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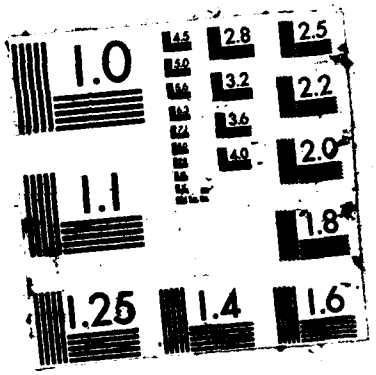
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CRREL REPORT 87-13

US Army Corps of Engineers
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Geochemistry of freezing brines

Low-temperature properties of sodium chloride

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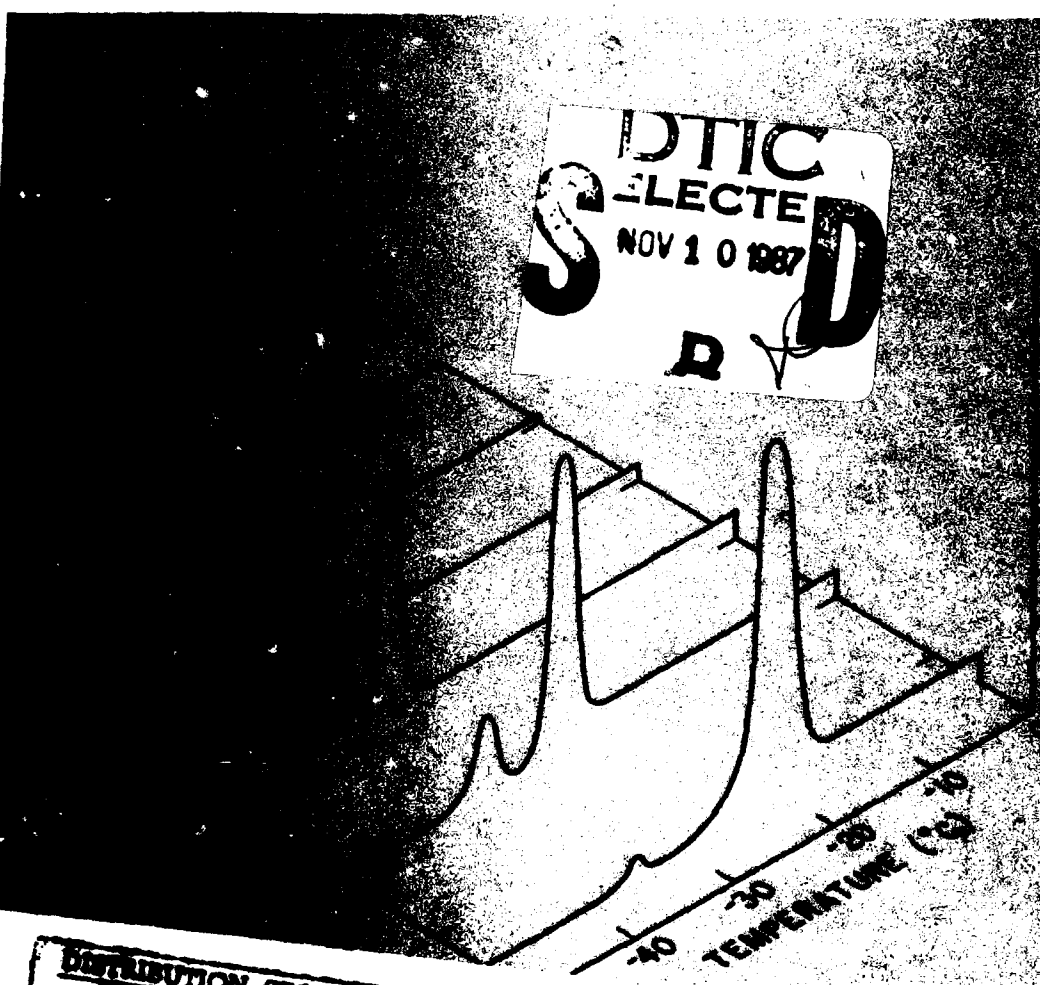

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Thermodynamic properties of electrolyte solutions change rapidly below 25°C, but these properties are seldom measured over the low temperature range (below 0°C), even though some salt solutions can remain unfrozen to -50°C. The heat capacities of concentrated solutions (0.5–6.0 molal) of NaCl-H_2O were measured from 25°C to -40°C as part of a study to provide thermodynamic data of salt solutions for use in cold regions chemical and geophysical studies. A differential scanning calorimeter was used to measure specific heat capacity from cooling scans as a function of temperature and concentration. The heat capacity data were fit to the equations of Pitzer and coworkers to obtain activity and osmotic coefficients of NaCl and H_2O, respectively, below 0°C. Supercooling of the solutions was encouraged by using a fast scan rate (10°/minute) so that specific heat could be measured to lower temperatures than would be possible if the solutions were allowed to equilibrate with the solid phases. The solubility of ice was calculated and compared to the experimental freezing point of NaCl solutions. Keywords:

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PREFACE

This report was prepared by Valerie L. Thurmond, graduate student, and Dr. Garrett W. Brass, Professor of Marine Geology and Geophysics at the Rosenstiel School of Marine and Atmospheric Science, University of Miami.

