Absorption and Desorption Accompanied by a Reversible Reaction

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The processes of absorption and desorption with reversible reaction are compared theoretically for reactions of the type $A \rightleftharpoons nB$. With the same concentration difference between bulk and interface, it is found that in general, the rate of desorption is lower than that of absorption. Under certain conditions the difference may be as much as 35%.

The analysis is based on the penetration theory. The numerical solution introduces a new transformation of the time and distance variables (based on the error function) which reduces the computing time required. An analytical examination of the penetration theory equations provides an explanation of the results of the numerical solution.

In recent years many papers have been published on the theory of gas absorption into a liquid accompanied by simultaneous chemical reaction [penetration theory (*1* to *4*); film theory (*5*) to (*7*)]. Very few papers are known to the authors on the reverse process desorption.

In this paper we calculate numerically and compare rates of absorption with those of desorption for reactions of the type $A \rightleftharpoons nB$, A being the absorbing gas and B a nonvolatile reaction product. This reversible reaction is an approximate description of, for example, sulfur dioxide, chlorine, or bromine gases dissolving in water.

The development of concentration profiles is dependent on the progress of the chemical reaction, which is in turn sensitive to the concentration level. Thus for this type of system the processes of absorption and desorption, with the same bulk to interface concentration difference, may not in general be the same. No previous work is known which investigates the effect of this on the rate of mass transfer.

This paper also introduces a mathematical device, an error function distance transformation. This permits the numerical solution of penetration theory absorption problems to be achieved in a significantly shorter time.

THE ABSORPTION-DESORPTION PROBLEM

The reaction in solution is

$$A \rightleftharpoons nB \tag{1}$$

Thus at equilibrium

$$\frac{B^n}{A} = K \tag{2}$$

The partial differential equations which govern the concentration profiles of A and B can be written as

$$\frac{\partial A}{\partial t} = D_A \frac{\partial^2 A}{\partial x^2} - k_1 A + k_2 B^n \tag{3}$$

$$\frac{\partial B}{\partial t} = D_B \frac{\partial^2 B}{\partial x^2} + nk_1 A - nk_2 B^n \tag{4}$$

The boundary conditions for penetration into or out of the semiinfinite medium are

$$\text{Initial:} \quad t = 0, \; A = A_B, \quad B = B_B, \quad x \geqq 0 \tag{5a}$$

$$\text{Interface:} \quad t > 0, \; A = A^*, \quad \frac{\partial B}{\partial x} = 0, \quad x = 0 \tag{5b}$$

$$\text{Bulk:} \quad t \geqq 0, \; A = A_B, \quad B = B_B, \quad x = \infty \tag{5c}$$

In Equation (5*b*) $\partial B/\partial x$ is put at zero since the nonvolatile reaction product B may not pass through the interface. Now consider two concentration levels A_1 and A_2, where A_1 is the larger of the two. We make the usual assumptions of penetration theory, that the concentration of the absorbing gas is constant at the interface (A^*) and in the bulk (A_B), and compare the rate of mass transfer for absorption ($A^* = A_1$, $A_B = A_2$) with desorption ($A^* = A_2$, $A_B = A_1$) for a particular reaction velocity constant after the same diffusion time. If the rate of reaction is very slow indeed, the process approximates that of physical diffusion of A alone and thus the absorption rate equals the desorption rate.

For equal diffusivities, the same follows for very fast reactions. Toor and Chiang (*4*) have shown that Equations (3) and (4) may be transformed to

$$\frac{\partial c_T}{\partial t} = D_A \frac{\partial^2 c_T}{\partial x^2} \tag{6}$$

where

$$c_T = A + B/n \tag{7}$$

For a very fast reaction we may assume that A and B are in equilibrium throughout the medium, and this defines c_T at the boundaries as

$$c_T^* = A^* + \sqrt[n]{KA^*}/n \tag{8a}$$

$$c_{T,B} = A_B + \sqrt[n]{KA_B}/n \tag{8b}$$

Thus the rate of mass transfer (M_t) for both absorption and desorption is given by

$$M_t = 2\sqrt{\frac{D_A}{\pi t}}\,(c_T^* - c_{T,B}) \tag{9}$$

However, for intermediate reaction velocities, we may expect differences between rates of absorption and desorption. Although both A and B are diffusing through the medium, only A may pass through the interface so that in general Equation (8*a*) does not hold. The equilibrium concentration ratio of A to B depends on the concentration level of A. This follows from the equilibrium relationship Equation (2). That is

$$\frac{B}{A} = \frac{n\sqrt{KA}}{A} \tag{10}$$

In general the lower the concentration level, the larger the equilibrium ratio of B to A. We assume in penetration theory that equilibrium is maintained in the bulk and that departures from equilibrium are found near the interface. This is the high concentration region for absorption and the low concentration region for desorption. Thus since reaction rate is proportional to the difference between local concentration and the equilibrium concentration, different reaction rates can be expected for absorption and desorption.

