Stepanova, G. S., and Y. I. Vybornova, "Study of Phase Equilibria of the Methane-*n*-Hexane System," Trudy Vesoyuz. *Nauchn.-Issled. Inst. Prirodnykh Gazov*, 17, 203 (1962).

Thompson, R. E., and W. C. Edmister, "Vapor-Liquid Equilibria in Hydrogen-Benzene and Hydrogen-Cyclohexane Mixtures," *AIChE J.*, 11, 457 (1965).

Won, K. W., and J. M. Prausnitz, "High-Pressure Vapor-Liquid Equilibria. Calculation of Partial Pressures from Total Pressure Data. Thermodynamic Consistency," *Ind. Eng. Chem. Fundamentals*, 12, 459 (1973).

Manuscript received September 25, 1973; revision received December 10 and accepted December 11, 1973.

Fast Fluxes with Supercritical Solvents

Measurements of iodine dissolution rates in supercritical carbon dioxide and other supercritical fluids show when the iodine flux in these systems can be made fast. For these systems, the dominant factor in achieving this fast flux is the solubility; increases in diffusion coefficient have less effect. An approximate guide for estimating these fluxes is developed and compared with the experimental results.

ROBERT W. RANCE
and E. L. CUSSLER
Department of Chemical Engineering
Carnegie-Mellon University
Pittsburgh, Pennsylvania

SCOPE

This work investigates mass fluxes in supercritical fluids. These fluids, an important class of solvents, are gases or liquids compressed above their critical pressures and heated above their critical temperatures. Their study is another of the projects in this laboratory which aim at making mass transfer fast and selective.

Fast fluxes are desirable in most areas of mass transfer. The expectation that fluxes in supercritical fluids can be increased depends primarily on the increase in diffusion coefficient in going from liquid to gas. This increase is big, about 10^5. However, in dissolution or extraction, the magnitude of the solute flux depends both on the diffusion coefficient and on the solubility of the solute in the solvent. The solubility can decrease sharply in going from a liquid to a gas. Thus whether a supercritical fluid can engender a high flux depends on the product of the increased diffusion coefficient and the decreased solubility. One hopes that such a fluid will prove the ultimate solvent, with transport properties analogous to those of a gas and solubility properties like those of a liquid.

The unique feature of this study is this concern with flux, in contrast with earlier studies which emphasize measurements of diffusion coefficients. These earlier studies have used a variety of experimental methods, for example, interferometry, NMR, and radioactive tracers (Robinson and Stewart, 1968; Woessner et al., 1969). The data are used as checks for kinetic theories or are collected in more general correlations (Slattery and Bird, 1958; Ramanan and Hamrin, 1972). The work most similar to ours does measure the flux, but primarily in the region of the critical point (Tsekhanshaya, 1971; Krichevskii et al., 1971). Since the flux at the critical point goes to zero, this is not a region of great practical interest.

CONCLUSIONS AND SIGNIFICANCE

We have found that the flux of a solute in a supercritical fluid will be fast if its solubility is large. The flux is less affected by the increases in the diffusion coefficient. Such increases in diffusion coefficient are offset by decreases in solubility.

Measurements of iodine dissolution using a spinning disk show that the iodine flux in supercritical carbon dioxide does increase about 5% per °C at constant density. However, this change with temperature is considerably less at constant pressure. In all cases, the increases in flux can be estimated from available methods for calculating solubilities in supercritical fluids.

Thus our experiments suggest that extreme temperatures and pressures are necessary to achieve increases in flux of several orders of magnitude. Whether a solute's flux in a supercritical fluid is significantly greater than in an ordinary liquid depends primarily on the relative solubilities in the specific case. Whether the flux in a supercritical fluid is of practical importance depends both on the possibility of increased mass transfer and on the economic restraints involved.

Correspondence concerning this paper should be addressed to E. L. Cussler. R. W. Rance is with Unilever Research, Isleworth Laboratory, 455 London Road, Isleworth, England.

The experiments reported below suggest that solubility is more important than diffusion in determining the flux in a supercritical fluid. To test this suggestion, we develop here a guide for estimating fluxes under these conditions. While this guide is approximate, it provides an initial value with which one can quickly evaluate the potential of a particular supercritical solvent.

