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Plate Efficiency with Chemical Reaction—Absorption of Carbon Dioxide in Monoethanolamine Solutions

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The effect of chemical reaction on plate efficiency has been given little attention in the determination of bubble-plate efficiencies, although it is of importance in many operations. A typical example is the absorption of carbon dioxide in monoethanolamine solutions.

The over-all Murphree gas-phase plate efficiency can be shown to be a function of $K_g(A/V)$ where A/V is the interfacial surface area formed per tray per unit volume of gas. In order to evaluate variations in tray efficiency due to factors influencing K_g, data available in the literature for the absorption of carbon dioxide in monoethanolamine were considered. These showed that the liquid film was controlling and that for a packed column at constant liquid rate the absorption coefficient could be satisfactorily expressed by an equation that resembles somewhat equations which have been developed for the effect of rapid second-order reactions on k_L. However, the observed effect of carbon dioxide partial pressure in the gas is not so great as the theoretical equations would predict.

By use of the equation mentioned above to predict K_g, satisfactory correlation of observed plate efficiencies is obtained for a commercial column over a considerable range of conditions. It appears that the correlation can be extended to other pressures, flow rates, and column designs by an evaluation of the effect of these variables on A/V and K_g.

The estimation of plate efficiencies has only recently been approached from a theoretical basis, and for the general cases of distillation and physical absorption some success has been noted. The effect on plate efficiency of chemical reaction in the liquid phase has apparently been given little attention, although a large number of industrial absorption operations depend upon processes of this type.

Methods of estimating plate efficiency based upon an attempted visualization of the actual bubbling action at a single point have been discussed by Geddes (*6*), West et al. (*20*), Chu (*2*, *3*), and others. The problem of predicting the effect of chemical reaction upon absorption has been treated by Sherwood and Pigford (*14*); by Van Krevelen and Hoftijzer (*17*); and recently by Perry and Pigford (*12*), who used a digital computer to solve the diffusion equations for the case of second-order reactions. The ultimate answer to the calculation of plate efficiency in the presence of chemical reaction would be to determine the effect of the reaction on the liquid-film coefficient by means of a fundamental treatment and, subsequently, to relate both liquid and gas film coefficients to the plate efficiency through an accurate analysis of phenomena occurring in the bubble zone. Unfortunately, it does not appear that this can be accomplished at the present time because of a lack of data on reaction kinetics and because of some fundamental inadequacies in the knowledge of what happens on bubble trays. It is therefore proposed that the problem be handled by an empirical technique.

The absorption of carbon dioxide by monoethanolamine solutions is an important commercial process particularly with regard to gas purification and dry-ice manufacture. In either application it is necessary to predict the number of plates required to effect the desired removal of carbon dioxide from the gas and to ascertain the degree of saturation which can be expected in the solution.

Equilibrium data for carbon dioxide over a typical aqueous monoethanolamine solution (15%) are presented in Figure 1. This chart is based on a cross plot of the data of Lyudkovskaya and Leibush (*8*), Mason and Dodge (*10*), and Reed and Wood (*13*). As can be seen for conditions encountered in the absorber, at solution concentrations below about 0.5 mole of carbon dioxide/mole of monoethanolamine and temperatures below about 150° F., the equilibrium partial pressure of carbon dioxide over the liquid is negligible. Stoichiometrically, 0.5 mole of carbon dioxide would be expected to react with 1 mole of monoethanolamine in water to form the compound monoethanolamine carbonate.

Although the liquid film resistance is apparently controlling in this system, gas-phase plate efficiency has been considered because the degree of carbon dioxide removal from the gas stream is normally more important than the solution concentration change per plate and because the gas-phase driving force can be estimated more readily. If it is assumed that the equilibrium at the interface is one of physical solubility, for which Henry's Law applies, and the concentration of molecular carbon dioxide in the body of the liquid is zero, the driving force in the liquid for unreacted carbon dioxide will be proportional to the carbon dioxide partial pressure.

BASIC EQUATIONS

The assumption of zero vapor pressure over the solution at equilibrium simplifies the efficiency equation. The equation for point efficiency on any tray becomes

$$E_{OG} = \frac{y_{n+1} - y_n}{y_{n+1}} \tag{1}$$

where

E_{OG} = Murphree point efficiency based on gas

y_{n+1} = mole fraction CO_2 entering point on tray n (leaving $n + 1$)

y_n = mole fraction CO_2 leaving point on tray n

Integration of the basic rate equation can be shown to yield an equation of the form

$$\ln (1 - E_{OG}) = -\frac{K_g a P h}{N} \tag{2}$$

where

K_g = over-all mass transfer coefficient

a = interfacial area per foot of depth

P = total pressure

h = height of contact zone

N = gas rate, moles per unit cross-sectional area

which may be simplified to

$$E_{OG} = 1 - e^{-\frac{K_g A R T_A}{V}} \tag{3}$$

in which A equals ah, the interfacial area per tray, T_A is the absolute temperature, and V is the actual volumetric gas rate.

