# A COMPUTER PROGRAM INCORPORATING PITZER'S EQUATIONS FOR CALCULATION OF GEOCHEMICAL REACTIONS IN BRINES

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U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 88-4153


Reston, Virginia

1988

DEPARTMENT OF THE INTERIOR

DONALD PAUL HODEL, Secretary

U.S. GEOLOGICAL SURVEY

Dallas L. Peck, Director

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For additional information write to:

Chief, Branch of Regional Research,
Northeastern Region
U.S. Geological Survey
432 National Center
12201 Sunrise Valley Drive
Reston, Virginia 22092

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2 Diskette containing a machine-readable copy of the source code to the interactive input program PITZINPT, and the files MINERALS.2.DATA and PHRQPITZ.DATA.

# A COMPUTER PROGRAM INCORPORATING PITZER'S EQUATIONS FOR CALCULATION OF GEOCHEMICAL REACTIONS IN BRINES[1]

L. Niel Plummer, D.L. Parkhurst, G.W. Fleming, and S.A. Dunkle

## ABSTRACT

The program named PHRQPITZ is a computer code capable of making geochemical calculations in brines and other electrolyte solutions to high concentrations using the Pitzer virial-coefficient approach for activity-coefficient corrections. Reaction-modeling capabilities include calculation of (1) aqueous speciation and mineral-saturation index, (2) mineral solubility, (3) mixing and titration of aqueous solutions, (4) irreversible reactions and mineral-water mass transfer, and (5) reaction path. The computed results for each aqueous solution include the osmotic coefficient, water activity, mineral saturation indices, mean activity coefficients, total activity coefficients, and scale-dependent values of pH, individual-ion activities and individual-ion activity coefficients. A data base of Pitzer interaction parameters is provided at 25 °C (Celsius) for the system: Na-K-Mg-Ca-H-Cl-$SO_4$-OH-$HCO_3$-$CO_3$-$CO_2$-$H_2O$, and extended to include largely untested literature data for Fe(II), Mn(II), Sr, Ba, Li, and Br with provision for calculations at temperatures other than 25 °C. An extensive literature review of published Pitzer interaction parameters for many inorganic salts is given. Also described is an interactive input code for PHRQPITZ called PITZINPT.

## INTRODUCTION

PHRQPITZ[2] is a FORTRAN 77[3] computer program that makes geochemical calculations in brines and other electrolyte solutions to high concentrations. PHRQPITZ has been adapted from the U.S. Geological Survey geochemical simulation computer code PHREEQE[4] of Parkhurst and others (1980) in which the aqueous model of PHREEQE has been replaced with the Pitzer virial coefficient approach (Pitzer, 1973; Pitzer and Mayorga, 1973, 1974; Pitzer and Kim, 1974; Pitzer, 1975). The PHRQPITZ code contains most of the reaction-modeling capabilities of the original PHREEQE code, including calculation of (1) aqueous speciation and mineral-saturation index, (2) mineral solubility, (3) mixing or titration of aqueous solutions, (4) irreversible reactions and mineral-water mass transfer, and (5) reaction path. The computed results for each aqueous solution include the osmotic coefficient, water activity, mineral saturation indices, mean-activity coefficients, total-activity coefficients, and scale-dependent values of pH, individual-ion activities and individual-ion activity coefficients.

The Pitzer treatment of the aqueous model is based largely on the equations as presented by Harvie and Weare (1980) and Harvie and others (1984). An expanded data base of Pitzer interaction parameters is provided that is identical to the partially validated data base of Harvie and others (1984) at 25 °C (Celsius) for the system Na-K-Mg-Ca-H-Cl-$SO_4$-OH-$HCO_3$-$CO_3$-$CO_2$-$H_2O$, and extended to include largely untested literature data for Fe(II), Mn(II), Sr, Ba, Li, and Br with provision for calculations at temperatures other than 25 °C. An extensive

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1 Manuscript approved for publication October 5, 1988.

2 **PH**-**R**edox-e**Qu**ilibrium-equations incorporating the **PITZ**er equations.

3 The use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

4 **PH**-**RE**dox-**EQ**uilibrium-Equations

literature review of published Pitzer interaction parameters for many inorganic salts is also given that may serve as a guide in selection of additional data for inclusion in PHRQPITZ. Some new data for the temperature dependence of mineral equilibrium constants accompanies the additional (untested) data. As with PHREEQE, the aqueous model and thermodynamic data of PHRQPITZ are user-definable and external to the code.

This report also describes an interactive input code for PHRQPITZ called PITZINPT, which is analogous to the PHREEQE input code, PHRQINPT (Fleming and Plummer, 1984). PITZINPT contains the mineral thermodynamic data base taken largely from Harvie and others (1984) and is used interactively to construct input data sets to PHRQPITZ.

Because most modeling aspects of PHRQPITZ are identical to the original PHREEQE treatment, the reader is referred to the PHREEQE documentation (Parkhurst and others, 1980) for background and modeling information. The current report focuses on extensions to the PHREEQE code including documentation of the Pitzer data base, explanation of the Pitzer equations as incorporated in PHRQPITZ, program limitations and instructions for use.

## PITZER EQUATIONS

The osmotic coefficient, $\phi$, and activity coefficients of the cations, $\gamma_M$, and anions, $\gamma_X$, are given by Harvie and Weare, 1980; Harvie and others, 1984),

$$(\phi - 1) = \frac{2}{\left(\sum_i m_i\right)} \left[ -\frac{A^\phi I^{3/2}}{1 + bI^{1/2}} + \sum_c \sum_a m_c m_a (B^\phi_{ca} + ZC_{ca}) \right.$$
$$+ \sum_{c<} \sum_{c'} m_c m_{c'} \left( \Phi^\phi_{cc'} + \sum_a m_a \psi_{cc'a} \right)$$
$$\left. + \sum_{a<} \sum_{a'} m_a m_{a'} \left( \Phi^\phi_{aa'} + \sum_c m_c \psi_{aa'c} \right) \right] \qquad (1)$$

$$\ln \gamma_M = z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c \left( 2\Phi_{Mc} + \sum_a m_a \psi_{Mca} \right)$$
$$+ \sum_{a<} \sum_{a'} m_a m_{a'} \psi_{aa'M} + |z_M| \sum_c \sum_a m_c m_a C_{ca} \quad , \qquad (2)$$

and

$$\ln \gamma_X = z_X^2 F + \sum_c m_c (2B_{cX} + ZC_{cX}) + \sum_a m_a \left( 2\Phi_{Xa} + \sum_c m_c \psi_{Xac} \right)$$
$$+ \sum_{c<} \sum_{c'} m_c m_{c'} \psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a C_{ca} \quad . \qquad (3)$$

Equations 1-3 use the notation of Harvie and Weare (1980). In equations 1-3 $m_i$ denotes molality of the *ith* ion (moles per kilogram) where the subscripts M, c, and c′ denote cations, and X, a, and a′ denote anions. The double summations c<c′ and a<a′ refer to all pairs of dissimilar cations and anions. The term $A^\phi$ is defined by

$$A^\phi = \frac{1}{3} (2\pi N_o \rho_w / 1000)^{1/2} (e^2 / DkT)^{3/2} \quad , \qquad (4)$$

where $N_o$ is Avagadro's number, $\rho_w$ is the density of water, e is the absolute electronic charge, k the Boltzman constant, D the static dielectric constant of pure water and T is temperature in Kelvins. $A^\phi$ then becomes

$$A^\phi = 1400684\left(\frac{\rho_w}{DT}\right)^{3/2} \quad . \tag{5}$$

In PHRQPITZ, values of $A^\phi$ are computed over the temperature range 0-350 °C. The total pressure is taken to be 1 atm. (atmosphere) between 0 and 100 °C and that of the vapor pressure curve for pure water of Haar and others (1984) beyond 100 °C. The dielectric constant of pure water is calculated from Bradley and Pitzer (1979). Values of $A^\phi$ are reported by Bradley and Pitzer (1979) to three significant figures between 0 and 350 °C and are identical to those calculated in PHRQPITZ. Between 0 and 100 °C at 1 atm. total pressure, $A^\phi$ calculated in PHRQPITZ agrees with values calculated by Ananthaswamy and Atkinson (1984) within 0.00004 or better. The computed value of $A^\phi$ from equation 5 in PHRQPITZ at 25 °C is 0.39148, which compares with 0.39145 reported by Ananthaswamy and Atkinson (1984) and 0.391 reported by Bradley and Pitzer (1979). Uncertainties beyond the third significant figure in $A^\phi$ lead to differences in thermodynamic calculations that are beyond the reliability of the parameterization of the model. However, to avoid introducing inconsistency with the Harvie and others (1984) data base, $A^\phi$ is defined to be 0.392 at 25 °C and 1 atm. total pressure in PHRQPITZ (Harvie and Weare, 1980). In their later paper (Harvie and others, 1984) these authors state that $A^\phi$ is 0.39 at 25 °C although calculations with their data base indicate it is consistent with the value 0.392. Because $A^\phi$ is defined to be 0.392 at 25 °C, small inconsistencies in calculations with PHRQPITZ may be observed between results at 25 °C and those very near 25 °C. Uncertainty in the value of $A^\phi$ is often a source of inconsistency in selecting literature data of Pitzer parameters.

The ionic strength, I, is given by

$$I = \frac{1}{2}\sum_i m_i z_i^2 \quad , \tag{6}$$

where $z_i$ is the charge of the *ith* ion. Because few ion pairs are considered in the Pitzer treatment, values of ionic strength computed for a given water sample tend to be larger in the Pitzer model than would be calculated using an ion-pairing model.

The term F in equations 2 and 3 is defined by

$$F = -A^\phi\left[\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b}\ln(1+b\sqrt{I})\right] + \sum_c\sum_a m_c m_a B'_{ca} + \sum_{c<}\sum_{c'} m_c m_{c'} \Phi'_{cc'} + \sum_{a<}\sum_{a'} m_a m_{a'} \Phi'_{aa'} \tag{7}$$

where b is 1.2. The parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and $C^\phi$ that define the variables B and C are fitted from single-salt data. For any salt containing a monovalent ion

$$B^\phi_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} e^{-\alpha\sqrt{I}} \tag{8}$$

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} g(\alpha\sqrt{I}) \tag{9}$$

$$B'_{MX} = \beta^{(1)}_{MX} g'(\alpha\sqrt{I})/I \quad , \tag{10}$$

where $\alpha$=2 (Pitzer, 1973). The functions g and g′ are

$$g(x) = 2[1 - (1 + x)e^{-x}]/x^2 \tag{11}$$

$$g'(x) = -2\left[1 - \left(1 + x + \frac{1}{2}x^2\right)e^{-x}\right]/x^2 \quad , \tag{12}$$

where x = $\alpha\sqrt{I}$. For 2-2 electrolytes and higher valence types

$$B^{\phi}_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}e^{-\alpha_1\sqrt{I}} + \beta^{(2)}_{MX}e^{-\alpha_2\sqrt{I}} \tag{13}$$

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}g(\alpha_1\sqrt{I}) + \beta^{(2)}_{MX}g(\alpha_2\sqrt{I}) \tag{14}$$

$$B'_{MX} = \beta^{(1)}_{MX}g'(\alpha_1\sqrt{I})/I + \beta^{(2)}_{MX}g'(\alpha_2\sqrt{I})/I \quad , \tag{15}$$

where, for 2-2 electrolytes, $\alpha_1$=1.4 and $\alpha_2$=12.0, and for 3-2 and 4-2 electrolytes $\alpha_1$=2.0 and $\alpha_2$=50. (Pitzer and Silvester, 1978). The other variable used to define the thermodynamic properties of single-salt solutions, $C_{MX}$, is given by

$$C_{MX} = C^{\phi}_{MX}/(2\sqrt{|z_M z_X|}) \tag{16}$$

and the coefficient to $C_{MX}$, Z, in equations 1 - 3 is given by

$$Z = \sum_i m_i |z_i| \quad . \tag{17}$$

The thermodynamic properties of aqueous solutions containing a single salt depend only on the interaction parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and $C^{\phi}$.

The parameters $\Phi$ and $\psi$ are determined from aqueous mixtures of two salts. $\Phi$ accounts for cation-cation and anion-anion interactions while the parameter $\psi$ is defined for cation-cation-anion and anion-anion-cation interactions. Values of $\Phi_{ij}$ are given by

$$\Phi^{\phi}_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) + I\,{}^{E}\theta'_{ij}(I) \tag{18}$$

$$\Phi_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) \tag{19}$$

$$\Phi'_{ij} = {}^{E}\theta'_{ij}(I) \quad , \tag{20}$$

where $\theta_{ij}$ is the only adjustable parameter and is defined for each pair of cations and each pair of anions. The terms ${}^{E}\theta_{ij}(I)$ and ${}^{E}\theta'_{ij}(I)$ account for electrostatic mixing effects of unsymmetrical cation-cation and anion-anion pairs as defined by Pitzer (1975). The higher-order electrostatic terms of equations 18-20 are calculated routinely in PHRQPITZ for all unsymmetrical pairs of cations or unsymmetrical pairs of anions using the Chebyshev approximation to the

integrals $J_0(x)$ and $J_1(x)$ (see Pitzer, 1975; Harvie and Weare, 1980). Test calculations showed, however, little difference from more simplified approximations to $J_0(x)$ and $J_1(x)$ given by Pitzer (1975). Values of ${}^{E}\theta_{ij}(I)$ and ${}^{E}\theta'_{ij}(I)$ depend only on ion charge and total ionic strength and are zero when ij cation or anion pairs have the same charge.

Caution should be exercised in using literature values of $\theta_{ij}$ (Reardon and Armstrong, 1987). Values of $\theta_{ij}$ must be compatible with the same single-salt data ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and $C^{\phi}$) used in the model and, for use in PHRQPITZ, their determination from mixed-salt solutions must include the higher-order electrostatic terms discussed above. Both types of $\theta_{ij}$ are reported in the literature (i.e., determined with and without provision for higher-order electrostatic terms). In PHRQPITZ the higher-order electrostatic terms are always included. This precaution applies to cation or anion pairs such as $Ca^{2+}$-$Na^{+}$ or $SO_4^{2-}$-$Cl^{-}$, but not to interactions such as $Cl^{-}$-$F^{-}$ or $Ca^{2+}$-$Mg^{2+}$ where, because of the identical charge, the higher-order electrostatic terms are zero. Values of $\theta_{ij}$ given by Pitzer and Mayorga (1974) and Pitzer (1979) do not include the higher-order electrostatic terms for unsymmetrical cation pairs and unsymmetrical anion pairs. The data of Harvie and Weare (1980) and Harvie and others (1984) include the higher-order electrostatic terms. Harvie and Weare (1980) found significant improvement in modeling the system Na-K-Mg-Ca-Cl-$SO_4$-$H_2O$ when the higher-order electrostatic terms were included.

Values of the parameters $\psi_{ijk}$ are included for all different combinations of two cations and an anion or two anions and a cation. $\psi$ is usually determined from the same two-salt mixture used to define $\theta_{ij}$ and is therefore internally consistent with that value of $\theta_{ij}$ as well as the individual single-salt interaction parameters.

Harvie and others (1984) have also included a model for calculation of the activity coefficients, $\gamma_N$, of neutral species in solution. In the Harvie and others (1984) data base, this calculation applies to the species $CO_2$(aq), $CaCO_3^{\circ}$ and $MgCO_3^{\circ}$. According to Harvie and others (1984), $\gamma_N$ is calculated from the relation

$$\ln \gamma_N = \sum_c m_c(2\lambda_{nc}) + \sum_a m_a(2\lambda_{na}) \quad , \tag{21}$$

where $\lambda_{nc}$ and $\lambda_{na}$ refer to interactions between neutral species and cations or anions.

## DATA BASE

Two data files are required to run PHRQPITZ. The first file, PHRQPITZ.DATA, is analogous to the thermodynamic data base of PHREEQE (though much smaller) and contains data under the keywords ELEMENTS, SPECIES, LOOK MIN and MEAN GAM. The first three of these keywords are identical to their usage in PHREEQE (Parkhurst and others, 1980). The keyword MEAN GAM is used in PHRQPITZ to define the stoichiometries of selected salts for calculation of the mean activity coefficient, $\gamma_{\pm}$. The mean activity coefficient is defined

$$\gamma_{\pm} = \left(\gamma_+^{\nu_+}\gamma_-^{\nu_-}\right)^{\frac{1}{\nu_+ + \nu_-}} \quad , \tag{22}$$

where $\gamma_+$ and $\gamma_-$ denote total-activity coefficients of cations (+) and anions (-) and $\nu_+$ and $\nu_-$ are the stoichiometric coefficients of the cation and anion in the neutral salt.

Equilibrium constants at 25 °C for (1) the formation of $OH^{-}$, $HCO_3^{-}$, $CO_2^{*}$(aq), $HSO_4^{-}$, $CaCO_3^{\circ}$, $MgOH^{+}$, and $MgCO_3^{\circ}$, and (2) dissolution of minerals listed under LOOK MIN in PHRQPITZ.DATA are computed from the free energies given by Harvie and others (1984).

Expressions for the temperature dependence of log K are of the form,

$$\log K = A_1 + A_2 T + A_3/T + A_4 \log T + A_5/T^2 \quad , \tag{23}$$

where $A_1$ - $A_5$ are constants and T is temperature in Kelvins. The form of equation 23 corresponds to the model for the heat capacity of Maier and Kelly (1932), as used in PHREEQE. Expressions of this form were either taken from the literature or fitted to solubility data reported by Linke (1965). In all cases the $A_1$ term has been adjusted to agree with the Harvie and others (1984) data base at 25 °C. In some cases the temperature dependence of log K is calculated from the van't Hoff equation using a value of $\Delta H_r^\circ$ at 25 °C. No data for the temperature dependence of the equilibrium constant are available for many of the minerals in the PHRQPITZ.DATA file and for these, PHRQPITZ computes the same value of the equilibrium constant at all temperatures. Table 1 summarizes data used to calculate the temperature dependence of the equilibria in PHRQPITZ. Line images of the file PHRQPITZ.DATA are listed in Attachment A. Coding format and description of input variables in PHRQPITZ.DATA are given in a later section of this report under "Description of Input".

The second data file read by PHRQPITZ is named PITZER.DATA and contains values of the interaction parameters to the Pitzer equations including values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $C^\phi$, $\theta$, $\lambda$, $\psi$, and limited data on the temperature dependence of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and $C^\phi$. The file PITZER.DATA is listed in Attachment B. For the chemical system Na-K-Mg-Ca-H-Cl-$SO_4$-OH-$HCO_3$-$CO_3$-$CO_2$-$H_2O$ at 25 °C, the data bases to PHRQPITZ (PHRQPITZ.DATA and PITZER.DATA) are identical to that of Harvie and others (1984), and in verification procedures have reproduced calculations reported in Harvie and others (1984).

## Extensions of the Data Base

Extensions beyond the Harvie and others (1984) data base are largely untested and include additions to PITZER.DATA for (1) calculation of the thermodynamic properties of aqueous solutions containing, in addition to the elements considered in the Harvie and others (1984) data base, Fe(II), Mn(II), $Sr^{2+}$, $Ba^{2+}$, $Li^+$, and $Br^-$; (2) estimation of the temperature dependence of many of the single-salt parameters from selected literature data for the first derivative with respect to temperature; and (3) calculation of the thermodynamic properties of NaCl solutions to approximately 300 °C following the vapor pressure curve of water beyond 100 °C. Except for the NaCl-$H_2O$ system, the PHRQPITZ aqueous model should be checked carefully before applications outside the temperature interval 0 to 60 °C are attempted. Several recent evaluations of the temperature dependence of Pitzer interaction parameters to relatively high temperatures (Pitzer, 1987; Moller, 1988) have not yet been incorporated in the PHRQPITZ data base.

Extensions to PHRQPITZ.DATA beyond that of Harvie and others (1984) include estimates of $\Delta H_r^\circ$ for the formation of the aqueous non-master species such as $OH^-$, $HCO_3^-$, $MgOH^+$, etc., and calculation of equilibrium constants for mineral dissolution reactions at temperatures other than 25 °C. Values of $\Delta H_r^\circ$ have been taken from the published literature, or, in some cases, calculated from speciation of mineral solubility data as a function of temperature such as from Linke (1965). The temperature dependence of the interaction parameters and $\Delta H^\circ_r$ is only partially complete. No data exist for the temperature dependence of the solubility of many minerals included in PHRQPITZ.DATA. In all cases, the data to PHRQPITZ reproduce the Harvie and others (1984) data base at 25 °C. If changes in the temperature-dependence of the Pitzer interaction parameters are made to the file PITZER.DATA, the appropriate mineral equilibrium constants and their temperature dependence will need to be examined in the file PHRQPITZ.DATA for consistency.

## Internal Consistency of the Data Base

It is important to stress the need to maintain the internal consistency of the Harvie and others (1984) data base. As an example, consider the solubility of nahcolite in $Na_2CO_3$ solutions. The results are given in Harvie and others (1984) (see their fig. 7c, p.734). Curve 1 of figure 1 shows the solubility of nahcolite in $Na_2CO_3$ solutions calculated from PHRQPITZ using the Harvie and others (1984) data base. The results are identical to those of Harvie and others (1984) and, of course, adequately reproduce the original experimental data. We will now examine the consequences of changing the Harvie and others (1984) data base as regards the solubility of nahcolite.

Table 1 -- Temperature dependence of equilibria in program PHRQPITZ

[--, no data; °C, degrees Celsius; kcal/mol, kilocalories per mole]

| Reaction | Mineral name | log K[1] 25 °C | $\Delta H_r^0$ 25 °C (kcal/mol) | $A_1$ (1) | $A_2$ (T) | $A_3$ (1/T) | $A_4$ (logT) | $A_5$ ($1/T^2$) | Source[1] |
|---|---|---|---|---|---|---|---|---|---|
| Aqueous Species | | | | | | | | | |
| 31 $H_2O = H^+ + OH^-$ | -- | -13.997 | 13.345 | -- | -- | -- | -- | -- | 2 |
| 34 $CO_3^{2-} + H^+ = HCO_3^-$ | -- | 10.339 | -- | 107.8975 | 0.03252849 | -5151.79 | -38.92561 | 563713.9 | 3 |
| 35 $CO_3^{2-} + 2H^+ = CO_{2(aq)} + H_2O$ | -- | 16.677 | -- | 464.1925 | .09344813 | -26986.16 | -165.75951 | 2248628.9 | 3 |
| 40 $SO_4^{2-} + H^+ = HSO_4^-$ | -- | 1.979 | -- | -5.3585 | .0183412 | 557.2461 | -- | -- | 4 |
| 76 $Ca^{2+} + CO_3^{2-} = CaCO_3^o$ | -- | 3.151 | -- | -1228.806 | -.299440 | 35512.75 | 485.818 | -- | 3 |
| 85 $Mg^{2+} + H_2O = MgOH^+ + H^+$ | -- | -11.809 | 15.419 | -- | -- | -- | -- | -- | 2 |
| 86 $Mg^{2+} + CO_3^{2-} = MgCO_3^o$ | -- | 2.928 | -- | -32.225 | -- | 1093.486 | 12.72433 | -- | 3 |
| Solids | | | | | | | | | |
| $CaSO_4 = Ca^{2+} + SO_4^{2-}$ | Anhydrite | -4.362 | -- | 422.950 | -- | -18431. | -147.708 | -- | 5 |
| $CaCO_3 = Ca^{2+} + CO_3^{2-}$ | Aragonite | -8.220 | -- | -171.8607 | -.077993 | 2903.293 | 71.595 | -- | 3 |
| $K_2SO_4 = 2K^+ + SO_4^{2-}$ | Arcanite | -1.776 | -- | 2.823 | -- | -1371.2 | -- | -- | 5 |
| $MgCl_2 \cdot 6H_2O = Mg^{2+} + 2Cl^- + 6H_2O$ | Bischofite | 4.455 | -- | 3.524 | -- | 277.6 | -- | -- | 5 |
| $Na_2Mg(SO_4)_2 \cdot 4H_2O = 2Na^+ + Mg^{2+} + 2SO_4^{2-} + 4H_2O$ | Bloedite | -2.347 | -- | -- | -- | -- | -- | -- | 1 |
| $Mg(OH)_2 = Mg^{2+} + 2OH^-$ | Brucite | -10.884 | .85 | -- | -- | -- | -- | -- | 6 |
| $Na_6CO_3(SO_4)_2 = 6Na^+ + CO_3^{2-} + 2SO_4^{2-}$ | Burkeite | -.772 | -- | -- | -- | -- | -- | -- | 1 |
| $CaCO_3 = Ca^{2+} + CO_3^{2-}$ | Calcite | -8.406 | -- | -171.8329 | -.077993 | 2839.319 | 71.595 | -- | 3 |
| $KMgCl_3 \cdot 6H_2O = K^+ + Mg^{2+} + 3Cl^- + 6H_2O$ | Carnallite | 4.330 | -- | -- | -- | -- | -- | -- | 1 |
| $CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$ | Dolomite | -17.083 | -9.436 | -- | -- | -- | -- | -- | 2 |
| $MgSO_4 \cdot 7H_2O = Mg^{2+} + SO_4^{2-} + 7H_2O$ | Epsomite | -1.881 | -- | 1.718 | -- | -1073. | -- | -- | 5 |
| $CaNa_2(CO_3)_2 \cdot 5H_2O = Ca^{2+} + 2Na^+ + 2CO_3^{2-} + 5H_2O$ | Gaylussite | -9.421 | -- | -- | -- | -- | -- | -- | 1 |
| $NaK_3(SO_4)_2 = Na^+ + 3K^+ + 2SO_4^{2-}$ | Glaserite | -3.803 | -- | -- | -- | -- | -- | -- | 1 |
| $Na_2Ca(SO_4)_2 = 2Na^+ + Ca^{2+} + 2SO_4^{2-}$ | Glauberite | -5.245 | -- | -- | -- | -- | -- | -- | 1 |
| $CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$ | Gypsum | -4.581 | -- | 90.318 | -- | -4213. | -32.641 | -- | 5 |
| $NaCl = Na^+ + Cl^-$ | Halite | 1.570 | -- | -713.4616 | -.1201241 | 37302.21 | 262.4583 | -2106915. | 7 |
| $MgSO_4 \cdot 6H_2O = Mg^{2+} + SO_4^{2-} + 6H_2O$ | Hexahydrate | -1.635 | -- | -62.666 | -- | 1828. | 22.187 | -- | 5 |
| $KMgClSO_4 \cdot 3H_2O = K^+ + Mg^{2+} + Cl^- + SO_4^{2-} + 3H_2O$ | Kainite | -.193 | -- | -- | -- | -- | -- | -- | 1 |
| $KHCO_3 = K^+ + H^+ + CO_3^{2-}$ | Kalicinite | -10.058 | -- | -- | -- | -- | -- | -- | 1 |
| $MgSO_4 \cdot H_2O = Mg^{2+} + SO_4^{2-} + H_2O$ | Kieserite | -.123 | -- | -- | -- | -- | -- | -- | 1 |
| $Na_4Ca(SO_4)_3 \cdot 2H_2O = 4Na^+ + Ca^{2+} + 3SO_4^{2-} + 2H_2O$ | Labile Salt | -5.672 | -- | -- | -- | -- | -- | -- | 1 |
| $MgSO_4 \cdot 4H_2O = Mg^{2+} + SO_4^{2-} + 4H_2O$ | Leonhadite | -.887 | -- | -- | -- | -- | -- | -- | 1 |

Table 1 -- Temperature dependence of equilibria in program PHRQPITZ (continued)

[--, no data; °C, degrees Celsius; kcal/mol, kilocalories per mole]

| Reaction | Mineral name | log K[1] 25 °C | $\Delta H_r^o$ 25 °C (kcal/mol) | $A_1$ (1) | $A_2$ (T) | $A_3$ (1/T) | $A_4$ (logT) | $A_5$ ($1/T^2$) | Source[1] |
|---|---|---|---|---|---|---|---|---|---|
| $K_2Mg(SO_4)_2 \cdot 4H_2O = 2K^+ + Mg^{2+} + 2SO_4^{2-} + 4H_2O$ | Leonite | -3.979 | -- | -- | -- | -- | -- | -- | 1 |
| $MgCO_3 = Mg^{2+} + CO_3^{2-}$ | Magnesite | -7.834 | -6.169 | -- | -- | -- | -- | -- | 6 |
| $Na_2SO_4 \cdot 10H_2O = 2Na^+ + SO_4^{2-} + 10H_2O$ | Mirabilite | -1.214 | -- | -3862.234 | -1.19856 | 93713.54 | 1577.756 | -- | 8 |
| $K_8H_6(SO_4)_7 = 8K^+ 6H^+ + 7SO_4^{2-}$ | Misenite | -10.806 | -- | -- | -- | -- | -- | -- | 1 |
| $NaHCO_3 = Na^+ + H^+ + CO_3^{2-}$ | Nahcolite | -10.742 | -- | -- | -- | -- | -- | -- | 1 |
| $Na_2CO_3 \cdot 10H_2O = 2Na^+ + CO_3^{2-} + 10H_2O$ | Natron | -.825 | -- | -- | -- | -- | -- | -- | 1 |
| $MgCO_3 \cdot 3H_2O = Mg^{2+} + CO_3^{2-} + 3H_2O$ | Nesquehonite | -5.167 | -- | -- | -- | -- | -- | -- | 1 |
| $CO_2(g) = CO_2(aq)$ | $PCO_2$ | -1.468 | -- | 108.3865 | .01985076 | -6919.53 | -40.45154 | 669365. | 3 |
| $MgSO_4 \cdot 5H_2O = Mg^{2+} + SO_4^{2-} + 5H_2O$ | Pentahydrite | -1.285 | -- | -- | -- | -- | -- | -- | 1 |
| $Na_2Ca(CO_3)_2 \cdot 2H_2O = 2Na^+ + Ca^{2+} + 2CO_3^{2-} + 2H_2O$ | Pirssonite | -9.234 | -- | -- | -- | -- | -- | -- | 1 |
| $K_2MgCa_2(SO_4)_4 \cdot 2H_2O = 2K^+ + Mg^{2+} + 2Ca^{2+} + 4SO_4 + 2H_2O$ | Polyhalite | -13.744 | -- | -- | -- | -- | -- | -- | 1 |
| $Ca(OH)_2 = Ca^{2+} + 2OH^-$ | Portlandite | -5.190 | -- | -- | -- | -- | -- | -- | 1 |
| $K_2Mg(SO_4)_2 \cdot 6H_2O = 2K^+ + Mg^{2+} + 2SO_4^{2-} + 6H_2O$ | Schoenite | -4.328 | -- | -- | -- | -- | -- | -- | 1 |
| $KCl = K^+ + Cl^-$ | Sylvite | .900 | -- | 3.984 | -- | -919.55 | -- | -- | 5 |
| $K_2Ca(SO_4)_2 \cdot H_2O = 2K^+ + Ca^{2+} + 2SO_4^{2-} + H_2O$ | Syngenite | -7.448 | -- | -- | -- | -- | -- | -- | 1 |
| $Na_3H(CO_3)_2 \cdot 2H_2O = 3Na^+ + H^+ + 2CO_3^{2-} + 2H_2O$ | Trona | -11.384 | -- | -- | -- | -- | -- | -- | 1 |

[1] References to values of log $K_T$:

1. Harvie and others (1984) unless otherwise indicated.
2. Parkhurst and others (1980).
3. Plummer and Busenberg (1982) with $A_1$ adjusted for consistency with (1).
4. Parkhurst and others (1980) with $A_1$ Adjusted for consistency with (1).
5. Solubility data from Linke (1965), speciated in PHRQPITZ, log K fitted to analytical expression as f(T) with $A_1$ adjusted to be consistent with (1).
6. Plummer and others (1976).
7. Halite solubility from Pitzer and others (1984) treated as in 5 (above).
8. Solubility data from Linke (1965) and Plummer and Busenberg (unpub. data, 1987). The revised value of log K at 25 C for mirabilite (-1.214) compares to -1.228 of Harvie and others (1984).

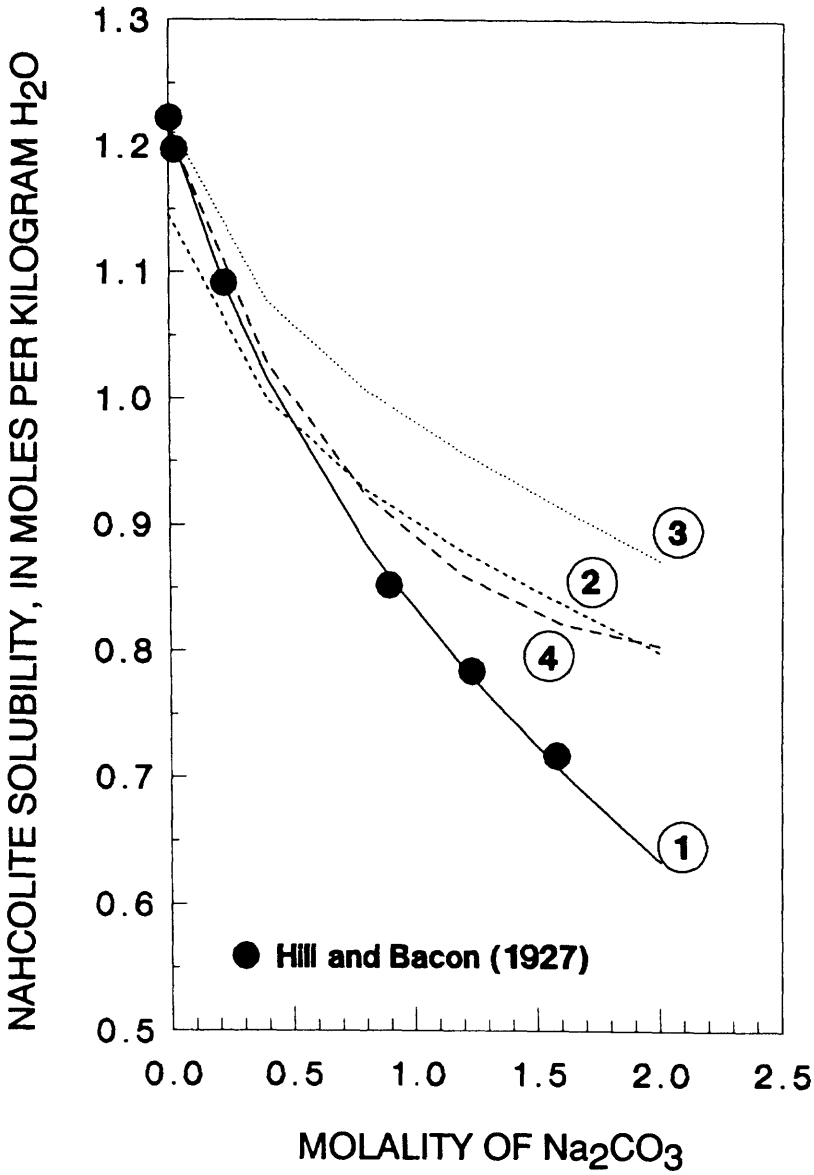


Figure 1 - Comparison of calculated solubility of nahcolite in aqueous solutions of $Na_2CO_3$ to 2 molal. (1) Calculated using the model of Harvie and others (1984), (2) Parameters $\beta^{\circ}$, $\beta^{1}$, and $C^{\phi}$ of $NaHCO_3$ changed to those of Sarbar and others (1982), (3) Same as curve 2 but with $K_{Nahcolite}$ changed to be consistent with Sarbar and others (1982), and (4) Same as curve 3 but with $\theta$ and $\psi$ for $NaHCO_3$-$Na_2CO_3$ mixtures changed to the values of Roy and others (1984) reported for $KHCO_3$-$K_2CO_3$ mixtures. Solid points are the experimental data of Hill and Bacon (1927).

The $Na^+$-$HCO_3^-$ interaction parameters in the Harvie and others (1984) data base were originally taken from Pitzer and Peiper (1980) based on an evaluation of the original electrochemical measurements of Harned and Davis (1943) and Harned and Bonner (1945) in $NaHCO_3$-NaCl aqueous solutions. Alternatively we have the Pitzer interaction parameters for $NaHCO_3$ of Sarbar and others (1982) determined from isopiestic measurements of mixed aqueous solutions of $NaHCO_3$ and $Na_2CO_3$ at 25 °C. Curve 2 of figure 1 shows the resulting calculated solubility of nahcolite in $Na_2CO_3$ solutions if the single-salt parameters of $NaHCO_3$ are arbitrarily changed from those of Pitzer and Peiper (1980) to those of Sarbar and others (1982). Curve 3 of figure 1 retains the Sarbar and others (1982) parameters for $NaHCO_3$ and adjusts the equilibrium constant of nahcolite to be internally consistent with the Sarbar and others (1982) parameters. Still the agreement is poor with the Harvie and others (1984) calculation (and experimental data).

One final adjustment is to change $\theta$ and $\psi$ for $CO_3^{2-}$ - $HCO_3^-$ - $Na^+$ interactions. Because no other values of $\theta$ and $\psi$ are known for $NaHCO_3$-$Na_2CO_3$ mixtures, we have substituted values of $\theta$ and $\psi$ determined by Roy and others (1984) for $KHCO_3$-$K_2CO_3$-KCl aqueous salt mixtures. Curve 4 of figure 1 shows marked improvement, but further adjustments in these parameters are clearly needed to obtain a revised data set for the $NaHCO_3$-$Na_2CO_3$ system consistent with the data of Sarbar and others (1982).

New values of $\theta$ and $\psi$ for $CO_3^{2-}$ - $HCO_3^-$ - $Na^+$ interactions that are internally consistent with the $NaHCO_3$ data of Sarbar and others (1982) and the known solubility of nahcolite in $Na_2CO_3$ solutions (Hill and Bacon, 1927) are compared with the Harvie and others (1984) data base in table 2. Both sets of parameters in table 2 will reproduce the experimental data for the solubility of nahcolite in $Na_2CO_3$ solutions (curve 1, fig. 1). This example demonstrates the need for internal consistency of all Pitzer interaction parameters and thermodynamic data for the given chemical system when changes to the Harvie and others (1984) data base are contemplated.

