Table I. Diffusion Coefficients of Selected Gases in Fluorinated Ethers

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

	Caroxin-D		Caroxin-F		FC-80	
Gas	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 N_2 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 $NaCl-MnCl_2-H_2O$ 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, 11*) 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 regularities 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 (*1*).

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 has 12 platinum dishes with gold alloy rims and tight-fitting titanium lids. In both cases during the equilibration period, the dishes rested in close-fitting wells in a gold-plated copper block 2.5-cm thick which was placed in a "Dry Seal" vacuum desiccator. During the equilibration period, which varied from four days to more than a week for some of the dilute solutions, the apparatus was thermostated at 25°C with variations of less than ±0.005°C. It was rocked through a small angle several times a minute to agitate the solutions gently.

Suitable portions of the mixtures were weighed into the dishes which were then placed on the block in the desiccator. After reducing the pressure in the desiccator below atmospheric (sufficient to ensure that no leaks occurred at the O ring seal), the apparatus was placed in the thermostat to reach thermal equilibrium before gradually reducing the pressure to the vapor pressure of the solutions. This was done by repeated equalizing of the pressure between the desiccator containing the apparatus and a similarly sized desiccator which had been evacuated.

At the end of the equilibration period, the apparatus was removed from the thermostat, dry air let in, the lids were closed, and then the weighing of the dishes was carried out as quickly as possible. Except where noted in Table I, duplicate solutions were used, and the mean values of the molality taken. The average difference in the molality of duplicates was less than 0.1%. New mixtures were prepared immediately before each experiment when the gold-plated silver dishes were used. Some sets of solutions in the platinum dishes were equilibrated more than once, and from the consistency of the results, the increased time of contact of the solutions with the atmosphere had no discernible effects.

Results

The compositions of the sets of solutions in isopiestic equilibrium are recorded in Table I in terms of the molalities of sodium chloride and manganous chloride, m_A and m_B, respectively. The first entry in each set in the column headed m_A gives the molality, m_{ref}, of the sodium chloride solution used as reference for that set. At vapor-pressure equilibrium

$$\phi = \frac{2m_{ref}}{2m_A + 3m_B}\phi_{ref} \qquad (1)$$

where ϕ is the osmotic coefficient. Osmotic coefficients of the reference sodium chloride solutions were obtained by interpolation of the data listed by Robinson and Stokes (*10*) by use of the same method and coefficients as before (*1*). In the analysis used to derive activity coefficients (see below), osmotic coefficients are required for pure sodium chloride and pure manganous chloride solutions at ionic strengths equal to the total ionic strength of each mixture. To facilitate the interpolation of the manganous chloride data, the same method as that used for sodium chloride was applied. The osmotic coefficients for pure manganous chloride listed in Table I were combined with the recalculated data of Robinson and Stokes for this salt [see earlier paper (*1*) for details] and fitted by least squares to give Equation 2 which is of the form suggested by Lietzke and Stoughton (*3*).

$$\phi = 1 - \frac{2 \times 1.17202}{a^3 I}\left[1 + aI^{1/2} - \frac{1}{1 + aI^{1/2}} - 2\ln(1 + aI^{1/2})\right] + 0.03745\, I + 0.0119905\, I^2 - 0.00147615\, I^3 + 0.00005287\, I^4 \qquad (2)$$

where $a = 1.60940$, and I is the ionic strength. The fit of the present experimental results for pure manganous chloride is indicated by the delta values at $m_A = 0$ given in Table I, whereas for the osmotic coefficients at 14 molalities determined by Robinson and Stokes, the average deviation is 0.0020 and the maximum 0.0047. The coefficients of Equation 2 differ from those given previously (*1*) because additional data have been included. However, smoothed osmotic and activity coefficients calculated from the two sets are almost identical, the differences being less than 0.002 up to $2m$. Osmotic and activity coefficients at rounded molalities calculated by use of the coefficients of Equation 2 are given in Table II.

