A First Course on Kinetics and Reaction Engineering

Example 1.2

Problem Purpose

This example shows how to determine when it is permissible to choose a basis for your calculations. It also illustrates how to use reaction progress variables and the initial composition to calculate the final composition of a reacting system.

Problem Statement

A new catalyst is being developed with the hope of generating ethylene by the oxidative dehydrogenation of ethane, reaction (1). Reaction (2) also takes place at the operating conditions of 1 atm and 150 °C. The process starts with 90% ethane and 10% air (you may take air to contain 79% N_2 and 21% O_2) and ends with a 50% conversion of O_2 and a selectivity of 3 C_2H_4/CO_2.

$$2\ C_2H_6 + O_2 \rightarrow 2\ C_2H_4 + 2\ H_2O \tag{1}$$

$$2\ C_2H_6 + 7\ O_2 \rightarrow 4\ CO_2 + 6\ H_2O \tag{2}$$

a. List all the quantities given in the problem statement and indicate whether they are intensive or extensive.
b. If none of the quantities specified in the problem statement are extensive, assume a basis of 100 starting moles of ethane for your solution.
c. Construct a mole table for this system and use it to calculate the final mole fraction of CO_2.

Problem Analysis

This problem clearly involves chemical reactions, but there is no mention of a reactor in the problem statement. Examining the problem statement more closely, we see that it provides information about the initial composition of the system along with values for selected reaction progress variables. It never mentions reaction kinetics or reaction thermodynamics (equilibrium). This suggests that this is a stoichiometry problem.

Problem Solution

(a) The quantities given in the problem statement are temperature, pressure, mole percents, percent conversion and a selectivity. In order to determine whether each of these quantities is intensive or extensive, one needs to ask whether knowing the value of that quantity reveals the size of the system. The temperature is specified as 150 °C, but the system could be any size and still have that temperature. The same is true for the pressure; the system could be any size and still have a pressure of 1 atm. Clearly, the mole percents don't fix the size of the system. All they say, for example, is that however large the system is, 90 % of it is ethane. Similarly, the conversion doesn't fix the size of the system; all it says is that however much oxygen was initially present in the system, half as much will be present at the end. The same is true for the selectivity; it doesn't say how much product there will be or how much ethylene or how much carbon dioxide; all it says is that for every carbon dioxide there will be three ethylenes. Thus, all of the variables are intensive.

(b) Whenever all of the variables given in a problem are intensive, it is permissible to assume a basis of calculation. That is, it is permissible to assume the value of any one extensive variable. Any other extensive quantities that are calculated using that basis are only valid for the chosen basis. However, any intensive quantities that are calculated using that basis will also be valid for any other basis that is chosen. Here we are told to choose a basis of 100 initial moles of ethane.

(c) A mole table is created with three columns (one for the species name, one for the initial number of moles and one for the moles after reaction) and a row for each species present in the system along with a row for the total moles:

Species, i	***Initial Moles,*** n_i^0	***Moles after Reaction,*** $n_i^0 + \sum_{j=1}^{N_{ind}} \nu_{i,j}\xi_j$
C_2H_6		
N_2		
O_2		
C_2H_4		
H_2O		
CO_2		
Total Moles	$n_{total}^0 = \sum_{all\ i} n_i^0$	$n_{total}^0 + \sum_{all\ i}\sum_{j=1}^{N_{ind}} \nu_{i,j}\xi_j$

The initial moles column is filled in based on information given in the problem statement. The initial species given in the problem statement are ethane and air (nitrogen and oxygen), so the initial moles of ethylene, steam and carbon dioxide are each 0 mol. The initial moles of ethane were assumed in (b) to equal 100 mol. The initial total moles are found from the statement that ethane comprises 90% of the initial moles.

$$n_{C_2H_6}^0 = 0.9 n_{initial}^0$$

$$n_{initial}^0 = \frac{n_{C_2H_6}^0}{0.9} = \frac{100 \text{ mol}}{0.9} = 111.1 \text{ mol}$$

The initial moles of air are then found using the statement 10% of the initial moles is air.

$$n_{air}^0 = 0.1 n_{total}^0 = 0.1\left(111.1 \text{ mol}\right) = 11.11 \text{ mol}$$

The initial moles of nitrogen and oxygen are then computed using the given approximate composition of air.

$$n_{N_2}^0 = 0.79 n_{air}^0 = 0.79\left(11.11 \text{ mol}\right) = 8.8 \text{ mol}$$

$$n_{O_2}^0 = 0.1 n_{air}^0 = 0.21\left(11.11 \text{ mol}\right) = 2.3 \text{ mol}$$

These values are entered into the mole table as shown below.

