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# CIRCULATION PHENOMENA IN STEFAN DIFFUSION*

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**Abstract**—Coupled diffusion and Navier–Stokes equations are used to analyze Stefan diffusion. Numerical solutions of the diffusion and hydrodynamic equations show the existence of circulation patterns for the "stagnant" species in a binary system. These results establish that the frequently made simplifying assumption that the non-volatile species in Stefan diffusion is stagnant is invalid. Results are presented showing how the flux and velocity profiles depend on the dimensions of the system.

## NOMENCLATURE

$a$, half-channel width;
$c$, total concentration;
$c_A$, concentration of $A$;
$c_B$, concentration of $B$;
$D$, diffusivity;
$\mathbf{F}_A$, dimensionless molar flux of $A$;
$\mathbf{F}_B$, dimensionless molar flux of $B$;
$F_{AZ}$, $z$-component of dimensionless molar flux of $A$;
$F_{Bz}$, $z$-component of dimensionless molar flux of $B$;
$L$, channel length;
$M_A$, molecular weight of $A$;
$M_B$, molecular weight of $B$;
$\mathbf{n}_A$, mass flux of $A$ relative to stationary coordinates;
$\mathbf{n}_B$, mass flux of $B$ relative to stationary coordinates;
$\mathbf{N}_A$, molar flux of $A$ relative to stationary coordinates;
$\mathbf{N}_B$, molar flux of $B$ relative to stationary coordinates;
$N_{Ax}$, $x$-component of the molar flux of $A$ relative to stationary coordinates;
$N_{Az}$, $z$-component of the molar flux of $A$ relative to stationary coordinates;
$N_{Bx}$, $x$-component of the molar flux of $B$ relative to stationary coordinates;
$N_{Bz}$, $z$-component of the molar flux of $B$ relative to stationary coordinates;
$p$, pressure;
$u$, $x$-component of the mass average velocity;
$U$, dimensionless $x$-component of the mass average velocity;
$v$, $z$-component of the mass average velocity;
$\bar{v}$, $z$-component of the mean mass average velocity;
$\mathbf{v}$, mass average velocity;
$V$, dimensionless $z$-component of the mass average velocity;
$\bar{V}$, dimensionless $z$-component of the mean mass average velocity;
$X$, dimensionless distance in $x$-direction;
$y_A$, mole fraction of $A$;
$y_B$, mole fraction of $B$;
$y_0$, mole fraction of $A$ at $z = 0$;
$y_L$, mole fraction of $A$ at $z = L$;
$Z$, dimensionless distance in $z$-direction.

Greek symbols

$\lambda$, ratio of channel length to half-channel width;
$\mu$, viscosity;
$\rho$, density;
$\psi$, stream function;
$\omega_A$, mass fraction of $A$;
$\omega_B$, mass fraction of $B$.

## INTRODUCTION

IN THIS paper we question the well known and widely accepted statement [1, 2] that the solvent in a tube or channel through which a solute is diffusing is stagnant. The study of the diffusion of a solute gas through a stagnant gas in a tube or channel is often referred to as Stefan diffusion. Heinzelmann *et al.* [3] have discussed difficulties in obtaining exact solutions to the Stefan diffusion problem and have used the Taylor diffusion model to estimate concentration profiles. Radial effects in a Stefan diffusion tube have been investigated by Rao and Bennett [4], who numerically solve a two-dimensional diffusion equation assuming a parabolic velocity profile. In a latter publication [5] they postulate, but do not confirm, the existence of circulation patterns in the Stefan diffusion tube. It is the purpose of this paper to obtain solutions to the coupled hydrodynamic and binary diffusion equations, which are applicable to Stefan diffusion. The existence of circulation patterns is established and results are obtained for the velocity profiles.

