Int. J. Heat Mass Transfer. Vol. 36, No. 2, pp. 347–351, 1993
Printed in Great Britain

0017-9310/93 $6.00 + 0.00

Convective diffusion near a consolute point

THOMAS F. FULLER and JOHN NEWMAN

Materials Sciences Division, Lawrence Berkeley Laboratory, and Department of Chemical Engineering, University of California, Berkeley, CA 94720, U.S.A.

(*Received* 12 *September* 1991 *and in final form* 10 *March* 1992)

Abstract—The equations for convective diffusion to a rotating disk are solved numerically for the case where a consolute point is found between the concentration in the bulk and that at the surface. A singular-perturbation expansion is presented for the condition where the bulk concentration is nearly equal to the consolute-point composition. Results are compared to Levich's solution for constant properties and with his analysis of an experimental system.

INTRODUCTION

THE DRIVING force for diffusion is the gradient of chemical potential of the diffusing species. Usually, one defines the diffusion coefficient in terms of a gradient in concentration. Thus, in the vicinity of a consolute point, the temperature and composition where two liquid phases become completely miscible, this diffusion coefficient becomes zero. Krichevski and Tshekhanskaya [1] and Vitagliano *et al.* [2] observed this experimentally in the water–triethylamine system. Krichevski and Tshekhanskaya also measured the rate of dissolution of a rotating disk of terephthalic acid in the water–triethylamine system. Levich [3] examined this system theoretically, accounting for variations in the diffusion coefficient with the concentration of triethylamine as well as the effects of variable physical properties on the hydrodynamics. However, Levich made a number of untenable assumptions, which call to question the validity of his conclusions. Although the behavior of transport properties at a consolute point is often discussed in the literature (see Sengers [4] and Cussler [5] for example), convective–diffusion problems when a consolute point is present in the system have not been addressed other than in Levich's original work.

Our objective is to re-examine convective diffusion to a rotating disk theoretically, without arbitrary assumptions, and to elucidate better the behavior of the system in the region of the consolute point. In the analysis below we do not consider variations in the density or viscosity. Clearly, variations in physical properties affect the hydrodynamics and convective diffusion to the disk. Nevertheless, these effects are omitted here for two reasons. First, Hsueh and Newman [6], and others [7, 8] have treated variable physical properties previously. Second, variations in the hydrodynamics will have only a secondary effect on convective diffusion near the consolute point and will add little to our understanding of the behavior in this region. The principal effect we wish to investigate is the consequence of a zero diffusion coefficient at a point in the flow and mass-transfer process.

ANALYSIS

The rotating disk is uniformly accessible to mass transfer. The convective diffusion equation in terms of the mass fraction of reacting species in a binary fluid is [9]

$$\rho v_z \frac{\mathrm{d}\omega}{\mathrm{d}z} = \frac{\mathrm{d}}{\mathrm{d}z}\left(\rho D \frac{\mathrm{d}\omega}{\mathrm{d}z}\right). \tag{1}$$

The general boundary conditions considered are

$$\omega = \omega_o \quad \text{at } z = 0$$

$$\omega = \omega_\infty \quad \text{at } z = \infty.$$

At high Schmidt number, the diffusion layer is much smaller than the hydrodynamic boundary layer, and the velocity normal to the surface of the disk may be accurately written as [3]

$$v_z = -Kz^2 = -a\Omega^{3/2}\nu^{-1/2}z^2. \tag{2}$$

With the dimensionless variable

$$\xi = \left(\frac{K}{3D_o}\right)^{1/3} z \tag{3}$$

where ξ can be regarded as the axial distance z divided by the thickness of the diffusion layer and D_o is the value of the diffusion coefficient at infinite dilution, equation (1) becomes

$$\xi^2 \frac{\mathrm{d}\omega}{\mathrm{d}\xi} = \frac{\mathrm{d}}{\mathrm{d}\xi}\left(\frac{D}{3D_o}\frac{\mathrm{d}\omega}{\mathrm{d}\xi}\right). \tag{4}$$

The implicit solution to equation (4) is

$$\Theta = \frac{\omega-\omega_o}{\omega_\infty-\omega_o} = \frac{\displaystyle\int_0^{\xi} \frac{D_o}{D}\exp\left\{\int_0^{\xi} -\frac{3D_o}{D}\xi^2\,\mathrm{d}\xi\right\}\mathrm{d}\xi}{\displaystyle\int_0^{\infty} \frac{D_o}{D}\exp\left\{\int_0^{\xi} -\frac{3D_o}{D}\xi^2\,\mathrm{d}\xi\right\}\mathrm{d}\xi}. \tag{5}$$

