Numerical solution of the Maxwell-Stefan equations modeling the n-component twin-bulb diffusion experiment using the finite volume method

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Introduction

The Maxwell-Stefan equations for multi-component diffusion are solved using the finite volume method. Time discretization is fully implicit. To validate the solution the Maxwell-Stefan equations are used to model the twin-bulb experiment and the results are compared with results obtained from other numerical schemes as well as experimental observations.

Twin-bulb model

The twin-bulb experiment [1] consists of two small compartments (bulbs) connected by a tube through which the components can diffuse. The compartments contain n components. Diffusion through the tube can be modeled by the Maxwell-Stefan equations [2]:

$$-\left(\frac{\partial \ln \gamma_i}{\partial \ln x_i} + 1\right) \nabla x_i = \sum_{j \neq i} \frac{x_j \mathbf{J}_i - x_i \mathbf{J}_j}{c_t D_{ij}} \tag{1}$$

For ideal systems the activity coefficient γ_i of component i is equal to unity. The left side of (1) then simplifies, resulting in:

$$-\nabla x_i = \sum_{j \neq i} \frac{x_j \mathbf{J}_i - x_i \mathbf{J}_j}{c_t D_{ij}} \tag{2}$$

From a mass balance follows that the change in local composition at any given time is:

$$c_t \frac{\partial x_i}{\partial t} = -\nabla \cdot \mathbf{J}_i \tag{3}$$

Diffusion occurs at constant pressure. To preserve the total concentration the fluxes of the different components sum up to zero:

$$\sum_i \mathbf{J}_i = 0 \tag{4}$$

Method

To compute the composition in the bulbs the model equations (2) - (4) are solved using the finite volume method. Time discretization is fully implicit, achieved by eliminating the flux-components from the model equations. Central differencing is used for the diffusion terms.

Two types of computation are performed. One where the model equations for the three-component system are solved and one where the model equations for a system containing four components are solved. The bulbs are filled with gaseous H_2, N_2, Ne and CO_2.

In the case of the three-component system the mole fractions of H_2, N_2 and CO_2 in the first compartment (bulb 1) are initially 0.501, 0.499 and 0.0, respectively. In the second compartment (bulb 2) the mole fractions of H_2, N_2 and CO_2 are initially 0.0, 0.501 and 0.499, respectively. The diffusivities are $D_{12} = 8.33e-5$ (m^2/s), $D_{13} = 6.8e-5$ (m^2/s) and $D_{23} = 1.68e-5$ (m^2/s). The volumes of the compartments are $5e-4$ (m^3) and the tube connecting the compartments has a length of $1e-2$ (m) and a diameter of $2e-3$ (m). To validate the solution it is compared with the results obtained from an implicit scheme designed specifically for the three-component system.

In the four-component case the mole fractions of H_2, N_2, Ne and CO_2 in bulb 1 are initially 0.501, 0.2, 0.15 and 0.149, respectively. In bulb 2 the mole fractions of H_2, N_2, Ne and CO_2 are initially 0.499, 0.0, 0.152 and 0.349, respectively. The diffusivities D_{12}, D_{13} and D_{23} are the same as those in the three-component case and in addition the diffusivities D_{14}, D_{24} and D_{34} are set arbitrarily and respectively to $3.8e-5$ (m^2/s), $4.68e-5$ (m^2/s) and $5.68e-5$ (m^2/s). The bulb parameters are the same as in the three-component case. To validate the solution it is compared with results obtained from an explicit scheme which supports arbitrary numbers of components.

Results

The results obtained from solving the model equations for the three-component case are shown in figure 1. The results are in excellent agreement with the results obtained from the reference three-component implicit scheme (results are not shown) and agree well with experimental observations [3].

The results for the four-component case are shown in figure 2. The results are in good agreement with the results obtained from the reference explicit scheme (results not shown).

Discussion

Explicit time discretization was only stable when small timesteps were used, whereas implicit discretization was stable even when large timesteps were used. The implicit schemes also had the shortest running times, suggesting that the efficiency gained by using implicit discretization and using fewer timesteps outweighs the cost associated with having to solve a linear system at each timestep.

Conclusion

The Maxwell-Stefan equations were solved using the finite volume method and the results were found to coincide with the results of the reference implicit and explicit methods and agree well with experimental observations, thereby validating the solution. Additionally, the implicit schemes were found to have the shortest running times.