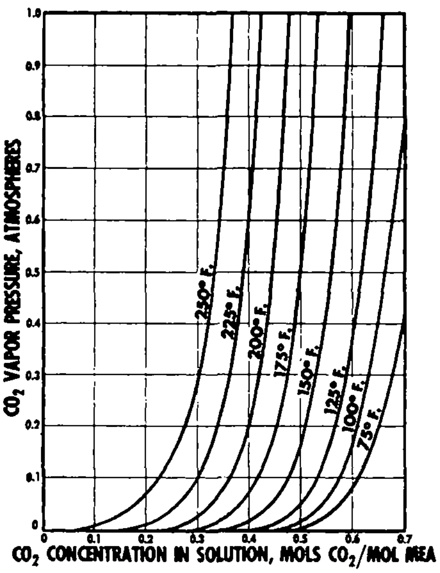

Fig. 1. Vapor pressure of carbon dioxide over 15% monoethanolamine (approx. 2.5*M*).

For the carbon dioxide–monoethanolamine system, the gas composition in equilibrium with the solution leaving each tray is essentially the same as it is with respect to the solution at any point on the tray, i.e., zero carbon dioxide. The Murphree vapor efficiency E_{MV} is therefore equal to the point efficiency E_{OG} expressed by the foregoing equations.

It is believed that A/V, the ratio of the area of surface formed to the actual volume rate of gas passed, is relatively constant for any given tray operating near design flow rates. For approximate efficiency estimates, it appears that an empirical correlation of A/V with physical properties of the system and operating characteristics of the tray is more satisfactory than an attempted theoretical analysis. With columns operating at the same pressure and employing approximately the same vapor velocity and tray design, it is convenient to assume that A/V is a constant. $K_g(A/V)$ can then be correlated much the same as $K_g a$ for packed towers.

The over-all coefficient K_g is related to the individual coefficients by

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{H}{k_L} \tag{4}$$

where the Henry's Law constant H refers to physical absorption at the interface and k_L represents the coefficient for the transfer of molecular carbon dioxide away from the interface. Because of the chemical reaction occurring in the liquid, k_L is greater than would be predicted for simple physical absorption. However, the observed low plate efficiencies of 8 to 25% indicate that the liquid film is largely controlling, as columns operating with gas film controlling (absorption of ammonia, evaporation of water) give plate efficiencies of 80% and higher.

On the basis of observed efficiencies, it is estimated that the liquid-film resistance comprises from 85 to 95% of the total for efficiencies typically encountered in the carbon dioxide absorption units. For the purpose of developing an empirical correlation, it is therefore assumed that $1/K_g$ is essentially equal to H/k_L. It should be noted, however, that k_g becomes more important at higher tray efficiencies and this simplification would introduce an appreciable error for cases where the total tray efficiency exceeds about 25%.

EVALUATION OF K_g

Effect of Carbon Dioxide Concentration

The data of Shneerson and Leibush (*16*) are valuable in establishing the nature of the reaction between carbon dioxide and dilute amines. They show $K_g a$ for a packed column to decrease linearly with carbon dioxide concentration in the solution, approaching zero at concentrations equivalent to about 0.5 mole of carbon dioxide/mole of monoethanolamine (MEA). This effect was also noted by Comstock (*5*). These studies were made at atmospheric pressure with relatively low carbon dioxide partial pressures, conditions under which a concentration of 0.5 mole of carbon dioxide/mole of monoethanolamine is a fair approximation of equilibrium. The relation undoubtedly does not hold at very high carbon dioxide partial pressures, for which the equilibrium concentration may be 0.7 mole of carbon dioxide/mole of amine or even higher. It is therefore suggested that for high-pressure operations the effective amine concentration be considered proportional to the difference between the equilibrium concentration of carbon dioxide and the actual concentra-

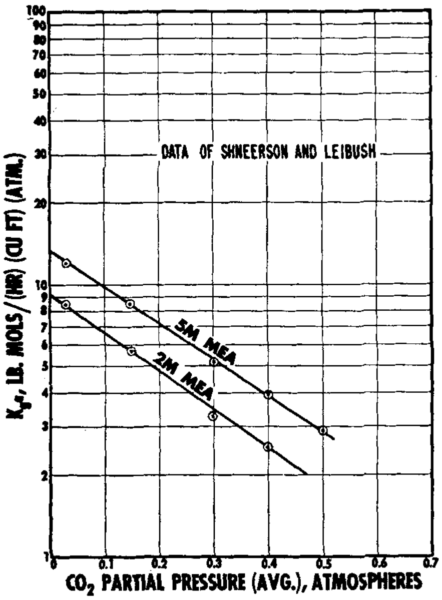

Fig. 2. Effect of carbon dioxide partial pressure on K_ga in packed column.

tion of carbon dioxide in the body of the liquid ($C_e - C$).