For the particular case of $n = 1$, the B to A equilibrium ratio is independent of concentration level. For this case we calculate below that the absorption and desorption rates are equal for all reaction velocities. A more explicit interpretation of the differences between absorption and desorption is given in the reaction rate interpretation near the end of the paper.

THE ABSORPTION-DESORPTION DEVICE

For the case of an infinitely fast reaction with all species having the same diffusivity, it has been shown that, assuming equilibrium throughout the medium, a total equivalent concentration (c_T) can be defined. The overall rate of diffusion for this case is proportional to Δc_T and the maximum relative increase in diffusion rate (ϕ_A) is given by $\Delta c_T/\Delta A$.

It is useful to define the problem in terms of concentration ratios:

$$\frac{A_B}{A^*} = q \tag{11}$$

$$\frac{A^*}{B_0} = s \tag{12}$$

These parameters can be set to such values that the equilibrium concentration profiles are exactly similar for desorption and absorption and at the same concentration level. Now for absorption

$$\frac{A_B}{A^*} = q_I \ ; \ \frac{A^*}{B_0} = s_I$$

and

$$\Delta c_T = \Delta\,(A + B/n) = A^*$$

$$\left[\left\{1 + \frac{1}{ns_I}\right\} - q_I\left\{1 + \frac{1}{ns_I\, q_I^{\frac{n-1}{n}}}\right\}\right]$$

Also

$$\Delta A = A^*\,(1 - q_I)$$

and hence

$$\phi_{A,I} = \frac{\Delta c_T}{\Delta A} = 1 + \frac{1}{ns_I}\left\{\frac{1 - q_I^{1/n}}{1 - q_I}\right\} \tag{13}$$

Similarly for desorption

$$\phi_{A,II} = 1 + \frac{1}{ns_{II}}\left\{\frac{1 - q_{II}^{1/n}}{1 - q_{II}}\right\} \tag{14}$$

Similarity criteria in terms of q and s for absorption and desorption can now be established.

$$q_I = \frac{A_1}{A_2} \text{ and } q_{II} = \frac{A_2}{A_1}$$

Hence

$$q_{II} = 1/q_I \tag{15}$$

For symmetrical equilibrium concentration profiles it is required that

$$\left(\frac{A_B}{B_B}\right)_{II} = \left(\frac{A^*}{B_0}\right)_I \tag{16}$$

but

$$s_{II} = \left(\frac{A^*}{B_0}\right)_{II} = \left(\frac{A^*}{A_B}\cdot\frac{A_B}{B_B}\cdot\frac{B_B}{B_0}\right)_{II}$$

and thus

$$s_{II} = s_I \cdot q_I^{\frac{n-1}{n}} \tag{17}$$

By substituting Equations (15) and (17) into (14) it is easily shown that

$$\phi_{A,I} = \phi_{A,II}$$

Thus, provided that we compare absorption and desorption in terms of s and q as defined by Equations (15) and (17), the dimensionless concentration level a (where $a = A/A^*$) is irrelevant and the concentration ratio $a = 1.0$ at the interface may be used for both absorption and desorption.

NUMERICAL TECHNIQUE

The differential Equations (3) and (4) can be put into the following dimensionless form:

$$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial y^2} - a + b^n \tag{18}$$

$$\frac{\partial b}{\partial \theta} = \frac{r\partial^2 b}{\partial y^2} + ns\,(a - b^n) \tag{19}$$

The boundary conditions for penetration theory become

Initial: $t = 0,\ a = q,\ b = q^{1/n},\ y \geqq 0$ (20*a*)

Interface: $t > 0,\ a = 1.0,\ \frac{\partial b}{\partial y} = 0,\ y = 0$ (20*b*)

Bulk: $t \geqq 0,\ a = q,\ b = q^{1/n},\ y = \infty$ (20*c*)

The two partial differential equations (18) and (19) are nonlinear and no analytical solutions can be expected except for simple cases such as $n = 0$ or 1.