Table 2. -- Comparison of two internally consistent sets of Pitzer interaction parameters for the system $NaHCO_3$-$Na_2CO_3$-$H_2O$ at 25 °Celsius [1]

| Harvie and others (1984) | Alternate parameter set |
|---|---|
| **$NaHCO_3$** [2] | **$NaHCO_3$** [3] |
| $\beta^\circ$ = 0.0277 | $\beta^\circ$ = -0.04096 |
| $\beta^1$ = .0411 | $\beta^1$ = .5062 |
| $C^\phi$ = 0 | $C^\phi$ = .005250 |
| **$Na_2CO_3$** [4] | **$Na_2CO_3$** [4] |
| $\beta^\circ$ = .0399 | $\beta^\circ$ = .0399 |
| $\beta^1$ = 1.389 | $\beta^1$ = 1.389 |
| $C^\phi$ = .0044 | $C^\phi$ = .0044 |
| $\theta_{CO3\text{-}HCO3}$ = -.04 | $\theta_{CO3\text{-}HCO3}$ = .111 |
| $\psi_{Na\text{-}CO3\text{-}HCO3}$ = .002 | $\psi_{Na\text{-}CO3\text{-}HCO3}$ = -.025 |
| Log $K_{Nahcolite}$ = -10.742 | Log $K_{Nahcolite}$ = -10.696 |

[1] $A^\phi$ = .392. Higher-order electrostatic terms included in calculation of $\theta$ and $\psi$.
[2] Pitzer and Peiper (1980).
[3] Sarbar and others (1982).
[4] Harvie and others (1984).

## Literature Sources of Pitzer Interaction Parameters

As an aid to future improvement of the Pitzer data base, and guide to interpretation of uncertainties of model results, a computer search of literature values of single and mixed inorganic salt data was conducted through March, 1988. The results are summarized in Attachment C, where Attachment C.1 lists a bibliography of 131 articles from which the data were selected. Attachment C.2 lists published values found for the single-salt parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and $C^{\phi}$. Attachment C.3 summarizes data for binary salt systems, $\theta$ and $\psi$. The asterisks assigned to values of $\theta$ on Attachment C.3 denote parameters for which higher-order electrostatic terms were not included in fitting to experimental data. Because PHRQPITZ automatically includes the higher-order electrostatic terms, these mixed-salt parameters cannot be used in PHRQPITZ without modification of the code. Attachment C.3 also summarizes values of the single-salt parameters used to define the mixed-salt parameters. Values of $\theta$ and $\psi$ from Attachment C.3 should not be used in PHRQPITZ unless they are consistent with the same single-salt parameters found in PITZER.DATA.

Attachment C.4 summarizes published values of the temperature derivative of the single-salt parameters. Additional temperature-dependent data are given in Attachment C.5. Numbers in parentheses on Attachments C.2-C.5 refer to bibliographic citations listed in Attachment C.1. Several advanced formulations of the temperature dependence of single-salt parameters have been proposed for NaCl, $CaCl_2$, NaOH, KCl, CsCl, HCl, LiCl, $MgSO_4$, $Na_2SO_4$, $K_2SO_4$, $MgCl_2$, and $CaSO_4$. Attachment C.5 lists these equations, fitted constants and sources of data. The reader is also referred to the recent papers of Pabalan and Pitzer (1987), Pitzer (1987) and Moller (1988) for additional high temperature data.

PHRQPITZ currently calculates values of the single-salt interaction parameters either using the 25 °C value and its first derivative with respect to temperature, or utilizes an expression of the form given by Silvester and Pitzer (1977) for NaCl (only). For more extensive data on NaCl the reader is referred to Pitzer and others (1984) and Weres and others (1987).

Because of our dependence in PHRQPITZ on the Harvie and others (1984) data base and its extensive origins from Pitzer and Mayorga (1973, 1974), and Pitzer and Kim (1974), Attachments C.2-C.4 are arranged to list single-salt parameters at 25 °C in the order: Harvie and others (1984), Harvie and Weare (1980), followed by Pitzer sources, and then the remaining literature. Attachment C.6 lists the PITZER.DATA file read by PHRQPITZ (see Attachment B) indicating sources of parameters in parentheses keyed to citations given in Attachment C.1.

## SCALE CONVENTION OF ACTIVITY COEFFICIENTS

As has long been recognized, individual-ion activities and activity coefficients cannot be measured independently. Equations 2 and 3 are valid only when individual-ion activity coefficients are combined to define properties of neutral combinations of ions such as in the calculation of mean activity coefficients, saturation indices, solubility, etc. Therefore, values of individual-ion activities and activity coefficients have meaning only in a relative sense and individual values depend on a particular choice of scale convention. The subject has received recent attention as applies to interpretation of pH in seawater (Bates, 1975; Bates and Culberson, 1977; Millero, 1979; Millero and Schreiber, 1982; Plummer and Sundquist, 1982; Millero, 1983; Dickson, 1984; Covington, Bates and Durst, 1985).

PHRQPITZ offers two scaling conventions based on the work of Harvie and others (1984). In the first case (IOPT(10)=0, see Description of Input) no scaling is performed and individual-ion activity coefficients are as computed by equations 2 and 3. In the second case, all individual-ion activity coefficients are scaled according to the MacInnes (1919) convention (IOPT(10)=1, see Description of Input). In this case the activity coefficient of Cl is defined to be equal to the mean activity coefficient of KCl in a KCl solution of equivalent ionic strength, $\gamma_{Cl(Mac)} \equiv \gamma_{\pm KCl}$. The scaling factor for the *ith* ion is computed from the term $(\gamma_{Cl(eqn.3)}/\gamma_{\pm KCl})^{z_i}$ and is multiplied through all other individual-ion activity coefficients computed from equations 2 and 3. That is

$$\gamma_{i(Mac)} = \gamma_i (\gamma_{Cl} / \gamma_{\pm KCl})^{z_i} \quad (24)$$

where $\gamma_{i(Mac)}$ is the individual ion activity coefficient of the *ith* ion converted to the MacInnes scale, $\gamma_i$ is the activity coefficient of the ion consistent with some other convention, such as equations 2 and 3, $\gamma_{Cl}$ is the activity coefficient of $Cl^-$ according to the alternate convention, $\gamma_{\pm KCl}$ is the mean activity coefficient of KCl in a pure KCl solution of equivalent ionic strength and $z_i$ is the charge of the *ith* ion (+ for cations, - for anions). The activity coefficients could be placed on other scales by substituting for $\gamma_{\pm KCl}$ or $\gamma_{Cl}/\gamma_{\pm KCl}$ in equation 24.

As an example, table 3 compares log values of the molality, activity, and activity coefficient of individual ions computed for sea water in equilibrium with aragonite at 25 °C and a $CO_2$ partial pressure of $10^{-3}$ atm. The results are presented for the problem computed on the MacInnes scale and without scaling as given by equations 2 and 3. In the problem, pH was calculated from the given equilibria and is therefore internally consistent with the aqueous model and respective scale. For this particular case, when all individual-ion activity coefficients are consistent with a single scale, the individual-ion molalities are independent of choice of scale, while the computed individual-ion activities and activity coefficients are scale-dependent. For example, the pH of sea water in equilibrium with aragonite at 25 °C and $10^{-3}$ atm. $P_{CO2}$ (using the Harvie and others (1984) data base) is 7.871 on the MacInnes scale and 7.828 without scaling equations 2 and 3, as shown in table 3.

Table 3. -- Sea water in equilibrium with aragonite at a $P_{CO2}$ of $10^{-3}$ atmospheres and 25 °Celsius on two different activity-coefficient scales

| | MacInnes scale | | | Unscaled | | |
|---|---|---|---|---|---|---|
| Species | Log molality | Log activity | Log gamma | Log molality | Log activity | Log gamma |
| $H^+$ | -7.694 | -7.871 | -0.178 | -7.694 | -7.828 | -0.134 |
| $H_2O$ | -.008 | -.008 | .000 | -.008 | -.008 | .000 |
| $Ca^{2+}$ | -1.981 | -2.795 | -.814 | -1.981 | -2.708 | -.726 |
| $Mg^{2+}$ | -1.259 | -2.034 | -.775 | -1.259 | -1.946 | -.687 |
| $Na^+$ | -.313 | -.552 | -.239 | -.313 | -.508 | -.195 |
| $K^+$ | -1.973 | -2.248 | -.274 | -1.973 | -2.204 | -.230 |
| $Cl^-$ | -.246 | -.363 | -.118 | -.246 | -.407 | -.162 |
| $CO_3^{2-}$ | -4.513 | -5.424 | -.911 | -4.513 | -5.512 | -.999 |
| $SO_4^{2-}$ | -1.532 | -2.419 | -.887 | -1.532 | -2.507 | -.975 |
| $OH^-$ | -5.938 | -6.134 | -.196 | -5.938 | -6.178 | -.240 |
| $HCO_3^-$ | -2.781 | -2.956 | -.176 | -2.781 | -3.000 | -.219 |
| $H_2CO_3$ | -4.535 | -4.482 | .053 | -4.535 | -4.482 | .053 |
| $HSO_4^-$ | -8.204 | -8.312 | -.108 | -8.204 | -8.356 | -.152 |
| $CaCO_3$ | -5.068 | -5.068 | .000 | -5.068 | -5.068 | .000 |
| $MgOH^+$ | -5.890 | -5.980 | -.100 | -5.890 | -5.936 | -.056 |
| $MgCO_3$ | -4.530 | -4.530 | .000 | -4.530 | -4.529 | .000 |

Combining the results of table 3 indicates that when different scales are used, which are in themselves internally consistent, all mean quantities such as $\gamma_\pm$, $a_\pm$, $m_\pm$ and other neutral salt combinations such as ion activity products, saturation indices, and therefore solubility, are independent of scale. Clearly then, we will reach the same thermodynamic conclusion for a

given data base regardless of scale when all individual-ion values are internally consistent with a single scale. However, no significance can be assigned to the individual-ion activities, individual-ion activity coefficients and pH in comparing results on differing scales.

The problem of activity-coefficient scale is more important when the measured pH is introduced in geochemical calculations. The measured pH is not likely to be on the same activity-coefficient scale as the aqueous model because the buffers used to define pH are conventional (Bates, 1973). Even if the measured pH were placed on the same scale as the aqueous model, uncertainties in the measurement of pH in brines, such as due to liquid-junction potentials (Bates, 1973; Wescott, 1978) will always introduce inconsistencies. Consequently, it is unlikely that the measured pH will be consistent with the particular scale used for the individual ions.

As an example of this problem, table 4 compares log activities, $\gamma_{\pm CaCO3}$, $a_{\pm CaCO3}$, $SI_{calcite}$ and log $P_{CO2}$ for two water samples, including the measured pH (courtesy of R. Spencer, written Comm., 1985) from Great Salt Lake, Utah in both scaled and unscaled calculations. When the measured pH is introduced in the speciation calculation, all individual ion and mean properties, including saturation indices, $P_{CO2}$, etc. are scale dependent. This dependency of thermodynamic properties on scale when the measured pH is used is particularly acute to the carbonate system and other chemical systems where the equilibria depend significantly on pH, but is not likely to be important to calculations involving chloride and sulfate minerals in most natural waters.

Table 4. -- Comparison of individual-ion activities using the measured pH[1]
[--, carbonate alkalinity included in bicarbonate]

| Great Salt Lake (Dilute)<br>pH = 8.056<br>$a_{H2O}$ = 0.986<br>Ionic Strength = 0.6712 | | | | Great Salt Lake (Evaporated)<br>pH = 8.26<br>$a_{H2O}$ = 0.730<br>Ionic Strength = 8.5313 | | | |
|---|---|---|---|---|---|---|---|
| Ion | Molality | Log activity | | Ion | Molality | Log activity | |
| | | MacInnes | Unscaled | | | MacInnes | Unscaled |
| Na | 0.4651 | -0.529 | -0.521 | Na | 6.5204 | 0.613 | 0.793 |
| K | .0204 | -1.915 | 1.907 | K | 1.1119 | -.462 | -.282 |
| Ca | .0096 | -2.862 | -2.845 | Ca | .0011 | -3.468 | -3.109 |
| Mg | .0170 | -2.556 | -2.539 | Mg | .0009 | -3.183 | -2.824 |
| Cl | .3263 | -.672 | -.680 | Cl | 5.8484 | .955 | .775 |
| $SO_4$ | .1058 | -1.899 | -1.916 | $SO_4$ | .8927 | -1.516 | -1.876 |
| $HCO_3$[2] | .0010 | -3.267 | -3.276 | $HCO_3$[2] | .0028 | -2.970 | -3.172 |
| $CO_3$ | -- | -5.551 | -5.560 | $CO_3$ | -- | -5.049 | -5.252 |
| $\gamma_{\pm CaCO3}$ | | .1082 | .1082 | $\gamma_{\pm CaCO3}$ | | .1387 | .1386 |
| log $a_{\pm CaCO3}$ | | -4.2063 | -4.2023 | log $a_{\pm CaCO3}$ | | -4.2585 | -4.1802 |
| $SI_{Calcite}$ | | -.0064 | .0014 | $SI_{Calcite}$ | | -.1107 | .0459 |
| log $Pco_2$ | | -3.51 | -3.52 | log $Pco_2$ | | -3.29 | -3.49 |

[1] All calculations at 25°C
[2] Carbonate alkalinity as $HCO_3^-$

The problem of inconsistency of the measured pH with the adopted scale is less important at relatively low ionic strengths. For example, for dilute Great Salt Lake (ionic strength = 0.67), the calcite saturation index varies from 0.001 to -0.006 between unscaled and scaled (MacInnes) calculations (table 4.) But at relatively high ionic strengths, such as evaporated Great Salt Lake (ionic strength = 8.53), the inconsistency in pH scale leads to differences in the calculated calcite saturation index of 0.05 to -0.11 between unscaled and scaled (MacInnes)

calculations (table 4). Therefore, in addition to the relatively formidable task of measuring pH in brines, it is important to recognize the magnitude of error that can result simply from differences in activity-coefficient scale.

## PRECAUTIONS AND LIMITATIONS

Because it was adapted from PHREEQE, PHRQPITZ retains some of the limitations of the original code. These are discussed in Parkhurst and others (1980) and reviewed here as they apply to geochemical reactions in brines.

All calculations are made relative to one kilogram (kg) of water. As there is no mass balance for the elements H and O, there is no formal provision for keeping track of the amount of water used in reactions such as hydration and dehydration of solids. This may be a source of error in simulation of the evaporation of brines where many of the minerals precipitated are often hydrated and remove water from solution.

PHRQPITZ retains the original logic of PHREEQE concerning oxidation-reduction reactions, but because an internally-consistent data base of Pitzer interaction parameters for multiple oxidation states is not currently available, geochemical redox reactions may not be attempted in PHRQPITZ. All redox equilibria used with PHREEQE have been removed from the PHRQPITZ data file PHRQPITZ.DATA. If PITZINPT is used interactively to construct input sets to PHRQPITZ, the pe is automatically set to 4.0 and the non-redox option is selected (IOPT(5)=0). Consequently, precautions in Parkhurst and others (1980) concerning possible formation of large amounts of $H_2$ or $O_2$ gas outside the stability field of $H_2O$ are not relevant in PHRQPITZ if these guidelines are adhered to.

Many of the original convergence problems of PHREEQE were redox-related. Improvements to the convergence criteria of PHREEQE (noted in the January, 1985 version) have been incorporated in PHRQPITZ. Precautions and comments on the use of ion exchange, and titration/mixing reactions in PHREEQE, and the lack of uniqueness of modeled reaction paths, discussed in Parkhurst and others (1980), also apply to PHRQPITZ.

The activity of water, $a_{H2O}$, in PHRQPITZ, is computed from the osmotic coefficient, $\phi$, given by equation 1, and is

$$\ln a_{H_2O} = -\frac{\phi \sum_i m_i}{55.50837} \qquad (25)$$

where $m_i$ is the molality of the *ith* ion in solution and there are 55.50837 moles of water per kg of water. Equation 25 represents a substantial improvement over water activity calculations in PHREEQE and is now determined directly from the Pitzer model.

Other precautions have been discussed earlier as they apply specifically to the Pitzer data base. These include the likelihood of introducing error in calculated mean activities and saturation indices (particularly for carbonates) when the measured pH is on a different activity coefficient scale than the aqueous model, and the need for internal consistency between mixed-salt and single-salt interaction parameters.

The pH problem is particularly important to carbonate calculations in high ionic strength brines and could easily introduce uncertainties of ±0.5 in the saturation index of calcite. Even larger errors in SI may be attributed to uncertainties in the measurement of pH in brines due to, for example, liquid-junction potentials (Bates, 1973; Westcott, 1978).

Although we have extended the Harvie and others (1984) data base to include $Fe^{2+}$, $Mn^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Li^+$, and $Br^-$, and limited temperature dependence, the data base has not been validated beyond that of Harvie and others (1984) at 25 °C. Any changes to the single-salt parameters of the Harvie and others (1984) data base will likely require extensive revision of the mixed-salt parameters and mineral free energies. Any new values of the mixed-salt parameters must be internally consistent with the single-salt parameters in the model and include the higher-order electrostatic terms, as discussed above. This requirement has been

followed in previously-discussed extensions to the Harvie and others (1984) data base given in PITZER.DATA, however, further testing is needed for calculations involving $Fe^{2+}$, $Mn^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Li^{+}$, and $Br^{-}$. Any changes to the mixed-salt parameters, even if consistent with the given single-salt parameters, will likely require changes to the mineral free energies. Because of the lack of Pitzer interaction parameters for aqueous aluminum and silica species, we are unable to make calculations with aluminosilicates in PHRQPITZ.

The temperature range for equilibria in the PHRQPITZ.DATA file is variable and is generally 0 to 60 °C if $\Delta H_f°$ is known. The NaCl system is valid to approximately 350 °C, and the carbonate system is reliable to about 100 °C. The temperature dependence of the solubility of many of the minerals in PHRQPITZ.DATA is not known and large errors could result if calculations are made at temperatures other than 25 °C for these solids. Limited temperature-dependent data for single salt parameters are included in PITZER.DATA. If the sample temperature is outside the interval 0 to 55 °C, PHRQPITZ prints a nonfatal warning.

## NUMERICAL METHOD

Much of the structure of PHREEQE is maintained in PHRQPITZ. PHRQPITZ still uses the Newton-Raphson approach to solve a set of algebraic equations by generating successively better estimates of the molalities and activity coefficients of the aqueous species. In effect, the only change in the results of simulations is caused by several new subroutines that calculate the activity coefficients and activity of water using the Pitzer equations. However, several major changes in the mechanics of the calculations have been made in order to deal with the large range of ionic strength for which the Pitzer formulations are applicable. At high ionic strengths, the activity coefficients and the activity of water have more extreme values. Thus, the numerical method has been changed to estimate changes in activity coefficients and the activity of water as part of refining the estimates of the unknowns.

### Basic Equations

The most fundamental change from PHREEQE is that the master variables are the molalities of the master species instead of the activities of the master species. The Newton-Raphson equations rely primarily on the total differential of the molality of each aqueous species with respect to the master variables. The following equations define the total differential of an arbitrary aqueous species, $m_i$:

$$m_i = K_i(\gamma_1 m_1)^{c_{1,i}}(\gamma_2 m_2)^{c_{2,i}} a_{H_2O}^{c_{H_2O,i}} / \gamma_i \quad , \tag{26}$$

where $m_i$ is the molality of the *ith* aqueous species, $m_1$ and $m_2$ are the molalities of the master species in the mass action expression for the aqueous species, $K_i$ is the equilibrium constant for the association reaction, $\gamma$ is the activity coefficient of a species, c is the stoichiometric coefficient for a master species in the *ith* species, and $a_{H2O}$ is the activity of water. The total differential is given by

$$dm_i = \frac{\partial m_i}{\partial \gamma_1} d\gamma_1 + \frac{\partial m_i}{\partial m_1} dm_1 + \frac{\partial m_i}{\partial \gamma_2} d\gamma_2 + \frac{\partial m_i}{\partial m_2} dm_2 + \frac{\partial m_i}{\partial a_{H_2O}} da_{H_2O} - \frac{\partial m_i}{\partial \gamma_i} d\gamma_i \quad . \tag{27}$$

An approximation is used at this point to reduce the activity coefficient terms in the equation to a single term which is dependent on ionic strength, I,

$$d\gamma \sim \frac{d\gamma}{dI} dI \quad . \tag{28}$$

The derivative of the activity coefficients with respect to ionic strength is calculated based on the values of the activity coefficient and ionic strength at a given iteration and the values at the last time the Newton-Raphson procedure was used. Thus there is little computational expense in calculating these derivatives. In testing the program with a wide range of salts, this approximation appears to be adequate. The total differential of the molality of an aqueous species then becomes

$$dm_i = c_{1,i} m_i \frac{dm_1}{m_1} + c_{2,i} m_i \frac{dm_2}{m_2} + c_{H_2O,i} m_i \frac{da_{H_2O}}{a_{H_2O}}$$

$$+ \left( c_{1,i} m_i \frac{1}{\gamma_1} \frac{d\gamma_1}{dI} + c_{2,i} m_i \frac{1}{\gamma_2} \frac{d\gamma_2}{dI} - m_i \frac{1}{\gamma_i} \frac{d\gamma_i}{dI} \right) dI \quad . \qquad (29)$$

This equation is the building block for the set of simultaneous equations which need to be solved. PHRQPITZ includes simultaneous equations for electroneutrality, mass balance for each element (except hydrogen and oxygen), and mineral mass action. Two equations that estimate the changes in the activity of water and the ionic strength are also included.

Electroneutrality error is defined

$$\sum_i z_i dm_i = E_{elect} \quad , \qquad (30)$$

where $z_i$ is the charge of the *ith* species and $E_{elect}$ is the electrical imbalance calculated from the molalities of the aqueous species at the current iteration.

Mass-balance error is defined

$$\sum_i c_{j,i} dm_i = E_{mass(j)} \quad , \qquad (31)$$

where $c_{j,i}$ is the stoichiometric coefficient of the master species j in the *ith* species, and $E_{mass(j)}$ is the error in the mass balance (the total concentration of the element j in solution minus the total concentration of j calculated from the molalities of the aqueous species at the current iteration).

Mineral mass action error is defined by

$$\sum_j c_{p,j} dm_j + \left( \sum_j c_{p,j} \frac{d\gamma_j}{dI} \right) dI = E_{IAP_p} \quad , \qquad (32)$$

where $c_{p,j}$ is the stoichiometric coefficient of master species j in the mass action expression for mineral p and $E_{IAP(p)}$ is the error in the saturation state (log K/IAP).

The change in the activity of water is estimated from

$$\sum_i DAW\, dm_i - da_{H_2O} = 0 \quad , \qquad (33)$$

where DAW is the decrease in the activity of water per mole of solute, $DAW = (1 - a_{H2O})/\Sigma m_i$, and $d(a_{H2O})$ is the estimate of the change in the activity of water for the iteration. The activity of water is calculated explicitly in the Pitzer equations, so the utility of including this equation is to estimate the effect of the change in the activity of water on the molalities of all of the aqueous species and mineral saturation indices.

The change in the ionic strength is estimated from

$$\frac{1}{2}\sum_i z_i^2 dm_i - dI = 0 \quad , \tag{34}$$

where dI is the estimated change in the ionic strength for the iteration. Through the approximation stated above (eq. 28), this equation allows for the estimation of the effects of activity coefficients on the molalities of the aqueous species.

All of the equations presented are linear with respect to changes in the master variables: The molalities of the master species, the mass of minerals, ionic strength, and activity of water. The equations are solved simultaneously to find new values for the molalities of the master species.

## Restrictions on the Newton-Raphson Approach

Though the Newton-Raphson approach is a very powerful technique for solving nonlinear equations, it is sensitive to poor estimates of the unknowns. Thus, PHRQPITZ applies the Newton-Raphson technique only after the estimates of the unknowns have satisfied certain criteria.

At each iteration, the sequence of calculations is as follows:

(1) The molalities of the species are used to calculate activity coefficients,
(2) the molalities of the master species and the activity coefficients are used to calculate the molalities of the aqueous complexes,
(3) the molalities of the master species of the elements are estimated using the technique described for PHREEQE (Parkhurst and others, 1980), and
(4) the molalities of the aqueous complexes are recalculated.

This sequence of calculations is repeated at least once to ensure that the molalities of the aqueous species are consistent with the activity coefficients and mass action expressions for the aqueous species. The sequence is repeated until the ionic strength has stabilized and the mass balance on the elements is satisfied within 10 percent. After these criteria are met, the Newton-Raphson equations are invoked. Until the electrical balance is less than 1.0 molal and the saturation indices of minerals are less than 0.5, no activity coefficient effects are included in the Newton-Raphson equations.

## Scaling the Newton-Raphson Results

The result of solving the simultaneous equations is a vector of additive changes to the master variables. The magnitude of the changes can be extremely large. In these cases the vector is assumed to be in the direction of decreasing the error terms but must be scaled to much smaller values in order to approach the correct solution. Several criteria are used to ensure that the changes in the master variables are relatively small.

The pH is constrained to change less than 0.5 units per iteration. The maximum change in ionic strength is 0.5 molal. The maximum amount of a mineral that can dissolve or precipitate is 0.5 moles per iteration. Precipitation of minerals is limited so that no negative molalities result. These restrictions make the program more reliable over a range of chemical compositions but cause the program to require more iterations to find a solution to the equations.

## DESCRIPTION OF INPUT

The user-defined input to PHRQPITZ is nearly identical to that of PHREEQE. Other input pertaining to the data file PITZER.DATA is new and described separately. Here we present the description of input section from Parkhurst and others (1980) which has been modified as needed to pertain to PHRQPITZ.

PHRQPITZ is designed to perform a sequence of simulations in a single computer run. Each simulation consists of two separate problems:

1. Process an initial solution or solutions and (or)

2. Model a reaction (starting from the initial solution(s)).

Many pathways for a simulation are accessible with a single input file; that is, no program modification should be necessary. Required input begins with a title line followed by a line of selected options. Depending on the options selected, additional data are supplied using various "Keyword" data blocks. A data block consists of a Keyword followed by appropriate data. The Keyword informs the program of the type and format of the data to follow. ELEMENTS and SPECIES, if they are used, should be the first two data blocks while the other keyword blocks may follow in any order. The keyword END denotes the end of the input data and is required once for each simulation. After the calculations for one simulation are completed, the program starts the data input process again, beginning with a new title and option line.

The general types of reactions that can be simulated are as follows:

1. Mixing of two solutions.
2. Titrating one solution with a second solution.
3. Adding or subtracting a net stoichiometric reaction (changing total concentrations of elements in proportion to a given stoichiometry).
4. Adding a net stoichiometric reaction until the phase boundary of a specified mineral is reached.
5. Equilibrating with mineral phases (mineral equilibrium can be specified with reaction types 1, 2, 3, 4, or 6 as well). Any condition which can be written in the form

$$\log(K_p) = \sum_i c_{p,i} \log(a_i) \quad ,$$

where $a_i$ is the activity of the *ith* aqueous species, $c_{p,i}$ is the stoichiometric coefficient of the *ith* aqueous species in the *pth* phase, and $K_p$ is the equilibrium constant for the *pth* phase, is considered a mineral phase. This definition of mineral equilibrium includes the following:

a. Maintaining the aqueous phase in equilibrium with one or more minerals;

b. Equilibration of a mineral-water system with a gas such as $CO_2$;

c. Apparent ion exchange in the sense that a ratio of two aqueous ion activities is kept constant.

Any combination of the above can be included in the MINERALS keyword input provided the Gibbs Phase Rule is not violated.

6. Changing temperature.

These six types of reaction (processes) may be used in various combinations. For example, one could add a net stoichiometric reaction to a starting solution while maintaining mineral equilibrium and increasing temperature.

In each type of reaction, an initial solution must be specified. There are three ways to provide a starting solution for a reaction. (1) The total concentrations of elements (and other necessary information such as pH, and temperature) may be input using the SOLUTION n keyword. n is either 1 or 2 and indicates the number of the array where the solution data will be stored. Any stoichiometric reaction or simple mineral equilibration is performed on solution number 1 alone. Solution number 2 is required only for mixing and titrating. (2) The second method of providing a starting solution for a reaction is to savé the final solution from the reaction step of the previous simulation (provided more than one simulation is made in a run). IOPT(7) is used to specify the solution number into which the final solution of a simulation will be saved. In the subsequent simulation no new solution should be read into that solution number. (3) Finally, if no reaction solution is saved and no new solutions are input, the solutions from the previous simulation remain in memory. Thus, a solution can be input once but can be used as the starting solution for multiple simulations.

One of the principle applications of PHRQPITZ is intended to be simulation of reactions based on observed water analyses, which will generally show an apparent electrical imbalance as a result of analytical errors. Because we use the electrical neutrality criterion in solving for pH, it is important to consider this apparent charge imbalance. Various options are available to achieve charge balance or to maintain a charge imbalance in the computations. Care should be taken in choosing the appropriate option and interpreting the results. Only perfect chemical analyses would produce electrical neutrality in an initial solution. Lacking these the solution may be left electrically unbalanced by setting IOPT(2) = 0. When a reaction is modeled the final calculated solution will have the same electrical imbalance as the initial solution. If IOPT(2) = 1, the pH of the initial solution will be adjusted to produce electrical neutrality in that solution. If the analytics are perfect, this places pH on the same activity coefficient scale as chosen for the aqueous model. It may be that the pH of the initial solution is relatively well known and it is more reasonable to add relatively inert ions like $K^+$ or $Cl^-$ to balance the charge. In this case set IOPT(2) = 2, and use the keyword NEUTRAL and associated input to specify K and Cl. The amount of K or Cl added will be listed in the output. One final alternative is to attribute the charge error to the most suspect analysis, e.g. carbon or sodium, or to a constituent known to be present for which one has no analytical data. Again, set IOPT(2) = 2 and use the NEUTRAL input. Lack of charge balance is a meaningful clue to the errors in analyses and a large error probably makes a solution unsuitable for reaction simulation. By using the various options of the program, one can investigate the significance of analytical errors and their effects on reaction simulations.

In the following description of the input, the Fortran format for each line is given. Any Fortran manual will provide a complete explanation of the symbols used in format statements. Format of input data sets is automatically controlled if PITZINPT is used to generate input data sets to PHRQPITZ.

A. Title and option lines.

1. TITLE LINE — TITLE

   FORMAT (20A4)

   Eighty characters of titles or comments.

2. OPTION LINE — (IOPT(I), I = 1,10), NSTEPS, NCOMPS, V0

   FORMAT (10I1,2I2, 6X, F10.5)

   IOPT(1) = 0, No print of thermodynamic data or coefficients of aqueous species.

   = 1, Print the aqueous model data (from PHRQPITZ.DATA) once during the entire computer run.

   IOPT(2) = 0, Initial solutions are not to be charge balanced. Reaction solutions maintain the initial charge imbalance.

   = 1, pH is adjusted in initial solution(s) to obtain charge balance. Caution: Large errors in pH can result from errors in analytical data, such as for water analyses that are not balanced in charge.

= 2, The total concentration of one of the elements (except H or O) is adjusted to obtain electrical balance. NEUTRAL input is required.

IOPT(3) = 0, No reactions are modeled. Only the initial solution is solved (speciated).

= 1, Solution 1 is mixed ( a hypothetical constant volume process) with solution 2 in specified reaction steps. STEPS input and a value of NSTEPS are required. MINERALS input may be included.

= 2, Solution 1 is titrated with solution 2 in specified reaction steps. STEPS input, a value for NSTEPS, and a value for V0 are required. MINERALS input may be included.

= 3, A stoichiometric reaction is added in specified reaction steps. REACTION input, STEPS input, a value for NSTEPS, and a value for NCOMPS are required. MINERALS input may be included.

= 4, A net stoichiometric reaction is added in NSTEPS equal increments. REACTION input, STEPS input, a value of NSTEPS, and a value for NCOMPS are required. MINERALS input may be included. Only one value for the total reaction is read in STEPS.

= 5, Solution number 1 is equilibrated with mineral phases only. No other reaction is performed. MINERALS input is required.

= 6, A reaction is added to solution 1 until equilibrium is attained with the first phase in MINERALS input (equilibrium with other MINERALS phases is maintained throughout the reaction). REACTION input, a value for NCOMPS, and MINERALS input is required. No STEPS input is required. Note: there should be a common element in the reaction and the first phase in MINERALS, unless the phase boundary depends only on the activity of water (such as anhydrite-gypsum) at constant temperature and pressure. To evaporate or dilute solution number 1 to reach a phase boundary, define the REACTION a 1.0 $H_2O$ (See description of REACTION input and Test Problem 6).

IOPT(4) = 0, The temperature of the reaction solution is (a) the same as the initial solution if adding a reaction, or (b) calculated linearly from the end members if mixing or titrating. No TEMP input is required.

= 1, The temperature is constant during the reaction steps and differs from that of the initial solution(s). One value is read in the TEMP input.

= 2, The temperature is varied from $T_o$ to $T_f$ in NSTEPS equal increments during the reaction steps. A value for NSTEPS and two values of temperature, $T_o$ and $T_f$, (in order) are required in the TEMP input, where $T_o$ is the initial temperature and $T_f$ is the final temperature.

= 3, The temperature of each reaction step is specified in TEMP input, in order. NSTEPS values are read. Note: If a change in temperature is the sole "reaction", then a (null) stoichiometric reaction adding 0.0 moles must be defined using REACTION and STEPS input (see test problem 4).

| | | |
|---|---|---|
| IOPT(5) | = 0, | The pe of the initial solution (defined to be 4.0 if PITZINPT is used to construct input sets) is held constant during all the reaction steps for the simulation. Redox reactions are currently not considered. |
| IOPT(6) | = 2, | Activity coefficients are calculated according to the Pitzer model. No other options are available. |
| IOPT(7) | = 0, | Do not save the aqueous phase composition at the end of a reaction for additional simulation. |
| | = 1, | Save the final reaction solution composition in solution number 1. |
| | = 2, | Save the final reaction solution composition in solution number 2. |
| IOPT(8) | = 0, | The debugging print routine is not called. |
| | = 1, | A long printout is output at each iteration in each problem. This print is to be used only if there are convergence problems with the program. (See discussion of subroutine PBUG given in Parkhurst and others (1980)). |
| IOPT(9) | = 0, | No printout of each array to be solved. |
| | = 1, | A long printout occurs of the entire array to be solved at each iteration. This print is used only if there are convergence problems. (See discussion of subroutine SLNQ given in Parkhurst and others (1980)). |
| IOPT(10) | = 0, | No scaling of the individual-ion activity coefficients is performed. |
| | = 1, | The individual-ion activity coefficients are scaled according to the MacInnes convention (see text). |
| NSTEPS | | The number of reaction steps. A value is required if IOPT(3) = 1, 2, 3, or 4, or if IOPT(4) = 2 or 3. (Right justified.) |
| NCOMPS | | The number of constituents in a net stoichiometric reaction. A constituent may be any element with an index number between 4 and 29 inclusive. No aqueous species with index numbers greater than 29 may be included as reaction constituents. A value of NCOMPS is required if IOPT(3) = 3, 4, or 6. |
| V0 | | The initial volume of solution 1 when modeling a titration. The unit of V0 must be the same as that of XSTEP (See STEPS input below) if IOPT(3) = 2. Otherwise, V0 is not required. |

B. Keyword data blocks. Blocks are preceded by a keyword line. The keywords are numbered and underlined in the following text. Each keyword must begin in the first column of the line. The appropriate lines, which are lettered in the text, must follow in order directly after the keyword.

1. ELEMENTS FORMAT (A8)

This input defines the names and indices of all elements in the aqueous model data base (PHRQPITZ.DATA). One of line 1.a is read for each element. The index numbers of the elements do not need to be consecutive or sequential. This input block must be terminated with one blank line. Generally these data will be part of the PHRQPITZ.DATA file stored on disk and read by the program at the beginning of each run. Only changes to the data base need to be in the input data file.

1.a. TNAME, NELT, TGFW
FORMAT (A8,2X,I2,3X,F10.0)

TNAME Alphanumeric name of the element.

NELT Index number assigned to the element. Number must be between 4 and 29, inclusive. (Right justified.)

TGFW Gram formula weight of the species used to report the analytical data. If solution data include alkalinity, TGFW for the element carbon must be the equivalent weight of the reported alkalinity species. TGFW is not used if the concentrations are entered as molality (IUNITS = 0 in SOLUTION input line 3.b).

1.b. Blank line. (Denotes end of ELEMENTS input).

2. SPECIES FORMAT (A8)

This input defines the names, index numbers and composition of all aqueous species in the aqueous model data base. Lines 2.a, 2.b, 2.c, and 2.d are read for each species. The index numbers for the species do not need to be sequential or consecutive. This input block must be terminated with one blank line. To eliminate a species (already in the PHRQPITZ.DATA file) from the aqueous model, only line 2.a followed by a blank line 2.b must be entered. More species changes could then follow or a second blank line would terminate this input block. All species must have association reactions which contain only master species (species numbers less than or equal to 29). Reactions containing non-master species must be converted to master species reactions and the appropriate association constants must be calculated before they can be entered into the program. These data are generally stored in the disk file PHRQPITZ.DATA which is read by the program at the beginning of each run and retained for the entire run. Only changes and additions to PHRQPITZ.DATA would appear in the input file.

2.a I

FORMAT (I3)

I The index number assigned to the aqueous species. Numbers 4 through 29 are reserved for master species. The maximum index number for an aqueous species is 250. (Right justified.)

2.b. SNAME, NSP, KFLAG, GFLAG, ZSP, THSP, DHA, ADHSP(1), ADHSP(2), ALKSP

FORMAT (A8,2X,I3,2I1,6F10.3)

SNAME Alphanumeric species name.

NSP The total number of master species in the association reaction that forms this species; do not count the species itself unless the species is a master species (index number of 1 - 29). (Right justified.)

KFLAG = 0. The van't Hoff equation is used to calculate the temperature dependence of the association constant for this species.

= 1. An analytical expression is used to calculate temperature dependence of the association constant. Values of ASP are required on line 2.c.

GFLAG Not used in PHRQPITZ. Read 0 or blank.

ZSP The charge on this aqueous species.

