Performance of Packed Columns

V. Effect of Solute Concentration on Gas-Phase Mass Transfer Rates

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In a determination of the effect of solute concentration on gas-phase mass transfer rates carbon tetrachloride was vaporized at three different concentration levels in a short 4.0-in.-diameter column packed with 0.5-in. Raschig rings.

The experimental data indicate that previous mass transfer correlations should be modified to include a term $(P_{BM}/P_T)^{2/3}$ and that the Schmidt number should be evaluated at average film conditions.

The correlation found is suitable for predicting gas-phase mass transfer coefficients which can be combined with effective interfacial areas reported previously to obtain volumetric mass transfer coefficients for any gas-liquid-solute system.

Parts I to III were published in volume 1; part IV appeared in volume 3.

In the previous papers (*4* to *7*) of this series a correlation was developed for the prediction of the gas-phase mass transfer coefficient in packings:

$$j_D = \left[\frac{k_G M_M P_{BM}}{G}\right]\left[\frac{\mu}{\rho D_V}\right]^{2/3} = 1.195\left[\frac{D_P G}{\mu(1-\epsilon)}\right]^{-0.36} \qquad (1)$$

This correlation was obtained from experimental work in which several gases and packings were employed at varying temperatures, pressures, and flow rates. As a result it can be said that this correlation has been checked for its ability to predict the effect on the mass transfer coefficient of varying every independent variable which appears in the equation with the exception of that of the mean partial pressure of the inert gas.

For a number of reasons it has been most convenient to do experimental mass transfer work with low solute concentrations, and as a result P_{BM} has always been almost equal to the total pressure on the experimental system. Thus in spite of the enormous amount of experimental mass transfer work which has been done and reported there are very few data available which can be used to check the effect of P_{BM}. Any correlating equation which employs P_{BM} can have it replaced by P_T without any significant effect on the degree of correlation obtained with low solute-concentration data.

The term P_{BM} appears in the equation for the steady state rate of molecular diffusion of one component through a stagnant layer of another gas.

$$N_A = \frac{D_V\, P_T(\Delta p)}{RTZ\, P_{BM})} \qquad (2)$$

As this equation does not describe the rate of mass transfer for physical systems in which turbulent motion of fluids occurs, a simpler empirical approach has been used which employs the gas-phase mass transfer coefficient:

$$N_A = k_G(\Delta p) \qquad (3)$$

Unfortunately Equations (2) and (3) have been compared to lead to some false conclusions, as shown in

$$k_G = \frac{D_V\, P_T}{RTZ\, P_{BM}} \qquad (4)$$

Chilton and Colburn (*2*), attempting to correlate mass transfer data by an analogy to work in heat transfer, introduced P_{BM} into the dimensionless group $k_G M_M P_{BM}/G$, which by the methods of dimensional analysis is found to be a function of the Schmidt number $(\mu/\rho D_V)$ and a Reynolds number. It was felt that since P_{BM} is associated with the diffusion coefficient, in relationships such as Equation (2), and diffusion plays a role in the over-all process of mass transfer, the use of P_{BM} was justified. Correlations of mass transfer data for many physical systems of practical importance by means of the Chilton and Colburn relationship have been successful because low solute-concentrations were employed. Under these conditions if P_T had been substituted for P_{BM}, the correlations would have been just as good.

Most correlations of the Chilton and Colburn type have shown that the exponent on the Schmidt number $(\mu/\rho D_V)$ is approximately 2/3 as in Equation (1). This implies that k_G is proportional to $(D_V)^{2/3}$. However the correlations also imply that k_G is inversely proportional to P_{BM}, which does not give the relationship between D_V and P_{BM} as expected from Equation (2) for a region in which molecular diffusion is the rate-controlling mechanism for mass transfer. By analogy with the effect found for D_V one might expect k_G to be inversely proportional to $(P_{BM})^{2/3}$.

