Gas Absorption Accompanied by Chemical Reaction:

A Study of the Absorption of Carbon Dioxide in Aqueous Solutions of Monoethanolamine

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Experiments were conducted on the absorption of carbon dioxide in aqueous solutions of monoethanolamine in a very short wetted-wall column.

When the absorption was effected from pure carbon dioxide streams, the results conformed to a theoretical relation for absorption combined with very fast second-order reaction. This is in accordance with expectations based on the probable mechanism and rate of the reaction. The data indicate that there is no appreciable effect of nonequilibrium at the interface for this particular reaction system over the range of exposure times studied.

When mixed gas streams were used, it was necessary to resort to empiricism to correlate the data, although the correlating expression arose from theoretical considerations.

The separation of components in a gas mixture is commonly effected by contacting the gas with a liquid which can selectively absorb either the desired component or the diluent. If the liquid contains a constituent which reacts with the dissolving gas, then both the rate of mass transfer and the capacity of the liquid for the gas are increased.

The design of contacting equipment for absorption requires a knowledge of rates of transfer and of equilibrium concentrations. This work is concerned with transfer rates and is confined to the liquid phase only, which usually is of primary importance when a reactant is present in the liquid. Successful predictions of liquid-phase mass transfer resistance in wetted-wall columns based on theoretical considerations of the molecular diffusion process can be made when no chemical reaction occurs and when the area of contact is known, as shown by Lynn, Straatemeier, and Kramers *(10)* and by Emmert and Pigford (3). This investigation was conducted in order to establish means of relating absorption rates when reaction occurs to those when there is no reaction.

The system chosen for experimental testing was carbon dioxide-monoethanolamine-water. This is one of the most widely used commercial systems in which a major portion of the resistance to mass transfer is in the liquid. Since the reaction between carbon dioxide and ethanolamine is a reversible one, regeneration of the amine and recovery of the carbon dioxide are accomplished by heating.

THEORY

Physical Absorption

It is common practice to relate mass transfer rates to a driving force in accordance with

$$\overline{N_A} = \overline{k_L}\,(A_i - A_o) \qquad (1)$$

When one deals with systems in which chemical reaction occurs in the liquid layer, the absorption rate may not be directly proportional to the driving force, but this relation still proves convenient.

Higbie (5) has derived a theoretical relation for $\overline{k_L}$ which applies to physical absorption into a laminar layer of liquid descending along a solid wall. It assumes that (1) the portion of the layer penetrated by diffusing molecules is moving at a uniform velocity, (2) the effect of diffusion in the direction of flow is negligible, and (3) the interfacial concentration has a constant value A_i^*. Emmert and Pigford (3) have presented experimental confirmation of this equation using a wetted-wall column and have shown that the first two assumptions are not seriously in error provided the time of contact is short and ripples are absent from the surface of the liquid. When there is no chemical reaction, Higbie's analysis shows that

$$\overline{k_L^o} = \frac{2}{\sqrt{\pi}}\sqrt{\frac{D_A}{t}} \qquad (2)$$

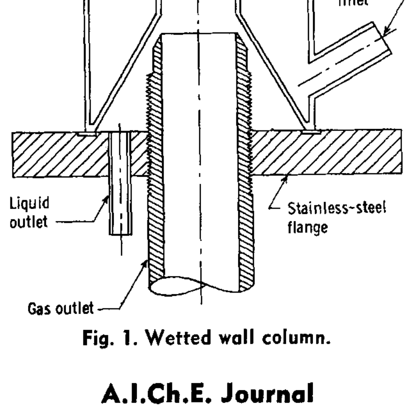

Fig. 1. Wetted wall column.

Theoretical relations for the effect of chemical reaction on absorption rate have been obtained for the cases of first- and second-order reversible reactions.

