

# The Influence of Gravitational Force on Gas Absorption in a Packed Column

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Carbon dioxide was desorbed from water in a packed column mounted on a large centrifuge. By varying the centrifuge rotational speed, the total body force acting upon the liquid was varied from 1 to 6.4 times the normal gravitational force. The results, obtained for  $\frac{3}{4}$  in. Raschig ring packing, showed  $k_L a$  varying with the body force to a power between 0.41 and 0.48, the exponent being larger at lower liquid flow rates. This effect of gravity is compared with penetration theory predictions and with those inferred from dimensional analysis and the effect of packing size.

Correlations of gas absorption data for the prediction of the individual phase coefficients are important for reliable design of gas absorption equipment.

In 1940, Sherwood and Holloway (9) published their classic paper on liquid-phase gas absorption coefficients in packed columns. By desorbing several slightly soluble gases from water, they obtained liquid-phase coefficients over a wide range of gas and liquid flow rates and temperatures for a number of sizes and types of packings. Similar experimental results were subsequently obtained by several other investigators (2, 6).

Although the experimental results of Sherwood and Holloway depicted the effects of a number of variables on the liquid-phase coefficient, no dimensionless correlation was proposed which could account for the effect of packing size for geometrically similar packings. Indeed, the results demonstrated clearly that a correlation involving only the Sherwood, Reynolds, and Schmidt numbers could not properly account for packing size variations.

In 1947, Van Krevelen and Hoftijzer (10) proposed a dimensionless correlation which included an effect of gravity:

$$\frac{k_L (\mu^2 / g \rho^2)^{1/3}}{D} = 0.015 \left( \frac{L}{a \mu} \right)^{2/3} (N_{Sc})^{1/3} \quad (1)$$

The effect of gravity was deduced from the theoretical relation for the thickness of a laminar falling liquid film and the use of this film thickness as the length dimension in the Sherwood number. In addition the correlation was based upon an interfacial area given by the expression

$$\frac{a}{a_r} = 1 - \exp(-0.4 L / \rho) \quad (2)$$

which is not dimensionless and which assumes that there is no effect of gravity upon the interfacial area.

The assumption that the effect of gravity on the liquid-phase coefficient could be accounted for by employing the liquid film thickness in the Sherwood number had no rigorous justification. Nevertheless, the work of Van Krevelen and Hoftijzer did call attention to the importance of the gravitational acceleration in determining the nature of the liquid flow over the packing and to the fact that a dimensionless correlation of liquid-phase coefficients in packed columns must include the effect of gravity.

In 1955, Vivian and Peaceman (13) presented a correlation for gas absorption in short wetted-wall columns:

$$\frac{k_L h}{D} = 0.443 \left( \frac{4\Gamma}{\mu} \right)^{0.4} (N_{Sc})^{1/3} (gh^3 \rho^2 / \mu^2)^{1/6} \quad (3)$$

The exponent of 1/6 on the gravity group was obtained from a theoretical analysis and was confirmed experimentally by the effect of variations in the column height. Later, Davidson (1) derived a similar expression for absorption coefficients in packed columns in which he obtained an exponent of 1/6 on the gravity group by theoretical considerations. Other workers between 1956 and 1958 attempted correlations with either a 1/6 or a 1/3 exponent on gravity.

In 1959, Onda, Sada, and Murase (8) proposed a dimensionless correlation for liquid-phase coefficients in columns packed with Rashig rings. The correlation was based upon separating the interfacial area from the mass transfer coefficient, and while  $k_L$  was depicted as varying with gravity, the interfacial area was assumed to be independent of the gravitational force. For the present discussion the many uncertainties involved in attempting to separate  $k_L$  from  $a$  are best avoided. Thus, combining the expressions for  $k_L$  and  $a$  proposed by Onda, Sada, and Murase and rearranging, one obtains

$$\frac{(k_L a) d^2}{D} = 0.023 (N_{Sc})^{1/2} \left( \frac{g d^3 \rho^2}{\mu^2} \right)^{0.38} \left( \frac{dL}{\mu} \right)^{1/2} \left\{ 1 - 1.02 \exp \left[ - (0.15) \left( \frac{dL}{\mu} \right)^{0.4} \right] \right\} \quad (4)$$

The effect of the gravity group was obtained from the effect of packing diameter on the assumption that the Sherwood group is a unique function of the Reynolds, Schmidt, and gravity groups. Experimental data on the effect of liquor rate and solute diffusivity were used to indicate the effect of the Reynolds and Schmidt numbers, respectively, and the residual effect of packing diameter at constant Reynolds and Schmidt numbers suggested an exponent of 0.38 on the gravity group.

