Polymath).

PART 2 STOICHIOMETRY

Now that we have shown how the rate law can be expressed as a function of concentrations, we need only express concentration as a function of conversion in order to carry out calculations similar to those presented in Chapter 2 to size reactors. If the rate law depends on more than one species, we must relate the concentrations of the different species to each other. This relationship is most easily established with the aid of a stoichiometric table. This table presents the stoichiometric relationships between reacting molecules for a single reaction. That is, it tells us how many molecules of one species will be formed during a chemical reaction when a given number of molecules of another species disappears. These relationships will be developed for the general reaction

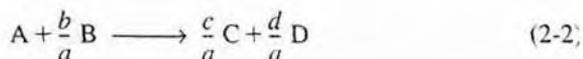


Recall that we have already used stoichiometry to relate the relative rates of reaction for Equation (2-1):

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d} \quad (3-1)$$

This stoichiometric relationship relating reaction rates will be used in Part 2 of Chapter 4.

In formulating our stoichiometric table, we shall take species A as our basis of calculation (i.e., limiting reactant) and then divide through by the stoichiometric coefficient of A,



in order to put everything on a basis of “per mole of A.”

Next, we develop the stoichiometric relationships for reacting species that give the change in the number of moles of each species (i.e., A, B, C, and D).

3.5 Batch Systems

Batch reactors are primarily used for the production of specialty chemicals and to obtain reaction rate data in order to determine reaction rate laws and rate law parameters such as k , the specific reaction rate.

Figure 3-4 shows an artist’s rendition of a batch system in which we will carry out the reaction given by Equation (2-2). At time $t = 0$, we will open the reactor and place a number of moles of species A, B, C, D, and I (N_{A0} , N_{B0} , N_{C0} , N_{D0} , and N_I , respectively) into the reactor.

Species A is our basis of calculation, and N_{A0} is the number of moles of A initially present in the reactor. Of these, $N_{A0}X$ moles of A are consumed in the system as a result of the chemical reaction, leaving $(N_{A0} - N_{A0}X)$ moles of A in the system. That is, the number of moles of A remaining in the reactor after a conversion X has been achieved is

$$N_A = N_{A0} - N_{A0}X = N_{A0}(1 - X)$$

We now will use conversion in this fashion to express the number of moles of B, C, and D in terms of conversion.

To determine the number of moles of each species remaining after $N_{A0}X$ moles of A have reacted, we form the stoichiometric table (Table 3-3). This stoichiometric table presents the following information:

Components of the
stoichiometric table

Column 1: the particular species

Column 2: the number of moles of each species initially present

Column 3: the change in the number of moles brought about by reaction

Column 4: the number of moles remaining in the system at time t

To calculate the number of moles of species B remaining at time t , we recall that at time t the number of moles of A that have reacted is $N_{A0}X$. For every mole of A that reacts, b/a moles of B must react; therefore, the total number of moles of B that have reacted is

$$\begin{aligned} \text{moles B reacted} &= \frac{\text{moles B reacted}}{\text{moles A reacted}} \cdot \text{moles A reacted} \\ &= \frac{b}{a} (N_{A0}X) \end{aligned}$$

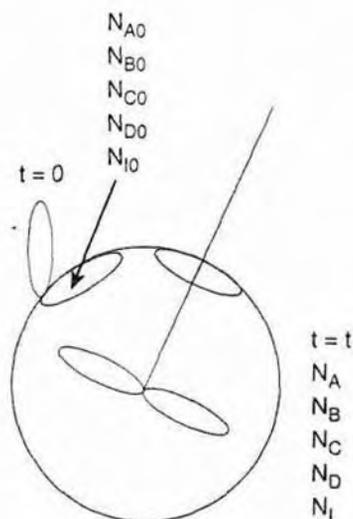


Figure 3-4 Batch reactor. (Schematic with permission by Renwahr.)

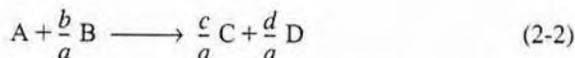
TABLE 3-3. STOICHIOMETRIC TABLE FOR A BATCH SYSTEM

| Species | Initially (mol) | Change (mol) | Remaining (mol) |
|------------|--------------------|-------------------------|--|
| A | N_{A0} | $-(N_{A0}X)$ | $N_A = N_{A0} - N_{A0}X$ |
| B | N_{B0} | $-\frac{b}{a}(N_{A0}X)$ | $N_B = N_{B0} - \frac{b}{a}N_{A0}X$ |
| C | N_{C0} | $\frac{c}{a}(N_{A0}X)$ | $N_C = N_{C0} + \frac{c}{a}N_{A0}X$ |
| D | N_{D0} | $\frac{d}{a}(N_{A0}X)$ | $N_D = N_{D0} + \frac{d}{a}N_{A0}X$ |
| I (inerts) | N_{I0} | — | $N_I = N_{I0}$ |
| Totals | N_{T0} | | $N_T = N_{T0} + \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)N_{A0}X$ |

Because B is disappearing from the system, the sign of the “change” is negative. N_{B0} is the number of moles initially in the system. Therefore, the number of moles of B remaining in the system, N_B , at a time t , is given in the last column of Table 3-3 as

$$N_B = N_{B0} - \frac{b}{a} N_{A0}X$$

The complete stoichiometric table delineated in Table 3-3 is for all species in the general reaction



Let's take a look at the totals in the last column of Table 3-3. The stoichiometric coefficients in parentheses ($d/a + c/a - b/a - 1$) represent the increase in the total number of moles per mole of A reacted. Because this term occurs so often in our calculations, it is given the symbol δ :

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \quad (3-23)$$

The parameter δ tells us the change in the total number of moles per mole of A reacted. The total number of moles can now be calculated from the equation

$$N_T = N_{T0} + \delta N_{A0} X$$

We want
 $C_j = h_j(X)$

We recall from Chapter 1 and Part 1 of this chapter that the kinetic rate law (e.g., $-r_A = kC_A^2$) is a function solely of the intensive properties of the reacting system (e.g., temperature, pressure, concentration, and catalysts, if any). The reaction rate, $-r_A$, usually depends on the concentration of the reacting species raised to some power. Consequently, to determine the reaction rate as a function of conversion X , we need to know the concentrations of the reacting species as a function of conversion.

