Performance of Packed Columns

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IV. Effect of Gas Properties, Temperature, and Pressure on Gas-phase Mass Transfer Coefficients

To test the applicability, over a wide range of temperatures, pressures, and gas physical properties, of the mass transfer correlation presented earlier, 0.5-in. naphthalene Berl saddles were vaporized into air, carbon dioxide, and Freon-12 in a 4.0-in. column. Temperatures from 15° to 73°C. and pressures from 0.26 to 1 atm. were covered.

The correlation was found to represent all the experimental data when the surface temperature of the naphthalene was used to evaluate the correct driving force.

This correlation, when combined with effective interfacial areas presented previously, makes it possible to estimate the volumetric mass transfer coefficient, k_Ga, for any gas-liquid-solute system.

In the first three papers (*10, 11, 12*) of this series devoted to packed columns, a method was proposed for predicting over-all mass transfer coefficients K_Ga from gas- and liquid-phase coefficients k_G and k_L and the effective interfacial area a. The correlation presented for estimating k_G

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

was based on data obtained with air as the inert gas at atmospheric pressure and room temperatures. Although this equation correlated the data of several previous investigators, obtained under similar conditions, there were no data to provide a suitable check on the ability of the equation to predict k_G over the wide range of temperatures, pressures and gas physical properties that may be encountered in design problems.

The object of this work is to study the effect of gas physical properties, temperature, and pressure on gas-phase mass transfer coefficients and the usefulness of Equation (1) for predicting coefficients under a variety of conditions.

An examination of the terms in Equation (1) indicates that k_G should be almost independent of temperature, being approximately proportional to $T^{0.11}$. The methods for estimating effective interfacial areas a presented previously (*10, 11, 12*) also predict small changes with temperature. For water systems k_Ga should be independent of temperature because small increases in k_G are counterbalanced by small decreases in a as temperature increases.

Decreases in k_Ga with increasing temperature for ammonia absorption work have been reported by Kowalke, Hougen, and Watson (*7*), Dodge and Dwyer (*3*), and Molstad, McKinney, and Abbey (*9*), these decreases ranging from 0.2 to 0.8 %/°C. based on the outlet water temperature. These data cannot be used for predicting the effect of temperature or checking Equation (1) because the gas temperatures were not varied over a wide range and the water temperature variations are peculiar to the conditions under which the columns were operated. In ammonia absorption it is possible to obtain a rise in water temperature when the ammonia dissolves and a fall in water temperature if the air used is not saturated. It should be pointed out that the effect of temperature on k_G should be determined by employing varying gas-phase temperatures rather than temperatures based on conditions in the liquid phase.

For low concentrations of the solute in the carrier gas, Equation (1) predicts that k_G should be inversely proportional to total pressure. This has been found to hold for absorption in packed columns over the range of 1 to 14 atm. by Zabban and Dodge (*14*). Goodman's (*4*) unpublished data for the vaporization of naphthalene Berl saddles into air, shown in Figure 5, cover the range 0.26 to 1 atm. and show the expected effect of pressure. Both sets of data mentioned were obtained at low solute concentration, thus leaving in doubt the use of P_{BM} in Equation (1) in place of the total pressure.

In the third paper of this series (*12*) it was shown that Equation (1) combined with effective interfacial areas made possible the correlation of packed-column data for absorption in water as well as the vaporization of several liquids when air was used as the inert gas. This implies that the correct exponent on the Schmidt number is ⅔. Recently two sets of data have become available for the vaporization of water into several inert gases, which raise the question as to whether or not the dimensionless groups of a correlating equation, such as Equation (1), satisfactorily represent the physical properties of all inert gases. Lynch and Wilke (*8*) vaporized water from a wet-bulb thermometer and 1-in. Raschig rings into helium, air, and Freon-12. They concluded that k_Ga was proportional to the Schmidt number raised to the −0.47 to −0.50 power and recommended that the H.T.U. $[G/(k_GaM_MP_{BM})]$ be compared at equal values of ρu^2 rather than at equal values of a Reynolds number. At equal values of Reynolds number, the H.T.U. was proportional to the Schmidt number raised to the 0.9 power. Yoshida (*13*) also vaporized water from 1-in. Raschig rings employing helium, air, and carbon dioxide as the inert gases. He concluded that the H.T.U. $[G/(k_GaM_MP_{BM})]$, when compared at equal values of Reynolds number, was proportional to the Schmidt number raised to the 0.77 power although the ⅔ power was also satisfactory.

