Unsteady Multicomponent Diffusional Evaporation

HSIEN-WEN HSU and R. BYRON BIRD
University of Wisconsin, Madison, Wisconsin

The unsteady diffusion-controlled evaporation of a pure fluid into a multicomponent mixture is studied by a boundary-layer method. An expression is obtained for the volume of vapor produced by the evaporating species as a function of time. It is shown that the result can be interpreted in terms of an effective diffusivity of the type proposed by Wilke and by Stewart. It is further demonstrated that the boundary-layer method predicts a sweep-diffusion effect.

A liquid 1 is placed in a long vertical tube in the region below $z = 0$ as shown in Figure 1. In the region above $z = 0$ there is initially a vapor containing species 2, 3, ... n; the initial composition in the gas is given by the mole fractions x^0_2, x^0_3, ... x^0_n. At time $t = 0$ liquid 1 begins to evaporate. It is desired to obtain information about the rate of evaporation if the system is maintained at constant temperature and pressure, and if the vapor of 1 is heavier than that of the gas mixture so that no free convection effects will occur. It is also desired to investigate the extent to which components 2, 3, ... n tend to separate as a result of the diffusion of species 1 through the mixture. It is presumed that 2, 3, ... n are all ideal gases and all insoluble in 1.

First the problem is reviewed for the two-component problem of 1 evaporating into pure 2. Then a boundary-layer solution for the binary problem is given. After that the same boundary-layer technique is applied to the multicomponent problem. Then these results are used to draw some conclusions regarding multicomponent diffusivities and sweep diffusion.

EXACT SOLUTION FOR THE BINARY PROBLEM

The equations describing the diffusion in this system are the equations of continuity (*2*) of 1 and 2:

$$\frac{\partial c_1}{\partial t} = -\frac{\partial N_1}{\partial z};\ \frac{\partial c_2}{\partial t} = -\frac{\partial N_2}{\partial z} \quad (1, 2)$$

and the expression for the molar flux[2] of 1 (with respect to a coordinate system fixed with respect to the stationary liquid-vapor interface):

$$N_1 = -c\mathcal{D}_{12}(\partial x_1/\partial z) + x_1(N_1+N_2) \quad (3)$$

When Equations (1) and (2) are added, and when use is made of the constancy of c for an ideal gas at constant temperature and pressure, it is concluded that (N_1+N_2) does not vary with z. Because there is no motion of 2 at $z = 0$, one can evaluate N_1 at $z = 0$ from Equation (3):

$$N_{10} = -\frac{c\mathcal{D}_{12}}{1-x_{10}}\left.\frac{\partial x_1}{\partial z}\right|_{z=0} \quad (4)$$

and this quantity must then be (N_1+N_2) at any position in the tube. Substitution of Equation (3) into Equation (1) and the use of Equation (4) for (N_1+N_2) gives

$$\frac{\partial x_1}{\partial t} = \mathcal{D}_{12}\frac{\partial^2 x_1}{\partial z^2}\Bigg| + \frac{\mathcal{D}_{12}}{1-x_{10}}\frac{\partial x_1}{\partial z}_{z=0}\frac{\partial x_1}{\partial z} \quad (5)$$

This equation has been solved by Arnold (*1*, 2) with the initial and boundary conditions: $x_1 = x_{10}$ at $z = 0$, and $x_1 = 0$ at $z = \infty$ and at $t = 0$. The solution is

$$\frac{x_1}{x_{10}} = \frac{1 - \operatorname{erf}\left(\frac{z}{\sqrt{4\mathcal{D}t}} - \phi\right)}{1 + \operatorname{erf}\phi} \quad (6)$$

where ϕ is a function of x_{10} given by

$$\frac{1}{x_{10}} = 1 + \frac{1}{\sqrt{\pi}\,(1+\operatorname{erf}\phi)\,\phi\exp\phi^2} \quad (7)$$

A few values of ϕ (x_{10}) are shown in Table 1.

By inserting this solution into Equation (5) one can get N_{10} and hence also the volume of species 1 produced up to time t:

$$V_1 = \int_0^t \frac{N_{10}\,S}{c}\,dt = S\,\phi\sqrt{4\mathcal{D}_{12}\,t} \quad (8)$$

which was obtained by Arnold (*1*). If the last term in Equation (5) had been omitted (that is, if Fick's second law of diffusion had been used), then instead of Equation (8) one would have gotten

$$V_1^{\mathrm{Fick}} = Sx_{10}\sqrt{4\mathcal{D}_{12}\,t/\pi} \quad (9)$$

Hence one can rewrite Equation (8). Thus (*1*)

$$V_1 = Sx_{10}\sqrt{\mathcal{D}_{12}\,t/\pi}\cdot\psi^{(2)} \quad (10)$$

where $\psi^{(2)} = \phi\sqrt{\pi}/x_{10}$; the function $\psi^{(2)}$, also shown in Table 1, gives the deviation from Fick's second law of the bulk flow.

