Liquid-side Resistance in Gas Absorption

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The film theory of liquid-side resistance to gas absorption, embodying the assumption of a thin stagnant liquid film adjacent to the interface in which steady state diffusion occurs, has long been open to question, particularly in packed columns. Higbie's penetration theory, believed to be more reasonable, pictures the liquid as flowing over a piece of packing for a very short period of time before being mixed as it flows to the next piece of packing. In the penetration model absorption occurs during a series of brief contacts, and unsteady state mass transfer conditions prevail in the liquid.

Several short glass wetted-wall columns 1.9 to 4.3 cm. long were constructed to simulate the assumptions of the penetration theory. Because of the short length ripples were absent except when the gas rate was higher than $Re_G = 2{,}200$. The desorption of carbon dioxide from water and of chlorine from dilute hydrochloric acid (0.16 to 0.18 N) was studied. The desorption rate of carbon dioxide was unaffected by gas velocity up to Re_G of 2,200 and increased 1.1%/°C. over the temperature range of 22° to 31°C.

Two theories have been proposed for the mechanism of the liquid-side resistance to gas absorption in packed towers. The first, and most widely used, is the film theory, which assumes the existence of a thin stagnant liquid film* adjacent to the interface while the rest of the liquid is well mixed. The film is considered to be sufficiently thin so that steady state mass transfer conditions exist within it. These assumptions lead to the following equation for the liquid-side coefficient, k_L:

$$k_L = D/x_f \qquad (1)$$

The driving force for this coefficient is the difference between the interfacial concentration and the average concentration in the bulk of the liquid.

Although the concept of a thin stagnant liquid film adjacent to the interface with steady state diffusion has proved to be extremely useful in providing a basis for defining a liquid-side coefficient which could be used in gas-absorption tower design, it has not permitted the prediction of liquid-side coefficients or their variation with physical and operating variables. As indicated by Equation (1), the coefficient should be proportional to the diffusivity and inversely proportional to the effective film thickness. There is no way of predicting the film thickness or of measuring it, and so it is a completely empirical quantity. Furthermore, experimental data of Sherwood and Holloway (*12*) indicate that the liquid-side coefficient varies as the 0.47 power of the diffusivity rather than the first power.

It should not be surprising that the film theory does not hold in a packed column. Considering the liquid flow conditions existing on the packing, it is difficult to conceive of the existence of a stagnant liquid film at the gas-liquid interface. As the liquid flows over a piece of packing, the stagnant portion of the liquid is expected to be adjacent to the solid packing, and the liquid at the gas-liquid interface should be the most rapidly moving portion.

Higbie (*6*) in 1935 proposed another theory of the liquid-side resistance, which he called the penetration theory. As the liquid flows over the packing, he pictured it as flowing over each piece in laminar flow. It is then partially or wholly mixed at the surface discontinuity in going from one piece of packing to the next. Absorption is considered to take place during a series of brief contacts between the liquid and gas in which the dissolved gas diffuses (or "penetrates") only a short distance into the liquid before the liquid is mixed.

As unsteady state conditions prevai in the liquid, the diffusion equation is

$$D\frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \qquad (2)$$

Since the dissolved gas penetrates only a short distance compared with the totall depth of the liquid layer, it makes little difference to the shape of the concentration vs. distance curve whether the depth of the liquid layer is assumed to be actual or infinite. In order to facilitate the mathematics, it is assumed that the liquid layer is of infinite extent away from the interface and also that there is no relative motion within the liquid. As long as the relative motion within the actual penetration zone is small, these assumptions are satisfactory. Then, if C_i is defined as the interfacial liquid concentration, the boundary condition at the interface is

$$\text{at} \quad x = 0, \quad t > 0, \quad C = C_i \qquad (3)$$

If C_o is the average concentration in the liquid, the initial condition corresponding to the instant just after mixing is

$$\text{at} \quad t = 0, \quad x > 0, \quad C = C_o \qquad (4)$$

Finally, since infinitely far from the interface the concentration undergoes no change in a finite time, the second boundary condition is

$$\text{at} \quad x = \infty, \quad t \geq 0, \quad C = C_o \qquad (5)$$

*It is necessary to make a distinction between the terms *film* and *layer*. Both have been applied both to the stagnant film at the interface referred to above and to the whole of the liquid layer running down a surface. In this paper, to avoid confusion, the term *film* is reserved for the former, and the latter is called a *layer*.

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Integration of these equations yields the result that the total amount absorbed per unit area in each absorption period of time t_E is

$$2(C_i - C_o)\sqrt{D\,t_E/\pi}$$

But this is also equal to

$$k_L(C_i - C_o)t_E$$

where k_L is the liquid-side coefficient averaged over the entire absorption period of time t_E. The penetration theory then yields the following equation for the liquid-side coefficient:

$$k_L = 2\sqrt{D/\pi t_E} \qquad (6)$$

The driving force for this coefficient is the difference between the interfacial concentration and the concentration in the liquid at the beginning of the short absorption period. Since the concentration change in the liquid in each absorption period is small compared with the over-all change in a packed column, this coefficient is practically equivalent to one based on the continuously changing driving force used in the film theory.

While the assumptions of the penetration theory may be an oversimplification of the conditions in the liquid phase in a packed column, they appear to be more reasonable than those of the film theory. Furthermore, the conclusion of Sherwood and Holloway (*12*) that the liquid-side coefficient varies as D to the 0.47 power is in remarkable agreement with the prediction of the penetration theory that it varies as D to the 0.5 power.

