

INTERPHASE MASS TRANSFER IN  
VARIOUS TYPES OF COLUMN

by

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## INTRODUCTION

The application of gas absorption accompanied by a chemical reaction in the liquid phase is attracting more and more attention today in chemical processes where higher purity of gas is demanded and where the gaseous products are to be recovered more completely. However, there are no general equations that can be used to correlate the characteristics of the absorption equipment, the properties of the gas and liquid material and the hydrodynamic conditions of the system for the purpose of design calculation.

The conventional design procedures for physical absorption stem from the two-film theory and they are essentially short range extrapolation of performance data obtained in the pilot plant under similar operating conditions as those anticipated in the full-scale installation. Hence each gas-liquid system and each piece of equipment usually has its own correlation equations describing only the performance carried out under the highly specified conditions. When the additional complication of a chemical reaction is involved, no correlation on the laboratory scale can be extrapolated to the plant conditions except in a few special cases.

The theoretical development on this subject has been difficult and slow and it still needs a great deal of experimental support. In many cases the physical constants involved in a theoretical equation are just as hard or even more difficult to obtain than the design data themselves. The Penetration theories proposed by Higbie (1) and Danckwerts (2) demand such physical

constants as "the fractional rate of surface renewal", "the transient absorption rate" and a knowledge of the distribution of local liquid film coefficient  $k_L$ , etc. It is obvious that such kind of treatment is still far from the practical application.

The purpose of the present investigation is to find some general, although empirical, correlation between the purely physical absorption and the absorption processes followed by chemical reaction. Only a few investigators have attempted this problem, but all followed different approach and no previous work has appeared in the literature that can be used for comparison. Roper (10, 11) has made a study of the effect of the concentration of the absorbent solution on the fractional increase of the liquid film coefficient due to chemical reaction. Data obtained from the absorption of chlorine gas in olefins with dissolved iodine as catalyst can be described by the equation

$$\phi - 1 = 39 \left\{ \frac{(C_c + 0.00005) C_B}{C_i} \right\}^{0.5}$$

Where  $\phi$  = the ratio of the liquid film coefficients

$\frac{k'_L}{k_L}$ , primed value refers to the case when chemical reaction is involved.

$C_c$  = Concentration of catalyst (iodine) lb - mole/ft<sup>3</sup>

$C_B$  = Log-mean concentration of the liquid phase reactant  
lb - mole/cu ft

$C_i$  = Concentration of dissolved, but unreacted, chlorine  
at the gas-liquid interface lb - mole/cu ft

Stephens and Morris (15) also studied the effect of concentration in the absorption of chlorine in aqueous solutions of ferrous chloride and ferric chloride. Danckwerts (2) attempted a theoretical treatment of the absorption process accompanied by an irreversible chemical reaction and it is from this theoretical analysis that the ideas of the present experimental approach evolved.

It is deduced, qualitatively, that perhaps the ratio of the absorption rate with chemical reaction to that without chemical reaction could be correlated to the "types" of column operating under "similar" conditions. Stated in a different way, the immediate problem is to obtain the necessary experimental data in order to see whether or not the effect of chemical reaction on absorption rate could be correlated between different types of columns and what would be the proper criterion for the "similarity" of operating conditions.

To achieve this object, three types of columns: a wetted-wall column, a disc column and a packed column were used in the present investigation. They constituted a series of flow patterns of progressing complexity. The  $\text{CO}_2 - \text{H}_2\text{O}$  and the  $\text{CO}_2 - \text{NaOH}$  systems were chosen because of the rapid irreversible (pseudo first order) reaction between  $\text{CO}_2$  and  $\text{NaOH}$  and because of the well-established fact that the absorption rate is liquid-film controlling. In the experimental runs with either of the two systems, all the variables except the liquid rate were maintained as nearly constant as possible so that the effect of the chemical reaction could be readily detected in the result.

## EXPERIMENTAL

## Equipment

Three types of columns were used in the present investigation. They were a disc column, a wetted-wall column and a packed column. A description of each is given below under separate paragraphs.

The wetted-wall column was designed and assembled by Lin (8). The short height of the side wall was designed purposely to eliminate the rippling effect. The Pyrex glass column was mounted between stainless steel end plates with Tygon sheet as gaskets. The absorbing liquid was introduced through two small glass tubes and it overflowed along the knife edge of the inner tube where the absorption takes place. The close-up view of the column and the detailed dimensions were shown in Fig. 1 and Fig. 2 in the Appendix.

The disc column consisted of a 1-1/8 inch Pyrex glass tube and 35 ceramic discs which were threaded on a fiberglass cord held in tension in the center of the tube. The discs were threaded in such a way that the successive discs were at right angle to each other.

The absorbing liquid was introduced at the top through a jet and it flowed downward over the surfaces of the discs. The distance between the jet and the first disc was 1 inch. The diameter and thickness of the disc and other principal constants of the column were given in the appendix and the general arrangement and the accessories were shown in Fig. 3 (Appendix).



The packed column was constructed with a 2-inch inside diameter pyrex glass tube packed with  $1/4$  inch glass Raschig rings. The total length of the column was  $2\frac{1}{2}$  inches while the packed portion was 6.5 inches in height. A perforated stainless steel plate was used to support the packings. In order to insure uniform distribution, the gas from the cylinder was split by a glass tee tube into two streams which were then introduced into the column at two different points on the diameter of the column. Also, the liquid was distributed over the packings by a Tygon distributor. A close-up view was given in Fig. 4 (Appendix).

#### Procedure

Liquid Stream. Distilled water was stored in a 50 gallon stainless tank and pumped to the top of each column by a  $1/30$  hp centrifugal pump. The flow rate was controlled and regulated by a calibrated C-clamp rotameter. Care must be taken to insure that no air bubbles were rising together. Entrained air bubbles in the liquid line leading to the column inlet could usually be eliminated by filling the pump with water before it was switched on. Before each run the absorbing surfaces would be completely wetted either by running the liquor through the column at its maximum flow rate or by filling up the entire column and then draining the liquor off. Incomplete wetting would cause serious error in the results.

The output of the centrifugal pump in the range of higher flow rates required frequent adjustment of the needle valves to keep the liquid flow rate constant.

Gas Stream. The  $\text{CO}_2$  gas was withdrawn from the gas cylinder at a controlled rate and measured by a Brooks rotameter. Problems of stoppage of flow due to expansion of  $\text{CO}_2$  gas in reducing valves were readily overcome. Even minor fluctuations in gas flow rate would not be serious, since it has been firmly established that the  $\text{CO}_2 - \text{H}_2\text{O}$  system is liquid-film controlling so that variation of gas flow rate over a moderate range would not have any effect on the gas absorption rate.

Before entering the column the  $\text{CO}_2$  gas was saturated with water by bubbling through two flasks in series. Two monometers connected to the inlet and outlet ends of the column were employed to measure the pressure difference of the entering and exit gas streams respectively.

Liquid Sampling. It took from 35 to 40 minutes to ensure that the steady state equilibrium conditions have been reached for each run. Samples were then taken at 10 to 15 minutes intervals until the last two samples gave identical chemical analyses.

Special techniques were developed for taking the liquid samples. The sampling device is shown in Plate I. It was necessary that the liquid sample be trapped as soon as it left the column. For the  $\text{CO}_2 - \text{H}_2\text{O}$  system,  $\text{Ba}(\text{OH})_2$  was used as the trapping solution; for the  $\text{NaOH} - \text{CO}_2$  system,  $\text{BaCl}_2$  was used. The tip of the sampling tube was submerged in the excess  $\text{Ba}(\text{OH})_2$  solution in a volumetric flask so that the liquid sample from the absorption column would have no chance to come into contact with the atmosphere. Just a short time of contact with the atmosphere could



have resulted in a considerable loss of  $\text{CO}_2$  from the sample. For the  $\text{NaOH} - \text{CO}_2$  system, the sampling technique was not as critical as in the case of  $\text{CO}_2 - \text{H}_2\text{O}$  system as the gas had been reacted with  $\text{NaOH}$  solution to form  $\text{Na}_2\text{CO}_3$ .

Temperature, Barometric Pressure, etc. In addition to the room temperature the inlet and outlet temperatures of the gas and liquid streams were carefully measured with mercury thermometers. The location of the thermometers are indicated in the schematic diagram, Plate III. Usually one barometric reading would be sufficient for an operation of not more than five or six hours.

#### Chemical Analysis

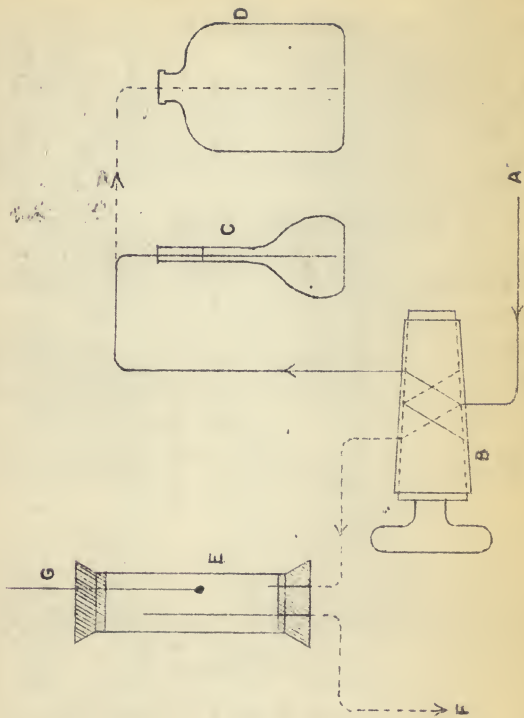
For the  $\text{CO}_2 - \text{H}_2\text{O}$  system, the absorbed carbon dioxide was precipitated as barium carbonate, then the excess barium hydroxide was determined by back titration against hydrochloric acid using phenolphthalein as indicator. For the  $\text{CO}_2 - \text{NaOH}$  system, the total amount of  $\text{CO}_2$  absorbed was determined by two titrations. The liquid sample was divided into two equal portions. The first portion was titrated against sulfuric acid using methyl orange as indicator while the second portion was titrated against the same acid using phenolphthalein as indicator. The difference of the amount of acid used in these two titrations determines the quantity of  $\text{CO}_2$  absorbed.

The detailed procedures and principles of the chemical analysis are discussed in the appendix.