THSP Not used in PHRQPITZ. Read 0.0, or blank.

DHA Not used in PHRQPITZ. Read 0.0, or blank.

ADHSP(1) Not used in PHRQPITZ. Read 0.0, or blank.

ADHSP(2) Not used in PHRQPITZ. Read 0.0, or blank.

ALKSP The alkalinity in equivalents assigned to this aqueous species. Such as 2.0 for carbonate species and 1.0 for bicarbonate. See discussion in Parkhurst and others (1980).

2.c. LKT0SP, DHSP, (ASP(I),I = 1,5)
FORMAT (2F10.3,5E12.5)

Constants used to evaluate the association constant as a function of temperature. The analytical expression has the form of equation 23.

LKT0SP $Log_{10}$ of the mass action association constant at 25 °C (used in van't Hoff equation).

DHSP Standard enthalpy of the association reaction at 25 °C ($\Delta H_r°$, in Kcal/mole); used in the van't Hoff equation.

ASP(1) Constant term in equation 23 for calculation of the temperature dependence of log K, (= $A_1$ in equation 3. The array ASP is used if KFLAG = 1.

ASP(2) Coefficient $A_2$ in equation 23.

ASP(3) Coefficient $A_3$ in equation 23.

ASP(4) Coefficient $A_4$ in equation 23.

ASP(5) Coefficient $A_5$ in equation 23.

2.d. (LSP(I), CSP(I), I = 1,NSP)
FORMAT 6(I3,F7.3)

List of master species numbers and their coefficients in the mass action association reaction. NSP pairs of values, LSP and CSP, are read. One and only one of these lines is required for each species.

LSP(I) Index number of master species. (Right justified.)

CSP(I) Stoichiometric coefficient of master species in this aqueous species.

See Parkhurst and others (1980) for further information.

3. SOLUTION n FORMAT (A8,1X,I1)

This input is used to define a starting solution. n can be either 1 or 2 and indicates the solution number of the data following. Lines 3.a and 3.b are required. Line 3.c is not included if NTOTS = 0. There must be as many line 3.c's as necessary to read NTOTS total concentrations.

3.a. HEAD
FORMAT (20A4)
Title or comments about the solution.
HEAD Alphanumeric heading

3.b. NTOTS, IALK, IUNITS, PH, PE, TEMP, SDENS
FORMAT (I2,I3,I2,3X,4F10.3)

NTOTS The number of total concentrations to be read from line 3.c input. For example, if the starting solution is a $MgCl_2$ - $NaHCO_3$ solution, NTOTS = 4 (for Mg, Cl, Na, and C). (Right justified.)

IALK Flag which indicates whether total carbon or total alkalinity is to be input. (Right justified.)

= 0 indicates the total concentration of carbon (not alkalinity) is input in the units specified by IUNITS (see below).

= n $4 \leq n \leq 29$ where n is the index number for the element carbon, (in PHRQPITZ.DATA, we have defined n = 15) and indicates total alkalinity is being entered. If alkalinity is used (n>0), then IOPT(2) cannot be equal to 1. It is theoretically impossible to use pH to achieve electrical neutrality if the alkalinity is fixed. ELEMENTS input may be required. The units of alkalinity are specified by IUNITS (below) and if IUNITS is greater than 0, the gram formula weight (GFW) of the element carbon is critically important. The GFW in the case of alkalinity must be the gram equivalent weight (grams/equivalent) of the chemical species in which the alkalinity is reported. The following is a list of species commonly used for reporting alkalinity and their corresponding equivalent weights:

$CaCO_3$ 50.0446 g/eq
$HCO_3^-$ 61.0171 g/eq
$CO_3^{2-}$ 30.0046 g/eq.

(Note that: Alkalinity (mg $HCO_3$/L) = Alkalinity (mg $CaCO_3$/L) x 1.21925.)

In PHRQPITZ.DATA 44.010 is the GFW of carbon which is suitable for entering carbon as total $CO_2$. This GFW must be changed via ELEMENTS input if alkalinity is to be entered as mg/L or ppm (IUNITS = 2 or 3). If IUNITS = 0, alkalinity must be input as eq/kg $H_2O$ and in this case the GFW need not be changed because no conversion of units is necessary. For a discussion of the contribution of different aqueous species to the total alkalinity see Parkhurst and others (1980).

IUNITS Flag describing units of input concentrations (right justified). The program makes all of its calculations in terms of molality and any other allowed concentration unit must be converted internally to molality before the calculations may begin. To make the conversions it is necessary to know the gram formula weight (GFW), in g/mole, of the chemical formula in which the elemental analyses are reported. The GFW is an input parameter under ELEMENTS input and must be in agreement with the analytical units for each solution data set. (If the units are molality, no conversion is necessary and the GFW's are not used.) Values of GFW currently in use are found in PHRQPITZ.DATA. Note: All elements must have the same units. It is not possible to enter mg/L of one element and molality of another.

= 0 Concentration of elements entered as molality of each element, or for alkalinity, eq/kg $H_2O$ (equivalents per kilogram).

= 1 Concentration of elements entered as mmol/L of each element, or for alkalinity, meq/L.

= 2 Concentration of elements entered as mg/L of the species which has a gram formula weight given in ELEMENTS input. (ELEMENTS input may be required.) For alkalinity see discussion under IALK above.

= 3 Concentration of elements entered as ppm of the species which has a gram formula weight given in ELEMENTS input. (ELEMENTS input may be required.) For alkalinity see discussion under IALK above.

= 4 Concentration of elements entered as millimoles per kilogram of solution, or for alkalinity as milliequivalents per kilogram of solution.

PH The pH of the solution (the estimated pH if IOPT(2) = 1). Required for all solutions.

PE The pe of the solution. It is suggested that the user enter 4.0 for this variable, as PHRQPITZ does not currently treat redox reactions.

TEMP The temperature of the solution in °Celsius.

SDENS The density of the solution. Required if concentrations are input in mmol/L or mg/L. If SDENS is omitted, 1.0 is assumed. Incorrect values of SDENS could lead to large errors in converting volume-based concentration units to molality.

3.c. (LT(I), DTOT(I), I = 1, NTOTS)
FORMAT 5(I4,D11.3)
Total concentrations of elements. Five values of LT. and DTOT are read on each line. The line may be repeated in order to enter all the elements desired. All data must appear consecutively in the fields, no blanks or zeros are allowed as values for LT. Omit this line if NTOTS is zero, the case of pure water.

LT Index number of the element, consistent with ELEMENTS data in PHRQPITZ.DATA. (Right justified.)

DTOT Total concentration of the element in molality, mmol/L, mg/L, ppm, or mmol/kg solution according to IUNITS.

4. MINERALS FORMAT (A8)
This input defines the phases which will be maintained at equilibrium with each of the reaction solutions. Lines 4.a and 4.b are required for each mineral. Line 4.c is optional for each mineral depending on the value of MFLAG. Unlike SPECIES, MINERALS may be defined in terms of any aqueous species, not just the master species. A maximum of 19 minerals is allowed. The input expression for the equilibrium constant must correspond with the input mass action coefficients. Mineral reactions are written as dissociation reactions. MINERALS input must be terminated with a blank line.

4.a. MNAME, NMIN0, THMIN, LKT0M, DHMIN, MFLAG, SIMIN
FORMAT (A8,2X,I2,3X,3F10.2,5X,I1,9X,F10.3)

MNAME Alphanumeric name of mineral.

NMIN0 Number of different species in the mineral dissociation reaction (including $H^+$ and $H_2O$). NMIN0 must be less than or equal to 10. (right justified.)

THMIN Not used in PHRQPITZ. Read 0.0.

LKT0M $Log_{10}$ of the equilibrium constant at 25 °C for the reaction.

DHMIN $\Delta H_r^\circ$ (Kcal/mole) for the van't Hoff equation.

MFLAG = 0. The van't Hoff equation is used to calculate the temperature dependence of the equilibrium constant.

= 1. The analytical expression is used to calculate the temperature dependence of the equilibrium constant. Line 4.c is required.

SIMIN — Saturation index ($\log_{10}$(Ion Activity Product/$K_{sp}$)) desired in the final solution. SIMIN = 0.0 would result in equilibrium with the (one component, or fixed composition) mineral, while 1.0 would produce a solution 10 times supersaturated (SI = 1.0). This variable is also useful in specifying the partial pressure of a gas. The Henry's law constant for the gas would be entered using the equilibrium constant (LKTOM) or analytical expression (AMIN) and the log of the partial pressure would be entered for SIMIN.

4.b. (LMIN(I), CMIN(I), I = 1,NMIN0)
FORMAT 5(I4,F11.3)

List of species index numbers and stoichiometric coefficients in the dissociation reaction for this mineral. NMIN0 pairs of numbers, LMIN and CMIN, are read. The maximum value of NMIN0 is 10. If NMIN0 is greater than 5, a second line 4.b is required.

LMIN(I) — Index number of species (not necessarily master species) in the dissociation reaction for this mineral. (Right justified.)

CMIN(I) — Stoichiometric coefficient of species in dissociation reaction.

For example, using the data for aqueous species index numbers in PHRQPITZ.DATA,

i. $CaCO_3 = Ca^{2+} + CO_3^{2-}$

NMIN0 = 2
LMIN(1) = 4, CMIN(1) = 1.0
LMIN(2) = 15, CMIN(2) = 1.0.

ii. $CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$

NMIN0 = 3
LMIN(1) = 4, CMIN(1) = 1.0
LMIN(2) = 16, CMIN(2) = 1.0
LMIN(3) = 3, CMIN(3) = 2.0.

iii. $Ca^{2+}$ - $Na^+$ ion exchange. (Assumes composition of exchanger does not change.)

$$Na_2(ex) + Ca^{2+} = Ca(ex) + 2Na^+$$

or

$$Na_2(ex) - Ca(ex) = 2Na^+ - Ca^{2+}$$

NMIN0 = 2
LMIN(1) = 6, CMIN(1) = 2.0
LMIN(2) = 4, CMIN(2) = -1.0.

$LKTOM = a^2_{Na+}/a_{Ca2+}$

iv. Fix $CO_2$ partial pressure.[5]

$$CO_{2(gas)} = CO_2^*(aq)$$

where $CO_2^*(aq)$ represents the sum of $CO_2°$ and $H_2CO_3°$

NMIN0 = 1
LMIN(1) = 35, CMIN(1) = 1.0
LKT0M = Henry's law constant for $CO_2$
SIMIN = Log $P_{CO2}$ desired.

4.c. AMIN(I), I =1,5
FORMAT (5E12.5)

Equilibrium constant expression of the form of equation 23 for the mineral dissociation reaction. This line is used only if MFLAG = 1.

AMIN(1) Coefficient $A_1$ of equation 23

AMIN(2) Coefficient $A_2$ of equation 23

AMIN(3) Coefficient $A_3$ of equation 23

AMIN(4) Coefficient $A_4$ of equation 23

AMIN(5) Coefficient $A_5$ of equation 23

4.d. Blank line.

5. LOOK MIN FORMAT (A8)

The purpose of this input is simply to provide information on the saturation state of the aqueous phase with respect to desired minerals. The minerals in this block of input do not affect the calculations of the initial solution or any of the reaction solutions. This input is never mandatory. The ion activity product (IAP) and saturation index (SI = log (IAP/K)) of each of these minerals is printed in the output following each solution description. Only the minerals which contain elements present in the solution are printed. The input following this line is identical to the input for MINERALS (see above). This input must be terminated with a blank line. The list of "look minerals" is maintained for the duration of the run and any new "look mineral" is simply added to the list. If a "look mineral" is added that has the identical 8 letter name as another mineral in the list, the new mineral replaces the old mineral. The word DELETE as a mineral name will eliminate all of the minerals in the list and new minerals may be added. Only 39 "look minerals" are allowed. LOOK MIN input is generally placed in PHRQPITZ.DATA and is read once for each run. The input file need not contain additions and changes to the PHRQPITZ.DATA list of "look minerals".

6. MEAN GAM FORMAT (A8)

This input allows the user to calculate the mean activity coefficient for any neutral salt combination of aqueous species. The input is optional. Data for calculation of 21 mean activity coefficients are included in PHRQPITZ.DATA. A total of 40 are allowed. MEAN GAM input can appear in the input data set as well as PHRQPITZ.DATA. The word DELETE is allowed and its usage is the same as in LOOK MIN input (see above).

---

5 The reaction is written for the predominant species, $CO_2°$.

6.a. NMEANG, IMEANG, (LMEANG(I), CMEANG(I), I = 1,3)
FORMAT (A8,I2,3(I4,F6.0))

This input defines the stoichiometry of neutral salts for calculation of mean activity coefficients.

NMEANG Alphanumeric name of salt or mineral.

IMEANG Number of different species in the salt. This number is usually 2 and may not exceed 3.

LMEANG(I) Index number of species (not necessarily a master species) in the salt. Index numbers are as defined under ELEMENTS and SPECIES input.

CMEANG(I) Stoichiometric coefficient of species in salt. For example, using SPECIES data from PHRQPITZ.DATA:

i. NaCl
IMEANG = 2
LMEANG(1) = 6, CMEANG(1) = 1.0
LMEANG(2) = 14, CMEANG(2) = 1.0

ii. $NaHCO_3$
IMEANG = 2
LMEANG(1) = 6, CMEANG(1) = 1.0
LMEANG(2) = 34, CMEANG(2) = 1.0

7. TEMP FORMAT (A8)

This input varies the temperature during the reaction steps. It is required input if IOPT(4) is greater than 0. Only one line 7.a. is necessary unless IOPT(4) = 3. In that case as many lines as necessary to input NSTEPS values are required. If TEMP input is included, REACTION input is required, even for a null reaction (see test problem 4).

7.a. XTEMP
FORMAT (8F10.1)

XTEMP Temperature in degrees Celsius.
If IOPT(4)=1, one value of XTEMP is read.
If IOPT(4)=2, two values of XTEMP are read, $T_0$ and $T_f$ (in order).
If IOPT(4)=3, NSTEPS values of XTEMP are read (no blank fields permitted).

8. STEPS FORMAT (A8)

This input defines the steps of the reaction progress. The input has a different meaning depending on the value of IOPT(3) (option line).

IOPT(3) = 1, XSTEP is the fraction of solution 1 to be mixed with solution 2. NSTEPS values are read.

IOPT(3) = 2, XSTEP is the volume of solution 2 to be titrated into solution 1. XSTEP must have the same units as V0 (option line). NSTEPS values are read.

IOPT(3) = 3, XSTEP is the number of moles of reaction to be added to solution 1. NSTEPS values are read.

IOPT(3) = 4, Only one value of XSTEP is read. XSTEP is the total number of moles of reaction to be added in NSTEPS steps. NSTEPS reaction solutions will be calculated. The I*th* solution will have I·XSTEP/NSTEPS moles of reaction added to solution 1.

8.a. XSTEP
FORMAT (8F10.3)

XSTEP Reaction increments as defined above.

9. REACTION FORMAT (A8)

This input describes the stoichiometry of the elements to be added as a reaction. STEPS input (see above) defines the total number of moles of this reaction to be added. The REACTION input changes the total aqueous concentration of an element by the stoichiometric coefficient (CREAC) times the total moles of reaction (XSTEP). (However, the final total concentration in the reaction solution may also be altered by mass transfer to achieve equilibrium with minerals specified in MINERALS input). It is necessary to consider the charge balance of the reaction which is added. A charge imbalance by an input error, or by intent, is equivalent to adding acid or base. If the reaction is a simulation from a known solution to another known solution, it is possible to add an amount of inert electrical charge equal to the difference in the charge imbalance between the two solutions. In this case, set LREAC(I)=0, CREAC(I)=Δcharge imbalance (equivalents per kilogram $H_2O$). This will eliminate implicit addition of acid or base. However, to add acid or base intentionally, simply add the anion for an acid (such as $Cl^-$ for HCl), or the cation for a base (such as $Na^+$ for NaOH) as a reaction. For the special case of evaporation or dilution to reach a phase boundary, set IOPT(3) = 6, define the phase boundary and appropriate equilibria with MINERALS input and set LREACT(1) = 3, and CREAC(1) = 1.0 (see Test Problem 6). Line 8.a is repeated as often as necessary to read NCOMPS (option line) reaction constituents. REACTION input is required for all changes in temperature, even if no reaction is intended. In this case a null reaction is defined using REACTION and STEPS input (see test problem 4).

9.a. (LREAC(I), CREAC(I), THMEAN(I), I = 1,NCOMPS)
FORMAT 4(I4,2F8.3)

This input defines a net stoichiometric reaction. Four triples of numbers are read on each line. Enough lines must be included to read NCOMPS triples of numbers.

LREAC(I) Index number of element for the reaction.

CREAC(I) Stoichiometric coefficient of the element in the reaction.

THMEAN(I) The operational valence of the element in the reaction. Not used in PHRQPITZ. Read 0.0.

The variables which affect a reaction simulation are IOPT(3), NSTEPS, and NCOMPS from the option line, REACTION input and STEPS input. The following examples use the species index numbers from PHRQPITZ.DATA.

i. Gypsum is added to the initial solution in 5 equal increments of 0.005 moles, to a total of 0.025 moles. Calcite equilibrium is maintained in each of the five steps.

IOPT(3) = 4 (net reaction linearly added).
NSTEPS = 5 (5 reaction steps)
NCOMPS = 2 (2 constituents, Ca and S)
LREAC(1) = 4, CREAC(1) = 1.0 (Ca)
LREAC(2) = 16, CREAC(2) = 1.0 (S)
MINERALS input, calcite.
XSTEP(1) = 0.025 (total moles of reaction to be added)

The total calcium at the completion of the first reaction step is given by:

$$Ca_{tot} = Ca_{tot(initial)} + 0.005 + MIN_{calcite}$$

ii. Suppose mass balance between two solutions shows calcite, gypsum, and dolomite dissolving (+) and precipitating (-) in proportions of -1:1.5:1. The net reaction is written:

| | | | | |
|---|---|---|---|---|
| -1Ca | - 1C | | = | -1 Calcite |
| +1.5Ca | | + 1.5S | = | 1.5 Gypsum |
| +1Ca + 1Mg + 2C | | | = | 1 Dolomite |
| 1.5Ca + 1Mg + 1C | | + 1.5S | = | NET |

Three points along this path are modeled by (arbitrarily) adding $10^{-4}$, $10^{-3}$, and $10^{-2}$ moles of the net reaction.

IOPT(3) = 3 (add net reaction in specified steps)
NSTEPS = 3 (number of steps)
NCOMPS = 4 (number of constituents in reaction)
LREAC(1) = 4 CREAC(1) = 1.5 (Ca)
LREAC(2) = 5 CREAC(2) = 1.0 (Mg)
LREAC(3) = 15 CREAC(3) = 1.0 (C)
LREAC(4) = 16 CREAC(4) = 1.5 (S)
XSTEP(1) = $10^{-4}$, XSTEP(2) = $10^{-3}$, XSTEP(3) = $10^{-2}$.
(Note that reaction increments are in moles, reaction progress is always from the defined solution 1 and is not cumulative)

10. NEUTRAL FORMAT (A8)

This input defines the elements to be used to adjust the initial solution(s) to electrical neutrality. One element with a master species cation and one element with a master species anion are input. $H^+$ (and $e^-$) are not valid entries. A master cation and anion are required in order to add one or the other element according to the charge imbalance. Species are not subtracted, eliminating the possibility of negative total concentrations. This input is required only if IOPT(2) = 2. (Note that this is not equivalent to adding or subtracting charge as discussed in REACTION; remember that IOPT(2) = 0 will maintain an original charge imbalance during a simulation.)

10.a. LPOS, LNEG
FORMAT (2I5)

LPOS Index number of an element with a cation master species. (Right justified.)

LNEG Index number of an element with an anion master species. (Right justified.)

11. SUMS FORMAT (A8)

This input sums molalities of aqueous species which are then printed in the output of the run. These sums do not affect the calculations in any way and are never mandatory. The "sums" are defined by lists of species numbers, so that each time a sequence number for a species is listed, the sum is incremented by the molality of that species. If the species has, for example, two carbonate ions and the total carbonate is the sum which is desired, then the species should be listed twice in that sum. Up to 10 different sums may be defined. Each sum may have up to 50 species. Lines 11.a and 11.b are required for each sum. This input, after all sums have been defined, must be terminated with one blank line.

As in LOOK MIN input, the sums are kept for the duration of the run, but it is possible to add or replace sums or delete the entire set in any single simulation. Any sum input in this data block will be added to the list of sums if the name (SUNAME) is different from all other sum names. A sum with the identical name will replace the sum already in the list. The word DELETE as a sum name will eliminate all the sums known to the computer.

11.a. SUNAME, NSUM
FORMAT (A8,2X,I2)

SUNAME Alphanumeric name to be printed to identify the sum.

NSUM The number of index numbers to be read on line(s) 11.b; NSUM cannot exceed 50. (Right justified.)

11.b. (LSUM(I,J), J = 1,NSUM)
FORMAT (20I4)

List of species numbers to define the sum. Twenty index numbers are read on this line. The line may be repeated as many times as necessary to input NSUM index numbers.

LSUM Index numbers of species in sum. (Right justified.)

Note: repeat lines 11.a and 11.b for each sum.

11.c. Blank line. One blank line at the end of all sums is required to terminate this input.

12. END FORMAT (A8)
This line terminates input operations for a single simulation. Initial solution(s) are computed as directed by the preceding input. Any computer run has at least one END line.

## DESCRIPTION OF PHRQPITZ.DATA FILE

The file PHRQPITZ.DATA contains blocks of KEYWORD information described above under "Description of Input". There is no title or option line in PHRQPITZ.DATA. The file begins with appropriate keywords such as ELEMENTS, SPECIES, LOOK MIN, and MEAN GAM, each with its associated input described above. The PHRQPITZ.DATA file (Attachment A) can be modified as needed to define any other aqueous model or chemical system that can be treated by the specific interaction approach. Data entered in PHRQPITZ.DATA are read automatically by PHRQPITZ and need not be included in the user-defined input file.

The PHRQPITZ.DATA file is read once for a given run (which may contain multiple, successive simulations) and remains in effect throughout the run, unless changed by user-defined input. The PHRQPITZ.DATA file may be changed, deleted, or supplemented by inclusion of appropriate keyword blocks and accompanying modifications in the user-defined input set. See "Description of Input" (above) and Parkhurst and others (1980) for further details.

## DESCRIPTION OF PITZER.DATA FILE

The file PITZER.DATA contains values of all the interaction parameters for the Pitzer model. The current file used with PHRQPITZ is listed in Attachment B. The Pitzer interaction parameters are defined by equations 1-21. The PITZER.DATA file defines all known interactions for the species included in the PHRQPITZ.DATA file (Attachment A). Interactions may be entered in PITZER.DATA only for species defined with appropriate ELEMENTS and SPECIES input in PHRQPITZ.DATA. Unknown values of interaction parameters are defined internally in PHRQPITZ as zero and may not be included in PITZER.DATA. Inclusion of zero values for any interaction parameter (except $\psi$, which is the last block of data read) will result in a read error. Species names used in PITZER.DATA must be exactly as they appear in PHRQPITZ.DATA. The input to PITZER.DATA is defined as follows.

1. SPEC1, IS
   FORMAT (A8,I3)

   SPEC1 — Type the word SPECIES for this variable to identify the input that follows. This variable is not used.

   IS — Total number of individual species in the Pitzer model.

1.a. (NS(I), I = 1,IS)
   FORMAT 18(1X,I3)

   NS — Index number assigned to the aqueous species as defined in PHRQPITZ.DATA. IS values are read and may appear in any order. Lines 1.a. are repeated as needed, provided no blank or zero values are read.

2. This input type contains all single salt interaction parameters and constants for defining their temperature dependence. The first line of this input requires a zero or blank entry for VALUE(1) in columns 21-32 (see description of input given below). The $\beta^{(0)}$ values must begin on the second line of input and continue for as many non-zero values of $\beta^{(0)}$ as to be defined. The second block of parameters contains values for $\beta^{(1)}$ followed by blocks of values for $\beta^{(2)}$ and then $C^{\phi}$. Each of these blocks of parameters must begin with a line containing a blank or zero value for VALUE(1) in columns 21-32. The names B0, B1, B2, and C0 in Attachment B are for identification purposes only and mark lines where zero or blank entries for VALUE(1) are given. The order of data blocks of this type must be $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and $C^{\phi}$. Zero values of the interaction parameters must not be entered unless to denote the beginning of a new data block.

2.a SPEC1, SPEC2, (VALUE(I), I = 1,5)
   FORMAT 2(2X,A8),5(1X,F11.0)

   SPEC1 — Name of the *ith* species exactly as used in PHRQPITZ.DATA for a particular ij cation-anion or anion-cation interaction.

   SPEC2 — Name of the *jth* species exactly as used in PHRQPITZ.DATA for a particular ij cation-anion or anion-cation interaction.

VALUE(I) Coefficients for the temperature dependence of the *pth* single-salt interaction parameter in the form

$$P_{ij} = c_1 + c_2\left(\frac{1}{T} - \frac{1}{T_R}\right) + c_3 \ln\left(\frac{T}{T_R}\right) + c_4(T - T_R) + c_5(T^2 - T_R^2)$$

where $T_R$=298.15, T is temperature in °K and $c_1$-$c_5$ are read as VALUE(I), I=1,5. VALUE(1) (= $c_1$) contains the value of the interaction parameter at the reference temperature. In many cases we only know the first derivative of an interaction parameter with respect to temperature and this then appears in VALUE(4) (= $c_4$).

Subsequent data blocks contain values of $\theta$, $\lambda$, and $\psi$ and, as before, each of these blocks begins with a zero or blank entry for the interaction parameter in VALUE(1). The order of these data blocks must appear as $\theta$, $\lambda$, and $\psi$. Zero or blank values for a given interaction are never required and are not permitted for $\theta$ and $\lambda$ data blocks.

3. Input format for $\theta_{ij}$ and $\lambda_{ij}$. The subscripts ij refer to dissimilar cation-cation or anion-anion pairs for $\theta_{ij}$ and ion-neutral species interactions for $\lambda_{ij}$. PHRQPITZ does not treat $\theta$, $\lambda$ and $\psi$ as functions of temperature. The Block of parameters for $\theta$ must precede the block for $\lambda$. Each block begins with a blank or zero value for VALUE(1).

3.a SPEC1, SPEC2, VALUE(1)
FORMAT 2(2X,A8),1X,F11.0

SPEC1 Name of *ith* species exactly as used in PHRQPITZ.DATA for a particular ij interaction.

SPEC2 Name of *jth* species exactly as used in PHRQPITZ.DATA for a particular ij interaction.

VALUE(1) Value of the parameter at 25 °C. Read a zero or blank entry for VALUE(1) for the first line of each block of input. Caution: as discussed in the text, $\theta_{ij}$ values must be internally consistent with the $\psi_{ijk}$ values, higher-order electrostatic terms and the single salt interaction parameters.

4. This data block contains entries for $\psi_{ijk}$, where ijk refer to dissimilar cation-cation-anion and anion-anion-cation interactions. The first line of data must contain a blank or zero entry for VALUE(1). Zero values of $\psi$ are permitted elsewhere in this block but are not required.

4.a SPEC1, SPEC2, SPEC3, VALUE(1)
FORMAT 3(2X,A8),2X,F10.0

SPEC1 Name of the *ith* species exactly as used in PHRQPITZ.DATA for the particular ijk interaction.

SPEC2 Name of the *jth* species exactly as used in PHRQPITZ.DATA for the particular ijk interaction.

SPEC3 Name of the k*th* species exactly as used in PHRQPITZ.DATA for the particular ijk interaction.

VALUE(1) Value of $\psi_{ijk}$ at 25 °C. Caution: values of $\psi_{ijk}$ must be internally consistent with values of $\theta_{ij}$, higher-order electrostatic terms, and the single-salt parameters (see text).

The final line of the file PITZER.DATA is the last entry of $\psi_{ijk}$.

## TEST PROBLEMS

The test problems that follow are designed to illustrate ways of setting up input sets for a wide range of problems that can be considered by PHRQPITZ. The problems also serve as a basis of comparison when transporting the code to other machines. For each problem the input set is given along with the printed output and a brief explanation. An example illustrating how to make temporary changes to the thermodynamic data base is given elsewhere (Parkhurst and others, 1980).

**Test problem 1: Speciate a brine sample and examine effects of changing activity-coefficient scale.**

This problem demonstrates how to speciate a brine solution for purposes of calculating mineral-water saturation state, activity coefficients, etc. The brine analysis is sample T-93 taken from Frape and others (1984) and is listed in table 5.

Table 5. -- Analytical data for Canadian Shield brine T-93 (mg/L)[1]

| Input # | Parameter | Value |
|---|---|---|
| --- | Temperature °C | 18.0 |
| --- | pH | 5.00 |
| --- | Density | 1.204 |
| 4 | Calcium | 64,000. |
| 5 | Magnesium | 5,100. |
| 6 | Sodium | 45,000. |
| 7 | Potassium | 199. |
| 12 | Strontium | 1,080. |
| 14 | Chloride | 207,000. |
| 15 | Alkalinity ($HCO_3^-$) | 19. |
| 16 | Sulfate | 284. |
| 22 | Bromide | 1,760. |

[1]From Frape and others (1984). Reported silica (4.80 mg/L $SiO_2$) not included.

In addition to examining the speciation calculation, this test problem demonstrates the significance of uncertainties in activity-coefficient scale on the predicted saturation state, particularly as they apply to the carbonate system. The problem is in 4 parts. In parts 1a and 1b the analysis of table 5 is speciated on the MacInnes scale, and unscaled, respectively, using the measured pH. Parts 1c and 1d attempt to resolve uncertainties in the carbonate system by assuming the water of table 5 is in equilibrium with calcite, on the MacInnes scale and unscaled, respectively. This procedure is preferable to alternate means of defining pH, such as through charge balance (using IOPT(2) = 1) owing to uncertainties in the analytical data. However, as we shall see, the analytical data are insufficient to fully resolve uncertainties in the carbonate system due to activity-coefficient scale.

The input data set for all four parts is listed in table 6. In all cases, the starting solution is as given in table 5, and IOPT(2) = 0 which retains the analytical charge imbalance (-0.30305 eq/kg $H_2O$) throughout the calculations. Consequently, it is not necessary to adjust the initial solution composition to obtain charge balance. Because total inorganic carbon is calculated from pH and alkalinity, it is theoretically impossible to adjust pH to obtain charge balance. In parts 1a and 1b IOPT(3) = 0 which indicates that SOLUTION 1 will be speciated only. IOPT(3) is 6 in parts 1c and 1d indicating that after speciation, an irreversible reaction will be added (or removed) to solution 1 to obtain equilibrium with one or more minerals. IOPT(6) is set to 2 indicating that the Pitzer equations will be used (no other choices are currently available). In parts 1a and 1c IOPT(10) is 1 which causes all activity coefficients to be scaled according to the MacInnes convention. IOPT(10) is 0 in parts 1b and 1d for unscaled activity

Table 6. -- Line images of the input file to test problem 1

```
Test Problem 1a:  Canadian Shield Brine T-93; Frape et al., 1984, Alk+Mac Scale
0000020001 0 0       0.0
ELEMENTS
C          15   61.0171

SOLUTION 1
Canadian Shield Brine T-93.
 9 15 2   5.         4.0      18.       1.204
   464000.        645000.        55100.         7199.         121080.
  14207000.      221760.        16284.         1519.
END
Test Problem 1b:  Canadian Shield Brine T-93; Frape et al., 1984, Alk + No scale
0000020000 0 0       0.0
ELEMENTS
C          15   61.0171

SOLUTION 1
Canadian Shield Brine T-93.
 9 15 2   5.         4.0      18.       1.204
   464000.        645000.        55100.         7199.         121080.
  14207000.      221760.        16284.         1519.
END
Test Problem 1c:  Canadian Shield Brine T-93; Frape et al., 1984, calcite + Mac
0060020001 0 1       0.0
ELEMENTS
C          15   61.0171

SOLUTION 1
Canadian Shield Brine T-93.
 9 15 2   5.         4.0      18.       1.204
   464000.        645000.        55100.         7199.         121080.
  14207000.      221760.        16284.         1519.
MINERALS
CALCITE    2          4.00   -8.406              1
  15 1.0          4 1.0
-171.8329   -.077993    2839.319    71.595

REACTION
  151.0     4.0
END
Test Problem 1d: Canadian Shield Brine T-93, calcite equil. No scale
0060020000 0 1       0.0
ELEMENTS
C          15   61.0171

SOLUTION 1
Canadian Shield Brine T-93.
 9 15 2   5.         4.0      18.       1.204
   464000.        645000.        55100.         7199.         121080.
  14207000.      221760.        16284.         1519.
MINERALS
CALCITE    2          4.00   -8.406              1
  15 1.0          4 1.0
-171.8329   -.077993    2839.319    71.595
```

```
REACTION
  151.0      4.0
END
```

coefficients. ELEMENTS input is used to redefine the molecular weight of the carbon input species from that of $CO_2$ (default in PHRQPITZ.DATA) to that of $HCO_3^-$ for input of total alkalinity as $HCO_3^-$ (table 5). The new molecular weight of the carbon input species is used internally during execution and not retained in PHRQPITZ.DATA. Permanent changes to PHRQPITZ.DATA must be made through normal editing procedures. MINERALS input is included in parts 1c and 1d to establish equilibrium with calcite, and REACTION input is used to adjust the total inorganic carbon content to establish calcite equilibrium.

The output for test problems 1a - 1d is listed in table 7. The output formats have been adjusted to accommodate screen widths of 80 characters. The printed output first lists all input to PHRQPITZ. The first 4 keywords printed (table 7), ELEMENTS, SPECIES, LOOK MIN, MEAN GAM were printed as appropriate data from PHRQPITZ.DATA were read. Computed output begins with a print of the total molalities of all elements in SOLUTION 1 followed by a description of the solution and distribution of species. Computed variables under "Description of Solution" include the activity of $H_2O$, osmotic coefficient, ionic strength, pressure (in atmospheres) along the vapor pressure line of pure water (if temperature is greater than 100 °C), the density of pure water at the given temperature and pressure, the electrical imbalance (in equivalents per kilogram $H_2O$), and the total concentration of inorganic carbon (moles per kg $H_2O$).

The molality, activity, and activity coefficient (and log values) of all aqueous species in the PHRQPITZ.DATA file for which an input concentration was given are listed under the "Distribution of Species". This output is followed by tables of total molalities, activities, activity coefficients, mean activity coefficients, and saturation indices. The saturation indices are given under the heading LOOK MIN IAP as log(IAP/KT). This output is repeated in part 1b for unscaled results.

In parts 1c and 1d the equilibration step (with calcite) appears under the heading "STEP NUMBER 1". The total molalities of the elements are printed first before the total molality of inorganic carbon is adjusted to bring the solution to equilibrium with calcite. The calcite mass transfer given under the heading "PHASE BOUNDARIES" is zero indicating that calcite has neither been dissolved or precipitated. The moles of inorganic carbon added or removed from the solution to reach calcite saturation follows. This is followed by an updated print of the saturation indices, revised total molalities, "Description of Solution", etc.

The results of test problem 1 are useful in illustrating some of the problems in making speciation calculations with the measured pH. Examination of the output from parts 1a and 1b (table 7) shows that for the same brine analysis, the saturation indices of calcite and dolomite vary, respectively, from -0.31 and -1.08 (MacInnes scale) to +0.16 and -0.13 (unscaled). The computed total concentration of inorganic carbon and log $PCO_2$, which is based on the pH and alkalinity measurements, varies from 32.43 mmol/kg $H_2O$ and 0.379 (MacInnes scale) to 10.25 mmol/kg $H_2O$ and -0.13 (unscaled), respectively. This is a change of more than 300 percent for these variables. Because total inorganic carbon, total alkalinity, and $PCO_2$ can be measured within ten percent or better in many brines, the thermodynamics of the carbonate system in this brine would be better defined by measuring total alkalinity and either total inorganic carbon or $PCO_2$. If such data are available, the carbonate system is unambiguously defined and independent of the measured pH and choice of scale convention. A value of pH would then be defined by the aqueous model according to any particular choice in activity-coefficient scale.

As a means of examining possible variations in the pH of brine T-93 (table 5), and in the absence of total inorganic carbon or $PCO_2$ data, the solution was equilibrated with calcite on both activity-coefficient scales (parts 1c and 1d) by adjusting the total inorganic carbon content. This caused outgassing (MacInnes scale) and ingassing (unscaled) of $CO_2$ to reach calcite saturation. The results suggest that pH could vary as much as 0.5 between the two scales. The carbonate system is more closely defined, as evidenced by the similarity in the calculated $PCO_2$ and total inorganic carbon. The total inorganic carbon and $PCO_2$ are not in complete agreement because of the inconsistency of the measured pH (5.00) with either scale. This inconsistency can be resolved only if total inorganic carbon or $PCO_2$ is measured in conjunction with the total alkalinity measurement.

