The Absorption of Carbon Dioxide in Aqueous Monoethanolamine in a Laminar Jet

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The mechanism of the absorption of carbon dioxide by an aqueous solution of monoethanolamine has been studied. Experimental results for the absorption of carbon dioxide into a laminar jet of amine solution have been used to examine the transfer process. Previously this process has been considered as pseudo unimolecular, but this has been disproved. When considered as a second-order, fast, irreversible reaction by the film, penetration, and corrected penetration theories, the results are most satisfactory. It is possible by the corrected penetration theory to correlate the results such as to predict k_L/k_{L_0} to within 3% of the experimentally determined value.

This system, of particular interest in industry today, has been examined by Emmert and Pigford (*1*), Astarita (*2*), and Clarke (*3*). Emmert and Pigford used a short wetted-wall column, and Astarita and Clarke used laminar jets.

The carbon dioxide may react as given below:

$$CO_2 + RNH_2 \rightleftharpoons R{\cdot}NH{\cdot}COOH \rightleftharpoons RNHCOO^- + H^+ \quad (1)$$

$$R{\cdot}NH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^- \quad (2a)$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \quad (2b)$$

$$HCO_3^- + OH^- \rightleftharpoons CO_3^= + H_2O \quad (2c)$$

$$RNH_2 + OH^- \rightleftharpoons {}^-OCH_2CH_2NH_2 + H_2O \quad (3a)$$

$$CO_2 + {}^-OCH_2CH_2NH_2 \rightleftharpoons {}^-OOCOCH_2CH_2NH_2 \quad (3b)$$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \quad (4)$$

The rates of these reactions are given in Table 1.

The overall reaction may be considered as

$$A + \nu B \rightarrow C \quad (5)$$

TABLE 1. REACTION RATE CONSTANTS

Reaction	Rate constant (25°C.)	Reference	d (carbon dioxide)/dt, moles/(sec.)(liter)
1	5,400 liters/(mole)(sec.)	*1*	175.2
2a	instantaneous		
2b	8,300 liters/(mole)(sec.)	*6*	1.54
2c	instantaneous		
3a	instantaneous		
3b	3,000 liters²/(mole²)(sec.)	*1, 7*	0.54
4	0.025 liter/(mole)(sec.)	*6*	
5	5,470 liters/(mole)(sec.)		177.28

TABLE 2. INITIAL SOLUTION CONCENTRATIONS
Concentrations of OH^- ions and free amine in monoethanolamine solutions (25°C.)

Total amine B_0 moles/liter	Free amine (RNH_2) moles/liter	Hydroxyl ion moles/liter
0.988	0.982	0.0056
2.036	2.028	0.008
2.878	2.868	0.0095
3.938	3.927	0.0112
4.738	4.726	0.0123

$$K_b = 3.18 \times 10^{-5} = \frac{[OH^-]^2}{[B_0 - OH^-]} \qquad \text{reference } 6$$

The value of ν, the stoichiometric factor, can be determined from a consideration of Equations (1) to (4) and the rate constants under initial conditions.

The values for the hydroxyl ion concentrations in the solutions given by Emmert and Pigford (*1*) are in error, due to a misreading of the dissociation constant of Pinching and Bates (*4*). Danckwerts (*5*) drew attention to this. Values are given also by Pinsent, Pearson, and Roughton (*6*) and by Jorgensen (*7*).

The concentrations of hydroxyl ion and free amine in the solutions of interest in the present work are given in Table 2, the activities being taken as unity.

The rates of removal of carbon dioxide by reactions (1), (2), and (3) are given in Table 1 for the initial conditions. It is assumed that reaction (4) is slow enough to be neglected. The stoichiometric factor is 1.01 and the overall reaction constant based on reaction (5) is 5,470 liters/(mole) (sec.) (25°C.). The contribution of reactions (2) and (3) to the removal of carbon dioxide is only about 1% of the removal due to reaction (1). Under these conditions the overall reaction rate constant should be little affected by the solution strength.

Clearly, the carbamate forming reaction (1) controls the absorption rate and reaction (2) affects the final equilibrium. Chemical equilibrium is not achieved in the contact times used in the laminar jet.

ABSORPTION THEORY

When there is no chemical reaction, we have from the penetration theory

$$k_{L_0} = 2\sqrt{\frac{D_A}{\pi t}} \tag{6}$$

The effect of reaction on the absorption rate is indicated by ϕ, the ratio of the mass transfer coefficients with and without reaction.