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Dr. Walter Stockmayer, Professor of Chemistry at Dartmouth College, and Dr. Frank J. Millero, Professor of Chemical Oceanography at the University of Miami, technically reviewed the report. The authors also thank Dr. Joseph L. Oliphant, formerly of CRREL, and Allen R. Tice of the Geochemical Sciences Branch, CRREL, for their assistance in the laboratory and their useful discussions.

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Geochemistry of Freezing Brines
Low-Temperature Properties of Sodium Chloride

VALERIE L. THURMOND AND GARRETT W. BRASS

INTRODUCTION

Brines that form by evaporation and mineral dissolution in regions that are cold or arid or both are common and have been the subject of many geochemical investigations because of their unusual chemical properties. We are unaccustomed to thinking of brine formation and mineral precipitation by freezing, although this is an important process in cold regions. Some brines, particularly those with a high concentration of calcium chloride, can remain entirely unfrozen at -50°C such as those in the dry valleys of Antarctica. Saline solutions in subsea permafrost are derived from seawater and concentrated by freeze–thaw processes and reactions with soil minerals. In frozen ground the unfrozen water due to the presence of salts changes the frost-heaving characteristics of soil and reduces the stability of structures such as buildings, roads and drilling platforms. Brine inclusions affect the properties of sea ice and the weathering of rocks, soils and building materials in cold climates.

These considerations make the phase relationships in freezing brines important to oceanography and cold regions studies. Other than several experimental studies of freezing seawater (Nelson and Thompson 1954, Thompson and Nelson 1956, Richardson 1976) and the binary and ternary solubility data in Linke (1958), little is known about the changes in phase composition that occur when brine mixtures are frozen. Calculating these changes is difficult since the thermodynamic properties of aqueous electrolytes below 0°C are virtually unknown, with the exception of some specific heat data for calcium and magnesium chloride (D'Ans et al. 1977). Thermodynamic quantities of interest to solubility studies, e.g. activity coefficients, enthalpies and heat capacities, change rapidly with concentration, especially at low temperatures, yet there are very few measurements below 0°C.

Recent improvements in the calculations of thermodynamic properties of mixed electrolytes at room temperature and above by Pitzer and his coworkers have been applied to the calculation of mineral solubilities in concentrated brines at 25°C (Eugster et al. 1980, Harvie and Weare 1980). These results shed light on old problems such as the mismatch between the calculated or experimentally determined solubility of salts and the observed sequences of minerals deposited by the evaporation of seawater. The model is now being extended to high temperatures and pressures by various workers for use in geothermal studies, petroleum engineering and mining geology (particularly hot-brine ore deposition). Up to now, however, temperatures below 25°C have not been included in these studies.

The purpose of this work is to extend the treatment of electrolytes to freezing temperatures (-40 °C), beginning with the properties of sodium chloride. Sodium chloride is a major constituent of many freezing brines, and the thermodynamic properties of its solution at room temperature are well known. We have measured heat capacities of sodium chloride solutions from 25°C to -40°C with a differential scanning calorimeter. Combining these results with literature values at 25°C, we have calculated the activity coefficients from 0.5 molal to saturation and down to -40°C using Pitzer's equations. The solubility of ice (freezing point curve) is accurately predicted from the low-temperature activities of the saturated solutions. The success of the method indicates that activities of other salts can be determined at very low temperatures and that these can be used to predict the properties of mixtures. Work is underway to ex-

tend the calculations to the seawater system Na-Ca-Mg-K-Cl-SO_4.

METHODS

Equations

The solubility product (K°) is a function of temperature and pressure only and for sodium chloride is given by

$$K^\circ(T, 1\text{ atm}) = m^2_{NaCl}\cdot\gamma^2_{\pm NaCl}(m, T, 1\text{ atm}) \quad (1)$$

where m = molality
$\gamma_\pm$ = activity coefficient at 1 atm pressure
T = temperature.

If the temperature variation of $\gamma_\pm$ is known, the equilibrium constant can be calculated at any temperature from $\gamma_\pm$ and the experimental solubility (m). The temperature dependence of $\gamma_\pm$ over a wide temperature range can be found by examining the temperature dependence of the partial molal free energy ($\Delta\bar{G}^\circ$) or the excess free energy (ΔG^{ex}). The different methods have been reviewed by Millero (1979).

The recent work of Silvester and Pitzer (1977) and Rogers and Pitzer (1981) demonstrates the use of excess free energies for determining the temperature dependence of $\gamma_\pm$ and the activity of water (a_w). The total excess free energy (G^{ex}) is given by

$$G^{ex} = n_w \nu m R T(1 - \phi + \ln\gamma_\pm) \quad (2)$$

where n_w = mass of water (kg)
ν = number of ions per formula unit
m = molality (mol kg^{-1})
ϕ = osmotic coefficient
R = gas constant
T = temperature (K).