To answer the questions which have been raised as to the usefulness of Equation (1) for predicting values of k_G over a wide range of temperatures, pressures, and physical properties of the inert gas, an experimental program was carried out to provide the required data. The temperature extremes were 15° and 73°C. Data are reported for pressures from 0.26 to 1 atm., and air, carbon dioxide, and Freon-12 were used to vaporize naphthalene 0.5-in. Berl saddles in a 4.0-in.-diam column.

Tabular material has been deposited as document 5211 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.

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TABLE 1. PACKING CHARACTERISTICS

Nominal size, in.	0.5
Void fraction, dry	0.660
Number of pieces/cu. ft.	15,000
Surface area/piece, sq. ft.	0.00888
Surface area, sq. ft./cu. ft.	133
Diameter of equivalent sphere, ft.	0.0532

TABLE 2. PHYSICAL PROPERTIES OF GASES USED AT 20°C.

Gas	Viscosity μ, lb./(ft.)(hr.)	Density ρ, lb./cu. ft.	Diffusivity* D_v sq. ft./hr.	Schmidt No. $(\mu/\rho D_v)$
Air	0.0439	0.0752	0.210	2.57
Carbon dioxide	0.0355	0.113	0.160	1.96
Freon-12	0.0299	0.313	0.085	1.12

*Diffusivities are reported for the naphthalene-gas systems.

EQUIPMENT

The equipment shown in Figure 1 was used in studying the temperature variation of k_G and that shown in Figure 2 in the study of the variation of k_G with gas properties. In the equipment used to study k_G temperature variations, the air was circulated by means of a U. S. Hoffman centrifugal blower. The air rate was measured with rotameters reading from 2 to 32 and 24 to 244 lb. air/hr. The rotameters were calibrated to read to within 2% of the actual flow rate. A thermometer and manometer were located at the rotameter exit so that corrections might be made for deviations from the conditions at which the rotameters were calibrated. The air rate was adjusted by means of valves beneath the rotameters. Since the blower heated up during operation, a packed humidifier was used to cool the air. The temperature was set with three 500-watt bayonet heaters connected to variable transformers.

The heated air was passed through an aluminum column 6 in. high by 4.0 in. in diameter. The column was packed with about 2.5 in. of 0.5-in. naphthalene Berl saddles. During a run the column usually contained 200 naphthalene saddles. A 1-in. layer of 0.5-in. ceramic saddles was located at the bottom of the column to insure characteristic gas distribution to the bottom layer of naphthalene saddles. The column was held in place with three quick-releasing, spring-loaded clamps and was gasketed at top and bottom.

Temperatures were indicated on two thermometers, one located 2 in. below the column and the other approximately 0.5 in. from the top layer of naphthalene. The thermometers read from −1.0° to 101.0°C. in tenths of a degree. Weighings were made on a torsion balance sensitive to a tenth of a gram in the range employed.

The naphthalene saddles, which were molded by Maurice A. Knight, have the same dimensions as the porcelain saddles supplied by this company and the characteristics given in Table 1. The naphthalene used was crushed refined Polar naphthalene from the Barrett Division of Allied Chemical and Dye Corporation.

The column was insulated by being wrapped with two electric heating pads. Running the column with 4 in. of ceramic packing at high gas rates at various temperatures ensured no heat loss from the column. A section of rubber hose was located above the column to facilitate its removal. After passing through the column the air was exhausted.

