

Vacuum Stripping of Refrigerants in Water Sprays

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The number of overall liquid transfer units as a function of the total pressure, flow rate, and nozzle height has been measured for the removal of butane and F-22 refrigerants from water for a flat spray nozzle in a vacuum spray chamber. The number of transfer units increases with the flow rate and with the total pressure with the increase proportional to 0.2 power of the Weber number in which the gas density is used. N_{OL} also increases linearly with length, but more than two-thirds of the mass transfer always takes place in liquid sheet attached to the nozzle. Because the rate of mass transfer in a spray chamber is much greater than in a packed column, vacuum spray stripping is recommended for the removal of refrigerants from water and brine in the freezing and hydrate processes for desalination and other slightly soluble gases from aqueous solution in other processes.

SCOPE

The separation of slightly soluble dissolved gases from aqueous solution is necessary to deaerate feedwaters to boilers, to remove volatile contaminants from process water, and to recover refrigerants in the freezing and hydrate processes for desalting seawater. This kind of separation usually has been carried out by steam or air stripping in packed towers with the subsequent separation of the stripping steam by condensation. This work is a study of vacuum spray stripping as an alternate process for the separation of refrigerants for use in the freezing and hydrate processes. The separation occurs as the liquid is sprayed into a vacuum chamber which is held at a pressure well below the equilibrium partial pressure of the dissolved refrigerant. Although considerable work

has been done on the fluid dynamic characteristics of sprays, little has been done to relate the liquid phase controlled mass transfer to the liquid flow rate, spray drop size, nozzle height, and chamber pressure. The objective of this work is to obtain experimental data on the mass transfer in a vacuum spray chamber and to correlate these data with the various experimental variables in a way which could be used for the design of vacuum spray stripping systems. Previous work has been concerned with mass transfer in spray absorption columns with counter-current gas flow, mass transfer in turbulent jets, and mass transfer from individual drops. These works do indicate that very rapid mass transfer occurs during the drop formation stage, with decreasing rate of transfer after the drops are formed.

CONCLUSIONS AND SIGNIFICANCE

A vacuum spray column has been used experimentally to successfully strip the refrigerants butane and F-22 (CHClF_2) from water. Most of the mass transfer was found to occur in the liquid sheet attached to the nozzle and not in the spray droplets. The number of transfer units for a small fan spray nozzle ($d = 0.038$ cm) was found to follow the correlation

$$N_{OL} = 2.4 \times 10^{-3} We^{0.2} (986 + Z/d).$$

Vacuum sprays for stripping can be used to obtain $N_{OL} = 2$ units with nozzle heights of only a few centimeters. This is far superior to packed columns, and vacuum spray chambers are advocated for removing dissolved slightly soluble gases from aqueous solutions.

In the freezing and hydrate processes for desalting seawater, in the deaeration of boiler feedwater, and in several process operations in the petroleum industry, relatively volatile but slightly soluble substances must be removed from water before it can be used, reused, or discharged. In the freezing process, these gases are refrigerants such as butane and the fluorinated hydrocar-

bons, while in the petroleum industry they are light hydrocarbons. For deaeration operations, the gases are those in air. All of these gases are only slightly soluble in water (up to several hundred parts per million), and consequently the liquid phase controls the mass transfer. Unless a third component such as air is used for stripping, the vapor mass flow rate in any mass transfer process

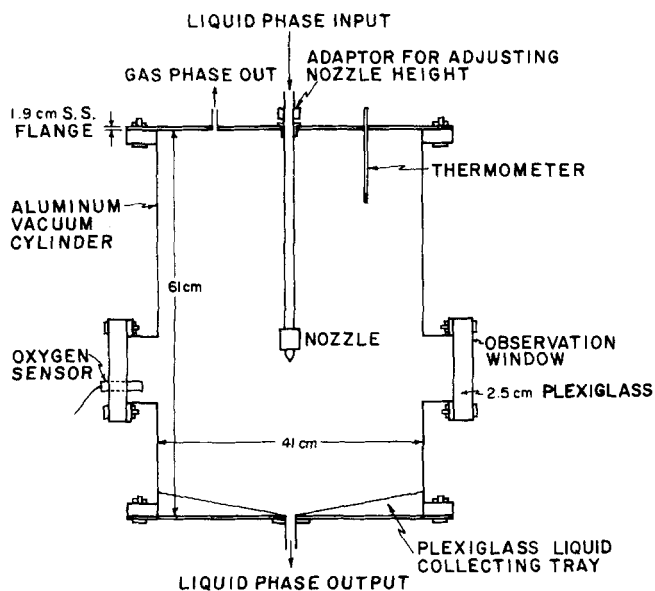


Fig. 1. Spray chamber.

