Simultaneous Heat and Mass Transfer in a Falling Laminar Film

A. D. MODINE, E. B. PARRISH, and H. L. TOOR
Carnegie Institute of Technology, Pittsburgh, Pennsylvania

In some recent ternary mass transfer studies in a wetted-wall column, (9) the mass transfer coefficients obtained when benzene and acetone were transferred in the presence of helium appeared to be unusually low. It seemed probable that this discrepancy was caused by neglect of the difference in temperature between the interface and bulk of the liquid film. If this were true, the same effect should appear in binary mass transfer. The binary experiments discussed below showed that this indeed was the case. It remains necessary to determine the interfacial temperature and its effect on the mass transfer.

When vaporization takes place from a liquid film as it flows down an adiabatic wall, the bulk and interfacial temperatures decrease if the gas temperature is not very much higher than the liquid temperature and the interfacial temperature falls below the bulk liquid temperature. The interfacial temperature can be calculated if the heat transfer coefficient in the liquid is known, but this coefficient depends upon the rate of mass transfer into the gas. This coupling of the liquid side heat transfer and the gas side mass transfer arises because the heat flux at the interface, which is a boundary condition on the heat conduction equation, is controlled by the gas side mass transfer. The mass transfer rate in turn depends upon the heat transfer in the liquid through the effect of the interfacial temperature on the partial or vapor pressure of the liquid.

The heat transfer coefficient in the liquid falls from an infinite value, in theory, at the point of introduction of the liquid to a constant value at large distances. The manner in which the coefficient varies with distance down the column, as well as the value of the coefficient at all points, depends upon the boundary conditions at the interface.

The approach taken here is to determine the liquid side heat transfer coefficient for any arbitrary variation of interfacial heat flux with position, and then to solve the resulting integral equation simultaneously with the gas side mass transfer equations.

THE MATHEMATICAL SOLUTION

Consider the steady laminar flow of a liquid film down a vertical tube. Temperature changes are assumed to be small enough so that the physical properties remain constant. If the curvature of the film is neglected, the problem reduces to flow of a film down a plane wall. Under these assumptions, the energy equation reduces to

$$u(y)\frac{\partial t}{\partial x} = \alpha \frac{\partial^2 t}{\partial y^2} \tag{1}$$

If the flow is assumed to be laminar and wave free, the velocity profile is given by

$$u(y) = \frac{3}{2}\bar{U}[1-(y/b)^2] \tag{2}$$

Combining Equations (1) and (2) and using reduced coordinates one obtains

$$\frac{3}{8}\frac{\partial T}{\partial \beta} = \frac{1}{1-\eta^2}\frac{\partial^2 T}{\partial \eta^2} \tag{3}$$

The solution to Equation (3) with an arbitrary heat flux at the interface, an adiabatic wall, and a constant initial temperature, may be obtained by the method of Sellars, et al. (7).

TABLE 1. VALUES OF λ_i AND a_i

λ_i	Pigford value	Asymptotic value	Pigford a_i
λ_0	2.2630	2.3333	—2.6869
λ_1	6.2700	6.3333	—2.5796
λ_2	10.2870	10.3333	—2.5601
λ_3	14.3090	14.3333	—2.3827

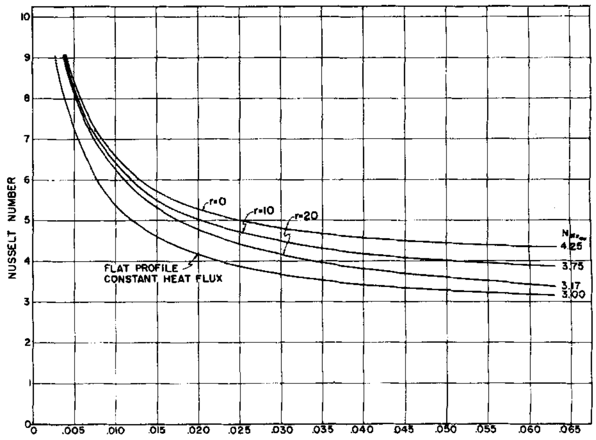

Fig. 1. Nusselt number vs. reduced distance.