BOUNDARY-LAYER SOLUTION FOR THE BINARY PROBLEM (5)

As the starting point for a boundary-layer development one takes the integrated form of Equation (1)

$$\frac{N_{10}}{c} = \frac{d}{dt}\int_0^\infty x_1\,dz \quad (11)$$

and Equation (3) written for $z = 0$ [that is Equation (4)]. When one equates these two expressions for N_{10}

$$\frac{d}{dt}\int_0^\infty x_1 dz = -\frac{\mathcal{D}_{12}}{1-x_{10}}\left.\frac{\partial x_1}{\partial z}\right|_{z=0} \quad (12)$$

Note that the same result could have been obtained by integrating Equation (5) over z from $z = 0$ to $z = \infty$.

One now assumes a concentration profile of the form

$$x_1/x_{10} = f(z/\delta) = f(\zeta) \qquad \zeta \leqq 1 \quad (13)$$

$$x_1/x_{10} = 0 \qquad \zeta \leqq 1 \quad (14)$$

where $\delta = \delta(t)$ is the concentration boundary-layer thickness. The function $f(\zeta)$ has the properties $f(0) = 1$, $f(1) = 0$, and $f'(1) = 0$.

Substitution of the above approximate profiles into Equation (12) gives

$$x_{10}\,\delta\int_0^1 f\,d\zeta = \frac{(\mathcal{D}_{12}x_{10}/\delta)}{1-x_{10}}\,(-f'(0)) \quad (15)$$

where $\delta = d\delta/dt$ and $f' = df/d\zeta$. This differential equation for $\delta(t)$ can be

---

Hsien-Wen Hsu is at Purdue University, Lafayette, Indiana.

Table 1

x_{10}	ϕ	$\psi^{(2)} = \phi\sqrt{\pi}/x_{10}$	$\psi^{(2)}_{\text{boundry layer}}$ $(1-\zeta)^2$	$\psi^{(2)}_{\text{boundry layer}}$ $(1-2\zeta+2\zeta^3-\zeta^4)$
0.00	0.0000	1.000	1.02	0.97
0.25	0.1562	1.108	1.18	1.12
0.50	0.3578	1.268	1.44	1.36
0.75	0.6618	1.564	2.04	1.93
1.00	∞	∞	∞	∞

integrated, with the initial condition $\delta(0) = 0$, to give

$$\delta = \sqrt{\frac{2\mathcal{D}_{12}t(-f'(0))}{(1-x_{10})\int_0^1 f d\zeta}} \qquad (16)$$

Once $\delta(t)$ is known, one can get the concentration profiles from Equation (13) and also the volume of 1 produced, namely

$$V_1 = Sx_{10}\sqrt{\frac{(\int_0^1 f d\zeta)(-f'(0))\cdot 2\mathcal{D}_{12}t}{(1-x_{10})}} \qquad (17)$$

Comparison with Equation (10) reveals that

$$\psi_{\text{bdry lyr}}^{(2)} = \sqrt{\frac{(\int_0^1 f d\zeta)(-f'(0))\pi}{2(1-x_{10})}} \qquad (18)$$

The values of $\psi_{\text{boundary layer}}^{(2)}$ for several trial functions $f(\zeta)$ are shown in Table 1 next to the values of $\psi^{(2)}$ obtained by the exact solution. It is seen that the dependence of $\psi_{\text{boundary layer}}^{(2)}$ on x_{10} is somewhat too strong.

BOUNDARY-LAYER SOLUTION FOR THE MULTICOMPONENT PROBLEM (5)

The equations describing the n-component system are the n equations of continuity:

$$\frac{\partial c_i}{\partial t} = -\frac{\partial N_i}{\partial z} \qquad i = 1,2,\ldots n \quad (19)$$

and the Stefan-Maxwell Equations (3) which describe the interrelation of the molar fluxes with the concentration gradients:

$$\partial x_i/\partial z = \sum_{j=1}^{n} (c\mathcal{D}_{ij})^{-1}(x_i N_j - x_j N_i) \qquad i = 1,2,\ldots n \quad (20)$$

