



## Absorption of Carbon Dioxide into Caustic Alkaline Solutions in a Wetted-wall Column

メタデータ	言語: eng 出版者: 公開日: 2010-04-05 キーワード (Ja): キーワード (En): 作成者: Hikita, Haruo, Asai, Satoru メールアドレス: 所属:
URL	<a href="https://doi.org/10.24729/00009047">https://doi.org/10.24729/00009047</a>

# Absorption of Carbon Dioxide into Caustic Alkaline Solutions in a Wetted-Wall Column

Haruo HIKITA\* and Satoru ASAI\*

(Received 31 January, 1961)

Experiments on the absorption of pure carbon dioxide into sodium and potassium hydroxide solutions of various concentrations were carried out in a wetted-wall column under the liquid flow conditions with and without rippling. The results for experiments without rippling agreed with the theory based on the unsteady-state diffusion accompanied by an instantaneous reaction. The absorption rate results for experiments with rippling did not agree with the theory and they were much higher than those obtained for the experiments without rippling. However, the values of  $\beta$ , the ratio of the absorption rates with and without chemical reaction, were in good agreement with the theoretical predictions.

## 1. Introduction

The wetted-wall column has been used for a fundamental study of the mechanism of the liquid phase mass transfer in packed columns, because of its advantage of fixed gas-liquid interfacial area. In the usual wetted-wall column with a length of about 20cm. or more, however, the flow pattern of the falling liquid film is complicated by the presence of ripples at the liquid surface, and then theoretical treatment of the results with liquid phase mass transfer rates in a long wetted-wall column has been unsuccessful. In several recent investigations, experiments have been performed under conditions such that rippling was eliminated by the addition of a small amount of wetting agent to the liquid. Under these conditions a falling liquid film may be assumed to be in laminar flow and the observed values of mass transfer rate can be compared with those predicted from the unsteady-state diffusion theory.

Most of the previous studies of the liquid phase transfer in wetted-wall columns have been concerned with the physical absorption and very few experimental works have been reported on the gas absorption accompanied by chemical reaction in liquid phase.

Pozin<sup>1)</sup> has studied the absorption of pure carbon dioxide or chlorine gas into 0.44 to 4 N sodium hydroxide solution in a column 30 cm. or 20 cm. long under conditions that wetting agent was not added to the solutions. He has shown that measured absorption rates agreed qualitatively with the theoretical equation of unsteady-state absorption with an instantaneous reaction between dissolved gas and hydroxide ion.

Fujita and others<sup>2)</sup> measured the rates of absorption of carbon dioxide from air into 0.001 to 3 N sodium hydroxide solution under conditions that ripples were present at the liquid surface, using a wetted-wall column of 134cm. or 42.4cm. length. They found that the values of  $\beta$ , the ratio of the absorption rates with and without chemical

---

\* Department of Chemical Engineering, College of Engineering.

reaction, were in good agreement with the theoretical equation assuming unsteady-state absorption accompanied with a pseudo first order reaction, but measured absorption rates themselves were much higher than theoretical predictions.

Nijsing, Hendriksz and Kramers<sup>3)</sup> studied the absorption of pure carbon dioxide into 0.1 and 0.5 N sodium and potassium hydroxide solutions containing a wetting agent to prevent rippling, varying the column height over a wide range, and showed that the absorption rates were in good agreement with the theoretical equation for an unsteady-state diffusion with a rapid second order reaction between carbon dioxide and hydroxide ion.

The present work was undertaken in order to reexamine the results obtained by previous investigators and gain a clearer insight into the effect of a chemical reaction on the mass transfer rate in liquid phase. Experiments were made on the absorption of pure carbon dioxide into sodium and potassium hydroxide solutions with and without wetting agent in a column of 20cm. length. Using the same apparatus, the absorption rates of pure carbon dioxide into water were also measured.

## 2. Apparatus and Procedure

The apparatus used in this work is shown in Fig. 1. The wetted-wall column was constructed of a vertical glass tube of 1.30 cm. in diameter and 20 cm. long.