When the packed column is used for a fundamental study of the mechanism of the liquid-side resistance to absorption, it suffers the severe disadvantage of unknown interfacial area. Other types of equipment have been used in the laboratory for the fundamental study of absorption; in general their main advantage has been that their interfacial area can be measured. One is the batch-adsorption flask, or beaker, in which the two phases are stirred; a second is the wetted-wall column. It is clear that the liquid flow conditions in the batch-absorption system bear no resemblance to those in the packed column. That the liquid flow conditions in conventional wetted-wall columns are different from those in a packed column is not so obvious. As the usual wetted-wall columns are about 1 ft. or so in length, a time of exposure of the liquid to the gas results that is much longer than on an individual piece of packing, which may run in size from ½ to 2 or at most 4 in. The result is that in the wetted-wall column the solute is able to penetrate well into the liquid layer and to change the concentration appreciably throughout the layer. In this case the assumption of infinite depth of liquid made in Equation (5) is no longer valid and Equation (6) can no longer be expected to hold. Another disadvantage of the usual wetted-wall column is the occurrence of ripples, which cause the area for mass transfer, assumed to be constant and known, actually to increase somewhat with the liquid rate. Further, the presence of ripples may either cause or indicate some mixing in the liquid, and a still greater mass transfer rate may result.

These disadvantages of the wetted-wall column may be overcome by reducing its length to ½ to 2 in. Observation of the longer wetted-wall columns shows that the ripples do not form until the liquid has traveled several inches down from the top. In a short wetted-wall column the absence of ripples is to be expected and, hence, the area for mass transfer is constant and known. Second, the time of exposure of the liquid to the gas in such a short column is about as long as on an individual piece of packing and is sufficiently short to justify the assumption of infinite depth of liquid. Data obtained in such an apparatus should be valuable in an understanding of the liquid-side resistance in a packed column.

To use Equation (6), one must determine the time of exposure, t_E. As the time of exposure is the time during which an element of the surface of the liquid is exposed to the gas, it may be calculated from the interfacial velocity of the liquid and the length of the column. If it is assumed that the interfacial velocity, v_i, is uniform, then

$$t_E = h/v_i \qquad (7)$$

where h is the length of the column. Combining Equations (6) and (7) gives the following equation for the liquid-side coefficient:

$$k_L = 2\sqrt{D\,v_i/\pi h} \qquad (8)$$

where v_i is some function of the liquid flow rate. Equation (8) may be tested by varying not only liquid rate, but also column length and the solute gas. How well the data for absorption or desorption in the short wetted-wall column fit the equation is a measure of the applicability of Higbie's penetration theory to the case where the liquid flow conditions are similar to those existing in a packed column.

DESCRIPTION OF SHORT WETTED-WALL COLUMN

In the usual wetted-wall column there are appreciable end effects due to the areas of contact between liquid and gas at the points where the liquid enters and leaves the wetted-wall section, apart from the area of contact on the wetted wall itself. Such end effects have usually been ignored by previous investigators. However, as the length of the column is reduced to the dimensions used here, these end effects could easily outweigh the mass transfer in the column itself. The primary requirement of the design of a short wetted-wall column, then, is that the liquid be brought into and out of the column without any gas-liquid contact other than on the wetted wall. This was done by having the liquid enter and leave through thin slots maintained completely full of liquid. In addition, all chambers and tubes through which the liquid passed in its journey to and from the column were kept completely full of liquid.

Drawings of the column assembly are shown in Figures 1 and 2. Liquid enters the outer glass chamber and flows through a thin entrance slot onto the inside of the inner glass tube. The inner tube, approximately 1 in. in diameter, constitutes the wetted-wall section. After flowing down this section, the liquid flows through an exit slot into the outlet chamber and then through the liquid outlet. Gas enters upward through a calming section of 1-in. glass tubing, 40 in. long, into the gas inlet tube, flows countercurrent to the liquid on the wetted wall, and then flows out the gas exit tube.

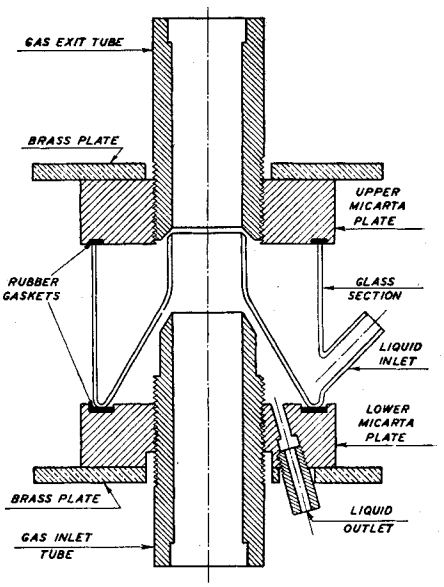

Fig. 1. Assembly of short wetted-wall column (upflow slot).

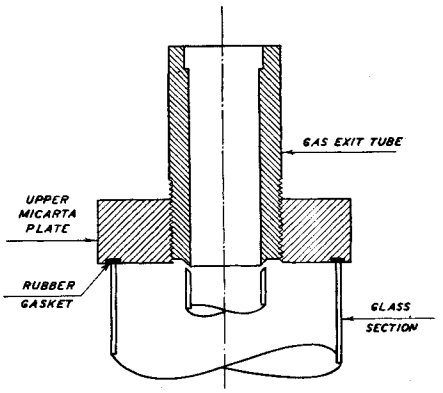

Fig. 2. Upper section of column assembly (downflow slot).

