Heat Transfer with Simultaneous Chemical Reaction: Film Theory for a Finite Reaction Rate

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Heat transfer rates between a fluid and a surface of different temperature may be appreciably modified if stable concentration gradients are established in the boundary layer. In such cases an enthalpy flux results from mass transfer, in addition to the heat transfer caused by temperature gradients.

If there is frosting of a humid air stream in the boundary layer near a cold wall, for example, the water molecules' diffusing to the wall and freezing will result in a net increase in the total heat transfer over that obtained where no frosting occurs.

A more interesting example appears in those cases where chemical reactions occur in the boundary layer or on the solid wall. The chemical transformations cause concentration gradients and enthalpy fluxes as the reactants diffuse into, and products diffuse out of, the boundary layer. In addition to the effect on the heat transfer rate, the effective heat capacity of the fluid may be greatly increased.

Recent interest in the effect of chemical reactions on heat transfer rates has stemmed from the fact that endothermic dissociation of air and other atmospheric gases takes place in the boundary layer of high-speed areodynamic vehicles. Such dissociation may significantly affect the rate of heat transfer (*1, 14, 25, 26, 27, 31, 39*). In this same general area, cooling of rocket motors is affected by the exothermic recombination of chemical fragments near the chamber walls (*31*). There are numerous instances in the chemical processing industries of heat transfer to reacting gas mixtures. An example is the thermal cracking of light paraffins to produce ethylene (*35*). Reacting gas mixtures have also been proposed for coolants in nuclear reactors.

In recent years a number of people have analyzed in some detail the interactions among the mass, momentum, and heat transfer rates (*1, 11, 15, 16, 21, 32, 33*), but few have considered the effect of finite chemical reaction rates. Very slow reactions have of course little effect on heat transfer, and very rapid rates result in the assumption of local chemical equilibrium at all points in the boundary layer. The latter case has been thoroughly studied by a number of investigators by means of the nitrogen tetroxide $\rightleftharpoons$ 2 nitrogen dioxide system (*6, 23, 24, 30, 34, 37*). The decompositions of iodine and oxygen have also been studied (*15, 21*).

The nitrogen tetroxide decomposition was chosen for most studies since it is a rapid, homogeneous reaction with a large endothermic enthalpy change. Also, for convenience of experimentation, wall temperatures between 100° and 300°F. are sufficiently high to result in almost complete decomposition. The necessary physical and thermodynamic properties of the system are known (*7, 9, 12, 13, 20, 22, 28, 29*), and experimental measurements of the heat transfer coefficients have covered a wide temperature range in both laminar and turbulent flow, with various system geometries (*6, 23, 24, 30, 34, 37*). Both experimental and theoretical studies have shown that the standard Nusselt-Reynolds-Prandtl–number correlations were applicable if effective heat capacities and thermal conductivities were employed and if allowances were made for the temperature variation in these properties in the boundary layer.

Thus the work to date has been concerned primarily with general review articles and detailed investigations of the heat transfer rates with nitrogen tetroxide decomposition. The case of heat transfer from dissociated air with a finite recombination rate has been examined by Fay and Riddell (*14*), who integrated the laminar-boundary-layer equations numerically. This same case, with a linearized reaction-rate expression, was examined by Broadwell (*5*) to determine the effect of various reaction rates on temperature and concentration gradients. Brokaw (*8*) adopted a similar approach in analyzing the effect of finite kinetics upon thermal conductivity. The approach taken in the present paper is similar in many respects to the approaches of Broadwell and Brokaw, but the results are presented in a different form and are interpreted from a different point of view. The present analysis is based upon a film theory model and is restricted to the case of a very small temperature-driving force. This permits the solution of the problem without reference to a particular reaction kinetic expression.

THEORY

For heat transfer between a gas and a solid wall, analytical relationships are desired which will delineate the effect of a chemical reaction occurring in the boundary layer at a finite rate. A convenient way to express the results is to calculate the ratio of the heat transfer coefficient with reaction to the coefficient without reaction, the bulk and wall temperatures and fluid mechanical parameters being comparable.

The Chemical Reaction

It will be assumed that the following reversible reaction occurs in a mixture of ideal gases:

$$aA + bB \rightleftharpoons uU + vV \qquad (1)$$

In addition to the components entering into the chemical reaction, the gas stream contains an inert component I. The homogeneous gas-phase reaction proceeds at a rate r defined by

$$\frac{\text{moles of A reacting}}{(\text{time})(\text{volume})} = r \qquad (2)$$

and r is a function of temperature and gas-phase composition at the fixed pressure under consideration:

$$r = f(T, y_A, y_B, y_U, y_V) \qquad (3)$$

It is assumed that reaction (1) may also occur by a heterogeneous mechanism on the wall. The rate of the heterogeneous reaction is defined by

$$\frac{\text{moles of A reacting}}{(\text{time})(\text{wall area})} = \mathcal{R} \qquad (4)$$

and $\mathcal{R}$ is related to the temperature and composition of the gas adjacent to the wall by

$$\mathcal{R} = F(T_w, y_{A_w}, y_{B_w}, y_{U_w}, y_{V_w}) \qquad (5)$$

The Film Model

In the film-theory model a thin, laminar film of gas is visualized adjacent to the solid wall, separating the wall and the turbulent core or bulk gas region. There is no turbulence within the film; the transport processes occur by molecular diffusion only. In the bulk gas region the eddy diffusivity is assumed to be infinite, and concentration and temperature gradients are absent. The film is so thin, relative to the bulk region, that the accumulation of a component or of energy within the film is negligible compared to the fluxes through the film; thus the film is assumed to be in a steady state condition.

Other Assumptions

Two major assumptions or limitations are imposed upon the analysis:

1. The gas in the bulk region is in chemical equilibrium.
2. The temperature difference between the wall and bulk gas is very small.

Because of the first assumption, $(T_w - T_o)$ is the driving force for chemical change as well as for thermal conduction. Because of the second assumption, the system will be in its linear range, and thus q_w will be proportional to $(T_w - T_o)$. These two assumptions permit the diffusion and reaction kinetic equations to be linearized in such a way that very simple and very general expression is given to the results. The significance of these assumptions and their limitation of the usefulness of the results are discussed later.

Effects such as frictional heating and perturbations in the fluid mechanical parameters due to the diffusion fluxes are of course not considered in this simplified film-theory analysis.

