Transfer Resistance and Fluid Mechanics

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Pure liquids were evaporated in a wetted-wall column into flowing streams of air to investigate the thickness and transfer resistance of gas films.

It was found necessary to express Reynolds number relative to the liquid surface to correlate transfer with gas flow.

Laminar and buffer layers in the gas phase were calculated from fluid-flow principles and compared to the effective film thickness calculated from mass transfer and molecular diffusivity. Good agreement was obtained, indicating applicability of fluid mechanics to mass transfer problems.

Eddy diffusivity was indicated to have a negligible effect upon the total resistance to transfer. Consequently it might be concluded that in packed towers where distances in the turbulent phase are shorter transfer between phases depends almost entirely upon molecular diffusivity.

Particularly fundamental to gas absorption theory has been the two-film concept first proposed by Whitman (*29*). This concept assumes that the principal resistances to interphase transfer are contained in stable fluid films on each side of the liquid-gas interface through through which material flows by molecular diffusion.

The object of this investigation was to evaluate the additional resistance that may be presented by eddy-diffusion transfer and to compare the film concept with the physical approximations of fluid mechanics. Summaries of fluid-flow knowledge as it pertains to this study are available in works by Bakhmeteff (*2*), McAdams (*18*), and Rouse (*23*).

EXPERIMENTAL APPARATUS

The wetted-wall column offers simplifying advantages for mass transfer studies. By evaporating pure liquids, liquid film resistances are eliminated as no concentration gradients exist in the liquid. The partial pressure of the diffusing material at the liquid-gas interface is the vapor pressure of the pure material. Compositions in the gas phase may be determined by simple measurement of material loss from the liquid system. The fluid-flow characteristics of the gas phase, as contained in a cylindrical duct, are the most standard and the best understood.

The apparatus was in principle similar to that used in previous studies but with the diameter of the wetted-wall section proportionately enlarged to intensify any possible resistance effects of eddy diffusivity. Thus the ratio of the volume in eddy-diffusion transfer to the area of molecular-diffusion flow was arranged as high as conveniently possible and exceeds that of previous work.

Figure 1 shows a schematic drawing of the apparatus. The column was constructed so that different sections of wetted height could be installed. A collar of 40-mesh screen assisted distribution of liquid at the entry slot. Another slot approximately 20 deg. from the vertical allowed exit of the liquid at the bottom of the wetted wall. Vapor seals in the inlet and outlet chambers were maintained by proper liquid levels. A planetary type of gear pump with valved bypass and ¼-in. copper tubing lines formed the liquid recirculation system. A liquid reservoir was formed by a section of ⅔-in. I.D. glass tubing placed vertically below the outlet line from the column. The level in this tube was sensitive to liquid losses from the system. Make-up liquid was added here from a burette at measured rates to maintain a constant level. Liquid circulation rates were obtained at the conclusion of runs by diverting the liquid flow into a volumetric container and timing with a stop watch. Liquid temperatures were measured by fine wire copper-constantan thermocouples and a precision potentiometer.

A ⅛ horsepower blower supplied air through a standard 2-in. steel pipe to the column. A valved line and side bleed allowed adjustment of rate. Measurement of air flow was made by standard orifice technique. Sufficient length was provided in the unwetted bottom section of the column to standardize the gas flow. Air temperatures were measured by thermometers. Inlet air humidity was determined by a standard ether-cooled dew point instrument.

Liquids for study were selected to give the widest practical variation in volatility and chemical nature with the limitation that sufficient physical properties be known for the necessary calculations. The availability of vapor-pressure and molecular-diffusivity data was of particular pertinence and eliminated many materials of interest. Benzyl chloride and *n*-amyl alcohol were selected as low volatility compounds; acetone and ethyl acetate as high volatility compounds; and water, toluene, and *n*-butanol as intermediates.