Equations (18) and (19) can however be converted to the equivalent finite-difference equations. The various numerical techniques are well described in the literature (*8* to *12*) and in this case a semi-implicit approach was found to be the most efficient.

Now for penetration theory boundary condition difficulties arise in the definition of a practical infinity and initially a region of very rapid change in concentration profiles is known to exist near the interface. Hence the definition of a distribution of mesh points is a critical factor for computational efficiency and stability. Secor and Beutler (*12*) suggest a distance transformation to z of the form

$$z = y/(y + C) \tag{21}$$

where C is an arbitrary constant. This transformation maps out the infinite range of y into a finite strip in z from 0 to 1. Ideally, C should be a function of time since the concentration profiles become less steep and require fewer mesh points near the interface as θ increases.

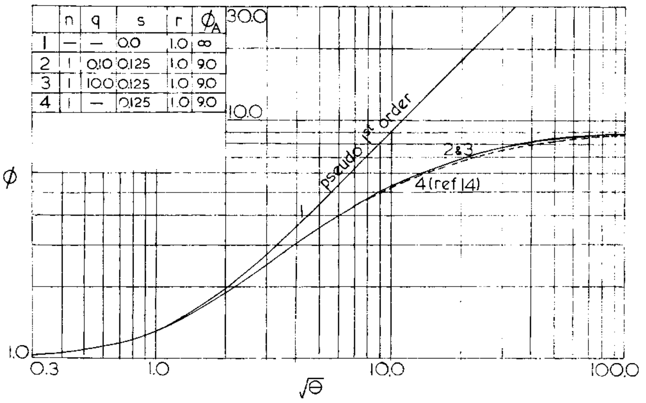

Fig. 1. Effect of first-order reaction absorption and desorption rates, $n = 1$.

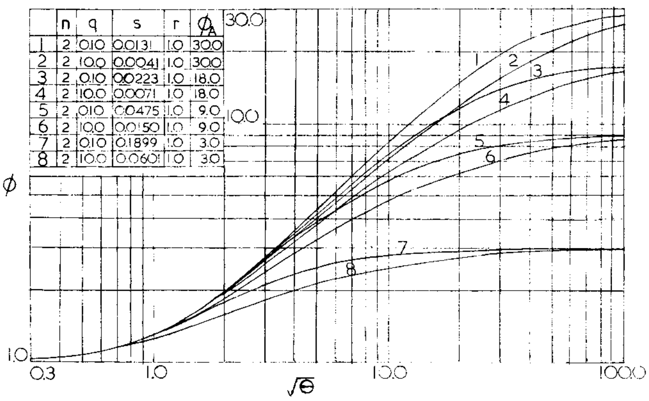

Fig. 2. Effect of second-order reaction on absorption and desorption rates, $n = 2$.

Brian and Beaverstock (*11*) suggest the use of the transform

$$z = y/C\sqrt{\theta + C'} \tag{22}$$

where C and C' are arbitrary constants which define the practical infinity and the distribution of the apparent mesh in y near the interface. This transformation also effects a continuous adjustment of the apparent mesh in y to suit the penetration of the concentration profiles as θ increases and results in a very large saving of computing time.

A further transformation, developed by the present authors, is one based on the solution of the diffusion equations without chemical reaction. This is given by Equation (23).

$$z = \text{erf}\,\frac{x}{2\sqrt{D_A t}} = \text{erf}\,\frac{y}{2\theta^{1/2}} \tag{23}$$

This transform has similar properties to Equations (21) and (22) but does not require the evaluation of any arbitrary constants or the definition of a practical infinity. Also the numerical instabilities caused by the step change of the interface concentration of A at $\theta = 0$ are avoided since all mesh points in z are concentrated on one line on the interface in y. Since no reaction can have taken place, the concentration profiles of a and b are straight lines in z. Consequently, $\partial a/\partial\theta$ and $\partial b/\partial\theta$ can be calculated for all mesh points by matrix inversion (see for example reference *13*) and initial instability is avoided.