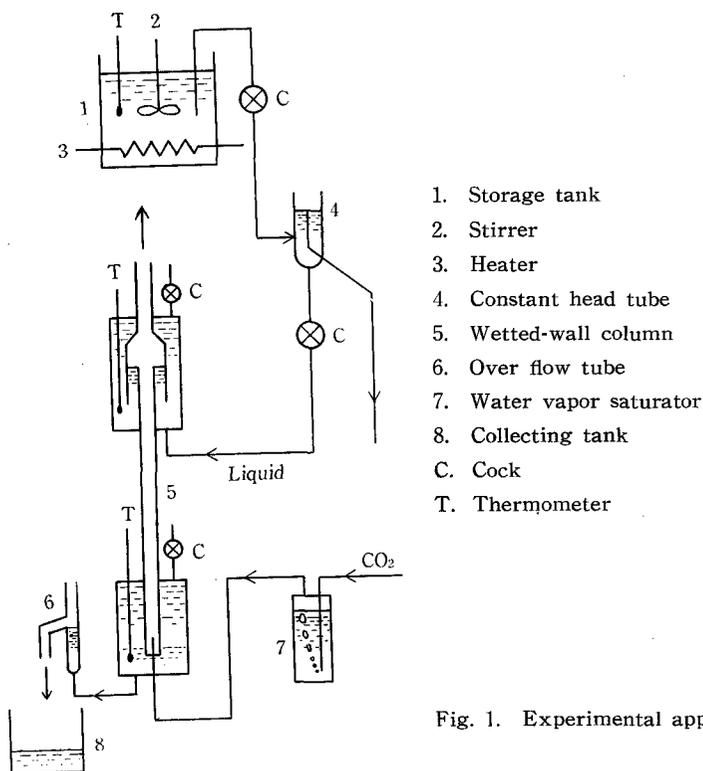


Fig. 1. Experimental apparatus.

The absorbing liquid passed from the storage tank with a constant temperature device through a constant head tube and a flow rate regulating cock to the top of

the column, and then flew down over the inner wall of the column. Liquid from the bottom of the column went through a overflow tube to a collecting tank. The upper and lower liquid chambers were filled with liquid during operation and the liquid level in the lower chamber was kept at the lowest end of the wetted-wall section to prevent the end effects as possible. Liquid temperature was held at 30°C. When water was used as the absorbing liquid, the top and the bottom temperatures agreed approximately. In the chemical absorption runs, however, the bottom temperature was somewhat higher than the top temperature, owing to the heat of reaction. Therefore, the average of the top and the bottom temperatures was adjusted to 30°C. The flow rates of liquid leaving the column were measured directly by the use of a stop-watch and a measuring cylinder.

Carbon dioxide gas (above 99% purity from a gas cylinder) was first bubbled through a water vapor saturator and then fed into the bottom of the column. The gas not absorbed was purged from the top of the column to the atmosphere. The temperature of the gas entering the column was controlled within 0.5°C of the liquid temperature. Gas flow rate was not measured exactly, but it was always greater than several times the absorption rate in the column. The column pressure was slightly above atmospheric.

The absorbing liquids used were water and aqueous solutions of sodium and potassium hydroxide varying concentrations from 0.125 to 1.0 N. For the experiment under the condition that rippling is absent at the liquid surface, a small amount of wetting agent (Emerl) was added to the solutions.

After all the operating variables had been adjusted to the desired values, 5 to 10 min. were needed for the conditions to reach steady-state. Liquid samples were taken from the inlet and the outlet of the column and analyzed. In the physical absorption experiments, the analysis for dissolving carbon dioxide in water was accomplished by precipitating the carbon dioxide as barium carbonate by use of a standard barium hydroxide solution. The excess barium hydroxide was then titrated with hydrochloric acid and phenolphthalein indicator. In the chemical absorption experiments, caustic alkaline and its carbonate in solutions was determined by the well known Warder method.

### **3. Results and Discussion**

#### **1. Results with no rippling**

##### (A) Physical absorption of carbon dioxide into water

The total absorption rate through the column was calculated from the liquid flow rate and the difference between the carbon dioxide concentrations in the outlet and inlet liquids, and the average absorption rate was obtained by dividing this value by the gas-liquid contact area. In the present experiment, in which rippling was absent and a liquid film seemed to be in laminar flow, the average absorption rate measured may be compared with the theoretical equation based on the penetration theory assuming

an unsteady-state diffusion in a liquid film and a very short contact time of gas and liquid, given by

$$N^* = 2c_{Ai}\sqrt{D_A/\pi t} = 0.727 c_{Ai}(D_A/z)Re^{1/3}Sc^{1/2}Ga^{1/6} \quad (1)$$

where

$$Re = 4\Gamma/\mu, \quad Sc = \mu/\rho D_A, \quad Ga = \rho^2 g z^3 / \mu^2$$

This comparison showed that the rate of absorption is slightly lower than that predicted by the theoretical equation. Similar results have been obtained by the previous investigators<sup>3)~5)</sup> and the discrepancy between the experiment and the theory has been attributed to the effect of the presence of a standing wave at the liquid surface near the bottom of the column. The liquid surface below the standing wave is nearly stagnant and this area is inactive for gas absorption. Nijsing and others<sup>3), 6)</sup> have shown that a good agreement between theory and experiment could be obtained if the total column was corrected for this negative end-effect by subtracting inactive film height of about 2 cm. This inactive film height was determined from the straight-line intercept on the abscissa in the plot of the square of total absorption rate against actual column height. The film height equivalent to the end-effect in the present work can not be determined by means of this method because of the only use of one kind of column height. Therefore, Hikita's data<sup>5)</sup> obtained in the physical absorption experiment, where pure carbon dioxide was absorbed into water containing a wetting agent and the same apparatus as in this work except for the variation of column height was employed, was used to estimate the end-effect in the present experiment. This estimated value was about 1 cm. Thus, effective column height in this work was assumed to be 19 cm.

