

# THE PERMEABILITY OF GASES THROUGH REACTING SOLUTIONS: THE CARBON DIOXIDE-BICARBONATE MEMBRANE SYSTEM

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**Abstract**—The transport of a gas across a stationary liquid film containing reactive species is investigated for the purpose of determining gas permeabilities or mass transfer coefficients in reacting solutions. Under limiting conditions when the reaction time constant far exceeds the diffusional time constant, the flux of the transported gas follows Fick's law of diffusion. Analytical series solution for the contribution of the chemical reaction to the transport process is obtained using the technique of perturbation analysis, criteria for the validity of various terms in the series solution are presented. The permeability of carbon dioxide in water and in 1N  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$  solution is estimated. It is shown that a high degree of accuracy in the data is necessary for obtaining separate estimates of diffusivity and solubility by this technique.

## INTRODUCTION

Several industrial processes involve gas absorption accompanied by chemical reaction, in the design of such equipment, pertinent information regarding diffusivity and *physical* solubility of the gas in the reacting solution is often necessary. A few semi-empirical correlations for predicting the same, based on mass transfer in non-reacting solutions, have been reported in the literature [1-3]. The absorption of carbon dioxide in  $\text{HCO}_3^-/\text{CO}_3^{2-}$  solution (ionic strength 1-3 gmol/l) has been studied for determining  $\sqrt{DC^*}$  (where  $D$  is the diffusivity and  $C^*$  is the physical solubility) using equipment of known surface area, such as the wetted-wall column [4, 5] and rotating drum [6]. The analysis in these studies conformed to the assumption that the reactions were irreversible.

In this article, an experimental approach is outlined for estimating the permeability (product of diffusivity and solubility) of gases in reacting solutions. The concept of permeability defined here is similar to, but not the same as, that of classical mass transfer coefficient in the film theory. Use is made of the fact that under a limiting condition, the contribution of the chemical reaction to the overall absorption process may be negligible. This limiting condition is realized whenever the time constant or the relaxation time for the chemical reaction is much larger than that for the diffusion process, the necessary criterion for such a condition is described. The analysis presented here is limited to

reversible reactions and one transferred (gas) species.

A similar concept has been described by Danckwerts [7] for the experimental determination of volumetric mass transfer coefficient,  $k_L a'$ , in absorption equipment. However, as Danckwerts has stated, "the condition for no-reaction in the film can be quite restrictive when the mass transfer coefficient is low" [7]. In the procedure described here, the film thickness is under direct experimental control, and the no-reaction condition has a greater possibility of being satisfied.

## MODEL DESCRIPTION AND ANALYSIS

The process governing the mass transfer, accompanied by reversible chemical reaction, of a gas across immobilized layers of liquid films or membranes falls under the category of 'facilitated' diffusion. Such systems have been studied for a number of years in the biological field, the model studies beginning with the transport of oxygen across layers of hemoglobin solutions [8, 9] are the most germane here. Although a comparatively large amount of literature has collected in this field (biological and otherwise), published literature on the industrial use of the 'facilitated' diffusion phenomenon in the separation of gases remains minimal.

### *Steady-state diffusion of a reacting gas across a planar liquid film*

Consider the diffusion of a dissolved gas,  $A_1$ , across a liquid film of thickness  $L$ . The film contains

'reacting' species,  $A_2$  and  $A_3$ , which react with  $A_1$  as shown in Fig 1. A partial pressure driving force in species  $A_1$ , namely  $\bar{p} - p$ , is maintained across the liquid film. Typical concentration profiles ( $C_i$ ) for the various species are also depicted in Fig 1. Several species ( $A_i, i = 2, 3, \dots, n$ ) may participate in other reactions, however, only the reaction involving species  $A_1$  is considered rate limiting in terms of kinetics of the reaction

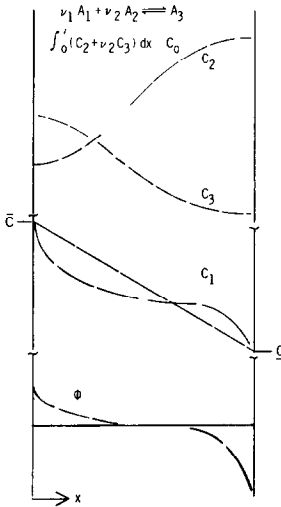


Fig 1 Concentration and reaction profiles within a film

Allowing for "dilute" solutions and binary diffusion coefficients, the governing one-dimensional diffusion-reaction equations at steady state, and the appropriate boundary conditions are

$$\frac{D_1}{\nu_1} \frac{d^2 \hat{C}_1}{dy^2} = \frac{D_2}{\nu_2} \frac{d^2 \hat{C}_2}{dy^2} = -D_3 \frac{d^2 \hat{C}_3}{dy^2} = -r_3 \quad (1)$$

and

$$\begin{aligned} @y=0, \hat{C}_1 &= \hat{C}_1(0), \frac{d\hat{C}_2}{dy} = \frac{d\hat{C}_3}{dy} = 0 \\ @y=L, \hat{C}_1 &= \hat{C}_1(1), \frac{d\hat{C}_2}{dy} = \frac{d\hat{C}_3}{dy} = 0 \end{aligned} \quad (2)$$

Only three of the four boundary conditions on the non-transferred are independent since one must satisfy the stoichiometric relationship for the "non-transferred" species,  $A_2$  and  $A_3$

$$\frac{1}{L} \int_0^L (\hat{C}_2 + \nu_2 \hat{C}_3) dy = \hat{C}_2^T \quad (3)$$

At this stage, the diffusion-reaction equations

and the boundary conditions are transposed to a dimensionless form in order to examine the relative importance of diffusion and chemical reaction terms. Thus,

$$\frac{d^2 C_i}{dx^2} = g_i \alpha^2 \phi \quad (4)$$

where

$$\alpha^2 = k \cdot C \cdot L^2 / D \cdot$$

$$\phi = -r_3 / k \cdot C \cdot C^{p-1}$$

$$C_i = \hat{C}_i / C \cdot$$

$$x = y / L$$

$$g_1 = D \cdot \nu_1 / D_1, \quad g_2 = D \cdot \nu_2 / D_2, \quad g_3 = -D \cdot / D_3$$

and  $C \cdot$ ,  $D \cdot$  and  $k \cdot$  are typical concentration, diffusivity and reaction rate constant, respectively. The dimensions of  $k \cdot C \cdot^p$  are  $[\text{sec}]^{-1}$