Effect of Amine Concentration and Viscosity

With increased amine concentration, Shneerson and Leibush found K_ga to increase up to 6 or 7 molar, then to decrease sharply. The latter effect is probably due principally to the viscosity increase, although it is expected that the decreased ionization of the amine at higher concentrations may also affect the transfer coefficient. In the region of concentrations normally used commercially (2 to 5 molar) K_ga appears to vary directly with amine concentration when corrected for viscosity change according to the relationship $K_ga \sim M/\mu^{0.68}$ where M is the amine concentration. Viscosity data for lean monoethanolamine solutions are available in the literature(*1*). The presence of carbon dioxide in the solution increases the viscosity somewhat; however, no published data on the relationship are available. For estimating purposes, it was assumed that the solution viscosity increased about 0.3% for each volume of carbon dioxide absorbed per volume of solution—a relationship indicated by limited tests on a 30% solution.

Effect of Temperature

Shneerson and Leibush (*16*) conducted tests at several temperatures ranging from 77° to 167°F. and found that K_ga increased with increased temperature up to 122°F. and leveled off or decreased in the range from 122° to 167°F. If the increase in the lower range is assumed to be due to viscosity change alone, it would be required that K_ga be proportional to $1/\mu^{1.3}$.

This is the same exponent observed by Walter and Sherwood (*19*) for the effect of viscosity change due to temperature variation on H_L (height of a liquid-phase transfer unit) for the desorption of carbon dioxide from water in a plate column. It is quite probable that the effect due to increased temperature is the result of viscosity decrease, reaction-rate increase, and other physical changes.

The data of Shneerson and Leibush (*16*) were plotted as $K_ga\mu^{0.68}$ vs. T °F. to determine the function of temperature after removal of the effect due to viscosity. This plot indicated that K_ga varies as $e^{0.0067T}$ at constant viscosity. This may be compared with $e^{-0.013T}$ reported by Sherwood and Pigford (*15*) as the effect of temperature on H_L. Their exponent, however, also includes the effect due to viscosity change with temperature. It should be pointed out that the foregoing relationship for effect of temperature on K_ga in carbon dioxide absorption, using monoethanolamine solutions, was found to hold reasonably well up to about 125°F. Above this point, increased temperature was found actually to decrease K_ga so that use of the relationship must obviously be limited accordingly.

It cannot be expected that viscosity will have exactly the same effect upon K_g in a plate column as it would upon K_ga in a packed absorber. However, it is of interest to note that a for packed columns is not generally considered to vary with viscosity, and studies with bubble-cap absorbers (*15*) indicate that the interfacial area in such devices is also unaffected by viscosity. If, then, the principal effect of viscosity change is on diffusion in the liquid film, it can be expected that μ will have approximately the same exponent in its effect on k_L in either plate or packed columns.

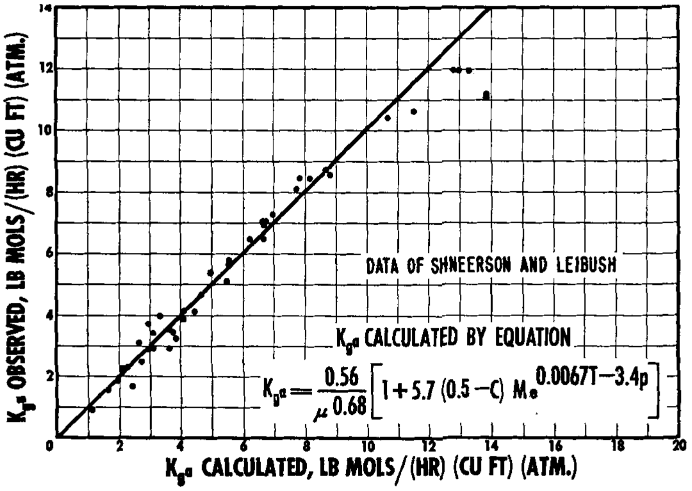

Fig. 3. K_ga correlation for packed column.

Carbon Dioxide Partial Pressure

The packed-column absorption data also show a marked effect of carbon dioxide partial pressure on K_ga. A decrease in k_L with increased concentration of carbon dioxide at the interface is predicted by Sherwood and Pigford (*14*) for a rapid second-order irreversible reaction. If, for example, it is assumed that $D_A/D_B = 2$ where A refers to carbon dioxide and B refers to monoethanolamine, these authors show that if a rapid second-order reaction occurs,

$$k_L/k_L' = 1 + (1/2)(q/C_{Ai}) \quad (5)$$

to a close degree of approximation. In this equation k_L' represents the liquid-film coefficient if no reaction occurs, q refers to the concentration of B (unreacted monoethanolamine) in the body of the liquid, and C_{Ai} refers to the concentration of A (carbon dioxide) at the interface. For the carbon dioxide–monoethanolamine system, q is approximately equal to $2(0.5 - C)M$. According to Equation (5), at very low partial pressures of carbon dioxide it is possible for k_L to become so large that the gas film would become controlling, and at very high partial pressures the liquid-film coefficient would approach that for no reaction.

