Computational Studies of the Simultaneous Chemical Absorption of Two Gases

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SCOPE

Comprehensive reviews of the effect of liquid phase chemical reaction on the rate of gas absorption in many common systems are given by Sherwood and Pigford (*14*), Astarita (*1*), and Danckwerts and Sharma (*8*). However, relatively little attention has been paid to the problem of simultaneous multicomponent absorption that involves strong interactions between the gaseous species through the reactions. This could seriously affect the individual absorption rates and hence the selectivity of the separation system.

The situation considered here is the simultaneous absorption of two gases into a reactive liquid containing a nonvolatile solute with which each reacts. The interesting feature of this problem is that the absorption of each gas affects that of the other through its consumption of the liquid reagent. Roper, Hatch, and Pigford (*13*) and Astarita and Gioia (*2*) treat this problem, but under the restriction that the chemical reactions of both gases are infinitely rapid.

In many practical situations this assumption is not valid. Some industrial scrubbing operations employ sodium hydroxide, carbonate/bicarbonate buffer solutions, or aqueous monoethanolamine solutions to simultaneously remove carbon dioxide and hydrogen sulfide from a gas stream. Although it is known that hydrogen sulfide reacts very quickly with hydroxyl ions, the reactions of carbon dioxide with monoethanolamine and hydroxyl ion cannot always be considered instantaneous. The conditions for an instantaneous reaction were not met in one study of the absorption of carbon dioxide into hydroxide solution in a packed column (*7*), and data on the simultaneous absorption of carbon dioxide and sulfur dioxide into aqueous sodium hydroxide show that such conditions are even more difficult to obtain in the presence of a second reactive gas (*9*). Moreover, some practical situations, such as the removal of carbon dioxide and carbonyl sulfide from natural gas and from synthesis gas made from fuel oil, involve the simultaneous absorption of two gases with finite reaction rates for both.

Thus, a complete solution to the simultaneous absorption of two gases must allow for finite reaction rates for both gases and contact (or diffusion) times of the same order as the reaction times. It is the purpose of this paper to derive and discuss solutions to the diffusion equations describing the simultaneous absorption of two gases followed by bimolecular second-order reaction of each with a liquid-phase reagent, when at least one of these reactions occurs at a finite rate. Then the reaction zone is diffuse, and the nonlinear differential equations cannot be solved exactly.

The penetration theory model is solved numerically on a digital computer for the case where both reaction rates are finite. The effect of chemical reaction on the absorption rate is described in terms of a reaction factor, the ratio of the mass transfer coefficient in a reacting system to that for the purely physical absorption of the same gas under the same physical conditions. Interactions between the gases in this general treatment are interpreted in terms of several limiting cases: pseudo first-order reaction, two infinitely fast reactions, and the absorption and slow reaction of a single gas.

Computation time requirements have limited the scope of the numerical solutions presented. Large changes in the parameter values have been chosen to outline the general behavior of the systems and to identify the conditions under which interaction between the absorbing gases is important.

Even when one of the gases does react infinitely fast, at a reaction plane, the other will still react in a diffuse region after diffusing across that plane. The film theory equations are formulated for that situation, solved numerically, and compared with approximate analytic solutions that have been presented previously (*10*, *11*).

SUMMARY

The solutions presented here describe how two gases will interact during chemical absorption over the complete range of kinetic conditions from very slow to very rapid reactions. The reaction factor, which is reported for one of the gaseous species arbitrarily selected as the reference gas, depends upon the ratio of liquid-phase contact time to a characteristic reaction time and five dimensionless parameters. These are the ratio of the reaction rate coefficients for the two gases, the diffusion coefficients of the second gas and of the nonvolatile liquid reagent relative to that of the reference gas, the total capacity of dissolved gas at the interface for consuming the liquid reagent, and the relative strengths of the two dissolved gases.

When the contact time is long or the reactions are very fast, the reaction zone in the liquid degenerates to a plane

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separating the dissolved gases from the liquid reagent. In this asymptotic condition, the reaction factor becomes independent of the first parameter. However, this limiting solution requires considerably faster reactions than when only one gas is present.

If the reaction rate constant for the second gas is not smaller than that for the reference gas, the reaction factor will be less than its asymptotic value for all contact times or reaction rates. However, when the second gas reacts more slowly, the average absorption rate can approach the asymptote from above as contact time increases. This unusual behavior does not occur in the absorption and simple reaction of a single gas. For sufficiently slow reactions or short contact times, the presence of a second gas may be neglected, especially when it is slower-reacting, but this could lead to large errors in the absorption rate when interactions are significant.

The effects of changes in the ratios of diffusion coefficients can be described in terms of the competition of the two gases for the liquid species. Thus, increasing the latter's diffusion coefficient or decreasing that of the second gas will increase the reaction factor for the reference gas.

When one of the gases reacts infinitely rapidly and the other at a finite rate, the film theory equations for the three species can be combined to yield a single nonlinear differential equation. An iterative solution stable for a slow reaction matches with an asymptotic approximation that is valid only when the finite reaction rate is moderately fast.

PENETRATION MODEL-FINITE REACTION RATES

If the contact time in the absorber is assumed to be short, the liquid can be considered a semi-infinite medium either moving at a uniform velocity or stagnant. Diffusion in the flow direction and convection normal to the interface are neglected. The liquid diffusion coefficients and the interfacial concentrations of dissolved gases are assumed to be constant.