to accomplish this separation is very small. Thus a process which enhances liquid phase mass transfer rates by mixing the liquid and creating a relatively large liquid-vapor interfacial area is advantageous. Spraying the product water or brine into a vacuum chamber accomplishes both of these objectives, since the liquid sheet attached to the nozzle fluctuates in thickness, creating waves which grow exponentially until ligaments of liquid finally break off to form the spray droplets. The liquid within the droplets also continues to circulate and oscillate for some time because of the original motion imparted during their formation and because of the shearing action of the vapor phase on the drop surface. Because of the high degree of liquid motion and the creation of a large mass transfer area, significant stripping of dissolved gases in a vacuum spray chamber can take place over relatively short distances, making the removal process compact. The only penalty incurred for this enhanced mass transfer is the energy necessary to create the pressure difference for spraying.

In this paper we discuss some of the mass transfer characteristics of a vacuum spray chamber. These include experimental measurements of the effect on refrigerant removal of the chamber pressure, the liquid flow rate, the height of the nozzle, and the nature of the refrigerant. The relative magnitude of the mass transfer in the sheet attached to the nozzle and in the spray droplets also is discussed.

PREVIOUS WORK

Previous work related to the vacuum spray process for stripping gases from water can be divided into several categories: the hydrodynamics of moving droplets, mass transfer from sheets and jets, and mass transfer from moving drops.

Considerable recent work on the hydrodynamics of jet and sheet breakup has been carried out by Dombrowski and co-workers (1960, 1962) and Fraser et al. (1962). They show that both jets and sheets are unstable, and, after flowing a distance which depends upon the flow rate and properties of the fluid, break into ligaments which coalesce into droplets. Before a sheet or jet breaks up, waves appear which grow in amplitude leading to the breakup. In fan spray nozzles or conical nozzles, the sheet also becomes thinner as the distance from the

nozzle increases. The pressure or density of the gas into which the liquid is sprayed also affects the liquid sheet, with fewer ripples forming at low gas densities.

Mass transfer from these sheets has been analyzed as mass transfer from a laminar falling film even though several experimental workers (Boyadzhiev et al., 1969; Goren and Mani, 1968; Stirba and Hurt, 1955; Muenz and Machello, 1966) have shown that the mass transfer rates may be twenty to eighty times greater than laminar theory predicts. Apparently mixing due to the wave-induced turbulence and the spreading of the sheet greatly increases the rate of transport.

The hydrodynamics of a moving droplet depend strongly on its Reynolds number. For low Reynolds number (<15), the steady circulation pattern for a falling drop has been calculated by Hadamard (1911). Using this flow distribution, mass transfer calculations have been made by Kronig and Brink (1950) showing that the rate of mass transfer is 2.7 times that of a stagnant drop. At higher Reynolds numbers (>400), the motion becomes turbulent and random. Radial motion due to vibrations has been combined with the fluid circulation to describe the fluid motion. At sufficiently large Reynolds numbers (>3000), the viscosity becomes unimportant and the velocity distribution in the drop approaches that corresponding to potential flow. Using this velocity distribution near the boundary, Ruckenstein (1967) has integrated the mass transfer equation to show that the mass transfer coefficient is given by

$$Sh = \frac{2}{\sqrt{\pi}} Pe^{1/2} \quad (1)$$

The experimental work on mass transfer from moving drops shows agreement with the prediction of the circulating drop model at low Reynolds number if sufficient time is allowed for the steady state circulation to be established. At higher Reynolds numbers, the mass transfer is much higher with the ratio of experimental diffusivity to molecular diffusivity approaching 80 (Garner and Lane, 1959; Garner and Skelland, 1954; Marsh and Heideger, 1965). Also, mass transfer rates are considerably higher even at the lower Reynolds numbers during the initial stages of drop formation before the steady state circulation pattern is established.

Considerable work also has been done on spray and jet columns, starting with Pigford and Pyle (1951), Fujita and Hayakawa (1956), Mada et al. (1964), and Mehta and Sharma (1970). This work shows that the efficiency of short spray or jet columns is at least comparable to packed columns when only one to three mass transfer units is required. The efficiency decreases with height because of drop coalescence and entrainment and also undoubtedly because of the decrease in mass transfer rate as the droplets approach a steady circulation pattern. The dependence of the number of transfer units on the liquid flow rate varies widely, depending apparently on the Weber number (Ross and Combe, 1966). At high Weber numbers (We), the number of liquid phase transfer units increases with the liquid velocity, becoming in some instances proportional to the velocity. At low Weber numbers, the number of liquid transfer units becomes independent of the liquid velocity and may even decrease slightly with increases in velocity.