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## HYDRODYNAMIC AND DIFFUSION EQUATIONS

The Navier–Stokes equations in two-dimensional rectangular coordinates are

$$\rho\frac{Du}{Dt} = -\frac{\partial p}{\partial x}+\frac{2}{3}\frac{\partial}{\partial x}\left[\mu\left(2\frac{\partial u}{\partial x}-\frac{\partial v}{\partial z}\right)\right] + \frac{\partial}{\partial z}\left[\mu\left(\frac{\partial u}{\partial z}+\frac{\partial v}{\partial x}\right)\right] \quad (1)$$

$$\rho\frac{Dv}{Dt} = -\frac{\partial p}{\partial z}+\frac{2}{3}\frac{\partial}{\partial z}\left[\mu\left(2\frac{\partial v}{\partial z}-\frac{\partial u}{\partial x}\right)\right] + \frac{\partial}{\partial x}\left[\mu\left(\frac{\partial u}{\partial z}+\frac{\partial v}{\partial x}\right)\right] \quad (2)$$

$$-a < x < a$$
$$0 < z < L$$

where $u$ and $v$ are the components of the mass average velocity in the transverse $x$-direction and axial $z$-direction, respectively. For a fluid in a channel, the boundary conditions at the wall $x = a$ and at the wall $x = -a$ are

$$u(\pm a, z) = 0 \quad (3)$$

$$v(\pm a, z) = 0. \quad (4)$$

At the inlet $z = 0$ and at the exit $z = L$ of the channel, the $x$-component of the velocity is taken to be zero:

$$u(x, 0) = 0 \quad (5)$$

$$u(x, L) = 0. \quad (6)$$

The $z$-component of the velocity at the exit of the channel is taken to be constant. The boundary condition for the $z$-component of the velocity at $z = 0$ is more complex, involving coupling between the hydrodynamic and diffusion equations. It is discussed below.

Solving the Navier–Stokes equations is greatly facilitated if the density $\rho$ and the viscosity $\mu$ are constant. For this case, it is convenient to introduce the stream function $\psi(x, z)$, which is related to the velocity components through the equations

$$u = \frac{\partial\psi}{\partial z} \quad (7)$$

$$v = -\frac{\partial\psi}{\partial x}. \quad (8)$$

For the case of steady creeping flow, the inertial terms can be neglected and the equation for the stream function becomes

$$\nabla^4\psi = 0. \quad (9)$$

The equations relating the mass fluxes to the mass fractions for a binary system are

$$\mathbf{n}_A = -\rho D\nabla\omega_A+\rho\omega_A\mathbf{v} \quad (10)$$

$$\mathbf{n}_B = -\rho D\nabla\omega_B+\rho\omega_B\mathbf{v} \quad (11)$$

where $\mathbf{n}_A$ and $\mathbf{n}_B$ are the mass fluxes relative to stationary coordinates of component $A$ and component $B$, respectively, and $\mathbf{v}$ is the mass average velocity. For a gaseous system, it is useful to formulate these equations in terms of molar fluxes and mole fractions. We obtain

$$\mathbf{N}_A = -cD(1+\alpha_{AB}y_A)^{-1}\nabla y_A+cy_A\mathbf{v} \quad (12)$$

$$\mathbf{N}_B = -cD(1+\alpha_{BA}y_B)^{-1}\nabla y_B+cy_B\mathbf{v} \quad (13)$$

$$\alpha_{AB} = \frac{M_A}{M_B}-1 \quad (14)$$

$$\alpha_{BA} = \frac{M_B}{M_A}-1 \quad (15)$$

where $\mathbf{N}_A$ and $\mathbf{N}_B$ are the molar fluxes relative to stationary coordinates of species $A$ and species $B$, respectively. For a system at steady-state, the diffusion equations are derived by combining the continuity equations with the flux equations

$$\nabla . \mathbf{N}_A = 0 \quad (16)$$

$$\nabla . \mathbf{N}_B = 0. \quad (17)$$

We consider the case where a gas mixture of species $A$ and $B$ is in contact with a liquid or solid of pure $A$ at the interface $z = 0$. The concentration $c_A$ of species $A$ at the interface is taken to be its equilibrium value $c_0$:

$$c_A(x, 0) = c_0. \quad (18)$$

At the exit of the channel, the concentration of species $A$ is taken to have the value $c_L$:

$$c_A(x, L) = c_L. \quad (19)$$

The boundary conditions at the walls of the channel are

$$N_{Ax}(\pm a, z) = 0 \quad (20)$$

$$N_{Bx}(\pm a, z) = 0. \quad (21)$$

For gaseous systems, it is common and convenient to consider the total concentration $c = c_A+c_B$ to be constant. For this case, the boundary conditions become

$$y_A(x, 0) = y_0 \quad (22)$$

$$y_A(x, L) = y_L \quad (23)$$

$$\frac{\partial y_A(\pm a, z)}{\partial x} = 0. \quad (24)$$

The important boundary condition coupling the hydrodynamic equations with the diffusion equation can be derived from the condition that $N_{Bz}(x, 0) = 0$. We obtain

$$v(x, 0) = [y_B(x, 0)]^{-1}[1+\alpha_{BA}y_B(x, 0)]^{-1} \times D\frac{\partial y_B(x, 0)}{\partial z}. \quad (25)$$

