Penetration Theory Applied to Unsteady Gas Absorption with Irreversible First–Order Reaction

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The absorption of reactive gases from bubbles into liquids in which an irreversible reaction occurs simultaneously with the diffusion process has been discussed by Lightfoot (*12*), Gill (*6*), and Gill and Nunge (*7*); the general treatment of Astarita (*1*) is also applicable. Of these Gill and Nunge have treated the process in which the liquid phase concentration changes with time, however, in general, the treatments have considered the steady state process. Here the absorption from a mixture of vapors in a bubble is considered, only one of which reacts with a component dissolved in the liquid so that the vapor undergoes a change in concentration. The liquid bulk concentration is taken to be constant. This process is studied here for times well after the bubble's initial generation. The basic ideas employed are extensions of those of Higbie (*9*) and Lightfoot (*12*) and may prove useful in describing other time dependent processes.

The model employed is that of Higbie (*9*) which has found good acceptance for the description of transport processes at interfaces in fairly complex geometries. The absorption process from bubbles as described by Levich (*10*) which makes use of potential flow theory in the liquid gives essentially the same results as penetration theory as ordinarily applied (*2, 11*). This aspect of the model has been studied in detail by Sideman (*13*).

The reactive gas in the bubble is assumed to dissolve and react within the liquid phase according to first-order or pseudo-first-order reaction kinetics. This gaseous component is present in only small amounts or the products of the reaction are gaseous and are passed into the bubble in an equal molal mass transfer process so that, in either case, the bubble does not change size to any significant degree. Although under some conditions the liquid phase concentrations may be relatively great, as with chlorine or hydrogen chloride dissolutions, a constant diffusion coefficient is assumed to apply. Further, the presence of the two components in the bubble imply the presence of a sizable display of resistance to mass transport in that phase. The work of Calderbank (*3*) has shown that this resistance is indeed small compared to that in the liquid surrounding the bubble for ordinary absorption processes. When the reaction occurring is rapid, the resistance to mass transport in the gas becomes increasingly important.

Consider a bubbling process in which little coalescence or breakage occur after the introduction of bubbles. The reactive component of the gas phase dissolves and reacts but the net process is such that the bubble diameter, $2R$, does not change. The relative flow of the liquid over the gas surface occurs with no frictional effects so that surface elements pass from the forward stagnation point to the rear stagnation point with no net stretching although they may distort to accommodate the spherical surface. The physical properties are constant and the process remains isothermal. An equivalent geometry may be visualized to be that of a vertical rectangular surface whose vertical dimension is $2R$ and whose width is

$$W \equiv \frac{4\Pi R^2}{2R} = 2\Pi R \tag{1}$$

This surface represents a gas volume $4/3\pi\ R^3$. Li, West, Vance and Moulton (*11*) describe the physical nature of the flow in this configuration more completely. The liquid surrounding the bubble but at some distance from it is well mixed and of constant composition.

The diffusion process associated with each liquid element may be introduced, in rectangular coordinates:

$$D\frac{\partial^2 C}{\partial Z^2} = \frac{\partial C}{\partial (T-t)} + kC \tag{2}$$

The two time variables are described as follows:

T = current time

t = that time at which the element contacted the bubble so that this time value identifies the element; the difference $T - t$ is the time of contact of the surface element.

The boundary and initial conditions are

$$C(T-t, 0) = C_o[t + (T-t)] \tag{2a}$$

$$C(T-t, \infty) = C_d e^{-k(T-t)} \tag{2b}$$

$$C(0, Z) = C_d \tag{2c}$$

The infinity condition is the same as that described by Lightfoot (*12*); it states that the mixing in the liquid is effective only well outside the diffusion boundary layer so that the bubble and its pertinent surroundings involve only a quiescent region in which reaction occurs. The interfacial condition reflects the concentration change within the bubble. This first boundary condition is written to indicate that the interfacial condition is a function of the current time and not merely $(T - t)$.