The dissolution of a solute in a pure solvent is described by the flux equation

$$j_2 = k_2 \Delta\rho_2 = k_2 \left(\frac{M_2}{M_1}\right) \rho_1 y_2^s \qquad (1)$$

The solvent density ρ_1 can be calculated from an equation of state. Thus estimating the flux requires estimating the solubility y_2^s and the mass transfer coefficient.

The simplest method for estimating solubilities is the theory of corresponding states (Prausnitz, 1969). While this method is of limited accuracy, its use is consistent with our objective of finding an approximate guide for these effects. In general, the solubility in a dense gas is

$$y_2^s = \frac{p_2^s}{p} E \qquad (2)$$

The solute's vapor pressure varies little with pressure, but is a strong function of temperature:

$$p_2^s = p_2^0 \exp\left(\frac{A}{T}\right) \qquad (3)$$

The enhancement factor E has the form

$$E = \frac{p}{f_1} \exp\left[\frac{\tilde{v}_m (p - p_2^s)}{RT} + y_1 \frac{\Delta H}{RT_{C1}}\left(\frac{1}{T}\frac{\partial T_C}{\partial y_2}\right)\right] \qquad (4)$$

where again we have used the limit of a dilute solution to simplify the more general equations (Lewis and Randall, 1961). The factors f_1/p and $\Delta H/RT_{C1}$ are known functions of temperature and pressure (Lewis and Randall, 1961), and the Poynting correction $v_m[p - p_2^s]/RT$ commonly does not change much. For the system iodine-carbon dioxide, we found by experiment that the temperature derivative given in parentheses is approximately unity.

Estimating the mass transfer coefficient requires a knowledge of the geometry and the solution properties. For example, because the experiments made in this work use a spinning disk (Levich, 1962),

$$k_2 \propto D_2^{2/3} \nu^{-1/6} \qquad (5)$$

We assume here that the diffusion coefficient is inversely proportional to the density of the solvent. This assumption is supported by available conductance data in supercritical water (Quist and Marshall, 1968) and is strongly implied by a recent corresponding states relation for self diffusivity (Ramanan and Hamrin, 1972). In addition, the kinematic viscosity is raised to such a small power that its variation under the range of experimental conditions important here is insignificant. Whether such assumptions are justified in more accurate work will require additional experiments.

We now can obtain the desired guide for the flux in supercritical fluids by combining Equations (1) to (5) and the assumed variation of diffusion to obtain

$$j_2 \propto \rho_1^{1/3} \frac{p_2^0}{p} \exp(a_1 + a_2) \qquad (6)$$

where

$$a_1 = \frac{\tilde{v}_m (p - p_2^s)}{RT} + y_1 \frac{\Delta H}{RT_{C1}}\left(\frac{1}{T}\frac{\partial T_C}{\partial y_2}\right) - \ln\left(\frac{f_1}{p}\right) \qquad (7)$$

and $a_2 = A/T$. Thus, a plot of flux versus the right-hand side of Equation (6) will be linear if the suggestion is correct that solubility is more important than diffusion in determining the flux in a supercritical fluid. This is evaluated below in terms of our experiments.

