



FREZCHEM2

A Chemical Thermodynamic Model for Electrolyte Solutions at Subzero Temperatures

Mikhail V. Mironenko, Steven A. Grant, Giles M. Marion,
and Ronald E. Farren

October 1997

9 - number of independent components

H2O 0 30 - the name of the independent component, its charge and its code (the codes in this model are the same as

Na+ 1 1
K+ 1 2
Ca2+ 2 3
Mg2+ 2 4
Cl- -1 11
SO4-2 -2 12
CO3-2 -2 15
H+ 1 6

5 -number of cations

	Na ²⁺	Mg ²⁺	Cl ⁻	SO ₄ -2	CO ₃ -2	H ⁺
Na+(aq)	.00	.00	.00	.00	.00	.00
K+(aq)	.00	.00	.00	.00	.00	.00
Ca ²⁺ (aq)	.00	.00	.00	.00	.00	.00
Mg ²⁺ (aq)	.00	1.00	.00	.00	.00	.00
H ⁺ (aq)	.00	.00	.00	.00	.00	1.00

5 -number of anions

	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ -2	CO ₃ -2	H ⁺
Cl ⁻ (aq)	.00	.00	.00	.00	1.00	.00	.00	.00
SO ₄ -2(aq)	.00	.00	.00	.00	.00	1.00	.00	.00
OH ⁻ (aq)	1.00	.00	.00	.00	.00	.00	.00	-1.00
HCO ₃ ⁻ (aq)	.00	.00	.00	.00	.00	.00	1.00	.00
CO ₃ -2(aq)	.00	.00	.00	.00	.00	.00	1.00	.00

4 -number of neutral species

	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ -2	CO ₃ -2	H ⁺
CO ₂ (aq)	.00	.00	.00	.00	.00	.00	.00	2.00
CaSO ₄ (aq)	.00	.00	.00	.00	.00	.00	.00	.00
MgSO ₄ (aq)	.00	.00	.00	.00	.00	.00	.00	.00
H ₂ O(l)	.00	.00	.00	.00	.00	.00	.00	.00

16 - number of solid phases

	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ -2	CO ₃ -2	H ⁺
H ₂ O(cr, I)	1.00	.00	.00	.00	.00	.00	.00	0.00
NaCl*2H ₂ O(cr)	.00	.00	.00	.00	1.00	.00	.00	.00
NaCl(cr)	.00	.00	.00	.00	1.00	.00	.00	.00
KCl(cr)	.00	.00	.00	.00	1.00	.00	.00	.00
CaCl ₂ *6H ₂ O(cr)	.00	.00	1.00	.00	2.00	.00	.00	.00
MgCl ₂ *6H ₂ O(cr)	.00	.00	.00	1.00	2.00	.00	.00	.00
MgCl ₂ *8H ₂ O(cr)	.00	.00	.00	1.00	2.00	.00	.00	.00
MgCl ₂ *12H ₂ O(cr)	.00	.00	.00	1.00	2.00	.00	.00	.00
KMgCl ₃ *6H ₂ O(cr)	.00	1.00	.00	.00	3.00	.00	.00	.00
CaCl ₂ *2MgCl ₂ *12H ₂ O(cr)	.00	.00	2.00	.00	6.00	.00	.00	.00
Na ₂ SO ₄ *10H ₂ O(cr)	.00	.00	.00	.00	1.00	.00	.00	.00
Na ₂ SO ₄ (cr)	.00	.00	.00	.00	1.00	.00	.00	.00
MgSO ₄ *6H ₂ O(cr)	.00	.00	.00	1.00	.00	1.00	.00	.00
MgSO ₄ *7H ₂ O(cr)	.00	.00	.00	1.00	.00	1.00	.00	.00
K ₂ SO ₄ (cr)	.00	2.00	.00	.00	.00	1.00	.00	.00
MgSO ₄ *K ₂ SO ₄ *6H ₂ O(cr)	.00	2.00	.00	.00	.00	2.00	.00	.00

Read input data

Choose needed data from data files

Homogeneous system

Local equilibrium computation

Call Pitzer

Call Gauss-Jordan

Phase removal

Phase addition (call Simplex)

Print results

yes

yes

no

yes

no

no

no

Abstract: This report documents a Fortran version of a chemical thermodynamic model for aqueous electrolyte solutions at subzero temperatures, FREZCHEM2, which is a further development of the FREZCHEM model. The model uses thermodynamic data of Spencer-Møller-Weare that permit the calculation of chemical equilibria in the Na-K-Ca-Mg-Cl-SO₄-H₂O system between -60 and 25°C at atmospheric pressure. It applies the Gibbs energy minimization method for chemical equilibrium computation combined with

Pitzer equations for activity coefficients and water activity calculation. The model includes both the freezing (melting) reaction pathway at fixed water amount and the evaporation (dilution) pathway at fixed temperature. The FREZCHEM2 model can be extended with respect to independent components, electrolyte species, and solids, and if corresponding thermodynamic data are available, the model may be used to compute chemical equilibria in any systems that include aqueous-solution and/or one-component solid phases.

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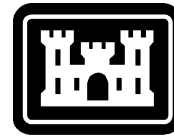
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PREFACE

This report was prepared by Dr. Mikhail V. Mironenko, Senior Researcher of the Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences, and Dr. Steven A. Grant, Dr. Giles M. Marion, and Dr. Ronald E. Farren, Research Physical Scientists of the Geochemical Sciences Branch, U.S. Army Cold Regions Research and Engineering Laboratory.

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FREZCHEM2

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MIKHAIL V. MIRONENKO, STEVEN A. GRANT, GILES M. MARION, AND RONALD E. FARREN

INTRODUCTION

The FREZCHEM model was developed by Marion and Grant (1994) to calculate chemical equilibria among aqueous electrolyte solutions, ice, and salts. The model applies the Pitzer equations for calculation of aqueous species and water activities. To find chemical equilibrium, this program solves sequentially a set of nonlinear equations that includes both solid-phase deposition and ion-pair formation using an individual subroutine for every reaction. FREZCHEM uses data on constants of chemical reactions and Pitzer equation parameters published by Spencer et al. (1990). The results of modeling show good agreement both with experimental data and with the results of the Spencer–Møller–Weare model. However, the FREZCHEM model has some limitations. One is convergence problems at high ionic strengths (>15 molal) and at junctions, where new phases begin to precipitate. Another is that addition of any new substance into this model requires changes not only in data but also in the program code.

The objective of this report is the further development of the chemical thermodynamic model FREZCHEM to make it more reliable, universal, and flexible. The point calculation reliability was improved by applying the Gibbs energy minimization approach to computing equilibrium. The thermodynamic information needed for computations is separated from the calculating routines. That allows components to be added to the system without code changes and the program code to be applied for other chemical systems. It should be noted that the Pitzer approach describes most interactions in aqueous solution as electro-

static and only explicitly recognizes a few chemical interactions, such as ion-pair formation. This is why the system under consideration is very simple from the viewpoint of chemical interactions, but it is very complex from the viewpoint of the influence of activity coefficients on the behavior of the Gibbs energy function.

MATHEMATICAL ALGORITHM

The system under investigation consists of the following components: 1) solid salts of fixed chemical composition and pure ice (so-called one-component phases), and 2) aqueous solutions consisting of water and dissolved electrolytes. The applied algorithms of chemical equilibria computation will be described in terms of these components.

The equilibrium composition of the system at constant T , P , and specified bulk composition may be found by minimizing the Gibbs energy function of the system under balance restrictions.

Local minimum computation

Local minimum is considered as an equilibrium composition of the system, in which all existing phases are specified before computation. The Gibbs energy function of the system that contains M solids and aqueous solution (water and J species) is as follows:

$$g = \frac{G}{RT} = \sum_{k=1}^M \mu_k^0 n_k + \mu_w n_w + \sum_{j=1}^J \mu_j n_j$$

where G = free energy of the system,
 n = the molal quantity of components,

μ_j = the chemical potential of species j ,
 μ_w = the chemical potential of water,
 μ_k^0 = the standard chemical potential of a
 one-component solid-phase k , and
 R = the universal gas constant.

The chemical potential of aqueous solution species j in terms of molality is defined by

$$\mu_j = \mu_j^0 + \ln a_j = \mu_j^0 + \ln(m_j \gamma_j)$$

where μ^0 is the standard chemical potential,

$$m_j = \frac{n_j}{n_w} \cdot 55.51$$

is the moles of the j^{th} species per 1 kg of water (molality), and γ is an activity coefficient.

The chemical potential of water may be written as

$$\mu_w = \mu_w^0 + \ln a_w$$

where water activity a_w , according to Pitzer (1987), is defined through the osmotic coefficient of the solution ϕ and molalities of species by

$$\ln a_w = -\phi \frac{W}{1000} \left(\sum_j m_j \right)$$

where W is the molecular weight of water (18.0153).

Accordingly, the free energy function of the system is as follows:

$$\begin{aligned}
 g(\bar{n}) = & \sum_{k=1}^M \mu_k^0 n_k + n_w \left(\mu_w^0 - \phi \frac{\sum n_j}{n_w} \right) \\
 & + \sum_{j=1}^J n_j \left[\mu_j^0 + \ln \left(\frac{n_j 55.51}{n_w} \gamma_j \right) \right]. \quad (1)
 \end{aligned}$$

Mass balance constraints, including the electroneutrality equation if necessary, may be written as a system of linear equations:

$$\sum_{j=1}^{M+1+J} v_{ij} n_j = b_i, \quad i = 1, P \quad (2)$$

where P is the number of independent chemical components in the system, and v_{ij} is the number of moles (stoichiometric units) of independent component i in one mole of component j . b_i represents the number of moles of independent com-

ponent i in the system. For the electroneutrality equation $b_1 = 0$ and $v_{1j} = z_j$, where z_j is the charge of the j^{th} component. In matrix notation, eq 2 may be written as

$$N\bar{n}^T = \bar{b}$$

where N is the stoichiometric matrix, \bar{n} is the vector of numbers of moles of species, and \bar{b} is the vector of bulk chemical composition of the system.

It is convenient to solve the system of linear equations (eq 2) with respect to P components, including M ($M \leq P$) solids,

$$n_k = B_k - \sum_{j=1}^{J+1} a_{kj} n_j \quad k = 1, M \quad (2a)$$

$$f_j = B_j - \sum_{j=1}^{J+1} a_{ij} n_j = 0 \quad i = M+1, P \quad (2b)$$

and in this way to switch to new independent components. In such a manner the stoichiometry of other $J+1-P$ components (vectors \bar{a}_i) and the matter balance \bar{B} are now defined through these independent components. This operation allows the number of active constraints to be reduced up to $P-M$. The thermodynamic meaning of this lies in the fact that the chemical potential of a one-component solid phase is equal to the standard Gibbs energy of formation and does not depend on its amount, until this phase is present. This is why the system can be considered to be open with respect to this component.

It is obvious that

$$n_w > 0 \text{ and } n_j > 0. \quad (3)$$

Minimization of the function in eq 1 under the constraints of eq 2 and eq 3 can be replaced by a search of the extremum of the Lagrangian function, which may be written as

$$\begin{aligned}
 \Phi(\bar{n}, \bar{\lambda}) = & g(\bar{n}) + \sum_{k=1}^M \mu_k^0 (B_k - \sum_{j=1}^{J+1} a_{kj} n_j) \\
 & + \sum_{i=m+1}^P \lambda_i (B_i - \sum_{j=1}^{J+1} a_{ij} n_j)
 \end{aligned}$$

where λ is a Lagrangian multiplier. It can be shown (Karpov et al. 1976) that λ is the chemical potential of the corresponding independent component of the system. In particular for solids, $\lambda_k = \mu_k^0$.