This equation system is written in dimensionless form to give the following:

$$\frac{\partial^2 C_1}{\partial \epsilon^2} = \frac{\partial C_1}{\partial \theta_T} + N_k C_1 \tag{3}$$

$$C_1(\theta_T, 0) = C_{10}\ (\theta + \theta_T) \tag{3a}$$

$$C_1(\theta_T, \infty) = e^{-N_k \theta_T} \tag{3b}$$

$$C_1(0, \epsilon) = 1 \tag{3c}$$

The dimensionless times are

$$\theta_T = \frac{D(T-t)}{(2R)^2} \tag{4}$$

$$\theta = \frac{Dt}{(2R)^2} \tag{5}$$

The transformation

$$C_1 = \phi(\theta_T, \epsilon)\ e^{-N_k(\theta+\theta_T)} + e^{-N_k\theta_T} \tag{6}$$

is applied to obtain

$$\frac{\partial^2 \phi}{\partial \epsilon^2} = \frac{\partial \phi}{\partial \theta_T} \tag{7}$$

$$\phi(\theta_T, 0) = C_{10}(\theta + \theta_T)\ e^{N_k(\theta+\theta_T)} - e^{N_k\theta} \tag{7a}$$

$$\phi(\theta_T, \infty) = 0 \tag{7b}$$

$$\phi(0, \epsilon) = 0 \tag{7c}$$

If $\phi(\theta_T, 0)$ were a constant, say, ϕ^*, the solution would be

$$\phi = \phi^* \text{ erfc } \left(\frac{\epsilon}{2\sqrt{\theta_T}}\right)$$

Since the boundary condition at $\epsilon = 0$ is not constant, the Duhamel theorem is applied, recognizing the zero initial condition (5), to give

$$\phi(\theta_T, \epsilon) = \int_0^{\theta_T} [C_{10}(\theta + \lambda)e^{N_k(\theta+\lambda)} - e^{N_k\theta}] \frac{\partial}{\partial\theta_T} \text{ erfc } \left(\frac{\epsilon}{2\sqrt{\theta_T - \lambda}}\right) d\lambda \quad (8)$$

The area over which mass transfer occurs for the element which was generated at time t (that is, between times $t - dt/2$ and $t + dt/2$) is

$$WU\ dt$$

and the relative velocity of the bubble to liquid, U, is equal to

$$U = \frac{2R}{t_e}$$

where t_e for the bubble under consideration is a constant representing the maximum value of the variable $(T - t)$. At current time T, then, the elements in contact with the bubble have initial contact times ranging from

$$t = T - t_e \left[\theta_T = \frac{t_e D}{(2R)^2} \equiv \theta_{Te}\right]$$

to

$$t = T\ (\theta_T = 0)$$

The rate of mass transfer into the contiguous liquid elements at any time, T, is the product of the diffusional flux and the total transfer area, such as

$$-DWU \int_{T-t_e}^{T} \left(\frac{\partial C}{\partial Z}\right)_{Z=0} dt = -DWU \int_0^{t_e} \left(\frac{\partial C}{\partial Z}\right)_{Z=0} d\ (T - t)$$

and transforming according to (6) the transfer is

$$-2RWUC_d \int_0^{\theta Te} e^{-N_k(\theta+\theta_T)} \left(\frac{\partial\phi}{\partial\epsilon}\right)_{\epsilon=0} d\theta_T \quad (9)$$

This expression is obtained from Equation (8) by multiplying both sides by $e^{-N_k(\theta+\theta_T)}$ and integrating from 0 to θ_{Te} with θ_T as the variable of integration. The order of integration can then be reversed and an integration by parts performed. This procedure avoids encountering integration difficulties. The differentiation with respect to ϵ is then carried out:

$$\int_0^{\theta_{Te}} \left(\frac{\partial\phi}{\partial\epsilon}\right)_{\epsilon=0} e^{-N_k(\theta_T+\theta)}\, d\theta_T = -\int_0^{\theta_{Te}} \{C_{10}(\theta + \lambda)e^{N_k(\theta+\lambda)} - e^{N_k\theta}\} \left\{\frac{e^{-N_k(\theta_{Te}+\theta)}}{\sqrt{\Pi}\sqrt{\theta_{Te} - \lambda}} + N_k \int_\lambda^{\theta_{Te}} \frac{e^{-N_k(\theta_T+\theta)}}{\sqrt{\Pi}\sqrt{\theta_T - \lambda}}\, d\theta_T\right\} dy \quad (10)$$