The absorption of carbon dioxide in aqueous monoethanolamine solutions apparently does not follow Equation (5) exactly, as the carbon dioxide partial pressure has not been found to have so great an effect on K_ga as does the amine concentration in the region of partial pressures investigated. Instead of an

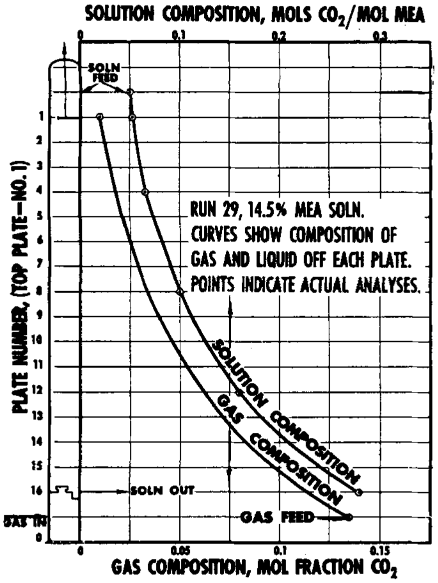

Fig. 4. Composition profile for commercial absorber.

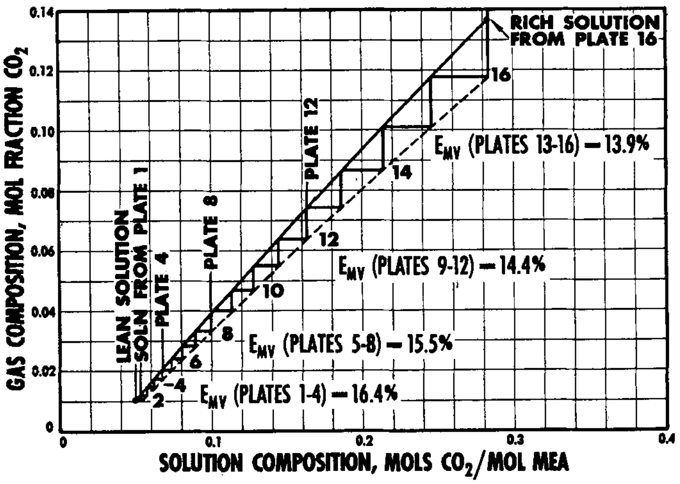

Fig. 5. Plate-efficiency diagram for run 29, solution 14.5 monoethanolamine, solution analyses at plates indicated.

approximately linear relationship with respect to $1/C_{A_i}$ (or $1/p$), $K_g a$ appears to vary with $e^{-3.4p}$, as shown in Figure 2. However, there is serious doubt that the coefficient would continue to decrease at the same rate at very high partial pressures of carbon dioxide, and so use of this equation appreciably above the range of the data may not be warranted. Insufficient data are available to prove or disprove the expression for absorption in bubble-tray equipment, but as the effect is apparently related to absorption through the liquid film, it seems reasonable to assume that a similar relationship holds.

Over-all Equation for $K_g a$

The various factors discussed above would yield an over-all equation for the absorption of carbon dioxide in aqueous monoethanolamine solutions in a packed tower at constant liquid rate of the form

$$K_g a = \frac{B(0.5 - C)Me^{0.0067T - 3.4p}}{\mu^{0.68}} \quad (6)$$

All the Shneerson and Leibush (*16*) runs for which sufficient data are available have been correlated by use of this equation, and B is indicated to be equal to 3.7. These data were obtained with a 1-in.-diam. column packed with 5- to 6-mm. glass rings at a liquid flow rate of 695 lb./(hr.)(sq. ft.) and for gas velocities varying from 0.09 to 0.55 ft./sec.

Somewhat better correlation of the data is obtained with the equation

$$K_g a = \frac{0.56}{\mu^{0.68}} [1 + 5.7(0.5 - C)M \cdot e^{0.0067T - 3.4p}] \quad (7)$$

A plot of the observed $K_g a$ vs. that calculated by this equation is given in Figure 3. Comparison of this equation with that given by Sherwood and Pigford (*14*) and described above for a rapid second-order irreversible reaction indicates that if the concentration of reactive amine q were reduced to zero (by M becoming 0 or by C becoming 0.5), $K_g a$ would be the same as for physical absorption, in this case equal to $0.56/\mu^{0.68}$.

