parallels the increase of the relative oxygen content of the ether molecules. We note that, in general, the excess enthalpy of cyclic ether + cyclohexene is distinctly smaller than that of the corresponding system cyclic ether + cyclohexane (*2*, *24*, *25*): at $x = 0.5$, these increments vary between ca. −400 and −700 J mol^{-1}.

Literature Cited

(1) Inglese, A.; Wilhelm, E.; Grolier, J.-P. E.; Kehiaian, H. V. *J. Chem. Thermodyn.* **1980**, *12*, 217.
(2) Inglese, A.; Wilhelm, E.; Grolier, J.-P. E.; Kehiaian, H. V. *J. Chem. Thermodyn.* **1980**, *12*, 1047.
(3) Inglese, A.; Wilhelm, E.; Grolier, J.-P. E.; Kehiaian, H. V. *J. Chem. Thermodyn.* **1981**, *13*, 229.
(4) Wilhelm, E.; Inglese, A.; Grolier, J.-P. E.; Kehiaian, H. V. *J. Chem. Thermodyn.* **1982**, *14*, 33.
(5) Wilhelm, E.; Inglese, A.; Grolier, J.-P. E.; Kehiaian, H. V. *J. Chem. Thermodyn.*, in press.
(6) Kehiaian, H. V.; Grolier, J.-P. E.; Benson, G. C. *J. Chim. Phys. Phys.-Chim. Biol.* **1978**, *75*, 1031.
(7) Andrews, A.; Morcom, K. W.; Duncan, W. A.; Swinton, F. L.; Pollock, J. M. *J. Chem. Thermodyn.* **1970**, *2*, 95.
(8) Wilhelm, E.; Grolier, J.-P. E.; Karbalai Ghassemi, M. H. *Monatsh. Chem.* **1978**, *109*, 369.
(9) Forziati, A. F.; Camin, D. I.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1950**, *45*, 406.
(10) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1950; Vol. 1.
(11) Harris, K. R.; Dunlop, P. J. *J. Chem. Thermodyn.* **1970**, *2*, 813.
(12) Wóycicky, W. *J. Chem. Thermodyn.* **1980**, *12*, 165.
(13) Letcher, T. M. *J. Chem. Thermodyn.* **1977**, *9*, 661.
(14) Riddick, J. A.; Bunger, W. B. "Techniques of Chemistry", 3rd ed.; Weissberger, A., Ed.; Wiley-Interscience: New York, 1970; Vol. 2.
(15) Landolt-Börnstein, Zahlenwerte und Funktionen, 2 Band, 1 Teil, 6 Auflage; Springer: West Berlin, 1971.
(16) Kiyohara, O.; D'Arcy, P. J.; Benson, G. C. *Can. J. Chem.* **1979**, *57*, 1006.
(17) Anand, S. C.; Grolier, J.-P. E.; Kiyohara, O.; Benson, G. C. *Can. J. Chem.* **1973**, *51*, 4140.
(18) Hammond, B. R.; Stokes, R. H. *Trans. Faraday Soc.* **1955**, *51*, 1641.
(19) Beilstein, "Handbuch der Organischen Chemie", 19 Band, 1 Ergänzungswerk, 4 Auflage; Springer: Berlin, 1934, p 609.
(20) Stokes, R. H.; Marsh, K. N.; Tomlins, R. P. *J. Chem. Thermodyn.* **1969**, *1*, 211. Marsh, K. N. *Int. Data Ser., Sel. Data Mixtures, Ser. A* **1973**, 2, 3.
(21) Günzel, K.; Bittrich, H. J. *Z. Phys. Chem.* (*Leipzig*) **1977**, *258*, 1073.
(22) Letcher, T. M.; Sack, J. *J. S. Afr. Chem. Inst.* **1975**, *28*, 316.
(23) Letcher, T. M.; Marsicano, F. *J. Chem. Thermodyn.* **1974**, *6*, 509.
(24) Andrews, A. W.; Morcom, K. W. *J. Chem. Thermodyn.* **1971**, *3*, 519.
(25) Cabani, S.; Ceccanti, N. *J. Chem. Thermodyn.* **1973**, *5*, 9.

Received for review November 3, 1981. Accepted April 13, 1982. Financial support within the frame of the Austrian–French treaty for scientific and technical cooperation is gratefully acknowledged by E.W.

Heat Capacities of Aqueous Solutions of $NiCl_2$ and $NiCl_2 \cdot 2NaCl$ from 0.12 to 3.0 mol kg^{-1} and 321 to 572 K at a Pressure of 17.7 MPa

David Smith-Magowan,[†] **Robert H. Wood,*** **and David M. Tillett**

Department of Chemistry, University of Delaware, Newark, Delaware 19711

The heat capacity of aqueous $NiCl_2$ and aqueous $NiCl_2 \cdot 2NaCl$ has been measured at temperatures from 321 to 572 K at a pressure of 17.7 MPa by using a new flow calorimeter. The results for $NiCl_2$ do not show the large negative apparent molar heat capacities characteristic of strong electrolytes at high temperatures and low molalities. This indicates that $NiCl_2$ at 572 K is mainly un-ionized. The apparent molar heat capacity of $NiCl_2 \cdot 2NaCl$ could be predicted with reasonable accuracy, by using Young's rule and the apparent molar heat capacities of pure $NiCl_2$ and NaCl. This success indicates that Young's rule can be used to calculate the heat capacity of $NiCl_2$ in any mixture with NaCl. Equations are derived which allow the present results together with room-temperature data to be used to calculate enthalpies and free energies of aqueous $NiCl_2$ at high temperatures. The integrals of the apparent molar and partial molar heat capacities needed in these equations are tabulated.

Introduction

This investigation of the heat capacities of $NiCl_2$ solutions at high temperatures, complementing our previous study of NaCl heat capacities (*1*), was undertaken for two reasons. First, we wanted to contrast the relatively simple behavior of NaCl solutions at high temperatures with a system more likely to exhibit complex thermodynamic behavior. Ludeman and Franck (*2*), in their spectroscopic investigation of aqueous $NiCl_2$ solutions, for example, found dramatic changes in the absorption spectrum near 200 °C. Second, we wanted to demonstrate that our calorimeter could be used to investigate industrial problems associated with high-temperature aqueous systems. Extensive use of nickel-containing alloys in nuclear power plants has resulted in several corrosion problems, yet very little is known about aqueous nickel species at high temperatures. These problems include stress-corrosion cracking which may result from $NiCl_2$ concentrations in crevices and sludge piles (*3*). Postlewait's investigation implicates chloride in the corrosion of nickel at temperatures up to 274 °C (*4*). Migration of radioactivity throughout steam-generating circuits is a serious problem which is dependent on nickel speciation at high temperatures (*5–7*).

