Gas-Liquid Kinetics: the Absorption of Carbon Dioxide in Diethanolamine

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The absorption of carbon dioxide in pure diethanolamine was studied in a gas-liquid stirred reactor at 85°, 95°, and 105°F. Over forty runs were made but only nineteen were reported here since several were invalidated by difficulties with the stirring mechanism and reaction-temperature control. The absorption was followed by pressure-time measurements with the carbon dioxide pressure ranging between 30 and 4 cm. of mercury. Experimental data were consistent and reproducible.

An equation describing the gas-liquid absorption system was derived and then simplified by considering only the kinetic region. The experimental data were correlated with the simplified equation by both integral and differential methods and indicate that the reaction follows a third-order rate equation: first order in carbon dioxide and second order in diethanolamine. A mechanism explaining the observed order is described.

Justification for assuming kinetic control of the absorption was demonstrated by doubling and tripling the stirring speed which produced no significant change in the absorption rate. Also, the temperature dependence of the pseudo-rate constants was out of the range of ordinary mass transfer control. This agrees with the results of a theoretical model reported previously (*6*).

The use of the ethanolamines (monoethanolamine, diethanolamine, triethanolamine) as industrial absorbents in an acid-gas removal process was developed by Bottoms (*1*). Basically the process involves the selective absorption of carbon dioxide and hydrogen sulfide with aqueous ethanolamine solutions at temperatures below 50°C., and subsequent regeneration of the absorbent at temperatures above 100°C. Carbon dioxide and hydrogen sulfide react with the ethanolamines to form thermally unstable products and therefore the absorbent can be regenerated by heating. The ethanolamines are economical for this process because of their low volatility, thermal stability, and high selectivity for the acid-gases (*1, 9*). Some absorbent losses occur in the regeneration process where the high temperatures cause carbon dioxide to form degradation products with the monoethanolamine and diethanolamine (*10, 11*). A complete review of the literature of the ethanolamines for acid-gas removal is given by Kohl (*9*).

The important reactions occurring in the absorption of the acid-gases in aqueous solutions of monoethanolamine are (*1, 3, 9*)

$$2RNH_2 + H_2S \rightleftharpoons (RNH_3)_2S \quad (1)$$

$$(RNH_3)_2S + H_2S \rightleftharpoons 2RNH_3HS \quad (2)$$

$$2RNH_2 + CO_2 + H_2O \rightleftharpoons (RNH_3)_2CO_3 \quad (3)$$

$$(RNH_3)_2CO_3 + CO_2 + H_2O \rightleftharpoons 2RNH_3HCO_3 \quad (4)$$

$$2RNH_2 + CO_2 \rightleftharpoons RNHCOONH_3R \quad (5)$$

where R is $(HOCH_2CH_2)$. Diethanolamine and triethanolamine undergo analogous reactions, but triethanolamine cannot react as shown in reaction (5) because it lacks the mobile hydrogen ion characteristic of mono- and diethanolamine (*7*).

Most existing experimental studies of carbon dioxide absorption in aqueous ethanolamine solutions have been conducted in industrial absorbers under operating conditions common to the industrial process. Separation of mass transfer effects in such equipment is complicated by multicomponent streams and the number of reactions possible. It has, therefore, been common to postulate a rate-controlling step, usually one of the carbon dioxide reactions, for the absorption. Complications exist here too for the mechanisms by which reactions (3) to (5) proceed have not been established. The results of Cryder and Maloney (*3*) were successfully correlated by van Krevelen (*13*) on the basis of a pseudo-third-order reaction suggested by the mechanism

$$2(CH_2CH_2OH)_2NH + H_2O \rightleftharpoons [(CH_2CH_2OH)_2NH]_2OH_2$$

$$[(CH_2CH_2OH)_2NH]_2OH_2 + CO_2 \rightleftharpoons \left[\left.\begin{matrix}(CH_2CH_2OH)_2NH_2^+\\(CH_2CH_2OH)_2NH_2^+\end{matrix}\right\rangle\right] CO_3^{=} \quad (6)$$

controlling. Others (*5*) propose the direct attack of carbon dioxide on the ethanolamine as the rate controlling step:

$$CO_2 + HOCH_2CH_2NH_2 \rightleftharpoons HOCH_2CH_2NHCOOH \rightleftharpoons HOCH_2CH_2NHCOO^- + H^+ \quad (7)$$