Development of Equations

At any point within the film at a distance x from the wall the following material balances may be written:

$$aN_U = -uN_A \tag{6}$$

$$aN_V = -vN_A \tag{7}$$

$$aN_B = bN_A \tag{8}$$

$$\frac{dN_A}{dx} = -r \tag{9}$$

The first law of thermodynamics can be expressed:

$$\frac{d}{dx}\left[k\left(\frac{dT}{dx}\right) + N_A\,\Delta H\right] = 0 \tag{10}$$

The multicomponent diffusion equation for any given component may be written

$$\frac{dy_k}{dx} = \frac{1}{\rho}\sum_{\text{all } j \neq k} \frac{y_k N_j - y_j N_k}{D_{jk}} \tag{11}$$

with the restriction that N_I, the mole flux of the inert component, is zero. For example, with Equation (11), for component A

$$\frac{dy_A}{dx} = \frac{1}{\rho}\left(\frac{y_A N_B - y_B N_A}{D_{AB}} + \frac{y_A N_U - y_U N_A}{D_{AU}} + \frac{y_A N_V - y_V N_A}{D_{AV}} - \frac{y_I N_A}{D_{AI}}\right) \tag{12}$$

and with Equations (6), (7), and (8)

$$\frac{dy_A}{dx} = \frac{N_A}{a\rho}\left[\left(\frac{by_A - ay_B}{D_{AB}}\right) - \left(\frac{uy_A + ay_U}{D_{AU}}\right) - \left(\frac{vy_A + ay_V}{D_{AV}}\right) - \frac{ay_I}{D_{AI}}\right] \tag{13}$$

Writing similar equations for (dy_B/dx), etc., and dividing by Equation (13), one finds the gradients of concentration relative to y_A; for example

$$\frac{dy_B}{dy_A} = \frac{\left[\dfrac{by_A - ay_B}{D_{AB}} + \dfrac{by_U + uy_B}{D_{BU}} + \dfrac{by_V + vy_B}{D_{BV}} + \dfrac{by_I}{D_{BI}}\right]}{\left[\dfrac{ay_B - by_A}{D_{AB}} + \dfrac{ay_U + uy_A}{D_{AU}} + \dfrac{ay_V + vy_A}{D_{AV}} + \dfrac{ay_I}{D_{AI}}\right]} \tag{14}$$

Solution of Equations

The general solution of the relations illustrated in Equation (14) is a mathematical challenge which need not be met in the present analysis. The two assumptions listed previously, that

$$(T_w - T_o) \rightarrow 0 \tag{15}$$

and

$$r_o = f(T_o, y_{A_o}, y_{B_o}, y_{U_o}, y_{V_o}) = 0 \tag{16}$$

ensure that variations in the mole fractions of the various components through the film will be vanishingly small. Thus a linearized solution of equations of the form of (14) can be obtained.

Definition of

$$\frac{1}{\mathcal{D}_k} \equiv \sum_{\text{all } j \neq k} \frac{y_{j_o} - \left(\dfrac{\omega_j}{\omega_k}\right) y_{k_o}}{D_{jk}} \tag{17}$$

and

$$S_{jk} \equiv \left(\frac{\mathcal{D}_k}{\mathcal{D}_j}\right)\left(\frac{\omega_j}{\omega_k}\right)$$

where ω_j is the stoichiometric multiplier of component j and is a positive value for reactants, a negative one for products, and zero for an inert gas, yields for example

$$\frac{y_B - y_{B_o}}{y_A - y_{A_o}} = \left(\frac{\mathcal{D}_A}{\mathcal{D}_B}\right)\left(\frac{b}{a}\right) \equiv S_{BA}$$

$$= \frac{\left[\dfrac{by_{A_o} - ay_{B_o}}{D_{AB}} + \dfrac{by_{U_o} + uy_{B_o}}{D_{BU}} + \dfrac{by_{V_o} + vy_{B_o}}{D_{BV}} + \dfrac{by_{I_o}}{D_{BI}}\right]}{\left[\dfrac{ay_{B_o} - by_{A_o}}{D_{AB}} + \dfrac{ay_{U_o} + uy_{A_o}}{D_{AU}} + \dfrac{ay_{V_o} + vy_{A_o}}{D_{AV}} + \dfrac{ay_{I_o}}{D_{AI}}\right]} \tag{18}$$

If the binary diffusion coefficients are all equal, Equation (18) collapses to

$$S_{BA} = \frac{b + \theta y_{B_o}}{a + \theta y_{A_o}} \tag{19}$$

where $\theta \equiv u + v - a - b$.

Returning to Equation (10), integrating once, and using the boundary condition at $x = 0$ to determine the constant of integration one obtains

$$k\left(\frac{dT}{dx}\right) + N_A\Delta H = -q_w \tag{20}$$

Equation (11), together with Equations (6), (7), (8), and (17), may be used to eliminate N_A from Equation (20) to yield a differential equation for which the linearized solution for vanishingly small variations in temperature and composition is

$$k(T - T_o) - \rho\mathcal{D}_A\Delta H(y_A - y_{A_o}) = -q_w(x - x_F) \tag{21}$$

Combining Equations (9) and (10), assuming k and ΔH to be independent of x, one gets

$$k\left(\frac{d^2T}{dx^2}\right) = r\Delta H \tag{22}$$

But the restrictions imposed by Equations (15) and (16) permit the expansion of r in a linear combination

$$r = f_T(T - T_o) + f_A(y_A - y_{A_o}) + f_B(y_B - y_{B_o}) + f_U(y_U - y_{U_o}) + f_V(y_V - y_{V_o}) \tag{23}$$

which may be written in a shorthand manner with the definitions expressed in Equations (17) and (18)

$$r = f_T(T - T_o) + f_y(y_A - y_{A_o}) \tag{24}$$

where

$$f_y \equiv f_A + f_B S_{BA} + f_U S_{UA} + f_V S_{VA} \tag{25}$$

Substitution of Equation (24) into Equation (22) and elimination of $(y_A - y_{A_o})$ by use of Equation (21) yields

$$\frac{d^2(T - T_o)}{dz^2} = m\,\eta\,(T - T_o) + \frac{mq_w}{h^*}(z - 1) \tag{26}$$

The solution of Equation (26), subject to the boundary conditions

$$\begin{aligned} &\text{At } z = 0, \quad T = T_w \\ &\text{At } z = 1, \quad T = T_o \end{aligned} \tag{27}$$

is then written:

$$T - T_o = \left(\frac{q_w}{h^*\eta}\right)(1 - z)$$

$$+\left[(T_w - T_o) - \frac{q_w}{h^*\eta}\right]$$

$$\left[\cosh(\sqrt{\eta m}\ z) - \frac{\sinh(\sqrt{\eta m}\ z)}{\tanh(\sqrt{\eta m}\ )}\right] \tag{28}$$

Differentiating Equation (28) one gets the temperature gradient in the film:

$$-\frac{dT}{dz} = \frac{q_w}{h^*\eta} - \left[(T_w - T_o) - \left(\frac{q_w}{h^*\eta}\right)\right] \left[\sqrt{m\eta}\ \sinh(\sqrt{m\eta}\ z) - \frac{\sqrt{m\eta}\ \cosh(\sqrt{m\eta}\ z)}{\tanh(\sqrt{m\eta})}\right] \tag{29}$$

To obtain an expression for h it is necessary to find q_w, and this is done by using Equation (20) at $z = 0$:

$$q_w = -\frac{k}{x_F}\left(\frac{dT}{dz}\right)_{z=0} - \Delta H(N_A)_{z=0} \tag{30}$$