Activity coefficients of each salt in the mixture were then obtained by the procedure used by Rush and Johnson (*12*). This involves finding the values of the b parameters of Equation 3 which best describe the observed osmotic coefficients.

$$(y_A + 1)\phi = 2\, y_A\phi_A{}^\circ + y_B\phi_B{}^\circ + y_A y_B \beta_0 + y_A y_B (y_A - y_B)\beta_1 \qquad (3)$$

where

$$\beta_0 = b_1 I + b_2 I^2 + b_3 I^3$$

and

$$\beta_1 = b_4 I^2 + b_5 I^3$$

In Equation 3, $\phi_A{}^\circ$ and $\phi_B{}^\circ$ are the osmotic coefficients of pure A and pure B at the same ionic strength I as the total ionic strength of the mixture, $I = m_A + 3m_B$, and y_A and y_B are the ionic strength fractions of A and B, $y_A = m_A/(m_A + 3m_B)$ and $y_B = 3m_B/(m_A + 3m_B)$. Results for solutions at total ionic strengths greater than 6, the limit of the data for pure sodium chloride, were omitted in this calculation. The best fitting parameters, obtained by the method of least squares, are $b_1 = 0.04940$, $b_2 = -0.01483$, and $b_4 = -0.00273$. Inclusion of the other parameters, b_3 and b_5, did not produce a significant improvement in the fit. These same b values were then used in the evaluation of activity coefficients from the expressions given by Rush and Johnson (*12*). It is convenient to summarize the behavior of the activity coefficients of the salts in the mixtures in terms of the Harned expressions, Equations 4 and 5.

$$\log \gamma_A = \log \gamma_A{}^\circ + Q_A y_B + R_A y_B{}^2 \qquad (4)$$

$$\log \gamma_B = \log \gamma_B{}^\circ + Q_B y_A + R_B y_A{}^2 \qquad (5)$$

In Equation 4, γ_A is the activity coefficient of A in the mixed solutions, $\gamma_A{}^\circ$ is the activity coefficient of A in a pure solution of A of the same ionic strength as the total ionic strength of the mixture, and Q_A and R_A are constants at constant total ionic strength. Similar definitions apply to Equation 5. The method described by Lietzke and Stoughton (*3*) was used to evaluate the activity coefficients of the pure salt solutions from an analysis of osmotic coefficient data. From the values of the coefficients listed in Table III, the quadratic terms in Equations 4 and 5 are significant, especially at the higher ionic strengths.

Our primary aim was to determine activity coefficients of trace amounts of manganous chloride γ^{tr} in the sodium chloride solutions, and these quantities, together with the corresponding values for sodium chloride, are given in Table III. Also listed are estimates based on data for the single electrolyte solutions alone [that is, taking all b's = 0 in the expressions given by Rush and Johnson (*12*)].

At all the ionic strengths studied, the activity coefficient of a trace of manganous chloride in a sodium chlo-