The steady-state flux of  $A_1$  across the liquid film,  $N_1$ , is given by

$$N_1 = -\frac{D_1 C \cdot}{L} \left[ \frac{dC_1}{dx} \right]_{x=0} \quad (5)$$

Defining  $N_0$  as the Fickian flux, that is, the flux obtained under conditions of physical absorption,

$$N_0 = \frac{D_1 C \cdot}{L} (\bar{C} - C) \quad (6)$$

we have

$$\frac{N_1}{N_0} = \frac{-1}{(\bar{C} - C)} \left[ \frac{dC_1}{dx} \right]_{x=0} \quad (7)$$

where

$$\bar{C} = \hat{C}_1(0) / C \cdot$$

$$C = \hat{C}_1(1) / C \cdot$$

The variable  $\alpha$  is a measure of diffusion and reaction resistances. For first order irreversible reaction in a slab of thickness  $L$ ,  $\alpha$  is related to the half-times for diffusion,  $t_D$ , and reaction,  $t_R$ , by a constant [10]

$$\alpha^2 \approx 3.5 t_D / t_R$$

For more complex reactions, such a simple correspondence may not be observed.

In a previous paper [11], two limiting regimes were defined based on the relative magnitude of reaction and diffusion terms

$\alpha \rightarrow 0$  "Near diffusion" regime

$\alpha \rightarrow \infty$  "Near equilibrium" regime

We are concerned here with the near diffusion regime in which the flux of the transported species *in excess of its diffusional flux* is small compared to that excess realized when all reactions are at equilibrium, that is,

$$N_1 - N_0 \ll N_1^E - N_0$$

where  $N_1^E$  is the flux of the transported species under the conditions of reaction equilibrium

A similar limiting condition is described by Danckwerts[7] for gas absorption with chemical reaction of species  $A_1$  in bulk of the liquid. For a first-order irreversible reaction, "the condition that a negligible amount of gas absorbed should react in the film" is given by[7]

$$\frac{D_1 k}{k_L^2} \ll 1$$

where  $k$  is the first order rate constant and  $k_L$  is the mass transfer coefficient

#### Asymptotic solution in the near diffusion regime

An asymptotic solution to the diffusion-reaction equations for the limit  $\alpha \rightarrow 0$  is derived below. The solution is non-singular, that is, valid in the entire distance field,  $0 \leq x \leq 1$ . Utilizing the techniques of perturbation theory, the concentration profiles are postulated to be of the form

$$C_i = C_i^{(0)} + \alpha^2 C_i^{(1)} + \alpha^4 C_i^{(2)} + \quad (8)$$

The dimensionless reaction-rate term  $\phi$  is expanded in a Taylor series around  $C_i^{(0)}$ . Subsequent substitution of Eq (8) in the Taylor series for  $\phi$  gives

$$\phi = \phi^{(0)} + \alpha^2 \sum_{j=1}^3 \phi^{(j)} C_i^{(j)} + \quad (9)$$

where

$$\phi^{(0)} = [\phi]_{C_i = C_i^{(0)}}$$

$$\phi^{(j)} = \left[ \frac{\partial \phi}{\partial C_i} \right]_{C_i = C_i^{(0)}}$$

The flux of the diffusing species  $A_1$  relative to its Fickian flux is given by

$$\frac{N_1}{N_0} = - \frac{1}{(\bar{C} - C)} \sum_{j=0}^p \alpha^{2j} \left[ \frac{dC_1^{(j)}}{dx} \right]_{x=0} + 0(\alpha^{2p+2}) \quad (10)$$

Substituting Eqs (8) and (9) into Eq (4), and equat-

ing terms in like powers of  $\alpha$ , we have

$$\frac{d^2 C_i^{(p)}}{dx^2} = g_i \delta^{(p)} \quad (11)$$

where

$$\delta^{(0)} = 0,$$

$$\delta^{(1)} = \phi^{(0)},$$

$$\delta^{(2)} = \sum_{j=1}^3 \phi^{(j)} C_i^{(j)}, \text{ etc}$$

Since the final solution to the problem must satisfy the boundary conditions and the stoichiometric relationship for any degree in  $\alpha$ , we may choose to assure consistency by requiring

$$\begin{aligned} @x = 0 & \quad C_1^{(0)} = \bar{C} \\ @x = 1 & \quad C_1^{(0)} = C \\ @x = 0, 1 & \quad \frac{dC_2^{(0)}}{dx} = 0 = \frac{dC_3^{(0)}}{dx} \end{aligned} \quad (12)$$

$$\int_0^1 (C_2^{(0)} + C_3^{(0)}) dx = C_0$$

and

$$\begin{aligned} @x = 0, 1 & \quad C_1^{(p)} = 0 \\ @x = 0, 1 & \quad \frac{dC_2^{(p)}}{dx} = 0 = \frac{dC_3^{(p)}}{dx} \end{aligned} \quad (13)$$

$$\int_0^1 (C_2^{(p)} + C_3^{(p)}) dx = 0$$

where  $C_0 = \hat{C}_2^T / C_*$ , and  $p = 1, 2$ . The non-linear set of diffusion-reaction equations, Eq (4), has been reduced to a series of ordinary linear differential equations, Eq (11), since for any degree of approximation  $p$ ,  $\delta^{(p)}$  is determined from the  $(p-1)$ th approximation. The zero-order solution to Eq (11), that is, for  $p = 0$ , is

$$\begin{aligned} C_1^{(0)} &= \bar{C} - (\bar{C} - C)x \\ C_i^{(0)} &= \gamma_i^{(0)}, \quad i = 2, 3 \end{aligned} \quad (14)$$

where  $\gamma_i^{(0)}$  are constants of integration. Note that the zero-order solution, Eq (14), predicts zero facilitation (or enhancement) in the flux of  $A_1$ . For  $p > 1$ , the solution to Eq (11) may be written in the following generalized form

$$C_i^{(p)} = g_i \lambda^{(p)} + \epsilon_i^{(p)} x + \gamma_i^{(p)} \quad (15)$$

$$\left[ \frac{dC_1^{(p)}}{dx} \right]_{x=0} = g_1 (f_0^{(p)} + \lambda_0^{(p)} - \lambda_1^{(p)}) \quad (16)$$

where

$$f^{(p)} = \int \delta^{(p)} dx,$$

$$\lambda^{(p)} = \int f^{(p)} dx,$$

and  $\epsilon^{(p)}$  and  $\gamma^{(p)}$  are constants of integration

Subscripts 0, 1 on  $f^{(p)}$  and  $\lambda^{(p)}$  denote evaluation at  $x=0, 1$ , respectively Equation (10) may therefore be written as

$$\frac{N_1}{N_0} = 1 + \frac{g_1}{(\bar{C} - \underline{C})} \times \sum_{j=1}^p \alpha^{2j} (\lambda_1^{(j)} - \lambda_0^{(j)} - f_0^{(j)}) + 0(\alpha^{2p+2}) \quad (17)$$

