SPECIAL REPORT 94-18

FREZCHEM: A Chemical-Thermodynamic Model for Aqueous Solutions at Subzero Temperatures

Giles M. Marion and Steven A. Grant

July 1994

Abstract

This report documents a FORTRAN version of the Spencer-Møller-Weare chemical thermodynamic model for aqueous electrolyte solutions at subzero temperatures (FREZCHEM). FREZCHEM is structured to predict the chemical composition and unfrozen water of aqueous solutions between –60 °C and +25 °C at atmospheric pressure (0.101325 MPa). FREZCHEM includes two reaction pathways: 1) freezing at variable temperature and fixed total water and 2) evaporation at variable water and fixed temperature. Activity coefficients and the activity of water are calculated using the Pitzer equations, which are valid to high solution ionic strengths (≈20 mol kg^{-1}). Fifteen chloride and sulfate salts of sodium, potassium, calcium, and magnesium are included in the model. Predicted and experimental measurements of solute molalities and the unfrozen water fraction during seawater freezing are in good agreement. At –50 °C, 0.3% of seawater remains unfrozen with 99.7% of Na and 95.5 % of Cl having precipitated into one of four salts. FREZCHEM should find many applications in physicochemical studies of aqueous solutions and freezing.

For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380-89a, *Standard Practice for Use of the International System of Units,* published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

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U.S. Army Corps of Engineers
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Prepared for
OFFICE OF THE CHIEF OF ENGINEERS

PREFACE

This report was prepared by Dr. Giles M. Marion and Dr. Steven A. Grant, Research Physical Scientists, of the Geochemical Sciences Branch, Research Division, U. S. Army Cold Regions Research and Engineering Laboratory. Funding was provided by DA Project 4A161102AT24, *Research in Snow, Ice and Frozen Ground*, Tasks EC and SC, Work Units B03, *Soil Solute Interactions at Low Temperature*, and F02, *Chemical Processes in Frozen Soil*, and by Strategic Environmental Research and Development Program (SERDP) Work Unit, *Fate and Transport in Seasonally Frozen Soil and Discontinuous Permafrost.*

The authors thank Andrew Sezak for assistance in translating the FREZCHEM program into the FORTRAN version, and Dr. Samuel C. Colbeck, James H. Cragin and David Fisk for technically reviewing earlier drafts of this report.

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FREZCHEM: A Chemical-Thermodynamic Model for Aqueous Solutions at Subzero Temperatures

GILES M. MARION AND STEVEN A. GRANT

INTRODUCTION

The presence of solutes lowers the freezing-point of aqueous solutions; and when solutions freeze, ice formation largely excludes solutes, concentrating them in the unfrozen brine which, in turn, further lowers the brine freezing point. For example, when the temperature of a 1.0 molal NaCl solution is lowered below 0 °C, ice starts to form at approximately –3 °C (Fig. 1). As ice forms, the NaCl molality increases and the temperature drops along the ice–solution line, assuming that equilibrium is maintained, until the eutectic is reached at –21.3 °C and 5.17 molal (Fig. 1). At this point, the residual solution freezes, forming a mixture of ice and hydrohalite [$NaCl \cdot 2H_2O(cr)$]. Clearly, complex interactions exist between solute concentrations and the freezing process.

A number of chemical thermodynamic models for aqueous electrolyte solutions have been developed in recent years (Sposito and Mattigod 1979, Plummer et al. 1988, Spencer et al. 1990). However, only the Spencer-Møller-Weare model deals explicitly with aqueous solutions at subzero temperatures. This model accounts for the precipitation of the chloride and sulfate salts of sodium, potassium, calcium, and magnesium over the temperature range from –60 °C to +25 °C at atmospheric pressure (0.101325 MPa). While the parameters used in the model have been published (Spencer et al. 1990), a working version of the model has not been published. Such a working model would be extremely useful for geochemists and geophysicists interested in the complex interactions between solutes and the freezing process. This preliminary report will document a FORTRAN version of the Spencer-Møller-Weare model, which we have chosen to call FREZCHEM.

MODEL STRUCTURE

FREZCHEM is a chemical thermodynamic "equilibrium" model. This model will calculate the equilibrium composition of aqueous solutions at specified temperatures, but will not provide any information on the time required to reach, or the path of change to, the equilibrium state. FREZCHEM calculates equilibrium between water and ice and between dissolved and solid phase salts.

For water and ice at equilibrium,

$$\mu_i = \mu_i^\circ + RT \ln\left(a_{H_2O(cr,I)}\right) = \mu_w = \mu_w^\circ + RT \ln\left(a_{H_2O(l)}\right) \quad (1)$$

where R is the gas constant, T is absolute temperature, μ_i and μ_w are the chemical potentials of ice and water, μ_i° and μ_w° are the standard chemical potentials, and $a_{H_2O(cr\,I)}$ and $a_{H_2O(l)}$ are the activities of water in the form of ice and liquid water. Equation 1 can be rearranged to yield

$$\frac{\mu_i^\circ - \mu_w^\circ}{RT} = \ln\left(a_{H_2O(l)}/a_{H_2O(cr,I)}\right) = \frac{\Delta_{fus}G^\circ}{RT} \quad (2)$$

where $\Delta_{fus}G^\circ$ is the standard Gibbs energy of fusion ($\mu_i^\circ - \mu_w^\circ$). At equilibrium with respect to pure ice, $a_{H_2O(cr,\,I)} = 1.0$. Therefore

$$\left(a_{H_2O(l)}\right) = \exp\left[\Delta_{fus}G^\circ/RT\right] = K \quad (3)$$

the activity of water is equal to the equilibrium constant (K) at a given temperature. For equilibrium with respect to a salt (e.g., hydrohalite)

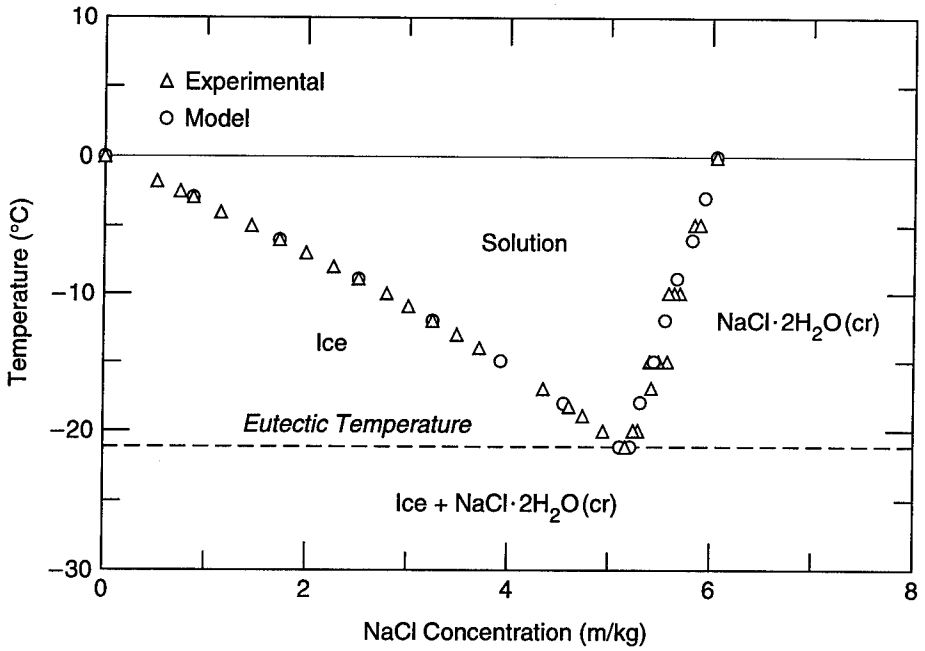

Figure 1. A stability diagram for the NaCl-H_2O system at subzero temperatures. Experimental measurements are from Bukshtein et al. (1953) and Hall et al. (1988).

$$NaCl \bullet 2H_2O(cr) \rightleftharpoons Na^+(aq) + Cl^-(aq) + 2\,H_2O(l) \quad (4)$$

and

$$(a_{Na^+(aq)})(a_{Cl^-(aq)})(a_{H_2O(l)})^2 = K \quad (5)$$

assuming that the activity of the pure salt [$NaCl \bullet 2H_2O(cr) = 1.0$. The relation between activity *(a)* and molality *(m)* of a substance "B" is given by

$$a_B = \gamma_B\, m_B \quad (6)$$

where γ is the activity coefficient. If molalities are given, to calculate activities requires an extra-thermodynamic model for activity coefficients.

The Pitzer equations are used to calculate the activity of water and the activity coefficients for soluble ions. These equations allow calculation of activity coefficients to high ionic strengths in complex solutions (Plummer et al. 1988, Spencer et al. 1990, Pitzer 1991).

The osmotic coefficient (ϕ), and single-ion activity coefficients for cations (γ_M) and anions (γ_X) are given by

$$(\phi - 1) = 2/(\Sigma m_i)\left\{-A^\phi I^{1.5}/(1 + b\,I^{0.5}) + \Sigma\Sigma m_c m_a\left(B^\phi_{ca} + ZC_{ca}\right) + \Sigma\Sigma m_c m_c\left(\Phi^\phi_{cc'} + \Sigma m_a\,\Psi_{cc'a}\right) + \Sigma\Sigma m_a m_a\left(\Phi^\phi_{aa'} + \Sigma m_c\,\Psi_{aa'c}\right)\right\} \quad (7)$$

$$\ln(\gamma_M) = z_M^2\,F + \Sigma m_a\left(2B_{Ma} + ZC_{Ma}\right) + \Sigma m_c\left(2\Phi_{Mc} + \Sigma m_a \Psi_{Mca}\right) + \Sigma\Sigma m_a m_{a'}\Psi_{aa'M} + |z_M|\,\Sigma\Sigma m_c m_a C_{ca} \quad (8)$$

$$\ln(\gamma_X) = z_X^2\,F + \Sigma m_c\left(2B_{cX} + ZC_{cX}\right) + \Sigma m_a\left(2\Phi_{Xa} + \Sigma m_c \Psi_{Xac}\right) + \Sigma\Sigma m_c m_{c'}\Psi_{cc'X} + |z_X|\,\Sigma\Sigma m_c m_a C_{ca} \quad (9)$$

where A^ϕ is the Debye-Huckel constant, b is a constant (=1.2), B^ϕ, C, Φ^ϕ, and Ψ are salt interaction coefficients, z_i is the charge number of the ith ion, I is the ionic strength defined by

$$I = 0.5\,\Sigma m_i z_i^2\,, \quad (10)$$

Z is defined by

Table 1. Minerals currently in the FREZCHEM model.

1. $Na_2SO_4 \cdot 10H_2O$(cr) (mirabilite)
2. Na_2SO_4(cr) (thenardite)
3. K_2SO_4(cr) (arcanite)
4. $MgSO_4 \cdot 6H_2O$(cr) (hexahydrite)
5. $MgSO_4 \cdot 7H_2O$(cr) (epsomite)
6. $MgSO_4 \cdot K_2SO_4\ 6H_2O$(cr) (picromerite)
7. NaCl(cr) (halite)
8. $NaCl \cdot 2H_2O$(cr) (hydrohalite)
9. KCl(cr) (sylvite)
10. $CaCl_2 \cdot 6H_2O$(cr) (antarcticite)
11. $MgCl_2 \cdot 6H_2O$(cr) (bischofite)
12. $MgCl_2 \cdot 8H_2O$(cr)
13. $MgCl_2 \cdot 12H_2O$(cr)
14. $KMgCl_3 \cdot 6H_2O$(cr) (carnallite)
15. $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$(cr) (tachyhydrite)

$$Z = \Sigma m_i |z_i| \tag{11}$$

and F is a complex function of $A\phi$, I, and the salt interaction coefficients (Plummer et al. 1988, Pitzer 1991). Given ϕ from eq 7, the activity of water is defined by

$$a_{H_2O(l)} = \exp(-\phi\ \Sigma m_i / 55.50837). \tag{12}$$

The equilibrium constants and the Pitzer equation parameters for the temperature range –60 °C to +25 °C were published by Spencer et al. (1990) as functions of temperature using equations of the form

$$P(T) = a_1 + a_2\,T + a_6\,T^2 + a_9\,T^3 + a_3/T + a_4\,\ln(T) \tag{13}$$

where $P(T)$ is the Pitzer equation parameter directly or the function, $[-\Delta_r G°/RT]$ (where $\Delta_r G°$ is the standard reaction Gibbs energy), for equilibrium constants $[K = \exp(-\Delta_r G°/RT)]$ and T is thermodynamic temperature (K). Refer to Spencer et al. (1990) for the specific parameters used in the model (their Tables 1, 2, and 3). The only additional parameter, beyond those used in the Spencer-Møller-Weare model, is $\Psi(Ca,Mg,SO_4) = 0.024$, which is treated as a constant independent of temperature (Pitzer 1991).

Table 2. A listing of chemical species and their numerical designation in the FREZCHEM model.