The osmotic coefficient is related to a_w by

$$\ln a_w = -\nu\frac{mM\phi}{1000} \quad (3)$$

where M is the molecular weight of water.

The variation of G^{ex} with temperature is given by

$$\frac{\partial G^{ex}/T}{\partial T} = \frac{-L}{T^2} \quad (4)$$

where L is the total relative enthalpy, i.e., the difference between the total enthalpy of the solution and the enthalpy of the components at infinite dilution. The temperature variation of L is given by

$$\frac{\partial L}{\partial T} = J \quad (5)$$

where J is the total relative heat capacity of the solution:

$$J = Cp_t - (n_1\bar{C}p_1^\circ + n_2\bar{C}p_2^\circ) \quad (6)$$

where Cp_t = total heat capacity
n_1 = number of moles of solvent
n_2 = number of moles of solute
$\bar{C}p_1^\circ$ and $\bar{C}p_2^\circ$ = partial molal heat capacities of water and solute, respectively, at infinite dilution.

From total heat capacity measurements the temperature dependence of the activity and osmotic coefficients can thus be found by integrating eq 4 and 5.

The prediction of activity coefficients of electrolytes has recently been improved by the specific interaction equations of Pitzer and coworkers (Pitzer 1973, 1975, Pitzer and Mayorga 1973, 1974, Pitzer and Kim 1974). The mean activity coefficient of a 1:1 salt as a function of concentration is given by a polynomial with second and third virial coefficients:

$$\ln\gamma_\pm = f^\gamma + mB^\gamma + m^2C^\gamma \quad (7)$$

and the osmotic coefficient by

$$\phi - 1 = f^\phi + mB^\phi + m^2C^\phi \quad (8)$$

where f^γ and f^ϕ represent the effects of long-range electrostatic interactions among ions. The parameters B^γ and B^ϕ are the second virial coefficients for short-range interactions between two ions ($m-m$, $x-x$, $m-x$). The terms C^γ and C^ϕ are the third virial coefficients for triplet interactions and are important at high concentrations.

By substitution of the expressions for $\gamma_\pm$ and $(\phi-1)$ (eq 7, 8) into eq 2, the excess free energy is now expressed in terms of Pitzer's equations by

$$G^{ex} = n_w RT(f + m^2B_{mx} + m^3C_{mx}) \quad (9)$$

where f is the long-range electrostatic term (f^γ –

f^{ϕ}), and B_{mx} and C_{mx} are the short-range interaction terms for excess free energy. The full forms of eq 7–9 are lengthy and are displayed in Appendix A.

The first and second temperature derivatives of eq 9 as prescribed by eq 4 and 5 yield a temperature-dependent equation that can be fit to total heat capacity data to find the parameters B_{mx} and C_{mx} at a given temperature:

$$Cp_t = n_w \bar{C}p_1^\circ + m\bar{C}p_2^\circ + m(f^J + mB_{mx}^J + m^2 C_{mx}^J) \quad (10)$$

where B_{mx}^J and C_{mx}^J are the second derivatives of the second and third virial coefficients and f^J is the second derivative of f. The Debye-Hückel slope, A_ϕ, which gives the relationship of thermodynamic properties to concentration at high dilution, is included in the f term (eq 7 in Appendix A). Also, A_ϕ depends on the density of water and the dielectric constant, which are functions of temperature. The derivatives of A_ϕ with respect to temperature have been calculated by Silvester and Pitzer (1978) from 0°C to high temperature. The equations for enthalpy and heat capacity in terms of Pitzer's equations have been derived by Silvester and Pitzer (1977) and are given in Appendix A.

Heat capacity measurements

The instrument used for measuring specific heat was a standard Perkin-Elmer Model DSC-2. Although the DSC-2 is not the most accurate instrument for certain types of calorimetric measurements, it is appropriate for the present purpose because heat capacities can be measured on solutions well below their normal freezing point by supercooling the solutions. The temperature that can be reached before freezing varies with the salt concentration. Typical thermograms are shown at several concentrations of NaCl in Figure 1. At 0.5 molal the solution was cooled to about 250 K before ice formed, as shown by the large exotherm at 250 K. As the concentration increases, first ice and then a eutectic mixture of ice and solid sodium chloride precipitates from the supersaturated solutions as the temperature decreases. With increasing concentration the ice and eutectic exotherms move closer together and both are shifted to lower temperatures. The 6.0-molal solution remained supersaturated to below 230 K (–43°C), which is the limit of temperature control of the calorimeter.