It is seen from the above discussion that various authors have suggested different effects of gravity upon the liquid-phase mass transfer coefficient in a packed column. Of the various proposed expressions the correlation of Onda,

Sada, and Murase, as given by Equation (4), appears to be the most complete. The procedure used to develop this correlation is supported by the theory of dimensional analysis and similitude if it can be assumed that all important parameters affecting the mass transfer process have been included. This assumption, however, is open to question, since the possibility of the liquid surface tension affecting the liquid flow in a packed column, and hence the mass transfer rate, has not been adequately considered. Also, for incompletely wetting systems, the interfacial free energies of the solid-liquid interface and the solid-gas interface may also be important because of their effect on wettability and spreading of the liquid on the solid packing. Even if these last two surface free energies are neglected, another dimensionless group must be added to the four contained in Equation (4) if surface tension is important; and this group will contain the packing diameter if it does not contain the liquid flow rate or the solute diffusivity. Under such conditions, the exponent on the gravity group cannot be obtained from the effect of packing diameter, and Equation (4) may misrepresent the effect of gravity. Experimental results (3, 15) for the absorption of carbon dioxide into methanol, in which the surface tension group ( $d\rho\sigma/\mu^2$ ) is different from that for water, appear to disagree with Equation (4), suggesting that perhaps the surface tension group is important and that the exponent of 0.38 for the gravity group might be in error.

The present study was undertaken to obtain a direct experimental measurement of the effect of the gravity group by measuring liquid phase-controlled mass transfer coefficients in a packed column under the influence of a centrifugal field.

## EXPERIMENTAL

The experimental program included a study of the rate of desorption of carbon dioxide from water into air in a packed column mounted on a rotating centrifuge. The column was 6 in. I.D. and was packed to a height of 1 ft. with new chemical stoneware Raschig rings obtained from U. S. Stoneware Corporation. The column design was similar to that described by Vivian and King (12), except for the water inlet distributor which consisted of a drilled plate fed with liquid from a weir.

The centrifuge, available through the cooperation of the M.I.T. Instrumentation Laboratory, had a 35-ft. horizontal arm which provided a stable platform capable of accelerating a 1-ton mass to a centrifugal acceleration equal to thirty times the normal gravitational acceleration. This was a precision machine designed for testing inertial guidance equipment and was therefore quite vibration-free. The assembly used to mount the column on the centrifuge allowed the column to swing freely outward at an angle from the vertical. Thus the column automatically aligned with the direction of the vector sum of the outward centrifugal field and the downward field due to the earth's gravity, with the result that the force on the liquid was also automatically aligned with the axis of the packed column. In these experiments, the packed column was mounted on the centrifuge arm at a distance of 21 ft. from the axis of rotation so that the variation in the centrifugal field over the 1-ft. height of the packed column was less than 5%.

Suspended above the center of the centrifuge arm was a stationary platform which contained the equipment for saturating the water feed with carbon dioxide and for collecting and analyzing the inlet and outlet water samples. Water containing dissolved carbon dioxide was pumped from an overhead storage tank through an orifice to one fixed port of a rotary union mounted on the stationary platform 2 ft. above the centrifuge. The water passed through the rotary union and to a pipe which extended out the centrifuge arm and carried the water to the distributor at the top of the packed column. Similarly, the water from the bottom of the column was pumped by a liquid return pump back to the center of the centrifuge and through another port of the rotary union to the operator's platform

where it was sampled. The liquid level in the bottom of the column was detected by electrical probes and was continuously monitored by the operator in the control room who regulated the return pumping rate to maintain the level constant.

Air from the room, drawn through a metering orifice by a centrifugal blower mounted on the arm of the centrifuge, passed through a spray tower water saturator to the bottom of the packed column. The air stream leaving the packed column was discharged to the room.

During a run measurements were made of the liquid and gas flow rates, the inlet and outlet liquid temperatures, the air temperature, and carbon dioxide and bicarbonate ion concentrations in the inlet and exit liquid samples. The column water temperature was not controlled but remained between 24° and 30°C.

Carbon dioxide concentration in the liquid was determined by collecting the sample under a barium hydroxide solution and back titrating the barium hydroxide with hydrochloric acid to a phenolphthalein endpoint. Bicarbonate ion was measured by titrating a sample with hydrochloric acid to a bromophenol blue endpoint. The carbon dioxide concentration was corrected for the bicarbonate ion present by subtracting half the bicarbonate ion from the total carbon dioxide concentration to yield the free carbon dioxide concentration according to the procedure of Sherwood and Holloway (9).