A. Solution and atmospheric species

#	*Species*	#	*Species*	#	*Species*
1	Na^+(aq)	11	Cl^-(aq)	21	CO_2(aq)
2	K^+(aq)	12	SO_4^{2-}(aq)	22	$CaSO_4°$(aq)
3	Ca^{2+}(aq)	13	OH^-(aq)	23	$MgSO_4°$(aq)
4	Mg^{2+}(aq)	14	HCO_3^-(aq)	24	
5	H^+(aq)	15	CO_3^{2-}(aq)	25	
6		16		26	
7		17		27	
8		18		28	
9		19		29	CO_2(g)
10		20		30	H_2O(l)

B. Solid phase species

#	*Species*	#	*Species*	#	*Species*
31	H_2O(cr,I)	41	$Na_2SO_4 \cdot 10H_2O$(cr)	51	
32	$NaCl \cdot 2H_2O$(cr)	42	Na_2SO_4(cr)	52	
33	NaCl(cr)	43	$MgSO_4 \cdot 6H_2O$(cr)	53	
34	KCl(cr)	44	$MgSO_4 \cdot 7H_2O$(cr)	54	
35	$CaCl_2 \cdot 6H_2O$(cr)	45	K_2SO_4(cr)	55	
36	$MgCl_2 \cdot 6H_2O$(cr)	46	$MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$(cr)	56	
37	$MgCl_2 \cdot 8H_2O$(cr)	47		57	
38	$MgCl_2 \cdot 12H_2O$(cr)	48		58	
39	$KMgCl_3 \cdot 6H_2O$(cr)	49		59	
40	$CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$(cr)	50		60	

Table 3. FREZCHEM model output for freezing of seawater at –30 °C.

Temp (K)	Ion. Str.	AH_2O	Phi	H_2O (g)	Ice (g)
243.15	7.8770	0.74696	1.6390	33.120	948.20
Solution Species	*Initial Conc.*	*Final Conc.*	*Act. Coef.*	*Activity*	*Moles*
Na	0.48695	1.6940	0.54243	0.91885	0.56104E–01
K	0.10630E–01	0.32095	0.19599	0.62905E–01	0.10630E–01
Ca	0.95300E–02	0.28673	0.51732	0.14833	0.94967E–02
Mg	0.55160E–01	1.6654	1.1282	1.8790	0.55160E–01
Cl	0.56818	5.9081	1.8095	10.691	0.19568
SO_4	0.29390E–01	0.55838E–02	0.32328	0.18051E–02	0.18494E–03
$CaSO_4$	0.00000	0.10058E–02	1.0000	0.10058E–02	0.33313E–04
$MgSO_4$	0.00000	0.42492E–05	1.0000	0.42492E–05	0.14074E–06
H_2O(l)				0.74696	1.8384
Solid Species	*Moles*	*Equil. Constant*			
Ice	52.633	0.74693			
$NaCl_2 \cdot 2H_2O$	0.37250	5.4770			
NaCl	0.00000	19.127			
KCl	0.00000	1.0399			
$CaCl_2 \cdot 6H_2O$	0.00000	695.12			
$MgCl_2 \cdot 6H_2O$	0.00000	40585.0			
$MgCl_2 \cdot 8H_2O$	0.00000	1403.3			
$MgCl_2 \cdot 12H_2O$	0.00000	27.775			
$KMgCl_3 \cdot 6H_2O$	0.00000	1054.2			
$CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$	0.00000	0.17775E+21			
$Na_2SO_4 \cdot 10H_2O$	0.29172E–01	0.81213E–04			
Na_2SO_4	0.00000	0.73236			
$MgSO_4 \cdot 6H_2O$	0.00000	3.1211			
$MgSO_4 \cdot 7H_2O$	0.00000	0.93967E–01			
K_2SO_4	0.00000	0.61722E–02			
$MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$	0.00000	0.21935E–04			
$CaSO_4$ (ion-pair)		0.26618			
$MgSO_4$ (ion-pair)		798.18			
Iterations = 39					

The specific salts included in the present model are listed in Table 1. In addition to these salts, the model also explicitly considers ion-pairs for $CaSO_4$ and $MgSO_4$.

MATHEMATICAL ALGORITHM

Two basic mathematical approaches are used in chemical thermodynamic models to calculate equilibrium concentrations and activities: Gibbs energy minimization or solution of sets of nonlinear equations. The Spencer et al. (1990) model explicitly uses Gibbs energy minimization. The PHRQPITZ model (Plummer et al. 1988) uses the nonlinear equation solution method. Both approaches ultimately provide the same answers.

The FREZCHEM model solves sets of nonlinear equations that include ice–water and mineral equilibria. These equations may, in principle, be solved either simultaneously or sequentially. FREZCHEM uses the sequential approach, which treats each reaction as an independent reaction (Fig. 2). The solution of the set of nonlinear equations occurs by iterating through the sequence many times. Advantages of the sequential approach vis-a-vis the simultaneous or Gibbs energy minimization approaches include l) programming

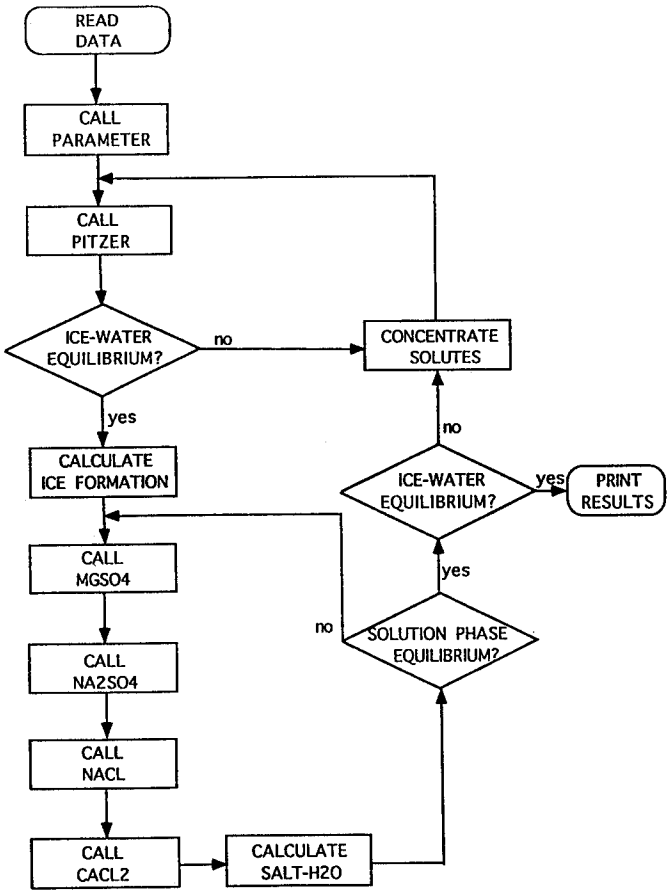

Figure 2. The FREZCHEM model flowchart.

simplicity since only one reaction is considered in separate subroutines, 2) ease of adding or subtracting new reactions since they can be inserted or deleted at any point in the sequence, and 3) the ease of program operation for both simple and complex aqueous solutions. With respect to the last point, only subroutines containing the elements in the "input" listing are used. For example, if only Na and Cl are present, then the program will only "call" the subroutine dealing with NaCl equilibrium and will bypass the remainder. For complex aqueous solutions such as seawater, the program will "call" every subroutine. The major disadvantage of the sequential approach is that it can be slow to converge. Another problem with the current model is convergence. At times, the program diverges or oscillates and never arrives at the equilibrium concentrations.

The program assumes that the initial aqueous solution is unfrozen and calculates the amount of ice, if any, that will form at the specified salt concentrations and temperature. The program first tests to see if ice and water are at equilibrium at the specified temperature. The criteria are

$$\text{IF } a_{H_2O(l)} > K \quad \text{THEN freeze} \tag{14}$$

$$\text{IF } a_{H_2O(l)} = K \quad \text{THEN equilibrium} \tag{15}$$

$$\text{IF } a_{H_2O(l)} < K \quad \text{THEN water is stable phase} \tag{16}$$

where $a_{H_2O(l)}$ is the activity of water calculated from the Pitzer equations (eq 7 and 12) and K *is* the equilibrium constant for ice-water (eq 3). If $a_{H_2O(l)} > K$, this implies that water is thermodynamically unstable and ice (stable phase) should form. Ice formation is calculated indirectly. First, solute concentrations are increased proportionally, which decreases $a_{H_2O(l)}$ (eq 12) until $a_{H_2O(l)} = K$ and equilibrium is reached. Ice formation is calculated by

$$\text{Ice} = \text{Total}H_2O - \text{Water}_f \quad (17)$$

$$\text{Water}_f = \text{Water}_i \left(\Sigma m_i / \Sigma m_f\right) \quad (18)$$

where Water_f, Water_i, and $\text{Total}H_2O$ are the final water, initial water, and total H_2O (ice and water), m_i are the initial molalities of solutes, and m_f are the final molalities. These calculations assume that the ice phase is a pure phase. If $a_{H_2O(l)} < K$, this implies that water is the thermodynamically stable phase and ice should not form at the specified salt concentrations and temperature.

In addition to freezing, FREZCHEM will also evaporate solutions. In contrast to freezing, the evaporation of water is not controlled by an equilibrium relation. The evaporation routine simply removes water incrementally from the solution, at a fixed temperature, according to the user's specifications. The program will not allow evaporation if ice is thermodynamically stable at the specified temperature and solution concentrations.

After ice and water are equilibrated, the program cycles through subroutines to handle mineral equilibria (Fig. 2). At present, there are 11 subroutines to handle the 15 mineral phases (Table 1) and the two ion-pair equilibria. Minerals that are identical in chemical composition except for waters of hydration are handled in the same subroutine [e.g., NaCl(cr) and $NaCl \cdot 2H_2O$(cr)].

After cycling through the mineral equilibrium equations, the program calculates the amount of water associated with hydrated salts (Fig. 2). Then the program tests for overall mineral equilibrium. In FREZCHEM, the initial and final solution phase concentrations must agree to within ±0.1 % for all solution phase cations and anions. In general if more than one mineral phase is precipitating, the first cycle through the mineral subroutines will not suffice to establish overall mineral equilibrium and the equations must be solved repeatedly.

Eventually mineral equilibrium is established. Then the program tests to see if ice and water are still in equilibrium or $a_{H_2O(l)} < K$. For equilibrium, $a_{H_2O(l)}$ must agree with K to within ±0.00005. If ice and water are not in equilibrium and $a_{H_2O(l)} > K$, then the program cycles through the ice-water equilibrium and subsequently mineral equilibrium subroutines. Eventually the program converges to within the numerical equilibrium criteria established in the program, and output is sent to the print files.

FREZCHEM PROGRAM

A listing of the FREZCHEM FORTRAN program is in Appendix A. A major effort was made to adhere to the FORTRAN 77 ANSI Standard in writing this program. For example, FREZCHEM uses an 80-column statement line where columns 1–5 are statement labels, column 6 is a continuation column, columns 7–72 are used for statements, and columns 73–80 are used for commentary. Variable names are ≤ 6 characters. FREZCHEM is a FORTRAN translation of an earlier program written in TrueBASIC. FORTRAN assumes, unless otherwise declared, that variables beginning with the letters "IJKLMN" are integer variables and all other initial letters refer to real variables. In order to retain the same variable names between programs, this restriction required formal declaration of some real variables in the FORTRAN version. FREZCHEM is currently running on a Macintosh Quadra 800 computer using the MacFortran II compiler (version 3.2, Absoft 1991).

The FREZCHEM program consists of a main program called *FREZCHEM* and 15 subroutines. *FREZCHEM* reads in data from screen queries, initializes some parameters, freezes or evaporates the aqueous solution, calculates the water of hydration, tests for chemical thermodynamic equilibria, and most importantly "calls" the various subroutines (Fig. 2).

Subroutine *PARAMETER* calculates the parameters for the Pitzer equations and the equilibrium constants as functions of temperature (eq 13). For the most part, these parameters are taken from Spencer et al. (1990). Subroutine *PITZER* calculates activity coefficients and the activity of water using the Pitzer and other equations (eq 7–12). Subroutine *INTERACTION* calculates the higher-order electrostatic interaction terms for the Pitzer equations. Subroutine *PPRINT* prints the results. The remaining 11 subroutines deal with mineral equilibria. For example, Subroutine *MGCL2* determines which $MgCl_2$ salt is thermodynamically stable and equilibrates, if necessary, the salt with the solution phase. Other mineral subroutines perform similar functions for specific minerals.

FREZCHEM was structured to be user-expandable. To alter the model requires knowing how chemical species are explicitly designated in the model. Table 2 summarizes the chemical species currently in or anticipated to be included in the

model in the near future. Species 1–10 are reserved for soluble cations; species 11–20 are reserved for soluble anions; species 21–30 are reserved for neutral species, both solution phase and gas phase. The solid phase species are designated with numbers 31–60. Blank spaces in Table 2 are available for future additions.

PROGRAM INPUT AND OUTPUT

Input to FREZCHEM is through screen queries that request the molal concentrations for Na, K, Ca, Mg, Cl, and SO_4. FREZCHEM is structured to cycle through a sequence of temperature changes (freezing) or water removals (evaporation). For a temperature change, the screen queries request the initial temperature, the final temperature, and the incremental temperature change. For example, to calculate the freezing of seawater between 273.15 K (0 °C) and 223.15 K (–50 °C) by 5 K intervals, enter: 273.15, 223.15, and 5.0. Because the model assumes an initially unfrozen solution, enter the temperature sequence from high (initial) to low (final). For evaporative removal, the screen queries request the temperature (assumed fixed for evaporation), the final total water content (grams), and the incremental water removal (grams). To evaporate water from 1000 g (the fixed initial water content for both freezing and evaporation) to 100 g by 50-g increments at 0.0 °C, enter 273.15, 100, and 50 for the evaporative screen queries.

