that the amount of deviation from the present results and those of Houghton et al. increases uniformly as the solubility of the gas decreases.

Gertz and Loeschcke (6) derived diffusivities from an experiment in which they passed water down through a downwardly divergent tube, 2.1 to 2.8 mm. in diameter and 30 cm. long. Bubbles of solute gas were introduced at the bottom of the tube and rose as dissolution took place. The rate of rise of the bubble gave a mass transfer coefficient, taken by Gertz and Loeschcke to be proportional to the first power of diffusivity. Calibration of the device was made by accepting the diffusivity given by Tammann and Jessen for hydrogen in water at 29°C.

A variation with the first power of diffusivity is unlikely in a system where there is flow around a bubble. More likely would be a variation with the 2/3 power of diffusivity, which is the case for flow of this magnitude about a solid sphere or a noncirculating bubble (5). The bubble rise time in all cases was over 30 sec., and it has been found by Deindorfer and Humphrey (4) and others recently that this should be more than time enough for cessation of circulation through accumulation of surfactant molecules or other causes. Figure 1 shows the reported diffusivities of Gertz and Loeschcke at 21°, 25°, 29°, 33°, and 37°C. plotted against the present values for helium, hydrogen, oxygen, and carbon dioxide and against the value of Houghton et al. (7) for nitrogen. The present diffusivities and that of Houghton et al. have been corrected for temperature by holding the group  $(D\mu/T)$  constant. It is apparent that the reported diffusivities of Gertz and Loeschcke correlate well with the 2/3 power of the present diffusivities. There is no apparent temperature effect other than that due to diffusivity, a fact in accord with predictions (5). Thus if one of the present values is used for calibration, and laminar boundary-layer theory for flow about a noncirculating spherical bubble is used for interpretation, the results of Gertz and Loeschcke agree well with the present diffusivities and those reported by Houghton et al.

# LITERATURE CITED

1. Aikazyan, E. A., and A. I. Federova, Dokl. Acad. Nauk. S.S.S.R., 86, 1187 (1952).

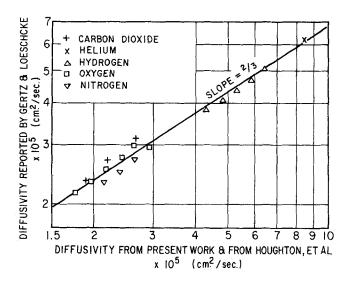


Fig. 1. Diffusivities reported by Gertz and Loeschcke (6).

- 2. Baird, M. H. I., and J. F. Davidson, Chem. Eng. Sci., 17,
- 3. Davidson, J. F., and E. J. Cullen, Trans. Inst. Chem. Engrs., **35**, 51 (1957)
- 4. Deindorfer, F. H., and A. E. Humphrey, Ind. Eng. Chem., **53**, 755 (1961).
- Friedlander, S. K., A.I.Ch.E. Journal, 7, 347 (1961).
   Gertz, K. H., and H. H. Loeschcke, Z. Naturforsch., 9b, I (1954); 11b, 61 (1956)
- 7. Houghton, G., P. D. Ritchie, and J. A. Thomson, Chem. Eng. Sci., 17, 221 (1962).
- 8. Ipatieff, V. V., and V. P. Teodorovich, Zh. Fiz. Khim., 10, 712 (1937).
- 9. King, C. J., Sc.D. thesis, Mass. Inst. Technol., Cambridge, Massachusetts (1960).
- Smith, R. E., E. T. Friess, and M. F. Morales, J. Phys. Chem., 59, 382 (1955).
- 11. Tammann, G., and V. Jessen, Z. Anorg. Allgem. Chem., 179, 125 (1929).
- 12. Vivian, J. E., and C. J. King, A.I.Ch.E. Journal, 10, p. 221 (1964).

# The Mechanism of Liquid-Phase Resistance to Gas Absorption in a Packed Column

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The descrption of five sparingly soluble gases from water into air in a packed tower was studied at five different flow conditions. At 25°C. these systems represent a range of liquidphase diffusivity from 1.4 imes 10 $^{-5}$  to 6.3 imes 10 $^{-5}$  sq. cm./sec. The mass transfer coefficient was found to vary as the 0.5 power of liquid-phase diffusivity in all cases. This result, obtained through the variation of diffusivity alone, is in agreement with the predictions of penetration theory and strongly suggests a penetration mechanism based on molecular processes and independent of eddy processes during a surface lifetime. A discussion of the nature of the diffusion and surface renewal process in flow over packing is included.