Before the packed column was operated on the centrifuge, a large number of runs were made to determine the packed column performance under normal gravity. Furthermore, after the runs at high centrifugal fields had been performed, the column was removed from the centrifuge and several additional runs were made to determine if the centrifugal field had caused settling or damage to the packing.

The details of the apparatus and procedure are given in reference 5.

## RESULTS AND DISCUSSION

The desorption results for 3/4-in. Raschig ring packing obtained under the normal gravitational force of the earth are presented in Figure 1. The height of a liquid-phase transfer unit  $H_L$  is plotted vs. the liquid flow rate per unit of column cross-sectional area. The values of  $H_L$  were corrected to 25°C. by the formula recommended by Vivian and King (12):

$$\frac{(H_L)_{25^\circ}}{(H_L)_T} = \exp [-0.02 (T - 25)] \quad (5)$$

although the temperature did not depart from 25°C. by more than 2° for the experiments shown in Figure 1. These results represent all the data collected for 3/4-in. Raschig rings at liquid and gas flow rates below the loading point at normal gravity;  $H_L$  is independent of the gas flow rate in agreement with the findings of previous investigators. A considerable number of experiments were performed at normal gravity for liquid and gas flow rates above the loading point, but these results will be presented elsewhere.

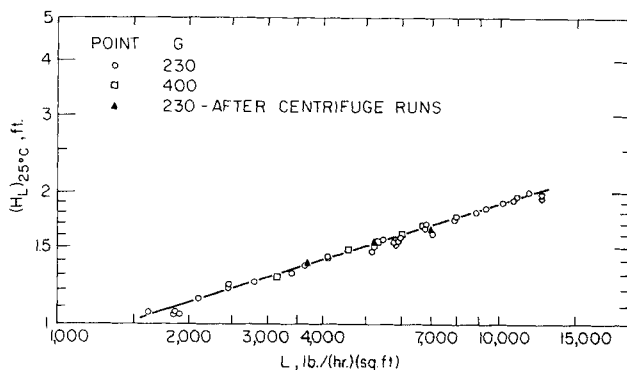


Fig. 1. Results at normal gravity, 3/4 in. Raschig rings.

The results shown in Figure 1 indicate the excellent reproducibility obtained in the present experiments in the absence of the centrifugal field. Similar results were obtained for  $\frac{1}{2}$  in. Raschig rings. The present results show approximately the same slopes as the results of Sherwood and Halloway (9) and Yoshida and Koyanagi (15), but the  $H_L$  values are approximately 20% higher. They are in better agreement with the data of Yoshida and Miura (16), Koch et al. (4), and Vassilatos et al. (11) in the region of overlap, but the present results have higher slopes than those of these investigators. In general, the present results agree with the results of these other investigators equally as well as these other investigators agree with each other. It should be noted that the different results of a single investigator show considerably better agreement than the agreement from one investigator to another. These differences probably result from end effects, different packing arrangements, incomplete wetting, or from the failure of some investigators to correct for bicarbonate ion concentration when carbon dioxide was used as the solute.

### Effect of Gravity

All the experimental results obtained in the presence of a centrifugal field are presented in Figure 2. These data are for carbon dioxide desorption with  $\frac{3}{4}$ -in. Raschig ring packing. The ordinate is the height of a liquid-phase transfer unit corrected to 25°C. by Equation (5). In these experiments the maximum deviation from 25°C. was 5°. The abscissa in Figure 2 is the body force on the liquid in the packed column, expressed as the vector sum of the normal gravitational force and the centrifugal force divided by the normal gravitational force. Results are presented for two liquid flow rates at a constant gas flow rate of 230 lb./ (hr.) (sq. ft.).

At a liquid rate of 5,200 lb./ (hr.) (sq. ft.), a total of nine runs were made with the packed column mounted on the centrifuge. The first run was made in the absence of rotation, and the  $H_L$  value of 1.48 obtained in this run agrees satisfactorily with the value of 1.51 obtained before mounting the column on the centrifuge and the value of

1.53 obtained after the completion of the runs on the centrifuge. The other eight runs were made at various values of the total body force up to a maximum of 6.36 times the normal gravitational force.

The slope of the line in Figure 2 indicates  $H_L$  to be proportional to the  $-0.41$  power of gravity, and the agreement of the data with this line is seen to be quite satisfactory. The chronology of the experiments did not correspond to increasing body force; the rotation speed of the centrifuge was varied back and forth during the sequence of experiments to provide an additional check on whether or not the high body forces were causing damage to the packing or other changes in bed characteristics. It can be concluded that these results indicate the effect of variation in body force on the absorption process and not settling or damage to the packing due to the large body forces.