Let A and B be two gases being simultaneously absorbed into a liquid containing a nonvolatile reagent C. A and B are unreactive toward each other in both the gas and the liquid phases, but each reacts with C according to a second-order bimolecular irreversible reaction.

$$A + \nu_A C \rightarrow \text{products} \tag{1}$$

$$\text{rate} = k_A AC \tag{2}$$

$$B + \nu_B C \rightarrow \text{products} \tag{3}$$

$$\text{rate} = k_B BC \tag{4}$$

A material balance over a differential element of liquid results in the unsteady state diffusion equations with reaction terms, here given in dimensionless form as

$$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial \eta^2} - ac \tag{5}$$

$$\frac{\partial b}{\partial \theta} = r_B \frac{\partial^2 b}{\partial \eta^2} - pbc \tag{6}$$

$$\frac{\partial c}{\partial \theta} = r_C \frac{\partial^2 c}{\partial \eta^2} - m_A ac - p m_B bc \tag{7}$$

where

$$\eta = (k_A C_o/D_A)^{1/2} x \qquad \theta = k_A C_o t$$

$$a = \frac{A}{A_i} \qquad b = \frac{B}{B_i} \qquad c = \frac{C}{C_o}$$

$$p = k_B/k_A$$

$$r_B = D_B/D_A \qquad r_C = D_C/D_A$$

$$m_A = \nu_A A_i/C_o \qquad m_B = \nu_B B_i/C_o$$

The boundary conditions are

$$\left.\begin{array}{lll} a(\eta, 0) = 0 & a(0, \theta) = 1 & a(\infty, \theta) = 0 \\ b(\eta, 0) = 0 & b(0, \theta) = 1 & b(\infty, \theta) = 0 \\ c(\eta, 0) = 1 & \dfrac{\partial c}{\partial \eta}(0, \theta) = 0 & c(\infty, \theta) = 1 \end{array}\right\} \tag{8}$$

These nonlinear, coupled differential equations will be solved numerically to give the concentration profiles as functions of θ. The liquid phase mass transfer coefficients, which describe the rates of absorption, are then calculated from the slopes of the concentration profiles and integrated over time to give the average coefficients.

$$k_{LA}(\theta) = -(D_A k_A C_o)^{1/2} \frac{\partial a}{\partial \eta}(0, \theta) \tag{9}$$

$$k_{LB}(\theta) = -\left(\frac{r_B}{p}\right)^{1/2} (D_B k_B C_o)^{1/2} \frac{\partial b}{\partial \eta}(0, \theta) \tag{10}$$

$$\bar{k}_{LA \text{ or } B}(\theta) = \frac{1}{\theta} \int_0^\theta k_{LA \text{ or } B}(s)\, ds \tag{11}$$

The reaction factors ϕ and $\bar{\phi}$ are the ratios of the instantaneous or average mass transfer coefficients to those for purely physical absorption. In this comparison it is assumed that the physical parameters are the same as in the absence of reaction. The reaction factor is then directly proportional to the mass transfer coefficient and to the absorption rate so that, under otherwise constant conditions, an increase in the reaction factor caused by a chemical effect indicates a proportionate change in the other quantities. In this sense the terminology can be used interchangeably.

Note that θ is a ratio of the actual time of contact which is available for diffusion to a characteristic reaction time $1/k_A C_o$. Thus, for long contact times the liquid reagent will be depleted near the interface by reactions of finite rate, and subsequent reaction must occur at greater distances into the liquid. This situation is similar to the consumption of C in short contact times by very fast reactions.

LIMITING CONDITIONS

No Reaction

At sufficiently small θ, either the reaction rate constant or the time for diffusion is too small for the chemical reaction to have any effect on the concentration profiles. Hence, the limiting value of the reaction factor as θ approaches 0 is unity.

Pseudo First-Order Reaction

If the sum of the interfacial concentrations of A and B is much less than the initial concentration of C, the latter will be consumed very slowly and $c \approx 1.0$ throughout the liquid. This behavior is always observed for sufficiently small values of θ. Under these conditions, Equations (5) and (6) become uncoupled, and the corresponding solutions for the mass transfer coefficients are given by Danckwerts (6). As θ approaches infinity a steady state is reached, for which

$$\lim_{\theta \to \infty} k_{LA} = k'_{LA} = (D_A k_A C_o)^{1/2} \tag{12}$$

$$\lim_{\theta \to \infty} k_{LB} = k'_{LB} = (D_B k_B C_o)^{1/2} \tag{13}$$

Note that these are the same dimensional quantities appearing in Equations (9) and (10). The ratios k_{LA}/k'_{LA} and k_{LB}/k'_{LB} then represent dimensionless mass transfer coefficients, which will be denoted by κ_A and κ_B. Pseudo first-order reactions represent an upperbound on the reaction factor ϕ as a function of θ. This is shown by the curves in Figures 4 to 8.

Infinitely Fast Chemical Reactions

If the reaction is not pseudo first order, the coupled Equations (5) to (8) possess no steady state solution for large θ. Instead, the solution approaches that for infinitely fast reactions as θ approaches infinity at constant p. Under these conditions neither absorbed gas can coexist with the nonvolatile solute, and a reaction plane exists in the liquid phase. This separation of the dissolved gases from the solute eliminates the reaction terms from the penetration theory equations and uncouples them, so that an analytic solution (*13*) is possible. The reaction factors are not time dependent, so that $\overline{\phi}_A = \phi_A$ and $\overline{\phi}_B = \phi_B$. They are given by the implicit algebraic equations

$$\phi_A = 1/\text{erf}\,(\beta)^{1/2}, \qquad \phi_B = 1/\text{erf}\,(\beta/r_B)^{1/2} \tag{14}$$

where β is given by

$$(r_C)^{1/2}\, e^{-\beta/r_C}/\text{erfc}\,(\beta/r_C)^{1/2} = m_A e^{-\beta}/\text{erf}\,(\beta)^{1/2} + m_B\,(r_B)^{1/2}\, e^{-\beta/r_B}/\text{erf}\,(\beta/r_B)^{1/2} \tag{15}$$

When m_A and m_B are small, Equations (14) and (15) can be approximated by

$$\phi_A \simeq r_C^{-1/2}\,(1 + r_C/(m_A + r_B\, m_B)) \tag{16}$$

$$\phi_B \simeq r_B^{1/2}\, \phi_A \tag{17}$$

Equations (16) and (17) become exact when $r_B = r_C = 1.0$ to give

$$\phi_A = \phi_B = 1 + 1/(m_A + m_B) \tag{18}$$

Because $(m_A + m_B)$ represents the total dissolved concentration at the interface relative to the initial concentration of liquid reagent, Equation (18) is like the corresponding equation for single gas absorption. The form of this equation suggests the use of $(m_A + m_B)$ and some other combination such as m_B/m_A rather than m_A and m_B separately as correlating parameters.