Now linearizing the heterogeneous reaction rate in the same manner as done with the homogeneous rate in Equation (24)

$$-(N_A)_{z=0} = \mathcal{R} = F_T(T_w - T_o) + F_y(y_{A_w} - y_{A_o}) \tag{31}$$

and eliminating $(y_{A_w} - y_{A_o})$ by means of Equation (21) one gets

$$-(N_A)_{z=0} = (T_w - T_o)\frac{Mh^*}{\Delta H}\left[1 + \frac{F_T\rho\mathcal{D}_A\Delta H}{F_y\ k}\right] - \left(\frac{M}{\Delta H}\right)(q_w) = (T_w - T_o)\left(\frac{Mh^*\eta}{\Delta H}\right) - \left(\frac{M}{\Delta H}\right)(q_w) \tag{32}$$

The substitution of η into Equation (32) is dependent upon the fact that

$$\frac{F_T}{F_y} = \frac{f_T}{f_y} \tag{33}$$

since, for any reacting component, for example A, the equilibrium relationships for the heterogeneous and homogeneous reactions must be identical:

$$-\left(\frac{\partial y_A}{\partial T}\right)_{\substack{\text{Ch. Equilibrium} \\ \text{const. } y_B,\ y_U,\ y_V}} = \frac{f_T}{f_A} = \frac{F_T}{F_A} \tag{34}$$

Equation (30) may now be solved by use of Equation (32) to determine the mole flux and Equation (29) to determine the temperature gradient at the wall. For the latter relationship

$$-\left(\frac{dT}{dz}\right)_{z=0} = \frac{q_w}{h^*\eta} + \left[(T_w - T_o) - \frac{q_w}{h^*\eta}\right]$$

$$\left[\frac{\sqrt{m\eta}}{\tanh\sqrt{m\eta}}\right] \tag{35}$$

Substitution of Equations (32) and (35) into Equation (30) and division by $(T_w - T_o)$ and by h^* yields the final result:

$$\phi \equiv \frac{h}{h^*} = \frac{M\eta + \dfrac{\sqrt{m\eta}}{\tanh\sqrt{m\eta}}}{1 + M + \left(\dfrac{1}{\eta}\right)\left[\dfrac{\sqrt{m\eta}}{\tanh\sqrt{m\eta}} - 1\right]} \tag{36}$$

It should be noted that Equation (36) is valid for either positive or negative values of $(T_w - T_o)$ and of q_w.

In a recent publication (*8*) Brokaw has presented an analysis of thermal conduction in gases accompanied by chemical reactions of finite rate. His model is quite general in regard to system geometry and thermal accommodation coefficients. When Equation (36) above is applied to the specific form of the reaction kinetic equation treated by Brokaw [his Equation (9)], the result agrees with Brokaw's result for flat-plate geometry with one wall completely catalytic (corresponding to the equilibrium in the bulk boundary condition adopted here).

DISCUSSION OF RESULTS

Noncatalytic Wall

In the absence of a heterogeneous reaction $M = 0$, and Equation (36) becomes

$$\phi = \frac{\dfrac{\sqrt{m\eta}}{\tanh\sqrt{m\eta}}}{1 + \left(\dfrac{1}{\eta}\right)\left[\dfrac{\sqrt{m\eta}}{\tanh\sqrt{m\eta}} - 1\right]} \tag{37}$$

Figure 1 shows a graphical representation of Equation (37) in which ϕ is plotted vs. $\sqrt{m}$ at several values of η. The variable ϕ is the factor by which the chemical reaction increases the heat transfer rate. The factor m is defined as

$$m \equiv \frac{f_y x_F{}^2}{\rho\mathcal{D}_A} \equiv \frac{f_y k^2}{\rho\mathcal{D}_A(h^*)^2} \tag{38}$$

from which it is clear that m is an index of how fast the homogeneous reaction is relative to rates of diffusion through the film. The dimensionless group m is similar to the Damköhler Group II (*2*) except that the derivative of the reaction rate f_y is used rather than the rate itself. When written in the form with h^*, m is expressed in terms not dependent upon the idealized film theory model. From Figure 1 it can be seen that, for a fixed value of η, ϕ approaches unity at low values of $\sqrt{m}$, and ϕ approaches η asymptotically at high values of $\sqrt{m}$. At the first extreme the reaction is too slow to affect significantly the heat transfer rate; at the second extreme the reaction is infinitely rapid, in comparison to diffusion rates, and departures from chemical equilibrium throughout the film are insignificant. In the intermediate region ϕ varies with h^* (or x_F) for fixed values of f_y, k, ρ, and $\mathcal{D}_A$. Thus for a given chemical system at a given pressure, temperature, and composition the effect of gas flow rate (for example) upon h will be quite different from the effect upon h^* when m is in this intermediate range. At very high values of the gas flow rate h^* is so large that the reaction is relatively slow and $\phi \cong 1$; thus $h \cong h^*$. At very low gas flow rates h^* is so small that the same chemical reaction now appears infinitely rapid, and $\phi \cong \eta$; thus the effect of G upon h is the same as the effect of G upon h^*. At intermediate values of the gas flow rate h is less sensitive to variations in G than is h^*. The reader will appreciate the analogy between this behavior and the behavior of certain systems which involve simultaneous gas absorption and chemical reaction (*3, 4, 18, 38*).

When the reaction rate is essentially infinite, that is at large values of $\sqrt{m}$

$$\phi_\infty = \eta \tag{39}$$

From the definition of η

$$\eta \equiv 1 + \frac{f_T\Delta H\rho\mathcal{D}_A}{kf_y} \tag{40}$$

it can be seen that $(\eta - 1)$ is a measure of how much the chemical equilibrium shifts with temperature (f_T/f_y), of the heat of reaction, and of the relative rates of diffusion and thermal conduction.

In order to give more meaning to the parameters m and η consider a simple example where the chemical reaction is homogeneous and written as

$$A \leftrightharpoons 2U \tag{41}$$

and the kinetic expression is assumed to be

$$r = k_F\left(y_A - \frac{Py^2_U}{K_P}\right)P \tag{42}$$

If there is no inert diluent in the gas stream, Equation (17) yields

$$\mathcal{D}_A = \frac{D_{AU}}{1 + y_{A_o}} \tag{43}$$

$$S_{UA} = -1 \tag{44}$$

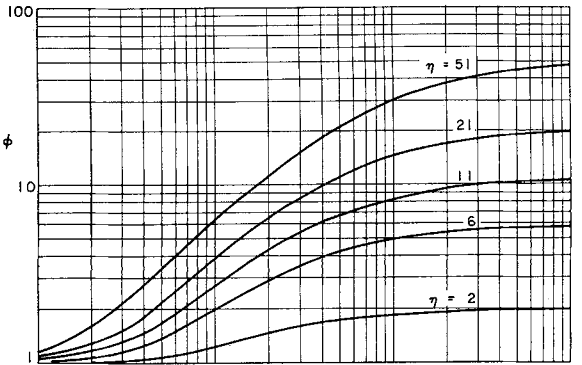

Fig. 1. Effect of a homogeneous reaction on the rate of heat transfer.

