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THE MASS TRANSFER BOUNDARY LAYER WITH FINITE TRANSFER RATE

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ass transfer with finite rates is usually passed over with only a brief mention in undergraduate transport courses because of the complexity of the coupled problem in mass and momentum transport. Solutions to classical problems are available; Bird, Stewart, and Lightfoot (BSL),^[1] for example, present an elegant similarity solution for simultaneous heat, mass, and momentum transfer in a laminar boundary layer. The similarity solution is of necessity numerical in the final stages, and the form is sufficiently complex in structure that it is difficult to obtain insight to the underlying physical process in a straightforward manner.

I have found that it is much more effective to introduce students, undergraduate and postgraduate alike, to the concept of finite transfer rates through the von Karman-Polhausen (vK-P) approximation. Undergraduates have often seen the method previously in their study of fluid mechanics (*e.g.*, Denn^[2]). With graduate students I precede this material with a scaling analysis to obtain the basic structure of the relation between the Sherwood, Schmidt, and Reynolds numbers (Denn^[3]). Standard texts often use the vK-P method for mass transfer boundary layers, but they fail to take advantage of one of its most significant pedagogical features: the finite-rate problem is no more complex than the uncoupled one. While there is no question but that the exact solution, as

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The solution given here is not completely new; the problem was considered within a broader class, for example, by Spalding.^[4,5] The analogous transpiration cooling problem in heat transfer was analyzed in part by Yuan and Ness.^[6] I believe it is useful, however, to present the specific case of finite mass transfer in laminar flow over a flat plate in a form that is easily accessible to students, who would find the original literature on vK-P solutions as difficult as the exact solutions. In that regard, this paper might be thought of as a lesson plan and a possible supplement to a course text.

PROBLEM FORMULATION

Consider flow of an incompressible Newtonian fluid with constant physical properties over a flat plate at zero angle of incidence. The flow direction is x and the transverse direction y. The surface contains a soluble species A, while the fluid phase is an ideal mixture of A and B. It is implicit in the standard problem formulation (cf BSL, p. 608 ff) that the molecular weights of A and B are equal ($M_A = M_B$). The overall continuity, momentum, and species continuity equations are, respectively,

$$\frac{\partial \mathbf{v}_{\mathbf{x}}}{\partial \mathbf{x}} + \frac{\partial \mathbf{v}_{\mathbf{y}}}{\partial \mathbf{y}} = 0 \tag{1}$$

$$v_{x} \frac{\partial v_{x}}{\partial x} + v_{y} \frac{\partial v_{x}}{\partial y} = v \frac{\partial^{2} v_{x}}{\partial y^{2}}$$
(2)

$$v_{x} \frac{\partial x_{A}}{\partial x} + v_{y} \frac{\partial x_{A}}{\partial y} = D_{AB} \frac{\partial^{2} x_{A}}{\partial y^{2}}$$
(3)

where

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elsewhere in this is

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$$v_x, v_y = x$$
- and y-components of velocity, respectively
 $x_A = mole \text{ fraction of } A$

υ,D_{AB} = kinematic viscosity and binary diffusivity, respectively

Boundary conditions are

$$y=0: v_{x}=0, x_{A}=x_{A0}, N_{B}=0 \qquad (4a,b,c)$$
$$x \le 0 \text{ and } y \to \infty: v_{a}=y_{ab}, x_{A}=x_{Ab}, \qquad (4d,e)$$

where

 $v_{\infty}, x_{A\infty}$ = "free-stream" values of velocity and mole fraction,

respectively ($x_{A\infty}$ will often be zero)

 x_{A0} = equilibrium or saturation level of A in the fluid phase at the surface y=0

 $N_{\rm B}$ = molar flux of B

It is also useful to record the molar flux of the transferring species A at y=0 as

$$N_{A0} = \frac{\rho v_{y0}}{M_A} = -\frac{c D_{AB}}{1 - x_{A0}} \left. \frac{\partial x_A}{\partial y} \right|_{y=0}$$
(5)

where v_{y0} is the transverse velocity at y=0 and c is the total molar concentration. Because $M_A = M_B$, $\rho = M_A c$. Equation (5) establishes the coupling between the mass and momentum equations.