The materials used in the column assembly were chosen primarily for their corrosion resistance. Glass was used for the wetted-wall section because of the ease with which it is wetted by water and because of its transparency, which permitted visual observation of the operation of the column. Teflon was chosen for the gas inlet and outlet tubes because it is machinable and not wetted by water. The latter property was valuable, as it constrained the liquid flowing through the slots to flow along the glass and not creep along the Teflon tubes. Micarta, a laminated phenolic plastic, was used for the upper and lower supporting plates because it is strong, corrosion resistant, and easy to machine. Rubber gaskets were used as seals. Brass plates and tie rods served to clamp the assembly together. A photograph of the column assembly is shown in Figure 3.

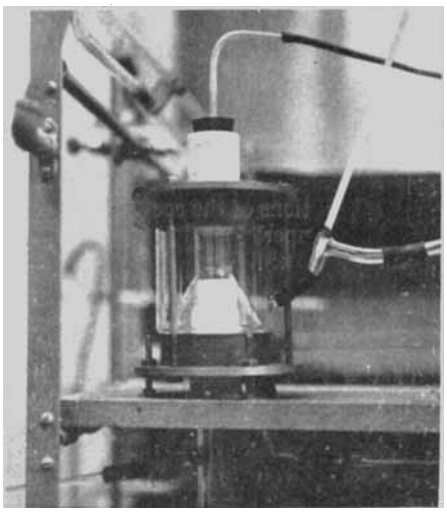

Fig. 3. Assembly of short wetted-wall column.

Two different types of entrance slots were used: upflow and downflow. (*Compare* Figures 1 and 2.) The gas entrance and exit tubes were threaded with twenty threads per inch so that the widths of the entrance and exit slots might be varied by turning the Teflon tubes. Two gas exit tubes were made, one with a bevel for the upflow slot and one with a bevel for the downflow slot. The inside of the gas inlet tube was recessed at the bottom to fit the 1-in. glass tubing which formed the calming section.

Five glass sections were made, three with bevels for upflow slots and two with bevels for downflow slots. Three column lengths were used, such that the straight sections of the inner glass tubes were approximately 0.5, 1.0, and 1.5 in. long. The dimensions

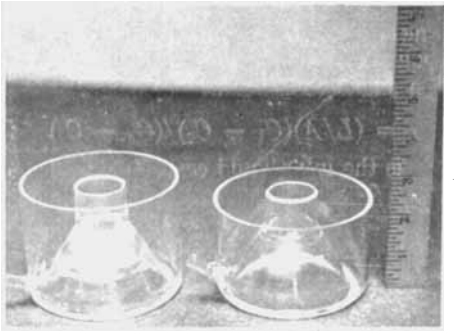

Fig. 4. Glass sections used in short wetted-wall columns.

and slot types of the five columns are given in Table 1. A photograph of two of the glass sections is shown in Figure 4.

The upper and lower edges of the outer glass cylinders were ground flat to form seals against the rubber gaskets set into the Micarta plates. The tops of the inner glass cylinders were first ground parallel with the bases and then ground to 45° bevels.

The liquid layer formed a very smooth cylinder inside the column with no distortion at the ends. The actual length of the layer was determined by inserting a depth gauge down from the top of the gas exit tube. When the downflow slot was used, the length was taken as the distance from the lowest extremity of the upper Teflon tube to the highest extremity of the lower Teflon tube. When the upflow slot was used, the top of the water layer was found always to be 0.14 cm. above the top extremity of the inner glass cylinder, the distance being independent of slot width and liquid rate. Consequently, with the upflow slot, the length of the gas-liquid interface was taken as the distance from the top of the inner glass cylinder to the top of the lower Teflon tube plus 0.14 cm.

PROCEDURE AND AUXILIARY APPARATUS

Two mass transfer processes were studied in the short wetted-wall column: desorption of carbon dioxide from water by air and of chlorine from dilute hydrochloric acid solution by air. These systems have the advantages that they are liquid-side controlled, have practically no chemical reaction occurring between solute and solvent, are comparatively easy to analyze, and have diffusivities known with comparative accuracy. Desorption was studied rather than absorption in order to use less solute gas; studying absorption without using an excessive quantity of solute gas would have required recirculation of the gas, thereby adding to the complication of the apparatus. That the coefficients of absorption and desorption are the same has been experimentally verified by Carlson (3), who found them to be the same for oxygen and carbon dioxide in water in a stirred flask, and by Allen, who found them to be the same for carbon dioxide in water in a packed column (12).

Ninety-seven runs were made on the CO_2–H_2O system, and the effects of temperature, air rate, liquid rate, entrance-slot width, slot type, and column length were investigated. Ten runs were made on the Cl_2–HCl–H_2O system, and the effects of liquid rate and chlorine concentration were measured. The auxiliary apparatus and analytical procedures for the two systems were different and are described separately below.

Desorption of Carbon Dioxide from Water

The liquid feed came from a constant-head tank where distilled water was about 90% saturated with carbon dioxide by bubbling the gas in considerable excess through the liquid. A glass cooling coil in the tank allowed control of the temperature of the liquid. From the head tank the liquid flowed by gravity through a calibrated orifice and through a valve into the column assembly. The temperature of the feed was indicated by a thermometer located in the feed line just before the entrance to the outer glass chamber. By adjusting a valve in the liquid exit line, the exit slot was kept completely full of liquid.