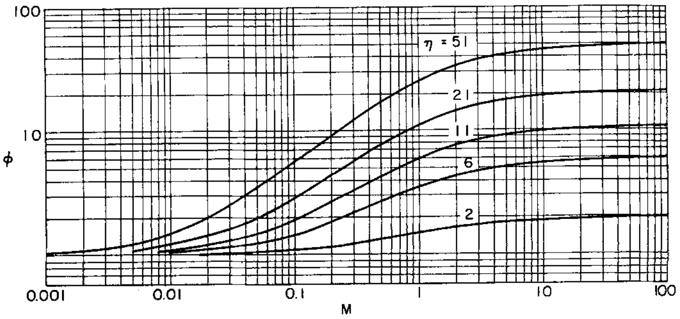

Fig. 2. Effect of a heterogeneous reaction on the rate of heat transfer.

Differentiating Equation (42) with respect to temperature one gets

$$f_T = P\left(y_{A_o} - \frac{Py^2_{U_o}}{K_{P_o}}\right)\left(\frac{dk_F}{dT}\right)_o + \frac{k_{F_o}P^2 y_{U_o}{}^2}{K^2_{P_o}}\left(\frac{dK_P}{dT}\right)_o \qquad (45)$$

The first term in Equation (45) is zero because chemical equilibrium has been assumed to prevail in the bulk (see Appendix); thus the energy of activation for the forward reaction does not contribute to f_T. The use of the van't Hoff equation to eliminate $(dK_P/dT)_o$ in Equation (45) yields

$$f_T = \frac{k_{F_o}P^2 y_{U_o}{}^2 \Delta H}{K_{P_o}RT_o{}^2} = \frac{k_{F_o}P\Delta H y_{A_o}}{RT_o{}^2} \qquad (46)$$

Differentiating Equation (42) with respect to y_A and y_U one gets

$$f_A = k_{F_o}P \qquad (47)$$

$$f_U = -2P^2\left(\frac{k_{F_o}}{K_{P_o}}\right)y_{U_o} \qquad (48)$$

Combining Equation (25), (44), (47), and (48) one obtains

$$f_y = k_{F_o}P\left(1 + 2P\frac{y_{U_o}}{K_{P_o}}\right) = k_{F_o}P\left[\frac{1 + y_{A_o}}{1 - y_{A_o}}\right] \qquad (49)$$

The use of Equations (43), (46), and (49) together with the definitions of m and η gives

$$m = \left[\frac{k_{F_o}P\,k^2}{\rho D_{AU}(h^*)^2}\right]\left[\frac{(1 + y_{A_o})^2}{1 - y_{A_o}}\right] \qquad (50)$$

$$\eta = 1 + \left(\frac{\Delta H^2}{RT_o{}^2}\right)\left(\frac{\rho D_{AU}}{k}\right)\left[\frac{y_{A_o}(1 - y_{A_o})}{(1 + y_{A_o})^2}\right] \qquad (51)$$

Catalytic Wall

If the homogeneous reaction rate is negligible

$$m \cong 0$$

and Equation (36) becomes

$$\phi = \frac{1 + M\eta}{1 + M} \qquad (52)$$

In Figure 2 Equation (52) is plotted as ϕ vs. M at several values of η. For any fixed value of η, ϕ approaches unity at low values of M, and ϕ approaches η asymptotically at high values of M. Thus it is seen that $\phi_\infty = \eta$ whether the reaction is completely homogeneous or completely heterogeneous.

Some cases of interest may involve both homogeneous and heterogeneous reaction rates of approximately equal importance. For such cases Equation (36) can be conveniently written as

$$\phi = \frac{\left(\dfrac{M}{\sqrt{m}}\right)\sqrt{m\eta} + \dfrac{\sqrt{m\eta}}{\tanh\sqrt{m\eta}}}{1 + \left(\dfrac{M}{\sqrt{m}}\right)\sqrt{m} + \left(\dfrac{1}{\eta}\right)\left[\dfrac{\sqrt{m\eta}}{\tanh\sqrt{m\eta}} - 1\right]} \qquad (36a)$$

It should be noted that

$$\frac{M}{\sqrt{m}} \equiv \frac{F_y}{\sqrt{\rho \mathcal{D}_A f_y}} \qquad (53)$$

and is therefore independent of h^* (or x_F); this group is an index of the rate of the heterogeneous reaction relative to that of the homogeneous reaction.

Figure 3 shows a plot of Equation (36*a*) as ϕ vs. $\sqrt{m}$ at several values of $M/\sqrt{m}$, all for $\eta = 11$. Physically this represents the effect of h^* (as affected by gas flow rate, for example) on ϕ for a given chemical system at given conditions of temperature and composition. As would be expected the presence of the heterogeneous reaction produces a ϕ value more nearly equal to ϕ_∞ for a given value of $\sqrt{m}$.

LIMITATIONS ON THE RESULTS

Small Temperature Driving Force

The results presented here are for the limiting case of

$$(T_w - T_o) \to 0$$

This imposes a limitation upon their usefulness, but it is believed that these results are still important and useful. Equation (36) and Figures 1, 2, and 3 evaluate the effects of finite reaction rates in terms of m and M and indicate the magnitudes of these two parameters which result in a reaction which is infinitely rapid or one which is too slow to affect the heat transfer rate. For moderate values of $(T_w - T_o)$ these results can probably be used

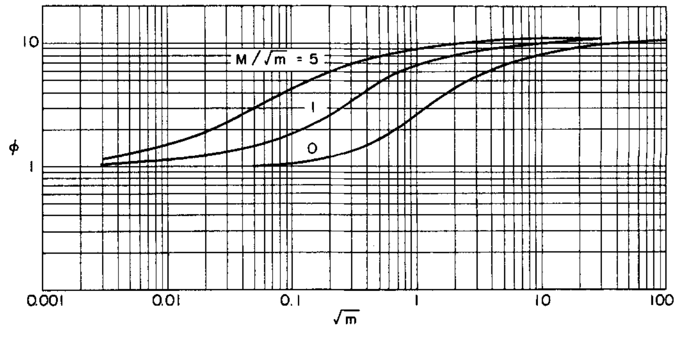

Fig. 3. Effect of homogeneous and heterogeneous reactions, $\eta = 11$.

with considerable confidence by evaluating η, m, and M at values of temperature and composition which represent average values in the film instead of bulk values. For larger values of $(T_w - T_o)$, for which the reaction rate constant varies greatly throughout the film, the linearized approach presented here is not applicable, but these results may still be of value in a qualitative evaluation of how rapid the reaction is relative to diffusion rates.