EXPLANATION OF PLATE I

- A: Sample liquid stream from the absorption column
- B: Three-way stopcock
- C: Sampling bottle
- D: Receiving bottle used to drain off the liquid in the hose before sampling
- E: Glass tube for the measurement of exit liquid temperature
- F: Drain Stream
- G: Thermometer

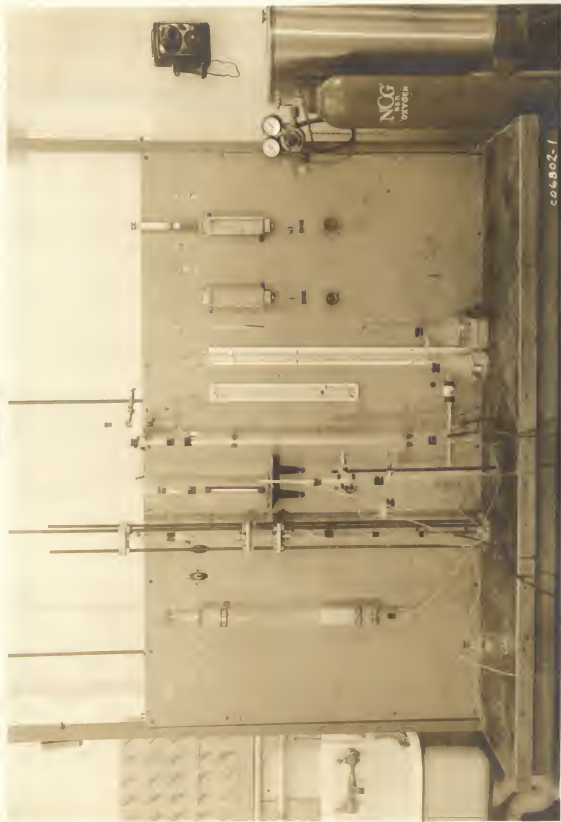
PLATE I



EXPLANATION OF PLATE II

A Picture of the Schematic Diagram  
of  
Plate III

PLATE II



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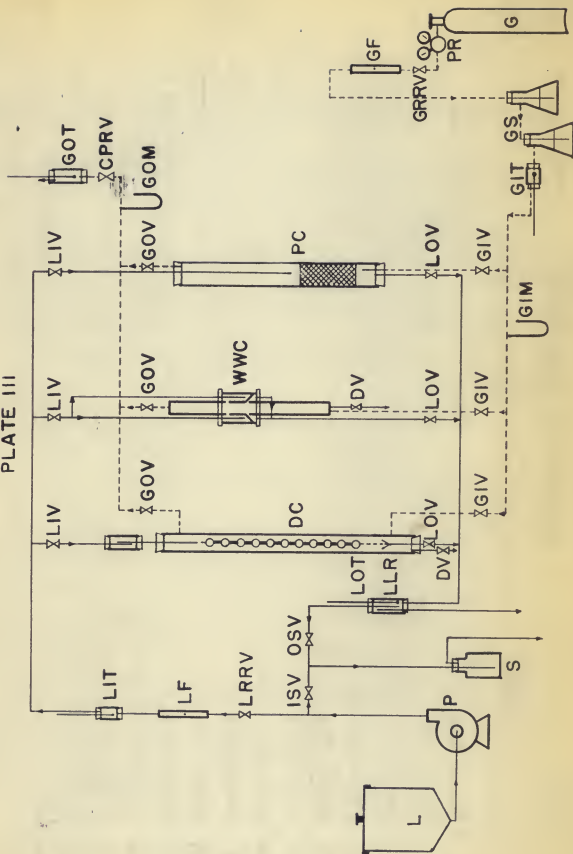
### EXPLANATION OF PLATE III

#### Schematic Diagram of Experimental Layout

L:	Liquid Tank	ISV:	Inlet liquid sampling valve
P:	Liquid pump	S:	Sampling bottle
LRRV:	Liquid rate regulating valve	G:	Cylinder Gas
LF:	Liquid flowmeter	PR:	Pressure regulator
LIT:	Liquid inlet temperature measuring thermometer	GRRV:	Gas rate regulating valve
DC:	Disc column	GF:	Gas flowmeter
WWC:	Wetted-wall column	GS:	Gas saturator
PC:	Packed column	GIT:	Gas inlet temperature measuring thermometer
LOV:	Liquid outlet valve	GIV:	Gas inlet valve
DV:	Drain valve	GIM:	Gas inlet pressure measuring manometer
LLR:	Liquid level regulator	GOV:	Gas outlet valve
LOT:	Liquid outlet temperature measuring thermometer	GOM:	Gas outlet pressure measuring manometer
OSV:	Outlet liquid sampling valve	CPRV:	Column pressure regulating valve
LIV:	Liquid inlet valve	GOT:	Gas outlet temperature measuring thermometer



PLATE III



## RESULTS AND DISCUSSION

## Summary of Experimental Data

CO<sub>2</sub> - H<sub>2</sub>O System. A total of 23 runs were carried out in the three columns for the absorption of carbon dioxide in water. Carbon dioxide gas from the gas cylinder was used without dilution. In all runs the flow rate of CO<sub>2</sub> gas was fixed at 3.1 cu. ft./hr. (at standard conditions) while the liquid rate varied from 2.0 lb./hr. to 24.8 lb./hr. During the months when these experiments were conducted, the room temperature ranged from 26° C to 30° C. In most runs there was no detectable rise in the liquid temperature as it passed through the column. In a few runs, however, the temperature did register a difference of 0.5 to 0.8° C. The carbon dioxide content of the inlet liquid was found negligible for all runs. The gas temperatures of all the runs ranged from 25° to 30° C. The absorption rates measured in these runs are given in Table 5 in the appendix. From the rate data the liquid film coefficient,  $k_L$ , was calculated for each run according to the following equation:

$$k_L = \frac{R}{\Delta G_{l,m}}$$

$$G_{l,m} = \frac{\{(Ce)_{out} - C_{in}\} - \{(Ce)_{in} - C_{out}\}}{\ln \frac{(Ce)_{out} - C_{in}}{(Ce)_{in} - C_{out}}}$$

$$(Ce)_{in} = \frac{P_{in}}{H}$$

$$(Ce)_{out} = \frac{P_{out}}{H}$$

Where  $R$  = Absorption rate  $\text{lb}/(\text{hr.})(\text{ft.}^2)$

$k_L$  = Liquid film coefficient  $\text{lb}/(\text{hr.})(\text{ft.}^2)$  ( $\text{lb}/\text{ft.}^3$ )

$\Delta C_{L,m}$  = Log mean concentration driving force  $\text{lb}/\text{ft.}^3$

$(C_e)_{out}$  = Liquid concentration in equilibrium with the outgoing gas stream expressed  $\text{lb.}/\text{ft.}^3$

$(C_e)_{in}$  = Liquid concentration in equilibrium with the incoming gas stream  $\text{lb.}/\text{ft.}^3$

$C_{out}$  = Outlet liquid concentration obtained from chemical analysis

$C_{in}$  = Inlet liquid concentration obtained from chemical analysis (zero in the present case)

$P_{in}$  = Partial pressure of inlet  $\text{CO}_2$  atm

$P_{out}$  = Partial pressure of outlet  $\text{CO}_2$  atm

$H$  = Henry's Law constant (available in Perry's Handbook), atm

The values of the calculated  $k_L$  range from 0.16 to 1.01 and they are given in the appendix.

$\text{CO}_2$  -  $\text{NaOH}$  System. A total of 27 runs were carried out under the same operating conditions as the  $\text{CO}_2$  -  $\text{H}_2\text{O}$  system except that the distilled water in the previous absorption system was replaced by 0.92 N  $\text{NaOH}$  solution. The absorption was studied at seven different liquid rates corresponding to those conducted in the  $\text{CO}_2$  -  $\text{H}_2\text{O}$  system. The method of calculation was the same as for the  $\text{CO}_2$  -  $\text{H}_2\text{O}$  system. It was assumed that the solution exerted no back pressure and the concentrations of  $\text{CO}_2$  in the solution were zero at both ends of the column. In other words  $C_{in}$  and  $C_{out}$  were both zero.

The heat of reaction between NaOH and CO<sub>2</sub> caused the outlet liquid temperature to increase by 2° to 6° C above the inlet temperature depending on the type of column. The liquid temperatures ranged from 27° C to 31° C for the wetted-wall column, from 26.7° C to 34.6° C from the disc column. The CO<sub>2</sub> content of the inlet NaOH solution was again found to be negligible.

Absorption rates measured in these runs are also given in the appendix.

#### Discussion of Experimental Results

Correlation of absorption rate with chemical reaction in the liquid phase from the rate of physical absorption.

In Plate III,  $k_L$  represents a correlation of the measured absorption rates of CO<sub>2</sub> in water and CO<sub>2</sub> in NaOH, respectively, in different columns. This graph was constructed from the experimental data for the disc and the wetted-wall columns as follows: In Tables 11 and 13 in the appendix, for each value of  $k_L$ , read off the corresponding value of liquid flow rate  $\Gamma$  and physical absorption rate  $R$ . Then in Tables 8 and 10 in the appendix, locate the identical flow rate  $\Gamma$  and read off the chemical absorption rate  $R'$ . The ratios between  $R'$  and  $R$  thus obtained at the same flow rate are given in Table 1 and plotted versus  $k_L$  in Plate IV.

The value of  $k_L$  in the wetted-wall column ranges from 0.174 to 0.660 lb./hr.)(ft.<sup>2</sup>) (lb./ft.<sup>3</sup>) corresponding to liquid rates from 2.0 to 24.8 lb./hr. The  $k_L$  values in the disc column are from 0.562 to 1.01 over the same range of liquid rates as above.

The two sets of data give rise to two smooth curves which overlap each other in the interval of  $k_L$  values between 0.562 and 0.66. However, upon closer inspection it is seen that the data for the two different columns can be represented by a single curve as described by the equation:

$$\alpha = 14.23 k_L - 0.697 \text{ --- (1)}$$

Where  $\alpha = \frac{R'}{R}$ , ratio of absorption rate with chemical reaction to that without chemical reaction (or to the physical absorption rate)

$k_L$  = Liquid film transfer coefficient for the physical absorption,

and the numerical coefficients were determined by the method of least squares. The complete data and the method of calculation are tabulated in the appendix.

This result is interpreted to mean that irrespective of the type of column in which the absorption is taking place, as long as the flow rates and other operating conditions are such that the value of  $k_L$  is the same, the effect of the chemical reaction on the absorption rate can be found either directly from the curve on Plate IV or by calculation with the empirical equation (1).

The proof of the independence of the effect of chemical reaction on the absorption rate with regard to the types of column in which the absorption process occurs would be stronger if the overlapping portion of the  $\frac{R'}{R}$  versus  $k_L$  were wider than the present results. However, in view of the coincidence of the general tendency of the curves and the actual overlapping of the

experimental data, it is believed that the results obtained in this investigation at least provide an indication that  $\alpha$  (which is the ratio of the absorption rates) is independent of the two types of column used. For further study it is suggested that, at least two more columns of larger dimensions be constructed and higher liquid rates, i.e. higher  $k_L$  values, be employed.

A plot of  $\alpha$  versus  $k_{Ga}$ . A similar plot with  $\alpha$  versus  $k_{Ga}$  for the packed column is also presented in Plate V for comparison. The general trend of the resultant curve is nearly the same as the plot for the disc and the wetted-wall columns. However, since the data here were obtained from a single packed column the results are not conclusive by themselves. Moreover, the absorption process in a packed tower is further complicated due to the fact that  $k_G$  and "a" (interfacial area per unit volume of packing) are both varying with the liquid rate. There is no way, so far, to predict the individual contribution of  $k_L$  and "a" to the combined effect observed in the laboratory. An attempt has been made to detect the change of "a" in the packed column due to the change in the liquid rate. By assuming that  $k_L$  could be predicted with the correlation developed for the disc column it was found that the absorption area (per unit packing volume) increased appreciably as the liquid rate became higher. A plot of the calculated "a" versus liquid rate is presented in Plate VI. The explanation of this phenomenon is that at lower liquid rates the packing surfaces might not have been completely wetted and were ineffective for absorption.