Ellis (*4*), in an attempt to explain his results for carbon dioxide absorption in monoethanolamine solutions, suggested that reaction (5) followed by hydrolysis to carbonate and bicarbonate products was in control. Until intermediates for the reactions have been successfully isolated and identified, uncertainties will remain about the mechanism and therefore the controlling step in the absorption.

No investigations of the rate of reaction between the pure ethanolamines and carbon dioxide are available in the literature. Goodridge (*7*) studied the initial absorption rate of carbon dioxide in pure monoethanolamine but found that the rate varied with the interfacial area which suggests mass transfer control.

In this study, a single component nonvolatile liquid absorbing a single component gas is considered. Gas-phase resistance and reaction in the gas phase are negligible, and the overall rate is controlled solely by the rates in the liquid phase.

EXPERIMENTAL

Measured amounts of carbon dioxide were absorbed isothermally in 250 ml. of non-volatile liquid diethanolamine. The absorption rate was determined by pressure-time measurements. Runs were made at reaction temperatures of 85°, 95°, and 105°F. The carbon dioxide pressure varied between 30 and 4 cm. of mercury and was measured to the nearest 0.5 mm. of mercury with mercury manometers. Stirring rates varied between 800 and 2,700 rev./min. Runs were made at diethanolamine conversions up to 50%, but the most useful data were taken at 10% or less.

In the experimental system, shown in Figure 1, flasks 1, 2, and 3 were used to store 15 liters of purified carbon dioxide slightly above atmospheric pressure. All significant volumes were calibrated to ± 1% by expanding carbon dioxide from flask 4 which had been calibrated before assembly.

The glass reactor, Figure 2, was a 500-ml. three-neck round-bottom flask modified with four equidistant baffles to insure adequate mixing. Gas entered the reactor from the feed section at A, passed through the sintered glass sparger at B, and impinged on the stirrer, C. During a run the reactor was submerged in an agitated water bath for temperature control. A thermowell was used to measure the absorption temperature. The stirrer shaft was sealed by a Teflon gland with rubber O-rings.

High-purity diethanolamine (mp. 26° to 28°C.) was used with no further purification. Anhydrous carbon dioxide was further purified by two successive freezing-sublimation processses, in traps 1 and 2 of Figure 1, during which 10 to 15% of both light and heavy ends were discarded.

The data and a detailed description of the apparatus and the experimental procedure used are available elsewhere (*14*). In general, the apparatus was similar to that used in a previous study (*15, 16*).

CORRELATION EQUATIONS

Consider the reaction

$$A(g) + 2D(l) \rightleftharpoons P(l) \tag{8}$$

taking place in the closed system illustrated in Figure 3. Carbon dioxide from a source volume, V_s, bubbles through liquid diethanolamine and also enters the liquid from a gas space above the liquid, V_r. The continuity equation for carbon dioxide in the liquid phase is

$$\frac{dC_A}{dt} = \frac{N_s + N_r}{V_l} - k_{nm}C^n{}_A C^m{}_D + k_a C^a{}_P \tag{9}$$

If we define a mass transfer coefficient, $k°$, by

$$\frac{N_s + N_r}{V_l} = k° \; (C_{Ai} - C_A) \tag{10}$$

and assume the interfacial concentration, C_{Ai}, to be equilibrium value given by Henry's law

$$C_{Ai} = p_l/H \tag{11}$$

then

$$\frac{N_s + N_r}{V_l} = k° \; (p_l/H - C_A) \tag{12}$$

From the gas law

$$N_s = -\frac{dn_s}{dt} = -\frac{V_s}{ZRT_s}\frac{dp_s}{dt} \tag{13a}$$

$$N_r = -\frac{dn_r}{dt} = -\frac{V_r}{ZRT_r}\frac{dp_r}{dt} \tag{13b}$$

Pressures in the two gas spaces differ by the liquid head, h, and the average pressure p_l is somewhere between these. The liquid head is small compared to p_s and p_r. These properties of the system lead to