Writing the flux equation in this form, we can see that the estimate of permeability is obtained from the experimental determination of  $N_1$  when the condition  $\alpha \rightarrow 0$  is satisfied since

$$\lim_{\alpha \rightarrow 0} N_1 = N_0 \quad (18)$$

The major theoretical question is to find a criterion for the magnitude of  $\alpha$  that would permit the extrapolation of  $N_1$  to  $N_0$  at  $\alpha = 0$ . This is determined by evaluating the various terms in the expansion series, Eq (17)

In as much as the first term in Eq (17),  $j=1$ , dominates the series, a linear extrapolation may be made in a plot of  $[(N_1/N_0) - 1]$  vs  $\alpha^2$ . The second-order correction term in Eq (17),  $j=2$ , is meaningful only in that a criterion for the validity of the first-order correction term is made available

The reader may easily verify that for any generalized reaction rate which is first-order in the transferred species  $A_1$ , namely, kinetic function of the form (where  $S$  is any function of  $C_2, C_3$ )

$$\phi = \frac{C_1 C_2^m - C_3^n K}{S(C_2, C_3)} \quad (19)$$

one always obtains

$$f_0^{(j)} = \lambda_0^{(j)} = 0, \quad j = 1, 2, \quad (20)$$

and Eq (17) reduces to the following simpler form

$$(\gamma_3^{(0n)}) / (\gamma_2^{(0m)}) = \frac{(\bar{C} + \underline{C})K}{2} \quad (21)$$

$$\frac{N_1}{N_0} = 1 + \frac{g_1}{(\bar{C} - \underline{C})} \sum_{j=1}^p \alpha^{2j} \lambda_1^{(j)} + 0(\alpha^{2p+2}) \quad (22)$$

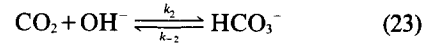
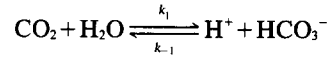
Note that  $\gamma_2^{(0)}$  and  $\gamma_3^{(0)}$ , as indicated by Eq (21), are equilibrium values for  $C_2$  and  $C_3$  determined at the

arithmetic average concentration of the transferred species  $A_1$  at the two interfaces ( $x=0$  and  $x=1$ ). A similar analysis for the specific case of oxygen facilitation across *thin* hemoglobin film is given by Smith *et al* [12]

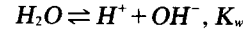
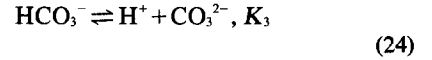
With a knowledge of the kinetics of the reaction and approximate value for the kinetic constants, one can evaluate the first few terms of the series indicated in Eq (22). This can then be utilized to determine the experimental range of parameters required to estimate  $N_0$  by extrapolation of Eq (22) to  $\alpha = 0$ . The procedure is illustrated in the following example

#### EXAMPLE $\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$ SYSTEM

The diffusion of carbon dioxide across a liquid film containing  $\text{HCO}_3^-/\text{CO}_3^{2-}$  is investigated herein. The rate controlling reactions for the process are



The following very fast reactions are assumed to be at equilibrium



The rate of depletion of carbon dioxide is given by [13]

$$r_1 = k_1 \hat{C}_1 - k_{-1} K_3 \frac{\hat{C}_3^2}{\hat{C}_2} + \frac{k_2 K_w}{K_3} \frac{\hat{C}_1 \hat{C}_2}{\hat{C}_3} - k_{-2} \hat{C}_3$$

which may be rearranged as follows

$$r_1 = k_1 \left( 1 + n \frac{2\hat{C}_2}{\hat{C}_3} \right) \left( \hat{C}_1 - \frac{1}{K} \frac{\hat{C}_3^2}{\hat{C}_2} \right) \quad (25)$$

where

$$n = \frac{k_2 K_w}{2k_1 K_3}$$

$$K = \frac{k_1}{k_{-1} K_3}$$

(Subscripts 1, 2, 3, on  $\hat{C}_i$  and  $D$ , refer to  $\text{CO}_2, \text{CO}_3^{2-}, \text{HCO}_3^-$  respectively.) Defining

$$x = y/L$$

$$C_1 = \hat{C}_1 / \hat{C}_1(0), \quad C_2 = \hat{C}_2 / \hat{C}_3^T, \quad C_3 = \hat{C}_3 / \hat{C}_3^T$$

$$\alpha^2 = k_1 L^2 / D_1$$

$$g_1 = 1, g_2 = \frac{D_1 \hat{C}_1(0)}{D_2 \hat{C}_3^T}, g_3 = \frac{-2D_1 \hat{C}_1(0)}{D_3 \hat{C}_3^T}$$

$$\phi = \left(1 + n \frac{2C_2}{C_3}\right) \left(\bar{C}_1 - m \frac{C_3^2}{2C_2}\right)$$

$$m = 2\hat{C}_3^T / K\hat{C}_1(0)$$

we have

$$\frac{d^2 C_1}{dx^2} = g_1 \alpha^2 \phi \quad (26)$$

For  $D_{HCO_3^-} \approx D_{CO_3^{2-}}$ , the solution of Eq (26) for  $\alpha \rightarrow 0$  is as follows (see Appendix 1)

$$\frac{N_1}{N_0} = 1 + \frac{1}{12} Y_0 \alpha^2 - \frac{Y_0}{720} \left[ Y_0 + g_2 Y_1 \left(6 - \frac{\alpha^2 \rho^2}{2}\right) \right] \alpha^4 \quad (27)$$

where

$$Y_0 = 1 + 2n \frac{\gamma_2^{(0)}}{\gamma_3^{(0)}}$$

$$Y_1 = m Y_0 \left[ 1 - \frac{1}{(1 - \gamma_3^{(0)})^2} \right]$$

$$Y_2 = n / \gamma_3^{(0)2}$$

$$\zeta = Y_2 / Y_1$$

$$a = -(1 - \rho)$$

and

$$N_0 = D_1 H_1 \bar{p} (1 - \rho) / L \quad (\bar{p} H_1 = \hat{C}_1(0), \rho = \underline{p} / \bar{p})$$