EXPERIMENTAL WORK

All of the experiments were carried out in the vacuum spray chamber shown schematically in Figure 1. The remaining ap-

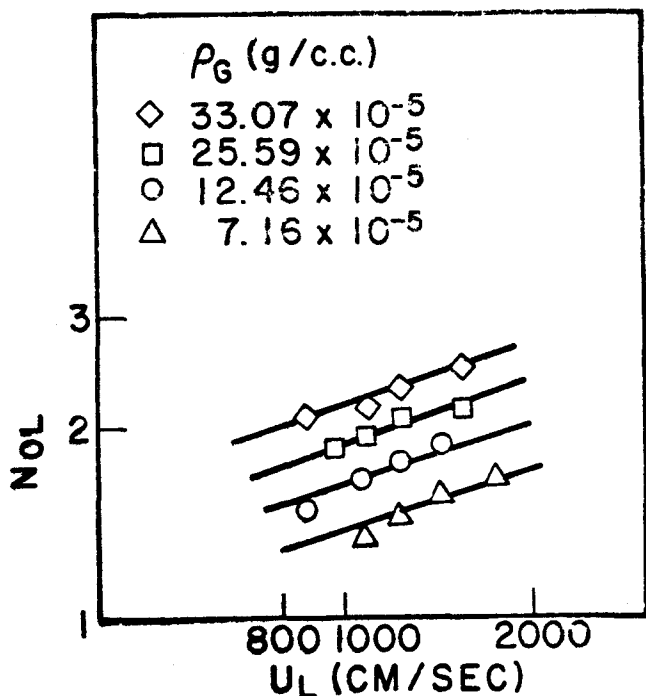


Fig. 2. N_{OL} vs. liquid velocity at $Z = 6$ cm, F-22-water system.

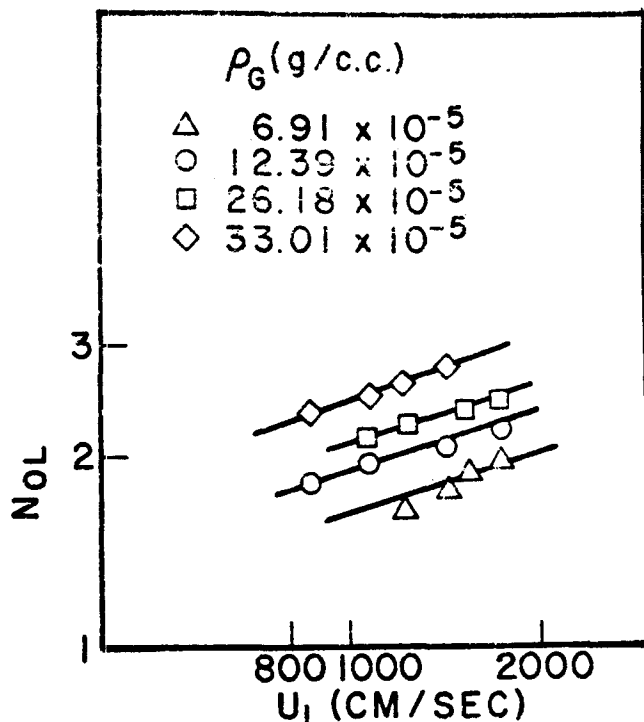


Fig. 3. N_{OL} vs. liquid velocity at $Z = 13$ cm, F-22-water system.

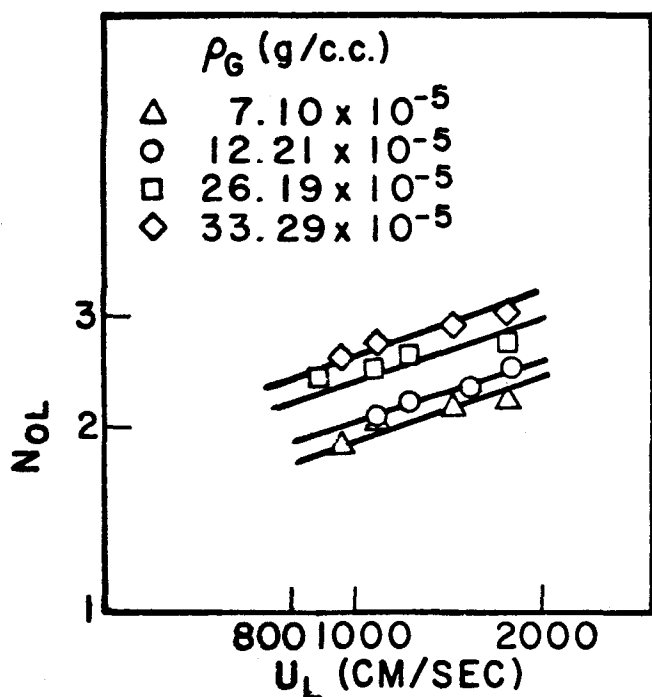


Fig. 4. N_{OL} vs. liquid velocity at $Z = 20$ cm, F-22-water system.