Output from the program is to a file called "FrData" which can be sent to a printer. A freezing simulation for seawater at 243.15 K (–30 °C) is given in Table 3, and an evaporative (1000 g to 100 g) simulation for seawater at 0 °C is given in Table 4. After the title, the first line of output gives the temperature, ionic strength, activity of water (AH_20), osmotic coefficient (phi), and the final calculated amounts of water and ice. The basic unit of mass in the model is 1.0 kg water. For the seawater simulation at –30 °C, the final distribution of water is 948.20 g of ice, 33.12 g water, 13.42 g of water in hydrohalite (0.3725 moles), and 5.26 g of water in mirabilite (0.0292 moles), which adds up to exactly 1000.00 g (Table 3). The final distribution of water in the evaporative scenario at 0 °C is 96.93 g water and 3.07 g water in mirabilite (0.017043 moles), which adds up to exactly 100.00 g (Table 4).

The solution phase species are grouped together in the output. This output includes initial concentration (the program input), final concentration, activity coefficient, activity, and the moles remaining in the solution phase. Because the basic unit of mass is 1.0 kg water, the initial concentration [moles/kg (water)] is also equal to the total moles. A difference between "Initial Conc." and "Moles" in the solution phase output is attributable to either salt precipitation or ion-pair formation. For example, the initial concentration (total moles) of Na is 0.48695. The distribution of Na at –30 °C is 0.05610 moles in the solution, 0.37250 moles as hydrohalite, and 0.05834 moles as mirabilite, which adds up to 0.48694 moles of Na (Table 3). For the seawater evaporative simulation, the final distribution of Na is 0.45286 moles in the solution and 0.03409 moles as mirabilite, which adds up to 0.48695 moles of Na (Table 4)

The solid phase species are also grouped together in the output. This output includes the moles of solid phase species and the equilibrium constant for the reaction. For the seawater freezing simulation, ice, hydrohalite, and mirabilite have precipitated at –30 °C (Table 3). For the seawater evaporative simulation, only mirabilite appears to have precipitated at 0 °C (Table 4); however, see *Program Limitations* (below) for a discussion of probable gypsum precipitation. Whenever ice is present, the activity of water (0.74696) must agree with the equilibrium constant for ice-water (0.74693) (Table 3) to within ±0.00005 units, which is the convergence criterion used in the model. For salts that are precipitating, the appropriate solution phase activity product should equal the equilibrium constant. For $NaCl \cdot 2H_2O(cr)$, the activity product is equal to $(0.91885) \times (10.691) \times (0.74696)^2 = 5.48$ which agrees with the equilibrium constant of 5.48 (Table 3).

The final output are the equilibrium constants for the $CaSO_4$ and $MgSO_4$ ion-pairs and the number of iterations through the equilibrium routines before convergence.

PROGRAM LIMITATIONS

FREZCHEM has convergence problems especially at high ionic strengths (>15 molal), where activity coefficients are rapidly changing, and at junctions, where new phases begin to precipitate. The program contains a routine to catch mathematical problems or special circumstances. If "iterations" reaches 300, a message to this effect is

Table 4. FREZCHEM model output for evaporation of seawater at 0 °C.

Temp (K)	Ion. Str.	AH_2O	Phi	H_2O (g)	Ice (g)
273.15	6.8871	0.75383	1.3728	96.930	0.00000
Solution Species	*Initial Conc.*	*Final Conc.*	*Act. Coef.*	*Activity*	*Moles*
Na	0.48695	4.6721	0.81929	3.8278	0.45286
K	0.10630E–01	0.10967	0.39751	0.43593E–01	0.10630E–01
Ca	0.95300E–02	0.92284E–01	1.0610	0.97912E–01	0.89451E–02
Mg	0.55160E–01	0.56905	2.1926	1.2477	0.55158E–01
Cl	0.56818	5.8618	1.2301	7.2105	0.56818
SO_4	0.29390E–01	0.12133	0.30951E–01	0.37552E–02	0.11760E–01
$CaSO_4$	0.00000	0.60346E–02	1.0000	0.60346E–02	0.58493E–03
$MgSO_4$	0.00000	0.19557E–04	1.0000	0.19557E–04	0.18957E–05
H_2O(l)				0.75383	5.3804
Solid Species	*Moles*	*Equil. Constant*			
Ice	0.00000	1.0002			
$NaCl•2H_2O$	0.00000	17.957			
NaCl	0.00000	31.339			
KCl	0.00000	3.7731			
$CaCl_2•6H_2O$	0.00000	1862.7			
$MgCl_2•6H_2O$	0.00000	55958.			
$MgCl_2•8H_2O$	0.00000	7080.2			
$MgCl_2•12H_2O$	0.00000	708.26			
$KMgCl_2•6H_2O$	0.00000	7819.3			
$CaCl_2•2MgCl_2•12H_2O$	0.00000	0.27626E+19			
$Na_2SO_4•10H_2O$	0.17043E–01	0.32600E–02			
Na_2SO_4	0.00000	0.69007			
$MgSO_4•6H_2O$	0.00000	0.18782			
$MgSO4•7H_2O$	0.00000	0.54675E–01			
K_2SO_4	0.00000	0.69458E–02			
$MgSO_4•K_2SO_4•6H_2O$	0.00000	0.50713E–04			
$CaSO_4$ (ion-pair)		0.60935E–01			
$MgSO_4$ (ion-pair)		239.57			
Iterations = 3					

printed and the program exits. The most likely explanations for nonconvergence within 300 iterations are divergence, oscillating around the correct solution, or the system is beyond the eutectic, at which point only solid phases are thermodynamically stable.

To rectify mathematical problems, try changing the temperature or evaporative increments, either increasing or decreasing their step size (e.g., change temperature decrement from 10 to 5 degrees or change water decrement from 50 to 100 g).

Generally one can tell the approximate eutectic of more complex mixtures from the behavior of pure salts. For example, the eutectic temperature for pure $CaCl_2$ is –50.4 °C (Spencer et al. 1990). Failure of the model to converge at –40 °C for a solution containing $CaCl_2$ such as seawater cannot be due to exceeding the eutectic, which must be lower in temperature than the eutectic of the pure solution. Failure of the model to converge within 300 iterations at –54 °C for seawater is caused by exceeding the eutectic at –53.6 °C (Spencer et al. 1990).

If you use FREZCHEM to identify "junctions" such as the eutectic, you need to carefully scrutinize the output for accuracy. For example, FREZCHEM prints results for seawater freezing down to –53.7 °C; at –53.8 °C, the program fails to converge within 300 iterations because the solution is beyond the eutectic temperature. If one examines the printed output at –53.7 °C, the solution is slightly supersaturated with respect to $CaCl_2$

(the last of the seawater salts to precipitate) based on calculated activity products, but the program indicates no precipitation of $CaCl_2$ (moles = 0.0). At –53.6 °C, the solution is undersaturated with respect to $CaCl_2$. The true eutectic lies between –53.7 °C and –53.6 °C, which agrees with Spencer et al. (1990) who place the seawater eutectic at –53.64 °C. Small errors can occur at junctions; therefore, these solutions need to be carefully scrutinized.

FREZCHEM is limited to applications where chloride and sulfate salts of sodium, potassium, calcium, and magnesium are dominant. Two common salts not currently in the model are gypsum [$CaSO_4 \cdot 2H_2O$(cr)] and calcite [$CaCO_3$(cr)]. In the evaporative scenario (Table 4), the calculated activity product for gypsum in seawater is 2.09×10^{-4} which is apparently supersaturated with respect to gypsum at 0 °C ($K = 2.33 \times 10^{-5}$, Plummer et al. 1988). The reason gypsum and calcite are missing from the current model is because these salts are relatively insoluble and as a consequence, there are few solubility data at subzero temperatures. Because neither gypsum nor calcite can be parameterized over the temperature range of interest (–60 to +25 °C), we have chosen not to include their solubility, even over a limited temperature range, in this preliminary version of FREZCHEM.

This is not to say that FREZCHEM cannot be used in circumstances where gypsum or calcite are precipitating, only that caution is necessary in interpreting the results. For example, calcite precipitates during both seawater freezing (Nelson and Thompson 1954) and seawater evaporation, as does gypsum during seawater evaporation (McCaffrey et al. 1987). However, the amounts of calcite precipitation are relatively minor and can apparently be ignored. Note the good agreement in Ca concentrations during seawater freezing between experimental data and the model that ignored both calcite and gypsum (Figs. 3 and 4). One cannot ignore gypsum during seawater evaporation (McCaffrey et al. 1987, Herut et al. 1990) where explicit recognition must be made of gypsum precipitation. As pointed out previously, a 10-fold concentration of seawater at 0 °C is likely to lead to the significant precipitation of both mirabilite (0.0170 moles) and gypsum (supersaturated) (Table 4). Where gypsum precipitation is possible, check the calculated gypsum activity product for apparent supersaturation. Unfortunately, reliable gypsum solubility products are available only for temperatures ≥ 0 °C (Plummer et al. 1988).

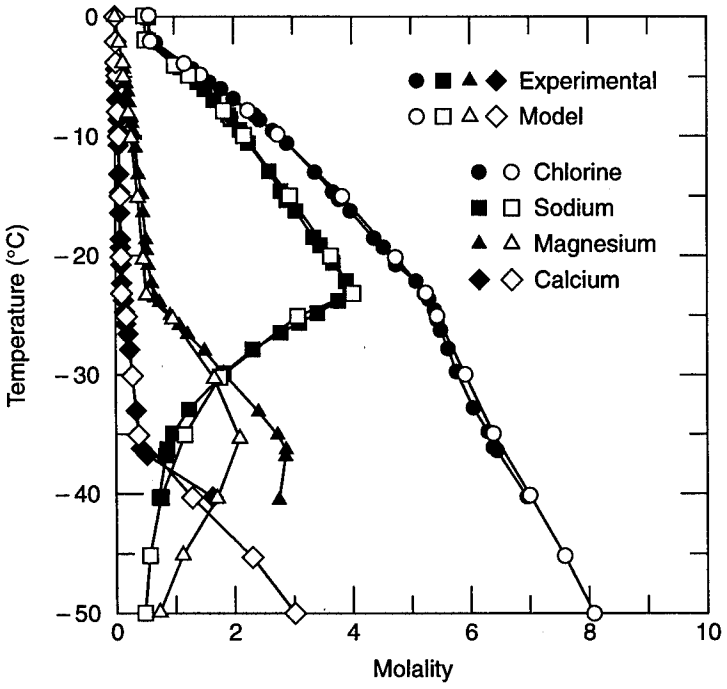

Figure 3. The concentrations of major seawater constituents during freezing. Experimental measurements are from Nelson and Thompson (1954).

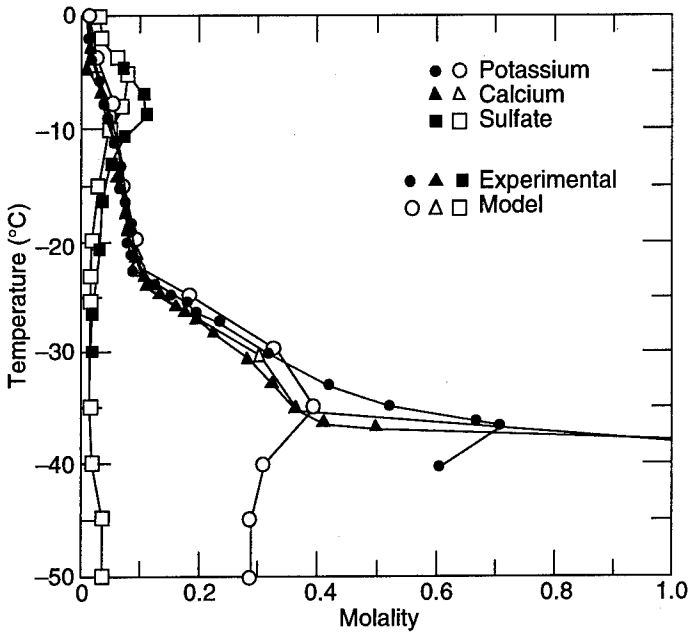

Figure 4. The concentrations of minor seawater constituents during freezing. Experimental measurements are from Nelson and Thompson (1954).

PROGRAM VALIDATION

The Spencer-Møller-Weare model and consequently the FREZCHEM model are parameterized primarily with data from pure binary and ternary salt solutions. Spencer et al. (1990) present 13 figures demonstrating how well their model fits the experimental data (e.g., Fig. 1). In general, the agreement is excellent, which is not surprising because this is the database used to parameterize the model, and as a consequence, this is not a true validation of the model.

The primary validation of the Spencer-Møller-Weare model is a comparison of model predictions for seawater freezing with experimental data from Nelson and Thompson (1954). The comparison of major (Fig. 3) and minor (Fig. 4) seawater constituents demonstrates good agreement except for Mg and K concentrations between –30° and –40 °C and SO_4 concentrations between –5° and –10 °C. The seawater experimental data between –30° and –40 °C show a great excess of cations over anions indicating a major problem with the analytical measurements. All of the discrepancy between measured and predicted Mg and K concentrations can be attributed to this charge imbalance. The model predicts that mirabilite precipitates at –5.9 °C, while experimental measurements suggest that precipitation begins at –8.2 °C. This is the largest discrepancy in the temperature of first appearance of salt between the model and the experimental data. We plan to address these problems with experimental work in the near future.

