concentration, indicating the structure-promoting nature of the solute.

The variation of $[\Delta T_{z,str}]_{expt}$ for this system is positive (Figure 6) and increases with the concentration of 3-pentanone.

All the three studies (TACM, TSVM, and TSAIM) indicate that the solute 3-pentanone behaves as a structure maker. It may be mentioned here that each study is confined to a different temperature range and all the three studies effectively cover a temperature range of 44–78 °C. The present results clearly show that the solute behaves as a structure maker in the temperature range studied.

Literature Cited

(1) Wada, G.; Umeda, S. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 646.
(2) Wada, G.; Umeda, S. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1797.
(3) Sakurai, M.; Komatsu, T.; Nakagama, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1038.
(4) Macdonald, D. D.; Hyne, J. B. *Can. J. Chem.* **1976**, *54*, 405.
(5) Macdonald, D. D.; Hyne, J. B. *J. Solution Chem.* **1976**, *5*, 405.
(6) Franks, F.; Watson, B. *Trans. Faraday Soc.* **1967**, *63*, 329.
(7) Subbarangaiah, K.; Manohara Murthy, N.; Subrahmanyam, S. V. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2200.
(8) Manohara Murthy, N.; Subrahmanyam, S. V. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 2069.
(9) Manohara Murthy, N.; Subrahmanyam, S. V. *Can. J. Chem.* **1978**, *56*, 2412.
(10) Subrahmanyam, S. V.; Manohara Murthy, N. *J. Solution Chem.* **1975**, *4*, 347.
(11) Ramanjappa, T.; Rajagopal, E. *Can. J. Chem.* **1988**, *66*, 371.
(12) Manohara Murthy, N.; Subrahmanyam, S. V. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2589.
(13) Subrahmanyam, S. V.; Manohara Murthy, N. *Z. Phys. Chem. Munich* **1974**, *88*, 116.
(14) Manohara Murthy, N.; Subrahmanyam, S. V. *J. Acoust. Soc. India* **1979**, *7*, 79.
(15) Subrahmanyam, S. V.; Raghavan, C. V. *Acustica* **1975**, *28*, 215.
(16) Ramanjappa, T.; Rajagopal, E. *Bull. Chem. Soc. Jpn.*, in press.
(17) Kiyohara, O.; Benson, G. C. *J. Chem. Thermodyn.* **1977**, *9*, 315.
(18) Roux, G.; Perron, G.; Desnoyers, J. E. *Can. J. Chem.* **1978**, *56*, 2808.
(19) Subrahmanyam, S. V.; Hyderkhan, V.; Raghavan, C. V. *J. Acoust. Soc. Am.* **1989**, *46*, 272.

Received January 20, 1988. Accepted June 13, 1988.

Heat Capacity of Aqueous $MgCl_2$ from 349 to 598 K

Dorothy E. White, Jeffrey A. Gates,† David M. Tillet, and Robert H. Wood*

Department of Chemistry, University of Delaware, Newark, Delaware 19716

A differential flow heat-capacity calorimeter has been used to measure the heat capacity of $MgCl_2$(aq) at molalities from 0.03 to 2.26 mol kg^{-1}, temperatures from 350 to 600 K, and pressures from 2 to 18 kPa. The results show the very large and negative apparent molar heat capacities at high temperatures and low molalities found previously for NaCl(aq), NaBr(aq), KCl(aq), LiCl(aq), and $CaCl_2$(aq).

Introduction

The work presented here is part of a continuing investigation of heat capacities of aqueous electrolytes at high temperatures using flow-calorimetric techniques (*1–6*). Very large and negative values of the apparent molar heat capacity, $C_{p,\phi}$, have been found for aqueous NaCl (*1*, *2*), KCl (*5*), NaBr (*4*), LiCl (*6*), and $CaCl_2$ (*3*) at high temperatures and low molalities. This has been attributed to large interactions between ions in water, together with the changes in properties of water as its critical point is approached (*1*, *7*). A knowledge of the properties of aqueous salt solutions at high temperature is important for understanding a variety of chemical processes that occur at high temperatures, including mineral geochemistry, the behavior of geothermal fluids, and corrosion in electric-power boilers. In this paper we report $C_{p,\phi}$ of $MgCl_2$(aq) at temperatures up to 600 K. For convenience in interpolating our results, the data are represented with a three-dimensional cubic spline.

Experimental Section

Solutions. A stock solution of approximately 3.0 mol kg^{-1} $MgCl_2$ was prepared from Baker Analyzed Reagent grade $MgCl_2 \cdot 6H_2O$ (less than 0.013% impurities) and distilled/deionized water. Other solutions were prepared by mass dilution of the stock solution. Concentrations of all solutions were determined (±0.1%) by titration with aqueous $AgNO_3$.

Heat Capacity Measurements. The high-temperature flow heat-capacity calorimeter has been described in detail previously (*1*, *14*). The calorimeter was operated at a water flow rate of 0.033 cm^3 s^{-1} and with heater power of 0.31 W, resulting in temperature rises of 1.1–1.8 K. The reported temperatures are the average of the initial and final temperatures of the solution. The back-pressure regulator was calibrated (±0.25 MPa) by using a Heise CM gauge (0–27 MPa). A minimum of three heat-capacity measurements were made for each molality. The instrument measured the electrical power necessary to give the same temperature rise when the sample solution and pure water were flowing in the calorimeter. The specific heat capacity of the sample solution at constant pressure, c_p, was then calculated by the equation

$$c_p/c_p^0 = \{1 + f(P_s - P_w)/P_w\}(d_w/d_s) \quad (1)$$

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 power when water is in the sample cell, f is a correction factor for heat losses (*15*), and d_w and d_s are the densities of water and of the aqueous salt solution at the experimental pressure and the temperature of the sample loop (298.15 K). The correction factor, f, was calculated at each temperature by using 3.0 mol kg^{-1} NaCl as a chemical standard (*15*). The solution densities were those of Gates and Wood (*16*). The densities of H_2O were obtained from the equation of state of Haar, Gallagher, and Kell (*17*).

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

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

where M_2 is the molar mass of the solute and m is the molality of the aqueous salt solution.

Boundary Effects. Fortier, Benson, and Picker (*18*) have shown that errors can arise in flow calorimeters because of mixing and volume changes at the boundary between the sample and reference solutions. This effect can be large when the sample and reference fluids are quite different but is normally

* To whom correspondence should be addressed.
† Present address: E. I. duPont de Nemours & Co., Inc., Experimental Station, Wilmington, DE 19898.

