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

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
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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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.

Funding was provided by the European Research Office of the U.S. Army, Project WK2Q6C-7411-EN09. Funding was also provided by U.S. Army Projects AT24-SC-F02, Chemical Processes in Frozen Soil, and BT25-EC-B03, Air–Snow–Ice–Soil Contaminant Interactions in Cold Regions.

The authors thank Dr. Virgil J. Lunardini of USACRREL and Dr. Jerry P. Greenberg of the University of California at San Diego for reviewing an earlier draft of this manuscript.

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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 electrostatic 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:

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

where \( G \) = free energy of the system,
\( n \) = the molal quantity of components,
\( \mu_j \) = the chemical potential of species \( j \),
\( \mu_w \) = the chemical potential of water,
\( \mu^0_k \) = 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 \( \mu_j^0 \) is the standard chemical potential,

\[
m_j = \frac{n_j}{n_w} \times 55.51
\]
is the moles of the \( j \)th species per 1 kg of water (molality), and \( \gamma_j \) 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 \( \phi \) and molalities of species by
\[
\ln a_w = -\phi \frac{W}{1000} \left( \sum m_j \right)
\]
where \( W \) is the molecular weight of water (18.0153).

Accordingly, the free energy function of the system is as follows:
\[
g(\tilde{n}) = \sum_{k=1}^{M} \mu_k^0 n_k + n_w (\mu_w^0 - \frac{\sum n_j}{n_w})
\]
\[
+ \sum_{j=1}^{J} n_j \left[ \mu_j^0 + \ln \left( \frac{n_j 55.51}{n_w} \gamma_j \right) \right].
\]

Mass balance constraints, including the electroneutrality equation if necessary, may be written as a system of linear equations:
\[
\sum_{j=1}^{J} v_{ij} n_j = b_i, \quad i = 1, P
\]
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 component \( i \) in the system. For the electroneutrality equation \( b_i = 0 \) and \( v_{ij} = z_j \), where \( z_j \) is the charge of the \( j \)th component. In matrix notation, eq 2 may be written as
\[
N\tilde{n}^T = \tilde{b}
\]
where \( N \) is the stoichiometric matrix, \( \tilde{n} \) is the vector of numbers of moles of species, and \( \tilde{b} \) 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,
\[
n_k = B_k - \sum_{j=1}^{J+1} a_{kj} n_j \quad k = 1, M
\]
and in this way to switch to new independent components. In such a manner the stoichiometry of other \( J+1-P \) components (vectors \( \tilde{a}_i \)) and the matter balance \( \tilde{B} \) 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
\[
n_w > 0 \quad \text{and} \quad n_j > 0.
\]

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
\[
\Phi(\tilde{n}, \lambda) = g(\tilde{n}) + \sum_{k=1}^{M} \mu_k^0 (B_k - \sum_{j=1}^{J+1} a_{kj} n_j)
\]
\[
+ \sum_{i=m+1}^{P} \lambda_i (B_i - \sum_{j=1}^{J+1} a_{ij} n_j)
\]
where \( \lambda \) is a Lagrangian multiplier. It can be shown (Karpov et al. 1976) that \( \lambda \) 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

\[
\frac{\partial \Phi}{\partial n_j} = (\mu_j^0 + \ln 55.51) + \ln \left(\frac{n_j}{n_w}\right)
- \sum_{k=1}^{M} \mu_k a_{kj} - \sum_{i=M+1}^{P} \lambda_i a_{ij} = 0
\]  

(4a)

\[
\frac{\partial \Phi}{\partial n_w} = -\frac{n_j}{n_w} - \sum_{k=1}^{M} \mu_k a_{kw}
- \sum_{i=M+1}^{P} \lambda_i a_{iw} = 0
\]  

(4b)

\[
\frac{\partial \Phi}{\partial \lambda_i} = B_i - \frac{1}{\sum_{j=1}^{J} a_{ij} n_j} - a_{iw} n_w = 0.
\]  

(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 (Khodakovskiy 1992). The idea of the method, as applied to the system under consideration, is as follows. Equation 4a may be solved with respect to \( n_j \):

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

(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 \( \lambda \) 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 \( \lambda_k \). 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

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

\[
\frac{\partial^2 \Phi}{\partial n_w \partial n_j} = \frac{1}{n_w}
\]

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

\[
\frac{\partial^2 \Phi}{\partial n_{w} \partial n_j} = -\phi \frac{1}{n_w}
\]

\[
\frac{\partial^2 \Phi}{\partial n_{w} \partial n_{j'}} = \frac{\partial^2 \Phi}{\partial n_{w} \partial n_{j'}} = -a_{ij}
\]

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:

$$\sum_{k=1}^{M} \mu_{k}^{0} a_{kK} + \sum_{i=M+1}^{P} \lambda_{i} a_{ik} - \mu_{K}^{0} < 0.$$  \hspace{1cm} (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 assemblage 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: $\gamma_i^{(k+1)} = \gamma_i^{(k)} + \Delta_i / \xi$. For a homogeneous system the value of $\xi$ 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 SIMFPL 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.