For constant diffusion coefficients, Levich gave the solution

NOMENCLATURE

a	constant, 0.51023
A	$\mathrm{d}W/\mathrm{d}x$ at $x = 0$
A^*_{12}	Margules constant
B	constant in equation (16)
B^*_{112}	Margules constant
D	diffusion coefficient [$\mathrm{cm}^2\,\mathrm{s}^{-1}$]
D_c	parameter used in equation (9)
$\tilde{G}$	Gibbs energy [$\mathrm{J\,mol}^{-1}$]
j	dimensionless flux defined in equation (24)
K	parameter in equation (2)
n	mass flux [$\mathrm{g\,cm}^{-2}\,\mathrm{s}^{-1}$]
v_z	velocity normal to disk [$\mathrm{cm\,s}^{-1}$]
W	dimensionless concentration
x	distorted dimensionless distance variable
x_i	mole fraction
z	distance from surface of disk [cm].

Greek symbols

Γ	gamma function
γ_i	activity coefficient
ε	parameter defined in equation (13)
Θ	dimensionless concentration
ν	kinematic viscosity [$\mathrm{cm}^2\,\mathrm{s}^{-1}$]
ξ	dimensionless distance
ρ	density [$\mathrm{g\,cm}^{-3}$]
Ω	rotation speed [$\mathrm{rad\,s}^{-1}$]
ω	mass fraction.

Subscripts

∞	far from disk
o	surface of disk, infinite dilution
c	critical or consolute value.

Superscripts

$-$	inner region variable
$\sim$	outer region variable.

$$\Theta = \frac{1}{\Gamma(4/3)}\int_0^{\xi} \mathrm{e}^{-x^3}\,\mathrm{d}x. \tag{6}$$

When the diffusion coefficient is a function of concentration, equation (5) can be integrated numerically, iteration being necessary because D depends on ω. For a solution with a consolute point, however, the diffusion coefficient becomes zero at some value of ξ, and equation (5) cannot be integrated directly.

The diffusion coefficient based on a concentration driving force can be related to a diffusion coefficient based on a chemical-potential driving force through an activity correction

$$D = D_o\left\{1+\frac{\mathrm{d}\ln\gamma_1}{\mathrm{d}\ln x_1}\right\}. \tag{7}$$

If the Gibbs energy is expressed by a three-suffix Margules equation, then the activity coefficient for a two-component solution is given by

$$\ln\gamma_1 = \frac{A^*_{12}}{RT}x_2^2+\frac{B^*_{112}}{RT}x_2^2(4x_1-1). \tag{8}$$

At the consolute point

$$\frac{\partial^2\tilde{G}}{\partial x_1^2} = \frac{\partial^3\tilde{G}}{\partial x_1^3} = 0.$$

If the concentration at the consolute point is known, these relationships allow the evaluation of the two constants in equation (8). Reference [1] gives the consolute point for the water–triethylamine system as 17°C and 0.261 mass fraction of triethylamine. These values are not in exact agreement with others reported in the literature [10] but suffice to illustrate our technique. Using a three-suffix Margules equation and the molar masses of the components, it is evident that the diffusion coefficient is zero at the consolute point. Additionally, one sees that in the vicinity of the consolute point the diffusion coefficient may be approximated by

$$D = D_c(\omega-\omega_c)^2. \tag{9}$$

Similar behavior is observed in other systems [11].

In order to solve the convective diffusion equation in the vicinity of the consolute point, we should formulate the problem so that the singularity is removed. The flux near the consolute point is

$$\frac{n}{\rho} = -D\frac{\mathrm{d}\omega}{\mathrm{d}z}+v_c\omega_c. \tag{10}$$

Variations in the velocity and flux are small compared to variations in the diffusion coefficient and concentration in this region; and, assuming that the diffusion coefficient is of the form given in equation (9), we conclude that in the vicinity of the consolute point

$$z-z_c \sim \frac{D_c}{3}(\omega-\omega_c)^3 \tag{11}$$

where z_c is the distance from the surface of the disk to the consolute point, also called the critical distance.