$\gamma_2^{(0)}$  and  $\gamma_3^{(0)}$  are related by the following two equations

$$2\gamma_2^{(0)} + \gamma_3^{(0)} = 1 \quad (28a)$$

$$\gamma_3^{(0)2} / \gamma_2^{(0)} = \frac{1 + \rho}{m} \quad (28b)$$

In an earlier paper by Otto and Quinn[13] on carbon dioxide facilitation through  $CO_3^{2-}$  films, an approximate solution to the diffusion-reaction equations was obtained on the assumption that the concentration of  $HCO_3^-$  and  $CO_3^{2-}$  was nearly constant throughout the film. The facilitation in the flux so obtained by them, as Eq (27) in their paper[13] is equivalent to the first term in Eq 27 namely

$$\frac{1}{12} Y_0 \alpha^2$$

(see Appendix 2)

For large values of  $(1 + \rho/m)$ , Eqs (28a) and (28b) may be approximated to

$$\gamma_3^{(0)} \approx 1 - \frac{2m}{1 + \rho}$$

$$\gamma_2^{(0)} \approx \frac{m}{1 + \rho}$$

Thus,

$$Y_0 \approx 1 + \frac{2mn}{1 + \rho}$$

$$Y_1 \approx -\frac{(1 + \rho)^2}{4m} Y_0$$

$$Y_2 \approx \frac{n}{\left[1 - \frac{4m}{1 + \rho}\right]}$$

The following literature values are used to evaluate  $m$  and  $n$  for a 1 N  $NaHCO_3$ - $Na_2CO_3$  solution ( $\hat{C}_3^T = 10^{-3}$  moles/cm<sup>3</sup>)

$$k_1 \quad 0.0375 \text{ sec}^{-1} [14]$$

$$\frac{k_2 K_w}{K_3} \quad 0.86 \text{ sec}^{-1} [5]$$

$$KH_1 \quad 0.1050 \text{ moles/cm}^3, \text{ atm} [15]$$

$$D_2 \quad 0.89 \times 10^{-5} \text{ cm}^2/\text{sec} [16]$$

Figure 2 shows a typical variation of facilitation factor,  $F$ , with respect to  $\alpha^2$  where

$$F = \frac{N_1}{N_0} - 1 \quad (29)$$

The numerical solution to Eq (26), based on a quasilinearization technique described in an earlier paper [11], is also included in Fig 2. The magnitude of the first and second order correction terms at various values of carbon dioxide partial pressure at  $x=0$  ( $\bar{p}$ ) are given in Table 1. Also included in Table 1 is the critical value  $\alpha_c$  defined as that  $\alpha^2$  for which the second order correction term contribution is equal to 10 per cent of the first order term contribution, that is

$$\alpha_c^2 = 0.1 \frac{M}{N}$$

Therefore, for  $\alpha < \alpha_c$ , the second order correction term may be neglected

Table 1

$F = M\alpha^2 - N\alpha^4$			
Correction terms (first and second) of Eq (27)			
$\rho = 0.01$			
$m = 0.019/\bar{p}$			
$n = 11.45$			
$-g_3 = 0.086\bar{p}$			
$\bar{p}$ , atm	$M$	$N$	$\alpha_c^2$
1	0.1156	0.0226	0.51
2/3	0.1350	0.0164	0.83
1/3	0.1820	0.0132	1.38
1/10	0.3637	0.0305	1.19

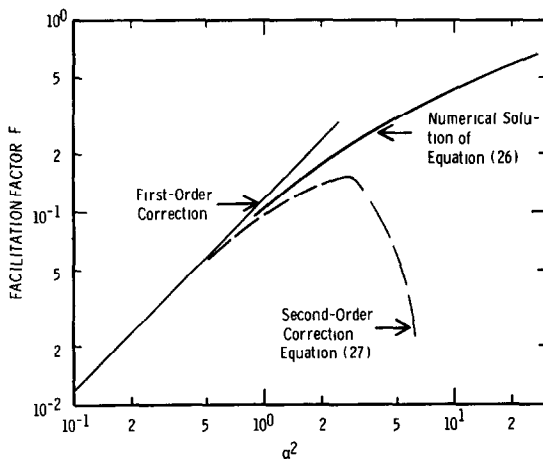


Fig 2 Facilitation factor as a function of  $\alpha^2$ , the ratio of diffusion to reaction resistance

As is evidenced from the numbers given in Table 1, the perturbation solution, Eq (27), remains convergent for  $\alpha$  in the vicinity of unity and for significant, though small, facilitation. The criterion for the convergence of the perturbation model is not that

$$M\alpha^2 \ll 1$$

but

$$N\alpha^4 \ll M\alpha^2$$

that is, the convergence of  $F$ , and not  $N_1/N_0$ , is desired. For the purpose of estimating  $D_1$  and  $H_1$ , Eq (27) may be rearranged as follows

$$\frac{N_1 L}{\bar{p} - p} = D_1 H_1 + \frac{1}{12} H_1 Y_0 (k_1 L^2) + \quad (30)$$

In Eq (30),  $N_1 L / (\bar{p} - p)$  may be recognized as the

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Table 2 Permeability of carbon dioxide in 1N  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$  solution

$D_1 H_1 \times 10^{10}$ moles/cm, atm, sec	Source
4.20	[3, 22]
4.35	[3, 4]
4.57	[3, 1]
$3.8 \pm 0.1$	This work

effective permeability of carbon dioxide through the  $\text{HCO}_3^-/\text{CO}_3^{2-}$  film

From the values given in Table 2, as long as  $\alpha^2$  is less than  $\alpha_c^2$ , the permeability data may be linearly extrapolated to find  $D_1 H_1$  by Eq (30)