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 $A^\phi$ 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):

$$-\frac{\Delta G}{RT} = a_1 + a_2T + a_6T^2 + a_9T^3$$

$$+ \frac{a_3}{T} + a_4 \ln(T)$$

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-
pendent components (presently Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, and CO₃²⁻ 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°C down to –40°C with a 2°C decrement.

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

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

\[
\text{NaCl} \cdot 2\text{H}_2\text{O}_{(cr)} \rightarrow \text{NaCl}_{(cr)} + 2\text{H}_2\text{O}_{(cr,I)}
\]

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

LITERATURE CITED


Mironenko, M.V., and A.N. Salaskin (1991) PTX-
Table 2. FREZCHEM2 model output for freezing seawater at –45°C and at –55°C.

Seawater freezing
temperature –45.00°C (228.15 K)

<table>
<thead>
<tr>
<th>SOLID PHASES</th>
<th>Phase</th>
<th>Moles</th>
<th>–G/RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂O(cr)</td>
<td>53.52785</td>
<td>–0.4278</td>
</tr>
<tr>
<td>2</td>
<td>NaCl₂H₂O(cr)</td>
<td>0.42624</td>
<td>1.0995</td>
</tr>
<tr>
<td>3</td>
<td>KCl(cr)</td>
<td>0.00948</td>
<td>–0.8002</td>
</tr>
<tr>
<td>4</td>
<td>MgCl₂*12H₂O(cr)</td>
<td>0.05052</td>
<td>1.2364</td>
</tr>
<tr>
<td>5</td>
<td>Na₂SO₄*10H₂O(cr)</td>
<td>0.02925</td>
<td>–12.2171</td>
</tr>
</tbody>
</table>

AQUEOUS SOLUTION

| Ionic strength | 11.0759 |
| Osmotic coefficient | 2.0008 |

<table>
<thead>
<tr>
<th>Species</th>
<th>Moles</th>
<th>Molality</th>
<th>Activity</th>
<th>Act. coef.</th>
<th>–G/RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺(aq)</td>
<td>0.22059D–02</td>
<td>0.53403D+00</td>
<td>0.23599D+00</td>
<td>0.4419</td>
<td>0.0000</td>
</tr>
<tr>
<td>K⁺(aq)</td>
<td>0.11533D–02</td>
<td>0.27920D+00</td>
<td>0.15016D–01</td>
<td>0.0538</td>
<td>0.0000</td>
</tr>
<tr>
<td>Ca⁺²</td>
<td>0.94653D–02</td>
<td>0.22914D+01</td>
<td>0.13724D+01</td>
<td>0.6862</td>
<td>0.0000</td>
</tr>
<tr>
<td>Mg⁺²</td>
<td>0.46407D–02</td>
<td>0.11235D+00</td>
<td>0.65163D+00</td>
<td>0.5800</td>
<td>0.0000</td>
</tr>
<tr>
<td>Cl⁻(aq)</td>
<td>0.31425D–01</td>
<td>0.76077D+01</td>
<td>0.29938D+00</td>
<td>3.9332</td>
<td>0.0000</td>
</tr>
<tr>
<td>SO₄⁻²(aq)</td>
<td>0.72974D–04</td>
<td>0.17666D–01</td>
<td>0.64149D–02</td>
<td>0.3631</td>
<td>0.0000</td>
</tr>
<tr>
<td>CaSO₄(aq)</td>
<td>0.64693D–04</td>
<td>0.15662D–01</td>
<td>0.15662D–01</td>
<td>1.0000</td>
<td>–0.4410</td>
</tr>
<tr>
<td>MgSO₄(aq)</td>
<td>0.87333D–07</td>
<td>0.21142D–04</td>
<td>0.21142D–04</td>
<td>1.0000</td>
<td>5.2851</td>
</tr>
<tr>
<td>H₂O(l)</td>
<td>0.22929D+00</td>
<td>0.65191D+00</td>
<td>0.00000</td>
<td>0.65191D+00</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