Air was blown through a small packed tower to saturate it with water and control its temperature to within 1°C. of the liquid temperature in order to minimize any mass transfer of water in the column. A calibrated orifice metered the air before it entered the calming section. A thermometer placed inside the glass-tube calming section, near the bottom, served to indicate the air temperature.

Glass "tees" were inserted in the liquid line just before the orifice and in the exit line just after the valve to provide sample outlets. A 25-ml. pipette was connected to each outlet with a short rubber tube and liquid was allowed to drain continuously through the pipette at a rate of about 150 ml./min. After all the operating variables had been adjusted to the desired values, a minimum of 5 min. was allowed for the apparatus to reach steady conditions before the samples were taken.

To take samples, the rubber tubes were pinched off, the one on the exit line first; the pipettes were then removed and allowed to drain to the graduation mark. The sample in each pipette was added to a known amount of barium hydroxide and, by measuring the electrical conductance of the supernatant liquid after the precipitate of barium carbonate had settled, the amount of barium hydroxide left was determined. The concentration of barium hydroxide to which the samples were added was adjusted so that nearly all the barium was precipitated. This procedure made it possible to determine the difference between the inlet and outlet concentrations of carbon dioxide in the liquid with an accuracy of about 2%.

Desorption of Chlorine from Dilute Hydrochloric Acid

Distilled water from a constant-head tank, chlorine from a cylinder metered by a Monel regulating valve, and 4*N* hydrochloric acid from a constant-head bottle were mixed together continuously in a glass

TABLE 1. COLUMN DIMENSIONS

Column	Slot type	h, cm.	Inside diameter, cm.
1*U*	Upflow	1.88	2.88
2*D*	Downflow	2.95 + w (runs 79–84) 2.99 + w (runs 85–91)	2.86
2*U*	Upflow	2.72	2.87
3*D*	Downflow	4.08 + w	2.87
3*U*	Upflow	4.25	2.88

tube packed with glass beads, the rates of each stream being adjusted to give a solution of the desired concentration. This solution flowed into a second constant-head tank, then through a calibrated glass flow meter, past the thermometer, and into the column.

A partial vacuum was applied at the gas exit to pull air through the system. The air flowed through the small packed tower, through the calming section, and then through the column. From the gas exit tube, the gas passed through an absorption train of three bottles in series, through a calibrated glass flow meter, and finally into the laboratory vacuum line. In the first two bottles of the absorption train, the gas bubbled through sodium hydroxide solutions; in the third bottle the gas bubbled through potassium iodide solution. Between runs, the gas coming from the column was passed through a single bottle containing sodium hydroxide solution, then through the flow meter, and into the vacuum line.

When the apparatus reached steady conditions, a run was started by rapidly switching the gas flow through the absorption train. At the end of the run, after a measured period of time ranging from 10 to 25 min., the gas flow was shut off from the absorption train and again shunted through the single bottle. The amount of chlorine contained in the exit gas during each run was then determined by analysis of the solutions of the absorption train. The third bottle always showed a negligible amount of chlorine.

To obtain inlet liquid samples, a portion of the inlet liquid was diverted from the liquid feed line just before the flow meter and allowed to flow continuously through a sampling tube. When each run was about half over, some of the sample stream was added to potassium iodide solution in a titration flask, care being taken to prevent desorption of chlorine from the sample. The size of the samples were determined by weighing the flasks before and after sampling, and the amount of chlorine was determined by titration with sodium thiosulfate.

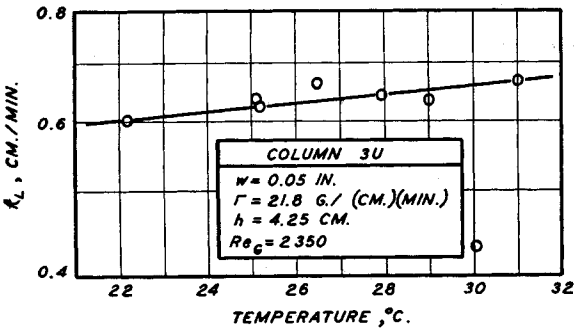

Fig. 5. Desorption of carbon dioxide from water, effect of temperature

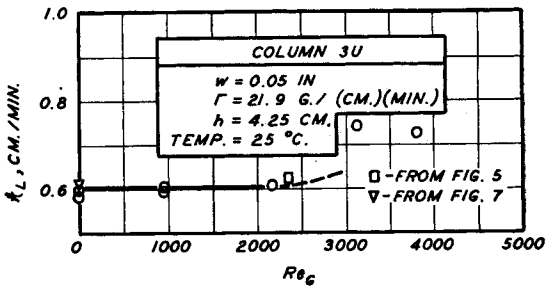

Fig. 6. Desorption of carbon dioxide from water, effect of air rate.