The conditions of extremum of the Lagrangian function are found where all first partial derivatives with respect to components and to Lagrangian multipliers are equal to zero. This gives

$$\begin{aligned} \frac{\partial \Phi}{\partial n_j} &= (\mu_j^0 + \ln 55.51) + \ln\left(\frac{n_j}{n_w} \gamma_j\right) \\ &- \sum_{k=1}^M \mu_k^0 a_{kj} - \sum_{i=M+1}^P \lambda_i a_{ij} = 0 \end{aligned} \quad (4a)$$

$$\begin{aligned} \frac{\partial \Phi}{\partial n_w} &= -\phi \frac{n_j}{n_w} - \sum_{k=1}^M \mu_k^0 a_{kw} \\ &- \sum_{i=M+1}^P \lambda_i a_{iw} = 0 \end{aligned} \quad (4b)$$

$$\frac{\partial \Phi}{\partial \lambda_i} = B_i - \sum_{j=1}^J a_{ij} n_j - a_{iw} n_w = 0. \quad (4c)$$

There are different approaches to searching the Lagrangian function extremum. One of them is the algorithm developed by White (1958, 1967) for homogeneous gas systems, which has been further developed for heterogeneous multiphase systems by Karpov (1976). This algorithm was applied by the senior author of this report for computation of a wide range of chemical equilibria (Mironenko 1991, 1992) and is build into the DiaNIK system (Khodakovsky 1992). The idea of the method, as applied to the system under consideration, is as follows. Equation 4a may be solved with respect to n_j :

$$n_j = \frac{n_w}{\gamma_j} \exp\left(\sum_{k=1}^M \mu_k^0 a_{kj} + \sum_{i=M+1}^P \lambda_i a_{ij} - \mu_j^0\right). \quad (5)$$

Substitution of these terms into eq 4b and c gives the system of $P - M + 1$ equations, which may be solved by Newton's method for λ and n_w . The advantages of this approach are a fast rate of computation, due to a small amount of variables (their amount does not depend on the number of species), and the lack of necessity to undertake special steps to calculate species at very low concentrations or to correct negative values of mass for species during iterations. Unfortunately, attempts to apply this approach to brine systems in combination with Pitzer's routine have demonstrated that the algorithm is not tolerant of oscillations of activity coefficient values, provided

by Pitzer's routine at every iteration. Because of this it was very difficult to reach the required precision of solution (0.1%), even when special steps were undertaken.

Another approach is to solve the whole system of $P - M + J + 1$ equations (eq 4 a,b,c) iteratively by Newton's method for n_j , n_w , and λ_k . This algorithm has been described in detail by Harvie et al. (1987). It has been successfully applied by Spencer et al. (1990) for strong electrolyte solution modeling, but a working version of the program has not been published. This algorithm also was applied by Mironenko (1983) for modeling fluid-rock interactions during hydrothermal uranium ore formation.

The second partial derivatives of the Lagrangian function are equal to

$$\frac{\partial^2 \Phi}{\partial n_j \partial n_{j1}} = \begin{cases} \frac{1}{n_j}, & \text{if } j = j1 \\ 0, & \text{if } j \neq j1 \end{cases}$$

$$\frac{\partial^2 \Phi}{\partial n_j \partial n_w} = -\frac{1}{n_w}$$

$$\frac{\partial^2 \Phi}{\partial n_j \partial \lambda_i} = \frac{\partial^2 \Phi}{\partial \lambda_i \partial n_j} = -a_{ij}$$

$$\frac{\partial^2 \Phi}{\partial n_w \partial n_j} = -\phi \frac{1}{n_w}$$

$$\frac{\partial^2 \Phi}{\partial n_w^2} = \frac{\sum n_j}{n_w^2} \phi$$

$$\frac{\partial^2 \Phi}{\partial n_w \partial \lambda_i} = \frac{\partial^2 \Phi}{\partial \lambda_i \partial n_w} = -a_{iw}$$

$$\frac{\partial^2 \Phi}{\partial \lambda_i \partial \lambda_{i1}} = 0.$$

This matrix of second partial derivatives is known as the Hessian matrix.

Activity coefficients of species and the osmotic coefficient are calculated at every iteration using Pitzer's model (Pitzer 1987). In FREZCHEM2, the Pitzer routines published by Marion and Grant (1994) were used, with insignificant changes dealing mainly with the interface with data files.

The molal amounts of solids are calculated after a local equilibrium has been achieved using eq 2a.

Search for the equilibrium phase assemblage

Solids

If a molal quantity of solid calculated using eq 2a was negative, this solid phase was considered as completely dissolved, and a new local equilibrium without this solid was computed. Then a search of new solid phases from the list of possible solids to be included into the system is undertaken. The criterion for the inclusion of phase K is as follows:

$$\sum_{k=1}^M \mu_k^0 a_{kK} + \sum_{i=M+1}^P \lambda_i a_{ik} - \mu_K^0 < 0. \quad (6)$$

The thermodynamic meaning of this expression is that the free energy of chemical reaction of a given solid substance formed from independent components of the system is negative, and therefore this solid is thermodynamically stable. If the condition (eq 6) asserts, this solid replaces one of the independent components of the system with which it is linearly dependent. Then the system of linear equations (eq 2a,b) is solved with respect to this new independent component. By this means the chemical composition of all components of the system will be expressed in terms of this and other independent components. This procedure is largely achieved by applying the Simplex routine. (Simplex is a classic finite iteration method of linear programming [Korn and Korn 1963].) Addition of each solid phase reduces the number of active linear restrictions by one. Calculations are continued until, in the list of possible phases, there is no phase that meets the condition in eq 6.

Aqueous solution

Aqueous solution is considered absent in the system when the number of active balance restrictions ($P - M$) is less than or equal to one and the amount of water is less than 0.001 moles.

Special steps

Usually, the approximate phase composition of a system may be determined at the first steps of calculation using the Simplex routine. Then the exact equilibrium composition may be computed using Newton's method for local equilibria determination and Simplex methods for addition or substitution of solids. Due to the very high non-ideality of brines, this technique collapsed, and some changes in the logical pattern of calculation were made:

1. At first, the system is considered homogeneous (no solids), then the solid-phase assem-

blage is calculated, not simultaneously during one application of the Simplex routine, but sequentially. Another phase is added after local equilibrium with previously added phases is achieved.

2. After the appearance of a new solid phase and before applying Newton's method, the current species concentrations have to be recalculated to be in better agreement with values of independent component chemical potentials. The relation between concentration of species and values of chemical potentials of independent components is expressed by eq 5 and can be also treated in terms of the free energy of the chemical reaction of species formation from independent components of the system.

3. Because of particularities of Pitzer's model, to prevent wide fluctuations during solution of the system of equations 4a,b,c by Newton's method, we have to smooth changes of activity coefficient and osmotic coefficient values, which are calculated at each iteration by Pitzer's routine. We use average values obtained at the current and previous iterations.

4. At every iteration a new approximation to the solution is provided by inversion of the Hessian matrix: $y_i^{(k+1)} = y_i^{(k)} + \Delta_i / \xi$. For a homogeneous system the value of ξ is equal to 1 and it increases by 0.5 with every new solid that precipitates.

FREZCHEM2 PROGRAM

A listing of the FREZCHEM2 Fortran program is in Appendix A. FREZCHEM2 consists of a main program called READWRITE and seven subroutines.

The READWRITE program reads input data from the file INPUT, according to these data forms independent components of the system, and reads the temperature interval and temperature step for freezing, or the water content interval and water decrement at a given temperature for the evaporation scenario. It calculates chemical potentials of the components as functions of temperature, calls various subroutines, and writes results of the chemical equilibria computation into the file RESULT.

Subroutine CHOICE is called from the main program and chooses components that may be formed in the system of given chemical composition as well as their stoichiometry. A data file for this routine is the DATABASE file.

Subroutine SOL is called from READWRITE

and is the main calculating routine. It computes the equilibrium composition of the system at given T and specified mass balance by searching for the global extremum of the Lagrangian function. It forms the Hessian matrix and calls various subroutines. Results of computations return to the READWRITE program to be written.

Subroutine SIMPL is called from the SOL subroutine to enter new solid phases into the system and to invert the stoichiometric matrix. This calls the GG1 routine, which is the short version of the Gauss–Jordan matrix method.

Subroutine PITZER is called from the main program to choose data for Pitzer parameters and to calculate them at various temperatures if the freezing scenario has been chosen. It is also called from the SOL routine to calculate activity coefficients of species and water activity, using the Pitzer model at every iteration while minimizing the free energy function by Newton’s method. In FREZCHEM2, the PITZER subroutine, as well as the INTERACT subroutine published by Marion and Grant (1994), were used with only insignificant changes dealing mainly with the interface with data files.

Subroutine INTERACT calculates the higher-order electrostatic interactions for the Pitzer equations.

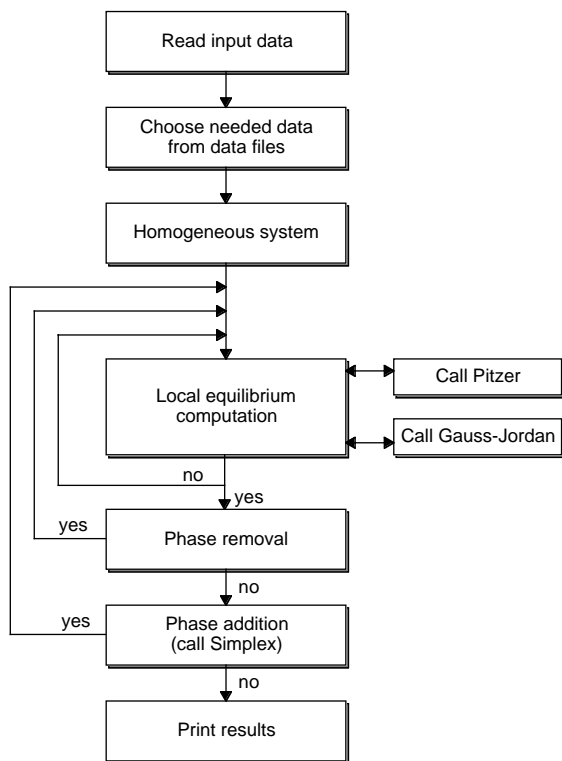


Figure 1. Flowchart of the FREZCHEM2 model.

Subroutine GG is called from the SOL subroutine and solves the system of linear equations by the Gauss–Jordan method.

The principal flowchart of FREZCHEM2 is shown in Figure 1. The FREZCHEM2 model is a universal model that may be used to compute chemical equilibrium in any system consisting of one-component solids and/or aqueous solution. For this goal, only additions in the data files are needed.

Data files

Files that contain the information needed for calculations and some remarks are listed in Appendix B.

File DATABASE contains a list of independent components, which can be taken into account, and lists of aqueous solution species (cations, anions, neutral species including water) and solid phases, consisting of given independent components as well as their stoichiometry. For the convenience of users, the same species numbers (coding) were used as in the FREZCHEM model. If necessary, additional information may be added for independent components as well as for species and solids. Requested formats for entering new data could be taken from the listing of the READWRITE program (Appendix A).