3.5.1 Equations for Batch Concentrations

Batch
concentration

The concentration of A is the number of moles of A per unit volume:

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

After writing similar equations for B, C, and D, we use the stoichiometric table to express the concentration of each component in terms of the conversion X :

$$\begin{aligned} C_A &= \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V} \\ C_B &= \frac{N_B}{V} = \frac{N_{B0} - (b/a)N_{A0}X}{V} \\ C_C &= \frac{N_C}{V} = \frac{N_{C0} + (c/a)N_{A0}X}{V} \\ C_D &= \frac{N_D}{V} = \frac{N_{D0} + (d/a)N_{A0}X}{V} \end{aligned} \quad (3-24)$$

We further simplify these equations by defining the parameter Θ_i , which allows us to factor N_{A0} in each of the expressions for concentration:

$$\Theta_i = \frac{N_{i0}}{N_{A0}} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$$

$$C_B = \frac{N_{A0}[N_{B0}/N_{A0} - (b/a)X]}{V} = \frac{N_{A0}[\Theta_B - (b/a)X]}{V}, \quad \text{with } \Theta_B = \frac{N_{B0}}{N_{A0}} \quad (3-25)$$

$$C_C = \frac{N_{A0}[\Theta_C + (c/a)X]}{V}, \quad \text{with } \Theta_C = \frac{N_{C0}}{N_{A0}}$$

$$C_D = \frac{N_{A0}[\Theta_D + (d/a)X]}{V}, \quad \text{with } \Theta_D = \frac{N_{D0}}{N_{A0}}$$

We need $V(X)$ to obtain $C_j = h_j(X)$.

We now need only to find volume as a function of conversion to obtain the species concentration as a function of conversion.

3.5.2 Constant-Volume Batch Reaction Systems

Some significant simplifications in the reactor design equations are possible when the reacting system undergoes no change in volume as the reaction progresses. These systems are called constant-volume, or constant-density, because of the invariance of either volume or density during the reaction process. This situation may arise from several causes. In gas-phase batch systems, the reactor is usually a sealed constant-volume vessel with appropriate instruments to measure pressure and temperature within the reactor. The volume within this vessel is fixed and will not change, and is therefore a constant-volume system ($V = V_0$). The laboratory bomb calorimeter reactor is a typical example of this type of reactor.

Another example of a constant-volume gas-phase isothermal reaction occurs when the number of moles of products equals the number of moles of reactants. The water-gas shift reaction, important in coal gasification and many other processes, is one of these:



In this reaction, 2 mol of reactant forms 2 mol of product. When the number of reactant molecules forms an equal number of product molecules at the *same* temperature and pressure, the volume of the reacting mixture will not change if the conditions are such that the ideal gas law is applicable, or if the compressibility factors of the products and reactants are approximately equal.

For liquid-phase reactions taking place in solution, the solvent usually dominates the situation. As a result, changes in the density of the solute **do not**

affect the overall density of the solution significantly and therefore it is essentially a constant-volume reaction process. Most liquid-phase organic reactions do not change density during the reaction and represent still another case to which the constant-volume simplifications apply. An important exception to this general rule exists for polymerization processes.

For the constant-volume systems described earlier, Equation (3-25) can be simplified to give the following expressions relating concentration and conversion:

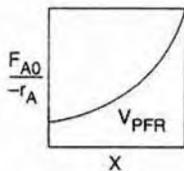
$$\begin{aligned}
 V &= V_0 \\
 C_A &= \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X) \\
 C_B &= N_{A0} \frac{[(N_{B0}/N_{A0}) - (b/a)X]}{V_0} = \frac{N_{A0}[\Theta_B - (b/a)X]}{V_0} = C_{A0} \left(\Theta_B - \frac{b}{a}X \right) \\
 C_C &= N_{A0} \frac{[(N_{C0}/N_{A0}) + (c/a)X]}{V_0} = C_{A0} \left(\Theta_C + \frac{c}{a}X \right) \\
 C_D &= N_{A0} \frac{[(N_{D0}/N_{A0}) + (d/a)X]}{V_0} = C_{A0} \left(\Theta_D + \frac{d}{a}X \right)
 \end{aligned} \quad (3-26)$$

Concentration as a function of conversion when no volume change occurs with reaction

To summarize for liquid-phase reactions (or as we will soon see for isothermic and isobaric gas-phase reactions with no change in the total number of moles) we can use a rate law for reaction (2-2) such as $-r_A = k_A C_A C_B$ to obtain $-r_A = f(X)$, that is,

$$-r_A = k C_A C_B = k C_{A0}^2 (1-X) \left(\Theta_B - \frac{b}{a}X \right) = f(X)$$

Substituting for the given parameters k , C_{A0} , and Θ_B , we can now use the techniques in Chapter 2 to size the CSTRs and PFRs for liquid-phase reactions.



Example 3-2 Expressing $C_j = h_j(X)$ for a Liquid-Phase Reaction

Soap consists of the sodium and potassium salts of various fatty acids such as oleic, stearic, palmitic, lauric, and myristic acids. The saponification for the formation of soap from aqueous caustic soda and glyceryl stearate is

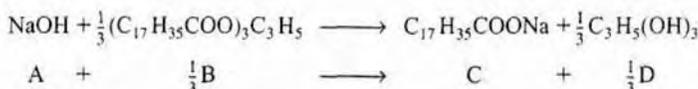


Letting X represent the conversion of sodium hydroxide (the moles of sodium hydroxide reacted per mole of sodium hydroxide initially present), set up a stoichiometric table expressing the concentration of each species in terms of its initial concentration and the conversion X .

Solution

Because we are taking sodium hydroxide as our basis, we divide through by the stoichiometric coefficient of sodium hydroxide to put the reaction expression in the form

Choosing a basis of calculation



We may then perform the calculations shown in Table E3-2.1. Because this is a liquid-phase reaction, the density ρ is considered to be constant; therefore, $V = V_0$.

