TABLE 5. EFFECT OF INITIAL SUBCOOLING ON θ_{sm}, θ_{fm} AND $\Delta\theta_m$ FOR THE MELTING OF A FINITE SLAB

B^*	ϕ_i	θ_{sm}	θ_{fm}	$\Delta\theta_m$
1.0	0	0	1.36	1.36
	−1.0	0.67	2.36	1.69
	−5.0	4.67	6.36	1.69
	−10.0	9.67	11.36	1.69
5.0	0	0	11.29	11.29
	−1.0	0.78	16.44	15.66
	−5.0	16.67	36.49	19.81
	−10.0	41.67	61.49	19.82

As expected, both θ_{sm} and $\Delta\theta_m$ increase as B^* increases and ϕ_i decreases. A thicker, cooler slab must be heated for a longer period of time before its surface reaches the melting temperature. It also has a longer melting time. But it is interesting to note that $\Delta\theta_m$ does not increase indefinitely as ϕ_i decreases. For a fixed B^*, $\Delta\theta_m$ approaches a constant limiting value as $\phi_i \to -\infty$. Physically, this phenomenon can be explained by considering the slab's temperature profile when melting begins. For small $|\phi_i|$, the surface of the slab remembers its initial temperature, since parts of the slab are still at that initial temperature. $\Delta\theta_m$ thus increases with increasing subcooling. For large $|\phi_i|$, on the other hand, a longer heating time is required before the slab's surface reaches the melting temperature. The slab forgets more of its initial temperature since the temperature at everywhere of the slab will be larger than ϕ_i when melting begins. Small differences in ϕ_i have little effect on the total melting time, and $\Delta\theta_m$ approaches a constant as $\phi_i \to -\infty$. The behavior of $\Delta\theta_m$ and its dependence on other physical parameters is clearly an interesting phenomenon which requires more detailed consideration. This work is currently under way, and results will be presented in future publications.

NOTATION

B = thickness of slab, m
B^* = dimensionless thickness defined by Equation (6)
c = specific heat, J/kg - °K
F = surface heat flux, W/m^2
H = location of interface, m
k = thermal conductivity, W/m-K
L = latent heat of fusion, J/kg
Q = heat fluxes defined in Equation (4c)
r_w = radius of inner cylinder in the sample cylindrical problem
t = time coordinate, s
T = temperature, °K
x = space coordinate, m
y = iterative solution to Equation (4f) defined by Equation (5)

Greek Letters

α = thermal diffusivity, m^2/s
δ = dimensionless melting thickness in the sample cylindrical problem
η = dimensionless space coordinate defined by Equation (6)
η_H = dimensionless location of interface defined by Equation (6)
θ = dimensionless time defined by Equation (6)
Θ = function defined by Equation (4f)
ρ = density, Kg/m^3
ϕ = dimensionless temperature defined by Equation (6)
τ = dimensionless time

Subscripts

c = cylindrical
i = interface
m = melting
l = liquid
s = solid
p = planar

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Gas Absorption with Consecutive Second-Order Reactions

For gas absorption accompanied by two consecutive second-order reactions, the reaction factors of the film and penetration theories were solved by the orthogonal collocation method. For equivalent definition of the other physico-chemical parameters, the reaction factors from the two theories differ only slightly. In film theory, it is shown that the film-bulk boundary condition is of importance only for small values of M. It is also shown that the difference between the point yields of the film and penetration theories is generally small, although it is larger than the difference in reaction factors for the two theories.

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SCOPE

The reaction (enhancement) factor, which shows the effect of chemical reaction on the rate of gas absorption, is of importance in the design of gas-liquid reactors (Hoffman et al., 1975; Sharma et al., 1976; Raghuram and Shah, 1977; Charpentier, 1978). In modeling gas-liquid reactors, it is usually preferable to use the reaction factor rather

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than the enhancement factor to describe the absorption rate.

Theoretical predictions of reaction factors or enhancement factors using the film and penetration theories have in general shown remarkable agreement between these two theories (Brian and Beaverstock, 1965; Danckwerts, 1970), although the case of a specific reaction scheme where large differences exist has been reported (Tavares Da Silva, 1974). Also in film theory, most previous works have applied the simplified film-bulk boundary condition: at $x = \delta, A = 0$, for the gas reactant A.

In this work, the reaction factors of the film and penetration theories, solved by the orthogonal collocation method, are compared for two consecutive second-order reactions: A (gas) + B (liq.) $\xrightarrow{k_1}$ C (liq.), A (gas) + C (liq.) $\xrightarrow{k_2}$ P (liq.). In the film theory, both the complete film-bulk boundary condition: at $x = \delta$, $-D_A \dfrac{dA}{dx} = \alpha\delta (k_1AB + k_2AC)$, and the simplified one as mentioned above are applied to investigate the effect of this condition on the reaction factors.

Evaluation of the point yield of the desired product (C) is also made for both the film and penetration theories, for the same reaction scheme.

