terfacial Reaction," Johns Hopkins University, Baltimore, Maryland (December, 28-29, 1959).
6. ———, Ph.D. dissertation, Princeton Univ., Princeton, New Jersey (October, 1960), University Microfilms, Ann Arbor, Michigan, Order No. 61-4825 (Microfilm $5.00; Xerox $17.55).
7. Schlicting, Hermann, "Boundary Layer Theory," Pergamon Press, London, England (1955).
8. Blasius, H., *Z. Math. u. Phys.*, **56**, 1 (1908).
9. Rosner, D. E., *J. Aero/Space Sci.*, **26**, 281-286 (1959).
10. Polhausen, E., *Z. angew. Math. Mech.*, **1**, 115-121 (1921).
11. Levich, B. G., *Acta Physicochim., U.R.S.S.*, **17**, 257-307 (1942); *ibid.*, **19**, 117-138 (1944); *Zhur. Fiz. Khim.*, **18**, 335-355 (1944).
12. Eckert, E. R. G., *VDI Forschungsheft 416* (1942).
13. Merk, H. J., *J. Fluid Mech.*, **5**, 460-480 (1959).
14. Sparrow, E. M., and J. L. Gregg, *Natl. Aeronaut. Space Admin. Memo. 2-27-59E* (February, 1959).
15. Fisher, F. D., and J. G. Knudsen, *Chem. Eng. Progr. Symposium Ser., No. 29*, **55**, 209 (1959).
16. Evans, H. L., *Intern. J. Heat Mass Transfer*, **5**, 35-57 (1962).
17. Carberry, J. J., *A.I.Ch.E. Journal*, **6**, 460 (1960).
18. Chambré, P. L., and Andreas Acrivos, *J. Appl. Phys.*, **27**, 1322-1328 (1956); *Ind. Eng. Chem.*, **49**, 1025-1029 (1957).
19. Ambrok, G. S., *Soviet Phys.—Tech. Phys.*, **2**, 1979-1986 (1957).
20. Rosner, D. E., *Chem. Eng. Sci.* to be published.
21. Lighthill, M. J., *Proc. Roy. Soc. (London)*, **202**, 359-377 (1950).
22. Boussinesq, J., *Gauthier-Villars*, Paris (1903); *J. Math Pures Appl.*, **1**, 285 (1905); Mixon, F. O., and J. J. Carberry, *Chem. Eng. Sci.*, **13**, 30 (1960).
23. Rosner, D. E., *AeroChem TP-16*, AFOSR TN 60-690, ASTIA AD 237-929 (April, 1960).
24. ———, *AeroChem TM-18*, AFOSR TN 60-331 (November, 1959).
25. Carslaw, H. S., and J. C. Jaeger, "Heat Conduction," Oxford, London, England (1947).
26. Sunderland, J. E., and R. J. Grosh, Document 6157, American Documents Institute, ADI Aux. Public. Project Photodup. Service, Library of Congress, Washington 25, D. C. ($1.25 for photoprints).
27. Shaaf, S. A., and F. S. Sherman, *J. Aeronaut. Sci.*, **21**, 85-90 (1954).
28. Levy, S., *ibid.*, **19**, 341 (1952).
29. Rosner, D. E., *AeroChem TP*, to be published.
30. Hougen, O. A., and K. M. Watson, *Ind. Eng. Chem.*, **35**, 529-541 (1943).
31. Rosner, D. E., Chemical Engineering Monograph, to be published.

Manuscript received January 30, 1962; revision received July 25, 1962; paper accepted July 30, 1962. Paper presented at A.I.Ch.E. New York meeting.

Effective Interfacial Area in Packed Columns for Absorption with Chemical Reaction

FUMITAKE YOSHIDA and YOSHIHARU MIURA

Kyoto University, Kyoto, Japan

A number of theoretical studies have been reported on gas absorption accompanied by a chemical reaction since the pioneering work of Hatta (*9, 10*). However the method of designing the packed column for chemical absorption has not been well established, partly because of insufficient knowledge of the effective interfacial area for chemical absorption. In the present work the effective interfacial area for chemical absorption was evaluated from data on absorption of carbon dioxide into aqueous solutions of sodium and potassium hydroxides in a packed column and in a bead column, that is a column of spheres connected in a vertical row. Theoretical relationships for the reaction factor, the ratio of the coefficient for chemical absorption to that for physical absorption, were confirmed. Physical absorption experiments were also performed to obtain the necessary data on the mass transfer rates in the liquid and gas phases.

EXPERIMENTAL

The setup of the apparatus for the physical absorption experiments was similar to the one reported elsewhere (*30, 31*). Figure 1 shows a schematic diagram of the apparatus for the chemical absorption experiments with the bead column. Carbon dioxide from a cylinder was absorbed into water in the saturating column, and the gas was stripped from the solution by air in the stripping column to give an air-carbon dioxide mixture of a given composition, which could be varied by controlling the rate of water to the stripping column. The bead column consisted of a jacketed glass tube, 40 mm. I.D. and a vertical row of porcelain spheres connected with a stainless steel wire at the axis of the column. Thirty 1-in. spheres, with 4-mm. clearances between adjacent spheres, and sixty ½-in. spheres, with 2-mm. clearances, were used. The temperature of the liquid through the bead column was controlled by means of the liquid feed preheater and the column jacket, through which water from a thermostated tank was passed.

The apparatus for the packed column experiments was similar to the one shown in Figure 1 except for the use of a packed column in place of the bead column. The packed column, made of glass, was 12.1 cm. I.D. and was packed with 1-in. and ½-in. porcelain Raschig rings to a

---

Yoshiharu Miura is at Himeji Technical College, Himeji, Japan.

Table 1. Reaction Rate Constant, k, of Reaction between Carbon Dioxide and Sodium Hydroxide

cu. m./kg.-mole sec.

