

tions are near zero at 0° and negative at 50°C. The effect of temperature on the b_V 's for all the electrolytes is similar in that $\partial b_V/\partial T$ is negative. The large positive deviations for most of the electrolytes at 0° and K_2SO_4 and $MgSO_4$ at 50°C may be due to cation-anion ion pair formation (10). The large negative deviations for $MgCl_2$ solutions at 50°C are what one might expect from the extended Debye-Hückel equation or if cation-cation and anion-anion interactions are more important than cation-anion interactions (10).

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Diffusion Coefficients of O_2 , N_2 , and CO_2 in Fluorinated Ethers

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Diffusion coefficients of O_2 , N_2 , and CO_2 in three fluorinated ethers are measured at 25° and 37°C. These coefficients are, in general, about twice as large as those in water.

Large gas solubilities in certain fluorinated ethers have stimulated considerable interest in their use as potential oxygen carriers in liquid breathing (5), in cardiopulmonary bypass machines (3), and as blood substitutes (8). To compute the mass-transfer rate during such processes, the diffusion coefficients of O_2 , N_2 , and CO_2 are needed. We have undertaken to measure these values for gases in fluorinated ethers at 25° and 37°C. The compounds studied were Caroxin-D (perfluoro-1,4 diisopropoxy butane) (Allied Chemical Corp., Morristown, N.J.), Caroxin-F (perfluoro-1-isopropoxy hexane) (Allied Chemical Corp., Morristown, N.J.), and FC-80 (perfluorobutyl perfluorotetrahydrofuran) (3M Co., St. Paul, Minn.).

Experimental

Materials. Minimum purities of O_2 , N_2 , and CO_2 were 99.6%. Caroxin-D and Caroxin-F were of greater than 99.9% purity as supplied, whereas FC-80 contains several isomers (2).

Procedure. Diffusion coefficients were measured with a modified Stokes' diaphragm cell (9). The procedure was described in detail by Tham and Gubbins (11), and we shall present only essential information here. The diaphragms were of porosity D (ASTM 10-20 μm), and stirring was accomplished with magnetic stirrers, rotating at 60 rpm. The diaphragm cells were immersed in a constant temperature bath controlled to within $\pm 0.02^\circ$ of the desired temperature with a proportional controller.

The cells were calibrated with 0.1N HCl, each cell being calibrated twice at the beginning of the work; cell constants were reproducible within $\pm 0.5\%$. [The diffusion coefficients are known accurately for the HCl-H₂O system (10).]

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The solvent-filled diaphragm method was used for both the calibration and diffusion coefficient measurement runs. Diffusion coefficients were calculated from the equation (1, 4)

$$D_{12} = \frac{1}{\beta t} \ln \left[\frac{C_B^\circ}{C_B - C_T} \right] \left[1 - \frac{\lambda}{6} \right] \quad (1)$$

where D_{12} is the differential diffusion coefficient of 1 in 2.

$$C_B^\circ = C_B \left[\frac{V_B + 1/2 V_D}{V_D} \right] + C_T \left[\frac{V_T + 1/2 V_D}{V_B} \right] \quad (2)$$

$$\lambda = \frac{V_D}{V_B + V_T} \quad (3)$$

β is the cell constant derived from calibration with HCl, and t is the time of diffusion; C is the concentration of diffusing substance, and V is the volume. Subscripts B , T , and D refer to bottom and top compartment and diaphragm, respectively.

The cell was first evacuated and then filled with the degassed fluorocarbon. It was equilibrated in a constant temperature bath for 2 hr with constant stirring; then, the bottom chamber was emptied and filled with solution containing the diffusing material. The method of preparing the gas solution and the precautions necessary in filling the cell have been described elsewhere (7, 12).