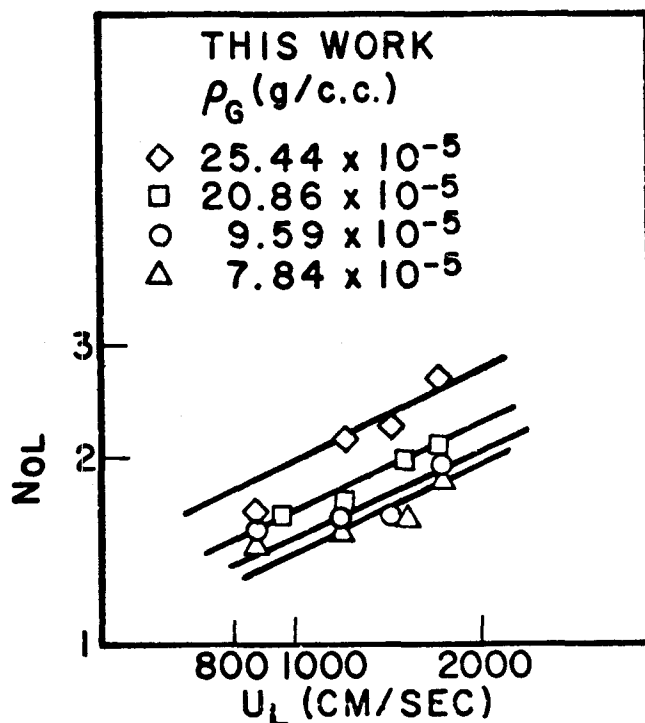


Fig. 5. N_{OL} vs. liquid velocity at $Z = 6$ cm, butane-water system.

paratus (Barduhn et al., 1974) consisted mainly of the feed tank in which water could be contacted with refrigerants, the liquid feed pump, the vacuum chamber into which the feed was sprayed, the liquid collection reservoir, the sample collection loop, and the vacuum system. A rotameter was located in the liquid feed line, and manometers registered the pressures in the spray chamber and in the feed tank. A thermometer recorded the spray chamber temperature. The diameter of the spray chamber was 40 cm, sufficiently large to prevent any direct contact of the spray with the wall at the highest nozzle height of 20 cm. The sample collection loop was situated so it could be flushed and filled completely with liquid to prevent any desorption of the refrigerant in the sample bulb. Refrigerant concentrations were determined using a Beckman 915 total organic

carbon analyzer. The estimated error in concentration measurements was ± 0.5 p.p.m. below 5 p.p.m. and approximately $\pm 10\%$ above 5 p.p.m.

The nozzle used in this work was a 1/4 T 65033 Tee jet nozzle from the Spraying Systems Company. This nozzle has an orifice diameter of 0.038 cm and produces a flat triangular spray with drop size in the range of 0.018 to 0.038 cm, depending on the flow rate.

Experiments were begun by evacuating the feed tank and filling it half full with distilled water. The gas space was filled with refrigerant gas, then reevacuated to the vapor pressure of water for several minutes to remove any dissolved air from the distilled water. Refrigerant gas was then readmitted to the tank and an immersion pump turned on for several hours to

mix the refrigerant with the water. Before the spraying of the liquid began, the spray chamber and liquid reservoir were evacuated to the vapor pressure of water for several minutes. Refrigerant was returned to the system to bring it to ambient pressure, and then the system was reevacuated to the desired system pressure.

In several runs an oxygen probe (96260 Oxygen Adaptor from Beckman Instruments, Inc.) was inserted into the chamber through the observation window. The oxygen partial pressure in the chamber was found to be zero within the precision of the instrument (0.25 torr).

Once the gas pressure in the chamber was set, the liquid spray was turned on. Steady refrigerant concentration measurements were obtained in about 20 to 30 min. Care was taken to prevent liquid accumulation in the bottom of the chamber which would increase the liquid residence time and possibly affect the total mass transferred. The gas pressure was maintained by regulating a valve in the vacuum line.

Usually concentration measurements were made at four different liquid flow rates (65, 75, 99, and 120 ml/min) for a given gas pressure. The gas pressure was then changed, and additional measurements at approximately the same set of flow rates were made. After a series of measurements at four different gas pressures (38, 48, 78, 94 torr), the height of the nozzle was changed (6, 13, 20 cm) and the procedure repeated. A complete set of measurement on F-22 (CHClF_2) and a set of measurements at a nozzle height of 6 cm on butane are reported here.