Sherwood and Pigford *(15)* treat the case of a first-order reversible reaction $A \rightleftharpoons C$ and obtain a solution which relates the mass transfer coefficient with reaction to that without. Their result is presented graphically and is of the form

$$\frac{\overline{k_L}}{\overline{k_L^o}} = f\,(k_c t, K) \qquad (3)$$

Perry and Pigford *(13)* have presented a theoretical treatment of the more general second-order reaction which is of the form

$$A + \nu B \rightleftharpoons C \qquad (4)$$

Their result is

$$\frac{k_L}{k_L^o} = g\,(k\,B_o t, B_o/\nu A_i^*, K) \qquad (5)$$

Care should be exercised in the use of this relation, since it is based on instantaneous or local coefficients rather than average coefficients as in Equation (3). Time-average coefficients are easily computed from the reported values however. In the limit, when $kB_o t$ becomes large, that is when the

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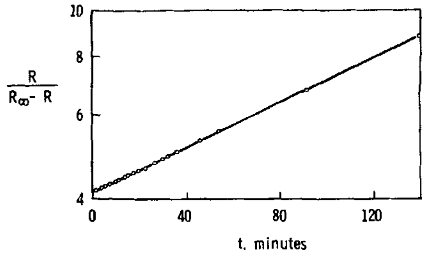

Fig. 2. Study of drift reaction.

reaction is very fast, this relation may be approximated by

$$\frac{\overline{k_L}}{\overline{k_L{}^o}} = \sqrt{\frac{D_A}{D_B}} \left(1 + \frac{D_B}{D_A} \frac{B_o}{\nu A_i{}^*} \right) \quad (6)$$

Here the mass transfer coefficients are averaged over the absorption period and may be compared directly with observed mean absorption rates.

APPARATUS AND PROCEDURE

The use of wetted-wall columns for investigating gas-liquid mass transfer has been widespread because of the ease of evaluating the interfacial area and the time of contact between the phases. Special measures should be adopted however to eliminate the increase in mass transfer resulting from ripples that appear on the surface of the liquid in a long column, as otherwise interpretation of the results is severely limited by lack of knowledge of the mass transfer resulting from the stirring action of the ripples. This may be achieved by using a very short column, since ripples do not begin until the liquid layer has descended several inches. This has the added advantages that the contact times are comparable to those in industrial contactors and are short enough that the absorbed gas molecules penetrate only a relatively short distance into the liquid layer, in accord with the assumption of nearly uniform fluid velocity made in deriving the theories for absorption.

Figure 1 shows the assembly of a short column, constructed of 0.95-in. I.D. glass tubing 1.524 in. long. The upper and lower gas calming sections were 4 ft. long and were constructed of 1-in. Lucite tubing threaded to permit vertical adjustment of the entrance and exit liquid slots.

In operation the liquid flowed in the nipple at the bottom, up the annular space, through the entrance slot (forming a layer on the inner wall of the inner cylinder), out the exit slot to the triangular cross-section reservoir, and then out the stainless steel nipple in the lower flange to the analytical apparatus. The gas flowed concurrent to the liquid. Liquid flow rates ranged from 2.27 to 14.23 g./sec. In order to avoid oxidation the liquid monoethanolamine solution was stored under nitrogen and was not recirculated.

Since the column was so short, the elimination of end effects took on particular importance. It was therefore necessary that the entrance and exit slots be kept full of liquid at all times and that no gas space or bubbles be present in the exit reservoir. The level in this outlet reservoir was maintained at the slot by means of an adjustable constant-level chamber combined with two screw clamps in series on the outlet line. Uncertainties in the surface liquid velocity due to gravitational acceleration of the film were estimated to be negligible; another effect due to accumulation of surface contaminants at the bottom of the film, described by Lynn, et al. (*10*), is more uncertain but is believed not to have been of major importance.

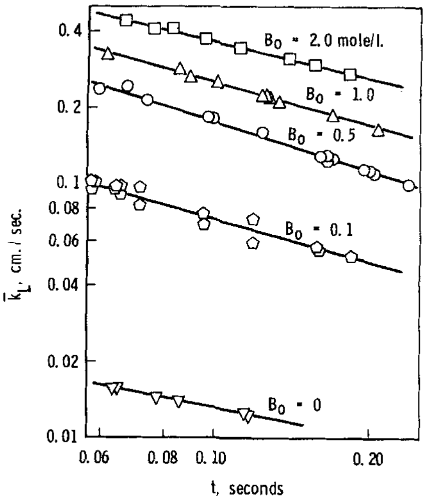

Fig. 3. Variation of absorption coefficient with contact time for absorption from pure carbon dioxide streams into monoethanolamine solutions. Coefficients were calculated on the assumption that the solubility is the same as that in water.