Temperature, °C.	10	15	20	25
Ionic strength, g.-ion/liter				
0	2,170	3,270	4,700	6,900
1.0	2,940	4,400	6,380	9,360
2.0	4,000	6,040	8,680	12,700

height of 30 in., which was equal to the height of the bead column.

To study the liquid phase mass transfer coefficients experiments on physical absorption of carbon dioxide of 98% purity into water were performed with the bead and packed columns. The gas-phase resistance in the bead column was studied by carrying out experiments on absorption of methanol vapor contained in air by water. The procedures for the physical absorption experiments are reported by Yoshida and Koyanagi (*30, 31*).

In the experiments on chemical absorption the air containing carbon dioxide of a given partial pressure was brought into contact with aqueous solutions of sodium and potassium hydroxides in the bead and the packed columns. Analyses were made of the gas and liquid samples taken at the top and the bottom of the columns. Carbon dioxide in the gas was analyzed by saturating water with the gas samples continuously withdrawn from the column and by titrating the solution in equilibrium with the gas by the conventional method. Liquid samples were analyzed for the concentrations of the total alkalis and hydroxides.

BASIS OF INTERPRETATION

The rate of absorption with a chemical reaction is expressed as

$$N_A = k'_L\,(C_{Ai} - C_{AL}) = \beta\, k_L\,(C_{Ai} - C_{AL}) \quad (1)$$

where β is the so-called *reaction factor.* The relationship between the overall coefficient and the individual phase coefficients is given as

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{H\,k'_L} \quad (2)$$

in which the Henry's law constant H is usually different from that for pure physical absorption owing to the presence of ions.

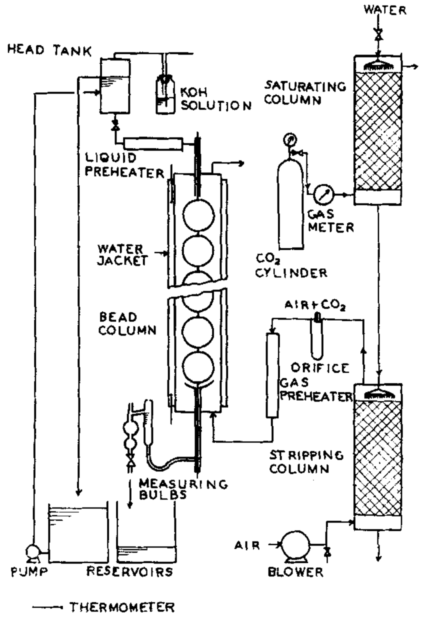

Fig. 1. Experimental apparatus.

The theoretical expressions for the reaction factor were first derived by Hatta (*9, 10*) on the assumption of steady state absorption across the stagnant liquid film at the interface. For a very rapid second-order irreversible reaction in the liquid phase he obtained

$$\beta = 1 + \frac{D_B\,C_B}{D_A\,C_{Ai}} \quad (3)$$

The reaction factor for a relatively slow first-order or pseudo first-order reaction is given by Hatta as

$$\beta = \frac{\gamma}{\tanh \gamma} \quad (4)$$

where

$$\gamma = (k\,C_B\,D_A)^{1/2}/k_L \quad (5)$$

When C_B is approximately constant, kC_B represents the pseudo first-order reaction rate constant. Equation (4) combined with Equation (1) holds for reversible as well as ireversible reactions. For the latter case the value of C_{AL} becomes zero.

The theoretical expressions for β can also be derived on the assumption of unsteady state absorption of solute into a stagnant medium. For a rapid second-order reaction Sherwood and Pigford (*22*) derived an equation similar to Equation (3), assuming unsteady state absorption. For the case of irreversible first-order or pseudo first-order reaction Danckwerts (*3*) obtained the following equation for the quantity Q absorbed in time t on the assumption of unsteady state absorption into a stagnant liquid:

$$Q = C_{Ai}\left(\frac{D_A}{k\,C_B}\right)^{1/2}\left[\left(k\,C_Bt + \frac{1}{2}\right)\operatorname{erf}\,(kC_Bt)^{1/2} + \left(\frac{kC_Bt}{\pi}\right)^{1/2} e^{-kC_Bt}\right] \quad (6)$$

Combining Equation (6) with the expression for k_L from the Higbie penetration theory (*11*) one obtains the following equation for β:

$$\beta = \left(\gamma + \frac{\pi}{8\gamma}\right)\operatorname{erf}\left(\frac{2\gamma}{\sqrt{\pi}}\right) + \frac{1}{2}\exp\,(-\,4\,\gamma^2/\pi) \quad (7)$$

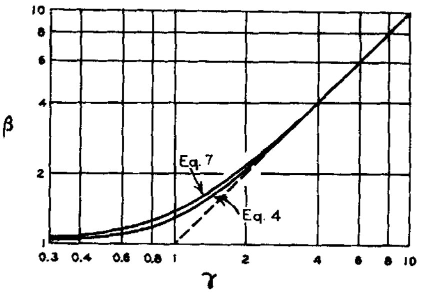

Fig. 2. Theoretical relationships between β and γ.

Figure 2, in which the values of β calculated by Equation (4) and (7) are compared, indicates that from the practical standpoint it is unimportant whether the film model or the penetration model is assumed in the derivation of the theoretical expressions for β. Another point of interest indicated in Figure 2 is that in the range where γ is greater than 5, β is practically equal to γ. Then from Equations (1) and (5)

$$N_A = (k\,C_B\,D_A)^{1/2}\,(C_{Ai} - C_{AL}) \quad (8)$$

Thus when absorption is accompanied by a moderately fast first-order or pseudo first-order reaction, the absorption rate is independent of the mass transfer coefficient k_L and of hydrodynamic conditions; in such cases the whole interfacial area is considered uniformly effective.