The fundamental equation of diffusion

$$Na = -D_v \frac{dc}{dL} \qquad (1)$$

is modified (24) for application to wetted-wall columns to

$$Na = \frac{D_v p}{RTx} \frac{\Delta p}{p_{bm}} \qquad (2)$$

where the effective film thickness is the desired result and represents the thickness of a purely stagnant gas film that would offer the same resistance as that encountered by the measured transfer.

EXPERIMENTAL PROCEDURE

The liquid system flow was adjusted to a rate sufficient to insure complete liquid coverage of the column wall without ripples upon the surface. Because of surface-tension effects this adjustment required care and close observation of the liquid surface. Generally the satisfactory range of flow was quite narrow. The view afforded through the glass wall of the column as well as that down the bore of the column were necessary to certify complete liquid coverage entirely in smooth laminar flow. Unwetted areas and particularly ripples are suspected as defects of some reported data. As wetting agents were not used, their possible influence on vapor pressure was not a factor. The air flow was adjusted to the desired rate by the line and bleed valves. The apparatus was run until temperature and rate equilibriums were obtained, and the previously enumerated measurements were then recorded. Measurements were continued until check results were obtained and large enough volumes of liquid had been evaporated to ensure volumetric accuracy. Successive air rates were varied as widely as possible within the turbulent range.

EXPERIMENTAL RESULTS

Table I exemplifies the experimental data (columns 1 to 6) and the transfer

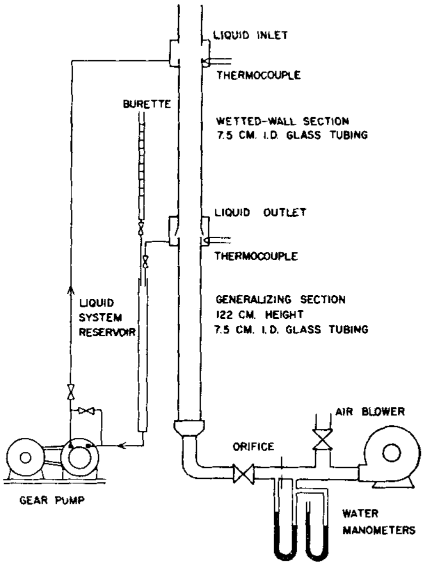

Fig. 1. Equipment.

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calculations (columns 7 to 11).* The gas-transfer coefficient was calculated and included for convenience to related studies.

To correlate film thickness with turbulence, it was necessary to relate the gas flow to the moving-liquid surface rather than the stationary column wall. Since the liquid surface was in direct contact with the gas film, its velocity would contribute to the shear forces determining the thickness of the laminar layer. Without inclusion of the effects of liquid motion, log-log plots of the column diameter to film thickness parameter vs. the Reynolds number of the gas flow yielded slopes varying from 0.56 to 0.80. This variation was unrelated to any apparent physical variable of the gas stream. However when the Reynolds number of the gas stream was calculated to relate to the liquid surface on the wetted wall (that is liquid surface velocity added to air flow velocity to obtain total flow velocity V), the plots of Figures 2 and 3 were obtained. All compounds correlated within the limits of experimental error with an 0.8 line slope, yielding an exponent common to transfer relations.

Surface velocities were estimated by the equation (*6, 28*)

$$u_s = 1/2\left(\frac{9g\rho q^2}{\mu}\right)^{1/3} \tag{4}$$

The viscosity of the air stream was calculated to be sufficiently low so that its effect on the liquid surface might be neglected.

Table 2 summarizes the calculations of layer thicknesses as predicted by fluid mechanics.* The data of Nikuradse (*21*) were used as reported by McAdams (*18*) and Rouse (*23*). Plots of Nikuradse's data consist of generalized velocity-distribution diagrams in which the parameter,

$$u^+ = u \bigg/ \sqrt{\frac{\tau_0 g}{\rho}},$$

is plotted as a function of the parameter,

$$y^+ = \frac{y\rho}{\mu}\sqrt{\frac{\tau_0 g}{\rho}}.$$

This distribution, derived from water data, has proved applicable to compressible fluids at moderate velocities. As reported by McAdams (*18*), the data permit the evaluation of the laminar layer (y^+ from $0 - 5$), the buffer layer (y^+ from $5 - 30$), and the turbulent core ($y^+ > 30$). However, Rouse (*23*) divides the intermediate or transition layer and reports only two zones, an effective laminar layer (y^+ from 0 to 11.6) and a turbulent core ($y^+ > 11.6$).