Another approach to validating the model, not used by Spencer et al. (1990), is to examine the distribution of water during seawater freezing. For a system starting with 1.0 kg of water at 0 °C, approximately 50% of the water has turned to ice by the time the temperature has dropped to –4 °C (Fig. 5). By –10°C, only 20% of the original water is unfrozen. At about –23 °C, hydrated salts become a significant sink for water; this is where hydrohalite begins to precipitate. At –50 °C, the original 1000 g of water is redistributed as 964.73 g of ice, 32.12 g of hydrated salts, and 3.15 g of unfrozen water. There is good agreement between calculated unfrozen water and experimental measurements (Richardson 1976) at least down to –36 °C (Fig. 6). Below –36 °C, the experimental and model estimates diverge but come back together at –50 °C where the model predicts 3.15 g water and the experimental measurement indicates 3.53 g water. The two curves diverge at the point where $MgCl_2 \cdot 12H_2O$(cr) begins to precipitate at –36 °C. Given major uncertainties in both model parameterization and experimental measurements, we cannot determine if the model or experimental measurements are more accurate at low temperature.

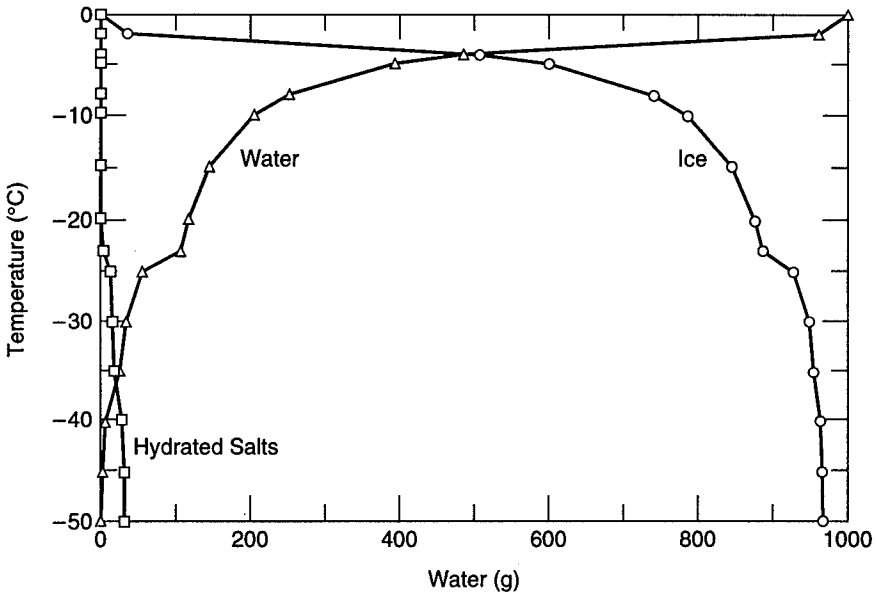

Figure 5. The model prediction of the distribution of water during seawater freezing.

The importance of salt precipitation in controlling seawater freezing is illustrated by examining the distribution of total Na and Cl during the freezing process (Fig. 7). At –50 °C, only 0.3 % and 4.5 % of the original soluble Na and Cl at 0 °C remain in the solution phase; 99.7 % and 95.5 % of the Na and Cl have precipitated in four salts.

The ionic strength of the unfrozen seawater changes from 0.72 to 11.85 molal between 0 °C and –50 °C. This large increase in salt concentration during the freezing process is the primary reason why it is necessary to use the Pitzer equations to evaluate the activity of water and activity coefficients.

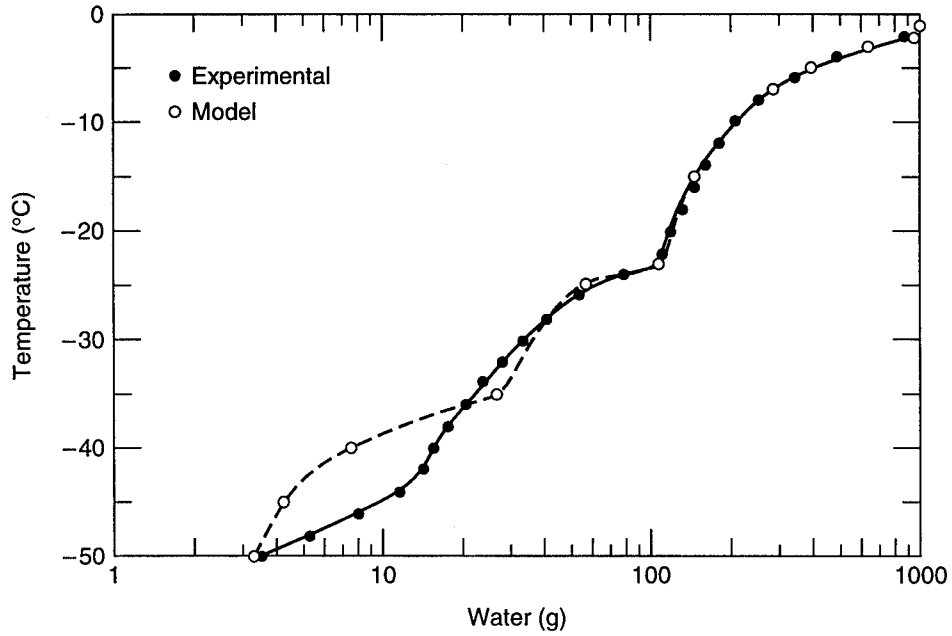

Figure 6. The amount of unfrozen water during seawater freezing. Experimental measurements are from Richardson (1976).

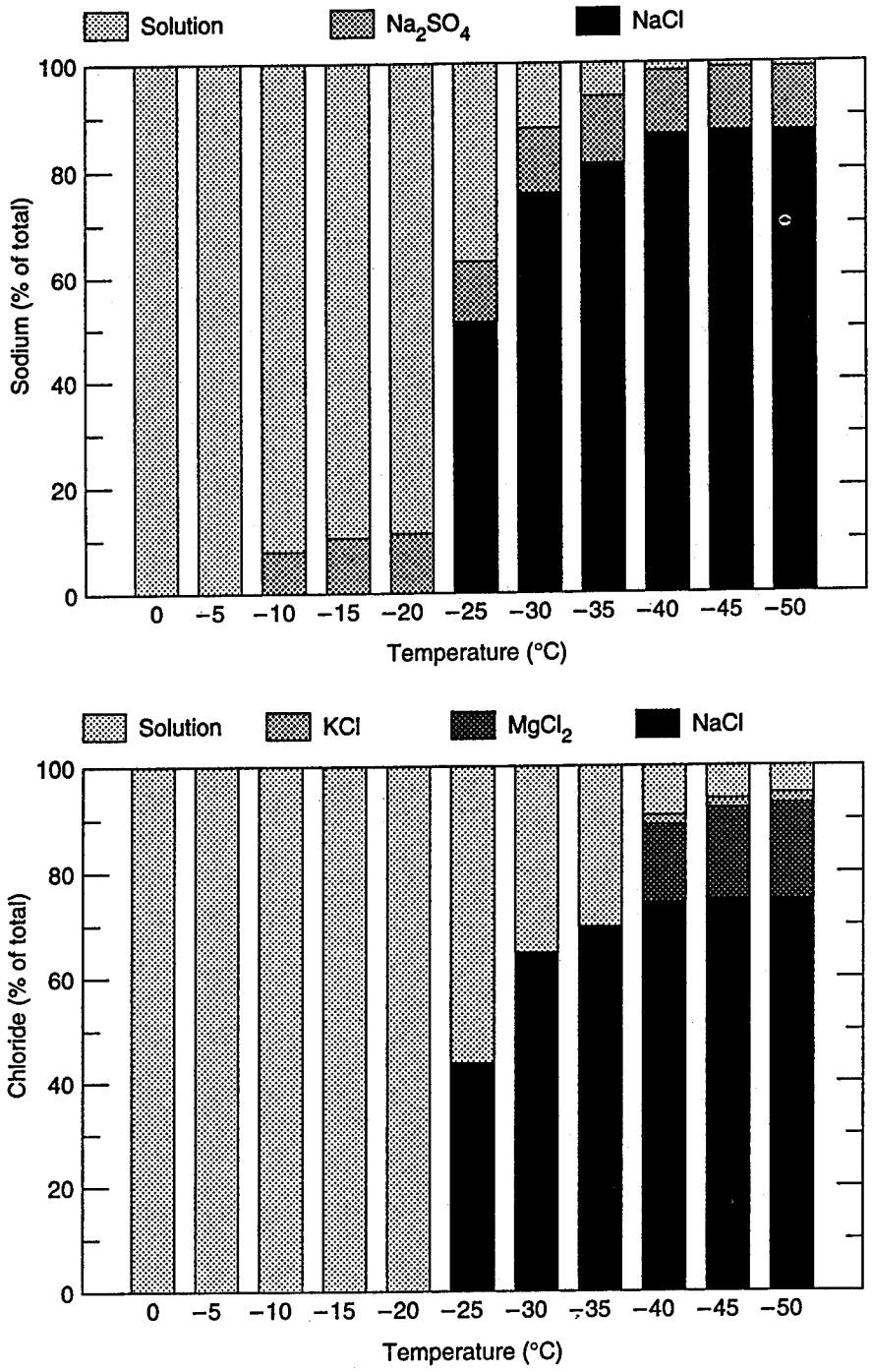

Figure 7. The model predictions of sodium and chloride distribution during seawater freezing.

FUTURE DIRECTIONS

The data presented in this report (Fig. 3–7) demonstrate the great complexity of the solute–freezing interaction and why this interaction must be considered to define accurately the freezing process, especially at high salinities. The FREZCHEM model can calculate the role of the Cl and SO_4 salts of Na, K, Ca, and Mg in the freezing process. The model is useful as is, but more work needs to be done in order to develop a new "state-of-the-art" model.

For the chloride salts, KCl solubility is the major uncertainty. The parameterization of KCl solubil-

ity by Spencer et al. (1990) is based on only one data point below –24 °C. We are beginning experiments to measure the solubility of KCl in KCl–$CaCl_2$ solutions to –50 °C. At a minimum, we want to add gypsum [$CaSO_4 \cdot 2H_2O$(cr)] solubility to the model and re-examine the solubility of Na_2SO_4, which is not predicted well by the current model (Fig. 4). And finally, we need to add calcite [$CaCO_3$(cr)] solubility to the model. Calcite and gypsum are common minerals that are present in many natural systems. Their inclusion in the model would be critical to many applications.

There are mathematical convergence problems, at times, with the FREZCHEM model, probably due to the sequential approach to solving a set of nonlinear equations used in the model. An alternative mathematical approach is the Gibbs energy minimization algorithm (Greenberg 1986, Harvie et al. 1987, Spencer et al. 1990). Our present strategy is to first document, by using the FREZCHEM model, where convergence problems exists. If these problems appear to be intractable using our present mathematical algorithm, we plan to try Gibbs energy minimization.