The principal limitation on the linear rate expression given by Equation (23) is probably the sensitivity of the reaction rate to temperature. For a kinetic equation of the form of Equation (42) the next term in the Taylor series expansion of f with respect to T will be negligible if (*17*)

$$\left| \left(\Delta E_o - \frac{\Delta H_o}{2} - RT_o\right) (T_w - T_o)/RT_o^2 \right| << 1 \quad (54)$$

Chemical Equilibrium in the Bulk

The assumption that chemical equilibrium prevails in the bulk imposes no real limitation on the usefulness of the results presented here for cases in which the homogeneous reaction predominates over the heterogeneous reaction in its effect on the heat transfer process. When the temperature driving force is small, if a reaction is sufficiently rapid to have an appreciable effect upon the heat transfer process, then it is sufficiently rapid to keep the bulk gas very near to chemical equilibrium in cases of practical importance (see Appendix for a quantitative demonstration of this assertion).

If the homogeneous reaction is slow but the heterogeneous reaction is fast on the other hand, the bulk gas will not necessarily be in chemical equilibrium. Then the assumption of equilibrium in the bulk limits the results to a very special case lacking in general interest. For these reasons the results presented in Figure 2 are not nearly so valuable as the other results of this study, although they do represent an interesting case for comparison with the other results.

Applicability of Film Theory

It is well to consider the extent to which these results, derived for the film theory model, might be applicable to heat transfer to a gas flowing in a pipe, for example. For an infinitely rapid reaction, as is approximated in the nitrogen tetroxide decomposition studies, it has been shown (*6, 23, 24, 30, 34, 37*) that for turbulent heat transfer

$$\phi_x = (k_{\text{eff}}/k)^{2/3} (C_{p_{\text{eff}}}/C_p)^{1/3} \quad (55)$$

but $(k_{\text{eff}}/k) = \eta$ as defined in this paper and

$$(C_{p_{\text{eff}}}/C_p) \equiv \eta' = 1 + \frac{f_T \, \Delta H}{f_y' C_p \, [1 + (\theta/a) \, y_{A_o}]}$$

If all binary pair diffusion coefficients are equal, then $f_y = f_y'$, and if in addition the Lewis number is unity, then $(C_{p_{\text{eff}}}/C_p) = (k_{\text{eff}}/k)$ and Equation (55) reduces to Equation (39). Equation (55) has been verified only for binary systems, but it might be expected to apply to multicomponent systems also.

For cases of finite reaction kinetics there are no experimental data at present to support the validity of Equation (36) or Figures 1 and 3 even for a Lewis number of unity. Fay and Riddell (*14*) obtained laminar boundary-layer solutions for heat transfer from dissociated air, but their calculations were for a case in which $(T_o - T_w)$ was of the order of 7,000°C., and no meaningful comparison can be made between their results and the present results for small values of $(T_o - T_w)$. Despite the lack of confirming experimental or analytical results, experience with the analogous problem of simultaneous gas absorption and chemical reaction (*4, 10, 16, 18, 19, 36, 38*) suggests that Equation (36) might be a good approximation to the real solution for turbulent flow if $N_{Le} = 1$. For Lewis numbers different from unity it is suggested that Equation (36) be used with η replaced by

$$(\eta)^{2/3} \; (\eta')^{1/3}$$

Such a procedure cannot be justified rigorously, but it is considered to be the best approximation available at present, and a similar procedure proved to be an excellent approximation in an analogous study involving simultaneous gas absorption and chemical reaction (*4*).

Complex Reaction Mechanism

Finally a word should be said about the effect of a successive-step chemical reaction mechanism. If a chemical reaction proceeds by a successive-step mechanism involving transient intermediate species, and the various steps add up to an overall reaction corresponding to Equation (1), the results of this study, applied by using the overall reaction equation and an overall kinetic equation, would probably describe the system if all of the intermediate species were relatively short-lived. On the other hand if some intermediate species were consumed at a rate which was slow relative to its formation rate and to diffusion rates, the application of these results based upon the overall reaction and an overall kinetic expression would be expected to result in serious errors. Such behavior was observed in an analogous problem involving gas absorption and simultaneous chemical reaction (*18*).

CONCLUSION

Through the use of a film theory model, the effect of a chemical reaction upon the rate of heat transfer from a solid wall to a gas has been derived for both a homogeneous reaction and a heterogeneous reaction on the wall. By limiting the analysis to the case of a very small temperature driving force and to the case where the bulk gas is essentially in chemical equilibrium, it has been possible to obtain a solution to the linearized problem which is given quite general expression in terms of partial derivatives of arbitrary chemical kinetic expressions.

The analysis results in defining two parameters, m and M, which express the magnitudes of the homogeneous and heterogeneous reaction rates, respectively, relative to the rates of diffusion in the boundary layer. Quantitative values of m and M, which define the regions of slow reaction, infinitely rapid reaction, and intermediate reaction rate, are presented. In addition in the intermediate rate range it is shown how the effect of Reynolds number on the heat transfer coefficient differs markedly from the effect in heat transfer systems which involve no chemical reaction.

The most serious limitation upon these results is the uncertainty associated with the use of the film theory model. These ideas are presently being extended to analysis of laminar and turbulent boundary-layer models, and these results will be reported later.

NOTATION

A = reactant in chemical reaction

a = stoichiometric factor of reactant A

B = reactant in chemical reaction

b = stoichiometric factor of reactant B

C_p = frozen isobaric heat capacity, cal./(mole)(°K.)

$C_{p_{\text{eff}}}$ = equilibrium isobaric heat capacity, cal./(mole)(°K.)

D_{AB} = binary diffusion coefficient for pair A, B; sq.cm./sec., analogous definitions for D_{AU}, D_{AV}, etc.

$\mathcal{D}_k$ = effective diffusion coefficient of component k, sq.cm./sec., defined by Equation (17)

F = function relating heterogeneous reaction rate to temperature and composition, moles/(sec.)(sq.cm.)

F_T = $(\partial F/\partial T) y_A$, y_B, y_U, y_V evaluated at bulk conditions; moles/(sec.)(sq.cm.)(°K.)

F_A = $(\partial F/\partial y_A)_{T,\, y_B,\, y_U,\, y_V}$ evaluated at bulk conditions; moles/(sec.)(sq.cm.); analogous definitions for F_B, F_U, F_V

F_y = $F_A + F_B S_{BA} + F_U S_{UA} + F_V S_{VA}$, moles/(sec.)(sq.cm.)

f = function relating homogeneous reaction rate to temperature and composition, moles/(sec.)(cc.)

f_T = $(\partial f/\partial T)_{y_A,\, y_B,\, y_U,\, y_V}$ evaluated at bulk conditions; moles/(sec.)(cc.)(°K.)

f_A = $(\partial f/\partial y_A)_{T,\, y_B,\, y_U,\, y_V}$ evaluated at bulk conditions moles/(sec.)(cc.); analogous definitions for f_B, f_U, f_V

f_y = $f_A + f_B S_{BA} + f_U S_{UA} + f_V S_{VA}$, moles/(sec.)(cc.) = (df/dy_A) when T is constant and y_B, y_U, and y_V vary with y_A as they do in the film, as dictated both by reaction stoichiometry and by the various diffusion coefficients

$$f_y' = f_A + \left(\frac{b + \theta y_{B_o}}{a + \theta y_{A_o}}\right) f_B + \left(\frac{-u + \theta y_{U_o}}{a + \theta y_{A_o}}\right) f_U + \left(\frac{-v + \theta y_{V_o}}{a + \theta y_{A_o}}\right) f_V$$

moles/(sec.)(cc.) = (df/dy_A) when T is constant and y_B, y_U, and y_V vary with y_A as they would in a closed reacting system, as dictated by stoichiometry alone