If both P_{BM} and P_T are employed, dimensional-analysis methods could yield a modified form of Equation (1) in which the ratio (P_{BM}/P_T) appears as an additional dimensionless group:

$$\left[\frac{k_G\, M_M\, P_T}{G}\right]\left[\frac{P_{BM}}{P_T}\right]^n\left[\frac{\mu}{\rho D_V}\right]^{2/3} = 1.195\left[\frac{D_P G}{\mu(1-\epsilon)}\right]^{-0.36} \qquad (5)$$

In this equation the exponent n on (P_{BM}/P_T) could be expected to be 2/3 on

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the basis of the preceding discussion. Regardless of the value of n, this equation will correlate low-solute-concentration data as well as Equation (1).

Two attempts have been made in recent years to obtain reliable gas-phase mass transfer data at high enough solute concentrations to investigate the effect of P_{BM} on the mass transfer coefficient. Cairns and Roper (*1*) employed a wetted-wall column to vaporize water into air at very high humidities. Their mass transfer data scattered badly possibly because they were operating in or near the critical zone by employing Reynolds numbers between 2,390 and 9,095; however they did offer a correlation which shows k_G inversely proportional to $(P_{BM}/P_T)^{0.83}$.

Westkaemper and White (*8*) obtained similar data by vaporizing carbon tetrchloride into an air stream flowing through a duct of rectangular cross section at Reynolds number between 600 and 15,000. By using the data for Reynolds numbers above 2,000 these investigators came to the unusual conclusion that their data could be correlated equally as well by the use of a (P_{BM}/P_T) term raised to the zero or first power. Their equations in rearranged form are

$$\left[\frac{k_G M_M P_T}{G}\right]\left[\frac{P_{BM}}{P_T}\right]^0\left[\frac{\mu}{\rho D_V}\right]^{0.56} = 0.00012\left[\frac{DG}{\mu}\right]^{0.42} \qquad (6)$$

and

$$\left[\frac{k_G M_M P_T}{G}\right]\left[\frac{P_{BM}}{P_T}\right]\left[\frac{\mu}{\rho D_V}\right]^{0.56} = 0.0014\left[\frac{DG}{\mu}\right]^{0.08} \qquad (7)$$

Both these equations are immediately open to suspicion because they imply that k_G is proportional to the gas rate raised to the 1.42 and 1.08 power, respectively. This is very unusual because extensive experience has shown this power to vary from about 0.60 to 0.83 for mass transfer.

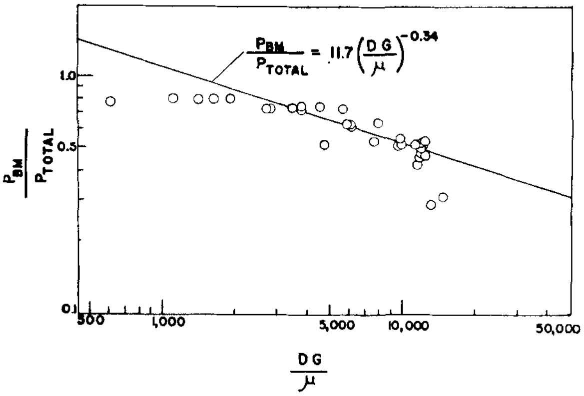

Fig. 2. Data of Westkaemper and White (*8*).

The unusual conclusions reached by these investigations can be explained easily as due to the unfortunate interpretation of a portion of their data and a coincidence in obtaining data in such a manner as to have introduced a relationship between (P_{BM}/P_T) and Reynolds number. These difficulties are shown in Figures 1 and 2. In Figure 1 Equation (7) is compared with the experimental data and a reference line showing the friction factor and the heat transfer factor for smooth round tubes. It can be seen that the data, although somewhat scattered, fall below but in a band parallel to the reference line. Unfortunately the investigators in attempting to obtain a correlation showing the minimum standard deviation ignored the data at low Reynolds numbers and obtained Equation (7). Cairns and Roper's (*1*) data are seen to scatter about the reference line. Figure 2 shows the coincidental relationship between (P_{BM}/P_T) and Reynolds number for the experimental data resulting in

$$\left[\frac{P_{BM}}{P_T}\right] = 11.7\left[\frac{DG}{\mu}\right]^{-0.34} \qquad (8)$$

for Reynolds numbers above 2,000. Because of this unfortunate coincidence the data can be correlated just as well by using any power on the (P_{BM}/P_T) term and obtaining the corresponding power on Reynolds number. It can be concluded that the data of Westkaemper and White (*8*) cannot be used to determine the effect of P_{BM} on k_G.