The Effect of Liquid Rate on the Ratio of Liquid Film Coefficient. To show the effect of liquid rate,  $\beta$ , the ratio of the liquid film coefficient with chemical reaction to that without, is plotted against the liquid rate for each column as shown in Plates VII, VIII, and IX. The complete data for these plots are given in Tables 2, 3, and 4 in appendix, respectively. All three curves show a negative slope, which can be interpreted to mean that the film coefficient of physical absorption is increasing faster with the liquid rate than that of the chemical absorption. Furthermore, the viscosity of 0.92N NaOH solution at the average operating temperature was 1.2 times as much as that of water. Therefore in the chemical absorption case where NaOH solution is used instead of water, the liquid film thickness, hence the observed coefficient  $k_L$  should be even less sensitive to any change in liquid rate.

Another significant feature of Plates VII, VIII, and IX is that the value of  $\beta = \frac{k'_L}{k_L}$  varies from column to column depending on its type. In the wetted-wall column, the value of  $k'_L$  (film coefficient with chemical reaction) is on the average about 30 times greater than that of  $k_L$  (film coefficient of physical absorption); in the disc column, the ratio of  $k'_L$  to  $k_L$  is about 11; while in the packed column, about 10.

Note that the wetted-wall column, the disc column and the packed column all together constitute a series of flow patterns of progressing complexity. For a given liquid rate, the ratio of the two coefficients ( $\beta$ ) is much higher in the wetted-wall column

than in the other two. The corresponding values of  $\phi$  in the disc and the packed columns are approximately the same, which is also to be expected because of their resemblance in flow pattern.

For the range of the liquid rate studied,  $k_L$  value varies from 0.16 to 0.66 in the wetted-wall column and from 0.56 to 1.01 in the disc column. The lower value of  $k_L$  in the wetted-wall column would account for the higher ratio of  $k'_L$  to  $k_L$ .

The quantity  $\frac{k'_L - k_L}{k_L}$  was used by Roper (10, 11) to represent the fractional increase in the liquid film coefficient due to chemical reaction. As the  $k_L$  value is continuously increasing with the liquid rate, the effect of chemical reaction, under the same operating conditions as that of the physical absorption, would become less important and finally as a limiting case at extremely high liquid rate, the value of  $k'_L$  (absorption with chemical reaction) would practically be the same as  $k_L$  (physical absorption). Then the fractional increase would become zero. On the other hand, if the  $k_L$  value for the physical absorption or the solubility of the solute gas in the absorbent liquid is so small that only a trace of the solute gas could be absorbed into the liquid, then the chemical reaction would bear a much more pronounced effect on the liquid film coefficient. The absorption process carried out in the wetted-wall column provides a direct experimental proof of the above statement because, again using Roper's terminology, the "fractional increase" in this case is expected to be a large number.

Effect of Liquid Rate on  $k_L$  in the Disc Column. The present data of the absorption of  $CO_2$  in water can be correlated by the method of least squares as follows:

$$k = 0.123 \Gamma^{0.37} \quad \text{for } 16 < \Gamma < 73 \text{ ef/hr. ft.}$$

$$k = 0.0386 \Gamma^{0.644} \quad \text{for } 73 < \Gamma < 200 \text{ lb/hr. ft.}$$

A plot of  $k_L$  versus  $\Gamma$  is shown in Plate IX.

Only a limited amount of data in the literature is available for comparison. These are plotted also in Plate IX. It shows that the present data are comparable to those obtained by Taylor and Robert (16) which are represented by the equations

$$(i) \quad k = 0.124 \Gamma^{0.4} \quad \text{for } \Gamma < 155 \text{ lb/hr. ft.}$$

$$(ii) \quad k = 0.0056 \Gamma^{1.0} \quad \text{for } \Gamma > 155 \text{ lb/hr. ft.}$$

Note that the break point on the curve occurs at a different liquid rate. This also agrees with Taylor and Robert's own observation that this critical flow rate where the break in the curve occurs varies with the dimensions of the discs used in each particular column.

The data of Stephens and Morris (15) are represented by the equation

$$k = 0.048 \Gamma^{0.7}$$

Again the apparent discrepancy may be attributed to the difference in the dimensions and the wetting properties of the discs used.

When the column used in the present study was first constructed by Hwu (6), it was tested at a higher liquid rate range. The equation  $k = 0.0075 \Gamma^{0.97}$  was tentatively proposed. The experimental points are also plotted in Plate XI.

Plate X is a plot of  $C$ , the concentration of  $\text{CO}_2$  in the exit liquid sample, versus the liquid rate. Hwu (6) explained that two opposing factors controlled the  $\text{CO}_2$  concentration in the exit liquid: One is the residence time or time of contact between the liquid and gas; the other is the degree of turbulence in the liquid stream. The plot in Plate X is consistent with this explanation. At the lower liquid rates, apparently the first factor predominates. Therefore the concentration first decreases, because of the shortened time of contact, as the liquid rate increases. At the higher liquid rate range, the second factor becomes more important. Therefore, then, as the liquid rate increases further, the concentration begins to level off as the effect of increased turbulence begins to compensate and may eventually overtake the effect of shortened contact time.

#### CONCLUSIONS

The findings of this investigation are summarized as follows:

The effect of chemical reaction on the absorption rate was studied and found amenable to correlation of the following form

$$\frac{R'}{R} = a(k_L)^b$$

where  $R'$  = Absorption rate per unit area when the liquid contains reagent which reacts with the solute.

$R$  = Absorption rate per unit area when the liquid contains no active reagent.

$k_L$  = Liquid film absorption coefficient when the liquid contains no active reagent.

$a, b$  = Empirical constants.

For the absorption of  $\text{CO}_2$  in  $\text{NaOH}$  solutions at room temperature, it was found that  $a = 14.23$  and  $b = -0.697$ . Furthermore, these same constants apply to both the short wetted column and the disc column within the entire flow range studied from 2 lb/hr. to 24.8 lb/hr. It is recommended that  $k_L$  for the physical absorption be used as the correlating variable, in preference to the modified Reynolds' number or the liquid flow rate itself. As long as the operating conditions (flow rates, physical properties, etc.) are such that  $k_L$  values in the two different types of columns are the same, the ratio  $R'/R$  in the two columns would be the same also. Upon further verification and modification, this method of correlation should be able to facilitate the design procedure involving new chemical reactions as follows:

(1) Determine the constants  $a$  and  $b$  with any convenient laboratory column such as the present disc column.

(2) Estimate  $k_L$  and  $R$  for the specified equipment and operating conditions by means of the existing design equations for physical absorption.

(3) Find the rate of chemical absorption in question:

$$R' = (R) a (k_L)^b.$$

The limitation of the proposed correlation is that it only accounts for the effect of chemical reaction. The present packed column data can not be correlated by the same constants as for the other two columns, although the form of the equation is still the same. In packed columns, in addition to the chemical effect, any change in the effective absorption area due to change in flow



conditions must also be accounted for. This, apart from the chemical reaction effect, has been the topic of a great deal of study in the past by various workers without much promise of success. This limitation imposes a restriction on the choice of laboratory column in step (1) of the design procedure above. It would be necessary to choose one for which the correlation of physical absorption is well known.

$\phi$ , the ratio of the liquid film coefficient for the absorption accompanied by chemical reaction,  $k'_L$ , to that of physical absorption,  $k_L$ , was found to vary from column to column depending on the characteristics of each individual piece of equipment. The fractional increase of the liquid film coefficient,  $\phi - 1 = \frac{k'_L - k_L}{k_L}$ , was found to be higher in a column where the  $k_L$  value range was lower. In other words, the effect of chemical reaction on the liquid film coefficient is more pronounced in a column of lower  $k_L$  value than those of higher values of  $k_L$ .

The measurement of the liquid film coefficient for the absorption of carbon dioxide in water in the disc column has been extended. They are consistent with those reported in the literature. Two empirical equations were proposed:

$$k_L = 0.123 \Gamma^{0.37} \quad \text{for } 16 < \Gamma < 73 \text{ lb/hr. ft.}$$

$$k_L = 0.0386 \Gamma^{0.644} \quad \text{for } 73 < \Gamma < 200 \text{ lb/hr. ft.}$$



Table 1. Effect of Chemical Reaction on the Absorption rate in the disc and the wetted-wall columns.

Run No	R	CO <sub>2</sub> absorbed without chem- ical reaction lb/hr ft <sup>2</sup>	Run No	CO <sub>2</sub> absorbed with chemical reaction lb/hr ft <sup>2</sup>	$\alpha$	$k_L$ Liquid absorp- tion constant lb/hr ft <sup>2</sup> lbs/ft <sup>3</sup>
5B4	0.0304	4.2B <sub>1</sub> , 4.3B <sub>1</sub>	0.525*	17.3	0.582	
5B4	0.0304	4.2B <sub>1</sub> , 4.3B <sub>1</sub>	0.525*	17.3	0.562	
7B1	0.0367	4.4B <sub>1</sub>	0.694	18.9	0.618	
7B2	0.0384	4.4B <sub>1</sub>	0.694	18.1	0.650	
8B2, B3	0.0472*	4.5B <sub>1</sub>	0.759	20.5	0.756*	
8B2, B3	0.0472*	4.6B <sub>1</sub>	0.740	14.9	0.705	
9B1	0.0588	4.7B <sub>1</sub>	0.917	15.6	0.935	
9B3	0.0602	4.7B <sub>1</sub>	0.917	15.2	1.011*	
10B1, B2, B3	0.0682*	4.8B <sub>1</sub>	1.11	16.3	0.174*	
22B3, B5, B6	0.01395*	6.6B <sub>1</sub>	0.686	49.2	0.303*	
21B1, B2	0.0252*	6.8B <sub>1</sub>	0.947	33.6	0.303*	
21B1, B2	0.0252*	6.7B <sub>1</sub>	0.752	30.2	0.348*	
23B2, B3, B6	0.0300*	6.4B <sub>1</sub>	0.845	28.2	0.348*	
23B2, B3, B6	0.0300*	6.4B <sub>2</sub>	0.852	28.4	0.318*	
24B1, B2, B3	0.036*	6.3B <sub>1</sub>	1.028	28.5	0.414	
24B1, B2, B3	0.036*	6.3B <sub>2</sub>	1.032	30.0	0.414	
24B1, B2, B3	0.036*	6.3B <sub>1</sub>	1.028	28.5	0.400	
24B1, B2, B3	0.036*	6.3B <sub>2</sub>	1.032	30.0	0.400	
25B3	0.0589	6.2B <sub>1</sub>	0.992	16.85	0.660	
25B4	0.0567	6.2B <sub>1</sub>	0.992	17.50	0.660	
26B2	0.0482	6.1B <sub>1</sub>	1.111	23.0	0.547	
26B4	0.0462	6.1B <sub>1</sub>	1.111	24.0	0.504	
27B1, B2	0.0519*	6.0B <sub>1</sub>	1.26	24.2	0.565	
27B3	0.0531	6.0B <sub>1</sub>	1.26	23.7	0.565	
27B1, B2	0.0519*	6.0B <sub>2</sub>	1.061	20.4	0.565	
27B3	0.0531	6.0B <sub>2</sub>	1.061	20.4	0.565	

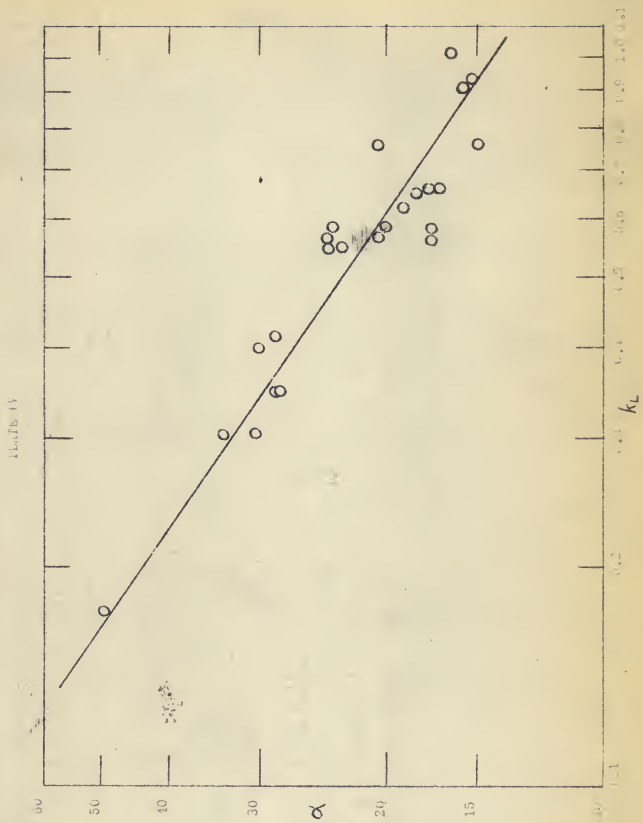
\* Average value for those runs indicated.