It is convenient to use the dimensionless variables

$$\mathbf{u} = \frac{\mathbf{v}_{\mathbf{x}}}{\mathbf{v}_{\infty}}, \quad \mathbf{v} = \frac{\mathbf{v}_{\mathbf{y}}}{\mathbf{v}_{\infty}}, \quad \mathbf{w} = \frac{\mathbf{x}_{\mathbf{A}0} - \mathbf{x}_{\mathbf{A}}}{\mathbf{x}_{\mathbf{A}0} - \mathbf{x}_{\mathbf{A}\infty}}$$
(6a, b, c)

Note that u and w range from zero to unity, but this is not true of v, so these are not appropriate variables for a scaling analysis (cf Denn^[3]). The dimensionless form of Eq. (5) is

$$v_{0} = \frac{D_{AB}}{v_{\infty}} \left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}} \right) \frac{\partial w}{\partial y} \bigg|_{y=0}$$
(7)

Equations (1) through (4) then become

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{8}$$

$$u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = \left(\frac{v}{v_{\infty}}\right)\frac{\partial^2 u}{\partial y^2}$$
(9)

$$u\frac{\partial w}{\partial x} + v\frac{\partial w}{\partial y} = \left(\frac{v}{v_{\infty}Sc}\right)\frac{\partial^2 w}{\partial y^2}$$
(10)

$$y = 0$$
 : $u = w = 0$ (11a, b)

$$x \le 0 \text{ and } y \to \infty$$
 : $u = w = 1$ (11c, d)

where $Sc = v/D_{AB}$ is the Schmidt number. When Sc = 1, Spring 1996 Eqs. (9) and (10) for u and w are identical with identical boundary conditions for any v, so it follows immediately that u = w and the dimensionless velocity and concentration profiles are the same.

vK-P FORMULATION

The vK-P approach converts the differential equations to an integral form. Firstly, the continuity equation is integrated to obtain

$$v_{y} = v_{0} - \int_{0}^{y} \frac{\partial u}{\partial x} dy$$
 (12)

Equations (9) and (10) are then integrated from y=0 to $y=\infty$; with some manipulation and the use of Eqs. (8) and (12), we obtain the starting point:

$$v_{0} + \int_{0}^{\infty} \frac{\partial}{\partial x} \left[u(u-1) \right] dy = -\frac{\upsilon}{v_{\infty}} \left. \frac{\partial u}{\partial y} \right|_{y=0}$$
(13)

$$\mathbf{v}_{0} + \int_{0}^{\infty} \frac{\partial}{\partial \mathbf{x}} \left[\mathbf{u}(\mathbf{w} - 1) \right] d\mathbf{y} = -\frac{\upsilon}{\mathbf{v}_{\infty} \mathbf{S} \mathbf{c}} \left. \frac{\partial \mathbf{w}}{\partial \mathbf{y}} \right|_{\mathbf{y} = 0}$$
(14)

We have assumed continuity of $\partial u / \partial y$ and $\partial w / \partial y$ throughout $0 \le y < \infty$. This is a subtlety that should be addressed in the classroom because it can become a problem for some students subsequently.