CONCLUSIONS AND SIGNIFICANCE

The difference between the reaction factors of the film and penetration theories is always found to be less than 2%. The numerical and approximate solutions also deviate only a few percent for both theories. Thus, the use of approximate solutions from either of the two theories in modeling both the steady state and dynamic behavior of gas-liquid reactors is justifiable; this dramatically simplifies theoretical studies of gas-liquid reactors. In film theory, the film-bulk boundary condition is shown to be of minor importance for most practical conditions; thus, the simplified condition may be used in its place. Finally, it is found that the difference between the point yields of the two theories is generally small, although it is larger than that for the reaction factor. Also, the van Krevelen-Hoftijzer approximation is not quite as good for the evaluation of the film yield as it is for the reaction factor.

For numerical solution, the orthogonal collocation method is shown to be as accurate as the conventional finite difference method. Considering the computer storage and computation time for the same accuracy, the orthogonal collocation method emerges superior to the finite difference method and is thus recommended for the solution of chemical absorption problems.

THEORY

Reaction-Zone Concept

Previous works indicate that the error introduced by the van Krevelen-Hoftijzer approximation for the estimation of the reaction factors is usually very small not only for film theory (van Krevelen and Hoftijzer, 1948; Onda et al., 1970) but also for penetration theory (Hikita and Asai, 1964; Onda et al., 1972) and surface-renewal theory (DeCoursey, 1974). This is because only the concentration profile of the gas reactant A near the gas-liquid interface is required to evaluate the reaction factor, defined as:

$$E_A^* \equiv \frac{N_A}{k_{L0}A_i} \tag{1}$$

where, in film theory,

$$N_A = -D_A \left(\frac{dA}{dx}\right)_{x=0} \tag{2a}$$

while in penetration theory,

$$N_A = \frac{1}{t}\int_0^t -D_A \left(\frac{\partial A}{\partial x}\right)_{x=0} dt' \tag{2b}$$

By applying the reaction-zone concept, following van Krevelen and Hoftijzer (1948), one may rather accurately estimate the reactant A profile near the gas-liquid interface by assuming an idealized profile for the liquid reactant B. The reaction factors can thus be estimated quite well using the reaction-zone concept.

This concept has also been applied in the numerical work of Brian and Beaverstock (1965) to obtain the penetration theory solution, with an enlarging-with-time reaction zone:

$$\eta = \frac{z}{z_R} \tag{3}$$

where

$$z_R = K(\theta+\epsilon)^{1/2} \tag{3a}$$

where z_R indicates the width of the reaction zone at time θ. The constant ϵ has to be chosen as some small value to retain proper behavior at $\theta = 0$, and also to adjust the dependence of the reaction zone on θ. The constant K is a scale factor which dictates the depth of penetration; i.e., the width of the reaction zone, at which η equals unity. K has to be chosen sufficiently large but as small as possible to cover properly the entire reaction zone. Eq. (3) is applied in this work to a reaction scheme different from that of Brian and Beaverstock (1965) to investigate its generality.

Reaction Scheme

The reaction scheme, for which we compare between the reaction factors of corresponding film and penetration models, is that studied by van de Vusse (1966):

$$A \text{ (gas)} + B \text{ (liq.)} \xrightarrow{k_1} C \text{ (liq)} \tag{4}$$

$$A \text{ (gas)} + C \text{ (liq.)} \xrightarrow{k_2} P \text{ (liq.)} \tag{5}$$

Many gas-liquid reactions belong to this class, such as chlorination or oxidation of liquid hydrocarbons, hydrogenation of diolefins, sulfonation of aromatics and olefins, etc. Specifically, chlorination of n-decane has been experimentally studied in gas-liquid stirred tank reactors by Ding et al. (1974), and numerically using the film theory by Sharma et al. (1976). To our knowledge, complete film and penetration theory solutions for this reaction scheme and a comparison between them have not been reported before.

Film Theory Equations

The film theory equations corresponding to reactions of Eqs. (4) and (5) can be expressed in the following dimensionless form (cf. van de Vusse, 1966):

$$\frac{d^2a}{dZ^2} = M\left(ab + \frac{p}{q}ac\right) \qquad (6)$$

$$\frac{d^2b}{dZ^2} = \frac{M}{r_B q}ab \qquad (7)$$

$$\frac{d^2c}{dZ^2} = \frac{M}{r_c}\left(\frac{p}{q}ac - ab\right) \qquad (8)$$

with boundary conditions

$$\text{at } Z = 0;\ a = 1,\ \frac{db}{dZ} = 0,\ \frac{dc}{dZ} = 0 \qquad (9)$$

$$\text{at } Z = 1;\ -\frac{da}{dZ} = \alpha M\left(1 + \frac{p}{q}c_L\right)a,\ b = 1,\ c = c_L \qquad (10a)$$

$$\text{or} \qquad a = 0,\ b = 1,\ c = 0 \qquad (10b)$$

where Eq. (10*a*) is the complete film-bulk condition for chemical absorption systems and Eq. (10*b*) is the simplified film-bulk condition. Note that for a reactor with a finite liquid residence time, the condition of Eq. (10*a*) should contain another term to account for the dissolved gas leaving in the liquid phase (Hoffman et al., 1975). From Eqs. (1) and (2*a*), the reaction factor is:

$$E_A^* = -\left(\frac{da}{dZ}\right)_{Z=0} \qquad (11a)$$

or combining with Eq. (6) and applying Eq. (10*a*)

$$E_A^* = \alpha M\left(1 + \frac{pc_L}{q}\right)a_L + \int_0^1 M\left(ab + \frac{p}{q}ac\right)dZ \qquad (11b)$$