EXPLANATION OF PLATE IV

Increase of Absorption Rate due to Chemical Reaction in the disc and the wetted-wall columns at different  $k_L$  values.

Ordinate:  $\alpha$ ,  $(\frac{R'}{R})$ , ratio of the absorption rate with chemical reaction in the liquid phase to that of physical absorption

Abscissa:  $k_L$ , Liquid Film Transfer Coefficient  
 $\text{lbs}/(\text{hr})(\text{ft}^2)(\text{lb}/\text{ft}^3)$



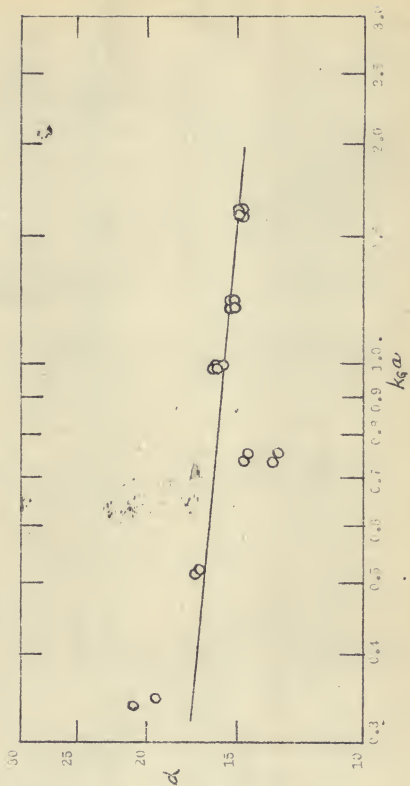
EXPLANATION OF PLATE V

Increase of Absorption Rate due to Chemical Reaction in the Packed Column at different  $k_{Ga}$  values.

Ordinate:  $\alpha$ ,  $(\frac{R_1}{R})$ , ratio of the absorption rate with chemical reaction in the liquid phase to that of physical absorption

Abscissa:  $k_{Ga}$ , Overall transfer coefficient based on the driving force of the gas side.  
 $\text{lbs}/(\text{hr})(\text{ft}^2)(\text{atm})$

PLATE 7



EXPLANATION OF PLATE VI

Effect of Liquid Rate on the Wetted Surface area per unit volume of packing.

Ordinate:  $a$ , effective wetted surface area per unit volume of packing,  $\text{ft}^2/\text{cu ft}$

Abscissa: Liquid rate  $G_L$  lbs/(hr)( $\text{ft}^2$ )



PLATE VI

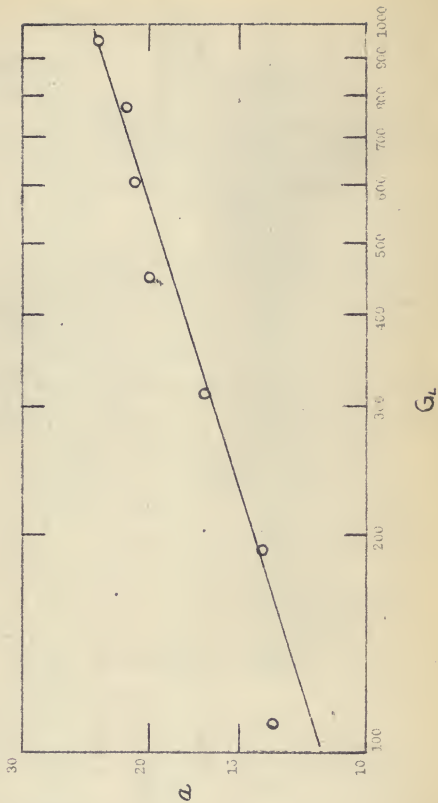


Table 2. Effect of liquid rate on the ratio of the liquid film coefficient with chemical reaction to that without in the disc column.

Run No	$k_L$ Liquid film con- stant without chemical reaction : lbs/(hr)(ft <sup>2</sup> )(lbs/ft <sup>3</sup> )	Run No	$k_L$ Liquid film constant with chemical reaction : lbs/(hr)(ft <sup>2</sup> )(lbs/ft <sup>3</sup> )	$\phi$	$\Gamma$ Liquid Flow rate : lb/(hr)(ft)
5B2	0.472	42B2	5.77	12.2	53.5
5B4	0.582	42B2	5.77	9.9	53.5
5B5	0.562	42B2	5.77	10.2	53.5
5B2	0.472	43B1	5.23	11.1	53.5
5B4	0.582	43B1	5.23	9.0	53.5
5B5	0.562	43B1	5.23	9.3	53.5
7B1	0.618	44B1	6.93	11.2	77.2
7B2	0.650	44B1	6.93	10.7	77.2
8B1	0.739	45B1	7.09	9.6	100.4
8B2, B3	0.756*	45B1	7.09	9.4	100.4
8B1	0.739	46B1	10.00	13.5	100.4
8B2, B3	0.756*	46B1	10.00	13.2	100.4
9B1	0.905	47B1	9.20	10.2	133
9B2	0.912	47B1	9.20	10.1	133
9B3	0.925	47B1	9.20	9.8	133
10B1	1.023	48B1	11.45	11.2	163
10B2	0.955	48B1	11.45	12.0	163
10B3	1.011	48B1	11.45	11.3	163

\* Average value for Run numbers indicated.

EXPLANATION OF PLATE VII

Effect of Liquid Rate on the ratio of the liquid film coefficient with chemical reaction to that without in the disc column.

Ordinate:  $\beta$ ,  $(\frac{k'}{k})$ , ratio of the liquid film coefficient with chemical reaction to that without

Abscissa:  $\Gamma$ , liquid rate lbs/(hr)(ft)

PLATE VII

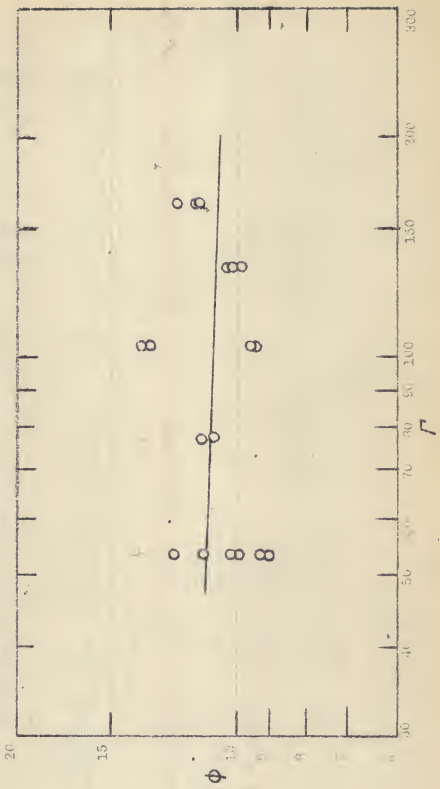


Table 3. Effect of liquid rate on the ratio of the liquid film coefficient with chemical reaction to that without in the wetted wall column.

Run No	$k_L$	$k_L$	Run No	$k_L$	$G$
	Liquid Absorption constant without chemical reaction, $lb/(hr)(ft^2)(lb/ft^3)$	Liquid Absorption constant with chemical reaction, $lb/(hr)(ft^2)(lb/ft^3)$		Liquid Absorption constant with chemical reaction, $lb/(hr)(ft^2)(lb/ft^3)$	Mass Flow Rate $lb/(hr)(ft^2)$
22B3, B5, B6	0.174*	6.9	66B1	39.7	366
21B1	0.311	7.7	67B1	24.8	770
21B2	0.2955	7.7	67B1	26.1	770
21B1	0.311	8.56	68B1	27.8	770
21B2	0.2955	8.56	68B1	29.0	770
23B2	0.348	9.16	64B1	26.3	1245
23B3	0.3415	9.16	64B1	26.8	1245
23B6	0.358	9.16	64B1	25.6	1245
23B2	0.348	9.26	64B2	27.2	1245
23B3	0.3415	9.26	64B2	27.1	1245
23B6	0.358	9.26	64B2	25.9	1245
24B2	0.400	9.9	63B1	24.8	1795
24B1, B3	0.4155*	9.9	63B1	23.8	1795
24B2	0.400	10.9	63B2	27.3	1795
24B1, B3	0.4155*	10.9	63B2	26.2	1795
25B3	0.604	10.0	62B1	15.1	2420
25B4	0.656	10.0	62B1	15.2	2420
26B2	0.547	11.3	61B1	20.7	3100
26B4	0.504	11.3	61B1	22.4	3100
27B1, B2	0.565*	12.3	60B1	3800	3800
27B3	0.585	12.3	60B2	21.0	3800
27B1, B2	0.565	10.7	60B1	18.9	3800
27B3	0.565	10.7	60B2	18.3	3800

\* Average values for those runs indicated.

EXPLANATION OF PLATE VIII

Effect of Liquid Rate on the Ratio of the Liquid Film Coefficient with Chemical Reaction to that without in the Wetted-Wall Column.

Ordinate:  $\beta, \left(\frac{k_1'}{k_2'}\right)$ , ratio of the liquid film coefficient with chemical reaction to that without

Abscissa:  $G_L$ , liquid rate lbs/(hr)(ft<sup>2</sup>)



PLATE VIII

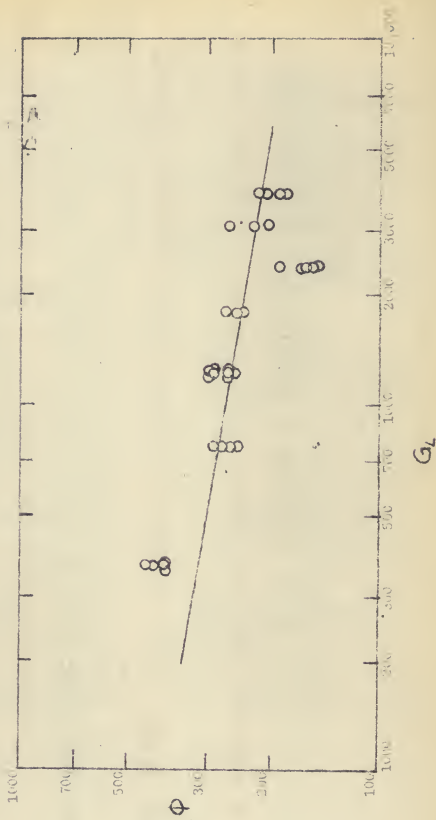


Table 4. Effect of Liquid Rate on the ratio of the liquid film coefficient with chemical reaction in the liquid phase to that without in the packed column.

