A MAXWELL-STEFAN EXPERIMENT

Pedro Taveira, Paulo Cruz, Adélio Mendes
University of Porto • 4099 Porto Codex, Portugal

Fickian mass transport is deeply rooted in the culture of many engineering institutions, universities, and companies. The mathematical equation that describes Fick's law is simple and intuitive, but it is only valid for binary mixtures or for diffusion of diluted species in a multicomponent mixture, in the absence of electrostatic or centrifugal force fields.[1]

The Maxwell-Stefan equation provides a better and a more general approach. To show its relevance, while keeping the mathematical treatment simple, we propose a ternary mass diffusion transport experiment and its simulation. The simulator was developed to solve the Maxwell-Stefan equation for multicomponent isobaric and isothermal systems and is readily available on the web (http://raff.fe.up.pt/~lepae/simulator.html).

The concepts presented in this work are particularly suited for both undergraduate and graduate chemical engineering students provided that they are familiar with the first and second Fick laws.

THEORETICAL BACKGROUND

The Maxwell-Stefan equation for an isothermal and isobaric multicomponent system, where only pressure forces act, is (a simple derivation of this equation is presented in the appendix)[1-3]

$$-\frac{x_i}{\Re T}\frac{d\mu_i}{dz}=\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{x_j N_i - x_i N_j}{c_t \mathfrak{D}_{ij}} \qquad (1)$$

where x_i is the i-solute molar fraction, T is the absolute temperature, $\Re$ is the ideal gas constant, μ_i is the molar chemical potential, z is the axial coordinate, c_t is the total molar concentration, N_i is the molar flux of the species i with respect to a fixed referential, and $\mathfrak{D}_{ij}$ is the Maxwell-Stefan i,j diffusivity, with $\mathfrak{D}_{ij}=\mathfrak{D}_{ji}$.[2]

For ideal gases, Eq. (1) becomes

$$\frac{1}{\Re T}\frac{dx_i}{dz}=-\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{x_j N_i - x_i N_j}{P_t \mathfrak{D}_{ij}}=-\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{x_j J_i - x_i J_j}{P_t \mathfrak{D}_{ij}} \qquad (2)$$

where P_t is the total pressure and J_i is the molar flux of the species i with respect to the mixture molar average velocity

$$J_i = N_i - x_i \sum_{k=1}^{n} N_k$$

For ternary systems, the Maxwell-Stefan equations are

$$\frac{dx_A}{dz}=\frac{x_A J_B - x_B J_A}{c_t \mathfrak{D}_{AB}}+\frac{x_A J_C - x_C J_A}{c_t \mathfrak{D}_{AC}} \qquad (3)$$

$$\frac{dx_B}{dz}=\frac{x_B J_A - x_A J_B}{c_t \mathfrak{D}_{AB}}+\frac{x_B J_C - x_C J_B}{c_T \mathfrak{D}_{BC}} \qquad (4)$$

and

$$\frac{dx_A}{dz}+\frac{dx_B}{dz}+\frac{dx_c}{dz}=0 \qquad (5)$$

Equation (2) is nonlinear and therefore when solving diffusion problems it is more practical to revert it to the Fickian form

$$(J)=-c_t[D]\frac{\partial(x)}{\partial z} \qquad (6)$$

where (J) and (x) are (n-1)-component column vectors of diffusion fluxes and molar fractions, respectively, and [D] is the (n-1)**x**(n-1) Maxwell-Stefan diffusion coefficient matrix

$$[D]=[B]^{-1} \qquad (7)$$

and [B] is the diffusion coefficient inverse matrix that is obtained from Eq. (2)

***Pedro Taveira** is a Ph.D. student in Chemical Engineering at the University of Porto, Portugal. He received his degree in Chemical Engineering from the same University in 1997. His research interests are in gas separation using membrane technology.*
***Paulo Cruz** is a first-year Ph.D. student in Chemical Engineering at the University of Porto, Portugal, where he received his degree in Chemical Engineering in 1998. His research interests are multicomponent mass transport and sorption in porous solids and membranes.*
***Adélio Mendes** received his degree and Ph.D. in Chemical Engineering from the University of Porto, Portugal, where he is currently Assistant Professor. He teaches Chemical Engineering Laboratories, Separation Processes, and Numerical Methods. His main research interests include membrane and sorption gas separations.*

$$B_{ij} = \frac{x_i}{\mathfrak{D}_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{x_k}{\mathfrak{D}_{ik}}, \quad B_{ij(i\neq j)} = -x_i\left(\frac{1}{\mathfrak{D}_{ij}} - \frac{1}{\mathfrak{D}_{in}}\right), \quad i,j=1,2,3,\cdots n-1 \tag{8}$$

