

$$C_B = C_{A0} \left( \Theta_B - \frac{b}{a} X \right) \quad (4-13)$$

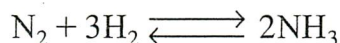
and so forth for  $C_C$  and  $C_D$ .

Consequently, using any one of the rate laws in Chapter 3, 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 (4-13) to express concentration as a function of conversion for gas-phase reactions.

### 4.2.3 Gas Phase Concentrations

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.

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.

**Flow Reactors with Variable Volumetric Flow Rate.** To derive the concentrations of each species in terms of conversion for a gas phase 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 (4-10)]. In the gas phase, the total concentration is also found from the gas law,  $C_T = P/ZRT$ . Equating these two relationships gives

$$C_T = \frac{F_T}{v} = \frac{P}{ZRT} \quad (4-14)$$

At the entrance to the reactor,

$$C_{T0} = \frac{F_{T0}}{v_0} = \frac{P_0}{Z_0 RT_0} \quad (4-15)$$

Taking the ratio of Equation (4-14) to Equation (4-15) and assuming negligible changes in the compressibility factor,  $Z$ , during the course of the reaction we have upon rearrangement

Gas Phase Reactions

$$v = v_0 \left( \frac{F_T}{F_{T0}} \right) \frac{P_0}{P} \left( \frac{T}{T_0} \right) \quad (4-16)$$

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,  $P$ .

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

Use this concentration equation for membrane reactors (Chapter 6) and for multiple reactions (Chapter 8).

$$C_j = C_{T0} \left( \frac{F_j}{F_T} \right) \left( \frac{P}{P_0} \right) \left( \frac{T_0}{T} \right) \quad (4-17)$$

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

$$F_T = F_A + F_B + F_C + F_D + F_I + \cdots = \sum_{j=1}^n F_j \quad (4-18)$$

The molar flow rates,  $F_j$ , are found by solving the mole balance equations. The concentration given by Equation (4-17) will be used for measures other than conversion when we discuss membrane reactors (Chapter 6) and multiple gas-phase reactions (Chapter 8).

Now let's express the concentration in terms of conversion for gas flow systems. From Table 4-2, the total molar flow rate can be written in terms of conversion and is

$$F_T = F_{T0} + F_{A0} \delta X \quad (4-19)$$

We divide Equation (4-19) through by  $F_{T0}$ :

$$\frac{F_T}{F_{T0}} = 1 + \frac{F_{A0}}{F_{T0}} \delta X = 1 + \overbrace{y_{A0}}^{\epsilon} \delta X$$

Then

$$\frac{F_T}{F_{T0}} = 1 + \varepsilon X \quad (4-20)$$

where  $y_{A0}$  is the mole fraction of A at the inlet, (i.e.,  $(F_{A0}/F_{T0})$ ) and where  $\delta$  is given by Equation (4-1) and  $\varepsilon$  is given by

Relationship  
between  
 $\delta$  and  $\varepsilon$

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

$$\boxed{\varepsilon = y_{A0} \delta} \quad (4-21)$$

Equation (4-21) holds for both batch and flow systems. To interpret  $\varepsilon$ , let's rearrange Equation (4-20) at complete conversion, (i.e.,  $X = 1$  and  $F_T = F_{Tf}$ )

$$\varepsilon = \frac{F_{Tf} - F_{T0}}{F_{T0}}$$

Interpretation of  $\varepsilon$

$$\boxed{\varepsilon = \frac{\text{Change in total number of moles for complete conversion}}{\text{Total moles fed}}} \quad (4-22)$$

Substituting for  $(F_T/F_{T0})$  in Equation (4-16) for the volumetric flow rate,  $v$ , we have

Gas-phase  
volumetric flow  
rate

$$\boxed{v = v_0(1 + \varepsilon X) \frac{P_0}{P} \left( \frac{T}{T_0} \right)} \quad (4-23)$$

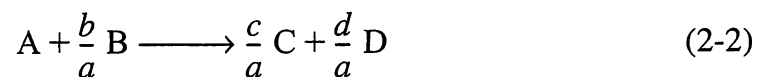
The concentration of species  $j$  in a flow system is

$$C_j = \frac{F_j}{v} \quad (4-24)$$

The molar flow rate of species  $j$  is

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

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



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

Substituting for  $v$  using Equation (4-23) and for  $F_j$ , we have

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

Rearranging

Gas-phase  
concentration as a  
function of  
conversion

$$C_j = \frac{C_{A0}(\Theta_j + v_j X)}{1 + \varepsilon X} \left( \frac{P}{P_0} \right) \frac{T_0}{T} \quad (4-25)$$

Recall that  $y_{A0} = F_{A0}/F_{T0}$ ,  $C_{A0} = y_{A0}C_{T0}$ , and  $\varepsilon$  is given by Equation (4-21) (i.e.,  $\varepsilon = y_{A0}\delta$ ).