Penetration Theory Equations

Corresponding to the reaction scheme of Eqs. (4) and (5), the penetration theory equations in dimensionless form are:

$$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial z^2} - (q\,ab + p\,ac) \qquad (12)$$

$$\frac{\partial b}{\partial \theta} = r_B\frac{\partial^2 b}{\partial z^2} - ab \qquad (13)$$

$$\frac{\partial c}{\partial \theta} = r_c\frac{\partial^2 c}{\partial z^2} - (p\,ac - q\,ab) \qquad (14)$$

with initial and boundary conditions

$$\text{at } \theta = 0,\ \text{any } z > 0;\ a = 0,\ b = 1,\ c = 0 \qquad (15)$$

$$\text{at } z = 0,\ \text{any } \theta > 0;\ a = 1,\ \frac{\partial b}{\partial z} = 0,\ \frac{\partial c}{\partial z} = 0 \qquad (16)$$

$$\text{as } z \to \infty,\ \text{any } \theta \quad;\ a = 0,\ b = 1,\ c = 0 \qquad (17)$$

The condition Eq. (17) is consistent with the film theory condition of Eq. (10*a*), since in the film theory reactant *A* and intermediate *C* diffusing into the bulk liquid react there, and their profiles should approach zero smoothly as Z goes to infinity, if it does.

From Eqs. (1) and (2*b*), the reaction factor for the penetration theory is:

$$E_A^* = \sqrt{\frac{\pi}{4\theta}}\int_0^\theta\left(-\frac{\partial a}{\partial z}\right)_{z=0}d\theta' \qquad (18)$$

After combining Eqs. (12), (13), and (14), applying conditions of Eqs. (15), (16) and (17), and using the fact that the concentration profiles should approach their values at infinity smoothly, Eq. (18) is transformed to:

$$E_A^* = \sqrt{\frac{\pi}{4\theta}}\int_0^\infty [a + 2q\,(1-b) - c]\,dz' \qquad (19)$$

Now, we apply Eq. (3) to test its applicability to the reaction scheme of Eqs. (4) and (5). Eqs. (12), (13), and (14) then become:

$$\frac{\partial a}{\partial \theta} = \frac{1}{K^2(\theta+\epsilon)}\frac{\partial^2 a}{\partial \eta^2} + \frac{\eta}{2(\theta+\epsilon)}\frac{\partial a}{\partial \eta} - (q\,ab + p\,ac) \qquad (20)$$

$$\frac{\partial b}{\partial \theta} = \frac{r_B}{K^2(\theta+\epsilon)}\frac{\partial^2 b}{\partial \eta^2} + \frac{\eta}{2(\theta+\epsilon)}\frac{\partial b}{\partial \eta} - ab \qquad (21)$$

$$\frac{\partial c}{\partial \theta} = \frac{r_c}{K^2(\theta+\epsilon)}\frac{\partial^2 c}{\partial \eta^2} + \frac{\eta}{2(\theta+\epsilon)}\frac{\partial c}{\partial \eta} - (p\,ac - q\,ab) \qquad (22)$$

while the initial and boundary conditions of Eqs. (15), (16), and (17) take the form

$$\text{at } \theta = 0,\ \text{any } \eta > 0;\ a = 0,\ b = 1,\ c = 0 \qquad (23)$$

$$\text{at } \eta = 0,\ \text{any } \theta > 0;\ a = 1,\ \frac{\partial b}{\partial \eta} = 0,\ \frac{\partial c}{\partial \eta} = 0 \qquad (24)$$

$$\text{at } \eta = 1,\ \text{any } \theta \quad;\ a = 0,\ b = 1,\ c = 0 \qquad (25)$$

and Eq. (19) becomes:

$$E_A^* = K\sqrt{\frac{\pi(\theta+\epsilon)}{4\theta}}\int_0^1 [a + 2q(1-b) - c]d\eta' \qquad (26)$$

RESULTS AND DISCUSSION

Orthogonal Collocation vs. Finite Difference Methods

We note that Eqs. (20), (21) and (22) with conditions of Eqs. (23), (24), and (25) are readily soluble by the method of orthogonal collocation (cf. Finlayson, 1972; Villadsen and Michelsen, 1978). Since it is conventional to use finite difference methods to solve problems of this type, it is interesting to compare these two numerical methods. The reaction scheme used by Brian and Beaverstock

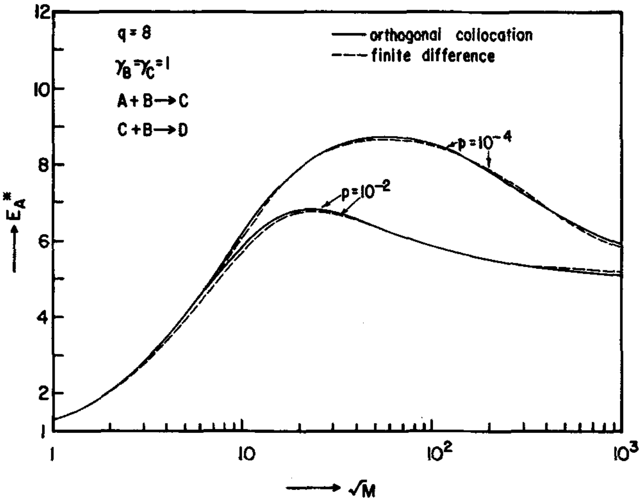

Figure 1. Comparison of the orthogonal collocation and finite difference methods: film model.