BALANCE

<table>
<thead>
<tr>
<th>Total</th>
<th>Solids</th>
<th>Solution</th>
<th>Total computed</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.555084E+02</td>
<td>0.552791E+02</td>
<td>0.229289E+00</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.486950E+00</td>
<td>0.484744E+00</td>
<td>0.000000E+00</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.010630E+01</td>
<td>0.947671E+02</td>
<td>0.000000E+00</td>
</tr>
<tr>
<td>Ca⁺²</td>
<td>0.095300E+02</td>
<td>0.000000E+00</td>
<td>0.095300E+02</td>
</tr>
<tr>
<td>Mg⁺²</td>
<td>0.055160E+01</td>
<td>0.505192E+00</td>
<td>0.000000E+00</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.568180E+00</td>
<td>0.536755E+00</td>
<td>0.000000E+00</td>
</tr>
<tr>
<td>SO₄⁻²</td>
<td>0.293900E+00</td>
<td>0.292522E+00</td>
<td>0.000000E+00</td>
</tr>
</tbody>
</table>

Number of iterations 93

Temperature –55.00°C (218.15 K)

<table>
<thead>
<tr>
<th>SOLID PHASES</th>
<th>Phase</th>
<th>Moles</th>
<th>–G/RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂O(cr,I)</td>
<td>53.63903</td>
<td>–0.5004</td>
</tr>
<tr>
<td>2</td>
<td>NaCl₂H₂O(cr)</td>
<td>0.42817</td>
<td>0.8123</td>
</tr>
<tr>
<td>3</td>
<td>KCl(cr)</td>
<td>0.01063</td>
<td>–1.4388</td>
</tr>
<tr>
<td>4</td>
<td>CaCl₂*6H₂O(cr)</td>
<td>0.00953</td>
<td>5.6614</td>
</tr>
<tr>
<td>5</td>
<td>MgCl₂*12H₂O(cr)</td>
<td>0.05516</td>
<td>–1.5678</td>
</tr>
<tr>
<td>6</td>
<td>Na₂SO₄*10H₂O(cr)</td>
<td>0.02939</td>
<td>–15.0450</td>
</tr>
</tbody>
</table>

BALANCE

<table>
<thead>
<tr>
<th>Total</th>
<th>Solids</th>
<th>Solution</th>
<th>Total computed</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.555084E+02</td>
<td>0.555084E+02</td>
<td>0.000000E+00</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.486950E+00</td>
<td>0.486950E+00</td>
<td>0.000000E+00</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.010630E+01</td>
<td>0.106300E+01</td>
<td>0.000000E+00</td>
</tr>
<tr>
<td>Ca⁺²</td>
<td>0.095300E+02</td>
<td>0.953000E+00</td>
<td>0.000000E+00</td>
</tr>
<tr>
<td>Mg⁺²</td>
<td>0.055160E+01</td>
<td>0.551600E–01</td>
<td>0.000000E+00</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.568180E+00</td>
<td>0.568180E+00</td>
<td>0.000000E+00</td>
</tr>
<tr>
<td>SO₄⁻²</td>
<td>0.293900E+00</td>
<td>0.293900E+00</td>
<td>0.000000E+00</td>
</tr>
</tbody>
</table>

Number of iterations 88
**Table 3. FREZCHEM2 model output for evaporation of seawater at 0°C.**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0.00°C (273.15 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water amount</td>
<td>50.00 g</td>
</tr>
</tbody>
</table>

### SOLID PHASES

<table>
<thead>
<tr>
<th>N</th>
<th>Phase</th>
<th>Moles –G/RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaCl(_{(cr)})</td>
<td>0.28103</td>
</tr>
<tr>
<td>2</td>
<td>Na(_2)SO(<em>4)s(</em>{10})H(<em>2)O(</em>{(cr)})</td>
<td>0.02021</td>
</tr>
</tbody>
</table>