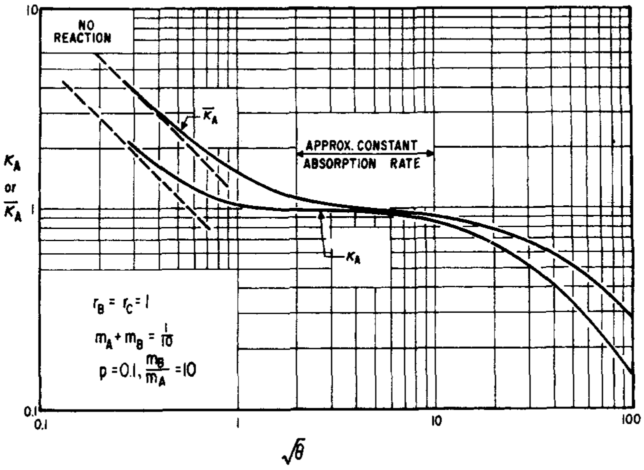

Fig. 1. Dimensionless mass transfer coefficient.

Notice that the infinite asymptotes for A and B are the same only when $D_B = D_A$. In contrast, the corresponding film theory solution predicts that

$$\overline{\phi}_A = \overline{\phi}_B = 1 + r_C/(m_A + r_B m_B) \tag{19}$$

even for unequal diffusivities. A comparison of Equations (16), (17), and (19) shows that, when m_A and m_B are small and r_B is approximately unity, the film theory result can be corrected by taking for the values of r_B and r_C the square roots of the ratios of diffusion coefficients.

Absorbed Gases Identical

When $D_B = D_A$ and $k_B = k_A$, the two absorbed gases cannot be distinguished. In this situation Equations (5) and (6) and the corresponding boundary conditions are identical. The solution reduces to that for single gas absorption with a value of $m = m_A + m_B$, as given in reference (*3*).

Before proceeding, let us note that the first three limiting conditions can be observed in the θ-dependence of the dimensionless mass transfer coefficients κ_A or $\overline{\kappa}_A$, which have been defined above. Such a plot, taken from the numerical solutions to be described, is shown in Figure 1. When $\theta \simeq 0$, the mass transfer coefficients are seen to be large and equal to those for absorption without reaction. For sufficiently small θ a pseudo first-order reaction takes place between the absorbed species and the liquid reagent, and the mass transfer coefficient decreases until some constant value is reached. This plateau level depends upon the diffusivity and reaction rate constant of the absorbed species and upon the liquid reagent concentration as shown by Equation (12). It represents absorption at a constant rate independent of the time of contact. Such behavior is in contrast to purely physical absorption, where the absorption rate continues to vary inversely with the square root of contact time. Further increase in θ will cause the absorption rate to decrease again and finally to vary inversely with $\sqrt{\theta}$, corresponding to the asymptotic value reached by ϕ_A. The plateau region is more pronounced when $m_A + m_B$ and p are small, and m_B/m_A is large.

NUMERICAL SOLUTION*

For conditions other than the limiting conditions enumerated above, the differential equations must be solved numerically. These equations are of the parabolic type, with boundary conditions specified on three sides of the $\eta - \theta$ region. For this problem, the infinite η-domain can be mapped into a finite one by transformations such as $\zeta = 1/(1 + h\eta)$, where h is an arbitrary constant. The solution is then projected from the initial condition at $\theta = 0$ in the direction of increasing θ, subject to the boundary conditions on ζ.

The Crank-Nicolson difference scheme (*5*) was selected for this problem because, for the simple linear diffusion equation $\partial a/\partial\theta = \partial^2 a/\partial\eta^2$, it is stable for all values of the modulus $\Delta\theta/(\Delta\eta)^2$. Although this desirable property is lost when nonlinearities occur, it is found that stability is maintained even when this modulus is much larger than the limit for a simple explicit scheme, enabling a faster solution. In some cases a value of two hundred could be used. A comparison of the numerical solutions for $m_A +$

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[*] The computer program and details of the numerical procedure have been deposited as Document No. 01454 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences Inc., 909 Third Ave., New York 10022 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

$m_B = 0$ with the exact solution for pseudo first-order reactions and changes in the solutions as the mesh size is refined indicated that the numerical solutions reported deviate from the exact solutions of the differential equations by less than two percent.

EFFECT OF A SECOND GAS ON THE SINGLE-GAS ABSORPTION RATE

Suppose that gas A is absorbed into a reactive liquid with no other reactive gas present. For $m_A = \nu_A A_i/C_o = 2/11$ and $B_i = 0$, $\bar{\phi}_A$ is given by the upper solid line in Figure 2. Equation (18) sets the asymptote at infinite θ for equal diffusivities at $\bar{\phi}_{A,\infty} = 1 + 1/(2/11 + 0) = 6.5$. The lower solid curve represents the absorption of another gas B in the same liquid without A present. If this gas is present at ten times the previously used concentration of A, and if the stoichiometric coefficients are assumed equal, $\bar{\phi}_{B,\infty} = 1 + 1/(0 + 20/11) = 1.55$. Now if the two gas streams are mixed and A and B are absorbed simultaneously, the total interfacial gas concentration corresponds to $m_A + m_B = 2.0$. Then Equation (18) predicts that $\bar{\phi}_{A,\infty} = \bar{\phi}_{B,\infty} = 1 + \frac{1}{2} = 1.5$.