It was necessary to consider the variable concentration of the diffusing material as it affected the physical properties of the various layers. The average concentration in the laminar layer was estimated upon the assumption that the transfer proceeded solely by molecular diffusion. Calculated densities and viscosities were correspondingly adjusted. A cut-and-try calculation was employed to obtain agreement between laminar-layer thickness (column 7) and average composition.

The distance from the liquid to the core edge of the buffer layer was similarly calculated. This distance less the laminar-layer thickness then represented the buffer-layer thickness (column 8). The average composition in the layer was estimated from the average of the partial pressures in the core and at the boundary of the laminar layer.

The McAdams laminar layer was multiplied by the ratio of $y^+ = 11.6$ to $y^+ = 5$ to obtain the Rouse laminar layer (column 9). This ignores the variation in average composition between the layers, but this difference was shown to have negligible effect.

Values of eddy diffusivity (column 6) were calculated from the Sherwood and Woertz (*26*) equation:

$$\delta_E = 0.08\bar{u}r\sqrt{f} \tag{5}$$

A previous investigation by the authors (*19*) verified the reliability of Equation (5) when applied to gases flowing in cylindrical ducts.

Discussion of Results

The 0.8 exponent obtained in Figures 2 and 3 is a further point of consistency with fluid mechanics.

An attempt to adjust these lines to a single correlation on the properties of the laminar gas layer resulted in the equation

$$D/x = 0.024(N_{Re})^{0.8}(N_{Sc})^{0.4} \tag{6}$$

where the Reynolds number of the gas flow is calculated relative to the liquid surface.

This equation correlated the lines with an average deviation of 12%. The range of the Schmidt number was not sufficient to lend precision to its exponent [derived by log-log plot of $D/x(N_{Re})^{0.8}$ vs. N_{Sc}]. The equation resembles prior results (*10*), but a quite different relationship is expressed at lower gas velocities due to a difference in definition of Reynolds number.