Substitution of Equation (23) into Equations (18) and (19) gives

$$\frac{\partial a}{\partial \theta} = \frac{\partial^2 a}{\partial z^2}\left[\frac{e^{-y^2/2\theta}}{\pi\,\theta}\right] - a + b^n \tag{24}$$

$$\frac{\partial b}{\partial \theta} = \frac{r\partial^2 b}{\partial z^2}\left[\frac{e^{-y^2/2\theta}}{\pi\,\theta}\right]$$

$$- (r-1)\frac{\partial b}{\partial z}\left[\frac{y\,e^{-y^2/4\theta}}{2\,\pi\,\theta^{3/2}}\right] + ns\,(a - b^n) \tag{25}$$

and the boundary conditions become

$$\theta = 0, \quad a = q, \quad b = q^{1/n}, \quad z \geqq 0 \tag{26a}$$

$$\theta > 0, \quad a = 1.0, \quad \frac{\partial b}{\partial z} = 0, \quad z = 0 \tag{26b}$$

$$\theta \geqq 0, \quad a = q, \quad b = q^{1/n}, \quad z = 1.0 \tag{26c}$$

The added complexity of the analysis is compensated for by the increase in accuracy given by the physical significance of the mesh distribution. Also the time required for computation is considerably reduced since the number of mesh points in both θ and z can be kept to a minimum.

The most convenient way to present the results of computation is in terms of an enhancement factor (ϕ) defined as the ratio of time-averaged mass transfer rates with and without chemical reaction.

$$\phi = \frac{k_L}{k_L^0} = \frac{M_t}{M_t^0} \tag{27}$$

Now

$$M_t = \frac{1}{t}\int_0^\infty \left\{(A - A_B) + \frac{1}{n}(B - B_B)\right\} dx$$

$$= A^*\left(\frac{\pi D_A}{t}\right)^{1/2}\int_0^{1.0}\left\{(a - q)\right.$$

$$\left. + \frac{1}{ns}(b - q^{1/n})\right\} e^{y^2/4\theta}\,dz \tag{28}$$

and

$$M_t^0 = 2\,A^*\left(\frac{\pi D_A}{t}\right)^{1/2}(1 - q)/\pi \tag{29}$$

Substitution of Equations (28) and (29) into (27) gives

$$\phi = \frac{\pi}{2(1-q)}\int_0^{1.0}\left\{(a - q)\right.$$

$$\left. + \frac{1}{ns}(b - q^{1/n})\right\} e^{y^2/4\theta}\,dz \tag{30}$$

Thus the concentration profiles of a and b can be integrated after each step in θ for particular values of q and s. Typical computation times to obtain each curve shown in Figures 1 et seq. were 10 to 16 min.

The preceding equations were incorporated into a Fortran IV program for an English Electric KDF9 computer.

RESULTS OF COMPUTATION

The results of the computation are presented in Figures 1 to 6. For absorption $q < 1.0$ and for desorption $q > 1.0$. The q values are related by Equation (15) and the s values by Equation (17), such that $\phi_{A,I} = \phi_{A,II}$; that is, we have the same bulk to interface concentration difference with the same value of the equilibrium constant K.

Equal Diffusivities ($D_B = D_A$)

Figure 1 shows that for a first-order backward reaction ($n = 1$) the enhancement factors for absorption and desorption are equal for all values of θ. Comparison with the analytical solution given in reference *14* shows the computed solution to be within 2% of the true solution.

Figure 2 shows calculated values for $n = 2$. Over a wide range of θ, the enhancement factor is lower for desorption than for absorption. For low values of θ, the solutions for both directions of mass transfer converge, and tend to follow the pseudofirst-order line. For large values of θ, the enhancement factors approach the same asymptotic value ϕ_A.

Similar trends but of greater magnitude are shown in Figures 3 and 4 for a third-order reaction ($n = 3$).

Figure 5 shows that the differences between absorption and desorption are less when the difference in concentration between bulk and interface is less.

Unequal Diffusivities

Inspection of Figure 6 shows that the difference between absorption and desorption enhancement factors increases with the diffusivity ratio r.

When $r > 1.0$, species B can move away from or to the interface more rapidly than species A. Thus the period of time required for species B to build up its equilibrium level with A^* is increased for both absorption and desorption. Hence the nonlinearity between absorption and desorption reaction driving forces will increase as D_B increases.