RESULTS AND DISCUSSSION

Equations

For use in calculating liquid-side coefficients from the data* taken on the carbon dioxide–water system, the following equation was derived from the rate equation and an over-all material balance on the liquid stream:

$$k_L = (L/A)(C_1 - C_2)/(C_o - C_i) \quad (9)$$

C_1 is the inlet liquid concentration (note that $C_1 = C_o$), C_2 the outlet liquid concentration, L is the total liquid flow rate through the column, and A is the interfacial area. For the conditions existing in these experiments, $C_i = 0$. The interfacial area was calculated from the length and diameter of the air-liquid interface. The diameter of the interface was obtained by subtracting twice the layer thickness, δ, from the inside diameter of the inner glass tube, where δ is given by streamline flow theory as

$$\delta = \sqrt[3]{3\mu\Gamma/(\rho^2 g)} \quad (10)$$

To calculate liquid-side coefficients for the chlorine-dilute hydrochloric acid system,* the following equation was used:

$$k_L = (N/A)/t_R(C_o - C_i) \quad (11)$$

N is the total amount of chlorine desorbed during the run, and t_R is the time of the run. Because of the presence of the hydrochloric acid, which suppresses the hydrolysis of the dissolved chlorine, C_o and C_i may be considered to be the concentrations of molecular chlorine in solution in the bulk of the liquid and at the interface. (In these experiments $C_i = 0$.)

For the purpose of discussing the effect of liquid rate on the performance of the column, the mass liquid rate per unit perimeter, Γ, g./(min.)(cm.), is used. The perimeter referred to is that of the inner glass tube.

Effect of Temperature

Results of eight carbon dioxide–water runs in which the temperature was varied and all other variables were held constant are shown in Figure 5, where k_L is plotted as a function of the liquid temperature. The best line through the experimental values on semilogarithmic coordinates gives a temperature relationship of the form

$$k_L \propto e^{mT} \quad (12)$$

where $m = 0.011$, and T is the liquid temperature, either degrees centigrade or degree Kelvin. The coefficients measured for the other carbon dioxide–water runs have been corrected to a standard temperature of 25°C. by the use of Equation (12).

No attempt was made to determine experimentally the effect of temperature on the chlorine coefficients. Equation (12) with $m = 0.019$, was used to make the small corrections of the coefficients to the standard temperature of 25°C. This value of m was obtained from Equation (17), developed below.

Effect of Air Rate

Results of seven carbon dioxide–water runs in which all variables but the air rate were held constant are plotted in Figure 6. The plot shows that there is no significant effect of gas rate on the desorption of carbon dioxide between a Reynolds number in the gas of 0 and 2,200. At higher values of the Reynolds number, ripples were observed in the liquid layer. These ripples account for the larger coefficients measured at the higher gas rates.

The fact that the coefficient is unaffected by gas rate down to zero gas rate may be explained by convection currents, set up in the gas by the moving liquid layer, which sweep away the small amount of carbon dioxide from the interface. Because of this lack of effect of gas rate, all but nineteen of the first seventy-eight carbon dioxide desorption runs were taken with zero gas rate in order to reduce the operating difficulties. Before each run was started, the blower was turned on for a short while to sweep out any accumulated carbon dioxide. For the remaining runs, because of improvements in the apparatus, it was not inconvenient to blow air through the column.

Effect of Entrance-slot Width and Type

Eleven runs were made on two different columns, one with an upflow slot and one with a downflow slot, to determine the effect of entrance-slot width and type. The results are shown in Figures 7 and 8. Because the length of the air-liquid interface varies with slot width for a downflow

*The data taken on both systems are filed as document 4959 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., available for $1.25 for photoprints or 35-mm. microfilm.

slot, the values of k_L shown in Figure 8 have been adjusted to a length of 4.21 cm. by multiplying by $(h/4.21)^{1/2}$ in accordance with Equation (8).

At the start of this work it was supposed that the interfacial velocity of the liquid is not constant with distance down the column but, rather, increases from the velocity at which the liquid enters the column through the inlet slot to some final velocity which depends on the liquid rate. Since the inlet velocity depends on whether the inlet slot is upflow or downflow, and also depends on the width of the inlet slot, it was expected that these variables would have an effect on the coefficients measured.

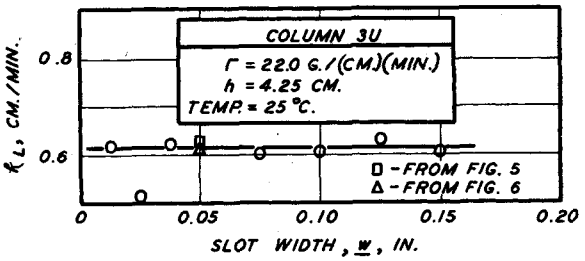

Fig. 7. Desorption of carbon dioxide from water, effect of entrance-slot width (upflow slot).

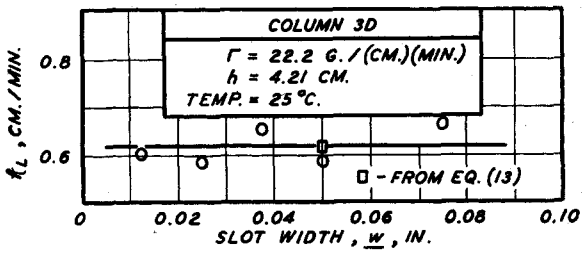

Fig. 8. Desorption of carbon dioxide from water, effect of entrance-slot width (downflow slot).

However, Figures 7 and 8 show that the slot width has no effect within the normal scatter of the data. Comparison of the two figures shows that the coefficients are practically the same for the upflow and downflow slots.

To make certain that the type of slot is immaterial, the remaining runs, which were made to determine the effect of liquid rate, were obtained on all five columns, three of which had upflow slots and two downflow slots. These runs are discussed below, but it may be pointed out here that the data obtained with the two types of slots fit equally well the correlation developed for these runs, despite the fact that the correlation does not take into account the entrance slot at all. In view of these results, it may be concluded that significant acceleration does not occur in the liquid later, but rather that the interfacial velocity is essentially uniform. This conclusion is further confirmed by the fact that the correlation just mentioned is developed on the assumption of uniform interfacial velocity.