0021-9568/88/1733-0485$01.50/0

Table I. Apparent Molar Heat Capacity of Aqueous $MgCl_2$

m/ mol kg^{-1}	P_s/P_w	c_p/c_p^0	$C_{p,\phi}{}^a$/ J K^{-1} mol^{-1}	δ^b	Δ^c	m/ mol kg^{-1}	P_s/P_w	c_p/c_p^0	$C_{p,\phi}{}^a$/ J K^{-1} mol^{-1}	δ^b	Δ^c
T/K = 349.07; P/MPa = 2.33; f^d = 1.046											
0.0311	0.9974	0.9948	−297.6	33.5	71.1	0.6725	0.9645	0.9167	−152.8	4.8	0.9
0.0311	0.9979	0.9953	−232.3	32.6	5.9	0.6725	0.9643	0.9166	−154.0	4.8	2.1
0.0311	0.9984	0.9958	−167.6	31.6	−58.7	0.6725	0.9645	0.9168	−152.4	4.8	0.5
0.0624	0.9960	0.9909	−214.0	18.2	−1.8	0.6725	0.9644	0.9167	−153.0	4.8	1.1
0.0624	0.9960	0.9909	−214.4	18.2	−1.4	1.4068	0.9326	0.8448	−125.2	3.8	2.6
0.1574	0.9906	0.9781	−193.8	9.5	−2.7	1.4068	0.9328	0.8449	−124.8	3.8	2.1
0.1574	0.9906	0.9781	−193.3	9.5	−3.2	1.4068	0.9326	0.8447	−125.3	3.8	2.7
0.1574	0.9905	0.9780	−194.9	9.5	−1.6	2.2616	0.9030	0.7784	−99.8	3.3	−1.2
0.1574	0.9905	0.9779	−196.6	9.5	0.1	2.2616	0.9031	0.7785	−99.6	3.3	−1.4
0.3358	0.9809	0.9554	−175.1	6.3	−0.3	2.2616	0.9030	0.7784	−100.0	3.3	−1.1
0.3358	0.9810	0.9555	−174.3	6.3	−1.1	2.2616	0.9030	0.7784	−100.0	3.3	−1.1
0.3358	0.9810	0.9554	−174.9	6.3	−0.5						
T/K = 349.10; P/MPa = 4.96; f^d = 1.046											
0.0311	0.9979	0.9953	−229.9	32.5	6.3	0.3358	0.9811	0.9556	−172.3	6.3	1.7
0.0311	0.9980	0.9954	−215.8	32.3	−7.8	0.6725	0.9645	0.9170	−151.1	4.8	3.8
0.0624	0.9961	0.9910	−206.2	18.1	−6.1	0.6725	0.9646	0.9171	−150.6	4.8	3.3
0.0624	0.9960	0.9909	−216.9	18.2	4.4	0.6725	0.9644	0.9169	−151.8	4.8	4.6
0.1574	0.9905	0.9780	−194.3	9.5	2.1	0.6725	0.9644	0.9169	−151.8	4.8	4.5
0.1574	0.9905	0.9781	−193.6	9.5	1.4	1.4068	0.9330	0.8453	−123.1	3.8	3.1
0.1574	0.9906	0.9781	−191.2	9.5	−0.9	1.4068	0.9329	0.8452	−123.4	3.8	3.4
0.3358	0.9811	0.9557	−171.1	6.3	0.5	1.4068	0.9329	0.8452	−123.4	3.8	3.4
0.3358	0.9811	0.9556	−171.8	6.3	1.2	2.2616	0.9032	0.7789	−98.6	3.3	−2.3
0.3358	0.9811	0.9557	−171.3	6.3	0.7	2.2616	0.9031	0.7789	−98.7	3.3	−2.1
T/K = 349.12; P/MPa = 10.10; f^d = 1.046											
0.0311	0.9981	0.9956	−199.1	32.0	−19.0	0.3358	0.9837	0.9585	−135.1	5.8	−25.8
0.0311	0.9980	0.9955	−214.1	32.2	−4.0	0.3358	0.9836	0.9584	−136.2	5.8	−24.8
0.0311	0.9980	0.9955	−208.3	32.1	−9.7	0.3358	0.9836	0.9584	−135.8	5.8	−25.1
0.0311	0.9979	0.9953	−231.4	32.5	13.2	0.6725	0.9662	0.9189	−138.0	4.6	−0.2
0.0311	0.9979	0.9954	−222.6	32.4	4.4	0.6725	0.9660	0.9187	−139.0	4.6	0.8
0.0311	0.9979	0.9954	−228.3	32.4	10.1	0.6725	0.9652	0.9179	−144.4	4.7	6.1
0.0624	0.9961	0.9910	−206.4	18.1	0.8	0.6725	0.9650	0.9178	−145.5	4.7	7.2
0.0624	0.9960	0.9910	−210.6	18.1	4.9	0.6725	0.9651	0.9178	−145.1	4.7	6.9
0.0624	0.9961	0.9911	−201.3	18.0	−4.3	1.4068	0.9332	0.8461	−120.2	3.8	5.5