The stoichiometric table for the gas-phase reaction (2-2) is given in Table 4-3.

TABLE 4-3 CONCENTRATIONS IN A VARIABLE-VOLUME GAS FLOW SYSTEM

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

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

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 4-3 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.

1. Reaction:

2. Basis:

3. Stoichiometric table:

<b><i>Species</i></b>	<b><i>Symbol</i></b>	<b><i>Initially</i></b>	<b><i>Change</i></b>	<b><i>Leaving/remaining</i></b>	<b><i>Concentration</i></b>
SO <sub>2</sub>	A				
O <sub>2</sub>	B				
SO <sub>3</sub>	C				
N <sub>2</sub>	I				
Totals					

4. What is known? Initial flows, mol fractions, etc

5. Other constants?

6. Rewrite concentrations only in terms of X

$C_A =$

$C_B =$

$C_C =$

$C_I =$

$$\text{O}_2 \quad C_B = C_{A0} \left( \frac{\Theta_B - \frac{1}{2}X}{1 + \varepsilon X} \right) = \frac{0.1(0.54 - 0.5X)}{1 - 0.14X} \text{ mol/dm}^3 \quad (\text{E4-3.7})$$

$$\text{SO}_3 \quad C_C = \frac{C_{A0}X}{1 + \varepsilon X} = \frac{0.1X}{1 - 0.14X} \text{ mol/dm}^3 \quad (\text{E4-3.8})$$

$$\text{N}_2 \quad C_I = \frac{C_{A0}\Theta_I}{1 + \varepsilon X} = \frac{(0.1)(2.03)}{1 - 0.14X} \text{ mol/dm}^3 \quad (\text{E4-3.9})$$

The concentrations of different species at various conversions are calculated in Table E4-3.1 and plotted in Figure E4-3.1. **Note** that the concentration of  $\text{N}_2$  is changing even though it is an inert species in this reaction!!

TABLE E4-3.2 CONCENTRATION AS A FUNCTION OF CONVERSION

Species		$C_i \text{ (mol/dm}^3\text{)}$				
		$X = 0.0$	$X = 0.25$	$X = 0.5$	$X = 0.75$	$X = 1.0$
$\text{SO}_2$	$C_A =$	0.100	0.078	0.054	0.028	0.000
$\text{O}_2$	$C_B =$	0.054	0.043	0.031	0.018	0.005
$\text{SO}_3$	$C_C =$	0.000	0.026	0.054	0.084	0.116
$\text{N}_2$	$C_I =$	<u>0.203</u>	<u>0.210</u>	<u>0.218</u>	<u>0.227</u>	<u>0.236</u>
Total	$C_T =$	0.357	0.357	0.357	0.357	0.357

*Note:* Because the volumetric flow rate varies with conversion,  $v = v_0(1 - 0.14X)$ , the concentration of inerts ( $\text{N}_2$ ) is *not* constant.

Now use techniques presented in Chapter 2 to size reactors.

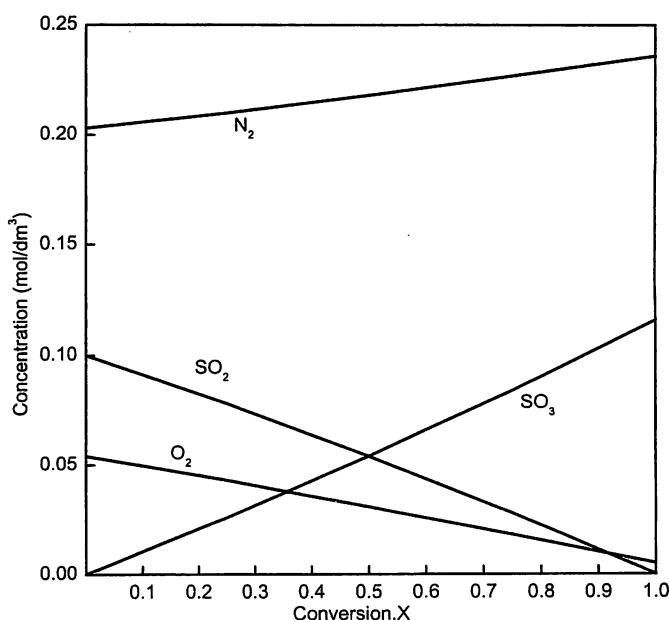


Figure E4-3.1 Concentration as a function of conversion.

We are now in a position to express  $-r_A$  as a function of  $X$  and use the techniques in Chapter 2. However, we will use a better method to solve CRE problems, namely the Polymath software, discussed in the next chapter.