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MASS TRANSFER IN LAMINAR FALLING LIQUID FILMS WITH ACCOMPANYING HEAT TRANSFER AND INTERFACIAL SHEAR

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Abstract – An analysis is made of mass transfer into a laminar finite falling film with accompanying heat transfer and interfacial shear. The analysis is extended to include chemical reaction with linear reaction kinetics. Variations of the liquid physical properties and kinetic rate constants with temperature are explicitly taken into account. Results are compared with the isothermal zero interfacial shear case. Average isothermal and nonisothermal enhancement factors are presented for first- and zero-order reactions. The analysis shows that the heat transfer and gas shear can have a profound influence on the mass transfer rate.

NOMENCLATURE

C, C^+, C^*,	concentration of absorbed gas; C/C_s;
C^+_{bulk},	$1 - C^+$; bulk;
C_i,	series expansion coefficients;
C_s,	gas solubility;
C_0,	initial concentration of absorbed gas;
D, D_0,	molecular diffusivity; at T_0;
$\hat{E}, E_a$,	activation energy for chemical reaction; for viscosity;
g,	gravitational acceleration constant;
h,	H_s/R_gE_a, dimensionless;
H_s,	heat of solution;
k_0, k_1,	reaction rate constant; for zero-order; for first-order;
k_{00}, k_{10},	rate constant for zero-order reaction at T_0, for first-order reaction at T_0;
k_0^*, k^*,	$k_{00}\Delta^2/D_0C_s(T_1)$, dimensionless; $k_{10}\Delta^2/D_0$, Damkohler Group II;
k',	mass transfer coefficient;
m,	$-\rho_1 g \sin\theta$;
m_1, m_2,	$\dfrac{-\alpha \pm \sqrt{(\alpha^2 + 4k_1^*)}}{2}$;
$N_{A_{\vert\eta=1}}$,	mass flux through interface;
N,	eigenfunction;
p,	$\hat{E}/E_aR_g$, dimensionless;
Q,	flow rate per unit width;
Sh^1, Sh, Sh^1_{00},	Sherwood number defined with respect to $(C_s - C_{\text{bulk}})$; defined with respect to $(C_s - C_0)$; limiting Sh^1;
T, T_0, T_1,	temperature; at the wall (also the reference temperature for isothermal condition); at the gas–liquid interface;
u,	'transient part' of solution;
U, U_1, $\langle U\rangle, U^*$,	X-component velocity; at gas–liquid interface; average; U/U_1;
v,	'steady part' of solution;
$W_A, \tilde{W}_A$, $\tilde{W}_{A_{sat}}$,	total absorption rate per unit width; $W_A/C_s(T_1)$; at saturation;
X, X^*,	axial distance or exposed film length; XD_0/Δ^2U_1, dimensionless;
Y,	normal distance from the wall.

Greek symbols

α,	$E_a(T_1 - T_0)/T_0^2$, dimensionless;
β,	$\dfrac{\tau_1\Delta}{\mu_0U_1}\,\dfrac{e^\alpha - 1}{\alpha}$, dimensionless;
Δ,	average film thickness;
η,	dimensionless Y-distance from the wall;
θ,	angle of inclination;
θ_c,	gas–liquid contact time;
λ,	eigenvalue;
μ, μ_0,	liquid viscosity; at T_0;
ρ_1,	liquid density;
τ_1,	constant interfacial stress;
ϕ, ϕ_I, ϕ_N,	enhancement factor; isothermal; nonisothermal.

INTRODUCTION

IN RECENT years extensive research efforts have been conducted on falling film flow because it has found wide application in modern process industries involving heat and mass transfer. Common process equipment utilizing film flow include heat exchangers, vertical condensers, film evaporators, distillation columns, packed and wetted-wall columns, trickling-type cooling or absorption towers, and annular two-phase flow in pipelines or boiler tubes. Wetted-wall columns and wetted spheres are common laboratory devices for measuring molecular diffusion coefficients and obtaining kinetic rate data in both Newtonian and non-Newtonian liquids.

The classical Graetz–Nusselt formulation which neglects axial diffusion has been traditionally used to describe physical absorption into a laminar finite falling film. For short contact times, Higbie's penetration theory gives nearly identical results. Olbrich and Wild [1] have solved the convective-diffusion equation for various flow geometries that have a certain degree of symmetry. The same kind of problem was treated by Tamir and Taitel [2] but they considered thermodynamic nonequilibrium at the gas–liquid interface by adding a constant interfacial resistance. Rotem and Neilson [3] analyzed low Peclet number film flow by including the axial diffusion term. Chavan and Mashelkar [4] and Mashelkar *et al.* [5] also solved the convective-diffusion equation for a non-Newtonian pseudoplastic liquid film. Most of the gas/liquid contacting processes in industry are accompanied by chemical reactions which have the favorable property of enhancing the absorption rate. Ratcliff and Holdcroft [6] measured the absorption rates of CO_2 and 1,1-dimethoxyethane vapor into a spherical liquid film undergoing first-order chemical reactions. The kinetic rate constant obtained was in good agreement with other independent kinetic measurements. Gottfredi *et al.* [7] presented both perturbation and numerical solutions for mass transfer with chemical reaction in a laminar falling film. Important contributions were made by Jameson *et al.* [8] who numerically solved the problem of diffusion with a generalized chemical reaction in a finite falling film obeying Nusselt's relation. Absorption enhancement rates were presented for higher orders of reaction between the gas absorbed and the liquid reactant.