The Maxwell-Stefan diffusivities can be estimated by the Chapman-Enskog Eq. (9)[4]

$$\mathfrak{D}_{ij} = 5.9543\times10^{-24}\frac{\sqrt{T^3\left(\frac{1}{M_i}+\frac{1}{M_j}\right)}}{P_T\sigma_{ij}^2\Omega_{D,ij}} \tag{9}$$

where σ_{ij} is collision diameter, $\Omega_{D,ij}$ is the collision integral, and M_i is the molecular mass of species i (all the units are in SI). The collision parameters can be found, for instance in Bird, et al.[4]

EXPERIMENTAL SETUP

The experiment described below shows the limitations of Fick's equation and introduces the Maxwell-Stefan equation for multicomponent diffusion. The setup is shown in Figure 1.

Typically, two tanks of about the same volume are connected by a 4.3-mm internal diameter pipe (1/4" nominal diameter) that is 15.3 cm long. Tank A has a 45.2-cm^3 volume, while tank B has a 41.5-cm^3 volume. An on/off valve divides the pipe at the middle and has about the same pipe internal diameter. A set of needle valves, on/off valves, and a pressure transducer are available to fill up the tanks. All the valves are made of stainless steel by Whitey. The pressure transducer (Druck model PDCR921) has an 0-70 kPa absolute pressure range with ±0.5% F.R.S. precision. Gas analysis is made at a high frequency by a mass spectrometer (Dataquad, from Spectramass, UK) connected to one tank at a time. The mass spectrometer sample probe is made of a 1-m long fused silica column with 50 μm internal diameter. After two hours the total pressure changes less than 1% due to this mass withdraw when the initial pressure is 40 kPa (absolute pressure). A vacuum pump evacuates the system to a pressure below 0.3 kPa. All data are recorded on a computer every 100 seconds.

Students evacuate both tanks and then fill them with equimolar binary gas mixtures with the help of the pressure transducer. They should fill both tanks with nitrogen at the same time, up to a pressure of 20 kPa (absolute pressure), and then add helium to tank A and carbon dioxide to tank B, up to a total pressure of 40 kPa. At the end, both tanks must have the same total pressure. When changing the feed gas, the filling circuit should be evacuated—otherwise the residual gas will enter with the new feed gas. Nitrogen is the common component in both tanks.

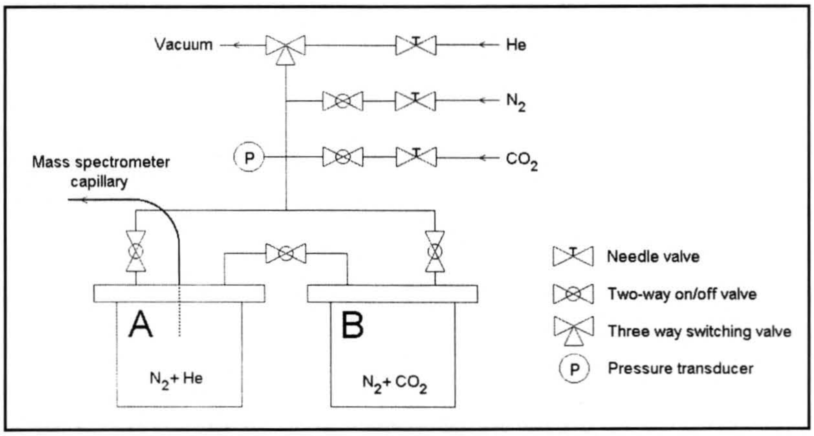

Figure 1. *Sketch of the experimental setup.*

After filling the tanks, students are asked to start the data acquisition software, to switch on the mass spectrometer, to read the temperature, and to open the switching valve connecting the tanks. Helium diffuses from tank A to tank B, and carbon dioxide diffuses from tank B to tank A. The total pressure difference between the tanks should be negligibly small, implying no viscous flow and so equimolar diffusion.

