are of equal magnitude, adsorption equilibrium for that component is not attained under steady state reactions and the assumption of a single rate controlling step is invalid; both adsorption and surface reaction become rate-controlling steps.

The information supplied by such experiments would also reveal whether or not all sites or only selective sites participate in the surface reaction. Adsorption equilibrium constants obtained from reaction rate data are independent of surface coverage or have been so assumed. This indicates that only a small fraction of surface coverage is involved or that only selective sites are involved. Equilibrium constants obtained from total adsorption experiments, on the other hand, decreases with surface coverage.

ACKNOWLEDGMENT

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NOTATION

C_A = concentration of adsorbed ethanol, g.-moles/g. cat.
C_{es} = equilibrium surface coverage of catalyst
C_l = concentration of empty active sites, g.-moles/g. cat.
C_{ss} = surface coverage at steady state
C_w = concentration of adsorbed water, g.-moles/g. cat.
k_A = adsorption velocity constant of ethanol, g.-moles/min. g. cat.
k'_A = desorption velocity constant of ethanol, g.-moles/min. g. cat.
k_s = kS = surface reaction velocity constant of dehydration reaction, g.-moles/min. g. cat.
k_w = adsorption velocity constant of water, g.-moles/min. g. cat. atm.
k'_w = desorption velocity constant of water, g.-moles/min. g. cat.
L = total adsorption sites on catalyst g.-moles of active sites, g.-moles/g. cat.
p_A = partial pressure of ethanol, atm.
p_w = partial pressure of water, atm.
R = k_A/k_s
r_A = adsorption velocity of ethanol, g.-moles/min. g. cat. atm.
r_A' = desorption velocity of ethanol, g.-moles/min. g. cat.
r_s = surface reaction velocity of dehydration reaction, g.-moles/min. g. cat.
S = number of equidistant active centers adjacent to each other
t = residence time, min.
κ_A = k_A'/k_A

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Mass Transfer Rates for Vaporization and Gas-Phase Controlled Desorption in a Short Wetted Wall Column

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In the experimental investigation of gas absorption in packed towers, investigators have studied the absorption or desorption of highly soluble gases, the vaporization of pure liquids into inert gas streams, and the absorption of gases which undergo a rapid chemical reaction with the absorbent liquid to determine individual gas phase absorption coefficients. Gas phase coefficients have also been reported based on studies of the absorption of moderately soluble gases in which allowance was made for the liquid phase resistance by simple additivity theory. It has long been recognized that unexplained discrepancies exist in the results obtained by the different systems.

In general, the mass transfer coefficients for vaporization are significantly higher than those for absorption of a highly soluble gas, although both processes would be expected to be essentially gas phase controlled. A comparison of the data of Fellinger (*5*) for the absorption of ammonia into water with the data of Sherwood and Holloway (*8*), and McAdams, et al. (*7*) for the vaporization of water into air shows the vaporization coefficients to be higher by factors of two to three. Gas phase coefficients estimated from data on the absorption of sulfur dioxide in water (*14*), a moderately soluble gas system, are also lower than the vaporization data and agree approximately with the ammonia data. The data on the absorption of chlorine into concentrated caustic solutions (*9*) agree approximately with the vaporization data. However, considering the general scatter of packed tower data when they are obtained by different investigators using different experimental equipment, the question of the significance of these discrepancies might well be raised.

In two recently reported studies, vaporization and absorption rates have been compared in the same apparatus. Yoshida and Koyanagi (*16*) studied methanol absorption and water vaporization in a single packed column under the same controlled operating conditions with careful allowance for end effects. After correcting for the difference in diffusivity, the methanol absorption data agree quite well with the ammonia data of Fellinger and the vaporization data agree quite well with the Sherwood and Pigford correlation of the data on vaporization and rapid chemical reaction (*9*). These data are shown in Figure 1 in which all data have been adjusted on the basis of the diffusivity of water vapor in air. The absorption data expressed as the height of a transfer unit, H_G, are shown by solid lines and the vaporization data by dotted lines. It is clear that the methanol absorption rates are substantially lower than the vaporization rates. Shulman, Savini,

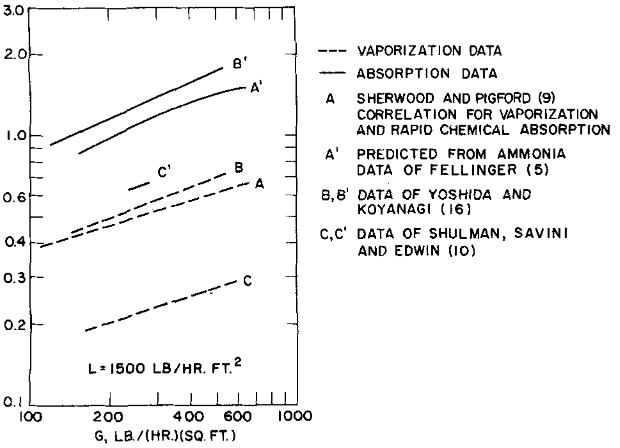

Fig. 1. Comparison of packed tower data on vaporization and absorption.

and Edwin (*10*) also studied methanol absorption and water vaporization in a single packed column. Again, substantially higher vaporization rates were obtained, although the absolute values of the H_G are not in good agreement with the results of Yoshida and Koyanagi.