The problem was reformulated with the following variables

$$x = \frac{-(z-z_c)^{1/3}}{z_c^{1/3}} \quad \text{and} \quad W = 1-\frac{\omega}{\omega_c}. \tag{12}$$

Thus equation (1) becomes

$$\varepsilon(1-x^3)^2\frac{\mathrm{d}W}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\dfrac{D}{D_c}}{\omega_c^2x^2}\frac{\mathrm{d}W}{\mathrm{d}x}\right) \tag{13}$$

where ε is defined by

$$\varepsilon = \frac{3Kz_c^3}{\omega_c^2 D_c}.$$

This can be split into two first-order differential equations

$$\frac{\mathrm{d}P}{\mathrm{d}x} = \varepsilon(1-x^3)^2 \frac{\omega_c^2 x^2}{\dfrac{D}{D_c}} P, \quad \frac{\mathrm{d}W}{\mathrm{d}x} = \frac{\omega_c^2 x^2}{\dfrac{D}{D_c}} P \tag{14}$$

and solved as an initial value problem with the boundary conditions

$$W = 0, \quad P = P_o \quad \text{at } x = 0.$$

Equations (14) were solved using a Runge–Kutta routine. ε was fixed, corresponding to a given critical distance. At $x = 0$ the value of P_o was adjusted until the calculated surface concentration was zero. Then with the known value of P_o, the equations were integrated from $x = 0$ to $-\infty$ to determine the value for the concentration far from the disk.

Assuming equation (9) is valid near the consolute point does not restrict the validity of the method. It is important that the diffusion coefficient does vary as shown in equation (9) only in the vicinity of the consolute point. In the analysis below, we assume that the functional form of equation (9) is valid over all compositions only to illustrate more clearly our method without the introduction of detailed physical-property variations, which would restrict our results to only one physical or chemical system. Figure 1 shows the concentration profiles plotted against ξ, which is related to x by

$$\xi = (1-x^3)\left(\frac{\varepsilon}{9}\right)^{1/3}. \tag{15}$$

As the bulk concentration is raised, the consolute point moves closer to the surface of the disk, and the slope $\mathrm{d}W/\mathrm{d}x$ at this critical distance increases. For values of $\varepsilon > 2$, solutions were not possible. We wished to investigate the behavior when the bulk concentration was arbitrarily close to that of the consolute composition, and to determine the maximum value of ε.

PERTURBATION ANALYSIS

As ω_∞ is lowered toward the consolute-point composition, ε increases, and $\mathrm{d}W/\mathrm{d}x$ at $x = 0$ appears to be approaching zero. Suppose there is a value of ε for which $\mathrm{d}W/\mathrm{d}x = 0$ at $x = 0$. The solution in the outer region would then be $W = 0$ for $x < 0$. For $x > 0$ look for a solution of the form

$$W = Ax + Bx^2 + \cdots \tag{16}$$

near $x = 0$. Substituting into the differential equation and equating equal powers of x gives

$$4AB = \varepsilon.$$

If ε approaches a limit, somewhat less than 1.8, then B approaches infinity as A goes to zero. The region where

$$Ax \approx Bx^2$$

defines an inner region (in the sense of a singular-perturbation expansion). Let

$$\bar{x} = \frac{x\varepsilon}{4A^2} \quad \text{and} \quad \bar{W} = \frac{\varepsilon}{4A^3} W. \tag{17}$$

The problem in the inner region becomes

$$\left(1 - \left(\frac{4A^2\bar{x}}{\varepsilon}\right)^3\right)^2 4\frac{\mathrm{d}\bar{W}}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}\bar{x}}\left(\frac{\bar{W}^2}{\bar{x}^2}\frac{\mathrm{d}\bar{W}}{\mathrm{d}x}\right) \tag{18}$$

with the boundary conditions

$$\bar{W} = 0 \quad \text{and} \quad \frac{\mathrm{d}\bar{W}}{\mathrm{d}x} = 1 \quad \text{at } x = 0.$$