The average absorption rates in the present experiment were calculated by use of this effective column height corrected for the end-effect. Fig. 2 shows the average absorption rates  $N^*$  plotted on a logarithmic scale against liquid Reynolds number  $Re$ . A straight line in this figure represents the theoretical equation given by Eq.(1). In the calculation of this theoretical line, the solubility of carbon dioxide in water at 30°C was taken as  $1.252 \times 10^{-3}$  g/cc. a value from Seidell,<sup>7)</sup> and for the diffusivity of carbon dioxide in water at 30°C,  $2.26 \times 10^{-5}$  cm<sup>2</sup>/sec., a value measured by Nijsing and others,<sup>3)</sup> was used. The agreement between the experimental absorption rates and the theoretical line is very good, as shown in Fig. 2. From these results, it is concluded that the penetration theory is applicable to liquid phase mass transfer in a wetted-wall column under conditions such that rippling is absent at the surface of a falling liquid film.

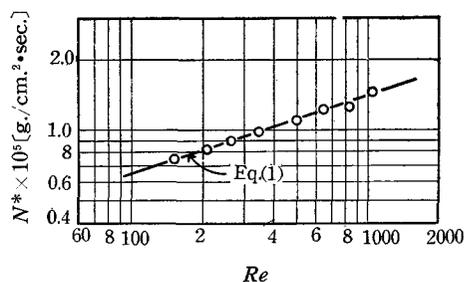


Fig. 2. CO<sub>2</sub> absorption into water with wetting agent, 30°C.

#### (B) Chemical absorption of carbon dioxide into caustic solutions

The average absorption rate was calculated from the liquid flow rate, gas-liquid

contact area and the difference between the hydroxide ion concentrations in the outlet and inlet solutions. In the calculation of the contact area, effective column height of 19cm. was used, assuming that the end-effect was the same as in the physical absorption experiment.

Fig. 3 shows the average absorption rates  $N$  for  $\text{CO}_2$ -NaOH system plotted on a logarithmic paper against liquid Reynolds number  $Re$ , with  $\text{OH}^-$  concentration as parameter. A dotted line in this figure represents the data for carbon dioxide-water runs given in Fig. 2. Fig. 4 shows the results for  $\text{CO}_2$ -KOH system as a plot similar to that in Fig. 3. From these figures, it can be seen that the average absorption rate is proportional to the  $1/3$  power of the liquid Reynolds number, as in the case of physical absorption, and increases as the concentration of hydroxide ion increases.

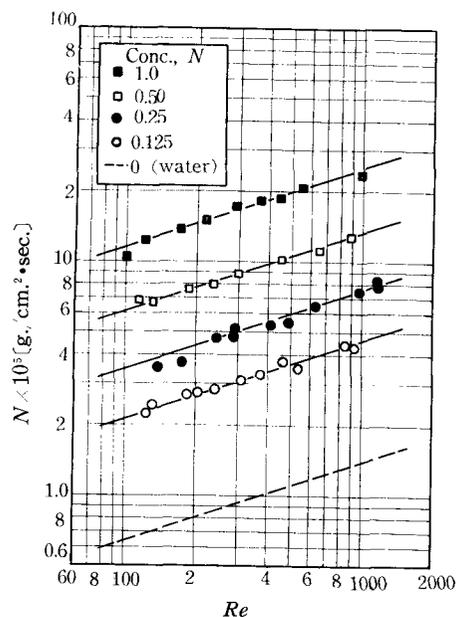


Fig. 3.  $\text{CO}_2$  absorption into aqueous solutions of NaOH with wetting agent,  $30^\circ\text{C}$ .

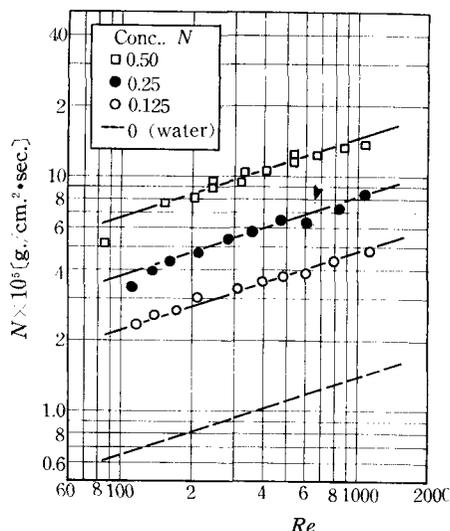
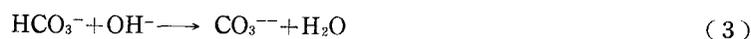


Fig. 4.  $\text{CO}_2$  absorption into aqueous solutions of KOH with wetting agent,  $30^\circ\text{C}$ .