File TABLE1 represents Table 1 of Spencer et al. (1990), which includes constants for the Debye–Hückel model parameter A^ϕ and for the binary interaction parameters as a function of temperature (K). File TABLE2 represents Table 2 of that paper for mixed-salt parameters. File TABLE3 contains coefficients for calculation of free energies of chemical reactions of formation for solids and ion pairs from aqueous solution species and liquid water as a function of temperature, using equations of the form published by Spencer et al. (1990):

$$\frac{-\Delta G}{RT} = a_1 + a_2 T + a_6 T^2 + a_9 T^3 + a_3 / T + a_4 \ln(T) \quad (7)$$

and represents a copy of Table 3 from their paper. In this convention, free energies of cations, anions, and liquid water are taken to be equal to zero at any temperature.

Program input and output

Input to FREZCHEM2 is through the file INPUT, which contains the molal amounts of inde-

Table 1. FREZCHEM2 model input for freezing seawater from 0°C down to -40°C with a 2°C decrement.

SMW seawater	Title of the task
0.48695	Sodium (mol/kg)
0.01063	Potassium (mol/kg)
0.00953	Calcium (mol/kg)
0.05516	Magnesium (mol/kg)
0.56818	Chloride (mol/kg)
0.02939	Sulfate (mol/kg)
0.0	Carbonate (mol/kg)
0.0	Hydrogen (mol/kg)
273.15	<i>initial temperature</i>
1	<i>freezing (2 for evaporation)</i>
233.15	<i>final temperature (final amount of water for evaporation)</i>
2.0	<i>temperature decrement (water decrement for evaporation)</i>

pendent components (presently Na⁺, K⁺, Ca⁺², Mg⁺², Cl⁻, SO₄⁻², and CO₃⁻² are included) per 1 kg of water. Thus, an initial amount of water in the system is equal to 1 kg or 55.51 moles. If the molal quantity of an independent component is equal to zero, all substances in the file DATABASE that contain it will be ignored. The program calculates a charge balance and, if it is different from zero, proposes to add some amount of any cation or anion depending on the value and the sign of the charge balance, after which the program starts its work. FREZCHEM2 is able to calculate both 1) a cooling/heating scenario (in this case one enters initial and final temperatures and temperature decrement/increment) and 2) an evaporation/dilution scenario at constant temperature (in this case it needs a temperature, a water amount decrement/increment, and a final mass of water). The model is also able to calculate the process of ice evaporation. An example of input (file INPUT) is present in Table 1 for seawater freezing from 0 to -40°C for a 2°C temperature decrement. The explanations are written in italics.

Output from the program is to the RESULT file. As examples of output, results of computation of seawater freezing at 228.15 K (-45°C) and at 218.15 K (-55°C) are given in Table 2. Output of evaporation of seawater at 273.15 K (0°C) down to 50 g of water is given in Table 3.

Distribution of the independent components among solids and solution phases is given in the BALANCE table at the bottom of the output table. The last column of this table has been printed to show the equivalence of input and computed balances.

Verification of the model

To verify the program, phase diagrams from Spencer et al. (1990) and point computations from Marion and Grant (1994) were recalculated. The model reproduces these computations with good accuracy. Table 4 shows the temperatures at the appearance of solids during seawater freezing, taken from Spencer et al. (1990) with an added column obtained by the FREZCHEM2 model using their thermodynamic data.

It is interesting to note that, according to the free energies of chemical reactions in the model, a solid reaction



takes place at temperatures lower than -57.15°C. To verify this independently, the heat capacity equations for these phases at low temperatures are needed.

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Table 2. FREZCHEM2 model output for freezing seawater at -45°C and at -55°C .

Seawater freezing

temperature -45.00°C (228.15 K)

SOLID PHASES

<i>N</i>	<i>Phase</i>	<i>Moles</i>	<i>-G/RT</i>
1	$\text{H}_2\text{O}_{(\text{cr},\text{l})}$	53.52785	-0.4278
2	$\text{NaCl}\cdot 2\text{H}_2\text{O}_{(\text{cr})}$	0.42624	1.0995
3	$\text{KCl}_{(\text{cr})}$	0.00948	-0.8002
4	$\text{MgCl}_2\cdot 12\text{H}_2\text{O}_{(\text{cr})}$	0.05052	1.2364
5	$\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}_{(\text{cr})}$	0.02925	-12.2171

AQUEOUS SOLUTION

Ionic strength 11.0759

Osmotic coefficient 2.0008

<i>N</i>	<i>Species</i>	<i>Moles</i>	<i>Molality</i>	<i>Activity</i>	<i>Act. coef.</i>	<i>-G/RT</i>
1	$\text{Na}^+_{(\text{aq})}$	0.22059D-02	0.53403D+00	0.23599D+00	0.4419	0.0000
2	$\text{K}^+_{(\text{aq})}$	0.11533D-02	0.27920D+00	0.15016D-01	0.0538	0.0000
3	Ca^{+2}	0.94653D-02	0.22914D+01	0.15724D+01	0.6862	0.0000
4	Mg^{+2}	0.46407D-02	0.11235D+01	0.65163D+00	0.5800	0.0000
5	$\text{Cl}^-_{(\text{aq})}$	0.31425D-01	0.76077D+01	0.29938D+02	3.9352	0.0000
6	$\text{SO}_4^{-2}_{(\text{aq})}$	0.72974D-04	0.17666D-01	0.64149D-02	0.3631	0.0000
7	$\text{CaSO}_4_{(\text{aq})}$	0.64693D-04	0.15662D-01	0.15662D-01	1.0000	-0.4410
8	$\text{MgSO}_4_{(\text{aq})}$	0.87333D-07	0.21142D-04	0.21142D-04	1.0000	5.2851
9	$\text{H}_2\text{O}(\text{l})$	0.22929D+00		0.65191D+00		0.0000

BALANCE

	<i>Total</i>	<i>Solids</i>	<i>Solution</i>	<i>Total computed</i>
H_2O	0.555084E+02	0.552791E+02	0.229289E+00	0.555084E+02
Na^+	0.486950E+00	0.484744E+00	0.220592E-02	0.486950E+00
K^+	0.106300E-01	0.947671E-02	0.115329E-02	0.106300E-01
Ca^{+2}	0.953000E-02	0.000000E+00	0.953000E-02	0.953000E-02
Mg^{+2}	0.551600E-01	0.505192E-01	0.464076E-02	0.551600E-01
Cl^-	0.568180E+00	0.536755E+00	0.314254E-01	0.568180E+00
SO_4^{-2}	0.293900E-01	0.292522E-01	0.137754E-03	0.293900E-01

Number of iterations 93

Temperature -55.00°C (218.15 K)

SOLID PHASES

<i>N</i>	<i>Phase</i>	<i>Moles</i>	<i>-G/RT</i>
1	$\text{H}_2\text{O}_{(\text{cr},\text{l})}$	53.63903	-0.5004
2	$\text{NaCl}\cdot 2\text{H}_2\text{O}_{(\text{cr})}$	0.42817	0.8123
3	$\text{KCl}_{(\text{cr})}$	0.01063	-1.4388
4	$\text{CaCl}_2\cdot 6\text{H}_2\text{O}_{(\text{cr})}$	0.00953	5.6614
5	$\text{MgCl}_2\cdot 12\text{H}_2\text{O}_{(\text{cr})}$	0.05516	-1.5678
6	$\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}_{(\text{cr})}$	0.02939	-15.0450

BALANCE

	<i>Total</i>	<i>Solids</i>	<i>Solution</i>	<i>Total computed</i>
H_2O	0.555084E+02	0.555084E+02	0.000000E+00	0.555084E+02
Na^+	0.486950E+00	0.486950E+00	0.000000E+00	0.486950E+00
K^+	0.106300E-01	0.106300E-01	0.000000E+00	0.106300E-01
Ca^{+2}	0.953000E-02	0.953000E-02	0.000000E+00	0.953000E-02
Mg^{+2}	0.551600E-01	0.551600E-01	0.000000E+00	0.551600E-01
Cl^-	0.568180E+00	0.568180E+00	0.000000E+00	0.568180E+00
SO_4^{-2}	0.293900E-01	0.293900E-01	0.000000E+00	0.293900E-01

Number of iterations 88

Table 3. FREZCHEM2 model output for evaporation of seawater at 0°C.

Temperature	0.00°C (273.15 K)					
Water amount	50.00 g					
SOLID PHASES						
<i>N</i>	<i>Phase</i>	<i>Moles</i>	<i>-G/RT</i>			
1	NaCl _(cr)	0.28103	3.4448			
2	Na ₂ SO ₄ *10H ₂ O _(cr)	0.02021	-5.7260			
AQUEOUS SOLUTION						
Ionic strength		8.0709				
Osmotic coefficient		1.5573				
<i>N</i>	<i>Species</i>	<i>Moles</i>	<i>Molality</i>	<i>Activity</i>	<i>Act. coef.</i>	<i>-G/RT</i>
1	Na ⁺ _(aq)	0.16551D+00	0.35701D+01	0.28612D+01	0.8014	0.0000
2	K ⁺ _(aq)	0.10630D-01	0.22929D+00	0.74428D-01	0.3246	0.0000
3	Ca ⁺²	0.82305D-02	0.17754D+00	0.16740D+00	0.9429	0.0000
4	Mg ⁺²	0.55155D-01	0.11897D+01	0.27250D+01	2.2905	0.0000
5	Cl ⁻ _(aq)	0.28715D+00	0.61941D+01	0.10952D+02	1.7681	0.0000
6	SO ₄ ⁻² _(aq)	0.78786D-02	0.16995D+00	0.10190D-01	0.0600	0.0000
7	CaSO ₄ _(aq)	0.12993D-02	0.28027D-01	0.28027D-01	1.0000	-2.7979
8	MgSO ₄ _(aq)	0.53787D-05	0.11602D-03	0.11602D-03	1.0000	5.4788
9	H ₂ O(l)	0.25733D+01		0.72306D+00	0.0000	
BALANCE						
		<i>Total</i>	<i>Solids</i>	<i>Solution</i>	<i>Total computed</i>	
H ₂ O		0.277542E+01	0.202067E+00	0.257334E+01	0.277541E+01	
Na ⁺		0.486950E+00	0.321441E+00	0.165509E+00	0.486950E+00	
K ⁺		0.106300E-01	0.000000E+00	0.106300E-01	0.106300E-01	
Ca ⁺²		0.953000E-02	0.000000E+00	0.952987E-02	0.952987E-02	
Mg ⁺²		0.551600E-01	0.000000E+00	0.551600E-01	0.551600E-01	
Cl ⁻		0.568180E+00	0.281028E+00	0.287154E+00	0.568182E+00	
SO ₄ ⁻²		0.293900E-01	0.202067E-01	0.918331E-02	0.293900E-01	
Number of iterations		45				

Table 4. Temperatures (°C) of first appearance of solid phases on chilling of seawater.

<i>Solid</i>	<i>Experiment</i>	<i>FREZCHEM2</i>	
		<i>Model</i> ^a	<i>model</i>
Ice	-1.921 ^b	-1.924	-1.921
Mirabilite	-8.2 ^c	-5.90	-5.87
Hydrohalite	-22.9 ^c	-22.84	-22.87
Sylvite	-36 ^c	-34.25	-34.30
MgCl ₂ · 12H ₂ O	-36 ^c	-36.82	-36.82
Antarcticite	-54 ^c	-53.64 ^d	-53.73

a. Spencer et al. (1990).

b. Fujino et al. (1974).

c. Nelson and Thompson (1954).

d. Calculated in sulfate-free system.