Absorption in Plate Columns

For the case where E_{MV} is the same for each plate in a column and both operating and equilibrium lines are straight, an equation has been developed which enables the number of actual plates to be calculated (*9*). For the highly simplified case where the equilibrium line lies on the x axis ($m = 0$ and $y_e = 0$), the equation reduces to the expression

$$n = \frac{\ln (y_1/y_2)}{-\ln (1 - E_{MV})} \quad (8)$$

Combining with Equation (3) yields an expression for $K_g(A/V)$ in terms of the inlet and outlet gas composition

$$K_g\left(\frac{A}{V}\right) = \frac{\ln (y_1/y_2)}{nRT} \quad (9)$$

where

n = number of plates
y_1 = composition of the feed gas
y_2 = mole fraction of solute in gas leaving

Operating data from a 4-ft.-diam. commercial absorber have been analyzed by use of the foregoing equation. The column contained sixteen trays at 2-ft. spacing with fifteen rectangular caps per tray. The design employed for the caps and overflow weir resulted in an average slot submergence of about 3 in. during normal operation. Gas rate through the column varied from about 0.6 × 10^6 to 3.3 × 10^6 std. cu. ft./day with the majority of runs made at a gas flow rate of approximately 3 × 10^6 std. cu. ft./day. The lean-solution flow rate varied from 120 to 180 gal./min. with most runs at about 160 gal./min. As plate-efficiency calculations were based entirely on analytical data, exact flow rates were not measured during each sampling period; however, occasional checks indicated material balances within about 5%. For the run illustrated by Figures 4 and 5, for example, the gas flow to the column was indicated to be 2.89 × 10^6 std. cu. ft./day and the lean-solution rate 152 gal./min. (of 14.5% monoethanolamine). On the basis of the gas-composition change from 13.7 to 1.0% carbon dioxide and the aforementioned gas rate 40.8 moles of carbon dioxide was absorbed from the gas/hour. This may be compared with 42.3 moles/hour indicated absorption on the basis of the solution rate and composition change from 0.050 to 0.283 mole carbon dioxide/mole monoethanolamine. (*See* Figure 5.)

As most of the data were for a gas flow rate of approximately 3 × 10^6 std. cu. ft./day through this column, the factor A/V was taken as unity for this rate, and $K_g(A/V)$ values based upon Equation (9) were correlated on the basis of an equation of the general form of (7) above. Equation (9) is, of course, most nearly correct for small sections of the column in which

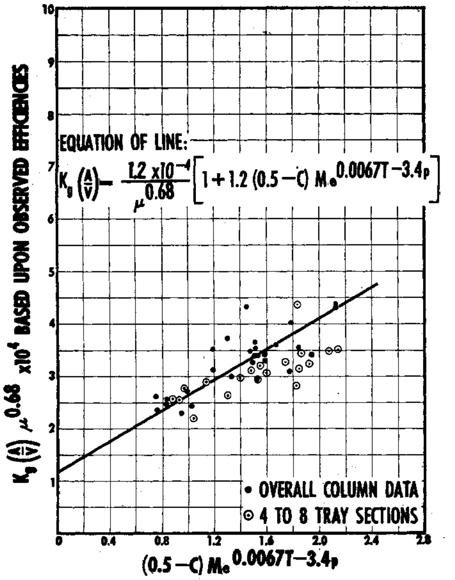

Fig. 6. Determination of $K_g(A/V)$ equation for carbon dioxide absorption in plate columns.

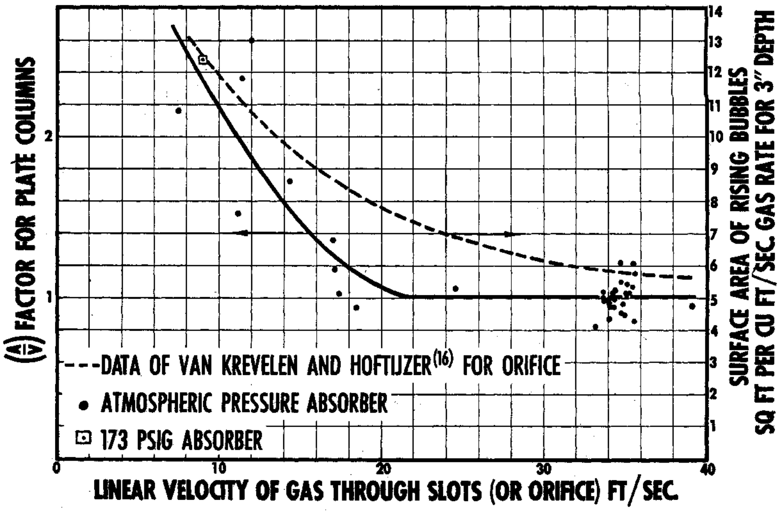

Fig. 7. Effect of gas velocity through slots on the interfacial area in bubble-plate columns.

it can be expected that the change in efficiency will not vary greatly. Available column-profile data were therefore considered first to determine the approximate efficiency range occurring throughout the column. A typical composition profile is shown in Figure 4. Because of the manner in which gas and liquid composition varied with column height, log mean values of these variables were used to express average conditions in column sections. A plate-efficiency diagram is shown in Figure 5 for a profile based upon solution analyses at three points in the column, plus inlet and outlet conditions. As can be seen, the efficiency variation was not very great throughout the entire column. This was due principally to the relatively small liquid-concentration change occurring in the test tower and is not generally true of plants of this type.

