A First Course on Kinetics and Reaction Engineering Example 1.3

Problem Purpose

This example illustrates how to write equations expressing any one composition or reaction progress variable in terms of others. It also gives a few examples of the relationship between environmental variables and reaction progress variables.

Problem Statement

Later in this course, you are going to learn how to analyze kinetics data. The analysis of kinetics data typically involves stoichiometry problems of the kind being considered here in Unit 1. As an example, suppose reaction (1) was studied in a closed, isothermal, constant-volume system. Suppose that in addition to the reagents of reaction (1), the system also contains nitrogen. In a typical experiment you would know the initial composition, so suppose here the system initially contained 0.5 mol of N₂O₅ and 0.5 mol of N₂ at 600K and 5 MPa. Here are three examples of stoichiometry problems you might have to solve during the analysis of the kinetics data.

(a) Suppose the conversion of N_2O_5 was measured in the experiment under consideration and found to equal 75%. Calculate the final moles of N_2O_5 , NO_2 , O_2 , and N_2 .

(b) Suppose that instead of measuring the fractional conversion, the final pressure was measured in the experiment under consideration and found to equal 7 MPa. Calculate the final moles of N_2O_5 , NO_2 , O_2 , and N_2 .

(c) The rate expression might contain the concentration of NO₂ and the concentration of N₂O₅, and it might be necessary to integrate that rate expression. Before the integration can be performed, it might be necessary to generate an expression for the concentration of NO₂ in terms of the initial composition and the concentration of N₂O₅. Generate such an expression for the experiment under consideration.

$$2 N_2 O_5 \rightleftharpoons 4 NO_2 + O_2 \tag{1}$$

Problem Solution

When solving stoichiometry problems, it is often useful to construct a mole table. Recall that a mole table has three columns (species, initial moles and moles at any later time) and rows for each of the species present plus a row for the total. In the column for the moles at later times, one inserts an expression for the moles of the corresponding species in terms of the extent(s) of reaction. In doing so, one must remember that by definition the stoichiometric coefficients of reactants are negative and those of products are positive. If a species does not participate in the reaction, its stoichiometric coefficient is zero. Hence, in the case of reaction (1) the values of the stoichiometric coefficients are as follows: $v_{N_2O_5,l} = -2$; $v_{NO_2,l} = 4$; $v_{O_2,l} = 1$ and $v_{N_2,l} = 0$. With these values, a mole table can be constructed as

shown at the top of the following page.

Species, i	<i>Initial Moles</i> , n_i^0	Moles after Reaction, $n_i^0 + \sum_{j=1}^{N_{ind}} v_{i,j} \xi_j$
N ₂ O ₅	$n_{N_2O_5}^0$	$n_{N_2O_5} = n_{N_2O_5}^0 - 2\xi_1$
NO ₂	$n_{\scriptscriptstyle NO_2}^0$	$n_{NO_2} = n_{NO_2}^0 + 4\xi_1$
O ₂	$n_{O_2}^0$	$n_{O_2} = n_{O_2}^0 + \xi_1$
N ₂	$n_{N_2}^0$	$n_{N_2} = n_{N_2}^0$
Total Moles	$n_{total}^{0} = n_{N_{2}O_{5}}^{0} + n_{NO_{2}}^{0} + n_{O_{2}}^{0} + n_{N_{2}}^{0}$	$n_{total} = n_{total}^0 + 3\xi_1$

For the experiment under consideration, the initial moles of each species are given.

$$n_{N_2O_5}^0 = 0.5 \text{ mol}$$
 (2)

$$n_{NO_2}^0 = 0 \text{ mol}$$
(3)

$$n_{O_2}^0 = 0 \text{ mol}$$
 (4)

$$n_{N_2}^0 = 0.5 \text{ mol}$$
 (5)

The total initial moles are found by summing the initial moles of each species.

$$n_{total}^{0} = n_{N_{2}O_{5}}^{0} + n_{NO_{2}}^{0} + n_{O_{2}}^{0} + n_{N_{2}}^{0} = 1.0$$
(6)

(a) If the N_2O_5 conversion is 75% (or equivalently, the fractional conversion is 0.75). The definition of conversion can be used to calculate the final moles of N_2O_5 .

$$n_{N_2O_5} = n_{N_2O_5}^0 \left(1 - f_{N_2O_5}\right) \tag{7}$$

$$n_{N_2O_5} = (0.5 \text{ mol})(1 - 0.75) = 0.125 \text{ mol}$$
 (8)

The extent of reaction can be calculated from the expression for the moles of N_2O_5 given in the mole table.

$$n_{N_2O_5} = n_{N_2O_5}^0 - 2\xi_1 \tag{9}$$

$$(0.125 \text{ mol}) = (0.5 \text{ mol}) - 2\xi_1$$
 (10)

$$\xi_1 = 0.188 \text{ mol}$$
 (11)