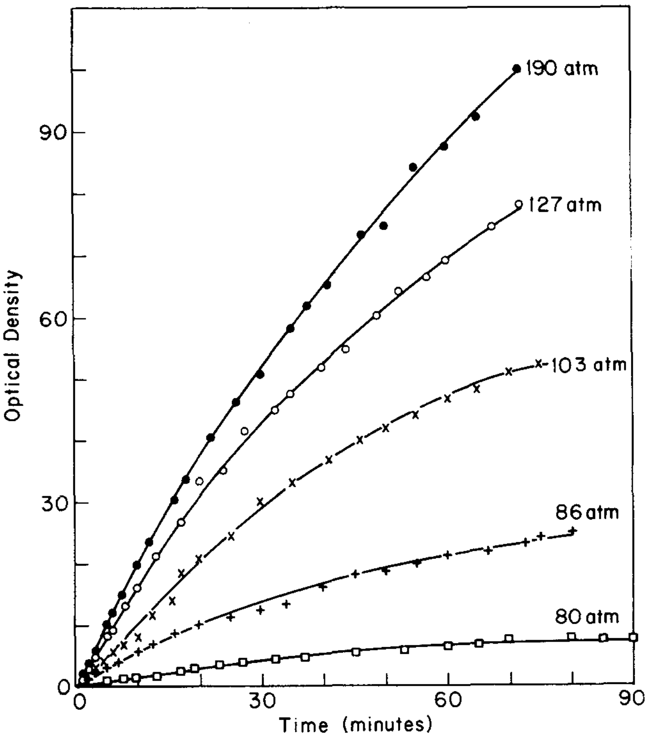

Fig. 1. Variation of optical density of iodine/carbon dioxide solutions with time at 40°C.

EXPERIMENT

The basic apparatus used in these experiments consists of a high pressure spectrophotometric cell containing a spinning disk of compressed iodine. The stainless steel cell volume contains two glass windows sealed in place with Teflon O-rings. Glass can be used as the window material because we are interested only in measuring the violet color of the iodine solutions and hence are working entirely within the visible range of the spectrum. Other common O-ring materials are chemically attacked by the supercritical fluids used here.

The iodine disk is spun with a high pressure stirrer, supplied by High Pressure Equipment Company. Initially the disk is covered by a screw cap lined with a Teflon gasket which prevents dissolution of the iodine before the desired temperature and pressure of the supercritical fluid are obtained. Starting the stirrer unscrews this cap, which then drops to the bottom of the cell below the level of the windows. The pressure in the cell is measured with a Heise bourdon tube gauge, and the entire cell was immersed in a water bath maintained constant to ±0.1°C. A more complete description of this apparatus, including drawings and dimensions, is given elsewhere (Kokini, 1974).

The changing concentration of the iodine solution is measured colormetrically using a Fisher Electrophotometer fitted with a 650 mμ filter. Concentration changes were proportional to the square root of rotational speed, indicating diffusion control (Levich, 1962). Typical optical density data measured at 120 rev./min. with this photocell are shown in Figure 1. The initial slopes of these curves provide a measure of the initial dissolution rate. The ability to monitor continuously the concentration of the solution gives this study a real advantage over previous efforts (Krichevskii et al., 1971), where dissolution rates were measured by determining the weight of material dis-

TABLE 1. RATES OF DISSOLUTION OF IODINE IN SUPERCRITICAL CARBON DIOXIDE[a]

	75°C			40°C	
p	Density	Flux	p	Density	Flux
282.3	0.75	25.9	190.5	0.83	7.4
227.9	0.69	23.7	153.1	0.80	6.6
189.8	0.60	19.2	127.2	0.75	5.7
155.8	0.50	13.7	102.7	0.65	3.7
146.3	0.44	10.4	90.1	0.52	2.6
138.1	0.41	8.1	85.7	0.40	2.2
115.6	0.31	4.8	80.3	0.30	0.7
88.4	0.20	3.0			
54.4	0.10	0.7		35°C	
			151.7	0.82	4.8
	70°C		112.2	0.76	4.4
226.5	0.72	21.8	92.5	0.70	2.4
			82.3	0.60	2.2
	60°C		79.6	0.53	2.2
270.7	0.80	15.9	77.9	0.40	1.5
197.3	0.72	14.4	75.5	0.30	0.2
165.3	0.66	12.6			
141.5	0.58	9.3		30°C	
122.4	0.44	5.9	136.1	0.83	5.6
101.4	0.31	1.3	106.8	0.79	5.2
75.5	0.18	1.3	81.6	0.71	3.0
			71.8	0.62	2.0
	50°C				
195.2	0.78	11.8		20°C	
153.7	0.71	8.9	95.2	0.85	3.7
130.6	0.65	6.3	71.4	0.83	3.7
119.1	0.58	5.9	62.9	0.81	3.0
106.1	0.47	3.7			
95.2	0.35	1.5			
81.0	0.23	0.7			

[a] Units: p [=] atm; density relative to water at 20°C; flux. [=] kg m^{-2} sec^{-1} × 10^2.