The procedure is first to find the solution for a constant interfacial temperature, that is, solve Equation (3) with the boundary conditions

$$T(0,\eta) = 1 \tag{4a}$$

$$T(\beta,0) = 0 \tag{4b}$$

$$\left.\frac{\partial T}{\partial \eta}\right|_{\beta,\eta=1} = 0 \tag{4c}$$

This is the analogue of a diffusion problem solved by Pigford (5). The solution is

$$T(\beta,\eta) = \sum_{i=0}^{\infty} a_i\,\phi_i\,(\eta,\lambda_i)\,e^{-\frac{8}{3}\lambda_i^2\beta} \tag{5}$$

where

$$\phi_i\,(\eta,\lambda_i) = e^{-\frac{\lambda_i^2\eta}{2}}\,\eta\left[1-\frac{\lambda_i}{3!}(\lambda_i-3)\eta^2+\frac{\lambda_i^2}{5!}(\lambda_i-7)(\lambda_i-3)\eta^4-\ldots\right] \tag{6}$$

$$a_i = \frac{\int_0^1 (1-\eta^2)\,\phi_i\,(\eta,\lambda_i)\,d\eta}{\int_0^1 (1-\eta^2)\,\phi_i^2\,(\eta,\lambda_i)\,d\eta} \tag{7}$$

The λ_i are the roots of

$$0 = (1-\lambda_i) - \frac{\lambda_i}{3!}(3-\lambda_i)(\lambda_i-3) +$$

A. D. Modine is with the Jersey Production Research Company, Tulsa, Oklahoma. E. B. Parrish is with the Sun Oil Company, Marcus Hook, New Jersey.

$$\frac{\lambda_i^2}{5!}(5-\lambda_i)(\lambda_i-7)(\lambda_i-5)\ \ldots \quad (8)$$

Solving Equation (8) for large values of λ_i is tedious. An asymptotic solution for the eigenvalues can be obtained by the method of Sellars, et al (7). This yields

$$\lambda_i = 4i + 7/3 \quad (9)$$

This expression is valid for large values of i and greatly simplifies evaluation of the characteristic constants a_i. Table 1 compares the λ_i given by Equation (8) with Pigford's values. The absolute error in the asymptotic value of λ_3 is 0.17%.

Applying Duhamel's theorem to Equation (5) one obtains

$$t(\beta, \eta) = t_o + \int_o^\beta [1 - T(\beta - \epsilon, \eta)]\, d\, t_s(\epsilon) \quad (10)$$

In Equation (10), $t(\beta, \eta)$ is the temperature at any point in the film when the interfacial temperature is $t_s(\beta)$. However, the desired solution must relate the temperature at the interface to the heat flux at the interface. Differentiating Equation (10) and using Equations (5) and (6) and the relation

$$q(\beta) = -\frac{k}{b}\left.\frac{\partial t}{\partial \eta}\right|_{\beta, \eta=0} \quad (11)$$

one obtains

$$q(\beta) = \frac{k}{b}\int_o^\beta \sum_{i=0}^{\infty} e^{-\frac{8}{3}\lambda_i^2(\beta-\epsilon)}\, a_i\, d\, t_s(\epsilon) \quad (12)$$

Taking the Laplace transform of Equation (12) and applying the convolution theorem one gets

$$\mathcal{L}\left[\frac{d\, t_s(\beta)}{d\, \beta}\right] = \frac{b}{k}\left[\frac{\mathcal{L}(q[\beta])}{p\displaystyle\sum_{i=0}^{\infty}\frac{a_i}{\left(p + \frac{8}{3}\lambda_i^2\right)}}\right] \quad (13)$$

Application of the residue theorem to Equation (13) yields the final solution

$$t_s(\beta) = t_o + \frac{b}{k}\int_o^\beta q(\epsilon)\left[4.0 - \sum_{m=0}^{\infty}\frac{e^{-\gamma_m^2(\beta-\epsilon)}}{\gamma_m^2\displaystyle\sum_{i=0}^{\infty}\frac{a_i}{\left(\frac{8}{3}\lambda_i^2 - \gamma_m^2\right)^2}}\right] d\epsilon \quad (14)$$

where the constants γ_m^2 are given by

$$\sum_{i=0}^{\infty}\frac{a_i}{\frac{8}{3}\lambda_i^2 - \gamma_m^2} = 0 \quad (15)$$

The first three values of γ_m^2 were determined with the aid of a digital computer and are given in Table 2. The values of γ_m^2 become large very rapidly. For this work, no more than the first three values were necessary.