To calculate theoretical values of β it is necessary to know the values of the reaction rate constant k of the con-

Table 2. Calculated Values of K

sec.$^{-1}$

Temperature, °C.		15*	20	25	100*
Ionic Strength g.-ion/liter					
0.5	CO_2-K_2CO_3	0.40	0.58	0.84	69
	CO_2-Na_2CO_3	0.38	0.55	0.8	65
2.0	CO_2-K_2CO_3	0.47	0.68	0.99	81
	CO_2-Na_2CO_3	0.38	0.55	0.8	65

* Values for 15° and 100°C. were extrapolated.

Table 3a. Diffusivity of Carbon Dioxide in Aqueous Solutions of Potassium and Sodium Carbonates × 10^5 sq. cm./sec.

Temperature, °C. Total sodium normality	OH⁻ ion conc. g.-ion/liter	10	15	20	25
0.5	0.01	1.18	1.38	1.58	1.81
	0.5	1.2	1.4	1.61	1.85
2.0	0.5	0.78	0.93	1.06	1.24
	2.0	0.83	0.98	1.12	1.31

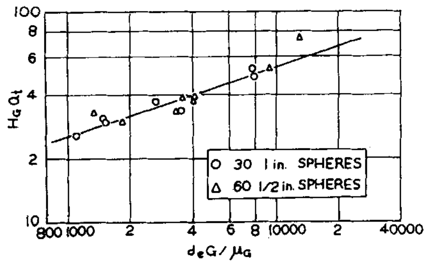

Fig. 3. Gas-phase mass transfer in bead columns.

trolling reaction as well as the values of C_B, D_A, and k_L. The reaction between dissolved carbon dioxide and the caustic alkali is known to take place in two steps:

$$CO_2 + OH^- = HCO_3^- \quad (9)$$

$$HCO_3^- + OH^- = CO_3^{--} + H_2O \quad (10)$$

Equation (9) is considered rate controlling, since (10) is thought to be very rapid (*4*). The reaction rate constant k of Equation (9) at infinite dilution was measured by Faurholt (*6*), Pinsent et al. (*19*), and Nijsing et al. (*17*). The variation of k with the ionic strength at a given temperature is given by Nijsing as

$$k = k_\infty 10^{\alpha I} \quad (11)$$

The value of α is 0.18 for potassium hydroxide solutions and 0.133 for sodium hydroxide solutions. Table 1 gives some calculated values of k in sodium hydroxide solutions based on the data of Faurholt and Nijsing.

In treating the literature data on absorption of carbon dioxide by sodium and potassium carbonates solutions the reaction mechanism was interpreted as follows after Danckwerts (*4*). The rate-controlling reaction in this case is again the Equation (9), that is reaction between dissolved carbon dioxide and the hydroxyl ions that are present in a carbonate solution due to the hydrolysis reaction:

$$CO_3^{--} + H_2O \underset{k_1}{\overset{k_2}{\rightleftarrows}} HCO_3^- + OH^- \quad (10a)$$

The concentration of OH^- is given as

$$[OH^-] = \frac{k_1 [H_2O] [CO_3^{--}]}{k_2 [HCO_3^-]} \quad (12)$$

Thus if absorption of carbon dioxide by Equation (9) is regarded as pseudo first-order with respect to the concentration of carbon dioxide

$$\frac{d[CO_2]}{dt} = k[OH^-] [CO_2] = k'[CO_2] \quad (13)$$

where

$$k' = \frac{k\, k_1[H_2O][CO_3^{--}]}{k_2[HCO_3^-]} = K \frac{[CO_3^{--}]}{[HCO_3^-]} \quad (14)$$

The value of K for sodium carbonate solutions at 25°C. was determined experimentally by Danckwerts and Kennedy (*4*) as 0.8 irrespective of the ionic strength, confirming the data of Nijsing and Kramers (*16*). The latter investigators also give values of K at 20°C. as 0.55. The values of the reaction rate constant for the absorption of carbon dioxide by potassium carbonate solutions are not available in the literature. But if it is assumed that Equation (9) controls the overall rate as in the case of sodium carbonate solutions, the only difference being the presence of K^+ ions in place of Na^+ ions, the values of K for the system carbon dioxide — potassium carbonate could be estimated from the ratio of the values of k for (9) with K^+ ions to that with Na^+ ions. Thus at an ionic strength I from Equation (11)

$$\frac{K_{K^+}}{K_{Na^+}} = \frac{k_{K^+}}{k_{Na^+}} = \frac{k_\infty 10^{0.18I}}{k_\infty 10^{0.133I}} = 10^{0.047I} \quad (15)$$

Table 2 gives some calculated values of K for sodium and potassium carbonate solutions as a function of the ionic strength and temperature based on the data of Danckwerts and Kennedy (*4*) and Nijsing and Kramers (*16*).

Diffusivity of carbon dioxide in caustic and carbonates solutions was estimated from the data of Arnold (*1*) on diffusivity of carbon dioxide in pure water on the assumption that diffusivity varies in proportion to the absolute temperature and to the reciprocal of viscosity. The latter assumption may not be greatly in error in dilute solutions, although Nijsing et al. (*16*) find that diffusivity of carbon dioxide in caustic solutions is inversely proportional to the 0.85 power of viscosity. Viscosities of caustic and carbonates solutions were estimated from the data of Hitchcock (*13*). Tables 3*a* and *b* list some calculated values of the diffusivity of carbon dioxide in caustic and carbonates solutions.