$$p_s = p_r + h \tag{14a}$$

$$\frac{dp_s}{dt} = \frac{dp_r}{dt} = \frac{dp}{dt} \tag{14b}$$

$$p_l = p_r + h/2 = p + h/2 \tag{14c}$$

where the subscripts are dropped for brevity. Note that all pressures are written in terms of the pressure of the gas phase in the reactor. Substituting Equations (13) and (14) in Equation (12) results in

$$C_A = \frac{1}{k° \, RV_l}\left(\frac{V_s}{Z_s T_s} + \frac{V_r}{Z_r T_r}\right)\frac{dp}{dt} + \frac{p + h/2}{H} \tag{15}$$

Assuming constant temperature and liquid volume, the derivative of (15) is

$$\frac{dC_A}{dt} = \frac{1}{k° RV_l}\left(\frac{V_s}{Z_s T_s} + \frac{V_r}{Z_r T_r}\right)\frac{d^2p}{dt^2} + \frac{1}{H}\frac{dp}{dt} \tag{16}$$

A material balance on the carbon dioxide yields an expression for the diethanolamine concentration:

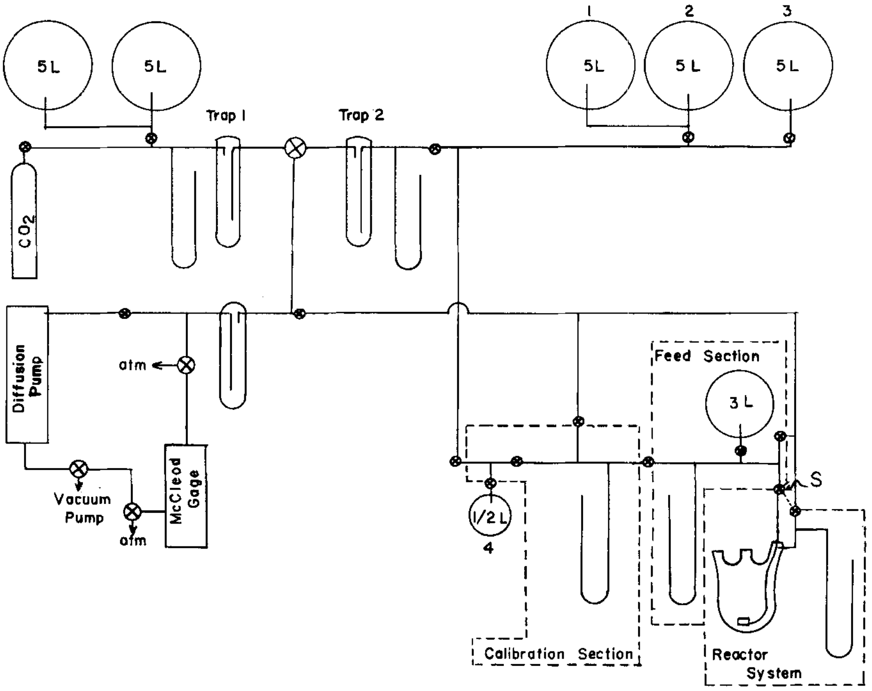

Fig. 1. Absorption apparatus.

