

# MEASUREMENT OF THE DIFFUSIVITY OF CO<sub>2</sub> IN LIQUID BY LIQUID JETS\*

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## I. Introduction

Diffusivities in liquids are essential factors in the mass-transfer process such as gas-absorption, distillation and extraction and have been measured for a long time. However the usual method such as partition-membrane method and capillary method must be carried out in the state of no convection of fluids. Thus the measurement needs very delicate technique and long time. On account of this, measured systems are very scarce. To make up the scarce data, many formulae<sup>1)13)15)20)</sup> have been recently presented. But their accuracies are not always satisfactory.

There are many methods to determine diffusivities as described in the paper of Johnson and Babb.<sup>8)</sup> The simplest one is that the diffusivity is calculated from the two results: one is the experimental gas absorption and the other is the theoretical result.

Davidson and Cullen<sup>5)</sup> measured the diffusivity of gas in water on a sphere, Lynn<sup>9)</sup> with wetted wall and Danckwerts and Kennedy<sup>4)</sup> with a rotating drum. But their accuracies are not satisfactory because of hydrodynamic defects.

The similar methods with this report were carried out by Vielstich<sup>19)</sup> and Toor and Chiang.<sup>17)</sup> The former determined the diffusivity of CO<sub>2</sub> in Decaline but failed in measuring the diffusivity in water. The latter measured only the effective diffusivity of SO<sub>2</sub> in water.

We have found that when the correction at the zero jet length is made and the so-called bell-shaped is used, the experimental value obtained by liquid-jet method coincides most accurately with the theoretical value.

The diffusivities of CO<sub>2</sub> in aqueous solution of glycerine, cane sugar, ethyl-alcohol, NaOH, KOH and CO<sub>2</sub> are measured in this paper.

## II. Absorption Experiment by Liquid-Jet Apparatus

As the absorption mechanism in a liquid-jet is considered to be in unsteady state, the penetration theory by Higbie<sup>7)</sup> is applied.

Taking the following two assumptions:

1) The equilibrium relation at the gas-liquid interface is immediately established.

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2) The diffusion is unidirection and the longitudinal diffusion is negligible.

The absorption quantity per unit time ( $N'$ ) by the penetration theory is expressed by Eq. (1)

$$N' = 2 \pi d(C^* - C) \sqrt{\frac{D_L v_m l}{\pi}} \tag{1}$$

Cullen and Davidson<sup>2)</sup> and Raimondi and Toor<sup>14)</sup> have pointed out that when the bell-shaped nozzle is used, the surface velocity of the liquid-jet is the same with the average velocity of it and this is quite different from the case using a long capillary nozzle.

We use the bell-shaped nozzles as shown in Fig. 2, then we take the third assumption:

3) The surface velocity of the liquid-jet is the same with its average velocity.

$$N' = 2 \pi d(C^* - C_0) \sqrt{\frac{D_L v_m l}{\pi}} \tag{2}$$

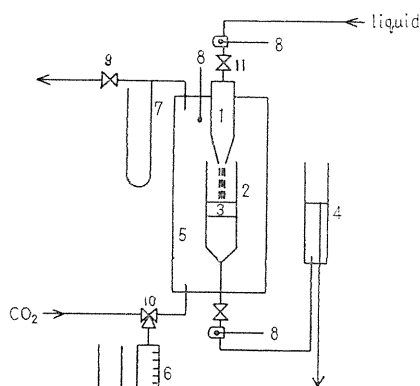
Putting  $v_m = 4L/\pi d^2$  in Eq. (2), Eq. (3) is obtained.

$$N' = 4(C^* - C_0) \sqrt{D_L L I} \tag{3}$$

*II-1. Apparatus and Procedure*

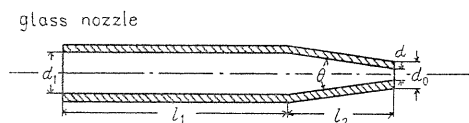
Fig. 1 shows the schematic diagram of the apparatus. The absorption chamber (5) is a glass cylinder of 4.5 cm inner dia. and 12 cm height. The liquid receiver (2) is a glass cylinder of 1.4 cm or 2.0 cm inner dia. and 5.5 cm height. As the so-called bell-shaped nozzles, four glass nozzles of 0.059, 0.086, 0.116 and 0.177 cm inner dia. and one brass nozzle of 0.080 cm inner dia. as shown in Fig. 2 were used.