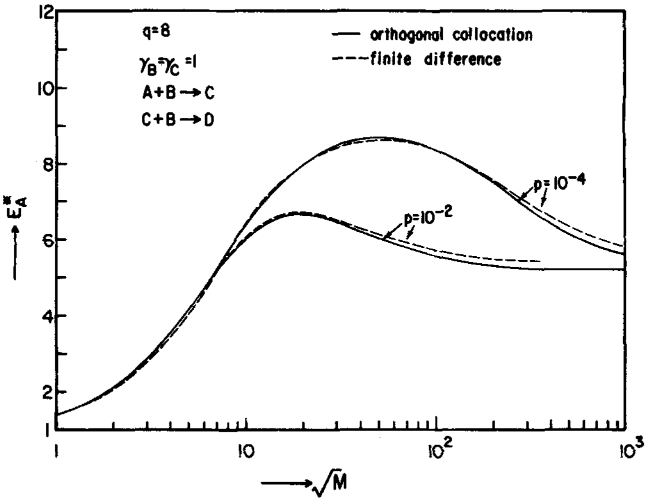

Figure 2. Comparison of the orthogonal collocation and finite difference methods: penetration model.

(1965) is adopted for this purpose as:

$$A\ (\text{gas}) + B\ (\text{liq.}) \rightarrow C\ (\text{liq.}) \tag{27}$$

$$C\ (\text{liq.}) + B\ (\text{liq.}) \rightarrow D\ (\text{liq.}) \tag{28}$$

The finite difference solutions of both the film and penetration theories corresponding to this reaction scheme are taken from Brian and Beaverstock (1965). The results are shown in Figures 1 and 2 for the film and the penetration theory, respectively. For the orthogonal collocation method, the convergence tests, in which the number of collocation points are increased and comparisons with known asymptotes made, show that the film theory solutions converge to within 0.6% and the penetration theory results are convergent to better than 1.3%. Only eight and 14 collocation points were used for the film and the penetration theory, respectively. The results show excellent agreement between the two numerical methods for both theories. If the computer storage and computation time are considered, the orthogonal collocation method would emerge superior and is thus recommended.

It is worth noting that the film theory equations are similar to the steady state diffusion-reaction problem in permeable catalyst pellets, for which the orthogonal collocation method has been extensively applied (cf. Finlayson, 1972; Villadsen and Michelsen, 1978). To our knowledge, the orthogonal collocation method has not been applied before to the penetration theory model, although Eqs. 20 to 22 except for nonconstant coefficients are qualitatively similar to those governing the transient axial dispersion model tubular reactor (cf. Varma and Aris, 1977). As in the catalyst effectiveness factor problem for large values of the Thiele modulus, the solutions for large M in the case of a gas-liquid reaction are difficult to obtain by any numerical method.

Film Theory Solutions

Applying the approximation method of van Krevelen and Hoftijzer (1948), Teramoto et al. (1969) derived the following approximate solution for the film theory Eqs. (6), (7), and (8) with boundary conditions of Eqs. (9) and (10*a*), which was adopted by Sharma et al. (1976) to analyze a gas-liquid CSTR:

$$E_A^* = \frac{\gamma'}{tanh\ \gamma'}\left(1 - \frac{a_L}{\cosh \gamma'}\right) \tag{29}$$

where

$$\gamma'^2 = Mb_i\left[1 + \frac{\dfrac{r_c c_L}{r_B q} + 1 - b_i}{1 + b_i\left(\dfrac{r_c}{r_B p} - 1\right)}\right] \tag{30}$$

with

$$b_i = 1/\left\{1 + \frac{M}{r_B q}\left[\frac{\coth \gamma'}{\gamma'} - \frac{1}{\gamma'^2} + \frac{\gamma'(\sinh \gamma' - \gamma')}{H}\right]\right\} \tag{30a}$$

$$H = \gamma'^2 \sinh \gamma' \left[\gamma' \cosh \gamma' + M\left(1 + \frac{pc_L}{q}\right)\alpha \sinh \gamma'\right] \tag{30b}$$

and

$$a_L = \gamma' / \left[\gamma' \cosh \gamma' + M\left(1 + \frac{pc_L}{q}\right)\alpha \sinh \gamma'\right] \tag{31}$$

Equation (30) with Eqs. (30*a*) and (30*b*) is a transcendental expression for γ', which has to be solved by trial and error. Once γ' is obtained, a_L can be found from Eq. (31) and then E_A^* from Eq. (29); the numerical results are shown in Figure 3.

The numerical solutions of the film theory are also presented in Figure 3, where 10 collocation points were used

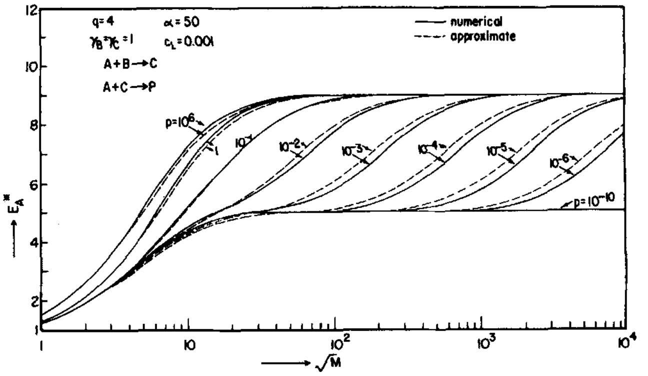

Figure 3. Comparison of the approximate and numerical solutions: film theory.