By changing the variable of integration of the inner integral to $\sqrt{\theta_T - \lambda}$, after some algebraic simplification this equation becomes

$$\int_0^{\theta_{Te}} e^{-N_k(\theta+\theta_T)} \left(\frac{\partial\phi}{\partial\epsilon}\right)_{\epsilon=0} d\theta_T = -\int_0^{\theta_{Te}} \{C_{10}(\theta + \lambda) - e^{-N_k\lambda}\}F\ d\lambda \quad (11)$$

where

$$F = \frac{e^{-N_k(\theta_{Te}-\lambda)}}{\sqrt{\Pi}\sqrt{\theta_{Te} - \lambda}} + N_k^{1/2} \text{ erf } [N_k^{1/2}\ (\theta_{Te} - \lambda)^{1/2}] \quad (12)$$

The right hand side of Equation (11) multiplied by $-2RWUC_d$ is the total transfer of active species leaving the bubble at any instant represented by θ. This representation is at best accurate to within an increment of time θ_{Te} since the first such increment occurs during formation of the bubble in the active liquid phase and cannot be described by the model. That is, this model avoids the discussion of the true initial condition at $T = 0$ and treats the process only for times greater than this. One attempt to do so might follow the notions of Groothuis and Kramers (8). This aspect of the problem is clearly described in the problem treated by Gill (6).

Since the bubble concentration is considered to be uniform at any instant because only the liquid phase resistance is assumed for the moment, and if equilibrium at the interface involves only a proportionality constant we obtain

$$HC_g = C_o$$

The rate of transfer of active species to the bubble is at any dimensionless time, θ, therefore

$$\left(\frac{DC_d}{(2R)^2}\right)\left(\frac{4\ \Pi R^3}{3\ H}\right)\frac{dC_{10}(\theta)}{d\theta}$$

Equating the expressions for transfer from the bubble gives

$$-\frac{6H}{\theta_{Te}} \int_0^{\theta_{Te}} \{C_{10}(\theta + \lambda) - e^{-N_k\lambda}\}\ F\ d\lambda = \frac{dC_{10}(\theta)}{d\theta} \quad (13)$$

Assume a solution of the form

$$C_{10} = Ae^{-a\theta} + B \quad (14)$$

with the initial condition $C_{10}(0)$, specified through some reasonable estimating procedure (6, 8). On insertion of this into Equation (13), and equating coefficients of $e^{-a\theta}$ there results

$$B = \frac{\int_0^{\theta_{Te}} e^{-N_k\lambda}\ Fd\lambda}{\int_0^{\theta_{Te}} Fd\lambda} \quad (15)$$

$$a = \frac{6H}{\theta_{Te}} \int_0^{\theta_{Te}} e^{-a\lambda}\ Fd\lambda \quad (16)$$

in which F is defined in Equation (12), and the initial condition gives

$$C_{10}(0) = A + B \quad (17)$$

The integrations may be carried out partially to give

$$\int_0^{\theta_{Te}} Fd\lambda = \frac{1}{N_K^{1/2}}\left[\left(\frac{1}{2} + N_k\theta_{Te}\right) \text{erf } \sqrt{N_k\theta_{Te}} + \frac{\sqrt{N_k\theta_{Te}}}{\sqrt{\Pi}}\ e^{-N_k\theta_{Te}}\right] \quad (18)$$

$$\int_0^{\theta_{Te}} e^{-a\lambda}\ Fd\lambda$$

$$= \frac{2}{\sqrt{\Pi}} \frac{e^{-a\theta_{Te}}}{N_k^{1/2}} \left(1 - \frac{N_k}{a}\right) \int_0^{\sqrt{N_k\theta_{Te}}} e^{-(1-a/N_k)\sigma^2}\, d\sigma + \frac{\sqrt{N_k}}{a} \operatorname{erf} \sqrt{N_k\theta_{Te}} \quad (19)$$

$$\int_0^{\theta_{Te}} e^{-N_k\lambda}\, F d\lambda = \frac{\operatorname{erf} \sqrt{N_k\theta_{Te}}}{N_k^{1/2}} \quad (20)$$