= f_y if all D_{ij} are equal

G = molal flow rate of gas per unit width of wall, moles/(sec.)(cm.)

h = heat transfer coefficient in presence of simultaneous chemical reaction, $\equiv q_w/(T_w - T_o)$; cal./(sec.)(sq.cm.)(°K.)

h^* = heat transfer coefficient that would be found in no chemical reaction were taking place, cal./(sec.)(sq.cm.)(°K.) = k/x_F for film theory

I = inert component in gas mixture

K_P = equilibrium constant for reaction in Equation (41)

k = frozen thermal conductivity, cal./(sec.)(cm.)(°K.)

k_{eff} = equilibrium thermal conductivity, cal./(sec.)(cm.)(°K.)

k_F = forward rate constant for reaction in Equation (41), moles/(sec.)(cc.)(atm.)

L = distance in direction of gas flow, cm.

M = $F_y x_F/\rho\mathcal{D}_A$ for film theory
$F_y k/\rho\mathcal{D}_A h^*$ in general

m = $f_y x_F^2/\rho\mathcal{D}_A$ for film theory
$f_y k^2/\rho\mathcal{D}_A (h^*)^2$ in general

N_j = molal flux of component j, relative to a stationary observer, moles/(sec.)(sq.cm.)

N_{Le} = Lewis number $(\mu/\rho D)/(C_p\mu/k)$, defined for the special case when all binary-pair diffusion coefficients are the same and equal to D

P = pressure, atm.

q_w = heat flux through wall, cal./(sec.)(sq.cm.); positive if heat removed from wall

R = ideal gas law constant = 1.987 cal./(mole)(°K.)

$\mathcal{R}$ = heterogeneous reaction rate, moles/(sec.)(sq.cm.)

r = homogeneous reaction rate, moles/(sec.)(cc.), Equation (2)

S_{BA} = $(\mathcal{D}_A/\mathcal{D}_B)(\omega_B/\omega_A)$ analogous definitions for S_{UA}, S_{VA}

T = temperature, °K.

U = product of chemical reaction

u = stoichiometric factor of component U

V = product of chemical reaction

v = stoichiometric factor of component V

x = distance from wall into film, cm.

x_F = thickness of film, cm.

x_o = thickness of bulk, cm.

y = mole fraction in gas phase

z = x/x_F

Greek Letters

θ = $u + v - a - b$

ΔE = energy of activation for forward reaction in Equation (41)

ΔH = enthalpy change of chemical reaction, cal./(mole of A reacting)

ϵ = $r_o x_F \Delta H/q_w$

$$\eta = 1 + \frac{f_T \Delta H \rho \mathcal{D}_A}{f_y\ k}$$

$$\eta' = C_{p_{eff}}/C_p = 1 + \frac{f_T\ \Delta H}{f_y'\, C_p \left[1 + \left(\frac{\theta}{a}\right) y_{A_o}\right]}$$

= $1 + (\eta - 1)N_{Le}$ if all D_{ij} are equal

ρ = molal density of gas, total moles/cc.

ϕ = h/h^*

ω_j = stoichiometric factor of component j, taken positive for reactants, negative for products, and zero for inert components

Subscripts

A = component A

B = component B

o = bulk

U = component U

V = component V

w = wall

∞ = infinitely rapid chemical reaction

LITERATURE CITED

1. Altman, David, and Henry Wise, *J. Am. Rocket Soc.*, **26**, 256 (1956).
2. Boucher, D. F., and G. E. Alves, *Chem. Eng. Progr.*, **55**, 55 (1959).
3. Brain, P. L. T., J. E. Vivian, and A. G. Habib, *A.I.Ch.E. Journal*, **8**, No. 2, p. 205 (1962).
4. Brian, P. L. T., J. F. Hurley, and E. H. Hasseltine, *ibid.*, **7**, 226 (1961).
5. Broadwell, J. E., *J. Fluid Mech.*, **4**, 113 (1958).
6. Brokaw, R. S., *Natl. Advisory Comm. Aeronaut., Reclassification Notice, E57K19a* (March, 1958).
7. ———, *J. Chem. Phys.*, **32**, 1005 (1960).
8. *Ibid.*, **35**, 1569 (1961).
9. Butler, J. N., and R. S. Brokaw, *ibid.*, **26**, 1636 (1957).
10. Chambre, P. L., and J. D. Young, *Phys. Fluids*, **1**, 48 (1958).
11. Clarke, J. F., *J. Fluid Mech.*, **4**, 441 (1958).
12. Coffin, K. P., and Cleveland O'Neal, Jr., *Natl. Advisory Comm. Aeronaut., Tech. Note 4209* (February, 1958).
13. Coffin, K. P., *J. Chem. Phys.*, **31**, 1290 (1959).
14. Fay, J. A., and F. R. Riddell, *J. Aeronaut. Sci.*, **25**, 73 (1958); *Res. Rept. No. 1*, Avco Corporation, Everett, Massachusetts (April, 1957).
15. Freedman, S. I., Sc.D. thesis, Mass. Inst. Technol., Cambridge, Massachusetts (1961).
16. Friedlander, S. K., and Mitchell Litt, *Chem. Eng. Sci.*, **7**, 229 (1958).
17. Friedlander, S. K., Private communication (January, 1962).
18. Gilliland, E. R., R. F. Baddour, and P. L. T. Brian, *A.I.Ch.E. Journal*, **4**, 223 (1958).
19. Hatta, S., *Technol. Repts. Tohoku Imp. Univ.*, **8**, 1 (1928-29).
20. Hirschfelder, J. O., "Sixth International Combustion Symposium," pp. 351 to 356, Reinhold, New York, (1957).
21. ———, *J. Chem. Phys.*, **26**, 274 (1957).
22. *Ibid.*, 282 (1957); *CM-880*, Univ. Wis., Madison, Wisconsin.
23. Irving, J. P., and J. M. Smith, *A.I.Ch.E. Journal*, **7**, 91 (1961).
24. Krieve, W. F., and D. M. Mason, *ibid.*, p. 277.
25. Lees, Lester, *Jet Propulsion*, **26**, 259 (1956).
26. Metzdorf, H. J., *J. Aeronaut. Sci.*, **25**, 200 (1958).
27. Moore, L. I., *ibid.*, **19**, 505 (1952).
28. Nernst, H. W., "Boltzmann-Festschrift," pp. 904-15, Johann Ambrosium Barth, Leipzig, Germany (1904).
29. Prigogine, I., and R. Buess, *Bull. classe. Sci., Acad. roy. Belg.*, **38**, 711 (1952).
30. Richardson, J. L., F. P. Boynton, K. Y. Eng, and D. M. Mason, *Chem. Eng. Sci.*, **13**, 130 (1961).
31. Rose, P. H., R. F. Probstein, and M. C. Adams, *J. Aeronaut. Sci.*, **25**, 751 (1958).

