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 modeling multi-component diffusion in the twin-bulb experiment are solved using the finite volume method. Time discretization is fully implicit. To validate the solution 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 bulbs 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.

Three cases are considered, the three-component (case 1), four-component (case 2) and five-component (case 3) systems. The bulbs are filled with gaseous H_2, N_2, Ne, Ar and CO_2. In all three cases the bulb parameters are the same. The volumes of the bulbs 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). The diffusivities and initial composition in the bulbs are given in table 1.

To validate the solution it is compared with the results obtained from other methods. In the case of the three-component system, case 1, results are compared with an implicit method designed specifically for the three-component system. To validate the solutions of cases 2 and 3, results are compared with the results from an explicit scheme based on a dynamic multi-directional search which supports arbitrary number of components.

Table 1: Diffusivities and initial bulb compositions.

Parameters	Case 3 components	Case 4 components	Case 5 components
D_{12} (m^2/s)	$8.33e-5$	$8.33e-5$	$8.33e-5$
D_{13} (m^2/s)	$6.8e-5$	$6.8e-5$	$6.8e-5$
D_{14} (m^2/s)	0	$3.8e-5$	$3.8e-5$
D_{15} (m^2/s)	0	0	$0.8e-5$
D_{23} (m^2/s)	$1.68e-5$	$1.68e-5$	$1.68e-5$
D_{24} (m^2/s)	0	$4.68e-5$	$4.68e-5$
D_{25} (m^2/s)	0	0	$9.68e-5$
D_{34} (m^2/s)	0	$5.68e-5$	$5.68e-5$
D_{35} (m^2/s)	0	0	$2.68e-5$
D_{45} (m^2/s)	0	0	$7.68e-5$
H_2 bulb 1	0.501	0.501	0.301
N_2 bulb 1	0.499	0.200	0.200
Ne bulb 1	0.0	0.150	0.150
Ar bulb 1	0.0	0.0	0.200
CO_2 bulb 1	0.0	0.149	0.149
H_2 bulb 2	0.0	0.499	0.299
N_2 bulb 2	0.501	0.0	0.0
Ne bulb 2	0.0	0.152	0.152
Ar bulb 2	0.0	0.0	0.075
CO_2 bulb 2	0.499	0.349	0.474

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).

Results of the five-component system as well as the results of the reference explicit scheme are shown in 3. The explicit method overshoots somewhat for two of the components, but the remaining results agree fairly well.

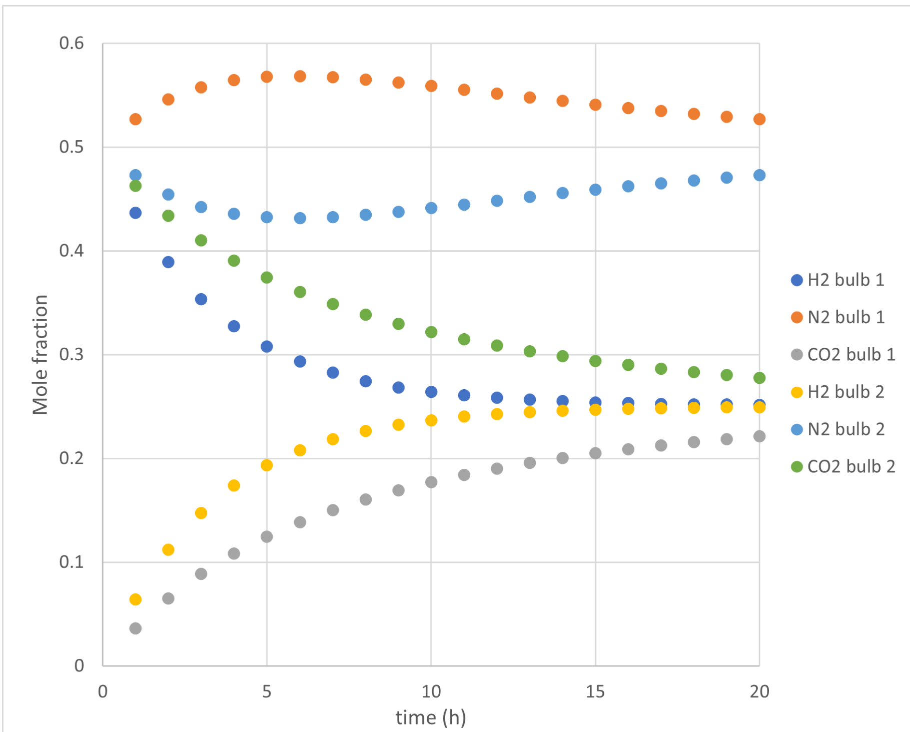

Figure 1: The mole fraction as a function of time (h).