For a laminar jet where the solute concentration in the bulk liquid is substantially zero

$$\phi = \frac{k_L}{k_{L_0}} = \frac{N_A}{C^* k_{L_0}} \tag{7}$$

A film theory solution for absorption accompanied by a second-order reaction such as Equation (5) has been proposed by Van Krevelen and Hoftijzer (*8*) and is given by

$$\phi = \frac{\sqrt{M}\sqrt{1-(\phi-1)/rq}}{\tanh\left[\sqrt{M}\sqrt{1-(\phi-1)/rq}\right]} \tag{8}$$

This approximate solution to the film theory ϕ has been shown by Peaceman (9) to differ from the true film theory solution by no more than 8%. The significance of Equation (8) has been discussed by Van Krevelen and Hoftijzer (*8*), Gilliland, Baddour, and Brian (*10*), and Brian, Hurley, and Hasseltine (*11*).

It will be seen from Equation (8) that ϕ approaches unity at low values of $\sqrt{M}$, so that a slow reaction will have little effect on the absorption coefficient. At large values of $\sqrt{M}$, ϕ approaches an asymptote for each value of rq. In the asymptotic region an increase in k, the reaction rate constant, produces no increase in ϕ. This region corresponds to a condition of very fast or infinitely fast reaction.

The asymptotic value of ϕ is given by

$$\phi_a = 1 + rq \tag{9}$$

A graphical representation of Equation (8) is given in Figure 1. As the asymptote is approached, the concentration of B becomes virtually constant throughout the liquid phase at a value of B_0. The reaction between A and B is then pseudo first-order, B being in considerable excess during reaction. For $\phi > 2$ the pseudo first-order curve is approximated by

$$\phi = \sqrt{M} \tag{10}$$

and under these conditions

$$k_L = \sqrt{k\,B_0\,D_A} \tag{11}$$

The same equation can be obtained from Danckwerts (*12*). When $kt > 2.5$

$$\frac{Q}{\pi dh} = C^* \sqrt{\frac{D_A}{kB_0}}\left[k\,B_0 t + \frac{1}{2}\right] \tag{12}$$

which reduces to Equation (11) if the second term is neglected.

A penetration theory solution for absorption, accompanied by a second-order reaction, is not available for the case when $r \neq 1$ and $k \neq \infty$. An approximate solution can be obtained from Equation (8) by replacing rq by $(\phi_a - 1)$. The equation then becomes

$$\phi = \frac{\sqrt{M}\sqrt{1-(\phi-1)/(\phi_a-1)}}{\tanh\left[\sqrt{M}\sqrt{1-(\phi-1)/(\phi_a-1)}\right]} \tag{13}$$

where

$$\phi_a = \frac{1}{\text{erf}(\sigma)} \tag{14}$$

$$q\sqrt{r} = \frac{1-\text{erf}(\sigma/\sqrt{r})}{\text{erf}(\sigma)\, e^{\sigma^2(1-1/r)}} \tag{15}$$

A graphical representation of Equation (13) is given in Figure 2 in which ϕ_a is approximated by

$$\phi_a = 1 + q\sqrt{r} \quad r \neq 1 \tag{16}$$

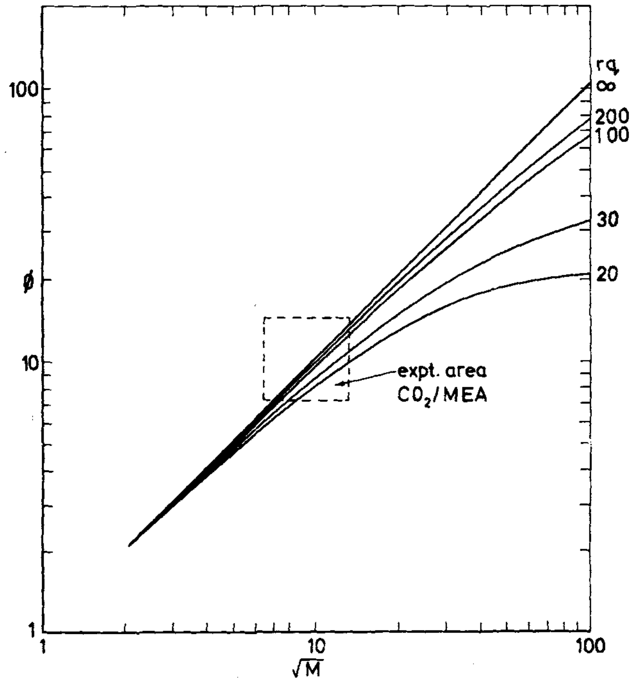

Fig. 1. Film theory; second-order reaction.