TABLE 2. VALUES OF γ_m^2

γ_1^2	51.914
γ_2^2	196.140
γ_3^2	436.84

The application of Equation (14) depends upon knowledge of the heat flux at the surface. One method of applying Equation (14) is to calculate the Nusselt number for various cases. The local heat transfer coefficient h is defined in the usual manner:

$$q(x) = h(x)\,[t_s(x) - \bar{t}(x)] \quad (16)$$

An overall heat balance on the liquid yields

$$\int_o^x q(x)\, dx = \rho\, \bar{U}\, C_P\, b\, [\bar{t}(x) - t_o] \quad (17)$$

Combining Equations (14), (16), and (17) gives the general form of the Nusselt number

$$N_{Nu} = \frac{-q(\beta)}{\displaystyle\int_o^\beta\left[q(\epsilon)\sum_{m=0}^{\infty}\frac{e^{-\gamma_m^2(\beta-\epsilon)}}{\gamma_m^2\displaystyle\sum_{i=0}^{\infty}\frac{a_i}{\left(\frac{8}{3}\lambda_i^2 - \gamma_m^2\right)^2}}\right]d\epsilon} \quad (18)$$

For a constant heat flux, Equation (18) reduces to

$$N_{Nu} = \frac{1}{-\displaystyle\sum_{m=0}^{\infty}\frac{1 - e^{-\gamma_m^2\beta}}{\gamma_m^4\displaystyle\sum_{i=0}^{\infty}\frac{a_i}{\left(\frac{8}{3}\lambda_i^2 - \gamma_m^2\right)^2}}} \quad (19)$$

The first series in the denominator is the asymptotic Nusselt number which can be obtained directly from the original differential equation so Equation (19) can be reduced to

$$N_{Nu} = \frac{1}{0.2357 + \displaystyle\sum_{m=0}^{\infty}\frac{e^{-\gamma_m^2\beta}}{\gamma_m^4\displaystyle\sum_{i=0}^{\infty}\frac{a_i}{\left(\frac{8}{3}\lambda_i^2 - \gamma_m^2\right)^2}}} \quad (20)$$

If the heat flux is given by

$$q(\beta) = C\, e^{-r\beta} \quad (21)$$

where r is a real positive constant, Equation (17) gives

$$N_{Nu} = \frac{-1}{\displaystyle\sum_{m=0}^{\infty}\frac{1 - e^{-(\gamma_m^2 - r)\beta}}{\gamma_m^2(\gamma_m^2 - r)\displaystyle\sum_{i=0}^{\infty}\frac{a_i}{\left(\frac{8}{3}\lambda_i^2 - \gamma_m^2\right)^2}}} \quad (22)$$

The Nusselt number is shown as a function of reduced length in Figure 1 for values of r of 0 (constant heat flux) 10 and 20 (a typical value in this work is 10) as well as for a constant interfacial temperature. In comparison, the Nusselt number for a constant flux at the interface with a flat-velocity profile is also included (1). It is noted that the exponential flux Nusselt number is not a strong function of r. This behavior is helpful in later calculations.

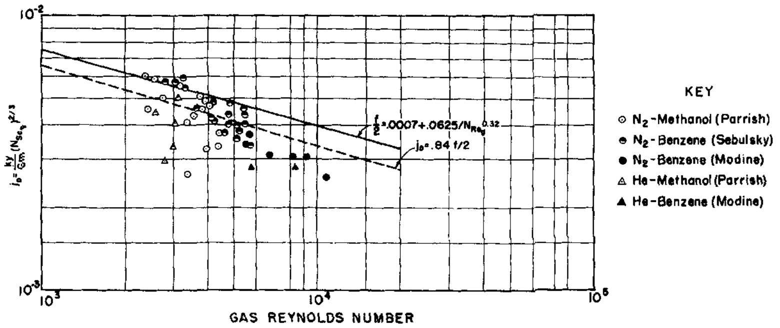

Fig. 2. Mass transfer coefficients, interfacial temperature assumed to be equal to bulk liquid temperature.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

The apparatus was that used by Toor and Sebulsky (9) with several modifications: the piping layout was altered to allow operation at higher gas Reynolds numbers; a gas-sampling technique was devised so that samples were fed directly to the gas chromotography column; the glass column was insulated from liquid contact in the liquid receivers; an additional mixing section was added to the exit gas line upstream from the sampling point.