The vK-P approximation is based on two fundamental hypotheses. Firstly, one assumes the asymptotic approach to free-stream conditions can be replaced by well-defined boundary layers $\delta(x)$ and $\delta_c(x)$ for velocity and concentration, respectively. For $y \leq \delta(x)[\delta_c]$ the velocity (concentration) varies continuously from the surface condition to the value at $y = \infty$; for greater values of y the velocity (concentration) is constant. Secondly, one assumes that u and w are unique functions of $y/\delta(x)$ and $y/\delta_c(x)$ respectively; this is a similarity assumption that is in fact rigorous for the problem at hand, but generally not for other problems in which the vK-P approach is employed. Students usually need some discussion of the physical meanings of both these (independent) assumptions. We therefore write u and w as the functions

$$u = \varphi[y / \delta(x)], y \le \delta; \quad u = 1, y > \delta$$
(15a)

$$w = \psi \left[y / \delta_c(x) \right], \ y \le \delta_c; \qquad w = 1, \ y > \delta_c \tag{15b}$$

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The functions φ and ψ must be continuously differentiable and satisfy boundary conditions

$$\varphi(0) = \psi(0) = 0, \quad \varphi(1) = \psi(1) = 1$$
 (16)

They are otherwise arbitrary. Equations (13) and (14) then become

$$\frac{\upsilon}{v_{\infty}Sc} \left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}} \right) \frac{1}{\delta_{c}} \psi'(0) + \int_{0}^{\delta} \frac{\partial}{\partial x} \left\{ \varphi\left(\frac{y}{\delta}\right) \left[\varphi\left(\frac{y}{\delta}\right) - 1 \right] \right\} dy = -\frac{\upsilon}{v_{\infty}} \frac{1}{\delta} \varphi'(0)$$
(17)

$$\frac{\upsilon}{v_{\infty}Sc} \left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}} \right) \frac{1}{\delta_{c}} \psi'(0) + \int_{0}^{\delta_{c}} \frac{\partial}{\partial x} \left\{ \varphi \left(\frac{y}{\delta} \right) \left[\psi \left(\frac{y}{\delta_{c}} \right) - 1 \right] \right\} dy = -\frac{\upsilon}{v_{\infty}Sc} \frac{1}{\delta_{c}} \psi'(0)$$
(18)

The upper limits of the integrals are δ and δ_c , respectively, because the integrands are identically zero beyond these points. It is important to remember that the argument of φ is $y/\delta(x)$ in both equations, whereas that of ψ is $y/\delta_c(x)$.

There is a very convenient variable change here, which is not necessary but simplifies the manipulations greatly. Students often have a problem with the details of the calculus. Define $\xi = y/\delta(x)$ in Eq. (17) and $\xi = y/\delta_c(x)$ in Eq. (18). The range of both integrals is then from $\xi = 0$ to $\xi = 1$; terms and operations involving only x are independent of ξ and can be taken outside the definite integrals. We thus obtain

$$\frac{\upsilon}{v_{\infty}Sc}\left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}}\right)\frac{1}{\delta_{c}}\psi'(0) + \frac{d\delta}{dx}\left\{\int_{0}^{1}\phi(\xi)[\phi(\xi) - 1]d\xi\right\} = -\frac{\upsilon}{v_{\infty}}\frac{1}{\delta}\psi'(0)$$
(19)

$$\frac{\upsilon}{\upsilon_{\infty}Sc} \left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}} \right) \frac{1}{\delta_{c}} \psi'(0) + \frac{d\delta_{c}}{dx} \left\{ \int_{0}^{1} \varphi \left(\xi \frac{\delta_{c}}{\delta} \right) [\varphi(\xi) - 1] d\xi \right\} = -\frac{\upsilon}{\upsilon_{\infty}Sc} \frac{1}{\delta_{c}} \psi'(0) \quad (20)$$

Now define $\Delta = \delta_c / \delta$, where we assume Δ is a constant. This assumption requires a consistency check later. With a bit of rearrangement, Eqs. (19) and (20) then become

$$\frac{1}{2} \frac{d\delta^2}{dx} \left\{ \int_0^1 \varphi(\xi) [\varphi(\xi) - 1] d\xi \right\}$$
$$= -\frac{\upsilon}{\upsilon_{\infty}} \left[\varphi'(0) + \frac{1}{\Delta Sc} \left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}} \right) \psi'(0) \right] \qquad (21)$$

$$\frac{1}{2} \frac{d\delta_c^2}{dx} \left\{ \int_0^1 \varphi(\Delta\xi) \left[\psi(\xi) - 1 \right] d\xi \right\}$$
$$= -\frac{\upsilon}{\upsilon_{\infty} Sc} \left[1 + \left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}} \right) \psi'(0) \right]$$
(22)