Run No	$k_L A$ Liquid film coef- ficient without chemical reaction $(lb/hr ft^3)(lb/ft^3)$	Run No	$k_L A$ Liquid film coefficient with chemical reaction $(lb/hr ft^3)(lb/ft^3)$	$k_L A$ Liquid film coefficient with chemical reaction $(lb/hr ft^3)(lb/ft^3)$	Gr flow rate $lb/hr ft^2$
15B <sub>3</sub> ,B <sub>4</sub>	5.96*	51B <sub>1</sub>	74.0	12.4	192.5
15B <sub>5</sub> ,B <sub>6</sub>	6.25*	51B <sub>1</sub>	74.0	11.8	192.5
14B <sub>3</sub> ,B <sub>4</sub>	9.45*	49B <sub>1</sub> ,B <sub>2</sub>	97.55*	10.3	312
14B <sub>5</sub> ,B <sub>6</sub>	9.28*	49B <sub>1</sub> ,B <sub>2</sub>	97.55*	10.5	312
13B <sub>1</sub> ,B <sub>2</sub>	12.95*	52B <sub>2</sub>	109	8.4	449.5
13B <sub>3</sub> ,B <sub>4</sub>	12.45*	52B <sub>2</sub>	109	8.8	449.5
13B <sub>1</sub> ,B <sub>2</sub>	12.95*	52B <sub>1</sub>	116.5	9.0	449.5
13B <sub>3</sub> ,B <sub>4</sub>	12.45*	52B <sub>1</sub>	116.5	9.4	449.5
17B <sub>2</sub>	15.69	53B <sub>1</sub>	162	10.5	605
17B <sub>3</sub> ,B <sub>4</sub>	16.19*	53B <sub>1</sub>	162	10.1	605
17B <sub>6</sub>	16.78	53B <sub>2</sub>	166	9.8	605
18B <sub>1</sub>	20.2	54B <sub>1</sub> ,B <sub>2</sub>	201*	9.95	775
18B <sub>2</sub> ,B <sub>3</sub>	19.39*	54B <sub>1</sub> ,B <sub>2</sub>	201*	10.4	775
19B <sub>1</sub> ,B <sub>2</sub>	23.6*	55B <sub>1</sub> ,B <sub>2</sub>	218*	9.2	950

\* Average value for runs indicated.

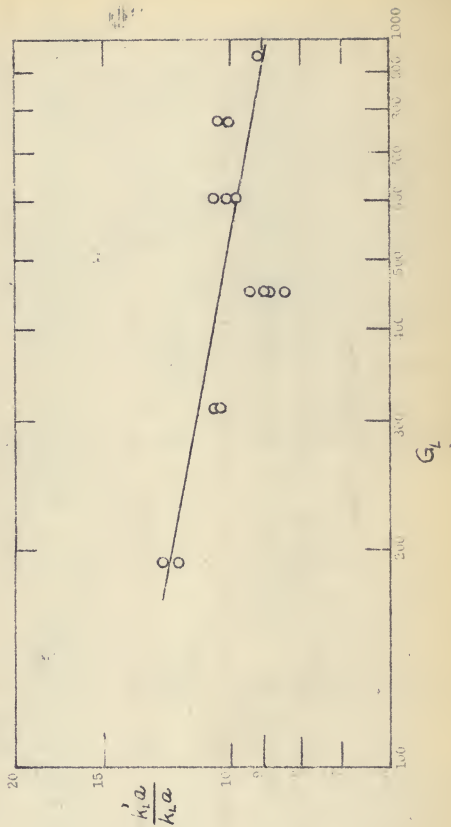
EXPLANATION OF PLATE IX

Effect of Liquid Rate on the Ratio of the Liquid Film Coefficient with Chemical Reaction in the Liquid Phase to that without in the Packed Column.

Ordinate:  $\frac{(k'_L)_a}{(k_L)_a}$ , ratio of the liquid film coefficient with chemical reaction to that without

Abscissa:  $G_L$ , liquid rate lbs/(hr)(ft<sup>2</sup>)

PLATE IX



EXPLANATION OF PLATE X

Plot of Liquid Film Coefficient,  $k_L$  vs the liquid rate,  $\Gamma$  in the disc column.

Ordinate: Liquid Film Coefficient  $k_L$  lbs/hr ( $ft^2$ )(lb/ $ft^3$ )

Abscissa: Liquid Rate  $\Gamma$  lbs/(hr)(ft)

Legend:

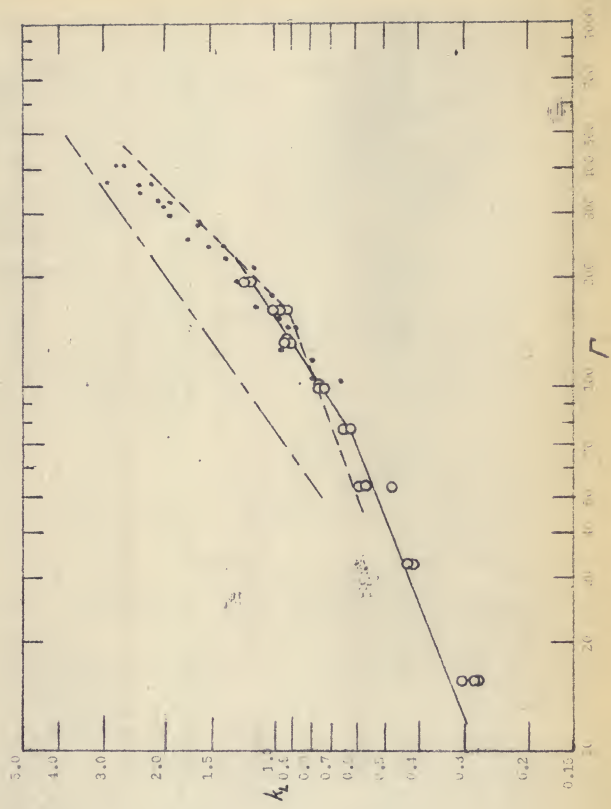
----- Reported by Stephens & Morris (15)

----- Reported by Taylor & Robert (16)

----- Present investigation

..... Data reported by Hwu (6)

PLATE X





EXPLANATION OF PLATE XI

Plot of Exit CO<sub>2</sub> concentration vs liquid rate.

Ordinate: Exit concentration CO<sub>2</sub> lb/cu ft

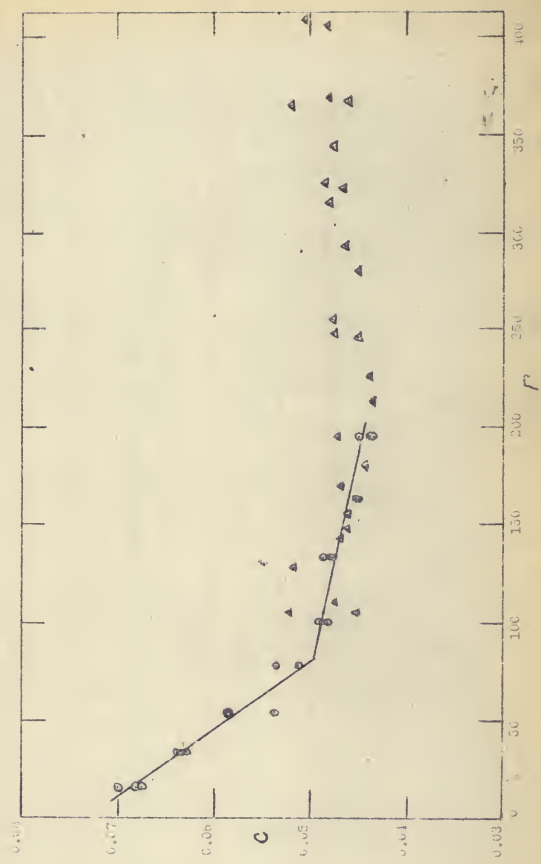
Abscissa: Liquid rate  $\bar{V}$  lbs/(hr)(ft)

Legend:

○ Data obtained from the present observation

△ Data reported by Hwu (6)

PLATE II



## ACKNOWLEDGMENTS

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**APPENDIX**





Fig. 1. Wetted-wall column.

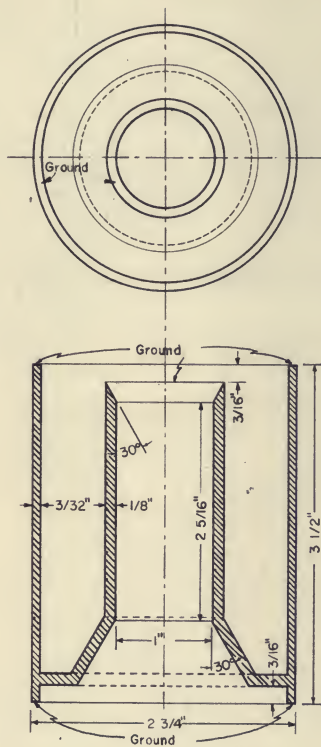


Fig. 2 Detailed Drawing of Fluted-Wall Column



Fig. 3. Disc column.



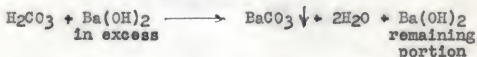
Fig. 4. Packed column.

### Chemical Analysis:

#### CO<sub>2</sub> - H<sub>2</sub>O System

The amount of the absorbed CO<sub>2</sub> precipitated as barium carbonate in the barium hydroxide solution was determined by back-titration of barium hydroxide against hydrochloric acid.

The method is based on the reaction:



the remaining portion of Ba(OH)<sub>2</sub> was then titrated against HCl (0.1N) using phenolphthalein as indicator. The results of this back titration method were generally less than 5 per cent in error.

The amount of CO<sub>2</sub> absorbed was calculated by the following formula

$$\begin{aligned} & \text{CO}_2 \text{ absorbed gr/c.c.} \\ & = \frac{C(Y-X) \times 0.022}{\text{Sample taken (c.c.)}} \end{aligned}$$

where Y = HCl (number of c.c.) required to neutralize the trapping solution Ba(OH)<sub>2</sub>

X = HCl (number of c.c.) required in the back titration

C = Concentration (number of normality of HCl used)

0.022 = Equivalent quantity of CO<sub>2</sub> (gram) for every c.c. of 1N HCl solution consumed in titration

All titrations were carried out in an Erlenmeyer flask free from carbon dioxide. A standard solution was prepared for the comparison of the color of the end point of titration.

CO<sub>2</sub> - NaOH System

In the present case, the sample liquid was a mixture of Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, NaOH, and H<sub>2</sub>O. The chemical reactions upon which the method of titration was based were listed as follows:



Methyl orange indicator



phenolphthalein indicator

To determine the total sodium ion concentration methyl orange was used as indicator as shown by the equations in group (A). To another portion of the same sample, excess BaCl<sub>2</sub> was added for the precipitation of BaCO<sub>3</sub> then the excess NaOH in the sample solution was back titrated against H<sub>2</sub>SO<sub>4</sub> using phenolphthalein as indication shown by the equations in group (B). This would determine the ionic strength of the remaining NaOH after a portion of it being reacted with the absorbed CO<sub>2</sub>.