Table I. Isopiestic Data for System $NaCl(A)-MnCl_2(B)-H_2O$ at 25°C

m_A, mol kg^{-1}	m_B, mol kg^{-1}	ϕ	Δ^a
1.1400	0.0	0.9407	
0.3148	0.5373	0.9569	15
0.5862	0.3606	0.9515	9
0.8284	0.2027	0.9470	7
0.9196	0.1443	0.9440	−9
0.0	0.7434	0.9617	1
1.2649	0.0	0.9461	
0.3920	0.5622	0.9687	9
0.6144	0.4192	0.9626	3
0.9612	0.1965	0.9528	−10
1.0364	0.1480	0.9510	−10
0.0	0.8154	0.9784	−3
1.2872	0.0	0.9471	
0.3518	0.6004	0.9734	21
0.6578	0.4045	0.9640	7
0.9332	0.2284	0.9555	−9
1.0363	0.1626	0.9522	−15
0.0	0.8279	0.9816	−1
1.2958	0.0	0.9474	
0.3543	0.6048	0.9734	8
0.6635	0.4080	0.9640	−18
0.9389	0.2298	0.9555	−5
1.0410	0.1634	0.9522	4
0.0	0.8326	0.9816	2
1.3921^b	0.0	0.9518	
0.1419	0.7953	0.9927	20
0.3039	0.6928	0.9866	12
0.6588	0.4652	0.9768	30
0.7231	0.4261	0.9727	6
0.9299	0.2949	0.9656	−3
0.9649	0.2745	0.9625	−26
0.0	0.8852	0.9979	24
1.4068	0.0	0.9525	
0.4322	0.6197	0.9840	12
0.6788	0.4631	0.9757	7
1.0653	0.2178	0.9627	−5
1.1502	0.1642	0.9596	−10
0.0	0.8954	0.9977	−3
1.7846	0.0	0.9715	
0.5377	0.7710	1.0233	0
0.8499	0.5798	1.0082	−17
1.3425	0.2744	0.9884	−9
1.4503	0.2071	0.9845	−3
0.0	1.1032	1.0477	−12
1.9038	0.0	0.9779	
0.5028	0.8582	1.0400	10
0.9512	0.5850	1.0181	−4
1.3590	0.3326	1.0021	18
1.5141	0.2376	0.9953	16
0.0	1.1655	1.0649	6
2.3655^b	0.0	1.0046	
0.4592	1.1356	1.0989	17
0.5487	1.0838	1.0929	5
1.2562	0.6608	1.0574	23
1.2864	0.6429	1.0559	22
1.5100	0.5108	1.0441	9
1.8938	0.2826	1.0254	−2
0.0	1.4091	1.1244	1
2.8553	0.0	1.0356	
0.9412	1.1194	1.1285	2
1.4152	0.8458	1.1017	−15
2.1338	0.4244	1.0673	−3
2.5118	0.2001	1.0516	15
0.0	1.6657	1.1835	−23
3.2192	0.0	1.0600	
0.9246	1.3258	1.1713	6
1.4844	1.0128	1.1361	−53
2.3965	0.4900	1.0897	−77
2.5832	0.3689	1.0880	14
0.0	1.8568	1.2252	−45
3.2586	0.0	1.0627	
1.0658	1.2677	1.1670	−3
1.6064	0.9599	1.1368	−17
2.4278	0.4828	1.0987	6
2.8654	0.2283	1.0795	7
0.0	1.8745	1.2316	21
3.3700^b	0.0	1.0705	
0.6156	1.5831	1.2064	2
0.8065	1.4764	1.1941	−9
1.4919	1.0824	1.1579	21
1.8416	0.8825	1.1397	17
2.1215	0.7234	1.1250	4
2.5104	0.5001	1.1064	−4
0.0	1.9311	1.2454	−9
3.6578	0.0	1.0908	
1.1904	1.4159	1.2039	−6
1.7966	1.0737	1.1711	−14
2.7210	0.5411	1.1295	11
3.2107	0.2558	1.1101	27
0.0	2.0814	1.2780	−7
4.4030	0.0	1.1458	
1.2514	1.7944	1.2795^c	...
2.0062	1.3687	1.2429^c	...
3.2538	0.6652	1.1866	12
3.5463	0.5064	1.1717	−46
0.0	2.4854	1.3533	−54
4.4742^b	0.0	1.1512	
0.5170	2.2346	1.3314^c	...
1.0247	1.9601	1.2991^c	...
1.9517	1.4469	1.2496^c	...
2.3091	1.2456	1.2330^c	...
2.8175	0.9543	1.2123	25
3.5331	0.5448	1.1840	19
0.0	2.5170	1.3643	−2
4.9623^b	0.0	1.1888	
0.5928	2.4676	1.3737^c	...
1.0224	2.2346	1.3486^c	...
2.2049	1.5834	1.2880^c	...
2.4840	1.4293	1.2746^c	...
3.1255	1.0688	1.2475^c	...
3.8734	0.6397	1.2206	2
0.0	2.7840	1.4126	15

Table I. Continued

m_A, mol kg^{-1}	m_B, mol kg^{-1}	ϕ	Δ[a]
5.7134[b]	0.0	1.2478	
0.7264	2.8266	1.4355	...
1.1936	2.5853	1.4057	...
2.1407	2.0806	1.3549	...
2.7467	1.7469	1.3283	...
3.6707	1.2212	1.2956	...
4.6764	0.6212	1.2712	...
0.0	3.2153	1.4782	−5
5.7801[b]	0.0	1.2531	
0.7896	2.8401	1.4343	...
1.2919	2.5754	1.4050	...
2.3987	1.9815	1.3486	...
2.8496	1.7334	1.3291	...
3.7015	1.2500	1.2988	...
4.8646	0.5573	1.2706	...
0.0	3.2530	1.4844	15

[a] Δ = (experimental osmotic coefficient − value calculated by using Equation 3 with $b_1 = 0.04940$, $b_2 = -0.01483$, $b_4 = -0.00273$, b_3, $b_5 = 0$) $\times 10^4$. [b] Means of triplicates. [c] These values, together with results for all mixtures in last two sets, were not used in the computation of b coefficients.