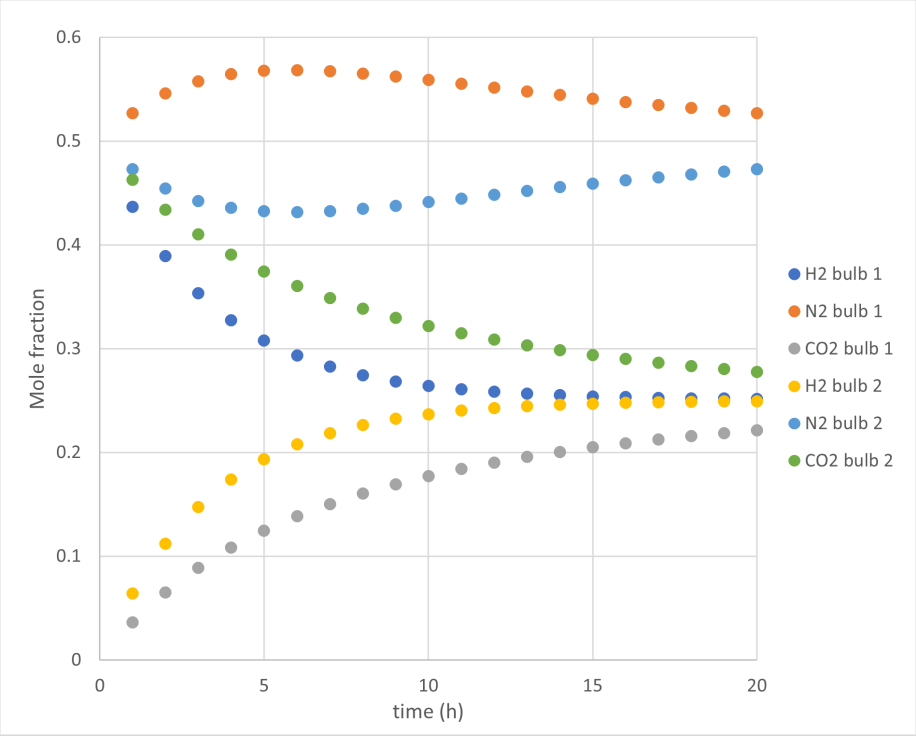

Figure 1: The mole fraction as a function of time (h).

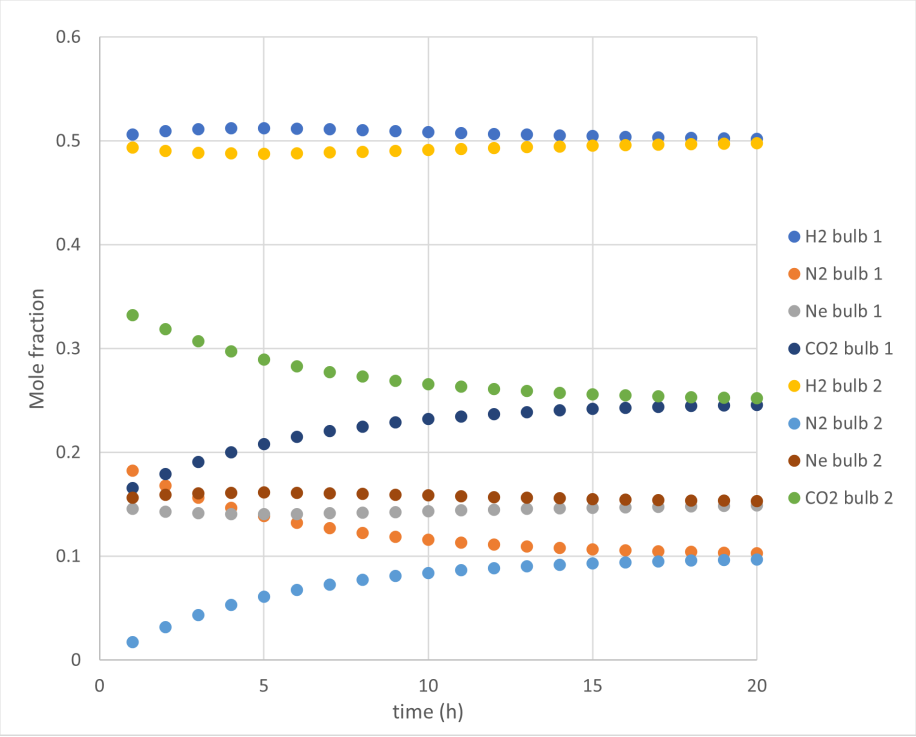

Figure 2: The mole fraction as a function of time (h).

Appendix

Here the one-dimensional case of the Maxwell-Stefan equations modeling the n-component twin-bulb experiment is elaborated on. The one-dimensional case of (2) is:

$$-c_t \frac{\partial x_i}{\partial z} = \sum_{i \neq j} \frac{x_j J_i - x_i J_j}{D_{ij}} \tag{5}$$

Equation (5) can be represented as a linear system:

$$A\mathbf{J} = \mathbf{b} \tag{6}$$

The elements of A are:

$$a_{ij} = \frac{x_i}{D_{in}} + \sum_{j \neq i} \frac{x_j}{D_{ij}} \quad , \; i = j \tag{7}$$

$$a_{ij} = -x_i \left(\frac{1}{D_{ij}} - \frac{1}{D_{in}} \right) \quad , \; i \neq j \tag{8}$$

The elements of $\mathbf{b}$ are:

$$b_i = -c_t \frac{\partial x_i}{\partial z} \tag{9}$$

To compute the local flux vector equation (6) is inverted:

$$\mathbf{J} = A^{-1}\mathbf{b} \tag{10}$$

Finally, the one-dimensional case of (3) is:

$$c_t \frac{\partial x_i}{\partial t} = -\frac{\partial J_i}{\partial z} \tag{11}$$

Equations (10) and (11) are the set of equations which model the n-component twin-bulb experiment.

Nomenclature

a_{ij}	Coefficient $(m^{-2} \cdot s)$
$\mathbf{b}$	Local composition gradient vector $(mol \cdot m^{-4})$
c_t	Concentration $(mol \cdot m^{-3})$
D_{ij}	Diffusivity $(m^2 \cdot s^{-1})$
$\mathbf{J}_i$	Flux vector $(mol \cdot m^{-2} \cdot s^{-1})$
$\mathbf{J}$	Local flux vector $(mol \cdot m^{-2} \cdot s^{-1})$
J_i	Flux component $(mol \cdot m^{-2} \cdot s^{-1})$
n	Number of components (-)
x_i	Mole fraction (-)
z	Axial coordinate (m)

Greek

γ_i Activity coefficient (-)

Subscripts

i Component index (-)
j Component index (-)
t Total (-)

References

[1] Duncan, J.B., Toor, H.L. *AIChE J.*, 1962, **8**, 38–41.

[2] Taylor, R., Krishna, R. *Multicomponent Mass Transfer*. New York: Wiley, 1993.

[3] Krishna, R. Uphill diffusion in multicomponent mixtures. *Chem. Soc. Rev.*, 2015, **44**, 2812.