Absorption of carbon dioxide in caustic solution is accompanied by the following reactions:



Reaction (3) has a much higher velocity constant than reaction (2). Thus, reaction (2) is the rate determining reaction of the overall reaction,



If the reaction rate of reaction (2) is extremely rapid compared with the rates of diffusion of  $\text{CO}_2$  and  $\text{OH}^-$ , the overall reaction (4) can be regarded as an instantaneous reaction and the absorption rate is controlled by the diffusion of  $\text{CO}_2$  and  $\text{OH}^-$  to a

reaction zone where the concentrations of both reactants are zero. The theoretical treatments for this case, on the basis of the penetration theory, have been developed by Danckwerts<sup>8)</sup> and Sherwood and Pigford.<sup>9)</sup> They have shown that the average absorption rate can be represented by the following equation:

$$N = \frac{2c_{Ai}}{\text{erf}(\alpha/D_A)^{1/2}} \sqrt{\frac{D_A}{\pi t}} = \frac{0.727c_{Ai}}{\text{erf}(\alpha/D_A)^{1/2}} \cdot \frac{D_A}{z} Re^{1/3} Sc^{1/2} Ga^{1/6} \quad (5)$$

where  $\alpha$  is the root of

$$\frac{c_{BO}}{\nu\sqrt{D_A}} \exp(\alpha/D_A) \text{erf}(\alpha/D_A)^{1/2} = \frac{c_{Ai}}{\sqrt{D_B}} \exp(\alpha/D_B) \text{erfc}(\alpha/D_B)^{1/2} \quad (6)$$

In general, it is convenient to use the ratio of the absorption rates with and without chemical reaction in order to indicate the effect of the reaction on the absorption rate. For the case of an infinitely rapid reaction, this ratio becomes

$$\beta = N/N^* = 1/\text{erf}(\alpha/D_A)^{1/2} \quad (7)$$

dividing Eq. (5) by Eq. (1), and when  $\beta \gg 1$ , Eqs. (6) and (7) are simplified as

$$\beta = \sqrt{\frac{D_A}{D_B}} + \sqrt{\frac{D_B}{D_A}} \cdot \frac{c_{BO}}{\nu c_{Ai}} \quad (8)$$

As described above, experimental results obtained in the present work show that the absorption rate is proportional to the 1/3 power of liquid Reynolds number and increases as  $\text{OH}^-$  concentration increases. These results agree qualitatively with those expected from the theoretical Eqs. (5) and (8), derived for the absorption accompanied with an instantaneous reaction. To make a more quantitative comparison between the theory and the experimental results, a plot of  $(\beta - \sqrt{D_A/D_B})$  vs.  $(\sqrt{D_B/D_A} \cdot c_{BO}/\nu c_{Ai})$  was attempted. For this plot, it is necessary to know the physical solubility of  $\text{CO}_2$ , the diffusivities of  $\text{CO}_2$  and  $\text{OH}^-$ , and other physical properties such as the viscosity and density of the solutions. These properties were predicted as follows:

a) Physical solubility of  $\text{CO}_2$

The physical solubility of a gas in an electrolyte solution at a given temperature is frequently represented by an empirical formula:

$$\log \frac{c^*}{c_w^*} = -k_s I \quad (9)$$

where  $c^*$  and  $c_w^*$  are the solubilities in the solution and in water respectively and  $I$  is the ionic strength.  $k_s$  is the salting-out parameter and can be predicted by the method proposed by van Krevelen and Hoftijzer.<sup>10)</sup> When an infinitely rapid reaction is assumed, the solution near the gas-liquid interface will contain no reactant. Under such a condition, the solubility in the solution containing the reaction product should be used. In this work, the solubility of  $\text{CO}_2$  in  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$  solution was calculated by the method mentioned above, and adopted as  $c_{Ai}$ .

b) Diffusivity of CO<sub>2</sub>

The diffusivity of CO<sub>2</sub> in the solution was estimated by correcting the value in pure water for the variations of viscosity, according to the Stokes-Einstein equation:

$$D\mu/T = \text{constant} \quad (10)$$

Also in this case, the value for carbonate solution was used as the viscosity of the solution.

c) Diffusivity of OH<sup>-</sup>

The diffusivity of OH<sup>-</sup> in a very dilute solution can be estimated from the Vinograd and McBain equation.<sup>11)</sup> This value was calculated as  $3.72 \times 10^{-5}$  cm<sup>2</sup>/sec., under the assumptions of a steady-state counter diffusion of OH<sup>-</sup> and CO<sub>3</sub><sup>-</sup> and the linear concentration gradients of both ions. After that, the diffusivity of OH<sup>-</sup> in the concentrated solution was predicted, assuming that the electrolyte concentration has the same effect on the diffusivity of OH<sup>-</sup> and that of CO<sub>2</sub> and then the ratio of both diffusivities is a constant which equals to  $1.65 (= 3.72 \times 10^{-5} / 2.26 \times 10^{-5})$ .

## d) Miscellaneous properties

Other physical properties such as viscosity or density of solutions were quoted from the data of Hitchcock and McIlhenny.<sup>12)</sup>

These predicted values are listed in Table 1.

Table 1. Physical Properties of Solutions at 30°C.