The amount of CO<sub>2</sub> absorbed was then calculated by the following formula.

$$\text{Gram CO}_2 \text{ absorbed} = \frac{C(A - B) \times 0.053}{106.1} \times 44$$

where A = H<sub>2</sub>SO<sub>4</sub> used in the first titration (group A).

B = H<sub>2</sub>SO<sub>4</sub> used in the second titration (group B).

C = concentration of H<sub>2</sub>SO<sub>4</sub> in normality.



In both of the titrations, magnetic stirrer was used to keep the solution being titrated well mixed at all times. Sufficient stirring was extremely important in the titration of the B part since the accumulation of acid at the dead corner of the titration flask could cause reaction with the precipitated  $\text{BaCO}_3$ .

#### Sample Calculation

Run No. 6B<sub>1</sub>

#### (1) Observed data:

Liquid rate 4.2 lb/hr  
 Gas rate 3.093 cu ft/hr  
 Liquid inlet temp. 29.9° C  
 Liquid outlet temp. 29.2° C  
 Gas inlet temp. 28.9° C  
 Gas outlet temp. 29.9° C  
 Gas inlet manometer pressure 2.72 mmHg  
 Gas outlet manometer pressure 0.59 mmHg  
 Henry's Law constant  $H_{in}$  (Perry's Handbook) 1864  
 Henry's Law constant  $H_{out}$  (Perry's Handbook) 1830  
 Temperature correction coefficient,  $\alpha$ , of barometric reading (Perry's Handbook) 0.12826  
 Barometric pressure 742.6 mmHg  
 Room temperature 29.4° C  
 Vapor pressure at 28.9° C - - - 29.87 mmHg  
 Vapor pressure at 29.9° C - - - 31.64 mmHg  
 Exit concentration of sample  $C_{out}$   $1.02 \times 10^{-3}$  lb/lb or  
 0.0634 lb/ft<sup>3</sup>

## (2) Calculation:

Corrected barometric pressure at 0° C is obtained by the following equation:

$$H_t = H'_t - \alpha(t' - t) \text{ where } H_t \text{ is the height at the standard temperature}$$

$$H'_t = \text{the observed height at the temperature } t'$$

$$t = 0^\circ \text{ C}$$

$$t' = \text{the room temperature}$$

$$H = 742.6 - 0.1283(294 - 0) = 738.8 \text{ mmHg}$$

$$(pCO_2)_{in} = (738.8 + 2.72) - 29.87 = 711.6 \text{ mmHg}$$

$$(pCO_2)_{out} = (738.8 + 0.59) - 31.64 = 707.8 \text{ mmHg}$$

$$G_{e_{in}} = \frac{(pCO_2)}{H} = \frac{707.8/760}{1864} \frac{44}{18} \times 62.2 = 0.0760 \text{ lb/ft}^3$$

$$G_{e_{out}} = \frac{(pCO_2)}{H} = \frac{711.6/760}{1830} \frac{44}{18} \times 62.2 = 0.0781 \text{ lb/ft}^3$$

$$\Delta C_{l.m.} = \frac{(C_e)_{out} - C_{in} - (C_e)_{in} - C_{out}}{\ln \frac{(C_e)_{out} - C_{in}}{(C_e)_{in} - C_{out}}} = \frac{0.0655}{\ln 6.2} =$$

$$0.036 \text{ lb/ft}^3$$

Absorption rate  $R$  lb/hr ft<sup>2</sup> was obtained as follows:

$$R = \frac{4.2 \times (1.02 \times 10^{-4})}{0.22} = 1.945 \times 10^{-2}$$

$$k = \frac{R}{C} = \frac{1.945 \times 10^{-2}}{0.036} = 0.54$$

$k$  was corrected to 20° C by the following equation:

$$(k_L)_{20^\circ \text{ C}} = (k_L)_{t^\circ \text{ C}} \frac{e^{0.023 \times 20}}{e^{0.023 \times t}}$$

$$= 0.54 \frac{e^{0.023 \times 20}}{e^{0.023 \times 29.55}} = 0.43$$

### Empirical Equation by Least Square Method

Data from Tables 5 to 16 show a straight line relationship on a full log scale.

It suggests that the empirical equation takes the form

$$\alpha = ak^b k_L \text{ or}$$

$$\log \alpha = \log a + b \log k_L$$

The least square method requires that the sum of the squares of the difference of the observed values  $\alpha$  and calculated values  $\alpha$  (where  $\alpha = a k^b k_L$ ) be minimum.

The empirical constants  $a$  and  $b$  are obtained by solving the following two equations simultaneously

$$\log \alpha = n \log a + b \sum \log k \quad (1)$$

$$\sum \log \alpha \log k = a \sum \log k + b \sum (\log k)^2 \quad (2)$$

where  $n$  = the number of points taken into calculation

log	log k	log log k	(log k) <sup>2</sup>
35.129	-7.355	-10.456	2.8249

substituting in (1) and (2) and solve for  $a$  and  $b$

$$a = 14.23$$

$$b = -0.697$$

Therefore, the empirical equation is  $\alpha = 14.23 k_L^{-0.697}$

Table 5. Absorption data of CO<sub>2</sub> - H<sub>2</sub>O system in disc column.

Run No	Barometric Pressure : mmHg	Room Temperature : °C	Liquid Rate : lb/hr	Liquid : Temperature-°C		Manometer : Reading - mmHg		Gas Temperature-°C	Gas Inlet : °C	Gas Outlet : °C	CO <sub>2</sub> / H <sub>2</sub> O
				Inlet	Outlet	Inlet	Outlet				
5B2	742.4	28	6.8	28.9	28.9	1.84	0	28.3	29.9	8.62x10 <sup>-4</sup>	
5B4	742.4	28	6.8	28.9	28.9	1.84	0	28.3	30	9.40x10 <sup>-4</sup>	
5B5	742.4	28	6.8	29.2	29.2	1.84	0	28.3	30	9.40x10 <sup>-4</sup>	
6B1	742.6	29.4	4.2	29.9	29.2	2.72	0.59	28.9	29.9	1.02x10 <sup>-3</sup>	
6B2	742.6	29.4	4.2	30.3	29.4	2.72	0.59	28.9	29.9	1.01x10 <sup>-3</sup>	
6B3	742.6	29.4	4.2	30.3	29.4	2.72	0.59	28.9	29.9	1.022x10 <sup>-3</sup>	
7B1	742.6	29.4	9.8	28.6	28.9	2.72	0.59	28.9	29.9	8.24x10 <sup>-4</sup>	
7B2	742.6	29.4	9.8	28.6	28.6	2.72	0.59	28.6	29.2	8.63x10 <sup>-4</sup>	
8B1	742.6	29.4	13.2	27.8	27.8	2.72	0.59	28.3	29.2	7.75x10 <sup>-4</sup>	
8B2	742.6	29.4	13.2	27.8	27.8	2.72	0.59	28.3	29.2	7.88x10 <sup>-4</sup>	
8B3	742.6	29.4	13.2	27.8	27.8	2.72	0.59	28.3	29.2	7.85x10 <sup>-4</sup>	
9B1	741.5	25.6	16.9	26.6	26.6	2.2	0.44	25.6	26.6	7.66x10 <sup>-4</sup>	
9B2	741.5	25.6	16.9	26.6	26.6	2.2	0.44	25.6	26.6	7.67x10 <sup>-4</sup>	
9B3	741.5	25.6	16.9	26.6	26.6	2.2	0.44	25.6	26.6	7.84x10 <sup>-4</sup>	
10B1	741.5	26	20.7	26.4	26.6	2.2	0.44	25.6	26.6	7.25x10 <sup>-4</sup>	
10B2	741.5	26	20.7	26.4	26.6	2.2	0.44	25.6	26.6	7.27x10 <sup>-4</sup>	
10B3	741.5	26	20.7	26.4	26.6	2.2	0.44	25.6	26.6	7.24x10 <sup>-4</sup>	
11B1	741.5	26	24.8	26.6	26.1	2.2	0.44	26.6	27.8	7.03x10 <sup>-4</sup>	
11B2	741.5	26	24.8	26.6	26.6	2.2	0.44	26.6	27.8	7.24x10 <sup>-4</sup>	
11B3	741.5	26	24.8	26.4	26.6	2.2	0.44	26.6	27.8	7.00x10 <sup>-4</sup>	
12B1	728.9	28	2.0	29.4	27.8	2.2	0.44	27.2	28.3	1.122x10 <sup>-3</sup>	
12B2	728.9	28.5	2.0	30.6	28.9	2.2	0.44	27.8	28.9	1.085x10 <sup>-3</sup>	
12B3	728.9	29	2.0	31.1	28.9	2.2	0.44	27.8	28.9	1.096x10 <sup>-3</sup>	

Table 6. Absorption data of CO<sub>2</sub>-H<sub>2</sub>O system in packed column.

Run No	Barometric		Room		Liquid		Liquid		Manometer		Gas		Out	
	Pressure	Temperature	Rate	Temperature	Inlet	Outlet	Inlet	Outlet	Reading	mmHg	Inlet	Outlet	Temperature	lbs CO <sub>2</sub> /lb H <sub>2</sub> O, 10 <sup>4</sup>
	mmHg	°C	lb/hr	°C	°C	°C	°C	°C			°C	°C	°C	
13B1	736	25.8	9.8	27.8	27.2	27.2	27.2	27.2	2.6	0.44	25.6	26.1	26.1	7.76
13B2	736	25.8	9.8	27.8	27.2	27.2	27.2	27.2	2.6	0.44	25.6	26.1	26.1	7.86
13B3	736	25.8	9.8	27.8	27.2	27.2	27.2	27.2	2.6	0.44	25.6	26.1	26.1	7.62
13B4	736	25.8	9.8	28.3	28.3	28.3	28.3	28.3	2.6	0.44	25.6	26.6	26.6	7.64
14B3	736	26.1	6.8	28.9	28.3	28.3	28.3	28.3	2.6	0.44	26.6	27.2	27.2	7.95
14B4	736	26.1	6.8	28.9	28.3	28.3	28.3	28.3	2.6	0.44	26.6	27.2	27.2	8.00
14B6	736	26.1	6.8	28.9	28.3	28.3	28.3	28.3	2.6	0.44	26.6	27.2	27.2	7.86
15B3	731.4	24.5	4.2	28	26.6	26.6	26.6	26.6	2.6	0.44	24.4	25.6	25.6	8.09
15B4	731.4	24.5	4.2	28.3	26.6	26.6	26.6	26.6	2.6	0.44	24.4	25.6	25.6	8.10
15B5	731.4	24.5	4.2	28.3	26.9	26.9	26.9	26.9	2.6	0.44	24.4	26.1	26.1	8.35
15B6	731.4	24.5	4.2	28.9	27.8	27.8	27.8	27.8	2.6	0.44	25.0	26.6	26.6	8.40
16B	731.4	26	2.0	28.9	26.1	26.1	26.1	26.1	2.9	0.59	25.6	26.6	26.6	9.22
16B	731.4	26	2.0	28.9	26.1	26.1	26.1	26.1	2.9	0.59	25.6	26.6	26.6	9.51
17B2	728.4	25.3	13.2	26.6	26.6	26.6	26.6	26.6	2.9	0.74	25.6	26.4	26.4	7.34
17B3	728.4	25.3	13.2	26.6	26.6	26.6	26.6	26.6	2.9	0.74	25.6	26.4	26.4	7.48
17B4	728.4	25.3	13.2	26.6	26.6	26.6	26.6	26.6	2.9	0.74	25.6	26.4	26.4	7.46
17B6	728.4	25.3	13.2	26.6	26.6	26.6	26.6	26.6	2.9	0.74	25.6	26.4	26.4	7.39
18B1	731	25	15.8	24.4	24.4	24.4	24.4	24.4	3.2	0.59	25.6	26.6	26.6	7.95
18B2	731	25	15.8	24.4	24.7	24.7	24.7	24.7	3.2	0.59	25.6	26.6	26.6	7.76
18B3	731	25	15.8	24.4	24.7	24.7	24.7	24.7	3.2	0.59	25.6	26.6	26.6	7.85
19B1	731	24.4	20.7	24.2	24.3	24.3	24.3	24.3	3.2	0.59	25.0	25.6	25.6	7.45
19B2	731	24.4	20.7	24.2	24.3	24.3	24.3	24.3	3.2	0.59	25.0	25.6	25.6	7.29
20B1	731	24.8	24.8	23.9	24.3	24.3	24.3	24.3	3.2	0.59	25.0	26.6	26.6	7.31
20B2	731	24.8	24.8	23.9	24.3	24.3	24.3	24.3	3.2	0.59	25.0	26.6	26.6	7.31

Table 7. Absorption data of CO<sub>2</sub>-H<sub>2</sub>O system in wetted-wall column.