The DSC-2 measures heat flow into a sample per unit time (dH/dt) relative to a known standard (usually sapphire). The specific heat C_p is related to the heat flow by

$$\frac{dH}{dt} = mC_p \frac{dT}{dt} . \quad (11)$$

The DSC-2 data are stored and processed by software written by New England Digital Corporation for an Able 60 computer located in the CRREL Soils Laboratory. The system collects data from the DSC-2 and computes specific heat at one-degree intervals. Energy calibration is afforded by data from a sapphire standard obtained over the

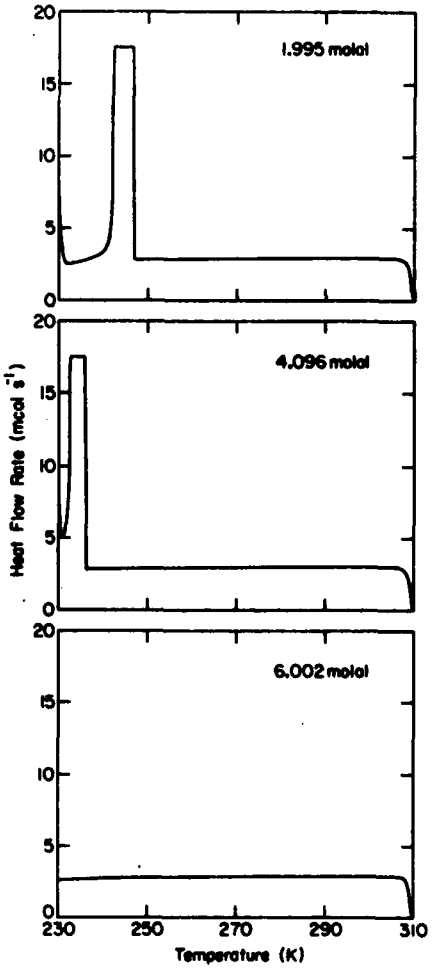

Figure 1. Thermograms of cooling scans at different concentrations of sodium chloride.

same temperature range. Temperature is calculated by measuring the freezing temperatures of pure water and mercury at a scan rate of 5 ° min^{-1} in the warming mode. An empty aluminum sample pan is run to establish the baseline. The samples, empty pan and sapphire were all run at a scan rate of -10° min^{-1} in the cooling mode at the highest instrument sensity (20 mcal s^{-1}). Sample weights averaged 20 mg and were weighed on a Perkin-Elmer TGS-2 thermobalance precise to 0.1 μg. A subambient kit was used which included a glove box and a helium purge gas supply. The system was cooled with a refrigeration unit supplied by CRREL.

The small sample size (about 0.025 cm^3) and low thermal resistance of the DSC-2 sample holder permits fast scan rates without temperature gradients and thermal lag in the sample. Specific heats can therefore be measured to low temperatures on supercooled solutions. Accuracy is sacrificed, however, especially at low concentration, as compared with some adiabatic and flow calorimeters, but these systems cannot be used on samples with decreasing temperature (adiabatic) or below 0°C. It will be shown that accurate high-dilution measurements are not needed to predict adequately the activities of saturated solutions below 0°C.

Three samples were prepared at each concentration with different sample pans. The sapphire standard and empty pans were rerun before each set of three samples. Temperature was recalibrated from thermograms of mercury and pure water before and after the standards and samples were run. The temperature calibrations were reproducible to about 0.05 K.

The heat flow (dH/dt) into each sample was converted to specific heat by eq 11. The specific heat values were smoothed over temperature by fitting the data at one-degree intervals to second-order polynomials in temperature. The standard error of a point from the smooth curve varied with temperature and concentration from 1.6% at 0.5 molal and 25°C to 0.8% at 6.0 molal and -40°C.

The average of the smoothed specific heat and the standard error for the three replicates at each concentration are given in Appendix B. The reproducibility of the values is 2.4% at 0.5 molal and 25°C, and decreases to 0.7% at 6.0 molal and -40°C.

Calculations

The calculation of low-temperature activities of sodium chloride and water begins by determining the temperature dependence of the adjustable parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ in Pitzer's equations. This dependence can be found by fitting activity or osmotic coefficient data directly to eq A7, if such data are available. For most salts, however, very few reliable activity measurements have been made below 10°C at high concentration. Silvester and Pitzer (1977) used apparent heat capacity data (ϕC_p) combined with other available thermodynamic data (enthalpy, activity and osmotic coefficients) to extend the ion-interaction equation of Pitzer from 25° to 300°C.

The heat capacities measured in this study can be used to improve the predictions from 25° to -40°C by fitting total heat capacity data to eq A14 and A15. The procedure is essentially the same as that described by Rogers and Pitzer (1981) for sodium sulfate solutions with the exception that total heat capacities instead of relative heat capacities are used in this study. The only difference is that the additional parameter, $\bar{C}p_1^\circ$, the molal heat capacity of pure water, must be fit to eq A14 at each temperature.

First, the specific heat of the sodium chloride solutions is converted to total heat capacity of an m-molal solution containing one kilogram of water by

$$Cp_t = C_p(1000 + mM) \qquad (12)$$

where M is the molecular weight of sodium chloride. The values of $\bar{C}p_1^\circ$ and $\bar{C}p_2^\circ$ are found by fitting Cp_t to eq A14 and treating $\bar{C}p_1^\circ$, $\bar{C}p_2^\circ$, B^J_{mx} and C^J_{mx} as adjustable parameters. A linear least-squares regression program (Davis 1973) was used to fit the data. Below 0°C the Debye-Hückel slope (A_ϕ, A_H and A_J) was extrapolated from Pitzer's values above 0°C.