0.1574	0.9907	0.9784	−184.3	9.4	0.7	1.4068	0.9333	0.8461	−120.1	3.8	5.4
0.1574	0.9905	0.9781	−192.1	9.5	8.5	1.4068	0.9335	0.8464	−119.2	3.8	4.5
0.1574	0.9908	0.9785	−181.9	9.3	−1.6	2.2616	0.9040	0.7803	−95.2	3.3	−5.3
0.1574	0.9908	0.9784	−184.1	9.4	0.5	2.2616	0.9034	0.7797	−96.5	3.3	−4.1
0.1574	0.9905	0.9781	−190.6	9.5	7.0	2.2616	0.9036	0.7800	−96.0	3.3	−4.5
0.3358	0.9832	0.9580	−141.1	5.9	−19.9	2.2616	0.9036	0.7799	−96.1	3.3	−4.5
T/K = 349.11; P/MPa = 17.70; f^d = 1.046											
0.0311	0.9981	0.9956	−192.3	31.9	−17.7	0.6725	0.9669	0.9201	−129.8	4.5	5.0
0.0311	0.9981	0.9956	−193.2	31.9	−16.8	0.6725	0.9670	0.9202	−128.9	4.5	4.1
0.0624	0.9963	0.9913	−186.0	17.8	−9.6	0.6725	0.9673	0.9204	−127.3	4.5	2.4
0.0624	0.9962	0.9912	−194.6	17.9	−1.0	0.6725	0.9670	0.9202	−129.2	4.5	4.3
0.0624	0.9963	0.9913	−187.7	17.8	−7.9	1.4068	0.9340	0.8476	−114.9	3.7	8.0
0.0624	0.9961	0.9911	−201.1	18.0	5.4	1.4068	0.9338	0.8474	−115.5	3.8	8.6
0.1574	0.9909	0.9787	−174.9	9.3	4.0	1.4068	0.9339	0.8474	−115.3	3.8	8.4
0.1574	0.9912	0.9790	−168.0	9.1	−2.8	1.4068	0.9338	0.8474	−115.5	3.8	8.6
0.1574	0.9907	0.9784	−181.8	9.4	10.9	1.4068	0.9339	0.8474	−115.4	3.8	8.5
0.3358	0.9856	0.9606	−107.0	5.4	−39.8	2.2616	0.9040	0.7812	−92.8	3.3	−7.3
0.3358	0.9854	0.9604	−109.5	5.4	−37.3	2.2616	0.9045	0.7817	−91.8	3.3	−8.2
0.3358	0.9855	0.9605	−108.3	5.4	−38.5	2.2616	0.9041	0.7813	−92.6	3.3	−7.5
T/K = 398.54; P/MPa = 2.33; f^d = 1.068											
0.0311	0.9974	0.9947	−322.0	35.0	10.9	0.3358	0.9785	0.9525	−216.0	7.1	−1.4
0.0311	0.9975	0.9948	−306.5	34.8	−4.5	0.3358	0.9785	0.9524	−216.9	7.1	−0.4
0.0311	0.9975	0.9949	−299.4	34.7	−11.6	0.6725	0.9621	0.9135	−176.9	5.2	−1.7
0.0624	0.9949	0.9896	−307.2	20.1	15.3	0.6725	0.9617	0.9132	−179.1	5.3	0.4
0.0624	0.9952	0.9900	−282.8	19.8	−9.0	0.6725	0.9616	0.9131	−179.9	5.3	1.3
0.0624	0.9953	0.9900	−280.0	19.7	−11.8	1.4068	0.9301	0.8409	−140.5	4.1	3.4
0.1574	0.9895	0.9767	−234.0	10.3	−21.2	1.4068	0.9302	0.8410	−140.2	4.1	3.1
0.1574	0.9894	0.9766	−237.2	10.4	−18.0	1.4068	0.9303	0.8411	−139.9	4.1	2.8
0.1574	0.9890	0.9762	−247.9	10.5	−7.4	2.2616	0.9022	0.7758	−107.5	3.5	−3.6
0.3358	0.9784	0.9523	−218.1	7.1	0.6	2.2616	0.9017	0.7753	−108.6	3.5	−2.4
0.3358	0.9789	0.9529	−211.3	7.0	−6.1	2.2616	0.9020	0.7756	−107.9	3.5	−3.1
0.3358	0.9793	0.9532	−206.2	6.9	−11.2						
T/K = 398.53; P/MPa = 4.96; f^d = 1.068											
0.0311	0.9977	0.9951	−273.9	34.2	−20.7	0.0624	0.9953	0.9901	−274.4	19.6	−3.0
0.0311	0.9974	0.9948	−308.3	34.7	13.6	0.0624	0.9955	0.9902	−263.5	19.5	−13.9
0.0311	0.9973	0.9947	−324.0	35.0	29.3	0.1574	0.9886	0.9759	−256.7	10.7	11.9
0.0624	0.9951	0.9899	−289.4	19.9	11.9	0.1574	0.9889	0.9762	−248.0	10.5	3.3
0.0624	0.9951	0.9899	−288.2	19.8	10.7	0.1574	0.9891	0.9764	−242.5	10.4	−2.2