Knowing the extent of reaction, the moles of other species can be calculated using the expressions in the mole table.

$$n_{NO_2} = n_{NO_2}^0 + 4\xi_1 = 0 + 4(0.188 \text{ mol}) = 0.75 \text{ mol}$$
 (12)

$$n_{O_2} = n_{O_2}^0 + \xi_1 = 0 + 0.188 \text{ mol} = 0.188 \text{ mol}$$
(13)

$$n_{N_2} = n_{N_2}^0 = 0.5 \text{ mol}$$
 (14)

$$n_{total} = n_{total}^{0} + 3\xi_{1} = 1 + 3(0.188 \text{ mol}) = 1.563 \text{ mol}$$
(15)

(b) In this case, the ideal gas law can be used to write expressions for the initial pressure and for the final pressure.

$$P^{0} = \frac{n_{total}^{0} R T^{0}}{V}$$
(16)

$$P = \frac{n_{total}RT}{V}$$
(17)

Noting that the gas constant, temperature and volume are all constant in this experiment, equations (16) and (17) can be combined, as shown in equation (19). Equation (19) can then be rearranged and used to calculate the total moles at the end of the experiment, equation (20).

$$\frac{P^0}{n_{total}^0} = \frac{RT}{V} = \frac{P}{n_{total}}$$
(18)

$$\frac{P^0}{n_{total}^0} = \frac{P}{n_{total}}$$
(19)

$$n_{total} = \frac{P}{P^0} n_{total}^0 = \frac{7 \text{ MPa}}{5 \text{ MPa}} (1 \text{ mol}) = 1.4 \text{ mol}$$
(20)

The total moles after reaction is related to the extent of reaction as seen at the bottom of the third column of the mole table, and so the extent of reaction can be calculated.

$$n_{total} = n_{total}^0 + 3\xi_1 \tag{21}$$

$$\xi_1 = \frac{n_{total} - n_{total}^0}{3} = \frac{1.4 - 1}{3} \text{ mol} = 0.133 \text{ mol}$$
(22)

As was the case in part (a), knowing the extent of reaction, the moles of other species can be calculated using the expressions in the mole table.

$$n_{N_2 O_5} = n_{N_2 O_5}^0 - 2\xi_1 = 0.5 \text{ mol} - 2(0.133 \text{ mol}) = 0.234 \text{ mol}$$
 (23)

$$n_{NO_2} = n_{NO_2}^0 + 4\xi_1 = 0 \text{ mol} + 4(0.133 \text{ mol}) = 0.532 \text{ mol}$$
 (24)

$$n_{O_2} = n_{O_2}^0 + \xi_1 = 0 \text{ mol} + 0.133 \text{ mol} = 0.133 \text{ mol}$$
 (25)

$$n_{N_2} = n_{N_2}^0 = 0.5 \text{ mol}$$
 (26)

(c) Here we seek an expression for $C_{_{NO_2}}$ in terms of $C_{_{N_2O_5}}$. We begin with the definition of $C_{_{N_2O_5}}$ in

terms of the moles of N_2O_5 , equation (27). The moles of N_2O_5 are then expressed in terms of the extent of reaction, as given in the mole table leading to equation (28), which can then be solved for the extent of reaction, equation (29).

$$C_{N_2 O_5} = \frac{n_{N_2 O_5}}{V}$$
(27)

$$C_{N_2O_5} = \frac{n_{N_2O_5}^0 - 2\xi_1}{V}$$
(28)

$$\xi_1 = \frac{n_{N_2O_5}^0 - C_{N_2O_5}V}{2} \tag{29}$$

Next, in an analogous manner, we write he definition of $C_{_{NO_2}}$ in terms of the moles of NO₂,

equation (30) and substitute the expression for the moles of NO₂ in terms of the extent of reaction from the mole table giving equation (31). Finally, substitution of equation (29) into equation (31) gives the desired expression for the concentration of NO₂ in terms of the initial composition and the concentration of N₂O₅.

$$C_{NO_2} = \frac{n_{NO_2}}{V} \tag{30}$$

$$C_{NO_2} = \frac{n_{NO_2}^0 + 4\xi_1}{V}$$
(31)

$$C_{NO_2} = \frac{n_{NO_2}^0 + 4\xi_1}{V} = \frac{n_{NO_2}^0}{V} + \frac{4}{V} \left(\frac{n_{N_2O_5}^0 - C_{N_2O_5}V}{2} \right) = \frac{n_{NO_2}^0}{V} + \frac{2n_{N_2O_5}^0}{V} - 2C_{N_2O_5}$$

$$= C_{NO_2}^0 + 2C_{N_2O_5}^0 - 2C_{N_2O_5}$$
(32)