Absorption liquid is fed from the constant temp. bath and is made into jet through the nozzle (1). In the upper part



- 1. nozzle
- 2. liquid receiver
- 3. kerosene
- 4. liquid level controller
- 5. absorption chamber
- 6. gas burette
- 7. manometer
- 8. thermometer

FIG. 1. Experimental apparatus,



No	d	d0	d1	l1	l2	θ
1	0.059	0.145	0.340	7.9	2.5	6° 26'
2	0.086	0.265	0.600	7.3	2.9	10° 8'
3	0.116	0.270	0.340	7.3	2.0	6° 24'
4	0.177	0.290	0.600	7.3	2.9	8° 20'

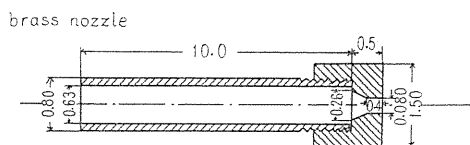


FIG. 2. Nozzle (unit: cm),

of the liquid receiver (2), there is a kerosene film (film thickness is 3~4 mm) to shut out further absorption of the gas by the liquid in the receiver.

The gas (CO<sub>2</sub> purity is more than 99%) is carried from the bomb and is saturated with the vapor of the liquid and is fed to the gas burette (6) and the absorption chamber (5). The gas burette and the absorption chamber is held to the constant temperature. The tip and the outer-side of the nozzle is covered by paraffin to avoid the creeping of the liquid. After the air in the burette and the absorption chamber is thoroughly replaced by CO<sub>2</sub>, the distance from the nozzle to the liquid surface in the liquid receiver is adjusted to a desired length by letting the liquid level controller (4) up or down. Then the liquid is flowed down from the nozzle to perform liquid jet.

After the constancy of temp. of the liquid and gas is ascertained, the out-let valve (9) is closed to shut off the absorption chamber from the atmosphere and the gas burette is connected to the gas absorption chamber through the three way cock (10). As the absorption of CO<sub>2</sub> by the jet proceeds, the pressure of CO<sub>2</sub> in the absorption chamber decreases and this is indicated by the manometer (7). CO<sub>2</sub> in the absorption chamber is supplied from the gas burette by raising the mercury level in the burette by means of the micro-raising apparatus and the pressure in the absorption chamber is maintained 2~3 mm. H<sub>2</sub>O column higher than the atmosphere. This is indicated by the manometer (7). By the raising rate of the mercury level in the gas burette, the absorption rate of CO<sub>2</sub> by the liquid is measured by means of a stop watch. But some absorption of CO<sub>2</sub> (about 15% of the total gas absorption) takes place at the surface of kerosene.

Then the level of the kerosene in the receiver is raised until the tip of the nozzle contacts with the surface of the kerosene, that is, the length of the jet becomes zero, and the same procedure with that described above is carried out. This value is subtracted from the total gas absorption value to get the true gas absorption value. This correction is necessary to get the accurate diffusivity of gas and is a key-point of our paper.

Liquid rate  $L$  [cm<sup>3</sup>/sec] was controlled by the controlling cock (11) above the nozzle and determined by measuring the outlet liquid by a measuring cylinder. Flow rate  $v_m$  [cm/sec] was determined by the liquid rate and inner dia.  $d$  [cm]. The contact time  $t_c$  [sec] of the gas with the liquid was calculated from the jet length and the flow rate  $v_m$ . The temperatures of the gas and the liquid were determined by thermometers placed in fluids, respectively. The temperatures of the inlet and outlet liquid were different within about 1° C in the experiment of CO<sub>2</sub> in KOH solution or NaOH solution. Then their arithmetic mean temperature was taken as the temp. of the liquid.