Run No	Barometric		Room		Liquid		Liquid		Manometer		Gas		C <sub>out</sub> : lbs CO <sub>2</sub> / : lb H <sub>2</sub> O, 10 <sup>4</sup>
	Pressure : mmHg	Temperature : °C	Rate : lb/hr	Temperature : °C	Rate : lb/hr	Temperature : °C	Temperature : °C	Reading - mmHg : Inlet : Outlet	Temperature : °C	Temperature : °C	Temperature : °C	Temperature : °C	
21B1	741	27.5	4.2	30	28.9	2.2	0.44	27.8	28.3	3.32			
21B2	741	27.5	4.2	30	28.9	2.2	0.44	27.8	28.3	3.16			
22B3	740.5	27.5	2.0	30	27.8	2.5	0.44	26.6	27.8	3.766			
22B5	740.5	27.5	2.0	30.6	28	2.5	0.44	27.2	28.3	3.78			
22B6	740.5	27.5	2.0	30.6	28	2.5	0.44	27.2	28.3	3.76			
23B2	740.5	27.5	6.8	29.4	29.2	2.2	0.44	27.8	28.3	2.38			
23B3	740.5	27.5	6.8	29.4	29.2	2.2	0.44	27.8	28.6	2.35			
23B6	740.5	27.5	6.8	29.4	29.2	2.2	0.44	27.8	29.2	2.44			
24B1	739.4	28.6	9.8	28.3	28.6	2.2	0.66	27.8	29.2	2.04			
24B2	739.4	28.6	9.8	28.3	28.6	2.2	0.66	27.8	29.2	1.98			
24B3	739.4	28.6	9.8	28	27.8	2.2	0.66	27.8	29.4	1.95			
25B3	734.5	27.5	13.2	27.5	27.5	2.6	0.29	27.2	28.3	2.41			
25B4	734.5	27.5	13.2	27.5	27.7	2.6	0.29	27.5	28.6	2.32			
26B1	730	29.2	16.9	27.2	27.2	2.2	0.59	28	28.9	1.34			
26B2	730	29.2	16.9	27.2	27.2	2.2	0.59	28	28.9	1.54			
26B3	730	29.2	16.9	27.2	27.2	2.2	0.59	28	28.9	1.30			
26B4	730	29.2	16.9	27.2	27.8	2.2	0.59	28.6	29.4	1.476			
27B1	730	30	20.7	27.2	27.2	2.2	0.59	28.9	29.4	1.37			
27B2	730	30	20.7	27.2	27.2	2.2	0.59	28.9	28.9	1.34			
27B3	730	30	20.7	27.2	27.2	2.2	0.59	28.9	28.9	1.385			
28B2	730	30	24.8	27.6	27.2	2.2	0.59	28.9	28.9	1.32			



Table 8. Absorption data of CO<sub>2</sub> - NaOH system in disc column.

Run No	Barometric		Room		Liquid		Liquid		Manometer		Gas		Cent					
	Pressure	mmHg	Temperature	°C	Rate	lb/hr	Temperature-°C	Inlet	Temperature-°C	Reading	mmHg	Temperature-°C		Inlet	Outlet	Temperature-°C	Outlet	Gas
42B <sub>2</sub>	734		27.2		6.8		26.7	33.6	2.06		0.514	26.7	27.2		0.01865			
43B <sub>1</sub>	734.3		26.1		6.8		26.7	33.3	2.06		0.514	26.7	27.2		0.01698			
44B <sub>1</sub>	734.3		26.1		9.8		27.2	34.6	2.06		0.514	26.7	27.7		0.01569			
45B <sub>1</sub>	734.3		26.1		12.5		27.2	34.4	2.06		0.514	26.7	27.7		0.01687			
46B <sub>1</sub>	734.3		26.1		11.8		27.2	35	2.06		0.514	26.7	27.8		0.01312			
47B <sub>1</sub>	734.3		26.1		16.9		26.7	33.9	2.06		0.514	26.9	27.8		0.01192			
48B <sub>1</sub>	734.3		26.1		20.4		26.7	33	2.06		0.514	27.2	28.3		0.01209			



Table 9. Absorption data of CO<sub>2</sub> - MeOH system in packed column.

Run No	Barometric Pressure : mmHg	Room Temperature : °C	Liquid Rate : lb/hr	Liquid Temperature : °C	Liquid		Monometer Reading - mmHg	Gas		Gas Temperature : °C	Gas : lbs CO <sub>2</sub> / lb H <sub>2</sub> O
					Inlet	Outlet		Inlet	Outlet		
49B <sub>1</sub>	734.6	27.8	6.3	26.7	32.6	2.64	0.294	26.1	27.2	0.01455	
49B <sub>2</sub>	734.6	27.8	6.6	27.2	32.2	2.64	0.294	26.1	27.2	0.01386	
51B <sub>1</sub>	734.6	27.8	3.7	28.9	33.2	2.94	0.514	26.7	28.3	0.01955	
52B <sub>1</sub>	734	26.1	9.8	26.7	32.2	2.94	0.514	26.7	27.2	0.01117	
52B <sub>2</sub>	734	26.1	9.8	26.7	31.9	2.94	0.514	26.0	27.2	0.01042	
53B <sub>1</sub>	734	25	13.2	26.7	32.2	2.94	0.514	26.7	27.2	0.01196	
53B <sub>2</sub>	734	26.1	13.2	26.7	32.3	2.94	0.514	26.7	27.8	0.01170	
54B <sub>1</sub>	734	25.6	16.9	26.7	32.8	2.82	0.368	26.7	27.8	0.01103	
54B <sub>2</sub>	734	25.6	16.6	26.7	32.8	2.82	0.368	26.7	27.8	0.01223	
55B <sub>1</sub>	734	27.8	20.7	27.2	33.2	2.35	0.294	27.8	28.9	0.01094	
55B <sub>2</sub>	734	27.8	20.7	27.2	33.2	2.35	0.294	27.8	28.9	0.01084	

Table 10. Absorption data of CO<sub>2</sub> - NaOH system in wetted-wall column.

Run No	Barometric Pressure : mmHg	Room Temperature : °C	Liquid Rate : lb/hr	Liquid Temperature : °C Inlet : Outlet :	Manometer Reading : mmHg Inlet : Outlet :	Gas Temperature : °C Inlet : Outlet :	Cent. lbs CO <sub>2</sub> / lb H <sub>2</sub> O
60B <sub>1</sub>	735.4	28.3	20.7	27.2 28.7	2.2 0.368	28.3 28.9	0.0033
60B <sub>2</sub>	735.4	28.3	20.7	27.2 28.7	2.2 0.368	28.3 28.9	0.00277
61B <sub>1</sub>	735.4	28.9	16.6	27.2 29.3	2.2 0.368	28.3 28.9	0.00361
62B <sub>1</sub>	735.4	28.9	13.2	27.8 29.7	2.06 0.44	28.3 28.9	0.00406
63B <sub>1</sub>	735.4	29.1	9.6	27.8 31.1	2.06 0.44	28.3 28.9	0.00577
63B <sub>2</sub>	735.4	28.9	9.6	28.1 30.9	2.06 0.44	28.3 28.9	0.00609
64B <sub>1</sub>	735.4	28.9	6.6	27.8 31	2.06 0.44	28.3 28.9	0.00691
64B <sub>2</sub>	735.4	28.9	6.0	27.8 31	2.06 0.44	28.3 28.9	0.00768
65B <sub>1</sub>	735.4	28.1	1.0	27.8 28.6	2.2 0.44	27.8 28.3	0.01931
66B <sub>1</sub>	735.4	28.3	2.0	28.3 29.4	2.2 0.44	28.3 28.9	0.01854
67B <sub>1</sub>	735.4	28.9	3.3	28.6 32.2	2.2 0.514	28.3 29.4	0.01247
68B <sub>1</sub>	735.4	28.9	4.0	28.6 32.2	2.2 0.514	28.3 29.4	0.00677
69B <sub>1</sub>	735.4	28.9	8.0	28.6 30.9	2.06 0.514	28.3 29.4	0.00677

Table 11. Liquid film coefficient for the absorption of  $\text{CO}_2$  in water in the disc column.

Run No	R Absorption Rate $\text{lb/hr ft}^2$	$(\Delta C)_{l,m}$ $\text{lb/ft}^3$	$k_L$ Liquid Film Coefficient $\text{lb}/(\text{hr ft}^2)$ $(\text{lb/ft}^3)$	$(k_L)_{20^\circ\text{C}}$ Liquid Film Coefficient $\text{lb}/(\text{hr ft}^2)$ $(\text{lb/ft}^3)$
5B <sub>2</sub>	0.0278	0.0480	0.579	0.472
5B <sub>4</sub>	0.0304	0.0419	0.725	0.582
5B <sub>5</sub>	0.0304	0.0438	0.694	0.562
6B <sub>1</sub>	0.0195	0.0360	0.540	0.430
6B <sub>2</sub>	0.0193	0.0356	0.544	0.434
6B <sub>3</sub>	0.0195	0.0347	0.562	0.448
7B <sub>1</sub>	0.0367	0.0486	0.755	0.618
7B <sub>2</sub>	0.0384	0.0486	0.790	0.650
8B <sub>1</sub>	0.0465	0.0526	0.884	0.739
8B <sub>2</sub>	0.0473	0.0522	0.906	0.758
8B <sub>3</sub>	0.0471	0.0522	0.902	0.754
9B <sub>1</sub>	0.0588	0.0559	1.052	0.905
9B <sub>2</sub>	0.0589	0.0555	1.061	0.912
9B <sub>3</sub>	0.0602	0.0553	1.089	0.935
10B <sub>1</sub>	0.0682	0.0580	1.176	1.023
10B <sub>2</sub>	0.0684	0.0618	1.107	0.955
10B <sub>3</sub>	0.0681	0.0581	1.172	1.011
11B <sub>1</sub>	0.0792	0.0594	1.332	1.151
11B <sub>2</sub>	0.0816	0.0578	1.412	1.213
11B <sub>3</sub>	0.0789	0.0581	1.359	1.170
12B <sub>1</sub>	0.0102	0.0289	0.353	0.282
12B <sub>2</sub>	0.00986	0.0286	0.345	0.276
12B <sub>3</sub>	0.00996	0.0263	0.379	0.304

Table 12. Liquid film coefficient for the absorption of CO<sub>2</sub> in water in the packed column.