Although an enormous quantity of research has been carried out for film flow under isothermal conditions, much less is known about the hydrodynamic and mass transfer behavior when significant temperature gradients exist in the liquid film. This occurs, for example, in the process of sulfonating and sulfating an organic acid in a wetted-wall column when the reaction between the organic acid with sulfur trioxide is highly exothermic. The color of the product, which is very sensitive to temperature, has to be carefully controlled by cooling through the walls. Chemical absorption studies have shown the importance of considering these heat effects. Since the film thickness is small and the liquid viscosity is a strong function of temperature, the velocity distribution in the film will change considerably when there is a large temperature gradient. Moreover, the molecular diffusion coefficient, kinetic rate constant and gas solubility are all functions of temperature. Another important parameter is the cocurrent or countercurrent gas shear which modifies not only the velocity distribution and transfer rates, but also has a dominant influence on the stability of the flow as studied by Yih and Seagrave [9, 10]. In analyzing dispersion in a falling film accompanied by heat transfer and interfacial shear, Shair [11] showed that the flow characteristics could be greatly affected by a change in the physical properties within the film and by the interfacial drag. Jennis [12] made a preliminary investigation on the mass transfer into a falling film by assuming a linear variation of viscosity and mass diffusion coefficient with temperature. The series solution obtained, however, was restricted to small changes in the temperature gradient with relatively large interfacial shear. The objective of the present study is to analyze mass transfer into a laminar finite falling film under different conditions of interfacial shear and heat transfer. The analysis is then extended to include first-order and zero-order chemical reactions. The problem is solved for a linear temperature drop across the liquid film and a constant cocurrent shear stress at the gas–liquid interface. The liquid viscosity, molecular diffusivity, kinetic rate constant and gas solubility are all assumed to vary with temperature in the liquid film. Absorption rates are predicted by an exact solution of the governing equations and compared with the isothermal, zero interfacial shear case. Average isothermal and nonisothermal enhancement factors are examined to determine the effects of heat transfer.

PHYSICAL ABSORPTION

A Newtonian liquid film of average thickness, Δ, is in steady, uniform laminar flow down an inclined plane under the action of gravity as shown in Fig. 1. The gas flow is downward and cocurrent to avoid flooding. A chemical component which is uniformly distributed in the gas phase is diffusing from the gas into the liquid film. Initially, the liquid phase contains only pure liquid reactant. A small linear temperature drop is imposed across the film and the gas–liquid interface is sheared by a constant tangential stress, τ_1. The liquid phase concentration $C_s(T_1)$ at the gas–liquid interface is assumed to be in equilibrium with the gas phase. Other assumptions involved in the present treatment are:

(1) The gas-phase mass transfer resistance is negligible.
(2) Volume change of the liquid phase due to absorption is negligible.
(3) The liquid phase is nonvolatile.
(4) Axial diffusion is neglected for high Peclet number film flow.
(5) Entrance effects are not considered.
(6) The viscosity of the liquid varies exponentially

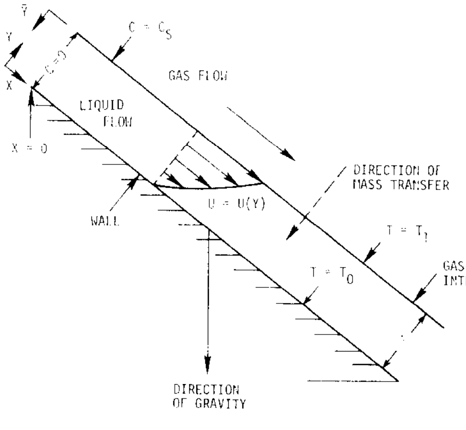

FIG. 1. Gas absorption in a laminar falling film.

with temperature, the molecular diffusion coefficient follows the Stokes–Einstein relation, the kinetic rate constant obeys the Arrhenius law, and the solubility of the gas is a linear function of the surface temperature.

Based on the physical model and the assumptions stated, the transport equations and boundary conditions may be expressed as in the following:

For heat transfer the energy equation is reduced to

$$\frac{\mathrm{d}^2T}{\mathrm{d}\eta^2} = 0 \tag{1}$$

with the boundary conditions

$$T = T_0 \quad \text{at } \eta = 0 \text{ (the wall)}, \tag{2}$$

$$T = T_1 \quad \text{at } \eta = 1 \text{ (the interface)}, \tag{3}$$

where $\eta = Y/\Delta$. The solution is simply

$$T = T_0 + (T_1 - T_0)\eta. \tag{4}$$

Since the temperature profile is known, the variation of viscosity and molecular diffusion coefficient with temperature can be determined. Employing the same assumptions as used by Shair [11], the viscosity–temperature dependence is of the form, for $(T_1 - T_0)/T_0 \ll 1$,

$$\mu = \mu_0 \,\mathrm{e}^{-\alpha\eta} \tag{5}$$

where $\alpha = E_a(T_1 - T_0)/T_0^2$. μ_0 is the viscosity at the reference wall temperature T_0, and E_a represents a free energy of activation. Values of the parameter E_a have been determined experimentally by Iyer [13] who examined 87 different liquids of diverse chemical constitution. The exponential dependency was found to be quite adequate in describing the temperature variation on liquid viscosity for a variety of pure liquids. Increasing values of α therefore denotes increasing variation of viscosity with temperature across the film. Typical values of α lie between 0 and 1.

For many liquid binary systems, $D\mu/T$ is essentially a constant. Substitution of equation (4) and (5) gives

$$D = D_0 \,\mathrm{e}^{\alpha\eta} \tag{6}$$

for $(T_1 - T_0)/T_0 \ll 1$.

By utilizing equation (5), the dimensionless form of the momentum equation reduces to

$$\frac{\mathrm{d}}{\mathrm{d}\eta}\left(\mathrm{e}^{-\alpha\eta}\frac{\mathrm{d}U^*}{\mathrm{d}\eta}\right) = \frac{m\Delta^2}{\mu_0 U_1} \tag{7}$$

with the boundary conditions

$$U^* = 0 \qquad \text{at } \eta = 0, \tag{8}$$

$$\frac{\mathrm{d}U^*}{\mathrm{d}\eta} = \frac{\tau_1 \Delta\,\mathrm{e}^{\alpha}}{\mu_0 U_1} \text{at } \eta = 1, \tag{9}$$

where $U^* = U/U_1$, $m = -\rho_1 g \sin\theta$, and U_1 is the surface velocity. The solution has been given by Shair [11]:

$$U^* = (1 - \beta)\left(\frac{\alpha\eta\,\mathrm{e}^{\alpha\eta} - \alpha\,\mathrm{e}^{\alpha\eta} - \mathrm{e}^{\alpha\eta} + \alpha + 1}{1 + \alpha - \mathrm{e}^{\alpha}}\right) + \beta\left(\frac{\mathrm{e}^{\alpha\eta} - 1}{\mathrm{e}^{\alpha} - 1}\right) \tag{10}$$

where

$$\beta = \frac{\tau_1 \Delta}{\mu_0 U_1}\left(\frac{\mathrm{e}^{\alpha} - 1}{\alpha}\right).$$

