Multicomponent Diffusion in Semi-Infinite Systems

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This paper provides a description of multicomponent diffusion in a one-dimensional semi-infinite system with finite net mass-transfer rate across the single bounding surface. Specifically, the time-dependent concentration profiles are calculated for a step change in interfacial conditions in a phase of previously uniform composition. These profiles are obtained as functions of the initial and final interfacial compositions, the necessary diffusion coefficients, and the ratio R of the absolute mass fluxes n_i of any two of the diffusing species. The mass flux of any component through the system boundary then may be calculated readily from these concentration profiles and the multicomponent analogue of Fick's first law of diffusion.

This development is thus a generalization of the Arnold problem (*1*) both to an arbitrary number of components and to arbitrary interfacial mass-flux ratios. This work was performed primarily to aid in the determination of multicomponent diffusion coefficients, but also may be used to extend penetration theory to multicomponent mixtures.

The flux equations chosen to express diffusion rates may be written as

$$\mathbf{n}_i = - \sum_{j=1}^{r-1} D^o_{ij} \nabla \rho_j + \rho_i v^o \tag{1}$$

Similar equations without the final term were used by Gosting and co-workers (*2, 3*). Equation (1) defines a nonsymmetric matrix $\mathbf{D}^o$ of diffusion coefficients consistent with the principles of irreversible thermodynamics and is of the type developed by Onsager (*4*). It is most useful for systems where the partial specific volumes may be assumed constant. This assumption is excellent for most gaseous and liquid systems. Formally identical sets of equations may be developed for other reference velocities, for example, the mass-average velocity which is the most useful reference for systems of constant density. These alternate expressions define different but related multicomponent diffusivities (*5, 6*), but may be treated in the same way as Equation (1).

MATHEMATICAL DESCRIPTION OF THE SYSTEM

This section gives the differential equations and boundary conditions necessary to calculate the concentration profiles. Equation (1) is introduced into the continuity equation for any species to obtain for the one-dimensional case, with $\mathbf{D}^o$ constant

$$\frac{\partial \rho_i}{\partial t} = \sum_{j=1}^{r-1} D^o_{ij} \frac{\partial^2 \rho_j}{\partial z^2} - v^o \frac{\partial}{\partial z} \rho_i \tag{2}$$

In Equation (2), use is made of the fact that $\frac{\partial v^o}{\partial z}$ is zero for a system in which the partial specific volumes are constant. Mathematically, this may be shown by multiplying the equation of continuity by $\overline{V}_i$, summing over all r species, and using the relation $\sum_{i=1}^{r} \rho_i \overline{V}_i = 1$. Equation (2) is to be solved with the initial and boundary conditions

for

$$t \leq 0,\ z > 0 \qquad \rho_i = \rho_{i\infty} \tag{3}$$

for

$$t > 0,\ z = 0 \qquad \rho_i = \rho_{io} \tag{4}$$

for

$$t < \infty,\ z = \infty \qquad \rho_i = \rho_{i\infty} \tag{5}$$

In addition, to evaluate the mass fluxes with respect to the interface (which is taken as the origin of the coordinate axes) one flux ratio is needed. This is stated as $n_r = R n_m$ where n_r is the component whose flux is not independent at the interface and n_m is the flux of any other component. One example is that of a liquid solution containing a single nonvolatile component exposed to a gas phase at $z = 0$. In this case $R = 0$ and $n_r = 0$ at the interface. To find v^o, one combines this relation and Equation (1), multiplies the result by $\overline{V}_i$, and sums from $i = 1$ to $i = (r - 1)$:

$$v^o = \frac{\sum_{i=1}^{r-1} \sum_{j=1}^{r-1} \overline{V}_i D^o_{ij} \frac{\partial \rho_j}{\partial z} + R \sum_{j=1}^{r-1} \overline{V}_r D^o_{mj} \frac{\partial \rho_j}{\partial z}}{V_r\ (\rho_r - R\, \rho_m)} \tag{6}$$

This result may be inserted as desired into Equation (2) to eliminate v^o.