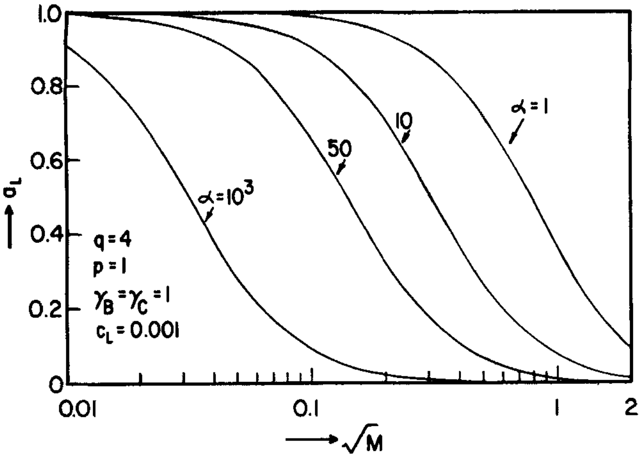

Figure 4. The effect of α on the film-bulk concentration of A.

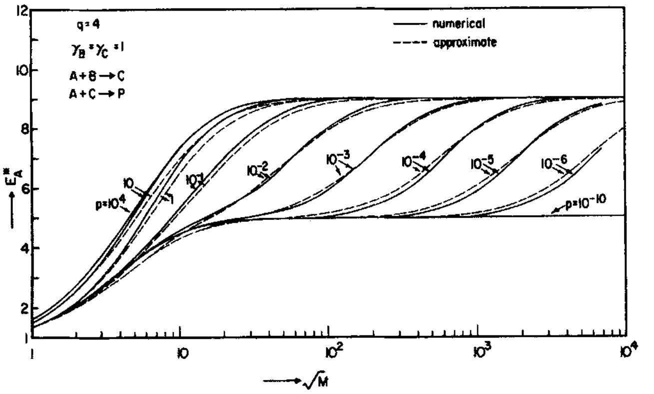

Figure 6. Comparison of the approximate and numerical solutions: penetration theory.

and the solutions are convergent to within 0.3%. From Figure 3, we note that for very small values of p, a two-step increase of E_A^* occurs. This is so because the second reaction Eq. (5) is negligible for relatively modest values of $\sqrt{M}$, and the problem thus reduces to gas absorption with a single chemical reaction Eq. (4) for which the asymptotic value is given by the Hatta equation:

$$E_{Aa,1}^* = 1 + r_B q \tag{32}$$

As $\sqrt{M}$ becomes very large, E_A^* increases again to approach its final asymptotic value, which is the same as that for large p. For large values of p, the second reaction is much faster than the first one so that the intermediate C in the reaction scheme of Eqs. (4) and (5) is consumed almost instantaneously. The overall stoichiometry is thus:

$$2A + B \rightarrow P \tag{33}$$

and the similar Hatta equation for this case is:

$$E_{Aa,2}^* = 1 + 2\,r_B q \tag{34}$$

From Figure 3, it may be observed that the numerical and approximate solutions agree well when p is not too small. For the case of very small p, where the two-step increase of E_A^* occurs, the agreement is excellent for first step, but the deviation can be as high as 6% for second step.

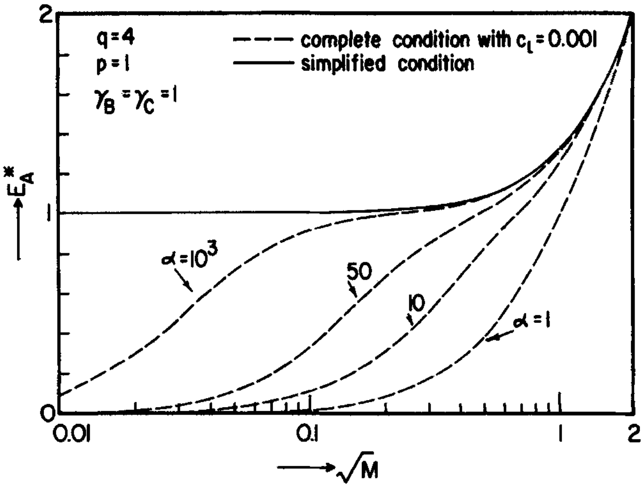

Figure 5. Comparison of the simplified and complete film-bulk boundary conditions.

The Effect of the Film-Bulk Condition

The two-step increase of E_A^* has also been observed by Onda et al. (1970) for film theory corresponding to the reaction scheme of Eqs. (4) and (6). The only difference between our model and theirs is the film-bulk boundary condition, where we used the complete condition (Eq. 10*a*) and they used the simplified one (Eq. 10*b*). It is, thus, interesting to investigate the effect of this condition on the evaluation of the reaction factors.