#### EXPERIMENTAL METHODS AND RESULTS

The experimental setup used in this study is identical to the one described by Bassett and Schultz [17]. The liquid film, constructed by soaking a highly porous cellulose acetate membrane (porosity 85%)\* in the test solution, is held firmly between two chambers of a diffusion cell. On the "upstream" side, a mixture of carbon dioxide and nitrogen (latter to obtain the desired carbon dioxide partial pressure) is passed continually at 20–40  $\text{cm}^3$  per min. On the "downstream" side, helium is used to sweep away the carbon dioxide that may have diffused across the liquid film. The total pressure in the entire apparatus is one atmosphere, all gases are saturated with water vapor prior to entry into the diffusion cell. Gas streams are analyzed by chromatography, and the flow rates measured with a 10  $\text{cm}^3$  soap bubble flow meter. The steady state transport rate of carbon dioxide across the membrane is estimated from the measured flow rate and composition of the "downstream" side.

The results of diffusion experiments for films containing water and 1N sodium bicarbonate are shown in Figs 3 and 4. In all the experimental runs reported here, the "downstream" carbon dioxide partial pressure was small

$$p \sim 0.01 \bar{p}$$

For transport across the water film, the proportionality between the carbon dioxide flux and its partial pressure driving force is observed, the Fick's Law of diffusion gives

$$\frac{V_1}{(\bar{p} - p)} = \frac{D_1^0 H_1^0 (A_m P)}{(L_m \tau)} \frac{v}{60} \text{ cm}^3/\text{min, atm}$$

where

- $V_1$  is the flux of carbon dioxide,  $\text{cm}^3/\text{min}$
- $A_m$  is the membrane transfer area,  $= 15.5 \text{ cm}^2$
- $P$  is the membrane porosity,  $= 0.88$
- $v$  is the molar volume at  $25^\circ\text{C}$ ,  $= 24,450 \text{ cm}^3/\text{gmole}$
- $L_m$  is the measured membrane thickness,  $= 162(\pm 11) \times 10^{-4} \text{ cm}$
- $\tau$  is the tortuosity of the membrane (unknown)

A least-squares fit through the origin for the data in Fig 3 gives

$$D_1^0 H_1^0 / \tau = 5.51 \times 10^{-10} \text{ gmoles/cm, atm, sec}$$

The literature values for  $H_1^0$  is  $3.39 \times 10^{-5}$  moles/cm, atm [18] and that for  $D_1$ , ranges from  $1.85 - 2.00 \times 10^{-5} \text{ cm}^2/\text{sec}$  [18, 19, 20]. Using a water film entrapped between two plastic films instead of the membrane soaked film employed in this study, Otto and Quinn [13] obtained a carbon dioxide permeability value of  $6.62 \times 10^{-10}$  gmoles/cm, atm, sec. One therefore is inclined to believe that the said difference lies in the fact that the tortuosity of the porous membrane used in this study is considerably higher than unity. Wittenberg [21] in his experiments on transfer of nitrogen and oxygen across hemoglobin solutions reports that the observed permeability (calculated as  $D_1^0 H_1^0 P / \tau$ ) of nitrogen across a water-soaked Millipore membrane was  $8.4 \times 10^{-12}$  gmoles/cm, atm, sec [18, 20]. Assuming that the porosity of the Gelman membrane and the Millipore membrane are the same order of magnitude, one estimates the tortuosity of the Millipore mem-

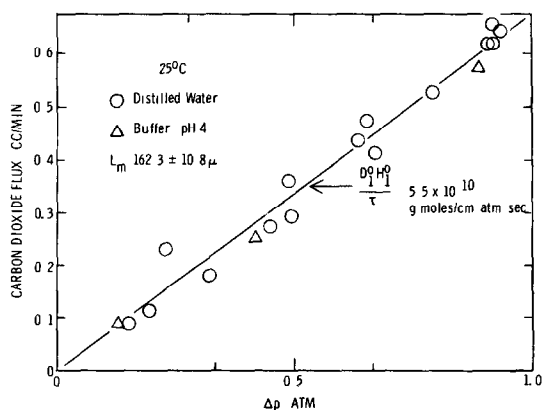


Fig 3 Flux of carbon dioxide across a water film

brane to be 1.37. In a similar experimental set up, Bassett and Schultz using a tortuosity of 1 obtained a diffusivity value, at  $25^\circ\text{C}$ , for oxygen and nitrogen of  $2.01 \times 10^{-5} \text{ cm}^2/\text{sec}$  [17]. The corresponding literature values range between  $1.87 - 3.25 \times 10^{-5}$  and  $1.8 - 2.25 \times 10^{-5} \text{ cm}^2/\text{sec}$ , respectively [20].

Based on a permeability value of  $6.6 \pm 0.2 \times 10^{-10}$  gmoles/cc, atm, sec, the tortuosity and, hence, the diffusion path length,  $L$ , of the Gelman membrane was calculated

$$L = L_m \tau = 200(\pm 20) \mu \text{ per membrane}$$

That the carbon dioxide flux across the water film was not facilitated by the bicarbonate reactions can be demonstrated by measuring the carbon dioxide flux across an acidic film, the results of such a measurement across a buffer solution, pH 4, are also included in Fig 3.

In Fig 4, the two separate lines for  $L = 0.06 \text{ cm}$  represent data obtained on two different occasions. Although the data for other values of thickness were also obtained on various occasions, the closeness of the data followed a single least-squares line fit for a given  $L$ . At  $L = 0.06 \text{ cm}$ , the difference in the two sets of data warranted that each be described by a least-square line separately. The discrepancy in this data remains unexplained. From the data reported in Fig 4, the carbon dioxide fluxes at a partial pressure differential across the

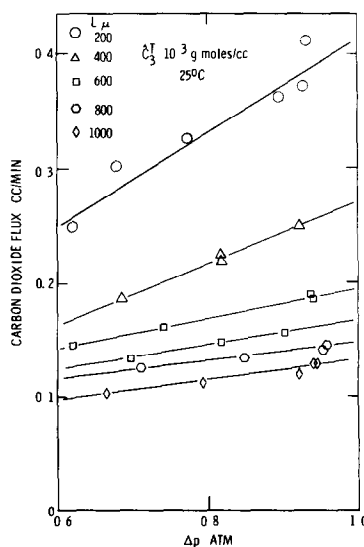


Fig 4 Flux of carbon dioxide across a  $\text{NaHCO}_3 - \text{Na}_2\text{CO}_3$  film for various diffusion lengths