Table 7. -- Listing of printout from test problem 1

```
         DATA READ FROM DISK

 ELEMENTS
 SPECIES
 LOOK MIN
 MEAN GAM
1Test Problem 1a:  Canadian Shield Brine T-93; Frape et al., 1984, Alk+Mac Scale
 0000020001 0 0          0.00000
 ELEMENTS
 C           15         0.61017E+02
              0         0.00000E+00
 SOLUTION 1
 Canadian Shield Brine T-93.
  9 15 2     5.00       4.00       18.0       1.20
    4  6.400D+04   6  4.500D+04   5  5.100D+03   7  1.990D+02  12  1.080D+03
   14  2.070D+05  22  1.760D+03  16  2.840D+02  15  1.900D+01
1SOLUTION NUMBER 1
 Canadian Shield Brine T-93.
```

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.815465D+00 | 0.2590 |
| MG | 2.385668D-01 | -0.6224 |
| NA | 2.225424D+00 | 0.3474 |
| K | 5.786697D-03 | -2.2376 |
| SR | 1.401380D-02 | -1.8534 |
| CL | 6.638239D+00 | 0.8221 |
| TOT ALK | 3.540280D-04 | -3.4510 |
| S | 3.361331D-03 | -2.4735 |
| BR | 2.504262D-02 | -1.6013 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 5.0000 |
| ACTIVITY H2O = | 0.7208 |
| OSMOTIC COEFFICIENT = | 1.6522 |
| IONIC STRENGTH = | 8.5902 |
| TEMPERATURE = | 18.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9986 G/CC |
| ELECTRICAL BALANCE = | -3.0305D-01 |
| TOTAL ALKALINITY = | 3.5403D-04 |
| ITERATIONS = | 5 |
| TOTAL CARBON = | 3.2432D-02 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | MACINNES SCALE ACTIVITY | MACINNES SCALE LOG ACT | MACINNES SCALE GAMMA | MACINNES SCALE LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 7.997E-06 | -5.097 | 1.000E-05 | -5.000 | 1.251E+00 | 0.097 |
| 3 | H2O | 0.0 | 7.208E-01 | -0.142 | 7.208E-01 | -0.142 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 1.815E+00 | 0.259 | 1.783E-01 | -0.749 | 9.823E-02 | -1.008 |
| 5 | MG+2 | 2.0 | 2.386E-01 | -0.622 | 4.144E-02 | -1.383 | 1.737E-01 | -0.760 |
| 6 | NA+ | 1.0 | 2.225E+00 | 0.347 | 6.252E-01 | -0.204 | 2.809E-01 | -0.551 |
| 7 | K+ | 1.0 | 5.787E-03 | -2.238 | 5.991E-04 | -3.222 | 1.035E-01 | -0.985 |
| 12 | SR+2 | 2.0 | 1.401E-02 | -1.853 | 7.035E-04 | -3.153 | 5.020E-02 | -1.299 |
| 14 | CL- | -1.0 | 6.638E+00 | 0.822 | 4.263E+01 | 1.630 | 6.422E+00 | 0.808 |
| 15 | CO3-2 | -2.0 | 3.764E-07 | -6.424 | 1.169E-08 | -7.932 | 3.106E-02 | -1.508 |
| 16 | SO4-2 | -2.0 | 3.361E-03 | -2.474 | 5.503E-04 | -3.259 | 1.637E-01 | -0.786 |
| 22 | BR- | -1.0 | 2.504E-02 | -1.601 | 2.389E-01 | -0.622 | 9.539E+00 | 0.979 |
| 31 | OH- | -1.0 | 1.797E-09 | -8.745 | 4.213E-10 | -9.375 | 2.345E-01 | -0.630 |
| 34 | HCO3- | -1.0 | 3.473E-04 | -3.459 | 2.980E-03 | -2.526 | 8.581E+00 | 0.934 |
| 35 | H2CO3 | 0.0 | 3.208E-02 | -1.494 | 9.948E-02 | -1.002 | 3.101E+00 | 0.491 |
| 40 | HSO4- | -1.0 | 9.753E-08 | -7.011 | 4.326E-07 | -6.364 | 4.436E+00 | 0.647 |
| 76 | CACO3 | 0.0 | 2.615E-06 | -5.583 | 2.615E-06 | -5.583 | 1.000E+00 | 0.000 |
| 85 | MGOH+ | 1.0 | 3.780E-08 | -7.423 | 2.480E-09 | -8.605 | 6.563E-02 | -1.183 |
| 86 | MGCO3 | 0.0 | 3.718E-07 | -6.430 | 3.718E-07 | -6.430 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | MACINNES ACTIVITY | MACINNES TOTAL GAMMA |
|---|---|---|---|
| H+ | 8.0943D-06 | 1.0000D-05 | 1.2354D+00 |
| CA+2 | 1.8155D+00 | 1.7834D-01 | 9.8232D-02 |
| MG+2 | 2.3857D-01 | 4.1441D-02 | 1.7371D-01 |
| NA+ | 2.2254D+00 | 6.2518D-01 | 2.8092D-01 |
| K+ | 5.7867D-03 | 5.9913D-04 | 1.0354D-01 |
| SR+2 | 1.4014D-02 | 7.0352D-04 | 5.0202D-02 |
| CL- | 6.6382D+00 | 4.2630D+01 | 6.4219D+00 |
| CO3-2 | 3.3633D-06 | 1.1691D-08 | 3.4761D-03 |
| SO4-2 | 3.3612D-03 | 5.5030D-04 | 1.6372D-01 |
| BR- | 2.5043D-02 | 2.3887D-01 | 9.5386D+00 |
| OH- | 3.9592D-08 | 4.2135D-10 | 1.0642D-02 |
| HCO3- | 3.4726D-04 | 2.9799D-03 | 8.5812D+00 |
| H2CO3 | 3.2081D-02 | 9.9484D-02 | 3.1010D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 1.5941D+00 |
| CASO4 | 1.2682D-01 |
| CACO3 | 1.8479D-02 |
| CA(OH)2 | 2.2324D-02 |
| MGCL2 | 1.9277D+00 |

| | |
|---|---|
| MGSO4 | 1.6864D-01 |
| MGCO3 | 2.4573D-02 |
| MG(OH)2 | 2.6995D-02 |
| NACL | 1.3432D+00 |
| NA2SO4 | 2.3465D-01 |
| NAHCO3 | 1.5526D+00 |
| NA2CO3 | 6.4976D-02 |
| NAOH | 5.4677D-02 |
| KCL | 8.1542D-01 |
| K2SO4 | 1.2062D-01 |
| KHCO3 | 9.4258D-01 |
| K2CO3 | 3.3401D-02 |
| KOH | 3.3194D-02 |
| HCL | 2.8167D+00 |
| H2SO4 | 6.2987D-01 |
| HBR | 3.4329D+00 |

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ANHYDRIT | -4.0082 | -4.3239 | 0.3157 |
| ARAGONIT | -8.6809 | -8.1781 | -0.5028 |
| ARCANITE | -9.7044 | -1.8866 | -7.8178 |
| BISCHOFI | 1.0238 | 4.4775 | -3.4536 |
| BLOEDITE | -8.8781 | -2.3470 | -6.5311 |
| BRUCITE | -20.1333 | -10.8990 | -9.2343 |
| BURKEITE | -15.6749 | -0.7720 | -14.9029 |
| CALCITE | -8.6809 | -8.3700 | -0.3109 |
| CARNALLI | -0.5689 | 4.3300 | -4.8989 |
| DOLOMITE | -17.9956 | -16.9167 | -1.0789 |
| EPSOMITE | -5.6372 | -1.9674 | -3.6698 |
| GAYLUSSI | -17.7319 | -9.4210 | -8.3109 |
| GLASERIT | -16.3902 | -3.8030 | -12.5872 |
| GLAUBERI | -7.6756 | -5.2450 | -2.4306 |
| GYPSUM | -4.2925 | -4.5834 | 0.2909 |
| HALITE | 1.4257 | 1.5574 | -0.1317 |
| HEXAHYDR | -5.4950 | -1.7161 | -3.7789 |
| KAINITE | -6.6613 | -0.1930 | -6.4683 |
| KALICINI | -16.1546 | -10.0580 | -6.0966 |
| KIESERIT | -4.7841 | -0.1230 | -4.6611 |
| LABILE S | -11.6273 | -5.6720 | -5.9553 |
| LEONHARD | -5.2107 | -0.8870 | -4.3237 |
| LEONITE | -14.9150 | -3.9790 | -10.9360 |
| MAGNESIT | -9.3147 | -7.7253 | -1.5894 |
| MIRABIL | -5.0891 | -1.5459 | -3.5432 |
| MISENITE | -78.5956 | -10.8060 | -67.7896 |
| NAHCOLIT | -13.1361 | -10.7420 | -2.3941 |
| NATRON | -9.7619 | -0.8250 | -8.9369 |
| NESQUEHO | -9.7412 | -5.1670 | -4.5742 |
| PCO2 | -1.0022 | -1.3811 | 0.3788 |
| PENTAHYD | -5.3528 | -1.2850 | -4.0678 |
| PIRSSONI | -17.3054 | -9.2340 | -8.0714 |
| POLYHALI | -22.6470 | -13.7440 | -8.9030 |
| PORTLAND | -19.4995 | -5.1900 | -14.3095 |

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              SCHOENIT      -15.1994      -4.3280      -10.8714
              SYLVITE        -1.5928       0.8257       -2.4184
              SYNGENIT      -13.8547      -7.4480       -6.4067
              TRONA         -21.7606     -11.3840      -10.3766
1Test Problem 1b:  Canadian Shield Brine T-93; Frape et al., 1984, Alk + No scal
 0000020000 0 0          0.00000
 ELEMENTS
 C           15         0.61017E+02
              0         0.00000E+00
 SOLUTION 1
 Canadian Shield Brine T-93.
  9 15 2      5.00       4.00       18.0       1.20
    4  6.400D+04   6  4.500D+04   5  5.100D+03   7  1.990D+02  12  1.080D+03
   14  2.070D+05  22  1.760D+03  16  2.840D+02  15  1.900D+01
1SOLUTION NUMBER 1
 Canadian Shield Brine T-93.
```

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.815465D+00 | 0.2590 |
| MG | 2.385668D-01 | -0.6224 |
| NA | 2.225424D+00 | 0.3474 |
| K | 5.786697D-03 | -2.2376 |
| SR | 1.401380D-02 | -1.8534 |
| CL | 6.638239D+00 | 0.8221 |
| TOT ALK | 3.540280D-04 | -3.4510 |
| S | 3.361331D-03 | -2.4735 |
| BR | 2.504262D-02 | -1.6013 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 5.0000 |
| ACTIVITY H2O = | 0.7214 |
| OSMOTIC COEFFICIENT = | 1.6512 |
| IONIC STRENGTH = | 8.5902 |
| TEMPERATURE = | 18.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9986 G/CC |
| ELECTRICAL BALANCE = | -3.0305D-01 |
| TOTAL ALKALINITY = | 3.5403D-04 |
| ITERATIONS = | 5 |
| TOTAL CARBON = | 1.0249D-02 |

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DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | UNSCALED LOG ACT | UNSCALED GAMMA | UNSCALED LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 2.570E-06 | -5.590 | 1.000E-05 | -5.000 | 3.891E+00 | 0.590 |
| 3 | H2O | 0.0 | 7.214E-01 | -0.142 | 7.214E-01 | -0.142 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 1.815E+00 | 0.259 | 1.713E+00 | 0.234 | 9.435E-01 | -0.025 |
| 5 | MG+2 | 2.0 | 2.386E-01 | -0.622 | 3.980E-01 | -0.400 | 1.668E+00 | 0.222 |
| 6 | NA+ | 1.0 | 2.225E+00 | 0.347 | 1.937E+00 | 0.287 | 8.703E-01 | -0.060 |
| 7 | K+ | 1.0 | 5.787E-03 | -2.238 | 1.860E-03 | -2.730 | 3.214E-01 | -0.493 |
| 12 | SR+2 | 2.0 | 1.401E-02 | -1.853 | 6.812E-03 | -2.167 | 4.861E-01 | -0.313 |
| 14 | CL- | -1.0 | 6.638E+00 | 0.822 | 1.370E+01 | 1.137 | 2.064E+00 | 0.315 |
| 15 | CO3-2 | -2.0 | 1.126E-06 | -5.948 | 3.613E-09 | -8.442 | 3.208E-03 | -2.494 |
| 16 | SO4-2 | -2.0 | 3.361E-03 | -2.473 | 5.659E-05 | -4.247 | 1.684E-02 | -1.774 |
| 22 | BR- | -1.0 | 2.504E-02 | -1.601 | 7.677E-02 | -1.115 | 3.065E+00 | 0.486 |
| 31 | OH- | -1.0 | 5.596E-09 | -8.252 | 4.217E-10 | -9.375 | 7.536E-02 | -1.123 |
| 34 | HCO3- | -1.0 | 3.339E-04 | -3.476 | 9.209E-04 | -3.036 | 2.758E+00 | 0.441 |
| 35 | H2CO3 | 0.0 | 9.905E-03 | -2.004 | 3.072E-02 | -1.513 | 3.101E+00 | 0.491 |
| 40 | HSO4- | -1.0 | 3.120E-08 | -7.506 | 4.449E-08 | -7.352 | 1.426E+00 | 0.154 |
| 76 | CACO3 | 0.0 | 7.762E-06 | -5.110 | 7.762E-06 | -5.110 | 1.000E+00 | 0.000 |
| 85 | MGOH+ | 1.0 | 1.168E-07 | -6.933 | 2.384E-08 | -7.623 | 2.042E-01 | -0.690 |
| 86 | MGCO3 | 0.0 | 1.103E-06 | -5.957 | 1.103E-06 | -5.957 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 2.6011D-06 | 1.0000D-05 | 3.8446D+00 |
| CA+2 | 1.8155D+00 | 1.7128D+00 | 9.4345D-01 |
| MG+2 | 2.3857D-01 | 3.9802D-01 | 1.6684D+00 |
| NA+ | 2.2254D+00 | 1.9368D+00 | 8.7029D-01 |
| K+ | 5.7867D-03 | 1.8601D-03 | 3.2145D-01 |
| SR+2 | 1.4014D-02 | 6.8121D-03 | 4.8610D-01 |
| CL- | 6.6382D+00 | 1.3703D+01 | 2.0642D+00 |
| CO3-2 | 9.9913D-06 | 3.6128D-09 | 3.6160D-04 |
| SO4-2 | 3.3613D-03 | 5.6590D-05 | 1.6836D-02 |
| BR- | 2.5043D-02 | 7.6765D-02 | 3.0654D+00 |
| OH- | 1.2235D-07 | 4.2171D-10 | 3.4466D-03 |
| HCO3- | 3.3392D-04 | 9.2086D-04 | 2.7577D+00 |
| H2CO3 | 9.9054D-03 | 3.0716D-02 | 3.1010D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 1.5901D+00 |
| CASO4 | 1.2603D-01 |
| CACO3 | 1.8470D-02 |
| CA(OH)2 | 2.2379D-02 |
| MGCL2 | 1.9228D+00 |
| MGSO4 | 1.6760D-01 |
| MGCO3 | 2.4562D-02 |
| MG(OH)2 | 2.7062D-02 |
| NACL | 1.3403D+00 |

| | |
|---|---|
| NA2SO4 | 2.3363D-01 |
| NAHCO3 | 1.5492D+00 |
| NA2CO3 | 6.4941D-02 |
| NAOH | 5.4768D-02 |
| KCL | 8.1458D-01 |
| K2SO4 | 1.2027D-01 |
| KHCO3 | 9.4152D-01 |
| K2CO3 | 3.3431D-02 |
| KOH | 3.3285D-02 |
| HCL | 2.8171D+00 |
| H2SO4 | 6.2899D-01 |
| HBR | 3.4329D+00 |

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ANHYDRIT | -4.0136 | -4.3239 | 0.3103 |
| ARAGONIT | -8.2084 | -8.1781 | -0.0303 |
| ARCANITE | -9.7082 | -1.8866 | -7.8216 |
| BISCHOFI | 1.0227 | 4.4775 | -3.4548 |
| BLOEDITE | -8.8877 | -2.3470 | -6.5407 |
| BRUCITE | -19.1501 | -10.8990 | -8.2511 |
| BURKEITE | -15.2142 | -0.7720 | -14.4422 |
| CALCITE | -8.2084 | -8.3700 | 0.1616 |
| CARNALLI | -0.5709 | 4.3300 | -4.9009 |
| DOLOMITE | -17.0507 | -16.9167 | -0.1340 |
| EPSOMITE | -5.6400 | -1.9674 | -3.6726 |
| GAYLUSSI | -16.7855 | -9.4210 | -7.3645 |
| GLASERIT | -16.3988 | -3.8030 | -12.5958 |
| GLAUBERI | -7.6867 | -5.2450 | -2.4417 |
| GYPSUM | -4.2972 | -4.5834 | 0.2863 |
| HALITE | 1.4239 | 1.5574 | -0.1336 |
| HEXAHYDR | -5.4982 | -1.7161 | -3.7821 |
| KAINITE | -6.6664 | -0.1930 | -6.4734 |
| KALICINI | -16.1726 | -10.0580 | -6.1146 |
| KIESERIT | -4.7892 | -0.1230 | -4.6662 |
| LABILE S | -11.6434 | -5.6720 | -5.9714 |
| LEONHARD | -5.2146 | -0.8870 | -4.3276 |
| LEONITE | -14.9228 | -3.9790 | -10.9438 |
| MAGNESIT | -8.8423 | -7.7253 | -1.1170 |
| MIRABIL | -5.0911 | -1.5459 | -3.5452 |
| MISENITE | -81.5745 | -10.8060 | -70.7685 |
| NAHCOLIT | -13.1551 | -10.7420 | -2.4131 |
| NATRON | -9.2860 | -0.8250 | -8.4610 |
| NESQUEHO | -9.2677 | -5.1670 | -4.1007 |
| PCO2 | -1.5126 | -1.3811 | -0.1316 |
| PENTAHYD | -5.3564 | -1.2850 | -4.0714 |
| PIRSSONI | -16.3601 | -9.2340 | -7.1261 |
| POLYHALI | -22.6662 | -13.7440 | -8.9222 |
| PORTLAND | -18.5163 | -5.1900 | -13.3263 |
| SCHOENIT | -15.2064 | -4.3280 | -10.8784 |
| SYLVITE | -1.5936 | 0.8257 | -2.4193 |
| SYNGENIT | -13.8635 | -7.4480 | -6.4155 |
| TRONA | -21.3067 | -11.3840 | -9.9227 |

```
1Test Problem 1c:  Canadian Shield Brine T-93; Frape et al., 1984, calcite + Mac
 0060020001 0 1          0.00000
 ELEMENTS
 C           15         0.61017E+02
              0         0.00000E+00
 SOLUTION 1
 Canadian Shield Brine T-93.
  9 15 2     5.00       4.00       18.0       1.20
    4  6.400D+04   6  4.500D+04   5  5.100D+03   7  1.990D+02  12  1.080D+03
   14  2.070D+05  22  1.760D+03  16  2.840D+02  15  1.900D+01
 MINERALS
 CALCITE    2       4.0       -8.4       0.00          1               0.000
   15   1.00        4   1.00
  -1.7183E+02 -7.7993E-02  2.8393E+03  7.1595E+01  0.0000E-01
            0     0.00       0.00       0.00          0               0.000
 REACTION
   15   1.000   4.000
1SOLUTION NUMBER 1
 Canadian Shield Brine T-93.
```

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.815465D+00 | 0.2590 |
| MG | 2.385668D-01 | -0.6224 |
| NA | 2.225424D+00 | 0.3474 |
| K | 5.786697D-03 | -2.2376 |
| SR | 1.401380D-02 | -1.8534 |
| CL | 6.638239D+00 | 0.8221 |
| TOT ALK | 3.540280D-04 | -3.4510 |
| S | 3.361331D-03 | -2.4735 |
| BR | 2.504262D-02 | -1.6013 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 5.0000 |
| ACTIVITY H2O = | 0.7208 |
| OSMOTIC COEFFICIENT = | 1.6522 |
| IONIC STRENGTH = | 8.5902 |
| TEMPERATURE = | 18.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9986 G/CC |
| ELECTRICAL BALANCE = | -3.0305D-01 |
| TOTAL ALKALINITY = | 3.5403D-04 |
| ITERATIONS = | 5 |
| TOTAL CARBON = | 3.2432D-02 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | MACINNES SCALE ACTIVITY | MACINNES SCALE LOG ACT | MACINNES SCALE GAMMA | MACINNES SCALE LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 7.997E-06 | -5.097 | 1.000E-05 | -5.000 | 1.251E+00 | 0.097 |
| 3 | H2O | 0.0 | 7.208E-01 | -0.142 | 7.208E-01 | -0.142 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 1.815E+00 | 0.259 | 1.783E-01 | -0.749 | 9.823E-02 | -1.008 |
| 5 | MG+2 | 2.0 | 2.386E-01 | -0.622 | 4.144E-02 | -1.383 | 1.737E-01 | -0.760 |
| 6 | NA+ | 1.0 | 2.225E+00 | 0.347 | 6.252E-01 | -0.204 | 2.809E-01 | -0.551 |
| 7 | K+ | 1.0 | 5.787E-03 | -2.238 | 5.991E-04 | -3.222 | 1.035E-01 | -0.985 |
| 12 | SR+2 | 2.0 | 1.401E-02 | -1.853 | 7.035E-04 | -3.153 | 5.020E-02 | -1.299 |
| 14 | CL- | -1.0 | 6.638E+00 | 0.822 | 4.263E+01 | 1.630 | 6.422E+00 | 0.808 |
| 15 | CO3-2 | -2.0 | 3.764E-07 | -6.424 | 1.169E-08 | -7.932 | 3.106E-02 | -1.508 |
| 16 | SO4-2 | -2.0 | 3.361E-03 | -2.474 | 5.503E-04 | -3.259 | 1.637E-01 | -0.786 |
| 22 | BR- | -1.0 | 2.504E-02 | -1.601 | 2.389E-01 | -0.622 | 9.539E+00 | 0.979 |
| 31 | OH- | -1.0 | 1.797E-09 | -8.745 | 4.213E-10 | -9.375 | 2.345E-01 | -0.630 |
| 34 | HCO3- | -1.0 | 3.473E-04 | -3.459 | 2.980E-03 | -2.526 | 8.581E+00 | 0.934 |
| 35 | H2CO3 | 0.0 | 3.208E-02 | -1.494 | 9.948E-02 | -1.002 | 3.101E+00 | 0.491 |
| 40 | HSO4- | -1.0 | 9.753E-08 | -7.011 | 4.326E-07 | -6.364 | 4.436E+00 | 0.647 |
| 76 | CACO3 | 0.0 | 2.615E-06 | -5.583 | 2.615E-06 | -5.583 | 1.000E+00 | 0.000 |
| 85 | MGOH+ | 1.0 | 3.780E-08 | -7.423 | 2.480E-09 | -8.605 | 6.563E-02 | -1.183 |
| 86 | MGCO3 | 0.0 | 3.718E-07 | -6.430 | 3.718E-07 | -6.430 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | MACINNES ACTIVITY | MACINNES TOTAL GAMMA |
|---|---|---|---|
| H+ | 8.0943D-06 | 1.0000D-05 | 1.2354D+00 |
| CA+2 | 1.8155D+00 | 1.7834D-01 | 9.8232D-02 |
| MG+2 | 2.3857D-01 | 4.1441D-02 | 1.7371D-01 |
| NA+ | 2.2254D+00 | 6.2518D-01 | 2.8092D-01 |
| K+ | 5.7867D-03 | 5.9913D-04 | 1.0354D-01 |
| SR+2 | 1.4014D-02 | 7.0352D-04 | 5.0202D-02 |
| CL- | 6.6382D+00 | 4.2630D+01 | 6.4219D+00 |
| CO3-2 | 3.3633D-06 | 1.1691D-08 | 3.4761D-03 |
| SO4-2 | 3.3612D-03 | 5.5030D-04 | 1.6372D-01 |
| BR- | 2.5043D-02 | 2.3887D-01 | 9.5386D+00 |
| OH- | 3.9592D-08 | 4.2135D-10 | 1.0642D-02 |
| HCO3- | 3.4726D-04 | 2.9799D-03 | 8.5812D+00 |
| H2CO3 | 3.2081D-02 | 9.9484D-02 | 3.1010D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 1.5941D+00 |
| CASO4 | 1.2682D-01 |
| CACO3 | 1.8479D-02 |
| CA(OH)2 | 2.2324D-02 |
| MGCL2 | 1.9277D+00 |
| MGSO4 | 1.6864D-01 |

| | |
|---|---|
| MGCO3 | 2.4573D-02 |
| MG(OH)2 | 2.6995D-02 |
| NACL | 1.3432D+00 |
| NA2SO4 | 2.3465D-01 |
| NAHCO3 | 1.5526D+00 |
| NA2CO3 | 6.4976D-02 |
| NAOH | 5.4677D-02 |
| KCL | 8.1542D-01 |
| K2SO4 | 1.2062D-01 |
| KHCO3 | 9.4258D-01 |
| K2CO3 | 3.3401D-02 |
| KOH | 3.3194D-02 |
| HCL | 2.8167D+00 |
| H2SO4 | 6.2987D-01 |
| HBR | 3.4329D+00 |

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ANHYDRIT | -4.0082 | -4.3239 | 0.3157 |
| ARAGONIT | -8.6809 | -8.1781 | -0.5028 |
| ARCANITE | -9.7044 | -1.8866 | -7.8178 |
| BISCHOFI | 1.0238 | 4.4775 | -3.4536 |
| BLOEDITE | -8.8781 | -2.3470 | -6.5311 |
| BRUCITE | -20.1333 | -10.8990 | -9.2343 |
| BURKEITE | -15.6749 | -0.7720 | -14.9029 |
| CALCITE | -8.6809 | -8.3700 | -0.3109 |
| CARNALLI | -0.5689 | 4.3300 | -4.8989 |
| DOLOMITE | -17.9956 | -16.9167 | -1.0789 |
| EPSOMITE | -5.6372 | -1.9674 | -3.6698 |
| GAYLUSSI | -17.7319 | -9.4210 | -8.3109 |
| GLASERIT | -16.3902 | -3.8030 | -12.5872 |
| GLAUBERI | -7.6756 | -5.2450 | -2.4306 |
| GYPSUM | -4.2925 | -4.5834 | 0.2909 |
| HALITE | 1.4257 | 1.5574 | -0.1317 |
| HEXAHYDR | -5.4950 | -1.7161 | -3.7789 |
| KAINITE | -6.6613 | -0.1930 | -6.4683 |
| KALICINI | -16.1546 | -10.0580 | -6.0966 |
| KIESERIT | -4.7841 | -0.1230 | -4.6611 |
| LABILE S | -11.6273 | -5.6720 | -5.9553 |
| LEONHARD | -5.2107 | -0.8870 | -4.3237 |
| LEONITE | -14.9150 | -3.9790 | -10.9360 |
| MAGNESIT | -9.3147 | -7.7253 | -1.5894 |
| MIRABIL | -5.0891 | -1.5459 | -3.5432 |
| MISENITE | -78.5956 | -10.8060 | -67.7896 |
| NAHCOLIT | -13.1361 | -10.7420 | -2.3941 |
| NATRON | -9.7619 | -0.8250 | -8.9369 |
| NESQUEHO | -9.7412 | -5.1670 | -4.5742 |
| PCO2 | -1.0022 | -1.3811 | 0.3788 |
| PENTAHYD | -5.3528 | -1.2850 | -4.0678 |
| PIRSSONI | -17.3054 | -9.2340 | -8.0714 |
| POLYHALI | -22.6470 | -13.7440 | -8.9030 |
| PORTLAND | -19.4995 | -5.1900 | -14.3095 |
| SCHOENIT | -15.1994 | -4.3280 | -10.8714 |

| | | | |
|---|---|---|---|
| SYLVITE | -1.5928 | 0.8257 | -2.4184 |
| SYNGENIT | -13.8547 | -7.4480 | -6.4067 |
| TRONA | -21.7606 | -11.3840 | -10.3766 |

1STEP NUMBER 1
0----------

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.815465D+00 | 0.2590 |
| MG | 2.385668D-01 | -0.6224 |
| NA | 2.225424D+00 | 0.3474 |
| K | 5.786697D-03 | -2.2376 |
| SR | 1.401380D-02 | -1.8534 |
| CL | 6.638239D+00 | 0.8221 |
| TOT ALK | 3.243193D-02 | -1.4890 |
| S | 3.361331D-03 | -2.4735 |
| BR | 2.504262D-02 | -1.6013 |

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| CALCITE | 0.000000D-01 | -8.3700 | -8.3700 | 0.0000 |

+ **

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

** -1.752259D-02 MOLES OF REACTION HAVE BEEN ADDED TO THE SOLUTION
TO REACH THE CALCITE PHASE BOUNDARY.

REACTION IS:
1.000000 MOLES OF C VALENCE = 4.000

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ANHYDRIT | -4.0124 | -4.3239 | 0.3115 |
| ARAGONIT | -8.3700 | -8.1781 | -0.1919 |
| ARCANITE | -9.7074 | -1.8866 | -7.8208 |
| BISCHOFI | 1.0229 | 4.4775 | -3.4545 |
| BLOEDITE | -8.8857 | -2.3470 | -6.5387 |
| BRUCITE | -19.4792 | -10.8990 | -8.5803 |

| | | | |
|---|---|---|---|
| BURKEITE | -15.3733 | -0.7720 | -14.6013 |
| CALCITE | -8.3700 | -8.3700 | 0.0000 |
| CARNALLI | -0.5705 | 4.3300 | -4.9005 |
| DOLOMITE | -17.3739 | -16.9167 | -0.4572 |
| EPSOMITE | -5.6394 | -1.9674 | -3.6720 |
| GAYLUSSI | -17.1090 | -9.4210 | -7.6880 |
| GLASERIT | -16.3970 | -3.8030 | -12.5940 |
| GLAUBERI | -7.6843 | -5.2450 | -2.4393 |
| GYPSUM | -4.2962 | -4.5834 | 0.2873 |
| HALITE | 1.4243 | 1.5574 | -0.1332 |
| HEXAHYDR | -5.4975 | -1.7161 | -3.7814 |
| KAINITE | -6.6653 | -0.1930 | -6.4723 |
| KALICINI | -16.1699 | -10.0580 | -6.1119 |
| KIESERIT | -4.7881 | -0.1230 | -4.6651 |
| LABILE S | -11.6400 | -5.6720 | -5.9680 |
| LEONHARD | -5.2138 | -0.8870 | -4.3268 |
| LEONITE | -14.9211 | -3.9790 | -10.9421 |
| MAGNESIT | -9.0038 | -7.7253 | -1.2786 |
| MIRABIL | -5.0907 | -1.5459 | -3.5448 |
| MISENITE | -80.5809 | -10.8060 | -69.7749 |
| NAHCOLIT | -13.1521 | -10.7420 | -2.4101 |
| NATRON | -9.4483 | -0.8250 | -8.6233 |
| NESQUEHO | -9.4295 | -5.1670 | -4.2625 |
| PCO2 | -1.3451 | -1.3811 | 0.0359 |
| PENTAHYD | -5.3556 | -1.2850 | -4.0706 |
| PIRSSONI | -16.6833 | -9.2340 | -7.4493 |
| POLYHALI | -22.6622 | -13.7440 | -8.9182 |
| PORTLAND | -18.8454 | -5.1900 | -13.6554 |
| SCHOENIT | -15.2049 | -4.3280 | -10.8769 |
| SYLVITE | -1.5935 | 0.8257 | -2.4191 |
| SYNGENIT | -13.8617 | -7.4480 | -6.4137 |
| TRONA | -21.4654 | -11.3840 | -10.0814 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.815465D+00 | 0.2590 |
| MG | 2.385668D-01 | -0.6224 |
| NA | 2.225424D+00 | 0.3474 |
| K | 5.786697D-03 | -2.2376 |
| SR | 1.401380D-02 | -1.8534 |
| CL | 6.638239D+00 | 0.8221 |
| C | 1.490935D-02 | -1.8265 |
| S | 3.361331D-03 | -2.4735 |
| BR | 2.504262D-02 | -1.6013 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 5.3282 |
| ACTIVITY H2O = | 0.7213 |
| OSMOTIC COEFFICIENT = | 1.6515 |
| IONIC STRENGTH = | 8.5902 |
| TEMPERATURE = | 18.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9986 G/CC |
| ELECTRICAL BALANCE = | -3.0305D-01 |
| TOTAL ALKALINITY = | 3.4974D-04 |
| ITERATIONS = | 5 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | MACINNES SCALE ACTIVITY | LOG ACT | MACINNES SCALE GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 3.756E-06 | -5.425 | 4.697E-06 | -5.328 | 1.250E+00 | 0.097 |
| 3 | H2O | 0.0 | 7.213E-01 | -0.142 | 7.213E-01 | -0.142 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 1.815E+00 | 0.259 | 1.771E-01 | -0.752 | 9.757E-02 | -1.011 |
| 5 | MG+2 | 2.0 | 2.386E-01 | -0.622 | 4.116E-02 | -1.386 | 1.725E-01 | -0.763 |
| 6 | NA+ | 1.0 | 2.225E+00 | 0.347 | 6.229E-01 | -0.206 | 2.799E-01 | -0.553 |
| 7 | K+ | 1.0 | 5.787E-03 | -2.238 | 5.980E-04 | -3.223 | 1.033E-01 | -0.986 |
| 12 | SR+2 | 2.0 | 1.401E-02 | -1.853 | 7.033E-04 | -3.153 | 5.019E-02 | -1.299 |
| 14 | CL- | -1.0 | 6.638E+00 | 0.822 | 4.264E+01 | 1.630 | 6.424E+00 | 0.808 |
| 15 | CO3-2 | -2.0 | 7.750E-07 | -6.111 | 2.408E-08 | -7.618 | 3.107E-02 | -1.508 |
| 16 | SO4-2 | -2.0 | 3.361E-03 | -2.473 | 5.486E-04 | -3.261 | 1.632E-01 | -0.787 |
| 22 | BR- | -1.0 | 2.504E-02 | -1.601 | 2.389E-01 | -0.622 | 9.540E+00 | 0.980 |
| 31 | OH- | -1.0 | 3.828E-09 | -8.417 | 8.977E-10 | -9.047 | 2.345E-01 | -0.630 |
| 34 | HCO3- | -1.0 | 3.359E-04 | -3.474 | 2.883E-03 | -2.540 | 8.583E+00 | 0.934 |
| 35 | H2CO3 | 0.0 | 1.457E-02 | -1.837 | 4.517E-02 | -1.345 | 3.101E+00 | 0.491 |
| 40 | HSO4- | -1.0 | 4.566E-08 | -7.341 | 2.026E-07 | -6.693 | 4.437E+00 | 0.647 |
| 76 | CACO3 | 0.0 | 5.350E-06 | -5.272 | 5.350E-06 | -5.272 | 1.000E+00 | 0.000 |
| 85 | MGOH+ | 1.0 | 8.000E-08 | -7.097 | 5.249E-09 | -8.280 | 6.561E-02 | -1.183 |
| 86 | MGCO3 | 0.0 | 7.606E-07 | -6.119 | 7.606E-07 | -6.119 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | MACINNES ACTIVITY | MACINNES TOTAL GAMMA |
|---|---|---|---|
| H+ | 3.8021D-06 | 4.6967D-06 | 1.2353D+00 |
| CA+2 | 1.8155D+00 | 1.7713D-01 | 9.7569D-02 |
| MG+2 | 2.3857D-01 | 4.1162D-02 | 1.7254D-01 |
| NA+ | 2.2254D+00 | 6.2288D-01 | 2.7989D-01 |
| K+ | 5.7867D-03 | 5.9796D-04 | 1.0333D-01 |
| SR+2 | 1.4014D-02 | 7.0328D-04 | 5.0185D-02 |
| CL- | 6.6382D+00 | 4.2645D+01 | 6.4241D+00 |
| CO3-2 | 6.8857D-06 | 2.4080D-08 | 3.4971D-03 |
| SO4-2 | 3.3613D-03 | 5.4863D-04 | 1.6322D-01 |
| BR- | 2.5043D-02 | 2.3891D-01 | 9.5403D+00 |
| OH- | 8.3826D-08 | 8.9771D-10 | 1.0709D-02 |
| HCO3- | 3.3588D-04 | 2.8827D-03 | 8.5827D+00 |
| H2CO3 | 1.4567D-02 | 4.5171D-02 | 3.1010D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 1.5909D+00 |
| CASO4 | 1.2620D-01 |
| CACO3 | 1.8472D-02 |
| CA(OH)2 | 2.2367D-02 |
| MGCL2 | 1.9238D+00 |
| MGSO4 | 1.6781D-01 |
| MGCO3 | 2.4564D-02 |
| MG(OH)2 | 2.7048D-02 |
| NACL | 1.3409D+00 |
| NA2SO4 | 2.3384D-01 |
| NAHCO3 | 1.5499D+00 |
| NA2CO3 | 6.4948D-02 |
| NAOH | 5.4749D-02 |
| KCL | 8.1476D-01 |
| K2SO4 | 1.2034D-01 |
| KHCO3 | 9.4174D-01 |
| K2CO3 | 3.3425D-02 |
| KOH | 3.3266D-02 |
| HCL | 2.8170D+00 |
| H2SO4 | 6.2917D-01 |
| HBR | 3.4329D+00 |