PHYSICAL ABSORPTION IN BEAD COLUMNS

Although in the case of chemical absorption the gas-phase resistance is relatively of minor importance, the gas-phase mass transfer coefficient in this particular experimental column was studied just to obtain the basis for corrections in later correlations. Experiments on absorption of methanol vapor contained in air into water were performed. The liquid-phase resistance is negligible for this particular system (*31*). Data for the two sizes of spheres, 1 and ½ in., are correlated by a single line as shown in Figure 3, in which the values of the dimensionless product of the gas-phase height of a transfer unit H_G and the surface area of the spheres per unit volume of the column a_t are plotted against the Reynolds number d_eG/μ_G of the gas stream through the channel between the spheres and the column wall. The equivalent diameter of the channel d_e was defined as four times the volume of the channel divided by the sum of the surface areas of the spheres and the column wall.

Table 3*b*. Diffusivity of Carbon Dioxide in Aqueous Solutions of Potassium and Sodium Carbonates × 10^6 sq. cm./sec.

Temperature, °C. Total alkali normality		15	20	25
0.5	K_2CO_3	1.46	1.67	1.91
	Na_2CO_3	1.38	1.58	1.81
2.0	K_2CO_3	1.16	1.34	1.58
	Na_2CO_3	0.90	1.03	1.22

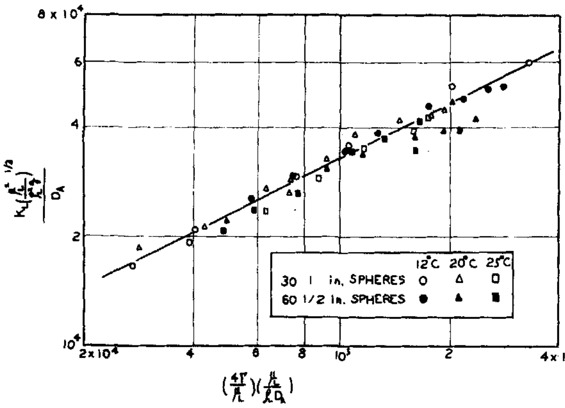

Fig. 4. Liquid-phase mass transfer in bead columns.

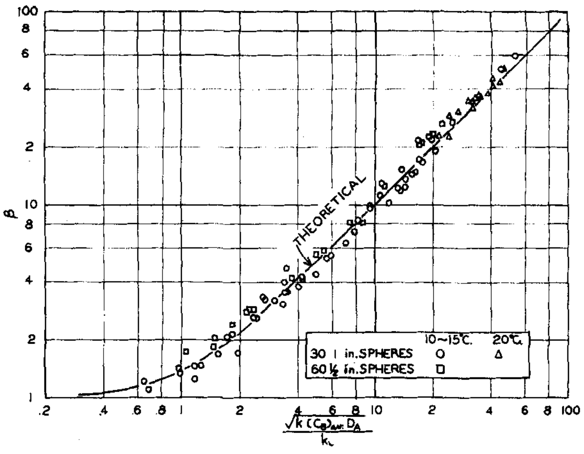

Fig. 6. Reaction factor β for the absorption of carbon dioxide in sodium hydroxide aqueous solution in bead columns.

No effect of the liquid rate was observed. In using this correlation it was assumed that H_G was proportional to the gas-phase Schmidt number raised to the 2/3 power.

The liquid-phase mass transfer coefficient k_L was studied by absorption of pure carbon dioxide into water at 12°, 20°, and 25°C. The results are plotted in Figure 4 and can be represented by

$$\frac{k_L}{D_A}\left(\frac{\mu_L^2}{\rho_L^2 g}\right)^{1/3} = 0.0105\left(\frac{4\Gamma}{\mu_L}\right)^{1/2}\left(\frac{\mu_L}{\rho_L D_A}\right)^{1/2} \quad (16)$$

This equation gives values of k_L about 10% lower than the equation of Yoshida and Koyanagi (*30*), which is based on the data with sixteen 1-in. spheres and thirty two ½-in spheres. The 10% difference can be accounted for if one considers that liquid mixing at the junctions between adjacent spheres is incomplete, since more spheres of the same size were used in the present experiments. Opinion differs (*5, 15, 20, 30*) on the extent of liquid mixing at the junctions in the column of spheres. It seems to the authors that the degree of mixing depends to some extent on the spacing between adjacent spheres. The columns employed by other investigators are different from the present apparatus in that they contained touching spheres.

PHYSICAL ABSORPTION IN PACKED COLUMNS

Data on physical absorption of pure carbon dioxide into water were taken at 12°C. with the packed column to obtain a basis for correlating the data on chemical absorption in the same column. In Figure 5 the values of the liquid-phase mass transfer coefficient k_La for the 1- and ½-in. Raschig rings are plotted against L/μ_L, a dimensional quantity proportional to the Reynolds number for a given size of packing. The broken lines in the figure represent the well-known data of Sherwood and Holloway (*21*) for desorption of oxygen from water.

CHEMICAL ABSORPTION IN BEAD COLUMNS

Experiments an absorption of carbon dioxide into aqueous solutions of sodium and potassium hydroxides were performed with the bead columns. The liquid-phase coefficient for chemical absorption k_L' was calculated from the observed values of the overall coefficient K_G, the gas phase mass transfer coefficient k_G estimated from the correlation in Figure 3, and the relationship expressed by Equation (2). In calculating the values of K_G the partial pressure of carbon dioxide in the bulk of liquid was assumed zero and the average of the partial pressure driving potentials at the top and the bottom was taken. The effect of the presence of electrolytes on the Henry's law constant was estimated by the method of Van Krevelen (*29*). The gas-phase resistance accounted for less than 10% of the overall resistance for the carbon dioxide-sodium hydroxide system and less than 30% for the carbon dioxide-potassium hydroxide system. Experimental values of the reaction factor β were calculated as the ratio of k_L' to k_L; the latter was calculated by Equation (16).