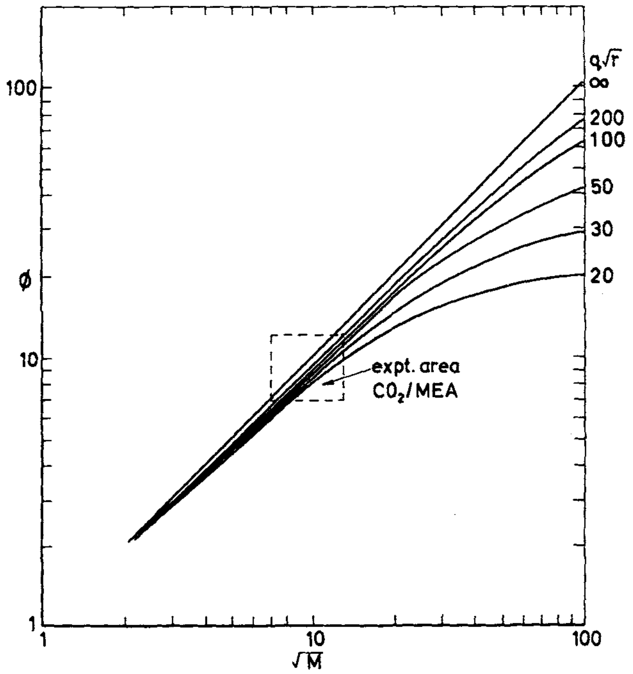

Fig. 2. Penetration theory; second-order reaction.

The ϕ_a approximation is more accurate at higher ϕ_a values and when r approaches 1.0.

Other solutions to the second-order reaction equations have been given by Emmert and Pigford (*1*) and by Nijsing, Hendrikse, and Kramers (*13*).

According to Emmert and Pigford (*1*)

$$\phi = \frac{1}{\sqrt{r}} [1 + rq] \tag{17}$$

According to Nijsing, Hendrikse, and Kramers for a fast second-order reaction

$$\phi = \frac{1}{\sqrt{r}} [1 + q] \tag{18}$$

NUMERICAL SOLUTIONS

Perry and Pigford (*14*) used a digital computer to solve the differential equations for a second-order reaction by a numerical method. Their analysis was restricted to $\sqrt{M} < 2.4$ and $r = 1$. However, Brian (*15*) has shown that in this range, ϕ, as given by Equation (8), shows a maximum deviation from the results of Perry and Pigford by only 9%. The comparison led Brian and Gilliland to suggest that Equation (13) could give an approximate penetration theory solution.

Brian, Hurley, and Hasseltine (*11*) obtained a solution to the differential equations for the second-order reaction over a much wider range of M values and when $r \neq 1$. They used a linearized, time-centered, implicit, finite-difference method for integrating the nonlinear partial differential equations.

They concluded that Equation (13) is a fair approximation to the penetration theory solution, and proposed a method for correcting the approximate value of ϕ obtained from Equation (13). They presented sets of curves similar to those shown in Figure 3, each set corresponding to a single value of ϕ_a. From a knowledge of ϕ_a and of the first approximation to ϕ, namely, ϕ obtained from Equation (13), a second approximation to ϕ can be obtained by interpolation from graphs such as Figure 3, this second approximation being within 3% of the true penetration theory solution.

This paper examines the experimental results for the absorption of carbon dioxide into aqueous monoethanolamine in a laminar jet in the light of the above theory, especially that of Brian, Hurley, and Hasseltine.

APPARATUS

The laminar jet apparatus used was of the conventional type. Great care was exercised in producing the jet orifice. Holes in a series of plates were produced by a drilling and lapping technique at the National Physical Laboratory, Teddington, England. These holes were examined microscopically and the best of ten plates were chosen. The orifice plate consisted of a disk of hard rolled 10% rhodium-platinum alloy 0.0102 cm. thick with 0.082-cm. hole size. The stainless steel orifice holder was screwed to a 1-cm. diameter × 60-cm. long stainless steel approach tube. Complete details of the system and jet are given by Adams (*16*) and by Thomas and Adams (*17*).

The equipment was housed in a thermostated room which could be maintained at temperatures between 18° to 25°C. with a variation of ± 0.5°C. Liquid temperatures entering and leaving the absorption chamber could be kept to within 0.1°C. for temperatures up to 45°C. All temperatures could be measured to 0.05°C.