RESULTS

Typical data for F-22 are shown in Figures 2 to 4 and the data for butane in Figure 5. In all these figures, N_{OL} is plotted against the liquid velocity, with gas density as a parameter. N_{OL} designates the number of overall liquid transfer units which was calculated from

$$N_{OL} = \ln \left(\frac{C_i - C^*}{C_o - C^*} \right) \quad (2)$$

where C^* is the concentration of refrigerant dissolved in the liquid which would be in equilibrium with the partial pressure of refrigerant in the gas. In the calculation of C^* , the partial pressure of water is taken to be the vapor pressure of water at the temperature of the chamber. N_{OL} is essentially equal to the N_L , the number of liquid transfer units, because the liquid phase refrigerant concentrations are several orders of magnitude less than the gas phase concentrations.

The liquid velocity U_L is calculated by dividing the liquid flow rate by the orifice area. This remains essentially constant as the liquid passes through the spray chamber (Naimpally, 1971).

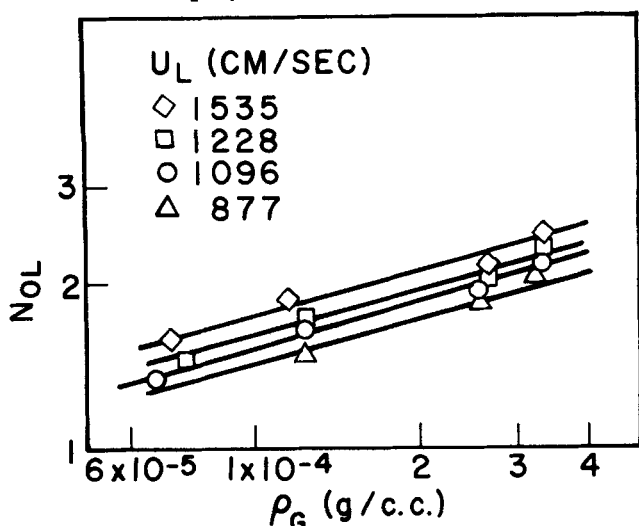


Fig. 6. N_{OL} vs. gas density at $Z = 6$ cm, F-22-water.

The solubility of F-22 in water was calculated from an equation derived by Parmelee (1953) for temperatures between 25° and 75°C:

$$\ln (C^*/P_F) = \frac{89.428}{T - 225.0} - 0.6485 \quad (3)$$

where C^* is in parts per million, P_F is the F-22 partial pressure in torr (equal to $P - P_w$), and T is in degrees Kelvin.

Similarly, the solubility of butane was estimated from an equation derived by Bajolle et al. (1971) for temperatures between 10° and 30°C:

$$P_B/C^* = 0.3513T - 93.84 \quad (4)$$

where C^* is in parts per million, P_B in torr, and T in degrees kelvin.

Cross plots of N_{OL} were also made against ρ_G , the gas density, and Z , the nozzle height for the F-22 data. An example of these cross plots is shown in Figure 6. All of the plots of the data involving U_L and ρ_G are log-log plots. Both log-log and linear plots of N_{OL} were made for Z with approximately the same scatter of data around a straight line. The linear plot was finally used because it differentiates more clearly between the mass transfer which occurs in the liquid sheet attached to the nozzle and the mass transfer in the spray droplets.

Additional butane data at different nozzle heights also have been collected by Cheng (in Barduhn et al., 1974). While these data show the same trends with respect to gas density, liquid velocity, and nozzle height as do the butane and F-22 data reported here, the number of transfer units under similar conditions averages about 15% higher (see dashed line on Figure 8). This difference may have been due to the presence of a small partial pressure of air in the chamber. For Cheng's lower feed concentrations, a partial pressure of air of only 5 torr is sufficient to account for the difference in the values of N_{OL} . One other contributing factor, also resulting from Cheng's lower feed concentrations, was the lower effluent concentrations. Errors in determining very low liquid butane concentrations (1 to 2 p.p.m.) tend to be biased on the positive side because negative values of concentration are not acceptable. Because of these possible discrepancies, only the data of Lin (1975) are analyzed here.

ANALYSIS OF THE RESULTS

In this analysis, the spray will be considered in two parts, the liquid sheet and the drops. Theoretical expressions for the rates of mass transfer in each part will be developed and then compared with the experimental results.