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

$$\Theta_B = \frac{C_{B0}}{C_{A0}} \quad \Theta_C = \frac{C_{C0}}{C_{A0}} \quad \Theta_D = \frac{C_{D0}}{C_{A0}}$$

TABLE E3-2.1. STOICHIOMETRIC TABLE FOR LIQUID-PHASE SOAP REACTION

Stoichiometric table (batch)

| Species | Symbol | Initially | Change | Remaining | Concentration |
|--|--------|-------------------------|-----------------------|---|---|
| NaOH | A | N_{A0} | $-N_{A0}X$ | $N_{A0}(1-X)$ | $C_{A0}(1-X)$ |
| $(\text{C}_{17}\text{H}_{35}\text{COO})_3\text{C}_3\text{H}_5$ | B | N_{B0} | $-\frac{1}{3}N_{A0}X$ | $N_{A0}\left(\Theta_B - \frac{X}{3}\right)$ | $C_{A0}\left(\Theta_B - \frac{X}{3}\right)$ |
| $\text{C}_{17}\text{H}_{35}\text{COONa}$ | C | N_{C0} | $N_{A0}X$ | $N_{A0}(\Theta_C + X)$ | $C_{A0}(\Theta_C + X)$ |
| $\text{C}_3\text{H}_5(\text{OH})_3$ | D | N_{D0} | $\frac{1}{3}N_{A0}X$ | $N_{A0}\left(\Theta_D + \frac{X}{3}\right)$ | $C_{A0}\left(\Theta_D + \frac{X}{3}\right)$ |
| Water (inert) | I | $\frac{N_{I0}}{N_{T0}}$ | $\frac{0}{0}$ | $\frac{N_{I0}}{N_T = N_{T0}}$ | C_{I0} |

Example 3-3 What Is the Limiting Reactant?

Having set up the stoichiometric table in Example 3-2, one can now readily use it to calculate the concentrations at a given conversion. If the initial mixture consists solely of sodium hydroxide at a concentration of 10 mol/dm³ (i.e., 10 mol/L or 10 kmol/m³) and of glyceryl stearate at a concentration of 2 mol/dm³, what is the concentration of glycerine when the conversion of sodium hydroxide is (a) 20% and (b) 90%?

Solution

Only the reactants NaOH and $(\text{C}_{17}\text{H}_{35}\text{COO})_3\text{C}_3\text{H}_5$ are initially present; therefore, $\Theta_C = \Theta_D = 0$.

(a) For 20% conversion of NaOH:

$$C_D = C_{A0} \left(\frac{X}{3} \right) = (10) \left(\frac{0.2}{3} \right) = 0.67 \text{ mol/L} = 0.67 \text{ mol/dm}^3$$

$$C_B = C_{A0} \left(\Theta_B - \frac{X}{3} \right) = 10 \left(\frac{2}{10} - \frac{0.2}{3} \right) = 10(0.133) = 1.33 \text{ mol/dm}^3$$

(b) For 90% conversion of NaOH:

$$C_D = C_{A0} \left(\frac{X}{3} \right) = 10 \left(\frac{0.9}{3} \right) = 3 \text{ mol/dm}^3$$

Let us find C_B :

$$C_B = 10 \left(\frac{2}{10} - \frac{0.9}{3} \right) = 10(0.2 - 0.3) = -1 \text{ mol/dm}^3$$

Oops!! Negative concentration—impossible! What went wrong?

Ninety percent conversion of NaOH is not possible, because glyceryl stearate is the limiting reactant. Consequently, all the glyceryl stearate is used up before 90% of the NaOH could be reacted. It is important to choose the limiting reactant as the basis of calculation.

The basis of calculation should be the limiting reactant.

3.6 Flow Systems

The form of the stoichiometric table for a continuous-flow system (see Figure 3-5) is virtually identical to that for a batch system (Table 3-3) except that we replace N_{j0} by F_{j0} and N_j by F_j (Table 3-4). Taking A as the basis, divide Equation (2-1) through by the stoichiometric coefficient of A to obtain

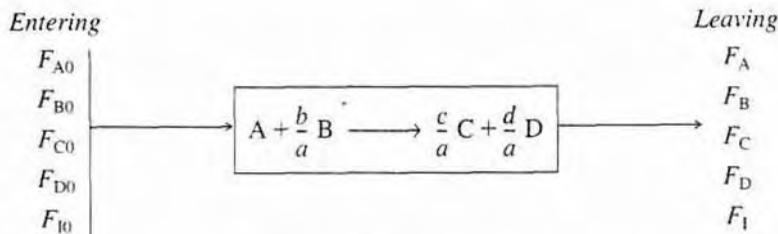
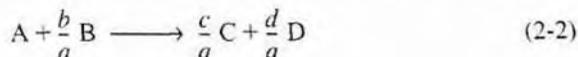


Figure 3-5 Flow reactor.

TABLE 3-4. STOICHIOMETRIC TABLE FOR A FLOW SYSTEM

| Species | Feed Rate to Reactor (mol/time) | Change within Reactor (mol/time) | Effluent Rate from Reactor (mol/time) |
|---------|---------------------------------|----------------------------------|---|
| A | F_{A0} | $-F_{A0}X$ | $F_A = F_{A0}(1-X)$ |
| B | $F_{B0} = \Theta_B F_{A0}$ | $-\frac{b}{a} F_{A0}X$ | $F_B = F_{A0} \left(\Theta_B - \frac{b}{a} X \right)$ |
| C | $F_{C0} = \Theta_C F_{A0}$ | $\frac{c}{a} F_{A0}X$ | $F_C = F_{A0} \left(\Theta_C + \frac{c}{a} X \right)$ |
| D | $F_{D0} = \Theta_D F_{A0}$ | $\frac{d}{a} F_{A0}X$ | $F_D = F_{A0} \left(\Theta_D + \frac{d}{a} X \right)$ |
| I | $F_{I0} = \Theta_I F_{A0}$ | — | $F_I = F_{A0} \Theta_I$ |
| | F_{T0} | | $F_T = F_{T0} + \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) F_{A0}X$ |
| | | | $F_T = F_{T0} + \delta F_{A0}X$ |

Stoichiometric table (flow)

where

$$\Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{C_{B0} v_0}{C_{A0} v_0} = \frac{C_{B0}}{C_{A0}} = \frac{y_{B0}}{y_{A0}}$$

and Θ_C , Θ_D , and Θ_I are defined similarly.