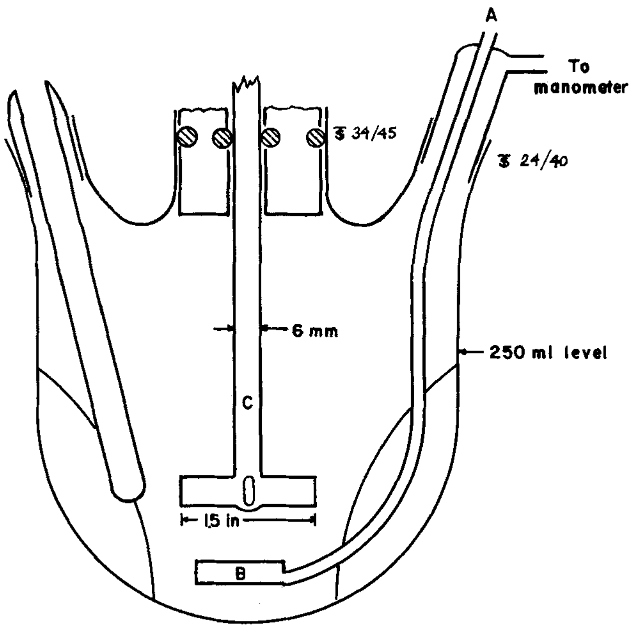

Fig. 2. Reactor.

$$C_D = 4\left\{G_0 - 2\left[n_0 - \frac{hV_s}{Z_sRT_s} - \frac{p}{R}\left(\frac{V_s}{Z_sT_s} + \frac{V_r}{Z_rT_r}\right) - V_lC_A\right]\right\} \tag{17}$$

Substituting Equations (12), (15), (16), and (17), in (9), ignoring the reverse reaction and assuming kinetic control ($k^\circ \rightarrow \infty$), gives

$$\Lambda\frac{dp}{dt} = -k_{nm}\,4^m\,V_l\left(\frac{p + h/2}{H}\right)^n (\xi + 2\Lambda p)^m \tag{18}$$

where

$$\Lambda = \frac{V_l}{H} + \frac{1}{R}\left(\frac{V_s}{Z_sT_s} + \frac{V_r}{Z_rT_r}\right) \tag{19}$$

$$\xi = G_0 - 2n_0 + \frac{2hV_s}{Z_sRT_s} + \frac{hV_l}{H} \tag{20}$$

Equation (18) was used to correlate the data.

ANALYSIS OF EXPERIMENTAL DATA

Both integral and differential techniques were used to analyze the experimental data. Each has its disadvantages. The integral method tends to eliminate differences between orders while the differential method requires differentiation of the data.

To determine the reaction order with respect to carbon dioxide it was assumed that C_D was constant, since changes in the diethanolamine conversion were very small during any one run. Equation (18) then reduces to

$$\frac{\Lambda\,dp}{(p + h/2)^n} = -\frac{k_q}{H^n}\,dt \tag{21}$$

When one plots the data in the integrated form of Equation (21), a first-order result for the order with respect to carbon dioxide is obtained.

To determine the order with respect to diethanolamine, Equation (18) was written with $n = 1$ and rearranged to

$$\frac{dp}{(p + h/2)\,(\xi + 2\Lambda p)^m} = -\frac{k_{1m}4^mV_l}{H}\,dt \tag{22}$$

Integrated forms of Equation (22) are given in Table 1.

If the differential method is used, Equation (22), after rearranging and taking logarithms, yields

$$\log - \left[\frac{\Lambda}{(p + h/2)}\,\frac{dp}{dt}\right] = m\log C_D + \log\frac{k_{1m}V_l}{H}$$

The integral method yielded inconclusive results, although a better correlation was obtained for $m = 2$. Repeated differentiations, however, clearly indicated that $m = 2$ as shown in Figure 4 wherein the results of two methods of differentiation are presented.

From these results it was concluded that the reaction was second order in diethanolamine and first order in carbon dioxide. Figure 5 shows the data plotted for $m = 2$ and $n = 1$, and Table 2 gives the pseudo-rate constants calculated from Equation (23). The integral method was used to calculate rate constants because of the error involved in differentiating the data.

DISCUSSION

Solubility Effects

An accurate evaluation of the solubility of carbon dioxide in diethanolamine is very difficult to give because the reaction between the two components cannot be stopped. Also, theoretical prediction of gas solubilities in polar solvents is highly uncertain. Therefore, the pseudo-rate constants contain the Henry's law constant for the system. An approximate value, $H \approx 5{,}000\ \frac{l\ \text{cm.}}{\text{c.m.-mole}}$ at 25°C., was calculated using Prausnitz's (12) method and showed that the terms $\frac{V_l}{H}\ln\Lambda$ and $\frac{hV_l}{H}$ in ξ were on the order of 10^{-2} and 4×10^{-5} and were negligible compared to other terms. Therefore, a negligible error was introduced by dropping these terms. The approximate H can also be used to estimate the absolute rate constant.

