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Convective Diffusion Near a Consolute Point

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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

Key words: variable physical properties, consolute temperature, critical point, singular perturbation
zero. Krichevskii and Tshekhanskaya [1] and Vitagliano et al. [2] observed this experimentally in the water-triethylamine system. Krichevskii 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 reexamine 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]

\[ \rho v \frac{dw}{dz} = d \left( \rho D \frac{dw}{dz} \right). \]  

The general boundary conditions considered are

\[ \omega = \omega_0 \text{ at } z = 0, \]
\[ \omega = \omega_\infty \text{ at } z = \infty. \]

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]

\[ v_z = -k z^2 = -\alpha \Omega^{3/2} \nu^{-1/2} z^2. \]  

With the dimensionless variable

\[ \xi = \left[ \frac{K}{3D_0} \right]^{1/3} z, \]

where \( \xi \) can be regarded as the axial distance \( z \) divided by the thickness of the diffusion layer and \( D_0 \) is the value of the diffusion coefficient at infinite dilution, equation 1 becomes

\[ \xi^2 \frac{d\omega}{d\xi} = d \left[ \frac{D}{3D_0} \frac{d\omega}{d\xi} \right]. \]
The implicit solution to equation 4 is

\[ \begin{align*}
\theta &= \frac{\omega - \omega^0}{\omega^\infty - \omega^0} = \frac{\int_0^\infty \frac{D^0}{D} \exp \left\{ \int_0^\xi - \frac{3D^0}{D} \xi^2 \right\} d\xi}{\int_0^\infty \frac{D^0}{D} \exp \left\{ \int_0^\xi - \frac{3D^0}{D} \xi^2 \right\} d\xi}.
\end{align*} \]

(5)

For constant diffusion coefficients, Levich gave the solution

\[ \theta = \frac{1}{\Gamma(4/3)} \int_0^\infty e^{-x^3} dx. \]

(6)

When the diffusion coefficient is a function of concentration, equation 5 can be integrated numerically, iteration being necessary because \( D \) depends on \( \omega \). For a solution with a consolute point, however, the diffusion coefficient becomes zero at some value of \( \xi \), 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

\[ D = D^0 \left\{ 1 + \frac{d \ln \gamma_1}{d \ln x_1} \right\}. \]

(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

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

(8)

At the consolute point
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. Figure 1 shows the activity factor for this system based on the 3-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

\[
D = D_c \left( \omega - \omega_c \right)^2.
\]

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

\[
\frac{n}{\rho} = -D \frac{d\omega}{dx} + v_c \omega_c.
\]

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
Figure 1. Activity-factor correction to the diffusion coefficient based on the 3-suffix Margules equation.
\[ z - z_c = \frac{D_c}{3} (\omega - \omega_c)^3, \quad (11) \]

where \( z_c \) is the distance from the surface of the disk to the consolute point, also called the critical distance. Therefore the \( z \) coordinate is stretched so that \( \omega \) is proportional to \( X \) near the consolute point:

\[ X^3 = z - z_c, \]

and equation 1 becomes

\[ \nabla_z \frac{d\omega}{dX} = \frac{d}{dX} \left( \frac{D}{3X^2} \frac{d\omega}{dX} \right). \quad (12) \]

Equation 12 was solved by breaking the problem into two regions: 1) from the consolute point to the surface of the disk, and 2) from the consolute point out to infinity. At the consolute point the concentration is known, but the position is not. The boundary conditions considered were

\[ \omega = \omega_c \text{ and } \frac{d\omega}{dX} = A \text{ at } X = 0, \]

\[ \omega = 0 \text{ at } X = -X_c. \]

The concentration at the surface was set equal to zero, representing the reaction of diffusing species at the surface of the disk with fast kinetics. For a given value of \( X_c \), the slope \( A \) at the critical point was adjusted to give a zero concentration at the surface. The bulk concentration was then determined by using the same value for the slope at the consolute point and integrating out to infinity. Equations 12 was
put in a form like equation 5 and solved by numerical integration, but this did not prove to be an efficient method.

The problem was reformulated with the following variables

\[ x = \frac{-X}{z_c^{1/3}}, \quad (13) \]

and

\[ W = 1 - \frac{\omega}{\omega_c}. \quad (14) \]

Thus equation 12 becomes

\[ \epsilon (1-x^3)^2 \frac{dW}{dx} = \frac{D}{D_c} \frac{D}{2\omega_c^2} \frac{d\omega}{dx}, \quad (15) \]

where \( \epsilon \) is defined by

\[ \epsilon = \frac{3Kz_c^3}{\omega_c^2 D_c}. \]

This can be split into two first-order differential equations

\[ \frac{dP}{dx} = \epsilon (1-x^3)^2 \frac{\omega_c^2}{D_c^2} \frac{x^2}{P}, \quad (16) \]

\[ \frac{d\omega}{dx} = \frac{\omega_c^2}{D_c^2} \frac{x^2}{P}, \quad (17) \]
and solved as an initial value problem with the boundary conditions

\[ w = 0, \quad P = P_0 \text{ at } x = 0. \]

Equations 16 and 17 were solved using a Runge-Kutta routine. \( \epsilon \) was fixed, corresponding to a given critical distance. At \( x=0 \) the value of \( P_\infty \) was adjusted until the calculated surface concentration was zero. Then with the known value of \( P_\infty \), the equations were integrated from \( x=0 \) to \( x=\infty \) to determine the value for the concentration far from the disk. The Runge-Kutta routine gave identical results to the previous method but was considerably more efficient.