3.6.1 Equations for Concentrations in Flow Systems

For a flow system, the concentration C_A at a given point can be determined from the molar flow rate F_A and the volumetric flow rate v at that point:

$$C_A = \frac{F_A}{v} = \frac{\text{moles/time}}{\text{liters/time}} = \frac{\text{moles}}{\text{liter}} \quad (3-27)$$

Definition of concentration for a flow system

Units of v are typically given in terms of liters per second, cubic decimeters per second, or cubic feet per minute. We now can write the concentrations of A, B, C, and D for the general reaction given by Equation (2-2) in terms of their respective entering molar flow rates (F_{A0} , F_{B0} , F_{C0} , F_{D0}), the conversion X , and the volumetric flow rate, v .

$$\begin{aligned} C_A &= \frac{F_A}{v} = \frac{F_{A0}}{v} (1-X) & C_B &= \frac{F_B}{v} = \frac{F_{B0} - (b/a) F_{A0} X}{v} \\ C_C &= \frac{F_C}{v} = \frac{F_{C0} + (c/a) F_{A0} X}{v} & C_D &= \frac{F_D}{v} = \frac{F_{D0} + (d/a) F_{A0} X}{v} \end{aligned} \quad (3-28)$$

3.6.2 Liquid-Phase Concentrations

For liquids, volume change with reaction is negligible when no phase changes are taking place. Consequently, we can take

$$v = v_0$$

For liquids

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

$$C_B = C_{A0} \left(\Theta_B - \frac{b}{a} X \right)$$

Therefore, for a given rate law we have
 $-r_A = g(X)$

Then

$$C_A = \frac{F_{A0}}{v_0} (1 - X) = C_{A0}(1 - X) \quad (3-29)$$

$$C_B = C_{A0} \left(\Theta_B - \frac{b}{a} X \right) \quad \text{etc.}$$

Consequently, using any one of the rate laws in Part 1 of this chapter, we can now find $-r_A = f(X)$ for liquid-phase reactions. However, for gas-phase reactions the volumetric flow rate most often changes during the course of the reaction because of a change in the total number of moles or in temperature or pressure. Hence, one cannot always use Equation (3-29) to express concentration as a function of conversion for gas-phase reactions.

3.6.3 Change in the Total Number of Moles with Reaction in the Gas Phase

In our previous discussions, we considered primarily systems in which the reaction volume or volumetric flow rate did not vary as the reaction progressed. Most batch and liquid-phase and some gas-phase systems fall into this category. There are other systems, though, in which either V or v do vary, and these will now be considered.

A situation where one encounters a varying flow rate occurs quite frequently in gas-phase reactions that do not have an equal number of product and reactant moles. For example, in the synthesis of ammonia,



4 mol of reactants gives 2 mol of product. In flow systems where this type of reaction occurs, the molar flow rate will be changing as the reaction progresses. Because equal numbers of moles occupy equal volumes in the gas phase at the same temperature and pressure, the volumetric flow rate will also change.

Another variable-volume situation, which occurs much less frequently, is in batch reactors where volume changes with time. Everyday examples of this situation are the combustion chamber of the internal-combustion engine and the expanding gases within the breech and barrel of a firearm as it is fired.

In the stoichiometric tables presented on the preceding pages, it was not necessary to make assumptions concerning a volume change in the first four columns of the table (i.e., the species, initial number of moles or molar feed

rate, change within the reactor, and the remaining number of moles or the molar effluent rate). All of these columns of the stoichiometric table are independent of the volume or density, and they are *identical* for constant-volume (constant-density) and varying-volume (varying-density) situations. Only when concentration is expressed as a function of conversion does variable density enter the picture.

Batch Reactors with Variable Volume Although variable volume batch reactors are seldom encountered because they are usually solid steel containers, we will develop the concentrations as a function of conversion because (1) they have been used to collect reaction data for gas-phase reactions, and (2) the development of the equations that express volume as a function of conversion will facilitate analyzing flow systems with variable volumetric flow rates.

Individual concentrations can be determined by expressing the volume V for a batch system, or volumetric flow rate v for a flow system, as a function of conversion using the following equation of state:

$$\text{Equation of state} \quad PV = ZN_T RT \quad (3-30)$$

in which V = volume and N_T = total number of moles as before and

T = temperature, K

P = total pressure, atm (kPa; 1 atm = 101.3 kPa)

Z = compressibility factor

R = gas constant = $0.08206 \text{ dm}^3 \cdot \text{atm/mol} \cdot \text{K}$

This equation is valid at any point in the system at any time t . At time $t = 0$ (i.e., when the reaction is initiated), Equation (3-30) becomes

$$P_0 V_0 = Z_0 N_{T0} R T_0 \quad (3-31)$$

Dividing Equation (3-30) by Equation (3-31) and rearranging yields

$$V = V_0 \left(\frac{P_0}{P} \right) \frac{T}{T_0} \left(\frac{Z}{Z_0} \right) \frac{N_T}{N_{T0}} \quad (3-32)$$

We now want to express the volume V as a function of the conversion X . Recalling the equation for the total number of moles in Table 3-3,

$$N_T = \dot{N}_{T0} + \delta N_{A0} X \quad (3-33)$$

where

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \quad (3-23)$$

$$\delta = \frac{\text{Change in total number of moles}}{\text{Mole of A reacted}}$$

We divide Equation (3-33) through by N_{T0} :

$$\frac{N_T}{N_{T0}} = 1 + \frac{N_{A0}\delta X}{N_{T0}} = 1 + \frac{\varepsilon}{\delta y_{A0}} X$$

Then

$$\frac{N_T}{N_{T0}} = 1 + \varepsilon X \quad (3-34)$$

Relationship between δ and ε

where y_{A0} is the mole fraction of A initially present, and where

$$\varepsilon = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) \frac{N_{A0}}{N_{T0}} = y_{A0}\delta \quad (3-35)$$

$$\varepsilon = y_{A0}\delta$$

Equation (3-35) holds for both batch and flow systems. To interpret ε , let's rearrange Equation (3-34)

$$\varepsilon = \frac{N_T - N_{T0}}{N_{T0}X}$$

Interpretation of ε

at complete conversion, (i.e., $X = 1$ and $N_T = N_{Tf}$)

$$\begin{aligned} \varepsilon &= \frac{N_{Tf} - N_{T0}}{N_{T0}} \\ &= \frac{\text{Change in total number of moles for complete conversion}}{\text{Total moles fed}} \end{aligned} \quad (3-36)$$

If all species in the generalized equation are in the gas phase, we can substitute Equation (3-34) with Equation (3-32) to arrive at

$$V = V_0 \left(\frac{P_0}{P} \right) \frac{T}{T_0} \left(\frac{Z}{Z_0} \right) (1 + \varepsilon X) \quad (3-37)$$

In the gas-phase systems that we shall be studying, the temperatures and pressures are such that the compressibility factor will not change significantly during the course of the reaction; hence $Z_0 \cong Z$. For a batch system, the volume of gas at any time t is

Volume of gas for a variable volume batch reaction

$$V = V_0 \left(\frac{P_0}{P} \right) (1 + \varepsilon X) \frac{T}{T_0} \quad (3-38)$$

Equation (3-38) applies only to a *variable-volume* batch reactor, where one can now substitute Equation (3-38) into Equation (3-25) to express $r_A = f(X)$. However, if the reactor is a rigid steel container of constant volume, then of course

$V = V_0$. For a constant-volume container, $V = V_0$, and Equation (3-38) can be used to calculate the gas pressure inside the reactor as a function of temperature and conversion.