The extent of conversion of ethanolamine with carbon dioxide was determined continuously by measuring the electrical conductivity of the inlet and outlet liquid streams. The conductivity bridge was constructed of a strip-chart recorder and a bridge box. The analyses were estimated to be accurate to within ± 0.5% of the total amine present. Since the conductivity is very sensitive to temperature, the liquid stream temperatures were controlled to within ± 0.05°C.

REACTION MECHANISM

Carbon dioxide may be consumed chemically by one of four routes which are possible because of the bifunctional nature of monoethanolamine. These are:

1. The direct attack of dissolved carbon dioxide by the amine functional group to form a carbamate, that is an amide of carbonic acid:

$$\begin{aligned} CO_2 + HOCH_2CH_2NH_2 &\rightleftharpoons \\ &HOCH_2CH_2NHCOOH \\ &\qquad\quad \upharpoonleft\downharpoonright \\ &HOCH_2CH_2NHCOO^- + H^+ \end{aligned}$$

2. The reaction of the amine with water to generate hydroxyl ion, followed by hydroxyl ion attack on dissolved carbon dioxide:

(a) $HOCH_2CH_2NH_2 + H_2O \rightleftharpoons HOCH_2CH_2NH_3{}^+ + OH^-$

(b) $CO_2 + OH^- \rightleftharpoons HCO_3{}^-$

(c) $HCO_3{}^- + OH^- \rightleftharpoons CO_3{}^= + H_2O$

3. The formation of the alkylate ion followed by attack on carbon dioxide by this ion, producing an ester of carbonic acid:

(a) $HOCH_2CH_2NH_2 + OH^- \rightleftharpoons {}^-OCH_2CH_2NH_2 + H_2O$

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

4. The reaction of carbon dioxide with water to form carbonic acid:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

Reaction (1) is presumably of primary importance. The rate constant is 3,190 liter/(mole)(sec.) at 18°C., according to Faurholt (*4*). Using the activation energy for the $CO_2 - OH^-$ reaction (*14*) for purposes of correcting the rate constant for temperature, one can estimate the rate constant to be 5,400 liter/(mole)(sec.) at 25°C.

Reaction (2a) occurs almost instantaneously and is doubtless not rate controlling, since it involves the transfer of a proton from an oxygen to a nitrogen. It is responsible for the alkalinity of the aqueous amine solutions. The rate constant (2b) is 8,300 liter/(mole)(sec.) at 25°C., as reported by Pinsent, Pearson, and Roughton (*14*).

This reaction is followed by instantaneous dissociation into the carbonate.

The rate constant for reactions (3) is probably about 3 × 10^4 liter^2/(mole)^2 (sec.) at 25°C., judging from the rate

TABLE 1. CONCENTRATIONS OF OH^- AND FREE MONOETHANOLAMINE IN SOLUTIONS OF VARIOUS STRENGTHS OF TOTAL AMINE BASED ON DATA OF BATES AND PINCHING (*1*)

B_o	(B)	(OH^-)	$(B)/(OH^-)$
0.01	0.00677	0.00323	2.1
0.1	0.0875	0.0125	7.0
0.5	0.472	0.0283	16.7
1.0	0.959	0.0412	23.2
2.0	1.942	0.0584	33.2

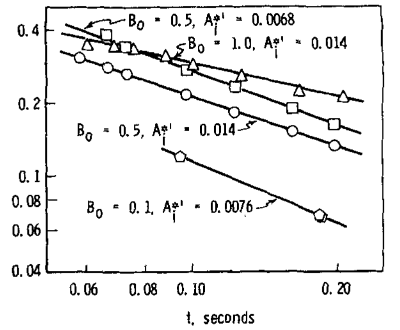

Fig. 4. Variation of absorption coefficient with contact time for absorption from mixtures of carbon dioxide with air into monoethanolamine solutions. Coefficients were calculated on the assumption that the solubility is the same as that in water.

measured for the analogous reaction with diethanolamine as reported by Jorgensen (*8*). This rate constant is a third-order constant expressed in terms of amine and hydroxyl ion and carbon dioxide concentrations. The basis for such a rate expression is that reaction (3a) is assumed to reach equilibrium instantaneously.