The only change in experimental technique from that of Toor and Sebulsky was in the method of gas-sample withdrawal. Gas samples were taken through a heated line connecting the gas lines and the chromotography column. This technique eliminated the use of a mercury displacement cell and allowed replicate samples to be taken in a short time.

CALCULATIONS

The local rate of mass transfer from the interface to the gas is written as

$$N_A = k_y \ln (\bar{y}_B/y_{Bs}) = \frac{dn_A}{\pi d\, dx} \quad (23)$$

where

$$y_{Bs} = 1 - P_A{}^o\,(t_s)/P_T \quad (24)$$

$$\bar{y}_B = n_A/(n_A + n_{B_o}) \quad (25)$$

The local mass transfer coefficient, k_y, is assumed to be given by

$$j_D = \frac{k_y}{G_m}\,(N_{Sc_g})^{2/3} = \sigma\, f/2 \quad (26)$$

where $f/2$ is the smooth tube friction factor, all properties are evaluated at the average gas-film composition, and σ is a constant to be determined by experiment.

For an isothermal experiment with a pure liquid, Equations (23) to (26) may be combined with a material balance in the usual manner, and the constant σ, which measures the error in the Colburn equation, may be determined from measurement of the terminal gas compositions and flow rate. In dilute systems with low transfer rates, σ is close to one (3, 8).

For a nonisothermal experiment, small changes in gas temperature may be ignored, but the interfacial temperature is required at each point in the column in order to evaluate y_{Bs}.

An enthalpy balance from the top of the column to any point yields

$$t_o - \bar{t}_{(\beta)} = \frac{K \int_0^\beta \lambda_A\, dn_A}{W\, C_P} \quad (27)$$

The factor K, which accounts for second-order terms in the enthalpy balance, is approximately constant throughout the column and is generally found to be about 0.9 in this work.

Analysis of previous calculations indicated that the flux of $N_A\lambda_A$ in the column varied exponentially with distance. Since the sensible heat transfer from the interface to the gas is small, $N_A\lambda_A$ may be taken as equal to q so Equation (21) holds. Combining Equations (21), (16), and (17) one obtains

$$t_s(\beta) = \bar{t}(\beta) - [t_o - \bar{t}(\beta)] \left(\frac{e^{-r\beta}}{1 - e^{-r\beta}}\right) \frac{r}{4\, N_{Nu}} \quad (28)$$

and since N_{Nu} is given by Equation (22), Equations (22) and (28) yield the interfacial temperature as a function of the amount of liquid vaporized. Equations (22) to (28) plus physical property data and measurements of inlet and exit temperatures, compositions, and pressures fix the parameters r, K and σ.

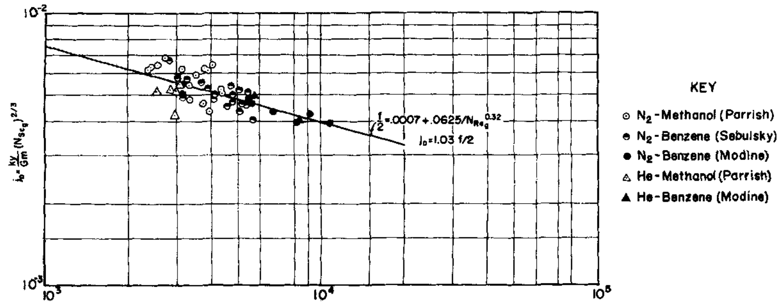

Fig. 3. Mass transfer coefficients.

The calculations were carried out on a digital computer, using the improved Euler method (2), in a manner similar to that used by Toor and Sebulsky (9). For comparison purposes, calculations were also carried out with the assumption that the interfacial temperature was equal to the bulk liquid temperature at all points in the column.