Table II. Osmotic and Activity Coefficients of Manganous Chloride at 25°C Calculated with Coefficients of Equation 2

m, mol kg^{-1}	ϕ	γ
0.1	0.851	0.518
0.2	0.855	0.469
0.3	0.869	0.450
0.4	0.887	0.442
0.5	0.907	0.441
0.6	0.929	0.443
0.7	0.952	0.449
0.8	0.975	0.458
0.9	0.999	0.468
1.0	1.023	0.480
1.2	1.073	0.509
1.4	1.122	0.543
1.6	1.170	0.581
1.8	1.217	0.623
2.0	1.261	0.667
2.2	1.303	0.715
2.4	1.343	0.765
2.6	1.379	0.817
2.8	1.414	0.871
3.0	1.446	0.926
3.2	1.476	0.984

Table III. Parameters of Equations 4 and 5 and Trace Activity Coefficients of Sodium Chloride (A) and Manganous Chloride (B)

	$I = 1$	$I = 2$	$I = 3$	$I = 4$	$I = 5$	$I = 6$
Q_A	0.0077	0.0011	−0.0169	−0.0457	−0.0849	−0.1341
R_A	0.0025	0.0101	0.0227	0.0403	0.0630	0.0907
Q_B	0.0144	0.0318	0.0464	0.0570	0.0626	0.0628
R_B	0.0014	0.0055	0.0123	0.0219	0.0343	0.0494
$\log \gamma_{A(A)}$	−0.1823	−0.1750	−0.1461	−0.1057	−0.0580	−0.0056
$\log \gamma_A^{tr}$[a]	−0.1719	−0.1637	−0.1403	−0.1111	−0.0801	−0.0493
$\log \gamma_A^{tr}$[b]	−0.1814	−0.1799	−0.1606	−0.1330	−0.1009	−0.0663
$\log \gamma_{B(B)}$	−0.3506	−0.3495	−0.3184	−0.2749	−0.2260	−0.1756
$\log \gamma_B^{tr}$[a]	−0.3349	−0.3120	−0.2593	−0.1954	−0.1283	−0.0626
$\log \gamma_B^{tr}$[b]	−0.3526	−0.3397	−0.2894	−0.2203	−0.1402	−0.0541

[a] Calculated from experimental results for mixtures. [b] Estimated from data for single-salt solutions.

Table IV. Excess Free Energy of Mixing, $\Delta_m G^e$, at $y_A = y_B = 1/2$ in J/kg of Water

Values for Alkaline Earth Systems Calculated with b Coefficients Tabulated by Rush (*11*)

	NaCl-$MnCl_2$[a]	NaCl-$MgCl_2$[b]	NaCl-$MgCl_2$[c]	NaCl-$CaCl_2$[d]	NaCl-$BaCl_2$[e]
$I = 1$	26	28	35	37	16
$I = 2$	86	108	125	126	39
$I = 3$	151	234	249	243	46
$I = 4$	196	401	400	375	27
$I = 5$	191	604	578	521	−11
$I = 6$	109	837	792	692	...

[a] Present work. [b] Data of Platford (*4*). [c] Data of Wu et al. (*13*). [d] Data of Robinson and Bower (*6*). [e] Data of Robinson and Bower (*5*).

ride solution is increased in relation to that of pure manganous chloride at the same ionic strength. The behavior of sodium chloride is more complicated in that at low ionic strengths the activity coefficient for a trace is higher than that of pure sodium chloride, whereas at the higher ionic strengths, it is lower. These characteristics are qualitatively the same as those found for the sodium chloride–calcium chloride system (*6*). The largest errors in the estimates of trace activity coefficients from single salt data amount to less than 7% in the case of manganous chloride and less than 5% for sodium chloride, and they occur near the middle of the ionic strength range studied.