The fitted values of $\bar{C}p_1^\circ$ and $\bar{C}p_2^\circ$ determined above were used to find the best values of the second temperature derivatives of $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ (App. A) at each temperature. The heat capacity data were refit to eq A14, and they reproduced the specific heat data to within 0.004 cal g^{-1} K^{-1}.

The temperature variation of the parameters $\partial^2\beta^{(0)}/\partial T^2$, $\partial^2\beta^{(1)}/\partial T^2$ and $\partial^2 C^\phi/\partial T^2$ is most simply represented by second-degree polynomials from 25° to -40°C. The polynomial equations are integrated by parts according to eq A16 and A17 after both sides are multiplied by T. The values of $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ and their first temperature derivatives at 25°C were used as the integration constants. Values of $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ at 25°C are from White and Bates (1980) and the first derivatives are from Silvester and Pitzer (1977). The tem-

perature dependence of the parameters is given by the following equations:

$$\beta^{(0)} = 2x_1 + 2x_2/T + x_3T^2/6 + x_4T^3/12 + x_5T^4/20 \quad (13)$$

$$\beta^{(1)} = 2x_6 + 2x_7/T + x_8T^2/6 + x_9T^3/12 + x_{10}T^4/20 \quad (14)$$

$$C^{\phi} = 2x_{11} + 2x_{12}/T + x_{13}T^2/6 + x_{14}T^3/12 + x_{15}T^4/20. \quad (15)$$

The coefficients of eq 13–15 are listed in Table 1.

Table 1. Coefficients of eq 13–15.

x_1 = 7.66249	x_9 = 4.49459 (10^{-5})
x_2 = -1.00472 (10^3)	x_{10} = -7.86640 (10^{-6})
x_3 = -1.79001 (10^{-3})	x_{11} = -1.06828
x_4 = 1.15601 (10^{-5})	x_{12} = 1.42620 (10^2)
x_5 = -1.90346 (10^{-8})	x_{13} = 2.44524 (10^{-4})
x_6 = 2.57468 (10^1)	x_{14} = -1.56052 (10^{-6})
x_7 = -3.25771 (10^3)	x_{15} = 2.54348 (10^{-9})
x_8 = -6.58529 (10^{-3})	

RESULTS

Values of $\gamma_{\pm}$ and a_w calculated over the entire temperature and concentration range of this study are listed in Table 2. The accuracy of these constants can be checked by independently calculating a_w from the thermodynamic properties of ice. In a solution of sodium chloride at the freezing point

$$\Delta G_s^{\circ}(\text{ice}) = -RT\ln a_w \quad (16)$$

where ΔG_s° is the free energy change in going from ice to infinite dilution at some temperature T.

To calculate the temperature dependence of ΔG_s°, the derivative with respect to temperature yields

$$\frac{\partial}{\partial T}\frac{\Delta G_s^{\circ}}{T} = \frac{-\Delta H_s^{\circ}}{T^2} \quad (17)$$

where ΔH_s° is the heat of solution at infinite dilution. At 0°C, $\Delta H_s^{\circ} = -1436$ cal. The variation of ΔH_s° is found from

$$\frac{\partial \Delta H_s^{\circ}}{\partial T} = \Delta Cp^{\circ} \quad (18)$$

where ΔCp° is the difference in heat capacity between ice and pure water:

$$\Delta Cp^{\circ}(\text{ice}) = Cp_i^{\circ} - Cp. \quad (19)$$

The value of Cp_i° is from the measured heat capacities of water emulsions down to -38°C (Angell et al. 1973). The heat capacity of ice (Cp) is from Dorsey (1940). The temperature variation of ΔCp° was fit to the following equation:

$$\Delta Cp^{\circ}(\text{ice}) = z_1 + z_2T + z_3T^2. \quad (20)$$

Integration of eq 20 with the values of ΔH_s° and ΔG_s° for ice at 0°C gives

$$\Delta G_s^{\circ}(\text{ice}) = -z_1T\ln T - \frac{z_2}{2}T^2 - \frac{z_3T^3}{6} + z_4T + z_5. \quad (21)$$

The coefficients of eq 20 and 21 are listed in Table 3. A comparison of the activity of water calculated from the properties of ice and from Pitzer's equations using the parameters determined above is given in Table 4. The average standard deviation is 0.0017. In Figure 2 the calculated solubility of ice is plotted against the experimental solubility; the agreement is good.

The activities of components in a salt mixture at low temperature can be calculated from the mixing equations of Pitzer and Kim (1974) by using the pure salt parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} as determined in this study and the mixing parameters θ and ψ for different ions of the same charge type. The terms θ and ψ are small at 25°C and probably will not require correction at low temperature.

Table 2. Values of $\gamma_{\pm}$ and a_w calculated below 0°C in this study.