Species, i	***Initial Moles,*** n_i^0	***Moles after Reaction,*** $n_i^0 + \sum_{j=1}^{N_{ind}} \nu_{i,j}\xi_j$
C_2H_6	100	
N_2	8.8	
O_2	2.3	
C_2H_4	0	
H_2O	0	
CO_2	0	
Total Moles	111.1	$n_{total}^0 + \sum_{all\ i} \sum_{j=1}^{N_{ind}} \nu_{i,j}\xi_j$

The numbers of moles after reaction are entered in the mole table in terms of the extents of the reactions, equation (3).

$$n_i = n_i^0 + \sum_{j=1}^{N_{ind}} \nu_{i,j}\xi_j \tag{3}$$

Before equation (3) can be used, an independent set of reactions must be identified. Here this is trivial because there are only 2 reactions taking place. Unless one of the reactions is a multiple of the other, they must be independent. It can be seen by inspection that they are not multiples of each other; for example, only reaction (1) contains ethylene, so it can't be a multiple of reaction (2). Hence the reactions are independent and the summation in equation (3) must include both reactions.

Recalling the sign convention for stoichiometric coefficients, their values are as follows:

$$\nu_{C_2H_6,1} = -2 \qquad \nu_{C_2H_6,2} = -2$$

$$\nu_{N_2,1} = 0 \qquad \nu_{N_2,2} = 0$$

$$\nu_{O_2,1} = -1 \qquad \nu_{O_2,2} = -7$$

$$\nu_{C_2H_4,1} = 2 \qquad \nu_{C_2H_4,2} = 0$$

$$\nu_{H_2O,1} = 2 \qquad \nu_{H_2O,2} = 6$$

$$\nu_{CO_2,1} = 0 \qquad \nu_{CO_2,2} = 4$$

These values are substituted into equation (3) to obtain the expressions for the moles of each of the species after reaction. For example, the expression for the moles of ethane is found as shown here.

$$n_i = n_i^0 + \sum_{j=1}^{2} \nu_{i,j}\xi_j$$

$$n_{C_2H_6} = n_{C_2H_6}^0 + \nu_{C_2H_6,1}\xi_1 + \nu_{C_2H_6,2}\xi_2$$

$$n_{C_2H_6} = 100 \text{ mol} + (-2)\xi_1 + (-2)\xi_2 = 100 \text{ mol} - 2\xi_1 - 2\xi_2$$

The expressions for the other species are found analogously, as shown below.

$$n_{N_2} = 8.8 \text{ mol}$$

$$n_{O_2} = 2.3 \text{ mol} - \xi_1 - 7\xi_2$$

$$n_{C_2H_4} = 2\xi_1$$

$$n_{H_2O} = 2\xi_1 + 6\xi_2$$

$$n_{CO_2} = 4\xi_2$$

To find the total moles after reaction, the moles of all the species are simply summed.

$$n_{total} = n_{C_2H_6} + n_{N_2} + n_{O_2} + n_{C_2H_4} + n_{H_2O} + n_{CO_2}$$

$$n_{total} = 100 \text{ mol} - 2\xi_1 - 2\xi_2 + 8.8 \text{ mol} + 2.3 \text{ mol} - \xi_1 - 7\xi_2 + 2\xi_1 + 2\xi_1 + 6\xi_2 + 4\xi_2$$

$$n_{total} = 111.1 \text{ mol} + \xi_1 + \xi_2$$

Upon substitution, the final mole table results, as shown at the top of the next page.

Species, i	***Initial Moles,*** n_i^0	***Moles after Reaction,*** $n_i^0 + \sum_{j=1}^{N_{ind}} \nu_{i,j}\xi_j$
C_2H_6	100	$100\text{ mol} - 2\xi_1 - 2\xi_2$
N_2	8.8	8.8 mol
O_2	2.3	$2.3\text{ mol} - \xi_1 - 7\xi_2$
C_2H_4	0	$2\xi_1$
H_2O	0	$2\xi_1 + 6\xi_2$
CO_2	0	$4\xi_2$
Total Moles	111.1 mol	$111.1\text{ mol} + \xi_1 + \xi_2$

The problem asks us to calculate the final mole fraction of CO_2. We begin with the definition of a mole fraction, substituting from the mole table to get equation (4).

$$y_{CO_2} = \frac{n_{CO_2}}{n_{total}} = \frac{4\xi_2}{111.1\text{ mol} + \xi_1 + \xi_2} \tag{4}$$

To calculate the mole fraction of CO_2 using equation (4), values are needed for ξ_1 and ξ_2. These can be found from two additional statements in the problem specification: the oxygen conversion is 50% and the ethylene to carbon dioxide selectivity is 3. These are written as equations and the mole quantities appearing in those equations are expressed in terms of the extents of the reactions using the mole table. This leads to equations (5) and (6).

$$f_{O_2} = 0.5 = \frac{n_{O_2}^0 - n_{O_2}}{n_{O_2}^0}$$

$$0.5 = \frac{2.3\text{ mol} - \left(2.3\text{ mol} - \xi_1 - 7\xi_2\right)}{2.3\text{ mol}} \tag{5}$$

$$S_{C_2H_4/CO_2} = 3 = \frac{n_{C_2H_4}}{n_{CO_2}}$$

$$3 = \frac{2\xi_1}{4\xi_2} \qquad (5)$$

Solving equations (5) and (6) gives ξ_1 = 0.53 mol and ξ_2 = 0.09 mol. Substituting these values into equation (4) reveals that the mole fraction of carbon dioxide is equal to 0.0032.