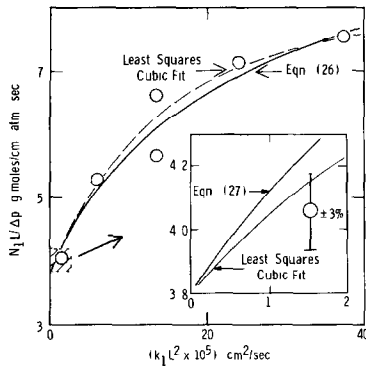


Fig 5 Effective permeability of  $\text{CO}_2$  through bicarbonate solution as a function of  $k_1 L^2$

film of  $\frac{2}{3}$  atm were obtained by interpolation. These results are plotted in Fig 5 in accordance with the co-ordinates of Eq (30) using a diffusion thickness per Gelman membrane of  $200\mu$ . A numerical solution to Eq (26) as well as a least-squares cubic fit are included in Fig 5 for comparison. Based on the correction terms given in Table 1, we note that for Eq (30) to be valid,  $\alpha^2 \leq 0.83$ . The extrapolated intercept at  $k_1 L^2 \rightarrow 0$  is

$$D_1 H_1 = 3.8 \pm 0.1 \times 10^{-10} \text{ moles/cm, atm, sec}$$

The difference between this value of permeability for  $\text{CO}_2$  in  $1\text{N NaHCO}_3\text{-Na}_2\text{CO}_3$  solution and that for  $\text{CO}_2$  in water ( $6.68 \times 10^{-10}$ ) is a result of the effect of chemical composition on permeability.

#### DISCUSSION

Estimates for the permeability of carbon dioxide in  $1\text{N NaHCO}_3\text{-Na}_2\text{CO}_3$  solution, based on literature correlations for gas diffusivity and solubility in electrolytes, are given in Table 2. The procedure used was to correct the values of  $D_1^\circ$  and  $H_1^\circ$  given earlier for the effects of viscosity on the diffusivity and the ionic strength on solubility of carbon dioxide.

A problem which immediately arises in implementing this procedure is that the composition of the solution is not known exactly, since the relative ratio of  $\text{NaHCO}_3$  to  $\text{Na}_2\text{CO}_3$  will depend on the carbon dioxide partial pressure. Therefore, in order to use these literature correlations, one must turn to the theoretical analysis presented in this paper. Based on Eqs (28a) and (28b), we estimate that about 94 per cent of the carrier is in the form of bicarbonate ion (that is,  $\gamma_3^{(0)} = 0.94$ ).

For estimating carbon dioxide diffusivity, literature correlations based on viscosity of the solution were used

$$\frac{D_1}{D_1^\circ} = \eta^{-m}$$

where  $\eta$  is the viscosity of the solution, relative to the solvent, and the empirical factor  $m$ , and carbon dioxide diffusivities calculated therefrom, are as follows

Source	$m$	$D_1 \times 10^5, \text{cm}^2/\text{sec}$
Wilke-Chang[22]	1	1.56
Nysing-Kramers[4]	0.85	1.62
Ratcliff-Holdcroft[1]	0.637	1.70

For the solution under study ( $\gamma_3^{(0)} = 0.94$ ), a relative viscosity of 1.26 was estimated from the viscosity data in International Critical Tables[23].

For estimating carbon dioxide solubility, the correlation of van Krevelen and Hoftizer[3] for predicting solubility of gases in non-reacting electrolytic solutions was used, the decrease in the solubility due to added salt is given by

$$\log \frac{H_1}{H_1^\circ} = -hI$$

where  $I$  is the ionic strength of the electrolyte, and  $h$  is defined as the sum of contributions of various species

$$h = h_+ + h_- + h_g$$

For a  $1\text{N NaHCO}_3\text{-Na}_2\text{CO}_3$  ( $\gamma_3^{(0)} = 0.94$ ), the values for  $h$  and  $I$  are 0.098[3] and 1.03, respectively.

The discrepancy between the various values of carbon dioxide permeability given in Table 2 remains unexplained. The work of Danckwerts and Kennedy[6] on absorption of carbon dioxide in neutral solutions ( $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$ ) indicates that the diffusivity of carbon dioxide in these solutions is less than or equal to that predicted by the Wilke-Chang correlation[22]. On the other hand, the work of Roberts and Danckwerts[5] on carbon dioxide absorption conforms to the Ratcliff-Holdcroft correlation[1]. Otto and Quinn[13] report a value of 0.9 for the ratio of observed carbon dioxide flux to the calculated Fick's Law flux (based on the diffusivity correlation of Wilke-Chang (that is,  $m = 1$ ) and solubility correlations of van Krevelen and Hoftizer). This conforms to our findings and further suggests that the use of a porous, tortuous membrane is not the only cause of our



lower observed permeability value Otto and Quinn[13] indicate that the discrepancy is possibly a result of inaccuracies in the viscosity data given in the literature

Theoretically, the solubility of carbon dioxide can be estimated from the slope, near the origin, of the curve in Fig 5 In the event that the first order correction term in the series is dominant, Eq (27) reduces to Eq (30), and Henry's Law constant is given by

$$H_1 = \text{Slope} \times \frac{12}{Y_0}$$

However, estimating the true limiting slope may be subject to errors in cases where the second-order correction term is a significant fraction of the first-order correction term One therefore must determine the permeability from plots such as Fig 4, and thereafter use Eq (27) in the form of Fig 2 to estimate  $D_1$  and  $H_1$  individually Unfortunately, plots such as Fig 2 demand a very high degree of accuracy in flux measurements for small values of facilitation factor  $F$ , for example, a 5 per cent error in carbon dioxide flux at a diffusion length of 200  $\mu$  results in an error in  $F$  value of 50–100 per cent