The film theory Eqs. (6), (7), and (8) with boundary conditions of Eqs. (9) and (10*a*) were solved to obtain the actual film-bulk concentration of reactant A, as shown in Figure 4. The reaction factor with the simplified condition (Eq. 10*b*) is shown in Figure 5 along with that from the complete condition (Eq. 10*a*). In the latter, for small values of $\sqrt{M}$, Eq. (11*b*) is used to compute the reaction factor and its accuracy, which is excellent, is checked against the approximate solution (Eq. 29). Note that for small $\sqrt{M}$ the approximate solution (Eq. 29) is virtually exact.

Figure 4 shows that although the actual concentration of A may differ significantly from zero, which is the simplified condition for A, as α or $\sqrt{M}$ increase the complete condition rapidly approaches the simplified condition. Figure 5 illustrates that the complete condition is important only for small values of both α and $\sqrt{M}$. In both Figures 4 and 5, if $c_L = 0$ instead of 0.001 for which the computations are made, the difference is less than 0.01% for the solutions presented. However, $c_L \neq 0$ is made to retain the completeness of condition (Eq. 10*a*).

Figures 4 and 5 also note the effect of α (the ratio of bulk liquid volume to film volume); that is, the larger the value of α, the smaller is the difference between the complete and simplified conditions. This effect is readily understood by viewing the problem as a perturbation problem for large α. Therefore, it may be concluded that for large α—which would normally be true—the complete condition is significant only for slow reactions, where $\sqrt{M}$ is much smaller than that for fast reactions.

Penetration Theory Solutions

Onda et al. (1972) have derived some approximate solutions of penetration theory by applying the Hikita and Asai approximation (1964). Adopting their general solution to the reaction scheme Eqs. (4) and (5), the approximate solution for the penetration theory Eqs. (12), (13), and (14) with conditions of Eqs. (15), (16), and (17) is:

$$E_A^* = 1 + 2\,r_B q\,(1-b_i) - r_B q c_i \tag{35}$$

and

$$E_A^* = \left(\sqrt{M_1} + \frac{\pi}{8\sqrt{M_1}}\right) \operatorname{erf}\left(2\sqrt{\frac{M_1}{\pi}}\right) + \frac{1}{2}\exp\left(-\frac{4M_1}{\pi}\right) \tag{36}$$

where

$$M_1 = M(b_i + p c_i) \tag{37}$$

and

$$c_i = \frac{1 - b_i}{1 + p\dfrac{r_B}{r_c}\left(\dfrac{1-b_i}{b_i}\right)} \tag{38}$$

Eqs. (35) and (36) are set equal and solved with Eqs. (37) and (38) by trial and error to get b_i for a given set of p, q, r_B, r_c, and M. Then, c_i is found through Eq. (38), and finally E_A^* from Eq. (35) or (36). The results are presented in Figure 6.

The numerical solutions of the penetration theory are also presented in Figure 6, where 14 collocation points were used and the solutions are believed to converge to better than 1.5%. The agreement between the numerical and approximate solutions is rather good for small values of p, and only a little poorer for large p. The overall agreement is much better than that for the film theory.

The numerical solutions of both the film and the penetration theories are shown in Figure 7. It may be seen that the two theories agree rather well, and the deviation is always less than 2%. Figure 6 already indicated that the approximate penetration theory solution deviates 2.5% at most from the corresponding numerical solution. Also, the difference between the approximate penetration theory solution and the numerical solution of the film theory is less than 6%. Therefore, it is justified to use approximate solutions from either theory in both steady state and dynamic models for the design of gas-liquid reactors.

In fact, we have observed that the approximate solutions for both the film and the penetration theories are nearly the same except for small $\sqrt{M}$. In this case, the reaction factor and the enhancement factor are identical for the penetration theory, and also for the film theory except for small $\sqrt{M}$, where the film-bulk concentration of reactant A does not vanish as seen from Figure 4. Note that the reaction factor may be less than unity and approaches zero as $\sqrt{M} \rightarrow 0$, but the enhancement factor is always above unity and approaches unity as $\sqrt{M} \rightarrow 0$.

Asymptotic Penetration Solution for Short Contact Time

For short contact time, that is, as $t \rightarrow 0$, it is apparent that $b \rightarrow 1$ and $c \rightarrow 0$, and thus the penetration model (Eq. 12) simplifies to:

$$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial z^2} - qa \tag{39}$$

with conditions reduced from Eqs. (15), (16), and (17):

$$\text{at } \theta = 0, \text{ any } z > 0, a = 0 \tag{39a}$$

$$\text{at } z = 0, \text{ any } \theta > 0, a = 1 \tag{39b}$$

$$\text{as } z \rightarrow \infty, \text{ any } \theta, a = 0 \tag{39c}$$

The mathematical problem of Eq. (39) has been solved by Danckwerts (1950). An analogy deduces, after transformation:

$$E_{A0}^* = \frac{\pi}{4\sqrt{M}}\left[\left(\frac{4M}{\pi} + \frac{1}{2}\right) \operatorname{erf}\left(\sqrt{\frac{4M}{\pi}}\right) + \frac{2\sqrt{M}}{\pi}\exp\left(-\frac{4M}{\pi}\right)\right] \tag{40}$$

This asymptote is used to test the numerical solution of the penetration theory, obtained by applying the orthogonal collocation method, for very small values of $\sqrt{M}$ (equivalent to $t \rightarrow 0$). The result is shown in Figure 8, where it may be seen that the numerical solution agrees rather well with the asymptotic solution for very small $\sqrt{M}$. This again supports the orthogonal collocation method and shows the applicability of Eq. (3) to the reaction scheme (Eqs. 4 and 5), and the validity of the reaction-zone concept in penetration theory as well.