The equipment used to study the variation of k_G with gas properties was, unlike the equipment previously described, a closed system. The gas, either air, carbon dioxide, or Freon-12, was blown through the rotameters by means of a Roots-Connersville gas pump. Coarse adjustments of the flow rate were made by means of a variable-speed motor drive and fine adjustments were made with the valves under the rotameters. The gas from the pump was cooled in a 13-ft. double-pipe heat exchanger with a 2-in.-diam. shell. The tube, supplied by the Brown Fintube Company, was 0.75-in. pipe with twenty 0.5-in. high axial fins. A thermometer and manometer were again located at the rotameter exit. The column packing and thermometers were the same as in the equipment described previously. The column was held between the top plate and bottom support with three 8-in. C clamps.

To make it possible to recycle the gas, the naphthalene was removed by means of activated carbon. The tank containing the carbon was 28 in. in diameter by 5.5 ft. high. It was filled with 220 lb. of 4- by 10-mesh activated carbon for the Freon and carbon dioxide runs. Before the Freon runs were made, the carbon was saturated with Freon.

The capacity of this activated carbon for naphthalene was roughly 15% by weight, or 33 lb. naphthalene in the carbon dioxide and Freon runs. Since the total weight of naphthalene vaporized was only 0.75 lb. for all the runs, it was assumed that the naphthalene concentration in the recycled gas could be taken as zero.

The compressed gas was supplied by the Matheson Chemical Company. The Freon-12 was at least 97% pure, and the carbon dioxide at least 99.8% pure. Atmospheric pressures were obtained from a Taylor recording barometer, and vacuum was obtained from a Cenco Hyvac pump.

PROCEDURE

The variation of k_G with temperature was studied by vaporizing naphthalene Berl saddles into air at temperatures from 20° to 70°C. Runs were made as follows.

A cardboard tube was inserted in the equipment in place of the aluminum column and the gas rate was adjusted. The temperature of the gas was set with the three bayonet heaters. The column, containing 1 in. of ceramic packing covered by a brass plate, was weighed in an insulated box. The naphthalene packing was then added and the column plus packing was put in an oven and heated to the temperature of the air passing through the cardboard tube.

When the naphthalene reached the proper temperature, the column was transferred into the insulated box, covered by the brass plate to eliminate vaporization, and weighed. The cardboard tube was then removed and the column inserted in its place. The necessary time, temperature, and pressure data were then taken. Temperatures were recorded every 2 min. for the first 10 min., every 5 min. for the next 20 min., and every 10 min. after that. At

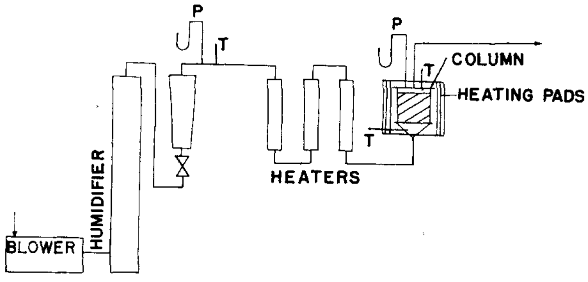

Fig. 1. Schematic diagram of apparatus, I.

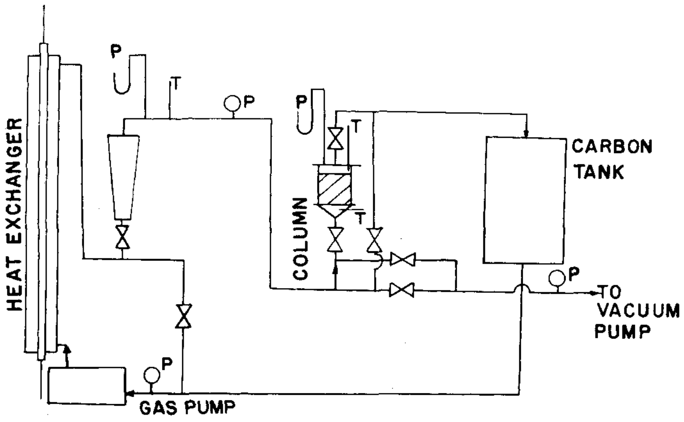

Fig. 2. Schematic diagram of apparatus, II.

the end of the run the column was covered by the brass plate, returned to the insulated box, and weighed.