```
1Test Problem 1d: Canadian Shield Brine T-93, calcite equil. No scale
 0060020000 0 1          0.00000
 ELEMENTS
 C           15         0.61017E+02
              0         0.00000E+00
 SOLUTION 1
 Canadian Shield Brine T-93.
  9 15 2     5.00       4.00       18.0       1.20
    4  6.400D+04   6  4.500D+04   5  5.100D+03   7  1.990D+02  12  1.080D+03
   14  2.070D+05  22  1.760D+03  16  2.840D+02  15  1.900D+01
 MINERALS
 CALCITE    2       4.0       -8.4       0.00          1                0.000
   15   1.00        4   1.00
 -1.7183E+02 -7.7993E-02  2.8393E+03  7.1595E+01  0.0000E-01
            0     0.00       0.00       0.00          0                0.000
 REACTION
   15   1.000   4.000
1SOLUTION NUMBER 1
 Canadian Shield Brine T-93.
```

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.815465D+00 | 0.2590 |
| MG | 2.385668D-01 | -0.6224 |

| | | |
|---|---|---|
| NA | 2.225424D+00 | 0.3474 |
| K | 5.786697D-03 | -2.2376 |
| SR | 1.401300D-02 | -1.8534 |
| CL | 6.638239D+00 | 0.8221 |
| TOT ALK | 3.540280D-04 | -3.4510 |
| S | 3.361331D-03 | -2.4735 |
| BR | 2.504262D-02 | -1.6013 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 5.0000 |
| ACTIVITY H2O = | 0.7214 |
| OSMOTIC COEFFICIENT = | 1.6512 |
| IONIC STRENGTH = | 8.5902 |
| TEMPERATURE = | 18.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9986 G/CC |
| ELECTRICAL BALANCE = | -3.0305D-01 |
| TOTAL ALKALINITY = | 3.5403D-04 |
| ITERATIONS = | 5 |
| TOTAL CARBON = | 1.0249D-02 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 2.570E-06 | -5.590 | 1.000E-05 | -5.000 | 3.891E+00 | 0.590 |
| 3 | H2O | 0.0 | 7.214E-01 | -0.142 | 7.214E-01 | -0.142 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 1.815E+00 | 0.259 | 1.713E+00 | 0.234 | 9.435E-01 | -0.025 |
| 5 | MG+2 | 2.0 | 2.386E-01 | -0.622 | 3.980E-01 | -0.400 | 1.668E+00 | 0.222 |
| 6 | NA+ | 1.0 | 2.225E+00 | 0.347 | 1.937E+00 | 0.287 | 8.703E-01 | -0.060 |
| 7 | K+ | 1.0 | 5.787E-03 | -2.238 | 1.860E-03 | -2.730 | 3.214E-01 | -0.493 |
| 12 | SR+2 | 2.0 | 1.401E-02 | -1.853 | 6.812E-03 | -2.167 | 4.861E-01 | -0.313 |
| 14 | CL- | -1.0 | 6.638E+00 | 0.822 | 1.370E+01 | 1.137 | 2.064E+00 | 0.315 |
| 15 | CO3-2 | -2.0 | 1.126E-06 | -5.948 | 3.613E-09 | -8.442 | 3.208E-03 | -2.494 |
| 16 | SO4-2 | -2.0 | 3.361E-03 | -2.473 | 5.659E-05 | -4.247 | 1.684E-02 | -1.774 |
| 22 | BR- | -1.0 | 2.504E-02 | -1.601 | 7.677E-02 | -1.115 | 3.065E+00 | 0.486 |
| 31 | OH- | -1.0 | 5.596E-09 | -8.252 | 4.217E-10 | -9.375 | 7.536E-02 | -1.123 |
| 34 | HCO3- | -1.0 | 3.339E-04 | -3.476 | 9.209E-04 | -3.036 | 2.758E+00 | 0.441 |
| 35 | H2CO3 | 0.0 | 9.905E-03 | -2.004 | 3.072E-02 | -1.513 | 3.101E+00 | 0.491 |
| 40 | HSO4- | -1.0 | 3.120E-08 | -7.506 | 4.449E-08 | -7.352 | 1.426E+00 | 0.154 |
| 76 | CACO3 | 0.0 | 7.762E-06 | -5.110 | 7.762E-06 | -5.110 | 1.000E+00 | 0.000 |
| 85 | MGOH+ | 1.0 | 1.168E-07 | -6.933 | 2.384E-08 | -7.623 | 2.042E-01 | -0.690 |
| 86 | MGCO3 | 0.0 | 1.103E-06 | -5.957 | 1.103E-06 | -5.957 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|

| | | | |
|---|---|---|---|
| H+ | 2.6011D-06 | 1.0000D-05 | 3.8446D+00 |
| CA+2 | 1.8155D+00 | 1.7128D+00 | 9.4345D-01 |
| MG+2 | 2.3857D-01 | 3.9802D-01 | 1.6684D+00 |
| NA+ | 2.2254D+00 | 1.9368D+00 | 8.7029D-01 |
| K+ | 5.7867D-03 | 1.8601D-03 | 3.2145D-01 |
| SR+2 | 1.4014D-02 | 6.8121D-03 | 4.8610D-01 |
| CL- | 6.6382D+00 | 1.3703D+01 | 2.0642D+00 |
| CO3-2 | 9.9913D-06 | 3.6128D-09 | 3.6160D-04 |
| SO4-2 | 3.3613D-03 | 5.6590D-05 | 1.6836D-02 |
| BR- | 2.5043D-02 | 7.6765D-02 | 3.0654D+00 |
| OH- | 1.2235D-07 | 4.2171D-10 | 3.4466D-03 |
| HCO3- | 3.3392D-04 | 9.2086D-04 | 2.7577D+00 |
| H2CO3 | 9.9054D-03 | 3.0716D-02 | 3.1010D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 1.5901D+00 |
| CASO4 | 1.2603D-01 |
| CACO3 | 1.8470D-02 |
| CA(OH)2 | 2.2379D-02 |
| MGCL2 | 1.9228D+00 |
| MGSO4 | 1.6760D-01 |
| MGCO3 | 2.4562D-02 |
| MG(OH)2 | 2.7062D-02 |
| NACL | 1.3403D+00 |
| NA2SO4 | 2.3363D-01 |
| NAHCO3 | 1.5492D+00 |
| NA2CO3 | 6.4941D-02 |
| NAOH | 5.4768D-02 |
| KCL | 8.1458D-01 |
| K2SO4 | 1.2027D-01 |
| KHCO3 | 9.4152D-01 |
| K2CO3 | 3.3431D-02 |
| KOH | 3.3285D-02 |
| HCL | 2.8171D+00 |
| H2SO4 | 6.2899D-01 |
| HBR | 3.4329D+00 |

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ANHYDRIT | -4.0136 | -4.3239 | 0.3103 |
| ARAGONIT | -8.2084 | -8.1781 | -0.0303 |
| ARCANITE | -9.7082 | -1.8866 | -7.8216 |
| BISCHOFI | 1.0227 | 4.4775 | -3.4548 |
| BLOEDITE | -8.8877 | -2.3470 | -6.5407 |
| BRUCITE | -19.1501 | -10.8990 | -8.2511 |
| BURKEITE | -15.2142 | -0.7720 | -14.4422 |
| CALCITE | -8.2084 | -8.3700 | 0.1616 |
| CARNALLI | -0.5709 | 4.3300 | -4.9009 |

| | | | |
|---|---|---|---|
| DOLOMITE | -17.0507 | -16.9167 | -0.1340 |
| EPSOMITE | -5.6400 | -1.9674 | -3.6726 |
| GAYLUSSI | -16.7855 | -9.4210 | -7.3645 |
| GLASERIT | -16.3988 | -3.8030 | -12.5958 |
| GLAUBERI | -7.6867 | -5.2450 | -2.4417 |
| GYPSUM | -4.2972 | -4.5834 | 0.2863 |
| HALITE | 1.4239 | 1.5574 | -0.1336 |
| HEXAHYDR | -5.4982 | -1.7161 | -3.7821 |
| KAINITE | -6.6664 | -0.1930 | -6.4734 |
| KALICINI | -16.1726 | -10.0580 | -6.1146 |
| KIESERIT | -4.7892 | -0.1230 | -4.6662 |
| LABILE S | -11.6434 | -5.6720 | -5.9714 |
| LEONHARD | -5.2146 | -0.8870 | -4.3276 |
| LEONITE | -14.9228 | -3.9790 | -10.9438 |
| MAGNESIT | -8.8423 | -7.7253 | -1.1170 |
| MIRABIL | -5.0911 | -1.5459 | -3.5452 |
| MISENITE | -81.5745 | -10.8060 | -70.7685 |
| NAHCOLIT | -13.1551 | -10.7420 | -2.4131 |
| NATRON | -9.2860 | -0.8250 | -8.4610 |
| NESQUEHO | -9.2677 | -5.1670 | -4.1007 |
| PCO2 | -1.5126 | -1.3811 | -0.1316 |
| PENTAHYD | -5.3564 | -1.2850 | -4.0714 |
| PIRSSONI | -16.3601 | -9.2340 | -7.1261 |
| POLYHALI | -22.6662 | -13.7440 | -8.9222 |
| PORTLAND | -18.5163 | -5.1900 | -13.3263 |
| SCHOENIT | -15.2064 | -4.3280 | -10.8784 |
| SYLVITE | -1.5936 | 0.8257 | -2.4193 |
| SYNGENIT | -13.8635 | -7.4480 | -6.4155 |
| TRONA | -21.3067 | -11.3840 | -9.9227 |

1STEP NUMBER 1
0--------------

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.815465D+00 | 0.2590 |
| MG | 2.385668D-01 | -0.6224 |
| NA | 2.225424D+00 | 0.3474 |
| K | 5.786697D-03 | -2.2376 |
| SR | 1.401380D-02 | -1.8534 |
| CL | 6.638239D+00 | 0.8221 |
| TOT ALK | 1.024929D-02 | -1.9893 |
| S | 3.361331D-03 | -2.4735 |
| BR | 2.504262D-02 | -1.6013 |

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| CALCITE | 0.000000D-01 | -8.3700 | -8.3700 | 0.0000 |

+ **

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

** 5.154798D-03 MOLES OF REACTION HAVE BEEN ADDED TO THE SOLUTION
TO REACH THE CALCITE PHASE BOUNDARY.

REACTION IS:
1.000000 MOLES OF C VALENCE = 4.000

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ANHYDRIT | -4.0123 | -4.3239 | 0.3116 |
| ARAGONIT | -8.3700 | -8.1781 | -0.1919 |
| ARCANITE | -9.7073 | -1.8866 | -7.8207 |
| BISCHOFI | 1.0230 | 4.4775 | -3.4545 |
| BLOEDITE | -8.8855 | -2.3470 | -6.5385 |
| BRUCITE | -19.4936 | -10.8990 | -8.5946 |
| BURKEITE | -15.3731 | -0.7720 | -14.6011 |
| CALCITE | -8.3700 | -8.3700 | 0.0000 |
| CARNALLI | -0.5705 | 4.3300 | -4.9005 |
| DOLOMITE | -17.3739 | -16.9167 | -0.4572 |
| EPSOMITE | -5.6393 | -1.9674 | -3.6720 |
| GAYLUSSI | -17.1090 | -9.4210 | -7.6880 |
| GLASERIT | -16.3968 | -3.8030 | -12.5938 |
| GLAUBERI | -7.6841 | -5.2450 | -2.4391 |
| GYPSUM | -4.2961 | -4.5834 | 0.2874 |
| HALITE | 1.4243 | 1.5574 | -0.1331 |
| HEXAHYDR | -5.4974 | -1.7161 | -3.7814 |
| KAINITE | -6.6652 | -0.1930 | -6.4722 |
| KALICINI | -16.1627 | -10.0580 | -6.1047 |
| KIESERIT | -4.7880 | -0.1230 | -4.6650 |
| LABILE S | -11.6396 | -5.6720 | -5.9676 |
| LEONHARD | -5.2137 | -0.8870 | -4.3267 |
| LEONITE | -14.9210 | -3.9790 | -10.9420 |
| MAGNESIT | -9.0038 | -7.7253 | -1.2786 |
| MIRABIL | -5.0907 | -1.5459 | -3.5447 |
| MISENITE | -80.5372 | -10.8060 | -69.7312 |
| NAHCOLIT | -13.1450 | -10.7420 | -2.4030 |
| NATRON | -9.4484 | -0.8250 | -8.6234 |
| NESQUEHO | -9.4295 | -5.1670 | -4.2625 |
| PCO2 | -1.3308 | -1.3811 | 0.0503 |
| PENTAHYD | -5.3556 | -1.2850 | -4.0706 |
| PIRSSONI | -16.6833 | -9.2340 | -7.4493 |
| POLYHALI | -22.6618 | -13.7440 | -8.9178 |
| PORTLAND | -18.8598 | -5.1900 | -13.6698 |
| SCHOENIT | -15.2047 | -4.3280 | -10.8767 |
| SYLVITE | -1.5934 | 0.8257 | -2.4191 |

| | | | |
|---|---|---|---|
| SYNGENIT | -13.8615 | -7.4480 | -6.4135 |
| TRONA | -21.4583 | -11.3840 | -10.0743 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.815465D+00 | 0.2590 |
| MG | 2.385668D-01 | -0.6224 |
| NA | 2.225424D+00 | 0.3474 |
| K | 5.786697D-03 | -2.2376 |
| SR | 1.401380D-02 | -1.8534 |
| CL | 6.638239D+00 | 0.8221 |
| C | 1.540409D-02 | -1.8124 |
| S | 3.361331D-03 | -2.4735 |
| BR | 2.504262D-02 | -1.6013 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 4.8279 |
| ACTIVITY H2O = | 0.7213 |
| OSMOTIC COEFFICIENT = | 1.6515 |
| IONIC STRENGTH = | 8.5902 |
| TEMPERATURE = | 18.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9986 G/CC |
| ELECTRICAL BALANCE = | -3.0305D-01 |
| TOTAL ALKALINITY = | 3.5529D-04 |
| ITERATIONS = | 7 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 3.819E-06 | -5.418 | 1.486E-05 | -4.828 | 3.891E+00 | 0.590 |
| 3 | H2O | 0.0 | 7.213E-01 | -0.142 | 7.213E-01 | -0.142 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 1.815E+00 | 0.259 | 1.716E+00 | 0.235 | 9.452E-01 | -0.024 |
| 5 | MG+2 | 2.0 | 2.386E-01 | -0.622 | 3.988E-01 | -0.399 | 1.672E+00 | 0.223 |
| 6 | NA+ | 1.0 | 2.225E+00 | 0.347 | 1.939E+00 | 0.288 | 8.712E-01 | -0.060 |
| 7 | K+ | 1.0 | 5.787E-03 | -2.238 | 1.861E-03 | -2.730 | 3.216E-01 | -0.493 |
| 12 | SR+2 | 2.0 | 1.401E-02 | -1.853 | 6.812E-03 | -2.167 | 4.861E-01 | -0.313 |
| 14 | CL- | -1.0 | 6.638E+00 | 0.822 | 1.370E+01 | 1.137 | 2.064E+00 | 0.315 |
| 15 | CO3-2 | -2.0 | 7.748E-07 | -6.111 | 2.486E-09 | -8.605 | 3.208E-03 | -2.494 |
| 16 | SO4-2 | -2.0 | 3.361E-03 | -2.473 | 5.665E-05 | -4.247 | 1.685E-02 | -1.773 |
| 22 | BR- | -1.0 | 2.504E-02 | -1.601 | 7.677E-02 | -1.115 | 3.065E+00 | 0.486 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 31 OH- | -1.0 | 3.765E-09 | -8.424 | 2.837E-10 | -9.547 | 7.535E-02 | -1.123 |
| 34 HCO3- | -1.0 | 3.414E-04 | -3.467 | 9.416E-04 | -3.026 | 2.758E+00 | 0.441 |
| 35 H2CO3 | 0.0 | 1.506E-02 | -1.822 | 4.669E-02 | -1.331 | 3.101E+00 | 0.491 |
| 40 HSO4- | -1.0 | 4.642E-08 | -7.333 | 6.618E-08 | -7.179 | 1.426E+00 | 0.154 |
| 76 CACO3 | 0.0 | 5.350E-06 | -5.272 | 5.350E-06 | -5.272 | 1.000E+00 | 0.000 |
| 85 MGOH+ | 1.0 | 7.869E-08 | -7.104 | 1.607E-08 | -7.794 | 2.042E-01 | -0.690 |
| 86 MGCO3 | 0.0 | 7.606E-07 | -6.119 | 7.606E-07 | -6.119 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 3.8658D-06 | 1.4862D-05 | 3.8445D+00 |
| CA+2 | 1.8155D+00 | 1.7160D+00 | 9.4524D-01 |
| MG+2 | 2.3857D-01 | 3.9877D-01 | 1.6715D+00 |
| NA+ | 2.2254D+00 | 1.9388D+00 | 8.7118D-01 |
| K+ | 5.7867D-03 | 1.8611D-03 | 3.2162D-01 |
| SR+2 | 1.4014D-02 | 6.8121D-03 | 4.8610D-01 |
| CL- | 6.6382D+00 | 1.3702D+01 | 2.0641D+00 |
| CO3-2 | 6.8856D-06 | 2.4856D-09 | 3.6099D-04 |
| SO4-2 | 3.3613D-03 | 5.6646D-05 | 1.6853D-02 |
| BR- | 2.5043D-02 | 7.6765D-02 | 3.0654D+00 |
| OH- | 8.2458D-08 | 2.8369D-10 | 3.4404D-03 |
| HCO3- | 3.4144D-04 | 9.4159D-04 | 2.7577D+00 |
| H2CO3 | 1.5056D-02 | 4.6688D-02 | 3.1010D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 1.5910D+00 |
| CASO4 | 1.2621D-01 |
| CACO3 | 1.8472D-02 |
| CA(OH)2 | 2.2366D-02 |
| MGCL2 | 1.9240D+00 |
| MGSO4 | 1.6784D-01 |
| MGCO3 | 2.4564D-02 |
| MG(OH)2 | 2.7047D-02 |
| NACL | 1.3410D+00 |
| NA2SO4 | 2.3386D-01 |
| NAHCO3 | 1.5500D+00 |
| NA2CO3 | 6.4949D-02 |
| NAOH | 5.4747D-02 |
| KCL | 8.1478D-01 |
| K2SO4 | 1.2035D-01 |
| KHCO3 | 9.4177D-01 |
| K2CO3 | 3.3424D-02 |
| KOH | 3.3264D-02 |
| HCL | 2.8170D+00 |
| H2SO4 | 6.2919D-01 |
| HBR | 3.4329D+00 |

**Test problem 2: Equilibration of pure water with a set of minerals accompanied by an irreversible reaction**

Using the computer code SNORM (Bodine and Jones, 1986) and the mineral stability data of Harvie and others (1984), it can be shown that the final equilibrium mineral assemblage upon evaporation of sea water to dryness in an environment open to air (log $PCO_2$ = -3.5) at 25 °C is anhydrite ($CaSO_4$), bischofite ($MgCl_2 \cdot 6H_2O$), carnallite ($KMgCl_3 \cdot 6H_2O$), halite (NaCl), kieserite ($MgSO_4 \cdot H_2O$), and magnesite ($MgCO_3$). According to the mineralogic phase rule this is an invariant system. That is, once evaporation of sea water reaches saturation with these phases, further evaporation of that solution or other inputs of calcium, magnesium, sodium, potassium, carbon, chloride or sulfate would change only the masses of the solids formed without altering the composition of the equilibrium solution. This test problem uses PHRQPITZ to test this reasoning and at the same time evaluate the internal consistency of SNORM and PHRQPITZ. Because both the SNORM and PHRQPITZ codes use the Harvie and others (1984) data base (though in very different ways) we expect to find with PHRQPITZ that no other phases than those listed above could precipitate from the final equilibrium solution, that is, that the saturation indices of all other minerals in the Harvie and others (1984) data base are less than zero in the equilibrium solution.

The input file for test problem 2 is listed in table 8. The starting solution was taken as pure water at 25 °C. IOPT(2) was arbitrarily selected to define the starting pH via electrical balance. The problem combines irreversible reaction with mineral equilibration (IOPT(3) = 3). An irreversible reaction (the addition of 0.0, 0.1 and 1.0 moles of "sea salt") is used as one means of modeling evaporation (of sea water). The second line of the input file indicates that there will be 3 increments of reaction (NSTEPS = 3) and there are 7 components in the reaction (NCOMPS = 7). The moles of each reaction increment and the stoichiometry of the reactant (sea salt) are defined under STEPS and REACTION input.

The computed results are listed in table 9. Following a print of the input data set, the starting solution, pure water, is speciated and the pH consistent with the thermodynamic data of PHRQPITZ.DATA is 6.9990. The calculations are performed in 3 similar steps, with each case beginning from the pure water starting point (solution 1). In step 1 zero moles of sea salt were added so that pure water could be equilibrated with the mineral set alone. The mass transfers of anhydrite, bischofite, carnallite, halite, kieserite, magnesite, and $CO_2$ appear under the heading "PHASE BOUNDARIES". The results show that all 6 minerals would dissolve and be accompanied by a small loss of $CO_2$ to the atmosphere. Examination of the saturation indices shows that all other minerals of the Harvie and others (1984) data base are undersaturated in the equilibrium solution. This confirms the prediction from SNORM and constitutes a partial validation of the two codes. The final equilibrium solution is predominantly a $MgCl_2$ solution of ionic strength 17.3873, pH 6.01 and water activity of 0.3382.

In steps 2 and 3 (table 9) we examine the capability of PHRQPITZ to perform calculations in invariant systems by irreversibly adding 0.1 and 1.0 moles of sea salt to pure water and again equilibrating with the same set of minerals. Comparison of the solution compositions from steps 2 and 3 with that from step 1 shows that all three are identical, as expected. The required mineral mass transfers are summarized under "PHASE BOUNDARIES".

Table 8. -- Line images of the input file to test problem 2

```
Test Problem 2: Sea Water Invariant Point (equilibration with reaction).
0130020000 3 7       0.0
SOLUTION 1
Pure water
 0  0 0    7.0       4.0       25.0      1.0
MINERALS
ANHYDRIT   2         6.00    -4.362              1
   4      1.000  16      1.000
422.950     0.0         -18431.     -147.708
BISCHOFI   3         0.00     4.455              1
   5      1.000  14      2.000   3      6.000
3.524       0.0         277.6
CARNALLI   4         0.00     4.330              0
   7      1.000   5      1.000  14      3.000   3      6.000
HALITE     2         0.00     1.570              1
   6      1.000  14      1.000
-713.4616   -.1201241   37302.21    262.4583    -2106915.
KIESERIT   3         6.00    -0.123              0
   5      1.000  16      1.000   3      1.000
MAGNESIT   2         4.00    -7.834     -6.169   0
   5      1.000  15      1.000
PCO2       1         4.0     -1.468     -4.776   1          -3.5
  35  1.0
108.3865    0.01985076  -6919.53    -40.45154    669365.0

STEPS
0.         .1        1.0
REACTION
   4.186    0.0        5.976    0.0        68.567   0.         7.181    0.
  149.958   0.        15.043    4.        16.514    6.
END
```

Table 9. -- Listing of printout from test problem 2

```
          DATA READ FROM DISK

 ELEMENTS
 SPECIES
 LOOK MIN
 MEAN GAM
1Test Problem 2: Sea Water Invariant Point (equilibration with reaction).
 0130020000 3 7         0.00000
 SOLUTION 1
 Pure water
  0  0 0     7.00       4.00       25.0       1.00
 MINERALS
 ANHYDRIT   2       6.0       -4.4       0.00          1                0.000
    4   1.00       16   1.00
   4.2295E+02  0.0000E-01 -1.8431E+04 -1.4771E+02  0.0000E-01
 BISCHOFI   3       0.00        4.5       0.00          1                0.000
    5   1.00       14   2.00        3   6.00
   3.5240E+00  0.0000E-01  2.7760E+02  0.0000E-01  0.0000E-01
 CARNALLI   4       0.00        4.3       0.00          0                0.000
    7   1.00        5   1.00       14   3.00        3   6.00
 HALITE     2       0.00        1.6       0.00          1                0.000
    6   1.00       14   1.00
  -7.1346E+02 -1.2012E-01  3.7302E+04  2.6246E+02 -2.1069E+06
 KIESERIT   3       6.0       -0.12      0.00          0                0.000
    5   1.00       16   1.00        3   1.00
 MAGNESIT   2       4.0       -7.8       -6.2          0                0.000
    5   1.00       15   1.00
 PCO2       1       4.0       -1.5       -4.8          1               -3.500
   35   1.00
   1.0839E+02  1.9851E-02 -6.9195E+03 -4.0452E+01  6.6936E+05
            0      0.00       0.00       0.00          0                0.000
 STEPS
  0.000      0.100      1.00
 REACTION
    4   0.186   0.000   5   0.976   0.000   6   8.567   0.000   7   0.181   0.00
   14   9.958   0.000  15   0.043   4.000  16   0.514   6.000
1SOLUTION NUMBER 1
 Pure water


                    TOTAL MOLALITIES OF ELEMENTS
                    ----- ---------- -- --------

               ELEMENT          MOLALITY         LOG MOLALITY

               PURE WATER


                    ----DESCRIPTION OF SOLUTION----
```

```
                                PH =   6.9990
                      ACTIVITY H2O =   1.0000
                OSMOTIC COEFFICIENT =   0.9999
                     IONIC STRENGTH =   0.0000
                       TEMPERATURE =  25.0000
                          PRESSURE =   1.0000 ATM
                     DENSITY OF H2O =   0.9971 G/CC
                  ELECTRICAL BALANCE = -2.2785D-19
                    TOTAL ALKALINITY =   1.0027D-07
                         ITERATIONS =   5
```

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 1.003E-07 | -6.999 | 1.002E-07 | -6.999 | 9.996E-01 | 0.000 |
| 3 | H2O | 0.0 | 1.000E+00 | 0.000 | 1.000E+00 | 0.000 | 1.000E+00 | 0.000 |
| 31 | OH- | -1.0 | 1.003E-07 | -6.999 | 1.002E-07 | -6.999 | 9.996E-01 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 1.0027D-07 | 1.0023D-07 | 9.9963D-01 |
| OH- | 1.0027D-07 | 1.0023D-07 | 9.9963D-01 |

```
1STEP NUMBER  1
0--------------
0 0.000D-01 MOLES OF REACTION HAVE BEEN ADDED.
```

REACTION IS:

```
          0.186000 MOLES OF CA        VALENCE =   0.000
          0.976000 MOLES OF MG        VALENCE =   0.000
          8.567000 MOLES OF NA        VALENCE =   0.000
          0.181000 MOLES OF K         VALENCE =   0.000
          9.958000 MOLES OF CL        VALENCE =   0.000
          0.043000 MOLES OF C         VALENCE =   4.000
          0.514000 MOLES OF S         VALENCE =   6.000
```

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| PURE WATER | | |

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| ANHYDRIT | 9.307528D-04 | -4.3617 | -4.3617 | 0.0000 |
| BISCHOFI | 5.651543D+00 | 4.4551 | 4.4551 | 0.0000 |
| CARNALLI | 2.151592D-02 | 4.3300 | 4.3300 | 0.0000 |
| HALITE | 9.313089D-02 | 1.5700 | 1.5700 | 0.0000 |
| KIESERIT | 6.246533D-02 | -0.1230 | -0.1230 | 0.0000 |
| MAGNESIT | 2.080462D-04 | -7.8340 | -7.8340 | 0.0000 |
| PCO2 | -1.508047D-04 | -4.9679 | -1.4679 | -3.5000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ANHYDRIT | -4.3617 | -4.3617 | 0.0000 |
| ARAGONIT | -12.5435 | -8.2195 | -4.3241 |
| ARCANITE | -7.1823 | -1.7760 | -5.4063 |
| BISCHOFI | 4.4551 | 4.4551 | 0.0000 |
| BLOEDITE | -5.3276 | -2.3470 | -2.9806 |
| BRUCITE | -14.6562 | -10.8840 | -3.7722 |
| BURKEITE | -19.5583 | -0.7720 | -18.7863 |
| CALCITE | -12.5435 | -8.4062 | -4.1373 |
| CARNALLI | 4.3300 | 4.3300 | 0.0000 |
| DOLOMITE | -20.3775 | -17.0830 | -3.2945 |
| EPSOMITE | -2.9479 | -1.8809 | -1.0670 |
| GAYLUSSI | -26.8716 | -9.4210 | -17.4506 |
| GLASERIT | -12.6695 | -3.8030 | -8.8665 |
| GLAUBERI | -8.1539 | -5.2450 | -2.9089 |
| GYPSUM | -5.3033 | -4.5805 | -0.7228 |
| HALITE | 1.5700 | 1.5700 | 0.0000 |
| HEXAHYDR | -2.4771 | -1.6346 | -0.8425 |
| KAINITE | -1.1897 | -0.1930 | -0.9967 |
| KALICINI | -18.7398 | -10.0580 | -8.6818 |
| KIESERIT | -0.1230 | -0.1230 | 0.0000 |
| LABILE S | -12.8877 | -5.6720 | -7.2157 |
| LEONHARD | -1.5354 | -0.8870 | -0.6484 |
| LEONITE | -8.7178 | -3.9790 | -4.7388 |
| MAGNESIT | -7.8340 | -7.8340 | 0.0000 |
| MIRABIL | -8.5003 | -1.2135 | -7.2868 |
| MISENITE | -70.5302 | -10.8060 | -59.7242 |
| NAHCOLIT | -17.0447 | -10.7420 | -6.3027 |
| NATRON | -16.6821 | -0.8250 | -15.8571 |
| NESQUEHO | -9.2464 | -5.1670 | -4.0794 |
| PCO2 | -4.9679 | -1.4679 | -3.5000 |
| PENTAHYD | -2.0063 | -1.2850 | -0.7213 |
| PIRSSONI | -25.4591 | -9.2340 | -16.2251 |
| POLYHALI | -16.4995 | -13.7440 | -2.7555 |
| PORTLAND | -19.3657 | -5.1900 | -14.1757 |
| SCHOENIT | -9.6594 | -4.3280 | -5.3314 |

| | | | |
|---|---|---|---|
| SYLVITE | -0.1251 | 0.8998 | -1.0249 |
| SYNGENIT | -12.0148 | -7.4480 | -4.5668 |
| TRONA | -29.9603 | -11.3840 | -18.5763 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 9.307528D-04 | -3.0312 |
| MG | 5.735732D+00 | 0.7586 |
| NA | 9.313089D-02 | -1.0309 |
| K | 2.151592D-02 | -1.6672 |
| CL | 1.146076D+01 | 1.0592 |
| C | 5.724154D-05 | -4.2423 |
| S | 6.339608D-02 | -1.1979 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 6.0119 |
| ACTIVITY H2O = | 0.3382 |
| OSMOTIC COEFFICIENT = | 3.4633 |
| IONIC STRENGTH = | 17.3873 |
| TEMPERATURE = | 25.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9971 G/CC |
| ELECTRICAL BALANCE = | 2.6802D-10 |
| TOTAL ALKALINITY = | 4.1616D-04 |
| ITERATIONS = | 66 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | UNSCALED LOG ACT | UNSCALED GAMMA | UNSCALED LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 5.297E-08 | -7.276 | 9.730E-07 | -6.012 | 1.837E+01 | 1.264 |
| 3 | H2O | 0.0 | 3.382E-01 | -0.471 | 3.382E-01 | -0.471 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 9.308E-04 | -3.031 | 3.533E-03 | -2.452 | 3.796E+00 | 0.579 |
| 5 | MG+2 | 2.0 | 5.735E+00 | 0.759 | 1.810E+02 | 2.258 | 3.156E+01 | 1.499 |
| 6 | NA+ | 1.0 | 9.313E-02 | -1.031 | 1.145E-01 | -0.941 | 1.230E+00 | 0.090 |
| 7 | K+ | 1.0 | 2.152E-02 | -1.667 | 2.311E-03 | -2.636 | 1.074E-01 | -0.969 |
| 14 | CL- | -1.0 | 1.146E+01 | 1.059 | 3.245E+02 | 2.511 | 2.831E+01 | 1.452 |
| 15 | CO3-2 | -2.0 | 1.448E-07 | -6.839 | 8.097E-11 | -10.092 | 5.590E-04 | -3.253 |
| 16 | SO4-2 | -2.0 | 6.340E-02 | -1.198 | 1.231E-02 | -1.910 | 1.941E-01 | -0.712 |
| 31 | OH- | -1.0 | 4.868E-08 | -7.313 | 3.492E-09 | -8.457 | 7.174E-02 | -1.144 |
| 34 | HCO3- | -1.0 | 4.325E-05 | -4.364 | 1.721E-06 | -5.764 | 3.979E-02 | -1.400 |
| 35 | H2CO3 | 0.0 | 1.431E-06 | -5.844 | 1.077E-05 | -4.968 | 7.523E+00 | 0.876 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 40 HSO4- | -1.0 | 1.462E-08 | -7.835 | 1.141E-06 | -5.943 | 7.805E+01 | 1.892 |
| 76 CACO3 | 0.0 | 4.053E-10 | -9.392 | 4.053E-10 | -9.392 | 1.000E+00 | 0.000 |
| 85 MGOH+ | 1.0 | 3.477E-04 | -3.459 | 9.767E-05 | -4.010 | 2.809E-01 | -0.551 |
| 86 MGCO3 | 0.0 | 1.242E-05 | -4.906 | 1.242E-05 | -4.906 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 6.7585D-08 | 9.7296D-07 | 1.4396D+01 |
| CA+2 | 9.3075D-04 | 3.5331D-03 | 3.7959D+00 |
| MG+2 | 5.7357D+00 | 1.8099D+02 | 3.1555D+01 |
| NA+ | 9.3131D-02 | 1.1451D-01 | 1.2296D+00 |
| K+ | 2.1516D-02 | 2.3108D-03 | 1.0740D-01 |
| CL- | 1.1461D+01 | 3.2445D+02 | 2.8310D+01 |
| CO3-2 | 1.2564D-05 | 8.0973D-11 | 6.4446D-06 |
| SO4-2 | 6.3396D-02 | 1.2307D-02 | 1.9413D-01 |
| OH- | 3.4778D-04 | 3.4921D-09 | 1.0041D-05 |
| HCO3- | 4.3246D-05 | 1.7206D-06 | 3.9787D-02 |
| H2CO3 | 1.4310D-06 | 1.0766D-05 | 7.5233D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 1.4490D+01 |
| CASO4 | 8.5843D-01 |
| CACO3 | 4.9460D-03 |
| CA(OH)2 | 7.2604D-04 |
| MGCL2 | 2.9353D+01 |
| MGSO4 | 2.4750D+00 |
| MGCO3 | 1.4260D-02 |
| MG(OH)2 | 1.4708D-03 |
| NACL | 5.8999D+00 |
| NA2SO4 | 6.6455D-01 |
| NAHCO3 | 2.2118D-01 |
| NA2CO3 | 2.1358D-02 |
| NAOH | 3.5137D-03 |
| KCL | 1.7437D+00 |
| K2SO4 | 1.3083D-01 |
| KHCO3 | 6.5370D-02 |
| K2CO3 | 4.2047D-03 |
| KOH | 1.0385D-03 |
| HCL | 2.0188D+01 |
| H2SO4 | 3.4266D+00 |

1STEP NUMBER 2
0----------
0 1.000D-01 MOLES OF REACTION HAVE BEEN ADDED.

REACTION IS:

| | |
|---|---|
| 0.186000 MOLES OF CA | VALENCE = 0.000 |
| 0.976000 MOLES OF MG | VALENCE = 0.000 |

| | | | |
|---|---|---|---|
| 8.567000 | MOLES OF NA | VALENCE = | 0.000 |
| 0.181000 | MOLES OF K | VALENCE = | 0.000 |
| 9.958000 | MOLES OF CL | VALENCE = | 0.000 |
| 0.043000 | MOLES OF C | VALENCE = | 4.000 |
| 0.514000 | MOLES OF S | VALENCE = | 6.000 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.860000D-02 | -1.7305 |
| MG | 9.760000D-02 | -1.0106 |
| NA | 8.567000D-01 | -0.0672 |
| K | 1.810000D-02 | -1.7423 |
| CL | 9.958000D-01 | -0.0018 |
| C | 4.300000D-03 | -2.3665 |
| S | 5.140000D-02 | -1.2890 |

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| ANHYDRIT | -1.766925D-02 | -4.3617 | -4.3617 | 0.0000 |
| BISCHOFI | 5.609147D+00 | 4.4551 | 4.4551 | 0.0000 |
| CARNALLI | 3.415878D-03 | 4.3300 | 4.3300 | 0.0000 |
| HALITE | -7.635695D-01 | 1.5700 | 1.5700 | 0.0000 |
| KIESERIT | 2.966496D-02 | -0.1230 | -0.1230 | 0.0000 |
| MAGNESIT | -4.091954D-03 | -7.8340 | -7.8340 | 0.0000 |
| PCO2 | -1.508049D-04 | -4.9679 | -1.4679 | -3.5000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ANHYDRIT | -4.3617 | -4.3617 | 0.0000 |
| ARAGONIT | -12.5435 | -8.2195 | -4.3241 |
| ARCANITE | -7.1823 | -1.7760 | -5.4063 |
| BISCHOFI | 4.4551 | 4.4551 | 0.0000 |
| BLOEDITE | -5.3276 | -2.3470 | -2.9806 |
| BRUCITE | -14.6562 | -10.8840 | -3.7722 |
| BURKEITE | -19.5583 | -0.7720 | -18.7863 |
| CALCITE | -12.5435 | -8.4062 | -4.1373 |
| CARNALLI | 4.3300 | 4.3300 | 0.0000 |
| DOLOMITE | -20.3775 | -17.0830 | -3.2945 |
| EPSOMITE | -2.9479 | -1.8809 | -1.0670 |
| GAYLUSSI | -26.8716 | -9.4210 | -17.4506 |
| GLASERIT | -12.6695 | -3.8030 | -8.8665 |

| | | | |
|---|---|---|---|
| GLAUBERI | -8.1539 | -5.2450 | -2.9089 |
| GYPSUM | -5.3033 | -4.5805 | -0.7228 |
| HALITE | 1.5700 | 1.5700 | 0.0000 |
| HEXAHYDR | -2.4771 | -1.6346 | -0.8425 |
| KAINITE | -1.1897 | -0.1930 | -0.9967 |
| KALICINI | -18.7398 | -10.0580 | -8.6818 |
| KIESERIT | -0.1230 | -0.1230 | 0.0000 |
| LABILE S | -12.8877 | -5.6720 | -7.2157 |
| LEONHARD | -1.5354 | -0.8870 | -0.6484 |
| LEONITE | -8.7178 | -3.9790 | -4.7388 |
| MAGNESIT | -7.8340 | -7.8340 | 0.0000 |
| MIRABIL | -8.5003 | -1.2135 | -7.2868 |
| MISENITE | -70.5302 | -10.8060 | -59.7242 |
| NAHCOLIT | -17.0447 | -10.7420 | -6.3027 |
| NATRON | -16.6822 | -0.8250 | -15.8572 |
| NESQUEHO | -9.2464 | -5.1670 | -4.0794 |
| PCO2 | -4.9679 | -1.4679 | -3.5000 |
| PENTAHYD | -2.0063 | -1.2850 | -0.7213 |
| PIRSSONI | -25.4591 | -9.2340 | -16.2251 |
| POLYHALI | -16.4995 | -13.7440 | -2.7555 |
| PORTLAND | -19.3657 | -5.1900 | -14.1757 |
| SCHOENIT | -9.6594 | -4.3280 | -5.3314 |
| SYLVITE | -0.1251 | 0.8998 | -1.0249 |
| SYNGENIT | -12.0148 | -7.4480 | -4.5668 |
| TRONA | -29.9604 | -11.3840 | -18.5764 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 9.307534D-04 | -3.0312 |
| MG | 5.735736D+00 | 0.7586 |
| NA | 9.313049D-02 | -1.0309 |
| K | 2.151588D-02 | -1.6672 |
| CL | 1.146077D+01 | 1.0592 |
| C | 5.724158D-05 | -4.2423 |
| S | 6.339571D-02 | -1.1979 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 6.0119 |
| ACTIVITY H2O = | 0.3382 |
| OSMOTIC COEFFICIENT = | 3.4633 |
| IONIC STRENGTH = | 17.3873 |
| TEMPERATURE = | 25.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9971 G/CC |
| ELECTRICAL BALANCE = | -7.8562D-11 |
| TOTAL ALKALINITY = | 4.1616D-04 |

ITERATIONS = 26

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | UNSCALED LOG ACT | UNSCALED GAMMA | UNSCALED LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 5.297E-08 | -7.276 | 9.730E-07 | -6.012 | 1.837E+01 | 1.264 |
| 3 | H2O | 0.0 | 3.382E-01 | -0.471 | 3.382E-01 | -0.471 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 9.308E-04 | -3.031 | 3.533E-03 | -2.452 | 3.796E+00 | 0.579 |
| 5 | MG+2 | 2.0 | 5.735E+00 | 0.759 | 1.810E+02 | 2.258 | 3.156E+01 | 1.499 |
| 6 | NA+ | 1.0 | 9.313E-02 | -1.031 | 1.145E-01 | -0.941 | 1.230E+00 | 0.090 |
| 7 | K+ | 1.0 | 2.152E-02 | -1.667 | 2.311E-03 | -2.636 | 1.074E-01 | -0.969 |
| 14 | CL- | -1.0 | 1.146E+01 | 1.059 | 3.245E+02 | 2.511 | 2.831E+01 | 1.452 |
| 15 | CO3-2 | -2.0 | 1.448E-07 | -6.839 | 8.097E-11 | -10.092 | 5.590E-04 | -3.253 |
| 16 | SO4-2 | -2.0 | 6.340E-02 | -1.198 | 1.231E-02 | -1.910 | 1.941E-01 | -0.712 |
| 31 | OH- | -1.0 | 4.868E-08 | -7.313 | 3.492E-09 | -8.457 | 7.174E-02 | -1.144 |
| 34 | HCO3- | -1.0 | 4.325E-05 | -4.364 | 1.721E-06 | -5.764 | 3.979E-02 | -1.400 |
| 35 | H2CO3 | 0.0 | 1.431E-06 | -5.844 | 1.077E-05 | -4.968 | 7.523E+00 | 0.876 |
| 40 | HSO4- | -1.0 | 1.462E-08 | -7.835 | 1.141E-06 | -5.943 | 7.805E+01 | 1.892 |
| 76 | CACO3 | 0.0 | 4.053E-10 | -9.392 | 4.053E-10 | -9.392 | 1.000E+00 | 0.000 |
| 85 | MGOH+ | 1.0 | 3.477E-04 | -3.459 | 9.767E-05 | -4.010 | 2.809E-01 | -0.551 |
| 86 | MGCO3 | 0.0 | 1.242E-05 | -4.906 | 1.242E-05 | -4.906 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 6.7585D-08 | 9.7296D-07 | 1.4396D+01 |
| CA+2 | 9.3075D-04 | 3.5331D-03 | 3.7959D+00 |
| MG+2 | 5.7357D+00 | 1.8099D+02 | 3.1555D+01 |
| NA+ | 9.3130D-02 | 1.1451D-01 | 1.2296D+00 |
| K+ | 2.1516D-02 | 2.3108D-03 | 1.0740D-01 |
| CL- | 1.1461D+01 | 3.2446D+02 | 2.8310D+01 |
| CO3-2 | 1.2564D-05 | 8.0972D-11 | 6.4445D-06 |
| SO4-2 | 6.3396D-02 | 1.2307D-02 | 1.9413D-01 |
| OH- | 3.4779D-04 | 3.4921D-09 | 1.0041D-05 |
| HCO3- | 4.3246D-05 | 1.7206D-06 | 3.9787D-02 |
| H2CO3 | 1.4310D-06 | 1.0766D-05 | 7.5233D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 1.4490D+01 |
| CASO4 | 8.5843D-01 |
| CACO3 | 4.9460D-03 |
| CA(OH)2 | 7.2604D-04 |
| MGCL2 | 2.9353D+01 |
| MGSO4 | 2.4750D+00 |
| MGCO3 | 1.4260D-02 |
| MG(OH)2 | 1.4708D-03 |

| | |
|---|---|
| NACL | 5.8999D+00 |
| NA2SO4 | 6.6455D-01 |
| NAHCO3 | 2.2118D-01 |
| NA2CO3 | 2.1358D-02 |
| NAOH | 3.5137D-03 |
| KCL | 1.7437D+00 |
| K2SO4 | 1.3083D-01 |
| KHCO3 | 6.5369D-02 |
| K2CO3 | 4.2047D-03 |
| KOH | 1.0385D-03 |
| HCL | 2.0188D+01 |
| H2SO4 | 3.4266D+00 |

1STEP NUMBER 3
0----------
0 1.000D+00 MOLES OF REACTION HAVE BEEN ADDED.

REACTION IS:

| | | |
|---|---|---|
| 0.186000 MOLES OF CA | VALENCE = | 0.000 |
| 0.976000 MOLES OF MG | VALENCE = | 0.000 |
| 8.567000 MOLES OF NA | VALENCE = | 0.000 |
| 0.181000 MOLES OF K | VALENCE = | 0.000 |
| 9.958000 MOLES OF CL | VALENCE = | 0.000 |
| 0.043000 MOLES OF C | VALENCE = | 4.000 |
| 0.514000 MOLES OF S | VALENCE = | 6.000 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.860000D-01 | -0.7305 |
| MG | 9.760000D-01 | -0.0106 |
| NA | 8.567000D+00 | 0.9328 |
| K | 1.810000D-01 | -0.7423 |
| CL | 9.958000D+00 | 0.9982 |
| C | 4.300000D-02 | -1.3665 |
| S | 5.140000D-01 | -0.2890 |

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| ANHYDRIT | -1.850692D-01 | -4.3617 | -4.3617 | 0.0000 |
| BISCHOFI | 5.227546D+00 | 4.4551 | 4.4551 | 0.0000 |
| CARNALLI | -1.594841D-01 | 4.3300 | 4.3300 | 0.0000 |
| HALITE | -8.473869D+00 | 1.5700 | 1.5700 | 0.0000 |
| KIESERIT | -2.655349D-01 | -0.1230 | -0.1230 | 0.0000 |
| MAGNESIT | -4.279195D-02 | -7.8340 | -7.8340 | 0.0000 |
| PCO2 | -1.508048D-04 | -4.9679 | -1.4679 | -3.5000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ANHYDRIT | -4.3617 | -4.3617 | 0.0000 |
| ARAGONIT | -12.5435 | -8.2195 | -4.3241 |
| ARCANITE | -7.1823 | -1.7760 | -5.4063 |
| BISCHOFI | 4.4551 | 4.4551 | 0.0000 |
| BLOEDITE | -5.3276 | -2.3470 | -2.9806 |
| BRUCITE | -14.6562 | -10.8840 | -3.7722 |
| BURKEITE | -19.5583 | -0.7720 | -18.7863 |
| CALCITE | -12.5435 | -8.4062 | -4.1373 |
| CARNALLI | 4.3300 | 4.3300 | 0.0000 |
| DOLOMITE | -20.3775 | -17.0830 | -3.2945 |
| EPSOMITE | -2.9479 | -1.8809 | -1.0670 |
| GAYLUSSI | -26.8716 | -9.4210 | -17.4506 |
| GLASERIT | -12.6695 | -3.8030 | -8.8665 |
| GLAUBERI | -8.1539 | -5.2450 | -2.9089 |
| GYPSUM | -5.3033 | -4.5805 | -0.7228 |
| HALITE | 1.5700 | 1.5700 | 0.0000 |
| HEXAHYDR | -2.4771 | -1.6346 | -0.8425 |
| KAINITE | -1.1897 | -0.1930 | -0.9967 |
| KALICINI | -18.7398 | -10.0580 | -8.6818 |
| KIESERIT | -0.1230 | -0.1230 | 0.0000 |
| LABILE S | -12.8877 | -5.6720 | -7.2157 |
| LEONHARD | -1.5354 | -0.8870 | -0.6484 |
| LEONITE | -8.7178 | -3.9790 | -4.7388 |
| MAGNESIT | -7.8340 | -7.8340 | 0.0000 |
| MIRABIL | -8.5003 | -1.2135 | -7.2868 |
| MISENITE | -70.5302 | -10.8060 | -59.7242 |
| NAHCOLIT | -17.0447 | -10.7420 | -6.3027 |
| NATRON | -16.6821 | -0.8250 | -15.8571 |
| NESQUEHO | -9.2464 | -5.1670 | -4.0794 |
| PCO2 | -4.9679 | -1.4679 | -3.5000 |
| PENTAHYD | -2.0063 | -1.2850 | -0.7213 |
| PIRSSONI | -25.4591 | -9.2340 | -16.2251 |
| POLYHALI | -16.4995 | -13.7440 | -2.7555 |
| PORTLAND | -19.3657 | -5.1900 | -14.1757 |
| SCHOENIT | -9.6594 | -4.3280 | -5.3314 |
| SYLVITE | -0.1251 | 0.8998 | -1.0249 |
| SYNGENIT | -12.0148 | -7.4480 | -4.5668 |
| TRONA | -29.9603 | -11.3840 | -18.5763 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 9.307531D-04 | -3.0312 |

| | | |
|---|---|---|
| MG | 5.735735D+00 | 0.7586 |
| NA | 9.313064D-02 | -1.0309 |
| K | 2.151589D-02 | -1.6672 |
| CL | 1.146077D+01 | 1.0592 |
| C | 5.724155D-05 | -4.2423 |
| S | 6.339584D-02 | -1.1979 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 6.0119 |
| ACTIVITY H2O = | 0.3382 |
| OSMOTIC COEFFICIENT = | 3.4633 |
| IONIC STRENGTH = | 17.3873 |
| TEMPERATURE = | 25.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9971 G/CC |
| ELECTRICAL BALANCE = | 1.1675D-10 |
| TOTAL ALKALINITY = | 4.1616D-04 |
| ITERATIONS = | 23 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | UNSCALED LOG ACT | UNSCALED GAMMA | UNSCALED LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 5.297E-08 | -7.276 | 9.730E-07 | -6.012 | 1.837E+01 | 1.264 |
| 3 | H2O | 0.0 | 3.382E-01 | -0.471 | 3.382E-01 | -0.471 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 9.308E-04 | -3.031 | 3.533E-03 | -2.452 | 3.796E+00 | 0.579 |
| 5 | MG+2 | 2.0 | 5.735E+00 | 0.759 | 1.810E+02 | 2.258 | 3.156E+01 | 1.499 |
| 6 | NA+ | 1.0 | 9.313E-02 | -1.031 | 1.145E-01 | -0.941 | 1.230E+00 | 0.090 |
| 7 | K+ | 1.0 | 2.152E-02 | -1.667 | 2.311E-03 | -2.636 | 1.074E-01 | -0.969 |
| 14 | CL- | -1.0 | 1.146E+01 | 1.059 | 3.245E+02 | 2.511 | 2.831E+01 | 1.452 |
| 15 | CO3-2 | -2.0 | 1.448E-07 | -6.839 | 8.097E-11 | -10.092 | 5.590E-04 | -3.253 |
| 16 | SO4-2 | -2.0 | 6.340E-02 | -1.198 | 1.231E-02 | -1.910 | 1.941E-01 | -0.712 |
| 31 | OH- | -1.0 | 4.868E-08 | -7.313 | 3.492E-09 | -8.457 | 7.174E-02 | -1.144 |
| 34 | HCO3- | -1.0 | 4.325E-05 | -4.364 | 1.721E-06 | -5.764 | 3.979E-02 | -1.400 |
| 35 | H2CO3 | 0.0 | 1.431E-06 | -5.844 | 1.077E-05 | -4.968 | 7.523E+00 | 0.876 |
| 40 | HSO4- | -1.0 | 1.462E-08 | -7.835 | 1.141E-06 | -5.943 | 7.805E+01 | 1.892 |
| 76 | CACO3 | 0.0 | 4.053E-10 | -9.392 | 4.053E-10 | -9.392 | 1.000E+00 | 0.000 |
| 85 | MGOH+ | 1.0 | 3.477E-04 | -3.459 | 9.767E-05 | -4.010 | 2.809E-01 | -0.551 |
| 86 | MGCO3 | 0.0 | 1.242E-05 | -4.906 | 1.242E-05 | -4.906 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 6.7585D-08 | 9.7296D-07 | 1.4396D+01 |
| CA+2 | 9.3075D-04 | 3.5331D-03 | 3.7959D+00 |
| MG+2 | 5.7357D+00 | 1.8099D+02 | 3.1555D+01 |

| | | | |
|---|---|---|---|
| NA+ | 9.3131D-02 | 1.1451D-01 | 1.2296D+00 |
| K+ | 2.1516D-02 | 2.3108D-03 | 1.0740D-01 |
| CL- | 1.1461D+01 | 3.2446D+02 | 2.8310D+01 |
| CO3-2 | 1.2564D-05 | 8.0972D-11 | 6.4445D-06 |
| SO4-2 | 6.3396D-02 | 1.2307D-02 | 1.9413D-01 |
| OH- | 3.4779D-04 | 3.4921D-09 | 1.0041D-05 |
| HCO3- | 4.3246D-05 | 1.7206D-06 | 3.9787D-02 |
| H2CO3 | 1.4310D-06 | 1.0766D-05 | 7.5233D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 1.4490D+01 |
| CASO4 | 8.5843D-01 |
| CACO3 | 4.9460D-03 |
| CA(OH)2 | 7.2604D-04 |
| MGCL2 | 2.9353D+01 |
| MGSO4 | 2.4750D+00 |
| MGCO3 | 1.4260D-02 |
| MG(OH)2 | 1.4708D-03 |
| NACL | 5.8999D+00 |
| NA2SO4 | 6.6455D-01 |
| NAHCO3 | 2.2118D-01 |
| NA2CO3 | 2.1358D-02 |
| NAOH | 3.5137D-03 |
| KCL | 1.7437D+00 |
| K2SO4 | 1.3083D-01 |
| KHCO3 | 6.5369D-02 |
| K2CO3 | 4.2047D-03 |
| KOH | 1.0385D-03 |
| HCL | 2.0188D+01 |
| H2SO4 | 3.4266D+00 |

**Test problem 3: The anhydrite-gypsum phase boundary in the system $NaCl-H_2O$ at 25 °Celsius**

At constant temperature and pressure equilibrium between anhydrite and gypsum occurs at a single value of the activity of $H_2O$. This follows from the dehydration reaction

$$CaSO_4 \cdot 2H_2O = CaSO_4 + 2H_2O$$

where the solids are in their standard state and the equilibrium constant for the reaction is equal to the square of the activity of $H_2O$ in solution. Using the standard free energy data of Harvie and others (1984), the anhydrite-gypsum phase boundary occurs at a water activity of 0.7773 at 25 °C and 1 atmosphere total pressure. In this test problem we locate the anhydrite-gypsum phase boundary in the $NaCl-H_2O$ system. This is accomplished by adding NaCl as an irreversible reaction until equilibrium with both anhydrite and gypsum occurs. Adding an irreversible reaction to reach a phase boundary is a special case of PHRQPITZ (and PHREEQE) made possible by setting IOPT(3) to 6. The program then adds (or subtracts) the irreversible reaction to solution 1 until saturation is just reached with the first mineral listed under MINERALS input. This first mineral will have zero mass transfer but will be just saturated as the reaction reaches the phase boundary. The mass transfers of other minerals in MINERALS input will vary with extent of reaction.

The input file for test problem 3 is listed in table 10. The second line of input selects IOPT(3) = 6 and there are 2 components in the reaction (Na and Cl) defined under REACTION input. The starting solution is pure water. By placing anhydrite first under MINERALS input we find the amount of NaCl to be dissolved in water, while maintaining equilibrium with gypsum to just reach saturation with anhydrite (though no solid anhydrite is yet present). More advanced problems of this type can be set up to define reaction paths in general (see test problem 5 of Parkhurst and others (1980), and test problem 6 of this report).

The computed results are listed in table 11 showing that dissolution of 5.5737 moles of halite per kg $H_2O$ is required to reach the gypsum-anhydrite phase boundary corresponding to a water activity of 0.7773. The solubility of gypsum in this NaCl solution is 48.01561 mmol per kg $H_2O$.

Table 10. -- Line images of the input file to test problem 3

```
Test Problem 3: Find the anhydrite-gypsum phase boundary with NaCl addition.
0060020000 0 2       0.0
SOLUTION 1
pure water
 0  0 0   7.         4.0      25.        1.0
MINERALS
ANHYDRIT   2         6.00    -4.362              1
   4      1.000  16      1.000
422.950     0.0          -18431.     -147.708
GYPSUM     3         6.00   -4.581               1
   4 1.0          16 1.0          3 2.0
90.318      0.0          -4213.      -32.641

REACTION
   61.      0.        141.      0.
END
```

Table 11. -- Listing of printout from test problem 3

```
         DATA READ FROM DISK

 ELEMENTS
 SPECIES
 LOOK MIN
 MEAN GAM
1Test Problem 3: Find the anhydrite-gypsum phase boundary with NaCl addition.
 0060020000 0 2          0.00000
 SOLUTION 1
 pure water
  0  0 0      7.00       4.00       25.0       1.00
 MINERALS
 ANHYDRIT    2       6.0       -4.4       0.00          1                0.000
    4   1.00       16   1.00
   4.2295E+02  0.0000E-01 -1.8431E+04 -1.4771E+02  0.0000E-01
 GYPSUM      3       6.0       -4.6       0.00          1                0.000
    4   1.00       16   1.00        3   2.00
   9.0318E+01  0.0000E-01 -4.2130E+03 -3.2641E+01  0.0000E-01
            0      0.00       0.00       0.00          0                0.000
 REACTION
    6   1.000   0.000  14   1.000   0.000
1SOLUTION NUMBER 1
 pure water
```

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|

PURE WATER

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 7.0000 |
| ACTIVITY H2O = | 1.0000 |
| OSMOTIC COEFFICIENT = | 0.9999 |
| IONIC STRENGTH = | 0.0000 |
| TEMPERATURE = | 25.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9971 G/CC |
| ELECTRICAL BALANCE = | -4.6175D-10 |
| TOTAL ALKALINITY = | 1.0050D-07 |
| ITERATIONS = | 5 |

---

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 1.000E-07 | -7.000 | 1.000E-07 | -7.000 | 9.996E-01 | 0.000 |
| 3 | H2O | 0.0 | 1.000E+00 | 0.000 | 1.000E+00 | 0.000 | 1.000E+00 | 0.000 |
| 31 | OH- | -1.0 | 1.005E-07 | -6.998 | 1.005E-07 | -6.998 | 9.996E-01 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 1.0004D-07 | 1.0000D-07 | 9.9963D-01 |
| OH- | 1.0050D-07 | 1.0046D-07 | 9.9963D-01 |

1STEP NUMBER 1
0----------

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| PURE WATER | | |

----PHASE BOUNDARIES----

| | PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|---|
| | ANHYDRIT | 0.000000D-01 | -4.3617 | -4.3617 | 0.0000 |
| + | ** | | | | |
| | GYPSUM | 4.801542D-02 | -4.5805 | -4.5805 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

** 5.573737D+00 MOLES OF REACTION HAVE BEEN ADDED TO THE SOLUTION
TO REACH THE ANHYDRIT PHASE BOUNDARY.

REACTION IS:

| | | |
|---|---|---|
| 1.000000 MOLES OF NA | VALENCE = | 0.000 |
| 1.000000 MOLES OF CL | VALENCE = | 0.000 |

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|

| | | | |
|---|---|---|---|
| ANHYDRIT | -4.3617 | -4.3617 | 0.0000 |
| GLAUBERI | -5.9695 | -5.2450 | -0.7245 |
| GYPSUM | -4.5805 | -4.5805 | 0.0000 |
| HALITE | 1.4407 | 1.5700 | -0.1293 |
| LABILE S | -7.7962 | -5.6720 | -2.1242 |
| MIRABIL | -2.7018 | -1.2135 | -1.4883 |
| PORTLAND | -16.0990 | -5.1900 | -10.9090 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 4.801542D-02 | -1.3186 |
| NA | 5.573737D+00 | 0.7461 |
| CL | 5.573737D+00 | 0.7461 |
| S | 4.801542D-02 | -1.3186 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 6.7203 |
| ACTIVITY H2O = | 0.7773 |
| OSMOTIC COEFFICIENT = | 1.2436 |
| IONIC STRENGTH = | 5.7658 |
| TEMPERATURE = | 25.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9971 G/CC |
| ELECTRICAL BALANCE = | -4.6196D-10 |
| TOTAL ALKALINITY = | 7.9772D-08 |
| ITERATIONS = | 28 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | UNSCALED LOG ACT | UNSCALED GAMMA | UNSCALED LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 4.983E-08 | -7.302 | 1.904E-07 | -6.720 | 3.821E+00 | 0.582 |
| 3 | H2O | 0.0 | 7.773E-01 | -0.109 | 7.773E-01 | -0.109 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 4.802E-02 | -1.319 | 4.734E-02 | -1.325 | 9.859E-01 | -0.006 |
| 6 | NA+ | 1.0 | 5.574E+00 | 0.746 | 5.182E+00 | 0.715 | 9.298E-01 | -0.032 |
| 14 | CL- | -1.0 | 5.574E+00 | 0.746 | 5.323E+00 | 0.726 | 9.549E-01 | -0.020 |
| 16 | SO4-2 | -2.0 | 4.802E-02 | -1.319 | 9.186E-04 | -3.037 | 1.913E-02 | -1.718 |
| 31 | OH- | -1.0 | 7.977E-08 | -7.098 | 4.101E-08 | -7.387 | 5.141E-01 | -0.289 |
| 40 | HSO4- | -1.0 | 2.948E-08 | -7.531 | 1.666E-08 | -7.778 | 5.653E-01 | -0.248 |

UNSCALED UNSCALED

| SPECIES | TOTAL MOL | ACTIVITY | TOTAL GAMMA |
|---|---|---|---|
| H+ | 7.9310D-08 | 1.9042D-07 | 2.4009D+00 |
| CA+2 | 4.8015D-02 | 4.7336D-02 | 9.8586D-01 |
| NA+ | 5.5737D+00 | 5.1824D+00 | 9.2979D-01 |
| CL- | 5.5737D+00 | 5.3226D+00 | 9.5494D-01 |
| SO4-2 | 4.8015D-02 | 9.1857D-04 | 1.9131D-02 |
| OH- | 7.9772D-08 | 4.1010D-08 | 5.1410D-01 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 9.6514D-01 |
| CASO4 | 1.3733D-01 |
| CA(OH)2 | 6.3871D-01 |
| NACL | 9.4228D-01 |
| NA2SO4 | 2.5478D-01 |
| NAOH | 6.9138D-01 |
| HCL | 1.5142D+00 |
| H2SO4 | 4.7954D-01 |

**Test problem 4: Solubility with incremental temperature variation: halite-water system**

PHRQPITZ does not allow the temperature to be varied incrementally without definition of a corresponding increment of reaction. Therefore, in order to calculate the solubility of a mineral at various temperatures, it is necessary to define a null irreversible reaction. In this problem we examine the solubility of halite in pure water between 0 and 300 °C. Halite is the only mineral in the PHRQPITZ data base for which the thermodynamic data are adequate for calculations beyond 100 °C. The input file is listed in table 12. IOPT(3) = 3 indicating that an irreversible reaction (null in this case) will be added at specified increments. IOPT(4) = 3 indicating that the temperature will be defined for each reaction step given under the keyword TEMP. There are 5 steps in the reaction (NSTEPS = 5) and 2 components in the reaction (NCOMPS = 2). We have arbitrarily defined the reaction to add NaCl (REACTION input) with the mass of NaCl added for each increment defined to be 0.0 (STEPS input). The starting solution is pure water and halite equilibrium is obtained by inclusion of the appropriate MINERALS data.

The computed results are listed in table 13. For each increment of null reaction a new temperature is defined and solution 1 (pure water) is equilibrated with halite at the new temperature. The computed solubilities all agree within 2 percent of values given in Pitzer, Peiper and Busey (1984) reflecting the accuracy of the fit of log K to these data (table 1). At temperatures greater than 100 °C the computed vapor pressure of pure water is identical to values given by Pitzer, Peiper and Busey (1984) reaching 84.7 atmospheres (85.5 bars) at 300 °C.

Table 12. -- Line images of the input file to test problem 4

```
Test Problem 4: Solubility with incremental temperature variation: halite-water
0033020000 5 2       0.0
SOLUTION 1
Pure water
 0  0 0    7.0       4.0       25.0      1.0
MINERALS
HALITE     2         0.00    1.570                1
   6      1.000  14      1.000
-713.4616   -.1201241   37302.21    262.4583    -2106915.

TEMP
0.        25.       100.      200.      300.
STEPS
0.        0.        0.        0.        0.
REACTION
   61.      0.        141.      0.
END
```

Table 13. -- Listing of printout from test problem 4

```
         DATA READ FROM DISK

 ELEMENTS
 SPECIES
 LOOK MIN
 MEAN GAM
1Test Problem 4: Solubility with incremental temperature variation: halite-water
 0033020000 5 2         0.00000
 SOLUTION 1
 Pure water
  0  0 0      7.00       4.00       25.0       1.00
 MINERALS
 HALITE      2      0.00        1.6       0.00          1                0.000
    6    1.00       14    1.00
  -7.1346E+02 -1.2012E-01  3.7302E+04  2.6246E+02 -2.1069E+06
             0      0.00       0.00       0.00          0                0.000
 TEMP
  0.000       25.0       100.       200.       300.
 STEPS
  0.000      0.000      0.000      0.000      0.000
 REACTION
    6    1.000    0.000   14    1.000    0.000
1SOLUTION NUMBER 1
 Pure water


                    TOTAL MOLALITIES OF ELEMENTS
                    ----- ---------- -- --------

               ELEMENT          MOLALITY         LOG MOLALITY

               PURE WATER


                    ----DESCRIPTION OF SOLUTION----

                                    PH =   7.0000
                          ACTIVITY H2O =   1.0000
                 OSMOTIC COEFFICIENT =   0.9999
                      IONIC STRENGTH =   0.0000
                         TEMPERATURE =  25.0000
                            PRESSURE =   1.0000 ATM
                       DENSITY OF H2O =   0.9971 G/CC
                   ELECTRICAL BALANCE =  -4.6175D-10
                     TOTAL ALKALINITY =   1.0050D-07
                           ITERATIONS =   5
```

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 1.000E-07 | -7.000 | 1.000E-07 | -7.000 | 9.996E-01 | 0.000 |
| 3 | H2O | 0.0 | 1.000E+00 | 0.000 | 1.000E+00 | 0.000 | 1.000E+00 | 0.000 |
| 31 | OH- | -1.0 | 1.005E-07 | -6.998 | 1.005E-07 | -6.998 | 9.996E-01 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 1.0004D-07 | 1.0000D-07 | 9.9963D-01 |
| OH- | 1.0050D-07 | 1.0046D-07 | 9.9963D-01 |

1STEP NUMBER 1
0----------
0 0.000D-01 MOLES OF REACTION HAVE BEEN ADDED.

REACTION IS:
1.000000 MOLES OF NA VALENCE = 0.000
1.000000 MOLES OF CL VALENCE = 0.000
0.00 = NEW TEMPERATURE (C).

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| PURE WATER | | |

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| HALITE | 6.093272D+00 | 1.5046 | 1.5046 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| HALITE | 1.5046 | 1.5046 | 0.0000 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| NA | 6.093272D+00 | 0.7849 |
| CL | 6.093272D+00 | 0.7849 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 7.0322 |
| ACTIVITY H2O = | 0.7577 |
| OSMOTIC COEFFICIENT = | 1.2641 |
| IONIC STRENGTH = | 6.0933 |
| TEMPERATURE = | 0.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9998 G/CC |
| ELECTRICAL BALANCE = | -4.6168D-10 |
| TOTAL ALKALINITY = | 1.7906D-08 |
| ITERATIONS = | 24 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 1.744E-08 | -7.758 | 9.284E-08 | -7.032 | 5.322E+00 | 0.726 |
| 3 | H2O | 0.0 | 7.577E-01 | -0.121 | 7.577E-01 | -0.121 | 1.000E+00 | 0.000 |
| 6 | NA+ | 1.0 | 6.093E+00 | 0.785 | 5.653E+00 | 0.752 | 9.278E-01 | -0.033 |
| 14 | CL- | -1.0 | 6.093E+00 | 0.785 | 5.653E+00 | 0.752 | 9.278E-01 | -0.033 |
| 31 | OH- | -1.0 | 1.791E-08 | -7.747 | 1.043E-08 | -7.982 | 5.827E-01 | -0.235 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 1.7444D-08 | 9.2844D-08 | 5.3223D+00 |
| NA+ | 6.0933D+00 | 5.6534D+00 | 9.2781D-01 |
| CL- | 6.0933D+00 | 5.6534D+00 | 9.2781D-01 |
| OH- | 1.7906D-08 | 1.0433D-08 | 5.8267D-01 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|

| | |
|---|---|
| NACL | 9.2781D-01 |
| NAOH | 7.3526D-01 |
| HCL | 2.2222D+00 |

1STEP NUMBER 2
0----------
0 0.000D-01 MOLES OF REACTION HAVE BEEN ADDED.

REACTION IS:

1.000000 MOLES OF NA VALENCE = 0.000
1.000000 MOLES OF CL VALENCE = 0.000
25.00 = NEW TEMPERATURE (C).

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|

PURE WATER

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| HALITE | 6.099676D+00 | 1.5700 | 1.5700 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| HALITE | 1.5700 | 1.5700 | 0.0000 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| NA | 6.099676D+00 | 0.7853 |
| CL | 6.099676D+00 | 0.7853 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 6.5971 |
| ACTIVITY H2O = | 0.7546 |
| OSMOTIC COEFFICIENT = | 1.2813 |
| IONIC STRENGTH = | 6.0997 |
| TEMPERATURE = | 25.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9971 G/CC |
| ELECTRICAL BALANCE = | -4.6169D-10 |
| TOTAL ALKALINITY = | 5.5149D-08 |
| ITERATIONS = | 24 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 5.469E-08 | -7.262 | 2.529E-07 | -6.597 | 4.624E+00 | 0.665 |
| 3 | H2O | 0.0 | 7.546E-01 | -0.122 | 7.546E-01 | -0.122 | 1.000E+00 | 0.000 |
| 6 | NA+ | 1.0 | 6.100E+00 | 0.785 | 6.095E+00 | 0.785 | 9.993E-01 | 0.000 |
| 14 | CL- | -1.0 | 6.100E+00 | 0.785 | 6.095E+00 | 0.785 | 9.993E-01 | 0.000 |
| 31 | OH- | -1.0 | 5.515E-08 | -7.258 | 2.998E-08 | -7.523 | 5.436E-01 | -0.265 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 5.4688D-08 | 2.5286D-07 | 4.6237D+00 |
| NA+ | 6.0997D+00 | 6.0953D+00 | 9.9929D-01 |
| CL- | 6.0997D+00 | 6.0953D+00 | 9.9929D-01 |
| OH- | 5.5149D-08 | 2.9980D-08 | 5.4361D-01 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| NACL | 9.9929D-01 |
| NAOH | 7.3704D-01 |
| HCL | 2.1495D+00 |

1STEP NUMBER 3
0----------
0 0.000D-01 MOLES OF REACTION HAVE BEEN ADDED.

REACTION IS:

| | | |
|---|---|---|
| 1.000000 MOLES OF NA | VALENCE = | 0.000 |
| 1.000000 MOLES OF CL | VALENCE = | 0.000 |

100.00 = NEW TEMPERATURE (C).

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|

PURE WATER

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| HALITE | 6.624753D+00 | 1.5605 | 1.5605 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| HALITE | 1.5605 | 1.5605 | 0.0000 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| NA | 6.624753D+00 | 0.8212 |
| CL | 6.624753D+00 | 0.8212 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 5.6149 |
| ACTIVITY H2O = | 0.7442 |
| OSMOTIC COEFFICIENT = | 1.2375 |
| IONIC STRENGTH = | 6.6248 |
| TEMPERATURE = | 100.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9584 G/CC |
| ELECTRICAL BALANCE = | -3.8820D-10 |
| TOTAL ALKALINITY = | 6.6989D-07 |

ITERATIONS = 24

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 6.695E-07 | -6.174 | 2.427E-06 | -5.615 | 3.626E+00 | 0.559 |
| 3 | H2O | 0.0 | 7.442E-01 | -0.128 | 7.442E-01 | -0.128 | 1.000E+00 | 0.000 |
| 6 | NA+ | 1.0 | 6.625E+00 | 0.821 | 6.029E+00 | 0.780 | 9.101E-01 | -0.041 |
| 14 | CL- | -1.0 | 6.625E+00 | 0.821 | 6.029E+00 | 0.780 | 9.101E-01 | -0.041 |
| 31 | OH- | -1.0 | 6.699E-07 | -6.174 | 2.849E-07 | -6.545 | 4.253E-01 | -0.371 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 6.6950D-07 | 2.4274D-06 | 3.6256D+00 |
| NA+ | 6.6248D+00 | 6.0293D+00 | 9.1012D-01 |
| CL- | 6.6248D+00 | 6.0293D+00 | 9.1012D-01 |
| OH- | 6.6989D-07 | 2.8490D-07 | 4.2529D-01 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| NACL | 9.1012D-01 |
| NAOH | 6.2215D-01 |
| HCL | 1.8165D+00 |

1STEP NUMBER 4
0----------
0 0.000D-01 MOLES OF REACTION HAVE BEEN ADDED.

REACTION IS:
1.000000 MOLES OF NA VALENCE = 0.000
1.000000 MOLES OF CL VALENCE = 0.000
200.00 = NEW TEMPERATURE (C).

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| PURE WATER | | |

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| HALITE | 7.837636D+00 | 1.2041 | 1.2041 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| HALITE | 1.2041 | 1.2041 | 0.0000 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| NA | 7.837636D+00 | 0.8942 |
| CL | 7.837636D+00 | 0.8942 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 4.6777 |
| ACTIVITY H2O = | 0.7415 |
| OSMOTIC COEFFICIENT = | 1.0589 |
| IONIC STRENGTH = | 7.8376 |
| TEMPERATURE = | 200.0000 |
| PRESSURE = | 15.3333 ATM |
| DENSITY OF H2O = | 0.8647 G/CC |
| ELECTRICAL BALANCE = | -4.4288D-10 |
| TOTAL ALKALINITY = | 7.5880D-06 |
| ITERATIONS = | 27 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 7.588E-06 | -5.120 | 2.100E-05 | -4.678 | 2.768E+00 | 0.442 |
| 3 | H2O | 0.0 | 7.415E-01 | -0.130 | 7.415E-01 | -0.130 | 1.000E+00 | 0.000 |
| 6 | NA+ | 1.0 | 7.838E+00 | 0.894 | 4.000E+00 | 0.602 | 5.103E-01 | -0.292 |

```
 14 CL-      -1.0  7.838E+00    0.894   4.000E+00    0.602  5.103E-01  -0.292
 31 OH-      -1.0  7.588E-06   -5.120   1.472E-06   -5.832  1.940E-01  -0.712
```

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 7.5876D-06 | 2.1002D-05 | 2.7680D+00 |
| NA+ | 7.8376D+00 | 3.9997D+00 | 5.1032D-01 |
| CL- | 7.8376D+00 | 3.9997D+00 | 5.1032D-01 |
| OH- | 7.5880D-06 | 1.4718D-06 | 1.9397D-01 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| NACL | 5.1032D-01 |
| NAOH | 3.1462D-01 |
| HCL | 1.1885D+00 |

```
1STEP NUMBER  5
0--------------
0 0.000D-01 MOLES OF REACTION HAVE BEEN ADDED.