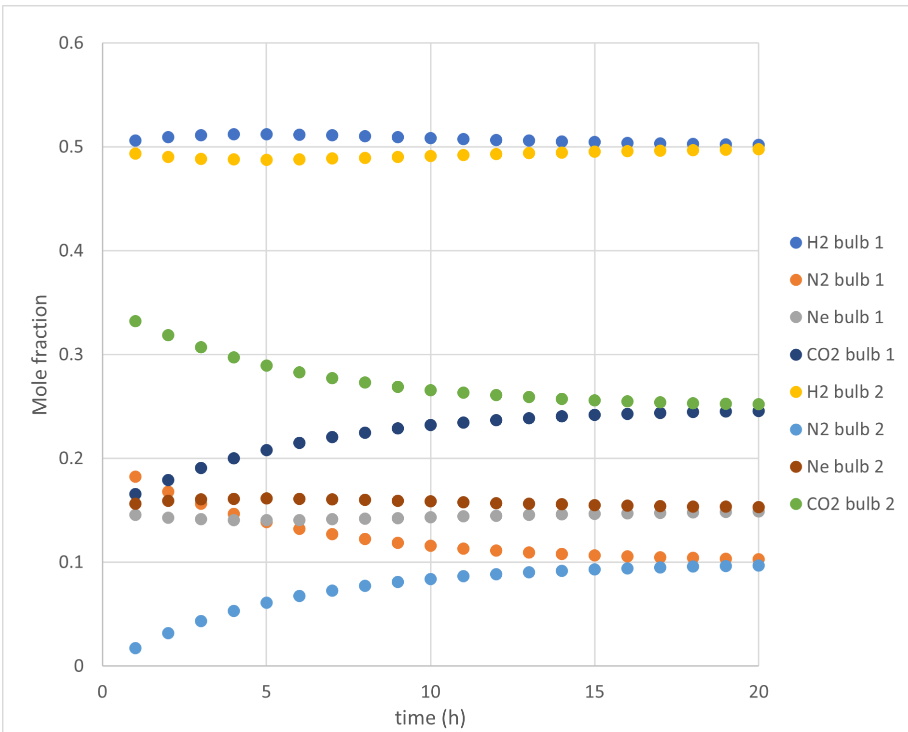

Figure 2: The mole fraction as a function of time (h).

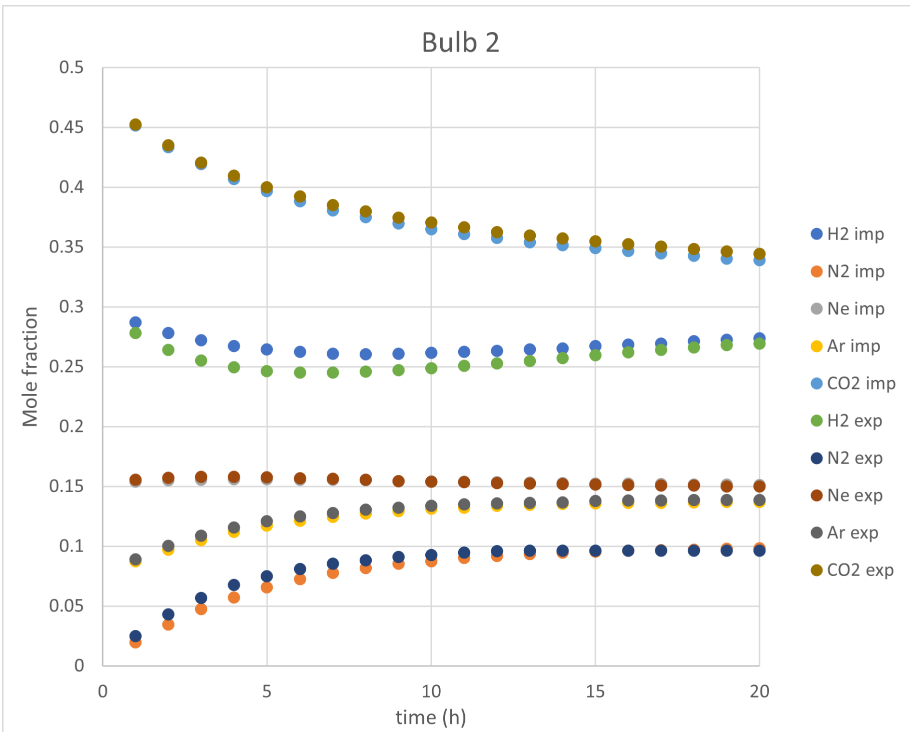

Figure 3: The mole fraction as a function of time (h).

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. The results of the three-component and four-component systems were found to coincide with the results of the reference implicit and explicit methods. In the five-component system some overshoot was observed in the explicit method, but generally the results agreed well with those obtained from applying the finite volume method. Also, the results were found to agree well with experimental observations, thereby validating the solution. Additionally, the implicit schemes were found to have the shortest running times.

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, obtained after eliminating the nth flux component J_n, are:

$$a_{ij} = \frac{x_i}{D_{in}} + \sum_{k \neq i}^{n} \frac{x_k}{D_{ik}} \quad , \ i = j \tag{7}$$

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

Elimination of J_n reduces the dimensions of A to $(n-1, n-1)$ and the bounds of the indices to $i, j \leq n-1$. The nth fraction x_n is computed from the other $n-1$ fractions:

$$x_n = 1 - \sum_{j}^{n-1} x_j \tag{9}$$

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

$$b_i = -c_t \frac{\partial x_i}{\partial z} \tag{10}$$

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

$$\mathbf{J} = A^{-1}\mathbf{b} \tag{11}$$

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

$$c_t \frac{\partial x_i}{\partial t} = -\frac{\partial J_i}{\partial z} \tag{12}$$

And from (11) follows that the flux components are related to the composition gradients:

$$J_i = -c_t \sum_j^{n-1} \alpha_{ij} \frac{\partial x_j}{\partial z} \tag{13}$$

The coefficients α_{ij} are the elements of the matrix inverse A^{-1}. Finally, after elimination of c_t one obtains a relation between the change in local composition with time and the composition gradients:

$$\frac{\partial x_i}{\partial t} = \frac{\partial}{\partial z} \sum_j^{n-1} \alpha_{ij} \frac{\partial x_j}{\partial z} \tag{14}$$

Equations represented by (14) 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 $(mol \cdot m^{-4})$
b_i	Element of vector of composition gradients $(mol \cdot m^{-4})$
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

α_{ij}	Coefficient of matrix inverse $(m^2 \cdot s^{-1})$
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.