Assuming equation 9 is valid near the consolute point does not restrict the validity of the method. It is important that the diffusion coefficient 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. The concentration profiles for \( \omega_\infty > \omega_c \) are shown in figure 2. Figure 3 shows the concentration profiles when the bulk concentration is below the consolute-point composition. In both cases the concentration is plotted against \( \xi \), which is related to \( x \) by

\[ \xi = (1-x^3) \left( \frac{\xi}{9} \right)^{1/3}. \]  

(18)

As the bulk concentration is raised, the consolute point moves closer to the surface of the disk, and the slope \( dW/dx \) at this critical
Figure 2. Concentration profiles for bulk concentrations above or at (dashed line) the consolute-point composition.
Figure 3. Concentration profiles for bulk concentrations below or at (dashed line) the consolute-point composition.
distance increases. Figure 4 shows the slope $dW/dx$ at the consolute point as a function of the concentration far from the disk. 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 $\varepsilon$.

**Perturbation Analysis**

Figure 5 shows $W$ against $x$, which is related to the distance from the critical point by equation 18. The stretching of the above formulation eliminated any sharp variation in this curve, in contrast to figure 2. As $\omega_0$ is lowered toward the consolute-point composition, $\varepsilon$ increases and $dW/dx$ at $x=0$ appears to be approaching zero. For $\varepsilon = 1.8$ the curve shows significant curvature. Suppose there is a value of $\varepsilon$ for which $dW/dx = 0$ 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

$$W = Ax + Bx^2 + \ldots$$

(19)

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

$$4AB = \varepsilon.$$ 

If $\varepsilon$ approaches a limit, somewhat greater than 1.8, then $B$ approaches infinity as $A$ goes to zero. The region where

$$Ax = Bx^2$$
Figure 4. The slope at the consolute point. Dashed line is the asymptote given in equation 28.
Figure 5. Concentration profiles as the bulk concentration approaches the consolute-point composition. Solid line is for the case when the bulk concentration nearly equals the consolute-point composition.
defines an inner region (in the sense of a singular-perturbation expansion). Let

\[ \frac{\bar{x}}{x} = \frac{x\epsilon}{4A^2}, \]  
\[ \frac{\bar{\omega}}{\omega} = \frac{\epsilon}{4A^3} \bar{\omega}. \]

The problem in the inner region becomes

\[ \left( 1 - \left( \frac{4A^2\bar{x}}{\epsilon} \right)^2 \right)^2 \frac{d\bar{w}}{d\bar{x}} = \frac{d}{d\bar{x}} \left( \frac{\bar{\omega}^2}{\bar{\omega}} \frac{d\bar{w}}{d\bar{x}} \right), \]

with the boundary conditions

\[ \bar{\omega} = 0 \text{ and } \frac{d\bar{w}}{d\bar{x}} = 1 \text{ at } \bar{x} = 0. \]

To a zeroth approximation, \( \bar{\omega} \) satisfies

\[ 4 \frac{d\bar{w}}{d\bar{x}} = \frac{d}{d\bar{x}} \left( \frac{\bar{\omega}^2}{\bar{\omega}} \frac{d\bar{w}}{d\bar{x}} \right), \]

with the implicit solution

\[ \frac{16\bar{x}^3}{3} = 2\bar{\omega}^2 - \bar{\omega} + \frac{1}{4} \ln(1 + 4\bar{\omega}). \]

As \( \bar{x} \rightarrow \infty \)

\[ \bar{\omega} \rightarrow \left( \frac{8}{3} \right)^{1/2} \frac{1}{\bar{x}^{3/2}}, \]

or
\[ W \rightarrow \left( \frac{2\varepsilon}{3} \right)^{1/2} x^{3/2}. \]  

(26)

The outer region satisfies equation 15. Let \( \bar{x} = x^{3/2} \), and the problem becomes

\[ \frac{2\varepsilon}{3} (1-\bar{x}^2)^2 \frac{d\bar{W}}{dx} = \frac{d}{dx} \left( \frac{\bar{W}^2}{\bar{x}} \frac{d\bar{W}}{dx} \right). \]  

(27)

The solution must match the inner solution as \( \bar{x} \rightarrow 0 \),

\[ W \rightarrow \left( \frac{2\varepsilon}{3} \right)^{1/2} \bar{x} \text{ as } \bar{x} \rightarrow 0, \]

and

\[ W = 1 \text{ at } \bar{x} = 1. \]

Thus \( \varepsilon \) can be adjusted to give \( W = 1 \) at \( \bar{x} = 1 \). The numerical solution gives \( \varepsilon = 1.9967 \). The concentration profiles for this condition are the dashed lines in figures 2 and 3 and the solid line in figure 5.