      REACTION IS:
                  1.000000 MOLES OF NA         VALENCE =    0.000
                  1.000000 MOLES OF CL         VALENCE =    0.000
                          300.00 = NEW TEMPERATURE (C).
```

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| PURE WATER | | |

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| HALITE | 1.020741D+01 | 0.2888 | 0.2888 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| HALITE | 0.2888 | 0.2888 | 0.0000 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| NA | 1.020741D+01 | 1.0089 |
| CL | 1.020741D+01 | 1.0089 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 3.6159 |
| ACTIVITY H2O = | 0.7658 |
| OSMOTIC COEFFICIENT = | 0.7256 |
| IONIC STRENGTH = | 10.2075 |
| TEMPERATURE = | 300.0000 |
| PRESSURE = | 84.7091 ATM |
| DENSITY OF H2O = | 0.7124 G/CC |
| ELECTRICAL BALANCE = | -6.5533D-10 |
| TOTAL ALKALINITY = | 1.0802D-04 |
| ITERATIONS = | 32 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 1.080E-04 | -3.967 | 2.421E-04 | -3.616 | 2.242E+00 | 0.351 |
| 3 | H2O | 0.0 | 7.658E-01 | -0.116 | 7.658E-01 | -0.116 | 1.000E+00 | 0.000 |
| 6 | NA+ | 1.0 | 1.021E+01 | 1.009 | 1.394E+00 | 0.144 | 1.366E-01 | -0.865 |
| 14 | CL- | -1.0 | 1.021E+01 | 1.009 | 1.394E+00 | 0.144 | 1.366E-01 | -0.865 |
| 31 | OH- | -1.0 | 1.080E-04 | -3.967 | 1.569E-06 | -5.805 | 1.452E-02 | -1.838 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 1.0802D-04 | 2.4214D-04 | 2.2417D+00 |
| NA+ | 1.0207D+01 | 1.3944D+00 | 1.3660D-01 |
| CL- | 1.0207D+01 | 1.3944D+00 | 1.3661D-01 |
| OH- | 1.0802D-04 | 1.5685D-06 | 1.4521D-02 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| NACL | 1.3660D-01 |
| NAOH | 4.4538D-02 |
| HCL | 5.5338D-01 |

**Test problem 5: Fresh water - brine mixing in a closed system.**

In this problem we use PHRQPITZ to calculate the solubility of calcite in mixtures of (1) a dilute water in equilibrium with calcite at log $PCO_2$ of -2.0 and (2) a sodium chloride brine in equilibrium with halite and calcite at log $PCO_2$ of -2.0. The mixing environment is assumed to be closed to $CO_2$. All calculations are at 25 °C. The problem is in 3 parts (table 14). The end-member waters are constructed in parts a and b by equilibrating pure water with calcite at a log $PCO_2$ of -2.0 (part a), and calcite-halite at log $PCO_2$ = -2.0 (part b). The final solution of part a is stored in solution 2 (IOPT(7)=2) and the final solution of part b is stored in solution 1 (IOPT(7)=1). In part c IOPT(3) is set to 1 selecting the mixing case and NSTEPS is 5 indicating that 5 mixtures will be solved. The fraction of solution 1 for each mixture is defined under STEPS input. Each mixture is equilibrated with calcite in a system closed to $CO_2$ gas. The results are listed in table 15.

Solution 2 (defined in part a) is representative of a dilute calcium bicarbonate ground water in equilibrium with calcite. Solution 1 is a hypothetical NaCl brine in equilibrium with calcite at the same $PCO_2$. The solubility of calcite is higher in the NaCl solution owing to the decrease in the mean activity coefficient of $CaCO_3$. Although both end-members are saturated with calcite, their mixtures are undersaturated and dissolve calcite owing to the non-linear variation in activity coefficients with concentration (table 15).

Table 14. -- Line images of the input file to test problem 5

```
Test Problem 5 (part a): Calcite-CO2-H2O equilibrium at log PCO2 = -2.
0050022000 0 0       0.0
SOLUTION 1
Pure water
 0  0 0    7.0       4.0       25.0      1.0
MINERALS
CALCITE    2         4.00   -8.406                1
  15 1.0          4 1.0
-171.8329   -.077993    2839.319    71.595
PCO2       1         4.0    -1.468     -4.776     1         -2.
  35  1.0
108.3865    0.01985076  -6919.53    -40.45154    669365.0

END
Test Problem 5 (part b): Calcite-Halite-CO2-H2O system at log PCO2 = -2.
0050021000 0 0       0.0
SOLUTION 1
Pure water
 0  0 0    7.0       4.0       25.0      1.0
MINERALS
CALCITE    2         4.00   -8.406                1
  15 1.0          4 1.0
-171.8329   -.077993    2839.319    71.595
PCO2       1         4.0    -1.468     -4.776     1         -2.
  35  1.0
108.3865    0.01985076  -6919.53    -40.45154    669365.0
HALITE     2         0.00    1.570                 1
   6      1.000  14       1.000
-713.4616   -.1201241   37302.21    262.4583    -2106915.

END
Test Problem 5 (part c): Mix solns. 1 and 2 maintaining calcite saturation.
0010020000 5 0       0.0
MINERALS
CALCITE    2         4.00   -8.406                1
  15 1.0          4 1.0
-171.8329   -.077993    2839.319    71.595

STEPS
 .1       .3        .5        .7        .9
END
```

Table 15. -- Listing of printout from test problem 5

```
         DATA READ FROM DISK

 ELEMENTS
 SPECIES
 LOOK MIN
 MEAN GAM
1Test Problem 5 (part a): Calcite-CO2-H2O equilibrium at log PCO2 = -2.
 0050022000 0 0         0.00000
 SOLUTION 1
 Pure water
  0  0 0     7.00       4.00       25.0       1.00
 MINERALS
 CALCITE    2       4.0       -8.4       0.00          1                0.000
   15   1.00        4   1.00
  -1.7183E+02 -7.7993E-02  2.8393E+03  7.1595E+01  0.0000E-01
 PCO2       1       4.0       -1.5       -4.8          1               -2.000
   35   1.00
   1.0839E+02  1.9851E-02 -6.9195E+03 -4.0452E+01  6.6936E+05
            0     0.00       0.00       0.00          0                0.000
1SOLUTION NUMBER 1
 Pure water
```

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|

PURE WATER

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 7.0000 |
| ACTIVITY H2O = | 1.0000 |
| OSMOTIC COEFFICIENT = | 0.9999 |
| IONIC STRENGTH = | 0.0000 |
| TEMPERATURE = | 25.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9971 G/CC |
| ELECTRICAL BALANCE = | -4.6175D-10 |
| TOTAL ALKALINITY = | 1.0050D-07 |
| ITERATIONS = | 5 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 1.000E-07 | -7.000 | 1.000E-07 | -7.000 | 9.996E-01 | 0.000 |
| 3 | H2O | 0.0 | 1.000E+00 | 0.000 | 1.000E+00 | 0.000 | 1.000E+00 | 0.000 |
| 31 | OH- | -1.0 | 1.005E-07 | -6.998 | 1.005E-07 | -6.998 | 9.996E-01 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 1.0004D-07 | 1.0000D-07 | 9.9963D-01 |
| OH- | 1.0050D-07 | 1.0046D-07 | 9.9963D-01 |

1STEP NUMBER 1
0----------

TOTAL MOLALITIES OF ELEMENTS
----- ---------- -- --------

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|

PURE WATER

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| CALCITE | 1.741541D-03 | -8.4062 | -8.4062 | 0.0000 |
| PCO2 | 2.071791D-03 | -3.4679 | -1.4679 | -2.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ARAGONIT | -8.4062 | -8.2195 | -0.1868 |
| CALCITE | -8.4062 | -8.4062 | 0.0000 |
| PCO2 | -3.4679 | -1.4679 | -2.0000 |
| PORTLAND | -16.2576 | -5.1900 | -11.0676 |

TOTAL MOLALITIES OF ELEMENTS
----- ---------- -- --------

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.741541D-03 | -2.7591 |
| C | 3.813332D-03 | -2.4187 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 7.3147 |
| ACTIVITY H2O = | 0.9999 |
| OSMOTIC COEFFICIENT = | 0.9576 |
| IONIC STRENGTH = | 0.0052 |
| TEMPERATURE = | 25.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9971 G/CC |
| ELECTRICAL BALANCE = | 4.3136D-09 |
| TOTAL ALKALINITY = | 3.4831D-03 |
| ITERATIONS = | 10 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 5.274E-08 | -7.278 | 4.845E-08 | -7.315 | 9.188E-01 | -0.037 |
| 3 | H2O | 0.0 | 9.999E-01 | 0.000 | 9.999E-01 | 0.000 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 1.736E-03 | -2.760 | 1.286E-03 | -2.891 | 7.406E-01 | -0.130 |
| 15 | CO3-2 | -2.0 | 4.251E-06 | -5.372 | 3.052E-06 | -5.515 | 7.181E-01 | -0.144 |
| 31 | OH- | -1.0 | 2.250E-07 | -6.648 | 2.073E-07 | -6.683 | 9.214E-01 | -0.036 |
| 34 | HCO3- | -1.0 | 3.463E-03 | -2.461 | 3.230E-03 | -2.491 | 9.327E-01 | -0.030 |
| 35 | H2CO3 | 0.0 | 3.402E-04 | -3.468 | 3.405E-04 | -3.468 | 1.001E+00 | 0.000 |
| 76 | CACO3 | 0.0 | 5.560E-06 | -5.255 | 5.560E-06 | -5.255 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 5.2736D-08 | 4.8455D-08 | 9.1882D-01 |
| CA+2 | 1.7415D-03 | 1.2857D-03 | 7.3826D-01 |
| CO3-2 | 9.8103D-06 | 3.0523D-06 | 3.1113D-01 |
| OH- | 2.2499D-07 | 2.0731D-07 | 9.2144D-01 |
| HCO3- | 3.4633D-03 | 3.2301D-03 | 9.3267D-01 |
| H2CO3 | 3.4024D-04 | 3.4045D-04 | 1.0006D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACO3 | 4.7926D-01 |

```
                          CA(OH)2       8.5582D-01
1Test Problem 5 (part b): Calcite-Halite-CO2-H2O system at log PCO2 = -2.
 0050021000 0 0         0.00000
 SOLUTION 1
 Pure water
  0  0 0     7.00       4.00       25.0       1.00
 MINERALS
 CALCITE     2        4.0        -8.4       0.00          1               0.000
   15   1.00         4    1.00
  -1.7183E+02 -7.7993E-02  2.8393E+03  7.1595E+01  0.0000E-01
 PCO2        1        4.0        -1.5       -4.8          1              -2.000
   35   1.00
   1.0839E+02  1.9851E-02 -6.9195E+03 -4.0452E+01  6.6936E+05
 HALITE      2        0.00        1.6       0.00          1               0.000
    6   1.00         14    1.00
  -7.1346E+02 -1.2012E-01  3.7302E+04  2.6246E+02 -2.1069E+06
            0        0.00       0.00       0.00          0               0.000
1SOLUTION NUMBER 1
 Pure water
```

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| PURE WATER | | |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 7.0000 |
| ACTIVITY H2O = | 1.0000 |
| OSMOTIC COEFFICIENT = | 0.9999 |
| IONIC STRENGTH = | 0.0000 |
| TEMPERATURE = | 25.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9971 G/CC |
| ELECTRICAL BALANCE = | -4.6175D-10 |
| TOTAL ALKALINITY = | 1.0050D-07 |
| ITERATIONS = | 5 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | UNSCALED LOG ACT | UNSCALED GAMMA | UNSCALED LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 1.000E-07 | -7.000 | 1.000E-07 | -7.000 | 9.996E-01 | 0.000 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 3 H2O | 0.0 | 1.000E+00 | 0.000 | 1.000E+00 | 0.000 | 1.000E+00 | 0.000 |
| 31 OH- | -1.0 | 1.005E-07 | -6.998 | 1.005E-07 | -6.998 | 9.996E-01 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 1.0004D-07 | 1.0000D-07 | 9.9963D-01 |
| OH- | 1.0050D-07 | 1.0046D-07 | 9.9963D-01 |

1STEP NUMBER 1
0----------

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|

PURE WATER

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| CALCITE | 2.544505D-03 | -8.4062 | -8.4062 | 0.0000 |
| PCO2 | 2.596886D-03 | -3.4679 | -1.4679 | -2.0000 |
| HALITE | 6.098571D+00 | 1.5700 | 1.5700 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ARAGONIT | -8.4062 | -8.2195 | -0.1868 |
| CALCITE | -8.4062 | -8.4062 | 0.0000 |
| GAYLUSSI | -13.3763 | -9.4210 | -3.9553 |
| HALITE | 1.5700 | 1.5700 | 0.0000 |
| NAHCOLIT | -12.3127 | -10.7420 | -1.5707 |
| NATRON | -5.5818 | -0.8250 | -4.7568 |
| PCO2 | -3.4679 | -1.4679 | -2.0000 |
| PIRSSONI | -13.0093 | -9.2340 | -3.7753 |
| PORTLAND | -16.3799 | -5.1900 | -11.1899 |
| TRONA | -16.9157 | -11.3840 | -5.5317 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 2.544505D-03 | -2.5944 |
| NA | 6.098571D+00 | 0.7852 |
| CL | 6.098571D+00 | 0.7852 |
| C | 5.141390D-03 | -2.2889 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 7.1698 |
| ACTIVITY H2O = | 0.7545 |
| OSMOTIC COEFFICIENT = | 1.2813 |
| IONIC STRENGTH = | 6.1062 |
| TEMPERATURE = | 25.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9971 G/CC |
| ELECTRICAL BALANCE = | -4.0491D-10 |
| TOTAL ALKALINITY = | 5.0890D-03 |
| ITERATIONS = | 24 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 1.464E-08 | -7.834 | 6.764E-08 | -7.170 | 4.619E+00 | 0.665 |
| 3 | H2O | 0.0 | 7.545E-01 | -0.122 | 7.545E-01 | -0.122 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 2.539E-03 | -2.595 | 3.320E-03 | -2.479 | 1.308E+00 | 0.117 |
| 6 | NA+ | 1.0 | 6.099E+00 | 0.785 | 6.089E+00 | 0.785 | 9.984E-01 | -0.001 |
| 14 | CL- | -1.0 | 6.099E+00 | 0.785 | 6.102E+00 | 0.785 | 1.001E+00 | 0.000 |
| 15 | CO3-2 | -2.0 | 4.863E-05 | -4.313 | 1.182E-06 | -5.927 | 2.430E-02 | -1.614 |
| 31 | OH- | -1.0 | 2.065E-07 | -6.685 | 1.121E-07 | -6.951 | 5.426E-01 | -0.266 |
| 34 | HCO3- | -1.0 | 4.980E-03 | -2.303 | 1.746E-03 | -2.758 | 3.506E-01 | -0.455 |
| 35 | H2CO3 | 0.0 | 1.068E-04 | -3.972 | 3.405E-04 | -3.468 | 3.189E+00 | 0.504 |
| 76 | CACO3 | 0.0 | 5.560E-06 | -5.255 | 5.560E-06 | -5.255 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 1.4644D-08 | 6.7638D-08 | 4.6187D+00 |
| CA+2 | 2.5445D-03 | 3.3202D-03 | 1.3048D+00 |
| NA+ | 6.0986D+00 | 6.0888D+00 | 9.9840D-01 |
| CL- | 6.0986D+00 | 6.1018D+00 | 1.0005D+00 |
| CO3-2 | 5.4192D-05 | 1.1820D-06 | 2.1811D-02 |
| OH- | 2.0652D-07 | 1.1206D-07 | 5.4261D-01 |

| | | | |
|---|---|---|---|
| HCO3- | 4.9804D-03 | 1.7460D-03 | 3.5058D-01 |
| H2CO3 | 1.0676D-04 | 3.4046D-04 | 3.1888D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 1.0931D+00 |
| CACO3 | 1.6870D-01 |
| CA(OH)2 | 7.2696D-01 |
| NACL | 9.9947D-01 |
| NAHCO3 | 5.9162D-01 |
| NA2CO3 | 2.7910D-01 |
| NAOH | 7.3603D-01 |
| HCL | 2.1497D+00 |

```
1Test Problem 5 (part c): Mix solns. 1 and 2 maintaining calcite saturation.
 0010020000 5 0         0.00000
 MINERALS
 CALCITE    2       4.0       -8.4       0.00          1              0.000
   15   1.00        4    1.00
  -1.7183E+02 -7.7993E-02  2.8393E+03  7.1595E+01  0.0000E-01
            0     0.00       0.00       0.00          0              0.000
 STEPS
  0.100      0.300      0.500      0.700      0.900

1STEP NUMBER  1
0--------------
0      0.100 = FRACTION OF SOLUTION 1.         0.900 = FRACTION OF SOLUTION 2.
```

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.821837D-03 | -2.7395 |
| NA | 6.098571D-01 | -0.2148 |
| CL | 6.098571D-01 | -0.2148 |
| C | 3.946138D-03 | -2.4038 |

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| CALCITE | 3.052849D-04 | -8.4062 | -8.4062 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ARAGONIT | -8.4062 | -8.2195 | -0.1868 |
| CALCITE | -8.4062 | -8.4062 | 0.0000 |
| GAYLUSSI | -14.3220 | -9.4210 | -4.9010 |
| HALITE | -0.7779 | 1.5700 | -2.3479 |
| NAHCOLIT | -13.3443 | -10.7420 | -2.6023 |
| NATRON | -5.9600 | -0.8250 | -5.1350 |
| PCO2 | -4.1316 | -1.4679 | -2.6637 |
| PIRSSONI | -14.2954 | -9.2340 | -5.0614 |
| PORTLAND | -15.6028 | -5.1900 | -10.4128 |
| TRONA | -19.2335 | -11.3840 | -7.8495 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 2.127122D-03 | -2.6722 |
| NA | 6.098571D-01 | -0.2148 |
| CL | 6.098571D-01 | -0.2148 |
| C | 4.251423D-03 | -2.3715 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 7.8627 |
| ACTIVITY H2O = | 0.9798 |
| OSMOTIC COEFFICIENT = | 0.9228 |
| IONIC STRENGTH = | 0.6163 |
| TEMPERATURE = | 25.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9971 G/CC |
| ELECTRICAL BALANCE = | -4.6165D-10 |
| TOTAL ALKALINITY = | 4.2543D-03 |
| ITERATIONS = | 6 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | UNSCALED LOG ACT | UNSCALED GAMMA | UNSCALED LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 1.718E-08 | -7.765 | 1.372E-08 | -7.863 | 7.984E-01 | -0.098 |
| 3 | H2O | 0.0 | 9.798E-01 | -0.009 | 9.798E-01 | -0.009 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 2.122E-03 | -2.673 | 4.847E-04 | -3.314 | 2.285E-01 | -0.641 |
| 6 | NA+ | 1.0 | 6.099E-01 | -0.215 | 4.075E-01 | -0.390 | 6.682E-01 | -0.175 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 14 CL- | -1.0 | 6.099E-01 | -0.215 | 4.092E-01 | -0.388 | 6.710E-01 | -0.173 |
| 15 CO3-2 | -2.0 | 6.187E-05 | -4.209 | 8.096E-06 | -5.092 | 1.309E-01 | -0.883 |
| 31 OH- | -1.0 | 1.137E-06 | -5.944 | 7.176E-07 | -6.144 | 6.310E-01 | -0.200 |
| 34 HCO3- | -1.0 | 4.118E-03 | -2.385 | 2.425E-03 | -2.615 | 5.890E-01 | -0.230 |
| 35 H2CO3 | 0.0 | 6.573E-05 | -4.182 | 7.386E-05 | -4.132 | 1.124E+00 | 0.051 |
| 76 CACO3 | 0.0 | 5.560E-06 | -5.255 | 5.560E-06 | -5.255 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 1.7181D-08 | 1.3718D-08 | 7.9842D-01 |
| CA+2 | 2.1271D-03 | 4.8474D-04 | 2.2789D-01 |
| NA+ | 6.0986D-01 | 4.0750D-01 | 6.6819D-01 |
| CL- | 6.0986D-01 | 4.0921D-01 | 6.7099D-01 |
| CO3-2 | 6.7429D-05 | 8.0958D-06 | 1.2006D-01 |
| OH- | 1.1371D-06 | 7.1756D-07 | 6.3104D-01 |
| HCO3- | 4.1183D-03 | 2.4255D-03 | 5.8896D-01 |
| H2CO3 | 6.5727D-05 | 7.3859D-05 | 1.1237D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 4.6815D-01 |
| CACO3 | 1.6541D-01 |
| CA(OH)2 | 4.4938D-01 |
| NACL | 6.6959D-01 |
| NAHCO3 | 6.2733D-01 |
| NA2CO3 | 3.7705D-01 |
| NAOH | 6.4935D-01 |
| HCL | 7.3194D-01 |

1STEP NUMBER 2
0--------------
0 0.300 = FRACTION OF SOLUTION 1. 0.700 = FRACTION OF SOLUTION 2.

TOTAL MOLALITIES OF ELEMENTS
----- ---------- -- --------

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.982430D-03 | -2.7028 |
| NA | 1.829571D+00 | 0.2623 |
| CL | 1.829571D+00 | 0.2623 |
| C | 4.211749D-03 | -2.3755 |

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| CALCITE | 3.191327D-04 | -8.4062 | -8.4062 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ARAGONIT | -8.4062 | -8.2195 | -0.1868 |
| CALCITE | -8.4062 | -8.4062 | 0.0000 |
| GAYLUSSI | -13.5474 | -9.4210 | -4.1264 |
| HALITE | 0.1659 | 1.5700 | -1.4041 |
| NAHCOLIT | -12.9227 | -10.7420 | -2.1807 |
| NATRON | -5.2809 | -0.8250 | -4.4559 |
| PCO2 | -4.1394 | -1.4679 | -2.6715 |
| PIRSSONI | -13.4635 | -9.2340 | -4.2295 |
| PORTLAND | -15.6140 | -5.1900 | -10.4240 |
| TRONA | -17.9800 | -11.3840 | -6.5960 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 2.301563D-03 | -2.6380 |
| NA | 1.829571D+00 | 0.2623 |
| CL | 1.829571D+00 | 0.2623 |
| C | 4.530882D-03 | -2.3438 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 7.8391 |
| ACTIVITY H2O = | 0.9377 |
| OSMOTIC COEFFICIENT = | 0.9748 |
| IONIC STRENGTH = | 1.8366 |
| TEMPERATURE = | 25.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9971 G/CC |
| ELECTRICAL BALANCE = | -4.6177D-10 |
| TOTAL ALKALINITY = | 4.6031D-03 |
| ITERATIONS = | 5 |

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DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 1.320E-08 | -7.879 | 1.449E-08 | -7.839 | 1.097E+00 | 0.040 |
| 3 | H2O | 0.0 | 9.377E-01 | -0.028 | 9.377E-01 | -0.028 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 2.296E-03 | -2.639 | 5.751E-04 | -3.240 | 2.505E-01 | -0.601 |
| 6 | NA+ | 1.0 | 1.830E+00 | 0.262 | 1.209E+00 | 0.082 | 6.607E-01 | -0.180 |
| 14 | CL- | -1.0 | 1.830E+00 | 0.262 | 1.212E+00 | 0.084 | 6.626E-01 | -0.179 |
| 15 | CO3-2 | -2.0 | 1.167E-04 | -3.933 | 6.824E-06 | -5.166 | 5.846E-02 | -1.233 |
| 31 | OH- | -1.0 | 1.164E-06 | -5.934 | 6.503E-07 | -6.187 | 5.587E-01 | -0.253 |
| 34 | HCO3- | -1.0 | 4.357E-03 | -2.361 | 2.159E-03 | -2.666 | 4.954E-01 | -0.305 |
| 35 | H2CO3 | 0.0 | 5.120E-05 | -4.291 | 7.254E-05 | -4.139 | 1.417E+00 | 0.151 |
| 76 | CACO3 | 0.0 | 5.560E-06 | -5.255 | 5.560E-06 | -5.255 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 1.3203D-08 | 1.4485D-08 | 1.0971D+00 |
| CA+2 | 2.3016D-03 | 5.7510D-04 | 2.4987D-01 |
| NA+ | 1.8296D+00 | 1.2087D+00 | 6.6065D-01 |
| CL- | 1.8296D+00 | 1.2123D+00 | 6.6262D-01 |
| CO3-2 | 1.2229D-04 | 6.8239D-06 | 5.5801D-02 |
| OH- | 1.1639D-06 | 6.5030D-07 | 5.5872D-01 |
| HCO3- | 4.3574D-03 | 2.1588D-03 | 4.9543D-01 |
| H2CO3 | 5.1195D-05 | 7.2537D-05 | 1.4169D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 4.7872D-01 |
| CACO3 | 1.1808D-01 |
| CA(OH)2 | 4.2727D-01 |
| NACL | 6.6163D-01 |
| NAHCO3 | 5.7211D-01 |
| NA2CO3 | 2.8987D-01 |
| NAOH | 6.0755D-01 |
| HCL | 8.5262D-01 |

1STEP NUMBER 3
0--------------
0 0.500 = FRACTION OF SOLUTION 1. 0.500 = FRACTION OF SOLUTION 2.

TOTAL MOLALITIES OF ELEMENTS
----- ---------- -- --------

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 2.143023D-03 | -2.6690 |

| | | |
|---|---|---|
| NA | 3.049286D+00 | 0.4842 |
| CL | 3.049286D+00 | 0.4842 |
| C | 4.477361D-03 | -2.3490 |

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| CALCITE | 2.584929D-04 | -8.4062 | -8.4062 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ARAGONIT | -8.4062 | -8.2195 | -0.1868 |
| CALCITE | -8.4062 | -8.4062 | 0.0000 |
| GAYLUSSI | -13.3252 | -9.4210 | -3.9042 |
| HALITE | 0.6773 | 1.5700 | -0.8927 |
| NAHCOLIT | -12.6872 | -10.7420 | -1.9452 |
| NATRON | -5.1695 | -0.8250 | -4.3445 |
| PCO2 | -3.9791 | -1.4679 | -2.5112 |
| PIRSSONI | -13.1749 | -9.2340 | -3.9409 |
| PORTLAND | -15.7965 | -5.1900 | -10.6065 |
| TRONA | -17.4559 | -11.3840 | -6.0719 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 2.401516D-03 | -2.6195 |
| NA | 3.049286D+00 | 0.4842 |
| CL | 3.049286D+00 | 0.4842 |
| C | 4.735854D-03 | -2.3246 |

----DESCRIPTION OF SOLUTION----

| | | |
|---|---|---|
| PH = | 7.6807 | |
| ACTIVITY H2O = | 0.8910 | |
| OSMOTIC COEFFICIENT = | 1.0489 | |
| IONIC STRENGTH = | 3.0566 | |
| TEMPERATURE = | 25.0000 | |
| PRESSURE = | 1.0000 | ATM |
| DENSITY OF H2O = | 0.9971 | G/CC |

ELECTRICAL BALANCE = -4.6177D-10
TOTAL ALKALINITY = 4.8030D-03
ITERATIONS = 5

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 1.289E-08 | -7.890 | 2.086E-08 | -7.681 | 1.619E+00 | 0.209 |
| 3 | H2O | 0.0 | 8.910E-01 | -0.050 | 8.910E-01 | -0.050 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 2.396E-03 | -2.621 | 8.678E-04 | -3.062 | 3.622E-01 | -0.441 |
| 6 | NA+ | 1.0 | 3.049E+00 | 0.484 | 2.178E+00 | 0.338 | 7.143E-01 | -0.146 |
| 14 | CL- | -1.0 | 3.049E+00 | 0.484 | 2.184E+00 | 0.339 | 7.161E-01 | -0.145 |
| 15 | CO3-2 | -2.0 | 1.196E-04 | -3.922 | 4.522E-06 | -5.345 | 3.782E-02 | -1.422 |
| 31 | OH- | -1.0 | 7.980E-07 | -6.098 | 4.291E-07 | -6.367 | 5.377E-01 | -0.269 |
| 34 | HCO3- | -1.0 | 4.552E-03 | -2.342 | 2.060E-03 | -2.686 | 4.526E-01 | -0.344 |
| 35 | H2CO3 | 0.0 | 5.873E-05 | -4.231 | 1.049E-04 | -3.979 | 1.786E+00 | 0.252 |
| 76 | CACO3 | 0.0 | 5.560E-06 | -5.255 | 5.560E-06 | -5.255 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 1.2888D-08 | 2.0861D-08 | 1.6187D+00 |
| CA+2 | 2.4015D-03 | 8.6777D-04 | 3.6134D-01 |
| NA+ | 3.0493D+00 | 2.1782D+00 | 7.1433D-01 |
| CL- | 3.0493D+00 | 2.1837D+00 | 7.1615D-01 |
| CO3-2 | 1.2512D-04 | 4.5224D-06 | 3.6143D-02 |
| OH- | 7.9797D-07 | 4.2910D-07 | 5.3774D-01 |
| HCO3- | 4.5520D-03 | 2.0604D-03 | 4.5264D-01 |
| H2CO3 | 5.8731D-05 | 1.0492D-04 | 1.7865D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 5.7013D-01 |
| CACO3 | 1.1428D-01 |
| CA(OH)2 | 4.7100D-01 |
| NACL | 7.1524D-01 |
| NAHCO3 | 5.6863D-01 |
| NA2CO3 | 2.6420D-01 |
| NAOH | 6.1978D-01 |
| HCL | 1.0767D+00 |

1STEP NUMBER 4
0----------
0 0.700 = FRACTION OF SOLUTION 1. 0.300 = FRACTION OF SOLUTION 2.

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 2.303616D-03 | -2.6376 |
| NA | 4.269000D+00 | 0.6303 |
| CL | 4.269000D+00 | 0.6303 |
| C | 4.742973D-03 | -2.3239 |

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| CALCITE | 1.619806D-04 | -8.4062 | -8.4062 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ARAGONIT | -8.4062 | -8.2195 | -0.1868 |
| CALCITE | -8.4062 | -8.4062 | 0.0000 |
| GAYLUSSI | -13.2781 | -9.4210 | -3.8571 |
| HALITE | 1.0707 | 1.5700 | -0.4993 |
| NAHCOLIT | -12.5115 | -10.7420 | -1.7695 |
| NATRON | -5.2514 | -0.8250 | -4.4264 |
| PCO2 | -3.7782 | -1.4679 | -2.3102 |
| PIRSSONI | -13.0504 | -9.2340 | -3.8164 |
| PORTLAND | -16.0233 | -5.1900 | -10.8333 |
| TRONA | -17.1557 | -11.3840 | -5.7717 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 2.465596D-03 | -2.6081 |
| NA | 4.269000D+00 | 0.6303 |
| CL | 4.269000D+00 | 0.6303 |
| C | 4.904953D-03 | -2.3094 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 7.4844 |
| ACTIVITY H2O = | 0.8396 |
| OSMOTIC COEFFICIENT = | 1.1354 |
| IONIC STRENGTH = | 4.2765 |
| TEMPERATURE = | 25.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9971 G/CC |
| ELECTRICAL BALANCE = | -4.6175D-10 |
| TOTAL ALKALINITY = | 4.9312D-03 |
| ITERATIONS = | 5 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 1.341E-08 | -7.873 | 3.278E-08 | -7.484 | 2.445E+00 | 0.388 |
| 3 | H2O | 0.0 | 8.396E-01 | -0.076 | 8.396E-01 | -0.076 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 2.460E-03 | -2.609 | 1.431E-03 | -2.844 | 5.818E-01 | -0.235 |
| 6 | NA+ | 1.0 | 4.269E+00 | 0.630 | 3.426E+00 | 0.535 | 8.026E-01 | -0.095 |
| 14 | CL- | -1.0 | 4.269E+00 | 0.630 | 3.434E+00 | 0.536 | 8.045E-01 | -0.094 |
| 15 | CO3-2 | -2.0 | 9.420E-05 | -4.026 | 2.742E-06 | -5.562 | 2.910E-02 | -1.536 |
| 31 | OH- | -1.0 | 4.822E-07 | -6.317 | 2.573E-07 | -6.590 | 5.337E-01 | -0.273 |
| 34 | HCO3- | -1.0 | 4.731E-03 | -2.325 | 1.963E-03 | -2.707 | 4.149E-01 | -0.382 |
| 35 | H2CO3 | 0.0 | 7.399E-05 | -4.131 | 1.667E-04 | -3.778 | 2.252E+00 | 0.353 |
| 76 | CACO3 | 0.0 | 5.560E-06 | -5.255 | 5.560E-06 | -5.255 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 1.3406D-08 | 3.2778D-08 | 2.4451D+00 |
| CA+2 | 2.4656D-03 | 1.4313D-03 | 5.8052D-01 |
| NA+ | 4.2690D+00 | 3.4264D+00 | 8.0262D-01 |
| CL- | 4.2690D+00 | 3.4344D+00 | 8.0449D-01 |
| CO3-2 | 9.9762D-05 | 2.7417D-06 | 2.7483D-02 |
| OH- | 4.8220D-07 | 2.5734D-07 | 5.3367D-01 |
| HCO3- | 4.7312D-03 | 1.9628D-03 | 4.1486D-01 |
| H2CO3 | 7.3992D-05 | 1.6666D-04 | 2.2524D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 7.2158D-01 |
| CACO3 | 1.2631D-01 |
| CA(OH)2 | 5.4885D-01 |
| NACL | 8.0355D-01 |
| NAHCO3 | 5.7704D-01 |
| NA2CO3 | 2.6063D-01 |
| NAOH | 6.5447D-01 |

HCL 1.4025D+00

1STEP NUMBER 5
0--------------
0 0.900 = FRACTION OF SOLUTION 1. 0.100 = FRACTION OF SOLUTION 2.

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 2.464208D-03 | -2.6083 |
| NA | 5.488714D+00 | 0.7395 |
| CL | 5.488714D+00 | 0.7395 |
| C | 5.008585D-03 | -2.3003 |

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| CALCITE | 5.382800D-05 | -8.4062 | -8.4062 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ARAGONIT | -8.4062 | -8.2195 | -0.1868 |
| CALCITE | -8.4062 | -8.4062 | 0.0000 |
| GAYLUSSI | -13.3265 | -9.4210 | -3.9055 |
| HALITE | 1.4113 | 1.5700 | -0.1587 |
| NAHCOLIT | -12.3719 | -10.7420 | -1.6299 |
| NATRON | -5.4492 | -0.8250 | -4.6242 |
| PCO2 | -3.5699 | -1.4679 | -2.1020 |
| PIRSSONI | -13.0092 | -9.2340 | -3.7752 |
| PORTLAND | -16.2614 | -5.1900 | -11.0714 |
| TRONA | -16.9748 | -11.3840 | -5.5908 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 2.518036D-03 | -2.5989 |
| NA | 5.488714D+00 | 0.7395 |

| | | |
|---|---|---|
| CL | 5.488714D+00 | 0.7395 |
| C | 5.062413D-03 | -2.2956 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 7.2754 |
| ACTIVITY H2O = | 0.7838 |
| OSMOTIC COEFFICIENT = | 1.2309 |
| IONIC STRENGTH = | 5.4963 |
| TEMPERATURE = | 25.0000 |
| PRESSURE = | 1.0000 ATM |
| DENSITY OF H2O = | 0.9971 G/CC |
| ELECTRICAL BALANCE = | -4.6175D-10 |
| TOTAL ALKALINITY = | 5.0361D-03 |
| ITERATIONS = | 5 |

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 1.421E-08 | -7.847 | 5.305E-08 | -7.275 | 3.732E+00 | 0.572 |
| 3 | H2O | 0.0 | 7.838E-01 | -0.106 | 7.838E-01 | -0.106 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 2.512E-03 | -2.600 | 2.486E-03 | -2.605 | 9.894E-01 | -0.005 |
| 6 | NA+ | 1.0 | 5.489E+00 | 0.739 | 5.072E+00 | 0.705 | 9.240E-01 | -0.034 |
| 14 | CL- | -1.0 | 5.489E+00 | 0.739 | 5.083E+00 | 0.706 | 9.261E-01 | -0.033 |
| 15 | CO3-2 | -2.0 | 6.264E-05 | -4.203 | 1.579E-06 | -5.802 | 2.520E-02 | -1.599 |
| 31 | OH- | -1.0 | 2.758E-07 | -6.559 | 1.484E-07 | -6.828 | 5.382E-01 | -0.269 |
| 34 | HCO3- | -1.0 | 4.899E-03 | -2.310 | 1.829E-03 | -2.738 | 3.733E-01 | -0.428 |
| 35 | H2CO3 | 0.0 | 9.480E-05 | -4.023 | 2.692E-04 | -3.570 | 2.840E+00 | 0.453 |
| 76 | CACO3 | 0.0 | 5.560E-06 | -5.255 | 5.560E-06 | -5.255 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 1.4215D-08 | 5.3045D-08 | 3.7318D+00 |
| CA+2 | 2.5180D-03 | 2.4858D-03 | 9.8720D-01 |
| NA+ | 5.4887D+00 | 5.0718D+00 | 9.2404D-01 |
| CL- | 5.4887D+00 | 5.0829D+00 | 9.2606D-01 |
| CO3-2 | 6.8196D-05 | 1.5787D-06 | 2.3149D-02 |
| OH- | 2.7580D-07 | 1.4844D-07 | 5.3824D-01 |
| HCO3- | 4.8994D-03 | 1.8290D-03 | 3.7330D-01 |
| H2CO3 | 9.4797D-05 | 2.6922D-04 | 2.8399D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|

| | |
|---|---|
| CACL2 | 9.4601D-01 |
| CACO3 | 1.5117D-01 |
| CA(OH)2 | 6.5885D-01 |
| NACL | 9.2505D-01 |
| NAHCO3 | 5.8732D-01 |
| NA2CO3 | 2.7038D-01 |
| NAOH | 7.0523D-01 |
| HCL | 1.8590D+00 |

**Test problem 6: Simulation of reaction path accompanying the evaporation of sea water**

Two limiting cases have traditionally been used to examine reaction paths in geochemical simulation: the open model and the zoned or closed model. In the open model, products formed earlier may re-react with the aqueous phase and form new products as reaction proceeds. In the closed model, products once formed are isolated (zoned, layered, buried) from the system and not allowed to re-react. Test problem 5 of Parkhurst and others (1980) is an example of the logic used in open system simulation, as used in the code PHREEQE. In closed system simulation of reaction paths, the MINERALS input is adjusted so that products once formed are not allowed to re-react with the aqueous solution.

Usually when we simulate reaction paths, the irreversible reactant is an unstable mineral or a suite of unstable minerals; that is, the stoichiometry of the irreversible reaction is fixed. Evaporation poses a special problem in reaction path simulation because the stoichiometry of the irreversible reaction (defined by the aqueous solution composition) continually changes. In test problem 2, REACTION input was used to simulate evaporation of sea water by irreversible addition of "sea salt", that is, a hypothetical solid containing calcium, magnesium, sodium, potassium, chloride, sulfate and carbon in stoichiometric proportion to sea water. The approach used was valid as long as we did not wish to examine details of the reaction path to reach the final equilibrium invariant point because the composition of the reactant (evaporated sea water) changes with reaction progress. The reaction path during evaporation could be solved by changing the stoichiometry of the irreversible reactant (altered "sea salt") at each new phase boundary but this method would be extremely laborious.

As a means of simplifying simulation of evaporation (in open or closed systems) a new feature has been added in PHRQPITZ that allows the user to automatically define the composition of solution 1 as a salt, without the necessity of entering the salt composition under REACTION input. This does not eliminate the need to locate each new phase boundary encountered during evaporation, but it is not necessary to define the stoichiometry of each new reactant (altered sea water for example) as evaporation proceeds. To use this new feature of PHRQPITZ, one first defines the composition of the starting solution. Evaporation of this solution is accomplished by setting IOPT(3) = 6 (specifying that a reaction will be added until the first mineral of MINERALS input is just saturated) and defining the reaction under REACTION input as water (LREAC(1) = 3 and CREAC(1) = 1.0). PHRQPITZ recognizes this combination of input as the special case of evaporation (or dilution, if the starting solution is oversaturated with the first mineral of MINERALS input) and additional output is provided. After the print of mass transfer under the heading "PHASE BOUNDARIES" is printed, PHRQPITZ prints the evaporation factor necessary to reach saturation with the first mineral in MINERALS input. For example an evaporation factor of 2.0 would mean that the concentration of an inert component in the starting solution would double upon evaporation to reach the phase boundary. (Similar logic applies to dilution where the evaporation factor would be less than unity.) Following a print of the evaporation factor, PHRQPITZ gives the total moles of each element remaining referenced to the initial condition defined in solution 1 (the initial condition being moles per one kilogram of water) and the amount of water (kg) remaining. Following an evaporation step, the total moles of each element should not be confused with the molality of the element, both of which are printed.

In test problem 6 we consider several steps in the evaporation of sea water in a closed system. The problem of sea water evaporation is too complex to be considered fully here. For example purposes, the evaporation of sea water is taken to the halite phase boundary only. The problem is solved in three parts and the input file listed in table 16. The starting solution (sea water) is defined in part a and equilibrated with dolomite in contact with air. Table 17 shows that this equilibration step causes precipitation of dolomite and outgassing of $CO_2$. This modified starting solution is now undersaturated with all other minerals in the LOOK MIN data base. The modified sea water was saved in solution 1 at completion of part a for use as the starting point of evaporation in part b by setting IOPT(7) to 1 (table 16). In all subsequent evaporation simulations the final solution may be stored in solution 1 to eliminate the need to re-define the starting solution (IOPT(7) = 1). In parts b and c IOPT(3) = 6 indicating that a reaction will be run until a phase boundary (defined by the first mineral under MINERALS input) is reached. The evaporation reaction (or dilution) is defined as 1.0 $H_2O$ under REACTION input and no STEPS input is needed. The first mineral under MINERALS input defines

Table 16. -- Line images of the input file to test problem 6