Table I (Continued)

m/ mol kg^{-1}	P_s/P_w	c_p/c_p^0	$C_{p,\phi}^a$/ J K^{-1} mol^{-1}	δ^b	Δ^c	m/ mol kg^{-1}	P_s/P_w	c_p/c_p^0	$C_{p,\phi}^a$/ J K^{-1} mol^{-1}	δ^b	Δ^c
0.3358	0.9791	0.9531	−207.2	6.9	−3.2	1.4068	0.9299	0.8410	−139.9	4.1	5.1
0.3358	0.9793	0.9534	−203.5	6.9	−6.8	1.4068	0.9303	0.8414	−138.4	4.1	3.7
0.3358	0.9789	0.9530	−209.3	7.0	−1.1	1.4068	0.9305	0.8415	−138.0	4.1	3.2
0.6725	0.9615	0.9131	−179.2	5.3	4.6	2.2616	0.9019	0.7759	−107.0	3.5	−1.5
0.6725	0.9623	0.9140	−173.8	5.2	−0.7	2.2616	0.9031	0.7770	−104.6	3.4	−3.9
0.6725	0.9615	0.9132	−179.1	5.3	4.5	2.2616	0.9026	0.7765	−105.6	3.5	−2.9
				T/K = 398.37; P/MPa = 10.10; f^d = 1.068							
0.0311	0.9976	0.9950	−281.2	34.3	18.7	0.3358	0.9792	0.9535	−202.4	6.9	5.8
0.0311	0.9979	0.9953	−234.0	33.6	−28.4	0.6725	0.9620	0.9140	−173.0	5.2	6.5
0.0311	0.9977	0.9951	−272.8	34.2	10.3	0.6725	0.9622	0.9142	−171.9	5.2	5.4
0.0624	0.9956	0.9905	−246.7	19.2	−2.4	0.6725	0.9621	0.9140	−172.6	5.2	6.1
0.0624	0.9954	0.9903	−261.8	19.4	12.6	1.4068	0.9309	0.8425	−134.5	4.1	4.4
0.0624	0.9956	0.9905	−247.5	19.2	−1.6	1.4068	0.9306	0.8422	−135.3	4.1	5.3
0.1574	0.9894	0.9768	−231.3	10.3	7.4	1.4068	0.9308	0.8424	−134.7	4.1	4.6
0.1574	0.9895	0.9768	−229.5	10.3	5.5	2.2616	0.9031	0.7776	−102.8	3.4	−0.8
0.1574	0.9894	0.9767	−232.7	10.3	8.8	2.2616	0.9033	0.7778	−102.3	3.4	−1.3
0.1574	0.9892	0.9766	−236.4	10.4	12.4	2.2616	0.9034	0.7779	−102.1	3.4	−1.5
0.3358	0.9793	0.9536	−201.0	6.9	4.4	2.2616	0.9028	0.7774	−103.3	3.4	−0.3
				T/K = 398.79; P/MPa = 17.90; f^d = 1.068							
0.0311	0.9980	0.9955	−215.0	33.2	0.6	0.3358	0.9810	0.9555	−174.6	6.5	−1.7
0.0311	0.9980	0.9954	−220.1	33.3	5.7	0.3358	0.9813	0.9559	−170.1	6.4	−6.2
0.0311	0.9982	0.9956	−191.7	32.9	−22.6	0.6725	0.9633	0.9157	−160.8	5.1	5.9
0.0624	0.9960	0.9909	−218.5	18.8	11.5	0.6725	0.9640	0.9164	−156.0	5.0	1.1
0.0624	0.9958	0.9907	−228.4	18.9	21.4	0.6725	0.9632	0.9156	−161.2	5.1	6.3
0.0624	0.9956	0.9905	−244.1	19.1	37.1	1.4068	0.9324	0.8447	−126.2	4.0	2.9
0.0624	0.9961	0.9910	−212.2	18.7	5.2	1.4068	0.9326	0.8449	−125.6	4.0	2.3
0.1574	0.9897	0.9772	−217.3	10.1	24.1	1.4068	0.9327	0.8450	−125.3	3.9	2.0
0.1574	0.9899	0.9775	−211.4	10.0	18.3	2.2616	0.9057	0.7810	−94.7	3.3	−1.6
0.1574	0.9898	0.9774	−214.2	10.1	21.1	2.2616	0.9052	0.7805	−95.8	3.4	−0.6
0.3358	0.9811	0.9557	−172.3	6.5	−3.9	2.2616	0.9054	0.7807	−95.3	3.4	−1.1
0.3358	0.9812	0.9558	−171.3	6.5	−4.9						
				T/K = 498.72; P/MPa = 4.96; f^d = 1.097							
0.0311	0.9954	0.9924	−687.7	44.0	9.0	0.3358	0.9653	0.9379	−442.5	10.9	−4.2
0.0311	0.9953	0.9924	−697.5	44.1	18.8	0.3358	0.9652	0.9377	−445.0	10.9	−1.6
0.0311	0.9955	0.9926	−669.9	43.7	−8.7	0.6725	0.9414	0.8911	−356.3	8.2	4.4
0.0311	0.9955	0.9926	−670.1	43.7	−8.5	0.6725	0.9414	0.8911	−356.6	8.2	4.7
0.0624	0.9915	0.9858	−617.5	26.6	−6.9	0.6725	0.9412	0.8909	−357.6	8.2	5.7
0.0624	0.9915	0.9858	−615.1	26.5	−9.3	0.6725	0.9413	0.8910	−357.3	8.2	5.4
0.0624	0.9916	0.9859	−611.5	26.5	−12.8	1.4068	0.9047	0.8141	−252.6	6.0	5.4
0.1574	0.9809	0.9671	−540.0	15.7	2.5	1.4068	0.9043	0.8137	−254.0	6.0	6.8
0.1574	0.9811	0.9674	−532.8	15.6	−4.6	1.4068	0.9047	0.8141	−252.6	6.0	5.3
0.1574	0.9809	0.9672	−538.0	15.7	0.4	2.2616	0.8798	0.7524	−174.9	4.7	−3.9
0.3358	0.9650	0.9375	−447.9	11.0	1.2	2.2616	0.8798	0.7524	−175.0	4.7	−3.9
0.3358	0.9651	0.9376	−445.7	10.9	−1.0	2.2616	0.8796	0.7522	−175.3	4.7	−3.6
				T/K = 498.85; P/MPa = 10.10; f^d = 1.097							
0.0311	0.9956	0.9927	−647.1	43.1	20.3	0.3358	0.9665	0.9393	−418.3	10.5	−4.7
0.0311	0.9956	0.9927	−644.2	43.1	17.4	0.6725	0.9435	0.8935	−335.4	7.9	−0.5
0.0311	0.9956	0.9928	−631.5	42.9	4.7	0.6725	0.9436	0.8937	−334.4	7.9	−1.5
0.0624	0.9918	0.9862	−583.6	26.0	3.2	0.6725	0.9437	0.8938	−333.5	7.9	−2.5
0.0624	0.9918	0.9862	−583.0	26.0	2.6	1.4068	0.9080	0.8178	−236.4	5.8	1.4
0.0624	0.9919	0.9863	−578.4	25.9	−2.0	1.4068	0.9080	0.8178	−236.5	5.8	1.4
0.1574	0.9818	0.9682	−503.1	15.1	−1.0	1.4068	0.9081	0.8180	−236.0	5.8	0.9
0.1574	0.9820	0.9684	−497.9	15.0	−6.2	2.2616	0.8832	0.7563	−163.8	4.5	−1.5
0.3358	0.9664	0.9392	−419.8	10.6	−3.3	2.2616	0.8835	0.7566	−163.0	4.5	−2.3
0.3358	0.9667	0.9394	−416.6	10.5	−6.4	2.2616	0.8835	0.7566	−163.1	4.5	−2.2
				T/K = 498.81; P/MPa = 17.20; f^d = 1.097							
0.0311	0.9961	0.9933	−546.3	41.3	−7.1	0.3358	0.9686	0.9418	−379.2	9.9	−10.3
0.0311	0.9962	0.9934	−529.6	41.0	−23.9	0.6725	0.9464	0.8970	−307.1	7.5	−6.2
0.0311	0.9961	0.9933	−546.1	41.3	−7.3	0.6725	0.9466	0.8972	−305.8	7.5	−7.5
0.0624	0.9930	0.9875	−480.6	24.3	−37.5	0.6725	0.9466	0.8972	−305.8	7.5	−7.6
0.0624	0.9927	0.9871	−507.9	24.7	−10.2	1.4068	0.9123	0.8227	−216.0	5.5	−1.7
0.0624	0.9928	0.9873	−495.2	24.5	−22.9	1.4068	0.9123	0.8227	−215.9	5.5	−1.8
0.1574	0.9833	0.9700	−445.9	14.2	−11.0	1.4068	0.9122	0.8227	−216.1	5.5	−1.6
0.1574	0.9834	0.9700	−444.2	14.2	−12.7	2.2616	0.8882	0.7619	−148.3	4.3	1.9
0.1574	0.9834	0.9701	−441.9	14.2	−14.9	2.2616	0.8886	0.7623	−147.4	4.3	1.0
0.3358	0.9690	0.9421	−374.1	9.9	−15.3	2.2616	0.8889	0.7625	−146.7	4.3	0.4
0.3358	0.9689	0.9420	−376.0	9.9	−13.5	2.2616	0.8887	0.7623	−147.3	4.3	0.9
				T/K = 549.02; P/MPa = 10.10; f^d = 1.188							
0.0311	0.9937	0.9901	−1153.4	57.6	7.6	0.0624	0.9882	0.9812	−1065.4	36.7	5.3
0.0311	0.9940	0.9904	−1094.6	56.7	−51.1	0.0624	0.9887	0.9817	−1017.6	36.0	−42.4
0.0311	0.9934	0.9898	−1202.3	58.3	56.4	0.0624	0.9882	0.9811	−1068.5	36.7	8.5