So that

$$B = \frac{e^{N_k\theta_{Te}} \operatorname{erf} \sqrt{N_k\theta_{Te}}}{\left(\frac{1}{2} + N_k\theta_{Te}\right) e^{N_k\theta_{Te}} \operatorname{erf} \sqrt{N_k\theta_{Te}} + \frac{\sqrt{N_k\theta_{Te}}}{\sqrt{\Pi}}} \quad (21)$$

and a is obtained from the implicit equation

$$\frac{a}{\left(\frac{12\ H}{\sqrt{\Pi}\ \theta_{Te}}\right)} = \frac{e^{-a\theta_{Te}}}{\sqrt{a\theta_{Te}}} \left[\left(\frac{a}{N_k}\right)^{1/2} - \left(\frac{N_k}{a}\right)^{1/2} \right] \int_0^{\sqrt{N_k\theta_{Te}}} e^{-(1-a/N_k)\sigma^2}\, d\sigma + \frac{\sqrt{\Pi}}{2\sqrt{a\theta_{Te}}} \left(\frac{N_k}{a}\right)^{1/2} \operatorname{erf} \sqrt{N_k\theta_{Te}} \quad (22)$$

The above has treated the adsorption process in the absence of gas phase resistance. When such resistance is present, and may be indicated simply as a mass transfer coefficient, k_g, then for any element of surface the transfer of mass is described by

$$-DWU \left(\frac{\partial C}{\partial Z}\right)_{Z=0} dt = k_g WU \left(C_g - \frac{C_o}{H}\right) dt \quad (23)$$

Also the continuity of active species requires, for time T,

$$-WU\ K_g \int_0^{te} \left(C_g(T) - \frac{C_o}{H}\right) [t + (T-t)]\, d(T-t) = \frac{4}{3} \Pi R^3 \frac{dC_g(T)}{dT} \quad (24)$$

The Equations (23) and (24) now describe C_o in boundary condition (2a) and thus replace the condition expressed in Equation (13). To provide an estimate, then, for the effect of gas phase resistance, Equation (23) is integrated over all instantaneous surface elements, that is, $T - t$ ranges from 0 to t_e for any T. The equations to be solved for C_g become, after nondimensionalizing

$$N_g \int_0^{\theta_{Te}} \{C_{10}(\theta + \lambda) - e^{-N_k\lambda}\}\, F d\lambda = \int_0^{\theta_{Te}} \left[C_{1g}(\theta) - \frac{C_{10}(\theta + \theta_T)}{H} \right] d\theta_T \quad (25)$$

$$-\frac{6}{N_g\theta_{Te}} \int_0^{\theta_{Te}} \left(C_{1g} - \frac{C_{10}}{H}\right) d\theta_T = \frac{dC_{1g}}{d\theta} \quad (26)$$

where $N_g = D/2(Rk_g)$, is a measure of the relative resistances to diffusion in the two phases. Again the liberty of expressing gas phase concentration as a function of t rather than T has been taken. For the description of the process given here, this is the same as saying that the marking of time is associated with the element at the forward stagnation point. These equations are satisfied by

$$C_{1g} = [C_{1g}(0) - L]\ e^{-a_1\theta} + L \quad (27)$$

where

$$L = \frac{1}{H} \cdot \frac{\int_0^{\theta_{Te}} e^{-N_k\lambda}\, F d\lambda}{\int_0^{\theta_{Te}} F d\lambda} \quad (28)$$

and a_1 is determined from the implicit equation

$$\int_0^{\theta_{Te}} e^{-a_1\lambda}\, F d\lambda = \frac{1}{H} \cdot \frac{1 - e^{-a_1\theta_{Te}}}{6 - a_1 N_g} \quad (29)$$

The integrals in these expressions have been described earlier.