A further complication was introduced by the changing composition of the liquid. Since concentration changes during any one run were small, H remains essentially constant. However, the concentration varies from run to run in any given series. In an investigation of how H is affected if the solubility of carbon dioxide in the product is different from its solubility in diethanolamine, it was assumed that H follows an additive law of the form

$$H = x_DH_D + x_PH_P \tag{25}$$

where H_P is some multiple, b, of H_D. With a 10% conversion

$$H = H_D\,(0.948 + 0.052b) \tag{26}$$

Table 1. Equation (23)

$m = 1$	$\pi_{11} = \Lambda\left[\frac{1}{(\xi - h\Lambda)}\ln\left(\frac{p + h/2}{\xi + 2\Lambda p}\right)\right] = -\frac{k_{11}\,4V_l}{H}t + \text{constant}$
$m = 2$	$\pi_{12} = \Lambda\left\{\frac{1}{(\xi - h\Lambda)}\left[\frac{1}{(\xi + 2\Lambda p)} + \frac{1}{(\xi + h\Lambda)}\ln\left(\frac{h/2 + p}{\xi + 2\Lambda p}\right)\right]\right\} = -\frac{k_{12}\,4^2V_l}{H}t + \text{constant}$

If $b = 2$, H increases by 5% over a 10% conversion; if $b = 1/2$, H decreases by 2.5% over the same conversion range. Since H is relatively insensitive to large differences in H_P and H_D, the assumption that H is independent of composition leads to small errors in the pseudo-rate constants.

Kinetic Control

The assumption of negligible mass transfer effects (kinetic control) appeared to be justified since no change in the calculated rate constant occurred when large increases in contact area were produced by doubling and tripling the stirring rate. This indicates that the absorption rate is independent of the stirrer speed and is a characteristic of kinetic control. The liquid volume increase owing to gas bubbles below the surface ranged from slightly less than 5% to greater than 30% with the stirring rates used. Conservatively, this reflects a five- to tenfold increase in contact area. Furthermore, because of the high viscosity of diethanolamine ($\mu \sim 150$ cp.) slippage effects were probably negligible.

The temperature dependence of the rate also gives an indication of the region in which the absorption is occurring with a strong dependence indicating kinetic control. Since the dependence of the Henry's law constant on temperature was unknown, it was necessary to assume H constant to make the customary Arrhenius plot. The activation energy calculated from such a plot, 13,000 cal./gm.-mole carbon dioxide, does not clearly establish kinetic control but is at least out of the range of ordinary mass transfer control. Furthermore, the calculated activation energy is probably less than the true value since the Henry's law constant generally increases with temperature. To illustrate this, suppose the temperature dependence of Henry's law constant is given by

$$H = H_o \, e^{\frac{-L}{RT}} \tag{27}$$

Then

$$\frac{k}{H} \propto e^{\left(\frac{-\Delta E + L}{RT}\right)} \tag{28}$$

and thus $\Delta E = 13{,}000 + L$.

Finally, criteria for eliminating diffusional effects, developed from a hypothetical model (*6*) which simulates the experimental system, predicted that the absorption would be kinetically controlled.

Runs at High Conversions

A majority of the runs were made at conversions of 10% or less to keep variations of H to a minimum. However, to investigate the absorption-system properties at higher conversions, runs were also made at 30 and 50% conversions, and the absorption continued until the product precipitated as a white solid at 68 ± 3% diethanolamine conversion.