In this method, it is necessary that there is no ripple in the surface of the jet and no entrainment of gas bubbles in the liquid receiver (2). Thus, the possible range of the measurement is confined and is as follows,

$$l=0.6\sim 3.25 \text{ cm.}, v_m=100\sim 250 \text{ cm/sec and } t_c=2/1,000\sim 3/100 \text{ sec.}$$

### *II-2. Experimental results on the jet*

First, the absorptions of CO<sub>2</sub> by distilled water using 0.059 cm, 0.086 cm, 0.116 cm inner dia. glass nozzles and 0.080 cm inner dia. brass nozzle, were carried out at 20° C and 25° C. Their results are shown in Fig. 3. Two straight lines in Fig. 3 are theoretical lines at 20° C and 25° C, respectively, in which  $C^*$  and  $D_L$  were

taken from I.C.T. Vol. 3, p. 260 and Vol. 5, p. 63 respectively and  $N'$  are calculated from Eq. (3). From Fig. 3, it is clear that the coincidence of the observed values with the theoretical is most satisfactory, and there is no influence of water vapor which Vielstich<sup>13)</sup> has pointed out and there is also no influence of the jet length which Matsuyama has described. So far as the nozzles are used, there is no influence of the inner dia. and the kinds of the nozzle.

Fig. 4 shows that there is no influence whether CO<sub>2</sub> is wet or dry under these conditions. This phenomena coincides with that of Raimondi and Toor<sup>14)</sup> and that of Scriven and Pigford<sup>15)</sup>.

Fig. 5 shows that the pressure in the absorption chamber has no influence till 30 mm. H<sub>2</sub>O column is higher than the atmospheric.

In this experiment, there is a limit in the length of jet. If it is too short, there occurs waves such as rings on the surface of the jet. If it is too long, the

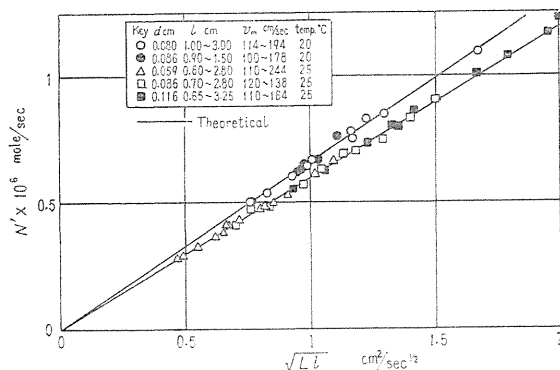


FIG. 3. Rate of CO<sub>2</sub> absorbed by water jet.

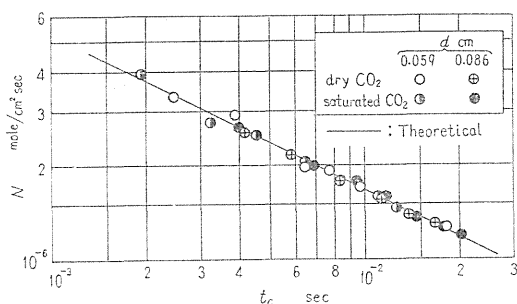


FIG. 4. Effect of presaturation of CO<sub>2</sub> with water vapor on absorption rate.

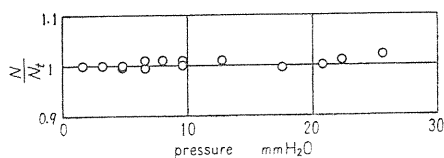


FIG. 5. Effect of pressure on absorption rate.

lower end of the jet scatters. Then there is a range for an adequate length of the jet between  $l_{min}$  and  $l_{max}$ .  $l_{min}$  is the length of the jet in which the ring wave begins to appear and  $l_{max}$  is the length of the jet in which the lower end of the jet begins to scatter.