The two dashed curves represent A and B absorbed simultaneously, and both approach an asymptote of 1.5 for large θ, as expected. For finite values of θ, however, the two additional parameters m_B/m_A and p also affect the solution. When $p = 1$ the reaction rate constants for A and B are equal, and $\bar{\phi}_A = \bar{\phi}_B$ for all θ because A and B are indistinguishable. The mass transfer coefficient or reaction factor $\bar{\phi}_B$ for B is affected only slightly, as the interfacial concentration of B is ten times that of A, and $m_B \approx m_A + m_B$.

However, because the total interfacial gas concentration changes by a factor of eleven when B is added to A, $\bar{\phi}_A$ is reduced significantly. But when $p = 0.1$, or A reacts ten times faster than B, the liquid reagent C is not consumed as rapidly and $\bar{\phi}_A$ is shown for small θ to approach the curve for the case where B is not present. Then, as the reaction rate constants of A and B increase with increasing θ at constant p, the effect of this difference in reactivity diminishes until at $\theta = \infty$ the ratio of mass transfer coefficients no longer depends on p and $\bar{\phi}_A$ again approaches 1.5.

Under these conditions the ratio of the *average* mass transfer coefficient for A to that for no reaction thus approaches its asymptotic value from above. Perry and Pigford (*12*) observed this behavior for the ratios of the *instantaneous* mass transfer coefficients in the absorption of a single gas. They concluded, by interpreting θ in terms of contact time, that the liquid reagent is preserved at the interface at short times when the reaction occurs with a finite rate constant, and its effect is felt at later times (larger θ) when the gas does not have to diffuse as far into the liquid to react.

The only previous known instance in which the ratio of average mass transfer coefficients was found to approach its asymptote from above occurred in the work of Brian and Beaverstock (*4*) concerning the reactions

$$A + C \rightarrow B$$

$$B + C \rightarrow \text{products}$$

where A is an absorbed gas, and B and C are nonvolatile species. If the second reaction has a smaller rate constant than the first, the reaction factor will, for small θ, tend to approach the asymptote for $\nu_A = 1$. For larger θ, however, the second reaction becomes important, C is consumed at a faster rate, and the reaction factor is reduced. The final asymptote corresponds to $\nu_A = 2$.

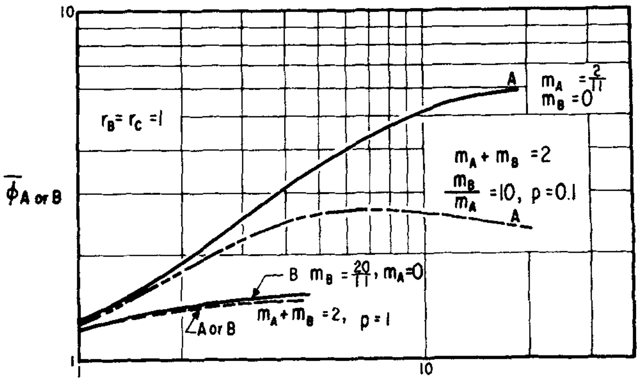

Fig. 2. Comparison of simultaneous and single-gas absorption.

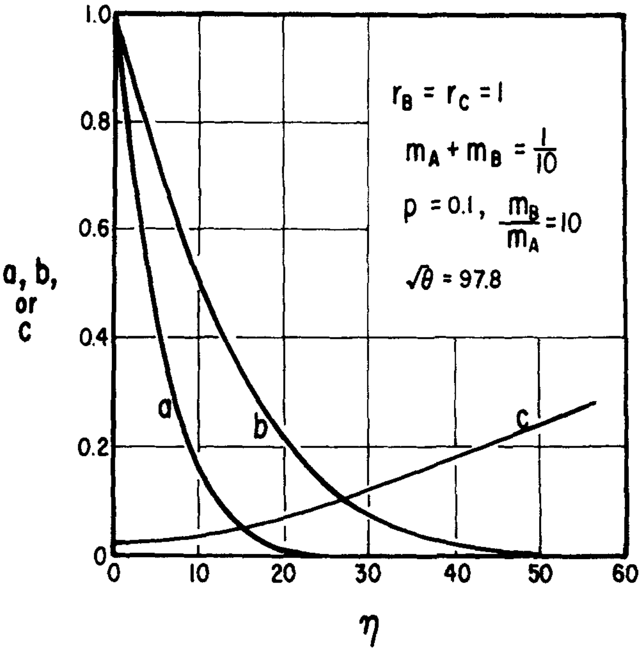

Fig. 3. Concentration profiles.

The common feature in all these cases is that the liquid reagent is consumed inordinately slowly for smaller θ. When the average reaction factors approach their asymptote from above, the change in consumption of C is seen to be caused by the increasing importance of a second reaction as θ increases.

PRESENTATION OF NUMERICAL SOLUTIONS

Most of the solutions were carried out for conditions of equal diffusivities, $D_A = D_B = D_C$. However, a few of the solutions were repeated at the same value of p, $(m_A + m_B)$, and m_B/m_A to show the effects of large changes in the diffusivity ratios r_B and r_C. Typical concentration profiles are shown in Figure 3.

The numerical procedure generated values for the ratio of mass transfer coefficients for both gases A and B. However, it is simpler and equally valid to interpret the solutions in terms of the effect of a second gas on the mass transfer of the first, rather than to present curves for both gases. Clearly, the results for gas B can be plotted and labeled on the graphs so that they refer to gas A. For example, the reaction factors for B for the parameter values

$r_B = f_1$, $r_C = f_2$, $(m_A + m_B) = f_3$, $m_B/m_A = f_4$ and $p = f_5$ are presented as results for A for the parameters $r_B = 1/f_1$, $r_C = f_2/f_1$, $(m_A + m_B) = f_3$, $m_B/m_A = 1/f_4$, and $p = 1/f_5$. Also, because $\theta = k_A C_o t$, the results for B are plotted as functions of $p\theta = k_B C_o t$. The resulting graphs can be used for either gas by considering the gas of interest to be A, and the other one, B.