Packed columns for gas absorption and distillation systems continue to assume importance in chemical opera-

This article is introduced by the communication to the editor on page 220.

tions, and many investigations have been carried out to provide a basis for their design. In general these investigations have had to depend on empirical analyses in view of the complex geometries and flow patterns encountered in industrial-sized equipment and have resulted in useful correlations valid for the conditions investigated.

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Such correlations however have limited applicability. Unless there is some indication of the mechanism of the processes involved together with all of the pertinent variables, these empirical correlations while dimensionally sound cannot be reliably used for scale-up purposes or extrapolation to conditions that have not been explicitly studied. Furthermore in the case of commercial packed columns considerable difficulty is encountered in obtaining adequate performance data to extend the design correlation except for the simplest systems and limited operating conditions. This is particularly the case where gas absorption with simultaneous chemical reaction is involved.

To supply fundamental information relative to the commercial absorption process a number of laboratory models have been proposed for the study of gas absorption. However for such model studies to be applicable in design the mechanisms of transport in model and in packed column must conform reasonably well, and to select or develop models of practical significance knowledge of the mechanisms involved in gas absorption in a packed column absorber is required.

There have been several theories proposed for the mechanisms of transport in gas absorption in a packed column. Basic to all theories is the assumption of individual-phase resistances adjacent to the gas-liquid interface (12) which can be studied independently in many cases in spite of the probable importance of their interaction. The work reported here was concerned only with the transport mechanism in the liquid phase in a packed column.

Two widely known theories used to describe the transport mechanism in the liquid phase are the so-called film and penetration theories. The film theory of Whitman and Lewis (17) considers the liquid-phase resistance to mass transfer to be concentrated in an effective stagnant film adjacent to the gas-liquid interface across which steady state transfer occurs by molecular diffusion. On this basis the mass transfer coefficient  $k_L$  is defined by the ratio of the molecular diffusivity  $D_L$  to the effective film thickness  $x_L$ .

The penetration theory of Higbie (2) pictures the absorption by the liquid phase as taking place by unsteady state diffusion into a laminar layer of liquid flowing over the surface of the packing. The liquid layer is assumed to be completely mixed in flowing from one piece of packing to the next and to be free of velocity gradients and turbulence near enough to the surface to affect the transport process adjacent to the gas-liquid interface. Since absorption is assumed to occur only during the laminar flow period, the absorption process is equivalent to transient diffusion into a stagnant liquid layer for an exposure time  $t_e$  equal to the surface lifetime between mixings. The mass transfer coefficient for this case, averaged over the time of exposure, is defined by

$$k_L = 2 \sqrt{\frac{D_L}{\pi t_c}} \tag{1}$$

Because of the irregularities of the flow path over packing and flow rates ordinarily used a degree of turbulence in the liquid layer can be expected which may vary with flow conditions and particularly with position in the packing. Consequently the degree to which such turbulence affects the transport mechanism may depend on operating conditions. This effect has been considered in what may be called *turbulence* theories. Kafarov and Murav'ev (4, 5) have proposed an effect of turbulence on the mass transfer process in a packed column at high liquid and gas flow rates through which the mass transfer coefficient can become independent of molecular diffusivity. Kishinev-

sky and Serebryansky (7), absorbing slightly soluble gases in water in a stirred vessel, have reported data which indicate the rate of absorption to be independent of molecular diffusivity at high rates of agitation.

Several possibilities can be suggested for the role of turbulence in the overall liquid-phase absorption process. Eddies generated at the mixing points at junctions of pieces of packing may extend into the layer of liquid flowing over the packing surfaces, thereby accelerating the transfer rate over that for diffusion into a truly laminar layer. Drag on the liquid surface at localized constrictions in the packing at high gas and liquid flow rates, recently discussed by Howkins and Davidson (3) as the cause of loading, may induce surface eddying. Rapid renewal of the surface by small-scale turbulence may result in rapid saturation of the surface liquid, and the overall liquidphase transport mechanism would then depend on removal of saturated liquid from the region of the interface by an eddy diffusion process. The effect of such processes superimposed on a process assumed to be dependent solely on molecular diffusion is to reduce the dependence on molecular diffusion.

Other models, such as the film-penetration theory of Toor and Marchello (14) or the assumption of significant velocity gradients near the interface due to drag of the gas on the liquid surface, would also alter the dependence on molecular diffusion.