The value of $\beta = 0$ corresponds to the freely falling film case while $\beta = 1$ corresponds to a highly stressed film or plane Couette flow. When $\alpha = 0$, application of L'Hospital's rule to equation (10) gives the expression for an isothermal film:

$$U^* = (\beta - 1)\eta^2 + (2 - \beta)\eta. \tag{11}$$

The average velocity is

$$\frac{\langle U \rangle}{U_1} = (1 - \beta)\left(\frac{\alpha^2 + 2\alpha + 2 - 2\,\mathrm{e}^{\alpha}}{\alpha^2 + \alpha - \alpha\,\mathrm{e}^{\alpha}}\right) + \beta\left(\frac{\mathrm{e}^{\alpha} - \alpha - 1}{\alpha\,\mathrm{e}^{\alpha} - \alpha}\right). \tag{12}$$

When $\alpha = 0$, equation (12) tends to

$$\frac{\langle U \rangle}{U_1} = \frac{4 - \beta}{6}. \tag{13}$$

Mass transfer begins at the axial distance $X = 0$. At steady state the concentration of the diffusing component satisfies the convective-diffusion equation

$$U^*\frac{\partial C^+}{\partial X^*} = \frac{\partial}{\partial \eta}\left(\mathrm{e}^{\alpha\eta}\frac{\partial C^+}{\partial \eta}\right), \tag{14}$$

with the boundary conditions

$$C^+ = 0 \quad \text{at } X^* = 0, \tag{15}$$

$$\frac{\partial C^+}{\partial \eta} = 0 \quad \text{at} \quad \eta = 0, \tag{16}$$

$$C^+ = 1 \quad \text{at} \quad \eta = 1, \tag{17}$$

where C^+ and X^* are the dimensionless concentration and axial length defined respectively as

$$C^+ = \frac{C}{C_s(T_1)}, \quad \text{and } X^* = \frac{XD_0}{\Delta^2 U_1}.$$

It should be noted that the equilibrium surface concentration, C_s, is a function of the surface temperature T_1. Therefore, C_s will decrease when α increases, that is, when T_1 is increased while a reference temperature T_0 is maintained constant for all the cases considered. Following an analysis by Shah [14], C_s is assumed to be a linear function of the temperature change, or, for $(T_1 - T_0)/T_0 \ll 1$,

$$C_s(T_1) = C_s(T_0)(1 - h\alpha) \tag{18}$$

where $h = H_s/(R_g E_a)$ is a constant dependent on the physical properties of the system. H_s is the heat of solution and R_g is the gas constant. The case of $h = 0$ represents an isothermal condition where $T_1 = T_0$. Typical values of h lie between 0.5 and 1.0. It should be noted that this solution model, along with assumptions (1) and (2), makes this analysis most appropriate for absorption of gases with low solubility.

Equation (14) can be solved by the method of separation of variables. The nonhomogeneous boundary conditions are rendered homogeneous by letting $C^* = 1 - C^+$ and substituting into equations (14)–(17). The analytical solution can thus be written as

$$C^+ = 1 - C^* = 1 - \sum_{i=1}^{\infty} C_i N_i(\eta) e^{-\lambda_i^2 X^*} \tag{19}$$

where λ_i and N_i are the eigenvalues and eigenfunctions, respectively, satisfying the following characteristic equation:

$$\frac{d}{d\eta}\left(e^{\alpha\eta}\frac{dN_i}{d\eta}\right) + \lambda_i^2 U^* N_i = 0, \tag{20}$$

with the boundary conditions

$$\frac{dN_i}{d\eta} = 0 \quad \text{at } \eta = 0, \tag{21}$$

$$N_i = 0 \quad \text{at } \eta = 1. \tag{22}$$

The eigenvalues are computed by a fourth-order Runge–Kutta–Gill method and Newton's iteration (1977). This method has also been applied successfully to mass transfer in turbulent falling films (1978). The series expansion coefficients are obtained by applying the orthogonality condition of eigenfunctions:

$$C_i = \frac{\int_0^1 U^* N_i \, d\eta}{\int_0^1 U^* N_i^2 \, d\eta} \tag{23}$$

$$= -\frac{2}{\lambda_i\left(\left.\frac{\partial N_i}{\partial \lambda_i}\right|_{\eta=1}\right)}. \tag{24}$$

The bulk concentration, Sherwood number and the absorption rate can be evaluated as in the following:

$$C_{bulk}^+ = \frac{\int_0^1 U^* C^+ \, d\eta}{\int_0^1 U^* \, d\eta} \tag{25}$$

$$= 1 - \frac{\sum_{i=1}^{\infty} C_i e^{-\lambda_i^2 X^*}\left(-\frac{e^{\alpha}}{\lambda_i^2}\left.\frac{\partial N_i}{\partial \eta}\right|_{\eta=1}\right)}{\langle U \rangle / U_1}. \tag{26}$$

The Sherwood number, Sh', is defined with respect to D_0 and the concentration difference $(C_s - C_{bulk})$:

$$Sh' = \frac{K^1 \Delta}{D_0} \tag{27}$$

$$= \frac{e^{\alpha}}{(C_{bulk}^+ - 1)} \sum_{i=1}^{\infty} C_i \left.\frac{\partial N_i}{\partial \eta}\right|_{\eta=1} e^{-\lambda_i^2 X^*}. \tag{28}$$

For large values of X^*, only the first term in the series will contribute significantly. Therefore, the fully developed Sherwood number is

$$Sh'_f = \frac{\langle U \rangle}{U_1}\lambda_1^2. \tag{29}$$

The total absorption rate per unit width, W_A, for an exposed film length, X, is calculated in terms of $\tilde{W}_A$

$$\tilde{W}_A = e^{\alpha} \Delta U_1 \sum_{i=1}^{\infty} C_i \left.\frac{\partial N_i}{\partial \eta}\right|_{\eta=1}\left[\frac{1}{\lambda_i^2}\left(e^{-\lambda_i^2 X^*} - 1\right)\right] \tag{30}$$

where

$$\tilde{W}_A = \frac{W_A}{C_s(T_1)}.$$

Equation (30) shows that the absorption rate will increase for an increase in the film thickness or the flow rate. The above analysis is useful for determining absorption rates at intermediate and long contact times.