Equal Diffusivities

The plot in Figure 4 shows the effects of p and m_B/m_A on ϕ_A for $\phi_{A,\infty} = 11$. For small θ the curves converge at the solution for pseudo first-order reactions. As already mentioned, when p equals unity the solution is identical to that for absorption of a single gas and passes through a slight maximum to approach the asymptotic value from above. This, of course, also occurs when $m_B/m_A = 0$, regardless of the value of p. This is shown by curve 4. When p is not equal to unity, the solution is also a function of m_B/m_A. Curves 1, 2, and 3 show that the ratio of mass transfer coefficients passes through a maximum whenever $p \leq 1$. As p approaches zero for a constant value of m_B/m_A, ϕ_A approaches the value it would have if B were not present, as determined by the magnitude of m_A. The presence of the second soluble gas is not felt if it is not reactive, for the model accounts only for chemical effects. For p greater than unity, the curves 5, 6, and 7 all lie below curve 4. Because the reactivity of B is greater than that of A, C is consumed more rapidly and the absorption rate of A is reduced. As p approaches infinity at constant m_B/m_A, a moving reaction plane will be formed since B will react with C immediately on contact. However, ϕ_A will not go to unity, for A will still be able to diffuse across the reaction plane to react with C. The solution for this special case is discussed later. The dashed lines in Figures 4 to 8 represent extrapolations of the computer solutions.

Figure 5 gives the average reaction factor $\overline{\phi}_A$ as a function of $\theta^{1/2}$ for the same conditions as shown in Figure 4. The same explanations also apply. For θ less than that corresponding to a maximum in $\overline{\phi}_A$, this ratio is smaller than ϕ_A. The ratio of average coefficients will also approach the asymptotic value more slowly. For $p = 10$ or 0.1, and $m_B/m_A = 10$, the curves deviate considerably from the asymptote even for $\theta^{1/2}$ greater than 100. Thus, application of the assumption of an infinitely fast reaction is more restricted than that for the absorption of a single gas.

For example, suppose that two gases are absorbed at a total concentration that gives a ratio of coefficients of 11 for infinitely fast reactions, and that B reacts ten times faster than A, but is present at the interface at only one tenth of the concentration. If the gases were both assumed to react with a rate constant k_A, the results, given by curve 4, would be identical to those for absorption of a single gas at the same total gas concentration. The asymptotic reaction factor would surely be approached within 10% at $\theta^{1/2} = 100$. Now, if the difference in reaction rate constants is considered, the results for A are given by curve 5. The deviation from the asymptotic value is slightly larger. But for B the reaction factor, given by curve 1 for the same contact time t at $\theta^{1/2} = (10)^{1/2}\,(100) = 316$, is twice that for infinitely fast reactions. In a similar manner Figure 5 shows that the assumption of infinitely fast reactions is also valid at smaller θ when each gas is absorbed separately at its same individual interfacial concentration.

Similar results for an asymptote of 1.5 are presented in Figure 6. Although the general behavior is the same as previously described, the ratio of coefficients approaches its asymptote more rapidly. The maximum in the curve for $p = 0.1$, $m_B/m_A = 10$ occurs at $\theta^{1/2} = 6.6$ as compared with $\theta^{1/2} = 105$ in Figure 5.

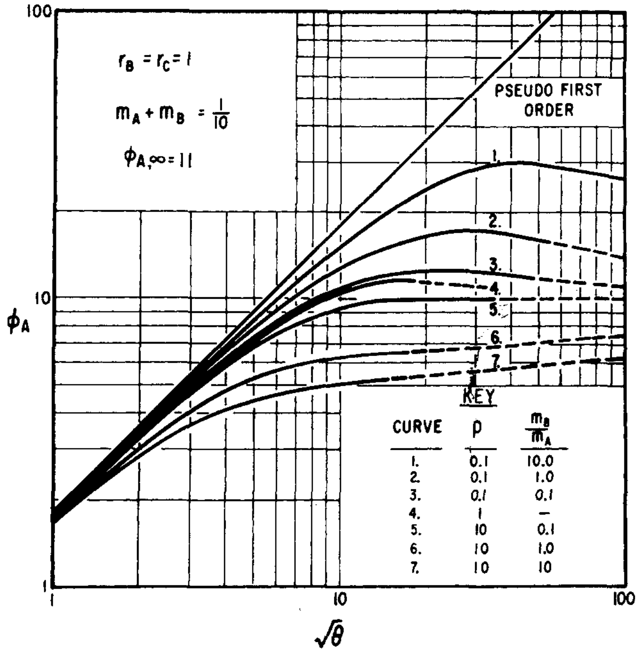

Fig. 4. Instantaneous reaction factor for equal diffusion coefficients, $\phi_{A,\infty} = 11$.

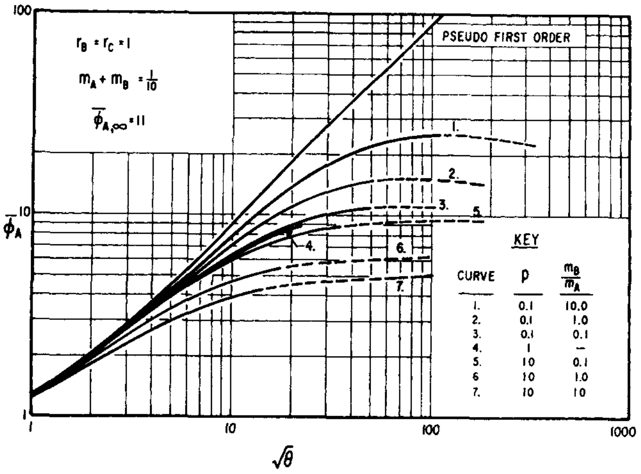

Fig. 5. Average reaction factor for equal diffusion coefficients, $\overline{\phi}_{A,\infty} = 11$.