Only three experimental points at a liquid rate of 3,700 lb./ (hr.) (sq. ft.) are shown in Figure 2. One of these, obtained in the absence of rotation after the entire series of runs with rotation, is in excellent agreement with the results obtained before the runs on the centrifuge, as shown in Figure 1. The other two runs were made with rotation at total body forces of 4.28 and 6.36 times normal gravity. These runs were made just after the runs at the higher liquid flow rate shown in Figure 2. The slope of the best line drawn through these data is  $-0.48$  in comparison with the slope of  $-0.41$  at the higher liquid rate. While only three points are available to determine the slope for the lower liquid rate, two of the points are at the high end of the body force range, and the third point at normal gravity is well established as shown in Figure 1. Thus the experiments performed at the lower liquid flow rate indicate the slope with considerable confidence, and the effect of the body force on  $H_L$  seems to be greater at the lower liquid flow rate.

The experimentally determined effect of gravity on the liquid-phase coefficient, as shown in Figure 2, is considerably greater than the  $1/6$  power deduced theoretically by Vivian and Peaceman (13) for a short wetted-wall column and by Davidson (1) for a packed column. The theoretical exponent of  $1/6$  was proposed for the effect of gravity upon  $k_L$ , while Figure 2 depicts the effect of gravity upon  $k_L a$ . It is quite probable that a major reason for the greater effect of body force shown in Figure 2 is an increase in interfacial area with increasing body force. This possibility was not considered by Van Krevelen and Hofstijzer (10) or by Onda, Sada, and Murase (8), but if the interfacial area is as sensitive to liquid flow rate as these investigators' correlations depict, it appears most unlikely that the interfacial area would be independent of the body force.

Another possible reason for the experimental effect of gravity being greater than the  $1/6$  power is the incompleteness of liquid mixing at the junctions between Raschig rings. The theoretical exponent of  $1/6$  is based on a penetration theory model in which the liquid is completely remixed at fixed points in the packing matrix. It is probable that liquid remixing between packing particles is not complete, and the degree of mixing might increase as the body force increases. Thus the effect of gravity upon  $k_L$  in a packed column could be greater than  $1/6$  power.

In view of these considerations and in view of the complex nature of liquid flow in a packed column, it is not surprising that  $k_L a$  is found to vary with gravity to a power considerably greater than the  $1/6$  power. It is also not surprising that the effect of gravity upon  $k_L a$  is found to vary with liquid flow rate.

### Effect of Surface Tension

The experimentally determined effect of gravity upon  $k_L a$  at the higher liquid flow rate is in close agreement

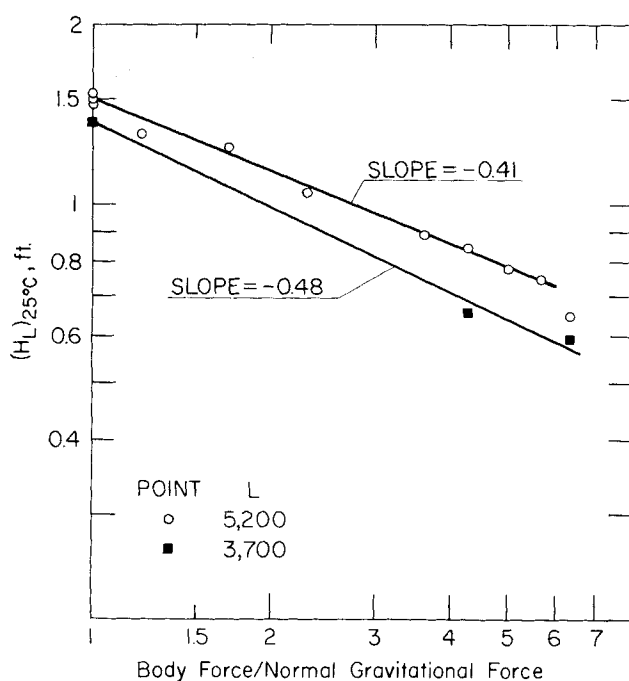


Fig. 2. Effect of body force,  $\frac{3}{4}$  in. Raschig rings ( $G = 230$ ).

with that shown in Equation (4). At the lower liquid flow rate the experimentally determined exponent on gravity is 0.48 vs. 0.38 in Equation (4). By comparing these two exponents, one might speculate that Equation (4) should contain a surface tension group,  $(d\rho\sigma/\mu^2)$ , to the  $-0.3$  power. This, together with an exponent of 0.48 on the gravity group, would preserve the effect of packing diameter shown in Equation (4). However, little confidence can be placed in this conclusion because of the variation in the exponent on the gravity group with liquid flow rate and because the effect of packing diameter shown in Equation (4) is averaged over a wide variety of conditions.