The description of this system is now complete, but further mathematical simplification is possible. When the system description is rewritten in terms of the new quantities

$$y = z/2\sqrt{t} \tag{7}$$

$$\chi_i = \frac{\rho_i - \rho_{i\infty}}{\rho_{io} - \rho_{i\infty}} \tag{8}$$

$$a_{ij} = \frac{\rho_{jo} - \rho_{j\infty}}{\rho_{io} - \rho_{i\infty}} \tag{9}$$

one obtains

$$\sum_{j=1}^{r-1} D^o{}_{ij}\, a_{ij} \frac{d^2\chi_j}{dy^2} + 2\,(y - \lambda)\,\frac{d\chi_i}{dy} = 0 \tag{10}$$

where λ is a constant

$$\lambda = -\frac{1}{2}\,\frac{\displaystyle\sum_{i=1}^{r-1}\sum_{j=1}^{r-1} \overline{V}_i D^o{}_{ij} \frac{d\rho_j}{dy} + R \sum_{j=1}^{r-1} \overline{V}_r D^o{}_{mj} \frac{d\rho_j}{dy}}{\overline{V}_r\,(\rho_r - R\,\rho_m)} \tag{11}$$

The boundary conditions become

$$\text{at } y = 0 \qquad \chi_i = 1 \tag{12}$$

$$\text{at } y = \infty \qquad \chi_i = 0 \tag{13}$$

SOLUTION FOR MASS CONCENTRATION PROFILES

Although Equation (10) is a second-order differential equation, it includes $(r - 1)$ concentration gradients. Thus the set of $(r - 1)$ Equation (12) must be solved simultaneously. First one allows that

$$\alpha_k = \sum_{j=1}^{r-1} D^o{}_{kj}\, a_{kj} \frac{dx_j}{dy} \tag{14}$$

If the determinant of $\mathbf{D^o a}$ is not zero, $\mathbf{E}$ may be defined as inverse matrix of $\mathbf{D^o a}$. When both sides of Equation (14) are multiplied by $\mathbf{E}$ and the result is substituted into Equation (10), one obtains

$$\frac{d\alpha_i}{d[(y - \lambda)^2]} + \sum_{k=1}^{r-1} E_{ik}\,\alpha_k = 0 \tag{15}$$

Equation (15) represents a set of simultaneous homogeneous linear equations (7). Since $\mathbf{E}$ and $d/d[(y - \lambda)^2]$ commute, solutions of the form $\exp\,(-\,\sigma(y - \lambda)^2)$ are assumed and a polynomial in σ is obtained:

$$\det\,[E_{ik} - \sigma\delta_{ik}] = 0 \tag{16}$$

The roots of this polynomial are known if there are five or fewer components. Equal roots may be handled by usual procedures. For unequal roots, the solution is

$$\alpha_k = \sum_{l=1}^{r-1} B_{kl} \exp\,[\sigma_l (y - \lambda)^2] \tag{17}$$

Because the α_k must satisfy Equation (15), there are additional restraints on the integration constants:

$$0 = \sum_{k=1}^{r-1} (E_{ik} - \delta_{ik}\,\sigma_l)\,B_{kl} = \sum_{k=1}^{r-1} F_{ik}\,B_{kl} \tag{18}$$

After Equation (17) is substituted into Equation (14) and multiplied by $\mathbf{E}$, one integrates and evaluates the boundary conditions and restraints by Cramer's rule. The resulting expression is

$$\chi_j = \sum_{l=1}^{r-1} M_{jl}\,\{M\}_{jl}\,\frac{1 - \operatorname{erf}\,[(y - \lambda)\sqrt{\sigma_l}]}{1 + \operatorname{erf}\,[\lambda\sqrt{\sigma_l}]} \tag{19}$$

where

$$M_{jl} = \sum_{k=1}^{r-1} E_{jk}\,\frac{\det\left[\displaystyle\sum_{m \neq k}^{r-1} (F_{km} - \delta_{kl}\,[F_{km} + E_{lm}])\right]}{\det\left[\displaystyle\sum_{m \neq k}^{r-1} F_{km}\right]} \tag{20}$$

and

$$\{M\}_{jl} = \frac{\det\,[M_{jk} - \delta_{kl}\,(1 + M_{jk})]}{\det \mathbf{M}} \tag{21}$$

Equation (19) gives the concentration profile of each component in terms of the diffusion coefficients, the concentration differences, and a constant λ, depending on the known flux ratio R. When this expression is inserted into Equation (11), the definition of λ, one obtains

$$\lambda = \frac{\displaystyle\sum_{l=1}^{r-1}\sum_{j=1}^{r-1} \frac{\left(\displaystyle\sum_{i=1}^{r-1} \overline{V}_i D^o{}_{ij} + R\,\overline{V}_r D^o{}_{mj}\right)(\rho_{jo} - \rho_{j\infty})\,M_{jl}\,\{M\}_{jl}}{[1 + \operatorname{erf}\lambda\sqrt{\sigma_l}\,]\,[\exp\,(\lambda^2\,\sigma_l)\,]\,/\sqrt{\sigma_l}}}{\overline{V}_r\,(\rho_r - R\,\rho_m)\,\sqrt{\pi}} \tag{22}$$

Equations (18) through (22) are sufficient for calculation of the concentration profiles.