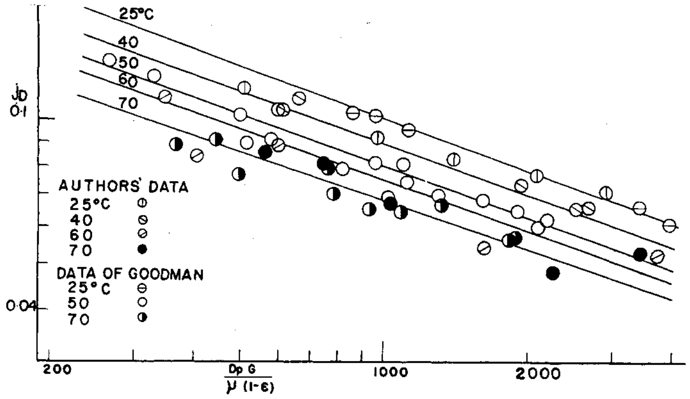

Fig. 3. Effect of temperature on j_D based on bulk-gas temperature.

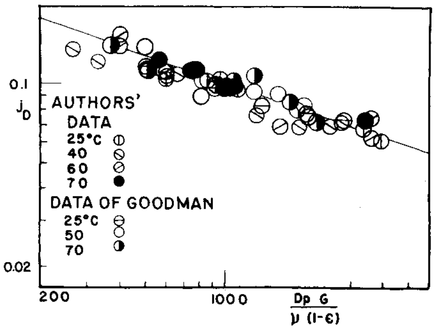

Fig. 4. Effect of temperature on j_D based on naphthalene-surface temperature.

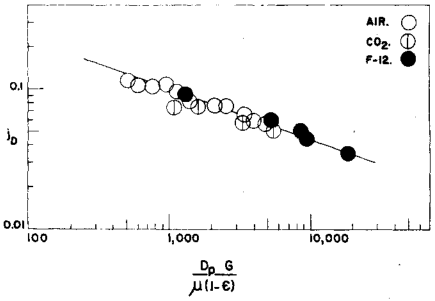

Fig. 6. Effect of carrier gas on j_D.

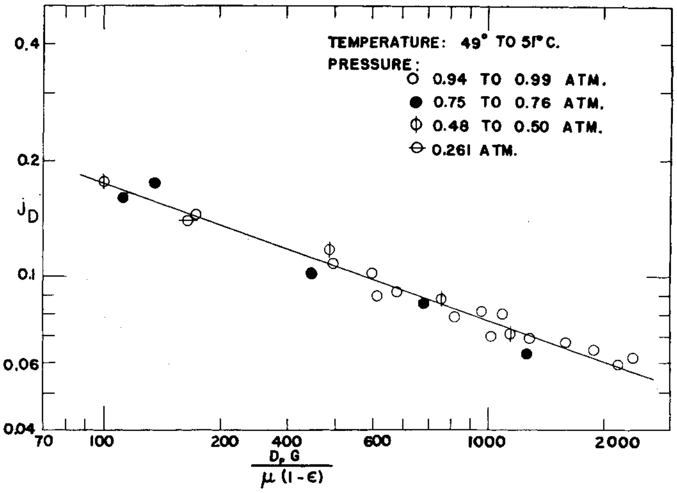

Fig. 5. Effect of pressure on mass transfer factor.

In the work with various carrier gases, the system was first evacuated to 27 in. Hg. below atmospheric pressure, filled with gas, evacuated again, and refilled with gas. The pressure at the suction end of the gas pump was always slightly above atmospheric pressure. During runs the pressure would fall slightly because of leakage past the stuffing boxes on the pump. To compensate, gas was continuously introduced.