The redistilled monoethanolamine boiled over a range of 0.8°C. and was shown to be 99.9% pure by acidimetric titration by using bromocresol green indicator. The water used was deaerated and passed through Permutit deminrolet deionizing unit which reduced dissolved carbon dioxide to 1 p.p.m. Jet length was measured with a cathetometer with an accuracy of 0.005 cm. Both entry and exit end effects were shown to be negligible.

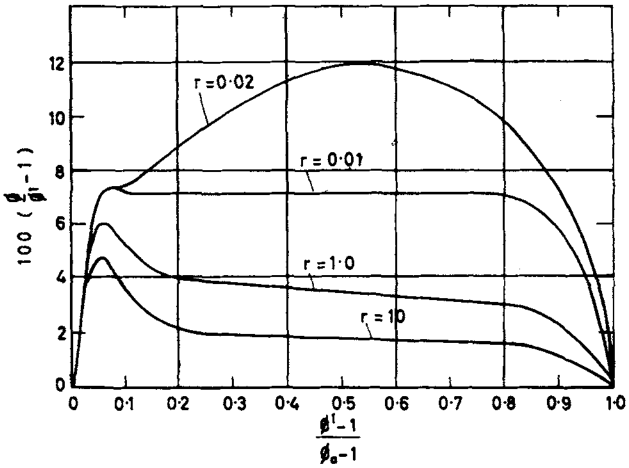

Fig. 3. Correction to Equation (13) ($\phi_a = 20$) (*11*).

EXPERIMENTAL RESULTS

Experimental results are given in Figure 4. A constant liquid rate of 2.5 cc./sec. was maintained throughout the experiments. The total gas pressure in the absorption chamber was 751 mm. Hg.

The calculated values of ϕ based on the experimental results and the value of C^* for carbon dioxide in water under the existing conditions by using Equation (7) are shown in Figures 5 and 6.

DIFFUSION COEFFICIENTS

The author is at present engaged in an extensive program of research into the measurement of diffusion coefficients in liquid systems by optical techniques. Diffusion coefficients for the water-amine systems are given by Thomas and Furzer (*18*) and some of the values for D_B are taken from this source. Work has been completed on a birefringent interferometer and some values for the water-monoethanolamine system are given by Thomas and McNicholl (*19*). Complete results will be published in the near future. Viscosity measurements were made on the solutions used, and D_A was obtained from the carbon dioxide–water coefficient with the data of Thomas and Adams (*17*).

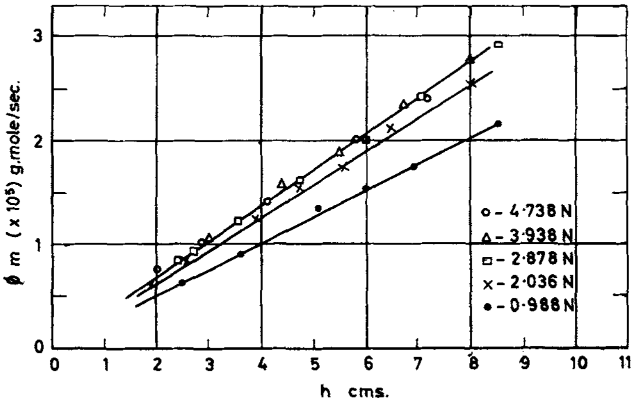

Fig. 4. Rate of absorption of carbon dioxide in MEA as a function of jet length and solution strength.

EQUILIBRIUM SOLUBILITY C*

The change in the value of C^*, the equilibrium solubility of carbon dioxide in water, with addition of monoethanolamine cannot be predicted theoretically. Clarke (*3*) has discussed this point and suggests that it is unlikely that C^* will be affected up to a strength of 5 N monoethanolamine solution. In the present work C^* is taken for carbon dioxide in water under the existing conditions. The considerable change in the C^* value in the presence of amine suggested by Emmert and Pigford (*1*) is unsupported and it is more likely to be due to errors in their equations.

INTERPRETATION ON THE BASIS OF A PSEUDO FIRST-ORDER REACTION

For a fast reaction there is the possibility of depletion of the reactant at the interface. This would invalidate the use of first-order equation. Clarke (3) drew attention to this fact when he criticized the work of Astarita (2) on a laminar jet in which the contact time between the gas and liquid was such as to allow appreciable surface amine depletion. The example given by Clarke does not highlight the problem.

According to Danckwerts (*20*) and Van der Vusse (*21*)

$$x_d = \frac{2C^*}{B_0}\left[2\sqrt{\frac{kt}{\pi}} - 1\right] \tag{19}$$

where x_d = fractional depletion of amine at the surface.