### AQUEOUS SOLUTION

#### Ionic strength

8.0709

#### Osmotic coefficient

1.5573

<table>
<thead>
<tr>
<th>N</th>
<th>Species</th>
<th>Moles (-G/RT)</th>
<th>Molality</th>
<th>Activity</th>
<th>Act. coef. (-G/RT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na(^+)(_{(aq)})</td>
<td>0.16551D+00</td>
<td>0.35701D+01</td>
<td>0.28612D+01</td>
<td>0.8014 0.0000</td>
</tr>
<tr>
<td>2</td>
<td>K(^+)(_{(aq)})</td>
<td>0.10630D–01</td>
<td>0.22929D+00</td>
<td>0.74428D–01</td>
<td>0.3246 0.0000</td>
</tr>
<tr>
<td>3</td>
<td>Ca(^{2+})</td>
<td>0.82305D–02</td>
<td>0.17754D+00</td>
<td>0.16740D+00</td>
<td>0.9429 0.0000</td>
</tr>
<tr>
<td>4</td>
<td>Mg(^{2+})</td>
<td>0.55155D–01</td>
<td>0.11897D+01</td>
<td>0.27250D+01</td>
<td>2.2905 0.0000</td>
</tr>
<tr>
<td>5</td>
<td>Cl(^–)(_{(aq)})</td>
<td>0.28715D+00</td>
<td>0.61941D+01</td>
<td>0.10952D+02</td>
<td>1.7681 0.0000</td>
</tr>
<tr>
<td>6</td>
<td>SO(<em>4^{2–})(</em>{(aq)})</td>
<td>0.78786D–02</td>
<td>0.16995D+00</td>
<td>0.10190D–01</td>
<td>0.0600 0.0000</td>
</tr>
<tr>
<td>7</td>
<td>CaSO(<em>4)(</em>{(aq)})</td>
<td>0.12993D–02</td>
<td>0.28027D–01</td>
<td>0.28027D–01</td>
<td>1.0000 –2.7979</td>
</tr>
<tr>
<td>8</td>
<td>MgSO(<em>4)(</em>{(aq)})</td>
<td>0.53787D–05</td>
<td>0.11602D–03</td>
<td>0.11602D–03</td>
<td>1.0000 5.4788</td>
</tr>
<tr>
<td>9</td>
<td>H(<em>2)O(</em>{(l)})</td>
<td>0.25733D+01</td>
<td>0.72306D+00</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

### BALANCE

<table>
<thead>
<tr>
<th></th>
<th>Total (-G/RT)</th>
<th>Solids (-G/RT)</th>
<th>Solution (-G/RT)</th>
<th>Total computed (-G/RT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>0.277542E+01</td>
<td>0.202067E+00</td>
<td>0.257334E+01</td>
<td>0.277541E+01</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>0.486950E+00</td>
<td>0.321441E+00</td>
<td>0.165509E+00</td>
<td>0.486950E+00</td>
</tr>
<tr>
<td>K(^+)</td>
<td>0.106300E–01</td>
<td>0.000000E+00</td>
<td>0.106300E–01</td>
<td>0.106300E–01</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>0.953000E–02</td>
<td>0.000000E+00</td>
<td>0.952987E–02</td>
<td>0.952987E–02</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>0.551600E–01</td>
<td>0.000000E+00</td>
<td>0.551600E–01</td>
<td>0.551600E–01</td>
</tr>
<tr>
<td>Cl(^–)</td>
<td>0.568180E+00</td>
<td>0.281028E+00</td>
<td>0.287154E+00</td>
<td>0.568182E+00</td>
</tr>
<tr>
<td>SO(_4^{2–})</td>
<td>0.293900E–01</td>
<td>0.202067E–01</td>
<td>0.918331E–02</td>
<td>0.293900E–01</td>
</tr>
</tbody>
</table>

Number of iterations 45

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

<table>
<thead>
<tr>
<th>Solid</th>
<th>Experiment</th>
<th>Model(^a)</th>
<th>FREZCHEM2 model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice</td>
<td>–1.921(^b)</td>
<td>–1.921</td>
<td>–1.921</td>
</tr>
<tr>
<td>Mirabilite</td>
<td>–8.2(^c)</td>
<td>–5.90</td>
<td>–5.87</td>
</tr>
<tr>
<td>Hydrohalite</td>
<td>–22.9(^c)</td>
<td>–22.84</td>
<td>–22.87</td>
</tr>
<tr>
<td>Sylvite</td>
<td>–36(^c)</td>
<td>–34.25</td>
<td>–34.30</td>
</tr>
<tr>
<td>MgCl(_2) · 12H(_2)O</td>
<td>–36(^c)</td>
<td>–36.82</td>
<td>–36.82</td>
</tr>
<tr>
<td>Antarticite</td>
<td>–54(^c)</td>
<td>–53.64(^d)</td>
<td>–53.73</td>
</tr>
</tbody>
</table>

\(^a\) Spencer et al. (1990).
\(^b\) Fujino et al. (1974).
\(^c\) Nelson and Thompson (1954).
\(^d\) Calculated in sulfate-free system.