Solutions containing the dissolved gas were analyzed with a Perkin-Elmer Model 900 gas chromatograph equipped with a thermal conductivity detector. The column was a $1/8$ -in. \times 12-ft Porapak Q column, which was kept at room temperature. The helium carrier gas flow rate was 40 ml/min; injector port and detector temperatures were kept at 100° and 200°C, respectively. Calibration of the chromatograph was done by injecting a known volume of pure gas into the chromatograph and measuring the peak area. Linear response was observed in the range of concentrations of interest. The chromatograph analyses were reproducible to $\pm 0.6\%$.

Table I. Diffusion Coefficients of Selected Gases in Fluorinated Ethers

$D_{1m} \times 10^5 \text{ cm}^2/\text{sec}$

Gas	Caroxin-D		Caroxin-F		FC-80	
	25°C	37°C	25°C	37°C	25°C	37°C
N ₂	4.22	5.70	4.20	5.75	4.26	5.81
O ₂	4.06	5.57	4.09	5.61	4.10	5.65
CO ₂	3.35	4.21	3.38	4.36	3.41	4.48

The dissolved gas concentrations are extremely low (0.2–1 mol %); hence, the diffusion coefficients measured are equivalent to differential diffusion coefficients; they can also be considered as diffusion coefficients at infinite dilution.

Results

The experimental results are tabulated in Table I. The values given are the averages of three measurements. It is estimated that 0.6% error in the analysis will introduce 2.4% error in the final diffusion coefficient calculation (4). This, together with 0.5% uncertainty in the calibration step and 2% error in handling, will result in an approximately 5.0% error in the diffusion measurements. No previous diffusivity measurements for these systems have been reported; however, Nakanishi et al. (6) measured the diffusion coefficients of N₂ in FC-43, and they reported a value at 25°C, about 20% lower than that found in this work.

Discussion and Conclusions

The diffusion coefficients of these gases do not differ significantly from one fluorocarbon to the other. The observed diffusion coefficients are about twice those in water. Since the solubilities of these gases in fluorocarbon are more than 10 times that in water, the fluxes (and mass-transfer rates) of these gases in the fluorocarbons will be high—generally 20–40 times higher than those in water.

Apparently, the diffusion coefficients in these systems exhibit similar temperature dependences, at least in the temperature range covered, 25–37°C.

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Osmotic and Activity Coefficients for System NaCl–MnCl₂–H₂O at 25°C

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Osmotic coefficients of aqueous mixtures of sodium and manganous chloride are obtained by the isopiestic method. The results for solutions up to an ionic strength of 6.0 mol kg⁻¹ are considered in the computation of the activity coefficients of each salt in the mixtures. Quadratic terms in the Harned expressions are important at the higher ionic strengths. The activity coefficient of a trace of manganous chloride in a sodium chloride solution is greater than that of a pure manganous chloride solution of the same ionic strength. At low total ionic strengths, the activity coefficient of a trace of sodium chloride is increased, and at the higher total ionic strengths, it is decreased in relation to the values for pure sodium chloride solutions.

There are now free energy data available (2, 17) for many mixed electrolyte solutions, but most of the systems investigated have consisted of mixtures of simple salts. To interpret the behavior of naturally occurring solutions, it is often necessary to estimate the activity coefficients of the component salts. As a guide to the best procedure to use, it is important to know if the regulari-

ties observed in the properties of mixtures of simple salts extend to other systems where ion association is expected to be more extensive. We are interested in the effect of the other salts on trace amounts of base metal cations in geochemical brines. To obtain an understanding of these systems, we are initially investigating two-salt solutions, and in this paper we report results for mixtures of manganous chloride and sodium chloride.

Experimental

Analar sodium chloride and manganous chloride were recrystallized, the latter from a slightly acidified solution. Concentrations of stock solutions were determined by gravimetric silver chloride analyses. The manganous chloride stock solutions were kept free of oxygen during storage (7).

Osmotic coefficients of the mixtures and the pure manganous chloride solutions were measured by the isopiestic vapor-pressure technique (9). A description of the particular apparatus and experimental conditions employed in this study is given below.

Two sets of isopiestic dishes were used. The first has 17 gold-plated silver dishes with flap lids, and the second