Table I (Continued)

m/ mol kg^{-1}	P_s/P_w	c_p/c_p^0	$C_{p,\phi}$[a]/ J K^{-1} mol^{-1}	δ[b]	Δ[c]	m/ mol kg^{-1}	P_s/P_w	c_p/c_p^0	$C_{p,\phi}$[a]/ J K^{-1} mol^{-1}	δ[b]	Δ[c]
0.0624	0.9880	0.9809	−1083.4	36.9	23.3	0.6725	0.9236	0.8661	−596.1	12.3	−0.6
0.1574	0.9740	0.9574	−918.2	22.8	3.8	0.6725	0.9235	0.8660	−596.6	12.3	−0.1
0.1574	0.9743	0.9578	−904.8	22.6	−9.6	1.4068	0.8814	0.7815	−413.5	8.8	3.7
0.1574	0.9743	0.9577	−906.7	22.6	−7.7	1.4068	0.8816	0.7816	−413.0	8.8	3.2
0.3358	0.9534	0.9211	−753.0	16.3	−7.6	1.4068	0.8816	0.7816	−413.0	8.8	3.2
0.3358	0.9528	0.9205	−762.8	16.5	2.2	1.4068	0.8811	0.7811	−415.0	8.8	5.2
0.3358	0.9528	0.9205	−762.5	16.5	1.8	2.2616	0.8577	0.7208	−280.2	6.6	−2.5
0.6725	0.9237	0.8663	−594.9	12.3	−1.9	2.2616	0.8582	0.7213	−278.7	6.5	−4.1
0.6725	0.9228	0.8652	−603.4	12.4	6.5	2.2616	0.8580	0.7211	−279.3	6.5	−3.4
				T/K = 548.91; P/MPa = 17.90; f[d] = 1.188							
0.0311	0.9950	0.9916	−873.5	52.3	38.2	0.3358	0.9601	0.9291	−608.5	14.1	2.5
0.0311	0.9954	0.9921	−785.9	51.0	−49.4	0.3358	0.9593	0.9282	−622.0	14.3	16.0
0.0311	0.9952	0.9919	−826.5	51.6	−8.7	0.6725	0.9325	0.8766	−496.3	10.7	3.1
0.0624	0.9900	0.9834	−855.9	33.0	70.0	0.6725	0.9326	0.8767	−495.4	10.7	2.3
0.0624	0.9907	0.9841	−797.0	32.1	11.1	0.6725	0.9322	0.8763	−498.7	10.8	5.6
0.0624	0.9904	0.9838	−819.8	32.5	33.9	1.4068	0.8944	0.7962	−342.7	7.7	0.2
0.1574	0.9783	0.9626	−724.6	19.7	23.1	1.4068	0.8947	0.7965	−341.3	7.7	−1.2
0.1574	0.9780	0.9622	−736.1	19.9	34.6	1.4068	0.8946	0.7964	−341.9	7.7	−0.5
0.1574	0.9781	0.9623	−733.6	19.8	32.0	2.2616	0.8730	0.7374	−227.8	5.7	4.0
0.1574	0.9780	0.9623	−734.9	19.9	33.3	2.2616	0.8726	0.7370	−228.7	5.8	4.9
0.3358	0.9595	0.9284	−619.9	14.2	13.9	2.2616	0.8747	0.7392	−222.9	5.7	−0.8
				T/K = 573.42; P/MPa = 17.90; f[d] = 1.248							
0.0311	0.9944	0.9906	−1127.2	61.4	−4.9	0.6725	0.9219	0.8602	−678.0	13.8	−10.2
0.0311	0.9953	0.9918	−918.5	58.3	0.0	0.6725	0.9213	0.8595	−683.9	13.9	−4.4
0.0311	0.9943	0.9905	−1137.2	61.6	5.0	0.6725	0.9198	0.8576	−699.4	14.2	11.0
0.0624	0.9893	0.9819	−1057.1	38.7	−9.7	1.4068	0.8796	0.7736	−469.6	9.8	−12.2
0.0624	0.9906	0.9835	−921.1	36.7	0.0	1.4068	0.8785	0.7723	−475.0	9.9	−6.9
0.0624	0.9895	0.9821	−1037.3	38.4	−29.4	1.4068	0.8784	0.7723	−475.3	9.9	−6.6
0.1574	0.9743	0.9563	−1003.0	25.0	42.4	1.4068	0.8789	0.7728	−472.8	9.9	−9.0
0.1574	0.9774	0.9602	−867.4	23.0	−93.1	1.4068	0.8778	0.7716	−478.0	10.0	−3.8
0.1574	0.9773	0.9600	−874.4	23.1	−86.2	2.2616	0.8552	0.7115	−321.7	7.4	7.3
0.3358	0.9524	0.9174	−853.2	18.4	15.7	2.2616	0.8561	0.7124	−319.0	7.3	4.5
0.3358	0.9522	0.9171	−857.7	18.4	20.1	2.2616	0.8565	0.7130	−317.6	7.3	3.1
0.3358	0.9532	0.9184	−836.3	18.1	−1.2						
				T/K = 597.81; P/MPa = 17.90; f[d] = 1.350							
0.0311	0.9919	0.9866	−2082.7	86.5	0.0	0.3358	0.9361	0.8912	−1476.9	28.9	−16.6
0.0311	0.9913	0.9859	−2233.0	88.7	−36.6	0.3358	0.9363	0.8915	−1472.7	28.9	−20.8
0.0311	0.9910	0.9854	−2319.2	90.0	49.5	0.3358	0.9347	0.8894	−1511.6	29.4	18.0
0.0311	0.9912	0.9857	−2268.7	89.2	−0.9	0.6725	0.8986	0.8226	−1145.6	21.6	−23.6
0.0624	0.9850	0.9750	−1904.1	56.9	0.0	0.6725	0.8972	0.8208	−1163.2	21.9	−6.0
0.0624	0.9843	0.9741	−1995.6	58.3	−88.6	0.6725	0.8972	0.8208	−1163.7	21.9	−5.5
0.0624	0.9838	0.9735	−2054.9	59.1	−29.4	1.4068	0.8476	0.7231	−790.7	15.2	−6.5
0.0624	0.9834	0.9728	−2117.2	60.1	32.9	1.4068	0.8475	0.7229	−791.6	15.2	−5.6
0.1574	0.9646	0.9409	−1767.0	38.8	−30.3	1.4068	0.8466	0.7219	−796.9	15.3	−0.3
0.1574	0.9634	0.9393	−1830.2	39.7	32.8	2.2616	0.8204	0.6579	−547.7	11.2	4.1
0.1574	0.9628	0.9385	−1861.7	40.2	64.3	2.2616	0.8197	0.6571	−550.3	11.3	6.8
0.1574	0.9625	0.9381	−1879.2	40.5	81.8	2.2616	0.8198	0.6572	−549.9	11.3	6.4