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APPENDIX A: FORTRAN LISTING OF THE FREZCHEM2 PROGRAM

```
PROGRAM READWRITE
IMPLICIT DOUBLE PRECISION (A-H,O-Z)

CHARACTER *40 NMC,NEL,NM,NMCOMP,TITLE

DIMENSION BAL(10),NEL(10),G0(40,6),G(40),GIN(40),BALS(10)
DIMENSION BALL(10),ACT(20)
DIMENSION BC(10,20),A(10,40),EX(40),NMC(20),NM(40),AIN(10,40)
DIMENSION IZC(20),IZ(20),NUM(40),NUMC(20),NUMIN(40),NMM(40)

COMMON /COMPNT/ NUR(10),IP,NUL(10),IPNUL,KCOMP
COMMON /NUMBER/ NCAT,NANI,NNEI,NMM
COMMON /MASS1/ A,G,NUM,X(40)
COMMON /MASS2/ NM
COMMON /INTGER/ NL,N,N1
COMMON /MATRIX/ ACT,UM,PHI,AH2O,IZ,IPP,NMV
COMMON /AIN/ AIN,GIN,T,NUMIN,IV
COMMON /OUTPUT/ JOOPEN(10),IOOPEN

10  FORMAT(A40)
11  FORMAT(A40/)
12  FORMAT(I3/)
13  FORMAT(A15,I3,1X,I2,A40,F12.6)
14  FORMAT(' THE CHARGE OF 1 KG OF THE SOLUTION IS EQUAL TO
$,F8.5)
15  FORMAT(/13X,'Temperature ',F7.2,' C (' ,F7.2,' K)')
16  FORMAT(' WATER AMOUNT ',F7.2,' GRAM'/
$      ' _____')
17  FORMAT(25X,'SOLID PHASES'/1X,'N   Phase ',
$ 16X,' Moles      -G/RT')
18  FORMAT(I2,1X,A23,F9.5,2X,F12.4)
19  FORMAT(21X,'Ionic strength ',F8.4/
$ 21X,'Osmotic coefficient ',F7.4)
20  FORMAT(1X,'N',2X,'Species      ',4X,'Moles',7X,
$ 'Molality ',3X,'Activity ', 'Act.coef.      -G/RT')
21  FORMAT(I2,1X,A16,3D12.5,2X,F8.4,F10.4)
22  FORMAT(I2,1X,A16,D12.5,12X,D12.5,8X,F10.4,)
23  FORMAT (26X,'BALANCE' /
$ 13X,'Total',9X,'Solids',8X,'Solution',5X,'Total computed')
24  FORMAT(1X,A8,4(2X,E12.6))
25  FORMAT(' Number of iterations ',I3)
26  FORMAT(' THE PROGRAM CANNOT CALCULATE THIS CHEMICAL
$EQUILIBRIUM')

OPEN(1,FILE='DBASE')
OPEN(9,FILE='INPUT')
OPEN(10,FILE='RESULT')

XW=55.50837

READ(9,10) TITLE
WRITE(10,11) TITLE
```

```

C..  READING  INDEPENDENT COMPONENTS AND GIVING THE BALANCE

      READ(1,12) KCOMP

C..  THE WATER BALANCE (1 KG H2O = 55.50837 MOLES )

      BAL(1)=XW
      NEL(1)='H2O'
      NUMIN(1)=1
      NMM(1)=30
      NM(1)=NEL(1)
      NUR(1)=1
      J=1
      J1=0
      CHARGE=0.

      DO 2000 I=2,KCOMP
        READ(1,13) NMCOMP,IIZ,NU
        READ(9,*) AA
        IF (AA.GT.1.D-20) THEN
          J=J+1
          BAL(J)=AA
          CHARGE=CHARGE+IIZ*AA
          NEL(J)=NMCOMP
          NM(J)=NEL(J)
          NMM(J)=NU
          NUMIN(J)=J
          NUR(J)=I
        ELSE
          J1=J1+1
          NUL(J1)=I
        END IF
2000  CONTINUE

      IF(DABS(CHARGE).GT.0.00001) THEN
        WRITE(*,*) 'THE SALT BALANCE IS NOT CORRECT'
        WRITE(*,14) CHARGE
        IF(CHARGE.GT.0.)WRITE(*,*)'ADD ANIONS OR SUBT. CATIONS IN
$INPUT'
        IF(CHARGE.LT.0.)WRITE(*,*)'ADD CATIONS OR SUBT. ANIONS IN
$INPUT'
        PAUSE
        GO TO 815
      END IF

      IP=J
      IPP=IP
      IPNUL=J1

      DO 2100 I=1,IP

        DO 2101 J=1,IP
          AIN(I,J)=0.
2101  CONTINUE

          AIN(I,I)=1.
          GIN(I)=0.
2100  CONTINUE

```



```

CALL CHOICE (NCAT,BC,NMC,NUMC,IZC)
NC=IP+NCAT

DO 2200 I=1, NCAT
  I1=I+IP

  DO 2201 J=1,IP
    AIN(J,I1)=BC(J,I)
2201  CONTINUE

  NM(I1)=NMC(I)
  NMM(I1)=NUMC(I)
  NUMIN(I1)=I1
  IZ(I1)=IZC(I)
2200  CONTINUE

CALL CHOICE (NANI,BC,NMC,NUMC,IZC)
NA=NC+NANI

DO 2300 I=1, NANI
  I1=I+NC

  DO 2301 J=1,IP
    AIN(J,I1)=BC(J,I)
2301  CONTINUE

  NM(I1)=NMC(I)
  NMM(I1)=NUMC(I)
  NUMIN(I1)=I1
  IZ(I1)=IZC(I)
2300  CONTINUE

CALL CHOICE (NNEI,BC,NMC,NUMC,IZC)
NL=NA+NNEI

DO 2400 I=1, NNEI
  I1=I+NA

  DO 2401 J=1,IP
    AIN(J,I1)=BC(J,I)
2401  CONTINUE

  NM(I1)=NMC(I)
  NMM(I1)=NUMC(I)
  IF(NMM(I1).EQ.30)IV=I1
  NUMIN(I1)=I1
  IZ(I1)=IZC(I)
2400  CONTINUE

CALL CHOICE (NSOL,BC,NMC,NUMC,IZC)

DO 2500 I=1, NSOL
  I1=I+NL

  DO 2501 J=1,IP
    AIN(J,I1)=BC(J,I)
2501  CONTINUE

```

```

        NM(I1)=NMC(I)
        NMM(I1)=NUMC(I)
        NUMIN(I1)=I1
2500  CONTINUE

        IP1=IP+1
        L=NCAT+NANI+NNEI
        N=NL+NSOL
        N1=N+1

        DO 2600 J=1,IP
            AIN(J,N1)=BAL(J)
2600  CONTINUE

        IJJ=0

        DO 2700 I=1, N1
            NUM(I)=NUMIN(I)
2700  CONTINUE

C..... READ TABLE 3 .....

        OPEN(5, FILE='TABLE3')

        DO 2800 I=IP+1,N
2810    READ(5,*, END=2820) NT1

            IF(NMM(I).EQ.NT1) THEN
                BACKSPACE(5)
                READ(5,*) NT1, (G0(I,K),K=1,6)
                REWIND(5)
            ELSE
                GO TO 2810
            END IF

2820    REWIND(5)
2800  CONTINUE

        CLOSE (5)
        CALL PITZER (T,0,EX)
        READ(9,*) TINIT
        READ(9,*) IPATH

        IF (IPATH.EQ.1) THEN
            READ(9,*) TFIN
            READ(9,*) DT
        ELSE
            READ(9,*) WFIN
            READ(9,*) DW
        END IF

        T=TINIT
        BALWAT=1000.

1    CONTINUE

        DO 2900 I=IP+1,N
            GIN(I)= PF(T,G0(I,1),G0(I,2),G0(I,3),G0(I,4),G0(I,5),
$          G0(I,6))
2900  CONTINUE

```

```

IF(IPATH.EQ.1) WRITE(*,*) `T=' , T
PHI=1.
CALL PITZER (T,1,EX)

2 CONTINUE

IF(IPATH.EQ.2) WRITE (*,*) `AMOUNT OF WATER=' , BALWAT
CALL SOL (ICK,EX,ISOLU,IPATH)
TC=T-273.15
WRITE(10,15) TC,T
IF(IPATH.EQ.2) WRITE(10,16) BALWAT

IF(ICK.GT.400) GO TO 5

IF(IOPEN.GT.0) THEN
  WRITE(10,17)

  DO 3000 I=1,IOPEN
    J=JOPEN(I)
    WRITE(10,18) I,NM(NUM(J)),X(J),G(J)
3000 CONTINUE

  END IF

  IF(ISOLU.EQ.0) GO TO 4

C..... START OF OUTPUT .....

WRITE(10,*) `
WRITE(10,19) UM, PHI
WRITE(10,20)
                                     AQUEOUS SOLUTION'

DO 3100 K=IP1,NL-1
  EX(K)=EX(K)*XW
  G(K)=G(K)-DLOG(XW)
  AC=EXP(ACT(K))
  WRITE(10,21) K-IP,NM(K),X(K),EX(K),EX(K)*AC,AC,G(K)
3100 CONTINUE

WRITE(10,22) NL-IP,NM(NL),X(NL),DEXP(AH2O),G(NL)
4 WRITE(10,23)

DO 3200 K=1,IP
  BALL(K)=0.
  BALS(K)=0.
3200 CONTINUE

DO 3300 I=1,IOPEN
  J=JOPEN(I)

  DO 3301 K=1,IP
    BALS(K)=BALS(K)+X(J)*AIN(K,NUM(J))
3301 CONTINUE

3300 CONTINUE

```

```

DO 3400 I=1,IP
      DO 3401 J=IP1,NL
        BALL(I)=BALL(I)+X(J)*AIN(I,J)
3401    CONTINUE

      WRITE(10,24)NEL(I),AIN(I,N1),BALS(I),BALL(I),BALS(I)+BALL(I)
3400    CONTINUE

5      WRITE(10,25) ICK

C..... FINISH .....
      IF(ICK.GT.400) WRITE (10,26)

      IF (IPATH.EQ.1) THEN
        T=T-DT
        IF(T.GE.TFIN-.001) GO TO 1
      ELSE
        BALWAT=BALWAT-DW
        IF(BALWAT.GE.WFIN) THEN
          AIN(1,N1)=BALWAT/18.0153
          GO TO 2
        END IF
      END IF

      CLOSE(3)

815    STOP
      END

```

```

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

```

```

      SUBROUTINE CHOICE (NCAT,BK,NMCUR,NUMCUR,IZC)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)

C.. SUBROUTINE FOR CHOOSING COMPONENTS FROM DATABASE ACCORDING TO
C.. THE GIVEN INDEPENDENT COMPONENTS

      CHARACTER *40 NM,NMCUR
      DIMENSION BK(10,20),NMCUR(20),NUMCUR(20),IZC(20),B(10)
      COMMON /COMPNT/ NUR(10),IP,NUL(10),IPNUL,KCOMP

3      FORMAT(A23,I2,1X,I2,1X,10F6.2)

      READ(1,*)NCAT
      J=0

      DO 2 I=1,NCAT
c      READ(1,3) NM,NUM,IZ, (B(I1),I1=1, KCOMP)
      READ(1,*) NM,NUM,IZ, (B(I1),I1=1, KCOMP)

      DO 2000 J1=1,IPNUL
        IF (B(NUL(J1)).NE.0.) GO TO 2
2000    CONTINUE