Pseudo-rate constants for the runs at higher conversions were considerably lower than those at lower conversions and show a large standard deviation. Two effects are possible explanations. It was noted that the viscosity of the liquid increased considerably with increasing conversion. The Stokes-Einstein equation (*2*)

$$D_v \mu / T = \text{constant} \tag{29}$$

shows that if μ increases at constant temperature, then the diffusivity must decrease. Increasing viscosity, then, has the dual effect of increasing mixing problems and decreasing D_v. Each effect increases the possibility that the absorption is mass transfer controlled. Furthermore, if these effects were eliminated, the possibility remains that

TABLE 2.
Pseudo-Rate constants

Run	rev./min.	Avg. conv. %	$\frac{4^2 k_{12} V_l^*}{H} 10^5$	Std. dev. $\times 10^5$
		85°F.		
14.1	900	1.8	2.39	0.17
14.3	900	8.0	2.36	0.11
20.1	900	2.3	2.52	0.18
20.2	900	4.9	2.45	0.16
20.3	810	8.2	2.41	0.13
20.4	850	10.7	2.33	0.25
20.5	1080	13.3	2.26	0.16
26.1	1800	2.4	2.43	0.13
26.2	1800	5.4	2.52	0.11
30.1	900	14.2	2.28	0.12
30.2	1080	32.6	1.81	0.36
30.3	1080	48.6	1.66	0.38
		95°F.		
21.2	950	5.7	3.50	0.07
21.3	950	9.3	3.41	0.03
27.1	1800	3.4	3.36	0.13
27.2	1800	7.7	3.59	0.14
27.3	2700	11.0	3.56	0.18
		105°F.		
24.1	900	2.8	4.04	0.11
24.2	900	6.9	4.05	0.09

* Units are $\left(\frac{1}{\text{min.}}\right)\left(\frac{\text{liter}}{\text{gm. moles (HOCH}_2\text{CH}_2)_2\text{NH}}\right)^2\left(\frac{\text{gm. moles CO}_2}{\text{cm. Hg-liter}}\right)\left(\text{liters}\right)$.

$V_l \sim 250$ ml.

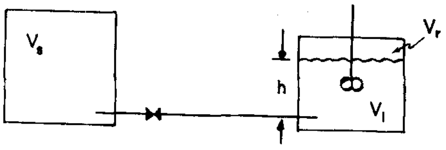

Fig. 3. Reactor schematic.

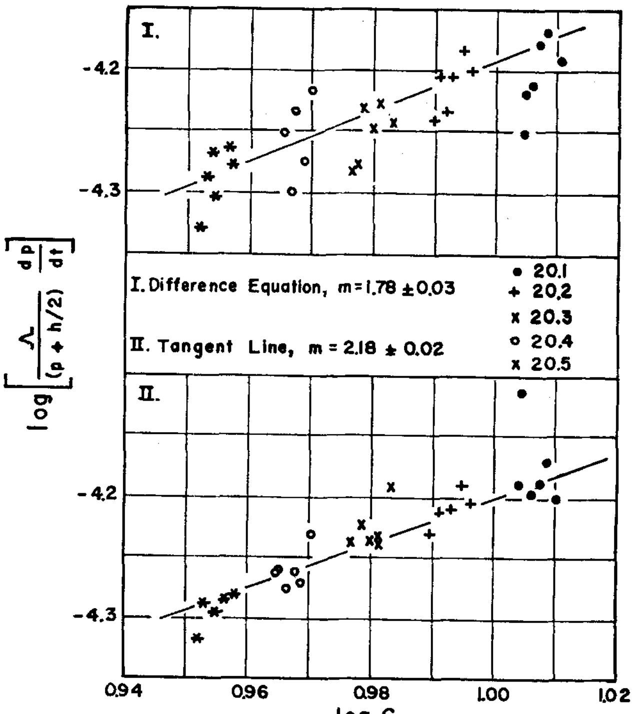

Fig. 4. Order determination, differential method.