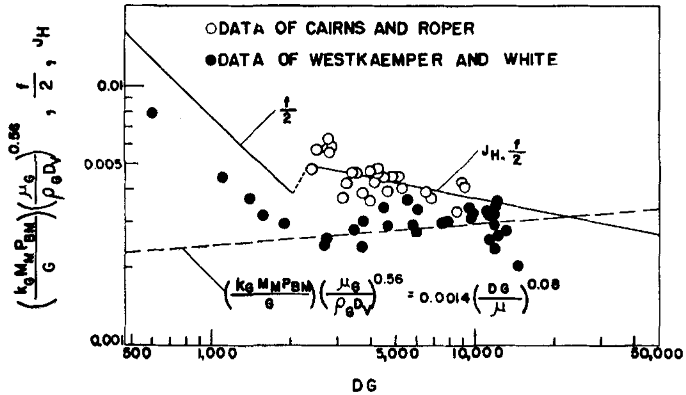

Fig. 1. Comparison of literature data.

The object of the present work is to determine the effect of P_{BM} on k_G for mass transfer in a packed column. A packed column avoids the difficulties inherent in operating in the ciritical and transition zones, such as encountered in wetted-wall columns. By vaporizing carbon tetrachloride into air streams of three different levels of concentration at varying gas rates one can avoid a coincidental relationship between (P_{BM}/P_T) and Reynolds number. The use of a short packed column results in a small gas-stream concentration change which makes it simple to employ average physical properties to interprete the data. Recycling the liquid carbon tetrachloride, one can adjust operating conditions to provide for little or no liquid temperature change throughout the column. This facilitates the determination of the liquid surface conditions required for the calculation of driving forces.

EQUIPMENT

Figure 3 shows a schematic diagram of the apparatus employed.

The experimental work was done in a Pyrex column 4 in. in diameter and packed with 1.75 in. of 0.5-in. Raschig rings. Air was obtained by means of a blower with a variable speed drive for coarse adjustments. Fine adjustments were made with valves located directly below the rotameters. The liquid rotameter was calibrated for a liquid rate of 3,000 lb./(hr.)(sq. ft.) in the liquid temperature range used. The column was heated with nichrome wire to avoid condensation and to maintain an essentially adiabatic operation.

The liquid receiving tank, a steel tank with a capacity of 5 gal., was located below the column. It was connected directly to a similar constant-head tank located 5 ft. above the top of the column. The liquid was circulated by a gear pump through a filter. An overflow line from the constant head tank to the receiving tank ensured a constant amount of liquid in the overhead tank at all times. The liquid was heated with a 1.5-kw. plate heater located directly

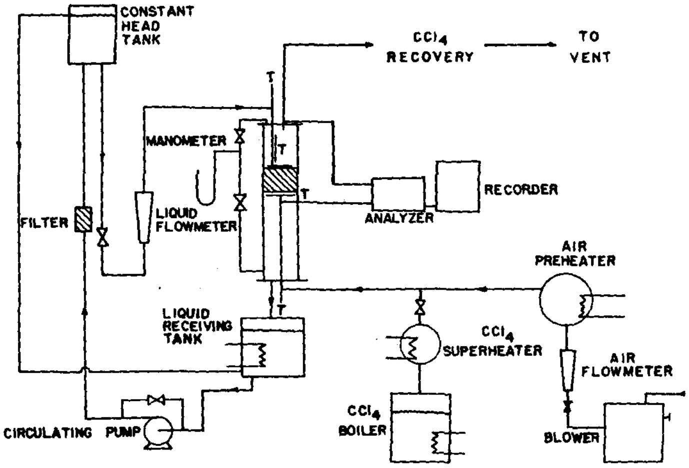

Fig. 3. Diagram of apparatus.

below the receiving tank. The temperature was controlled with a variable transformer used to adjust the power input. The copper lines were insulated with asbestos tape and covered with aluminum foil.