In the final analysis, one concludes that a fairly accurate determination of permeability may be obtained by the procedure outlined herein It is noted that the criterion for such determinations is not that the reaction be virtually absent (that is,  $\alpha \ll 1$ ), but that a small, although finite, reaction rate is permissible (that is,  $\alpha < \alpha_c$ ) When  $\alpha_c \gg 1$ , we note that fairly accurate estimates of diffusivity and solubility could have been obtained for the case under study However, for the experimental situation described here ( $\alpha_c \sim 0.8$ ) the estimates of individual values that make up the permeability term, namely, diffusivity and solubility, are subject to large errors and are therefore not included

An alternate method for permeability determination via the "carrier" facilitated mechanism described here seems proper as a closing remark In cases where the critical value of diffusion-reaction parameter  $\alpha_c$  results in too small a film thickness, one may eliminate the facilitation effect, that is, the gradient in "carrier" concentrations, by operating at sufficiently high upstream and downstream gas pressures For example, in the transfer of oxygen across a 150  $\mu$  film containing hemoglobin, a minimum oxygen partial pressure of 40 mmHg, that is  $\bar{p}_0, p_1 \geq 40$  mmHg, is sufficient to transform hemoglobin completely into the oxy-hemoglobin form Thus, the flux of oxygen across such a

hemoglobin film for  $\bar{p}_0 > p_1 \geq 40$  mmHg would represent the 'Fickian' flux and thereby permit reasonable estimation of oxygen permeability through such reacting solutions This concept has been utilized by Keller and Friedlander[24] as well as Kutcha and Staub[25]

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#### NOTATION

$A_i$	species $i$
$\hat{C}_i$	concentration of $A_i$ , moles/cm <sup>3</sup>
$C_i$	dimensionless concentration of $A_i$
$\hat{C}_i(0), \hat{C}_i(1)$	concentration of transferred species at $y = 0, L$ , respectively, moles/cm <sup>3</sup>
$C_3^T$	total "carrier" concentration, moles/cm <sup>3</sup>
$D_i$	binary diffusivity of $A_i$ , cm <sup>2</sup> /sec
$F$	facilitation factor defined in Eq (29)
$f$	integral defined in Eq (16)
$g_i$	ratio of stoichiometric to diffusion terms
$H_1$	solubility of carbon dioxide, moles/cm <sup>3</sup> , atm
$K$	overall equilibrium constant for $\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$ reactions
$K_s, K_w$	equilibrium constants for reaction Eq (24)
$k_i, k_{-i}$	rate constants for reaction Eq (23)
$k_L$	liquid mass transfer coefficient, cm/sec
$L$	diffusion path length, cm
$m$	equilibrium constant defined in Eq (26)
$N_0$	"Fickian" flux, moles/cm <sup>2</sup> , sec
$N_1$	reaction facilitated flux, moles/cm <sup>2</sup> , sec
$n$	hydroxyl ion effect defined in Eq (25)
$\bar{p}, p$	partial pressure of $A_i$ at $y = 0, L$ , respectively, atm
$r_i$	rate of depletion of $A_i$ , moles/cm <sup>3</sup> , sec
$t_D, t_R$	half times for diffusion and reaction, respectively, sec
$x$	dimensionless distance
$y$	distance variable within the film, cm

#### Greek symbols

$\alpha$	ratio of reaction of diffusion term
$\gamma_i$	constant of integration defined in Eq (14)

- $\delta$  perturbation coefficient of reaction rate defined in Eq (11)  
 $\epsilon_i$  constant of integration defined in Eq (15)  
 $\lambda$  integral defined in Eq (20)  
 $\nu_i$  stoichiometric ratio for A,  
 $\phi$  dimensionless kinetic function

### Superscripts

- (k) kth order perturbation parameter  
 0 for estimation in water

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### APPENDIX 1

Solution to Eq (26) for  $\alpha \rightarrow 0$

$$\frac{d^2 C_i}{dx^2} = g_i \alpha^2 \phi \quad (26)$$

Zero-order term

$$\begin{aligned} \delta^{(0)} &= 0 \\ C_1^{(0)} &= 1 - (1 - \rho)x \\ C_2^{(0)} &= \gamma_2^{(0)} \\ C_3^{(0)} &= \gamma_3^{(0)} \\ \gamma_3^{(0)} + 2\gamma_2^{(0)} &= 1 \end{aligned} \quad (1 1)$$

A second relationship between  $\gamma_2^{(0)}$  and  $\gamma_3^{(0)}$  is obtained by solving for the First-order term

$$\delta^{(1)} = Y_0 \left[ 1 - (1 - \rho)x - m \frac{\gamma_3^{(0)2}}{2\gamma_2^{(0)}} \right] \quad (1 2)$$

$$\begin{aligned} f^{(1)} &= \int \delta^{(1)} d\bar{x} \\ &= Y_0 \left[ x - (1 - \rho) \frac{x^2}{2} - m \frac{\gamma_3^{(0)2}}{2\gamma_2^{(0)}} x \right] \end{aligned} \quad (1 3)$$

At  $x = 0$ ,  $f^{(1)} = f_0^{(1)} = 0$

At  $x = 1$ ,  $f^{(1)} = f_1^{(1)}$

$$= \left[ \frac{1 + \rho}{2} - m \frac{\gamma_3^{(0)2}}{2\gamma_2^{(0)}} \right]$$

$f_0^{(1)} = f_1^{(1)}$  gives

$$\frac{\gamma_3^{(0)2}}{\gamma_2^{(0)}} = \frac{1 + \rho}{m} \quad (1 4)$$

Substituting Eq (1 4) into Eq (1 3), we have

$$f^{(1)} = -a Y_0 / 2 (x - x^2) \quad (1 5)$$

Therefore

$$\begin{aligned} \lambda^{(1)} &= \int f^{(1)} dx \\ &= -a Y_0 / 12 (3x^2 - 2x^3) \end{aligned}$$

At  $x = 0$ ,

$$\begin{aligned} \lambda^{(1)} &= \lambda_1^{(1)} \\ &= -a Y_0 / 12 \end{aligned} \quad (1 6)$$

The first-order concentration profiles for  $D_2 = D_3$ , are

$$C_i^{(1)} = g_i \lambda^{(1)} + \epsilon_i^{(1)} x + \gamma_i^{(1)}$$

where

$$\begin{aligned} \lambda^{(1)} &= -a Y_0 / 12 (3x^2 - 2x^3) \\ \epsilon_1^{(1)} &= -g_1 \lambda_1^{(1)}, \gamma_1^{(1)} = 0 \\ \epsilon_2^{(1)} &= \epsilon_3^{(1)} = 0 \\ \gamma_3^{(1)} + 2\gamma_2^{(1)} &= 0 \end{aligned} \quad (1 7)$$