As the starting point for the boundary-layer development one takes the integrated form of Equation (19) for component 1 and the Stefan-Maxwell equations written for $z = 0$:

$$\frac{N_{10}}{c} = \frac{d}{dt}\int_0^\infty x_1\,dz \qquad (21)$$

$$\frac{N_{10}}{c} = -\left[\sum_{i=2}^{n}\frac{x_{i0}}{\mathcal{D}_{1i}}\right]^{-1}\frac{\partial x_1}{\partial z}\bigg|_{z=0} \qquad (22)$$

$$\frac{N_{10}}{c} = +\left[\frac{\mathcal{D}_{1j}}{x_{j0}}\right]\frac{\partial x_j}{\partial z}\bigg|_{z=0} \qquad j = 2,3,\ldots n \quad (23)$$

in which the x_{j0} are the vapor phase mole fractions at the gas-liquid interface, assumed to be independent of time. It is not known how good this assumption is; furthermore the interfacial condition will depend on the mechanism for forming the interface.

One now uses the following concentration profiles:

$$\frac{x_1}{x_{10}} = f_1\left(\frac{z}{\delta_1}\right) = f_1(\zeta_1) \qquad \zeta_1 \leq 1 \quad (24)$$

$$\frac{x_j^0 - x_j}{x_j^0 - x_{j0}} = f_j\left(\frac{z}{\delta_j}\right) = f_j(\zeta_j) \qquad \zeta_j \leq 1 \qquad j = 2,3,\ldots n \quad (25)$$

where x_j^0 is the concentration of species j at $t = 0$ in the gas mixture; that is each species has its own concentration boundary-layer thickness $\delta_j(t)$, and the authors specify that $f_j(0) = 1$, $f_j(1) = 0$, and $f'_j(1) = 0$ for all j.

The introduction of $f_1(\zeta_1)$ into Equations (21) and (22) gives two expressions for N_{10}/c. When these are equated one gets a differential equation for $\delta_1(t)$, which yields

$$\delta_1 = \sqrt{\frac{2(-f_1'(0))t}{\int_0^1 f_1 d\zeta}\left[\sum_{i=2}^{n}\frac{x_{i0}}{\mathcal{D}_{1i}}\right]^{-1/2}} \qquad (26)$$

A similar operation on Equations (21) and (23) gives

$$\delta_j = \sqrt{\frac{2(-f_j'(0))^2 t}{(-f_1'(0))\int_0^1 f_1 d\zeta_1}\,\mathcal{D}_{1j}\left[\sum_{i=2}^{n}\frac{x_{i0}}{\mathcal{D}_{1i}}\right]^{1/2}\left(\frac{x_j^0 - x_{j0}}{x_{j0}x_{10}}\right)} \qquad (27)$$

Once these boundary-layer thicknesses are known, one may get the concentration profiles from Equations (24) and (25). By the same procedure as in the previous section one can find the volume component 1 produced:

$$V_1 = Sx_{10}\sqrt{(\int_0^1 f_1 d\zeta_1)(-f_1'(0))\cdot 2t}\left[\sum_{i=2}^{n}\frac{x_{i0}}{\mathcal{D}_{1i}}\right]^{-1/2} = Sx_{10}\sqrt{4\mathcal{D}_{12}t/\pi}\cdot\psi_{\text{bdry lyr}}^{(n)} \qquad (28)$$

This last relation serves to define a $\psi^{(n)}$ analogous to the $\psi^{(2)}$ of Equation (10). There is little reason to believe that the result in Equation (28) would give quantitative results any better than those in Equation (18).

REMARKS ABOUT THE EFFECTIVE DIFFUSIVITY

If it be assumed that the function $f(\zeta)$ in Equations (13) and (14) is the same as the function $f_1(\zeta_1)$ in Equations (24) and (25), then comparison of Equations (18) and (28) shows that

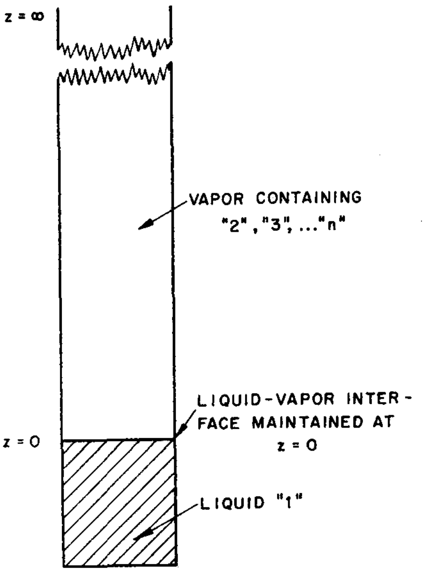

Fig. 1. Evaporation of "1" into a gaseous mixture of n-1 components.