32. Rosner, D. E., *J. Am. Rocket Soc.*, **31**, 816 (1961).
33. Scala, S. M., and G. W. Sutton, *ibid.*, **29**, 141 (1959).
34. Schotte, William, *Ind. Eng. Chem.*, **50**, 683 (1958).
35. Schutt, H. C., and S. B. Zodonic, *Oil and Gas J.*, **54**, No. 41, p. 98; No. 48, p. 99; No. 54, p. 149; No. 60, p. 92; No. 65, p. 175; No. 71, p. 133 (1956).
36. Sherwood, T. K., and J. M. Ryan, *Chem. Eng. Sci.*, **11**, 81 (1959).
37. Thievon, W. J., G. A. Sterbutzel, and J. L. Beal, *Wright Air Develop. Center, Tech. Rpt. 59-450* (June, 1959).
38. Van Krevelen, D. W., and P. J. Hoftijzer, *Rec. trav. chim.*, **67**, 563 (1948).
39. Ziebland, H., *J. Brit. Interplanet. Soc.*, **14**, 249 (1955).

Manuscript received December 1, 1961; revision received March 12, 1962; paper accepted March 12, 1962.

APPENDIX

It was asserted in the discussion that, when the temperature driving force is small and the homogeneous reaction rate is sufficiently rapid to have an appreciable effect upon the heat transfer process, the assumption that chemical equilibrium prevails in the bulk is a good one for cases of practical importance. It is the purpose of this development to demonstrate the truth of this assertion.

Consider first the effect of a departure from equilibrium in the bulk. The mathematical development presented previously is altered in the following respects:
Equation (24) is changed to

$$r = f_T(T - T_o) + f_y(y_A - y_{A_o}) + r_o \qquad \text{(A1)}$$

where r_o is the homogeneous reaction rate in the bulk. This results in Equation (26) being changed to

$$\frac{d^2(T - T_o)}{dz^2} = m\eta(T - T_o) + \frac{mq_w}{h^*}(z - 1) + \frac{r_o x_F{}^2 \Delta H}{k} \qquad \text{(A2)}$$

Equation (29) becomes

$$-\frac{dT}{dz} = \frac{q_w}{\eta h^*} + \left[q_w/\eta h^* - (T_w - T_o) - \frac{r_o x_F{}^2 \Delta H}{km\eta} \right] \sqrt{m\eta} \sinh(\sqrt{m\eta}\, z) - \left\{ \frac{\dfrac{q_w}{\eta h^*} - (T_w - T_o) - \dfrac{r_o x_F{}^2 \Delta H}{km\eta}}{\tanh \sqrt{m\eta}} + \frac{\dfrac{r_o x_F{}^2 \Delta H}{km\eta}}{\sinh \sqrt{m\eta}} \right\} \sqrt{m\eta} \cosh(\sqrt{m\eta}\, z) \qquad \text{(A3)}$$

Equation (31) is changed to

$$-(N_A)_{z=0} = \mathcal{R} = F_T(T_w - T_o) + F_y(y_{A_w} - y_{A_o}) + \mathcal{R}_o \qquad \text{(A4)}$$

where $\mathcal{R}_o$ is the heterogeneous reaction rate that would result at a wall contacted with a gas at the temperature and composition of the bulk gas. Equation (36) is changed to

$$\phi = \frac{M\eta + \dfrac{\sqrt{m\eta}}{\tanh \sqrt{m\eta}}}{\left[1 + M + \dfrac{1}{\eta}\left(\dfrac{\sqrt{m\eta}}{\tanh \sqrt{m\eta}} - 1\right) + \dfrac{\sqrt{m\eta}}{\tanh \sqrt{m\eta}}\left(\dfrac{1}{\cosh \sqrt{m\eta}} - 1\right) \dfrac{(r_o x_F \Delta H/q_w)}{m\eta} - (\mathcal{R}_o \Delta H/q_w) \right]} \qquad \text{(A5)}$$

Figure A1 is a plot of Equation (A5) for $\eta = 11$ and for $\mathcal{R}_o = 0$ and $M = 0$, at various values of

$$\epsilon \equiv \frac{r_o x_F \Delta H}{q_w}$$

It can be seen from Figure A1 that, in the absence of a heterogeneous reaction, if

$$|\epsilon| < 0.1$$

the departure from equilibrium in the bulk has a very small effect upon the computed answer, except at values of $\sqrt{m}$ so low that $\phi \cong 1$ as read from Figure 1.

The next problem is to evaluate the magnitude of ϵ to be encountered in cases of practical importance. Consider the flow of a reacting gas past a wall of different temperature, as sketched in Figure A2. Even if the bulk gas is in chemical equilibrium when the gas contacts the leading edge of the wall, as it flows down in the L direction there will generally be an imbalance between the heat transfer rate to the bulk gas and the diffusion of reactants from the bulk gas which will cause the bulk gas to depart from chemical equilibrium. When it does, the homogeneous reaction rate in the bulk r_o will build up tending to cancel this imbalance. At some point r_o will be at a steady state value, and it will not change appreciably with distance in the L direction. The magnitude of this steady state value of r_o will be determined in the following analysis.

For simplicity it will be assumed that the heterogeneous reaction rate is negligible. When one refers to Figure A2 and remembers that the accumulation of matter or of energy in the film is negligible, a material balance on the bulk gas gives

$$\frac{G\,(dy_{A_o}/dL)}{1 + \left(\dfrac{\theta}{a}\right)(y_{A_o})} = (N_A)_{z=1} - r_o x_o \qquad \text{(A6)}$$

with piston flow of the gas in the bulk and axial diffusion neglected. Likewise applying the first law of thermodynamics to the bulk, neglecting axial conduction, one gets

$$GC_p\,(dT_o/dL) = q_w + \Delta H (N_A)_{z=1} - x_o r_o \Delta H \qquad \text{(A7)}$$

assuming that the heat capacity of the gas stream is constant.