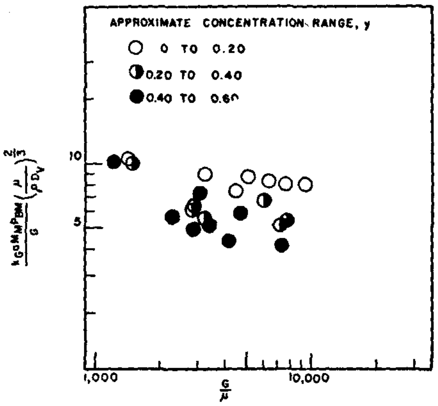

Fig. 4. Experimental data with Schmidt number based on average bulk composition.

A carbon tetrachloride boiler was used to give gas mixtures of the desired composition. Heat was supplied to the boiler by an immersion heater with the power input controlled by a variable transformer. The carbon tetrachloride vapor was passed through a 2-ft. length of copper tubing covered with a 400-watt jacket type of heater and mixed with air that had been heated to 800°F. The air heater was a 4.5-kw. Chromalox heater equipped with automatic temperature controls.

The heated gases were brought into the base of the column where the temperature was measured with an iron-constantan thermocouple. The gas distributor was a cross made of a brass stock bar ⅝ in. wide and ⅜ in. deep. Two grooves were cut along the underside of each arm of the cross, and six 0.125-in. holes were drilled along each groove from the end to the center of the cross, making a total of forty-eight discharge holes.

The liquid entered the top of the column and was discharged directly above the packing to minimize end effects. The liquid distributor was made of 0.25-in. copper tubing forming a continuous coil of two turns, with fifty holes 0.031 in. in diameter drilled radially along the underside. The temperature of the liquid was measured with a thermocouple just before being discharged into the packing; then a portion of the liquid leaving the packing was collected in a shallow trough and the temperature was measured there with a thermocouple which was always immersed in fresh liquid coming from the packing. The temperature of the gas leaving the column was measured with a thermometer placed above the liquid distributor. The carbon tetrachloride recovery system consisted of two double-pipe heat exchangers connected in series. The condensate was returned to the boiler.

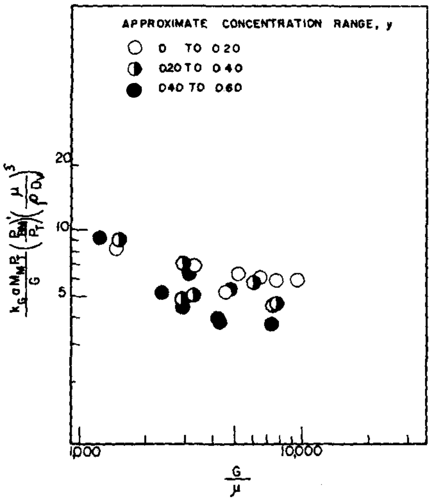

Fig. 5. Correlation of data with Schmidt number based on average film composition and $(P_{BM}/P_T)^1$.

Inlet gas samples were taken from the inlet gas line ½ in. below the distributor, and outlet samples were taken as the gas left the column. The samples were drawn through 0.125-in. copper tubing by slight suction, which was kept constant once the runs were started. An analysis was made for air, and carbon tetrachloride concentration was calculated by difference. The concentration of air was given by comparison of the peak height of pure air with the peak height for the air of the mixtures; because it was found that the width of the air peak was constant, peak heights were used rather than the area under the curve. Peak heights for pure air were reproducible within 0.2%.