```

```

        IS=0

        DO 3000 J1=1,IP
            IF (DABS(B(NUR(J1))).GT.1D-20) IS=IS+1
3000    CONTINUE

        IF (IS.EQ.0) GO TO 2
        J=J+1

        DO 4 J1=1,IP
            BK(J1,J)=B(NUR(J1))
4        CONTINUE

        NMCUR(J)=NM
        NUMCUR(J)=NUM
        IZC(J)=IZ
2        CONTINUE

        NCAT=J

        RETURN
        END
C-----C
C-----C
        SUBROUTINE INTACT(Z1,Z2,UM,A,PHIPHI,PHIPRI,PHIIJ,THETA)
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)

C    THIS SUBROUTINE CALCULATES THE HIGHER-ORDER ELECTROSTATIC
C    INTERACTION TERMS FOR PITZER EQUATIONS.

        DIMENSION B(0:22), D(0:22), ZA(2), XA(2,2),XJ(2,2),XJPRIM(2,2)
        DIMENSION AKI(0:20), AKII(0:20)

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

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

        B(21)=0.
        B(22)=0.
        D(21)=0.
        D(22)=0.
        ZA(1)=Z1
        ZA(2)=Z2
        SQ=SQRT(UM)

```

```

DO 2000 J=1,2

      DO 2001 I =1,2
        XA(J,I)=6.*ZA(I)*ZA(J)*A*SQ
        X=XA(J,I)
        IF (X.LT.1.) THEN
          ZZ=4.*X**0.2-2.0
          DZ=.8*X**(-.8)

          DO 2002 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)
2002      CONTINUE

          ELSE
            ZZ=40./9.*X**(-.1)-22./9.
            DZ=-40./90.*X**(-1.1)

            DO 2003 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)
2003      CONTINUE

          END IF
        XJ(J,I)=.25*X-1.+5*(B(0)-B(2))
        XJPRIM(J,I)=.25+.5*DZ*(D(0)-D(2))
2001      CONTINUE

2000  CONTINUE

      ETHETA=(Z1*Z2/4./UM)*(XJ(1,2)-.5*XJ(1,1)-.5*XJ(2,2))
      ETHPRI=-ETHETA/UM+(Z1*Z2/8./UM**2)*(XA(1,2)*XJPRIM(1,2)-
$      .5*XA(1,1)*XJPRIM(1,1)-.5*XA(2,2)*XJPRIM(2,2))
      PHIPHI=THETA+ETHETA+UM*ETHPRI
      PHIIJ=THETA+ETHETA
      PHIPRI=ETHPRI

      RETURN
      END

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

      SUBROUTINE PITZER (T,IFLAG,EX)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)

      DIMENSION A0M(6),NMM(40),NAQ(20),Z(20),EX(20)
      DIMENSION BPRIME(10,10),BPHI(10,10),C(10,10),PHIIJ(10,10),
$      SUMCA(10),SUMCAT(10),SUMAN(10),SUMZ(10),SUMAC(10),ACT(20),
$      PHIPHI(10,10),PHIPRI(10,10),XM(40),IZ(20)
      DIMENSION SUMAA(10),SUMCC(10),SUMK(10)
      DIMENSION BET0(10,10),BET1(10,10),C0(10,10), BET2(10,10),
$      TET(10,10),PSI(10,10,10),B(10,10)
      DIMENSION BET0M(10,10,6),BET1M(10,10,6),COM(10,10,6),
$      BET2M(10,10,6),TETM(10,10,6),PSIM(10,10,10,6)

      COMMON /NUMBER/NCAT,NANI, NNEI,NMM

```

```

COMMON /MATRIX/ ACT,UM,PHI,AH2O,IZ,IP,NMV

IF (IFLAG.EQ.1) GO TO 1
IF (IFLAG.EQ.2) GO TO 2

ICOL=6
NN=NCAT+NANI
NC1=NCAT+1

DO 2000 I=1,NN
    Z(I)=IZ(I+IP)
    NAQ(I)=NMM(I+IP)
2000 CONTINUE

C..... READ TABLES 1 AND 2 .....

OPEN(3, FILE='TABLE1')

C..... READ TABLE 1 .....

DO 3000 I=1,NN
    DO 3001 J=1,NN
        DO 3002 K=1,6
            COM(I,J,K)=0.
            BET2M(I,J,K)=0.
3002 CONTINUE
3001 CONTINUE
3000 CONTINUE

READ(3,*) (AOM(I), I=1,6)

DO 4000 I=1,NCAT
    DO 4001 J=NC1,NN
101 READ(3,FMT='(2I3)') NT1,NT2

    IF(NAQ(I).EQ.NT1.AND.NAQ(J).EQ.NT2) THEN
        READ(3,*) (BET0M(I,J,K),K=1,6)
        READ(3,*) (BET1M(I,J,K),K=1,6)

        IF((NT1.EQ.3 .OR. NT1.EQ.4) .AND. NT2.EQ.12) THEN
            READ(3,*) (BET2M(I,J,K),K=1,6)
            READ(3,*) (COM(I,J,K),K=1,6)
        ELSE
            READ(3,*) (COM(I,J,K),K=1,6)
        END IF

    ELSE

        IF((NT1.EQ.3 .OR. NT1.EQ.4) .AND. NT2.EQ.12) THEN
            READ(3,FMT='(///)',END=910)
        ELSE
            READ(3,FMT='(//)',END=910)
        END IF

```

```

                                GO TO 101

                                END IF
4001      CONTINUE

4000  CONTINUE

      CLOSE(3)

C..... READ TABLE 2 .....

      OPEN(4, FILE='TABLE2')

      DO 5000 I=1,NCAT-1

102      DO 5001 J=I+1,NCAT
          READ(4,*) NT1,NT2,NT3

          IF(NAQ(I).EQ.NT1.AND.NAQ(J).EQ.NT2.AND.NT3.EQ.0)THEN
              BACKSPACE(4)
              READ(4,*) NT1,NT2,NT3,(TETM(I,J,K),K=1,6)
              REWIND(4)
          ELSE
              GO TO 102
          END IF

5001      CONTINUE

5000  CONTINUE

      DO 6000 I=1,NCAT-1

          DO 6001 J=I+1,NCAT

              DO 6002 IJ = NC1,NN
105          READ(4,*) NT1,NT2,NT3

              IF(NAQ(I).EQ.NT1
$              .AND. NAQ(J).EQ.NT2
$              .AND. NAQ(IJ).EQ.NT3) THEN
                  BACKSPACE(4)
                  READ(4,*)NT1,NT2,NT3,(PSIM(I,J,IJ,K),K=1,6)
                  REWIND(4)
              ELSE
                  GO TO 105
              END IF

6002      CONTINUE

6001      CONTINUE

6000  CONTINUE

      DO 7000 I=NC1,NN-1

          DO 7001 J=I+1,NN
103          READ(4,*) NT1,NT2,NT3

```



```

                IF(NAQ(I) .EQ. NT1
$                .AND.  NAQ(J) .EQ. NT2
$                .AND.  NT3.EQ.0) THEN
                BACKSPACE(4)
                READ(4,*) NT1,NT2,NT3,(TETM(I,J,K),K=1,6)
                REWIND(4)
                ELSE
                GO TO 103
                END IF

7001          CONTINUE

7000  CONTINUE

        DO 8000 I=NC1,NN-1

                DO 8001 J=I+1,NN

                        DO 8002 IA=1,NCAT
106          READ(4,*) NT1,NT2,NT3

                                IF(NAQ(I) .EQ. NT1
$                                .AND.  NAQ(J) .EQ. NT2
$                                .AND.  NAQ(IA) .EQ. NT3) THEN
                                BACKSPACE(4)
                                READ(4,*)NT1,NT2,NT3,(PSIM(I,J,IA,K),K=1,6)
                                REWIND(4)
                                ELSE
                                GO TO 106
                                END IF

8002          CONTINUE

8001          CONTINUE

8000  CONTINUE

104  CLOSE(4)

C..... END OF READING .....

        RETURN

1    CONTINUE

C.. CALCULATION OF VALUES OF THE PARAMETERES FOR CURRENT TEMPERATURE

        A0= PF(T,A0M(1),A0M(2),A0M(3),A0M(4),A0M(5),A0M(6))

        DO 9000 I=1,NCAT

                DO 9001 J=NC1,NN
                BET0(I,J)= PF(T,BET0M(I,J,1),BET0M(I,J,2),
$BET0M(I,J,3),BET0M(I,J,4),BET0M(I,J,5),BET0M(I,J,6) )
                BET1(I,J)= PF(T,BET1M(I,J,1),BET1M(I,J,2),
$BET1M(I,J,3),BET1M(I,J,4),BET1M(I,J,5),BET1M(I,J,6) )
                BET2(I,J)= PF(T,BET2M(I,J,1),BET2M(I,J,2),
$BET2M(I,J,3),BET2M(I,J,4),BET2M(I,J,5),BET2M(I,J,6) )
                C0(I,J)= PF(T,C0M(I,J,1),C0M(I,J,2),C0M(I,J,3),

```

```

          $          COM(I,J,4),COM(I,J,5),COM(I,J,6) )
9001      CONTINUE

9000      CONTINUE

          DO 10000 I=1,NN-1

              DO 10001 J=I+1,NN
                  TET(I,J)= PF(T,TETM(I,J,1),TETM(I,J,2),TETM(I,J,3),
$                      TETM(I,J,4),TETM(I,J,5),TETM(I,J,6))

              DO 10002 IA=1,NN
                  PSI(I,J,IA)=PF(T,PSIM(I,J,IA,1),PSIM(I,J,IA,2),
$                      PSIM(I,J,IA,3),PSIM(I,J,IA,4),
$                      PSIM(I,J,IA,5),PSIM(I,J,IA,6))
10002      CONTINUE

10001      CONTINUE

10000      CONTINUE

          RETURN

2          CONTINUE

          DO 11000 I = 1, 10
              SUMCA(I) = 0.
              SUMCAT(I) = 0.
              SUMAN(I) = 0.
              SUMZ(I) = 0.
              SUMAC(I) = 0.
              SUMAA(I) = 0.
              SUMCC(I) = 0.
              SUMK(I) = 0.
11000      CONTINUE

          SMX=0.
          ZZ=0.
          UM=0.

          DO 12000 I=IP+1,NMV
              J=I-IP
              XM(J)=EX(I)*55.50837
              ZZ=ZZ+XM(J)*DABS(Z(J))
              UM=UM+XM(J)*Z(J)**2
              SMX=SMX+XM(J)
12000      CONTINUE

          UM=UM/2.
          SQ=SQRT(UM)
          ALPHA=2.*SQ
          ALPHA1=1.4*SQ
          ALPHA2=12.*SQ
          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 13000 J=1,NCAT
    DO 13001 I=NC1,NN
        IF (Z(J)*ABS(Z(I)).EQ.4) THEN
            BPHI(J,I)=BET0(J,I)+BET1(J,I)*EXP(-ALPHA1)+
            $      BET2(J,I)*EXP(-ALPHA2)
            B(J,I)=BET0(J,I)+BET1(J,I)*G1+BET2(J,I)*G2
            BPRIME(J,I)=BET1(J,I)*GPR11/UM+BET2(J,I)*GPR12/UM
        ELSE
            BPHI(J,I)=BET0(J,I)+BET1(J,I)*EXP(-ALPHA)
            B(J,I)=BET0(J,I)+BET1(J,I)*G
            BPRIME(J,I)=BET1(J,I)*GPRIME/UM
        END IF

        C(J,I)=C0(J,I)/2./SQRT(Z(J)*DABS(Z(I)))
13001    CONTINUE

13000 CONTINUE

    DO 14000 J=1,NCAT-1
        DO 14001 I=J+1,NCAT
            CALL INTACT(Z(J),Z(I),UM,A0,PHIPHI(J,I),
            $      PHIPRI(J,I),PHIIJ(J,I),TET(J,I))
14001    CONTINUE

14000 CONTINUE

    DO 15000 J=NC1,NN-1
        DO 15001 I=J+1,NN
            CALL INTACT(Z(J),Z(I),UM,A0,PHIPHI(J,I),
            $      PHIPRI(J,I),PHIIJ(J,I),TET(J,I))
15001    CONTINUE

15000 CONTINUE

C..    CALCULATION OF SUMMATION TERMS FOR F AND PHI.

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

DO 16000 J=1,NCAT-1

    DO 16001 J1=J+1,NCAT

        DO 16002 I=NC1,NN
            SUBSUM=SUBSUM+PSI(J,J1,I)*XM(I)
16002    CONTINUE

            SCATON=SCATON+(SUBSUM+PHIPHI(J,J1))*XM(J)*XM(J1)
            SUMCAF=SUMCAF+PHIPRI(J,J1)*XM(J)*XM(J1)
            SUBSUM=0.
16001    CONTINUE