Sherwood and Holloway (11) in a study of the rate of desorption of insoluble gases from water into air obtained data which give the only previous indication of the mechanism of mass transfer in the liquid phase in a large-scale packed column. The Nusselt or Sherwood group was found to vary as the 0.5 power of the Schmidt group for a given Reynolds number and packing, thus making kla proportional to the square root of the diffusivity, suggestive of a penetration-theory mechanism. The variation in the Schmidt group was obtained mainly by varying the temperature for the desorption of carbon dioxide and oxygen, since the diffusivities of carbon dioxide and oxygen in water are approximately the same. However, since other temperature-dependent dimensionless groups such as a surface tension group and the so-called gravity group were not included, the effect of diffusivity could not be definitely ascertained from the effect of temperature. Limited data obtained with hydrogen as solute were taken to provide only qualitative substantiation of the exponent for the Schmidt group. Thus the conclusion regarding a penetration-theory mechanism was considered tentative.

The experiment of desorbing slightly soluble gases from water under carefully controlled fluid dynamic conditions is a powerful tool for determining the effect of diffusivity on the liquid-phase absorption coefficient, and thus indicating the mechanism. The absorption or desorption of slightly soluble gases is entirely liquid phase controlled. In solution these gases do not perceptibly affect the physical flow or spreading qualities of the solvent and give such low rates of transfer that for reasonable values of gas and liquid flow rate there is negligible solute build up in the gas stream. Thus a comparison of the mass transfer coefficients for desorption from water into air of various slightly soluble gases having significantly different diffusivities on the same packing and at the same flow rates and temperature should give the effect of solute diffusivity without altering any other variables in the system. Such an experiment was carried out with the aim of contributing to a better understanding of the mechanism of liquid-phase transfer in flow over packing.

The five solute gases listed in Table 1 were chosen for study; they are all of low enough solubility to provide liquid phase controlled systems and show a wide range

TABLE 1. DIFFUSIVITIES OF SOLUTE GASES IN WATER AT 25°C.

Gas	Diffusivity $ imes 10^5$ (sq. cm./sec.)		
Propylene	1.44		
Carbon dioxide	2.00		
Oxygen	2.41		
Hydrogen	4.8		
Helium	6.3		

of diffusivities. In a preliminary set of experiments the diffusivities of these gases in water were measured with a fritted glass diaphragm cell (15), and the results are summarized in Table 1.

# EXPERIMENTAL APPARATUS

One and one-half inch ceramic Raschig rings were used in a 12-in. diameter tower. Packed heights of 1 and 2 ft. were allowed for as a compromise between appreciable end effects and a measurable bottom driving force.

A schematic flow sheet is shown in Figure 1. A water recirculation system was provided, capable of producing flow rates equivalent to flooding at various gas rates. A bypass arrangement gave control of the water flow rate, which was measured by one of three calibrated orifices. Water temperature control was achieved by a steam injection system which held the water entering the column at 25°C. Control of the concentration of solute in water entering the column was achieved by a solute gas injection system. The solute gas flow was monitored with capillary flow meters. Several fittings followed the tees through which steam and solute gas were injected; these gave efficient absorption of both.

All surfaces in contact with water were either made of brass or copper, or covered with three coats of paint. All water piping was 1½-in. copper tubing. The air stream was provided by a variable speed, D.C., rotary blower through a standard butt mounted orifice. The inlet air stream to the column was saturated with water at 25°C. in a spray column with facilities for both steam and water injection. The entire air line was made of 4-in. galvanized sheet metal pipe except for the spray tower which was 6 ft. of 8-in. sheet metal pipe.

Details of the packed column are shown in Figure 2. The tower consisted of four sections of 12-in. steel pipe. The normal operation was with a 1-ft. packed height and the section labelled optional omitted. This section could be used to give either a second foot of packed height or additional head on the

Upon entering the top of the tower the water flowed over a liquid seal and through twenty-three lengths of copper tubing which discharged on the packing surface. At the bottom of the bed the water fell into a pool, from which the water returned to the storage tanks by gravity flow. A levelling tee and sight glass made it possible to maintain the height of the pool con-

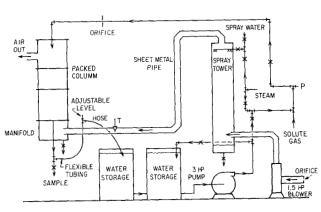


Fig. 1. Flow diagram of apparatus.

stant, just below the points of air entry. To minimize end effects and provide for liquid and gas distribution the distribution and take-off systems were made similar to those used by Whitney and Vivian (18).