Strictly speaking, this equation only applies over a limited range where pseudo first-order conditions apply. Table 3 shows how rapidly depletion occurs even though at the higher times the values are not exact. In the present experiments $t_{\min} = 0.005$ sec.; Clarke $t_{\min} = 0.00217$ sec.; Astarita $t_{\min} > 0.02$ sec.

Even at the smallest contact time used in the present work, the depletion of amine at the surface is such as to make it most unlikely that a first-order condition applies. Little importance therefore can be attached to the conclusions of Clarke and Astarita at carbon dioxide gas pressure near 1 atm. The use of low carbon dioxide partial pressures may satisfy the conditions, but such an approach is made unnecessary by the following study on the bimolecular reaction.

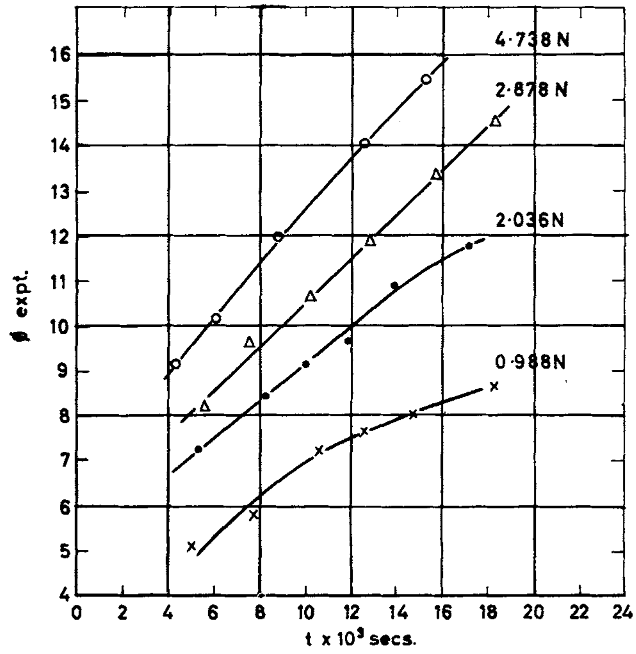

Fig. 5. Experimental values of ϕ for a range of jet contact times and solution strengths.

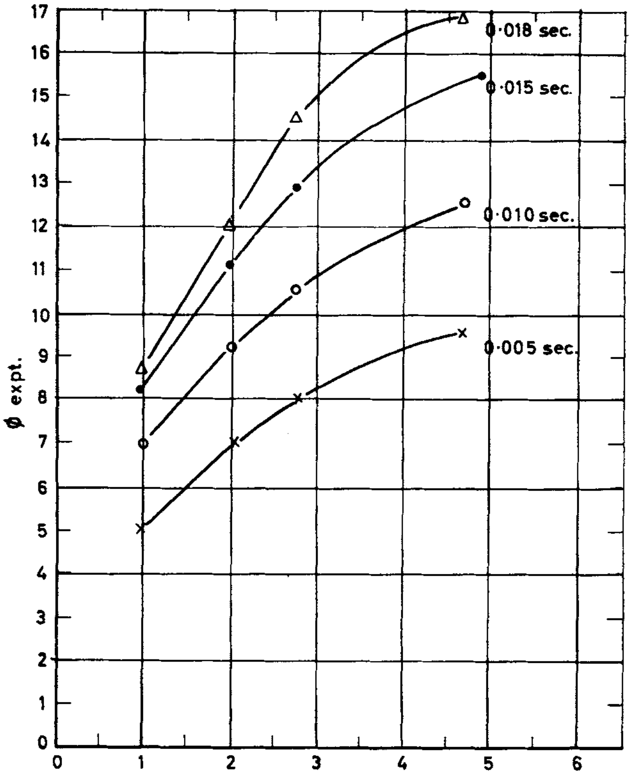

Fig. 6. Experimental values of ϕ for a range of MEA solution strengths.

Emmert and Pigford *(1)*

They proposed Equation (17) for the carbon dioxide–monoethanolamine system. For a 0.988 N solution when $q = 30$, $r = 0.613$, and by assuming $\nu = 1.0$, Equation (17) gives $\phi_{\text{theor}} = 24.8$. The experimental value of ϕ varies between 5 and 9, depending upon the contact time as shown in Figure 5. The agreement is most unsatisfactory.

Nijsing, Hendrikse, and Kramers *(13)*

Equation (18) has been proposed with the assumptions that $\nu = 1.0$, $q = 30$, $r = 0.613$ for 0.988 N solution $\phi_{\text{theor}} = 39.6$ calculated from Equation (18). The experimental ϕ value is 5 to 9 from Figure 5. The equation is not reliable under the existing circumstances.