```

```

16000 CONTINUE

      SUBSUM=0.

      DO 17000 J=NC1,NN-1

          DO 17001 J1=J+1,NN

              DO 17002 I=1,NCAT
                  SUBSUM=SUBSUM+PSI(J,J1,I)*XM(I)
17002          CONTINUE

                  SANON=SANON+(SUBSUM+PHIPHI(J,J1))*XM(J)*XM(J1)
                  SUMANF=SUMANF+PHIPRI(J,J1)*XM(J)*XM(J1)
                  SUBSUM=0.
17001          CONTINUE

17000 CONTINUE

      SUMB=0.
      SUMPHI=0.

      DO 18000 J=1,NCAT

          DO 18001 I=NC1,NN
              SUMB=SUMB+XM(J)*XM(I)*BPRIME(J,I)
              SUMPHI=SUMPHI+XM(J)*XM(I)*(BPHI(J,I)+ZZ*C(J,I))
18001          CONTINUE

18000 CONTINUE

      F=-A0*(SQ/(1.+1.2*SQ)+2.*DLOG(1.+1.2*SQ)/1.2)+
      $   SUMB+SUMCAF+SUMANF
      PHI=1.+2./SMX*(-A0*UM**1.5/(1.+1.2*SQ)+SUMPHI+SCATON+SANON)
      AH2O=-PHI*SMX/55.50837

      C..... CALCULATION OF TERMS FOR ACTIVITY COEFFICIENTS(GAMMA).....

      SUM=0.

      DO 19000 J=1, NCAT-1

          DO 19001 J1=J+1, NCAT

              DO 19002 I=NC1,NN
                  PSI(J1,J,I)=PSI(J,J1,I)
19002          CONTINUE

                  PHIIJ(J1,J)=PHIIJ(J,J1)
19001          CONTINUE

19000 CONTINUE

      DO 20000 I=NC1, NN-1

          DO 20001 I1=I+1, NN

              DO 20002 J=1, NCAT
                  PSI(I1,I,J)=PSI(I,I1,J)

```

```

20002          CONTINUE

                PHIIJ(I1,I)=PHIIJ(I,I1)
20001          CONTINUE

20000 CONTINUE

        DO 21000 J=1, NCAT

                DO 21001 I=NC1,NN
                SUMCA(J)=SUMCA(J)+XM(I)*(2.*(B(J,I))+ZZ*C(J,I))
21001          CONTINUE

21000 CONTINUE

        DO 22000 J=1, NCAT

                DO 10 J1=1,NCAT
                IF (J.EQ.J1) GO TO 10

                DO 22001 I=NC1, NN
                SUM=SUM+XM(I)*PSI(J,J1,I)
22001          CONTINUE

                SUMCAT(J)=SUMCAT(J)+XM(J1)*(SUM+2.*PHIIJ(J,J1))
                SUM=0.
10          CONTINUE

22000 CONTINUE

        DO 23000 J=1, NCAT

                DO 23001 J1=NC1,NN-1

                DO 23002 I=J1+1, NN
                SUMAN(J)=SUMAN(J)+XM(J1)*XM(I)*PSI(J1,I,J)
23002          CONTINUE

23001          CONTINUE

23000 CONTINUE

                SUM=0.

        DO 24000 J=1,NCAT

                DO 24001 I=NC1,NN
                SUM=SUM+XM(J)*XM(I)*C(J,I)
24001          CONTINUE

24000 CONTINUE

        DO 25000 J=1,NCAT
                SUMZ(J)=SUM*DABS(Z(J))
25000 CONTINUE

        DO 26000 J=1,NCAT
                ACT(J+IP)=Z(J)**2*F+SUMCA(J)+SUMCAT(J)+SUMAN(J)+SUMZ(J)

```

```

26000 CONTINUE

      SUM=0.

      DO 27000 I=NC1, NN

          DO 27001 J=1, NCAT
              SUMAC(I)=SUMAC(I)+XM(J)*(2.*(B(J,I))+ZZ*C(J,I))
27001          CONTINUE

27000 CONTINUE

      DO 28000 I=NC1, NN

          DO 20 I1=NC1,NN
              IF (I.EQ.I1) GO TO 20

              DO 28001 J=1, NCAT
                  SUM=SUM+XM(J)*PSI(I,I1,J)
28001          CONTINUE

                  SUMAA(I)=SUMAA(I)+XM(I1)*(SUM+2.*PHIIJ(I,I1))
                  SUM=0.
20          CONTINUE

28000 CONTINUE

      DO 29000 I=NC1, NN

          DO 29001 J=1,NCAT-1

              DO 29002 J1=J+1, NCAT
                  SUMCC(I)=SUMCC(I)+XM(J)*XM(J1)*PSI(J,J1,I)
29002          CONTINUE

29001          CONTINUE

29000 CONTINUE

      SUM=0.

      DO 30000 J=1,NCAT

          DO 30001 I=NC1,NN
              SUM=SUM+XM(J)*XM(I)*C(J,I)
30001          CONTINUE

30000 CONTINUE

      DO 31000 I=NC1,NN
          SUMK(I)=SUM*ABS(Z(I))
31000 CONTINUE

      DO 32000 J=NC1,NN
          ACT(J+IP)=Z(J)**2*F+SUMAC(J)+SUMAA(J)+SUMCC(J)+SUMK(J)
32000 CONTINUE

      DO 33000 I=1,NMV-IP
          IF(ACT(I+IP).GT.ALOG(10000.)) ACT(I+IP)=ALOG(10000.)

```

33000 CONTINUE

```
      RETURN
910  WRITE(*,1910) NAQ(I),NAQ(J)
1910 FORMAT(2(1X,I3),/,',', '!! TABLE 1 IS NOT COMPLETE !!' /
      $'          !! OR WRONG COMPONENT WAS ENTERED !!')
      STOP
      END
```

C-----C

C-----C

```
      SUBROUTINE SIMPL (IP1,M,IOP1,IP,N1,K,IR)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON /MASS1/ A,G,NUM,X(40)
      COMMON /ENTER/ ISIM,ISIMIN
      DIMENSION A(10,40),G(40),NUM(40)
```

C IP1 - BEGINING J, M - FINISH J, IOP1- BEGINING I, IP -FINISH I
C.....LOOKING FOR A NEW PHASE FOR INCLUDING INTO BASIS.....

```
      ISIM=0
1111  DEL=0.DO
      IK=0
      K=0
```

```
      DO 1001 J=IP1,M
      P=0.
```

```
      DO 1002 I=1,IP
      P=P+G(I)*A(I,J)
1002  CONTINUE
```

```
      DELTA=G(J)-P
      IF(DELTA.GE.DEL) GO TO 1001
      DEL=DELTA
      K=J
      ISIM=1
```

1001 CONTINUE

```
      IF(K.EQ.0) GO TO 1000
```

C.....LOOKING FOR PLACE IN THE BASIS TO BE SUBSTITUTED.....

```
      BMIN=1D+20
```

```
      DO 1005 I=IOP1,IP
      IF(A(I,K).LE.0.) GO TO 1005
      BTEK=A(I,N1)/A(I,K)
      IF(BTEK.GE.BMIN) GO TO 1005
      BMIN=BTEK
      IR=I
1005  CONTINUE
```

```
      DO 1007 I=1,IP
      A(I,IR)=A(I,K)
1007  CONTINUE
```

```

NUM(IR)=NUM(K)
G(IR)=G(K)
CALL GG1(IR,IP+1,IP,N1)

C..      IF(ISIMIN.EQ.0) GO TO 1111

1000 CONTINUE

      RETURN
      END

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

      SUBROUTINE GG1(ICOL,IP1,IPS,N1)
      DOUBLE PRECISION A,G,X
      DIMENSION A(10,40),G(40),NUM(40)
      COMMON /MASS1/ A,G,NUM,X(40)

      DO 1 I=IP1,N1
          A(ICOL,I)=A(ICOL,I)/A(ICOL,ICOL)
1 CONTINUE

      A(ICOL,ICOL)=1.

      DO 2 J=1,IPS
          IF(J.EQ.ICOL) GO TO 2

          DO 3 I=IP1,N1
              A(J,I)=A(J,I)-A(ICOL,I)*A(J,ICOL)
3 CONTINUE

          A(J,ICOL)=0.
2 CONTINUE

      RETURN
      END

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

      SUBROUTINE GG(INI,NP,NP1)
      DOUBLE PRECISION P1,AM,AT
      COMMON/COMGG/ P1(20,21)

      DO 201 I=INI,NP
          AM=P1(I,I)
          I1=I
          IJ=I+1

          DO 202 K=IJ,NP
              IF(ABS(AM).GE.DABS(P1(K,I))) GO TO 202
              AM=P1(K,I)
              I1=K
202 CONTINUE

```



```

                DO 203 K=I,NP1
                  AT=P1(I1,K)
                  P1(I1,K)=P1(I,K)
                  P1(I,K)=AT/AM
203             CONTINUE

                DO 241 J=INI,NP
                  AM=P1(J,I)
                  IF(J.EQ.I) GO TO 241

                  DO 204 K=I,NP1
                    P1(J,K)=P1(J,K)-P1(I,K)*AM
204             CONTINUE

241             CONTINUE

201             CONTINUE

                RETURN
                END

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

C..  THE ROUTINE FOR CALCULATION OF CHEMICAL EQUILIBRIA
C..  IN WATER-SALT SYSTEMS AT THE TEMPERATURE RANGE 25- -60 C.

                DOUBLE PRECISION FUNCTION PF(T,A1,A2,A6,A9,A3,A4)
                IMPLICIT DOUBLE PRECISION (A-H,O-Z)

                PF=A1+A2*T+A6*T**2+A9*T**3+A3/T+A4*LOG(T)

                RETURN
                END

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

                SUBROUTINE SOL (ICK,EX,ISOLU,IPATH)
                IMPLICIT DOUBLE PRECISION (A-H,O-Z)
                CHARACTER *40 NM

                DIMENSION G(40),X(40),EX(20),EXTMP(20),A(10,40),ACT(20),NM(40)
                DIMENSION  JOPEN(10),JCLOS(10),SU(20),P1(20,21),AIN(10,40)
                DIMENSION  NUMIN(40),NUM(40),GIN(40),ACTT(20),IZ(20)
                COMMON /NUMBER/NCAT,NANI,NNEI,NMM(40)
                COMMON /MASS1/ A,G,NUM,X
                COMMON /MASS2/ NM
                COMMON /INTGER/ NL,N,N1
                COMMON /MATRIX/ ACT,UM,PHI,AH2O,IZ,IP,NMV
                COMMON /AIN/ AIN,GIN,T,NUMIN,IV
                COMMON /COMGG/ P1
                COMMON /ENTER/ ISIM,ISIMIN
                COMMON /OUTPUT/JOPEN,IOPEN

                DO 1000 I = 1, 20
                  ACT(I) = 0.D0
1000             CONTINUE