Flow Reactors with Variable Volumetric Flow Rate. An expression similar to Equation (3-38) for a variable-volume batch reactor exists for a variable-volume flow system. To derive the concentrations of each species in terms of conversion for a variable-volume flow system, we shall use the relationships for the total concentration. The total concentration, C_T , at any point in the reactor is the total molar flow rate, F_T , divided by volumetric flow rate v [cf. Equation (3-27)]. In the gas phase, the total concentration is also found from the gas law, $C_T = P/ZRT$. Equating these two relationships gives

$$C_T = \frac{F_T}{v} = \frac{P}{ZRT} \quad (3-39)$$

At the entrance to the reactor,

$$C_{T0} = \frac{F_{T0}}{v_0} = \frac{P_0}{Z_0RT_0} \quad (3-40)$$

Taking the ratio of Equation (3-40) to Equation (3-39) and assuming negligible changes in the compressibility factor, we have upon rearrangement

$$v = v_0 \left(\frac{F_T}{F_{T0}} \right) \frac{P_0}{P} \left(\frac{T}{T_0} \right) \quad (3-41)$$

We can now express the concentration of species j for a flow system in terms of its flow rate, F_j , the temperature, T , and total pressure, P .

$$C_j = \frac{F_j}{v} = \frac{F_j}{v_0 \left(\frac{F_T}{F_{T0}} \right) \frac{P_0}{P} \left(\frac{T}{T_0} \right)} = \left(\frac{F_{T0}}{v_0} \right) \left(\frac{F_j}{F_T} \right) \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

Use this form for
membrane reactors
(Chapter 4)
and for multiple
reactions
(Chapter 6)

$$C_j = C_{T0} \left(\frac{F_j}{F_T} \right) \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right) \quad (3-42)$$

The total molar flow rate is just the sum of the molar flow rates of each of the species in the system and is

$$F_T = F_A + F_B + F_C + F_D + F_I + \cdots = \sum_{j=1}^n F_j$$

One of the major objectives of this chapter is to learn how to express any given rate law $-r_A$ as a function of conversion. The schematic diagram in Figure 3-6 helps to summarize our discussion on this point. The concentration of the key reactant, A (the basis of our calculations), is expressed as a function of conversion in both flow and batch systems, for various conditions of temperature, pressure, and volume.

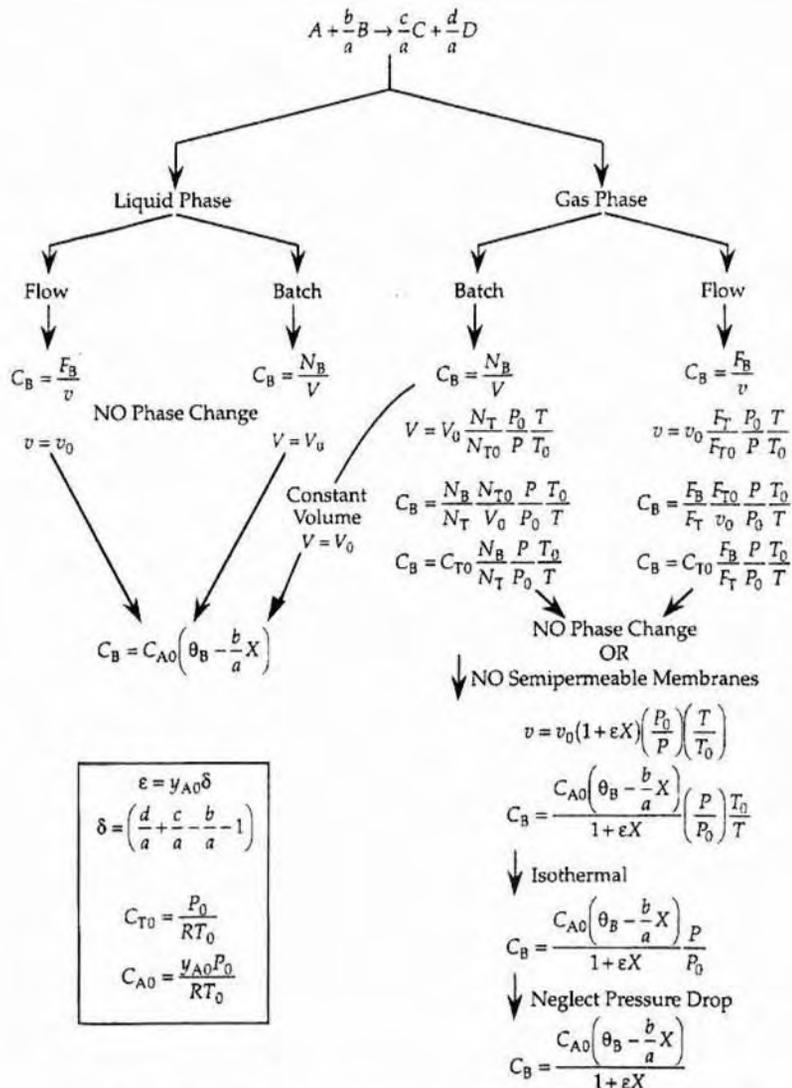


Figure 3-6 Expressing concentration as a function of conversion.

We see that conversion is not used in this sum. The molar flow rates, F_j , are found by solving the mole balance equations. Equation (3-42) will be used for measures other than conversion when we discuss membrane reactors (Chapter 4 Part 2) and multiple reactions (Chapter 6). We will use this form of the concentration equation for multiple gas-phase reactions and for membrane reactors.