A study of the profile data indicated that for this particular operation over-all efficiencies could be used for correlation purposes. This would permit use of test data covering a much wider range of conditions. A summary of these data is presented in Table 1.* The temperature given for each run represents a simple average between the feed and exit solution temperatures. Solution viscosity at this average temperature was used for correlation purposes. $K_g(A/V)\mu^{0.68}$, based upon the observed efficiency, was first plotted against $(0.5 - C)M\ e^{0.0067T-3.4p}$ for average conditions in the column to obtain the intercept and slope. This plot, which is given in Figure 6, indicated that $K_g(A/V)$ for these operations can best be expressed by the equation

$$K_g\left(\frac{A}{V}\right) = \frac{1.2 \times 10^{-4}}{\mu^{0.68}} \cdot \left[1 + 1.2(0.5 - C)Me^{0.0067T-3.4p}\right] \tag{10}$$

Points representing small sections of the column derived from profile data are also shown on the chart. As the profile points represent only five runs and because they are somewhat less certain, owing to the large effect of minor analytical errors on observed $K_g(A/V)$ for the column sections, the position of the line was based on the over-all column data. In order to use the data from a few tests in which the operating temperature was above the range for which the relationship $K_g \sim e^{0.0067T}$ was known to hold, it was assumed that the temperature effect had an equal reverse slope above 125°F. A corrected value for T was therefore used for these high-temperature runs, obtained by subtracting from 125°F. a figure equal to the number of degrees by which the actual temperature exceeded 125°F. This relationship is not included in the final correlation because of its uncertainty. Comparison of Equation (10) with the analogous one obtained for the packed-column data [Equation (7)] reveals that the portion of the equation which represents the influence of the reaction is appreciably smaller in the case of the plate columns. The reason for this is not known, although it is possible that the use of data representing several trays or the entire column, instead of point conditions, may have contributed to this effect.

Effect of Gas Rate

It was noted that at low gas velocities in the atmospheric-pressure carbon dioxide absorber appreciably higher efficiencies were obtained. The increased efficiency was considerably above what could be expected on the basis of decreased carbon dioxide concentration in the liquid. Data from a high-pressure column (which was designed for a lower gas velocity) also showed appreciably higher efficiency at design conditions than the low-pressure absorber operated at its design gas rate.

As bubble size and, in fact, the bubbling mechanism on the plate are greatly influenced by gas rate, it is expected that this would be an important variable. Although the data are inadequate for a satisfactory analysis, they show a definite trend which may be of value in utilizing the basic correlation for other columns. These data are plotted in Figure 7 as the A/V factor vs. the linear velocity of gas through the bubble-cap slots. The A/V factor was obtained by dividing $K_g(A/V)$, based on observed column efficiency, by the $K_g(A/V)$ obtained by the use of Equation (10). This, of course, results in an average A/V factor of 1.0 for the runs used as a basis for the equation.

For comparison purposes, a curve has been included on the figure which is based upon the data of Van Krevelen and Hoftijzer (*18*) for air bubbles formed at a single orifice 2.3 mm. in diam. submerged in water and in glycerol solutions. This curve indicates the effect of linear velocity through the orifice on the surface area of the rising bubbles per unit rate of gas flow. The values have been calculated for a 3-in. liquid depth to make the work more comparable with the commer-

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*Table 1, as published, presents sample runs. Data for the complete series of forty-three runs may be obtained as document 4794 from the Photoduplication Service, American Documentation Institute, Library of Congress, Washington 25, D. C., for $1.25 for photoprints or 35-mm. microfilm.

Table 1A. Atmospheric-pressure Absorber (Sixteen Trays 48-in. I.D., 24-in. Tray Spacing)—Gas Rate Constant—Slot Velocity Approximately 35 Ft./Sec.

Run	CO$_2$ in gas y_1	CO$_2$ in gas y_2	E_{MV}, avg. observed, %	CO$_2$ in soln., moles/mole MEA In	CO$_2$ in soln., moles/mole MEA Out	MEA conc. molarity, M	Temp., °F., avg. in column	$K_g(A/V)$ observed, $\times 10^{-4}$	$K_g(A/V)$ calculated, $\times 10^{-4}$	E_{MV}, avg. calculated, %
1	0.0940	0.0190	9.5	0.068	0.244	1.73	92	2.49	2.39	9.16
6	0.0960	0.0140	11.3	0.079	0.300	1.53	127	2.82	3.13	12.49
11	0.0950	0.0085	14.0	0.135	0.256	2.70	108	3.54	3.24	12.52
16	0.0950	0.0080	14.3	0.119	0.219	3.60	104	3.76	3.73	14.18
21	0.1350	0.0185	11.6	0.046	0.274	2.16	109	3.00	3.11	12.07
26	0.1058	0.0060	16.2	0.053	0.230	2.21	147	4.06	3.91	15.89

Table 1B. Atmospheric-pressure Absorber—Profile Data—Gas Rate Constant—Slot Velocity Approximately 35 Ft./Sec.