FIRST-ORDER AND ZERO-ORDER REACTIONS

The momentum and energy transport equations remain the same. The diffusion equation becomes

$$U(Y)\frac{\partial C}{\partial X} = \frac{\partial}{\partial Y}\left[D(T)\frac{\partial C}{\partial Y}\right] - \begin{cases} k_1(T)C & \text{(first-order)} \\ k_0(T) & \text{(zero-order)} \end{cases} \tag{31}$$

where k_1 and k_0 are the first-order and zero-order reaction rate constants respectively. All the rate constants are assumed to obey the Arrhenius relation. Using the same kind of reasoning in deriving $\mu(\eta)$, $D(\eta)$, and C_s we arrive at

$$k_1 = k_{10}\, e^{p\alpha\eta}, \quad k_0 = k_{00}\, e^{p\alpha\eta} \tag{32}$$

where $p = \hat{E}/R_g E_a$ is a constant depending on the physical properties of the system. $\hat{E}$ is the activation energy, k_{10} and k_{00} are the rate constants at T_0. By letting $C^+(X^*, \eta) = v(\eta) + u(X^*, \eta)$, the dimensionless form of equation (31) can be reduced to two equivalent sets of equations by linear superposition:

(1) 'transient part'

$$U^*\frac{\partial u}{\partial X^*} = \frac{\partial}{\partial \eta}\left(e^{\alpha\eta}\frac{\partial u}{\partial \eta}\right) - \begin{cases} k_1^* e^{p\alpha\eta} u & \text{(first-order)} \quad (33) \\ 0 & \text{(zero-order)} \quad (34) \end{cases}$$

with the boundary conditions

$$u = -v \quad \text{at } X^* = 0, \tag{35}$$

$$\frac{\partial u}{\partial \eta} = 0 \quad \text{at } \eta = 0, \tag{36}$$

$$u = 0 \quad \text{at } \eta = 1, \tag{37}$$

(2) 'steady part'

$$\frac{d}{d\eta}\left(e^{\alpha\eta}\frac{dv}{d\eta}\right) - \begin{cases} k_1^* e^{p\alpha\eta} v = 0 & \text{(first-order)} \quad (38) \\ k_0^* e^{p\alpha\eta} = 0 & \text{(zero-order)} \quad (39) \end{cases}$$

with the boundary conditions

$$\frac{dv}{d\eta} = 0 \quad \text{at } \eta = 0, \tag{40}$$

$$v = 1 \quad \text{at } \eta = 1, \tag{41}$$

where $k_1^* = \Delta^2 k_{10}/D_0$ is the Damkohler Group II and $k_0^* = k_{00}\Delta^2/[D_0 C_s(T_1)]$. The first set of equations, which we shall designate the 'transient part', still constitute a proper Sturm–Liouville system and can be solved by the same method of separation of variables as described for the case of physical absorption. The characteristic equation for the first-order reaction case is

$$\frac{\mathrm{d}}{\mathrm{d}\eta}\left(\mathrm{e}^{\alpha\eta}\frac{\mathrm{d}N_i}{\mathrm{d}\eta}\right) + (\lambda_i^2 U^* - k_1^*\,\mathrm{e}^{p\alpha\eta})N_i = 0 \qquad (42)$$

with the boundary conditions given by equations (21) and (22).

The general solution of the second set of equations, which we shall designate the 'steady part', will require a numerical solution. For a value of $p = 1$, however, an analytical solution can be obtained. For a first-order reaction the solution is given by

$$v = \frac{m_2\,\mathrm{e}^{m_1\eta} - m_1\,\mathrm{e}^{m_2\eta}}{m_2\,\mathrm{e}^{m_1} - m_1\,\mathrm{e}^{m_2}} \qquad (43)$$

where

$$m_1 = \frac{-\alpha + (\alpha^2 + 4k_1^*)^{1/2}}{2},$$

and

$$m_2 = \frac{-\alpha - (\alpha^2 + 4k_1^*)^{1/2}}{2}. \qquad (44)$$

The dimensionless mass flux at the gas–liquid interface for a first-order reaction is given by

$$\frac{N_A|_{\eta=1}\Delta}{D_0 C_s(T_1)} = \mathrm{e}^{\alpha}\left[\sum_{i=1}^{\infty} C_i \frac{\partial N_i}{\partial\eta}\bigg|_{\eta=1} \mathrm{e}^{-\lambda_i^2 X^*} + \frac{m_1 m_2(\mathrm{e}^{m_1} - \mathrm{e}^{m_2})}{m_2\,\mathrm{e}^{m_1} - m_1\,\mathrm{e}^{m_2}}\right]. \qquad (45)$$

The solution for a zero-order reaction contains two different cases.

For $\alpha = 0$,

$$v = 1 - \frac{k_0^*}{2} + \frac{k_0^*}{2}\eta_2 \quad \text{if } k_0^* \le 2. \qquad (46)$$

For $\alpha \neq 0$,

$$v = \frac{k_0^*}{\alpha^2}(\mathrm{e}^{-\alpha\eta} - \mathrm{e}^{-\alpha}) + \frac{k_0^*}{\alpha}(n - 1) + 1$$

$$\text{if } k_0^* \le \frac{\alpha^2}{\mathrm{e}^{-\alpha} - 1 + \alpha}. \qquad (47)$$