	0°C		−5°C		−10°C	
m	$\gamma_{\pm}$	a_w	$\gamma_{\pm}$	a_w	$\gamma_{\pm}$	a_w
0.5	0.656	0.9839	0.646	0.9840	0.633	0.9842
1.0	0.614	0.9679	0.598	0.9684	0.578	0.9688
2.0	0.599	0.9347	0.574	0.9358	0.546	0.9372
3.0	0.623	0.8982	0.592	0.9001	0.556	0.9023
4.0	0.676	0.8576	0.639	0.8598	0.598	0.8624
5.0	0.756	0.8122	0.716	0.8142	0.670	0.8165
6.0	0.870	0.7620	0.829	0.7629	0.780	0.7641

	−15°C		−20°C		−25°C	
m	$\gamma_{\pm}$	a_w	$\gamma_{\pm}$	a_w	$\gamma_{\pm}$	a_w
0.5	0.618	0.9844	0.600	0.9846	0.580*	0.9849*
1.0	0.556	0.9694	0.530	0.9702	0.501*	0.9710*
2.0	0.513	0.9389	0.477	0.9408	0.438	0.9431
3.0	0.516	0.9049	0.473	0.9080	0.426	0.9117
4.0	0.552	0.8656	0.501	0.8693	0.448	0.8736
5.0	0.619	0.8193	0.563	0.8227	0.504	0.8266
6.0	0.726	0.7655	0.667	0.7673	0.603	0.7693

	−30°C		−35°C		−40°C	
m	$\gamma_{\pm}$	a_w	$\gamma_{\pm}$	a_w	$\gamma_{\pm}$	a_w
0.5	0.557*	0.9852*	0.513*	0.9856*	0.503*	0.9860*
1.0	0.469*	0.9720*	0.434*	0.9731*	0.397*	0.9744*
2.0	0.396*	0.9458*	0.352*	0.9489*	0.307*	0.9526*
3.0	0.377	0.9160	0.327*	0.9210*	0.278*	0.9268*
4.0	0.393	0.8788	0.317	0.8848	0.282*	0.8918*
5.0	0.443	0.8313	0.380	0.8368	0.319	0.8432*
6.0	0.536	0.7718	0.467	0.7748	0.397	0.7784

* Values exceed temperature range of heat capacity equations.

Table 3. Coefficients of eq 20 and 21.

z_1	3.0256 (10^1)
z_2	−1.1274 (10^{-1})
z_3	1.2876 (10^{-4})
z_4	1.68746 (10^3)
z_5	−3.49782 (10^5)

Table 4. Activity of water (a_w) at freezing point calculated from Pitzer's equations compared to values from ΔG_s^0(ice) and solubility data.

	a_w *from*		
T (°C)	*Pitzer's equation*	*Solubility data*	*Difference*
−3.48	0.9666	0.9668	0.0002
−5.17	0.9515	0.9510	−0.0005
−6.32	0.9414	0.9405	−0.0009
−8.52	0.9222	0.9205	−0.0017
−9.41	0.9150	0.9126	−0.0024
−11.04	0.9007	0.8982	−0.0025
−14.77	0.8682	0.8660	−0.0022
−16.21	0.8562	0.8539	−0.0023
−18.73	0.8346	0.8331	−0.0015
−20.85	0.8129	0.8160	0.0031

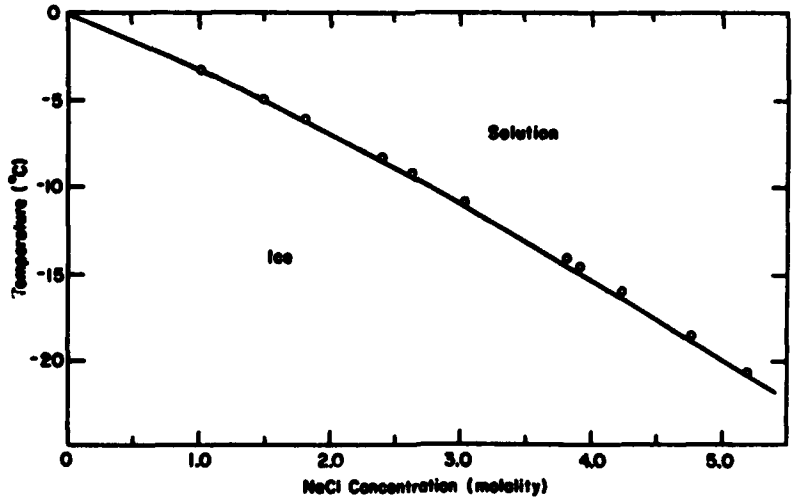

Figure 2. Freezing point of ice in sodium chloride solutions. The curve is the experimental solubility from Linke (1958). The points are from this study.

CONCLUSION

This work demonstrates that total heat capacity data can be used to improve calculations of activities of salts at freezing temperatures. Now that the usefulness of the method has been shown, additional salts will be investigated so that mineral equilibria can be determined in common brine mixtures. In mixtures with many possible phases, the phase and solution composition can be found from the temperature dependence of the free energy of all species that can be present by using one of the free energy minimization methods that are in use (Storey and Van Zeggeren 1964, Harvie and Weare 1980).