Effect of Liquid Rate

The remaining seventy runs on the carbon dioxide–water system were made to determine the effect of liquid rate on the performance of each of the five columns. In addition, ten runs were made on the chlorine-dilute hydrochloric acid system, with one column, to determine the effect of liquid rate for that system. The dashed line on the plot was calculated by the method of least squares, with each point being weighted by the number of runs that it represents. The slope of the least squares line is −0.46. Considering the precision of the data, this slope is in excellent agreement with Equation (8), which predicts that k_L varies inversely as the square root of h.

Logarithmic plots of k_L vs. Γ were constructed for each set of runs, and the best lines through the data were drawn. These lines are represented by the equation

$$k_L = b\Gamma^n \qquad (13)$$

where b and n have the values shown in Table 2. The units of k_L and Γ to be used with these constants are centimeters/minutes and grams/(centimeters)(minutes), respectively.

Although there appears to be a trend in the exponent, n, it is not significant, especially since the smallest and largest values were obtained on the same column, although with different solutes. Considering the precision of the data, the second figure in n cannot be considered significant. Consequently, an average value for n of 0.4 was chosen. The quantity $k_L/\Gamma^{0.4}$ was evaluated for each run and averaged for each series of runs. These average values are listed in Table 2. Several runs were omitted from these averages because the deviation from the mean of these runs exceeded four times the average deviation.

Effect of Length of Column

In order to determine the effect of length, the average values of $k_L/\Gamma^{0.4}$ for the CO_2-H_2O runs are plotted vs. length on logarithmic coordinates in Figure 9.

Effect of Diffusivity

Measurements of the diffusion coefficient of chlorine in solutions of hydrochloric acid were made with a diaphragm cell (10). The diffusion coefficient of molecular chlorine in water at 25°C. was found to be 1.475×10^{-5} sq. cm./sec. Because of the slightly higher viscosity of the hydrochloric acid solutions used here, compared with water, the diffusion coefficient of chlorine in the hydrochloric acid solution is corrected to 1.46×10^{-5} sq. cm./sec.

Some measurements of the diffusion rate of carbon dioxide in water at 30°C. were also made in the diaphram cell. A summary of these values of the diffusion coefficient of CO_2, as well as those found in the literature, together with the corresponding temperatures, is given in Table 3. The best line on a plot of log D vs. $1/T$ was found by the method of least squares, and the value at 25°C. was estimated from this line to be 1.96×10^{-5} sq. cm./sec.

By comparing the data on the desorp-

Table 2. Constants for Equation (13)

Column	System	No. of runs	b	n	h, cm.	Average $k_L/\Gamma^{0.4}$
3*U*	CO_2–H_2O	43	0.150	0.45	4.25	0.174
3*D*	CO_2–H_2O	13	0.167	0.42	4.21	0.180
2*U*	CO_2–H_2O	19	0.224	0.39	2.72	0.212
2*D*	CO_2–H_2O	13	0.224	0.39	3.09	0.218
1*U*	CO_2–H_2O	6	0.292	0.36	1.88	0.255
3*D*	Cl_2–HCl–H_2O	10	0.177	0.36	4.14	0.155

Table 3. Diffusivity of Carbon Dioxide in Water

Investigator	Temp., °C.	$D \times 10^5$, sq. cm./sec.
Stefan (*7*, *1*)	17	1.63
	17	1.57
Hüfner (*7*, *1*)	16	1.59
	10.3	1.46
	15.2	1.60
	20.4	1.78
Carlson (*2*)	18.2	1.70
	18.2	1.72
	18.2	1.69
Ringbom (*11*)	25	1.82
	30	2.08
	40	2.75
	50	3.26
Present authors	30	2.29

tion of chlorine from dilute hydrochloric acid with the data on desorption of carbon dioxide from water at the same column length, the effect of diffusivity can be determined. For the chlorine runs, in which the length of the column was 4.14 cm., the average value of $k_L/\Gamma^{0.4}$ is 0.155. From the least squares line of Figure 9 the value of $k_L/\Gamma^{0.4}$ for carbon dioxide at this length is found to be 0.178. The ratio of k_L for carbon dioxide to k_L for chlorine, then, is 0.178/0.155, and the ratio of the diffusion coefficient of carbon dioxide to that of chlorine is 1.96/1.46. The liquid-side coefficient of desorption, therefore, is found to vary as D to the 0.47 power, in very good agreement with the 0.5 power predicted by the penetration theory.

Correlation of Data

So far it has been shown that the liquid-side coefficient of desorption varies as the square root of the diffusion coefficient and inversely as the square root of column length, in agreement with Equation (8). Consequently, to correlate all the data on a single graph, $k_L\sqrt{h/D}$ is plotted vs. Γ on logarithmic coordinates in Figure 10.

The best line through the data is expressed by the equation

$$k_L\sqrt{h/D} = 7.13\Gamma^{0.4} \qquad (14)$$

where k_L is the liquid-side coefficient in centimeters per second, h is the height in centimeters, D is the diffusivity in square centimeters per second and Γ is the liquid rate in grams per (minute)(centimeter). Equation (14) is also plotted on Figure 9, which shows the effect of length on the coefficient. In that figure, of course, the line has a slope of -0.5, and the two points on the right of the graph have the greatest influence on the position of the line because they represent over half the runs.