PROCEDURE

The chromatographic analyzer required approximately 3 hr. to reach equilibrium, and therefore the analyzer was set well in advance of an actual run. Helium was the carrier gas, and a flow rate was used that gave reproducible peaks for pure air.

When runs were to be made with carbon tetrachloride from the boiler, the power for the boiler was turned on first. Air was then sent through the column. The thermostatic control on the air heater was set at 800°F. to bring the piping and insulation to equilibrium. The jacketed heater on the carbon tetrachloride line was also turned on to superheat the vapor before it was mixed with air. The liquid heater under the liquid receiver tank was turned on and then the nichrome heating wire on the column. The equipment required about 1 hr. to come to operating conditions.

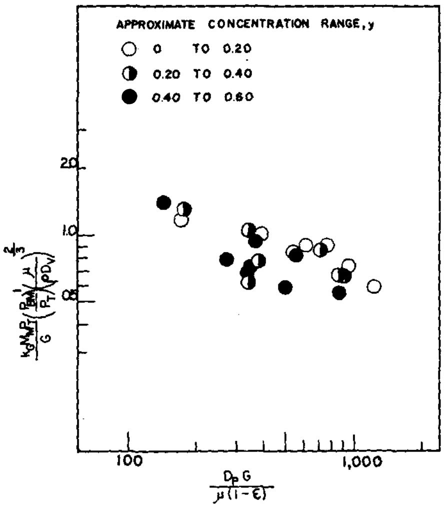

Fig. 6. Correlation of data with Schmidt number based on average film composition and $(P_{BM}/P_T)^1$.

A series of pure air peaks was then taken to be compared with actual heights taken during runs. Inlet compositions were set by the adjustment of the power input to the boiler following analysis of the inlet stream. When the desired inlet composition was reached, the heated liquid from the constant head tank was started through the column and adjusted to a rate of 3,000 lb./(hr.)(sq. ft.). The system was allowed to run about 15 min. while the liquid temperature was being adjusted so that its temperature remained fairly constant as it passed through the packing.

The analyzer required 6 min. to analyze a sample. To make a given measurement the sample valve was opened to bring the sample from the top of the column into the analyzer. Temperature and pressure measurements required about 2 min. to be recorded, which was about the time required for the analyzer to produce the analysis for air. The sample line for the inlet concentration was then connected to the analyzer. After the analysis of the top sample for air was complete, the bottom sample had about 3 min. to flush out the sample valve. The inlet stream was then analyzed and the inlet concentration was found to remain constant over a period of time with the same boiler setting. The settings were changed on the boiler and air rate, and the procedure was repeated. Intermittent pure-air samples were taken to make sure that there was no variation in the pure-air peak height.

The high concentration runs were done as the first series, then the medium concentration runs, and finally the low concentration runs. The packing and the distributor were not disturbed once actual runs were being made. Typical experimental data for five runs are presented in Table 1.

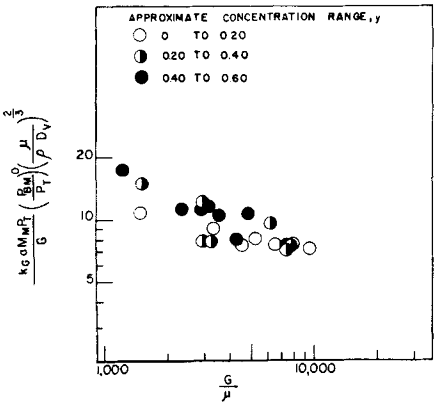

Fig. 7. Correlation of data with Schmidt number based on average film composition and $(P_{BM}/P_T)^0$.