DISCUSSION

In this section, the binary and ternary cases are examined in more detail. Because of the complexity of the terms involved, the four- and five-component cases are not discussed, but they are of similar form and may be found by expanding the general equations of the previous section. The results of the binary case are particularly simple, since

$$E_{ii} = \sigma_i = \frac{1}{D^o{}_{ii}} \tag{23}$$

and

$$D^o{}_{11} = D^o{}_{22} = D^o \tag{24}$$

This gives the solution

$$\chi_i = \frac{1 - \operatorname{erf}\,[(y - \lambda)/D^o]}{1 + \operatorname{erf}\,[\lambda/D^o]} \tag{25}$$

If $n_2 = Rn_1$ at $z = 0$, then λ may be found from the relation

$$\frac{\rho - \rho_{10}\,(1 + R)}{\rho_{10} - \rho_{1\infty}} = \left(\frac{\overline{V}_1 + R\,\overline{V}_2}{\overline{V}_2}\right)$$

$$\left(\frac{\lambda}{\sqrt{D^o}}\,e^{\left(\frac{\lambda}{D_o}\right)^2}\left(1 + \operatorname{erf}\frac{\lambda}{\sqrt{D^o}}\right)\right)^{-1} \tag{26}$$

The case in which concentration is constant, $R = 0$, and $\rho_{1\infty} = 0$ was derived by Arnold (*1*).

TABLE 1. CONSTANT EVAPORATING COMPOSITIONS
A COMPARISON OF THREE CALCULATION PROCEDURES

Result	Coupling of flows considered: Diffusivities at interfacial composition	Coupling of flows considered: Arithmetic average composition	Coupling neglected: Binary diffusivities in air
D^o_{TT} .10^2	4.39	5.01	7.15
D^o_{TE} .10^2	0.42	0.31	0.0
D^o_{ET} .10^2	0.21	0.19	0.0
D^o_{EE} .10^2	8.48	9.50	12.9
Const.-evap. comp. % toluene in liquid	17.4	17.1	16.5
Flux toluene relative to flux calculated from avg. diffusion coefficient	0.96	1.00	1.14

Although the results of the ternary case have a similar form, they are more complex:

$$\mathbf{E} = \begin{bmatrix} \left(\dfrac{D^o_{22}}{\det \mathbf{D}^o}\right) & \left[\dfrac{-D^o_{12}}{\det \mathbf{D}^o}\left(\dfrac{\rho_{20}-\rho_{2\infty}}{\rho_{10}-\rho_{1\infty}}\right)\right] \\ \left[\dfrac{-D^o_{21}}{\det \mathbf{D}^o}\left(\dfrac{\rho_{10}-\rho_{1\infty}}{\rho_{20}-\rho_{2\infty}}\right)\right] & \left(\dfrac{D^o_{11}}{\det \mathbf{D}^o}\right) \end{bmatrix} \tag{27}$$

$$\sigma_1 = \frac{1}{2}\left(E_{11} + E_{22} + \sqrt{(E_{22} - E_{11})^2 + 4\,E_{12}\,E_{21}}\right) \tag{28a}$$

$$\sigma_2 = \frac{1}{2}\left(E_{11} + E_{22} - \sqrt{(E_{22} - E_{11})^2 + 4\,E_{12}\,E_{21}}\right) \tag{28b}$$

The profiles are

$$\chi_1 = \left(\frac{\sigma_2 - E_{11} - E_{12}}{-\sigma_1 + \sigma_2}\right)\left(\frac{1 - \text{erf}\,[(y-\lambda)\sqrt{\sigma_1}]}{1 + \text{erf}\,[\lambda\sqrt{\sigma_1}]}\right) + \left(\frac{\sigma_1 - E_{11} - E_{12}}{-\sigma_2 + \sigma_1}\right)\left(\frac{1 - \text{erf}\,[(y-\lambda)\sqrt{\sigma_2}]}{1 + \text{erf}\,[\lambda\sqrt{\sigma_2}]}\right) \tag{29}$$

$$\chi_2 = \left(\frac{\sigma_2 - E_{22} - E_{21}}{-\sigma_1 + \sigma_2}\right)\left(\frac{1 - \text{erf}\,[(y-\lambda)\sqrt{\sigma_1}]}{1 + \text{erf}\,[\lambda\sqrt{\sigma_1}]}\right) + \left(\frac{\sigma_1 - E_{22} - E_{21}}{-\sigma_2 + \sigma_1}\right)\left(\frac{1 - \text{erf}\,[(y-\lambda)\sqrt{\sigma_2}]}{1 + \text{erf}\,[\lambda\sqrt{\sigma_2}]}\right) \tag{30}$$

λ is found from Equation (11). In the limit where $\lambda = 0$, these results reduce to those derived for the infinite case (*3*).