## **PROCEDURE**

#### Experimental

Before solute gas was injected in a run, the tower was operated for 15 min. at the desired air flow rate and a water flow rate 25 to 50% higher than that desired for the run; this established the water holdup in the tower. The water flow rate was then brought back to the desired value, and temperatures, humidity, and pool height were adjusted to the operating conditions. After 10 minutes samples were taken of the inlet and exit water streams. The sample was kept enclosed by taking it either in a closed bulb or a stoppered flask. The vessel was always flushed with 5 to 10 vol. of water solution. At least one more set of samples was taken in each run, 5 min. or more later. At all flow conditions at least two duplicate runs were made for each solute (in addition to the duplicate samples within a run). For conditions where data tended to scatter, still more runs were made. The total number of runs was seventy.

Oxygen solution samples were taken in 250-ml. flasks and analyzed by the Winkler technique (6, 11). All other solutions were sampled in 100-ml. two-arm glass bulbs. In the case of carbon dioxide the solution was forced by mercury from the bulb through a glass jet delivering under the surface of a standard barium hydroxide solution. The amount of solution introduced was determined by weight differences, and the excess hydroxyl was titrated against hydrochloric acid to a phenolphthalein end point (6, 11).

Sample solutions of the other three gases were analyzed by removing all dissolved gas from a known quantity of sample. The amount of solute in this extracted gas was found quantitatively by injecting the gas into a gas chromatograph, with a 6-ft. silica gel column. For hydrogen and helium samples a nitrogen carrier was used, whereas helium was employed as the carrier for propylene samples.

The apparatus used for separating the dissolved gas was patterned closely after that used by Rakestraw and Emmel (9). Basically the operation consisted of taking a measured water sample into a bulb. The water was then passed through a fine nozzle into an evacuated chamber; the water was removed, and the extracted gas forced in to a gas collection

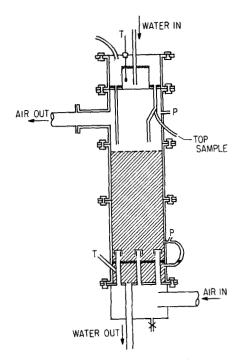


Fig. 2. Packed column assembly.

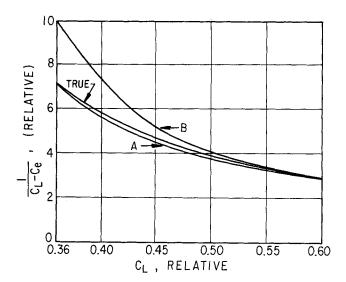


Fig. 3. (NTU) $_{
m OL}$  integral for oxygen desorption runs.

bulb. The process was repeated two or three more times. More details of this technique are given elsewhere (6).

## Calculational

The following three equations are applicable by definition to transfer rates in dilute solutions:

$$K_{L}a = \frac{L}{\rho_{L}(HTU)\rho_{L}} \tag{2}$$

$$(NTU)_{OL} = \frac{h_t}{(HTU)_{OL}} \tag{3}$$

$$(NTU)_{OL} = \int_{C_B}^{C_T} \frac{dC_L}{C_L - C_e}$$
 (4)

In the cases of helium, hydrogen, and propylene desorption there is no significant content of the gases in the air stream, and the solubilities are so low that at all points  $C_e$  was negligible in comparison to  $C_L$ . For these solutes then Equation (4) is readily integrated to give

$$(NTU)_{OL} = \ln \frac{C_T}{C_B} \tag{5}$$

For carbon dioxide desorption there is a slight buildup of carbon dioxide in the gas phase which eventually causes  $C_e$  to become significant. A material balance on carbon dioxide

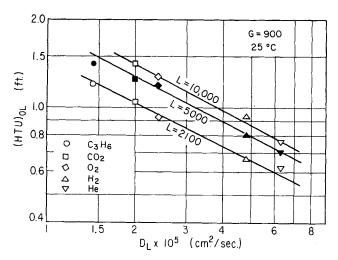


Fig. 4. (HTU) $_{\rm OL}$  vs. D $_{\rm L}$ , at constant G.