The column plus the ceramic and napththalene packing was weighed before and after each run. The equipment was set up so that the section containing the column might be isolated from the rest of the system and evacuated separately. When the column was replaced in the equipment after the initial weighing, it was evacuated to 28 in. Hg. below atmospheric pressure before the valves connecting it to the rest of the system were opened. The weight loss during this evacuation period was not detectable on the balance used.

METHOD OF CALCULATION

The expression used to calculate k_G is

$$k_G = \frac{N_A}{A(\Delta p)_{\rm lm}} \tag{2}$$

where

$$(\Delta p)_{\rm lm} = \frac{(p_{s_1} - p_1) - (p_{s_2} - p_2)}{\ln\left[\frac{(p_{s_1} - p_1)}{(p_{s_2} - p_2)}\right]} \tag{3}$$

Since the inlet gas did not contain naphthalene, p_1 was always taken as zero and p_2 was calculated from a naphthalene material balance.

It can be shown that when equilibrium conditions are reached in the column, the surface temperature of the naphthalene packing will be lower than the bulk temperature of the gas passing the surface. At room temperature this temperature difference is small enough to be neglected and the partial pressure of the naphthalene at the surface of the packing can be taken as equal to the vapor pressure of naphthalene at the bulk gas temperature. For the runs at the higher temperatures, however, it was necessary to calculate the surface temperatures at the bottom and top of the naphthalene packing in order to evaluate the true driving force. This was done by writing an equation for the wet-bulb temperature of naphthalene in terms of the bulk temperature t and bulk partial pressure p of the gas passing the surface:

$$p_s = 0.642(t - t_s) + p \tag{4}$$

The constant, 0.642, was obtained by using the psychrometric ratio for the naphthalene-air system reported by Bedingfield and Drew (*1*). The surface temperature t_s and partial pressure p_s can be obtained by solving Equation (4) simultaneously with the equation for the vapor pressure of naphthalene reported in the "International Critical Tables" (*6*).

$$\log p_s = -\frac{3{,}729}{t_s + 273.1} + 11.450 \tag{5}$$

The constants in Equations (4) and (5) require temperatures to be expressed in degrees centigrade and pressures in millimeters of mercury. These equations were solved simultaneously either by the use of charts which were prepared for this purpose or by trial and error.

An experimental value of the diffusivity is available for the naphthalene-air system (6) but not for the naphthalene-

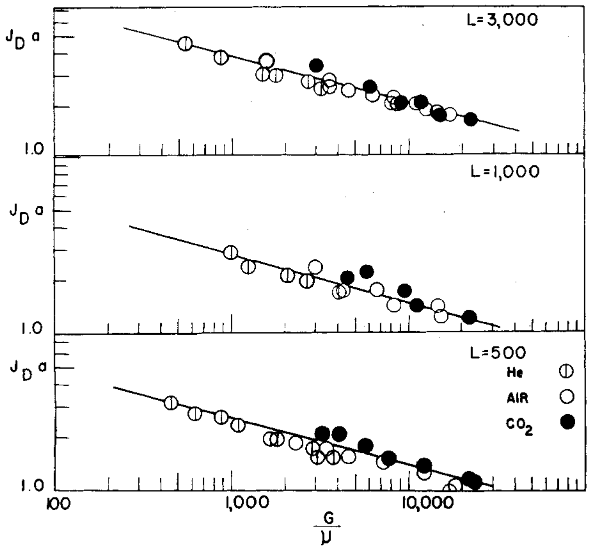

Fig. 7. Data of Yoshida.

carbon dioxide and naphthalene–Freon-12 systems. These diffusivities were estimated by the method suggested by Hirschfelder, Bird, and Spotz (*5*) using the collision radius for Freon-12 reported by Buddenburg and Wilke (*2*) and a force constant estimated from the critical temperature. The collision radius of naphthalene was estimated from its critical volume, and a force constant was estimated from the critical temperature.

The viscosities of Freon-12 and carbon dioxide are reported by Buddenburg and Wilke (*2*). The physical properties of the gases employed are tabulated for 20°C. in Table 2.

The naphthalene saddles retained their shape even when more than one quarter of their weight was lost by vaporization. This made it possible to assume constant surface area during a run.