Solution	C <sub>BO</sub> (g·mole/lit.)	C <sub>Ai</sub> × 10 <sup>3</sup> (g./cm. <sup>3</sup> )	D <sub>A</sub> × 10 <sup>5</sup> (cm. <sup>2</sup> /sec.)	D <sub>B</sub> × 10 <sup>5</sup> (cm. <sup>2</sup> /sec.)	
				(calc.)	(obs.)
NaOH	0.125	1.202	2.19	3.61	2.80
	0.25	1.154	2.12	3.50	2.71
	0.50	1.063	1.99	3.28	2.54
	1.0	0.903	1.75	2.89	2.23
KOH	0.125	1.214	2.22	3.66	2.83
	0.25	1.177	2.18	3.60	2.78
	0.50	1.107	2.09	3.45	2.67

In Fig. 5, the values of  $(\beta - \sqrt{D_A/D_B})$  calculated from the results shown in Figs. 3 and 4, are plotted against the values of  $(\sqrt{D_B/D_A} \cdot c_{BO}/\nu c_{Ai})$  on a logarithmic scale, and compared with the theoretical Eq. (8). The experimental results are 10 to 20% lower than the theoretical line and the discrepancy increases with the increase of the value of  $(\sqrt{D_B/D_A} \cdot c_{BO}/\nu c_{Ai})$ . Fig. 5 also includes some data of Nijsing and others<sup>3)</sup> obtained with the absorption of pure carbon dioxide into NaOH and KOH solutions. Their results show a similar tendency, too.

The deviation from the theoretical line may be attributed to the inaccurate prediction of the diffusivity of OH<sup>-</sup>, in which the diffusivity ratio  $D_B/D_A$  for the concentrated solution is assumed to be the same as for the very dilute solution. If the value of

$D_B/D_A$  is taken as 1.28 in place of 1.65, a much better agreement between the experimental results and the theoretical line can be obtained, as shown in Fig. 6. For the re-calculation of Nijssing and others' data,<sup>3)</sup> the value of 1.28 was used for the diffusivity ratio, assuming that this ratio was constant independent of the liquid temperature. These results are included in Fig. 6, where a good agreement with the theoretical line can be seen, too. Thus, the value of 1.28 seems to be a plausible one as the average value of the diffusivity ratio for  $\text{CO}_2\text{-OH}^-$  system over the range of  $\text{OH}^-$  concentrations used by the present authors and Nijssing *et al.*

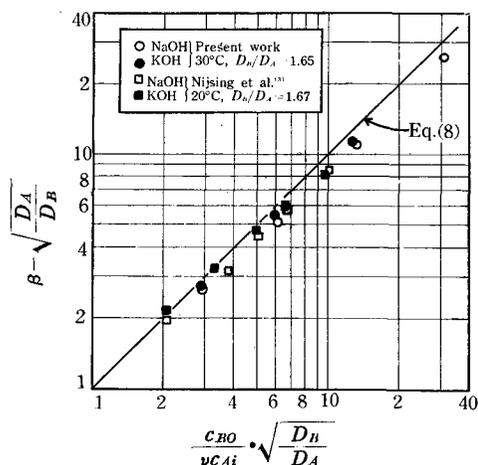


Fig. 5. Comparison between experimental and theoretical values. ( $D_B/D_A=1.65$ )

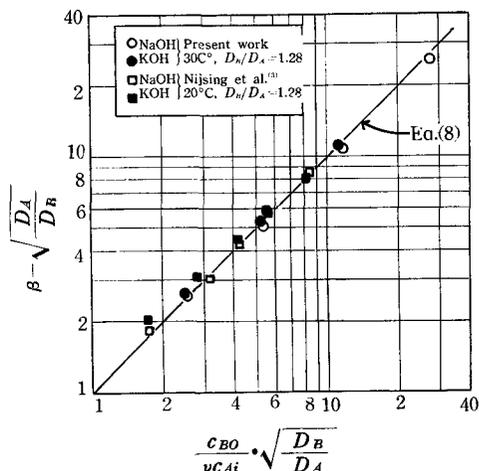


Fig. 6. Comparison between experimental and theoretical values. ( $D_B/D_A=1.28$ )

From the foregoing results, it is concluded that the absorption rates of carbon dioxide into caustic alkaline solutions are in good accordance with the theoretical equation derived for an unsteady-state absorption accompanied with an instantaneous reaction, under the conditions such that rippling does not exist at the surface of the liquid film.

## 2. Results with rippling

### (A) Physical absorption of carbon dioxide into water

When a wetting agent was not added to the absorbing liquid, considerably violent rippling was observed at the surface of the liquid film. Fig. 7 shows the results obtained under such conditions for the absorption of carbon dioxide into water, as a plot of average absorption rate  $N^*$  vs. liquid Reynolds number  $Re$  on a logarithmic scale. The absorption rates are considerably higher than

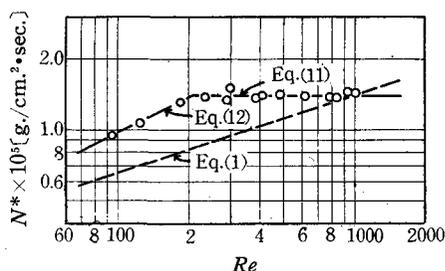


Fig. 7.  $\text{CO}_2$  absorption into water with no wetting agent,  $30^\circ\text{C}$ .

those predicted from the penetration theory, which are given by Eq. (1) and represented as a dotted line in this figure. Experimental results were represented by two straight lines having the slopes of 0 and 1/2 respectively, above and below about 200 of  $Re$ . The increased rate of absorption may be caused by the increase in the surface area and the mixing of the liquid near the surface due to the presence of ripples. Furthermore, the different slopes of the experimental lines may be attributed to the variation of the flow pattern of liquid film. The flow mechanism of liquid film accompanied with rippling is so complicated that the theoretical treatment for absorption rate has been unsuccessful.