The diffusion constant is approximately inversely proportional to the total pressure. A total pressure of 40 kPa allows students to complete the diffusion experiment within the three-hour laboratory session.

The experiment should be performed twice, switching the tanks' contents on the second run in order to record the concentration history of both tanks. This can be done in two consecutive classes of three hours each by two different student groups. The two groups, working as a team, should exchange their results and draw the nitrogen molar fraction curves as a function of time. Then they can simulate their experimental system with the available simulator and comment on the results.

DATA TREATMENT AND DISCUSSION OF RESULTS

After opening the connecting valve, the gas mixtures in the tanks enter in contact (see Figure 1). The connecting pipe mass balance can be written as[4]

$$\frac{\partial N_i}{\partial z} + \frac{\partial c_i}{\partial t} = 0 \tag{10}$$

Since the total pressure gradient between the tanks can be neglected, there is no viscous flow, and therefore the total flux, N_t, is zero. Introducing Eqs. (6) and (7) into the mass balance, the following expression is obtained for constant temperature and pressure:

$$\frac{\partial(N)}{\partial z}+\frac{\partial(c)}{\partial t}=\frac{\partial}{\partial z}\left[-c_t[D]\frac{\partial(x)}{\partial z}\right]+c_t\frac{\partial(x)}{\partial z}=$$

$$c_t[B]^{-1}\frac{\partial[B]}{\partial z}[B]^{-1}\frac{\partial(x)}{\partial z}-c_T[B]^{-1}\frac{\partial^2(x)}{\partial z^2}+c_t\frac{\partial(x)}{\partial z} \qquad (11)$$

where the matrix product is not commutative. In the case of three-component diffusion, a two-component matrix equation (Eq. 11) must be considered along with the total flux: $N_t=0$. Assuming that the diffusion time constant inside the tanks is much smaller than the diffusion time constant in the pipe, the tanks can be considered as completely stirred. The mass balance of the complete system (Figure 1) is

$$V_A\frac{\partial c_i\big|_{z=0}}{\partial t}-A\,N_i\big|_{z=0}=0 \qquad (12)$$

for tank A, and

$$V_A\frac{\partial c_i\big|_{z=0}}{\partial t}-A\,N_i\big|_{z=0}=0 \qquad (12)$$

for tank B. L is the pipe length.

A fortran program, using an MS Excel interface, was written to solve this problem. The program is also available on the web <http://raff.fe.up.pt/~lepae/simulator.html> for remote simulation. It can be applied to mixtures of 3 to 7 components. For solving the partial differential equations, along with the ordinary differential equations, the package FORSIM VI[5] was used.

At the beginning the nitrogen concentration is the same in both tanks and therefore, according to the Fick equation, nothing should happen to it. Figure 2 shows the concentration curves for the three gases in both tanks. As can be seen, the concentration of nitrogen starts to decrease in tank B and to increase in tank A! Why? Helium and carbon dioxide seem to behave as Fickian gases: helium concentration decreases in tank A and carbon dioxide in tank B until equilibrium is reached. The step-like behavior of some experimental points in Figure is related to the mass spectrometer resolution.

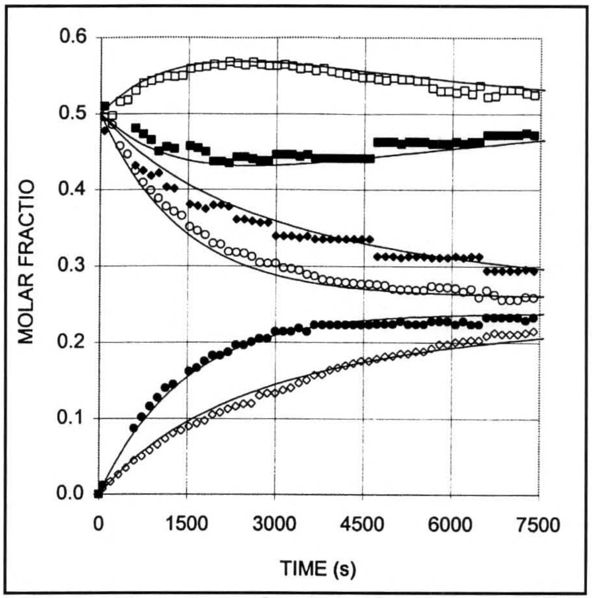

Figure 2. *Experimental and simulated nitrogen (■), helium (●), and carbon dioxide (◆) molar fraction curves as a function of time. Open symbols refer to tank A and closed symbols to tank B. The solid lines represent the simulated results.*