ANALYSIS OF EXPERIMENTAL RESULTS

Four cases are discussed and are chosen to give values at each solution normality with a spread of contact times. The details relative to these cases are given in Table 4.

TABLE 3. AMINE DEPLETION AT THE INTERFACE
0.988N monoethanolamine
k = 5,460 liters/(mole)(sec.)
$C^* = 3.3 \times 10^{-5}$ g.-mole/cc.

t, sec.	x_d
0.001	0.11
0.005	0.33
0.010	0.49
0.020	0.73

x_d = fractional depletion of amine at the interface

Table 4. Interpretation of Experimental Jet Results

	I	II	III	IV
B_0, g.-mole/liter	0.988	2.036	2.878	4.738
d, cm.	0.082	0.082	0.082	0.082
h, cm.	6.0	8.05	2.61	2.06
L, cc./sec.	2.5	2.5	2.5	2.5
t, sec.	0.0126	0.0171	0.0055	0.00436
D_A, sq. cm./sec. × 10^5	1.63	1.35	1.10	0.80
D_B, sq. cm./sec. × 10^5	1.00	0.90	0.83	0.70
k, liter/(mole)(sec.)	5,460	5,460	5,460	5,460
C^*, g.-mole/liter 25°C. 727 mm. Hg pp carbon dioxide	0.033	0.033	0.033	0.033
r	0.613	0.668	0.755	0.870
q	30.0	61.6	87.4	146
rq	18.4	41.2	66.0	127
$q\sqrt{r}$	23.5	50.2	75.6	136
ϕ_m (exp) mole/sec. × 10^5	1.56	2.55	0.91	0.77
$\overline{k}_{L0}$, cm./sec.	0.04	0.0318	0.0503	0.0484
$\overline{k}_L$, cm./sec.	0.307	0.372	0.410	0.443
ϕ (exp)	7.67	11.70	8.15	9.17
$\sqrt{M}$	7.45	12.25	8.25	9.40
$\phi_a = 1 + rq$ (film theory) Equation (9)	19.4	42.2	67.0	128
$\phi_a = 1 + q\sqrt{r}$ (penetration theory) Equation (16)	24.5	51.2	76.6	137
ϕ_1 (film theory) Equation (8), Figure 1	6.1	10.5	7.5	8.9
$\Delta\phi$	22%	10%	8%	4%
ϕ_2 (penetration theory) Equation (13) Figure 2	6.6	10.8	7.5	8.8
$\Delta\phi$	15%	7.7%	8%	4%
ϕ_3 (penetration theory corrected by the method of Brian et al.) Equation (13)	7.65	11.4	8.1	9.1
$\Delta\phi$	0.26%	2.6%	0.6%	0.66%
Criteria for speed of reaction	Fast	Fast	Fast	Fast
Fast reaction $\phi_a >> \sqrt{M} >> 1$	but not	but not	but not	but not
Very fast reaction $\sqrt{M} >> \phi_a$	very fast	very fast	very fast	very fast

ϕ_{exp}

Obtained directly from the jet experiments in which ϕ_m, C^*, t, D_A, d, and h are known.

ϕ_1 Film Theory Solution

The values of r, q, and $\sqrt{M}$ are known from experiment so that ϕ_1 can be found from Equation (8). Alternatively, ϕ_1 can be obtained directly from Figure 1 at given values of r, q, and $\sqrt{M}$. It is seen that the calculated value of ϕ differs from ϕ_{exp} by as much as 10%.

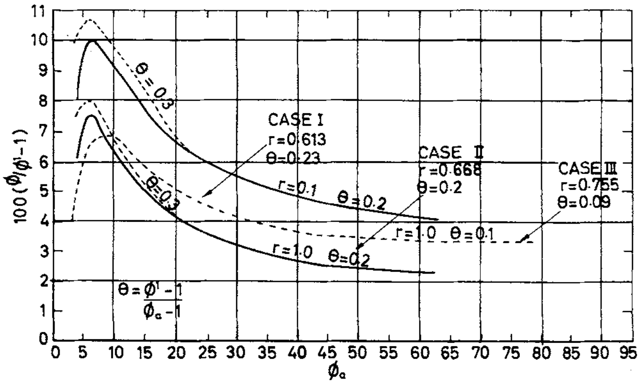

Fig. 7. Interpolated curves for correction by the method of Brian, Hurley, and Hasseltine.