First approximations to K and r were fed into the computer as input data. During the iteration procedure, the value of K was readjusted by using Equation (27) over the entire column and the measured exit temperature [K varied slightly during the iteration because the physical properties in Equation (27) depend upon the integration path] while the value of r was recomputed from the calculated heat flux distance profile. The column calculations were iterated on until the calculated exit liquid temperature was within 0.2°C. of the measured value. The value of r converged rapidly, generally well before the temperature convergence. Usually five iterations of the column were required with a total computing time of approximately 1 min.

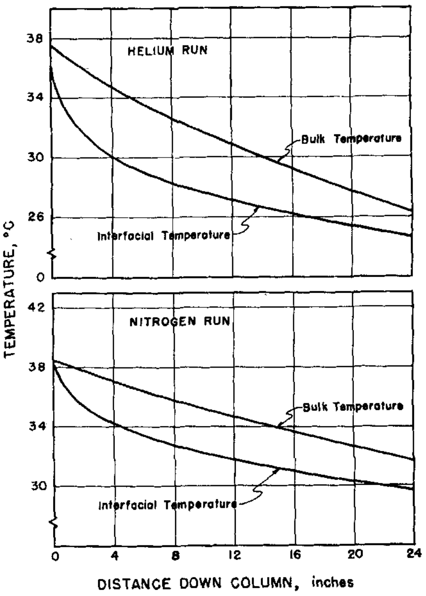

Fig. 4. Typical liquid temperature profiles.

RESULTS

Toor and Sebulsky (9) had already vaporized benzene into nitrogen. Further measurements were carried out at higher gas Reynolds numbers and at

TABLE 3. RANGES OF VARIABLES

Column pressure	1-1.4 atm.; average ΔP across column—60 mm.
Gas Reynolds number	2,400-11,000; average 6% change across column
Liquid Reynolds number	430-500
Inlet gas and liquid temperature	35-40°C.
Change in liquid temperature across column	2.4-12.3°C.; average for N_2 runs—6.9°C., average for He runs—8.3°C.
Kinematic viscosity of gas	

Benzene: N_2-0.36 at interface to maximum of 0.64 sq. ft./hr. in bulk
Benzene: He-0.67 at interface to maximum of 5.0 sq. ft./hr. in bulk

higher fluxes with this system and the benzene-helium system. Parrish's (*4*) data obtained with methanol-nitrogen and methanol-helium are also included.

Experiments were carried out over the range of conditions shown in Table 3. β at the column exit ranged between 0.75 and 0.83.

The measured j_D is $\sigma\, f/2$ and these values are plotted as a function of the arithmetic average of the inlet and exit gas Reynolds numbers in Figures 2 and 3. Figure 2 shows the results obtained when the interfacial temperature is assumed to be the bulk temperature and Figure 3 the results when the interfacial temperature is computed in the manner described earlier. The average value of σ is 0.84 in the former case and 1.03 in the latter.

Figure 4 shows typical bulk liquid and interfacial temperature profiles in the column. It is noted that the largest difference between the interfacial and bulk temperature occurs near the top of the column.

DISCUSSION

The low values of j_D in Figure 2 differ significantly from the $f/2$ line and correspond to high flux runs.

When the lowering of the interfacial temperature is accounted for, as in Figure 3, there is no significant difference between the results of the high and low flux runs. The quite large variations in physical properties from the interface to the bulk of the gas (Table 3) have little apparent effect on the mass transfer.

The ripples which are present on the liquid surface raise some uncertainty about the gas side mass transfer coefficients (3), but previous studies (8) indicate that for the conditions of this work the expected value of α is near one. What is probably more important, the ripples increase the heat transfer in the liquid so the liquid side heat transfer coefficient should be greater and the gas side mass transfer coefficient less than calculated. Thus, the consistency of the mass transfer results is probably less of an indication of the exactness of the heat transfer calculations than an indication of the lack of high sensitivity of the mass transfer coefficient to the heat transfer coefficient.

It is concluded that the low apparent values of j_D obtained in this study and earlier studies are caused by a lowering of the interfacial temperature, and that the proposed method of computing the interfacial temperature is satisfactory insofar as mass transfer calculations are concerned.