The deviation of $k_L\sqrt{h/D}$ from the value given by Equation (14) was calculated for each run, and the following statistics were determined: the average deviation is 7.7%, the standard deviation is 11.0%, 44% of the points lie within 5% of the line, and 78% of the points lie within 10% of the line.

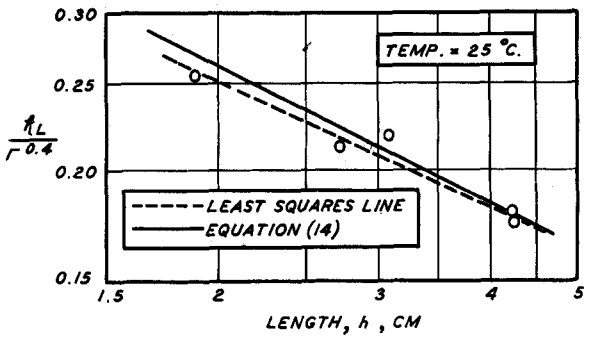

Fig. 9. Desorption of carbon dioxide from water, effect of length of column.

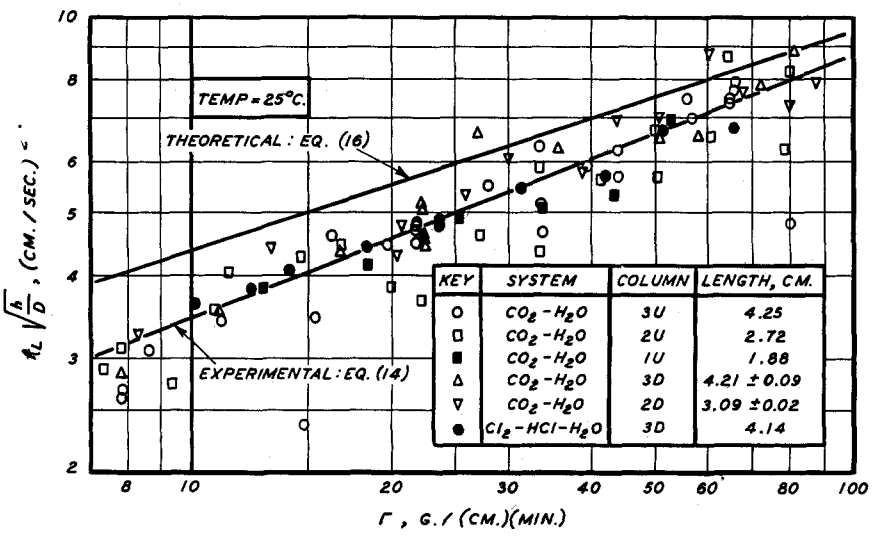

Fig. 10. Correlation of data on short wetted-wall columns.

Comparison with Streamline Flow Theory

The interfacial velocity of a liquid layer flowing down a wall is given by streamline flow theory as

$$v_i = (9g\Gamma^2/8\mu\rho)^{1/3} \qquad (15)$$

Substituting Equation (15) into Equation (8) gives a theoretical equation for k_L:

$$k_L = 2\sqrt{D/\pi h}\,(9g\Gamma^2/8\mu\rho)^{1/6} \qquad (16)$$

Equation (16), with the values of ρ and μ for water at 25°C. substituted, is plotted on Figure 10 for comparison with the experimental data. The experimental line falls below the theoretical line, the deviation being about 30% at the lowest flow rate and about 10% at the highest.

A possible explanation for the discrepancy is the fact that the falling liquid layer is actually finite in thickness and has a parabolic velocity gradient. The possibility exists that the depth of the region in which the concentration is affected by the interface is sufficiently great that the assumptions of infinite depth and uniform liquid velocity used in deriving Equation (16) are not valid. Johnstone and Pigford (*8*) solved the problem of diffusion into a finite liquid layer with a parabolic velocity gradient. Comparison of their solution with Equation (16) for the most unfavorable of the conditions that existed in the short column shows that the difference is negligible.

Another possible explanation for the fact that the experimental line falls below the theoretical line is lack of equilibrium at the gas-liquid interface, as suggested by the work of Danckwerts (*4*) and Emmert and Pigford (*5*). The failure of equilibrium to be established at the interface may be interpreted in terms of the presence of an extra, interfacial resistance. However, if the interfacial resistance is assumed to be constant, it can be shown that the shorter the period of exposure, the greater is the effect of the interfacial resistance. Then, as the liquid rate increases and the time of exposure decreases, the deviation between the two lines should increase, but this is contrary to the trend actually found. In order to account for the observed trend, it would be necessary to assume that the interfacial resistance increases rapidly with the time of exposure.

A more likely explanation of the discrepancy between theory and experiment may be found in the nature of the liquid flow. It is difficult to conceive of the liquid entering through the inlet slot and immediately assuming the velocity given by streamline flow theory. From physical considerations it is clear that it must take a finite time for the liquid to accelerate from the entrance velocity to the final velocity. It was shown above that the lack of an effect of entrance-slot width or type on the desorption coefficient indicates that such an acceleration period is absent, but it may well be that there is

some effect which could not be detected because the data were not sufficiently precise. The presence of an acceleration period does account for the low coefficients, as well as for the trend in the deviation. The entrance velocity varies directly as Γ, and the final interfacial velocity varies as $\Gamma^{2/3}$. At sufficiently high flow rates the two velocities would be equal; there would be no acceleration period, and the experimental coefficient would approach the theoretical value. At lower flow rates there appears to be an acceleration period, increasing the time of exposure above that given by streamline flow theory and causing the observed coefficient to be lower than the theoretical value. Furthermore, the lower the flow rate, the greater the deviation.