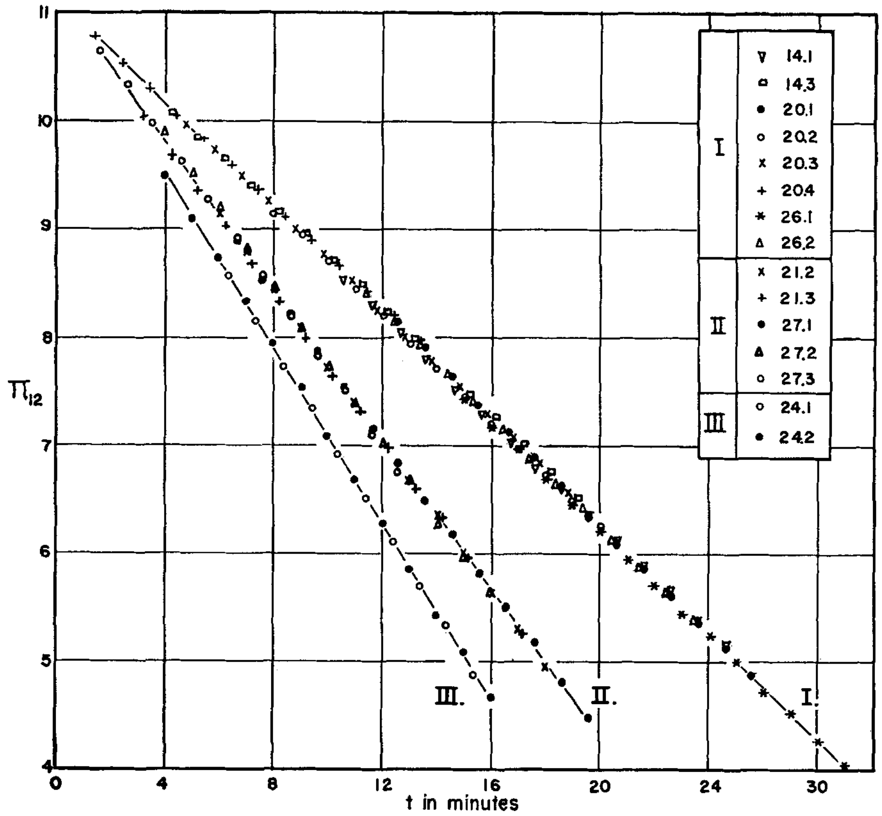

Fig. 5. Order determination, $m=2$, $n=1$.

the reverse reaction, which was not considered in the analysis, becomes important as the conversion increases, thereby invalidating the analysis. For these reasons the runs at higher conversions were not used in calculating average pseudo-rate constants.

Mechanism Speculation

The overall reaction between carbon dioxide and diethanolamine is presumably (*7*, *8*, *9*)

$$CO_2 + 2(CH_2CH_2OH)_2NH \rightarrow (CH_2CH_2OH)_2NCOONH_2(CH_2CH_2OH)_2 \qquad (30)$$

Experimentally the rate equation was found to be second-order in the diethanolamine and first-order in the carbon dioxide. That the mechanism follows the stoichiometry given above is highly unlikely since the simultaneous joining of three molecules is infrequent. Therefore a more reasonable mechanism explaining the derived order was sought.

The equation for the direct attack of carbon dioxide on diethanolamine is (*5*, *7*)

$$CO_2 + (CH_2CH_2OH)_2NH \rightleftharpoons (CH_2CH_2OH)_2NCOOH \rightleftharpoons (CH_2CH_2OH)_2NCOO^- + H^+ \qquad (31)$$

with a rate constant on the order of 3,000 liter/(mole sec.) at 18°C. Using this as a starting point the following reactions are possible steps in the mechanism of reaction (30):

$$(CH_2CH_2OH)_2NH + H^+ \rightleftharpoons (CH_2CH_2OH)_2NH_2^+ \qquad (32)$$

$$(CH_2CH_2OH)_2NH_2^+ + (CH_2CH_2OH)_2NCOO^- \rightarrow (CH_2CH_2OH)_2NCOONH_2(CH_2CH_2OH)_2 \qquad (33)$$