The diffusion coefficients of the three gas pairs at 40 kPa and 20°C are

$$\mathcal{D}_{He-N_2}=\mathcal{D}_{N_2-He}=1.7076\times10^{-4}\ m^2/s$$

$$\mathcal{D}_{He-CO_2}=\mathcal{D}_{CO_2-He}=1.4172\times10^{-4}\ m^2/s$$

$$\mathcal{D}_{N_2-CO_2}=\mathcal{D}_{CO_2-N_2}=0.3688\times10^{-4}\ m^2/s$$

Helium binary coefficients are high and it readily moves from tank A to tank B while carbon dioxide moves slowly from tank B to tank A. Nitrogen should balance these effects, and so it first moves with carbon dioxide from tank B to tank A, to balance the very fast helium, and then returns to tank A. Students are asked to internalize this picture in opposition to the one given by Fick's law, where mass transport is viewed as depending only on each component concentration gradient.

The mass spectrometer allows for an almost continuous concentration measurement. If not available, a different experiment can be performed using a gas chromatograph. Two samples can be collected from each tank using a syringe. In this case, the tanks' total pressure should be 1 atm or more, to allow sampling. The samples can be collected at the highest and lowest nitrogen partial pressures, and the time at which this happens can be estimated from the simulation program.

CONCLUSIONS

Fick's equation is "intuitive" and deeply rooted in the culture of many engineering institutions. While very simple, it is only valid for binary systems or multicomponent diluted systems. To change the Fickian culture and internalize a new feeling in the diffusion area, we propose to the students a ternary diffusion lab exercise. The gases considered (helium, carbon dioxide, and nitrogen) are neither dangerous nor expensive. The experimental setup is also inexpensive, provided that a mass spectrometer is available.

The experiment is very simple and can be easily performed in 3 hours. It also strongly demonstrates the inaccurate results that Fick's equation can lead to under some circumstances. The simulation program that supports this experiment allows students to play at home with different systems, helping them to gain a new feeling for multicomponent diffusion mass transport.

ACKNOWLEDGMENTS

The authors wish to thank Professors Carlos Costa and Fernao Magalhaes for their careful review of this manuscript.

NOMENCLATURE

A connecting pipe cross-section area (m^2)

c_i	molar concentration of species i (mol m^{-3})
c_t	total molar concentration (mol m^{-3})
D_{AB}	Fickian A,B diffusivity (m^{2}s^{-1})
D_{AM}	Fickian diffusivity of species A in a mixture (m^{2}s^{-1})
$\mathcal{D}_{AB}$	Maxwell-Stefan A,B diffusivity (m^{2}s^{-1})
F	molar force (N mol^{-1})
J_i	molar flux of species i with respect to the mixture molar average velocity (mol m^{-2}s^{-1})
(J)	(n-1)-component column vector of diffusion fluxes (mol m^{-2}s^{-1})
L	connecting pipe length (m)
M_i	molecular mass of species i (kg mol^{-1})
N_i	molar flux of species i with respect to a fixed referential (mol m^{-2}s^{-1})
N_t	total molar flux with respect to a fixed referential (mol m^{-2}s^{-1})
p_i	partial pressure of species i (Pa)
P_t	total pressure (Pa)
$\Re$	ideal gas constant (J mol^{-1}K^{-1})
t	time (s)
T	absolute temperature (K)
V_A,V_B	volume of tanks A and B, respectively (m^3)
u_i	velocity of species i (ms^{-1})
x_i	molar fraction of species i (dimensionless)
(x)	(n-1)-component molar fractions vector
z	axial coordinate (m)

Greek Letters

μ_i	molar chemical potential (J mol^{-1})
σ_{ij}	collision diameter (m)
$\Omega_{D,ij}$	collision integral (dimensionless)