We measured this  $l_{min}$  and  $l_{max}$  using 5 nozzles in Fig. 2, and H<sub>2</sub>O, aqueous cane sugar solution, aqueous glycerine solution, CCl<sub>4</sub> and ethylalcohol as absorbing liquids.

Fig. 6 shows  $l_{min}/d$  vs.  $v_m$  and all the observed values take place on one curve. From Fig. 6, it is shown that  $l_{min}$  should be larger than  $8d$  till  $v_m=100$ , but when  $v_m$  becomes larger,  $l_{min}$  can be smaller.

Fig. 7 shows that  $l_{max}$  does not depend on the viscosity of the liquid to the contrary of the experiment of Merrington and Richardson.<sup>11)</sup>

Fig. 8 shows the relation of  $l_{max}/d$  vs. Weber number  $[\frac{dv_m^2 \rho}{\sigma}]$ .  $l_{max}/d$  can be represented by the following Eq. (5) within  $\pm 15\%$  error.

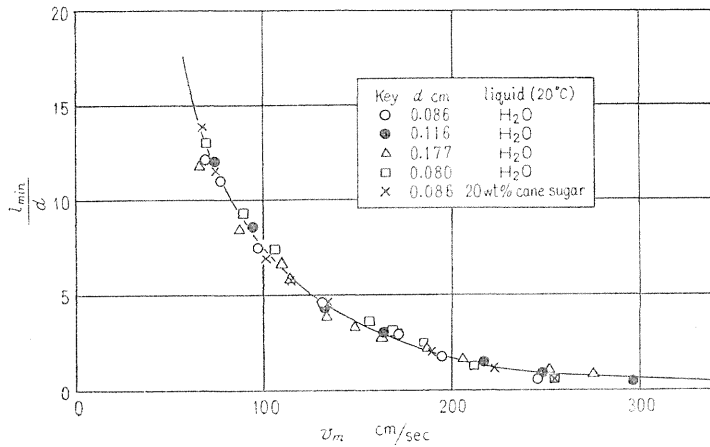


FIG. 6. Minimum jet length:  $\frac{l_{min}}{d}$  vs.  $v_m$ .

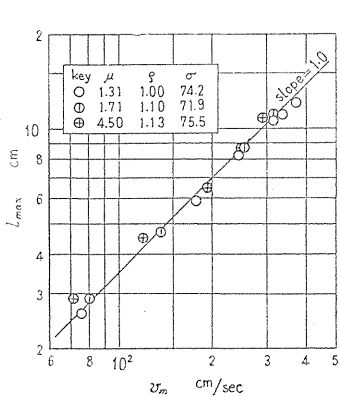


FIG. 7. Effect of viscosity on maximum jet length.

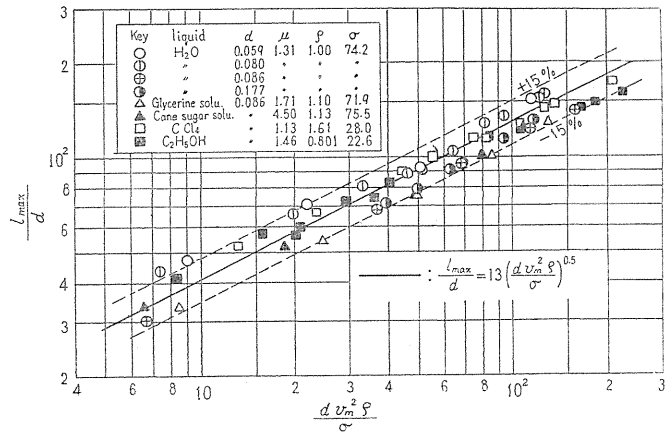


FIG. 8. Maximum jet length:  $\frac{l_{max}}{d}$  vs.  $\frac{dv_m^2 \rho}{\sigma}$

$$l_{\max}/d = 13 \left( \frac{d v_m^2 \rho}{\sigma} \right)^{0.5} \quad (5)$$

The exponent of  $We$ , that is 0.5, is in accord with that of Merrington and Richardson<sup>11)</sup> and that of Toshima.<sup>13)</sup>

From the experiments above described, it is clear that when the measurement is carried within the range of an adequate length, that is, between  $l_{\min}$  and  $l_{\max}$ , the diffusivity of  $CO_2$  in liquids can be easily and accurately determined by Eq. (3) or (4).