```

```

ISIMIN=1
ISOLU=1
ICK=0
ICE=0
XW=55.50837

DO 2000 I = 1, 10

    DO 2001 J = 1, 40
        A(I,J)=AIN(I,J)
2001    CONTINUE

2000 CONTINUE

DO 2100 I = 1, 40
    NUM(I)=NUMIN(I)
    G(I)=GIN(I)
2100 CONTINUE

EPS=.001
IP1=IP+1
NUM(N1)=N1
NM(N1)='DEL'
PHI=1.
IP1=IP+1
NL1=NL+1
L=NL-IP
NMV=NL-1
N1=N+1

DO 2200 I=IP1,NMV
    G(I)=G(I)+DLOG(XW)
2200 CONTINUE

DO 2300 I=1,IP

    DO 2301 J=IP1,NL
        IF(NMM(I).EQ.NMM(J)) THEN
            NUM(I)=J
            NUMIN(I)=J
            G(I)=G(J)
        END IF
2301 CONTINUE

    IF(NMM(I).EQ.30) THEN
        IVV=I
        X(IV)=A(I,N1)
    END IF
2300 CONTINUE

SUM=0.D0

DO 2400 I=1,IP
    NI=NUM(I)
    IF (I.NE.IVV) THEN
        X(NI)=A(I,N1)
        EX(NI)=A(I,N1)/X(IV)
        G(I)=G(NUM(I))+DLOG(EX(NUM(I)))

```

```

                END IF
2400 CONTINUE

CALL PITZER (T,2,EX)
G(IVV)=AH2O

DO 2500 I=1,IP
    NI=NUM(I)
    IF (I.NE.IVV) THEN
        G(I)=G(NI)+DLOG(EX(NI))+ACT(NI)
    END IF
2500 CONTINUE

DO 2600 J=IP1,NMV
    SU(J)=-G(J)

        DO 2601 K=1,IP
            SU(J)=SU(J)+A(K,J)*G(K)
2601 CONTINUE

        EX(J)=DEXP(SU(J)-ACT(J))
        X(J)=X(IV)*EX(J)
2600 CONTINUE

CALL SIMPL (NL1,NL1,1,IP,N1,IK,IR)
DELL=1.
75 CONTINUE
76 ICLOS=0
    IOOPEN=0

DO 2700 I=1,IP
    IF (NUM(I).GE.NL1.AND.NUM(I).LE.N) THEN
        IOOPEN=IOOPEN+1
        JOOPEN(IOOPEN)=I
    ELSE
        ICLOS=ICLOS+1
        JCLOS(ICLOS)=I
    END IF
2700 CONTINUE

IF (IOOPEN.GT.0) THEN
    IF (IOOPEN.EQ.1.AND.NMM(NUM(JOOPEN(1))).EQ.31) THEN
        ICE=1
        SU(IV)=-G(IV)

        DO 2800 K=1,IP
            SU(IV)=SU(IV)+A(K,IV)*G(K)
2800 CONTINUE

        XMN=1.

        DO 2900 K=1,10
            XMN=XMN*1.5

            DO 2901 J=IP1,NMV
                EXTMP(J)=EX(J)*XMN
                SUMS=SUM*XMN
2901 CONTINUE

```

```

                CALL PITZER (T,2,EXTMP)
                IF (AH2O.LE.SU(IV)) GO TO 10
2900          CONTINUE
10            X(IV)=X(IV)/XMN*1.2

                DO 3000 I=1,ICLOS
                  J=JCLOS(I)
                  NJ=NUM(J)
                  EX(NJ)=EXTMP(NJ)/1.2
                  G(J)=G(NJ)+DLOG(EX(NJ))+ACT(NJ)
3000          CONTINUE
                ELSE

                  DO 3200 I=1,IP

                    DO 3201 J=IP1, NL
                      IF(NUMIN(I).EQ.J) THEN
                        X(J)=X(J)-.95*A(IR,N1)*AIN(I,IK)
                        IF(X(J).LE.0.)X(J)=1.E-5
                      END IF
3201          CONTINUE

3200          CONTINUE

                  IF(ICE.EQ.1) THEN
                    SU(IV)=-G(IV)

                    DO 3300 K=1,IP
                      SU(IV)=SU(IV)+A(K,IV)*G(K)
3300          CONTINUE

                    III=0
                  END IF

11            DO 3400 J=IP1,NMV
                  EX(J)=X(J)/X(IV)
3400          CONTINUE

                III=III+1

                CALL PITZER (T,2,EX)

                IF(ICE.EQ.1.AND.IPATH.EQ.1) THEN
                  IF(AH2O.GT.SU(IV))THEN
                    X(IV)=X(IV)/1.2
                    GO TO 11
                  ELSE
                    IF(III.GT.1)X(IV)=X(IV)*1.1
3          END IF
                END IF

                DO 3500 I=1,ICLOS
                  J=JCLOS(I)
                  NJ=NUM(J)
                  IF(NJ.LT.NL) G(J)=G(NJ)+DLOG(EX(NJ))+ACT(NJ)
3500          CONTINUE

```

```

DO 3600 J=IP1,NMV
    SU(J)=-G(J)

DO 3601 K=1,IP
    SU(J)=SU(J)+A(K,J)*G(K)
3601 CONTINUE

    IF(J.NE.IV) EX(J)=DEXP(SU(J)-ACT(J))
    X(J)=EX(J)*X(IV)
3600 CONTINUE

    END IF
END IF

IN=ICLOS+L
IN1=IN+1

5 IF(ICK.GT.400) RETURN
ICK=ICK+1

C.. EXAMINE FOR AQUEOUS SOLUTION PRESENCE.....

IF(ICLOS.LE.1) THEN
    ISOLU=0

DO 3700 I=IP1,NL
    X(I)=0.
3700 CONTINUE

GO TO 400
END IF

ISL=0

DO 3800 J=IP1,NL
    SU(J)=G(J)

DO 3801 K=1,IP
    SU(J)=SU(J)-A(K,J)*G(K)
3801 CONTINUE

EX(J)=X(J)/X(IV)
ACTT(J)=ACT(J)
IF(IS.EQ.1)ACTT(J)=0.
3800 CONTINUE

IS=IS+1
PHITT=PHI

CALL PITZER (T,2,EX)

PHI=(PHITT+PHI)/2
SUM=0.

DO 3900 J=IP1,NMV
    ACT(J)=(ACT(J)+ACTT(J))/2.
    JI=J-IP
    P1(JI,JI)=1./X(J)

```

```

        P1(JI,IN1)=DLOG(X(J))+ACT(J)-DLOG(X(IV))+SU(J)
        P1(JI,L)=-1./X(IV)
        P1(L,JI)=-1./X(IV)*PHI
        SUM=SUM+EX(J)
3900  CONTINUE

        P1(L,L)=SUM*PHI/X(IV)
        P1(L,IN1)=SU(NL)-SUM*PHI

        DO 4000 I=1,ICLOS
            K=L+I
            II=JCLOS(I)
            P1(K,K)=0.
            P1(K,IN1)=A(II,N1)

            DO 4001 J=IP1,NL
                P1(K,IN1)=P1(K,IN1)-A(II,J)*X(J)
                IJ=J-IP
                P1(K,IJ)=-A(II,J)
                P1(IJ,K)=-A(II,J)
4001  CONTINUE

4000  CONTINUE

        CALL GG(1,IN,IN1)

        DO 4100 I=1,ICLOS
            K=L+I
            II=JCLOS(I)
            YLI=G(II)-P1(K,IN1)/DELL
            XBS=DABS(YLI-G(II))
            IF(XBS.LE.EPS) ISL=ISL+1
            G(II)=YLI
4100  CONTINUE

        DO 4200 I=1,L
            J=I+IP
            YLI=X(J)-P1(I,IN1)/DELL
            IF(YLI.LE.1.D-10) YLI=1.D-6
            XBS=DABS((YLI-X(J))/X(J))
            IF(XBS.LE.EPS) ISL=ISL+1
            X(J)=YLI
4200  CONTINUE

        IF(X(NL).LE.1.D-3) X(NL)=1.D-3
        IF(ISL.LT.IN) GO TO 5

C..    DELETING OF FIXED COMPOSITION PHASES

400  XX=0.
     IMIN=0

        DO 3100 I=1,IOPEN
            JO=JOPEN(I)
            SUM=0.

            DO 3101 J=IP1,NL
                SUM=SUM+A(JO,J)*X(J)
3101  CONTINUE

```

```

        X(JO)=A(JO,N1)-SUM
        IF(X(JO).GT.XX)GO TO 3100
        XX=X(JO)
        IMIN=JO
3100  CONTINUE

        IF (ISOLU.EQ.0) RETURN
        IF (IMIN.EQ.0) GO TO 1025
        NUM(IMIN)=N1
        GO TO 76

1025  CALL SIMPL(NL1,N,1,IP,N1,IK,IR)

        IF(ISIM.EQ.1) THEN
            DELL=DELL+.5
            GO TO 75
        END IF

7000  CONTINUE

        RETURN
        END

```

APPENDIX B: DATA FILES FOR PROGRAM FREZCHEM2

File DATABASE

9 - number of independent components

H2O	0	30	- the name of the independent component, its charge and its
Na+	1	1	code (the codes in this model are the same as
K+	1	2	in the FREZCHEM model)
Ca2+	2	3	
Mg2+	2	4	
Cl-	-1	11	
SO4-2	-2	12	
CO3-2	-2	15	
H+	1	6	

5 -number of cations

			H2O	Na+	K+	Ca2+	Mg2+	Cl-	SO4-2	CO3-2	H+
Na+(aq)	1	1	.00	1.00	.00	.00	.00	.00	.00	.00	.00
K+(aq)	2	1	.00	.00	1.00	.00	.00	.00	.00	.00	.00
Ca2+(aq)	3	2	.00	.00	.00	1.00	.00	.00	.00	.00	.00
Mg2+(aq)	4	2	.00	.00	.00	.00	1.00	.00	.00	.00	.00
H+(aq)	5	1	.00	.00	.00	.00	.00	.00	.00	.00	1.00

5 -number of anions

Cl- (aq)	11	-1	.00	.00	.00	.00	.00	1.00	.00	.00	.00
SO4-2(aq)	12	-2	.00	.00	.00	.00	.00	.00	1.00	.00	.00
OH-(aq)	13	-1	1.00	.00	.00	.00	.00	.00	.00	.00	-1.00
HCO3-(aq)	14	-1	.00	.00	.00	.00	.00	.00	.00	1.00	1.00
CO3-2(aq)	15	-2	.00	.00	.00	.00	.00	.00	.00	1.00	.00