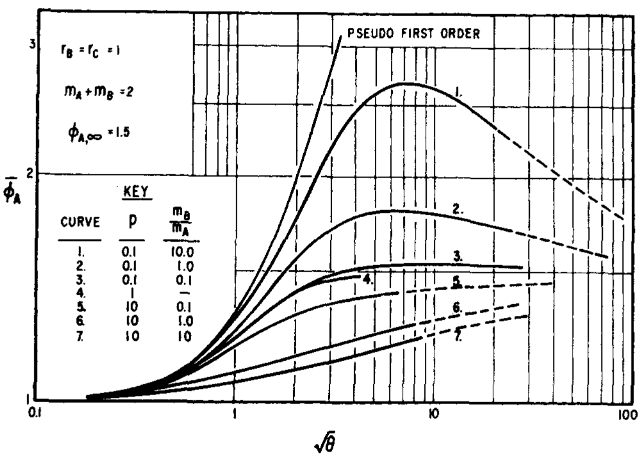

Fig. 6. Average reaction factor for equal diffusion coefficients, $\overline{\phi}_{A,\infty} = 1.5$.

Unequal Diffusivities

All solutions for the absorption of a single gas that approach a common asymptote can be described by a single curve for a wide range of the diffusivity and concentration ratios (3). However, when two reactive gases are competing for the same liquid reagent, conditions may occur for which this correlation (with p and m_B/m_A held fixed) is no longer valid.

The solutions for $p = 0.1$, $m_B/m_A = 10$, and $m_A + m_B = 0.1$ are compared in Figure 7 for various values of the ratios of diffusion coefficients. If r_B and r_C were both unity, $\bar{\phi}_A$ would reach an asymptotic value of 11, as shown by the upper solid curve. However, when the diffusivity of C is reduced so that $r_C = 0.16$, a solution of Equations (14) and (15) shows that the asymptote decreases to 6. In fact, the ratio of coefficients is smaller for all θ because C is not supplied to the interface as rapidly, and A and B must diffuse farther into the liquid to react. A solution for $p = 0.1$ and $m_B/m_A = 10$, but with $m_A + m_B = 0.2$ and equal diffusivities, is shown for comparison. This solution also has an asymptote of 6 and agrees with the previous case of reduced r_C within 2% up to the maximum point in the curves. The numerical calculations were not continued to larger values of θ.

When $r_B = 21.3$ and $r_C = 2.66$, the asymptote is reduced to 1.5. Again a solution with the same asymptote and the same p and m_B/m_A but for equal diffusivities is shown for comparison. The two solutions agree only for $\theta^{1/2}$ less than 2 and deviate widely for larger θ. The agreement of the asymptotes is caused by the large diffusion coefficient of B in the former case, but at finite θ B's low reactivity relative to A makes its diffusivity a less important factor. The smaller dissolved gas concentrations and the somewhat larger diffusivity of C in the solution for unequal diffusivities then favor a higher concentration of C near the interface where A reacts. This accounts for the greater absorption rate of A at finite θ.

Solutions for $p = 10$, $m_B/m_A = 0.1$, and $m_A + m_B = 0.1$ are presented in Figure 8 to illustrate the change from $r_B = r_C = 1$ to $r_B = 1$, $r_C = 0.16$ and $r_B = 0.047$, $r_C = 0.125$. If the diffusivity ratios were unity, these curves would approach an asymptote of 11, but the changes in the diffusivities reduce the asymptotic value to 6 in each case. The solid lines in the figure represent solutions for equal diffusivities and asymptotes of 11 and 6. When the diffusivity of C is reduced, the absorption rate of A decreases, for less C is available near the interface. When the diffusivity of B is also made very small, somewhat less C is consumed by reaction, but the absorption rate of A is only slightly increased over the previous solution. The small magnitude of the increase in $\bar{\phi}_A$ over the entire range of θ probably occurs for two reasons. First, r_C has also been altered to make the asymptotes agree at infinite θ. Secondly, in the example given, B is present at only a small concentration relative to A and C, so that any change in its parameters in this case would not have much effect. Both the solutions agree with that for $r_B = r_C = 1$ and the same asymptote of 6 with maximum deviations of 2.5 and 9.5%.

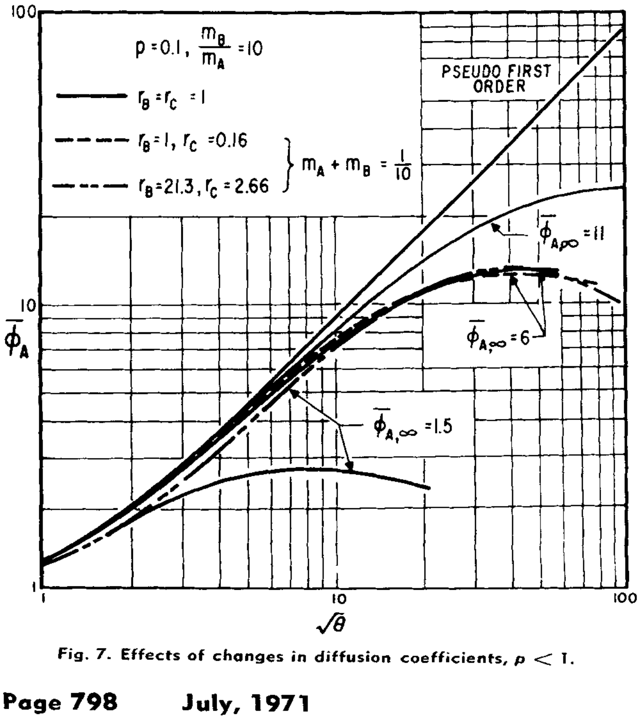

Fig. 7. Effects of changes in diffusion coefficients, $p < 1$.