Equations (46) and (47) can only be used for $k_0^* \le 2$ and

$$k_0^* < \frac{\alpha^2}{\mathrm{e}^{-\alpha} - 1 + \alpha},$$

respectively, because above these values, the solution v becomes negative somewhere in the liquid film which is physically impossible. For larger k_0^*, the gas can only penetrate a short distance beneath the liquid film before it is consumed completely by the reaction. Clearly, then, the boundary condition of zero mass flux at the wall equations (16) or (40) cannot be used when k_0^* is large. The solution for large k_0^* is available from Astarita and Marruci [16]. It is convenient to define an average isothermal and nonisothermal enhancement factor respectively as:

$$\Phi_I = \left(\frac{W_{A,\text{reaction}}}{W_{A,\text{physical}}}\right)_{\alpha} = 0$$

$$\Phi_N = \left(\frac{W_{A,\text{reaction}}}{W_{A,\text{physical}}}\right)_{\alpha} \neq 0 \qquad (49)$$

where the ratio is based on the same α and β for W_A, and for a first-order reaction,

$$\Phi = \frac{\left\{\sum_{i=1}^{\infty} -C_i\frac{\partial N_i}{\partial\eta}\bigg|_{\eta=1}\left[\frac{1}{\lambda_i^2}(1 - \mathrm{e}^{-\lambda_i^2 X^*})\right] + X^*\frac{m_1 m_2(\mathrm{e}^{m_1} - \mathrm{e}^{m_2})}{m_2\,\mathrm{e}^{m_1} - m_1\,\mathrm{e}^{m_2}}\right\}_{\text{reaction}}}{\left\{\sum_{i=1}^{\infty} C_i\frac{\partial N_i}{\partial\eta}\bigg|_{\eta=1}\left[\frac{1}{\lambda_i^2}(\mathrm{e}^{-\lambda_i^2 X^*} - 1)\right]\right\}_{\text{physical}}}. \qquad (50)$$

For a zero-order reaction:

$$\Phi_I = \frac{\left\{\sum_{i=1}^{\infty} -C_i\frac{\partial N_i}{\partial\eta}\bigg|_{\eta=1}\left[\frac{1}{\lambda_i^2}(1 - \mathrm{e}^{-\lambda_i^2 X^*})\right] + k_0^* X^*\right\}}{\left\{\sum_{i=1}^{\infty} C_i\frac{\partial N_i}{\partial\eta}\bigg|_{\eta=1}\left[\frac{1}{\lambda_i^2}(\mathrm{e}^{-\lambda_i^2 X^*} - 1)\right]\right\}_{\text{physical},\alpha=0}} \qquad (51)$$

$$\Phi_N = \frac{\left\{\sum_{i=1}^{\infty} -C_i\frac{\partial N_i}{\partial\eta}\bigg|_{\eta=1}\left[\frac{1}{\lambda_i^2}(1 - \mathrm{e}^{-\lambda_i^2 X^*})\right] + \frac{k_0^*}{\alpha}(1 - \mathrm{e}^{-\alpha})X^*\right\}}{\left\{\sum_{i=1}^{\infty} C_i\frac{\partial N_i}{\partial\eta}\bigg|_{\eta=1}\left[\frac{1}{\lambda_i^2}(\mathrm{e}^{-\lambda_i^2 X^*} - 1)\right]\right\}_{\text{physical},\alpha\neq 0}} \qquad (52)$$

where the expansion coefficients are now given by

$$C_i = \frac{\int_0^1 (-v)U^*N_i\,\mathrm{d}\eta}{\int_0^1 U^*N_i^2\,\mathrm{d}\eta}. \tag{53}$$

It should be noted that the nonisothermal enhancement factor, Φ_N, is the ratio of the chemical absorption rate at a certain α and β to the physical absorption rate at the same α and β.

Asymptotic solutions have been obtained for the isothermal, zero interfacial shear case in the light of penetration theory. For a first-order reaction (see Danckwerts [17] or Astarita [18]):

$$\frac{W_A}{C_sQ} = \frac{U_1}{\langle U\rangle}\frac{1}{\sqrt{k_1^*}}\left[\left(k_1^*X^* + \frac{1}{2}\right)\mathrm{erf}(k_1^*X^*)^{1/2} + \frac{1}{\sqrt{\pi}}(k_1^*X^*)^{1/2}\exp(-k_1^*X^*)\right]. \tag{54}$$

For very slow reaction or $k_1^*X^* \ll 1$

$$\frac{W_A}{C_sQ} = \frac{U_1}{\langle U\rangle}\left[\frac{2}{\sqrt{\pi}}(X^*)^{1/2} + \frac{1}{2\sqrt{\pi}}k_1^*(X^*)^{3/2}\right]. \tag{55}$$

As $k_1^*X^* \rightarrow 0$, the solution approaches the penetration theory for physical absorption;

$$\frac{W_A}{C_sQ} = \frac{U_1}{\langle U\rangle}\frac{2}{\sqrt{\pi}}(X^*)^{1/2}. \tag{56}$$

For very fast reaction or $k_1^*X^* \gg 1$

$$\frac{W_A}{C_sQ} = \frac{U_1}{\langle U\rangle}\frac{1}{\sqrt{k_1^*}}(k_1^*X^* + \tfrac{1}{2}). \tag{57}$$

The error is less than 3% when $k_1^*X^* > 2$.

As $k_1^*X^* \rightarrow \infty$

$$\frac{W_A}{C_sQ} = \frac{U_1}{\langle U\rangle}\sqrt{k_1^*}\,X^*. \tag{57a}$$

The error is within 5% when $k_1^*X^* > 10$.

For a zero-order reaction, (see Astarita [18]), the solutions are available from Astarita and Marrucci [16], when $k_0^*X^* \rightarrow 0$, the solution approaches penetration theory for physical absorption [equation (56)].