Reaction (4) proceeds very slowly with a rate constant of 0.025 liter/(mole)(sec.) at 25°C. (*14*). This is so slow that the reaction will have a negligible effect on absorption rate.

Reaction (1) depends on the residual amine concentration alone, but (2) and (3) depend on the hydroxyl-ion concentration as well. The only source of hydroxyl ion is reaction (2*a*), which has been studied by Bates and Pinching (*1*). They report

$$K_b = \frac{(BH^+)(OH^-)}{(B)(H_2O)} \cdot \frac{\gamma_{BH^+}\gamma_{OH^-}}{\gamma_B} = 3.18 \times 10^{-5}\ (25°C.)$$

or

$$\frac{(BH^+)(OH^-)}{(B)} \approx 1.77 \times 10^{-3}\ \text{mole/liter}$$

where the activity coefficients are taken as unity. Table 1 shows the calculated concentrations of hydroxyl ion and free amine in solutions of various total amine strengths.

Based on these relative quantities of amine and hydroxyl ion an estimate may be made of the relative contributions of the various reactions in consuming carbon dioxide (when one considers initial rates only). Since in reaction (1) only 1 mole of amine is consumed per mole of carbon dioxide absorbed, while in reactions (2) and (3) 2 moles are consumed, an estimate may also be made of the average amine consumption or apparent stoichiometric factor ν. These estimates are presented in Table 2.

This has the consequence that as the absorption proceeds and amine is depleted, the relative amounts of carbon dioxide consumed by the different reactions change slightly, and the apparent stoichiometric factor governing the rate of absorption according to Equation (6) also changes correspondingly.

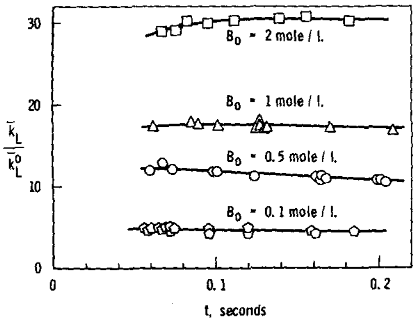

Fig. 5. Absorption of carbon dioxide from pure streams into solutions of monoethanolamine. Absorption coefficients $\bar{k}_L$ were calculated on the assumption that the solubility of unreacted carbon dioxide is the same as that in water.

TABLE 2. RELATIVE INFLUENCE OF PARALLEL, FAST-REACTION PATHS IN CONSUMING CARBON DIOXIDE (BASED ON INITIAL RATES)

	% of CO_2 consumed by reaction			Moles amine consumed per mole CO_2
B_o	*a*	*b*	*c*	Reacting, ν
0.01	57	42	1	1.4_3
0.1	78	17	5	1.2_2
0.5	83	8	9	1.1_7
1.0	79	5	16	1.2_1
2.0	76	4	20	1.2_4

In general it is evident that reaction (1), the carbamate-forming reaction, is most important in influencing absorption rate. However Lund and Faurholt (*9*) have shown that the eventual chemical equilibrium favors the formation of carbonate by reaction (2), so that after the carbamate is formed rapidly, it slowly reverts through free carbon dioxide to the carbonate. Consequently, while reaction (1) controls absorption rate, reaction (2) is of prime importance in affecting the final equilibrium.

Lund and Faurholt (*9*) have obtained a rate expression for this slow reversal reaction in terms of the known rate and equilibrium constants for the component reactions. From this rate expression the rate constant for the carbamate-to-carbonate reaction may be calculated for various concentrations of amine. Experimental confirmation of this expression has been provided by Jensen, Jorgensen, and Faurholt (*7*). The rate constants are expressed as pseudo first order in terms of carbamate or carbonate, respectively.