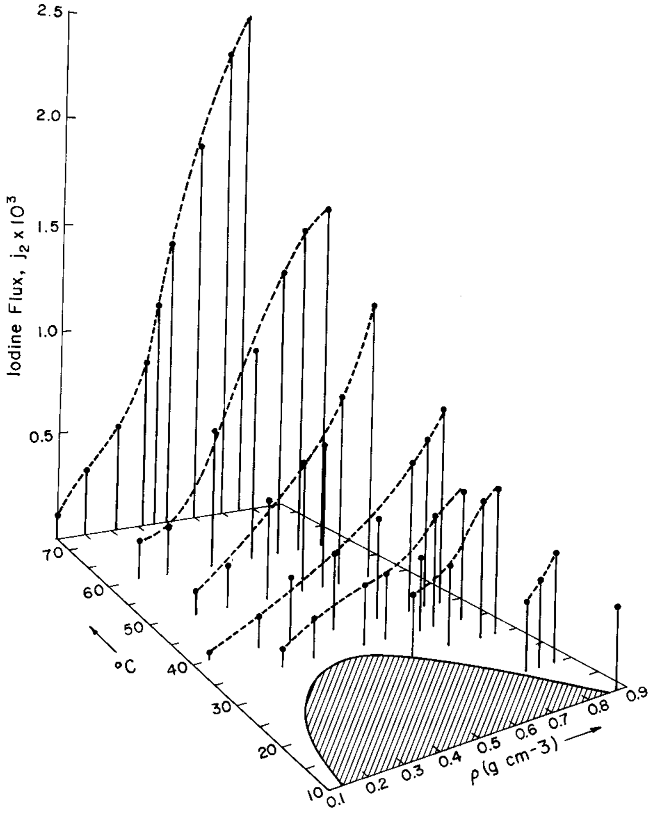

Fig. 2. Rate of iodine dissolving in supercritical carbon dioxide. With the theory developed here, these results can be reduced to the single line in Figure 3.

solved in a given time.

In a typical experiment, the optical density of the solution is measured until twice the time at which the dissolution rate became noticeably nonlinear. The initial slopes of duplicate experiments agreed within 10%. They also agreed with separate experiments in which we measured the loss in weight of the disk. The exact relation between optical density and iodine concentration was determined by measuring the optical density of iodine solutions of known composition. This relation obeys the Beer-Lambert law over the entire concentration range studied, that is, the optical density is linearly related to the concentration. However, since this constant is specific to our particular apparatus, it is not given here.

RESULTS AND DISCUSSION

The measured fluxes of iodine dissolving in carbon dioxide are shown as a function of temperature and solvent density in Table 1 and Figure 2. Densities were found from measurements of temperature and pressure using available *p-V-T* data (Michels et al., 1957). Most of the data are in the supercritical region, above the two phase region shaded in the figure. Values below the critical temperature and at high density are fluxes in the liquid region; values below the critical temperature but at low density would be in the gaseous region.

We have reported the data in Figure 2 as a function of density because this seems to us to give a better indication of the state of the fluid. The alternative would be to plot the data as a function of pressure, the variable measured directly in our experiments. A plot of flux versus temperature and pressure, or versus the corresponding reduced quantities, would have the same general appearance as Figure 2 but would be strongly skewed along the pressure axis. This is because reaching a specific value for density requires higher and higher pressures as the temperature is increased.

The general rule drawn from Table 1 and Figure 2 is that the flux is greatest when the supercritical solvent is hot and dense. At a constant temperature, the flux increases with increases in pressure or density. Still greater fluxes should be possible at higher densities than those given here, although the high pressures required are of limited utility. Eventually, increases in pressure will produce decreases in flux because the free volume between solvent molecules will be reduced sufficiently to decrease the solute's solubility.

The increases of flux with increasing pressure are in the opposite direction from those expected from changes in diffusion alone. In a dilute gas, the diffusion coefficient is inversely proportional to the pressure; in a liquid, it decreases relatively slightly with increasing pressure. Thus the diffusion coefficient would be expected to decrease with increasing pressure. That the flux increases under these conditions indicates how solubility dominates this behavior.