ϕ_2 Penetration Theory Solution

The values of $q\sqrt{r}$ and $\sqrt{M}$ are known from experiment so that ϕ_2 can be found from Equation (13). Figure 2 can be used to give values directly. The agreement between ϕ_2 and ϕ_{exp} is better than the case of ϕ_1.

ϕ_3 Corrected Penetration Theory Solution

ϕ_3 was calculated by the method of Brian, Hurley, and Hasseltine. Because Brian et al. limited their graphs up to $\phi_a = 21$, it was necessary to interpolate, as for the four cases $\phi_a = 24.5, 51.2, 76.6$, and 137. The interpolation for three cases is shown in Figure 7; case IV is an extension of this graph.

Specimen Calculation Case II

$$\sqrt{M} = 12.25 \quad \phi_a = 51 \quad r = 0.668$$

$$\phi' = 12.25\sqrt{1 - (\phi' - 1)/50}$$

Let $\phi^1 = 11.3$

$$\phi' = 12.5\sqrt{1 - 10.3/50} = 10.9$$

$$\theta = \frac{\phi' - 1}{\phi_a - 1} = \frac{10.3}{50} = 0.2$$

From Figure 7 $100\left(\frac{\phi}{\phi'} - 1\right) = 3.5$

$$\phi = 1.035 \times 10.9 = 11.3$$
$$\phi = 11.3 \text{ is correct.}$$

Several trials were necessary to arrive at this value. The experimental value of $\phi = \phi_{\text{exp}} = 11.70$. The values for the other cases are given in Table 4.

The values of $\Delta\phi$ in Table 4 speak for themselves. The error of about 10% between the film theory solution and experiment is of the order of magnitude given by Peaceman. The penetration theory solution gives an improved agreement with the experimental result and is of the order of magnitude quoted by Brian et al.: The corrected penetration theory solution gives good agreement with the experimental value.

The accuracy of the calculated ϕ value by the method of Brian improves with the amine solution strength. Probably this is not a function of physical properties but rather of the numerical solution of Equation (13). The value of ϕ_a depends upon q and $\sqrt{r}$. In the present experiments r has a limited range (0.78 to 0.93) but q changes fivefold. For large ϕ_a values $\phi - 1/\phi_a - 1$ becomes small and $\sqrt{1 - \frac{\phi - 1}{\phi_a - 1}}$ has a limited effect on the calculation of ϕ^1.

When ϕ_a is small (low normality of amine solution) $\frac{\phi - 1}{\phi_a - 1}$, is large and the value of $\sqrt{1 - \frac{\phi - 1}{\phi_a - 1}}$ can change considerably. An error in r or q will therefore be significant in predicting the value of ϕ, especially in the case of r, as accurate values of D_B and D_A are needed. The author has established D_B accurately (*19*) but D_A is an approximation based on a viscosity change at constant temperature. Work being carried out at present by the author to establish D_A accurately for amine solutions will help to clarify the position.

Reaction Rate

It is of interest to show the rate of reaction relative to diffusion. One may refer to the reaction as being fast or very fast, but it should be remembered that this bears no relationship to the speed of ionic reactions which have velocity constants of the order of 10^{10} and greater. The work of Van Krevelen and Hoftijzer can be used to establish a simple criterion as shown in Table 4. It is seen that in each case the reaction may be considered as fast but not very fast relative to diffusion.

A similar conclusion is evident from an observation of Figure 2. The area in which the experimental results fall is indicated. Within this area the criteria in Table 4 are seen to hold; and an observation of the approach of an experimental ϕ value at a given $\sqrt{M}$ to ϕ_a, and the magnitude of the experimental $\sqrt{M}$ itself, will give an indication of the speed of the reaction. An advantage of the Gilliland and Brian methods is that the rate of reaction requires no assumption as to the probable position of the reaction zone.

SUMMARY

1. The kinetics of the reactions between carbon dioxide and aqueous monoethanolamine has been considered. The only reaction of importance in the short time of exposure to a laminar liquid jet is that in which carbamate is formed. An overall second-order reaction velocity constant is proposed.
2. The interpretation of the mass transfer process on the basis of a pseudo unimolecular reaction is untenable due to excessive depletion of amine at the surface.
3. The experimental results for carbon dioxide absorption into MEA solution are examined on the basis of Van Krevelen and Hoftijzer, film theory; Gilliland et al., penetration theory; and Brian et al., modified penetration theory. The accuracy of the calculation is improved in that order. The results for the Brian modified penetration theory solution are accurate to approximately 3%.