The results are shown in Table 3. The forward rate constants are from seven to ten orders of magnitude slower than reaction (1), so it is apparent they will have a negligible effect on rate of absorption. However the reverse rate constants are much smaller than the forward ones, showing that the equilibrium favors the carbonate form.

Total equilibrium data, such as those of Mason and Dodge (*11*), should be used only in evaluating absorption capacity of a solution fed to an absorber from a storage vessel, but not absorption rate as influenced by the chemical conversion of amine in the absorber. When one refers to Equation (1), A_i is the interfacial concentration of dissolving gas, which is equivalent to the equilibrium solubility of unreacted A in the liquid A_i^*. The presence of amine affects this only because of the salting-out effect. On the other hand A_o, which represents unreacted *A* in the bulk of the liquid, is reduced by the presence of a reaction which serves to fix *A*. Hence the driving force $A_i - A_o$ for absorption is increased when free amine is consumed by reaction; in addition the transfer coefficient $\bar{k}_L$ is enhanced. A_o should not be based on the ultimate equilibrium resulting from the reversion of carbamate to carbonate, as has sometimes been assumed (*2, 16*), but on the intermediate, temporary equilibrium resulting from the reactions that occur rapidly enough to be effective in an absorption tower. Also total equilibrium data should not be used in evaluating the effect of reaction on $\bar{k}_L$ by means of Equation (6).

TABLE 3. RATE CONSTANTS FOR REACTION $HOC_2H_4NHCOOH + H_2O \rightleftharpoons HOC_2H_4NH_4CO_3$ CALCULATED FROM DATA OF FAURHOLT (18°C.) (CARBAMATE + $H_2O \rightleftharpoons$ CARBONATE)

B_o	$k_{forward}$, (sec.$^{-1}$)	$k_{reverse}$, (sec.$^{-1}$)
1.0	1.5×10^{-6}	0.20×10^{-6}
0.1	1.5×10^{-5}	0.067×10^{-5}
0.01	1.4×10^{-4}	0.025×10^{-4}

Experimental confirmation of the carbamate-to-carbonate reversion reported by Lund and Faurholt (*9*) was obtained by the authors. While the conductivity apparatus was calibrated, it was observed that the conductivity of a freshly prepared solution containing carbon dioxide and monoethanolamine changed upon standing for several hours. This effect was more noticeable with low amine concentrations. An experiment was conducted in which the variation of conductivity with time was measured for a 0.1-N amine solution which was 4% converted to carbamate. If the initial concentration of carbamate is termed c_o, and the concentration at time *t* is *c*, then for a pseudo first-order reaction

$$\ln \frac{c_o}{c_o - c} = k_c t \qquad (7)$$

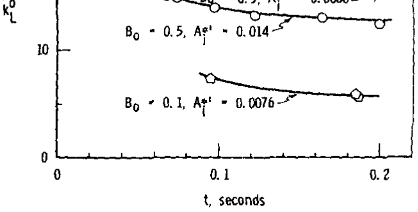

Fig. 6. Absorption of carbon dioxide from mixed streams into solutions of monoethanolamine. Absorption coefficients $\bar{k}_L$ were calculated on the assumption that the solubility of unreacted carbon dioxide is the same as that in water.

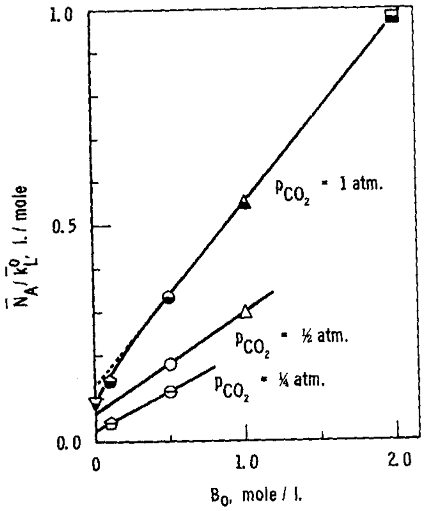

Fig. 7. Effect of amine concentration on rate of absorption of carbon dioxide.