A preferred method of ascertaining the effect of the surface tension group is to compare experimental results for carbon dioxide absorption into methanol (3, 15) with results for absorption into water at the same values of the Reynolds and gravity groups. Such a comparison (5) suggests that  $N_{sh}/\sqrt{N_{so}}$  varies with the surface tension group to the  $-0.25$  power. However, these conclusions are based upon the use of a value of  $3.6 \times 10^{-5}$  sq. cm./sec. for the diffusion coefficient of carbon dioxide in methanol, as obtained from the Wilke-Chang correlation (14), because no experimental value is available. Since the Wilke-Chang correlation yields a diffusion coefficient which is approximately half the experimental value reported (7) for the diffusion coefficient of carbon dioxide in ethanol, this casts considerable doubt upon the reliability of the diffusivity for carbon dioxide in methanol used in inferring the effect of the surface tension group. Thus it seems inappropriate to attempt at this time to draw a conclusion regarding the effect of surface tension, and these considerations point to the need for experimental values for the diffusivity of carbon dioxide in methanol. They also point to the need for experiments on gas absorption into liquids with considerably different surface tension groups, achieved by variations in liquid surface tension and also by variations in liquid viscosity.

## CONCLUSIONS

The effect of gravitational force upon the liquid-phase mass transfer coefficient in a packed column absorber had been inferred by previous investigators from theoretical considerations and from dimensionless correlation of the effects of other parameters, but no experimental measurements of the effect of gravity had been reported. This paper reports experiments in which this effect was measured directly by subjecting the packed column to a centrifugal field.

The results show that  $k_L a$  varies with gravity to a power between 0.41 and 0.48, the effect of gravity increasing as the liquid flow rate decreases. This effect of gravity is much larger than the  $1/6$  exponent deduced from penetration theory for the effect of gravity on  $k_L$ , suggesting that the interfacial area probably increases as gravity increases. It is also likely that incomplete liquid remixing at contact points between Raschig rings increases the sensitivity of  $k_L$  to gravity above the theoretical exponent of  $1/6$ .

An attempt to obtain a dimensionless correlation for liquid-phase coefficients to account for the experimentally observed effects of body force, solute diffusivity, liquid flow rate, and packing size leads to the inference that a surface tension group is needed also. More data are needed to resolve this point.

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## NOTATION

- $a$  = gas-liquid interfacial area per unit of column volume,  $\text{ft.}^{-1}$
- $a_T$  = total dry surface area of packing per unit of column volume,  $\text{ft.}^{-1}$
- $D$  = liquid-phase diffusion coefficient, sq. ft./hr.
- $d$  = diameter (or characteristic dimension) of packing, ft.
- $G$  = gas rate,  $\text{lb.}/(\text{hr.})(\text{sq. ft.})$
- $g$  = gravitational acceleration normally, or the acceleration due to the total body force in general,  $\text{ft./sec.}^2$
- $H_L$  = height of a liquid-phase transfer unit =  $N_{re}N_{sc}d/N_{sh}$ , ft.
- $h$  = height of short wetted-wall column, ft.
- $k_L$  = liquid-phase mass transfer coefficient,  $\text{ft./hr.}$
- $L$  = liquid flow rate per unit of column cross-sectional area,  $\text{lb.}/(\text{hr.})(\text{sq. ft.})$
- $N_{Gv}$  = gravity group =  $g d^3 \rho^2 / \mu^2$
- $N_{Re}$  = Reynolds number =  $dL/\mu$
- $N_{so}$  = Schmidt group =  $\mu/\rho D$
- $N_{sh}$  = Sherwood group =  $k_L a d^2/D$
- $N_s$  = surface tension group =  $d\rho\sigma/\mu^2$
- $T$  = temperature,  $^{\circ}\text{C.}$

## Greek Letters

- $\Gamma$  = liquid flow rate per unit perimeter in wetted-wall column,  $\text{lb.}/(\text{hr.})(\text{ft.})$
- $\mu$  = liquid viscosity,  $\text{lb.}/(\text{hr.})(\text{ft.})$
- $\rho$  = liquid density,  $\text{lb./cu. ft.}$
- $\sigma$  = gas-liquid surface tension,  $\text{lb./hr.}^2$

## Subscripts

- $T$  = at temperature  $T$
- $25^{\circ}$  = corrected to  $25^{\circ}\text{C.}$  by Equation (5)

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