If r_o has reached its steady state value

$$\frac{dr_o}{dL} \cong 0 \qquad \text{(A8)}$$

and thus

$$\frac{(dy_{A_o}/dL)}{(dT_o/dL)} = -f_T/f'_y \qquad \text{(A9)}$$

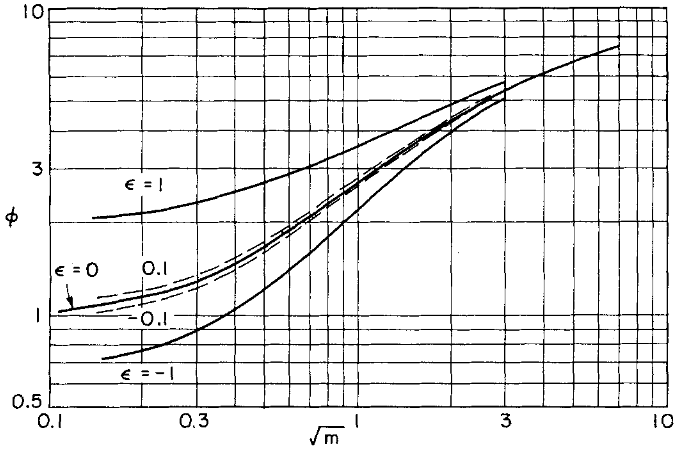

Fig. A1. Effect of departure from chemical equilibrium in the bulk, $\eta = 11$, no heterogeneous reaction

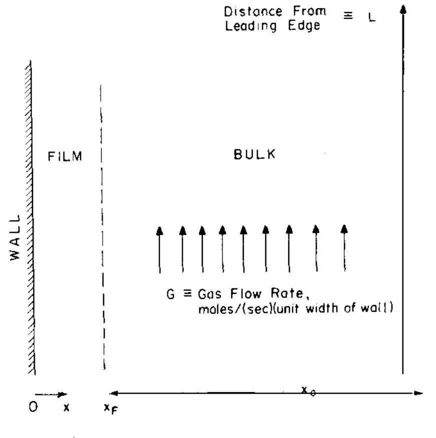

Fig. A2. The heat transfer system.

Dividing Equation (A6) by Equation (A7) and then using Equation (A9) to eliminate $(dy_{A_o}/dL)/(dT_o/dL)$ one gets

$$r_o x_o - (N_A)_{z=1} = \frac{q_w/\Delta H}{1 + \dfrac{1}{(\eta' - 1)}} \qquad \text{(A10)}$$

Now in the absence of a heterogeneous reaction

$$-(N_A)_{z=1} = \bar{r}_F x_F \qquad \text{(A11)}$$

where $\bar{r}_F$ is the average value of r in the film. Thus Equation (A10) can be written

$$\frac{\bar{r}_F x_F \Delta H}{q_w} + \left(\frac{r_o x_F \Delta H}{q_w}\right)\left(\frac{x_o}{x_F}\right) = \frac{1}{1 + \dfrac{1}{(\eta' - 1)}} \qquad \text{(A12)}$$

There remains the problem of evaluating the first term in Equation (A12). This term is the ratio of the energy absorbed by the chemical reaction within the film to the wall heat flux, and it is given by

$$\frac{\bar{r}_F x_F \Delta H}{q_w} = 1 - \frac{(dT/dz)_{z=1}}{(dT/dz)_{z=0}} \qquad \text{(A13)}$$

TABLE A1. STEADY STATE VALUES OF THE BULK REACTION RATE

$\eta = 11, \quad \eta' = 11$

$\sqrt{m}$	$\epsilon \equiv \dfrac{r_o x_F \Delta H}{q_w}$	
	$x_o/x_F = 100$	$x_o/x_F = 10$
0.15	0.008	0.075
0.3	0.006	0.055
0.9	0.0009	0.0087
1.66	0.000074	0.00074

when one assumes that the heterogeneous reaction rate is negligible. Evaluating the (dT/dz) terms in Equation (A13) by using Equation (A3) and then eliminating $(\bar{r}_F x_F \Delta H/q_w)$ by using Equation (A12) one gets

$$\frac{1}{\eta'} + \left(\frac{x_o}{x_F}\right)\epsilon = \frac{\dfrac{\phi}{\eta} + (1 - \phi/\eta)\left(\dfrac{\sqrt{m\eta}}{\sinh\sqrt{m\eta}}\right) - \left(\dfrac{\sqrt{m\eta}}{\tanh\sqrt{m\eta}}\right)\left(1 - \dfrac{1}{\cosh\sqrt{m\eta}}\right)\left(\dfrac{\phi}{m\eta}\right)\epsilon}{\dfrac{\phi}{\eta} + (1 - \phi/\eta)\left(\dfrac{\sqrt{m\eta}}{\tanh\sqrt{m\eta}}\right) + \left(\dfrac{\sqrt{m\eta}}{\tanh\sqrt{m\eta}}\right)\left(1 - \dfrac{1}{\cosh\sqrt{m\eta}}\right)\left(\dfrac{\phi}{m\eta}\right)\epsilon} \qquad \text{(A14)}$$

For given values of (x_o/x_F), m, η, and η' Equation (A14) can be solved simultaneously with Figure A1 [or Equation (A5) with no heterogeneous reaction] to yield the value of ϵ.

For the simple case in which all binary-pair diffusion coefficients are equal

$$\eta' - 1 = (\eta - 1)\, N_{Le} \qquad \text{(A15)}$$

With this simplification for $\eta = 11$ and $N_{Le} = 1$, $\eta' = 11$. The solution to Equation (A14) for this case is shown in Table A1.

When one compares Table A1 with Figure A1, it is clear that the assumption that $r_o = 0$ is an excellent one if

$$x_o/x_F > 10 \qquad \text{(A16)}$$

If inequality (A16) did not hold, the basic notion of the film theory, that the film holdup is negligible, is open to serious question. Furthermore for most practical cases involving turbulent flow inequality (A16) should surely be satisfied.

The foregoing analysis leads to the conclusion that for cases of practical importance the steady state value of r_o required to account for the imbalance in heat transfer to the bulk and diffusion of reactants from the bulk is so small that it has a negligible effect upon the results as presented in Figure 1. It is also clear that if r_o is not equal to its steady state value at the leading edge of the wall (that is the inflow boundary condition), it will rapidly approach that steady state value as the gas flows down in the L direction. This basic conclusion is unaltered if the foregoing analysis is repeated for other values of η and for other values of the Lewis number.

On the other hand if the heterogeneous reaction is rapid enough to produce a large value of $(\phi - 1)$ while the homogeneous reaction is so slow that it would, in the absence of the heterogeneous reaction, produce a small value of $(\phi - 1)$, then clearly the assumption of chemical equilibrium in the bulk is not justified in general.

Binary Liquid Diffusion Coefficients

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The present work proposes a new approach for the calculation of the diffusion coefficients in binary liquid systems. The proposed equation is based on the results obtained by statistical mechanics of transport phenomena in dense media. It does not include viscosity explicitly, and the variables required for the calculation are fundamental in nature; these are the free volume of a molecule obtainable from physical measurements such as velocity of sound and the heat of vaporization of the solute. In spite of its theoretical background, the proposed correlation obtains results on fifty-six different solute-solvent systems with about 13% deviation from the experimental results. The effect of concentration on the diffusion coefficient is very easy to determine and is more in accord with experimental results than can be predicted by other available correlations.

The available correlations for the prediction of diffusion coefficients may be divided into two classes. In the first class theoretical correlations based on the works of Einstein (*11*), Eyring (*12, 14*) and Hill (*18, 19*) are included. Einstein's approach is based on the kinetic theory and Brownian motion. Eyring employs the hole theory for the liquid state and the activation energy consideration to obtain an

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