At $y_A = y_B = 1/2$ the excess free energy of mixing, $\Delta_m G^e$, is given (*14*) by Equation 6.

$$\Delta_m G^e = \tfrac{1}{4} RTI \left(b_1 I + \tfrac{1}{2} b_2 I^2 + \tfrac{1}{3} b_3 I^3\right) \qquad (6)$$

Values for $\Delta_m G^e$ are given in Table IV and may be compared with results for mixtures of sodium chloride with magnesium, calcium, and barium chloride. The values for the last three systems have been computed by use of the b coefficients tabulated by Rush (*11*). As noted by Robinson and Covington (*7*), comparatively large changes in the activity coefficients with composition at constant total ionic strength need not be reflected in the magnitude of $\Delta_m G^e$. For example, at an ionic strength of 6.0 mol kg^{-1}, the changes in the activity coefficients of sodium chloride and manganous chloride in the NaCl–$MnCl_2$ system are about the same as for sodium chloride and magnesium chloride in the NaCl–$MgCl_2$ system; yet, the excess free energy of mixing is much less.

In conclusion, the behavior of the sodium chloride–manganous chloride system is only moderately complicated in that quadratic terms in the Harned expressions are sufficient to give an accurate description of the activity coefficients and that estimates of trace activity coefficients from single salt data are in reasonable agreement with experimental values.

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Equilibrium-Phase Properties of *n*-Pentane–Carbon Dioxide System

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Vapor and liquid equilibrium-phase compositions and refractive indices were determined for the *n*-pentane–carbon dioxide system at 40.1°, 100.2°, 159.8°, and 220.0°F from the vapor pressure of *n*-pentane to pressures in the critical region. The equilibrium ratios for each component were calculated at each temperature from the phase composition data. The equilibrium-phase densities were calculated from the measured phase composition and refractive index by use of the Lorentz-Lorenz molar refractivity relationship.

As a continuation of a program to provide data on binary systems of interest to the petroleum and natural gas industry, the behavior of the *n*-pentane–carbon dioxide system was studied. This system was studied earlier by Poettman and Katz (*5*) in the temperature range from about 80° to 280°F, but it was suspected that substantial errors might exist in the data.

The first indication of this possibility arose when a considerable discrepancy existed between the data for the *n*-butane–carbon dioxide system reported in the same work and the data of Olds et al. (*4*) and data taken by Besserer and Robinson (*1*). In this system the liquid-phase compositions were generally too lean in *n*-butane, thus suggesting the possibility of some consistent error in the liquid-phase compositions. From this it was reasoned that a similar error might exist in the *n*-pentane–carbon dioxide data. The second indication was that the Henry's Law constant for carbon dioxide dissolved in *n*-pentane, defined by

$$H = \lim_{x \to 0} \frac{f}{x}$$

was about 30% lower than would have been expected by comparison with values of the constant for other carbon dioxide–paraffin binaries.

Experimental

The experimental equipment and procedure were described in detail in earlier papers by Besserer and Robinson (*1, 3*). Experiments were carried out at each of four temperatures which were nominally 40°, 100°, 160°, and 220°F. At each temperature, measurements of equilibrium-phase compositions and refractive indices were made at a series of pressures between the vapor pressure of *n*-pentane and the vapor pressure of carbon dioxide or the critical pressure for the system. The temperature was measured with a calibrated pair of iron-constantan thermocouples with the reference junction kept in an ice bath and is believed known to ±0.1°F. The pressure was measured with a strain gauge pressure transducer calibrated against the vapor pressure of carbon dioxide at 70°F and is believed known to ±3 psi.

The phase compositions were determined with a Hewlett-Packard Model 700 gas chromatograph equipped with a thermal conductivity cell detector. The column used was a 3-ft by $\frac{1}{8}$-in. diameter stainless steel column packed with Poropak QS maintained at 170°C. The response factors for conversion from area fraction to mole fraction were 1.903 for *n*-pentane compared to 1.000 for carbon dioxide. These factors were obtained by calibration by use of pure component samples in a 1-cc sample loop at pressures up to 0.3 atm. The compositions are believed known to ±0.004 mole fraction.

Materials

The carbon dioxide used in the experiments was obtained from Canadian Liquid Air and the *n*-pentane was pesticide grade obtained from the Fisher Scientific Co. Both had a purity of better than 99.9 mol %.

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