Table I. Densities of the Solutions at 1 atm and 25 °C[a]

m/(mol kg^{-1})	d/(g cm^{-3}) $NiCl_2$	d/(g cm^{-3}) $NiCl_2 \cdot$ 2NaCl	m/(mol kg^{-1})	d/(g cm^{-3}) $NiCl_2$	d/(g cm^{-3}) $NiCl_2 \cdot$ 2NaCl
0.1202	0.985 45	0.976 11	0.9940	0.885 42	0.899 32
0.5286	0.937 78	0.949 44	2.995	0.681 25	0.821 32

[a] The density of water used was 0.997 04 g cm^{-3}.

The measurements reported here allow the calculation of the apparent molar and partial molar heat capacities, the change in the enthalpy and the partial molar enthalpy, and the change in the chemical potential as functions of molality and temperature for aqueous $NiCl_2$ and $NiCl_2 \cdot 2NaCl$. The results allow the calculation of equilibria involving aqueous $NiCl_2$ alone or in the presence of NaCl at molalities from 0.12 to 3.0 mol kg^{-1} and temperatures from 298 to 575 K.

Experimental Section

Solutions. A stock solution of approximately 3.0 mol kg^{-1} $NiCl_2$ was prepared from Fisher certified $NiCl_2 \cdot 2H_2O$, the actual

---

[†] Current address: Westinghouse Research and Development Center, Pittsburgh, PA 15235.

0021-9568/82/1727-0335$01.25/0

Table II. Experimental Results, P_s/P_w, and Calculated Values of $c_p/c_p{}^0$ and $C_{p,\phi}$ for $NiCl_2$ and $NiCl_2 \cdot NaCl$ at 17.7 MPa

m^a/(mol kg^{-1})	P_s/P_w	$c_p/c_p{}^{0\,b}$	$C_{p,\phi}{}^c$/ (J mol^{-1} K^{-1})
	(A) $NiCl_2$ at pH 2^d		
	T/K = 322.8, f = 1.01^e		
0.1202	0.9930	0.9785	−215
0.5286	0.9736	0.9127	−194
0.9940	0.9554	0.8456	−189
2.9950	0.9111	0.6201	−192
	T/K = 359.29, f = 1.07		
0.1202	0.9934	0.9875	−216
0.5286	0.9765	0.9143	−182
0.9940	0.9619	0.8494	−172
2.9950	0.9297	0.6302	−174
	T/K = 398.79, f = 1.06		
0.1202	0.9930	0.9782	−230
0.5286	0.9778	0.9158	−171
0.9940	0.9662	0.8538	−153
2.9950	0.9450	0.6417	−154
	T/K = 453.31, f = 1.08		
0.1202	0.9914	0.9763	−307
0.5286	0.9721	0.9096	−230
0.9940	0.9717	0.8585	−135
2.9950	0.9634	0.6544	−133
	T/K = 498.49, f = 1.09		
0.1202	0.9917	0.9765	−311
0.5286	0.9810	0.9184	−160
0.9940	0.9772	0.8634	−116
2.9950	0.9878	0.6722	−101
	T/K = 549.72, f = 1.19		
0.1202	0.9927	0.9769	−326
0.5286	0.9880	0.9244	−115
0.9940	0.9914	0.8764	−54
	T/K = 572.73, f = 1.08		
0.1202	0.9924	0.9773	−334
0.5286	0.9898	0.9275	−91
0.9940	0.9934	0.8791	−41
	(B) $NiCl_2$ at pH 3^d		
	T/K = 322.18, f = 1.01		
0.1202	0.9932	0.9787	−209
0.5286	0.9737	0.9128	−193
0.9940	0.9554	0.8456	−189
2.9950	0.9111	0.6201	−192
	T/K = 359.29, f = 1.07		
0.1202	0.9934	0.9785	−216
0.5286	0.9767	0.9145	−180
0.9940	0.9616	0.8492	−173
2.9950	0.9297	0.6302	−174
	T/K = 398.79, f = 1.06		
0.1202	0.9931	0.9783	−228
0.5286	0.9779	0.9160	−170
0.9940	0.9662	0.8539	−153
2.9950	0.9451	0.6418	−153
	T/K = 453.31, f = 1.08		
0.1202	0.9921	0.9770	−279
0.5286	0.9789	0.9165	−170
0.9940	0.9711	0.8578	−138
2.9950	0.9636	0.6545	−132
	T/K = 498.49, f = 1.09		
0.1202	0.9915	0.9763	−318
0.5286	0.9809	0.9183	−161
0.9940	0.9773	0.8635	−115
	T/K = 549.72, f = 1.19		
0.1202	0.9928	0.9770	−323
0.5286	0.9880	0.9243	−116
0.9940	0.9910	0.8759	−56
	T/K = 572.73, f = 1.08		
0.1202	0.9923	0.9773	−336
0.5286	0.9895	0.9271	−95
0.9940	0.9941	0.8798	−37

m^a/(mol kg^{-1})	P_s/P_w	$c_p/c_p{}^{0\,b}$	$C_{p,\phi}{}^c$/ (J mol^{-1} K^{-1})
	(C) $NiCl_2 \cdot 2NaCl$ at pH 2		
	T/K = 322.37, f = 1.01		
0.1200	0.9876	0.9639	−263
0.2582	0.9758	0.9263	−237
0.5283	0.9574	0.8607	−214
0.9967	0.9382	0.7701	−169
	T/K = 359.29, f = 1.07		
0.1200	0.9880	0.9636	−274
0.2582	0.9770	0.9262	−240
0.5283	0.9610	0.8619	−204
0.9967	0.9430	0.7714	−163
	T/K = 398.79, f = 1.06		
0.1200	0.9870	0.9627	−310
0.2582	0.9760	0.9254	−257
0.5283	0.9606	0.8620	−206
0.9967	0.9447	0.7734	−154
	T/K = 453.31, f = 1.08		
0.1200	0.9840	0.9593	−447
0.2582	0.9724	0.9212	−339
0.5283	0.9574	0.8581	−248
0.9967	0.9429	0.7708	−173
	T/K = 498.49, f = 1.09		
0.1200	0.9811	0.9559	−596
0.2582	0.9681	0.9164	−443
0.5283	0.9528	0.8530	−308
0.9967	0.9455	0.7724	−172
	T/K = 549.72, f = 1.19		
0.1200	0.9763	0.9485	−969
0.2582	0.9634	0.9080	−658
0.5283	0.9546	0.8507	−362
0.9967	0.9577	0.7799	−142
	T/K = 572.73, f = 1.08		
0.1200	0.9694	0.9437	−1272
0.2582	0.9534	0.9015	−857
0.5287	0.9429	0.8437	−471
0.9967	0.9395	0.7674	−237
	(D) $NiCl_2 \cdot 2NaCl$ at pH 3		
	T/K = 322.37, f = 1.01		
0.1200	0.9878	0.9641	−256
0.2582	0.9757	0.9262	−238
0.5283	0.9574	0.8606	−214
0.9967	0.9382	0.7700	−169
	T/K = 359.29, f = 1.07		
0.1200	0.9880	0.9637	−272
0.2582	0.9782	0.9274	−220
0.5283	0.9601	0.8611	−211
0.9967	0.9433	0.7717	−162
	T/K = 398.79, f = 1.06		
0.1200	0.9871	0.9629	−303
0.2582	0.9760	0.9254	−256
0.5283	0.9609	0.8622	−204
0.9967	0.9448	0.7735	−154
	T/K = 453.31, f = 1.08		
0.1200	0.9840	0.9593	−446
0.2582	0.9725	0.9214	−336
0.5283	0.9565	0.8572	−256
0.9967	0.9428	0.7707	−174
	T/K = 498.49, f = 1.09		
0.1200	0.9812	0.9560	−592
0.2582	0.9686	0.9169	−433
0.5283	0.9530	0.8531	−307
0.9967	0.9451	0.7721	−174
	T/K = 549.72, f = 1.19		
0.1200	0.9766	0.9489	−955
0.2582	0.9635	0.9082	−655
0.5283	0.9644	0.8611	−251
0.9967	0.9573	0.7796	−144