## RESULTS AND DISCUSSION

The diffusion equations and the stream function equation for the case of $M_A = M_B$ were solved on a digital computer by the method of finite differences. In solving these equations it was convenient to introduce the dimensionless variables

$$X = x/a \quad (26)$$

$$Z = z/L \quad (27)$$

$$V = vL/D \quad (28)$$

$$U = uL/D \quad (29)$$

$$\lambda = L/a \quad (30)$$

$$\mathbf{F}_A = \mathbf{N}_A L/cD \quad (31)$$

$$\mathbf{F}_B = \mathbf{N}_B L/cD. \quad (32)$$

The $z$-component of the mean velocity and the $z$-component of the mean dimensionless velocity are given by

$$\bar{v} = \frac{1}{2a}\int_{-a}^{a} v(x, z)\,\mathrm{d}x \qquad (33)$$

$$\bar{V} = \tfrac{1}{2}\int_{-1}^{1} V(X, Z)\,\mathrm{d}X. \qquad (34)$$

According to the equation of continuity, $\bar{V}$ is independent of $Z$. In the calculations the mole fraction of the volatile species $A$ at the liquid–gas interface ($Z = 0$) was 0·25 and the mole fraction of species $A$ at the exit ($Z = 1$) was 0·0. Figure 1 shows $N_{Bz}$, the $z$-component of the molar flux of species $B$, divided by $c\bar{v}$ as a function of $X$ for $Z = 0{\cdot}25$, $Z = 0{\cdot}50$, and $Z = 0{\cdot}75$.

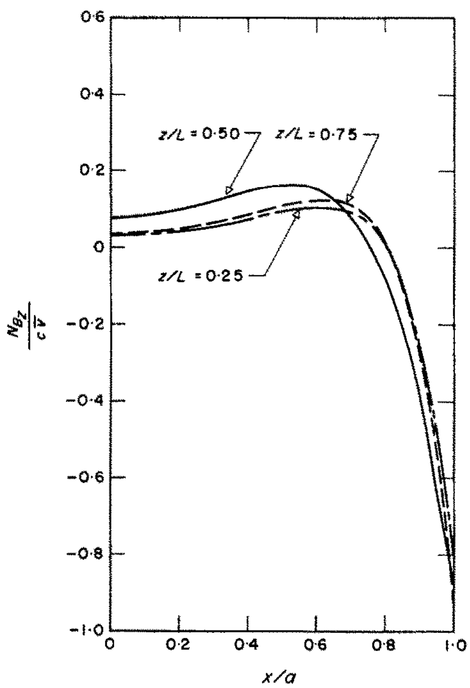


FIG. 1. Molar flux of species $B$ in $z$-direction as a function of $x/a$ at $z/L = 0{\cdot}25$, 0·50 and 0·75. Here $L/a = 1$.

The value of $\lambda = L/a$ for this system is $\lambda = 1$. The quantity $N_{Bz}/c\bar{v}$ of the ordinate is equal to

$$N_{Bz}/c\bar{v} = N_{Bz}/\bar{N}_{Az} = F_{Bz}/\bar{F}_{Az} = F_{Bz}/\bar{V}. \qquad (35)$$

These results show that the diffusion of the volatile species $A$ from the liquid–gas interface to the exit produces a flux of species $B$, which moves down the sides of the channel and up the center. Figures 2–4 show similar results for systems in which $\lambda = 2{\cdot}5$, $\lambda = 5$ and $\lambda = 10$. Interesting relations can be seen in this series of figures. For example, when $\lambda = 10$, the center-line ($X = 0$) flux of component $B$ at $Z = 0{\cdot}75$ is greater than the center-line flux at $Z = 0{\cdot}50$. On the other hand, when $\lambda = 1$, the reverse is true. Figures 2 and 3 give intermediate cases. It can be seen from these figures that as $\lambda$ is decreased, the magnitude of the center-line flux of species $B$ divided by $c\bar{v}$ is also on the average decreased. Figures 1–4 show that species $B$, which is frequently referred to as the "stagnant" species, exhibits significant circulation.