Hikita and others<sup>13)</sup> have presented the empirical equations for liquid phase  $H.T.U.$  in a wetted-wall column. These equations are rewritten as follows:

For A region of pseudo stream-line flow, where the absorption rate is independent of liquid Reynolds number,

$$N^* = 0.106 c_{Ai} (D_A/z) Sc^{1/2} Ga^{1/3} \quad (11)$$

and for B region of pseudo stream-line flow, where the absorption rate is proportional to the 1/2 power of  $Re$ ,

$$N^* = 0.011 c_{Ai} (D_A/z) Re^{1/2} Sc^{0.62} Ga^{0.29} \quad (12)$$

The solid lines in Fig. 7 indicate Eqs. (11) and (12) and are in close agreement with the observed values.

#### (B) Chemical absorption of carbon dioxide into caustic solutions

Results for the absorption of  $CO_2$  into NaOH and KOH solutions are shown in Fig. 8 and 9 respectively, where the absorption rates  $N$  are plotted against liquid Reynolds number  $Re$  on the logarithmic scales. In these figures, physical absorption results shown in Fig. 7 are represented as dotted lines for the comparison. The results for chemical absorption indicate a similar tendency as those for physical absorption except for the slight movement of the break point to the right with the increases of the  $OH^-$  concentrations. Furthermore, the comparison of Figs. 8 and 9 with Figs. 3 and 4 show that the absorption results with rippling are considerably higher than those without rippling, which are in agreement with Eq. (5) based on the penetration theory for gas absorption with an infinitely rapid reaction.

Fig. 8 includes the data of Pozin<sup>1)</sup> for the absorption of pure carbon dioxide into 1.0 and 3.97 N NaOH solutions. Two dotted lines representing his data were drawn by means of the following empirical equation:

$$k_L' = b \sqrt{u_{av}} \quad (13)$$

where  $k_L'$  is Pozin's coefficient defined by  $k_L' = N/c_{RO}$ ,  $u_{av}$  is the average velocity of liquid film, given by

$$u_{av} = (g\mu/48\rho)^{1/3} Re^{2/3} \quad (14)$$

and  $b$  is an empirical constant having the values of 17.7 and 8.0 for 1.0 and 3.97 N

solutions respectively.

Pozin's results indicate that the absorption rate is proportional to the 1/3 power of the Reynolds number, and this trend with  $Re$  is different from those observed in the present experiments.

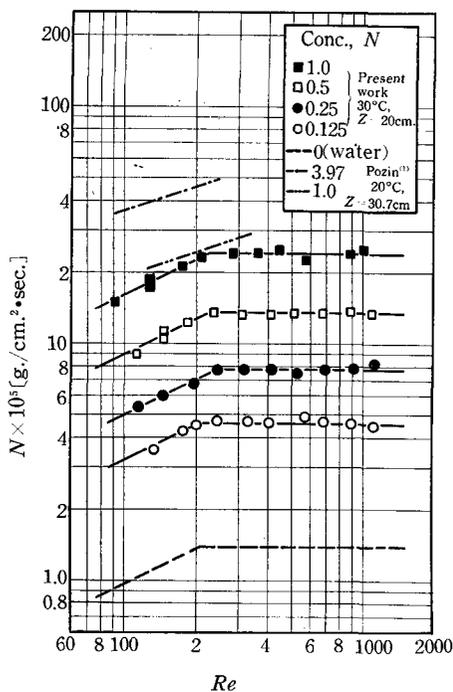


Fig. 8.  $\text{CO}_2$  absorption into aqueous solutions of NaOH with no wetting agent.

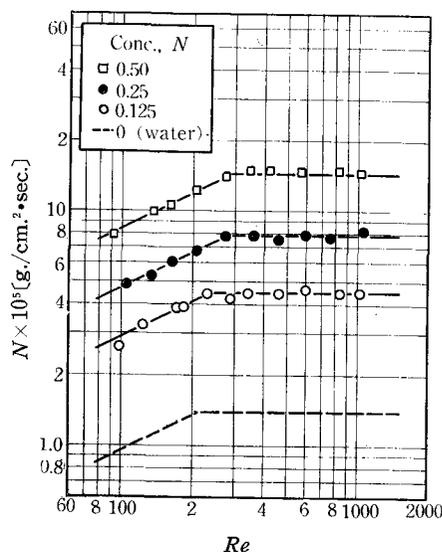


Fig. 9.  $\text{CO}_2$  absorption into aqueous solutions of KOH with no wetting agent,  $30^\circ\text{C}$ .