Now let's express the concentration in terms of conversion for gas flow systems. From Table 3-4, the total molar flow rate can be written in terms of conversion and is

$$F_T = F_{T0} + F_{A0} \delta X \quad (3-43)$$

Substituting for F_T in Equation (3-41) gives

$$\begin{aligned} v &= v_0 \frac{F_{T0} + F_{A0} \delta X}{F_{T0}} \left(\frac{P_0}{P} \right) \frac{T}{T_0} \\ &= v_0 \left(1 + \frac{F_{A0}}{F_{T0}} \delta X \right) \frac{P_0}{P} \left(\frac{T}{T_0} \right) = v_0 (1 + y_{A0} \delta X) \frac{P_0}{P} \left(\frac{T}{T_0} \right) \end{aligned} \quad (3-44)$$

Gas-phase
volumetric flow
rate

$$\boxed{v = v_0 (1 + \varepsilon X) \frac{P_0}{P} \left(\frac{T}{T_0} \right)} \quad (3-45)$$

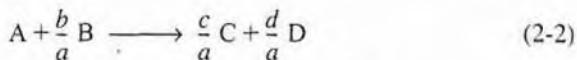
The concentration of species j is

$$C_j = \frac{F_j}{v}$$

The molar flow rate of species j is

$$F_j = F_{j0} + v_j (F_{A0} X) = F_{A0} (\Theta_j + v_j X)$$

where v_j is the stoichiometric coefficient, which is negative for reactants and positive for products. For example, for the reaction



$v_A = -1$, $v_B = -b/a$, $v_C = c/a$, $v_D = d/a$, and $\Theta_j = F_{j0}/F_{A0}$.

Substituting for v using Equation (3-42) and for F_j , we have

$$C_j = \frac{F_{A0} (\Theta_j + v_j X)}{v_0 (1 + \varepsilon X) \frac{P_0}{P} \frac{T}{T_0}}$$

Rearranging

Gas-phase
concentration as a
function of
conversion

$$C_j = \frac{C_{A0}(\Theta_j + \nu_j X)}{1 + \epsilon X} \left(\frac{P}{P_0} \right) \frac{T_0}{T} \quad (3-46)$$

Recall that $y_{A0} = F_{A0}/F_{T0}$, $C_{A0} = y_{A0}C_{T0}$, and ϵ from Equation (3-35) (i.e., $\epsilon = y_{A0}\delta$).

The stoichiometric table for the gas-phase reaction (2-2) is given in Table 3-5.

TABLE 3-5. CONCENTRATIONS IN A VARIABLE-VOLUME GAS FLOW SYSTEM

| | | | |
|--|---|--|---|
| | $C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v}$ | $= \frac{F_{A0}(1-X)}{v_0(1+\epsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0}$ | $= C_{A0} \left(\frac{1-X}{1+\epsilon X} \right) \frac{T_0}{T} \left(\frac{P}{P_0} \right)$ |
| | $C_B = \frac{F_B}{v} = \frac{F_{A0}[\Theta_B - (b/a)X]}{v}$ | $= \frac{F_{A0}[\Theta_B - (b/a)X]}{v_0(1+\epsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0}$ | $= C_{A0} \left(\frac{\Theta_B - (b/a)X}{1+\epsilon X} \right) \frac{T_0}{T} \left(\frac{P}{P_0} \right)$ |
| | $C_C = \frac{F_C}{v} = \frac{F_{A0}[\Theta_C + (c/a)X]}{v}$ | $= \frac{F_{A0}[\Theta_C + (c/a)X]}{v_0(1+\epsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0}$ | $= C_{A0} \left(\frac{\Theta_C + (c/a)X}{1+\epsilon X} \right) \frac{T_0}{T} \left(\frac{P}{P_0} \right)$ |
| | $C_D = \frac{F_D}{v} = \frac{F_{A0}[\Theta_D + (d/a)X]}{v}$ | $= \frac{F_{A0}[\Theta_D + (d/a)X]}{v_0(1+\epsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0}$ | $= C_{A0} \left(\frac{\Theta_D + (d/a)X}{1+\epsilon X} \right) \frac{T_0}{T} \left(\frac{P}{P_0} \right)$ |
| | $C_I = \frac{F_I}{v} = \frac{F_{A0}\Theta_I}{v}$ | $= \frac{F_{A0}\Theta_I}{v_0(1+\epsilon X)} \left(\frac{T_0}{T} \right) \frac{P}{P_0}$ | $= \frac{C_{A0}\Theta_I}{1+\epsilon X} \left(\frac{T_0}{T} \right) \frac{P}{P_0}$ |

At last!
We now have
 $C_j = h_j(X)$
and
and
 $-r_A = g(X)$
for variable-volume
gas-phase reactions

Example 3-4 Manipulation of the Equation for $C_B = h_j(X)$

Show under what conditions and manipulation the expression for C_B for a gas flow system reduces to that given in Table 3-5.

Solution

For a flow system the concentration is defined as

$$C_B = \frac{F_B}{v} \quad (E3-4.1)$$

From Table 3-4, the molar flow rate and conversion are related by

$$F_B = F_{A0} \left(\Theta_B - \frac{b}{a} X \right) \quad (E3-4.2)$$

Combining Equations (E3-4.1) and (E3-4.2) yields

$$C_B = \frac{F_{A0}[\Theta_B - (b/a)X]}{v} \quad (E3-4.3)$$

This equation for v is only for a gas-phase reaction

Using Equation (3-45) gives us

$$v = v_0(1 + \varepsilon X) \frac{P_0}{P} \left(\frac{T}{T_0} \right) \quad (3-45)$$

to substitute for the volumetric flow rate gives

$$C_B = \frac{F_B}{v} = \frac{F_{A0}[\Theta_B - (b/a)X]}{v_0(1 + \varepsilon X)} \left(\frac{P}{P_0} \right) \frac{T_0}{T} \quad (\text{E3-4.4})$$

Recalling $\frac{F_{A0}}{v_0} = C_{A0}$, we obtain

$$C_B = C_{A0} \left[\frac{\Theta_B - (b/a)X}{1 + \varepsilon X} \right] \frac{P}{P_0} \left(\frac{T_0}{T} \right)$$

which is identical to the concentration expression for a variable-volume batch reactor.

Example 3-5 Determining $C_j = h_j(X)$ for a Gas-Phase Reaction

A mixture of 28% SO_2 and 72% air is charged to a flow reactor in which SO_2 is oxidized.



First, set up a stoichiometric table using only the symbols (i.e., Θ_i, F_i) and then prepare a second stoichiometric table evaluating numerically as many symbols as possible for the case when the total pressure is 1485 kPa (14.7 atm) and the temperature is constant at 227°C.

Solution

Taking SO_2 as the basis of calculation, we divide the reaction through by the stoichiometric coefficient of our chosen basis of calculation:



The initial stoichiometric table is given as Table E3-5.1. Initially, 72% of the total number of moles is air containing (21% O_2 and 79% N_2) along with 28% SO_2 .

$$\begin{aligned} F_{A0} &= (0.28)(F_{T0}) \\ F_{B0} &= (0.72)(0.21)(F_{T0}) \\ \Theta_B &= \frac{F_{B0}}{F_{A0}} = \frac{(0.72)(0.21)}{0.28} = 0.54 \\ \Theta_1 &= \frac{F_{I0}}{F_{A0}} = \frac{(0.72)(0.79)}{0.28} = 2.03 \end{aligned}$$

From the definition of conversion, we substitute not only for the molar flow rate of SO_2 (A) in terms of conversion but also for the volumetric flow rate as a function of conversion.