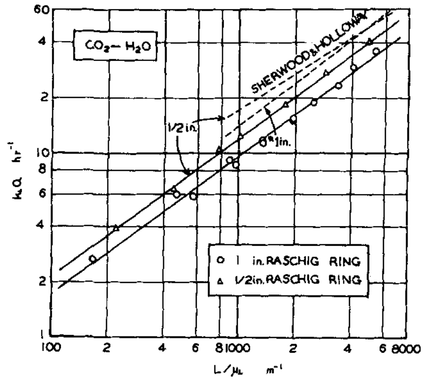

Fig. 5. Liquid-phase mass transfer in packed columns.

Experimental values of β obtained from the data on absorption of carbon dioxide by sodium hydroxide solutions in the bead columns were compared with theoretical values. Runs with sodium hydroxide solutions were so planned that variation of the concentration of the hydroxide through the column was less than 10% of the inlet concentration, and arithmetic average values were used for C_B in Equation (5). Thus it was assumed that the reaction was approximately pseudo first order with respect to the concentration of carbon dioxide, and Equation (4) or (7) was valid. Variation of the partial pressure of carbon dioxide in the gas through the columns was made less than 5%.

In Figure 6 the data points show the experimental values of β for absorption of carbon dioxide by sodium hydroxide solutions of concentrations below 2N and at temperatures below 20°C. in the bead columns with 1- and ½-in. spheres. The curve in the figure represents Equation (7). Fair agreement between theoretical and experimental values may indicate that for absorption accompanied by a first-order or pseudo first-order chemical reaction in the bead column, and presumably in the packed column, in which hydroxynamic conditions in the liquid phase are considered to be quite similar to those in the bead column, the reaction factor can be predicted by Equations (7) or (4) accurately enough for design purposes.

Data for the carbon dioxide-sodium hydroxide system at 30°C. can also be represented approximately by Equation (7) or (4), but in this case an equation of the type of Equation (3) gives a somewhat better correlation. The lower line in Figure 7 is a log-log plot of the values of $(\beta - 1)$ against the ratio C_B/C_{Ai}. The line is expressed by

$$\beta = 1 + 0.33\,(C_B/C_{Ai})^{0.7} \qquad (17)$$

This empirical equation resembles the equation obtained by Stephens and Morris (*25*) for absorption of chlorine by aqueous solutions of ferrous chloride, with the values of the constant and exponent of 0.46 and 0.83 instead of 0.33 and 0.7, respectively. The fact that the values of the exponent on (C_B/C_{Ai}) are less than unity may imply that these reactions are not so rapid as was assumed by Hatta in the derivation of Equation (3).

According to Spector and Dodge (*24*) the rate of absorption of carbon dioxide into a potassium hydroxide solution is slightly faster than that into a sodium hydroxide solution of a corresponding concentration. The upper line in Figure 7 represents the present data on absorption of carbon dioxide by potassium hydroxide solutions at 30°C. in the bead columns with 1- and ½-in. spheres. The line can be expressed by

$$\beta = 1 + 0.27\,(C_B/C_{Ai})^{0.9} \qquad (18)$$

The higher value of the exponent on (C_B/C_{Ai}) indicates that the reaction between carbon dioxide and potassium hydroxide is faster than the reaction between carbon dioxide and sodium hydroxide.

CHEMICAL ABSORPTION IN PACKED COLUMNS

Van Krevelen and Hoftijzer (*28*) were the first to adopt the reaction factor in correlating data on chemical absorption in packed columns. They assumed that the effective area for chemical absorption was the same as that for physical absorption. This assumption seems doubtful to the authors, because the effective interfacial area for physical absorption depends on hydrodynamic conditions, whereas, under certain conditions, the effective area for chemical absorption is not affected by flow conditions as mentioned before. When the value of γ is greater than 5, the absorption rate is given by Equation (8) which does not involve k_L.

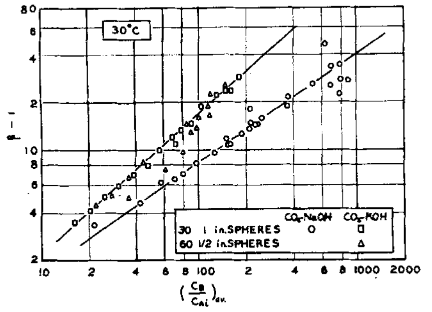

Fig. 7. Reaction factor β for the absorption of carbon dioxide in sodium and potassium hydroxide aqueous solution in bead columns.

In the present work experimental values of $k_L'a$ were obtained from the values of the overall coefficient K_Ga by Equation (2) as in the case of the bead column. The gas-phase coefficient k_Ga was estimated from the correlation for the gas-phase mass transfer rate proposed by Yoshida and Koyanagi (*31*) on the basis of their data on absorption of methanol vapor by water in a packed column of the same size as used in the present work. The gas-phase resistance accounted for less than 5% of the overall resistance in the carbon dioxide-sodium hydroxide runs and less than 30% in the carbon dioxide- potassium hydroxide runs.

Some carbon dioxide-sodium hydroxide runs were made under conditions such that Equation (8) was valid. It was possible to find, by trial experiments, the range of C_B where $k_L'a$ was proportional to the square root of the arithmetic average value of C_B, other factors being kept constant. Figure 8 is a log-log plot of $k_L'a$ vs. the square root of $(k\,C_B\,D_A)$ calculated from the data on such runs in the column packed with ½-in. Raschig rings. A similar plot was obtained from the data with 1-in. Raschig rings. The slope of unity of all the straight lines, corresponding to various liquid rates, indicates that Equation (8) did hold for these runs. Thus it was possible to evaluate the effective area for these runs by dividing the values of the ordinates by those of abscissas. In Figure 9 the effective area a_{et} thus calculated for the 1- and ½-in. Raschig rings are plotted as fraction of the total packing surface a_t against the superficial liquid mass velocity. The data points show remarkable agreement with the broken lines representing the wetted area calculated by the following equation of Hikita (*12*) based on his measurement of the wetted area of paper Raschig rings:

$$\frac{a_w}{a_t} = 0.046\,L^{1/3}\left(\frac{\sigma}{20}\right)^q \qquad (19)$$

in which

$$q = -1.42\,d_p^{-0.70}$$

Agreement between the wetted area and the effective interfacial area might be a coincidence, but this seems to imply that when absorption is accompanied by a moderately fast chemical reaction and γ is greater than 5, nearly the whole interfacial area is effective. The fact that the whole interface including the semistagnant part continues to be effective over a prolonged period could be explained by slow turnover or diffusion between the semistagnant and the moving parts. Shulman (*23*) noted that the gas-phase coefficient k_Ga for ammonia absorption by sulfuric acid increases with acid concentration. He states that when ammonia is absorbed in water or very dilute acid, the effective area is that of the moving liquid, but as acid concentration increases, the semistagnant part becomes as effective as the moving liquid.

The next problem is how to evaluate the effective area for absorption accompanied by a relatively slow reaction. If γ is smaller than 5, then from Equation (5)

$$k_L > (k\,C_B\,D_A)^{1/2}/5 \qquad (20)$$

This inequality should hold if k and/or C_B is relatively small or k_L is large. However even when this is the case with the moving part of the interface, there should be the slowly moving, or semistagnant, part of the interface where k_L is so small that the above inequality does not hold; that is γ is greater than 5. Thus if one assumes that the interface consists of two parts, that is the moving part where γ is smaller than 5 and the semistagnant part where γ is greater than 5, the average coefficient for chemical absorption per unit packed volume $k_L'a$ can be given as

$$k_L'a = \beta k_L\,a_{ep} + (k\,C_B\,D_A)^{1/2}(a_{et} - a_{ep}) \qquad (21)$$

The total interfacial area a_{et} can be evaluated by the aforementioned method and is practically equal to the wetted area given by the Hikita equation. The area of the moving part of

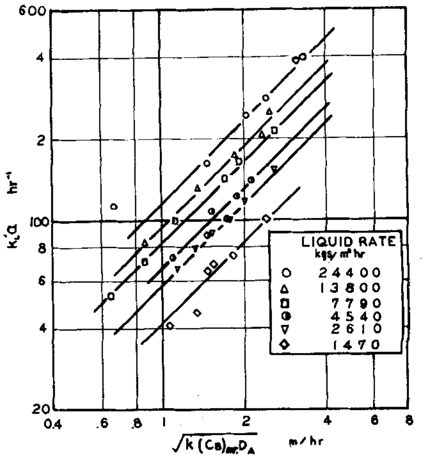

Fig. 8. The values of k'_La for the absorption of carbon dioxide in sodium hydroxide aqueous solution in ½-in. Raschig ring packed column when γ is greater than 5.

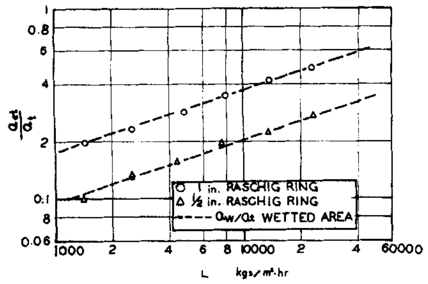

Fig. 9. Effective interfacial area in packed columns for the absorption with moderately fast chemical reaction.

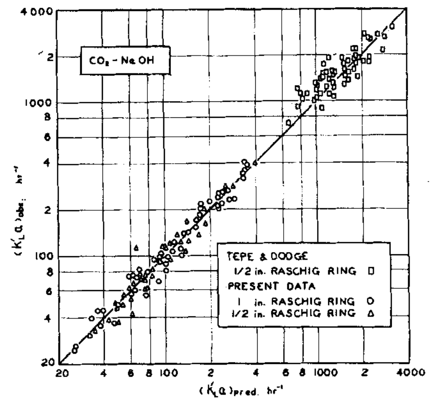

Fig. 10. Predicted and observed values of k'_La for the absorption of carbon dioxide in sodium hydroxide aqueous solution.

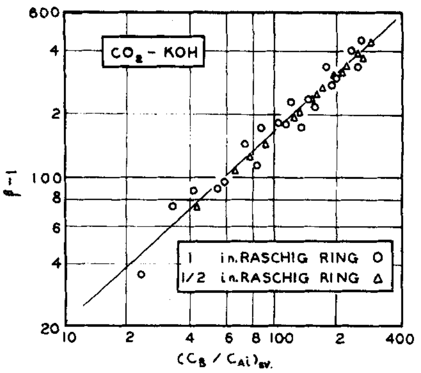

Fig. 11. Reaction factor β for the absorption of carbon dioxide in potassium hydroxide aqueous solution in packed columns.

the interface is considered substantially equal to the effective interfacial area for physical absorption a_{ep}. The latter can be evaluated by comparing the values of the capacity coefficient for physical absorption such as k_Ga or k_La in a packed column with the k_G or k_L values obtained with some reference apparatus (*30, 31*). The magnitude of a_{ep} depends to some extent on the choice of the reference apparatus. However slight variation of a_{ep} would affect the calculated value of $k_L'a$ very little, since at the border line between the moving and the semistagnant areas, which is not a distinct one, the values of βk_L and $(k C_B D_A)^{1/2}$ should approach to each other. It should be mentioned that the assumption that the value of γ is 5 at the border line between the moving and the semistagnant areas is entirely arbitrary; drawing a line of demarcation between the two areas is also arbitrary because variation of the local liquid velocity should be continuous. However the fact that calculations based on the above assumptions give $k_L'a$ values that are in fair agreement with the experimental values, as will be shown below, seems to indicate that such assumptions are justifiable at least from the practical standpoint.