A coefficient obtained in a packed tower study is a volumetric coefficient and depends on the interfacial area per unit volume as well as on the transfer rate per unit area. The usual correlating techniques for k_g are based on the predictions of diffusion theory and the assumption that interfacial effects are the same for vaporization and absorption. To explain the discrepancies it has been suggested (*11, 15*) that there are different effective areas for absorption and vaporization. In fact, the Shulman (*10*) and Yoshida (*16*) studies were aimed at elucidating information about interfacial areas.

Considering the nature of the liquid flow in a packed column one would expect to find a wide variation of local liquid flow rates and path lengths, resulting in a wide distribution of surface element lifetimes. Since the liquid phase coefficient varies inversely as the square root of the time of exposure, the slowest moving parts of the liquid surface may present a significant liquid phase resistance to a system which would be predicted on the basis of average coefficients to be a gas phase controlled absorption process. Thus, the relatively slow moving parts of the liquid surface can be viewed as being relatively ineffective for absorption, as compared to the rapidly moving regions. On the other hand, in a vaporization process there is no question of liquid phase diffusion rates influencing the overall mass transfer coefficient, whatever the liquid-fluid mechanics, and there would be only a single level of effectiveness of the interfacial area.

A more quantitative way of describing this phenomenon is through the use of a surface lifetime distribution function (*3, 4, 6*), with which one can compute an average liquid phase coefficient to use in the additivity equation to obtain an overall coefficient. Apparently, the nature of the distribution has a marked effect on the proper averaging procedure. King (*6*) shows, for example, that the packed tower discrepancies may be explained by postulating the existence of a binodal liquid surface lifetime distribution having a wide spread in lifetime values between the two nodes of the distribution.

If we assume that the discrepancies between packed tower absorption and vaporization coefficients are the result of some type of surface lifetime distribution, then similar measurements carried out in an apparatus where all the liquid surface is moving rapidly should give results that do not exhibit the discrepancy. The short wetted wall column is a device well suited to a study of this type. The wetted interfacial area is well defined. The liquid flow pattern simulates penetration theory behavior in liquid phase-controlled absorption processes (*1, 13*), and the countercurrent contacting has some resemblance to mass transfer on a single packing piece. For these reasons this device was chosen as the experimental contactor for this study.

The experimental program consisted of measurements of the vaporization rate of water and of the desorption rate of methanol from dilute aqueous solutions in a short wetted wall column. The concentrations of the latter were chosen so as to correspond to an interfacial partial pressure of methanol equal in value to the vapor pressure of water at the same temperature that affords a comparison of the two systems on an equal driving force basis.

The assembly of the short wetted wall column section was similar to that used by Vivian and Behrmann (*12*). The liquid entered the 1 in. diam. by 4 in. long cylindrical glass column through a horizontal slot formed by the top of the glass column and an upper teflon section. It flowed down the contacting section in a smooth film and was withdrawn from the bottom of the column through a slot formed by the glass column and a lower teflon piece. The flow rates and temperatures of the liquid and gas streams were controlled by auxiliary apparatus.

The air used as the carrier gas flowed upward through a glass calming section to the short wetted wall column.

During the methanol desorption runs, a packed tower was used to humidify the air supplied to the wetted wall column to prevent simultaneous water vapor transfer in the short wetted wall column. No attempt was made to match the partial pressure of water vapor in the air supplied exactly with the vapor pressure of water over the methanol solution, since calculations indicated the interaction of water vapor and methanol transfer would be small for such a dilute system and short exposure time. During the water vaporization runs, the air was heated such that the wet bulb temperature of the air entering the short wetted wall column was about equal to the entering water temperature. With these conditions, the heat of vaporization is supplied from the gas phase, thus avoiding a drop in the water temperature at the interface which would represent an additional resistance to the transfer.