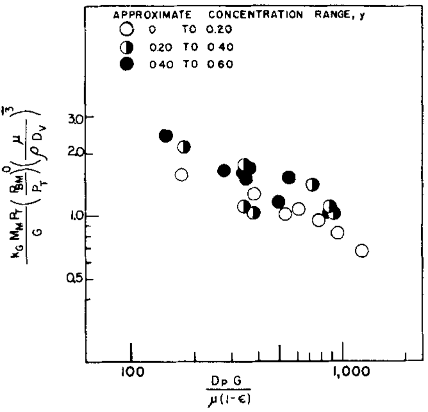

Fig. 8. Correlation of data with Schmidt number based on average film composition and $(P_{BM}/P_T)^0$.

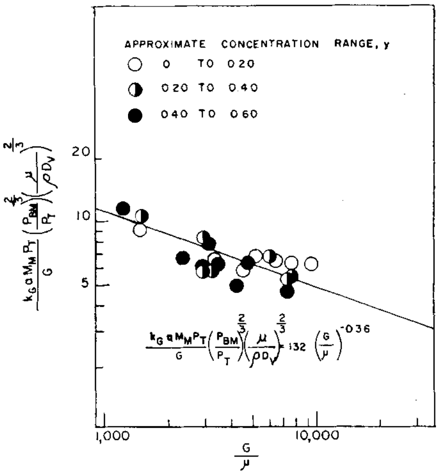

Fig. 9. Correlation of data with Schmidt number based on average film composition and $(P_{BM}/P_T)^{2/3}$.

METHODS OF CALCULATION

The volumetric mass transfer coefficient is calculated from

$$k_G a = \frac{(N_A a)}{(\Delta p)_{lm}} \tag{9}$$

where

$$(\Delta p)_{lm} = \frac{(p_i - p)_1 - (p_i - p)_2}{\ln \frac{(p_i - p)_1}{(p_i - p)_2}} \tag{10}$$

and $N_A a$ is obtained from the measured air rate and the analysis of the inlet and outlet streams.

The mass transfer coefficient is calculated from $k_G a$ by estimating a with the methods developed previously (*4* to *7*). Viscosities and diffusivities are calculated by the methods outlined in the text of Hirschfelder, Curtis, and Bird (*3*). The void fraction in the irrigated packing is estimated by methods presented preciously (*4, 6, 7*). The reported gas rates are an average of the inlet and outlet rates. Molecular weights and physical properties are determined from an average of the inlet and outlet compositions and temperatures except as otherwise noted. The reported values of P_{BM} are the arithmetic average of the P_{BM} at the inlet and outlet ends of the packed column. The Schmidt number varies rapidly with changing composition but is almost independent of temperature changes. As a result it was evaluated and used in two ways, first at the average bulk composition and second at what might be called "film" conditions, that is an average of the inlet, outlet, bulk, and interfacial conditions. The second composition corresponds closely to the value value obtained by the subtraction of P_{BM} from P_T for this work.

The gas rate was read on a rotameter calibrated to within 3%. Air concentrations could be determined to better than 1%. The carbon tetrachloride concentrations, obtained by difference, were reproducible to within 1% at high concentration and about 2% at low concentrations. As a result it can be estimated that the calculated $k_G a$ values are reproducible to better than 10% at low concentrations and 30% at the very high concentrations where a close approach to equilibrium introduces appreciable uncertainty in the driving forces. The final correlation of the data (Figure 10) shows scatter of the experimental data at the various concentration levels within the limits estimated.

EXPERIMENTAL RESULTS

An attempt was made to obtain data at three concentration levels with varying gas rates. This was done by introducing gas to the column roughly at the 0, 0.20, and 0.40 mole fraction carbon tetrachloride levels. When one vaporized additional carbon tetrachloride in the column, the outlet concentrations rose approximately 15 to 25 mole % above the inlet concentrations. The highest outlet concentration obtained was 0.616 mole fraction carbon tetrachloride. The data obtained are shown in Figures 4 through 10 with the three different concentration levels indicated. It should be realized that since it was impractical to hold the inlet concentrations constant for each level, the concentration differences between points at the three levels are not uniform and the scatter at any one level may be due in part to concentration differences.