Comparisons were made between the values of $k_L'a$ predicted by means of Equation (21) and experimental values of $k_L'a$ for all the additional carbon dioxide-sodium hydroxide runs at various liquid rates, temperatures, and sodium hydroxide concentrations including the runs for the range of C_B where $k_L'a$ was not proportional to the square root of $(k C_B D_A)$. The values of a_{et} were estimated from Figure 9 and the values of a_{ep} from the correlation of the effective interfacial area for physical absorption (*31*) based on the data of Fellinger (*7*) on ammonia absorption and the Taecker-Hougen data (*26*) on the vaporization of water from all-wet packings. The values of k_L were estimated from the correlation of Yoshida and Koyanagi (*31*). The observed and predicted values of $k_L'a$ are in agreement within 20% as shown in Figure 10.

Another evidence to show that the effective area for absorption with a slow or moderately fast chemical reaction is not the same as that for physical absorption is a plot against γ of the ratio of the $k_L'a$ values from the above mentioned data to the k_La values for physical absorption shown in Figure 5. If the effective area for chemical absorption were the same as that for physical absorption, the data points should fall around the theoretical line shown in Figures 2 and 6. The points scattered badly above the theoretical curve.

When absorption is accompanied by a rapid second-order irreversible reaction, it is considered that the absorption rate is controlled by diffusion of the solute gas and the reactant through the liquid film to the thin reaction zone. Thus in this case the effective area in the packed column should be the same as that for physical absorption, and the reaction factor β should simply be the ratio of the volumetric coefficient for chemical absorption $k_L'a$ to that for physical absorption k_La in the same column under corresponding conditions. This means that the absorption rate at the moving part of the interface is so high that absorption at the semistagnant part becomes insignificant in comparison with that at the moving part. The experimental values of β were calculated from the present $k_L'a$ data on absorption of carbon dioxide into aqueous potassium hydroxide solutions and the correlation for k_La for physical absorption, shown in Figure 5, with corrections for variations in viscosity and diffusivity due to temperature change by means of the correlation by Yoshida and Koyanagi (*31*). The calculated values of $(\beta - 1)$ are plotted in Figure 11 against (C_B/C_{Ai}) showing good agreement with the line representing β for the bead column. This agreement is a verification that the effective area in packed columns for absorption with a rapid second-order irreversible reaction is the same as that for physical absorption.

PREVIOUS DATA ON CHEMICAL ABSORPTION IN PACKED COLUMNS

Extensive experiments on absorption of carbon dioxide by sodium hydroxide solutions and by sodium and potassium carbonates solutions in packed column were carried out by Dodge and coworkers (*2, 18, 27*). Furnas and Bellinger (*8*) also studied absorption of carbon dioxide into sodium carbonate solutions. In these papers effects of such factors as liquid and gas rates, temperature, and concentrations of the reactive liquid component are presented rather qualitatively. To test the present method of correlation the data of references *2, 8, 18,* and *27* listed in Table 4[*] were used. Data of other investigations were not useable either because the size of the apparatus used was not comparable with the one used in the present work or because values of the reaction rate constants and/or solubility were not available.

Values of the mass transfer coefficients for the liquid and gas phases and the overall coefficient were calculated by the aforementioned procedure. With previous data for large packed heights the effect of packed height on k_La was taken into account on the assumption that the liquid-phase height of a transfer unit was proportional to the packed height raised to the 0.15 power (*14*). The reaction rate constants for the controlling reactions were estimated as aforementioned.

Predicted and experimental values of $k_L'a$ from the data of Tepe and Dodge (*27*) on absorption of carbon

---

[*] Tabular material has been deposited as document 7419 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

dioxide in sodium hydroxide solutions are shown in Figure 10 along with the present data on the same system.

Similar comparisons were made with the data of Payne and Dodge (*18*), Comstock and Dodge (*2*), and Furnas and Bellinger (*8*) on absorption of carbon dioxide in sodium carbonate solutions and with the data of Comstock and Dodge on absorption of carbon dioxide in potassium carbonate solutions. Predicted and observed values of $k_L'a$ showed agreement within 30%.

CONCLUSIONS

The capacity coefficient for chemical absorption in packed columns can be predicted from the mass transfer coefficients for the individual phases, solubility of the gas with the effect of the presence of ions taken into consideration, the reaction factor, which in turn depends on the reaction rate constant and other factors, and the effective interfacial area. The effective interfacial area for chemical absorption in packed columns is the same as that for physical absorption only when absorption is accompanied by a rapid second-order reaction. For absorption with a moderately fast first-order or pseudo first-order reaction the whole interfacial area is uniformly effective. For absorption with a slower reaction the moving part of the interface is more effective than the semistagnant part, and the two parts should be treated separately.

For a new system, with no reaction rate constant available, experimental determination of the reaction factor with use of a bead column would serve as a guide. With known values of the reaction factor the volumetric coefficient for chemical absorption can be estimated provided that correlations are available for the gas phase and the liquid phase mass transfer coefficients, the total interfacial area or the wetted area of packing, and/or the effective interfacial area for physical absorption.

NOTATION

a = effective interfacial area in packing, sq. m./cu. m.

a_{ep} = effective interfacial area for physical absorption, sq. m./cu. m.

a_{et} = total interfacial area, sq. m./cu. m.

a_t = total surface area of packing, sq. m./cu. m.

a_w = wetted area of packing, sq. m./cu. m.

C_{Ai}, C_{AL} = concentrations of the component absorbed at the interface and in the bulk of liquid, respectively, kg.-moles/cu. m.

C_B = concentration of the reactive component in the bulk of liquid, kg.-moles/cu. m.