Rate measurements were made at liquid rates of about 55 g./cm. min. and at gas phase Reynolds numbers from about 3,000 to 6,000. The temperature was 25°C. and the pressure was 1 atm. approximately. The mass transfer coefficients were obtained from a knowledge of stream flow rates and concentrations. In the water vaporization runs, the humidity of the entering and leaving gas streams was

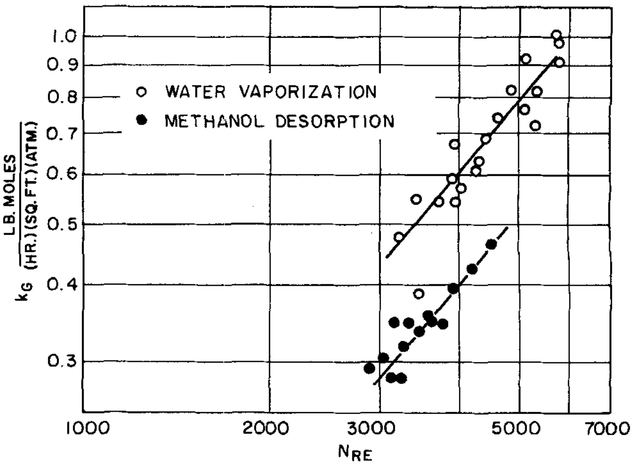

Fig. 2. Experimental data on water vaporization and methanol desorption in a short wetted wall column.

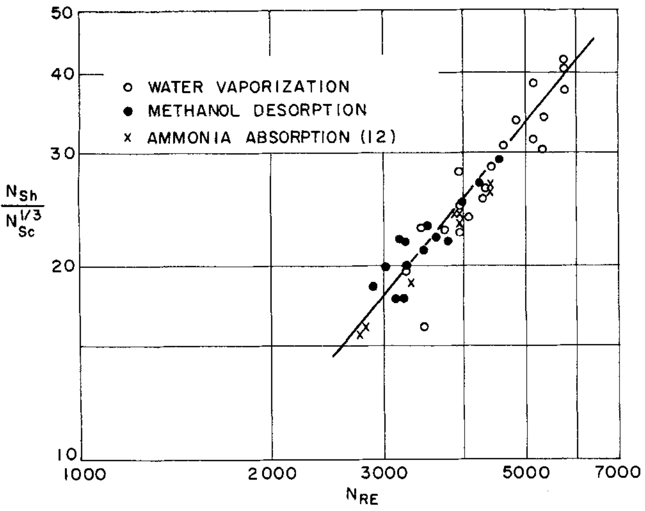

Fig. 3. Correlating of vaporization, absorption and desorption data.

determined from the gain in weight of drying tubes associated with a measured volume of gas sample. In the methanol desorption runs, the methanol concentration of the inlet liquid and outlet gas streams was determined chromatographically. The relative response of a thermal conductivity detector with the solvent water as a reference substance was used for the liquid samples. A flame ionization detector was used for the gas samples, and secondary butanol was added to the gas samples as a reference substance. Carbowax 1500 columns were used for both the liquid and gas samples.

The results of the vaporization and desorption experiments are shown in Figure 2. The water vaporization coefficients are higher than the methanol desorption coefficients. When allowance is made, however, for the different gas phase diffusivities of water and methanol, the data for the two systems agree well as shown in Figure 3. Since in both systems, solute concentrations in the gas phase are very low, gas phase diffusivity is the only gas phase property which is significantly different. Data for ammonia absorption into water (*12*) in a short wetted wall column are also shown in Figure 3 to agree well with the water vapor and methanol data. Use of the ratio $(Sh)/(Sc)^{1/3}$ in this case is equivalent to a 2/3 power adjustment of the gas phase diffusivity as suggested by the Chilton-Colburn correlation (*2*).

The agreement between the data on absorption and desorption of highly soluble gases and vaporization shown in Figure 3 indicates the similarity of these processes; the agreement tends to substantiate the suggestion that the discrepancies observed in packed tower data are in fact the result of liquid phase resistance due to elements of the liquid surface having a wide distribution of lifetimes.

NOTATION

d = short wetted wall column diameter
D = diffusivity of solute in gas phase
G = gas mass velocity, lb./hr.-sq.ft.
H_G = height of a transfer unit (gas phase), ft.
k_G = gas phase coefficient, lb. moles/hr.-sq.ft.-atm.
N_{Re} = Reynolds number, dG/μ
N_{Sc} = Schmidt number, $\mu/\rho D$
N_{Sh} = Sherwood number, $k_G\ RTd/D$
R = gas constant
T = temperature
μ = viscosity
ρ = density

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A Thermodynamic Relationship between Integral Heat of Vaporization and Isobaric Equilibrium Vapor-Liquid Compositions

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A rigorous thermodynamic equation relating the phase composition and the phase enthalpy difference for an isobaric, multicomponent vapor-liquid equilibrium system was recently proposed by me (*1*). That equation establishes a useful relationship in estimating the enthalpy-composition space between the two saturated phases for the design of distillation equipment. This paper shows an analogous derivation that results in an equation containing the commonly used integral heat of vaporization instead of the phase enthalpy difference.

The integral heat of vaporization is defined by Equation (1); the right side of which consists of three groups.