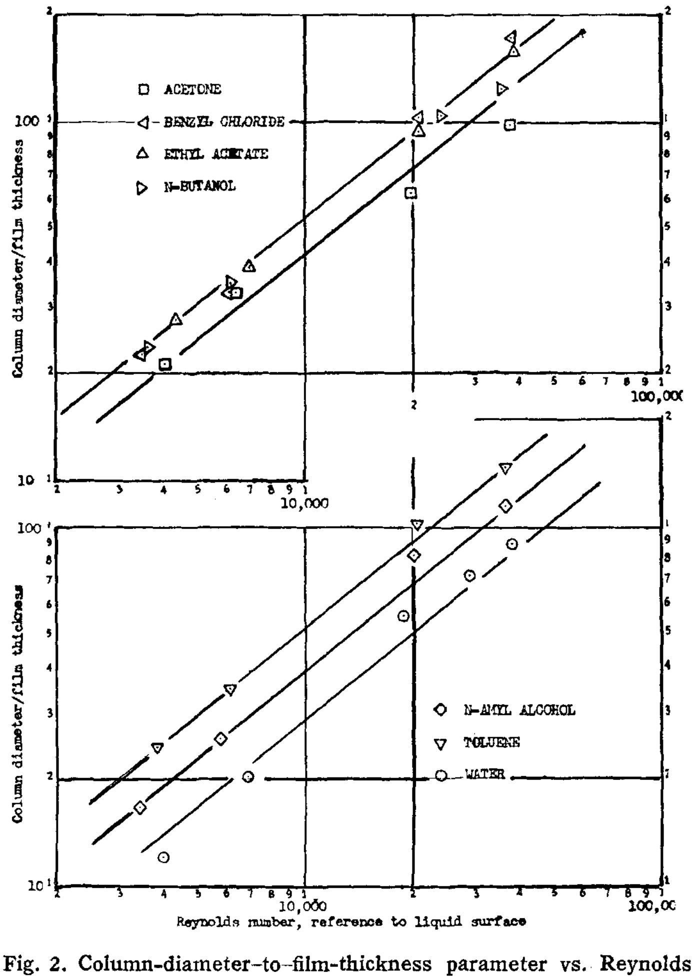

Fig. 2. Column-diameter-to-film-thickness parameter vs. Reynolds number. Evaporation of pure liquids into air in a 3-in.-diameter wetted-wall column, 40-in. wetted height.

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*Tabular material has been deposited as document 6053 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

*See footnote in column 1.

It may be noted that the correlation lines for acetone in Figures 2 and 3 are weighted to the data points at lower Reynolds numbers. After experiments were concluded, heat balances disclosed that evaporation was no longer adiabatic at the highest flow rates for acetone. Thus at the most severe conditions heat transfer of effect had occurred through the column wall. Hence the liquid surface temperature in this case was less than that indicated by measurement, and in turn the partial pressure driving force was less, the effective film thickness less, and the diameter to thickness parameter greater. Appropriate wall insulation would have eliminated this effect.

No appreciable difference in results occurred with the different heights of wetted section. Thus eddy diffusivity was indicated to add little additional transfer resistance in the taller wetted wall.

The simplest correlation of the Table 2 data is the agreement between Rouse laminar-layer thickness (column 9) and effective film thickness (column 10). Apparently the Rouse arbitrary boundary limit results in a division of zones that gives a reasonable physical representation in terms of resistance to mass transfer. However the transfer data would favor a slightly thicker laminar layer, as indicated by the effective film thickness exceeding the Rouse laminar layer in nearly all cases. A division of zones at about $y^+ = 13.5$ would be inferred from the transfer data, as displayed by Figure 4 (estimate of y^+ derived by linear plot of

$$x\rho/\mu \text{ vs. } \sqrt{\frac{\rho}{\tau_0 g}}, \text{ where } \sqrt{\frac{\tau_0 g}{\rho}} = u^*$$

the friction velocity).