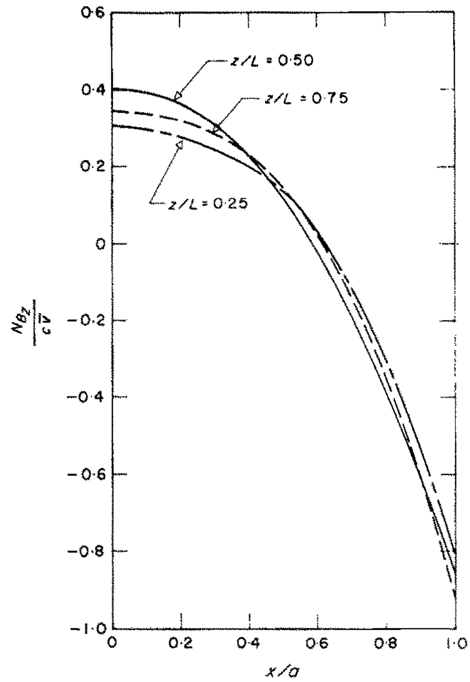


FIG. 2. Molar flux of species $B$ in $z$-direction as a function of $x/a$ at $z/L = 0{\cdot}25$, 0·50 and 0·75. Here $L/a = 2{\cdot}5$.

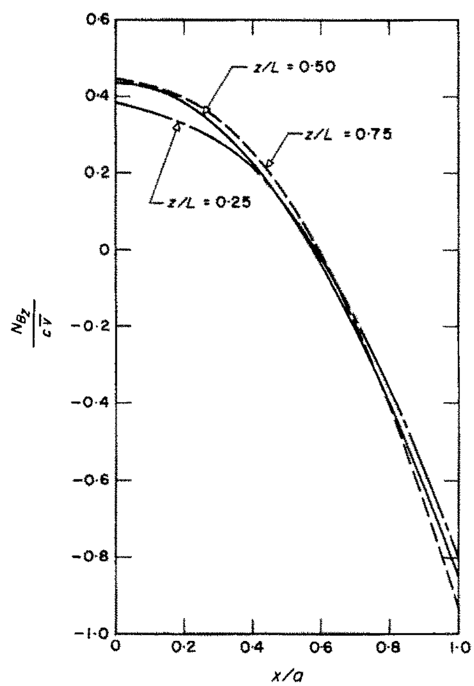


FIG. 3. Molar flux of species $B$ in $z$-direction as a function of $x/a$ at $z/L = 0{\cdot}25$, 0·50 and 0·75. Here $L/a = 5$.

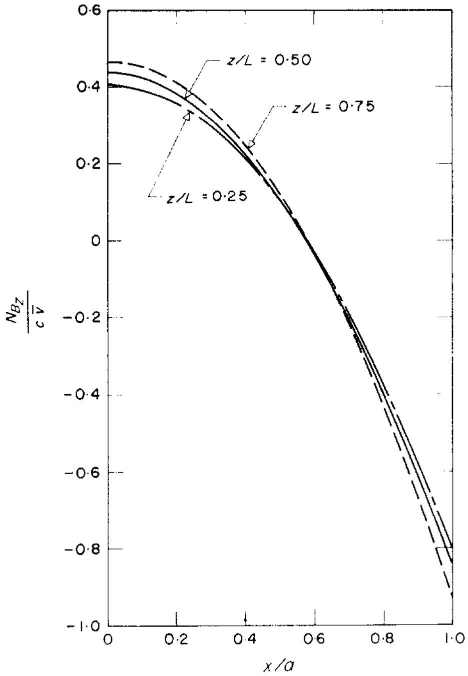


FIG. 4. Molar flux of species $B$ in $z$-direction as a function of $x/a$ at $z/L = 0{\cdot}25$, $0{\cdot}50$ and $0{\cdot}75$. Here $L/a = 10$.