Table II (*Continued*)

m^a/(mol kg^{-1})	P_s/P_w	$c_p/c_p{}^{0\ b}$	$C_{p,\phi}{}^c$/ (J mol^{-1} K^{-1})	m^a/(mol kg^{-1})	P_s/P_w	$c_p/c_p{}^{0\ b}$	$C_{p,\phi}{}^c$/ (J mol^{-1} K^{-1})
	T/K = 572.72, f = 1.08			0.5287	0.9407	0.8415	−496
0.1200	0.9694	0.9438	−1268	0.9967	0.9381	0.7662	−245
0.2582	0.9532	0.9013	−860				

[a] Moles of $NiCl_2$ or of $NiCl_2 \cdot 2NaCl$ per kilogram of water. [b] Calculated from eq 1 by using the correction factor, f = 1.02, 1.04, 1.04, 1.04, 1,05, 1.05, and 1.05 at T = 321, 358, 398, 452, 498, 549, and 572 K (*1*). [c] Calculated from eq 2 by using the specific heat capacity of pure water, $c_p{}^0$, given by ref *18*. The values (in J mol^{-1} g^{-1}) used are 4.139 at 321 K, 4.156 at 358.4 K, 4.215 at 398 K, 4.341 at 452.6 K, 4.966 at 549.1 K, and 5.350 at 572.1 K. [d] The results (*8*) at a molality of 0.2578 mol kg^{-1} were not used because the density of the solution did not agree with literature values. [e] The values of the heat loss correction factor, f, were determined by using 3.0 mol kg^{-1} NaCl as a chemical standard as recommended by White and Wood (*9*). The values of P_s/P_w for 3.000 mol kg^{-1} NaCl at the temperatures 322.18, 359.29, 398.79, 453.31, 498.49, 549.72, and 572.73 K were 0.9504, 0.9489, 0.9405, 0.9247, 0.9037, 0.8681, and 0.8150, respectively.

concentration determined by titration with $AgNO_3$. Other solutions were prepared by weight dilutions (corrected to vacuum) of this stock solution. The pH of the solutions was then adjusted by dropwise addition of 12 mol dm^{-3} HCl using a glass electrode as a pH indicator. Solutions at pH 2 and 3 were prepared.

The $NiCl_2 \cdot 2NaCl$ solutions were prepared in the same manner except that 2 mol of NaCl solid was added per mole of $NiCl_2$ to each solution before adjusting the pH. The Fisher certified NaCl was dried for 24 h at 498 K before use.

Calorimetric Apparatus. The calorimeter is a flow, heat capacity calorimeter described in detail previously (*8*). The instrument measures the electrical power necessary to give the same temperature rise when the sample solution and pure water are flowing in the calorimeter. The specific heat capacity of the solution at constant pressure, c_p, is then calculated by the equation

$$c_p/c_p{}^0 = [1 - f(P_s - P_w)/P_w](d_w/d_s) \qquad (1)$$

where c_p is the specific heat capacity of the solution, $c_p{}^0$ is the specific heat capacity of pure water at the experimental temperature and pressure, P_s is the electrical power when the sample solution is in the sample cell, P_w is the power when water is in the sample cell, f is a correction factor for heat losses, and d_w and d_s are the densities of water and of the aqueous solution at the experimental pressure and the temperature of the sample delay loop (25.0 °C). The correction factor, f, was calculated by using 3.000 mol kg^{-1} aqueous NaCl as a chemical standard (*9*).

The densities of the experimental solutions were determined at atmospheric pressure by using a Sodev vibrating tube densimeter (*10*, *11*). The results of the measurements are given in Table I. It was assumed that the ratio of the density of water to the density of the solution did not change as the pressure was increased from 1 atm to 17.7 MPa. Changes in d_w/d_s range from 0.02% at the lowest concentrations to 0.08% at the highest concentrations for the NaCl solutions (*1*). This can be considered an estimate of possible errors introduced by this assumption.

The apparent molar heat capacity, $C_{p,\phi}$, can be calculated from the specific heat capacity ratio, $c_p/c_p{}^0$, by using

$$C_{p,\phi} = (M_2 + 1/m)(c_p/c_p{}^0) - (1/m)c_p{}^0 \qquad (2)$$

where M_2 is the molar mass of the solute and m is the molality of the solution. (Note that, if M_2 is in grams, m must be in moles per gram of solvent to have consistent units.)