Run No	R Absorption Rate lb/hr ft <sup>2</sup>	( $\Delta C$ ) <sub>l,m.</sub> lb/ft <sup>3</sup>	k <sub>ya</sub> Liquid Film Coefficient lb/(hr ft <sup>2</sup> ) (lb/ft <sup>3</sup> )	(k <sub>ya</sub> ) 20° C Liquid Film Coefficient lb/(hr ft <sup>2</sup> ) (lb/ft <sup>3</sup> )
13B <sub>1</sub>	0.805	0.0532	15.32	12.9
13B <sub>2</sub>	0.815	0.0528	15.436	13.0
13B <sub>3</sub>	0.790	0.0537	14.711	12.39
13B <sub>4</sub>	0.792	0.0527	15.028	12.5
14B <sub>3</sub>	0.572	0.0500	11.440	9.4
14B <sub>4</sub>	0.576	0.0498	11.566	9.5
14B <sub>5</sub>	0.565	0.05045	11.192	9.21
14B <sub>6</sub>	0.570	0.0501	11.377	9.35
15B <sub>3</sub>	0.360	0.0515	6.990	5.93
15B <sub>4</sub>	0.360	0.0510	7.059	5.99
15B <sub>5</sub>	0.372	0.0501	7.425	6.25
15B <sub>6</sub>	0.374	0.0496	7.540	6.25
16B <sub>7</sub>	0.195	0.0453	4.305	3.62
16B <sub>8</sub>	0.202	0.0406	4.975	4.18
17B <sub>2</sub>	1.030	0.05647	18.240	15.69
17B <sub>3</sub>	1.050	0.0556	18.885	16.20
17B <sub>4</sub>	1.050	0.05575	18.82	16.18
17B <sub>6</sub>	1.030	0.05624	18.35	16.78
18B <sub>1</sub>	1.330	0.0596	22.3	20.2
18B <sub>2</sub>	1.300	0.0601	21.3	19.38
18B <sub>3</sub>	1.320	0.06151	21.45	19.40
19B <sub>1</sub>	1.630	0.0620	26.3	23.8
19B <sub>2</sub>	1.600	0.0626	25.6	23.2
20B <sub>1</sub>	1.920	0.0627	30.65	28.1
20B <sub>2</sub>	1.920	0.0627	30.65	27.65

Table 13. Liquid film coefficient for the absorption of CO<sub>2</sub> in NaOH solution in the wetted-wall column.

Run No	R <sup>1</sup> Absorption Rate lb/hr ft <sup>2</sup>	(ΔC) <sub>1,m.</sub> lb/ft <sup>3</sup>	k <sup>1</sup> L Liquid Film Coefficient lb/(hr ft <sup>2</sup> ) (lb/ft <sup>3</sup> )	(k <sup>1</sup> L) <sub>20° C</sub> Liquid Film Coefficient lb/(hr ft <sup>2</sup> ) (lb/ft <sup>3</sup> )
60B <sub>1</sub>	1.260	0.0831	14.75	12.3
60B <sub>2</sub>	1.061	0.0831	12.79	10.7
61B <sub>1</sub>	1.111	0.0819	13.55	11.3
62B <sub>1</sub>	0.992	0.0813	12.21	10.0
63B <sub>1</sub>	1.028	0.0798	12.88	9.9
63B <sub>2</sub>	1.082	0.0798	13.58	10.9
64B <sub>1</sub>	0.845	0.0742	11.39	9.16
64B <sub>2</sub>	0.852	0.0742	11.48	9.26
65B <sub>1</sub>	0.358	0.0820	4.25	3.6
66B <sub>1</sub>	0.686	0.0810	8.45	6.9
67B <sub>1</sub>	0.762	0.0780	9.78	7.7
68B <sub>1</sub>	0.847	0.0780	10.86	8.56
69B <sub>1</sub>	1.001	0.0794	12.62	10.1

Table 14. Liquid film coefficient for the absorption of  $\text{CO}_2$  in NaOH solution in the disc column.

Run No	R' : Absorption : Rate : lb/hr ft <sup>2</sup> :	( $\Delta C$ ) <sub>l.m.</sub> : lb/ft <sup>3</sup> :	k' <sub>L</sub> : Liquid Film : Coefficient : lb/(hr ft <sup>2</sup> ) : (lb/ft <sup>3</sup> ) :	(k' <sub>L</sub> ) 20° C : Liquid Film : Coefficient : lb/(hr ft <sup>2</sup> ) : (lb/ft <sup>3</sup> ) :
42B <sub>2</sub>	0.575	0.0789	7.30	5.77
43B <sub>1</sub>	0.524	0.0794	6.61	5.23
44B <sub>1</sub>	0.694	0.0776	8.93	6.93
45B <sub>1</sub>	0.959	0.0740	12.95	10.00
46B <sub>1</sub>	0.704	0.0768	9.16	7.09
47B <sub>1</sub>	0.917	0.0787	11.65	9.20
48B <sub>1</sub>	1.110	0.0798	14.32	11.45



Table 15. Liquid film coefficient for the absorption of CO<sub>2</sub> in NaOH solution in the packed column.

Run No	R <sup>*</sup> Absorption Rate lb/hr ft <sup>3</sup>	(ΔC) <sub>l.m.</sub> lb/ft <sup>3</sup>	k <sub>L</sub> a Liquid Film Coefficient lb/(hr ft <sup>3</sup> ) (lb/ft <sup>3</sup> )	(k <sub>L</sub> a) <sub>20° C</sub> Liquid Film Coefficient lb/(hr ft <sup>3</sup> ) (lb/ft <sup>3</sup> )
49B <sub>1</sub>	9.69	0.0796	121.9	97.5
49B <sub>2</sub>	9.69	0.0794	122.1	97.6
51B <sub>1</sub>	7.23	0.0771	93.9	74.0
52B <sub>1</sub>	11.6	0.0802	144.9	116.5
52B <sub>2</sub>	10.62	0.0789	134.9	109
53B <sub>1</sub>	16.6	0.0829	200.5	162
53B <sub>2</sub>	16.38	0.0796	205.9	166
54B <sub>1</sub>	20.00	0.0798	250.5	200
54B <sub>2</sub>	20.19	0.0798	253.0	202
55B <sub>1</sub>	24.01	0.0876	254.2	219
55B <sub>2</sub>	23.79	0.0876	271.0	217



Table 16. Liquid film coefficient for the absorption of CO<sub>2</sub> in water in the wetted-wall column.

Run No	R Absorption Rate lb/hr ft <sup>2</sup>	(ΔC) <sub>l.m.</sub> lb/ft <sup>3</sup>	k <sub>L</sub> Liquid Film Coefficient lb/(hr ft <sup>2</sup> ) (lb/ft <sup>3</sup> )	(k <sub>L</sub> ) 20° C Liquid Film Coefficient lb/(hr ft <sup>2</sup> ) (lb/ft <sup>3</sup> )
21B <sub>1</sub>	0.0258	0.06668	0.387	0.311
21B <sub>2</sub>	0.0246	0.06620	0.372	0.2955
22B <sub>3</sub>	0.01395	0.06589	0.212	0.173
22B <sub>5</sub>	0.0140	0.06488	0.216	0.175
22B <sub>6</sub>	0.01393	0.06474	0.2155	0.174
23B <sub>2</sub>	0.0300	0.06969	0.431	0.348
23B <sub>3</sub>	0.0296	0.0702	0.422	0.3435
23B <sub>6</sub>	0.0307	0.06932	0.443	0.358
24B <sub>1</sub>	0.0370	0.07352	0.504	0.414
24B <sub>2</sub>	0.0359	0.07353	0.487	0.400
24B <sub>3</sub>	0.0354	0.07075	0.500	0.417
25B <sub>3</sub>	0.0589	0.07478	0.787	0.664
25B <sub>4</sub>	0.0567	0.07262	0.780	0.656
26B <sub>1</sub>	0.0419	0.07677	0.545	0.547
26B <sub>2</sub>	0.0482	0.07487	0.645	0.504
26B <sub>3</sub>	0.0407	0.08059	0.505	0.429
26B <sub>4</sub>	0.0462	0.07742	0.598	0.504
27B <sub>1</sub>	0.0525	0.0788	0.666	0.565
27B <sub>2</sub>	0.0514	0.0773	0.666	0.565
27B <sub>3</sub>	0.0531	0.0768	0.690	0.585
28B <sub>2</sub>	0.0606	0.0732	0.830	0.704

Principal Constants of Disc Column

Number of discs	35
Diameter of the disc	1.5 cm (0.594 inches)
Thickness of the disc	0.48 cm (0.188 inches)
Diameter of the Pyrex column	1 1/8 inches
Mean perimeter for liquid flow	0.127 ft.
Equivalent diameter for gas flow	0.059 ft.
Absorption surface (dry)	0.22 sq. ft.

Constants of Wetted-wall Column

Liquid inlet opening gas =	1/16"
Liquid outlet opening gas =	7/64"
Absorption area (dry) =	0.054 sq. ft.

INTERPHASE MASS TRANSFER IN  
VARIOUS TYPES OF COLUMN

by

I-cheng Chu

B. S. National Taiwan University, China, 1953

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AN ABSTRACT OF A THESIS

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MASTER OF SCIENCE

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The application of gas absorption accompanied by a chemical reaction in the liquid phase is attracting more and more attention today in chemical processes where higher purity of gas is demanded and where the gaseous products are to be recovered more completely. However, there are no general equations that can be used to correlate the characteristics of the absorption equipment, the properties of the liquid and gas material, and the hydrodynamic condition of the system for the purpose of design calculations.

The purpose of the present investigation is to find some empirical correlation between the purely physical absorption and the absorption processes accompanied by a chemical reaction in different types of absorption equipment. Three columns: a wetted-wall column, a disc column and a packed column, which constitute a series of flow pattern of progressing complexity, were used and the  $\text{CO}_2 - \text{H}_2\text{O}$  and  $\text{CO}_2 - \text{NaOH}$  systems were chosen for the study because of the rapid irreversible reaction between  $\text{CO}_2$  and  $\text{NaOH}$  and because of the well-established fact that the absorption rate is liquid-film controlling.

An empirical equation for the correlation of the effect of chemical reaction on absorption rate was developed in the following form:

$$\frac{R'}{R} = 14.23 k_L^{-0.697}$$

It is recommended that  $k_L$  for the physical absorption be used as the correlating variable in reference to the Reynold's number or the liquid flow rate. The equation is applicable to both wetted-

wall and disc columns used in this study and is independent of the individual characteristics of each column. This equation can be used for design calculations of absorption towers where a chemical reaction is involved provided that the  $k_L$  and  $R$  values for physical absorption are known.

The experimental results are also interpreted as indicating that the effect of chemical reaction on the film coefficient is more pronounced in an absorption where the range of  $k_L$  value is lower. In other words the ratio of  $k'_L$  (film coefficient with chemical reaction) to  $k_L$  is higher in a column of lower  $k_L$  value.