Run	Plate section	CO$_2$ in gas y_1	CO$_2$ in gas y_2	E_{MV}, avg. observed, %	CO$_2$ in soln. mean conc., moles/mole MEA	MEA conc. molarity, M	Temp. (avg.), °F.	$K_g(A/V)$, observed $\times 10^{-4}$	$K_g(A/V)$, calculated $\times 10^{-4}$	E_{MV}, avg., calculated, %
29	1–4	0.0205	0.0100	16.40	0.058	2.37	133	4.16	5.09	19.8
	5–8	0.0403	0.0205	15.52	0.084	2.37	135	3.89	4.79	18.6
	9–12	0.0752	0.0403	14.37	0.132	2.37	137	3.57	4.56	17.9
	13–16	0.1370	0.0752	13.89	0.223	2.37	139	3.43	3.47	14.0
31	1–4	0.0260	0.0160	11.43	0.061	2.32	113	2.91	4.01	12.8
	5–8	0.0458	0.0260	13.18	0.090	2.32	118	3.36	4.16	16.1
	9–12	0.0818	0.0458	13.49	0.145	2.32	123	3.41	3.67	14.4
	13–16	0.1340	0.0818	11.61	0.246	2.32	127	2.89	2.88	11.6

Table 1C. Atmospheric-pressure Absorber—Gas Rate Variable

Run	CO$_2$ in gas y_1	CO$_2$ in gas y_2	E_{MV}, avg. observed, %	CO$_2$ in soln., moles/mole MEA In	CO$_2$ in soln., moles/mole MEA Out	MEA conc. M	Temp. (avg.), °F.	$K_g(A/V)$, observed $\times 10^{-4}$	Slot velocity, ft./sec.	(A/V), factor	$K_g(A/V)$, calculated $\times 10^{-4}$	E_{MV}, avg., calculated, %
35	0.0935	0.0025	20.2	0.084	0.111	1.75	90	5.65	7.5	2.60	6.79	22.9
37	0.0960	0.0050	16.8	0.093	0.195	1.79	97	4.55	14.4	1.53	4.04	15.0
40	0.1020	0.0100	13.5	0.148	0.234	3.32	103	3.54	24.6	1.00	3.34	12.7

Table 1D. High-pressure Absorber (Sixteen Trays 84-in. I.D., 24-in. Tray Spacing) 173 Lb./Sq. In. Gauge

Run	CO$_2$ in gas y_1	CO$_2$ in gas y_2	E_{MV}, avg., observed, %	CO$_2$ in soln., moles/mole MEA In	CO$_2$ in soln., moles/mole MEA Out	MEA conc., M	Temp. (avg.), °F.	$K_g(A/V)$, observed $\times 10^{-4}$	Slot velocity, ft./sec.	(A/V) factor	$K_g(A/V)$, calculated $\times 10^{-4}$	E_{MV}, avg., calculated, %
43	0.0641	0.003	17.5	0.204	0.529	2.34	115	4.57	9.0	2.33	4.32	16.5

cial-column data. In view of the wide divergence in conditions between the plate-column operations and the Van Krevelen and Hoftijzer (*18*) experiments, it is interesting to note that the same general shape of curve is obtained.

Further indications of the effect of gas velocity are presented by the data of West et al. (*20*), who show that the interfacial area for bubble-cap plates used in the desorption of oxygen decreased markedly with increased air rate.

It cannot be expected that results from the high-pressure column will be in close agreement with those from the atmospheric absorber, as the high-pressure plant operated on a gas stream which contained hydrogen sulfide in addition to carbon dioxide and attained a much higher degree of saturation of the solution. The position of this point with respect to the line may therefore be more of a coincidence than evidence of a good correlation.

By use of the curve shown on Figure 7 to correct (A/V) for all tests in the atmospheric column at gas rates appreciably different from design and for the test in the high-pressure column, $K_g(A/V)$ has been estimated for all runs and converted to E_{MV} by use of Equation (3). These values are compared to the observed E_{MV} calculated from the inlet and outlet gas compositions by use of Equation (8) in Figure 8.