In order to examine the effect of chemical reaction on the absorption rate, the plots of  $(\beta - \sqrt{D_A/D_B})$  vs.  $(\sqrt{D_B/D_A} \cdot c_{B0}/\nu c_{Ai})$  similar to that in Fig. 5 or 6, were made. Figs. 10 and 11 show these plots for the results in  $A$  and  $B$  regions of pseudo stream-line flow respectively. The diffusivity ratio of 1.28 was also used for these plots. The results for  $A$  region of pseudo stream-line flow are in good agreement with Eq. (8). However, the agreement between the results for  $B$  region and Eq. (8) is not so good as those for  $A$  region. This may be due to the poor uniformity of liquid film thickness caused by lower liquid flow rate.

Pozin's data shown in Fig. 8 are also plotted in Figs. 10 and 11. The break point between  $A$  and  $B$  regions of pseudo stream-line flow was not observed in his experiment, so that the Reynolds number corresponding to this point was estimated by the use of Eqs. (11) and (12), and then the maximum and the minimum values of  $(\beta - \sqrt{D_A/D_B})$  for each region were calculated, taking the diffusivity ratio as 1.28. His results also agree with the theoretical line.

From the above results, it is concluded that the  $\beta$  values for the chemical absorption of  $\text{CO}_2$  into caustic solutions, under the liquid flow conditions where ripples exist at

the liquid surface, are in fair agreement with the theoretical Eq. (8) based on the unsteady-state absorption with an instantaneous reaction, although the absorption rates themselves do not agree with the theoretical predictions.

In general, for the gas absorption accompanied by a second order reaction of finite reaction rate, no analytical solution has been developed. However, analytical solutions have been developed for the special cases. Theoretical treatment for the absorption accompanied with an instantaneous reaction, discussed in this work, is one of such cases. The condition must be fulfilled for this case is that the value of  $\sqrt{kc_{BO}D_A}/k_i^{1/2}$  is much larger than 1 and at the same time the value of  $c_{BO}/c_{Ai}$  is not so large. It seems that this condition has been satisfied in the present experiment. On the other hand, when the value of  $\sqrt{kc_{BO}D_A}/k_i^{1/2}$  is not so large and the value of  $c_{BO}/c_{Ai}$  is very high, the depletion of  $C_B$  at the gas-liquid interface is small and then the reaction is regarded as a pseudo first order reaction. The  $\beta$  value for this case is given by the following equation<sup>8)</sup>:

$$\beta = (\gamma + \pi/8\gamma) \operatorname{erf}(2\gamma/\sqrt{\pi}) + \frac{1}{2} e^{-(2\gamma/\sqrt{\pi})^2} \quad (15)$$

where

$$\gamma = \sqrt{kc_{BO}D_A}/k_i^{1/2} \quad (16)$$

Fujita and others<sup>2)</sup> have performed the experiment on the absorption of carbon dioxide from air into sodium hydroxide solutions. In their experiment, the values of  $c_{BO}/c_{Ai}$  were considerably higher than in the present work, because of the use of CO<sub>2</sub>-air mixture, then the condition for the absorption with a pseudo first order reaction would be fulfilled. Their results have shown that the values are in fair agreement

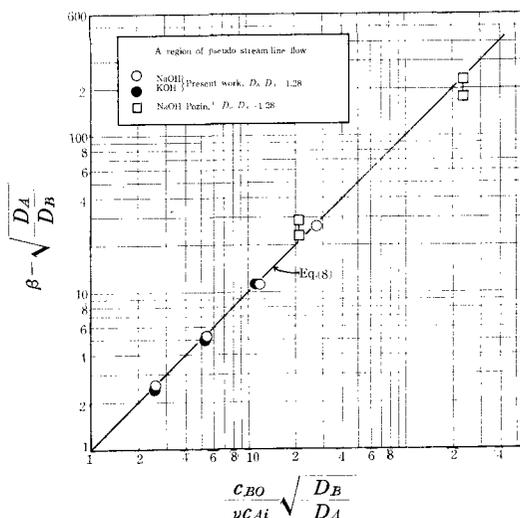


Fig. 10. Comparison between experimental and theoretical values.

(A region of pseudo stream-line flow).

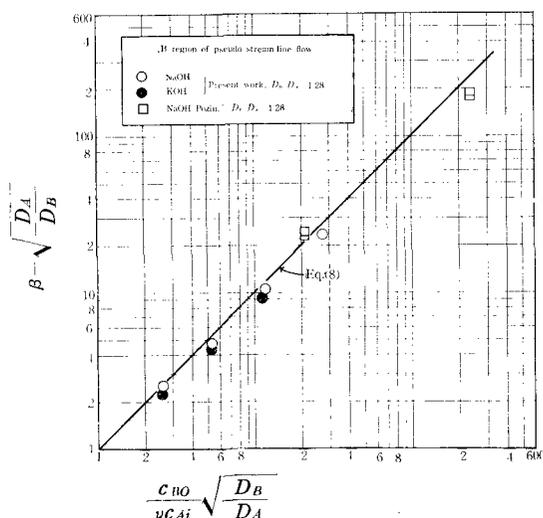


Fig. 11. Comparison between experimental and theoretical values.