In an attempt to correlate the data to determine the true effect of P_{BM} a problem is encountered which one does have to face at low concentrations or with a system such as air and water. This is the change in physical properties with changes in concentration and

Table 1. Typical Experimental Data

Run	1	7	10	17	21
Liquid rate, lb./(hr.)(sq. ft.)	3,000	3,000	3,000	3,000	3,000
Pure-air rate, lb./hr.	4.78	3.41	4.80	1.36	2.38
Mole fraction CCl$_4$, inlet, y_1	0.360	0.229	0	0.433	0.276
Mole fraction CCl$_4$, outlet, y_2	0.504	0.359	0.245	0.616	0.454
Liquid temperature, bottom, °C.	57.6	48.2	43.2	62.6	53.2
Liquid temperature, top, °C.	59.4	50.1	45.9	63.6	54.8
Gas temperature, bottom, °C.	144	111	211	175	115
Gas temperature, top, °C.	71	65	63	92	76
Total pressure, atm.	0.973	0.976	1.000	0.988	1.000

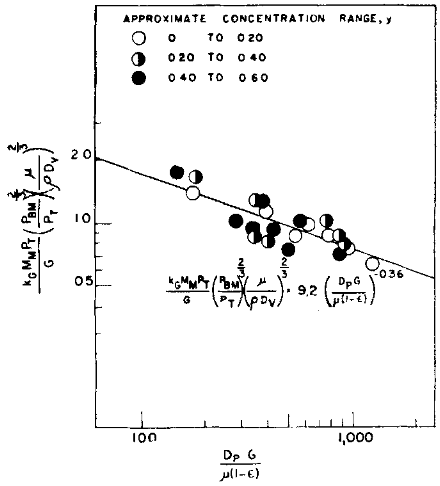

Fig. 10. Correlation of data with Schmidt number based on average film composition and $(P_{BM}/P_T)^{2/3}$.

especially the great variation in Schmidt number with changing concentration.

The first attempt to correlate the data is shown in Figure 4, where physical properties are based on a composition which is the arithmetic average of the inlet and outlet concentrations. It can be seen that the data fall into three bands depending upon concentration level and that the effect of gas rate is different for the three. Further attempts to correlate the date with Schmidt numbers based on average column compositions were not successful because the effect of gas rate found did not agree with Equation (1), and the power on the (P_{BM}/P_T) term as shown in Equation (5) was zero or negative.

All further attempts at correlation employed Schmidt numbers evaluated at average film conditions; that is the inlet, outlet, bulk, and interfacial, concentrations were averaged. Figure 5 shows the data with a $(P_{BM}/P_T)^1$ term used. The points still show an effect of concentration but an effect of gas rate closer to that expected from Equation (1). Since the low concentration runs at the higher gas rates were taken near loading conditions, it was felt that the removal of the effective interfacial area would make it possible to test Equation (5) to find the best power on the (P_{BM}/P_T). This was accomplished by estimating a and ϵ as described under methods of calculation. Figure 6 shows further improvement in correlation by the use of this method, but an effect of concentration is still present. Figures 7 and 8 show attempts with $(P_{BM}/P_T)^0$ employed. Again the proper effect of gas rate is indicated, but the effect of concentration is reversed; that is the low concentration data now fall below the high concentration data. It appears therefore that the best power on (P_{BM}/P_T) lies between zero and one. Several additional trials indicated that the use of $(P_{BM}/P_T)^{2/3}$ would correlate the data to give the effect of gas rate called for by Equations (1) and (5) and eliminate scatter which could be attributed to concentration level. Figures 9 and 10 show the data with $(P_{BM}/P_T)^{2/3}$.

The difference between the coefficient of the equation shown on Figure 10 and that of Equation (5) is probably due to a number of factors, several of which can be shown to predict a higher coefficient for this work. Since a very short column was used, end effects and excellent gas and liquid distribution would tend to provide a much higher coefficient. In addition there is some question as to the reliability of estimating a and ϵ for carbon tetrachloride because it has a density well above that used in developing the methods of predicting these quantities.

