R3.4 Expressing Concentrations in Terms Other Than Conversion

As we shall see later in the book, there are some instances in which it is much more convenient to work in terms of the number of moles (N_A, N_B) or molar flow rates (F_A, F_B, etc.) rather than conversion. Membrane reactors and gas-phase multiple reactions are two such cases where molar flow rates rather than conversion are preferred. Consequently, the concentrations in the rate laws need to be expressed in terms of the molar flow rates. We start by recalling and combining Equations (3-40) and (3-41):

$$C_{T0} = \frac{F_{T0}}{v_0} = \frac{P_0}{Z_0 R T_0} \tag{3-40}$$

Used for:
• Multiple rxns
• Membranes
• Unsteady state

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

to give for the case of an ideal gas ($Z = 1$),

$$v = \frac{F_T}{C_{T0}} \frac{P_0}{P} \frac{T}{T_0} \tag{R 1-1}$$

the concentration species A is

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

Substituting for v gives

$$\boxed{C_A = C_{T0} \frac{F_A}{F_T} \frac{P}{P_0} \frac{T_0}{T}} \tag{R 1-2}$$

In general (j = A, B, C, D, I)

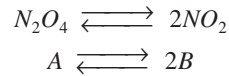$$\boxed{C_j = C_{T0} \frac{F_j}{F_T} \frac{P}{P_0} \frac{T_0}{T}} \tag{3-45}$$

with the total molar flow rate given as the sum of the flow rates of the individual species:

$$F_T = F_A + F_B + F_C + F_D + F_I \tag{R3.1-3}$$

The molar flow rate of each species F_j is obtained from a mole balance on each species.

Example R3–1 PFR Mole Balances in Terms of Molar Flow Rates

Reconsider the elementary gas reaction discussed in Example 3-5.

$$N_2O_4 \rightleftarrows 2NO_2$$
$$A \rightleftarrows 2B$$

The reaction is to be carried out isothermally ($T = T_0$) and isobarically ($P = P_0$) in a PFR. Express the rate law and mole balances in terms of the molar flow rates.

Solution

Mole balance:
$$\frac{dF_A}{dV} = r_A \qquad \text{(RE3-1.1)}$$

$$\frac{dF_B}{dV} = r_B \qquad \text{(RE3-1.2)}$$

Rate law:
$$-r_A = k_A\left[C_A - \frac{C_B^2}{K_C}\right] \qquad \text{(RE3-1.3)}$$

Stoichiometry:
$$\frac{r_A}{-1} = \frac{r_B}{2}$$

Then

$$r_B = -2r_A \qquad \text{(RE3-1.4)}$$

Combine:

Using Equation (3-45) to substitute for the concentrations of A and B when $T = T_0$ and $P = P_0$, Equation (E3-9.3) becomes

$$-r_A = k_A\left[C_{T0}\left(\frac{F_A}{F_T}\right) - \frac{C_{T0}^2}{K_C}\left(\frac{F_B}{F_T}\right)^2\right] \qquad \text{(RE3-1.5)}$$

where the total molar flow rate is just the sum of the flow rates of A and B:

$$F_T = F_A + F_B \qquad \text{(RE3-1.6)}$$

and the total concentration of the entrance to the reactor (P_0, T_0) is calculated from the equation

$$C_{T0} = \frac{P_0}{RT_0} \qquad \text{(RE3-1.7)}$$

Combining Equations (E3-9.5) and (E3-9.6), we obtain

$$\frac{dF_A}{dV} = r_A = -k_A C_{T0}\left[\frac{F_A}{F_A + F_B} - \frac{C_{T0}}{K_C}\left(\frac{F_B}{F_A + F_B}\right)^2\right] \qquad \text{(RE3-1.8)}$$

and combining Equations (RE3-1.2), (RE3-1.4), and (RE3-1.8) gives

$$\frac{dF_B}{dV} = r_B = -2r_A = 2k_A C_{T0}\left[\frac{F_A}{F_A + F_B} - \frac{C_{T0}}{K_C}\left(\frac{F_B}{F_A + F_B}\right)^2\right] \quad (RE3\text{-}1.9)$$

Equations (RE3-1.8) and (RE3-1.9) can now be solved numerically, preferably by a software package such as Polymath or Matlab. (See Chapter 4.)

Polymath will combine all these equations for us and insert the parameter values in the appropriate spots. The Polymath program and outputs are shown in Table PRS3D-1 and Figure PRS 3D-1.

TABLE PRS3D-1.   POLYMATH RESULTS

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	80	80
Fa	0.72	0.4211651	0.72	0.4211651
Fb	0	0	0.5976697	0.5976697
Kc	0.06	0.06	0.06	0.06
Cao	0.072	0.072	0.072	0.072
Cto	0.072	0.072	0.072	0.072
Ft	0.72	0.72	1.0188349	1.0188349
ka	0.4	0.4	0.4	0.4
Cb	0	0	0.0422367	0.0422367
Ca	0.072	0.0297633	0.072	0.0297633
ra	-0.0288	-0.0288	-1.24E-05	-1.24E-05
rb	0.0576	2.479E-05	0.0576	2.479E-05
rate	0.0288	1.24E-05	0.0288	1.24E-05

ODE Report (RKF45)

Differential equations as entered by the user

[1]   d(Fa)/d(V) = ra
[2]   d(Fb)/d(V) = rb

Explicit equations as entered by the user

[1]   Kc= 0.06
[2]   Cao = 0.072
[3]   Cto = Cao
[4]   Ft = Fa + Fb
[5]   ka = 0.4
[6]   Cb = Cto*(Fb/Ft)
[7]   Ca = Cto*(Fa/Ft)
[8]   ra = -ka*(Ca-Cb^2/Kc)
[9]   rb = -2*ra
[10]   rate = -ra