Since resistance is inversely proportional to concentration

$$\frac{c_o}{c_o - c} = \frac{1/R_\infty - 1/R_o}{1/R_\infty - 1/R} = \frac{(R_\infty - R_o)R}{R_o(R_\infty - R)} \quad (8)$$

Consequently a plot of log $(R)/(R_\infty - R)$ vs. t should give a straight line if the reaction is psuedo first order, as implied by Faurholt's mechanism. Figure 2 shows such a plot, and it does give a straight line. From the slope the rate constant is estimated to be 4×10^{-5} sec.$^{-1}$ at 25°C. When one refers to Table 3, the rate constant predicted from Faurholt's mechanism is 1.5×10^{-5} sec.$^{-1}$ at 18°C., which, when extrapolated to 25°C., is 3×10^{-5} sec.$^{-1}$, a good check with the experimental determination with the resistance method.

RESULTS OF ABSORPTION STUDIES

Figures 3 and 4 show the data for the absorption of carbon dioxide into aqueous monoethanolamine solutions from pure carbon dioxide streams and from mixtures of carbon dioxide with air, respectively. A correction has been applied to the data to account for the slight effect of gas-phase resistance due to air. Figures 5 and 6 show the data plotted in a fashion suggested by the theoretical treatment discussed earlier. The values of $\overline{k}_L^{\circ}$ were calculated from the theoretical Equation (2) with the observed solution viscosity used to adjust the diffusion coefficient.

The important feature of Figure 5 is that $\overline{k}_L/\overline{k}_L^{\circ}$ is virtually independent of contact time. This has two significant implications. First, the effect of nonequilibrium at the interface is apparently negligible judging from equations resulting from the assumption of a time-independent interfacial coefficient. Second, the influence of the reaction rate is also probably negligible, since the theory of Perry and Pigford (*13*) for bimolecular reaction without interfacial resistance indicates that if the reaction is slow enough that its rate influences the absorption rate, $\overline{k}_L/\overline{k}_L^{\circ}$ will increase with increasing contact time. Also a calculation with the rate data of Faurholt (*4*) for this reaction combined with the theory of Perry and Pigford (*13*) shows that kB_ot is so large that the chemical rate phenomena should not be important. This suggests that the approximate theory for infinitely-fast reaction without interfacial resistance [Equation (6)] might be suitable for describing the experimental results.

Equation (6) indicates that, provided the carbon dioxide solubility is independent of amine concentration, a plot of $\overline{N}_A/\overline{k}_L^{\circ}$ vs. B_o should give a straight line with a slope of $\sqrt{D_B/D_A}/\nu$ and an intercept of $A_i^* \sqrt{D_A/D_B}$. Also $\overline{N}_A/\overline{k}_L^{\circ} = A_i^*$ when $B_o/\nu A_i^* = 0$, so such a plot should give a straight line for high values of $B_o/\nu A_i^*$, curving into $\overline{N}_A/\overline{k}_L^{\circ} = A_i^*$ at $B_o/\nu A_i^* = 0$. The upper line of Figure 7 shows such a plot based on the asymptotic levels from Figure 5, and it does indeed follow the predicted form. The two lower lines on this figure are for absorption from mixed streams, which will be discussed later. Based on the estimated diffusivity of monoethanolamine through water from the Wilke (*18*) correlation, and experimental values of D for carbon dioxide in water, suitably corrected for the viscosity of the solution, $\sqrt{D_B/D_A} = 0.765$; on this basis apparently $\nu = 1.78$, and $A_i^* = 0.092$ mole/liter.

Whether these values are the true ones cannot be ascertained at this time, since there are no independent means of determining A_i^* and since its effect on the absorption rate is small. The solubility of carbon dioxide in water is 0.034 mole/liter, but this would be affected by the presence of the amine and the ions in the solution. A_i^* is the equilibrium concentration of dissolved but unreacted carbon dioxide, which cannot be measured directly. In any case the value of A_i^* resulting from the absorption data is about three times the solubility in water.