ACKNOWLEDGMENT

This research was supported by a grant from The Petroleum Research Fund and administered by the American Chemical Society. Grateful acknowledgement is hereby made to the donors of the said fund.

NOTATION

a_i = characteristic constants as defined by Equation (7)
b = film thickness, ft.
C_P = heat capacity, B.t.u./lb. °F.
d = tube diameter, ft.
D = diffusion coefficient, sq. ft./hr.
$f/2$ = friction factor
G_m = molar gas velocity, lb. moles/sq. ft. hr.
h = heat transfer coefficient, B.t.u./hr. sq. ft. °F.
j_D = Colburn j factor for mass
k = thermal conductivity, B.t.u/hr. sq. ft. °F./ft.
k_y = mass transfer coefficient, lb. moles/sq. ft. hr.
K = constant in heat balance as defined by Equation (27)
$\mathcal{L}$ = LaPlace transform operator
N = point mass transfer rate, lb. moles/sq. ft. hr.
n = molar gas flow rate, lb. moles/hr.
p = independent variable in transform equation
$P°$ = vapor pressure, atm.
P_T = column pressure, atm.
q = heat flux, B.t.u./hr. sq. ft.
r = constant as defined by Equation (21)
t_o = inlet liquid temperature, °F.
t = point liquid temperature, °F.
$\bar{t}$ = bulk liquid temperature, °F.
T = reduced temperature, $(t - t_s)/(t_o - t_s)$
u = point liquid velocity, ft./hr.
$\bar{U}$ = mean liquid velocity, ft./hr.
W = liquid flow rate, lb./hr.
x = distance down column, ft.
y = distance from interface, ft.
$y_{A,B}$ = gas phase mole fractions

Greek Symbols

α = thermal diffusivity sq. ft./hr.
β = reduced axial distance, $(x/b)(N_{Re}\, N_{Pr})^{-1}$
$\gamma_m{}^2$ = constants as defined by Equation (15)
Γ = mass liquid flow rate per unit perimeter, lb./ft. hr.
ϵ = dummy variable of integration
η = reduced distance from the interface, y/b
λ_i = eigenvalue as defined by Equation (8)
λ_A = latent heat of vaporization, B.t.u./lb. mole
μ = viscosity, lb./ft. hr.
ρ = density, lb./cu. ft.
σ = constant defined by Equation (26)
ϕ_i = eigenfunctions defined by Equation (6)

Dimensionless Groups

N_{Re} = Reynolds number, dG/μ_g for the gas and $4\Gamma/\mu$ for the liquid
N_{Pr} = Prandtl number, $C_P\mu/k$
N_{Nu} = Nusselt number, hb/k
N_{Sc} = Schmidt number, $\mu/\rho D$

Subscripts

g = gas phase quantity, no subscript liquid phase quantity
s = value at interface
A,B = species A and B

LITERATURE CITED

1. Carslaw, H. S., and J. C. Jaeger, "Conduction of Heat in Solids," Oxford Univ. Press, Oxford, England (1947).
2. Henrici, P., "Discrete Variable Methods in Ordinary Differential Equations," Wiley, New York (1962).
3. Kafesjian, Ralph, C. A. Plank, and E. R. Gerhard, *A.I.Ch.E. Journal*, **7**, 463 (1961).
4. Parrish, E. B., M.S. thesis, Carnegie Inst. of Technol., Pittsburgh, Pennsylvania (1960).
5. Pigford, R. L., Ph.D. thesis, Univ. Illinois, Urbana, Illinois (1941).
6. Sebulsky, R. T., Ph.D. thesis, Carnegie Inst. of Technol., Pittsburgh, Pennsylvania (1961).
7. Sellars, J. R., Myron Tribus, and J. S. Klein, *Trans. Am. Soc. Mech. Engrs.*, **78**, 441 (1956).
8. Sherwood, T. K., and R. L. Pigford, "Absorption and Extraction," p. 79, McGraw-Hill, New York (1952).
9. Toor, H. L., and R. T. Sebulsky, *A.I.Ch.E. Journal*, **7**, 558 (1961).

Manuscript received May 10, 1962; revision received October 24, 1962; paper accepted October 31, 1962.