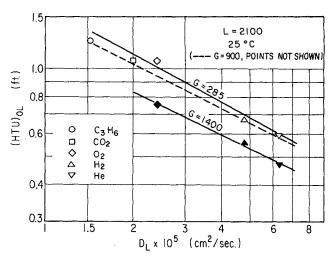


Fig. 5. (HTU)OL vs. D at constant L.

$$\frac{L}{\rho_L}(C_L - C_B) = \frac{C}{\rho_A RT}(p - p_B) \tag{6}$$

combined with Henry's law  $(p = HC_L)$ 

$$C_e = \frac{1}{H} \left[ \frac{L \rho_A RT}{G \rho_L} \left( C_L - C_B \right) + p_B \right] \tag{7}$$

shows however that  $C_e$  is linear in  $C_L$ , and thus Equation (4) may be integrated to give

$$(NTU)oL = \frac{C_T - C_B}{(C_L - C_e)_T - (C_L - C_e)_B} \ln \frac{(C_L - C_e)_T}{(C_L - C_e)_B}$$
(8)

 $C_e$  at the top and bottom comes from Equation (7). Variations in temperature, and thus in H, could make  $C_e$  nonlinear in  $C_L$ , but in practice the effect of changing  $C_L$  was much greater, and changes in H could be neglected. The solubility data of Bohr (10) for carbon dioxide in water were employed.

In the case of oxygen desorption  $C_e$  at any point is again given by Equation (7), but now  $p_B$  is highly important, amounting to 0.21 atm. This fact also produces a close approach of  $C_L$  to  $C_e$  at the tower bottom and makes small changes in H significant. Temperature usually did differ by half a degree or so from top to bottom of the tower. This temperature effect was the result of heat transfer to the atmosphere, which is nearly linear in tower height. This serves to make  $C_e$  remain closer to  $C_{eB}$  than it would for a linear variation with  $C_L$ . The effect is shown qualitatively in Figure 3, where line A represents  $C_e$  linear in  $C_L$ , and line B represents the situation if  $C_e$  were constant throughout and equal to  $C_{eB}$ . A computation shows that the true result for NTU is different from the result obtained from curve A by about 20% of the difference in areas given by curves A and B.\*

The solubility data of Winkler (10) for oxygen in water were employed for calculational purposes.

### EXPERIMENTAL RESULTS AND DISCUSSION

## **Effect of Diffusivity**

Figures 4 and 5 show the main experimental results with one foot of packed height at  $25^{\circ}$ C., giving  $(HTU)_{OL}$  as a function of solute liquid diffusivity at constant air and water flow rates.† Table 2 shows the slopes of straight

$$(NTU)_{OL} = \ln \frac{(C_L - C_e)_T}{(C_L - C_e)_B}$$

which is not necessarily correct. The correction becomes significant only for runs made at different temperature levels or with large bed heights (6).

 $^{\dagger}$  A complete tabulation of experimental data and results is available (6).

<sup>\*</sup> The oxygen results of Sherwood and Holloway (11) were calculated with

TABLE 2. SLOPES OF LOG (HTU)OL VS. LOG (DL)

L, (lb./hr. ft.)	G, (lb./hr. ft.)	% of flooding G	Slope	Standard dev./slope
2,100	900	52	0.50	4%
2,100	285	16	0.53	5%
5,000	900	73	0.54	6%
10,000	900	91	-0.53	5%
2,100	1,400	80	0.48	6%

Table 3. Experimental Data at  $L=2,100,\,G=900$ 

	Median			
Solute	No. of sample sets	$(HTU)_{OL}$ at $25^{\circ}$ C. (ft.)	Standard deviation	
Propylene	4	1.20	5%	
Carbon dioxide	7	1.05	5%	
Oxygen	10	0.93	2%	
Hydrogen	4	0.66	5%	
Helium	7	0.62	8%	

lines on the logarithmic plots statistically fitted to these data for the indicated gas and liquid rates. The third column refers the air rate to that air rate which would correspond to flooding at the particular water rate. Table 3 shows the results and reproducibility obtained for the various solutes at one set of flow conditions.

These slopes are strikingly constant over the range of flow conditions and are equal to  $-\frac{1}{2}$  within expected deviations. There is no confirmed trend in slopes with respect to air or water rates. Furthermore the data taken by Sherwood and Holloway at G=230 and L=2,000 (13% of flooding) give a slope of -0.48 when the present diffusivity values are employed.

Since for these sparingly soluble gases  $(HTU)_{OL} = (HTU)_{L'}$  it may be reasonably concluded that  $(HTU)_{L}$  varies at  $D_L^{-0.50}$  and  $k_L a$  varies as  $D_L^{0.50}$  over the entire range of flow conditions studied. This result is in excellent agreement with the prediction of penetration theory that  $k_L$  varies as the square root of  $D_L$  [Equation (1)]. This square-root variation characterizes the unsteady state molecular diffusion of solute into an element of fluid without a velocity gradient, and this appears to be the case for L/G ratios of 1.5 to 11 and for flow conditions corresponding to 16 to 91% of flooding. There is furthermore no indication that the mass transfer process becomes less dependent on molecular diffusivity as flooding is approached.