Additional uncertainty in the nature of the liquid flow is introduced by the exit slot, which tends to retard the liquid at the bottom of the column. This effect also results in an increase in the time of exposure above that given by streamline flow theory and a coefficient lower than the theoretical value. A similar effect has been observed by Lynn, Straatemeier and Kramers (*9*) in their study of absorption by liquid films flowing outside short tubes.

Dimensionless Correlation

Equation (14), which was developed to correlate the data, is a dimensional equation. It is desirable for some purposes to express it in dimensionless form. To develop a dimensionless equation, it is necessary to list all the variables which are expected to affect k_L: diffusivity, D; length, h; liquid flow rate, Γ; viscosity of liquid, μ; density of liquid, ρ; and acceleration due to gravity, g. Dimensional analysis shows that these variables can be arranged in four dimensionless groups, which may be taken as

$$\frac{k_L h}{D} \qquad \frac{\mu}{\rho D} \qquad \frac{\rho^2 g h^3}{\mu^2} \qquad \frac{4\Gamma}{\mu}$$

The last group is the Reynolds number for a liquid flowing down a wall. Comparison with Equation (14) shows that the dimensionless equation should be

$$\frac{k_L h}{D} = 0.433\left(\frac{\mu}{\rho D}\right)^{1/2}\left(\frac{\rho^2 g h^3}{\mu^2}\right)^{1/6}\left(\frac{4\Gamma}{\mu}\right)^{0.4} \tag{17}$$

Equation (17) may be used to predict the coefficient for systems where the viscosity and density are different from those of water at 25°C. It should be remembered, however, that the effect of these variables is predicted solely on the basis of dimensional analysis and that there is no experimental evidence regarding these effects. Therefore, the equation should be used for this purpose with caution.

CONCLUSION

The experimental results obtained with the short wetted-wall column indicate that the liquid-side resistance to mass transfer between gas and an initially well-mixed liquid, exposed for short periods between mixing, follows closely predictions based on the penetration mass transfer theory and streamline liquid flow theory. The liquid-side coefficient, k_L, appears to vary as the square root of the diffusivity, in agreement with the penetration theory.

The assumption of streamline liquid flow predicts that the time of exposure should be proportional to the height of the column and inversely proportional to the 2/3 power of the liquid rate. The penetration theory predicts that the coefficient should be inversely proportional to the square root of the time of exposure and, hence, inversely proportional to the square root of the height and proportional to the ⅓ power of the liquid rate. The experimental data verify the effect of height but indicate that the k_L varies as the 0.4 power of the liquid rate instead of the ⅓ power and that they are 10 to 30% below the theoretical values. This discrepancy is attributed to uncertainty in defining the true nature of the liquid flow over the surface of the column. While the agreement between theory and experiment is good, further study of the fluid dynamics is required before this agreement can be improved and the theory applied directly to packed-tower absorbers.

One of the aims of fundamental studies of mass transfer is to provide a basis for correlating and predicting coefficients for design of commercial equipment. In this respect the short wetted-wall column appears to provide a model in which liquid flow conditions are somewhat similar to those existing when liquid flows over discontinuous packing and yet are amenable to analytical treatment and reproducible results.

The literature on liquid-side coefficients measured in conventional wetted-wall columns shows great disagreement among the results obtained by various investigators. This disagreement appears to be caused in part by the presence of rippling, which changes both the interfacial area and the mass transfer process in the liquid. It is not unlikely that the rippling conditions vary widely among the various experimental columns.

The use of the short wetted-wall column avoids rippling and provides short contact time between gas and liquid. Because it is subject to theoretical analysis and further provides liquid flow conditions similar to those found in a packed column, it should prove useful for further study of liquid-side–controlled mass transfer between gas and liquid.

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NOTATION

- A = interfacial area, sq. cm.
- C = concentration of solute in liquid, moles/liter
- C_i = interfacial concentration, moles/liter
- C_o = average concentration at start of absorption period, moles/liter
- C_1 = concentration in inlet liquid, moles/liter
- C_2 = concentration in outlet liquid, moles/liter
- D = diffusion coefficient of solute in liquid, sq. cm./sec.
- g = acceleration due to gravity, cm./sec.^{2}
- h = length of wetted-wall column, cm.
- k_L = liquid-side coefficient of absorption or desorption, cm./min. or cm./sec.
- L = volumetric rate of flow of liquid, cc./min.
- N = total solute desorbed in a run, moles
- Re_G = Reynolds number in gas stream
- t = time, sec.
- t_E = time of exposure of liquid to gas, sec.
- t_R = time of a run, sec. or min.
- v_i = interfacial velocity of liquid, cm./sec.
- w = width of entrance slot, cm. or in.
- x = distance in liquid from interface, cm.
- x_f = film thickness, cm.
- Γ = mass flow rate of liquid per unit perimeter, g./(min.)(cm.)
- δ = thickness of liquid layer, cm.
- μ = viscosity of liquid, g./(cm.)(sec.)
- π = 3.14159 . . .
- ρ = density of liquid, g./cc.

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