Numerical difficulties were encountered for $r > 1$ using the transform given by Equation (23). This was overcome by modifying the transform so that the mesh distribution is based on the physical diffusion of B, that is

$$z = \operatorname{erf}\left(\frac{x}{2\sqrt{D_B t}}\right) = \operatorname{erf}\left(\frac{y}{2\sqrt{r\theta}}\right) \tag{31}$$

The solutions for r close to unity were found to converge to within 5% of ϕ_A ($0.5 < r < 1.5$), given by Equation (32), which is similar to an expression given in reference 2.

$$\phi_A = \frac{1}{\sqrt{r}} + \frac{\sqrt{r}}{ns}\frac{(1 - q^{1/n})}{(1 - q)} \tag{32}$$

AN EXPLANATION FOR THE DIFFERENCE BETWEEN ABSORPTION AND DESORPTION

By consideration of the reaction terms in Equations (3) and (4), we can demonstrate the essential difference between the development of concentration profiles for absorption and desorption.

The concentrations A and B at any point and time may be put in terms of the initial concentrations plus a contribution due to diffusion and reaction, that is

$$A = A_B + A' \tag{33}$$

$$B = B_B + B' \tag{34}$$

where A' and B' are positive for absorption and negative for desorption.

The average mass transfer rate through the interface after time t is given by

$$M_t = \frac{1}{t}\int_0^\infty (A' + B'/n)\, dx \tag{35}$$

Equations (33) and (34) may be inserted into Equation (3) to give

$$\frac{\partial A'}{\partial t} = D_A \frac{\partial^2 A'}{\partial x^2} - k_1 (A_B + A') + k_2 (B_B + B')^n \tag{36}$$

Expansion of the terms on the right of Equation (36) gives

$$\frac{\partial A'}{\partial t} = D_A \frac{\partial^2 A'}{\partial x^2} - k_1 (A_B + A') + k_2 \sum_{m=0}^{m=n} \frac{n!}{(n-m)!} B_B^{n-m} B'^m \tag{37}$$

where $m = 0, 1 \ldots\ldots n$.

We note that before the concentrations have been changed by the diffusion process, the rate of the forward reaction ($k_1 A_B$) is equal to that of the backward reaction ($k_2 B_B^n$), so that Equation (38) may be written as

$$\frac{\partial A'}{\partial t} = D_A \frac{\partial^2 A'}{\partial x^2} - k_1 A' - k_2 \sum_{m=1}^{m=n} \frac{n!}{(n-m)!} B_B^{n-m} B'^m \tag{38}$$

where $k_1 A' = R'_{A'}$, the change in the rate of the forward reaction due to the change in concentration A' and

$$k_2 \sum_{m=1}^{m=n} \frac{n!}{(n-m)!} B_B^{n-m} B'^m = R'_B$$

the change in the rate of the backward reaction due to the change in concentration B'.

Now only A may pass through the interface; B is considered to be nonvolatile [see Equation (5b)]. The initial equilibrium is disturbed by loss of A. The reaction then proceeds toward a new equilibrium by converting A into B or B into A. In general then R'_A is numerically greater than R'_B. The contribution of the reaction to the change in concentration is given by $(R'_A - R'_B)$. For an infinitely fast reaction R'_B is equal to R'_A and chemical equilibrium exists always at all points. For this case $\phi = \phi_A$.

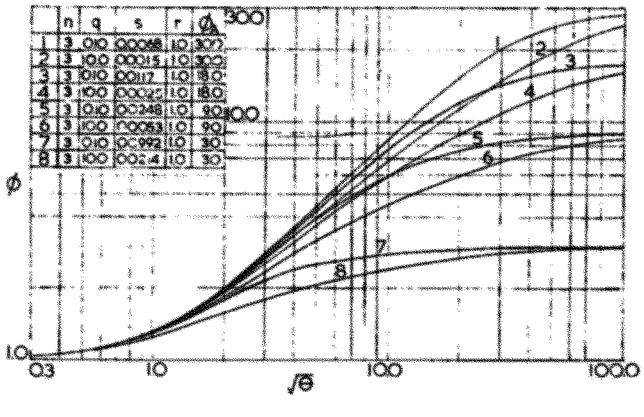

Fig. 3. Effect of third reaction on absorption and desorption rates, $n = 3$.