EXAMPLE: CALCULATION OF THE CONSTANT-EVAPORATING COMPOSITION OF A TOLUENE-ETHANOL MIXTURE

A problem of practical utility in the lacquer industry, the calculation of the composition of a constant-evaporating mixture, is considered here. To avoid excessive complication discussion is restricted to isothermal evaporation from a binary mixture of ethanol and toluene into stagnant air at 1 atm. absolute pressure. Then the fluxes are fixed by the insolubility of air in the liquid and by the requirement that the toluene and ethanol fluxes be in the same ratio as the liquid-phase compositions. There may be no mass transfer resistance in the liquid phase. This idealized system then may be described by the above development if $\mathbf{D}^o$ is known for an average composition.

Binary diffusivities for the system are $\mathcal{D}_{TE} = 0.0365$, $\mathcal{D}_{TA} = 0.0715$, and $\mathcal{D}_{EA} = 0.129$ where T, E, and A refer to toluene, ethanol, and air, respectively (*8* to *10*). The vapor-pressure data is that of Lewis and Squires (*11*). For gases and dilute vapors, the multicomponent-diffusion coefficients may be found from this binary data. First, the Onsager coefficients are calculated (*12*), and the results are used to find the $\mathbf{D}^o$ (*6*). Although an average composition must be assumed, this assumption does not significantly affect the calculated flux ratio.

When the multicomponent-diffusion coefficients are known, the fluxes may be calculated from the above equations. First, $\mathbf{E}$ *is* found from $\mathbf{D}^o a$, σ_i from Equation (28), and λ from Equation (11) with $R = 0$. Combination of these values gives the concentration profiles [Equations (29), (30)]. The derivatives of these profiles are substituted into Equation (1) to obtain the fluxes. The results of these calculations are shown in Table 1.

NOTATION

a_{ij} = mass-density ratio, Equation (9)
det = determinental operator
$\mathbf{D}^o$ = nonsymmetric matrix
D^o_{ij} = diffusion coefficients based on volume-average velocity, Equation (1)
$\mathcal{D}_{ij}$ = binary diffusivity for mixtures of species i and j
E_{ij} = inverse matrix of diffusion coefficients and mass-density ratio
F_{ik} = matrix of restraints on integration constants, Equation (18)
M_{il} = integration constants, Equation (20)
n_i = mass flux = $\rho_i v_i$, Equation (1)
R = ratio of r-th flux
t = time
$\overline{V}_i$ = partial specific volume
v^o = volume-average velocity, Equation (1)
y = combined cell coordinate, Equation (7)
z = cell coordinate, Equation (2)

Greek Letters

α_i = reduced flux, Equation (14)
λ = constant, a function of R, Equation (11)
σ_i = root of polynomial, Equation (16)
ρ_i = mass density of component i, Equation (1)
χ_i = reduced mass density, Equation (8).

Subscripts

i, j, k, l, m = components of the mixture

LITERATURE CITED

1. Arnold, J. H., *Trans. Am. Inst. Chem. Engrs.*, **40**, 361 (1944).
2. Dunlop, P. J., and L. J. Gosting, *J. Am. Chem. Soc.*, **77**, 5238 (1955).
3. Fujita, H., and L. J. Gosting, *ibid.*, **78**, 1099 (1956).
4. Onsager, Lars, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).
5. Fitts, D. D., "Nonequilibrium Thermodynamics," pp. 78-82, McGraw-Hill, New York (1962).
6. de Groot, S. R., and P. Mazur, "Non-Equilibrium Thermodynamics," pp. 239-246, North-Holland (1962).
7. Hildebrand, F. B., "Advanced Calculus for Engineers," pp. 21-26, Prentice-Hall, Englewood Cliffs, New Jersey (1949).
8. Flynn, L. W., and George Thodos, *A.I.Ch.E. Journal*, **8**, 362 (1962).
9. Monchick, L., and E. A. Mason, *J. Chem. Phys.*, **35**, 1676 (1961).
10. Lee, C. Y., and C. R. Wilke, *Ind. Eng. Chem.*, **46**, 2381 (1954).
11. Lewis, W. K., and L. Squires, *ibid.*, **29**, 109 (1937).
12. Curtiss, C. F., and J. O. Hirschfelder, *J. Chem. Phys.* **17**, 550 (1949).

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