### III. Determination of the Diffusivity of $CO_2$ in Liquids

To determine the diffusivity, the same procedure with that described in II-1 are carried out and the absorption rate  $N'$  or  $N$  are measured. Then  $N'$  vs.  $\sqrt{Ll}$  or  $N$  vs.  $1/\sqrt{t_c}$  are plotted in section paper. From the straight line thus derived, the diffusivity is calculated using Eq. (3) or (4).

#### III-1. The diffusivity of $CO_2$ in aqueous glycerine and cane sugar solutions

The diffusivities of  $CO_2$  in 5, 10, 17.5, 25, 35 and 45 wt% aqueous glycerine solution at 15° C ( $C_0=0$ ) and in 10, 20, 30 and 40 wt% aqueous cane sugar solution at 20° C ( $C_0=0$ ) are plotted in Fig. 9. In Fig. 9, the values calculated by Othmer-Thakar method<sup>13)</sup> are also plotted. Their coincidence is satisfactory. In Fig. 10, it is shown that  $D_L$  is approximately inversely proportional to  $\mu$ .

$D_L$  of  $CO_2$  in 25 wt% glycerine solution and 20 wt% cane sugar solution were measured at 5~25° C to see its temperature-dependence. From Fig. 11, it is shown that their temperature-dependence is the same with that in water, that is Eq. (6)

$$D_{Lt} = \frac{D_{L20}}{1.6} (1 + 0.03 t) \quad (6)$$

In Eq. (6),  $D_{Lt}$  means  $D_L$  at  $t^\circ$  C and  $D_{L20}$  is  $D_L$  at 20° C. For  $C^*$  in calculating  $D_L$ , the value in I.C.T. was used.

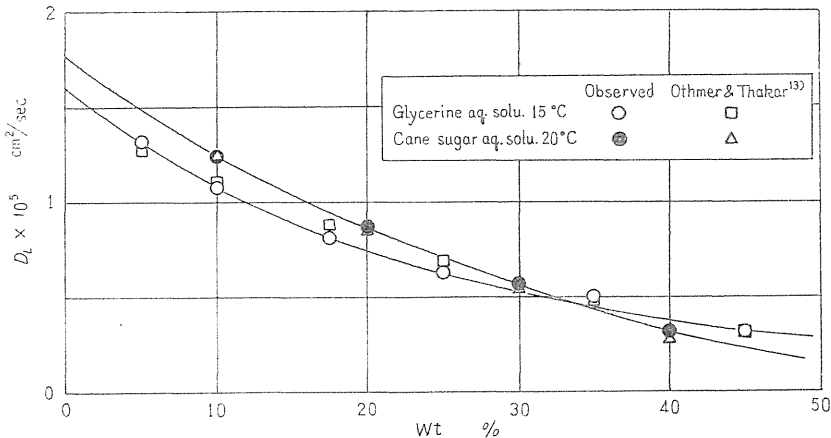


FIG. 9. Diffusivity of  $CO_2$  in glycerine and cane sugar aqueous solutions.

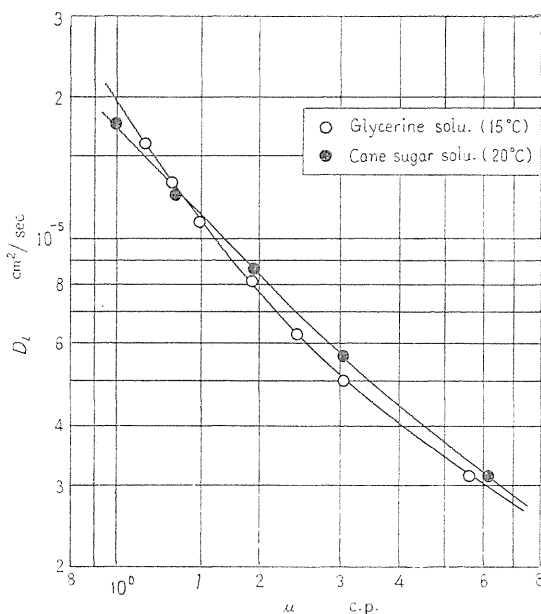


FIG. 10. Effect of viscosity of CO<sub>2</sub> in glycerine and cane sugar aqueous solutions.