Theories based on turbulent transport operating in parallel with molecular diffusion either do not predict an exponent of 0.50 on diffusivity or else suggest that the exponent should vary with flow conditions. Although some mode of turbulence near the interface in conjunction with molecular diffusion resulting in an exponent of 0.50 is possible, it would be unlikely that such behavior would produce the same effect of diffusivity at five very different flow conditions. Thus, to the extent that the present experimental results tend to indicate a constant exponent of 0.50 on DL, a mechanism other than unsteady-state penetration into an element of surface liquid with negligible velocity gradient and with negligible turbulent transport within the transport zone adjacent to the interface does not appear reasonable. This conclusion does not preclude an effect of larger scale turbulence on the frequency of surface renewal, as discussed below. A distinction should be drawn between large scale eddies which accomplish a surface renewal process and smaller scale eddies which act in parallel with molecular diffusion during a given surface exposure.

# **Effect of Temperature**

The effect of temperature upon  $(HTU)_L$  was studied and deserves some attention. The experimental results for

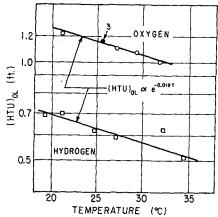


Fig. 6.  $(HTU)_{\rm OL}$  vs. temperature.

the desorption of oxygen and of hydrogen at various temperatures are shown in Figure 6. A comparison of these results with the results of other investigators is shown in Figure 7. The oxygen data of Sherwood and Holloway have been recalculated by the method described above. From Figure 7 it appears that the best representation of the various sets of data for aqueous systems including those of the present investigation is given by  $(HTU)_{L^-}$   $\alpha e^{-0.020T}$ , where T is in degrees Centigrade.

The exponent of -0.019 found by Vivian and Whitney (15) for chlorine absorption is also in agreement, although it would be expected that the simultaneous chemical reaction would introduce a complicated temperature effect.

#### **Effect of Other Variables**

The experimental data for each solute system showed the same effects of gas and liquid rates as found by Sherwood and Holloway (11); namely (HTU)oL was independent of gas rate below loading and dependent on the 0.2 power of the liquid rate. Repacking the tower with the 1½-in. Raschig rings gave reproducible data within 3%. A few data obtained with approximately a 2-ft. packed height gave essentially the same results except that the (HTU)oL were about 10% higher than with the 1-ft. packed height.

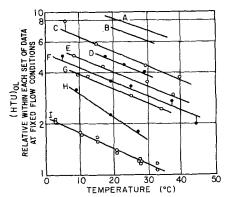


Fig. 7. Effect of temperature: comparison of data for aqueous systems. Key: A—present data—hydrogen— —0.019°C.—1, B—present data—oxygen— —0.019, C—Sherwood and Holloway (11)—carbon dioxide— —0.020, D—Sherwood and Holloway (11)—hydrogen—0.020, E—Sherwood and Holloway (11)—oxygen (L = 10,000)— —0.020, F—Sherwood and Holloway (11)—oxygen (L = 2,000)—0.020, G—Sherwood and Holloway (11)—oxygen (L = 400)—0.020, H—Molstad et al. (8)—oxygen—0.031, I—Vivian and Whitney (15)—chlorine—0.019.

Certain runs made with propylene as the solute gave scattered results and a tendency toward low values of (HTU)oL. These were instances in which the combined content of dissolved propylene and air in the inlet water was equivalent to nearly complete saturation. Apparently the higher diffusivity of absorbing air, as compared with the lower diffusivity of desorbing propylene, caused local supersaturations to develop within the water in the course of the mass transfer process, with consequent acceleration of the propylene desorption.

When steam-deaerated make-up water was employed, the values of  $(HTU)_{OL}$  were normal.

#### Surface Renewal Mechanism

As noted above the experimental results on the effect of diffusivity indicate the penetration type of mechanism for transfer at the liquid-gas interface in the absence of flow-induced small scale turbulence at the interface. Characteristic of this mechanism is the lifetime during which fluid surface elements are exposed. With liquid flowing over packing each packing produces a distribution of surface lifetimes, and this distribution of lifetimes can be expected to be dependent on packing geometry. Insofar as packing geometry is taken to be the only factor affecting lifetime distribution, penetration theory with its assumption of laminar flow between surface renewals predicts that the liquid phase  $(HTU)_L$  will be proportional to the liquid flow rate per unit wetted perimeter I to the 2/3 power, equivalent to  $L/a_e$  to the 2/3 power (1, 12).