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Appendix A: FORTRAN listing of the FREZCHEM program.


```
      PROGRAM FREZCHEM

C  FREZCHEM: This is a chemical thermodynamic model for aqueous
C  solutions over the temperature range from +25C to -60C.  This
C  model uses the Pitzer equations for activity coefficients and
C  the activity of water and is valid to high ionic strengths
C  (20 M).  The model considers the precipitation-dissolution of
C  the chloride and sulfate salts of calcium, magnesium, sodium,
C  and potassium.

      REAL IX,INIT(20),I,K
      DIMENSION FINAL(20)
      CHARACTER*50 TITLE
      DOUBLE PRECISION AKI,AKII,ISALGM,SALGM,DELGM,SALH2O,X
      DOUBLE PRECISION M,MO,H2O

      COMMON /A/ MAXCAT,MAXAN,AKI(0:20),AKII(0:20),BET0(10,11:20),
     xBET1(10,11:20),BET2(10,11:20),C(10,11:20),CPHI(10,11:20),
     xPSI(20,20,20),THETA(20,20),A,Z(30)
      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI

      OPEN (UNIT = 2, FILE = "FrData")

C  Read in or initialize run parameters.

      PRINT*, 'TITLE ='
      READ(*,1) TITLE
1     FORMAT (A50)
      PRINT*, 'FREEZE(1) OR EVAPORATION(2) SCENARIO ?'
      READ*, PATH
      PRINT*, 'SODIUM (M/KG) ='
      READ*, IX(1)
      PRINT*, 'POTASSIUM (M/KG) ='
      READ*, IX(2)
      PRINT*, 'CALCIUM (M/KG) ='
      READ*, IX(3)
      PRINT*, 'MAGNESIUM (M/KG) ='
      READ*, IX(4)
      PRINT*, 'CHLORIDE (M/KG) ='
      READ*, IX(11)
      PRINT*, 'SULFATE (M/KG) ='
      READ*, IX(12)
      PRINT*, 'INITIAL TEMPERATURE (K) ='
      READ*, TEMP
      IF (PATH.EQ.1) THEN
            PRINT*, 'FINAL TEMPERATURE (K) ='
            READ*, FINTEM
            PRINT*, 'TEMPERATURE DECREMENT (K) ='
            READ*, DELTEM
      ELSE
            PRINT*, 'FINAL WATER (G) = '
            READ*, FINWAT
            PRINT*, 'WATER DECREMENT (G) = '
            READ*, DELWAT
      END IF
      DATA DEL / 1.25, 1.10, 1.01, 1.001, 1.0001 /
      X(1) = IX(1)
      X(2) = IX(2)
      X(3) = IX(3)
      X(4) = IX(4)
      MAXCAT = 4
      X(11) = IX(11)
```

```
      X(12) = IX(12)
      MAXAN = 12
      X(30) = 1000
      X(31) = 0
      ISALGM = 0
3     ITER = 0

      CALL PARAMETER
5     CALL PITZER

C  Test for supersaturation with respect to ice phase and freeze
C  if necessary.

      IF (AH2O .GT. K(31)) THEN
            IF (PATH.EQ.2) THEN
                  WRITE(2,*)'THEORETICALLY THIS SOLUTION SHOULD FREEZE.'
                  WRITE (2,*) 'THEREFORE, CAN NOT EVALUATE THIS USING AN
     X EVAPORATIVE SCENARIO.'
                  FINTEM=TEMP
                  DELTEM=1.0
                  PATH=1
            END IF
            MO = 0
            M = 0
            H2O = X(30) + X(31)
            DO 10 J = 1, 25
                  MO = MO + X(J)
10          CONTINUE
            DO 70 KA = 1, 5
20                DO 30 J = 1, 25
                        X(J) = X(J) * DEL(KA)
30                CONTINUE
                  DO 40 J = 32, 60
                        X(J) = X(J) * DEL(KA)
40                CONTINUE
                  CALL PITZER
                  IF (AH2O .GT. K(31)) GOTO 20
                  DO 50 J = 1, 25
                        X(J) = X(J) / DEL(KA)
50                CONTINUE
                  DO 60 J = 32, 60
                        X(J) = X(J) / DEL(KA)
60                CONTINUE
70          CONTINUE
            DO 80 J = 1, 25
                  M = M + X(J)
80          CONTINUE
            X(30) = X(30) * MO / M
            X(31) = H2O - X(30)
      END IF

C  Test for mineral saturation and equilibrate solutions.

200   DO 210 J = 1, 20
            INIT(J) = X(J)
210   CONTINUE
      CALL PITZER
      ITER = ITER + 1
      IF ((IX(3) .GT. 0) .AND. (IX(12) .GT. 0)) CALL CASO4
      IF ((IX(4) .GT. 0) .AND. (IX(12) .GT. 0)) CALL MGSO4
      IF ((IX(1) .GT. 0) .AND. (IX(12) .GT. 0)) CALL NA2SO4
      IF ((IX(2) .GT. 0) .AND. (IX(12) .GT. 0)) CALL ARCANITE
      IF ((IX(2) .GT. 0) .AND. (IX(4) .GT. 0) .AND. (IX(12) .GT. 0))
```

```
     x      CALL PICROMERITE
      IF ((IX(2) .GT. 0) .AND. (IX(11) .GT. 0)) CALL SYLVITE
      IF ((IX(1) .GT. 0) .AND. (IX(11) .GT. 0)) CALL NACL
      IF ((IX(4) .GT. 0) .AND. (IX(11) .GT. 0)) CALL MGCL2
      IF ((IX(3) .GT. 0) .AND. (IX(11) .GT. 0)) CALL ANTARCTICITE
      IF ((IX(2) .GT. 0) .AND. (IX(4) .GT. 0) .AND. (IX(11) .GT. 0))
     x      CALL CARNALLITE
      IF ((IX(3) .GT. 0) .AND. (IX(4) .GT. 0) .AND. (IX(11) .GT. 0))
     x      CALL TACHYHYDRITE
      IF (ITER .EQ. 300) THEN
            WRITE (2,*) 'THIS RUN IS NOT CONVERGING AFTER 300
     xINTERATIONS'
            GOTO 270
      END IF

C  Calculate water associated with hydrated salts.

      SALH2O=2*X(32)+6*X(35)+6*X(36)+8*X(37)+12*X(38)+6*X(39)+12*X(40)
      SALH2O=SALH2O+10*X(41)+6*X(43)+7*X(44)+6*X(46)
      SALGM = SALH2O * X(30) * 18.0153 / 1000
      DELGM = SALGM - ISALGM
      X(30) = X(30) - DELGM
      DO 220 J = 1, 25
            X(J) = X(J) * (X(30) + DELGM) / X(30)
220   CONTINUE
      DO 230 J = 32, 60
            X(J) = X(J) * (X(30) + DELGM) / X(30)
230   CONTINUE
      ISALGM = SALGM

C  Test for mineral equilibria.

235   DO 240 J = 1, 20
            FINAL(J) = X(J)
            IF (FINAL(J) .EQ. 0) GOTO 240
            IF ((ABS(FINAL(J)-INIT(J))/FINAL(J))*1000 .GT. 1) GOTO 200
240   CONTINUE

C Test for ice-water equilibrium

      CALL PITZER
      IF (AH2O-K(31) .GT. 0.00005) GOTO 5

C  Print Results.

260   CALL PPRINT

C Update Temperature or Water Content

      IF (PATH.EQ.1) THEN
            TEMP = TEMP - DELTEM
            IF (TEMP .GE. FINTEM) GOTO 3
      ELSE
            X(30)=X(30)-DELWAT
            TH2O = SALGM+X(30)
            IF (TH2O.LT.FINWAT) GOTO 270
            DO 263 IJK=1,25
                  X(IJK)=X(IJK)*(X(30)+DELWAT)/X(30)
263         CONTINUE
            DO 265 IJK=32,60
                  X(IJK)=X(IJK)*(X(30)+DELWAT)/X(30)
265         CONTINUE
            GO TO 3
```

```
      END IF

270   END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------

      SUBROUTINE PARAMETER

C  This subroutine calculates the parameters and their temperature
C  dependence for the Pitzer equations and mineral solubility products.

      REAL IX,I,K
      CHARACTER*50 TITLE
      DOUBLE PRECISION D(64,6), P(64),AKI,AKII,T,X

      COMMON /A/ MAXCAT,MAXAN,AKI(0:20),AKII(0:20),BET0(10,11:20),
     xBET1(10,11:20),BET2(10,11:20),C(10,11:20),CPHI(10,11:20),
     xPSI(20,20,20),THETA(20,20),A,Z(30)
      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI

      DATA AKI / 1.925154014814667, -0.060076477753119,
     x      -0.029779077456514, -0.007299499690937,
     x      0.000388260636404, 0.000636874599598,
     x      0.000036583601823, -0.000045036975204,
     x      -0.000004537895710, 0.000002937706971,
     x      0.000000396566462, -0.000000202099617,
     x      -0.000000025267769, 0.000000013522610,
     x      0.000000001229405, -0.000000000821969,
     x      -0.000000000050847, 0.000000000046333,
     x      0.000000000001943, -0.000000000002563,
     x      -0.000000000010991 /

      DATA AKII / 0.628023320520852, 0.462762985338493,
     x      0.150044637187895, -0.028796057604906,
     x      -0.036552745910311, -0.001668087945272,
     x      0.006519840398744, 0.001130378079086,
     x      -0.000887171310131, -0.000242107641309,
     x      0.000087294451594, 0.000034682122751,
     x      -0.000004583768938, -0.000003548684306,
     x      -0.000000250453880, 0.000000216991779,
     x      0.000000080779570, 0.000000004558555,
     x      -0.000000006944757, -0.000000002849257,
     x      0.000000000237816 /

      DATA Z / 1,1,2,2,1,0,0,0,0,0,-1,-2,-1,-1,-2,
     x      0,0,0,0,0,0,0,0,0,0,0,0,0,0,0 /

C  Data Stored in D(I,J) are from Spencer et al. (1990)

      DATA ((D(I,J),J=1,6),I=1,64) /
     x      86.6836498, 0.0848795942, -8.8878515D-5,
     x      4.88096393D-8, -1.32731477D3, -17.6460172,
     x      7.87239712, -8.3864096D-3, 1.44137774D-5,
     x      -8.7820301D-9, -496.920671, -0.820972560,
     x      866.915291, 0.606166931, -4.8048921D-4,
     x      1.88503857D-7, -1.70460145D4, -167.171296,
     x      1.70761824, 2.32970177D-3, -2.46665619D-6,
     x      1.21543380D-9, -1.35583596, -0.387767714,
     x      26.5718766, 9.92715099D-3, -3.62323330D-6,
     x      -6.28427180D-11, -755.707220, -4.67300770,
```

```
     x      1.69742977D3, 1.22270943, -9.99044490D-4,
     x      4.04786721D-7, -3.28684422D4, -328.813848,
     x      -3.27571680, -1.27222054D-3, 4.71374283D-7,
     x      1.1162507D-11, 90.7747666, 0.580513562,
     x      -5.62764702D1, -3.00771997D-2, 1.05630400D-5,
     x      3.3331626D-9, 1.11730349D3, 1.06664743D1,
     x      3.4787, -1.5417D-2, 3.1791D-5, 0, 0, 0,
     x      2.64231655D1, 2.46922993D-2, -2.48298510D-5,
     x      1.22421864D-8, -4.18098427D2, -5.35350322,
     x      3.13852913D2, 2.61769099D-1, -2.46268460D-4,
     x      1.15764787D-7, -5.53133381D3, -6.21616862D1,
     x      -3.18432525D4, -2.86710358D1, 2.78892838D-2,
     x      -1.3279705D-5, 5.24032958D5, 6.40770396D3,
     x      5.9532D-2, -2.49949D-4, 2.41831D-7, 0, 0, 0,
     x      -3.32486330D3, -2.9297353, 2.8024367D-3,
     x      -1.316883D-6, 5.53958527D4, 6.66660369D2,
     x      -3.57406160D3, -3.0011206, 2.73660950D-3,
     x      -1.219171D-6, 6.09716482D4, 7.11613120D2,
     x      3.68520478D2, 3.16243995D-1, -2.95372760D-4,
     x      1.35491104D-7, -6.22607913D3, -7.35844094D1,
     x      4.07908797D1, 8.26906675D-3, 0,0, -1.41842998D3,-6.74728848,
     x      -1.31669651D1, 2.35793239D-2, 0, 0, 2.06712594D3, 0,
     x      -1.88D-2, 0, 0, 0, 0, 0,
     x      1.50D-1, 0, 0, 0, 0, 0,
     x      3.00, 0, 0, 0, 0, 0,
     x      -1.29399287D2, 4.00431027D-1, 0, 0, 0, 0,
     x      5.40007849D3, 4.90576884, -4.80489750D-3,
     x      2.31126994D-6, -8.80664146D4, -1.08839565D3,
     x      2.78730869, 4.30077440D-3, 0, 0, 0, 0,
     x      -5.88623653D2, -5.0552280D-1, 4.8277657D-4,
     x      -2.3029838D-7, 1.02002016D4, 1.17303808D2,
     x      -18.2266741, -3.69038470D-3, 0,
     x      0, 612.415011, 3.02994981,
     x      6.48108127, 1.46803468D-3, 0,
     x      0, -204.354019, -1.09448043,
     x      3.48120D-2, 0, 0, 0, -8.21660, 0,
     x      5.0D-2, 0, 0, 0, 0, 0,
     x      -7.63980, -1.2990D-2, 1.1060D-5, 0, 0, 1.8475,
     x      -1.20D-2, 0, 0, 0, 0, 0,