Since the effect of gas rate found is identical to that found in previous studies with packings, it is believed that the data are valid for conditions representative of flow patterns in packings and that the effect of P_{BM} can be predicted by the use of $(P_{BM}/P_T)^{2/3}$ in an expression such as Equation (5). The 2/3 power is also in agreement with the effect of D_V found previously, and it is logical to expect the same relationship between P_{BM} and D_V as is found for molecular diffusion to hold for systems where molecular diffusion plays a part in the over-all process of mass transfer.

SUMMARY AND CONCLUSIONS

Mass transfer data including data obtained at three concentration levels indicate that mass transfer coefficients for packings can be correlated by

$$\left[\frac{k_G\, M_M\, P_T}{G}\right]\left[\frac{P_{BM}}{P_T}\right]^{2/3}\left[\frac{\mu}{\rho D_V}\right]^{2/3} = 1.195\left[\frac{D_P G}{\mu(1-\epsilon)}\right]^{-0.36} \tag{11}$$

when the Schmidt number is evaluated at average film conditions.

This equation makes it possible to predict a k_G which can be combined with effective interfacial areas reported previously (*4* to *7*) to obtain a $k_G a$ for any desired gas-liquid-solute system for which physical properties are available.

ACKNOWLEDGMENT

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NOTATION

a = effective interfacial area, sq. ft./cu. ft.
D = equivalent diameter or characteristic dimension, ft.
D_P = diameter of sphere possessing the same surface area as a piece of packing, ft.
D_V = diffusivity of solute in gas, sq. ft./hr.
f = friction factor for smooth tubes
G = superficial gas rate, lb./(hr.)(sq. ft.)
j_D = mass transfer factor, defined by Equation (1)
j_H = heat transfer factor for smooth tubes
k_G = gas-phase mass transfer coefficient, lb.-moles/(hr.) (sq. ft.) (atm.)
$k_G a$ = volumetric mass transfer coefficient
M_M = mean molecular weight of gas, lb./lb.-mole
n = exponent on (P_{BM}/P_T) in Equation (5)
N_A = rate of mass transfer, lb.-moles/(hr.) (sq. ft.)
$N_A a$ = lb.-moles of carbon tetrachloride vaporized/hr./cu. ft. of packing
p = partial pressure of carbon tetrachloride in gas, atm.
Δp = solute partial pressure difference, atm.
$(\Delta p)_{lm}$ = logarithmic mean driving force, atm.
P_{BM} = mean partial pressure of inert gas in the gas phase, atm.
p_i = partial pressure of carbon tetrachloride at liquid surface, atm.
P_T = total pressure, atm.
R = gas-law constant
T = absolute temperature, °K.
y = solute mole fraction
Z = diffusion path length, ft.
ϵ = void fraction, cu. ft./cu. ft.
μ = gas viscosity, lb./(hr.) (ft.)
ρ = gas density, lb./cu. ft.

Subscripts

1 = bottom of packing
2 = top of packing

LITERATURE CITED

1. Cairns, R. C., and G. H. Roper, *Chem. Eng. Sci.*, **3**, 97 (1954).
2. Chilton, T. H., and A. P. Colburn, *Ind. Eng. Chem.*, **26**, 1183 (1934).
3. Hirschfelder, J. O., C. F. Curtis, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York (1954).
4. Shulman, H. L., C. F. Ullrich, and N. Wells, *A.I.Ch.E. Journal*, **1**, 247 (1955).
5. Shulman, H. L., C. F. Ullrich, A. Z. Proulx, and J. O. Zimmerman, *ibid.*, p. 253.
6. Shulman, H. L., C. F. Ullrich, N. Wells, and A. Z. Proulx, *ibid.*, p. 259.
7. Shulman, H. L., and J. E. Margolis, *ibid.*, **3**, 157 (1957).
8. Westkaemper, L. E., and R. R. White, *ibid.*, p. 69.

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