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APPENDIX A: PITZER'S EQUATIONS FOR THE ACTIVITY, EXCESS FREE ENERGY, ENTHALPY AND HEAT CAPACITY OF A SINGLE ELECTROLYTE

Osmotic coefficient

$$\phi - 1 = -|Z_m Z_x| A_\phi \frac{I^{1/2}}{1+1.2I^{1/2}} + \frac{m2\nu_m\nu_m}{\nu} B^\phi_{mx} + m^2 2 \frac{(\nu_m\nu_x)^{3/2}}{\nu} C^\phi_{mx} \quad \text{(A1)}$$

$$B^\phi_{mx} = \beta^{(0)} + \beta^{(1)} \exp(-\alpha I^{1/2}) \quad \text{(A2)}$$

Activity coefficient

$$\ln \gamma_\pm = -|Z_m Z_x| A_\phi \left[\frac{I^{1/2}}{1+1.2I^{1/2}} + \frac{2}{b} \ln(1+1.2I^{1/2})\right] + \frac{m2\nu_m\nu_x}{\nu} B^\gamma_{mx} + m^2 \frac{2(\nu_m\nu_x)^{3/2}}{\nu} C^\gamma_{mx} \quad \text{(A3)}$$

$$B^\gamma_{mx} = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2 I}\left[1-(1+\alpha I^{1/2} - \frac{\alpha^2 I}{2}\exp(-\alpha I^{1/2})\right] \quad \text{(A4)}$$

$$C^\gamma_{mx} = 3/2\, C^\phi_{mx} \quad \text{(A5)}$$

Excess Gibbs free energy

$$\Delta G^{ex} = n_w \nu m R T (1 - \phi + \ln \gamma_\pm) \quad \text{(A6)}$$

$$\Delta G^{ex} = n_w RT\left[-A_\phi \frac{4I}{1.2} \ln(1+1.2I^{1/2}) + m^2 2\nu_m\nu_x B_{mx} + m^3 2(\nu_m\nu_x)^{3/2} C_{mx}\right] \quad \text{(A7)}$$

$$B_{mx} = \beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2 I}\left[1-(1+\alpha I^{1/2})\exp(-\alpha I^{1/2})\right] \quad \text{(A8)}$$

$$C_{mx} = \frac{C^\phi}{2} \quad \text{(A9)}$$

Relative enthalpy

$$L = m\nu|Z_m Z_x| \frac{A_H}{3.6} \ln(1+1.2I^{1/2}) - 2\nu_m\nu_x RT^2 m^2 B^L_{mx} + 2(\nu_m\nu_x)^{3/2} RT^2 m^3 C^L_{mx} \quad \text{(A10)}$$

$$B^L_{mx} = (\partial B_{mx}/\partial T)_{P,I} = \left(\frac{\partial \beta^{(0)}}{\partial T}\right)_P + \left(\frac{\partial \beta^{(1)}}{\partial T}\right)_P \left(\frac{2}{\alpha^2 I}\right)\left[1-(1+\alpha I^{1/2})\exp(-\alpha I^{1/2})\right] \quad \text{(A11)}$$

$$C^L_{mx} = \left(\frac{\partial C_{mx}}{\partial T}\right)_P = \frac{1}{2}\left(\frac{\partial C^\phi}{\partial T}\right)_P \quad \text{(A12)}$$

$$A_H = 6RT^2\left(\frac{\partial A_\phi}{\partial T}\right)_P \quad \text{(A13)}$$

Relative heat capacity

$$J = m\nu|Z_m Z_x|\frac{A_J}{3.6}\ \ln(1+1.2I^{1/2}) - 2\nu_m\nu_x RT^2m^2B^J_{mx} - 2(\nu_m\nu_x)^{3/2}RT^2m^3C^J_{mx} \quad \text{(A14)}$$

$$J = Cp_t - n_w\bar{C}p_i^\circ - m\bar{C}p_2^\circ \quad \text{(A15)}$$

$$B^J_{mx} = \left(\frac{\partial^2 B_{mx}}{\partial T^2}\right)_{P,I} + \frac{2}{T}\left(\frac{\partial B_{mx}}{\partial T}\right)_{P,I} \quad \text{(A16)}$$

$$= \left(\frac{\partial^2\beta^{(0)}}{\partial T^2}\right)_P + \frac{2}{T}\left(\frac{\partial\beta^{(0)}}{\partial T}\right)_P + \left[\left(\frac{\partial^2\beta^{(1)}}{\partial T^2}\right)_P + \frac{2}{T}\left(\frac{\partial\beta^{(1)}}{\partial T}\right)_P\right]\frac{2}{\alpha^2 I}$$

$$\times\ [1-(1+\alpha I^{1/2})\exp(-\alpha I^{1/2})]$$

$$C^J_{mx} = \left(\frac{\partial^2 C_{mx}}{\partial T^2}\right)_P + \frac{2}{T}\left(\frac{\partial C_{mx}}{\partial T}\right)_P \quad \text{(A17)}$$