TABLE E3-5.1. STOICHIOMETRIC TABLE FOR $\text{SO}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{SO}_3$

| Species | Symbol | Initially | Change | Remaining |
|---------------|--------|----------------------------|----------------------|--|
| SO_2 | A | F_{A0} | $-F_{A0}X$ | $F_A = F_{A0}(1-X)$ |
| O_2 | B | $F_{B0} = \Theta_B F_{A0}$ | $-\frac{F_{A0}X}{2}$ | $F_B = F_{A0}\left(\Theta_B - \frac{1}{2}X\right)$ |
| SO_3 | C | 0 | $+F_{A0}X$ | $F_C = F_{A0}X$ |
| N_2 | I | $F_{I0} = \Theta_I F_{A0}$ | — | $F_I = F_{I0} = \Theta_I F_{A0}$ |
| | | F_{T0} | | $F_T = F_{T0} - \frac{F_{A0}X}{2}$ |

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

Recalling Equation (3-45), we have

$$v = v_0(1 + \varepsilon X) \frac{P_0}{P} \left(\frac{T}{T_0} \right) \quad (3-45)$$

Neglecting
pressure
drop, $P = P_0$

Neglecting pressure drop in the reaction, $P = P_0$, yields

$$v = v_0(1 + \varepsilon X) \frac{T}{T_0}$$

If the reaction is also carried out isothermally, $T = T_0$, we obtain

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

Isothermal
operation, $T = T_0$

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

The concentration of A initially is equal to the mole fraction of A initially multiplied by the total concentration. The total concentration can be calculated from an equation of state such as the ideal gas law. Recall that $y_{A0} = 0.28$, $T_0 = 500$ K, and $P_0 = 1485$ kPa.

$$\begin{aligned} C_{A0} &= y_{A0} C_{T0} = y_{A0} \left(\frac{P_0}{RT_0} \right) \\ &= 0.28 \left[\frac{1485 \text{ kPa}}{8.314 \text{ kPa} \cdot \text{dm}^3 / (\text{mol} \cdot \text{K}) \times 500 \text{ K}} \right] \\ &= 0.1 \text{ mol/dm}^3 \end{aligned}$$

The total concentration is

$$C_T = \frac{F_T}{v} = \frac{F_{T0} + y_{A0}\delta X F_{T0}}{v_0(1 + \varepsilon X)} = \frac{F_{T0}(1 + \varepsilon X)}{v_0(1 + \varepsilon X)} = \frac{F_{T0}}{v_0} = C_{T0} = \frac{P_0}{RT_0}$$

$$= \frac{1485 \text{ kPa}}{[8.314 \text{ kPa} \cdot \text{dm}^3/(\text{mol} \cdot \text{K})](500 \text{ K})} = 0.357 \frac{\text{mol}}{\text{dm}^3}$$

We now evaluate ε .

$$\varepsilon = y_{A0} \delta = (0.28)(1 - 1 - \frac{1}{2}) = -0.14$$

$$C_A = C_{A0} \left(\frac{1 - X}{1 + \varepsilon X} \right) = 0.1 \left(\frac{1 - X}{1 - 0.14X} \right) \text{ mol/dm}^3$$

$$C_B = C_{A0} \left(\frac{\Theta_B - \frac{1}{2}X}{1 + \varepsilon X} \right) = \frac{0.1(0.54 - 0.5X)}{1 - 0.14X} \text{ mol/dm}^3$$

$$C_C = \frac{C_{A0}X}{1 + \varepsilon X} = \frac{0.1X}{1 - 0.14X} \text{ mol/dm}^3$$

$$C_I = \frac{C_{A0}\Theta_I}{1 + \varepsilon X} = \frac{(0.1)(2.03)}{1 - 0.14X} \text{ mol/dm}^3$$

The concentrations of different species at various conversions are calculated in Table E3-5.2 and plotted in Figure E3-5.1. *Note* that the concentration of N_2 is changing even though it is an inert species in this reaction!!

TABLE E3-5.2. CONCENTRATION AS A FUNCTION OF CONVERSION

| Species | | C_i (mol/dm ³) | | | | |
|-----------------|---------|------------------------------|--------------|--------------|--------------|--------------|
| | | $X = 0.0$ | $X = 0.25$ | $X = 0.5$ | $X = 0.75$ | $X = 1.0$ |
| SO ₂ | $C_A =$ | 0.100 | 0.078 | 0.054 | 0.028 | 0.000 |
| O ₂ | $C_B =$ | 0.054 | 0.043 | 0.031 | 0.018 | 0.005 |
| SO ₃ | $C_C =$ | 0.000 | 0.026 | 0.054 | 0.084 | 0.116 |
| N ₂ | $C_I =$ | <u>0.203</u> | <u>0.210</u> | <u>0.218</u> | <u>0.227</u> | <u>0.236</u> |
| | $C_T =$ | 0.357 | 0.357 | 0.357 | 0.357 | 0.357 |

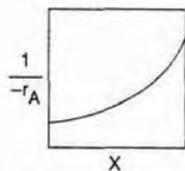
The concentration of the inert is not constant!

We are now in a position to express $-r_A$ as a function of X . For example, if the rate law for this reaction were first order in SO₂ (i.e., A) and in O₂ (i.e., B), with $k = 200 \text{ dm}^3/\text{mol} \cdot \text{s}$, then the rate law becomes

$$-r_A = kC_A C_B = kC_{A0}^2 \frac{(1 - X)(\Theta_B - 0.5X)}{(1 + \varepsilon X)^2} = \frac{2(1 - X)(0.54 - 0.5X)}{(1 - 0.14X)^2} \quad (\text{E3-5.1})$$

Note: Because the volumetric flow rate varies with conversion, the concentration of inerts (N_2) is *not* constant.

Now use techniques presented in Chapter 2 to size reactors.