These considerations infer the correlation of packed tower (liquid phase) absorption data on the basis of  $(HTU)_L$  as a function of the Reynolds number to the 2/3 power and the Schmidt number to the 1/2 power. Several investigators have used these groups for empirical correlation, but recently Davidson (1) attempted to develop a similar correlation on a more fundamental basis. With three models predicated on penetration theory with the assumption of vertical surfaces of specified length, random surface orientation of specified length, and random surface orientation and random surface length, together with the estimates of  $a_e$  given by Shulman (13), remarkably improved predictions involving the above functions of Re and Sc with theoretically derived numerical constants were obtained.

As is shown by Davidson's comparison of theory with data a value of the exponent on the Reynolds number appreciably less than 2/3 is indicated by the data. This is especially the case if individual packings are considered, as shown in Figure 8 where the slope indicates  $(HTU)_L$  proportional to about the 0.4 power of the Reynolds number. This fact suggests that the average length of flow path between surface renewals decreases with increasing Reynolds number. Furthermore, values of  $(HTU)_L$  are lower than predicted by models of the

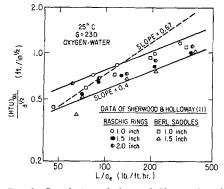


Fig. 8. Correlation of data of Sherwood and Holloway (11) for desorption of oxygen from water at 25°C.

Davidson type when a reasonable average surface orientation and a reasonable average flow path length between packing discontinuities are assumed. (For example a preference toward vertical surface flow would be expected even though the packing may be truly randomly oriented, and flow path length would be expected to have a distribution which peaked at some large fraction of a packing length.) It seems evident therefore that surface renewal by gross turbulence in the course of flow over a continuous length of packing is a factor in the performance of a packing and becomes more and more important as the flow rate increases. These renewals occur without the simultaneous appearance of smaller scale eddies near the interface such as would provide an eddy diffusivity to affect the molecular transport process during a given surface exposure.

# ACKNOWLEDGMENT

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## NOMENCLATURE

a<sub>e</sub> = effective interfacial area between gas and liquid phases, (length²)

C<sub>B</sub> = concentration of solute in liquid at bottom of tower, (moles/length³)

Ce = concentration of solute in liquid that would be at equilibrium with solute partial pressure in gas phase, (moles/length³)

C<sub>L</sub> = concentration of solute in liquid phase, (moles/ length<sup>3</sup>)

C<sub>T</sub> = concentration of solute in liquid at top of tower, (moles/length³)

d = nominal dimension of packing, (length)

D<sub>L</sub> = diffusivity of solute in liquid phase, (length<sup>2</sup>/time)

g = acceleration due to gravity, (length/time<sup>2</sup>)

G = gas flow rate per unit superficial area, (mass/time length<sup>2</sup>)

 $h_t$  = height of tower, (length)

H = Henry's law constant, (pressure length³/mole)
 (HTU)o<sub>L</sub> = height of an overall liquid-phase transfer unit, (length)

 $(HTU)_L$  = height of an individual liquid-phase transfer unit, (length)

k<sub>L</sub> = individual liquid-phase mass transfer coefficient, (length/time)

 $K_{La}$  = volumetric overall liquid-phase mass transfer coefficient (1/time)

L = liquid flow rate per unit superficial area, (mass/time length<sup>2</sup>)

(NTU) o<sub>L</sub> = number of transfer units based on overall liquid-phase driving force

p = partial pressure of solute gas, (pressure)

p<sub>B</sub> = partial pressure of solute gas at bottom of tower, (pressure)

R = gas constant, (pressure length<sup>3</sup>/mole deg.)

t = age of liquid surface, (time)

te = lifetime of liquid surface before renewal, (time)

T = temperature, (deg.)

 $x_L$  = film thickness in film theory, (length)  $\mu$  = viscosity of liquid, (mass/length time)  $\rho_A$  = density of air stream, (mass/length<sup>3</sup>)  $\rho_L$  = density of liquid stream, (mass/length<sup>3</sup>)

# LITERATURE CITED

Davidson, J. F., Trans. Inst. Chem. Engrs., 37, 131 (1959).
 Higbie, Ralph, Trans. Am. Inst. Chem. Engrs., 31, 365 (1935).