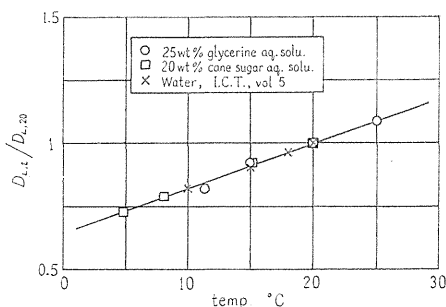


FIG. 11. Variation with temperature of CO<sub>2</sub> diffusivity in 25 wt% glycerine and 20 wt% cane sugar aqueous solutions.

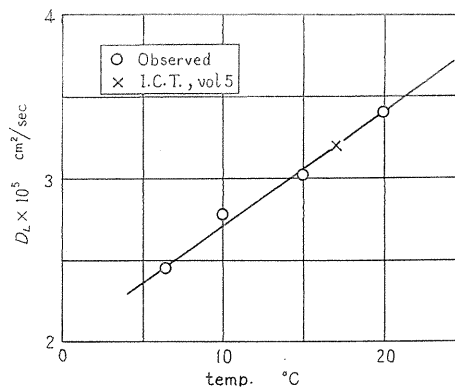


FIG. 12. Diffusivity of CO<sub>2</sub> in 99% ethylalcohol.

### III-2. The diffusivity of CO<sub>2</sub> in ethylalcohol

In Table 1 and Fig. 12, the diffusivities of CO<sub>2</sub> in 99% ethylalcohol ( $C_0=0$ ) at 6.4°, 10°, 15° and 20° C are shown where the correction due to the large vapor pressure of ethylalcohol was introduced and  $C^*$  was taken from I.C.T. Its dependence on the temperatures is shown as Eq. (7).

$$D_{Lt} = \frac{D_{L20}}{1.7} (1 + 0.35 t) \quad (7)$$

From Table 1, it is shown that  $D_L \mu / T$  is constant and  $1.40 \times 10^{-7}$  [cm<sup>2</sup>c.p./sec.°K] at any temperature (6°~20° C).

TABLE 1. Diffusivities of CO<sub>2</sub> in 99% Ethanol at Different Temperatures

Temp. [° C]	$D_L \times 10^5$ [cm <sup>2</sup> /sec]	$\mu^*$ [c.p.]	$D_L \mu / T \times 10^7$ [cm <sup>2</sup> c.p./sec.°K]
6.4	2.45	1.57	1.38
10	2.78	1.47	1.44
15	3.02	1.33	1.38
20	3.40	1.20	1.39
			mean 1.40

\*  $\mu$  is taken from Bingham, E. C. and Jackson, R. F.: Bull. Bur. Stds., 14, 59 (1918~1919).

### III-3. The diffusivity of CO<sub>2</sub> in NaOH and KOH solution

As the absorption of CO<sub>2</sub> by alkaline solution is not physical gas absorption but chemical one, the equations described above should not be applied.

CO<sub>2</sub> absorbed by the alkaline solution diffuses in the solution where OH' is uniformly distributed, and reacts in the following mechanism:



But in this mechanism, the reaction (9) is so faster than the latter (8) and the reaction (8) is the rate controlling. In this case, the contact time of CO<sub>2</sub> with the liquid is so short that the concentration of CO<sub>2</sub> in the liquid is very small compared with the concentration of OH'.

Then the reaction mechanism (8) may be regarded as a pseudo-1st order irreversible reaction.