Results and Data Treatment

The results of the heat capacity measurements are given in Table II. The random errors experienced with the operation of this instrument indicate a limit of sensitivity of about 0.0001 in P_s/P_w and an accuracy of 1% in the measurement of $(P_s - P_w)/P_w$. In addition, there is a possible 5% systematic error in the measurement of the calibration factor f in eq 1. An examination of the results in Table II shows that almost all of the results are well within the expected accuracy calculated from the above *random* errors (the expected accuracy in $C_{p,\phi}$ varies from about 6 to 2 J mol^{-1} K^{-1} for $NiCl_2$ and from 16 to 3 J mol^{-1} K^{-1} for $NiCl_2 \cdot 2NaCl$ as the concentration goes from 0.12 to 3.0 mol kg^{-1}). The general agreement of the results at pH 2 and 3 indicates that hydrolysis effects are negligible. There are two regions where the difference in the results reported at pH 2 and 3 exceed those limits. For $NiCl_2$ at 453.31 K, the results at 0.1200 and 0.5286 mol kg^{-1} have errors of ±14 and ±30 J mol^{-1} K^{-1}, respectively. For the $NiCl_2 \cdot 2NaCl$, the results at 549.73 K and 0.5283 mol kg^{-1} have an error of ±56 J mol^{-1} K^{-1}. Both this point and the point at 1.0 mol kg^{-1} appear to be much lower than the result expected by drawing a smooth curve through the other points. It is most likely that this increased scatter is due to improper operation of the calorimeter, perhaps a small leak in the sample valve. However, it is also possible that there is a slow equilibrium taking place in solution (for instance, $Ni^{2+} + Cl^- \rightarrow NiCl^+$) which is incomplete during the time of the experiment (about 20 s). In the data treatment below we have used an average of the results at pH 2 and 3 as our best estimate of the true heat capacity.

Values of the apparent molar heat capacity at 298.15 K and 17.7 MPa were estimated by extrapolation of the present results. The extrapolated values were as follows: $C_{p,\phi}$ = −223, −210, −209, and −206 J mol^{-1} K^{-1} for $NiCl_2$ at m = 0.1202, 0.5286, 0.994, and 2.995 mol kg^{-1}, respectively, and $C_{p,\phi}$ = −282, −260, −231, and −183 J mol^{-1} K^{-1} for $NiCl_2 \cdot 2NaCl$ at m = 0.1200, 0.2582, 0.5283, and 0.9967 mol kg^{-1}, respectively. The extrapolated values should be only slightly less accurate than the measured values.

Discussion

Comparison with Other Results. The heat capacities given in Table II are quite different from the results for NaCl of Smith-Magowan and Wood (*1*). The striking difference is that for $NiCl_2$ the heat capacities are fairly constant as a function of temperature, whereas, for NaCl at low concentrations, the heat capacities become very large and negative. Smith-Magowan and Wood attributed this behavior for the NaCl solutions to the electrostatic effects of the ions on the solvent at low concentrations. This effect is predicted by the Born equation (*1*), so that for any strong electrolyte the large negative apparent molar heat capacities at low concentrations and high temperatures are expected. The present results, then, indicate that $NiCl_2$ at high temperatures is mainly un-ionized. Previous spectroscopic measurements on $NiCl_2$ solutions at high temperatures have shown an increased degree of association of this electrolyte (*2*), so the present indication that it is mainly un-ionized at 572 K is reasonable.

Examining the results of mixtures of NaCl and $NiCl_2$ shows that the apparent molar heat capacity becomes large and

Table III. Values of the Apparent Molar Heat Capacity, $C_{p,\phi}$, and Partial Molar Heat Capacity and Their Integrals for $NiCl_2$ and $NiCl_2 \cdot 2NaCl$ at 17.7 MPa

(A) $C_{p,\phi}$

m	T/K	298.15	350.00	400.00	450.00	500.00	550.00	575.00
				(1) $NiCl_2$				
0.10		−224	−217	−235	−297	−329	−344	−359
0.20		−219	−205	−212	−267	−267	−260	−259
0.30		−215	−196	−195	−244	−223	−200	−187
0.40		−212	−190	−182	−224	−189	−155	−136
0.50		−210	−185	−173	−205	−165	−123	−99
0.60		−209	−182	−166	−188	−147	−100	−75
0.70		−209	−180	−161	−172	−135	−84	−60
0.80		−209	−178	−157	−159	−126	−72	−50
0.90		−209	−177	−155	−147	−119	−62	−43
1.00		−209	−177	−153	−137	−114	−54	−38
1.50		−209	−175	−148	−113	−99		
2.00		−208	−176	−148	−112	−94		
2.50		−207	−177	−150	−120	−92		
3.00		−206	−178	−152	−130	−91		
				(2) $NiCl_2 \cdot 2NaCl$				
0.10		−286	−275	−319	−458	−632	−1023	−1386
0.20		−269	−241	−276	−368	−497	−774	−1029
0.30		−255	−223	−246	−311	−411	−586	−794
0.40		−244	−215	−225	−277	−357	−439	−639
0.50		−234	−210	−209	−252	−316	−331	−530
0.60		−223	−203	−195	−233	−282	−259	−449
0.70		−213	−194	−183	−215	−251	−213	−387
0.80		−202	−184	−173	−199	−222	−182	−335
0.90		−192	−174	−163	−185	−195	−161	−292
1.00		−183	−164	−154	−171	−170	−143	−252

(B) $[1/(T-298.15\ \mathrm{K})]\int_{298.15\,\mathrm{K}}^{T} C_{p,\phi}\,\mathrm{d}T$

m	T/K	350.00	400.00	450.00	500.00	550.00	575.00
			(1) $NiCl_2$				
0.10		−216	−220	−235	−255	−271	−278
0.20		−208	−207	−217	−231	−237	−239
0.30		−202	−198	−205	−213	−213	−211
0.40		−198	−191	−195	−199	−194	−189
0.50		−195	−186	−187	−188	−179	−173
0.60		−193	−183	−181	−179	−168	−160
0.70		−191	−181	−176	−172	−159	−151
0.80		−191	−179	−172	−166	−152	−144
0.90		−190	−178	−169	−161	−147	−138
1.00		−190	−178	−167	−157	−142	−134
1.50		−190	−177	−161	−148		
2.00		−190	−177	−161	−149		
2.50		−191	−178	−162	−153		
3.00		−192	−179	−165	−159		
			(2) $NiCl_2 \cdot 2NaCl$				
0.10		−270	−281	−315	−370	−454	−522
0.20		−248	−251	−273	−311	−371	−419
0.30		−235	−233	−247	−275	−315	−349
0.40		−226	−222	−230	−253	−277	−300
0.50		−218	−213	−217	−236	−249	−264
0.60		−209	−204	−205	−221	−226	−237
0.70		−199	−194	−194	−207	−207	−214
0.80		−189	−184	−183	−193	−190	−196
0.90		−180	−174	−173	−179	−175	−179
1.00		−170	−164	−163	−167	−162	−164