[a] The apparent molar heat capacity, $C_{p,\phi}$, was calculated from eq 1 and 2. [b] The estimated accuracy, δ, of each $C_{p,\phi}$/(J K^{-1} mol^{-1}) value was calculated assuming absolute errors of ±0.00015 and relative errors of 1% in $\Delta P/P$. [c] Δ is the value of $\{C_{p,\phi}(\text{calcd}) - C_{p,\phi}\}$/(J K^{-1} mol^{-1}). The calculated value is from a cubic spline interpolation of the knots in Table II. [d] The value of the heat loss correction factor, f, was calculated by using the heat capacity of 2.9836 mol kg^{-1} NaCl as a chemical standard (*15*). The NaCl experiments were run concurrently with $MgCl_2$ and $\Delta P/P$ for the NaCl runs have already been reported (*2*).

negligible with aqueous salt solutions (m = <5.0 mol kg^{-1}). As a check for this error, the sample loop was loaded with water, followed by 1.5 mL of 2.2616 mol kg^{-1} $MgCl_2$(aq). At equilibrium and before the $MgCl_2$(aq) arrives at the heater we measured the heat-capacity ratio of water-to-water with two water-to-$MgCl_2$(aq) interfaces in the sample loop. The $\Delta P/P$ measured ($\Delta P/P$ = 0.000 21) should be twice the effect of one water-to-$MgCl_2$(aq) interface. The effects of interfacial mixing ($\Delta P/P$ = 0.0001) are negligible at 2.26 mol kg^{-1} compared to the chemical effects ($\Delta P/P$ = −0.097 to −0.180 at 348–600 K). These effects should be even smaller at lower molalities.

Results

The results of the heat-capacity measurements on $MgCl_2$(aq) are given in Table I, together with estimates of the accuracy of the individual measurements. The apparent molar heat capacities were fitted by the multidimensional cubic-spline method described previously (*2*, *19*). The knot positions and fitted values are presented in Table II. Table III gives values of $C_{p,\phi}$ of a variety of temperatures and molalities. The Debye–Hückel slopes for $C_{p,\phi}$ as a function of molality, A_J, have been included in Table II. These have been calculated by using Haar, Gallagher, and Kell's equation of state for water (*17*) with Uematsu and Franck's equation for the dielectric properties of water (*20*). As with the $C_{p,\phi}$ surfaces presented previously (*1–6*), the $MgCl_2$ surface required knots at three molalities, six temperatures, and two pressures. The surface was extended to 298.15 K by using the measurements of Perron, Roux, and Desnoyers (*21*) at 1 atm. The pressure dependence at 298.15 K was estimated by graphically extrapolating the high-temperature, elevated pressure results to 298.15 K. The fit of the 357 points to the cubic-spline surface resulted in a sum of the squares of the residuals of 107 000 and a standard error of 18.3 J K^{-1} mol^{-1}. A direct comparison of the estimated uncertainty of these results and the residuals from the fit (Table I) dem-

Table II. $MgCl_2$ Knot Positions, Knot Values, and Debye-Hückel Slopes, A_J/(J mol$^{-3/2}$ K^{-1} kg$^{1/2}$), for Calculating $C_{p,\phi}$ of $MgCl_2$(aq)[a]

$m^{1/2}$/ mol kg^{-1}		T/K					
		298.15	340.00	450.00	550.00	575.00	600.00
				P = 12.5 MPa			
	A_J	184.9	235.6	609.1	3354.1	7388.2	28147.8
				$C_{p,\phi}$/(J K^{-1} mol^{-1})			
0.0000		-231.5	-250.0	-433.3	-1429.0	-1776.9	-2258.2
0.2500		-195.9	-200.2	-342.7	-986.3	-1286.9	-1615.5
1.6000		-121.6	-100.4	-107.3	-231.8	-349.5	-631.2
				P = 17.9 MPa			
	A_J	182.4	232.2	584.7	2876.1	5699.9	15795.4
				$C_{p,\phi}$/(J K^{-1} mol^{-1})			
0.000		-216.6	-248.2	-364.4	-1133.8	-1720.1	-3910.1
0.2500		-177.5	-194.0	-296.2	-791.4	-1108.7	-2195.9
1.6000		-123.2	-102.4	-95.3	-190.7	-273.9	-494.0

[a] This fit is a representation of 357 data points. The sum of the squares of the residuals is 107 000 resulting in a standard error of the fit of 18.3 J K^{-1} mol^{-1}. The minimum sum of the squares for this data set is 62 900.

onstrates the quality of the fit. Another way of showing the quality of the fit is to compare the sum of the squares of the residuals (s = 107 000) with the sum of the squares of the residuals for a surface which passed through the average of each duplicate set of results (s = 62 900).