To a zeroth approximation, $\bar{W}$ satisfies

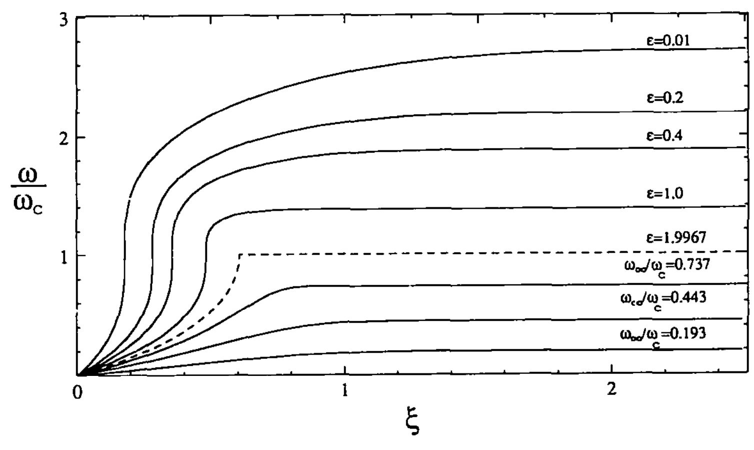

FIG. 1. Concentration profiles for bulk concentrations above, below, and at (dashed line) the consolute-point composition.

$$4\frac{\mathrm{d}\bar{W}}{\mathrm{d}\bar{x}} = \frac{\mathrm{d}}{\mathrm{d}\bar{x}}\left(\frac{\bar{W}^2}{\bar{x}^2}\frac{\mathrm{d}\bar{W}}{\mathrm{d}\bar{x}}\right) \tag{19}$$

with the implicit solution

$$\frac{16\bar{x}^3}{3} = 2\bar{W}^2 - \bar{W} + \frac{1}{4}\ln(1+4\bar{W}). \tag{20}$$

As $\bar{x} \to \infty$

$$\bar{W} \to \left(\frac{8}{3}\right)^{1/2}\bar{x}^{3/2}, \quad \text{or} \quad W \to \left(\frac{2\varepsilon}{3}\right)^{1/2} x^{3/2}. \tag{21}$$

The outer region satisfies equation (14). Let $\tilde{x} = x^{3/2}$, and the problem becomes

$$\frac{2\varepsilon}{3}(1-\tilde{x}^2)^2\frac{\mathrm{d}W}{\mathrm{d}\tilde{x}} = \frac{\mathrm{d}}{\mathrm{d}\tilde{x}}\left(\frac{W^2}{\tilde{x}}\frac{\mathrm{d}W}{\mathrm{d}\tilde{x}}\right). \tag{22}$$

The solution must match the inner solution as $\tilde{x} \to 0$

$$W \to \left(\frac{2\varepsilon}{3}\right)^{1/2}\tilde{x} \quad \text{as } \tilde{x} \to 0,$$

and

$$W = 1 \quad \text{at } \tilde{x} = 1.$$

Thus ε can be adjusted to give $W = 1$ at $\tilde{x} = 1$. The numerical solution gives $\varepsilon = 1.9967$. The concentration profile for this condition is the dashed line in Fig. 1.

MASS TRANSFER

The rate of mass transfer to the surface of the disk is given by

$$\frac{n}{\rho} = -D\left.\frac{\mathrm{d}\omega}{\mathrm{d}z}\right|_{z=0}. \tag{23}$$

The coordinate transformation allows us to define a dimensionless rate of mass transfer j and to express it as

$$j = \frac{1}{\omega_c}\left(\frac{3D_o}{K}\right)^{1/3}\left.\frac{\mathrm{d}\omega}{\mathrm{d}z}\right|_{z=0} = \frac{1}{(3\varepsilon)^{1/3}}\left.\frac{\mathrm{d}W}{\mathrm{d}x}\right|_{x=1}. \tag{24}$$

For a constant coefficient of diffusion, equation (6) shows that j takes the limiting form

$$j = \frac{1}{\omega_c}\left(\frac{3D_o}{K}\right)^{1/3}\left.\frac{\mathrm{d}\omega}{\mathrm{d}z}\right|_{z=0} = \frac{1}{\Gamma(4/3)}\frac{\omega_\infty}{\omega_c}. \tag{25}$$

Figure 2 shows the flux to the surface of the disk from our numerical calculation as compared with the theoretical line predicted by equation (25).

DISCUSSION

From Fig. 1, one observes that the consolute point moves farther from the surface of the disk as the bulk concentration is decreased and reaches a maximum distance $\xi = 0.6054$ when the bulk concentration equals the consolute composition. As the concentration becomes closer to ω_c from below the critical value, the slope of the concentration profile increases sharply and is infinite when the consolute point is reached.