A second relationship between  $\gamma_2^{(1)}$  and  $\gamma_3^{(1)}$  is obtained by solving for the

Second-order term

$$\delta^{(2)} = Y_0 C_1^{(1)} + [Y_1 - a Y_2 (x - \frac{1}{2})] C_2^{(1)} \quad (18)$$

$$\begin{aligned} f^{(2)} &= \int \delta^{(2)} dx \\ &= a Y_0^2 / 24 (x^2 - 2x^3 + x^4) \\ &\quad + a g_2 Y_0 Y_1 / 24 (x^4 - 2x^3) \\ &\quad - a^2 g_2 Y_0 Y_2 / 120 (5x^3 - 10x^4 + 4x^5) \\ &\quad + \gamma_2^{(1)} [Y_1 x - a Y_2 / 2 (x^2 - x)] \end{aligned} \quad (19)$$

At  $x=0$ ,  $f^{(2)} = f_0^{(2)} = 0$

At  $x=1$ ,  $f^{(2)} = f_1^{(2)}$

$$= -a g_2 Y_0 Y_1 / 24 + a^2 g_2 Y_0 Y_2 / 120 + \gamma_3^{(1)} Y_1$$

Further,  $f_0^{(2)} = f_1^{(2)}$  gives

$$\gamma_3^{(1)} = a g_2 / 24 \left( 1 - \frac{a g_2}{5} \right) \quad (110)$$

Integrating Eq (19), we have

$$\begin{aligned} \lambda^{(2)} &= \int f^{(2)} dx \\ &= a Y_0^2 / 720 (10x^3 - 15x^4 + 6x^5) \\ &\quad + a g_2 Y_0 Y_1 / 240 (2x^5 - 5x^4) \\ &\quad - a^2 g_2 Y_0 Y_2 / 1440 (8x^6 - 24x^5 + 15x^4) \\ &\quad + \gamma_3^{(1)} / 2 [Y_1 x^2 - a Y_2 / 6 (2x^3 - 3x^2)] \end{aligned} \quad (111)$$

Substituting Eq (110) for  $\gamma_3^{(1)}$  into Eq (111) and determining at  $x=1$ , we have

$$\lambda_1^{(2)} = a Y_0 / 720 \left[ Y_0 + g_2 Y_1 \left( 6 - \frac{a g_2^2}{2} \right) \right] \quad (112)$$

The second-order concentration profiles need be determined only if the third-order correction term is desired Up to second-order correction term,

$$\frac{N_1}{N_0} = 1 + \frac{\lambda_1^{(1)} \alpha^2 + \lambda_1^{(2)} \alpha^4}{(1-\rho)} + 0(\alpha^6) \quad (113)$$

where

$$\lambda_1^{(1)} = (1-\rho) Y_0 / 12$$

$$\lambda_1^{(2)} = -(1-\rho) Y_0 / 720 \left[ Y_0 + g_2 Y_1 \left( 6 - \frac{a^2 g_2^2}{2} \right) \right]$$

## APPENDIX 2

Constant carrier concentration an approximation

Recalling the diffusion-reaction equation, namely,

$$\frac{d^2 C_i}{dx^2} = g_i \alpha^2 \phi \quad (26)$$

it is assumed that under limiting conditions, the concentration of the carrier species, that is,  $C_2$  and  $C_3$ , may be

treated as constants

$$C_2 = \gamma_2^{(0)}$$

$$C_3 = \gamma_3^{(0)}$$

$$(21)$$

Thus,

$$\frac{d^2 C_1}{dx^2} = \alpha^2 Y_0 \left( C_1 - m \frac{\gamma_3^{(0)2}}{2 \gamma_2^{(0)}} \right) \quad (22)$$

The solution to the ordinary differential equation, Eq (22), is

$$\begin{aligned} C_1 &= M_1 \cosh(\alpha \sqrt{Y_0} x) \\ &\quad + M_2 \sinh(\alpha \sqrt{Y_0} x) \\ &\quad + m \frac{\gamma_3^{(0)2}}{2 \gamma_2^{(0)}} \end{aligned} \quad (23)$$

The four unknowns,  $\gamma_3^{(0)}$ ,  $M_1$ ,  $M_2$ ,  $\gamma_2^{(0)}$  and  $\gamma_3^{(0)}$ , are determined from the following conditions

$$\left. \begin{aligned} C_1 &= 1 @ x = 0 \\ C_1 &= \rho @ x = 1 \\ \left[ \frac{dC_1}{dx} \right]_{x=0} &= \left[ \frac{dC_1}{dx} \right]_{x=1} \\ \int_0^1 (C_3 + 2C_2) dx &= 1 \end{aligned} \right\} \quad (24)$$

Thus,

$$\left. \begin{aligned} \frac{\gamma_3^{(0)2}}{\gamma_2^{(0)}} &= \frac{1+\rho}{m} \\ M_1 &= -M_2 \tanh\left(\frac{1}{2} \alpha \sqrt{Y_0}\right) \\ M_2 &= -(1-\rho) / 2 \coth\left(\frac{1}{2} \alpha \sqrt{Y_0}\right) \\ \gamma_3^{(0)} + 2\gamma_2^{(0)} &= 1 \end{aligned} \right\} \quad (25)$$

The flux of carbon dioxide relative to its Fickian flux is

$$\begin{aligned} \frac{N_1}{N_0} &= -\frac{1}{(1-\rho)} \left[ \frac{dC_1}{dx} \right]_{x=0} \\ &= \frac{-\alpha \sqrt{Y_0}}{(1-\rho)} M_2 \end{aligned} \quad (26)$$

Substituting for  $M_2$ , we have

$$\frac{N_1}{N_0} = \frac{\alpha \sqrt{Y_0}}{2} \coth\left(\frac{\alpha \sqrt{Y_0}}{2}\right) \quad (27)$$

In the limit, that is,  $q \ll 1$

$$q \coth q \approx 1 + q^2/3$$

Hence,

$$\frac{N_1}{N_0} = 1 + \frac{1}{12} \alpha^2 Y_0 \quad (28)$$