(C) $[1/(T-298.15\ \mathrm{K})]\{\int_{298.15\,\mathrm{K}}^{T} C_{p,\phi}\mathrm{d}T' - T\int_{298.15\,\mathrm{K}}^{T}(C_{p,\phi}/T')\mathrm{d}T'\}$

m	T/K	350.00	400.00	450.00	500.00	550.00	575.00
			(1) $NiCl_2$				
0.10		17.8	33.6	48.6	64.4	80.4	88.4
0.20		17.2	32.1	45.9	60.2	74.1	80.8
0.30		16.8	31.1	43.9	57.1	69.5	75.2
0.40		16.5	30.4	42.4	54.8	65.9	71.0
0.50		16.3	29.8	41.4	53.0	63.2	67.7
0.60		16.2	29.5	40.7	51.6	61.1	65.2
0.70		16.1	29.2	40.2	50.6	59.4	63.3
0.80		16.1	29.1	39.9	49.8	58.2	61.8
0.90		16.1	29.0	39.7	49.2	57.2	60.6
1.00		16.1	28.9	39.6	48.7	56.5	59.7
1.50		16.1	28.8	39.3	47.6		
2.00		16.1	28.8	39.5	47.7		

Table III (*Continued*)

m	T/K	350.00	400.00	450.00	500.00	550.00	575.00
2.50		16.2	28.9	39.8	48.1		
3.00		16.2	29.0	40.3	48.7		
(2) $NiCl_2 \cdot 2NaCl$							
0.10		22.3	42.4	62.4	85.2	112.0	127.5
0.20		20.8	38.5	56.0	75.0	96.7	109.0
0.30		19.8	36.2	52.1	68.6	87.1	97.1
0.40		19.0	34.7	49.6	64.6	81.1	89.5
0.50		18.3	33.5	47.6	61.4	76.4	83.7
0.60		17.5	32.1	45.5	58.3	72.1	78.4
0.70		16.7	30.6	43.2	55.2	67.8	73.5
0.80		15.8	29.1	41.0	52.2	63.7	68.9
0.90		15.0	27.6	38.7	49.3	59.8	64.5
1.00		14.3	26.1	36.6	46.5	56.0	60.3

(D) $\overline{C}_{p,2}$

m	T/K	298.15	350.00	400.00	450.00	500.00	550.00	575.00
(1) $NiCl_2$								
0.10		−217	−202	−207	−261	−254	−242	−237
0.20		−209	−185	−173	−216	−164	−120	−92
0.30		−205	−174	−151	−180	−108	−45	−5
0.40		−203	−168	−139	−147	−75	−2	39
0.50		−204	−166	−132	−117	−60	15	50
0.60		−206	−166	−131	−89	−59	14	38
0.70		−208	−167	−131	−68	−61	12	25
0.80		−209	−169	−132	−55	−64	11	14
0.90		−210	−170	−133	−49	−66	15	10
1.00		−210	−171	−135	−50	−67	24	14
1.50		−207	−175	−143	−86	−74		
2.00		−205	−180	−153	−131	−83		
2.50		−202	−183	−162	−167	−87		
3.00		−200	−185	−167	−187	−81		
(2) $NiCl_2 \cdot 2NaCl$								
0.10		−265	−232	−267	−347	−467	−721	−949
0.20		−238	−189	−206	−224	−281	−350	−451
0.30		−219	−191	−173	−183	−212	−86	−232
0.40		−201	−193	−152	−164	−174	68	−127
0.50		−181	−180	−135	−145	−133	115	−67
0.60		−160	−153	−119	−122	−86	84	−27
0.70		−140	−126	−105	−100	−42	47	6
0.80		−122	−102	−92	−79	−1	19	40
0.90		−105	−82	−79	−59	38	9	82
1.00		−90	−65	−66	−39	76	22	134

(E) $[1/(T-298.15\ \mathrm{K})]\int_{298.15\ \mathrm{K}}^{T}\overline{C}_{p,\phi}\,\mathrm{d}T$

m	T/K	350.00	400.00	450.00	500.00	550.00	575.00
(1) $NiCl_2$							
0.10		−206	−204	−214	−226	−230	−231
0.20		−194	−185	−189	−190	−181	−174
0.30		−187	−174	−172	−166	−148	−137
0.40		−183	−168	−160	−149	−127	−114
0.50		−182	−166	−152	−138	−115	−101
0.60		−183	−167	−148	−130	−109	−97
0.70		−185	−169	−145	−125	−106	−94
0.80		−186	−171	−144	−123	−104	−93
0.90		−187	−172	−144	−123	−103	−93
1.00		−188	−173	−145	−124	−103	−92
1.50		−190	−176	−154	−140		
2.00		−193	−180	−165	−161		
2.50		−195	−184	−173	−181		
3.00		−196	−187	−177	−196		
(2) $NiCl_2 \cdot 2NaCl$							
0.10		−243	−244	−264	−298	−353	−396
0.20		−213	−203	−207	−218	−235	−250
0.30		−204	−193	−186	−193	−180	−177
0.40		−194	−185	−173	−179	−147	−135
0.50		−177	−170	−157	−159	−123	−108
0.60		−153	−146	−136	−133	−102	−90
0.70		−131	−124	−117	−107	−83	−73
0.80		−110	−104	−99	−84	−65	−57
0.90		−92	−86	−83	−63	−47	−39
1.00		−77	−70	−68	−44	−27	−19

Table III (*Continued*)

(F) $[1/(T - 298.15\ \mathrm{K})]\{\int_{298.15\mathrm{K}}^{T}\overline{C}_{p,2}\mathrm{d}T' - T\int_{298.15\mathrm{K}}^{T}(\overline{C}_{p,2}/T')\mathrm{d}T'\}$

m	T/K	350.00	400.00	450.00	500.00	550.00	575.00
(1) $NiCl_2$							
0.10		17.1	31.8	45.3	59.3	72.7	79.2
0.20		16.3	29.7	41.3	53.2	63.4	68.0
0.30		15.8	28.5	38.8	49.2	57.4	60.8
0.40		15.6	27.8	37.5	46.6	53.4	56.1
0.50		15.5	27.6	37.1	45.1	51.1	53.3
0.60		15.7	27.7	37.3	44.5	50.1	52.1
0.70		15.8	27.9	37.6	44.3	49.6	51.5
0.80		15.9	28.1	37.9	44.3	49.5	51.3
0.90		16.0	28.2	38.2	44.4	49.6	51.4
1.00		16.1	28.3	38.4	44.6	49.9	51.6
1.50		16.2	28.7	39.3	46.6		
2.00		16.3	29.1	40.6	49.0		
2.50		16.5	29.4	41.8	50.9		
3.00		16.6	29.5	43.0	52.0		
(2) $NiCl_2 \cdot 2NaCl$							
0.10		20.5	37.6	54.6	72.7	93.2	104.8
0.20		18.5	32.4	45.9	58.7	72.3	79.2
0.30		17.2	31.0	43.2	54.0	65.1	69.5
0.40		16.0	29.6	41.1	50.8	60.7	63.6
0.50		14.4	27.1	37.4	46.0	54.5	56.6
0.60		12.6	23.5	32.3	39.8	46.3	48.1
0.70		10.9	20.0	27.4	33.8	38.6	40.1
0.80		9.4	16.8	23.0	28.3	31.5	32.7
0.90		8.0	14.1	19.0	23.4	25.1	25.8
1.00		6.8	11.7	15.6	19.0	19.3	19.4

negative at low concentrations and high temperatures, indicating that there are substantial quantities of ions present in these solutions. The results cannot distinguish whether the anion present is Cl^-, $NiCl_3^-$, or $NiCl_4^{-2}$.

