# 10.8 SIMULTANEOUS MULTICOMPONENT DIFFUSION OF GASES

### 10.8.1 Concepts Demonstrated

Application of the Stefan-Maxwell equations to describe the multicomponent molecular diffusion of gases.

### 10.8.2 Numerical Methods Utilized

Numerical integration of a system of simultaneous ordinary differential equations with optimization of two parameters in order to match split boundary conditions.

### 10.8.3 Problem Statement*

Gases A and B are diffusing through stagnant gas C at a temperature of 55 °C and a pressure of 0.2 atmospheres. This process involves molecular diffusion between two points, where the compositions are known, as summarized in Table 10–9. The distance between the points is $10^{-3}$ m.

(a) Use the Stefan Maxwell equations to calculate the molar fluxes of both gases A and B from point 1 to point 2. Suggestion: An initial approximate solution can be determined by first considering the binary diffusion of only A through component C and then separately considering the binary diffusion of only B through component C.

(b) Plot the mole fractions of the gases as a function of distance from point 1 to point 2.

**Table 10–9** Data for Multicomponent Diffusion (from Geankoplis[5] with permission)

| Component | Point 1 Concentration kg-mol/m$^3$ | Point 2 Concentration kg-mol/m$^3$ | Diffusivities at 0.2 atm m$^2$/s |
|---|---|---|---|
| A | $2.229 \times 10^{-4}$ | 0 | $D_{AC} = 1.075 \times 10^{-4}$ |
| B | 0 | $2.701 \times 10^{-3}$ | $D_{BC} = 1.245 \times 10^{-4}$ |
| C | $7.208 \times 10^{-3}$ | $4.730 \times 10^{-3}$ | $D_{AB} = 1.47 \times 10^{-4}$ |

### Additional Information and Data

The kinetic theory of gases can be used to derive the Stefan-Maxwell equations

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* This problem is adapted from Geankoplis[5] with permission.

in the $z$ direction as (see Bird et al.[2] or Geankoplis[5])

$$\frac{dC_i}{dz} = \sum_{i=1}^{n} \frac{(x_i N_j - x_j N_i)}{D_{ij}} \tag{10-75}$$

where $C_i$ represent the concentration of diffusing component $i$ in kg-mol/m$^3$, $x_i$ is the mole fraction of component $i$, $N_i$ is the molar flux of component $i$ in kg-mol/m$^2\cdot$s, $n$ is the number of components, and $D_{ij}$ is the binary molecular diffusivity for components $i$ and $j$ in m$^2$/s.

Application of Equation (10-75) to a three-component mixture yields the equations

$$\frac{dC_A}{dz} = \frac{(x_A N_B - x_B N_A)}{D_{AB}} + \frac{(x_A N_C - x_C N_A)}{D_{AC}} \tag{10-76}$$

$$\frac{dC_B}{dz} = \frac{(x_B N_A - x_A N_B)}{D_{AB}} + \frac{(x_B N_C - x_C N_B)}{D_{BC}} \tag{10-77}$$

$$\frac{dC_C}{dz} = \frac{(x_C N_A - x_A N_C)}{D_{AC}} + \frac{(x_C N_B - x_B N_C)}{D_{BC}} \tag{10-78}$$

where the appropriate equalities for the binary molecular diffusivities have been substituted for $D_{BA} = D_{AB}$, $D_{CA} = D_{AC}$, and $D_{CB} = D_{BC}$.

Typical boundary conditions for the preceding equations are dictated by the physical or chemical process. For example, if the diffusion is to a catalyst surface where the reaction rate is very fast, then the corresponding concentration of the limiting reactant at the catalyst surface may be assumed to be zero. If the diffusion process leads to a bulk stream, then the concentrations in the bulk stream are usually assumed to be at the bulk stream concentrations and diffusing components not in the bulk stream will have zero concentrations. Often the boundary conditions involving concentrations are split between two locations.

If relationships are known between the fluxes due to reaction stoichiometry or any of the fluxes are zero (stagnant component), then these relationships can be substituted into the preceding equations or expressed separately.

### 10.8.4 Solution

For the three-component system of this problem, the differential equations of Equations (10-76) to (10-78) directly apply. Since component C is stagnant, then the flux of this component is zero. Thus $N_C = 0$. The problem solution requires that the two fluxes $N_A$ and $N_B$ must be optimized until the boundary conditions of the concentrations of Table 10–9 are satisfied. The initial conditions are the known concentrations at point 1, and the final conditions are the known concentrations at point 2.

**(a) & (b)** The POLYMATH *Simultaneous Differential Equation Solver* can be used to solve the differential equations as a split boundary value problem with the initial conditions at point 1. In order to converge on the values of fluxes $N_A$ and $N_B$, error functions for the matching of the boundary conditions at point 2 can be defined by

$$\varepsilon(C_A) = 0 - C_A\big|_{z\,=\,0.001} \tag{10-79}$$

$$\varepsilon(C_B) = 2.701\times 10^{-3} - C_B\big|_{z\,=\,0.001} \tag{10-80}$$

Note that these error functions should go to zero when convergence is obtained.