D_A, D_B = liquid diffusivities of the component absorbed and the reactive component, respectively, sq. m./hr.

d_e = equivalent diameter of the channel for gas flow in bead column defined in the text, m.

d_p = size of Raschig ring, cm.

erf = Gauss' error function defined as $\text{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-u^2}\,du$

G = superficial mass velocity of gas with respect to the total cross section of column, kg./(sq. m.)(hr.)

g = gravitational constant, m./hr.^{2}

H = Henry's constant defined by $C = pH$, kg.-moles/(cu. m.)(atm.)

H_G = gas-phase height of a transfer unit, m.

I = ionic strength, that is $(\frac{1}{2})\,\Sigma c_i Z_i^2$, where c_i is concentration of ion i and z_i is its valency, kg.-ions/cu. m.

K = constant in Equation (14), sec.$^{-1}$

K_G = overall coefficient, kg.-moles/(sq. m.)(hr.)(atm.)

k_G = gas-phase mass transfer coefficient, kg.-moles/(sq. m.)(hr.)(atm.)

k_L = liquid-phase mass transfer coefficient, m./hr.

k_L' = liquid-phase coefficient for chemical absorption, m./hr.

k, k_1, k_2 = reaction rate constants for second-order reaction, cu. m./(kg.-mole)(sec.)

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

k_∞ = k at infinite dilution, cu. m./(kg.-mole)(sec.)

L = superficial mass velocity of liquid with respect to the total cross section of column, kg./(sq. m.)(hr.)

N_A = rate of absorption, kg.-moles/(sq. m.)(hr.)

Q = quantity absorbed in time t, kg.-moles/sq. m.

T = absolute temperature, °K.

t = time, hr.

Greek Letters

β = reaction factor defined as k_L'/k_L, dimensionless

Γ = liquid rate per unit of perimeter of the spheres, kg./(m.)(hr.)

γ = ratio defined by Equation (5)

μ_G = gas viscosity, kg./(m.)(hr.)

μ_L = liquid viscosity, kg./(m.)(hr.)

ρ_L = liquid density kg./cu. m.

σ = surface tension, dynes/cm.

LITERATURE CITED

1. Arnold, J. H., *J. Am. Chem. Soc.*, **52**, 3937 (1930).
2. Comstock, C. S., and B. F. Dodge, *Ind. Eng. Chem.*, **29**, 520 (1937).
3. Danckwerts, P. V., *Trans. Faraday Soc.*, **46**, 300 (1950).
4. ———, and A. M. Kennedy, *Chem. Eng. Sci.*, **8**, 201 (1958).
5. Davidson, J. F., and E. J. Cullen, *Trans. Inst. Chem. Engrs.*, **35**, 51 (1957).
6. Faurholt, C., *J. Chim. Physique*, **21**, 400 (1924).
7. Fellinger, L., Sc.D. thesis, Mass. Inst. Technol., Cambridge, Massachusetts (1941).
8. Furnas, C. C., and F. Bellinger, *Trans. Am. Inst. Chem. Engrs.*, **34**, 251 (1938).
9. Hatta, S., *J. Soc. Chem. Ind. (Japan)*, **31**, 869 (1928).
10. *Ibid.*, **35**, 1389 (1932).
11. Higbie, Ralph, *Trans. Am. Inst. Chem. Engrs.*, **31**, 365 (1935).
12. Hikita, H., and K. Kataoka, *Chem. Eng. (Japan)*, **20**, 528 (1956).
13. Hitchcock, L. B., and J. S. McIlhenny, *Ind. Eng. Chem.*, **27**, 461 (1935).
14. Knapp, W. G., and J. R. Fair, *Chem. Eng. Progr.*, **56**, 68 (1960).
15. Lynn, S., J. R. Staatmeier, and H. Kramers, *Chem. Eng. Sci.*, **4**, 63 (1955).
16. Nijsing, R. A. T. O., and H. Kramers, "Chemical Reaction Engineering," p. 81, Pergamon Press, London, England (1958).
17. ———, R. H. Hendriksz, and H. Kramers, *Chem. Eng. Sci.*, **10**, 88 (1959).
18. Payne, J. W., and B. F. Dodge, *Ind. Eng. Chem.*, **24**, 630 (1932).
19. Pinsent, B. R. W., L. Pearson, and F. J. W. Roughton, *Trans. Faraday Soc.*, **52**, 1512 (1956).
20. Ratchliff, G. A., and K. J. Reid, *Trans. Inst. Chem. Engrs.*, **40**, 69 (1962).
21. Sherwood, T. K., and F. A. L. Holloway, *Trans. Am. Inst. Chem. Engrs.*, **36**, 39 (1940).
22. Sherwood, T. K., and R. L. Pigford, "Absorption and Extraction," 2 ed., p. 332, McGraw-Hill, New York (1952).
23. Shulman, H. L., C. F. Ullrich, and N. Wells, *A.I.Ch.E. Journal*, **1**, 247 (1955).
24. Spector, N. A., and B. F. Dodge, *Trans. Am. Inst. Chem. Engrs.*, **42**, 827 (1946).
25. Stephens, E. J., and G. A. Morris, *Chem. Eng. Progr.*, **47**, 232 (1951).
26. Taecker, R. G., and O. A. Hougen, *ibid.*, **45**, 188 (1949).
27. Tepe, J. B., and B. F. Dodge, *Trans. Am. Inst. Chem. Engrs.*, **39**, 255 (1943).
28. Van Krevelen, D. W., and P. J. Hoftijzer, *Chem. Eng. Progr.*, **44**, 529 (1948).
29. ————————, Chim. Industr. XXI Congr. Int. Chim. Industr., 168 (1948).
30. Yoshida, F., and T. Koyanagi, *Ind. Eng. Chem.*, **50**, 365 (1958).
31. ————————, *A.I.Ch.E. Journal*, **8**, 309 (1962).

Manuscript received June 1, 1962; revision received August 29, 1962; paper accepted October 30, 1962.