(B region of pseudo stream-line flow).

with the theoretical equation derived for the absorption with a pseudo first order reaction, given by Eq. (15), although the absorption rates themselves do not accord with the theoretical predictions.

Thus, it will be concluded that under the liquid flow conditions where rippling is present at the liquid surface, the theory of simultaneous gas absorption and chemical reaction is not applicable directly to the absorption rate, but for the  $\beta$  value such theory can be applied.

#### 4. Conclusion

Absorption of pure carbon dioxide into sodium and potassium hydroxide solutions of various concentrations was carried out in a wetted-wall column of 20 cm. height, under the liquid flow conditions with and without rippling at the liquid surface.

The results obtained with no rippling were in good agreement with the theoretical predictions based on the unsteady-state gas absorption accompanied by an instantaneous reaction between  $\text{CO}_2$  and  $\text{OH}^-$ .

The absorption rates observed in the experiment with rippling did not agree with the theory, but the values of  $\beta$  accorded with the theoretical predictions as in the case of no rippling.

#### Notation

$b$  = constant in Eq. (13)

$c^*$  = physical solubility of gas in electrolyte solution, g./cm<sup>3</sup>.

$c_w^*$  = physical solubility of gas in water, g./cm<sup>3</sup>.

$c$  = liquid concentration, g./cm<sup>3</sup>. or g.-mol/lit.

$D$  = liquid phase diffusivity, cm.<sup>2</sup>/sec.

$g$  = acceleration due to gravity, cm./sec.<sup>2</sup>

$Ga$  = Galilei number,  $\rho^2 g z^3 / \mu^2$ , —

$I$  = ionic strength of solution, g.-ion/lit.

$k$  = second order reaction rate constant, lit./ (g.-mol)(sec.)

$k_r$  = liquid-phase mass transfer coefficient, cm./sec.

$k_r'$  = Pozin's coefficient, kg./ (hr.)(m.<sup>2</sup>)(mole fraction of NaOH)

$k_s$  = salting out parameter in Eq. (9), lit./g.-ion

$N$  = average absorption rate, g./ (cm.<sup>2</sup>)(sec.)

$Re$  = liquid Reynolds number,  $4\Gamma/\mu$ , —

$Sc$  = Schmidt number,  $\mu/\rho D$ , —

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

$T$  = absolute temperature, °K.

$u_{av}$  = average velocity of falling liquid film, m./hr.

$z$  = height of wetted-wall column, cm.

#### Greek Letters

$\alpha$  = root of Eq. (6)

$\beta$  =ratio of absorption rates with and without chemical reaction,  $N/N^*$ , —

$r = \sqrt{kc_{B0}D_A}/k_L^*$ , —

$\Gamma$  =liquid mass flow rate per unit perimeter of column, g./cm.(sec.)

$\mu$  =liquid viscosity, g./cm.(sec.)

$\nu$  =number of moles of  $B$  reacting with one mole of  $A$ ,  $\nu=2$  in this work.

$\rho$  =liquid density, g./cm.<sup>3</sup>

### Subscripts

$A$  =species  $A$ , the gas being absorbed

$B$  =species  $B$ , the reactant in solution

$i$  =gas-liquid interface

$o$  =initial condition

### Superscripts

\* =physical absorption

### References

- 1) M. E. Pozin, J. Applied Chem. (U.S.S.R.), **20**, 963 (1947); Chem. Abst., **43**, 23 (1949).
- 2) S. Fujita, A. Tanimoto, H. Hijikata, H. Shiina and Y. Nakane, Chem. Eng. (Japan), **18**, 73 (1954).
- 3) R. A. T. O. Nijsing, R. H. Hendriksz and H. Kramers. Chem. Eng. Sci., **10**, 88 (1959).
- 4) S. Lynn, J. R. Straatmeier and H. Kramers, *ibid.*, **4**, 58 (1955).
- 5) H. Hikita, Chem. Eng. (Japan), **23**, 23 (1959).
- 6) R. A. T. O. Nijsing and H. Kramers, Chem. Eng. Sci., **8**, 81 (1958).
- 7) A. Seidell, *Solubilities of Inorganic and Metal Organic Compounds*, 3rd. ed., pp. 221, D. Van Nostrand, New York, (1953).
- 8) P. V. Danckwerts, Trans. Faraday Soc., **46**, 300 (1950).
- 9) T. K. Sherwood and R. L. Pigford, *Absorption and Extraction*, 2nd. ed., pp. 317, McGraw-Hill, New York, (1952).
- 10) D. W. Van Krevelen and P. J. Hoftijzer, *Chim. Indust., XXI<sup>eme</sup> Congres Int. Chim. Indust.*, pp. 168 (1948).
- 11) J. R. Vinograd and J. W. McBain. J. Am. Chem. Soc., **163**, 2008 (1941).
- 12) L. B. Hitchcock and J. S. McIlhenny, Ind. Eng. Chem., **27**, 461 (1935).
- 13) H. Hikita, K. Nakanishi and T. Kataoka, Chem. Eng. (Japan), **23**, 459 (1959).