EXPERIMENTAL RESULTS

Effect of Temperature

The experimental data obtained with air as the inert gas at temperatures from 25° to 70°C. are shown in Figures 3 and 4 with some similar data of Goodman (*4*). For Figure 3 the data have been calculated with driving forces based on bulk gas temperatures. The same data are shown in Figure 4 with driving forces based on naphthalene surface temperatures obtained as outlined under the discussion of the method of calculation. The solid line through the data in Figure 4, as well as the 25°C. line in Figure 3, represents Equation (1), which satisfactorily correlates these data when the true driving force is employed. Figure 3 is an excellent illustration of how false conclusions can be reached as to the effect of temperature if the bulk gas temperature is employed instead of the temperature existing at the phase boundary.

These results raise some questions as to the evaluation of driving forces in packed absorption columns. If the surface temperature of the liquid differs substantially from the bulk liquid temperature, which is commonly used as the basis for evaluating the driving force, there may appear to be some effect of temperature. The direction of this effect will depend upon the heat effects at the surface and, as pointed out for ammonia absorption, the surface temperature may be above or below the bulk liquid temperature for different operating conditions. Unfortunately, nothing is known about the temperature gradient in the liquid phase in packed columns, and so it is impossible to estimate actual surface temperatures except for special cases.

Effect of Pressure

Figure 5 presents the previously unpublished data of Goodman (*4*) obtained by vaporizing 0.5-in. naphthalene Berl saddles into air at approximately 50°C. and pressures varying from 0.261 to 0.99 atm. As data are based on bulk gas temperatures, the line corresponds to the 50°C. line of Figure 3. If these points were corrected for surface temperature, they would fall on the line representing Equation (1) in Figure 4. It is obvious that on a j_D vs. modified-Reynolds-number plot there is no effect of pressure. This means that k_G is inversely proportional to pressure as observed by Zabban and Dodge (*14*), who used packed columns for absorption at pressures above 1 atm.

Effect of Properties of Inert Gas

The data obtained with air, carbon dioxide, and Freon-12 as carrier gases are shown in Figure 6. The solid line, again, represents Equation (1), and it can be seen that this equation satisfactorily represents the data for inert gases of different physical properties.

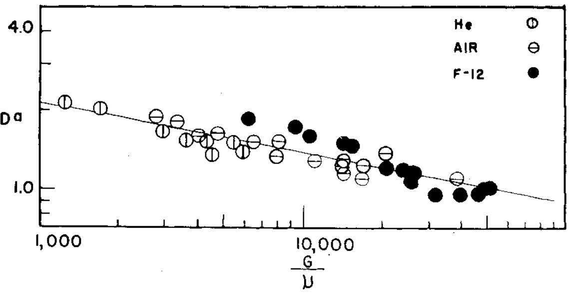

Fig. 8. Data of Lynch and Wilke.

Tests of this method of correlation for packed columns are shown in Figures 7 and 8. The product of j_D and the effective interfacial area $j_D a$ is plotted vs. G/μ, which is proportional to the Reynolds number for any one packing. In Figure 7 the water-vaporization data of Yoshida (*13*) are brought together for three different inert gases. Similar results are shown in Figure 8 for the data of Lynch and Wilke (*8*).

There is always difficulty in correlating $k_G a$ data because k_G and a are not affected by the same variables in the same way. For example, at a given liquid rate a is relatively independent of G, up to the loading point. Lynch and Wilke (*8*), using a 1-ft.-diam. column packed with 1-in. rings, operated at gas rates up to and in the neighborhood of the loading point. Yoshida (*13*), by using the same packing in a 4-in. column, avoided loading conditions although he operated at similar gas and liquid rates. For a given liquid rate, therefore, Yoshida could maintain a constant effective interfacial area, whereas Lynch and Wilke could not. Yoshida's data, therefore, are brought together better than the data of Lynch and Wilke on $j_D a$ vs. modified Reynolds-number plots such as Figures 7 and 8.