RESULTS AND DISCUSSION

When N_k is permitted to approach zero in Equation (22) the following equation results:

$$\frac{a}{\left(\frac{12H}{\sqrt{\Pi\theta_{Te}}}\right)} = \frac{e^{-a\theta_{Te}}}{\sqrt{a\theta_{Te}}} \int_0^{\sqrt{a\theta_{Te}}} e^{x^2}\, dx \quad (30)$$

The denominator on the left is the coefficient for θ which appears in the exponent when the penetration theory with no chemical reaction is used to describe an absorption problem (2) and the effect of changing concentration in the gas upon the coefficient is disregarded. Therefore the left hand side is the ratio of mass transfer coefficients, the coefficient with reaction and changing gas concentration to that when no change occurs. Equations (22) and (30) are described in Figure 1. It is seen there that the effect of changing gas phase concentration influences the mass transfer coefficient when H is greater than 10 or so. It may be seen directly from Equation (30) that the right side approaches unity as $\sqrt{a\theta_{Te}}$ approaches zero by application of L'Hopital's rule. Thus large H and large θ_{Te} tend to decrease the liquid phase coefficient below that value given by ordinary penetration theory; this occurs in the mathematics through the dependence of a upon H and θ_{Te}.

The effect of gas phase resistance as described in Equation (29) may be noted by comparison with Equation (16) obtained under conditions of no resistance in the bubble. When $N_g \to 0$, the two equations become the same when $a_1\theta_{Te}$ is small as it appears to be under ordinary circumstances. As N_g becomes increasingly greater than zero its effect is seen to be the same as increasing H values, discussed in the above paragraph, through its influence upon a_1.

From Equation (14) the term B is seen to be the value of the concentration at the interface, C_o/C_d, as θ approaches infinity. The nature of B is shown in Figure 2 and is noted to be generally less than unity. Since C_d

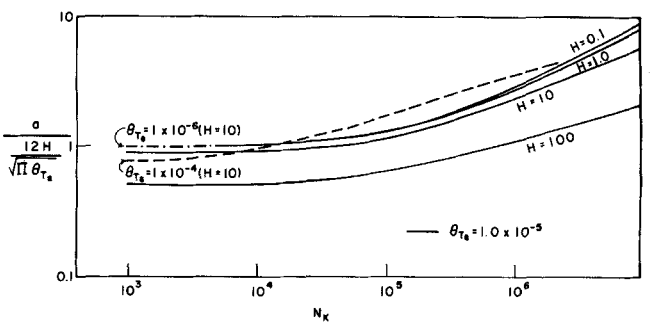

Fig. 1. Effect of reaction rate number, N_k, upon the mass transfer. Effects upon mass transfer of θ_{Te} and solubility coefficient, H, because of changing bubble concentration are indicated.

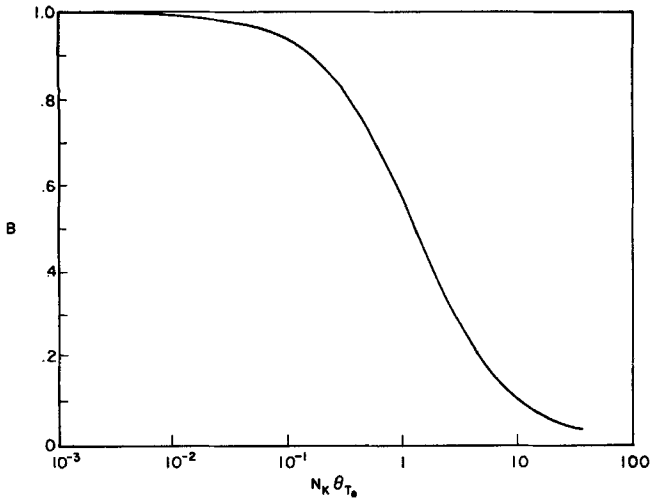

Fig. 2. Final interface concentrations after large contact times, θ. [$B = C_o/C_d\ (\infty)$]

would approach zero when the reaction rate constant, k, is large and since $N_k\theta_{Te}$ is kt_e, physically a low value for $C_o/C_d(\infty)$, that is, much less than unity, is possible when t_e is very large as might occur in a viscous liquid. Since the bulk liquid is assumed to be well mixed in the process visualized here, this situation is not likely (nor is it accurately described in the model).