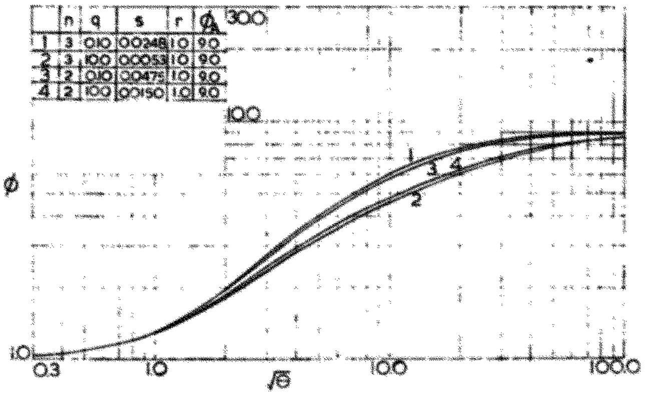

Fig. 4. Effect of reaction order on absorption and desorption rates, $n = 2$ and 3.

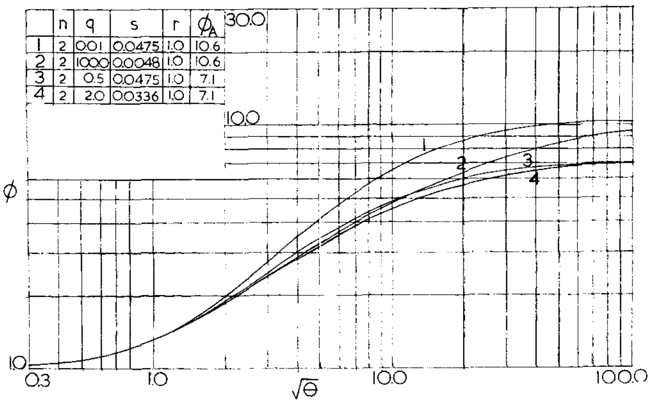

Fig. 5. Effect of concentration gradients on absorption and desorption rates, $n = 2$.

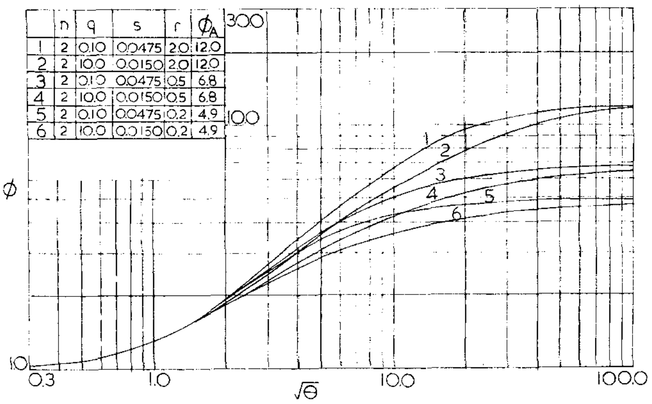

Fig. 6. Effect of diffusivity ratio on absorption and desorption rates, $n = 2$.

Now consider a slower rate of reaction and compare absorption and desorption by considering a hypothetical situation where the A' and B' concentration fields at time (t) are numerically the same but of opposite sign. If desorption is to proceed at the same rate as absorption, the $(R'_A - R'_B)$ terms must be equal.

In the general case for $n > 1$ this condition can never be met for finite reaction speeds since the bulk concentration B_B is higher for desorption $(B_B = B_1)$ than for absorption $(B_B = B_2)$. Thus $(R'_A - R'_B)$ is higher for absorption than for desorption and absorption rates can be expected to be higher than desorption rates due to the more rapid chemical reaction in the case of absorption.

Several limiting cases can now be examined.

First-Order Reaction, $n = 1$

If the backwards reaction is first order with respect to A, then Equation (39) becomes identical for both absorption and desorption:

$$\frac{\partial A'}{\partial t} = D_A \frac{\partial^2 A'}{\partial x^2} - k_1 A' + k_2 B' \qquad (39)$$

Equation (39) is independent of the concentration level of B and the solutions will be the same for desorption as for absorption. This explains the calculated result shown in Figure 1 that the mass tranfer rates are also equal.