Because the Reynolds number of the liquid in the spray is less than 10 000, the flow in the liquid sheet according to Fraser is laminar but at the same time is wavy, with number of waves and the length of the sheet depending to some extent on the chamber pressure (Fraser et al., 1962). The expression for the mass transfer coefficient from a laminar sheet is (for example, Bird et al., 1960)

$$k_{OLL} = (4D_L/\pi t)^{1/2} \quad (5)$$

Introducing this into the mass balance equation for the dissolved refrigerant in the liquid sheet

$$dC/dt = k_{OL}a(C - C^*) \quad (6)$$

we get

$$N_{OLL} = a(16D_L r_o / U_L)^{1/2} \quad (7)$$

For a triangular fan spray sheet, the product of the film thickness and the radial distance is a constant; that is

$$hr = K \quad (8)$$

K can be found from

$$K = \frac{\pi d^2}{8 \sin(\theta_T/2)} \quad (9)$$

These expressions can be used as follows to calculate a for a sheet which disintegrates into droplets at radial distance r_o :

$$a = \frac{r_o^2 \theta_T}{\int_{\pi/2-\theta_T/2}^{\pi/2+\theta_T/2} \int_0^{r_o} \int_0^\eta 2r d\theta dr dZ} = \frac{r_o^2 \theta_T}{K r_o \theta_T} = \frac{r_o}{K} \quad (10)$$

The order of a is about 10^{-3} cm^{-1} . Equation (7) indicates that N_{OLL} should be inversely proportional to $U_L^{1/2}$ and proportional to $D_L^{1/2}$.

For the droplet part of the spray, Ruckenstein's (1967) expression for the mass transfer coefficient from drops at large Reynolds number is most appropriate. From Equation (1)

$$k_{OLD} = 2(U_L D_L / \pi d_s)^{1/2} \quad (11)$$

The specific interfacial area is given by

$$a = 6/d_s \quad (12)$$

For the droplets in the sprays discussed here (Sauter mean diameter from 0.018 to 0.038 cm), this is about an order of magnitude lower than a for the liquid sheet. Substituting this relation and Equation (11) into Equation (6), now applied to the drop portion of the spray, and integrating, we get

$$12[\sqrt{(U_L D_L)/(\pi d_s^3)}]t \quad (13)$$

Setting $t = Z/U_L$ and substituting Dombrowski and Hooper's (1962) empirical expression for the Sauter mean diameter

$$d_s = Cd \left(\frac{\rho_L}{\rho_G} \right)^{1/8} \left(\frac{\sigma}{\rho_L U_L^2 d} \right)^{1/3} \quad (14)$$

into Equation (13), we get

$$N_{OLD} = C \left(\frac{\rho_L U_L^2 d}{\sigma} \right)^{1/2} \left(\frac{\rho_G}{\rho_L} \right)^{1/4} \left(\frac{D_L}{U_L d} \right)^{1/2} \frac{Z}{d} \quad (15)$$

where C is a constant depending on the nozzle. This relationship indicates that N_{OLD} should be proportional to $U_L^{1/2}$, $\rho_G^{1/4}$, Z , and $D_L^{1/2}$ (the variables of the experiments reported here). The appropriate dimensionless groups are the liquid Weber number ($\rho_L U_L^2 d / \sigma$), the density ratio (ρ_G / ρ_L), the Peclet number ($D_L / U_L d$), and a distance ratio (Z/d).

The experimental mass transfer results expressed in terms of N_{OL} can also be separated into two parts by plotting N_{OL} vs. Z for constant sets of values of U_L and ρ_G . Figure 7 shows some of the F-22 data plotted this way and indicates that within the experimental error, N_{OL} is linear with Z , the result expected from Equation (15) above. Extrapolation of N_{OL} to $Z = 1 \text{ cm}$ on the same figure shows that most of the mass transfer takes place from the liquid sheet attached to the nozzle and that N_{OL} increases only slowly with Z after the drops are formed. Least-square slopes of the dependence of $\log N_{OL}$ on $\log U_L$ and $\log \rho_G$ showed no significant difference between the data for F-22 and butane. Also within the

errors of estimate, the power dependence of N_{OL} on U_L ($U_L^{0.39}$) was twice that of the dependence of ($\rho_G^{0.23}$). This, too, is consistent with Equation (15). By combining several groups, Equation (15) can also be written as

$$N_{OLD} = C \left(\frac{\mu^2}{d \rho_L \sigma} \right)^{1/4} (Sc)^{-1/2} (We)^{1/4} \frac{Z}{d} \quad (16)$$

where the group $(\mu^2 / d \rho_L \sigma)$ is a constant for all of the experiments reported here and $We = (\rho_G U_L^2 d / \sigma)$ and $Sc = (U_L / \rho_L D_L)$. Because of the linear dependence of N_{OL} on Z , an expression for the entire spray of the form