When $k_D^* \gg 2$, or fast reaction

$$\frac{W_A}{C_sQ} = \frac{U_1}{\langle U\rangle}\sqrt{(2k_0^*\,X^*}. \tag{57b}$$

RESULTS AND DISCUSSION

For physical absorption, the eigenvalues and the related quantities for $\alpha = 1$, $\beta = 0$ are reported in Table 1 for the first ten eigenvalues. Other cases for various α and β can be found in Yih [15]. The eigenvalues computed for $\alpha = 0$, $\beta = 0$ agree exactly with those of Tamir and Taitel [2] and Rotem and Neilson [3], showing that the solution is accurate. The eigenvalues are also compared with the series solution by Jennis [12] who used the assumptions of linear dependency of viscosity and molecular diffusivity on temperature. Agreement is very close showing that for small α, preferably $0 \le \alpha \le 0.3$, the two models are invariably the same. However, the two models deviate considerably for increasing values of α and β. This is because of the differences in average velocity between the two models for various values of α and β. The average velocity for a linear temperature dependency of μ and D can be derived as

$$\frac{\langle U\rangle}{U_1} = (1-\beta)\left[\frac{1.5\alpha^2 - \alpha - (1-\alpha)^2\ln(1-\alpha)}{\alpha^2 + \alpha(1-\alpha)\ln(1-\alpha)}\right] - \beta\left[\frac{(1-\alpha)\ln(1-\alpha) + \alpha}{\alpha\ln(1-\alpha)}\right]. \tag{58}$$

Equation (58) is not valid for $\alpha \ge 1$. The analysis of Jennis is restricted only to small α terms with relatively large β terms. This is primarily because of the linear assumptions used. The present work represents a substantial improvement by employing a more realistic assumption—the exponential dependency of viscosity on temperature and the Stokes–Einstein relation for the molecular diffusivity. Also, by invoking a quasi-numerical solution, the analysis is applicable to all ranges of α and β.

The variation of the bulk concentration with the dimensionless axial distance is presented in Fig. 2. In order to compare adsorption under nonisothermal conditions with that of isothermal conditions, the dimensionless bulk concentration with respect to the surface concentration at the reference temperature T_0

Table 1. Eigenvalues and related quantities for $\alpha = 1$, $\beta = 0$

i	λ_i	$\left.\frac{\partial N_i}{\partial \lambda_i}\right\|_{\eta=1}$	$\left.\frac{\partial N_i}{\partial \eta}\right\|_{\eta=1}$	C_i
1	3.587407	−0.387773	−1.477908	1.437713
2	9.065506	0.307105	3.021233	−0.718373
3	14.652242	−0.278843	−4.437974	0.489516
4	20.261025	0.262188	5.771499	−0.376492
5	25.878222	−0.250585	−7.046154	0.308419
6	31.499615	0.241778	8.275979	−0.262607
7	37.123439	−0.234734	−9.469927	0.229512
8	42.748822	0.228894	10.634134	−0.204395
9	48.375282	−0.223926	−11.773037	0.184630
10	54.002535	0.219614	12.889964	−0.168638

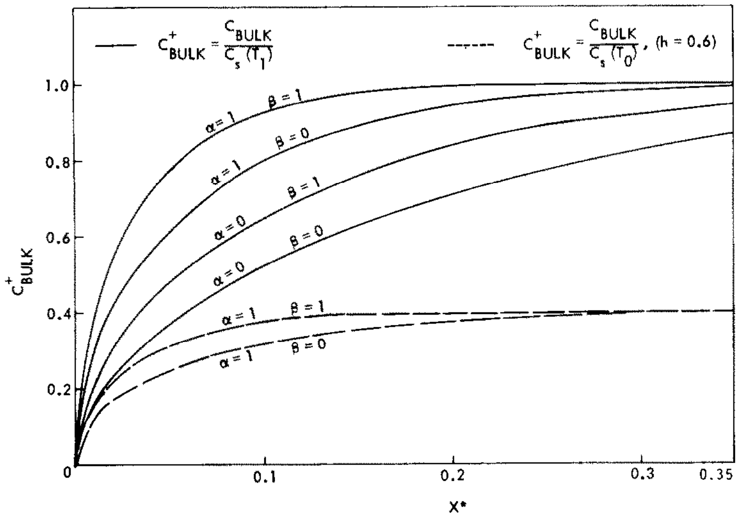

FIG. 2. Dimensionless bulk concentration as a function of dimensionless axial length for various values of α and β.

is also plotted for a typical value of $h = 0.6$ using equation (18). When compared with the case of $\alpha = 0$, $\beta = 0$ under the same $C_s(T_0)$, it is observed that at a fixed X^* in the film, an increase in β increases the bulk concentration while an increase in α may increase or decrease the bulk concentration depending on the value of h. This shows that in order to correctly analyze the effects of heat transfer on the absorption rates, the variation of gas solubility with surface temperature must be accounted for. Since in most typical gas–liquid systems, the gas solubility decreases with increasing temperature and the value of α is usually greater than 0.5, an increase in α usually decreases the bulk concentration. High values of α and β cause saturation to be reached more quickly. In order to assess the influence of heat transfer and cocurrent gas shear on the total absorption rate, it is necessary to compare several extreme operating conditions with the $\alpha = 0$, $\beta = 0$ case under the same flow rate. Since both the film thickness and surface velocity change under the same flow rate for different values of α and β, the dimensionless axial length, X^*, cannot be used as a basis for comparison. In fact, no convenient dimensionless quantity can be used. Therefore, a comparison is made by plotting the dimensional total absorption rate, $\tilde{W}_A$, vs the exposed film length, X. For a given flow rate per unit width, Q, a given $-m/\mu_0$ (i.e. a given slope) and a given τ_1/μ_0 (i.e. a given β), the film thickness, the average velocity and the surface velocity can be calculated. The procedure was shown in Yih [15]. For a given X and D_0, X^* is obtained at a given Q. From Fig. 2, the appropriate values of C^+_{bulk} can thus be found. The total absorption rate $\tilde{W}_A = C^+_{bulk}Q$ is then plotted vs the exposed film length in Fig. 3 for a given flow rate. An increase in flow rate will increase the absorption rate regardless of the values of α and β. The film reaches saturation more quickly at lower Q. An increase in cocurrent gas shear decreases the film thickness and increases the absorption rate. An increase in α also decreases the film thickness and increases the molecular diffusivity but may increase or decrease the absorption rate depending on the gas solubility–temperature relationship as expressed by the parameter h. For a countercurrent gas shear in which the film is still flowing downward or a temperature gradient in which $T_1 < T_0$ (i.e. $-\alpha$), the film thickness increases. Conclusions regarding their effects on mass transfer cannot readily be drawn because of the change in velocity profile in the liquid film. However, it can be reasoned from the above that a countercurrent gas shear (in which the film is still flowing downward) will decrease the mass transfer rate because of an increase in film thickness. A temperature gradient in which $T_1 < T_0$ will increase or decrease the