TABLE 4. APPARENT SOLUBILITIES OF UNCOMBINED CARBON DIOXIDE IN AMINE SOLUTIONS FROM EXPERIMENTAL DATA (25°C.)

p_{CO_2}, atm.	A_i^*, mole/liter
1	0.092
0.5	0.046
0.25	0.023

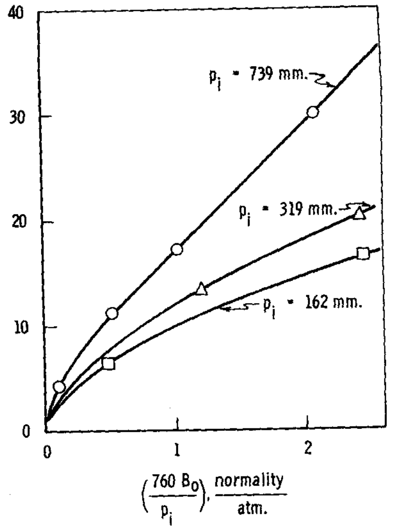

Fig. 8. Effect of partial pressure on rate coefficient.

The authors have previously concluded from the probable reaction mechanism that the stoichiometric coefficient should be between 1 and 2, which apparently it is. So the experimental results are in general accord with the predictions of the theory for bimolecular infinitely-fast reaction. However, as shown by Table 2, the expected value of ν is about 1.2 instead of 1.78.

Consider now the results of experiments on absorption from mixed gas streams containing carbon dioxide and nitrogen. Figure 6 shows that $\overline{k}_L/\overline{k}_L^{\circ}$ varies to some extent with contact time. Analysis following the scheme adopted for absorption from pure streams according to Equation (6) can be applied, therefore, only to the asymptotic levels of these curves. The validity of such an approach is uncertain here, since variation with exposure time may result from a changing reaction mechanism as suggested earlier or possibly from an influence of interfacial resistance, but it will be attempted anyway. With reference to Figure 7, the two lower lines represent absorption from mixed gas streams. Only two levels of B_o are available for each value of carbon dioxide partial pressure, so whether a straight line really results is questionable. However the intercepts indicate values of A_i^* proportional to the gas partial pressure as shown by Table 4. Based on the slopes of the lower lines shown in Figure 7, the calculated values of the stoichiometric coefficient are 3.2 and 4.2 for $p_{CO_2} = 0.5$ and 0.25 atm., respectively. In view of the earlier discussion regarding the reaction mechanism, these values seem unrealistically high. It is possible that these high values of ν are merely a reflection of the failure of the theory to account for an interfacial contaminant. Based on Equation (6) and with $\nu = 1.78$, the two lower lines should be parallel to the upper one, the decrease in $\bar{N}_A$ being proportional to the decrease in p_i regardless of the value of B_o, that is $\partial \bar{N}_A / \partial p_i =$ constant. The observed reduction in rate is greater than this and is evidently dependent on the amine strength. This is further illustrated in Figure 8, where a single correlating line would be expected regardless of the level of p_i. The presence of the nitrogen in the gas seems to be causing an extra resistance not accounted for by partial pressure considerations alone.

Empirical Correlation

This behavior suggests plotting the data as shown in Figure 9, where $\bar{k}_L/\bar{k}_L^{o}$ is plotted vs. B_o with $B_o/A_i^{*\prime}$ as a parameter. The value of $A_i^{*\prime}$ chosen for calculation of $\bar{k}_L$ and $B_o/A_i^{*\prime}$ was the solubility in water. Whether or not this is the actual value of A_i^{*} in amine solutions is immaterial, since this merely affects the level of $\bar{k}_L/\bar{k}_L^{o}$ and $B_o/A_i^{*\prime}$. In order to make this plot it was necessary to correct $\bar{k}_L/\bar{k}_L^{o}$ values to nominal values of $B_o/A_i^{*\prime}$. It is evident that the dependence of $\bar{k}_L/\bar{k}_L^{o}$ on $B_o/A_i^{*\prime}$ or on $A_i^{*\prime}$ is small compared with its dependence on B_o. Although this is contrary to the theoretical predictions, it is in accord with the data of Shneerson and Leibush (*16*) on monoethanolamine and diethanolamine and of Cryder and Maloney (*2*) on diethanolamine, both taken in packed columns.