The right-hand sides and the coefficients in braces on the left are all constants in these equations for specified φ and ψ , so the square-root dependence of the boundary layer development is established. For $(x_{A0} - x_{A\infty})/(1 - x_{A\infty}) << 1$ the problems uncouple, in that Eq. (21) involves only fluid-mechanical variables. We can write the solution to the coupled problem as

$$\delta^{2} = \frac{-\frac{2\nu}{\nu_{\infty}} \left(\varphi'(0) + \frac{1}{\Delta Sc} \left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}}\right) \psi'(0)\right) x}{\int_{0}^{1} \varphi(\xi) [\varphi(\xi) - 1] d\xi}$$
(23)
$$\delta_{c}^{2} = \frac{-\frac{2\nu}{\nu_{\infty} Sc} \left(1 + \left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}}\right) \psi'(0)\right) x}{\int_{0}^{1} \varphi(\Delta \xi) [\psi(\xi) - 1] d\xi}$$
(24)

The equation for Δ is obtained by setting $\Delta^2 = \delta^2 / \delta_c^2$; this ratio is clearly independent of x, establishing that Δ is indeed a constant.

CLOSED-FORM SOLUTION

The functions φ and ψ are typically taken to be polynomials, usually cubics. The structure of the solution is best revealed by taking $\varphi(\xi) = \psi(\xi) = \xi$, since in that case Δ simply factors out of the integral involving $\varphi(\Delta\xi)$. There is a problem at $\xi = 1$, where the derivatives are not continuous, which will be a concern to some students, but it is a technical detail; the function can be taken as linear arbitrarily close to $\xi = 1$ and then rounded suitably to provide continuity of the derivative without changing the integrals in Eqs. (13) and (14) by more than an infinitesimal amount. With

 $\phi = \psi = \xi$, $\phi' = \psi' = 1$, and $\int_{0}^{1} \xi(\xi - 1) d\xi = -\frac{1}{6}$

we have

$$\delta^{2} = \frac{12 \upsilon}{v_{\infty}} \left[1 + \frac{1}{\Delta Sc} \left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}} \right) \right] x$$
(25)

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$$\delta_{\rm c}^2 = \frac{12\nu}{v_{\infty}\Delta \operatorname{Sc}} \left[1 + \left(\frac{x_{\rm A0} - x_{\rm A\infty}}{1 - x_{\rm A0}} \right) \right] {\rm x}$$
(26)

and

$$\Delta^{3} \text{Sc} + \left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}}\right) \Delta^{2} = 1 + \left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}}\right)$$
(27)

To first order in $(x_{A0} - x_{A\infty})/(1 - x_{A0})$ the solution to Eq. (27) is

$$\Delta \sim \mathrm{Sc}^{-\frac{1}{3}} \left[1 + \frac{1}{3} \left(\frac{\mathrm{x}_{\mathrm{A0}} - \mathrm{x}_{\mathrm{A\infty}}}{1 - \mathrm{x}_{\mathrm{A0}}} \right) \left(1 - \mathrm{Sc}^{-\frac{2}{3}} \right) \right]$$
(28)

Defining $\operatorname{Re}_{x} = xv_{\infty} / v$ we obtain, to the same order in $(x_{A0} - x_{A\infty})/(1 - x_{A\infty})$,

$$\frac{\delta}{x} = 3.46 \operatorname{Re}_{x}^{-\frac{1}{2}} \left[1 + \frac{1}{2} \left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}} \right) \operatorname{Sc}^{-\frac{2}{3}} \right]$$
(29)

$$\frac{\delta_{\rm c}}{\rm x} = 3.46 \ {\rm Re}_{\rm x}^{-\frac{1}{2}} \, {\rm Sc}^{-\frac{1}{3}} \left[1 + \frac{1}{6} \left(\frac{{\rm x}_{\rm A0} - {\rm x}_{\rm A\infty}}{1 - {\rm x}_{\rm A0}} \right) \left(2 + {\rm Sc}^{-\frac{2}{3}} \right) \right]$$
(30)