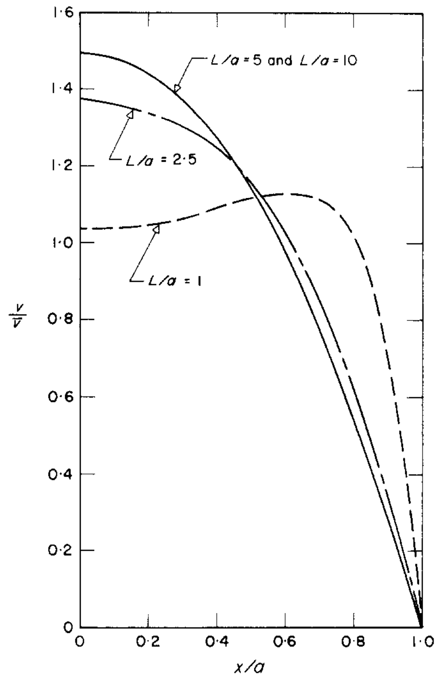


FIG. 5. Mass average velocity in $z$-direction as a function of $x/a$ at $z/L = 0{\cdot}25$ for four different systems ($L/a = 1, 2{\cdot}5, 5, 10$).

Figure 5 gives the velocity ratio $v/\bar{v} = V/\bar{V}$ as a function of $X$ at $Z = 0{\cdot}25$ for four different systems ($L/a = 1, 2{\cdot}5, 5, 10$). The velocity profiles for systems where $L/a = 5$ and $L/a = 10$ are essentially parabolic. For the system where $L/a = 2{\cdot}5$, a slight deviation from the parabolic velocity profile is noted. Finally, for the system where $L/a = 1$, a substantial deviation from the parabolic velocity profile is seen.

In summary, the coupled equations of diffusion and fluid mechanics have been solved numerically for the Stefan diffusion problem, and numerical results have been presented for the flux and velocity profiles. These results have established the existence of circulation patterns and have shown that the widely accepted statement that the solvent in Stefan diffusion is stagnant is invalid.

## REFERENCES

1. R. B. Bird, W. E. Stewart and E. N. Lightfoot, *Transport Phenomena*. John Wiley, New York (1960).
2. L. E. Sissom and D. R. Pitts, *Elements of Transport Phenomena*. McGraw-Hill, New York (1972).
3. F. J. Heinzelmann, D. T. Wasan and C. R. Wilke, Concentration profiles in a Stefan diffusion tube, *I/EC Fundamentals* **4**, 55–61 (1965).
4. S. S. Rao and C. O. Bennett, Radial Effects in a Stefan diffusion tube, *I/EC Fundamentals* **5**, 573–575 (1966).
5. S. S. Rao and C. O. Bennett, Velocity profile in the Stefan diffusion tube, *I/EC Fundamentals* **6**, 477 (1967).

## PHENOMENE DE CIRCULATION EN DIFFUSION DE STEFAN

**Résumé**—Les équations couplées de la diffusion et de Navier–Stokes sont utilisées afin d'analyser la diffusion de Stefan. Les solutions numériques des équations de diffusion et de Navier–Stokes montrent l'existence de contours de circulation pour les espèces "immobiles" dans un système binaire. Ces résultats établissent que l'hypothèse simplificatrice fréquemment utilisée suivant laquelle les espèces non volatiles demeurent immobiles dans la diffusion de Stefan n'est pas valable. Des résultats sont présentées qui montrent la dépendance des profils de flux et de vitesse sur les dimensions du système.

## ZIRKULATIONSERSCHEINUNGEN IM STEFAN-STROM

**Zusammenfassung**—Der Stefan-Strom wird mit gekoppelten Diffusions- und Navier–Stokes-Gleichungen untersucht. Die numerischen Lösungen der Diffusionsgleichungen und der hydrodynamischen Gleichungen zeigen das Vorhandensein von Zirkulationserscheinungen für die schwerer flüchtige Komponente eines binären Systems. Diese Ergebnisse belegen, daß die häufig getroffene vereinfachende Voraussetzung des Stillstehens der weniger flüchtigen Komponente ungültig ist. Die Ergebnisse zeigen die Abhängigkeit der Strömungs- und Geschwindigkeitsprofile von den Abmessungen des Systems.

## ЯВЛЕНИЕ ЦИРКУЛЯЦИИ ПРИ ДИФФУЗИИ СТЕФАНОВСКОГО ТИПА

**Аннотация** — Для анализа диффузии стефановского типа используются уравнения диффузии и Навье-Стокса. Численные решения уравнений диффузии и гидродинамики показывают наличие циркуляции для «застоявшихся» частиц в бинарных системах. Эти результаты не подтверждают справедливость часто высказываемого предположения о неподвижности нелетучих частиц при диффузии стефановского типа. Приводятся данные, показывающие зависимость профилей потока и скорости от характерных размеров системы.