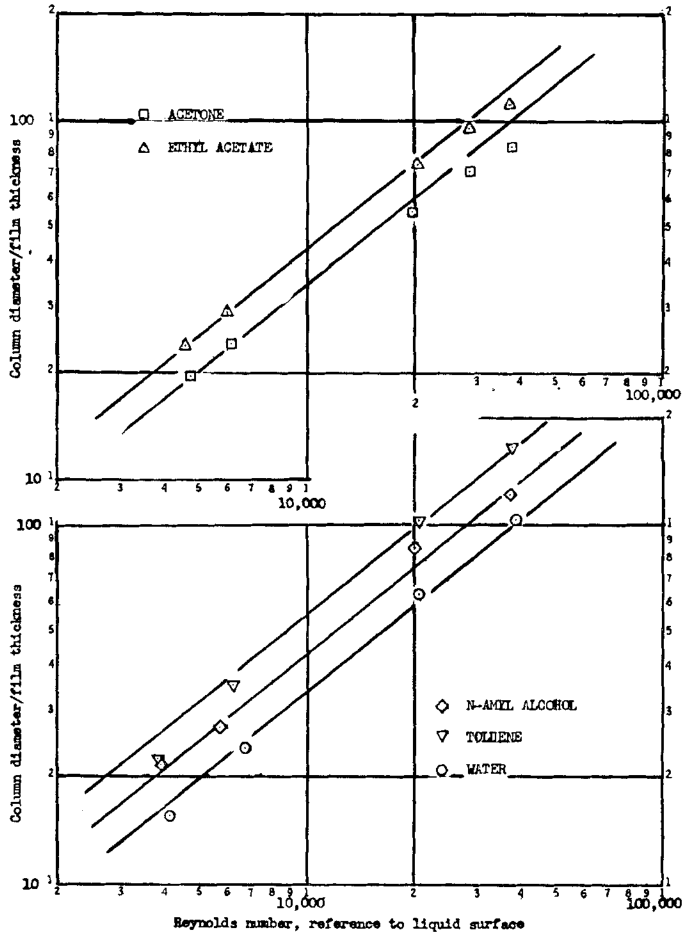

Fig. 3. Column-diameter-to-film-thickness parameter vs. Reynolds number. Evaporation of pure liquids into air in a 3-in.-diameter wetted-wall column, 14-in. wetted height.

If this relationship to fluid dynamics might be firmly defined by further work, it is suggested that the wetted-wall column could then become a relatively simple means to experimentally determine values of molecular diffusivity. The complications of other apparatus are testified to by the scarcity and variance of molecular diffusivity data in the literature. A considerable service would be performed by such determinations, as evidenced by numerous pleas for such data originating from several fields of inquiry.

Evaluation of most aspects of the results is obstructed by the uncertainty attached to molecular diffusivity values. Additionally at the conditions of this study the very low concentration of diffusing material (for example about 0.02 mole fraction water or 0.0015 mole fraction of benzyl chloride) in the gas layer of interest raises the question of how molecular diffusivity may vary with concentration. The literature contains theory (*7, 9, 11, 12, 15, 20*) about the amount of such variation, but a conclusive answer is not available. No adjustment of values was made in this study. Water, the only strongly polar compound used, would be a prime suspect in this respect. Looser confidence limits would be attached to the molecular diffusivity values for acetone as derived from an empirical formula. The largest discrepancies from the mean of the correlations were obtained with water and with acetone, producing a temptation to improve the derived correlations by deleting the data for these two materials.

Inspection of the relative extension of effective film thickness into the buffer layer revealed only a linear correlation and indicated no dependence upon eddy diffusivity. Further calculations upon the influence of eddy diffusivity were pursued in which it was assumed that the magnitude of eddy diffusivity was proportional to the gas velocity from the center of the core to the edge of the buffer layer. These calculations indicated a very minor contribution to resistance by eddy diffusivity in the turbulent core.

CONCLUSIONS

The velocity of the liquid surface influenced the transfer resistance encountered, and inclusion of this effect allowed correlation of the film data with the 0.8 exponent common to transfer relations.

Reasonable agreement was obtained between laminar gas layers calculated from fluid-flow theory and effective film thicknesses derived experimentally, in view of the uncertainties in the accuracy of molecular diffusivity values. The division of fluid characteristics into two zones of laminar and turbulent flow as advocated by Rouse (*23*) represented a reasonable approximation to the physical transfer resistances measured in the wetted-wall column, although a slightly thicker laminar layer would be estimated from the transfer data. If this relationship were proven and refined, the wetted-wall column might then usefully serve to determine diffusivity values.

No correlative effect of eddy diffusivity could be found upon transfer through the buffer zone as defined by fluid-flow theory. No appreciable difference in results was obtained by a threefold change in wetted-wall height. This, combined with the calculated relative values of eddy diffusivity, indicated a negligible contribution by eddy diffusivity to the total transfer resistance with the dimensions of transfer as employed. The dimensions of most gas absorption in comparison are such that eddy diffusivity is indicated to be an unimportant factor.