Discussion

Saluja and LeBlanc (*22*) have measured the heat capacity of $MgCl_2$(aq) for molalities from 0.1 to 0.5 mol kg^{-1} and temperatures from 298.15 to 373.15 K at 0.6 MPa. At low concentrations our results agree with their results well within the expected experimental errors (±14 J mol^{-1} K^{-1} at 0.1 mol kg^{-1}). At 0.5 mol kg^{-1} and 373.15 K the results of Saluja and LeBlanc are 15 J mol^{-1} K^{-1} more negative than our results. This difference is a little more than the estimated experimental errors (±5 J mol^{-1} K^{-1} for our experiments, somewhat less for Saluja and LeBlanc).

Likke and Bromley (*23*) have published data on $MgCl_2$(aq) from 353 to 473 K at the saturation vapor pressure. Likke and Bromley's reported uncertainty of 0.3% in specific heat capacity is approximately 10 times the expected uncertainty of the present data at low molalities, and 3 times the expected uncertainty at the highest molality. A comparison of Likke and Bromley's results with values calculated from the fitted spline surface demonstrates excellent agreement except at 373 K above 1.0 mol kg^{-1}. Their molality dependence is negative in this region while it is positive everywhere else, and our results have a positive molality dependence. The earlier results of Eigen and Wicke (*24*) from 298 to 393 K are in reasonable agreement with the present results considering the expected experimental errors. The data of Rutskov (*25*) measured from 298 to 348 K at atmospheric pressure agree with the present results within the error estimates provided by Rutskov. Examination of many individual isothermal, isobaric groups of data may give the appearance of some systematic errors; however, consideration of the entire surface dispels these concerns. The quality of the fit degrades above 573 K (half of the sum of the squares of the errors result from the fit above 573 K). As with the NaCl representation, the knots at 575 and 600 K at 12.5 MPa are solely for convenience. The pressure dependence has not been measured above 550 K. The two pressure knots

Table III. Apparent Molar Heat Capacity, $C_{p,\phi}$ /(J K^{-1} mol^{-1}), of $MgCl_2$(aq)

T/K	m/mol kg^{-1}						
	0	0.100	0.250	0.500	1.000	2.000	2.250
				P = 10.0 MPa			
298.15	-238.4	-197.8	-181.2	-165.5	-147.8	-128.5	-125.0
303.15	-240.3	-196.6	-178.9	-162.6	-144.5	-125.3	-121.9
313.15	-243.9	-194.4	-174.8	-157.0	-138.0	-119.2	-115.9
323.15	-247.1	-192.9	-171.4	-152.3	-132.4	-113.6	-110.4
333.15	-249.6	-192.5	-169.4	-149.0	-128.1	-108.9	-105.7
343.15	-251.3	-193.7	-169.4	-147.8	-125.8	-105.5	-102.2
353.15	-252.2	-196.9	-171.5	-148.9	-125.6	-103.7	-100.0
363.15	-253.7	-202.0	-175.9	-152.3	-127.4	-103.3	-99.1
373.15	-256.7	-209.3	-182.4	-157.8	-131.2	-104.1	-99.3
398.15	-279.6	-237.5	-208.0	-179.8	-147.3	-110.8	-104.0
423.15	-339.1	-280.9	-246.0	-211.9	-171.0	-122.7	-113.4
448.15	-454.0	-341.0	-295.9	-251.9	-199.4	-137.5	-125.7
473.15	-639.0	-421.8	-359.7	-300.4	-232.0	-155.1	-140.7
498.15	-889.1	-541.3	-453.9	-372.2	-281.0	-183.3	-165.5
523.15	-1192.7	-721.3	-599.4	-486.7	-362.5	-232.7	-209.4
548.15	-1538.7	-983.8	-817.2	-662.9	-492.7	-314.0	-281.9
573.15	-1803.4	-1396.6	-1438.3	-1381.2	-1151.8	-634.8	-512.8
				P = 17.5 MPa			
298.15	-217.7	-170.7	-152.2	-137.9	-126.7	-122.8	-122.9
303.15	-222.5	-172.3	-152.3	-136.7	-124.5	-120.1	-120.2
313.15	-231.9	-175.5	-152.5	-134.6	-120.4	-114.9	-114.9
323.15	-239.9	-178.4	-153.0	-133.0	-117.0	-110.2	-110.0
333.15	-245.9	-181.0	-154.0	-132.4	-114.7	-106.1	-105.6
343.15	-248.9	-183.1	-155.5	-133.1	-114.0	-103.0	-102.0
353.15	-248.9	-184.8	-157.9	-135.4	-115.1	-101.0	-99.2
363.15	-247.2	-186.6	-161.2	-139.3	-117.9	-100.0	-97.3
373.15	-245.3	-189.1	-165.8	-144.8	-122.3	-100.1	-96.2
398.15	-248.1	-202.0	-184.2	-165.0	-139.1	-104.1	-97.0
423.15	-279.4	-231.3	-215.0	-194.5	-162.4	-112.8	-102.3
448.15	-360.9	-285.7	-261.7	-233.0	-189.7	-125.1	-111.5
473.15	-508.0	-371.6	-327.4	-281.0	-220.3	-140.8	-124.9
498.15	-704.4	-484.0	-413.5	-344.4	-261.8	-164.3	-145.6
523.15	-924.0	-614.6	-521.0	-430.5	-324.1	-201.3	-178.1
548.15	-1140.5	-755.0	-651.1	-546.7	-417.2	-257.7	-226.4
573.15	-1633.1	-1031.1	-912.8	-784.5	-610.2	-373.1	-324.8
598.15	-3607.4	-1974.4	-1736.2	-1481.5	-1141.0	-685.0	-592.5

enforce linearity in the pressure dependence of $C_{p,\phi}$.

Previous results on $C_{p,\phi}$ and $\{C_{p,\phi}(m_1) - C_{p,\phi}(m_2)\}$ for 1-1 electrolytes (*4*, *6*) have shown that absolute differences between the salts tend to increase as temperature increases but on a relative scale the opposite is true. This means that, as a fraction of the total effect, individuality decreases. A comparison of the present results for $MgCl_2$(aq) with previous results for $CaCl_2$(aq) shows the same trends: absolute differences increase with increasing temperature and relative differences (except at 0 mol kg^{-1} and 600 K) decrease. The exception for $C_{p,\phi}^{\circ}$ at 600 K may be due to the great inaccuracy of determining $C_{p,\phi}^{\circ}$ by extrapolation of the experimental measurements. Both $CaCl_2$(aq) and $MgCl_2$(aq) are strongly ion paired at the lowest experimental concentrations (*26*) and plots of $C_{p,\phi}$ vs $m^{1/2}$ exhibit slopes which are much less than the Debye-Hückel limiting law even at the lowest experimental molalities (*3*).