For design purposes the k_G, obtained from Equation (1), can be combined with the effective interfacial areas a obtained from the plots of a vs. G reported previously (*11*). For inert gases other than air these plots should be taken as a vs. $G/\sqrt{\rho/0.075}$ because loading and flooding points as well as pressure drops can be correlated for various gases with this term.

SUMMARY OF RESULTS AND CONCLUSIONS

The equation

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

has been shown to correlate mass transfer data for a wide variety of packings, operating conditions, and physical properties of the solute and inert gases.

A design method is now available whereby the k_G obtained from Equation (1) can be combined with effective interfacial areas a reported previously (*10, 11, 12*) to obtain a k_Ga for any desired gas-liquid-solute system for which physical properties are available.

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NOTATION

A = total surface area of packing, sq. ft.
a = effective interfacial area, sq. ft./cu. ft.
D_v = diffusivity of solute in gas, sq. ft./hr.
D_P = diameter of sphere possessing the same surface area as a piece of packing, ft.
G = superficial gas rate, lb./(hr.) (sq. ft.)
H.T.U. = height of a gas-phase transfer unit, ft., $(G/k_GaM_MP_{BM})$
j_D = mass transfer factor, defined by Equation (1)
K_G = over-all mass transfer coefficient, lb. moles/(hr.) (sq. ft.) (atm.)
k_G = gas-phase mass transfer coefficient, lb. moles/(hr.) (sq. ft.) (atm.)
k_L = liquid-phase mass transfer coefficient, lb. moles/(hr.)(sq. ft.) (lb. moles/cu. ft.)
M_M = mean molecular weight of gas, lb./lb. mole
N_A = rate of mass transfer, lb. moles/hr.
p = partial pressure of naphthalene in the gas, atm.
$(\Delta p)_{lm}$ = logarithmic mean driving force, atm.
P_{BM} = mean partial pressure of inert gas in the gas phase, atm.
T = absolute temperature, °K.
t = temperature of the gas, °C.
u = gas velocity, ft./sec.

Greek Letters

ϵ = void fraction, cu. ft./cu. ft.
μ = gas viscosity, lb./(hr.)(ft.)
ρ = gas density, lb./cu. ft.

Subscripts

S = at the naphthalene surface
S_1 = at the naphthalene surface, bottom of packing
S_2 = at the naphthalene surface, top of packing
1 = bottom of packing
2 = top of packing

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Densities of Liquid-acetone-water Solutions up to Their Normal Boiling Points

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The densities of acetone-water liquid solutions have been measured over the entire composition range from 20°C. to within 3° to 7°C. of the normal boiling point of the mixture. The density was measured with a Robertson pycnometer (*13*), which was modified slightly. The density values are thought to be accurate to within ±0.00005 density units. The technique for determining density values of the volatile mixture near the boiling temperature is given in some detail. The refractive index (n_D^{25}) of pure acetone has been redetermined and equals 1.35596 ± 0.00003.

In a study of the effect of the physical properties on the efficiency of distillation in the binary acetone-water system, physical properties such as density, viscosity, molecular diffusivity, and surface tension were needed at the boiling temperature. No density data of acetone-water mixtures above 25°C. could be found in the literature; furthermore, no reliable method was known whereby the density data could be extrapolated 30° to 75°C. to the boiling points with confidence. It was resolved to measure the density precisely (at least to ±0.01%) from 20°C. to within a few degrees of the boiling temperature. These data could then be used to extrapolate accurately to the boiling points. Measurements and correlations of other physical properties such as the absolute viscosity, the surface tension, and molecular diffusivity require accurate density values, and the density data would also be useful in this respect.

Several early investigators (*8, 10*) have reported the densities of acetone-water mixtures at 15°, 20°, and 25°C. Their results, however, scatter considerably, probably because of the inferior quality of the acetone available to them. The most recent, and presumably the best, determinations of the densities of acetone-water mixtures were done by Young (*16*) at 20°C. and by Griffiths (*5*) at 25°C.

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