$$N_{OL} = A(We)^{0.2} \left(B + \frac{Z}{d} \right) \quad (17)$$

was proposed for both the F-22 and the butane data, where A presumably is a function of D_L and B represents the contribution of the liquid sheet to the mass transfer. This form does assume that the dependence of N_{OL} in the liquid sheet on ρ_G and U_L is the same as in the drops. The form of this equation was checked by plotting $N_{OL}/(We)^{0.2}$ vs. Z/d . This plot indicated a linear relationship with Z and gives the values the constants A (2.4×10^{-3}) and $B(986)$. The dependence of A on the liquid diffusivity should have been indicated on the same plot by the difference between the butane data and the F-22 data. Surprisingly, there was no apparent difference, even though the liquid diffusivity for F-22 in water as calculated from the Wilke-Chang correlation (1955) is about 50% greater than the experimental or calculated value of the diffusivity of butane in water (Witherspoon and Bonoli, 1969). Thus, both the F-22 and the butane data can be represented by the equation

$$N_{OL} = 2.4 \times 10^{-3} We^{0.2} \left(986 + \frac{Z}{d} \right) \quad (18)$$

A plot of this equation and a comparison of it with the experimental data is shown in Figure 8.

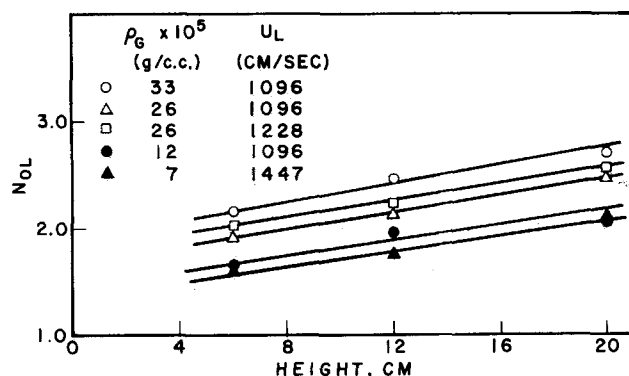


Fig. 7. N_{OL} vs. nozzle height, F-22-water system.

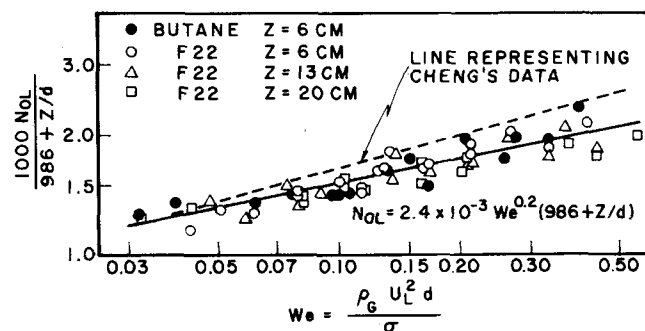


Fig. 8. Correlation of vacuum spray stripping data.

DISCUSSION OF THE RESULTS

Experimental results show that most of the mass transfer in the sprays takes place from the liquid sheet and not from the drops. The length of this sheet is 1 to 2 cm, making the term $986 + Z/d$ for the sheet alone equals 1012 to 1039. At the highest nozzle height tested, $Z = 20$ cm, $986 + Z/d = 1512$, implying that at most only one third of the mass transfer takes place in the droplets. This suggests that refrigerant removal processes based on the vacuum spray chamber should be low in height and staged if necessary.

The rate of mass transfer from the liquid sheet does not agree at all with the predictions of the laminar theory. Experimentally, N_{OL} increases as $U_L^{0.4}$, while laminar theory implies that it should decrease as $U_L^{-0.5}$ and, in addition, the experimental values of N_{OL} are five to ten times those predicted from the laminar theory. These differences undoubtedly are due to mixing induced in the sheet by the wavy instabilities which gradually disintegrate the sheet into drops.

The agreement of the theory with experiment for mass transfer during the droplet phase is better, and in fact the data for both the sheet and droplet portions of the spray seem to fit the form of Equation (15) which was derived from Ruckenstein's formula for mass transfer from turbulent droplets, if one allows a much greater rate of change of mass transfer with distance in the liquid sheet. This perhaps is not too surprising, since the same forces which give rise to mixing in the droplets also generate mixing in the sheet.

Another interesting result is the lack of dependence of the rate of mass transfer on the liquid diffusivity. This effect may be masked by the not too large a difference in the values of the diffusivities and may also be because the true diffusivity for F-22 is less than that predicted by the Wilke-Chang correlation. In any event, it is difficult to believe that a mass transfer process does not in some way depend on the fundamental mass transfer parameter, the diffusivity, if only in a relatively weak fashion.