Effect of Slot Submergence

In the commercial-column tests described herein, the slot submergence (height of liquid above the centers of bubble-cap slots) varied within a relatively narrow range (i.e., 3 to 4 in.) and so an accurate evaluation of the effect of this factor on efficiency was not possible. If the correlation were to be applied to columns of appreciably different design, however, it is apparent that the effect of slot submergence would have to be considered. Various investigators have studied this variable and in general agreed that increased submergence provides an increased efficiency. Walter and Sherwood (*19*) suggest a general equation in which the contact is assumed to be proportional to h (height of solution above slot centers). Geddes (*6*) used the height of liquid over the midpoint of the slot opening under operating conditions

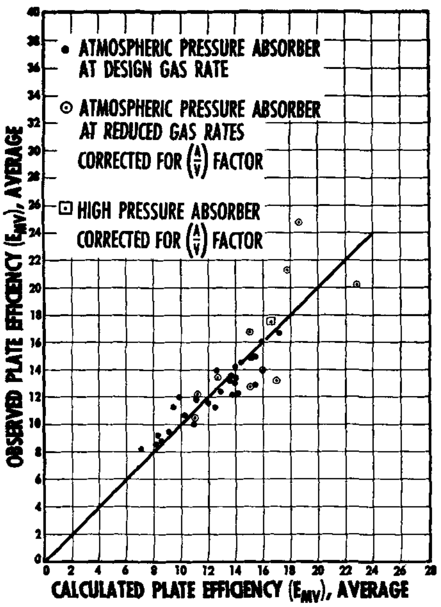

Fig. 8. Plate-efficiency correlation for carbon dioxide absorption in plate columns.

and assumed that the time of contact would be proportional to this height. Chu et al. (*4*) analyzed the data of Peavy and Baker (*11*) and determined a factor *B* for correcting over-all plate efficiencies for effective submergence. Their correlation leads to the conclusion that a zero effective slot depth (static submergence plus one-half slot height) would result in a plate efficiency equal to 87% of that calculated for a 0.7-in. submergence, and a 2.5-in. depth would result in an efficiency equal to 143% of the base value. In a more recent article by Chu et al. (*2*) it is pointed out that a substantial portion of the mass transfer appears to occur in the bubble-formation zone where the gas jets through the slots at high velocities. This would indicate a fallacy in assuming the interfacial area or the time of contact to be directly proportional to liquid height above the slots.

SUMMARY

For the absorption of carbon dioxide in aqueous solutions of monoethanolamine in bubble-plate columns, it is proposed that the Murphree vapor-phase efficiency E_{MV} be calculated from the equation

$$E_{MV} = 1 - e^{-K_g(A/V)RT_A}$$

$K_g(A/V)$ for the specific column tested, at a gas rate which results in a superficial velocity of about 35 ft./sec. through the bubble-cap slots, can be estimated from the equation

$$K_g\left(\frac{A}{V}\right) = \frac{1.2 \times 10^{-4}}{\mu^{0.68}} \cdot [1 + 1.2(0.5 - C)Me^{0.0067T - 3.4p}]$$

The indicated temperature effect holds only up to about 125°F.; so the equation should not be used above this value unless a suitable correction is applied. For high-pressure operations, it appears that the value $(0.5 - C)$, which indicates the fraction of amine unconverted, should be replaced by $(C_e - C)$ where C_e is the concentration in equilibrium with the gas.

The data indicate that $K_g(A/V)$ increases appreciably at decreased gas rates, presumably owing to an increase in A/V. The magnitude of the A/V correction at various gas velocities is indicated by a plot of the data which includes several gas rates in the atmospheric-pressure absorber and one operation at higher pressure.

The equation for calculating E_{MV} can be used for single plates or for groups of plates where concentration changes are not extreme. A simplified equation for calculating the number of plates required after E_{MV} has been estimated is

$$n = \frac{\ln (y_1/y_2)}{-\ln (1 - E_{MV})}$$

This assumes constant plate efficiency and no vapor pressure of carbon dioxide over the amine solution. If the plate efficiency varies appreciably throughout the column, a conventional graphical method may be employed.

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NOTATION

a = interfacial area, sq. ft./(ft. of depth) (sq. ft. of tray) or sq. ft./cu. ft. of packing.
A = ah; contact area, sq. ft./sq. ft. of tray
B, B' = constants
C = concentration of carbon dioxide in the solution, moles/mole MEA
C_e = equilibrium concentration of carbon dioxide in solution
D = diffusivity
E_{OG} = Murphree point efficiency based on gas
E_{MV} = Murphree vapor efficiency for entire plate
h = height of contact zone, ft.
H = p/C, Henry's Law coefficient
k_g = gas-film coefficient, lb. moles/(hr.)(sq. ft.)(atm.)
K_g = over-all gas-film coefficient, lb. moles/(hr.)(sq. ft.)(atm.)
k_L = liquid-film coefficient
k_L' = liquid-film coefficient based upon physical absorption
m = y/x, slope of equilibrium line
M = amine concentration of solution (molarity, gram moles/liter)
n = number of plates
N = total gas rate, moles/(hr.)(sq. ft.)
p = partial pressure, atm.
P = total pressure, atm.
q = concentration of unreacted amine in solution
R = gas constant
T = temperature, °F.
T_A = absolute temperature, °R.
V = actual gas volume, cu. ft./(hr.)(sq. ft. of tray)
y = mole fraction carbon dioxide in gas
μ = viscosity, centipoises

Subscripts

g = gas
L = liquid
e = equilibrium
i = interface
1 = feed condition
2 = exit condition

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