The theoretical absorption rate by the pseudo-1st order irreversible reaction was derived by Danckwerts<sup>3)</sup>, that is:

$$N = (C^* - C_0) \sqrt{\frac{D_L}{k_r[\text{OH}']}} \left( k_r[\text{OH}'] + \frac{1}{2t_c} \right) \text{erf} \left( k_r[\text{OH}']t_c \right) + \sqrt{\frac{k_r[\text{OH}']}{\pi t_c}} \exp \left( -k_r[\text{OH}']t_c \right) \quad (10)$$

where  $k_r$  is the reaction velocity constant of Eq. (8).

When  $k_r[\text{OH}']t_c > 4$ , Eq. (10) may be approximated in Eq. (11) within the error of 2%,

$$N = (C^* - C_0) \sqrt{D_L k_r [\text{OH}']} \left( 1 + \frac{1}{2 k_r [\text{OH}'] t_c} \right) \quad (11)$$

In the liquid jet, the contact area is  $\pi dl$ . Then, the absorption quantity per unit time ( $N'$ ) can be represented by Eq. (12) which is a linear function of the jet length ( $l$ ),

$$N' = \pi (C^* - C_0) dl \sqrt{D_L k_r [\text{OH}']} + \frac{\pi (C^* - C_0) dv_s}{2} \sqrt{\frac{D_L}{k_r [\text{OH}']}} \quad (12)$$

Fig. 13 shows this relation at 20° C. From the slopes of the straight line,  $D_L$  can be calculated. In Table 2, the diffusivities of CO<sub>2</sub> in each alkaline solution



TABLE 2. Diffusivities of CO<sub>2</sub> in Caustic solution at 20° C

Solution	$D_L \times 10^5$ [cm <sup>2</sup> /sec]	$\mu^*$ [c.p.]	$D_L \mu \times 10^5$ [cm <sup>2</sup> c.p./sec]
0.137 N NaOH	1.72	1.03	1.77
0.282 N	1.59	1.06	1.68
0.462 N	1.58	1.10	1.74
1.33 N	1.37	1.33	1.82
0.244 N KOH	1.73	1.03	1.78
			mean 1.77

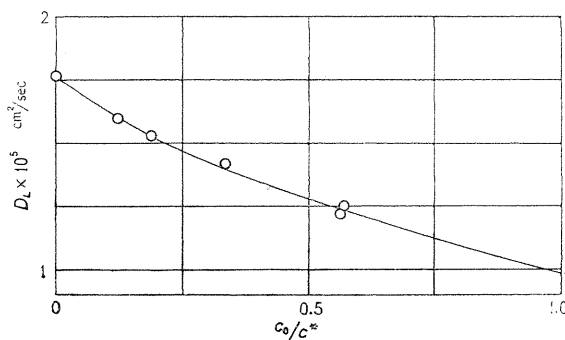
\*  $\mu$  is taken from Hitchcock, L. B. and McIlhenny, J. S.: Ind. Eng. Chem. 27, 461 (1935).

are described where  $C^*$  for NaOH solution was taken from Matsuyama,<sup>10)</sup>  $C^*$  for KOH solution was taken from Nijsing's equation<sup>12)</sup> and  $k_r$  was taken from the data of Faurholt,<sup>6)</sup> that is  $k_r = 4.6 \times 10^6$  cm<sup>3</sup>/mole·sec.

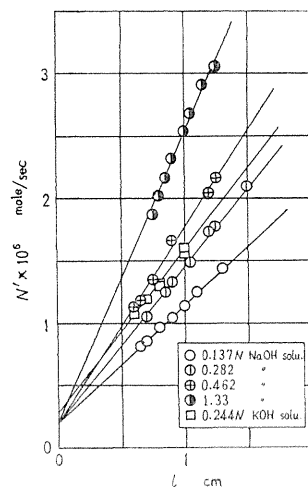
From Table 2, it is shown that  $D_L \mu$  is almost constant at a constant temperature and coincides with the value ( $1.79 \times 10^{-5}$  cm<sup>2</sup>c.p./sec) in CO<sub>2</sub>-H<sub>2</sub>O system at 20° C.