Table 2. Values of the Quantity Δ.

	$R = ½$				$R = 2$		
ζ_j / x_{10}	0.1	0.2	0.5	ζ_j / x_{10}	0.1	0.2	0.5
0.1	0.010	0.022	0.078	0.1	−0.018	−0.041	−0.143
0.2	0.018	0.039	0.125	0.2	−0.030	−0.064	−0.206
0.5	0.032	0.066	0.179	0.5	−0.026	−0.053	−0.143
0.9	0.029	0.059	0.147	0.9	−0.001	−0.002	−0.005

$$\cdot\ \frac{\psi_{\text{bdry lyr}}^{(n)}}{\psi_{\text{bdry lyr}}^{(2)}} = \left[\frac{\dfrac{1-x_{10}}{\mathcal{D}_{12}}}{\displaystyle\sum_{i=2}^{n}\frac{x_{i0}}{\mathcal{D}_{1i}}}\right]^{+1/2} \qquad (29)$$

If it further be assumed that $x_{20}/x_2^0 = x_{30}/x_3^0 = \ldots\ldots = x_{n0}/x_n^0$, then Equation (29) assumes the very simple form

$$\frac{\psi_{\text{bdry lyr}}^{(n)}}{\psi_{\text{bdry lyr}}^{(2)}} = \left[\frac{\dfrac{1}{\mathcal{D}_{12}}}{\displaystyle\sum_{i=2}^{n}\frac{x_i^0}{\mathcal{D}_{1i}}}\right]^{+1/2} \qquad (30)$$

One can hope that although the individual $\psi_{\text{boundary layer}}^{(k)}$ are not very accurate, the ratio may be rather good. If one assumes that the ratio of boundary-layer quantities is exactly the same as the ratio of rigorously calculated quantities, then Equation (28) becomes

$$V_1 = Sx_{10}\sqrt{4\mathcal{D}_{1,\text{eff}}t/\pi}\cdot\psi^{(2)} \qquad (31)$$

where $\psi^{(2)}$ is the function of x_{10} given in Table 1 and $\mathcal{D}_{1,\text{eff}}$ is defined by

$$\mathcal{D}_{1,\text{eff}} = \frac{1-x_{10}}{\displaystyle\sum_{j=2}^{n}\frac{x_{j0}}{\mathcal{D}_{1j}}} = \frac{1}{\displaystyle\sum_{j=2}^{n}\frac{x_j^0}{\mathcal{D}_{1j}}} \qquad (32)$$

That is Equation (31) has exactly the same form as the binary relation in Equation (10), when the effective diffusivity $\mathcal{D}_{1,\text{eff}}$, defined by Equation (32), is used.

It is interesting to note that the effective diffusivity $\mathcal{D}_{1,\text{eff}}$ defined above is exactly the same as that proposed by Wilke (*8*) by a development different from that given above. Furthermore Fairbanks and Wilke (*4*) have found that the above definition of $\mathcal{D}_{1,\text{eff}}$ gave a very good description of the evaporation rate of ethyl propionate into air-hydrogen mixtures and of toluene into hydrogen-argon mixtures.

It is also informative to compare $\mathcal{D}_{1,\text{eff}}$ with the $\mathcal{D}_{1m}$ proposed by Stewart (*7*), which is defined by

$$N_1 = -c\mathcal{D}_{1m}(\partial x_1/\partial z) + x_1\sum_{j=1}^{n} N_j \qquad (33)$$

That is one regards $\mathcal{D}_{1m}$ as the binary diffusivity of 1 into a mixture consisting of all other components. When Equation (33) is solved for $(\partial x_1/\partial z)$ and this quantity equated to $(\partial x_i/\partial z)$ in Equation (20) one obtains the relation between $\mathcal{D}_{1m}$ and the usual binary $\mathcal{D}_{ij}$:

$$\mathcal{D}_{1m}(z,t) = \frac{N_1 - x_1\sum\limits_{j=1}^{n} N_j}{\displaystyle\sum_{j=2}^{n}\left(\frac{N_1x_j - N_jx_1}{\mathcal{D}_{1j}}\right)} \qquad (34)$$

In the evaporating system considered here $\mathcal{D}_{1m}$ is clearly a function of z and t. At $z = 0$ the molar fluxes of components $2,3,\ldots.n$ are zero, and hence $\mathcal{D}_{1m}(0,t)$ is exactly the same as $\mathcal{D}_{1,\text{eff}}$ defined in Equation (32). Hence the boundary-layer treatment (with f_1 selected to be the same function as f) gives the same result as would be obtained by treating the multicomponent problem as a binary one and using $\mathcal{D}_{1m}$ evaluated at $z = 0$.