While the largest fluxes occur in the hot, dense solvent, the smallest occur in the dilute gas and at the critical point, at 31.5°C and 0.467 g cm^{-3}. Indeed, the flux at the critical point is predicted to be zero because chemical potential gradients are zero at this point (Khazanova, 1962). We made some approximate experiments which tended to support this, but these results were compromised by our limited temperature control. This prediction has been verified much more exactly for the present system (Krichevskii, 1961a; Krichevskii, 1961b), for naphthalene/CO$_2$ (Tsekhanskaya, 1971; Krichevskii, 1971), and for liquid-liquid critical points (Tsekhanskaya, 1968). Since this region is of such minor industrial utility, we have not studied it in detail.

The approximate guide for estimating supercritical

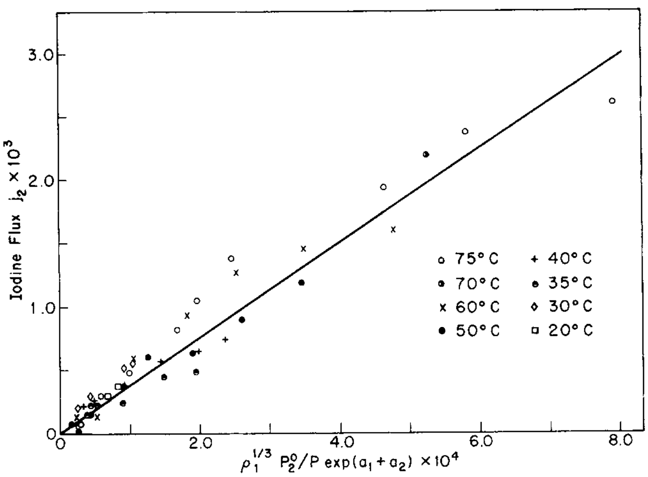

Fig. 3. Predicted variation of supercritical fluxes. These estimates, based on Equation (6), assume that diffusion is inversely proportional to density and that solubilities can be calculated from the theory of corresponding states.

fluxes is tested in Figure 3. In this figure, the measured iodine fluxes, accurate to about 20%, are plotted versus the right-hand side of Equation (6). This equation is developed by assuming diffusion is inversely proportional to density and by estimating the solubility from the theory of corresponding states. The success of this guide in reducing the data in Figure 2 to the simpler form in Figure 3 justifies our contention that solubility, not diffusion, dominates supercritical fluxes.

This method of estimation can also be used to decide between various supercritical solvents. To show this, we measured iodine dissolution rates at 50°C in other supercritical solvents, including nitrogen and hydrogen chloride. For example, the dissolution rate in nitrogen at 130 atm is predicted to be 2% of that in carbon dioxide at the same pressure; experimentally it is 3%. Similarly, at 80 atm. the dissolution rate in hydrogen chloride is predicted to be 370% of that in carbon dioxide; experimentally it is 350%. However, while these relative magnitudes may be estimated successfully, the correlation of data in these solvents is less exact than that shown in Figure 3.

The guide developed here cannot be used to predict accurately dissolution rates in ordinary liquids. In these cases, specific chemical interactions can dominate the solubility and thus can greatly enhance or diminish the flux. For example, at 25°C, the dissolution rate of iodine in carbon disulfide at 1 atm is 40 times greater than in carbon dioxide at 140 atm, while the rate in water at 1 atm is about 15 times less. There is no general way to predict these changes. For ordinary liquids, there is no substitute for a quick experiment. In contrast, for solutes of low volatility in supercritical solvents, the guide developed in this paper provides a useful tool.

ACKNOWLEDGMENTS

The authors had many helpful discussions with J. L. Kokini. This work was supported by the Petroleum Research Fund, Grant PRF #6376-AC7. R.W.R. is grateful to Unilever, Ltd., for a leave of absence and the Fulbright Commission for a travel grant. E. L. Cussler is supported by the NIH Career Development 1 K04 AM070461.