Calculation of Enthalpy and Free Energy at High Temperatures. The heat capacity measurements at the lowest concentrations reported in this paper do not approach the Debye–Hückel limiting law. For this reason, the results cannot be extrapolated to infinite dilution and the standard-state thermodynamic properties at infinite dilution cannot be determined. However, we can calculate changes in free energies and enthalpies for the concentrated solution, and this allows calculation of high-temperature thermodynamic equilibria even when the standard-state values are unknown. The development of appropriate equations for these calculations is given below. We start with the chemical potential defined in the usual way

$$\mu_i = [\partial G/\partial n_i]_{n_j,T,p} = \mu_i^{\theta} + RT \ln \gamma_i + RT \ln m_i \tag{3}$$

where γ_i is the molal scale activity coefficient. In order to get equations for the changes in chemical potential and enthalpy as a function of temperature, we use the standard thermodynamic relations

$$[\partial(\mu_i/T)/\partial(1/T)]_p = \bar{H}_i \tag{4}$$

$$\partial\bar{H}_i/\partial T = \bar{C}_{p,i} \tag{5}$$

where $\bar{H}_i$ is the partial molar enthalpy and $\bar{C}_{p,i}$ is the partial molar heat capacity of the solute species, i. The partial molar heat capacity, $\bar{C}_{p,i}$, is calculated from the measured apparent molar heat capacity, $C_{p,\phi}$, using

$$\bar{C}_{p,i} = C_{p,\phi} + m_i[\partial C_{p,\phi}/\partial m_i]_{T,p,m_j} \tag{6}$$

Integration of eq 5 gives

$$\bar{H}_i(T,p,m_i) = \bar{H}_i(T_{\mathrm{R}},p,m_i) + \int_{T_{\mathrm{R}}}^{T} \bar{C}_{p,i}(T,p,m_i)\,\mathrm{d}T \tag{7}$$

for the partial molar enthalpy, $\bar{H}_i$. Similarly, the apparent molar enthalpy, H_{ϕ}, is given by

$$H_{\phi}(T,p,m) = H_{\phi}(T_{\mathrm{R}},p,m) + \int_{T_{\mathrm{R}}}^{T} C_{p,\phi}(T,p,m)\,\mathrm{d}T \tag{8}$$

Integrating eq 4 and using eq 7 gives us the final result

$$\mu_i(T,p,m_i)/T = \mu_i(T_{\mathrm{R}},p,m_i)/T_{\mathrm{R}} + \bar{H}_i(T_{\mathrm{R}},p,m_i) \times (1/T - 1/T_{\mathrm{R}}) + \int_{T_{\mathrm{R}}}^{T}\left[\int_{T_{\mathrm{R}}}^{T'} \bar{C}_{p,i}(T'',p,m_i)\,(\mathrm{d}T'')\right] \mathrm{d}(1/T') \tag{9}$$

where T_{R} is a reference temperature (normally 298.15 K). Integrating by parts yields

$$\mu_i(T,p,m_i)/T = \mu_i(T_{\mathrm{R}},p,m_i)/T_{\mathrm{R}} + \bar{H}_i(T_{\mathrm{R}},p,m_i)(1/T - 1/T_{\mathrm{R}}) + (1/T)\int_{T_{\mathrm{R}}}^{T} \bar{C}_{p,i}(T,p,m_i)\,\mathrm{d}T - \int_{T_{\mathrm{R}}}^{T} (\bar{C}_{p,i}(T,p,m_i)/T)\,\mathrm{d}T \tag{10}$$

where we have now indicated the specific temperature, pressure, and molality dependence for μ_i, $\bar{H}_i$, and $\bar{C}_{p,i}$.

Normally, the integrals in eq 10 are broken into their standard-state and excess parts, but this is not necessary in order to calculate high-temperature equilibria at finite concentrations. The equations above allow the calculation of chemical potentials, partial molar and apparent molar enthalpies for any species, given their values at room temperature and the appropriate integrals of the apparent molar and partial molar heat capacities. If the terms in eq 10 are known for all of the species participating in a chemical equilibrium, then the stoichiometric equilibrium constant, $K_m(T,p,m)$, can be calculated by combining eq 10 for each species in the equilibrium with the standard definition of the equilibrium constant ($K_a(T,p)$). The result is

$$-R \ln K_m(T,p,m) = -R \ln \{(K_a(T,p)/(\prod_i \gamma_{i,T}^{\nu_i})\}$$
$$= -R \ln \{K_a(T_R,p)/(\prod_i \gamma_{i,T_R}^{\nu_i})\} + \sum_i \nu_i \bar{H}_i(T_R,p,m)(1/T - 1/T_R) + (1/T) \times \int_{T_R}^{T} \sum_i \nu_i \bar{C}_{p,i}(T,p,m_i)\,\mathrm{d}T - \int_{T_R}^{T} [\sum \nu_i \bar{C}_{p,i}(T,p,m_i)/T]\,\mathrm{d}T \quad (11)$$

where the ν_i values are the species coefficients in the balanced chemical equation. Thus, using eq 11, one can calculate the stoichiometric equilibrium constant at T, p, and m given room-temperature values for the thermodynamic equilibrium constant ($K_a(T_R,p)$), the activity coefficients, and the partial molar enthalpies at room temperature, together with partial molar heat capacity integrals as a function of temperature at the molality and pressure of interest.

For convenience in using the present results for calculating high-temperature thermodynamic equilibrium, we have evaluated the integrals appearing in eq 7–10 using a cubic spline fit of the experimental measurements. The procedure was to use a cubic spline to fit the heat capacity results at each temperature as a function of molality and calculate values of the apparent molar and partial molar heat capacity at round values of molality. This was then repeated at each experimental temperature and the integrals were then calculated by fitting the apparent molar and partial molar heat capacities as a function of temperature at the rounded molalities with a cubic spline. The results of these calculations are given in Table III. For convenience in interpolating the tables, the integrals are divided by the difference in temperature to give a more slowly varying function of temperature.