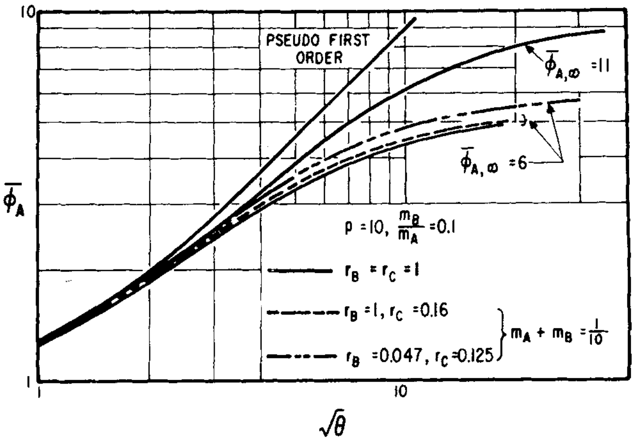

Fig. 8. Effects of changes in diffusion coefficients, $p > 1$.

A SOLUTION WHEN ONE GAS REACTS INFINITELY RAPIDLY

If the reaction rate constant for one of the gases approaches infinity as that for the other gas remains finite, the parameter p must also become infinite. Such a condition cannot be handled by the numerical technique just described. It is also not possible to obtain an accurate extrapolation of the computer results to conditions for $p = \infty$. This situation has industrial importance because the rate constants of both hydrogen sulfide and sulfur dioxide for reaction with hydroxyl ions are much greater than the rate constants for the corresponding reactions of carbon dioxide ($p > 10^5$) or carbonyl sulfide ($p > 10^8$).

Since one of the gases reacts infinitely fast, a reaction plane is formed in the liquid. But the second gas can still react with the liquid reagent by diffusing across the reaction plane. The reaction factor for the fast-reacting gas will decrease as θ for the other gas increases. The presence of the slow-reacting gas affects the position of the reaction plane, and neither reaction factor can be given by the simpler theories which assume only one or two infinitely fast reactions. The mathematical formulation in terms of the penetration theory is especially complex as it must include the determination of the velocity of the reaction plane.

In this work, the simpler film theory equations are solved for the reactions

$$A + \nu_A\,C \longrightarrow \text{products}, \qquad \text{rate} = k_A AC \tag{20}$$

$$B + \nu_B\,C \xrightarrow[\text{fast}]{} \text{products}. \tag{21}$$

The equations describing diffusion and reaction between the interface at $x = 0$ and the film boundary at $x = x_L$ are

$$d^2a/d\xi^2 = Mac \tag{22}$$

$$r_B(d^2b/d\xi^2) = pMbc \tag{23}$$

$$r_C(d^2c/d\xi^2) = M\ (m_Aac + pm_Bbc) \tag{24}$$

with the boundary conditions

$$\left.\begin{array}{ll} a(0) = 1 & a(1) = 0 \\ b(0) = 1 & b(1) = 0 \\ dc/d\xi\ (0) = 0 & c(1) = 1 \end{array}\right\} \tag{25}$$

where $\xi = x/x_L$ and $M = k_AC_ox_L{}^2/D_A = k_AC_oD_A/\bar{k}^0{}_{LA}{}^2$. By reinterpreting the physical mass transfer coefficient in terms of contact time according to the penetration model, it can be shown that M is equivalent to $(\pi/4)\theta$.

When B reacts infinitely fast, p is infinite. Then by rearrangement of Equation (23)

$$\lim_{p\to\infty} bc = \lim_{p\to\infty} (r_B/Mp)(d^2b/d\xi^2) = 0 \tag{26}$$

which suggests the existence of a reaction plane at $\xi = \xi^*$ such that $c = 0$ for $0 \leqq \xi \leqq \xi^*$ and $b = 0$ for $\xi^* \leqq \xi \leqq 1$. In the first region there is no chemical reaction. The concentration profiles are linear so that

$$\bar{\phi}_A = (1 - a^*)/\xi^* \tag{27}$$

and

$$\bar{\phi}_B = 1/\xi^* \tag{28}$$

where

$$a^* = a\ (\xi^*)$$

Equations (22) and

$$r_C(d^2c/d\xi^2) = M\ m_A\ ac \tag{29}$$

subject to the boundary conditions

$$\left.\begin{array}{ll} a(\xi^*) = a^* & a(1) = 0 \\ c(\xi^*) = 0 & c(1) = 1 \end{array}\right\} \tag{30}$$

apply to the region where $b = 0$. These may be combined to eliminate the nonlinear reaction terms and the result can be integrated twice to give

$$m_Aa - r_Cc = (m_Aa^* + r_C\xi^* - (m_Aa^* + r_C)\xi)/(1 - \xi^*) \tag{31}$$

Some additional constraints apply to the first derivatives at the reaction plane

$$da/d\xi(\xi^{*-}) = da/d\xi(0) = -\ (1 - a^*)/\xi^* \tag{32}$$

and $da/d\xi$ is continuous across the reaction plane.

$$r_C(dc/d\xi)(\xi^{*+}) = -\ r_B\ m_B(db/d\xi)(\xi^{*-}) = r_B\ m_B/\xi^* \tag{33}$$

Differentiating Equation (31), evaluating the terms at $\xi = \xi^*$, and substituting for the derivatives from above gives a relationship between a^* and ξ^*

$$m_Aa^* = m_A + r_B\ m_B - (m_A + r_B\ m_B + r_C)\ \xi^* \tag{34}$$

Thus, the problem of predicting the reaction factors $\bar{\phi}_A$ and $\bar{\phi}_B$ reduces to a solution of the nonlinear differential Equations (22) and (29) subject to (30). The differential equation for c may be eliminated by Equation (31). Either Equations (32) and (33) or (32) and (34) are used to evaluate a^* and ξ^*. Substitution into Equations (27) and (28) gives the reaction factors as functions of M.

A numerical solution was performed by choosing consistent values for the reaction factors and the input parameters, except for M, which was then determined by solving the boundary value problem iteratively. The results of the calculations on a digital computer appear in Figures 9 and 10. These are both for equal diffusion coefficients, and show the effects of changes in m_A and m_B on the reaction factor $\bar{\phi}_A$ for the slower reacting gas. In all cases the asymptote is calculated from Equation (18).