Pseudofirst-Order Reaction

The condition for this situation is that the concentration of B throughout the medium should have changed very little, that is, $B' = 0$. Equation (38) then becomes

$$\frac{\partial A'}{\partial t} = D_A \frac{\partial^2 A'}{\partial x^2} - k_1 A' \qquad (40)$$

Thus equal rates of mass transfer may be expected for absorption and desorption.

Effect of Concentration Difference

The above analysis has demonstrated the dependence of the rate of reaction on the concentration level of B in the bulk liquid. In general the larger the concentration gradient, the greater will be the difference between B_1 and B_2. Thus for small concentration gradients the rates of absorption and desorption will be nearly equal. For larger gradients the absorption rates will be higher than the corresponding desorption rates.

CONCLUSIONS

Similarity criteria have been established for the processes of absorption and desorption accompanied by a chemical reaction of the type $A \rightleftharpoons nB$. Furthermore this theoretical study predicts that under certain circumstances, desorption may be expected to progress at a rate up to 35% lower than the corresponding absorption rate.

In practical situations this effect is likely to appear where the product of reaction velocity constant and contact time is in the range 10 to 10^3. The greatest differences between absorption and desorption rates are found for situations wherein exist large bulk to interface concentration gradients and relatively high equilibrium constants, that is, ϕ_A in the range 3 to 30.

The low computing costs of solution of error function transformed equations should permit a more direct and flexible comparison of experimental results with theoretical models of diffusion with reaction. The computer program written to solve Equations (18) and (19) may be modified to deal with other reaction schemes simply by changing the relevant boundary conditions and the terms a and b in the equations.

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NOTATION

a = A/A^*
A = concentration species A, moles/cu.cm.
A^* = interfacial concentration of species A, moles/cu.cm.
b = B/B_0
B = concentration species B, moles/cu.cm.
B_0 = concentration species B in equilibrium with A^*, moles/cu.cm.
c_T = $A + B/n$
D_A = diffusivity of species A, sq.cm./sec.
D_B = diffusivity of species B, sq.cm./sec.
k_1 = forward reaction velocity constant, sec.$^{-1}$
k_2 = reverse reaction velocity constant, [(moles)/(cu.cm.)]$^{1-n}$/sec.
K = equilibrium constant
M_t = time-averaged mass transfer rate with reaction, moles/(sq.cm.)(sec.)
M_t^0 = time-averaged mass transfer rate without reaction, moles/(sq.cm.)(sec.)
n = order of reverse reactions with respect to series A
r = D_B/D_A
t = time, sec.
x = distance from the interface into liquid, cm.
y = $k_1/D_A\,x$

z = transformed distance variable as defined by Equations (21), (22) or (23)

Greek Letters

θ = $k_1 t$

ϕ = enhancement factor. M_t/M_t^0

ϕ_A = maximum relative increase in diffusion rate

Subscripts

B = located in liquid bulk

I = absorption situation

II = desorption situation

Superscript

* = located at gas/liquid interface

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Convective Dispersion of Blood Gases in Curved Channel Exchangers

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The rates of hemoglobin saturation and carbon dioxide reduction in blood flowing in a curved channel membrane exchanger were studied theoretically by considering the fluid-limited process and the wall-limited process. The fluid-limited process was studied for laminar flows with and without secondary circulations. The relatively nontraumatic centrifugally induced circulations in the curved channel can reduce the required channel length to less than 1/500 that required for unperturbed flow. Such improvement, however, is practical only if very permeable membranes are available. If the P_{O_2} = 715 mm. Hg and P_{CO_2} = 0 mm. Hg at the walls, the fluid-limited analyses show oxygenation to be the slower process and the wall-limited analyses indicate CO_2 removal to be the limiting process. If the best available silicone rubber membranes are used, the process will be fluid limited for the unperturbed flow and wall limited for the flow with secondary circulations.

The use of auxiliary respiratory gas exchangers to restore venous blood to arterial conditions is commonplace today in cardiac surgical procedures. Nevertheless, the need remains for better designed exchangers, and much of the current interest centers on development of membrane exchangers. Recent analyses have described the characteristics of membrane exchangers consisting of straight tubes (*23*, *2*), coiled tubes (*24*, *6*), oscillating coiled tubes (*8*), annuli with stationary walls (*4*), annuli with an outer moving wall (*12*), and a rectangular channel with one moving wall (*22*). With the presently available membranes and with reasonable sizes, the analyses indicate that the process is limited by the gas transfer in the fluid phase

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