     x      7.0D-2, 0, 0, 0, 0, 0,
     x      -3.109870D-2, 5.4464780D-5, 0, 0, 1.99404210, 0,
     x      1.1750520D-1, 0, 0, 0, -4.198620D1, 0,
     x      2.365710, -4.540D-3, 0, 0, -2.84940D2, 0,
     x      -5.930D-2, 2.54280D-4, 0, 0, -1.34390D1, 0,
     x      1.1670D-1, 0, 0, 0, 0, 0,
     x      5.0362230D-2, -8.750820D-6, 0, 0, -2.899090D1, 0,
     x      -1.3679157, 4.24016653D-3, 0, 0, 0, 0,
     x      5.31274136, -6.3424248D-3, 0, 0, -9.83113847D2, 0,
     x      4.15790220D1, 1.30377312D-2, 0,0, -9.81658526D2, -7.4061986,
     x      7.00D-2, 0, 0, 0, 0, 0,
     x      4.0209775, 1.1286005D-3, 0, 0, -1.01169260D2, -7.060798D-1,
     x      -2.124815D-1, 2.8469833D-4, 0, 0, 3.75619614D1, 0,
     x      -1.80D-2, 0, 0, 0, 0, 0,
     x      -1.839158D-1, 1.429444D-4, 0, 0, 3.263D1, 0,
     x      -1.62917341D3, -1.51940390, 1.45249679D-3,
     x      -6.9427505D-7, 2.26012743D4, 333.075506,
     x      7.875060393D3, 11.69118490, -1.7183789D-2,
     x      1.24395543D-5, -9.3314790D4, -1.7287461D3,
     x      -1.2222551D4, -9.8806459, 8.46685083D-3,
     x      -3.4459117D-6, 2.09823965D5, 2.42328528D3,
     x      -1.47477745D1, 0, 0, 0, 3.26409496D3, 0,
     x      3.65283115D2, -7.1578257D-1, 0, 0, -4.48753391D4, 0,
     x      9.14839001D3, 8.22348745, -8.1288759D-3,
```

```
     x      3.95552403D-6, -1.54040868D5, -1.83624247D3,
     x      1.42290062D5, 1.61973105D2, -1.95332071D-1,
     x      1.17636119D-4, -2.04059847D6, -2.97464810D4,
     x      7.52225099D2, 1.17584653D-1,0,0,-2.43223909D4,-1.21990076D2,
     x      2.27801976D3, 6.49361616D-1,0,0,-6.23075123D4,-3.95438891D2,
     x      2.55008896D5, 2.44532240D2, -2.48807876D-1,
     x      1.22425236D-4, -4.02988342D6, -5.18668604D4,
     x      -4.45702171D1, 2.32023790D-1, -7.14935692D-4,
     x      5.32658215D-7, -4.24817923D3, 8.59110245,
     x      8.03777918D1, -1.388069D-1, 0, 0, 0, 0,
     x      8.44728050D4, 7.68443387D1, -7.4825816D-2,
     x      3.51806085D-5, -1.3881852D6, -1.7026778D4,
     x      -3.9635632D3, -5.8114490, 7.59799462D-3,
     x      -4.6571737D-6, 3.93454893D4, 8.79598423D2,
     x      2.39166461D1, -9.3680744D-2, 0, 0, 0, 0,
     x      2.02443627, -1.8051586D-2, 0, 0, 0, 0,
     x      -3.53346251D4, -2.76809991D1, 2.39856021D-2,
     x      -1.0201845D-5, 6.37561988D5, 6.94737787D3,
     x      -1.75203509D1, 2.793713D-2, 0, 0, 0, 0 /
      T=TEMP
      DO 730 J = 1, 64
          P(J)=D(J,1)+D(J,2)*T+D(J,3)*T**2+D(J,4)*T**3+D(J,5)
     x            /T+D(J,6)*LOG(T)
730   CONTINUE

      A = P(1)
      BET0(1,11) = P(2)
      BET1(1,11) = P(3)
      CPHI(1,11) = P(4)
      BET0(2,11) = P(5)
      BET1(2,11) = P(6)
      CPHI(2,11) = P(7)
      BET0(3,11) = P(8)
      BET1(3,11) = P(9)
      CPHI(3,11) = P(10)
      BET0(4,11) = P(11)
      BET1(4,11) = P(12)
      CPHI(4,11) = P(13)
      BET0(1,12) = P(14)
      BET1(1,12) = P(15)
      CPHI(1,12) = P(16)
      BET0(2,12) = P(17)
      BET1(2,12) = P(18)
      CPHI(2,12) = P(19)
      BET0(3,12) = P(20)
      BET1(3,12) = P(21)
      BET2(3,12) = P(22)
      BET0(4,12) = P(23)
      BET1(4,12) = P(24)
      CPHI(4,12) = P(25)
      THETA(1,2) = P(26)
      PSI(1,2,11) = P(27)
      PSI(1,2,12) = P(28)
      THETA(1,3) = P(29)
      PSI(1,3,11) = P(30)
      PSI(1,3,12) = P(31)
      THETA(1,4) = P(32)
      PSI(1,4,11) = P(33)
      PSI(1,4,12) = P(34)
      THETA(2,3) = P(35)
      PSI(2,3,11) = P(36)
      THETA(2,4) = P(37)
      PSI(2,4,11) = P(38)
```

```
      PSI(2,4,12) = P(39)
      THETA(3,4) = P(40)
      PSI(3,4,11) = P(41)
      PSI(3,4,12) = 0.024
      THETA(11,12) = P(42)
      PSI(11,12,1) = P(43)
      PSI(11,12,2) = P(44)
      PSI(11,12,3) = P(45)
      PSI(11,12,4) = P(46)
      K(34) = EXP(P(47))
      K(31) = EXP(P(48))
      K(32) = EXP(P(49))
      K(22) = EXP(P(50))
      K(23) = EXP(P(51))
      K(33) = EXP(P(52))
      K(35) = EXP(P(53))
      K(36) = EXP(P(54))
      K(37) = EXP(P(55))
      K(38) = EXP(P(56))
      K(39) = EXP(P(57))
      K(40) = EXP(P(58))
      K(41) = EXP(P(59))
      K(42) = EXP(P(60))
      K(43) = EXP(P(61))
      K(44) = EXP(P(62))
      K(45) = EXP(P(63))
      K(46) = EXP(P(64))
      RETURN
      END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------

      SUBROUTINE PITZER

C  This subroutine calculates activity coefficients and the activity
C  of water using the Pitzer equations.

      REAL I,IX,K
      CHARACTER*50 TITLE
      DOUBLE PRECISION AKI,AKII,X
      DIMENSION SUMCA(10), SUMCAT(10), SUMAN(10), SUMZ(10),
     x      SUMAC(11:20), SUMAA(11:20), SUMCC(11:20), SUMK(11:20),
     x      BPHI(10,11:20), B(10,11:20), BPRIME(10,11:20),
     x      PHIPHI(20,20), PHIPRI(20,20), PHIIJ(20,20)

      COMMON /A/ MAXCAT,MAXAN,AKI(0:20),AKII(0:20),BET0(10,11:20),
     xBET1(10,11:20),BET2(10,11:20),C(10,11:20),CPHI(10,11:20),
     xPSI(20,20,20),THETA(20,20),A,Z(30)
      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI

      ZZ = 0
      SM = 0
      I = 0
      DO 280 J = 1, 20
            ZZ = ZZ + X(J) * ABS(Z(J))
            I = I + .5 * (X(J) * Z(J)**2)
            SM = SM + X(J)
280   CONTINUE

      DATA SUMCA / 10*0 /
```

```
      DATA SUMCAT / 10*0 /
      DATA SUMAN / 10*0 /
      DATA SUMZ / 10*0 /
      DATA SUMAC / 10*0 /
      DATA SUMAA / 10*0 /
      DATA SUMCC / 10*0 /
      DATA SUMK / 10*0 /

      ALPHA = 2 * SQRT(I)
      ALPHA1 = 1.4 * SQRT(I)
      ALPHA2 = 12 * SQRT(I)
      G1 = 2*(1-(1+ALPHA1)*EXP(-ALPHA1))/ALPHA1**2
      G2 = 2*(1-(1+ALPHA2)*EXP(-ALPHA2))/ALPHA2**2
      GPRI1 = -2*(1-(1+ALPHA1+ALPHA1**2/2)*EXP(-ALPHA1))/ALPHA1**2
      GPRI2 = -2*(1-(1+ALPHA2+ALPHA2**2/2)*EXP(-ALPHA2))/ALPHA2**2
      G = 2*(1-(1+ALPHA)*EXP(-ALPHA))/ALPHA**2
      GPRIME = -2*(1-(1+ALPHA+ALPHA**2/2)*EXP(-ALPHA))/ALPHA**2
      DO 300 J = 1, MAXCAT
            DO 290 IK = 11, MAXAN
                  IF (Z(J)*ABS(Z(IK)) .EQ. 4) THEN
                        BPHI(J,IK)=BET0(J,IK)+BET1(J,IK)*EXP(-ALPHA1)+
     x                        BET2(J,IK)*EXP(-ALPHA2)
                        B(J,IK)=BET0(J,IK)+BET1(J,IK)*G1+BET2(J,IK)*G2
                        BPRIME(J,IK)=BET1(J,IK)*GPRI1/I+BET2(J,IK)*
     x                        GPRI2/I
                  ELSE
                        BPHI(J,IK)=BET0(J,IK)+BET1(J,IK)*EXP(-ALPHA)
                        B(J,IK)=BET0(J,IK)+BET1(J,IK)*G
                        BPRIME(J,IK)=BET1(J,IK)*GPRIME/I
                  END IF
                  C(J,IK)=CPHI(J,IK)/(2*SQRT(Z(J)*ABS(Z(IK))))
290         CONTINUE
300   CONTINUE
      DO 320 J = 1, MAXCAT - 1
            DO 310 IK = J + 1, MAXCAT
                  IF ((Z(J) .EQ. 0) .OR. (Z(IK) .EQ. 0)) GOTO 310
                  CALL INTERACTION(Z(J),Z(IK),I,A,PHIPHI(J,IK),
     x                  PHIPRI(J,IK),PHIIJ(J,IK),THETA(J,IK),AKI,AKII)
310         CONTINUE
320   CONTINUE
      DO 340 J = 11, MAXAN - 1
            DO 330 IK = J + 1, MAXAN
                  IF ((Z(J) .EQ. 0) .OR. (Z(IK) .EQ. 0)) GOTO 330
                  CALL INTERACTION(Z(J),Z(IK),I,A,PHIPHI(J,IK),
     x                  PHIPRI(J,IK),PHIIJ(J,IK),THETA(J,IK),AKI,AKII)
330         CONTINUE
340   CONTINUE

C  Calculation of summation terms for F and PHI.

      SCATON = 0
      SUBSUM = 0
      SANON = 0
      SUMCAF = 0
      SUMANF = 0

      DO 370 J = 1, MAXCAT - 1
            DO 360 IK = J + 1, MAXCAT
                  DO 350 L = 11, MAXAN
                        SUBSUM  = SUBSUM + PSI(J,IK,L) * X(L)
350               CONTINUE
                  SCATON=SCATON+(SUBSUM+PHIPHI(J,IK))*X(J)*X(IK)
                  SUMCAF=SUMCAF+PHIPRI(J,IK)*X(J)*X(IK)
```

```
                  SUBSUM = 0
360         CONTINUE
370   CONTINUE
      SUBSUM = 0
      DO 400 J = 11, MAXAN - 1
            DO 390 IK = J + 1, MAXAN
                  DO 380 L = 1, MAXCAT
                        SUBSUM=SUBSUM+PSI(J,IK,L)*X(L)
380               CONTINUE
                  SANON=SANON+(SUBSUM+PHIPHI(J,IK))*X(J)*X(IK)
                  SUMANF=SUMANF+PHIPRI(J,IK)*X(J)*X(IK)
                  SUBSUM = 0
390         CONTINUE
400   CONTINUE
      SUMB = 0
      SUMPHI = 0
      DO 420 J = 1, MAXCAT
            DO 410 IK = 11, MAXAN
                  SUMB=SUMB+X(J)*X(IK)*BPRIME(J,IK)
                  SUMPHI=SUMPHI+X(J)*X(IK)*(BPHI(J,IK)+ZZ*C(J,IK))
410         CONTINUE
420   CONTINUE
      F=-A*(SQRT(I)/(1+1.2*SQRT(I))+2*LOG(1+1.2*SQRT(I))/1.2)+SUMB+
     x      SUMCAF+SUMANF
      PHI=1+(2/SM)*((-A*I**1.5)/(1+1.2*SQRT(I))+SUMPHI+SCATON+
     x      SANON)
      AH2O = EXP(-PHI*SM/55.50837)

C  Calculation of terms for activity coefficients (gamma).

      SUM = 0
      DO 450 J = 1, MAXCAT - 1
            DO 440 IK = J + 1, MAXCAT
                  DO 430 L = 11, MAXAN
                        PSI(IK,J,L) = PSI(J,IK,L)
                        PHIIJ(IK,J) = PHIIJ(J,IK)
430               CONTINUE
440         CONTINUE
450   CONTINUE
      DO 480 L = 11, MAXAN - 1
            DO 470 IK = L + 1, MAXAN
                  DO 460 J = 1, MAXCAT
                        PSI(IK,L,J) = PSI(L,IK,J)
                        PHIIJ(IK,L) = PHIIJ(L,IK)
460               CONTINUE
470         CONTINUE
480   CONTINUE
      DO 500 J = 1, MAXCAT
            DO 490 IK = 11, MAXAN
                  SUMCA(J) = SUMCA(J)+X(IK)*(2*(B(J,IK))+ZZ*C(J,IK))
490         CONTINUE
500   CONTINUE
      DO 530 J = 1, MAXCAT
            DO 520 IK = 1, MAXCAT
                  IF (J .EQ. IK) GOTO 520
                  DO 510 L = 11, MAXAN
                        SUM=SUM+X(L)*PSI(J,IK,L)
510               CONTINUE
                  SUMCAT(J)=SUMCAT(J)+X(IK)*(SUM+2*PHIIJ(J,IK))
                  SUM = 0
520         CONTINUE
530   CONTINUE
      DO 560 J = 1, MAXCAT
```

```
            DO 550 IK = 11, MAXAN-1
                  DO 540 L = IK + 1, MAXAN
                        SUMAN(J) = SUMAN(J)+X(IK)*X(L)*PSI(IK,L,J)
540               CONTINUE
550         CONTINUE
560   CONTINUE
      SUM = 0
      DO 580 J = 1, MAXCAT
            DO 570 IK = 11, MAXAN
                  SUM = SUM + X(J)*X(IK)*C(J,IK)
570         CONTINUE
580   CONTINUE
      DO 590 J = 1, MAXCAT
            SUMZ(J) = SUM*ABS(Z(J))
590   CONTINUE
      DO 600 J = 1, MAXCAT
             GX(J)=EXP(Z(J)**2*F+SUMCA(J)+SUMCAT(J)+SUMAN(J)+SUMZ(J))
600   CONTINUE
      SUM = 0
      DO 620 IK = 11, MAXAN
            DO 610 J = 1, MAXCAT