NOTATION

A = constant in Equation (4)
D_2 = diffusivity of solute, m^2/s
E = enhancement factor in corresponding states theory
f_1 = solvent fugacity, atm
ΔH = molar enthalpy of mixture at T and zero pressure minus that at T and P, Nm/°K/mole
j_2 = solute flux, kg/m^2/s
k_2 = solute mass transfer coefficient, m/s
M_1 = solvent molecular weight
M_2 = solute molecular weight
p = total pressure, atm
p_2^s = solute vapor pressure, atm
R = gas constant, Nm/°K/mole
T = absolute temperature, °K
T_{C1} = solvent critical temperature, °K
T_{C2} = solute critical temperature, °K
y_1 = mole fraction of solvent
y_2^s = solubility of solute, mole fraction
v_m = solute molar volume, m^3/mole
ρ_1 = solvent density, kg/m^3
ρ_2^s = solute solubility

LITERATURE CITED

Khazanova, I. R., N. E. Khazanova and L. D. Lesnevskaya, "The Fick Diffusion Equation," *Inzh.-Fiz. Zh. Akad. Nauk Belorussk. SSR*, **5**, 101 (1962).

Kokini, J. L., "Fast Extractions from Dead-end Pores," M.S. thesis, Carnegie-Mellon Univ., Pittsburgh, Penn. (1974).

Krichevskii, I. R., N. E. Khazanova, and L. F. Linshits, "Diffusion of Gases near the Critical Point of Liquid-Vapor Equilibrium," *Teplo i Massoperenos, Pervoe Vses, Soveshch., Minsk*, **2**, 132 (1961a).

————., "Iodine Diffusion in Carbon Dioxide near its Critical Point," *Dokl. Akad. Nauk SSSR*, **141**, 397 (1961b).

Krichevŝkii, I. R., Yu. V. Tsekhanskaya, and I. I. Sokolinskaya, "Rate of Naphthalene Dissolution in Carbon Dioxide near its Critical Point," *Dokl. Akad. Nauk SSR*, **196**, 1129 (1971).

Levich, V. G., *Physiochemical Hydrodynamics*, p. 70, Prentice-Hall, Englewood Cliffs, N. J. (1962).

Lewis, G. N., and M. Randall, *Thermodynamics*, 2nd Edit. Revised by K. S. Pitzer, and L. Brewer, Appendix I., McGraw-Hill, New York (1961).

Michels, A., A. Botzen and W. Schuurman, "Viscosity of Carbon Dioxide Between 0° and 75°C at pressures up to 2000 Atmosphere," *Physica*, **23**, 95 (1957).

Prausnitz, J. M., *Molecular Thermodynamics of Fluid-Phase Equilibria*, p. 146 et seq., Prentice-Hall, Englewood Cliffs, N. J. (1969).

Quist, A. S., and W. L. Marshall, "Electrical Conductances of Aqueous Sodium Chloride Solutions from 0 to 800° and at Pressures to 4000 Bars," *J. Phys. Chem.*, **72**, 684 (1968).

Ramanan, P., and C. E. Hamrin, Jr., "Friction Coefficients and Self-Diffusivity Reduced State Correlations and Interrelationships," *AIChE J.*, **18**, 333 (1972).

Robinson, R. C., and W. E. Stewart, "Self-Diffusion in Liquid Carbon Dioxide and Propane," *Ind. Eng. Chem. Fundamentals*, **7**, 90 (1968).

Slattery, J. C., and R. B. Bird, "Calculation of the Diffusion Coefficients of Dilute Gases and of the Self-Diffusion Coefficients of Dense Gases," *AIChE J.*, **4**, 137 (1958).

Tsekhanskaya, Yu. V., "Diffusion in a p-Nitrophenol-Water Systems in the Critical Region," *Zh. Fiz. Khim.*, **42**, 1014 (1968).

————., "Diffusion of Naphthalene in Carbon Dioxide near the Critical Point of the Liquid-Gas Equilibrium," *ibid.*, **45**, 1306 (1971).

Woessner, D. E., B. C. Snowden, R. A. George, and J. C. Melrose, "Dense Gas Diffusion Coefficients for the Methane-Propane System," *Ind. Eng. Chem. Fundamentals*, **8**, 779 (1969).

Manuscript received June 1, 1973; revision received and accepted November 9, 1973.