MASS-TRANSFER COEFFICIENT

There are a number of ways in which the mass-transfer coefficient can be defined. In my opinion the transport coefficients need to be viewed as quantities defined by experiment; for mass transfer the interfacial flux N_{A0} and driving force $x_{A0} - x_{A\infty}$ are the quantities that can be measured in principle, so the proper operational definition for the mass transfer coefficient k_x is

$$k_{x} \equiv \frac{N_{A0}}{c(x_{A0} - x_{A\infty})}$$
(31a)

BSL choose to define the transport coefficient relative to the molar average velocity, so their definition would be

$$k_{x}^{*} = \frac{N_{A0} (1 - x_{A0})}{c (x_{A0} - x_{A\infty})}$$
(31b)

Failure to distinguish between these definitions can cause a great deal of confusion. (There is a dimensionality difference between both these definitions and those used by BSL; k, as defined here, has dimensions of velocity.) The Sherwood number, $Sh_x = xk_x / D_{AB}$, then follows from Eqs. (7) and (30) to first order as

$$Sh_{x} = 0.289 \text{ Re}^{\frac{1}{2}} Sc^{\frac{1}{3}} \frac{1}{1 - x_{A0}} \left[1 - \frac{1}{6} \left(2 + Sc^{-\frac{2}{3}} \right) \left(\frac{x_{A0} - x_{A\infty}}{1 - x_{A0}} \right) \right] (32)$$

(The coefficient for the exact solution is 0.332. The form

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Re^{1/2}Sc^{1/3} follows directly from scaling arguments; cf Denn.^[3]) The correction relative to the low-flux limit is therefore

$$\frac{\mathrm{Sh}_{\mathrm{x}}}{\mathrm{Sh}_{0\mathrm{x}}} = \frac{1}{1 - \mathrm{x}_{\mathrm{A0}}} \left[1 - \frac{1}{6} \left(2 + \mathrm{Sc}^{-\frac{2}{3}} \right) \left(\frac{\mathrm{x}_{\mathrm{A0}} - \mathrm{x}_{\mathrm{A\infty}}}{1 - \mathrm{x}_{\mathrm{A0}}} \right) \right]$$
(33)

There are two contributions to the correction term. The term in brackets, which reflects the contribution of the driving force, is less than unity; this term corresponds to the effect of thickening the boundary layer with a constant driving force, hence reducing the gradient for diffusion. The demoninator term $1 - x_{A0}$ reflects the convective contribution to the total flux. The net effect of the two terms is to increase the Sherwood number relative to the zero-flux limit. (This is most easily seen by setting $x_{A0} = 0$, $x_{A0} <<1$, in

which case
$$\frac{Sh_x}{Sh_{0x}} \sim 1 + \left(\frac{2}{3} - \frac{1}{6}Sc^{-\frac{2}{3}}\right) x_{A0} > 1.$$
 A Sherwood

number based on k_x^* would decrease, however, since the thickened boundary layer decreases the diffusive flux.

CONCLUDING REMARKS

I have found this example to be effective in introducing students to the concept of corrections for finite mass-transfer rates because it uses a methodology with which they are (or should be) familiar and leads to a reasonably accurate result in closed form. I like to emphasize the limitations inherent in the usual assumption of no surface flux and the breakdown of transport analogies at high rates of mass transfer. The boundary layer, approached in the manner outlined here, is an excellent vehicle for doing so, and at no "cost" since the same methodology is likely to be used for the solution of the uncoupled problem in order to establish the Sc^{1/3} dependence in the Sherwood number relation.

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Warren Stewart called my attention to the papers by Spalding and Yuan.

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