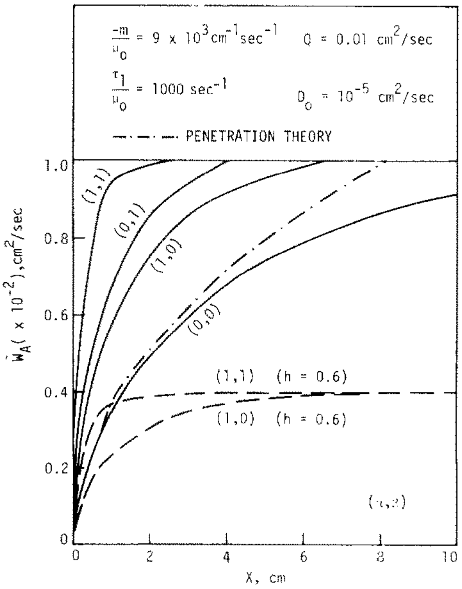

FIG. 3. Total absorption rate as a function of exposed film length; $Q = 0.01$ cm²/s.

mass transfer rate depending on the gas solubility–temperature relationship.

For a first-order reaction, two cases, $\alpha = 0, \beta = 0$; $\alpha = 1, \beta = 1$, are analyzed with different values of the Damkohler Group II, k_1^*. As an illustration, eigenvalues and the associated quantities are reported in Table 2 for $k_1^* = 50$ and $\alpha = 1, \beta = 1$. When k_1^* increases, the eigenvalues increase in magnitude showing that the 'transient part' decays rapidly. In Fig. 4, the local dimensionless mass flux is plotted as a function of the dimensionless axial length for different values of k_1^*. For $k_1^* = 1$, the mass transfer rate is only slightly influenced by the presence of the chemical reaction and the transfer rate approaches that of physical absorption. For $k_1^* = 50$ and 100, the transfer rate reaches its 'steady-state' value at a relatively small X^* implying that the length of the 'transient part' varies inversely with the reaction rate. At such high values of k_1^*, the system is essentially governed by the process of steady diffusion with chemical reaction and the effect of hydrodynamics is unimportant. For a zero-order reaction, the eigenvalues are the same as computed from the section on physical absorption. The only difference is the expansion coefficients which have to be obtained from equation (53). In Table 3, the expansion coefficients are reported for $k_0^* = 0.1$ and 1. In order to compare the reaction enhancement, the isothermal and nonisothermal enhancement factors based on equations (50)–(52) are plotted vs X^* for some values of k_1^* and k_0^* in Fig. 5. Evidently, the enhancement factors increase with X^*. At a fixed X^*, ϕ_N is larger than the corresponding ϕ_I for a given k_1^* or k_0^*. For example, ϕ_N for $k_1^* = 50$ is about two to three times greater than ϕ_1. This is probably due to the fact that an increase in α increases the molecular diffusivity, and above all, increases the Arrhenius reaction rate as

Table 2. Eigenvalues and related quantities for $\alpha = 1, \beta = 1$, $k_1^* = 50$, $p = 1$

i	λ_i	$\left.\frac{\partial N_i}{\partial \eta}\right\|_{\eta=1}$	C_i
1	15.455304	−30.149808	−0.037842
2	20.203396	14.388184	0.110398
3	25.494639	−10.711065	−0.177463
4	31.238910	9.832896	0.216354
5	37.337411	−9.981843	−0.229432
6	43.695594	10.585973	0.227118
7	50.236941	−11.410922	−0.217669
8	56.906721	12.348738	0.205685
9	63.667773	−13.345794	−0.193348
10	70.495088	14.373806	0.181595

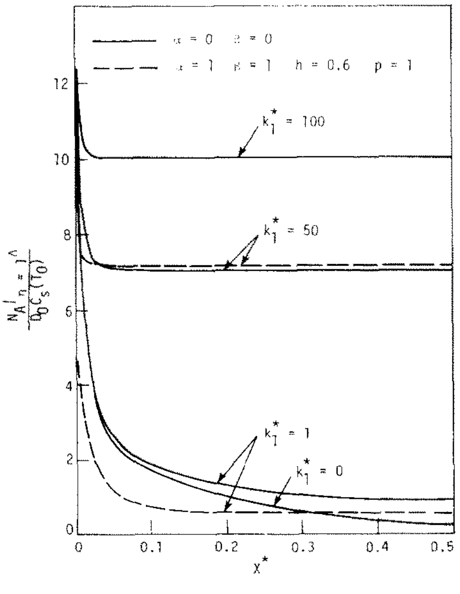

FIG. 4. Local dimensionless mass flux as a function of dimensionless axial length for different values of Damkohler Group II, k_1^*.

Table 3. Expansion coefficients, C_i, for zero-order reactions

	$\alpha = 0, \beta = 0$		$\alpha = 1, \beta = 1, p = 1$
i	$k_0^* = 0.1$	$k_0^* = 1$	$k_0^* = 1$
1	−1.291444	−0.870757	−1.157568
2	0.546601	0.556374	0.828685
3	−0.357798	−0.347899	−0.559626
4	0.272303	0.274340	0.445431
5	−0.220842	−0.218438	−0.361922
6	0.187394	0.188202	0.312382
7	−0.163000	−0.162009	−0.271564
8	0.144917	0.145337	0.243708
9	−0.130531	−0.130011	−0.219322
10	0.119106	0.119358	0.201344

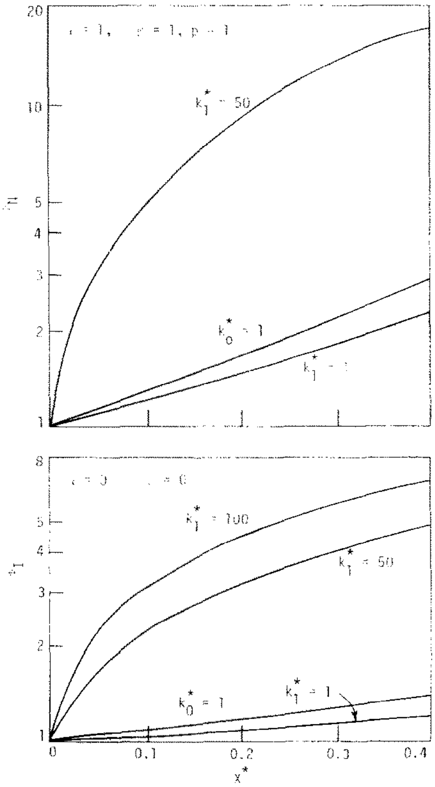

FIG. 5. Average isothermal and nonisothermal enhancement factors for first-order and zero-order reactions.