                  SUMAC(IK) = SUMAC(IK)+X(J)*(2*B(J,IK)+ZZ*C(J,IK))
610         CONTINUE
620   CONTINUE
      DO 650 IK = 11, MAXAN
            DO 640 L = 11, MAXAN
                  IF (IK .EQ. L) GOTO 640
                  DO 630 J = 1, MAXCAT
                        SUM = SUM+X(J)*PSI(IK,L,J)
630               CONTINUE
                  SUMAA(IK)=SUMAA(IK)+X(L)*(2*PHIIJ(IK,L)+SUM)
                  SUM = 0
640         CONTINUE
650   CONTINUE
      DO 680 IK = 11, MAXAN
            DO 670 J = 1, MAXCAT - 1
                  DO 660 L = J + 1, MAXCAT
                        SUMCC(IK)=SUMCC(IK)+X(J)*X(L)*PSI(J,L,IK)
660               CONTINUE
670         CONTINUE
680   CONTINUE
      SUM = 0
      DO 700 J = 1, MAXCAT
            DO 690 IK = 11, MAXAN
                  SUM = SUM+X(J)*X(IK)*C(J,IK)
690         CONTINUE
700   CONTINUE
      DO 710 IK = 11, MAXAN
            SUMK(IK) = SUM * ABS(Z(IK))
710   CONTINUE
      DO 720 IK = 11, MAXAN
         GX(IK)=EXP(Z(IK)**2*F+SUMAC(IK)+SUMAA(IK)+SUMCC(IK)+SUMK(IK))
720   CONTINUE
      RETURN
      END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------

      SUBROUTINE INTERACTION(Z1,Z2,I,A,PHIPHI,PHIPRI,PHIIJ,THETA,
     xAKI,AKII)
```

```
C  This subroutine calculates the higher-order electrostatic
C  interaction terms for the Pitzer equations.

      REAL I, JX(2,2), JXPRIME(2,2)
      DIMENSION B(0:22), D(0:22),ZA(2), XA(2,2)
      DOUBLE PRECISION AKI(0:20),AKII(0:20)

      B(21) = 0
      B(22) = 0
      D(21) = 0
      D(22) = 0
      ZA(1) = Z1
      ZA(2) = Z2

      DO 770 JJ = 1, 2
            DO 760 IJ = 1, 2
                  XA(JJ,IJ)=6*ZA(IJ)*ZA(JJ)*A*SQRT(I)
                  X=XA(JJ,IJ)
                  IF (X .LT. 1) THEN
                        ZZ =4*X**0.20-2.0
                        DZ = 0.80*X**(-0.80)
                        DO 740 K = 20, 0, -1
                              B(K) = ZZ*B(K+1)-B(K+2)+AKI(K)
                              D(K) = B(K+1)+ZZ*D(K+1)-D(K+2)
740                     CONTINUE
                  ELSE
                        ZZ = (40/9)*X**(-0.10)-22/9
                        DZ = (-40/90)*X**(-1.10)
                        DO 750 K = 20, 0, -1
                              B(K) = ZZ*B(K+1)-B(K+2)+AKII(K)
                              D(K) = B(K+1)+ZZ*D(K+1)-D(K+2)
750                     CONTINUE
                  END IF
                  JX(JJ,IJ) = .25*X-1+.5*(B(0)-B(2))
                  JXPRIME(JJ,IJ) = .25+.5*DZ*(D(0)-D(2))
760         CONTINUE
770   CONTINUE
      ETHETA=(Z1*Z2/(4*I))*(JX(1,2)-.5*JX(1,1)-.5*JX(2,2))
      ETHPRI=-ETHETA/I+(Z1*Z2/(8*I**2))*(XA(1,2)*JXPRIME(1,2)-.5*
     x      XA(1,1)*JXPRIME(1,1)-.5*XA(2,2)*JXPRIME(2,2))
      PHIPHI=THETA+ETHETA+I*ETHPRI
      PHIIJ=THETA+ETHETA
      PHIPRI=ETHPRI
      RETURN
      END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------

      SUBROUTINE PPRINT

C  Subroutine prints the results.

      REAL MOLE, K, IX, I
      CHARACTER*20 SPECIS(30), SOLID(31:60)
      CHARACTER*50 TITLE
      DIMENSION AX(60)
      DOUBLE PRECISION X

      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI
```

```
      DATA SPECIS / 'NA','K','CA','MG','H',0,0,0,0,0,
     x      'CL','SO4','OH','HCO3','CO3',0,0,0,0,0,
     x      'CO2(AQ)','CASO4','MGSO4',0,0,0,0,0,'CO2(ATM)','H2O(L)' /
      DATA SOLID / 'ICE','NACL.2H2O','NACL','KCL','CACL2.6H2O',
     x      'MGCL2.6H2O','MGCL2.8H2O','MGCL2.12H2O','KMGCL3.6H2O',
     x      'CACL2.2MGCL2.12H2O','NA2SO4.10H2O','NA2SO4','MGSO4.6H2O',
     x      'MGSO4.7H2O','K2SO4','MGSO4.K2SO4.6H2O',
     x      0,0,0,0,0,0,0,0,0,0,0,0,0,0 /
      GX(22) = 1
      GX(23) = 1
      CALL PITZER
      DO 780 J = 1, 30
            AX(J) = X(J) * GX(J)
780   CONTINUE
      WRITE(2,785) TITLE
785   FORMAT(A50)
      WRITE (2,*)
      WRITE (2,787) "Temp(K)","Ion.Str.","AH2O","Phi","H2O(g)","Ice(g)"
787   FORMAT (1X, A7, A15, A10, A13, A14, A13)
      WRITE (2,790) TEMP,I,AH2O,PHI,X(30),X(31)
790   FORMAT (1X, G10.5, 1X, 5G13.5)
      WRITE (2,*)
      WRITE (2,795) "Solution","Initial","Final"
795   FORMAT (1X, A8, A13, A11)
      WRITE (2,797) "SPECIES","Conc.","Conc.","Act.Coef.","Activity",
     x      "Moles"
797   FORMAT (1X, A7, A12, A13, A17, A12, A10)
      DO 810 J = 1, 23
            MOLE = X(J)*X(30)/1000
            IF (MOLE .EQ. 0) GOTO 810
            WRITE(2,800) SPECIS(J), IX(J), X(J), GX(J), AX(J), MOLE
800         FORMAT(1X, A11, 5G13.5)
810   CONTINUE
      MOLE = X(30) / 18.0153
      WRITE (2,812) SPECIS(30), AH2O, MOLE
812   FORMAT (1X, A11, 42X, G10.5,G12.5)
      WRITE (2,*)
      WRITE (2,815) "Solid","Equil."
815   FORMAT (1X, A5,30X,A7)
      WRITE (2,817) "SPECIES","Moles","Constant"
817   FORMAT (1X, A7, A21, A16)
      DO 840 J = 31, 46
            MOLE = X(J)*X(30)/1000
            IF (J .EQ. 31) MOLE = X(31) / 18.0153
            WRITE (2,830) SOLID(J), MOLE, K(J)
830         FORMAT (1X, A20,2G13.5)
840   CONTINUE
      WRITE (2,*)
      WRITE (2,845) "CaSO4 (ionpair)", K(22)
845   FORMAT (1X, A15, G31.5)
      WRITE (2,850) "MgSO4 (ionpair)", K(23)
850   FORMAT (1X, A15, G30.5)
      WRITE (2,*)
      WRITE (2,*) " Iterations =", ITER
      WRITE (2,*)
      WRITE (2,*)
      RETURN
      END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------
```

```
      SUBROUTINE NACL

C  Subroutine for NaCl equilibrium.

      REAL IX,I,K
      CHARACTER*50 TITLE
      DOUBLE PRECISION NAT,CLT,KPRIME,X,DELTA

      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI

      DELTA=0
      HHALIT = K(32) / AH2O**2
      HALITE = K(33)
      NAT = X(1) + X(32) + X(33)
      CLT = X(11) + X(32) + X(33)
      IF (HHALIT .GT. HALITE) KPRIME = K(33)/(GX(1)*GX(11))
      IF (HALITE .GT. HHALIT) KPRIME = K(32)/(GX(1)*GX(11)*AH2O**2)
      IF (NAT*CLT-KPRIME .GT. 0) GOTO 860
855   X(1) = NAT
      X(11) = CLT
      X(32) = 0
      X(33) = 0
      GOTO 880
860   DECREM = MIN(NAT,CLT)
      DO 870 KA = 2, 5
865         DELTA = DELTA+DECREM*(DEL(KA)-1)
            IF (DELTA .LT. 0) GOTO 855
            X(1) = NAT - DELTA
            X(11) = CLT - DELTA
            IF (KA .EQ. 5) CALL PITZER
            HHALIT = K(32) / AH2O**2
            HALITE = K(33)
            IF (HHALIT .GT. HALITE) KPRIME = K(33)/(GX(1)*GX(11))
            IF (HALITE .GT. HHALIT) KPRIME = K(32)/(GX(1)*GX(11)*
     x            AH2O**2)
            IF (X(1)*X(11)-KPRIME .GT. 0) GOTO 865
            DELTA = DELTA-DECREM*(DEL(KA)-1)
870   CONTINUE
      X(1) = NAT - DELTA
      X(11) = CLT - DELTA
      IF (HHALIT .GT. HALITE) THEN
            X(33) = DELTA
            X(32) = 0
      ELSE
            X(32) = DELTA
            X(33) = 0
      END IF
880   RETURN
      END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------

      SUBROUTINE SYLVITE

C  Subroutine for KCl equilibrium.

      REAL  IX,I,K
      CHARACTER*50 TITLE
      DOUBLE PRECISION KT,CLT,KPRIME,X,DELTA
```

```
      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI

      DELTA=0
      KT = X(2) + X(34)
      CLT = X(11) + X(34)
      KPRIME = K(34) / (GX(2)*GX(11))
      IF (KT*CLT-KPRIME .GT. 0) GOTO 890
885   X(2) = KT
      X(11) = CLT
      X(34) = 0
      GOTO 910
890   DECREM = MIN(KT,CLT)
      DO 900 KA = 2, 5
895         DELTA = DELTA+DECREM*(DEL(KA)-1)
            IF (DELTA .LT. 0) GOTO 885
            X(2) = KT - DELTA
            X(11) = CLT - DELTA
            IF (KA .EQ. 5) CALL PITZER
            KPRIME = K(34)/(GX(2)*GX(11))
            IF (X(2)*X(11)-KPRIME .GT. 0) GOTO 895
            DELTA = DELTA-DECREM*(DEL(KA)-1)
900   CONTINUE
      X(2) = KT-DELTA
      X(11) = CLT-DELTA
      X(34) = DELTA
910   RETURN
      END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------

      SUBROUTINE ANTARCTICITE

C  Subroutine for CaCl2 equilibrium.

      REAL IX,I,K
      CHARACTER*50 TITLE
      DOUBLE PRECISION CAT,CLT,KPRIME,X,DELTA

      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI

      DELTA=0
      CAT = X(3) + X(35)
      CLT = X(11) + 2*X(35)
      KPRIME = K(35)/(GX(3)*GX(11)**2*AH2O**6)
      IF (CAT*CLT**2-KPRIME .GT. 0) GOTO 920
915   X(3) = CAT
      X(11) = CLT
      X(35) = 0
      GOTO 940
920   DECREM = MIN(CAT,CLT)
      DO 930 KA = 2, 5
925         DELTA = DELTA+DECREM*(DEL(KA)-1)
            IF (DELTA .LT. 0) GOTO 915
            X(3) = CAT - DELTA
            X(11) = CLT - 2*DELTA
            IF (KA .EQ. 5) CALL PITZER
            KPRIME = K(35)/(GX(3)*GX(11)**2*AH2O**6)
            IF (X(3)*X(11)**2-KPRIME .GT. 0) GOTO 925
            DELTA = DELTA - DECREM*(DEL(KA)-1)
```

```
930   CONTINUE
      X(3) = CAT-DELTA
      X(11) = CLT - 2*DELTA
      X(35) = DELTA
940   RETURN
      END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------

      SUBROUTINE MGCL2

C     Subroutine for MgCl2 equilibrium.

      REAL IX,I,K
      CHARACTER*50 TITLE
      DOUBLE PRECISION MGT,CLT,KPRIME,X,DELTA,KPRIM1,KPRIM2,KPRIM3

      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI

      DELTA=0
      MGT = X(4)+X(36)+X(37)+X(38)
      CLT = X(11)+2*X(36)+2*X(37)+2*X(38)
      KPRIM1 = K(36)/(GX(4)*GX(11)**2*AH2O**6)
      KPRIM2 = K(37)/(GX(4)*GX(11)**2*AH2O**8)
      KPRIM3 = K(38)/(GX(4)*GX(11)**2*AH2O**12)
      KPRIME=MIN(KPRIM1,KPRIM2,KPRIM3)
      IF (MGT*CLT**2-KPRIME .GT. 0) GOTO 960
950   X(4) = MGT
      X(11) = CLT
      X(36) = 0
      X(37) = 0
      X(38) = 0
      GOTO 990
960   DECREM = MIN(MGT,CLT)
      DO 980 KA = 2, 5
970         DELTA = DELTA+DECREM*(DEL(KA)-1)
            IF (DELTA .LT. 0) GOTO 950
            X(4) = MGT - DELTA
            X(11) = CLT-2*DELTA
            IF (KA .EQ. 5) CALL PITZER
            KPRIM1 = K(36)/(GX(4)*GX(11)**2*AH2O**6)
            KPRIM2 = K(37)/(GX(4)*GX(11)**2*AH2O**8)
            KPRIM3 = K(38)/(GX(4)*GX(11)**2*AH2O**12)
            KPRIME=MIN(KPRIM1,KPRIM2,KPRIM3)
            IF (X(4)*X(11)**2-KPRIME .GT. 0) GOTO 970
            DELTA = DELTA - DECREM*(DEL(KA)-1)
980   CONTINUE
      X(4) = MGT - DELTA
      X(11) = CLT - 2*DELTA
      IF (KPRIM1 .EQ. KPRIME) THEN
            X(36) = DELTA
            X(37) = 0
            X(38) = 0
      END IF
      IF (KPRIM2 .EQ. KPRIME) THEN
            X(37) = DELTA
            X(36) = 0
            X(38) = 0
      END IF
      IF (KPRIM3 .EQ. KPRIME) THEN
```

```
            X(38) = DELTA
            X(36) = 0
            X(37) = 0
      END IF
990   RETURN