Need to first calculate X_r

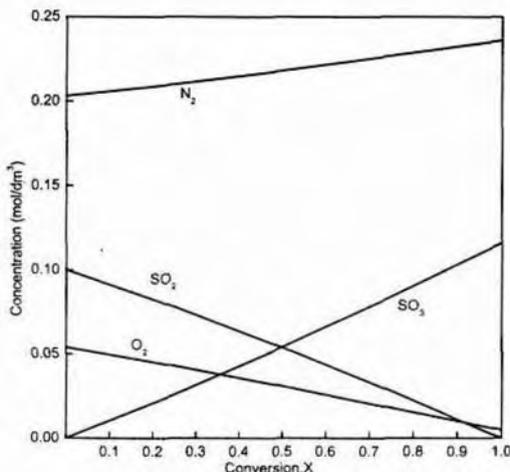


Figure E3-5.1 Concentration as a function of conversion.

Taking the reciprocal of $-r_A$ yields

$$\frac{1}{-r_A} = \frac{0.5(1 - 0.14X)^2}{(1 - X)(0.54 - 0.5X)} \quad (\text{E3-5})$$

We see that we could size a variety of combinations of *isothermal reactors* using the techniques discussed in Chapter 2.

Thus far in this chapter, we have focused mostly on irreversible reactions. The procedure one uses for the isothermal reactor design of reversible reactions is virtually the same as that for irreversible reactions, with one notable exception. First calculate the maximum conversion that can be achieved at the isothermal reaction temperature. This value is the equilibrium conversion. In the following example it will be shown how our algorithm for reactor design is easily extended to reversible reactions.

Example 3-6 Calculating the Equilibrium Conversion

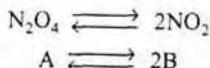
The reversible gas-phase decomposition of nitrogen tetroxide, N_2O_4 , to nitrogen dioxide, NO_2 ,



is to be carried out at constant temperature. The feed consists of pure N_2O_4 at 340 K and 202.6 kPa (2 atm). The concentration equilibrium constant, K_C , at 340 K is 0.1 mol/dm^3 .

- Calculate the equilibrium conversion of N_2O_4 in a constant-volume batch reactor.
- Calculate the equilibrium conversion of N_2O_4 in a flow reactor.
- Assuming the reaction is elementary, express the rate of reaction solely as a function of conversion for a flow system and for a batch system.
- Determine the CSTR volume necessary to achieve 80% of the equilibrium conversion.

Solution



At equilibrium the concentrations of the reacting species are related by the relationship dictated by thermodynamics [see Equation (3-10) and Appendix C]

$$K_C = \frac{C_{Be}^2}{C_{Ae}} \quad (\text{E3-6.1})$$

(a) **Batch system—constant volume, $V = V_0$.** See Table E3-6.1.

TABLE E3-6.1. STOICHIOMETRIC TABLE

| Species | Symbol | Initial | Change | Remaining |
|----------|--------|-------------------|-------------|--------------------------|
| N_2O_4 | A | N_{A0} | $-N_{A0}X$ | $N_A = N_{A0}(1-X)$ |
| NO_2 | B | 0 | $+2N_{A0}X$ | $N_B = 2N_{A0}X$ |
| | | $N_{T0} = N_{A0}$ | | $N_T = N_{T0} + N_{A0}X$ |

For batch systems $C_i = N_i/V$,

$$C_A = \frac{N_A}{V} = \frac{N_A}{V_0} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X) \quad (\text{E3-6.2})$$

$$C_B = \frac{N_B}{V} = \frac{N_B}{V_0} = \frac{2N_{A0}X}{V_0} = 2C_{A0}X \quad (\text{E3-6.3})$$

$$\begin{aligned} C_{A0} &= \frac{y_{A0}P_0}{RT_0} = \frac{(1)(2 \text{ atm})}{(0.082 \text{ atm} \cdot \text{dm}^3/\text{mol} \cdot \text{K})(340 \text{ K})} \\ &= 0.07174 \text{ mol/dm}^3 \end{aligned}$$

At equilibrium, $X = X_e$, and we substitute Equations (E3-6.2) and (E3-6.3) into Equation (E3-6.1),

$$K_C = \frac{C_{Be}^2}{C_{Ae}} = \frac{4C_{A0}^2X_e^2}{C_{A0}(1-X_e)} = \frac{4C_{A0}X_e^2}{1-X_e}$$



$$X_e = \sqrt{\frac{K_C(1-X_e)}{4C_{A0}}} \quad (\text{E3-6.})$$

-math-math-math-math

We will use Polymath to solve for the equilibrium conversion and let x_{eb} represent the equilibrium conversion in a constant-volume batch reactor. Equation (E3-6.) written in Polymath format becomes

$$f(x_{eb}) = x_{eb} - [k_c(1-x_{eb})/(4C_{A0})]^{0.5}$$

The Polymath program and solution are given in Table E3-6.2.

When looking at Equation (E3-6.4), you probably asked yourself, "Why not use the quadratic formula to solve for the equilibrium conversion in both batch and flow systems?" That is,

$$\text{Batch: } X_e = \frac{1}{8}[-1 + \sqrt{1 + 16C_{A0}/K_C}]/(C_{A0}/K_C)$$

$$\text{Flow: } X_e = \frac{[(\epsilon - 1) + \sqrt{(\epsilon - 1)^2 + 4(\epsilon + 4C_{A0}/K_C)}]}{2(\epsilon + 4C_{A0}/K_C)}$$

There is a Polymath tutorial in the summary Notes of Chapter 1

The answer is that future problems will be nonlinear and require Polymath solutions and I wanted to increase the reader's ease in using Polymath.

TABLE E3-6.2. POLYMATH PROGRAM AND SOLUTION FOR BOTH BATCH AND FLOW SYSTEMS.

NLES Solution

| Variable | Value | f(x) | Ini Guess |
|----------|-----------|-----------|-----------|
| Xeb | 0.4412598 | 4.078E-08 | 0.5 |
| Xef | 0.5083548 | 2.622E-10 | 0.5 |
| Kc | 0.1 | | |
| Cao | 0.07174 | | |
| eps | 1 | | |

NLES Report (safenewt)

Nonlinear equations

[1] $f(X_{eb}) = X_{eb} - (K_c(1-X_{eb})/(4*C_{A0}))^{0.5} = 0$

[2] $f(X_{ef}) = X_{ef} - (K_c(1-X_{ef})^{1+eps}*X_{ef}/(4*C_{A0}))^{0.5} = 0$

Explicit equations

[1] $K_c = 0.1$

[2] $C_{A0} = 0.07174$

[3] $eps = 1$

The equilibrium conversion in a constant-volume batch reactor is

$$X_{eb} = 0.44$$