Calculations for Any Mixture of $NiCl_2$ and NaCl. There are a variety of mixture rules that allow the estimation of the properties of any mixture of electrolytes from the properties of the pure solutions. The present data, together with the data of Smith-Magowan and Wood (*1*) on pure NaCl, allow a test of these mixture rules. The most common mixture rule is that of Young and Smith, now known as Young's rule (*12*). This states that the apparent molar properties of a solution (free energy, enthalpy, volume, or heat capacity) are to a first approximation unchanged if the solutions to be mixed are at the same concentration. Young only applied this rule to mixtures of the same charged type. For mixtures of differing charged type, it is necessary to choose the concentration scale. Both experiment and theory indicate that constant ionic strength is the appropriate rule for low concentrations where the Debye–Hückel effects predomininate. However, at very high concentrations where ion association is beginning to occur, mixing at constant equivalents per kilogram of solvent is more appropriate (*13*, *14*). The mixing equations of Reilley and Wood also show that the rule is best applied to mixtures with either a common anion or a common cation and that the rule need not be applied to any other kind of mixture (*16*, *17*). Applying this rule at constant ionic strength to the apparent molar heat capacity gives the following equation:

$$n_{Na_2NiCl_4} C_{p,\phi}(NiCl_2{\cdot}2NaCl, I) = n_{NaCl} C'_{p,\phi}(NaCl, I) + n_{NiCl_2} C'_{p,\phi}(NiCl_2, I) \quad (12)$$

or

$$C_{p,\phi}(NiCl_2{\cdot}2NaCl, I) = 2C'_{p,\phi}(NaCl, I) + C'_{p,\phi}(NiCl_2, I) \quad (13)$$

where the superscript prime indicates the apparent molar heat capacity of the solute in a pure solution of that solute. As an example of the use of this equation at an ionic strength of 3, we would look up the apparent molar heat capacity of NaCl in a 3 *m* NaCl solution ($I = 3$), multiply this by 2, and add the apparent molar heat capacity of a pure $NiCl_2$ solution at a molality of 1 ($I = 3$) and compare it with the experimental apparent molar heat capacity of $NiCl_2{\cdot}2NaCl$ at a molality of 0.6 ($I = 3$).

Table IV. Predictions of $C_{p,\phi}$ ($NiCl_2{\cdot}2NaCl$)[a] According to Eq 13

	I/(mol kg^{-1}) = 3		I/(mol kg^{-1}) = 1		I/ (mol kg^{-1}) = 0.5	
T/K	$C_{p,\phi}$	Δ[b]	$C_{p,\phi}$	Δ[b]	$C_{p,\phi}$	Δ[b]
350	−165	38	−230	11	−256	+19
400	−171	24	−262	14	−321	−2
450	−207	26	−393	−25	−478	−20
500	−272	10	−511	−14	−667	−35
550	−404	−91	−844	−70	−1054	−31
600	−610	−161	−1174	−145	−1564	−178

[a] Units: J mol^{-1} K^{-1}. [b] $\Delta = C_{p,\phi}(\text{calcd}) - C_{p,\phi}(\text{exptl})$.

Equation 13 was tested by using the present results together with a spline fit of the NaCl data of Smith-Magowan and Wood (*1*). The results are given in Table IV at ionic strengths of 3, 1, and 0.5. The predicted apparent molar heat capacities are not much different from the experimental ones, particularly at low temperatures, where both electrolytes are strong electrolytes. At high temperatures, the calculation is still a useful approximation.

Young's rule for mixing at a constant equivalence per kilogram (E) was also tried. The equation for this mixture rule is the same as eq 13 except that the heat capacities of all of the solutions are looked up at the same value of $E = \Sigma m_+ z_+$; that is, at $E = 3$ we would add twice the apparent molar heat capacity of 3 *m* NaCl to the apparent molar heat capacity of 1.5 *m* $NiCl_2$ to get the apparent molar heat capacity of $NiCl_2{\cdot}2NaCl$ at molality of 0.75 mol of $NiCl_2{\cdot}2NaCl$ per kilogram of water. This mixing rule proved to be slightly better at the low temperatures but considerably poorer at high temperatures, so that overall the constant ionic strength rule is preferred for this system.

There is another mixing rule that is appropriate for a mixture of a nonelectrolyte with an electrolyte. This would be appropriate if $NiCl_2$ is un-ionized in these solutions at high concentrations. This rule ignores the interactions of the nonelectrolyte ($NiCl_2$) with the salt (NaCl) and states that the change upon mixing of apparent molar free energy, enthalpy, volume, or heat capacity is zero after the two solutions are mixed and water is extracted from the mixture such that the concentrations of the two solutes are the same in the initial and final solutions (*17*). The resulting equation for the apparent molar heat capacity is again identical with eq 13 except that now the apparent molar heat capacities are looked up at molalities that are identical in the initial and final solutions. That is, the apparent molar heat capacity of a 1.5 *m* $NiCl_2{\cdot}2NaCl$ solution is equal to twice the apparent molar heat capacity of a 3 *m* NaCl plus the heat capacity of 1.5 *m* $NiCl_2$. A test of this equation with the present data showed that the results were not nearly as good as the other two rules, particularly at the high temperatures. The failure of this mixing rule would be expected if, when mixed with NaCl, the un-ionized $NiCl_2$ reacts to form either $NiCl_3^-$ or $NiCl_4^{2-}$. So the present results indicate that these species become more important at higher temperatures.

Calculation of Equilibria in Any Mixture of $NiCl_2$ and NaCl. Assuming that Young's mixture rule at constant ionic strength is exactly correct, we can calculate the partial molar heat capacity of $NiCl_2$ in any mixture with NaCl. From eq 13 we can calculate the heat capacity of a solution containing 1000 g of water, C_p, as

$$C_p = 1000c_p^{\,0} + m_{NaCl} C'_{p,\phi}(NaCl, I) + m_{NiCl_2} C'_{p,\phi}(NiCl_2, I) \quad (14)$$

(The accuracy of the present data does not warrant adding correction terms to account for systematic deviations from

Young's rule. The first-order correction would involve adding $y(1-y)I^2Rc_0$ to eq 14 (*12*, *16*, *17*) and adjusting c_0 to fit the experimental results on mixtures.) The partial molar heat capacity of $NiCl_2$ in this mixed solution is then given by

$$\bar{C}_p(\mathrm{NiCl_2}) = (\partial C_p/\partial m_{\mathrm{NiCl_2}})_{T,P,m_{\mathrm{NaCl}}} = \\ C'_{p,\phi}(\mathrm{NiCl_2},I) + m_{\mathrm{NiCl_2}}(\partial C'_{p,\phi}(\mathrm{NiCl_2},I)/\partial m_{\mathrm{NiCl_2}}) \quad (15)$$