$$A_J = \left(\frac{\partial A_H}{\partial T}\right)_P \quad \text{(A18)}$$

Nomenclature

A_ϕ	Debye-Hückel slope for the activity and osmotic coefficient
A_H	Debye-Hückel slope for enthalpy
A_J	Debye-Hückel slope for heat capacity
z_m, z_x	charge on cation and anion, respectively
ν_m, ν_x	number of cations and anions, respectively, per formula weight in a strong electrolyte mx
α	2.0, a constant
I	ionic strength, $I = \frac{1}{2}m(\nu_m z_m^2 + \nu_x z_x^2)$
n_w	mass of water (kg)
m	molality (mol salt·kg H_2O^{-1})
Cp_t	total heat capacity (cal K^{-1} mol^{-1})
$\bar{C}p_i^\circ$	molal heat capacity of pure water (cal K^{-1} mol^{-1})
$\bar{C}p_2^\circ$	partial molal heat capacity of solute at infinite dilution (cal K^{-1} mol^{-1})
$\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ_{mx}	fitted parameters
ΔG^{ex}	excess free energy
R	gas constant
T	temperature (K)
L	total relative enthalpy
J	total relative heat capacity

APPENDIX B: AVERAGE VALUES OF SPECIFIC HEAT AND STANDARD ERRORS FOR THREE RUNS AT EACH CONCENTRATION

Concentration	25°C		20°C		15°C		10°C		5°C		0°C		-5°C	
(mol kg^{-1})	Cp	S.E.	Cp	S.E.	Cp	S.E.	Cp	S.E.	Cp	S.E.	Cp	S.E.	Cp	S.E.
0.502	1.000	0.026	1.001	0.026	1.002	0.0264	1.003	0.0266	1.003	0.0267	1.0038	0.0264	1.005	0.026
1.008	0.9488	0.0039	0.9498	0.0038	0.9504	0.0036	0.9506	0.0034	0.9504	0.0031	0.9499	0.0029	0.9490	0.0027
1.995	0.9076	0.0106	0.9081	0.011	0.9081	0.0111	0.9075	0.0110	0.9064	0.0106	0.9048	0.0098	0.9024	0.009
2.558	0.8815	0.0040	0.8830	0.003	0.8838	0.0022	0.8837	0.0017	0.8828	0.0013	0.8812	0.0013	0.8770	0.0042
3.075	0.8549	0.0175	0.8557	0.019	0.8558	0.0193	0.8555	0.0196	0.8546	0.0196	0.8531	0.0193	0.8510	0.0187
4.096	0.8310	0.0050	0.8323	0.0059	0.8329	0.0066	0.8328	0.0072	0.8319	0.0077	0.8303	0.0078	0.8280	0.0079
5.027	0.8088	0.0147	0.8111	0.0150	0.8126	0.0151	0.8133	0.0150	0.8133	0.0147	0.8125	0.0140	0.8110	0.0132
6.002	0.7873	0.0120	0.7891	0.0115	0.7903	0.0109	0.7909	0.0104	0.7909	0.0099	0.7903	0.0094	0.7891	0.0088

Concentration	-10°C		-15°C		-20°C		-25°C		-30°C		-35°C		-40°C	
(mol kg^{-1})	Cp	S.E.	Cp	S.E.	Cp	S.E.	Cp	S.E.	Cp	S.E.	Cp	S.E.	Cp	S.E.
0.502	1.0051	0.0258	1.0059	0.0258	1.0068	0.0258	1.0073	0.025	1.0079	0.0250	1.0086	0.0246	1.0092	0.0244
1.008	0.9477	0.0026	0.9460	0.0025	0.9440	0.0027	0.9416	0.0030	0.9388	0.0055	0.9357	0.0041	0.9322	0.0050
1.995	0.8997	0.0077	0.8963	0.0063	0.8925	0.0050	0.8880	0.0042	0.8831	0.0048	0.8776	0.0068	0.8715	0.0096
2.558	0.8754	0.0018	0.8713	0.0022	0.8665	0.0028	0.8608	0.0035	0.8636	0.0119	0.8470	0.0055	0.8389	0.0069
3.075	0.8484	0.0178	0.8452	0.0166	0.8415	0.0151	0.8372	0.0135	0.8323	0.0117	0.8269	0.0099	0.8209	0.0086
4.096	0.8250	0.0078	0.8213	0.0075	0.8168	0.0072	0.8117	0.0067	0.8058	0.0062	0.7992	0.0058	0.7918	0.0057
5.027	0.8067	0.0120	0.8056	0.0106	0.8018	0.0089	0.7973	0.0071	0.7919	0.0054	0.7859	0.0044	0.7790	0.0053
6.002	0.7873	0.0082	0.7850	0.0076	0.7820	0.0071	0.7784	0.0066	0.7743	0.0061	0.7696	0.0056	0.7642	0.0054

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