- 3. Howkins, J. E., and J. F. Davidson, A.I.Ch.E. Journal, 4, 324 (1958).
- 32, 2042 (1959).
- King, C. J., Sc.D. thesis, Mass. Inst. Technol., Cambridge, Massachusetts (1960).
- 7. Kishinevsky, M. K., and V. T. Serebryansky, J. Appl. Chem. (USSR), 29, 29 (1956).
- Molstad, M. C., R. G. Abbey, A. R. Thompson, and J. F. McKinney, Trans. Am. Inst. Chem. Engrs., 38, 410 (1942). Rakestraw, N. W., and V. M. Emmel, Ind. Eng. Chem.
- Anal. Ed., 9, 344 (1937).

  10. Seidell, A., "Solubilities of Inorganic and Metal Organic Compounds," 3 ed., Van Nostrand, New York (1940).

- 11. Sherwood, T. K., and F. A. L. Holloway, Trans. Am. Inst. Chem. Engrs., 36, 39 (1940).
- 12. Sherwood, T. K., and R. L. Pigford, "Absorption and Extraction," 2 ed., McGraw-Hill, New York (1952).
- 13. Shulman, H. F., C. F. Ullrich, A. Z. Proulx, and J. O. Zimmerman, A.I.Ch.E. Journal, 1, 253 (1955).
- 14. Toor, H. L., and J. M. Marchello, ibid., 4, 97 (1958).
- 15. Vivian, J. E., and C. J. King, ibid., 10, p. 220 (1964).
- 16. Vivian, J. E., and R. P. Whitney, Chem. Eng. Progr., 43,
- 17. Whitman, W. G., Chem. Met. Eng., 29, 146 (1923).
- 18. Whitney, R. P., and J. E. Vivian, Chem. Eng. Progr., 45, 323 (1949)

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# A Relation Between Steam Quality and Void Fraction in Two-Phase Flow

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The prediction of void fraction in two-phase flow is very important to determine reactivities of boiling water reactors and circulation rates of water in boilers.

Most of the work to date has been of an experimental nature. Theoretical attempts for this problem have been made by Levy (1) and Bankoff (2). The results of these treatments agree with the results of experiments under some flow conditions, but they are not adequate.

A theoretical treatment which deals with the annular flow regime is proposed in this paper. To deal with a twophase flow in which water evaporates into vapor the twophase flow system is considered to consist of three regions. One of the regions is occupied by liquid only, another is occupied by vapor, and a third region provides for the phase exchanges (evaporation). From the equations of force balance for these three regions, and an assumption for the forces between these regions, a relationship between steam quality and void fraction and a relationship between steam quality and two-phase frictional losses are derived.

The effects of entrained liquid quantity on the void fractions as well as on the momentum changes are neglected because in accordance with Dukler (3) the entrained liquid quantity is small compared with the quantity of the film along the wall, unless the gas velocity in the core exceeds 100 ft./sec.

The derived formulas offer explanations for differences arising between the use of vertical and horizontal pipes, the effect of the total flow rate for vertical flow, and the effect of evaporation on the relationship between the steam quality and void fraction.

## BASIC EQUATIONS

An evaporating two-phase flow is considered to consist of three regions, A, B, and C (see Figure 1). Regions A and C are respectively occupied by liquid and vapor whose velocity can change between sections I and II, but the mass flow rate does not change. Region B is occupied by liquid only at section I, and all the liquid vaporizes into vapor between section I and II.

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The equation of the force balance for each region has been simplified as follows:

$$\frac{1}{g}G_{l}\frac{dV_{l}}{dL} = A_{l}\frac{dP}{dL} - A_{l}\rho_{l}\sin\theta - \frac{1}{g}AF_{wl} + \frac{1}{g}F_{lt}$$

$$\frac{1}{g}V_{R}\frac{dG_{g}}{dL} = \frac{1}{g}(F_{gt} - F_{lt})$$
(2)

$$\frac{1}{g}G_g\frac{dV_g}{dL} = A_g\frac{dP}{dL} - A_g\rho_g\sin\theta - \frac{1}{g}F_{gt} \qquad (3)$$

Adding Equations (1), (2), and (3) one obtains the equation of force balance for the whole two-phase flow system:

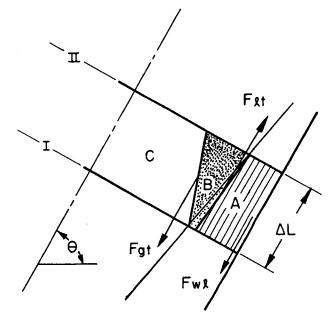


Fig. 1. Model of evaporating two-phase flow.