4 -number of neutral species

CO2(aq)	21	0	-1.00	.00	.00	.00	.00	.00	.00	1.00	2.00
CaSO4(aq)	22	0	.00	.00	.00	1.00	.00	.00	1.00	.00	.00
MgSO4(aq)	23	0	.00	.00	.00	.00	1.00	.00	1.00	.00	.00
H2O(l)	30	0	1.00	.00	.00	.00	.00	.00	.00	.00	.00

16 - number of solid phases

			H2O	Na+	K+	Ca2+	Mg2+	Cl-	SO4-2	CO3-2	H+
H2O(cr,I)	31	0	1.00	.00	.00	.00	.00	.00	.00	.00	0.00
NaCl*2H2O(cr)	32	0	2.00	1.00	.00	.00	.00	1.00	.00	.00	0.00
NaCl(cr)	33	0	.00	1.00	.00	.00	.00	1.00	.00	.00	.00
KCl(cr)	34	0	.00	.00	1.00	.00	.00	1.00	.00	.00	.00
CaCl2*6H2O(cr)	35	0	6.00	.00	.00	1.00	.00	2.00	.00	.00	.00
MgCl2*6H2O(cr)	36	0	6.00	.00	.00	.00	1.00	2.00	.00	.00	.00
MgCl2*8H2O(cr)	37	0	8.00	.00	.00	.00	1.00	2.00	.00	.00	.00
MgCl2*12H2O(cr)	38	0	12.00	.00	.00	.00	1.00	2.00	.00	.00	.00
KMgCl3*6H2O(cr)	39	0	6.00	.00	1.00	.00	1.00	3.00	.00	.00	.00
CaCl2*2MgCl2*12H2O(cr)	40	0	12.00	.00	.00	1.00	2.00	6.00	.00	.00	.00
Na2SO4*10H2O(cr)	41	0	10.00	2.00	.00	.00	.00	.00	1.00	.00	.00
Na2SO4(cr)	42	0	.00	2.00	.00	.00	.00	.00	1.00	.00	.00
MgSO4*6H2O(cr)	43	0	6.00	.00	.00	.00	1.00	.00	1.00	.00	.00
MgSO4*7H2O(cr)	44	0	7.00	.00	.00	.00	1.00	.00	1.00	.00	.00
K2SO4(cr)	45	0	.00	.00	2.00	.00	.00	.00	1.00	.00	.00
MgSO4*K2SO4*6H2O(cr)	46	0	6.00	.00	2.00	.00	1.00	.00	2.00	.00	.00

•

File TABLE1

8.66836498d+01 8.48795942d-02 -8.88785150d-05 4.88096393d-08 -1.32731477d+03 -1.76460172d+01
 1 11
 7.87239712d+00 -8.3864096d-03 1.44137774d-05 -8.7820301d-09 -4.96920671d+02 -8.20972560d-01
 8.66915291d+02 6.06166931d-01 -4.80489210d-04 1.88503857d-07 -1.70460145d+04 -1.67171296d+02
 1.70761824d+00 2.32970177d-03 -2.46665619d-06 1.21543380d-09 -1.35583596d+00 -3.87767714d-01
 1 12
 -3.32486330d+03 -2.9297353d+00 2.8024367d-03 -1.316883d-06 5.53958527d+04 6.66660369d+02
 -3.57406160d+03 -3.0011206d+00 2.73660950d-03 -1.219171d-06 6.09716482d+04 7.11613120d+02
 3.68520478d+02 3.16243995d-01 -2.95372760d-04 1.35491104d-07 -6.22607913d+03 -7.35844094d+01
 2 11
 2.65718766d+01 9.92715099d-03 -3.62323330d-06 -6.28427180d-11 -7.55707220d+02 -4.67300770d+00
 1.69742977d+03 1.22270943d+00 -9.99044490d-04 4.04786721d-07 -3.28684422d+04 -3.28813848d+02
 -3.27571680d+00 -1.27222054d-03 4.71374283d-07 1.1162507d-11 9.07747666d+01 5.80513562d-01
 2 12
 4.07908797d+01 8.26906675d-03 0. 0. -1.41842998d+03 -6.74728848d+00
 -1.31669651d+01 2.35793239d-02 0. 0. 2.06712594d+03 0.
 -1.88d-02 0. 0. 0. 0. 0.
 3 11
 -5.62764702d+01 -3.00771997d-02 1.05630400d-05 3.3331626d-09 1.11730349d+03 1.06664743d+01
 3.4787d+00 -1.5417d-02 3.1791d-05 0. 0. 0.
 2.64231655d+01 2.46922993d-02 -2.48298510d-05 1.22421864d-08 -4.18098427d+02 -5.35350322d+00
 3 12
 1.50d-01 0. 0. 0. 0. 0.
 3.00d+00 0. 0. 0. 0. 0.
 -1.29399287d+02 4.00431027d-01 0. 0. 0. 0.
 0. 0. 0. 0. 0. 0.
 4 11
 3.13852913d+02 2.61769099d-01 -2.46268460d-04 1.15764787d-07 -5.53133381d+03 -6.21616862d+01
 -3.18432525d+04 -2.86710358d+01 2.78892838d-02 -1.3279705d-05 5.24032958d+05 6.40770396d+03
 5.9532d-02 -2.49949d-04 2.41831d-07 0. 0. 0.
 4 12
 5.40007849d+03 4.90576884d+00 -4.80489750d-03 2.31126994d-06 -8.80664146d+04 -1.08839565d+03
 2.78730869d+00 4.30077440d-03 0. 0. 0.
 0. 0. 0. 0. 0. 0.
 -5.88623653d+02 -5.05522880d-01 4.8277657d-04 -2.3029838d-07 1.02002016d+04 1.17303808d+02
 .

File TABLE2

1	2	0	-1.82266741d+01	-3.69038470d-03	0.	0.	6.12415011d+02	
3.02994981d+00								
1	2	11	6.48108127d+00	1.46803468d-03	0.	0.	-2.04354019d+02	-
1.09448043d+00								
1	2	12	3.48120d-02	0.	0.	0.	-8.21660d+00	0.
1	3	0	5.0d-02	0.	0.	0.	0.	0.
1	3	11	-7.63980d+00	-1.2990d-02	1.1060d-05	0.	0.	
1.8475d+00								
1	3	12	-1.20d-02	0.	0.	0.	0.	0.
1	4	0	7.0d-02	0.	0.	0.	0.	0.
1	4	11	-3.109870d-02	5.4464780d-05	0.	0.	1.99404210d+00	0.
1	4	12	1.1750520d-01	0.	0.	0.	-4.198620d+01	0.
2	3	0	2.365710d+00	-4.540d-03	0.	0.	-2.84940d+02	0.
2	3	11	-5.930d-02	2.54280d-04	0.	0.	-1.34390d+01	0.
2	3	12	0.	0.	0.	0.	0.	0.
2	4	0	1.1670d-01	0.	0.	0.	0.	0.
2	4	11	5.0362230d-02	-8.750820d-06	0.	0.	-2.899090d+01	0.
2	4	12	-1.3679157d+00	4.24016653d-03	0.	0.	0.	0.
3	4	0	5.31274136d+00	-6.3424248d-03	0.	0.	-9.83113847d+02	0.
3	4	11	4.15790220d+01	1.30377312d-02	0.	0.	-9.81658526d+02	
-7.4061986d+00								
3	4	12	0.	0.	0.	0.	0.	0.
11	12	0	7.00d-02	0.	0.	0.	0.	0.
11	12	1	4.0209775d+00	1.1286005d-03	0.	0.	-1.01169260d+02	-
7.060798d-01								
11	12	2	-2.124815d-01	2.8469833d-04	0.	0.	3.75619614d+01	0.
11	12	3	-1.80d-02	0.	0.	0.	0.	0.
11	12	4	-1.839158d-01	1.429444d-04	0.	0.	3.263d+01	0.

File TABLE3

22	-1.47477745d+01	0.	0.	0.	3.26409496d+03	0.	CaSO4(aq)
23	3.65283115d+02	-7.1578257d-01	0.	0.	-4.48753391d+04	0.	MgSO4(aq)
31	7.875060393d+03	1.169118490d+01	-1.7183789d-02	1.24395543d-05	-9.3314790d+04	-1.7287461d+03	ice
32	-1.2222551d+04	-9.8806459d+00	8.46685083d-03	-3.4459117d-06	2.09823965d+05	2.42328528d+03	hydrohilite
33	9.14839001d+03	8.22348745d+00	-8.1288759d-03	3.95552403d-06	-1.54040868d+05	-1.83624247d+03	halite
34	-1.62917341d+03	-1.51940390d+00	1.45249679d-03	-6.9427505d-07	2.26012743d+04	3.33075506d+02	syllite
35	1.42290062d+05	1.61973105d+02	-1.95332071d-01	1.17636119d-04	-2.04059847d+06	-2.97464810d+04	antarcticite
36	7.52225099d+02	1.17584653d-01	0.	0.	-2.43223909d+04	-1.21990076d+02	bischofite
37	2.27801976d+03	6.49361616d-01	0.	0.	-6.23075123d+04	-3.95438891d+02	MGCL8
38	2.55008896d+05	2.44532240d+02	-2.48807876d-01	1.22425236d-04	-4.02988342d+06	-5.18668604d+04	MGCL12
39	-4.45702171d+01	2.32023790d-01	-7.14935692d-04	5.32658215d-07	-4.24817923d+03	8.59110245d+00	carnallite
40	8.03777918d+01	-1.388069d-01	0.	0.	0.	0.	tachyhydrite
41	8.44728050d+04	7.68443387d+01	-7.4825816d-02	3.51806085d-05	-1.3881852d+06	-1.7026778d+04	mirabilite
42	-3.9635632d+03	-5.8114490d+00	7.59799462d-03	-4.6571737d-06	3.93454893d+04	8.79598423d+02	thenardite
43	2.39166461d+01	-9.3680744d-02	0.	0.	0.	0.	hexahydrite
44	2.02443627d+00	-1.8051586d-02	0.	0.	0.	0.	epsomite
45	-3.53346251d+04	-2.76809991d+01	2.39856021d-02	-1.0201845d-05	6.37561988d+05	6.94737787d+03	arcanite
46	-1.75203509d+01	2.793713d-02	0.	0.	0.	0.	picromerite

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13. ABSTRACT (Maximum 200 words) This report documents a Fortran version of a chemical thermodynamic model for aqueous electrolyte solutions at subzero temperatures, FREZCHEM2, which is a further development of the FREZCHEM model. The model uses thermodynamic data of Spencer-Møller-Weare that permit the calculation of chemical equilibria in the Na-K-Ca-Mg-Cl-SO ₄ -H ₂ O system between -60 and 25°C at atmospheric pressure. It applies the Gibbs energy minimization method for chemical equilibrium computation combined with Pitzer equations for activity coefficients and water activity calculation. The model includes both the freezing (melting) reaction pathway at fixed water amount and the evaporation (dilution) pathway at fixed temperature. The FREZCHEM2 model can be extended with respect to independent components, electrolyte species, and solids, and if corresponding thermodynamic data are available, the model may be used to compute chemical equilibria in any systems that include aqueous-solution and/or one-component solid phases.					
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