The diffusivity $\mathcal{D}_{1m}$ has recently been found by the authors to be useful for describing some three component diffusion problems with chemical reactions (*6*).

REMARKS ABOUT THE SWEEP-DIFFUSION EFFECT

It is now desired to establish some measure of the extent to which the initial relative concentration is disturbed by the diffusion of component 1 through the mixture. If there were no sweep diffusion, then the initial relative concentration would be preserved; the concentration of j at any position and any time would just be $x_j^0(1-x_1)$, where x_1 is the composition at the same position and the same time. Hence the quantity

$$\Delta = \frac{x_j - x_j^0(1-x_1)}{x_j} \qquad (35)$$

will give the fractional error one would make by assuming there is no sweep diffusion. If, as above, one assumes $f_1 = f_2 = \ldots f_n = f$ and that all x_{j0}/x_j^0 are the same, then one finds from Equations (26) and (27) that

$$R \equiv \delta_j/\delta_1 = (\mathcal{D}_{1j}/\mathcal{D}_{1,\text{eff}}) \qquad (36)$$

and that Equation (35) can be written

$$\Delta = \frac{x_{10}[f(\zeta,R) - f(\zeta_j)]}{1 - x_{10}f(\zeta_j)} \qquad (37)$$

A few sample values of $\Delta = \Delta(x_{10}, R, \zeta_j)$ calculated for $f(\zeta_j) = (1-\zeta_j)^2$ are given in Table 2, to illustrate the order of magnitude of the sweep diffusion effect.

CONCLUSIONS

The boundary-layer treatment gives a new interpretation to the effective diffusivity formula as proposed earlier by Wilke and tested experimentally by Fairbanks and Wilke. It further gives information as to the order of magnitude of the sweep-diffusion effect. Unfortunately there seem to be no experimental measurements of the concentration profiles in evaporation systems to allow any comparisons to be made with measured separations.

ACKNOWLEDGMENT

H. W. Hsu wishes to thank the Wisconsin Alumni Research Foundation for financial support during this work.

NOTATION

c = total molar concentration of mixture
c_i = molar concentration of i-th species
$\mathcal{D}_{ij}$ = binary diffusivity of system i-j
$\mathcal{D}_{1,\text{eff}}$ = effective binary diffusivity for i in evaporating system
$\mathcal{D}_{1m}$ = effective binary diffusivity for i in a mixture
f = assumed form for concentration profile
N_i = molar flux of species i with respect to a stationary coordinate system
R = ratio of boundary-layer thicknesses
S = surface area exposed for evaporation
t = time elapsed since beginning of evaporation
V_1 = volume of vapor of 1 produced up to time t
x_i = mole fraction of species i
z = distance in gas phase from the liquid-vapor interface

Greek Letters

$\delta(t)$ = instantaneous concentration boundary layer thickness
Δ = sweep diffusion factor
ζ = z/δ = dimensionless distance
π = 3.14159 . . . . .
ϕ = Arnold's evaporation function
$\psi^{(j)}$ = correction factor in a j-component system
0 = subscript indicating evaluated at $z = 0$; also superscript indicating evaluated at $t = 0$

LITERATURE CITED

1. Arnold, J. H., *Trans. Am. Inst. Chem. Engrs.*, **40**, 361 (1944).
2. Bird, R. B., "Theory of Diffusion," Chapter in Vol. I of "Advances in Chemical Engineering," p. 220, Academic Press, New York (1956).
3. ———, W. E. Stewart, and E. N. Lightfoot, "Notes on Transport Phenomena," p. 353, Wiley, New York (1958).
4. Fairbanks, D. F., and C. R. Wilke, *Ind. Eng. Chem.*, **42**, 471 (1950).
5. Hsu, H. W., Ph.D. thesis, Univ. Wisconsin, Madison, Wisconsin (1959).
6. ———, and R. B. Bird, *A.I.Ch.E. Journal*, to be published.
7. Stewart, W. E., unpublished analysis (see also Reference 3, pp. 390-391).
8. Wilke, C. R., *Chem. Eng. Progr.*, **46**, 95 (1950).

Manuscript received October 29, 1959; revision received February 1, 1960; paper accepted February 3, 1960.