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 I2C(20), I2(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, I2, IPP, NMV
COMMON /AIN/ AIN, GIN, T, NUMIN, IV
COMMON /OUTPUT/ JOPEN(10), IOPEN

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(I2, ‘IONIC strength ‘, F8.4/
$\,$ 21X,’Osmotic coefficient ‘, F7.4)
20 FORMAT(I2, ‘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(I1X, 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
READING INDEPENDENT COMPONENTS AND GIVING THE BALANCE

READ(1,12) KCOMP

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, I2C)  
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) = I2C(I)
2200 CONTINUE

CALL CHOICE (NANI, BC, NMC, NUMC, I2C)  
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) = I2C(I)
2300 CONTINUE

CALL CHOICE (NNEI, BC, NMC, NUMC, I2C)  
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) = I2C(I)
2400 CONTINUE

CALL CHOICE (NSOL, BC, NMC, NUMC, I2C)

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

IP1=IP+1
I=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,*) '                      AQUEOUS SOLUTION'
WRITE(10,19) UM, PHI

WRITE(10,20)

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)
    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

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
   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

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,
$   0.00036583601823, -0.00045036975204,
$  -0.00002937706971,  0.000039664662,
$ -0.0000025267769,  0.000001352610,
$  0.000000001943,  0.000000002563,
$  -0.000000000010991/

DATA AKII/0.6280232320520852,  0.4627629853338493,
$  0.150044637187895, -0.028796057604906, -0.036552745910311,
$  0.006519840398744,  0.001130378079086,
$  0.000242107641309, -0.000087294451594,
$ -0.0000000483768938, -0.000003548684306,
$  0.000000216991779,  0.00000080779570,
$  0.000000006944757, -0.0000002849257,
$  0.00000000237816/

B(21)=0.
B(22)=0.
D(21)=0.
D(22)=0.
ZA(1)=21
ZA(2)=22
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 BETOM(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,*) (A0M(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
    END IF
101  CONTINUE

END IF

ELSE

END
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
   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
         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
      READ(4,*) NT1,NT2,NT3
   7001 CONTINUE
  7000 CONTINUE

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 PARAMETERS FOR CURRENT TEMPERATURE

A0= PF(T,AOM(1),AOM(2),AOM(3),AOM(4),AOM(5),AOM(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),
$ \text{COM}(I,J,4), \text{COM}(I,J,5), \text{COM}(I,J,6) )$

9001 \hspace{1em} \text{CONTINUE}

9000 \hspace{1em} \text{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),
    $ \text{TETM}(I,J,4), \text{TETM}(I,J,5), \text{TETM}(I,J,6))$
  10001 \hspace{1em} \text{CONTINUE}
  10000 \hspace{1em} \text{CONTINUE}

RETURN

2 \hspace{1em} \text{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 \hspace{1em} \text{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 \hspace{1em} \text{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
GPR11=-2.* (1.-(1.+ALPHA1+ALPHA1**2/2.)*EXP(-ALPHA1))/ALPHA1**2
GPR12=-2.* (1.-(1.+ALPHA2+ALPHA2**2/2.)*EXP(-ALPHA2))/ALPHA2**2
G=2.* (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)*GPRI1/UM+BET2(J,I)*GPRI2/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
            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)
    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
      PHIJJ(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
  20001 CONTINUE

24
20002    CONTINUE

        PHIJI(J1,I)=PHIJI(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 22001 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.*PHIJI(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
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.D0
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————————————————————

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————————————————————

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),I2(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,I2,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.

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
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)
   ELSE IF (I.LE.IVV) THEN
      G(I)=G(IVV)
   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
IOPEN=0

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

IF (IOPEN.GT.0) THEN
   IF (IOPEN.EQ.1.AND.NMM(NUM(JOPEN(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
   2900         CONTINUE
   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
ENDIF

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
    END IF
    END IF

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)
   CONTINUE
3601
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.
   CONTINUE
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)
   CONTINUE
3801 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
   3100 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

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16 - number of solid phases

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FREZCHEM2: A Chemical Thermodynamic Model for Electrolyte Solutions at Subzero Temperatures

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

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.