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NOTATION

c = concentration, g. mole/cc.
D = column diameter, cm.
D_v = molecular diffusivity, sq. cm./sec.*
f = Fanning friction factor, dimensionless
g = acceleration of gravity, cm./sec.^{2}
kg = gas-transfer coefficient
L = distance, cm.
Na = rate of diffusion, g. mole/sq. cm. sec.**
N_{Re} = Reynolds number, $DV\rho/\mu$, dimensionless
N_{Sc} = Schmidt number, $\mu/\rho D_v$, dimensionless
p = total pressure, mm.Hg***
Δp = average partial pressure driving force effecting transfer, mm.Hg†
p_{bm} = average partial pressure of inerts, mm.Hg††
q = volumetric flow per width of film, cc./cm. sec.
r = distance from wall to center of duct, cm.
R = gas law constant, mm.Hg cc./g. mole °K.
T = absolute temperature, °K.†††
u = local gas velocity, cm./sec.
$\bar{u}$ = average gas velocity, cm./sec.
u^* = friction velocity, cm./sec.
u_s = liquid surface velocity, cm./sec.
V = flow velocity, cm./sec. (herein equal to the sum of air flow and liquid surface velocities)
x = effective film thickness, cm.
y = distance from wall, cm.
ρ = density, g./cc.
μ = absolute viscosity, g./cm. sec.
τ_0 = shearing force at wall, g./sq. cm.
δ_E = eddy diffusivity, sq. cm./sec.

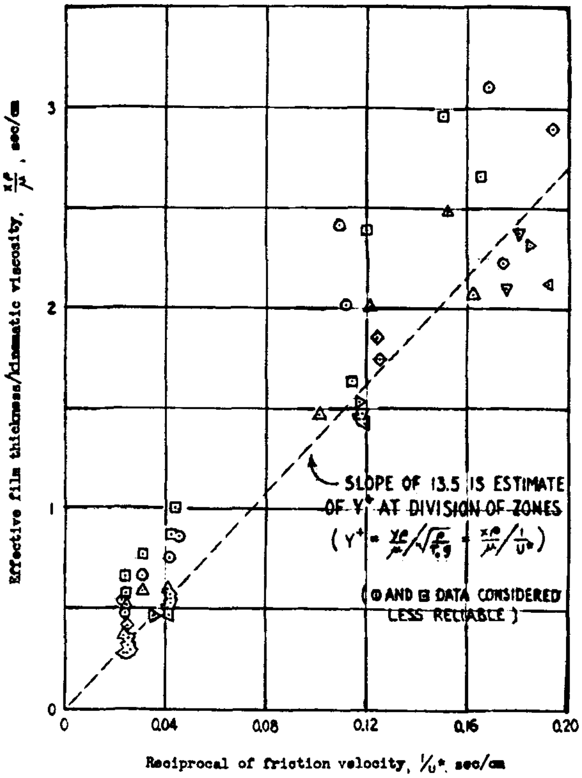

Fig. 4. Estimate of zone division from transfer data.

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*Calculated from experimental values presented in the International Critical Tables, with the exception that an empirical formula (11) was used for acetone.

**Calculated from measurement of the rate of material volume loss from the liquid circulation system, the density and molecular weight of the evaporating material, and the wetted area of the column.

***Measured by barometer.

†Calculated as the log mean difference between the liquid vapor pressures and the partial pressures of the diffusing material in the air stream at the top and bottom of the wetted-wall section. The liquid vapor pressures (or interface partial pressures) were calculated from the determined inlet and outlet liquid temperatures and vapor-pressure data compiled by Stull (*27*). The partial pressure of the diffusing material in the inlet air was zero, with the exception of the water case where the inlet humidity was determined by dew point. The partial pressure in the outlet air was calculated from a material balance of the liquid evaporation rate and air flow rate. The discrepancy between this average partial pressure and the exact partial pressure at the limit of the gas film at the outlet was calculated to be small, since a majority of the transfer resistance was indicated to be contained in the laminar and buffer layers and the outlet partial pressures were generally small in comparison to liquid vapor pressures.

††Calculated as the total pressure minus the arithmetric average of the interface and air stream partial pressures of the diffusing material at inlet and outlet of the wetted-wall section.

†††Calculated for the gas film as the arithmetric average of the inlet and outlet liquid temperatures and inlet and outlet gas temperatures.