Comparison of Film and Penetration Point Yields

Szekely and Bridgwater (1967) found that for the irreversible first-order consecutive reaction sequence $A \rightarrow B \rightarrow C$ in gas-liquid reactors, the yields predicted by the film and penetration models may differ significantly. In this work corresponding to reactions (Eqs. 4 and 5), the film yield is defined as:

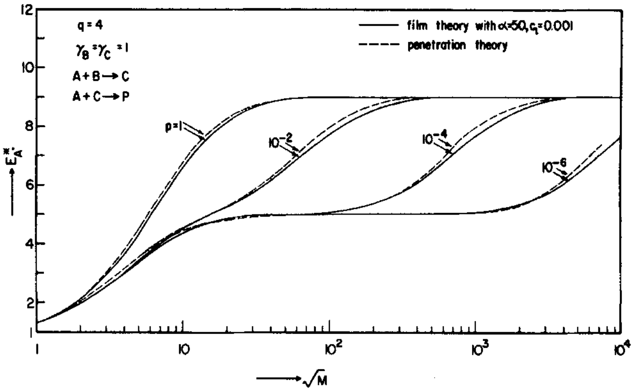

Figure 7. Comparison of the film and penetration theories: numerical solutions.

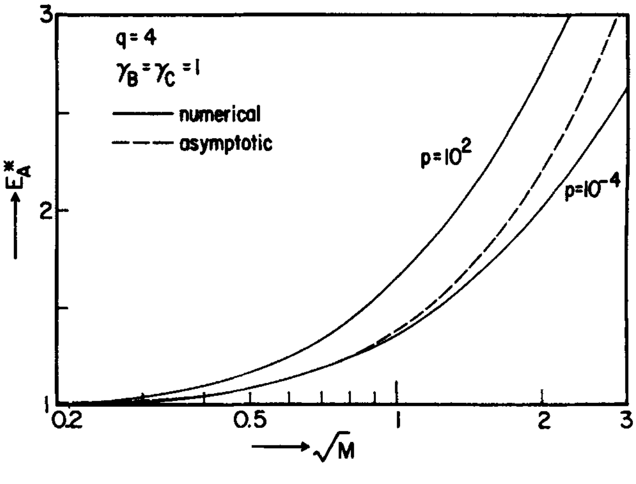

Figure 8. Penetration theory: comparison of the numerical and asymptotic solutions for short contact time.

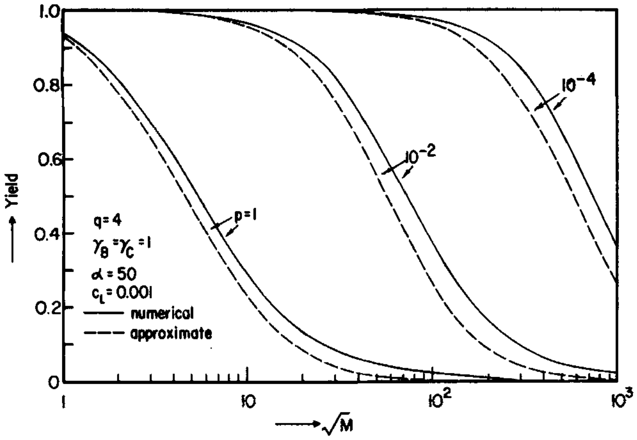

Figure 9. Comparison of the film and penetration point yields.

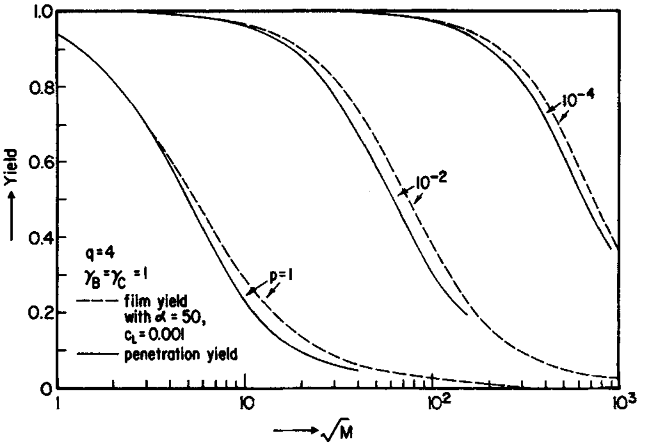

Figure 10. Comparison of the approximate and numerical solutions: film yield.

$$Y_f \equiv \frac{\int_0^\delta (k_1AB - k_2AC)dx}{\int_0^\delta k_1AB\, dx} \tag{41}$$

or in dimensionless form,

$$Y_f = \frac{\int_0^1 (qab - pac)dZ}{\int_0^1 q\, ab\, dZ} \tag{42}$$

From Eqs. (7) and (8), and using condition (Eq. 9), Eq. (42) becomes

$$Y_f = -\frac{r_c}{r_B q} \frac{\left(\frac{dc}{dZ}\right)_{z=1}}{\left(\frac{db}{dZ}\right)_{z=1}} \tag{43}$$

It is, thus, clear that the definition (Eq. 41) is equivalent to:

$$Y_f \equiv \frac{N_C}{N_B} \tag{44}$$

which is the one most frequently used for the film yield. Since the slopes of the concentration profiles of B and C at the film-bulk boundary are almost zero as $\sqrt{M} \rightarrow 0$, it may not be accurate to use Eq. (43) to calculate the film yield for very small values of $\sqrt{M}$; it is then better to use Eq. (42) instead. Note that Eq. (42) is accurate through the whole range investigated by applying the orthogonal collocation method.