Figure 9 shows the effect of increasing the concentration of liquid reagent when the effective concentration of both gases are the same. As expected, a more concentrated solution will give larger reaction factors. The effect of a change in the relative amounts of gases A and B present at the interface for a fixed total amount of A and B is shown in Figure 10. Both curves in this case approach the same asymptote. The reaction factor is larger when less B is present, because more C is then available for reaction with A.

Unfortunately, the computer solution becomes unstable for large M. However, an approximate analytic solution has also been obtained by taking the concentration of C to be linear in the region from the bulk liquid to the reaction plane (*10*). This will be valid for sufficiently large M, when the size of the diffuse zone for the reaction of A with C is small. Operations in which the slower reacting gas is carbon dioxide usually fall in this range. An asymptotic expansion of the resulting Airy functions results in the simple form

$$M^{1/3} = 1.3717\,\frac{(1 - \xi^*)^{1/3}\,(1 - a^*)}{\xi^*\ a^*} \tag{35}$$

A comparison with the more exact computer solutions is shown in Figure 9. It can be seen that the asymptotic approximation is in error for $\sqrt{M} < 6$.

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The numerical solutions were performed at the University of Delaware Computing Center. Lloyd A. Goettler held a Na-

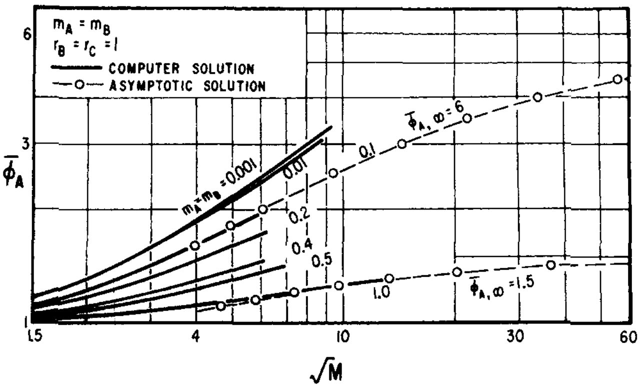

Fig. 9. Effect of $(m_A + m_B)$ on $\bar{\phi}_A$ when B reacts infinitely fast.

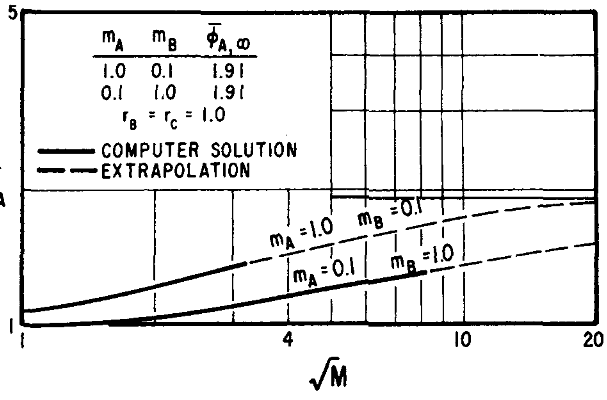

Fig. 10. Effect of m_B/m_A on $\bar{\phi}_A$ when B reacts infinitely fast.

tional Defense Act Fellowship during the course of the work.

NOTATION

A = molar concentration of absorbed gas A
a = A/A_i, dimensionless concentration of A
B = molar concentration of absorbed gas B
b = B/B_i, dimensionless concentration of B
C = molar concentration of nonvolatile liquid reagent
c = C/C_o, dimensionless concentration of C
D = diffusion coefficient in the liquid
h = arbitrary constant
k = bimolecular reaction rate constant
k_L = mass transfer coefficient for the liquid phase
M = measure of the rate of the chemical reaction, or the ratio of diffusion time to reaction time in the film theory
m_A = $\nu_A A_i/C_o$, the ratio of the effective interfacial concentration of dissolved gas A to the concentration of liquid reagent; similarly for m_B
p = k_B/k_A, ratio of reaction rate constants
r_B = D_B/D_A, ratio of diffusion coefficients
r_C = D_C/D_A, ratio of diffusion coefficients
t = contact time
x = distance coordinate normal to the interface
x_L = film thickness in the film theory

Greek Symbols

β = parameter defined by Equation (15)
Δ = indication of difference
ζ = transformed distance coordinate in the penetration theory
η = dimensionless distance normal to the interface in the penetration theory
θ = dimensionless time for the penetration theory
κ = k_L/k_L', dimensionless mass transfer coefficient
ν = stoichiometric coefficient
ξ = x/x_L, dimensionless distance in the film theory
ϕ = reaction factor, the ratio of the liquid phase mass transfer coefficient to that for no reaction under otherwise similar conditions

Subscripts

i = interfacial conditions
o = bulk liquid concentration
A, B = reference to the two absorbed gases
C = reference to the nonvolatile liquid reagent
∞ = condition at very large M or θ

Superscripts

— = average over contact time
$*$ = reference to concentrations at the reaction plane
$'$ = asymptotic value, with first-order reaction
0 = physical absorption without chemical reaction

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Diffusion of Urea in Flowing Blood

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SCOPE

It is well recognized (*1, 2*) that in hemodialysis for the replacement of renal function, the rate of removal of toxic molecules, particularly low molecular weight solutes, is often limited by transport within the blood. For this reason, application of mathematical models for the prediction of solute transport rates in hemodialyzers requires reasonably accurate knowledge of diffusion coefficients in flowing blood.

In an earlier study (*3*), diffusion coefficients of urea in stagnant plasma and red blood cell solutions were reported, and the latter were found to correlate well with the model of Fricke (*4*) for the electrical conductivity of a suspension of oblate ellipsoids. However, it has been suggested (*5, 6*) that rotation and migration of red cells in the presence of a velocity gradient, and the resulting secondary fluid motion, may materially increase transport rates. Hence, application to flowing blood of results obtained in stagnant solutions requires verification.

The present work is concerned with measurement of the

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