expressed by the parameter p. It must be remembered, however, that ϕ_N compares the total chemical absorption rate to the total physical absorption rate at the same α and β. It does not afford a comparison between the chemical absorption rate at a certain α and β with the physical absorption rate at $\alpha = 0, \beta = 0$. Such a comparison would have to be made on a dimensional basis such as under a given flow rate, slope and gas shear. Certain deductions, however, can be made regarding the effects of heat transfer and chemical reaction on the mass transfer rate. In physical absorption, heat transfer ($T_1 > T_0$) increases the molecular diffusivity and decreases the film thickness. This leads to an increase in mass transfer rate. However, the decrease of gas solubility with increasing α acts as an opposing factor in decreasing the mass transfer rate. So, an increase in α may increase or decrease the mass transfer rate depending on the value of h. In the presence of chemical reactions, heat transfer will further increase the Arrhenius reaction rate. The larger the rate constant, the more effective is the increase in mass transfer rate. Therefore, the reaction enhancement for a certain α and β as compared to $\alpha = 0, \beta = 0$ may be greater, less or even equal to 1.0 depending on the relative importance of several factors: the magnitudes of α, β, h and p.

CONCLUSIONS

A model which incorporates the effects of heat transfer and interfacial shear is developed for mass transfer with or without chemical reaction in a laminar falling film. Effects of heat transfer on liquid viscosity, molecular diffusivity, reaction rate constant and gas solubility are explicitly taken into account. The analysis shows that the heat transfer and interfacial shear can have a profound influence on the mass transfer rate. A cocurrent gas shear decreases the film thickness and increases the mass transfer rate. A linear temperature drop in the liquid film in which the wall is cooled also decreases the film thickness, but the mass transfer rate can be reduced or increased depending on the gas solubility–temperature relationship. For most gases under practical conditions, the gas solubility decreases with increasing temperature and so the mass transfer rate will be reduced. The assumptions that the viscosity varies exponentially with temperature and that $D\mu/T$ is constant represent a much better approximation than the assumptions of linear dependency of viscosity and molecular diffusivity on temperature as used by Jennis [12]. Moreover, this enables the analysis to be carried out for all ranges of the temperature gradient and interfacial shear, which is not possible in the work by Jennis. In the presence of chemical reactions, the heat transfer increases the Arrhenius reaction rate such that the reaction enhancement for finite values of α and β as compared to an isothermal, zero interfacial shear film ($\alpha = 0, \beta = 0$) may be greater, less or even equal to 1.0 depending on the relative importance of the dimensionless parameters α, β, h, and p. α, h, and p represent the effects of heat transfer on liquid viscosity, gas solubility, and reaction rate respectively, and β represents the interfacial shear. The parametric study presented here should be a useful guide to the development of experimental testing of certain extreme operating conditions of mass transfer into falling films involving heat transfer and interfacial shear.

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TRANSFERT MASSIQUE DANS DES FILMS TOMBANTS, LAMINAIRES, AVEC TRANSFERT THERMIQUE ET CISAILLEMENT INTERFACIAL

Résumé—On analyse le transfert massique dans un film laminaire tombant, avec transfert thermique et cisaillement à l'interface, en incluant une réaction chimique à cinétique linéaire. On tient compte des variations des propriétés physiques du liquide et des paramètres de la cinétique chimique en fonction de la température. Les résultats sont comparés avec le cas isotherme et à cisaillement interfacial nul. On considère des réactions du premier et du second ordre. L'analyse montre que le transfert thermique et le cisaillement dû au gaz ont une influence profonde sur le flux de transfert massique.

STOFFÜBERGANG AN LAMINAREN RIESELFILMEN, VERBUNDEN MIT WÄRMEÜBERGANG UND GRENZFLÄCHENSCHUBSPANNUNG

Zusammenfassung—Der Stoffübergang an einen laminaren endlichen Rieselfilm, der mit Wärmeübergang und Grenzflächenschubspannung verbunden ist, wird analytisch behandelt. Die Analyse wird auf den Einfluß chemischer Reaktionen mit linearer Reaktionskinetik ausgedehnt. Änderungen der physikalischen Eigenschaften der Flüssigkeit und der Reaktionsgeschwindigkeit mit der Temperatur werden ausdrücklich in Betracht gezogen. Die Ergebnisse werden mit dem isothermen Fall ohne Grenzflächenschubspannung verglichen. Es werden mittlere isotherme und nichtisotherme Verstärkungsfaktoren für Reaktionen ersten und nullten Grades mitgeteilt. Die Berechnung zeigt, daß der Wärmeübergang und die Gasschubspannung einen starken Einfluß auf die Stofftransportrate haben können.

МАССООБМЕН В ЛАМИНАРНЫХ СТЕКАЮЩИХ ПЛЕНКАХ ЖИДКОСТИ ПРИ НАЛИЧИИ ТЕПЛОПЕРЕНОСА И МЕЖФАЗНОГО НАПРЯЖЕНИЯ СДВИГА

Аннотация — Рассматривается массообмен ограниченной ламинарной стекающей пленки жидкости при наличии переноса тепла и межфазного напряжения сдвига. Анализ обобщен на случай линейной кинетики химической реакции. Учитываются температурные зависимости физических свойств жидкости и кинетических констант скорости реакции. Проведено сравнение с данными для изотермической задачи при отсутствии сдвига на поверхности раздела. Приводятся средние изотермические и неизотермические характеристики интенсификации массопереноса для реакций нулевого и первого порядков. Отмечается, что теплоперенос и сдвиг в газовой фазе могут существенно влиять на интенсивность массопереноса.