The $C_{p,\phi}$s presented in this paper, together with experimental standard Gibbs free energies and enthalpies at 298.15 K, allow calculations of the thermodynamic properties of $MgCl_2$(aq) at temperatures to 600 K. Calculation of standard Gibbs free energies by this route allows the calculation of equilibrium constants for chemical reactions involving $MgCl_2$(aq) under these conditions. The details of the calculations have been reported elsewhere (*27*, *28*).

Registry No. $MgCl_2$, 7786-30-3.

Literature Cited

(1) Smith-Magowan, D.; Wood, R. H. *J. Chem. Thermodyn.* **1981**, *13*, 1047.
(2) Gates, J. A.; Tillett, D. M.; White, D. E.; Wood, R. H. *J. Chem. Thermodyn.* **1987**, *19*, 131.
(3) White, D. E.; Doberstein, A. L.; Gates, J. A.; Tillett, D. M.; Wood, R. H. *J. Chem. Thermodyn.* **1987**, *19*, 251.
(4) White, D. E.; Gates, J. A.; Wood, R. H. *J. Chem. Thermodyn.* **1967**, *19*, 493.
(5) White, D. E.; Ryan, M. A.; Cavalucci Armstrong, M.; Gates, J. A.; Wood, R. H. *J. Chem. Thermodyn.* **1987**, *19*, 1023.
(6) White, D. E.; Gates, J. A.; Wood, R. H. *J. Chem. Thermodyn.* **1987**, *19*, 1037.
(7) Wood, R. H.; Quint, J. R.; Grolier, J.-P. *J. Phys. Chem.* **1981**, *85*, 3944.
(8) Wood, R. H.; Quint, J. R. *J. Chem. Thermodyn.* **1982**, *14*, 1069.
(9) Wheeler, J. C. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *76*, 308.
(10) Gates, J. A.; Wood, R. H.; Quint, J. R. *J. Phys. Chem.* **1982**, *86*, 4948.
(11) Helgeson, H. C.; Kirkham, D. H. *Abstracts of Papers*, 174th National Meeting of the American Chemical Society, New Orleans, LA, March 1977; American Chemical Society: Washington, DC, 1977.
(12) Cobble, J. W.; Murray, R. C., Jr. *Discuss. Faraday Soc.* **1977**, *64*, 144.
(13) Chang, R. F.; Morrison, G.; Levelt Sengers, J. M. H. *J. Phys. Chem.* **1984**, *88*, 3389.
(14) Smith-Magowan, D. Ph.D. Dissertation, University of Delaware, May 1980.
(15) White, D. E.; Wood, R. H. *J. Solution Chem.* **1982**, *8*, 289.
(16) Gates, J. A.; Wood, R. H. *J. Chem. Eng. Data* **1985**, *30*, 44.
(17) Haar, L.; Gallagher, J. S.; Kell, G. S. *NBS/NRC Steam Tables*; Hemisphere: Washington, DC, 1984.
(18) Fortier, J.-L.; Benson, G. C.; Picker, P. *J. Chem. Thermodyn.* **1976**, *8*, 289.
(19) Gates, J. A. Ph.D. Dissertation, University of Delaware, June 1985.
(20) Uematsu, M.; Franck, E. U. *J. Phys. Chem. Ref. Data* **1980**, *9*, 1291.
(21) Perron, G.; Roux, A.; Desnoyers, J. E. *Can. J. Chem.* **1981**, *52*, 3049.
(22) Saluja, P. P. S.; LeBlanc, J. C. *J. Chem. Eng. Data* **1987**, *32*, 72.
(23) Likke, S.; Bromley, L. A. *J. Chem. Eng. Data* **1973**, *18*, 189.
(24) Eigen, M.; Wicke, E. *Z. Elektrochem Angew. Phys. Chem.* **1951**, *55*, 354.
(25) Rutskov, A. *Zh. Prikl. Chem.* **1948**, *21*, 820.
(26) Franz, J. D.; Marshall, W. L. *Am. J. Sci.* **1982**, *282*, 166.
(27) Smith-Magowan, D.; Wood, R. H.; Tillett, D. M. *J. Chem. Eng. Data* **1982**, *27*, 335.
(28) Wood, R. H. "High Temperature Thermodynamic Data for Aqueous Salt Solutions." Final report on research project RP1167-4, Electric Power Research Institute, December 1984.

Received for review February 22, 1988. Accepted April 26, 1988. This work was supported by the Electric Power Research Institute under Contract No. RP1167-4 and by the National Science Foundation under grant nos. CHE8412592 and CHE8009672 and by the Office of Standard Reference Data of the National Bureau of Standards.

Thermodynamics of "Scale" Mineral Solubilities. 1. $BaSO_4$(s) in H_2O and Aqueous NaCl

Krishnam Raju[†] and Gordon Atkinson*

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019

A review of the solubilities of barium sulfate in water and aqueous NaCl is given. Equations to calculate C_p°, ΔH°, ΔS°, ΔG° for all of the species in the solubility equilibrium are presented and the coefficients are computed. With these coefficients, all of the thermodynamic quantities and the equilibrium constant are expressed as a function of temperature. The calculated thermodynamic values are compared with the available literature values. Activity coefficients are calculated at the given NaCl concentration and temperature by using the Pitzer formalism. The best literature solubility data are used to calculate the needed coefficients. A computer program is used with these coefficients to predict the solubility of $BaSO_4$(s) in NaCl solutions up to 300 °C.

[†] On leave from the Department of Chemistry, Osmania University, Hyderabad 500 007, India.

Introduction

"Scale" formation is the precipitation of a solid mineral from a brine. Although there are many industrial processes where scaling can be a concern there are and many possible scales, we have focused on those most common in oil and gas production. All petroleum reservoirs contain connate brines. These are ancient sea water modified chemically by millenia of interaction with the gas phase and the reservoir rock/clay matrix. In the reservoir the brine is in equilibria with its surroundings at their temperature and pressure. But as the brine is produced with the oil/gas, the equilibrium is disturbed by going to a lower temperature and pressure. This can lead to the precipitation of scale ranging from a minor annoyance to massive clogging of production tubing and above ground equipment. Scale formation can also be a problem during "water flood" operations. Here, water or brine is injected into a reservoir to maintain production pressure. If the injected water is quite different in composition with the connate brine,

0021-9568/88/1733-0490$01.50/0