NOTATION

A = concentration of species A, the gas being absorbed (carbon dioxide), g.-mole/liter
B = concentration of species B, the reactant in solution (MEA), g.-mole/liter
B_0 = initial concentration of B in solution when $t = 0$, g.-mole/liter
C^* = equilibrium solubility of A (carbon dioxide) in the liquid at the interface, g.-mole/liter
d = diameter of jet orifice, cm.
D_A = diffusion coefficient of A (carbon dioxide) in solution, sq.cm./sec.
D_B = diffusion coefficient of B (MEA) in solution, sq. cm./sec.
h = height of laminar jet, cm.
k_L = average liquid mass transfer coefficient (subscript 0 refers to coefficient without reaction), cm./sec.
k = second-order reaction rate constant, liter/(mole) (sec.)
$M = \frac{k \cdot D_A B_0}{{k_{L_0}}^2}$
N_A = average absorption rate $= \frac{Q}{\pi d h t}$ g.-mole/(sq. cm.) (sec.)
Q = absorption of carbon dioxide in t sec., g.-mole
$q = B_0/C^*$
$r = D_B/D_A$
t = time of exposure of jet, sec.

Greek Letters

σ = parameter in parametric equations
$\text{erf}(\sigma) = \frac{2}{\sqrt{\pi}} \int_0^{\sigma} e^{-y^2}\, dy$
$\phi = k_L/k_{L_0}$
ϕ_{exp} = experimental value of k_L/k_{L_0}
ϕ_1 = film theory solution
ϕ_2 = penetration theory solution
ϕ_3 = Brian et al. modified calculation from ϕ_2
ϕ^1 = approximation to ϕ for use in Brian equation
$\Delta\phi = \frac{\phi_{\text{exp}} - \phi_{1.2.3}}{\phi_{\text{exp}}} \times 100$
ϕ_a = asymptotic value of ϕ for an infinitely fast reaction or large $\sqrt{M}$ values
$\theta = \frac{\phi^1 - 1}{\phi_a - 1}$
ν = stoichiometric factor

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The Dynamic Behavior of a Fixed-Bed Catalytic Reactor

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The dynamic behavior of a fixed-bed catalytic reactor was studied under isothermal conditions by means of frequency response analysis. The investigation was conducted over a range of nonreacting and reacting conditions by using the hydrogen-oxygen combination over supported platinum as the reaction system. The kinetics of the surface catalysis of this reaction were investigated separately and then were incorporated into the analysis of frequency response data under reaction conditions.

A method was developed whereby nonlinear chemical reaction effects appearing in the frequency response measurements could be separated from hydrodynamic factors for a plug flow reactor. Use is made of the describing function technique, often used to approximate nonlinear servomechanism response, to accomplish this. It is shown by this method that Peclet numbers measured for the reacting system agree with those measured in the absence of reaction.

Based on the semitheoretical value of 2 for the Peclet group at high Reynolds numbers, a value of 0.73 sq. cm./min. was determined for the effective diffusion coefficient of hydrogen at 100°C. within the porous catalyst particles. Analysis of frequency response data in which this diffusion is not accounted for leads to Peclet numbers which are unreasonable in view of previously reported results.

Although there is a great deal of work in the recent literature on the characterization of flow and dispersion of fluids in beds of nonporous packing, and some work on porous packing, there are few data available concerning these effects under reaction conditions. Furthermore, there have been until recently no reported measurements of the dynamic behavior of a catalyst surface. It is, therefore, the primary purpose of this work to apply existing techniques of transient analysis to a study of the dynamic behavior of a fixed bed of porous catalytic particles under conditions of chemical reaction, and to define the pertinent adsorption, flow, and diffusion parameters.

Tinkler (*1*) and Sinai (*2*) have investigated by frequency response analysis related problems of flow through beds packed with inert solid in which a homogeneous chemical reaction took place in a liquid phase. Axial dispersion effects were neglected and nonlinearities were handled by Taylor series expansion. These workers studied both the temperature and concentration response in their systems; work in the present study is limited to the isothermal case.

The general problem of flow patterns and residence time in fixed beds has been considered by many workers and two distinct approaches have evolved. One considers the bed as a series of mixing cells in which the fluid in each cell is perfectly mixed and then passed on to the next cell; this approach has its most complete expression in the computational model of Deans and Lapidus (*3*). The other approach involves expression of the conservation equations as material balances over a segment of the bed in which a continuous (fluid) phase and a discontinuous (solid) phase are visualized. Numerous workers have employed this type of description; the well-known, one-dimensional, axial dispersion model of fixed beds has been thoroughly explored in the literature (*4* to *8*).

For such axial mixing or dispersion, the fundamental step in the mixing process is considered to be a random

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