      END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------

      SUBROUTINE CARNALLITE

C  Subroutine for KMgCl3.6H2O equilibrium.

      REAL IX,I,K
      CHARACTER*50 TITLE
      DOUBLE PRECISION KT,MGT,CLT,KPRIME,X,DELTA

      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI

      DELTA=0
      KT = X(2) + X(39)
      MGT = X(4) + X(39)
      CLT = X(11) + 3*X(39)
      KPRIME = K(39)/(GX(2)*GX(4)*GX(11)**3*AH2O**6)
      IF (KT*MGT*CLT**3-KPRIME .GT. 0) GOTO 1005
1000  X(2) = KT
      X(11) = CLT
      X(4) = MGT
      X(39) = 0
      GOTO 1030
1005  DECREM = MIN(KT,MGT,CLT)
      DO 1020 KA = 2, 5
1010        DELTA = DELTA+DECREM*(DEL(KA)-1)
            IF (DELTA .LT. 0) GOTO 1000
            X(2) = KT - DELTA
            X(4) = MGT - DELTA
            X(11) = CLT - 3*DELTA
            IF (KA .EQ. 5) CALL PITZER
            KPRIME = K(39)/(GX(2)*GX(4)*GX(11)**3*AH2O**6)
            IF (X(2)*X(4)*X(11)**3-KPRIME .GT. 0) GOTO 1010
            DELTA = DELTA - DECREM*(DEL(KA)-1)
1020  CONTINUE
      X(2) = KT - DELTA
      X(4) = MGT - DELTA
      X(11) = CLT - 3*DELTA
      X(39) = DELTA
1030  RETURN
      END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------

      SUBROUTINE TACHYHYDRITE

C  Subroutine for CaMg2Cl6.12H2O equilibrium.

      REAL IX,I,K
      CHARACTER*50 TITLE
```

```
      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI
        DOUBLE PRECISION KPRIME,CAT,MGT,CLT,X,DELTA

      DELTA=0
      CAT = X(3) + X(40)
      MGT = X(4) + 2*X(40)
      CLT = X(11) + 6*X(40)
      KPRIME = K(40)/(GX(3)*GX(4)**2*GX(11)**6*AH2O**12)
      IF (CAT*MGT**2*CLT**6-KPRIME .LT. 0) GOTO 1050
1040  X(3) = CAT
      X(11) = CLT
      X(4) = MGT
      X(40) = 0
      GOTO 1080
1050  DECREM = MIN(CAT,MGT,CLT)
      DO 1070 KA = 2, 5
1060        DELTA = DELTA+DECREM*(DEL(KA)-1)
            IF (DELTA .LT. 0) GOTO 1040
            X(3) = CAT - DELTA
            X(4) = MGT - 2*DELTA
            X(11) = CLT - 6*DELTA
            IF (KA .EQ. 5) CALL PITZER
            KPRIME = K(40)/(GX(3)*GX(4)**2*GX(11)**6*AH2O**12)
            IF (X(3)*X(4)**2*X(11)**6-KPRIME .GT. 0) GOTO 1060
            DELTA = DELTA-DECREM*(DEL(KA)-1)
1070  CONTINUE
      X(3) = CAT - DELTA
      X(4) = MGT - 2*DELTA
      X(11) = CLT - 6*DELTA
      X(40) = DELTA
1080  RETURN
      END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------

      SUBROUTINE ARCANITE

C  Subroutine for K2SO4 equilibrium.

      REAL IX,I,K
      CHARACTER*50 TITLE
      DOUBLE PRECISION KT,SO4T,KPRIME,X,DELTA

      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI

      DELTA=0
      KT = X(2) + 2*X(45)
      SO4T = X(12) + X(45)
      KPRIME = K(45)/(GX(2)**2*GX(12))
      IF (KT**2*SO4T-KPRIME .GT. 0) GOTO 1100
1090  X(2) = KT
      X(12) = SO4T
      X(45) = 0
      GOTO 1130
1100  DECREM = MIN(KT,SO4T)
      DO 1120 KA = 2, 5
1110        DELTA = DELTA+DECREM*(DEL(KA)-1)
            IF (DELTA .LT. 0) GOTO 1090
            X(2) = KT - 2*DELTA
```

```
            X(12) = SO4T - DELTA
            IF (KA .EQ. 5) CALL PITZER
            KPRIME = K(45)/(GX(2)**2*GX(12))
            IF (X(2)**2*X(12)-KPRIME .GT. 0) GOTO 1110
            DELTA = DELTA - DECREM*(DEL(KA)-1)
1120  CONTINUE
      X(2) = KT - 2*DELTA
      X(12) = SO4T - DELTA
      X(45) = DELTA
1130  RETURN
      END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------

      SUBROUTINE NA2SO4

C  Subroutine for Na2SO4 equilibrium.

      REAL MIRAB,IX,I,K
      CHARACTER*50 TITLE
      DOUBLE PRECISION NAT,SO4T,KPRIME,X,DELTA

      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI

      DELTA=0
      NAT = X(1)+2*X(41)+2*X(42)
      SO4T = X(12)+X(41)+X(42)
      MIRAB  = K(41)/AH2O**10
      TENAR = K(42)
      IF (MIRAB .GT. TENAR) THEN
            KPRIME = K(42)/(GX(1)**2*GX(12))
      ELSE
            KPRIME = K(41)/(GX(1)**2*GX(12)*AH2O**10)
      END IF
      IF (NAT**2*SO4T-KPRIME .GT. 0) GOTO 1150
1140  X(1) = NAT
      X(12) = SO4T
      X(41) = 0
      X(42) = 0
      GOTO 1180
1150  DECREM = MIN(NAT,SO4T)
      DO 1170 KA = 2, 5
1160        DELTA = DELTA+DECREM*(DEL(KA)-1)
            IF (DELTA .LT. 0) GOTO 1140
            X(1) = NAT - 2*DELTA
            X(12) = SO4T - DELTA
            IF (KA .EQ. 5) CALL PITZER
            MIRAB = K(41)/AH2O**10
            TENAR = K(42)
            IF (MIRAB .GT. TENAR) THEN
                  KPRIME = K(42)/(GX(1)**2*GX(12))
            ELSE
                  KPRIME = K(41)/(GX(1)**2*GX(12)*AH2O**10)
            END IF
            IF (X(1)**2*X(12)-KPRIME .GT. 0) GOTO 1160
            DELTA = DELTA - DECREM*(DEL(KA)-1)
1170  CONTINUE
      X(1) = NAT - 2*DELTA
      X(12) = SO4T - DELTA
      IF (MIRAB .LT. TENAR) THEN
```

```
            X(41) = DELTA
            X(42) = 0
      ELSE
            X(42) = DELTA
            X(41) = 0
      END IF
1180  RETURN
      END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------

      SUBROUTINE MGSO4

C  Subroutine for MgSO4 equilibrium.


      REAL  IX,I,K
      CHARACTER*50 TITLE
      DOUBLE PRECISION A,B,C,XA,MGT,SO4T,KPRIME,KIONPR,X,DELTA

      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI

      DELTA=0
      MGT = X(4)+X(43)+X(44)+X(23)
      SO4T = X(12)+X(43)+X(44)+X(23)
      HEXAHY = K(43)/AH2O**6
      EPSOM = K(44) / AH2O**7
      IF (HEXAHY .LT. EPSOM) THEN
            KPRIME = K(43)/(GX(4)*GX(12)*AH2O**6)
      ELSE
            KPRIME = K(44)/(GX(4)*GX(12)*AH2O**7)
      END IF
      IF (MGT*SO4T-KPRIME .GT. 0) GOTO 1200
1190  KIONPR = K(23)/(GX(4)*GX(12))
      A = 1
      B = -1*(MGT+SO4T+KIONPR)
      C = MGT*SO4T
      XA = (-B-SQRT(B**2-4*A*C))/(2*A)
      X(4) = MGT - XA
      X(12) = SO4T - XA
      X(23) = XA
      X(43) = 0
      X(44) = 0
      GOTO 1230
1200  DECREM = MIN(MGT,SO4T)
      DO 1220 KA = 2, 5
1210        DELTA = DELTA+DECREM*(DEL(KA)-1)
            IF (DELTA .LT. 0) GOTO 1190
            KIONPR = K(23)/(GX(4)*GX(12))
            X(23) = KPRIME/KIONPR
            X(4) = MGT - DELTA - X(23)
            X(12) = SO4T - DELTA - X(23)
            IF (KA .EQ. 5) CALL PITZER
            HEXAHY = K(43)/AH2O**6
            EPSOM = K(44)/AH2O**7
            IF (HEXAHY .LT. EPSOM) THEN
                  KPRIME = K(43)/(GX(4)*GX(12)*AH2O**6)
            ELSE
                  KPRIME = K(44)/(GX(4)*GX(12)*AH2O**7)
            END IF
```

```
            IF (X(4)*X(12)-KPRIME .GT. 0) GOTO 1210
            DELTA = DELTA-DECREM*(DEL(KA)-1)
1220  CONTINUE
      X(23) = KPRIME/KIONPR
      X(4) = MGT - DELTA - X(23)
      X(12) = SO4T - DELTA - X(23)
      IF (HEXAHY .LT. EPSOM) THEN
            X(43) = DELTA
            X(44) = 0
      ELSE
            X(44) = DELTA
            X(43) = 0
      END IF
1230  RETURN
      END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------

      SUBROUTINE PICROMERITE

C  Subroutine for K2Mg(SO4)2.6H2O equilibrium.

      REAL IX,I,K
      CHARACTER*50 TITLE
      DOUBLE PRECISION A,B,C,XA,MGT,KT,SO4T,KPRIME,KIONPR,X,DELTA

      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI

      PHASE = PHASE + 1
      DELTA=0
      KPRIME = K(46)/(GX(4)*GX(2)**2*GX(12)**2*AH2O**6)
      MGT = X(4) + X(46) + X(23)
      KT = X(2) + 2*X(46)
      SO4T = X(12) +2*X(46) + X(23)
      IF (MGT*KT**2*SO4T**2-KPRIME .GT. 0) GOTO 1250
1240  KIONPR  = K(23)/(GX(4)*GX(12))
      A = 1
      B = -1*(MGT+SO4T+KIONPR)
      C = MGT*SO4T
      XA = (-B-SQRT(B**2-4*A*C))/(2*A)
      X(4) = MGT - XA
      X(12) = SO4T - XA
      X(23) = XA
      X(2) = KT
      X(46) = 0
      GOTO 1280
1250  DECREM = MIN(MGT,SO4T,KT)
      DO 1270 KA = 2, 5
1260        DELTA = DELTA+DECREM*(DEL(KA)-1)
            IF (DELTA .LT. 0) GOTO 1240
            KIONPR = K(23)/(GX(4)*GX(12))
            X(23) = KPRIME/KIONPR
            X(4) = MGT - DELTA - X(23)
            X(12) = SO4T - 2*DELTA - X(23)
            X(2) = KT - 2*DELTA
            IF (KA .EQ. 5) CALL PITZER
            KPRIME = K(46)/(GX(4)*GX(2)**2*GX(12)**2*AH2O**6)
            IF (X(4)*X(2)**2*X(12)**2-KPRIME .GT. 0) GOTO 1260
            DELTA = DELTA-DECREM*(DEL(KA)-1)
1270  CONTINUE
```

```
      X(23) = KPRIME/KIONPR
      X(4) = MGT - DELTA - X(23)
      X(12) = SO4T - 2*DELTA - X(23)
      X(2) = KT - 2*DELTA
      X(46) = DELTA
1280  RETURN
      END

C-----------------------------------------------------------------------

C-----------------------------------------------------------------------

      SUBROUTINE CASO4

C  Subroutine for CaSO4 equilibrium.

      REAL IX,I,K
      CHARACTER*50 TITLE
      DOUBLE PRECISION A,B,C,XA,CAT,SO4T,KIONPR,IXA,X

      COMMON /B/ X(60),GX(60),K(20:60),AH2O,DEL(5),
     xIX(30),TITLE,ITER,AX(60),TEMP,I,PHI

1290  CALL PITZER
      KIONPR = K(22)/(GX(3)*GX(12))
      CAT = X(3) + X(22)
      SO4T = X(12) + X(22)
      IXA = X(22)
      A = 1
      B = -1*(CAT + SO4T + KIONPR)
      C = CAT*SO4T
      XA = (-B-SQRT(B**2-4*A*C))/(2*A)
      X(3) = CAT - XA
      X(12) = SO4T - XA
      X(22) = XA
      IF ((ABS(IXA-XA)/XA)*100 .GT. 1) GOTO 1290
      RETURN
      END

C-----------------------------------------------------------------------
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This report documents a FORTRAN version of the Spencer-Møller-Weare chemical thermodynamic model for aqueous electrolyte solutions at subzero temperatures (FREZCHEM). FREZCHEM is structured to predict the chemical composition and unfrozen water of aqueous solutions between –60 °C and +25 °C at atmospheric pressure (0.101325 MPa). FREZCHEM includes two reaction pathways: 1) freezing at variable temperature and fixed total water and 2) evaporation at variable water and fixed temperature. Activity coefficients and the activity of water are calculated using the Pitzer equations, which are valid to high solution ionic strengths (≈20 mol kg^{-1}). Fifteen chloride and sulfate salts of sodium, potassium, calcium, and magnesium are included in the model. Predicted and experimental measurements of solute molalities and the unfrozen water fraction during seawater freezing are in good agreement. At –50 °C, 0.3% of seawater remains unfrozen with 99.7% of Na and 95.5 % of Cl having precipitated into one of four salts. FREZCHEM should find many applications in physicochemical studies of aqueous solutions and freezing.

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