At low values of ω_∞, the diffusion coefficient is nearly constant, and the profile approaches that predicted by equation (6). The rate of mass transfer is therefore identical to that predicted by equation (25), the dashed line in Fig. 2.

As the consolute point is approached, the diffusion coefficient becomes smaller, and the rate of mass transfer is reduced as seen by the leveling off of the solid line in Fig. 2. This does not continue indefinitely because there is a competing effect. As the bulk concentration is increased above the consolute-point composition, the diffusion coefficient increases sharply, and the critical distance moves toward the disk. Thus, the rate of mass transfer becomes larger than that predicted by equation (25). The leveling off was observed experimentally by Krichevski and

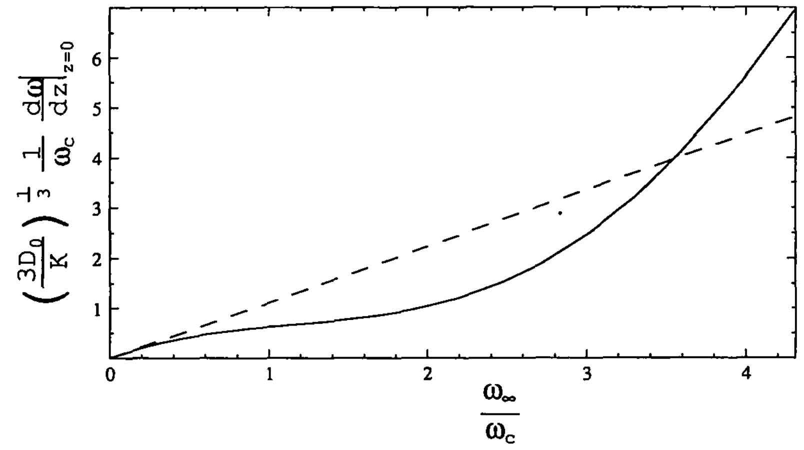

FIG. 2. Rate of mass transfer to the surface of a rotating disk. Dashed line is that predicted by equation (25) for a constant diffusion coefficient.

Tshekhanskaya [1] and predicted by Levich [3]. The concentration range of Krichevski and Tshekhanskaya's experiments was not large enough to verify the up-turn in the rate of mass transfer.

Levich arbitrarily divided the problem into three regions: (a) far from the disk the concentration was constant and equal to the bulk concentration; (2) close to the disk the concentration varied approximately linearly with distance from zero to the consolute composition; and (3) a thin intermediate region showed negligible resistance to mass transfer. Figure 1 clearly contradicts this picture.

Acknowledgements—This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

REFERENCES

1. I. R. Krichevski and Yu. V. Tshekhanskaya, Diffuziya i rastvoreniya v zhudkik rastvorak v kriticheskoy oblasty, *Zh. Fiz. Khim.* **30,** 2315–2326 (1956).
2. V. Vitagliano, R. Sartorio, E. Chiaravalle and O. Ortona, Diffusion and viscosity in water–triethylamine mixtures at 19 and 20°C, *J. Chem. Engng Data* **25,** 121–124 (1980).
3. V. G. Levich, *Physicochemical Hydrodynamics.* Prentice-Hall, Englewood Cliffs, New Jersey (1962).
4. J. V. Sengers, Transport processes near the critical point of gases and binary liquids in the hydrodynamic regime, *Ber. Busenges. Phys. Chem.* **76,** 234–249 (1972).
5. E. L. Cussler, *Multicomponent Diffusion.* Elsevier Scientific, Amsterdam (1976).
6. L. Hsueh and J. Newman, The effect of variable transport properties on mass transfer to a rotating disk, *Electrochim. Acta* **12,** 417–427 (1967).
7. R. Pollard and J. Newman, Silicon deposition on a rotating disk, *J. Electrochem. Soc.* **127,** 744–752 (1980).
8. A. Acrivos, Solution of the laminar boundary layer energy equations at high Prandtl numbers, *Physics Fluids* **3,** 657–658 (1960).
9. R. B. Bird, W. E. Stewart and E. N. Lightfoot, *Transport Phenomena.* Wiley, New York (1960).
10. F. Kohler and O. K. Rice, Coexistence curve of the triethylamine–water system, *J. Chem. Phys.* **26,** 1614–1618 (1957).
11. W. M. Clark and R. L. Rowley, The mutual diffusion coefficient of methanol–n-hexane near the consolute point, *A.I.Ch.E. Jl* **32,** 1125–1131 (1986).