ACKNOWLEDGMENT

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NOTATION

a	= specific interfacial area, cm^2/m^3
C	= concentration of refrigerant in the liquid
C_1	= inlet liquid refrigerant concentration
C_o	= outlet liquid refrigerant concentration
C^*	= equilibrium liquid refrigerant concentration
d	= orifice diameter
d_s	= Sauter mean diameter of the drops
D	= drop diameter
D_L	= diffusivity of the refrigerant in the liquid,
h	= sheet thickness
k_L	= liquid phase mass transfer coefficient, cm/s
k_{OL}	= overall liquid phase mass transfer coefficient
k_{OLD}	= overall liquid phase mass transfer coefficient for the drops
k_{OLL}	= overall liquid phase mass transfer coefficient for the liquid sheet
K_{OLL}	= liquid sheet thickness parameter
N_L	= number of liquid phase transfer units
N_{OL}	= number of overall liquid transfer units
N_{OLD}	= number of overall liquid transfer units in the droplet portion of the spray

N_{OLL}	= number of overall liquid transfer units in the liquid sheet
Pe	= Peclet number = DU_L/D_L
P	= total pressure, torr
P_B	= partial pressure of butane, torr
P_F	= partial pressure of F-22, torr
P_w	= vapor pressure of water, torr
r	= measure of the liquid sheet length
r_o	= total length of the liquid sheet
Sh	= Sherwood number = $K_{OL}D/D_L$
t	= residence time
T	= temperature, $^{\circ}\text{K}$
U_L	= liquid velocity
Z	= height of the nozzle, cm
We	= Weber number using the gas density = $(\rho_G U_L^2 d)/\sigma$
ρ_G	= gas density
ρ	= liquid density
θ	= total included angle of the liquid sheet
σ	= surface tension of the liquid

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Photoassisted Heterogeneous Catalysis with Optical Fibers:

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I. Isolated Single Fiber

Recently reported varieties of photoassisted heterogeneous catalysts are summarized. A cylindrical, light carrying, optical fiber coated with a catalyst layer is evaluated as a novel configuration for all such light assisted catalysis. Equations are obtained which describe the light intensity in the fiber and its surrounding catalyst layer. A dimensionless group of the form $\Phi = (4\alpha_c\beta_c dL)/(d_f)$ [$d = d_c$ for $d_c < \lambda$, $d = 0(\lambda)$ for $d_c > \lambda$] determines the relative influence of light loss by all absorption and scattering to light transported in the fiber length. An effectiveness factor η_I for heterogeneous photoassisted catalysis is determined for reactions which are first order in intensity and without mass transport limitations. Asymptotic forms of η_I are $\eta_I = 1.0$ ($\Phi \ll 1.0$) and $\eta_I = \Phi^{-1}$ ($\Phi \gg 1.0$).

SCOPE

Heterogeneously catalyzed photoassisted reactions occur at ambient temperature and low pressures. If the corresponding present or future photoassisted heterogeneous catalysts are to be useful, scale-up configurations which contain both high surface areas per volume and convenient light-distribution to the catalyst phase must be developed. One such general configuration, conceptually applicable to all such reported catalysts, is an optical fiber which is coated with a layer of the photo-utilizing catalyst. The present paper evaluates the change in light intensity as a light beam, entering the fiber end, is repeatedly internally reflected down the fiber length, contacting the catalyst

coating at each reflection. The principles of fiber optics and Internal Reflection Spectroscopy determine which factors influence the transport of light in the presence of scattering and absorption. A review of the extant photoassisted catalysts indicates that the analysis should include thin ($d_c \ll \lambda$), thick ($d_c \gg \lambda$), and intermediate catalyst films. In all cases, an effectiveness factor for light transport is defined and evaluated, its asymptotic forms being the same as are well known for mass diffusion, even though the appropriate equations are first rather than second order. Assembly of such fibers into a macroscopic bundle is considered in a subsequent paper (Marinangeli and Ollis, 1977).

CONCLUSIONS AND SIGNIFICANCE

For thin, thick, or intermediate thickness concentric catalyst coatings, an equation of the form $d\psi/d\xi + \Phi\psi = 0$ determines the axial profile of light intensity ψ with axial distance ξ in the optical fiber. Thus, the appropriately defined effectiveness factor for light transport depends on the

single dimensionless group Φ which is a function of fiber length, fiber diameter, catalyst film thickness, catalyst absorption, and illumination wavelength. The single fiber effectiveness factor offers a means for correlating experimental data obtained from single, optical, fiber-catalyst systems. Effectiveness factors for macroscopic (multifiber) configurations including simultaneous influences of light, heat, and mass transfer are reported in a subsequent paper.

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