Using the definition for the partial molar heat capacity of a pure solution, eq 8, and $I = 3m$ in a pure $NiCl_2$ solution, we find

$$\bar{C}_p(\mathrm{NiCl_2}) = (1 - 3m/I)C'_{p,\phi}(\mathrm{NiCl_2},I) + (3m/I)\bar{C}'_p(\mathrm{NiCl_2},I) \\ = (1-y)C'_{p,\phi}(\mathrm{NiCl_2},I) + y\bar{C}'_p(\mathrm{NiCl_2},I) \quad (16)$$

where y is the ionic strength fraction of $NiCl_2$ in the mixture. Thus, using eq 16 we can estimate the partial molar heat capacity of $NiCl_2$ in any mixture, and this estimate has been found to be reasonably accurate in the case of $NiCl_2$–NaCl mixtures. (This prediction would probably be reasonably accurate for mixtures with other alkali metal chlorides. It could be very inaccurate in mixtures with other anions because of the change in nickel complexes formed.) To calculate the partial molar heat capacity of $NiCl_2$ in any mixture, we use eq 16 and the present results for $C'_{p,\phi}$ and $\bar{C}'_p$ in Table III, parts A1 and D1. If integrals of the partial molar heat capacity are desired, they can be obtained by integrating eq 16 and using the integrals in Table III, parts B1 and E1.

It is interesting to note the two extreme cases of eq 16; in a pure $NiCl_2$ solution ($y = 1$) the partial molar heat capacity is, of course, just the partial molar heat capacity of pure $NiCl_2$. However, in a NaCl solution with just a trace of $NiCl_2$ ($y = 0$), the *partial* molar heat capacity of $NiCl_2$ is equal to the *apparent* molar heat capacity of pure $NiCl_2$ at the same ionic strength as the NaCl solution. Thus, if Young's rule is accurate, the partial molar heat capacity of $NiCl_2$ at low concentrations in any mixture of electrolytes is equal to the apparent molar heat capacity of pure $NiCl_2$ at the ionic strength of the mixture.

Literature Cited

(1) Smith-Magowan, D.; Wood, R. H. *J. Chem. Thermodyn.* **1981**, *13*, 1047.
(2) Lüdemann, Von H.-D.; Franck, E. U. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 514.
(3) Garnsey, R. Central Electricity Research Laboratories, Leatherhead, G. B., Laboratory Note No. RD/L/N, March 1979.
(4) Postlethwaite, J. *Electrochim. Acta* **1967**, *12*, 33.
(5) Tomlinson, M. "High Temperature High Pressure Electrochemistry in Aqueous Solutions"; Jones, D. de G., Slater, J., Staehle, R. W., Eds.; National Association of Corrosion Engineers: Houston, TX, 1976.
(6) MacDonald, D. D. Pinawa, Manitoba, Canada, 1972, Atomic Energy of Canada Limited Report No. AECL-4139.
(7) Tremaine, P. R.; LeBlanc, J. C. *J. Chem. Thermodyn.* **1980**, *12*, 521.
(8) Smith-Magowan, D. Ph.D. Dissertation, University of Delaware, Newark, DE, May 1980.
(9) White, D. E.; Wood, R. H. *J. Solution Chem.*, in press.
(10) Picker, P.; Tremblay, E.; Jolicoeur, D. *J. Solution Chem.* **1974**, *3*, 377.
(11) Sodev Inc., P.O. Box 1060, Sherbrooke, Quebec, Canada J1H 5L3; Model 01D.
(12) Young, T. F.; Smith, M. B. *J. Phys. Chem.* **1954**, *58*, 716.
(13) Reilly, P. J.; Wood, R. H. *J. Phys. Chem.* **1972**, *76*, 3474.
(14) Wood, R. H.; Smith, D. E.; Chen, H. K. W.; Thompson, P. T. *J. Phys. Chem.* **1975**, *79*, 1532.
(15) Wood, R. H.; Falcone, M. V. *J. Phys. Chem.* **1975**, *79*, 1540.
(16) Reilly, P. J.; Wood, R. H. *J. Phys. Chem.* **1969**, *73*, 4292.
(17) Andersen, W. L.; Wood, R. H. "Water: A Comprehensive Treatise"; Franks, F., Ed.; Plenum Press: New York, 1973; Vol. 3, Chapter 2.
(18) Cassel, R. B.; Wood, R. H. *J. Phys. Chem.* **1974**, *78*, 2460.
(19) Haar, L.; Gallagher, J.; Kell, G. S. Proceedings of the International Association for the Properties of Steam, Sept 1979. See also National Bureau of Standards Internal Report No. 81-2253.

Received for review November 6, 1981. Accepted April 14, 1982. We thank the Electric Power Research Institute (contract no. RP 1167-4) for their support of this work.

Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous Mixtures of NaCl and $SrCl_2$ at 25 °C

Joseph A. Rard* and Donald G. Miller

University of California, Lawrence Livermore National Laboratory, Livermore, California 94550

The osmotic and activity coefficients of aqueous mixtures of NaCl and $SrCl_2$ have been determined at 25 °C by the isopiestic method. These measurements extend from moderate concentrations to the crystallization limits of the mixtures; results are in excellent agreement (0.1–0.2%) with published isopiestic data in overlapping regions of concentration. Osmotic and activity coefficients for NaCl–$SrCl_2$ mixtures are reliably represented by both Pitzer's equations and Scatchard's neutral electrolyte equations.

Introduction

Mixed electrolyte solutions occur in many important geochemical, biochemical, and industrial systems. Activity coefficient data are important for understanding chemical speciation, reactions, and solubility for these solutions.

Activity measurements are available for a fair number of mixed electrolyte aqueous solutions (*1*), mainly at 25 °C. Analysis of activity data for mixed electrolyte solutions involves relating these data to activities of the constituent binary solutions, generally at the total ionic strength of the mixture. However, the ionic strengths of concentrated mixtures can become higher than that of the least-soluble constituent in its binary solution. Most experimenters restrict their mixed-electrolyte measurements to ionic strengths for which binary data exist. This is unfortunate since some important processes, such as dissolution and leaching in salt beds, may require activity data at higher concentrations. Also, data for these higher concentrations will become analyzable by standard methods when better estimation procedures become available for properties of supersaturated binary solutions.

Macaskill et al. (*2*) have recently published highly accurate isopiestic data for NaCl–$SrCl_2$ mixtures to ionic strengths at 4.3–5.9. In the present publication these measurements are extended to the highest accessible concentrations for these mixtures ($I = 6.7$–11.2), thereby completing the study at 25 °C. These data have potential applications to the transport of ^{90}Sr in the natural environment.

Experimental Section

The isopiestic measurements were performed at 25.00 ± 0.005 °C (IPTS-68) using chambers that have previously been

0021-9568/82/1727-0342$01.25/0