We are also able to find an asymptote for \( \frac{dW}{dx} \big|_{x=0} \). As \( \bar{x} \rightarrow -\infty \)

\[ \bar{W} \rightarrow -\frac{1}{4} - \frac{1}{4} \exp \left( \frac{6\varepsilon x^3}{3} \right), \]

and since \( A = \frac{dW}{dx} \big|_{x=0} \)

\[ \frac{dW}{dx} \big|_{x=0} \rightarrow \left( \frac{\omega}{\omega_c} - 1 \right)^{1/3}. \]

(28)

This is the dashed line on figure 4.
Mass Transfer

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

\[ \frac{n}{\rho} = -D \frac{dw}{dz} \bigg|_{z=0}. \]  

(29)

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

\[ j = \frac{1}{w_c} \left( \frac{3D \omega}{K} \right)^{1/3} \frac{dw}{dz} \bigg|_{z=0} = \frac{1}{(3\varepsilon)^{1/3}} \frac{dw}{dx} \bigg|_{x=1}. \]  

(30)

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

\[ j = \frac{1}{w_c} \left( \frac{3D \omega}{K} \right)^{1/3} \frac{dw}{dz} \bigg|_{z=0} = \frac{1}{\Gamma(4/3)} \frac{\omega}{w_c}. \]  

(31)

Figure 6 shows the flux to the surface of the disk from our numerical calculation as compared with the theoretical line predicted by equation 31. The results are summarized below in table 1.

Discussion

From figure 2 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. The slope at the consolute point is infinite when plotted against \( \xi \). Figure 3 shows the behavior as a consolute point is approached from concentrations below the critical value. As
Figure 6. Rate of mass transfer to the surface of a rotating disk. Dashed line is that predicted by equation 31 for a constant diffusion coefficient.
Table 1.

<table>
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<th>ε</th>
<th>(\frac{dW}{dx})</th>
<th>(x=0)</th>
<th>(\frac{dW}{dx})</th>
<th>(x=1)</th>
<th>(\frac{\omega_c}{\omega})</th>
<th>(j)</th>
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the concentration becomes closer to \(\omega_c\), the slope increases sharply and is infinite when the consolute point is reached.

At low values of \(\omega_c\), 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 31, the dashed line in figure 6.

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 figure 6. 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 31. The leveling off was observed experimentally by Krichevski and Tshekhanskaya [1] and predicted by Levich [3]. The concentration range in 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: 1) 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. Figures 2 and 3 clearly contradict this picture.

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List of Symbols

\[ a \quad \text{constant} = 0.51023 \]
\[ A \quad \frac{dW}{dx} \text{ at } x=0 \]
\[ A_{12}^* \quad \text{Margules constant} \]
\[ B \quad \text{constant in equation 19} \]
\[ B_{112}^* \quad \text{Margules constant} \]
\[ D \quad \text{diffusion coefficient, } \text{cm}^2/\text{s} \]
\[ D_c \quad \text{parameter used in equation 9} \]
\[ \tilde{G} \quad \text{Gibbs energy, J/mol} \]
\[ j \quad \text{dimensionless flux defined in equation 30} \]
\[ K \quad \text{parameter in equation 2} \]
\( n \) \hspace{1cm} \text{mass flux, g/cm}^2\cdot\text{s}

\( v_z \) \hspace{1cm} \text{velocity normal to disk, cm/s}

\( \dot{W} \) \hspace{1cm} \text{dimensionless concentration}

\( x \) \hspace{1cm} \text{distorted dimensionless distance variable}

\( x_i \) \hspace{1cm} \text{mole fraction}

\( X \) \hspace{1cm} \text{variable defined below equation 11, cm}^{1/3}

\( z \) \hspace{1cm} \text{distance from surface of disk, cm}

\( \gamma_i \) \hspace{1cm} \text{activity coefficient}

\( \Gamma \) \hspace{1cm} \text{gamma function}

\( c \) \hspace{1cm} \text{parameter defined in equation 15}

\( \Theta \) \hspace{1cm} \text{dimensionless concentration defined by equation 5}

\( \nu \) \hspace{1cm} \text{kinematic viscosity, cm}^2/\text{s}

\( \xi \) \hspace{1cm} \text{dimensionless distance}

\( \rho \) \hspace{1cm} \text{density, g/cm}^3

\( \omega \) \hspace{1cm} \text{mass fraction}

\( \Omega \) \hspace{1cm} \text{rotation speed, rad/s}

\textbf{Subscripts}

\( \infty \) \hspace{1cm} \text{far from disk}

\( \circ \) \hspace{1cm} \text{surface of disk, infinite dilution}

\( \ast \) \hspace{1cm} \text{critical or consolute value}

\textbf{Superscripts}

\( \cdot \) \hspace{1cm} \text{inner region variable}

\( \prime \) \hspace{1cm} \text{outer region variable}
References