When the bulk concentration C_d is desired it may be ordinarily well estimated

$$\frac{Q}{H}\left[\frac{C_o(0)}{C_d} - C_{10f}\right] = V_T k \qquad (31)$$

in which

Q = volumetric rate of gas feed at concentration $C_o(0)$

V_T = total volume of liquid

$\left(\frac{C_{10f}}{H}\right)$ = dimensionless concentration of bubbles leaving liquid as obtained from Equation (14) after a residence time of $\theta = \theta_f$; and $\theta_f >> \theta_{Te}$.

This equation assumes that the fraction of the reaction which occurs in the vicinity of the bubble is small compared to that which occurs in the bulk of the liquid.

It should be noted that under ordinary bubbling conditions encountered in the Chemical Industry, such as are described by Calderbank and Moo-Young (4), and in which the gas discharged from the contactor has not been completely depleted of reactive component, the mass transfer characteristics of the operation are not affected greatly because of the chemical reaction. Further, it must be pointed out that the concluding comments made above are strongly dependent upon the condition of a mobile interface.

CONCLUSIONS

The Higbie model for mass transfer to bubbles is modified to include chemical reaction and changing gas phase concentration. The equations involved are solved, at least in the range of concentration change which can be given exponentially in time, and discussed.

The effect of bubble phase concentration-time dependence is important in its effects on mass transfer rate when the gas component dissolving and reacting is very soluble, for example, $H > 10$. Aside from this, the effect of chemical reaction and changing bubble concentration upon the mass transfer process, does not appear to be significant for the ranges of parameters, N_k, θ_{Te} and H, ordinarily encountered.

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NOTATION

B = dimensionless interfacial concentration after an infinite time period, $\frac{C_o}{C_d}(\infty)$

C = volumetric concentration of liquid, moles/(cu.ft.)

C_d = volumetric concentration in bulk liquid, moles/(cu.ft.)

C_o = volumetric concentration in liquid at bubble interface, moles/(cu.ft.)

C_1 = dimensionless concentration, C/C_d

C_{1g} = dimensionless concentration in gas phase, C_g/C_d

D = molecular diffusion coefficient of reactive, absorbed component in liquid phase, (sq.ft.)/sec.

H = equilibrium constant, C_o/C_g

k = first-order reaction rate constant, $(\text{sec.})^{-1}$

L = dimensionless gas phase concentration after infinite time, $\frac{C_g}{C_d}(\infty)$

k_g = mass transfer coefficient in gas phase, ft./sec.

N_k = dimensionless reaction parameter, $k(2R)^2/D$

N_g = dimensionless mass transfer parameter, $D/(2Rk_g)$

R = radius of bubble, ft.

T = time, sec.

t = time, and in the expressions referring to a liquid element, t refers to the time at which the element first contacted the bubble, sec.

t_e = duration of time of contact of liquid element on bubble surface, sec.

U = bubble rise velocity taken to be equal to $2R/t_e$, ft./sec.

W = equivalent width of bubble, ft.

Z = distance into liquid away from interface, ft.

Greek Letters

ϵ = dimensionless distance into liquid, $Z/(2R)$

θ = dimensionless time, $Dt/(2R)^2$

θ_T = dimensionless time, $D(T-t)/(2R)^2$

θ_{Te} = dimensionless contact time, $Dt_e/(2R)^2$

λ = dummy variable occurring on application of the Duhamel theorem in Equation (8)

σ^2 = $N_K(\theta_{Te} - \lambda)$, used as a variable of integration

ϕ = transformed concentration given in Equation (6)

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