REFERENCES

1. Krishna, R., and J.A. Wesselingh, "The Maxwell-Stefan Approach to Mass Transfer," *Chem. Eng. Sci.*, **52**, 861 (1997)
2. Taylor, R., and R. Krishna, *Multicomponent Mass Transfer,* John Wiley & Sons, New York, NY (1993)
3. Wesselingh, J.A., and R. Krishna, *Mass Transfer,* Ellis Horwood, New York, NY (1990)
4. Bird, R.B., W.E. Stewart, and E.N. Lightfoot, *Transport Phenomena,* John Wiley & Sons, New York, NY (1960)
5. Carver, M., D. Stewart, J. Blair, and W. Selander, *Forsim VI,* Chalk River Nuclear Laboratories, Ontario, Canada (1979)

APPENDIX

Derivation of the Maxwell-Stefan Equation (Based on References 1, 2, and 3)

Consider a pipe filled with an isobaric binary gas mixture, components A and B. When moving, component A exerts a force on B. This drag force should be proportional to the molar concentrations of B and A and to the relative velocity of both components

$$F \propto c_A c_B (u_A - u_B) \tag{A1}$$

where c_i is the i-component molar concentration, u_i is the i-solute velocity referred to a fixed referential, and F is the drag force. On the other hand, when considering an infinitesimal pipe slice, the pressure exerted by component A on the imaginary left boundary is $p_{A|z=z}$ and on the right boundary is $p_{A|z=z+dz}$, where p_A is the partial pressure of A. The partial pressure gradient $-dp_A/dz$ is the driving force for component A to move inside the pipe and should be balanced by the drag force

$$-\frac{dp_A}{dz} \propto c_A c_B (u_A - u_B) \tag{A2}$$

Calling $\mathcal{D}_{AB}/\Re T$ to the proportional factor, we obtain

$$-\frac{dp_A}{dz} = \frac{c_A c_B (u_A - u_B)}{\mathcal{D}_{AB}/\Re T} \tag{A3}$$

For ideal gas mixtures, Eq. A3 simplifies to

$$-\frac{dx_A}{dz} = \frac{x_A x_B (u_A - u_B)}{\mathcal{D}_{AB}} \tag{A4}$$

For ternary mixtures, we must add an additional drag force term to the right-hand side of Eq. A4 to account for A-C interactions

$$-\frac{dx_A}{dz} = \frac{x_A x_B (u_A - u_B)}{\mathcal{D}_{AB}} + \frac{x_A x_C (u_A - u_C)}{\mathcal{D}_{AC}} \tag{A5}$$

and for multicomponent systems

$$-\frac{dx_i}{dz} = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_i x_j (u_i - u_j)}{\mathcal{D}_{ij}} \tag{A6}$$

The Maxwell-Stefan equation is usually written in terms of molar fluxes: $N_i = c_i u_i$. Replacing the velocities in Eq. A6 by molar fluxes, we obtain

$$-\frac{dx_i}{dz} = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_i N_j - x_j N_i}{c_t \mathcal{D}_{ij}} \tag{A7}$$

The driving force is better represented by the chemical potential gradient

$$-\frac{dx_i}{dz} = -\frac{x_i}{\Re T} \frac{d(\Re T \,\ell n\, x_i)}{dz} \approx -\frac{x_i}{\Re T} \frac{d\mu_i}{dz} \tag{A8}$$

and introducing this result into Eq. A7, we obtain

$$-\frac{x_i}{\Re T} \frac{d\mu_i}{dz} = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_i N_j - x_j N_i}{c_t \mathcal{D}_{ij}} = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_i J_j - x_j J_i}{c_t \mathcal{D}_{ij}} \tag{A9}$$

This is the usual form of the Maxwell-Stefan equation for isobaric and isothermal systems, where only pressure forces are present.

For binary mixtures, the Maxwell-Stefan equation reduces to the Fick equation

$$J_A = -c_t D_{AB} \frac{dx_A}{dz} \tag{A10}$$

and the Maxwell-Stefan diffusivity is the same as the Fickian binary diffusivity. For multicomponent systems, the Fick equation is written as

$$J_A = -c_t D_{AM} \frac{dx_A}{dz} \tag{A11}$$

where D_{AM} is the diffusion coefficient of A in the multicomponent mixture. While the Maxwell-Stefan diffusion coefficients can be considered essentially constant with the composition, the Fickian diffusivity cannot, even for ideal gases and equimolar diffusion.[4] ❐