Utilizing the preceding error functions and adding definitions for the mole fractions of the three components, one can write an initial POLYMATH equation set as given in Table 10–10.

**Table 10–10** POLYMATH Program - File **P10-08AB1.POL**

| Line | Equation |
|---|---|
| 1 | d(CA)/d(z)=(xA*NB-xB*NA)/DAB+(xA*NC-xC*NA)/DAC |
| 2 | d(CB)/d(z)=(xB*NA-xA*NB)/DAB+(xB*NC-xC*NB)/DBC |
| 3 | d(CC)/d(z)=(xC*NA-xA*NC)/DAC+(xC*NB-xB*NC)/DBC |
| 4 | NA=2.396E-5 |
| 5 | NB=-3.363E-4 |
| 6 | DAB=1.47E-4 |
| 7 | NC=0 |
| 8 | DBC=1.245E-4 |
| 9 | DAC=1.075E-4 |
| 10 | CT=0.2/(82.057E-3*328) |
| 11 | errA=CA-0 |
| 12 | errB=CB-2.701E-3 |
| 13 | xB=CB/CT |
| 14 | xA=CA/CT |
| 15 | xC=CC/CT |
| 16 | z(0)=0 |
| 17 | CA(0)=0.0002229 |
| 18 | CB(0)=0 |
| 19 | CC(0)=0.007208 |
| 20 | z(f)=0.001 |

Note that the initial estimate for $N_A$ in the preceding POLYMATH equation set is obtained from an application of Fick's law for just simple binary diffusion of A in C while the other diffusional transport is neglected. Thus the initial estimate for $N_A$ is

$$N_A = -D_{AC}\frac{(C_A|_2 - C_A|_1)}{(z|_2 - z|_1)} = -1.075\times 10^{-4}\frac{(0 - 2.229\times 10^{-4})}{(0.001 - 0)} = 2.396\times 10^{-5} \tag{10-81}$$

Similarly, for $N_B$ the initial estimate is

$$N_B = -D_{BC}\frac{(C_B|_2 - C_B|_1)}{(z|_2 - z|_1)} = -1.245\times 10^{-4}\frac{(2.701\times 10^{-3} - 0)}{(0.001 - 0)} = -3.363\times 10^{-4} \qquad \textbf{(10-82)}$$

The POLYMATH problem solution file for the initial solution is found in directory CHAPTER 10 with file named **P10-08AB1.POL**.

### Optimization of $N_A$ and $N_B$

A simple way to optimize these two fluxes is first to hold $N_B$ fixed and then to converge upon an improved value of $N_A$ by minimizing the error calculated in Equation (10-79). This iterative shooting method solution can be easily accomplished by trial and error or by the secant method, as discussed in Problem 6.5. Then the improved value of $N_A$ can be held fixed, and an improved value of $N_B$ can be obtained by minimizing the error calculated by Equation (10-80). Note that this simple optimization technique really involves searching along each parameter until a local minimum is obtained in an objective function, and then searching in turn along the other parameter to satisfy another objective function.

Typical progress in the solution for these local searches of this problem is summarized in Table 10–11. Note that the initial optimization holds $N_B$ and searches for the value of $N_A$. Then the next step involves holding $N_A$ and searching for an improved value of $N_B$. Convergence is obtained with just two searches for each flux, and the resulting values are found to be $N_A = 2.12\times 10^{-5}$ kg-mol/m$^2\cdot$s and $N_B = -4.14\times 10^{-4}$ kg-mol/m$^2\cdot$s. The resulting mole fraction profiles are nonlinear, as shown in Figure 10–7, and the final result is significantly different from the initial solution calculated from binary diffusion consideration only.

**Table 10–11** Iterative Search for Fluxes $N_A$ and $N_B$

| Search | $N_A$ | $\varepsilon(C_A)$ | $N_B$ | $\varepsilon(C_B)$ |
|---|---|---|---|---|
| Start | $2.396\times 10^{-5}$ | $-1.692\times 10^{-5}$ | $-3.363\times 10^{-4}$ | $-4.170\times 10^{-4}$ |
| 1 | $2.174\times 10^{-5}$ | $4.224\times 10^{-8}$ | $-3.363\times 10^{-4}$ | $-4.196\times 10^{-4}$ |
| 2 | $2.174\times 10^{-5}$ | $-4.309\times 10^{-8}$ | $-4.141\times 10^{-4}$ | $6.325\times 10^{-8}$ |
| 3 | $2.115\times 10^{-5}$ | $9.811\times 10^{-10}$ | $-4.141\times 10^{-4}$ | $-7.510\times 10^{-7}$ |
| 4 | $2.115\times 10^{-5}$ | $-1.017\times 10^{-8}$ | $-4.143\times 10^{-4}$ | $2.827\times 10^{-7}$ |