#### III-4. Dependence of the diffusivities of CO<sub>2</sub> on the concentration of CO<sub>2</sub> in water

The dependence of the diffusivities of CO<sub>2</sub> on the concentration of CO<sub>2</sub> in water, that is, the diffusivities of CO<sub>2</sub> in the case of  $C_0 \doteq 0$  in water are shown in Fig. 14. In this case, the absorbed quantity of CO<sub>2</sub> is very small (less than 3% of the saturated value), then the arithmetic mean value of the concentration of CO<sub>2</sub> in water before and after the absorption process was taken as the value ( $C_0$ ) for  $C_0/C^*$  in Fig. 14.

FIG. 14. Variation of CO<sub>2</sub> diffusivity in water with its concentration.

From Fig. 14, it is shown that  $D_L$  decreases almost linearly till  $C_0/C^* \doteq 0.6$  as it does in many liquid-liquid systems.

FIG. 13. Absorption rate of CO<sub>2</sub> in caustic solutions.

#### IV. Conclusion

1) An easy and reliable method for determining the diffusivities of CO<sub>2</sub> in liquids was obtained from the experiment in which the so-called bell-shaped nozzles as shown in Fig. 2 and the jet-receiver calibrated in degrees of absorption were employed, while the pressure in the absorption chamber was held as high as 2~3 mmH<sub>2</sub>O.

2) To practice the above method, the stationary range of the jet, *i.e.*, the minimum jet length ( $l_{\min}$ ) and the maximum jet length ( $l_{\max}$ ), was determined as in Fig. 6 and 8 and  $l_{\max}/d$  was confirmed to be proportional to  $We^{0.5}$ .

3) The diffusivities of CO<sub>2</sub> in glycerine and cane sugar aqueous solutions were measured. The results shown in Fig. 9 and 11 proved to be in good agreement with the values obtained from the correlation of Othmer and Thakar<sup>13)</sup>, by calculation.

4) The diffusivities of CO<sub>2</sub> in ethanol were measured in the temperature range of 6.4~20° C. The results are shown in Fig. 12 and Table 1.

5) The diffusivities of CO<sub>2</sub> in NaOH and KOH solutions were measured at 20° C. The results are shown in Table 2. Their values of  $D_L\mu$  are mostly constant and in accord with the value ( $1.79 \times 10^{-5}$  cm<sup>2</sup>c.p./sec) in H<sub>2</sub>O.

6) Dependence of the concentration of CO<sub>2</sub> on the diffusivity of CO<sub>2</sub> in H<sub>2</sub>O was investigated at 20° C. The results are shown in Fig. 14.

#### Nomenclature

- $C_0$  : initial concentration of gas in liquid [mole/cm<sup>3</sup>],  
 $C^*$  : saturated concentration of gas in liquid [mole/cm<sup>3</sup>],  
 $d$  : nozzle diameter [cm],  
 $D_L$  : diffusivity of gas in liquid [cm<sup>2</sup>/sec],  
 $k_r$  : second-order reaction velocity constant [cm<sup>3</sup>/mole·sec],  
 $l$  : jet length [cm],  
 $l_{\max}$  : maximum jet length [cm],  
 $l_{\min}$  : minimum jet length [cm],  
 $L$  : liquid flow rate [cm<sup>3</sup>/sec],  
 $N$  : mean absorption rate per unit area [mole/cm<sup>2</sup>·sec],  
 $N_t$  : theoretical absorption rate per unit area [mole/cm<sup>2</sup>·sec],  
 $N'$  : amount of gas absorbed per unit contact time [mole/sec],  
 $t_c$  : contact time [sec],  
 $T$  : absolute temperature [°K],  
 $v_m$  : mean jet velocity [cm/sec],  
 $v_s$  : jet surface velocity [cm/sec],  
 $\rho$  : density of liquid [g/cm<sup>3</sup>],  
 $\mu$  : viscosity of liquid [c.p.],  
 $\sigma$  : surface tension of liquid [dyne/cm].

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