In view of the high rate constant for Equation (31), the experimental absorption rate was too slow to be governed by this reaction. Reaction (32) probably occurs instantaneously since it involves the transfer of a proton. Clearly, if the mechanism holds, reaction (33) must be the slow step and the others can be considered to be at equilibrium. The rate relationship for (33) is

$$d\,[R_2NCOONH_2R_2]/dt = k\,[R_2NH_2^+]\,[R_2NCOO^-] \qquad (34)$$

Using the equilibrium expressions

$$\frac{[R_2NCOOH]}{[CO_2][R_2NH]} = K \qquad (35a)$$

$$\frac{[H^+][R_2NCOO^-]}{[R_2NCOOH]} = K' \qquad (35b)$$

$$\frac{[R_2NH_2^+]}{[R_2NH][H^+]} = K'' \qquad (35c)$$

and the expression for one-to-one correspondence between moles produced and consumed

$$d\,[R_2NCOONH_2R_2]/dt = -\,d\,[CO_2]/dt \qquad (36)$$

the rate at which carbon dioxide is used by the reaction is

$$-\,d\,[CO_2]/dt = kKK'K''\,[CO_2][R_2NH]^2 \qquad (37)$$

which agrees with the experimentally determined orders.

Ellis (*4*) has suggested reaction (30) as a possible controlling step in the mechanism of carbon dioxide absorption in aqueous solutions of the ethanolamines. In view of present experimental results, it is unlikely that this reaction is significant in the mechanism since the absorption would then be much slower than Ellis observed.

CONCLUSIONS

1. The reaction between carbon dioxide and anhydrous diethanolamine was studied in the kinetic region. Pseudo-rate constants involving the Henry's law constant for the system were determined.
2. Consistent and reproducible data were obtained and

successfully correlated by the relationship developed for kinetic control.

3. The reaction between carbon dioxide and diethanolamine is third-order; first-order in carbon dioxide and second order in diethanolamine.

4. A speculative mechanism explaining the observed order was developed.

5. It seems improbable that the reaction

$$CO_2 + 2(HOCH_2CH_2)_2NH \rightleftharpoons \text{product} \qquad (38)$$

is the controlling step in the absorption of carbon dioxide in aqueous solutions.

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NOTATION

A = gaseous reaction component
a = reaction order with respect to component P
C = concentration
D = liquid reaction component
G = moles of diethanolamine
H = Henry's law constant defined by Equation (11)
ΔE = activation energy
h = liquid head illustrated in Figure 3
K, K', K'' = equilibrium constants defined by Equation (35)
k = reaction rate constant
k° = mass transfer coefficient defined by Equation (10)
L = temperature coefficient for H
m = reaction order with respect to component D
N = gas flux across gas-liquid interface
n = reaction order with respect to component A
P = component P
p = gas pressure
R = gas constant
T = absolute temperature
t = temperature
V = volume
x = mole fraction
Z = compressibility
Λ = defined by Equation (19)
μ = viscosity
ξ = defined by Equation (20)
Π_{11}, Π_{12} = defined by Equation (23)

Subscripts

A = component A
a = reaction order of component P
D = component D
i = interfacial
l = liquid phase
n = moles
P = component P
q = pseudo-value
r, s = gas phases of Figure 3
0 = initial value

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Effects of Solute Purity, Temperature, and Surfactants on Solid-Liquid Mass Transfer

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Mass transfer in solid-liquid systems has been investigated widely in a variety of geometries and for a number of solute-solvent combinations. The literature in this area emphasizes the effects of agitation and the physical properties of diffusivity and kinematic viscosity. Data are generally correlated by the dimensionless grouping

$$N_{Sh} = aN^{\alpha}_{Re} N^{\beta}_{Sc} \qquad (1)$$

The variables that are used in defining the Sherwood and Reynolds numbers depend on the system geometry. In particular, for mixed vessels of various types, the Sherwood number includes a linear dimension characteristic of the container or impeller size, and the Reynolds number is based on the rotational speed of the mixing device. This method of correlation was motivated at least in part by the great interest in the analogy between momentum, heat, and mass transfer.

In the present work the effects on mass transfer of solute purity, temperature, and the concentration of surface-active agents were studied. No previous work on solute purity could be found in the literature; however, several earlier investigations did study the effect of temperature. The experiments of Johnson and Huang (*21*) included a series at 10°C., 25°C., and 40°C. for the