The penetration yield is defined as:

$$Y_p \equiv \frac{\int_0^t \int_0^\infty (k_1AB - k_2AC)dxdt}{\int_0^t \int_0^\infty k_1ABdxdt} \tag{45}$$

and, after transformation, this becomes:

$$Y_p = \frac{\int_0^1 c\, d\eta}{q\int_0^1 (1-b)d\eta} \tag{46}$$

Both the film and penetration yields are presented in Figure 9. Although the difference of the yields between the two theories is generally small, it is much higher than that of the reaction factors, as was also observed by Szekely and Bridgwater (1967) for a different reaction scheme.

It is worth stressing that the yields computed here are *point* yields, and that the difference between the two theories for a *reactor* yield would indeed be magnified.

Approximate Film Yield

Using Eq. (43) and the results of Teramoto et al. (1969), as mentioned in previous section, an approximate solution of the film yield is:

$$Y_f = 1 - \frac{p\, c_i}{q\, b_i} \tag{47}$$

where

$$c_i = \frac{c_L + \frac{r_B\, q}{r_c}(1-b_i)}{1 + \frac{r_B\, p}{r_c\, b_i}(1-b_i)} \tag{48}$$

and b_i is obtained from Eq. (30*a*) by the same trial-and-error procedure used for calculating the approximate film reaction factor.

Figure 10 indicates that the difference between the approximate and numerical solutions becomes relatively larger, as $\sqrt{M}$ increases and as p decreases. This, thus, shows that the van Krevelen and Hoftijzer approximation method is not quite as good for the evaluation of the film yield as it was for the reaction factor, Figure 3. It is so, because the approximation does not accurately estimate the concentration profiles of B and C near the film-bulk boundary, since its purpose was originally in evaluating the concentration profile of A near the gas-liquid boundary.

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NOTATION

A,B,C = concentrations of species A, B, and C, respectively
a = dimensionless concentration, A/A_i

b = dimensionless concentration, B/B_L
c = dimensionless concentration, C/A_i
D = molecular diffusivity
E_A^* = reaction factor, defined by Eq. (1)
E_{A0}^* = asymptotic value of E_A^* in penetration theory for short contact time, Eq. (40)
$E_{Aa,1}^*$ = asymptotic value of E_A^*, Eq. (32)
$E_{Aa,2}^*$ = asymptotic value of E_A^*, Eq. (34)
K = constant defined by Eq. (3*a*)
k_1,k_2 = rate constants of reactions, Eqs. (4) and (5) respectively
k_{L0} = physical mass transfer coefficient: $2\sqrt{\frac{D_A}{\pi t}}$ in penetration theory; $\frac{D_A}{\delta}$ in film theory
M = $k_1 B_L D_A / k_{L0}^2$ in general; $\pi q \theta / 4$ in penetration theory; $k_1 B_L \delta^2 / D_A$ in film theory
N = mass transfer rate
p = k_2/k_1
q = B_L/A_i
r_B,r_C = defined by D_B/D_A and D_C/D_A, respectively
t = contact time in penetration theory
x = distance into the liquid phase
Z = dimensionless distance in film theory, x/δ
z = dimensionless distance in penetration theory, $x\sqrt{k_1 A_i / D_A}$
z_R = defined by Eq. (3*a*)

Greek Letters

α = ratio of the bulk liquid volume to film volume in film theory
γ' = constant defined by Eq. (30)
δ = film thickness in film theory
θ = dimensionless contact time, $k_1 A_i t$
ϵ = constant defined by Eq. (3*a*)
η = dimensionless distance defined by Eq. (3)

Subscripts

A,B,C = species A, B, and C, respectively
i = gas-liquid interface
L = bulk liquid in film theory

Superscript

= dummy variable in definite integral

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Separation of Proteins Via Multicolumn *p*H Parametric Pumping

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Fractionation of protein mixtures by multicolumn *p*H parametric pumping is investigated theoretically and experimentally. The parapumps considered consist of a series of columns packed alternately with cation and anion exchangers. Various methods of operation of the parapumps are discussed. Two separation problems are examined: enrichment and splitting. Experimental data were obtained for two-column systems and compared with the calculated results based on an equilibrium theory.

SCOPE

The name 'parametric pumping' was applied to the separation process in 1966 by the inventor of the batch pump, the late R. H. Wilhelm of Princeton University. Since the time of that invention, much experimental and theoretical work has been done on thermal and pressure cycling parametric pumping. Comprehensive reviews of the subject have been written by Sweed (1971), Wankat (1974*a*), Rice (1976) and Chen (1979*c*). By contrast, very little work has been done on the *p*H paramet-

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