Consideration of Figure 9 leads to an empirical equation which represents the data on both absorption from pure and mixed streams. This results from the following analysis. The lines for the three values of $B_o/A_i^{*\prime}$ are parallel, terminating in the line for pure gas streams. The intercepts of these lines are linear in $B_o/A_i^{*\prime}$, as shown by the small plot in the upper left-hand corner. The empirical equation that represents these data is

$$\frac{\bar{k}_L}{\bar{k}_L^{o}} = 0.077\,\frac{B_o}{A_i^{*\prime}} + 10.8\,B_o + 4.2 \qquad (8)$$

$$\bar{N}_A = 2\sqrt{\frac{D_A}{\pi t}}\,[0.077\,B_o + 10.8\,B_o\,A_i^{*\prime} + 4.2\,A_i^{*\prime}] \qquad (9)$$

where B_o is expressed in mole/liter, and $A_i^{*\prime}$ is the solubility in water. This equation represents all the data taken at high contact times to within ± 10% but does not account for the variation with contact time, so that an error as great as 30% may result at the lower times of exposure for mixed streams. However the theoretical equation for pure streams is as much as 50% in error when applied to mixed streams.

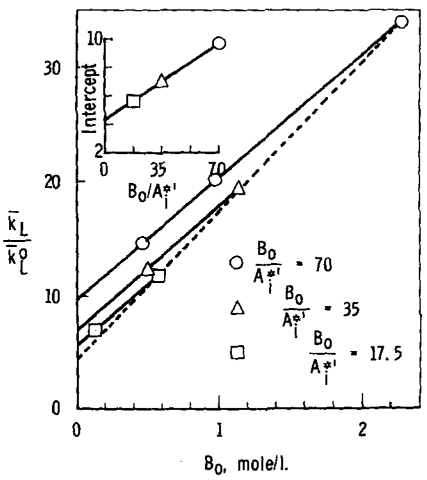

Fig. 9. Absorption of carbon dioxide from both pure and mixed streams into solutions of monoethanolamine (based on solubility in water for evaluating $A_i^{*\prime}$).

The fact that the dependence of $\bar{k}_L/\bar{k}_L^{o}$ on $A_i^{*\prime}$ is less than anticipated from the bimolecular, infinitely-fast theory suggests the possibility of pseudo first-order behavior. However this would require that $\bar{k}_L$ be independent of contact time, which is certainly not observed.

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NOTATION

A_i = liquid concentration of A at the interface, g.moles/liter

A_i^{*} = liquid concentration of A in equilibrium with the gas, g.moles/liter; prime indicates value computed from solubility of carbon dioxide in water

A_o = concentration of A in the bulk of the liquid, g.moles/liter

B = concentration of reagent B, g.moles/liter; subscript o signifies initial concentration

c = concentration of carbamate, g.moles/liter; subscript o designates initial concentration

D_A = diffusion coefficient of A in liquid, sq. cm./sec.

D_B = diffusion coefficient of B in liquid, sq. cm./sec.

K = equilibrium constant

K_b = basic dissociation constant

k = second-order reaction rate constant, liter/(mole) (sec.)

k_e = pseudo first-order reaction rate constant, sec.$^{-1}$

$\bar{k}_L$ = average liquid-side mass transfer coefficient, cm./sec.; superscript o indicates coefficient with no chemical reaction. Absence of bar indicates instantaneous coefficient

$\bar{N}_A$ = average absorption rate, g.moles/(sec.) (sq. cm.)

p_i = partial pressure of carbon dioxide at interface, atm.

p_{CO_2} = partial pressure of carbon dioxide in gas, atm.

R = resistance of carbon dioxide-amine solution, ohms; subscript ∞ indicates resistance after the completion of the reaction; subscript o indicates initial resistance

t = time of contact of gas and liquid, sec.

γ = activity coefficient of component denoted by subscript

ν = stoichiometric coefficient

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