```
Test Problem 6 (part a): Equilibrate sea water with dolomite and air.
0050021000 0 0       0.0
ELEMENTS
C         15   61.0171

SOLUTION 1
SEAWATER FROM NORDSTROM ET AL. (1979) TEST CASE IN PPM.
 8 15 3   8.22      8.451     25.0      1.023
   4 412.3        5 1291.8       6 10768.0      7 399.1       22 67.3
  14 19353.0     15 141.682     16 2712.0
MINERALS
PCO2       1          4.0    -1.468     -4.776     1          -3.5
  35  1.0
108.3865    0.01985076  -6919.53    -40.45154    669365.0
DOLOMITE   3          8.00  -17.083 -9.436          0
   4 1.0          5 1.0          15 2.0

END
#6 (part b): Evaporate final solution of part a to gypsum saturation.
0060021000 1 1       0.0
MINERALS
GYPSUM     3          6.00   -4.581                 1
   4 1.0          16 1.0           3 2.0
90.318      0.0           -4213.       -32.641
PCO2       1          4.0    -1.468     -4.776     1          -3.5
  35  1.0
108.3865    0.01985076  -6919.53    -40.45154    669365.0
DOLOMITE   3          8.00  -17.083 -9.436          0
   4 1.0          5 1.0          15 2.0

REACTION
   3 1.0
END
#6 (part c): Evaporate final solution of part b to halite saturation.
0060021000 1 1       0.0
MINERALS
HALITE     2          0.00    1.570                  1
   6      1.000  14       1.000
-713.4616   -.1201241   37302.21    262.4583    -2106915.
GYPSUM     3          6.00   -4.581                 1
   4 1.0          16 1.0           3 2.0
90.318      0.0           -4213.       -32.641
PCO2       1          4.0    -1.468     -4.776     1          -3.5
  35  1.0
108.3865    0.01985076  -6919.53    -40.45154    669365.0
DOLOMITE   3          8.00  -17.083 -9.436          0
   4 1.0          5 1.0          15 2.0

REACTION
   3 1.0
END
```

Table 17. -- Listing of printout from test problem 6

```
         DATA READ FROM DISK

 ELEMENTS
 SPECIES
 LOOK MIN
 MEAN GAM
1Test Problem 6 (part a): Equilibrate sea water with dolomite and air.
 0050021000 0 0          0.00000
 ELEMENTS
 C           15         0.61017E+02
              0         0.00000E+00
 SOLUTION 1
 SEAWATER FROM NORDSTROM ET AL. (1979) TEST CASE IN PPM.
  8 15 3     8.22       4.00       25.0       1.02
    4  4.123D+02   5  1.292D+03   6  1.077D+04   7  3.991D+02  22  6.730D+01
   14  1.935D+04  15  1.417D+02  16  2.712D+03
 MINERALS
 PCO2        1       4.0       -1.5       -4.8          1              -3.500
   35   1.00
   1.0839E+02  1.9851E-02 -6.9195E+03 -4.0452E+01  6.6936E+05
 DOLOMITE    3       8.0       -17.       -9.4          0               0.000
    4   1.00         5   1.00        15   2.00
            0      0.00       0.00       0.00          0               0.000
1SOLUTION NUMBER 1
 SEAWATER FROM NORDSTROM ET AL. (1979) TEST CASE IN PPM.
```

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.066163D-02 | -1.9722 |
| MG | 5.508555D-02 | -1.2590 |
| NA | 4.854426D-01 | -0.3139 |
| K | 1.057942D-02 | -1.9755 |
| CL | 5.657614D-01 | -0.2474 |
| TOT ALK | 2.406585D-03 | -2.6186 |
| S | 2.926073D-02 | -1.5337 |
| BR | 8.729404D-04 | -3.0590 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 8.2200 |
| ACTIVITY H2O = | 0.9813 |
| OSMOTIC COEFFICIENT = | 0.9035 |
| IONIC STRENGTH = | 0.7223 |
| TEMPERATURE = | 25.0000 |

PRESSURE = 1.0000 ATM
DENSITY OF H2O = 0.9971 G/CC
ELECTRICAL BALANCE = -4.6020D-05
TOTAL ALKALINITY = 2.4066D-03
ITERATIONS = 9
TOTAL CARBON = 2.2098D-03

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 8.201E-09 | -8.086 | 6.026E-09 | -8.220 | 7.347E-01 | -0.134 |
| 3 | H2O | 0.0 | 9.813E-01 | -0.008 | 9.813E-01 | -0.008 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 1.064E-02 | -1.973 | 1.999E-03 | -2.699 | 1.879E-01 | -0.726 |
| 5 | MG+2 | 2.0 | 5.499E-02 | -1.260 | 1.130E-02 | -1.947 | 2.054E-01 | -0.687 |
| 6 | NA+ | 1.0 | 4.854E-01 | -0.314 | 3.096E-01 | -0.509 | 6.378E-01 | -0.195 |
| 7 | K+ | 1.0 | 1.058E-02 | -1.976 | 6.226E-03 | -2.206 | 5.885E-01 | -0.230 |
| 14 | CL- | -1.0 | 5.658E-01 | -0.247 | 3.900E-01 | -0.409 | 6.893E-01 | -0.162 |
| 15 | CO3-2 | -2.0 | 9.105E-05 | -4.041 | 9.137E-06 | -5.039 | 1.004E-01 | -0.998 |
| 16 | SO4-2 | -2.0 | 2.926E-02 | -1.534 | 3.100E-03 | -2.509 | 1.060E-01 | -0.975 |
| 22 | BR- | -1.0 | 8.729E-04 | -3.059 | 6.243E-04 | -3.205 | 7.151E-01 | -0.146 |
| 31 | OH- | -1.0 | 2.841E-06 | -5.547 | 1.636E-06 | -5.786 | 5.759E-01 | -0.240 |
| 34 | HCO3- | -1.0 | 1.992E-03 | -2.701 | 1.202E-03 | -2.920 | 6.037E-01 | -0.219 |
| 35 | H2CO3 | 0.0 | 1.421E-05 | -4.847 | 1.606E-05 | -4.794 | 1.130E+00 | 0.053 |
| 40 | HSO4- | -1.0 | 2.523E-09 | -8.598 | 1.780E-09 | -8.750 | 7.055E-01 | -0.152 |
| 76 | CACO3 | 0.0 | 2.588E-05 | -4.587 | 2.588E-05 | -4.587 | 1.000E+00 | 0.000 |
| 85 | MGOH+ | 1.0 | 3.252E-06 | -5.488 | 2.856E-06 | -5.544 | 8.782E-01 | -0.056 |
| 86 | MGCO3 | 0.0 | 8.747E-05 | -4.058 | 8.747E-05 | -4.058 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 1.0724D-08 | 6.0256D-09 | 5.6187D-01 |
| CA+2 | 1.0662D-02 | 1.9990D-03 | 1.8749D-01 |
| MG+2 | 5.5086D-02 | 1.1297D-02 | 2.0508D-01 |
| NA+ | 4.8544D-01 | 3.0960D-01 | 6.3777D-01 |
| K+ | 1.0579D-02 | 6.2260D-03 | 5.8850D-01 |
| CL- | 5.6576D-01 | 3.8998D-01 | 6.8931D-01 |
| CO3-2 | 2.0439D-04 | 9.1369D-06 | 4.4702D-02 |
| SO4-2 | 2.9261D-02 | 3.1005D-03 | 1.0596D-01 |
| BR- | 8.7294D-04 | 6.2425D-04 | 7.1511D-01 |
| OH- | 6.0930D-06 | 1.6361D-06 | 2.6852D-01 |
| HCO3- | 1.9917D-03 | 1.2024D-03 | 6.0371D-01 |
| H2CO3 | 1.4212D-05 | 1.6059D-05 | 1.1300D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 4.4662D-01 |

| | |
|---|---|
| CASO4 | 1.4095D-01 |
| CACO3 | 9.1550D-02 |
| CA(OH)2 | 2.3822D-01 |
| MGCL2 | 4.6017D-01 |
| MGSO4 | 1.4741D-01 |
| MGCO3 | 9.5748D-02 |
| MG(OH)2 | 2.4545D-01 |
| NACL | 6.6304D-01 |
| NA2SO4 | 3.5061D-01 |
| NAHCO3 | 6.2051D-01 |
| NA2CO3 | 2.6296D-01 |
| NAOH | 4.1383D-01 |
| KCL | 6.3691D-01 |
| K2SO4 | 3.3231D-01 |
| KHCO3 | 5.9606D-01 |
| K2CO3 | 2.4923D-01 |
| KOH | 3.9752D-01 |
| HCL | 6.2233D-01 |
| H2SO4 | 3.2221D-01 |
| HBR | 6.3388D-01 |

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ANHYDRIT | -5.2078 | -4.3617 | -0.8461 |
| ARAGONIT | -7.7384 | -8.2195 | 0.4811 |
| ARCANITE | -6.9202 | -1.7760 | -5.1441 |
| BISCHOFI | -2.8141 | 4.4551 | -7.2692 |
| BLOEDITE | -8.0154 | -2.3470 | -5.6684 |
| BRUCITE | -13.5194 | -10.8840 | -2.6354 |
| BURKEITE | -13.1115 | -0.7720 | -12.3395 |
| CALCITE | -7.7384 | -8.4062 | 0.6678 |
| CARNALLI | -5.4289 | 4.3300 | -9.7589 |
| DOLOMITE | -14.7246 | -17.0830 | 2.3584 |
| EPSOMITE | -4.5130 | -1.8809 | -2.6321 |
| GAYLUSSI | -13.8370 | -9.4210 | -4.4160 |
| GLASERIT | -12.1437 | -3.8030 | -8.3407 |
| GLAUBERI | -8.7347 | -5.2450 | -3.4897 |
| GYPSUM | -5.2242 | -4.5805 | -0.6437 |
| HALITE | -0.9182 | 1.5700 | -2.4881 |
| HEXAHYDR | -4.5048 | -1.6346 | -2.8702 |
| KAINITE | -7.0949 | -0.1930 | -6.9019 |
| KALICINI | -15.4650 | -10.0580 | -5.4070 |
| KIESERIT | -4.4638 | -0.1230 | -4.3408 |
| LABILE S | -12.2781 | -5.6720 | -6.6061 |
| LEONHARD | -4.4884 | -0.8870 | -3.6014 |
| LEONITE | -11.4085 | -3.9790 | -7.4295 |
| MAGNESIT | -6.9862 | -7.8340 | 0.8478 |
| MIRABIL | -3.6089 | -1.2135 | -2.3954 |
| MISENITE | -84.5263 | -10.8060 | -73.7203 |
| NAHCOLIT | -13.7684 | -10.7420 | -3.0264 |
| NATRON | -6.1396 | -0.8250 | -5.3146 |
| NESQUEHO | -7.0108 | -5.1670 | -1.8438 |
| PCO2 | -4.7943 | -1.4679 | -3.3263 |

| | | | |
|---|---|---|---|
| PENTAHYD | -4.4966 | -1.2850 | -3.2116 |
| PIRSSONI | -13.8124 | -9.2340 | -4.5784 |
| POLYHALI | -21.8077 | -13.7440 | -8.0637 |
| PORTLAND | -14.2716 | -5.1900 | -9.0816 |
| SCHOENIT | -11.4249 | -4.3280 | -7.0969 |
| SYLVITE | -2.6147 | 0.8998 | -3.5146 |
| SYNGENIT | -12.1361 | -7.4480 | -4.6881 |
| TRONA | -19.8424 | -11.3840 | -8.4584 |

1STEP NUMBER 1
0----------

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.066163D-02 | -1.9722 |
| MG | 5.508555D-02 | -1.2590 |
| NA | 4.854426D-01 | -0.3139 |
| K | 1.057942D-02 | -1.9755 |
| CL | 5.657614D-01 | -0.2474 |
| TOT ALK | 2.209828D-03 | -2.6556 |
| S | 2.926073D-02 | -1.5337 |
| BR | 8.729404D-04 | -3.0590 |

----PHASE BOUNDARIES----

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| PCO2 | -7.853663D-04 | -4.9679 | -1.4679 | -3.5000 |
| DOLOMITE | -4.880043D-04 | -17.0830 | -17.0830 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ANHYDRIT | -5.2262 | -4.3617 | -0.8645 |
| ARAGONIT | -8.9263 | -8.2195 | -0.7069 |
| ARCANITE | -6.9181 | -1.7760 | -5.1421 |
| BISCHOFI | -2.8166 | 4.4551 | -7.2716 |
| BLOEDITE | -8.0143 | -2.3470 | -5.6673 |
| BRUCITE | -14.5162 | -10.8840 | -3.6322 |
| BURKEITE | -14.2751 | -0.7720 | -13.5031 |
| CALCITE | -8.9263 | -8.4062 | -0.5201 |

| | | | |
|---|---|---|---|
| CARNALLI | -5.4311 | 4.3300 | -9.7611 |
| DOLOMITE | -17.0830 | -17.0830 | 0.0000 |
| EPSOMITE | -4.5138 | -1.8809 | -2.6330 |
| GAYLUSSI | -16.1923 | -9.4210 | -6.7713 |
| GLASERIT | -12.1397 | -3.8030 | -8.3367 |
| GLAUBERI | -8.7512 | -5.2450 | -3.5062 |
| GYPSUM | -5.2426 | -4.5805 | -0.6621 |
| HALITE | -0.9179 | 1.5700 | -2.4879 |
| HEXAHYDR | -4.5057 | -1.6346 | -2.8711 |
| KAINITE | -7.0956 | -0.1930 | -6.9026 |
| KALICINI | -16.1355 | -10.0580 | -6.0775 |
| KIESERIT | -4.4647 | -0.1230 | -4.3417 |
| LABILE S | -12.2925 | -5.6720 | -6.6205 |
| LEONHARD | -4.4893 | -0.8870 | -3.6023 |
| LEONITE | -11.4074 | -3.9790 | -7.4284 |
| MAGNESIT | -8.1567 | -7.8340 | -0.3227 |
| MIRABIL | -3.6068 | -1.2135 | -2.3933 |
| MISENITE | -81.5306 | -10.8060 | -70.7246 |
| NAHCOLIT | -14.4390 | -10.7420 | -3.6970 |
| NATRON | -7.3069 | -0.8250 | -6.4819 |
| NESQUEHO | -8.1812 | -5.1670 | -3.0142 |
| PCO2 | -4.9679 | -1.4679 | -3.5000 |
| PENTAHYD | -4.4975 | -1.2850 | -3.2125 |
| PIRSSONI | -16.1678 | -9.2340 | -6.9338 |
| POLYHALI | -21.8435 | -13.7440 | -8.0995 |
| PORTLAND | -15.2858 | -5.1900 | -10.0958 |
| SCHOENIT | -11.4238 | -4.3280 | -7.0958 |
| SYLVITE | -2.6145 | 0.8998 | -3.5143 |
| SYNGENIT | -12.1525 | -7.4480 | -4.7045 |
| TRONA | -21.6804 | -11.3840 | -10.2964 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.017363D-02 | -1.9925 |
| MG | 5.459755D-02 | -1.2628 |
| NA | 4.854426D-01 | -0.3139 |
| K | 1.057942D-02 | -1.9755 |
| CL | 5.657614D-01 | -0.2474 |
| C | 4.484536D-04 | -3.3483 |
| S | 2.926073D-02 | -1.5337 |
| BR | 8.729404D-04 | -3.0590 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 7.7226 |
| ACTIVITY H2O = | 0.9813 |
| OSMOTIC COEFFICIENT = | 0.9036 |

IONIC STRENGTH = 0.7196
TEMPERATURE = 25.0000
PRESSURE = 1.0000 ATM
DENSITY OF H2O = 0.9971 G/CC
ELECTRICAL BALANCE = -4.6020D-05
TOTAL ALKALINITY = 4.5459D-04
ITERATIONS = 7

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | UNSCALED LOG ACT | UNSCALED GAMMA | UNSCALED LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 2.575E-08 | -7.589 | 1.894E-08 | -7.723 | 7.355E-01 | -0.133 |
| 3 | H2O | 0.0 | 9.813E-01 | -0.008 | 9.813E-01 | -0.008 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 1.017E-02 | -1.993 | 1.911E-03 | -2.719 | 1.879E-01 | -0.726 |
| 5 | MG+2 | 2.0 | 5.459E-02 | -1.263 | 1.124E-02 | -1.949 | 2.059E-01 | -0.686 |
| 6 | NA+ | 1.0 | 4.854E-01 | -0.314 | 3.099E-01 | -0.509 | 6.384E-01 | -0.195 |
| 7 | K+ | 1.0 | 1.058E-02 | -1.976 | 6.233E-03 | -2.205 | 5.891E-01 | -0.230 |
| 14 | CL- | -1.0 | 5.658E-01 | -0.247 | 3.898E-01 | -0.409 | 6.890E-01 | -0.162 |
| 15 | CO3-2 | -2.0 | 6.151E-06 | -5.211 | 6.201E-07 | -6.208 | 1.008E-01 | -0.997 |
| 16 | SO4-2 | -2.0 | 2.926E-02 | -1.534 | 3.109E-03 | -2.507 | 1.062E-01 | -0.974 |
| 22 | BR- | -1.0 | 8.729E-04 | -3.059 | 6.239E-04 | -3.205 | 7.147E-01 | -0.146 |
| 31 | OH- | -1.0 | 9.027E-07 | -6.044 | 5.205E-07 | -6.284 | 5.766E-01 | -0.239 |
| 34 | HCO3- | -1.0 | 4.252E-04 | -3.371 | 2.565E-04 | -3.591 | 6.032E-01 | -0.220 |
| 35 | H2CO3 | 0.0 | 9.531E-06 | -5.021 | 1.077E-05 | -4.968 | 1.130E+00 | 0.053 |
| 40 | HSO4- | -1.0 | 7.955E-09 | -8.099 | 5.609E-09 | -8.251 | 7.050E-01 | -0.152 |
| 76 | CACO3 | 0.0 | 1.679E-06 | -5.775 | 1.679E-06 | -5.775 | 1.000E+00 | 0.000 |
| 85 | MGOH+ | 1.0 | 1.027E-06 | -5.988 | 9.044E-07 | -6.044 | 8.802E-01 | -0.055 |
| 86 | MGCO3 | 0.0 | 5.908E-06 | -5.229 | 5.908E-06 | -5.229 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 3.3704D-08 | 1.8939D-08 | 5.6192D-01 |
| CA+2 | 1.0174D-02 | 1.9109D-03 | 1.8783D-01 |
| MG+2 | 5.4598D-02 | 1.1243D-02 | 2.0592D-01 |
| NA+ | 4.8544D-01 | 3.0991D-01 | 6.3840D-01 |
| K+ | 1.0579D-02 | 6.2326D-03 | 5.8913D-01 |
| CL- | 5.6576D-01 | 3.8978D-01 | 6.8895D-01 |
| CO3-2 | 1.3738D-05 | 6.2007D-07 | 4.5137D-02 |
| SO4-2 | 2.9261D-02 | 3.1085D-03 | 1.0624D-01 |
| BR- | 8.7294D-04 | 6.2389D-04 | 7.1470D-01 |
| OH- | 1.9302D-06 | 5.2055D-07 | 2.6968D-01 |
| HCO3- | 4.2519D-04 | 2.5648D-04 | 6.0322D-01 |
| H2CO3 | 9.5307D-06 | 1.0766D-05 | 1.1296D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

FORMULA MEAN GAMMA

| | |
|---|---|
| CACL2 | 4.4673D-01 |
| CASO4 | 1.4126D-01 |
| CACO3 | 9.2076D-02 |
| CA(OH)2 | 2.3905D-01 |
| MGCL2 | 4.6064D-01 |
| MGSO4 | 1.4791D-01 |
| MGCO3 | 9.6409D-02 |
| MG(OH)2 | 2.4649D-01 |
| NACL | 6.6320D-01 |
| NA2SO4 | 3.5114D-01 |
| NAHCO3 | 6.2056D-01 |
| NA2CO3 | 2.6398D-01 |
| NAOH | 4.1493D-01 |
| KCL | 6.3709D-01 |
| K2SO4 | 3.3283D-01 |
| KHCO3 | 5.9613D-01 |
| K2CO3 | 2.5022D-01 |
| KOH | 3.9859D-01 |
| HCL | 6.2221D-01 |
| H2SO4 | 3.2251D-01 |
| HBR | 6.3373D-01 |

```
1#6 (part b): Evaporate final solution of part a to gypsum saturation.
 0060021000 1 1          0.00000
 MINERALS
 GYPSUM     3       6.0       -4.6       0.00          1                0.000
    4   1.00       16   1.00        3   2.00
  9.0318E+01  0.0000E-01 -4.2130E+03 -3.2641E+01  0.0000E-01
 PCO2       1       4.0       -1.5       -4.8          1               -3.500
   35   1.00
  1.0839E+02  1.9851E-02 -6.9195E+03 -4.0452E+01  6.6936E+05
 DOLOMITE   3       8.0       -17.       -9.4          0                0.000
    4   1.00        5   1.00       15   2.00
            0     0.00       0.00       0.00          0                0.000
 REACTION
    3   1.000   0.000

1STEP NUMBER  1
0--------------
```

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.017363D-02 | -1.9925 |
| MG | 5.459755D-02 | -1.2628 |
| NA | 4.854426D-01 | -0.3139 |
| K | 1.057942D-02 | -1.9755 |
| CL | 5.657614D-01 | -0.2474 |
| C | 4.484536D-04 | -3.3483 |
| S | 2.926073D-02 | -1.5337 |

| | | |
|---|---|---|
| BR | 8.729404D-04 | -3.0590 |

----PHASE BOUNDARIES----

MASS PRECIPITATED/DISSOLVED FROM INITIAL KILOGRAM WATER

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| GYPSUM | 0.000000D-01 | -4.5805 | -4.5805 | 0.0000 |
| ** | | | | |
| PCO2 | -2.017398D-04 | -4.9679 | -1.4679 | -3.5000 |
| DOLOMITE | -8.623117D-05 | -17.0830 | -17.0830 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

** 3.487807D+00 IS THE EVAPORATION FACTOR NECESSARY TO REACH THE GYPSUM PHASE BOUNDARY.

MOLES OF ELEMENTS REMAINING AFTER REACTION

| ELEMENT | MOLES | LOG MOLES |
|---|---|---|
| CA | 1.008740D-02 | -1.9962 |
| MG | 5.451131D-02 | -1.2635 |
| NA | 4.854426D-01 | -0.3139 |
| K | 1.057942D-02 | -1.9755 |
| CL | 5.657614D-01 | -0.2474 |
| C | 7.425143D-05 | -4.1293 |
| S | 2.926073D-02 | -1.5337 |
| BR | 8.729404D-04 | -3.0590 |

2.867131D-01 KILOGRAMS OF WATER REMAINING

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ANHYDRIT | -4.5181 | -4.3617 | -0.1564 |
| ARAGONIT | -8.9579 | -8.2195 | -0.7385 |
| ARCANITE | -5.8520 | -1.7760 | -4.0760 |
| BISCHOFI | -1.1940 | 4.4551 | -5.6491 |
| BLOEDITE | -6.1270 | -2.3470 | -3.7800 |
| BRUCITE | -14.5076 | -10.8840 | -3.6236 |
| BURKEITE | -11.3906 | -0.7720 | -10.6186 |
| CALCITE | -8.9579 | -8.4062 | -0.5517 |
| CARNALLI | -2.7808 | 4.3300 | -7.1108 |

| | | | |
|---|---|---|---|
| DOLOMITE | -17.0830 | -17.0830 | 0.0000 |
| EPSOMITE | -3.9037 | -1.8809 | -2.0229 |
| GAYLUSSI | -15.8708 | -9.4210 | -6.4498 |
| GLASERIT | -9.9365 | -3.8030 | -6.1335 |
| GLAUBERI | -6.8350 | -5.2450 | -1.5900 |
| GYPSUM | -4.5805 | -4.5805 | 0.0000 |
| HALITE | 0.1808 | 1.5700 | -1.3892 |
| HEXAHYDR | -3.8725 | -1.6346 | -2.2379 |
| KAINITE | -5.3656 | -0.1930 | -5.1726 |
| KALICINI | -15.9839 | -10.0580 | -5.9259 |
| KIESERIT | -3.7164 | -0.1230 | -3.5934 |
| LABILE S | -9.2143 | -5.6720 | -3.5423 |
| LEONHARD | -3.8101 | -0.8870 | -2.9231 |
| LEONITE | -9.6621 | -3.9790 | -5.6831 |
| MAGNESIT | -8.1251 | -7.8340 | -0.2911 |
| MIRABIL | -2.6291 | -1.2135 | -1.4156 |
| MISENITE | -75.1160 | -10.8060 | -64.3100 |
| NAHCOLIT | -14.2163 | -10.7420 | -3.4743 |
| NATRON | -7.0690 | -0.8250 | -6.2440 |
| NESQUEHO | -8.2187 | -5.1670 | -3.0517 |
| PCO2 | -4.9679 | -1.4679 | -3.5000 |
| PENTAHYD | -3.8413 | -1.2850 | -2.5563 |
| PIRSSONI | -15.7772 | -9.2340 | -6.5432 |
| POLYHALI | -18.6357 | -13.7440 | -4.8917 |
| PORTLAND | -15.3405 | -5.1900 | -10.1505 |
| SCHOENIT | -9.7245 | -4.3280 | -5.3965 |
| SYLVITE | -1.5868 | 0.8998 | -2.4866 |
| SYNGENIT | -10.4013 | -7.4480 | -2.9533 |
| TRONA | -21.0356 | -11.3840 | -9.6516 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 3.518289D-02 | -1.4537 |
| MG | 1.901250D-01 | -0.7210 |
| NA | 1.693130D+00 | 0.2287 |
| K | 3.689898D-02 | -1.4330 |
| CL | 1.973267D+00 | 0.2952 |
| C | 2.589747D-04 | -3.5867 |
| S | 1.020558D-01 | -0.9912 |
| BR | 3.044648D-03 | -2.5165 |

----DESCRIPTION OF SOLUTION----

| | |
|---|---|
| PH = | 7.4400 |
| ACTIVITY H2O = | 0.9306 |
| OSMOTIC COEFFICIENT = | 0.9892 |
| IONIC STRENGTH = | 2.5080 |

TEMPERATURE = 25.0000
PRESSURE = 1.0000 ATM
DENSITY OF H2O = 0.9971 G/CC
ELECTRICAL BALANCE = -4.6020D-05
TOTAL ALKALINITY = 2.6794D-04
ITERATIONS = 10

---

DISTRIBUTION OF SPECIES

---

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | LOG ACT | UNSCALED GAMMA | LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 3.532E-08 | -7.452 | 3.630E-08 | -7.440 | 1.028E+00 | 0.012 |
| 3 | H2O | 0.0 | 9.306E-01 | -0.031 | 9.306E-01 | -0.031 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 3.518E-02 | -1.454 | 6.884E-03 | -2.162 | 1.957E-01 | -0.708 |
| 5 | MG+2 | 2.0 | 1.901E-01 | -0.721 | 4.685E-02 | -1.329 | 2.464E-01 | -0.608 |
| 6 | NA+ | 1.0 | 1.693E+00 | 0.229 | 1.046E+00 | 0.020 | 6.178E-01 | -0.209 |
| 7 | K+ | 1.0 | 3.690E-02 | -1.433 | 1.786E-02 | -1.748 | 4.841E-01 | -0.315 |
| 14 | CL- | -1.0 | 1.973E+00 | 0.295 | 1.450E+00 | 0.161 | 7.347E-01 | -0.134 |
| 15 | CO3-2 | -2.0 | 4.914E-06 | -5.309 | 1.600E-07 | -6.796 | 3.257E-02 | -1.487 |
| 16 | SO4-2 | -2.0 | 1.021E-01 | -0.991 | 4.406E-03 | -2.356 | 4.318E-02 | -1.365 |
| 22 | BR- | -1.0 | 3.045E-03 | -2.516 | 2.514E-03 | -2.600 | 8.259E-01 | -0.083 |
| 31 | OH- | -1.0 | 5.637E-07 | -6.249 | 2.575E-07 | -6.589 | 4.569E-01 | -0.340 |
| 34 | HCO3- | -1.0 | 2.391E-04 | -3.621 | 1.269E-04 | -3.897 | 5.307E-01 | -0.275 |
| 35 | H2CO3 | 0.0 | 7.039E-06 | -5.152 | 1.077E-05 | -4.968 | 1.529E+00 | 0.185 |
| 40 | HSO4- | -1.0 | 2.149E-08 | -7.668 | 1.524E-08 | -7.817 | 7.092E-01 | -0.149 |
| 76 | CACO3 | 0.0 | 1.561E-06 | -5.807 | 1.561E-06 | -5.807 | 1.000E+00 | 0.000 |
| 85 | MGOH+ | 1.0 | 2.616E-06 | -5.582 | 1.864E-06 | -5.729 | 7.126E-01 | -0.147 |
| 86 | MGCO3 | 0.0 | 6.354E-06 | -5.197 | 6.354E-06 | -5.197 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 5.6808D-08 | 3.6304D-08 | 6.3907D-01 |
| CA+2 | 3.5183D-02 | 6.8842D-03 | 1.9567D-01 |
| MG+2 | 1.9012D-01 | 4.6852D-02 | 2.4643D-01 |
| NA+ | 1.6931D+00 | 1.0459D+00 | 6.1775D-01 |
| K+ | 3.6899D-02 | 1.7863D-02 | 4.8410D-01 |
| CL- | 1.9733D+00 | 1.4497D+00 | 7.3467D-01 |
| CO3-2 | 1.2828D-05 | 1.6003D-07 | 1.2475D-02 |
| SO4-2 | 1.0206D-01 | 4.4064D-03 | 4.3177D-02 |
| BR- | 3.0446D-03 | 2.5144D-03 | 8.2585D-01 |
| OH- | 3.1799D-06 | 2.5753D-07 | 8.0985D-02 |
| HCO3- | 2.3911D-04 | 1.2689D-04 | 5.3067D-01 |
| H2CO3 | 7.0392D-06 | 1.0766D-05 | 1.5295D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 4.7268D-01 |

| | |
|---|---|
| CASO4 | 9.1915D-02 |
| CACO3 | 4.9406D-02 |
| CA(OH)2 | 1.0867D-01 |
| MGCL2 | 5.1045D-01 |
| MGSO4 | 1.0315D-01 |
| MGCO3 | 5.5445D-02 |
| MG(OH)2 | 1.1735D-01 |
| NACL | 6.7368D-01 |
| NA2SO4 | 2.5446D-01 |
| NAHCO3 | 5.7256D-01 |
| NA2CO3 | 1.6822D-01 |
| NAOH | 2.2367D-01 |
| KCL | 5.9637D-01 |
| K2SO4 | 2.1629D-01 |
| KHCO3 | 5.0685D-01 |
| K2CO3 | 1.4299D-01 |
| KOH | 1.9800D-01 |
| HCL | 6.8520D-01 |
| H2SO4 | 2.6028D-01 |
| HBR | 7.2648D-01 |

```
1#6 (part c): Evaporate final solution of part b to halite saturation.
 0060021000 1 1          0.00000
 MINERALS
 HALITE      2      0.00        1.6       0.00          1                0.000
    6   1.00       14   1.00
  -7.1346E+02 -1.2012E-01  3.7302E+04  2.6246E+02 -2.1069E+06
 GYPSUM      3       6.0       -4.6       0.00          1                0.000
    4   1.00       16   1.00        3   2.00
   9.0318E+01  0.0000E-01 -4.2130E+03 -3.2641E+01  0.0000E-01
 PCO2        1       4.0       -1.5       -4.8          1               -3.500
   35   1.00
   1.0839E+02  1.9851E-02 -6.9195E+03 -4.0452E+01  6.6936E+05
 DOLOMITE    3       8.0       -17.       -9.4          0                0.000
    4   1.00        5   1.00       15   2.00
             0      0.00       0.00       0.00          0                0.000
 REACTION
    3   1.000   0.000

'STEP NUMBER  1
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```

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 3.518289D-02 | -1.4537 |
| MG | 1.901250D-01 | -0.7210 |
| NA | 1.693130D+00 | 0.2287 |
| K | 3.689898D-02 | -1.4330 |
| CL | 1.973267D+00 | 0.2952 |

| | | |
|---|---|---|
| C | 2.589747D-04 | -3.5867 |
| S | 1.020558D-01 | -0.9912 |
| BR | 3.044648D-03 | -2.5165 |

----PHASE BOUNDARIES----

MASS PRECIPITATED/DISSOLVED FROM INITIAL KILOGRAM WATER

| PHASE | DELTA PHASE* | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|---|
| HALITE | 0.000000D-01 | 1.5700 | 1.5700 | 0.0000 |
| ** | | | | |
| GYPSUM | -3.155443D-02 | -4.5805 | -4.5805 | 0.0000 |
| PCO2 | -1.255065D-04 | -4.9679 | -1.4679 | -3.5000 |
| DOLOMITE | -4.023108D-05 | -17.0830 | -17.0830 | 0.0000 |

* NEGATIVE DELTA PHASE INDICATES PRECIPITATION
AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

** 3.057208D+00 IS THE EVAPORATION FACTOR NECESSARY TO REACH THE
HALITE PHASE BOUNDARY.

MOLES OF ELEMENTS REMAINING AFTER REACTION

| ELEMENT | MOLES | LOG MOLES |
|---|---|---|
| CA | 3.588229D-03 | -2.4451 |
| MG | 1.900847D-01 | -0.7211 |
| NA | 1.693130D+00 | 0.2287 |
| K | 3.689898D-02 | -1.4330 |
| CL | 1.973267D+00 | 0.2952 |
| C | 5.300600D-05 | -4.2757 |
| S | 7.050135D-02 | -1.1518 |
| BR | 3.044648D-03 | -2.5165 |

3.270959D-01 KILOGRAMS OF WATER REMAINING

---- LOOK MIN IAP ----

| PHASE | LOG IAP | LOG KT | LOG IAP/KT |
|---|---|---|---|
| ANHYDRIT | -4.3204 | -4.3617 | 0.0413 |
| ARAGONIT | -9.5397 | -8.2195 | -1.3202 |
| ARCANITE | -4.9697 | -1.7760 | -3.1937 |
| BISCHOFI | 1.0046 | 4.4551 | -3.4504 |
| BLOEDITE | -3.8133 | -2.3470 | -1.4663 |
| BRUCITE | -14.0247 | -10.8840 | -3.1407 |

| | | | |
|---|---|---|---|
| BURKEITE | -8.1263 | -0.7720 | -7.3543 |
| CALCITE | -9.5397 | -8.4062 | -1.1334 |
| CARNALLI | 0.5743 | 4.3300 | -3.7557 |
| DOLOMITE | -17.0830 | -17.0830 | 0.0000 |
| EPSOMITE | -3.2344 | -1.8809 | -1.3536 |
| GAYLUSSI | -16.3782 | -9.4210 | -6.9572 |
| GLASERIT | -7.9391 | -3.8030 | -4.1361 |
| GLAUBERI | -5.2894 | -5.2450 | -0.0444 |
| GYPSUM | -4.5805 | -4.5805 | 0.0000 |
| HALITE | 1.5700 | 1.5700 | 0.0000 |
| HEXAHYDR | -3.1044 | -1.6346 | -1.4698 |
| KAINITE | -3.1446 | -0.1930 | -2.9516 |
| KALICINI | -15.9819 | -10.0580 | -5.9239 |
| KIESERIT | -2.4541 | -0.1230 | -2.3311 |
| LABILE S | -6.5185 | -5.6720 | -0.8465 |
| LEONHARD | -2.8443 | -0.8870 | -1.9573 |
| LEONITE | -7.8140 | -3.9790 | -3.8350 |
| MAGNESIT | -7.5433 | -7.8340 | 0.2907 |
| MIRABIL | -2.2696 | -1.2135 | -1.0560 |
| MISENITE | -69.5451 | -10.8060 | -58.7391 |
| NAHCOLIT | -13.9815 | -10.7420 | -3.2395 |
| NATRON | -7.4889 | -0.8250 | -6.6639 |
| NESQUEHO | -7.9335 | -5.1670 | -2.7665 |
| PCO2 | -4.9679 | -1.4679 | -3.5000 |
| PENTAHYD | -2.9743 | -1.2850 | -1.6893 |
| PIRSSONI | -15.9881 | -9.2340 | -6.7541 |
| POLYHALI | -16.1946 | -13.7440 | -2.4506 |
| PORTLAND | -16.0211 | -5.1900 | -10.8311 |
| SCHOENIT | -8.0741 | -4.3280 | -3.7461 |
| SYLVITE | -0.4304 | 0.8998 | -1.3302 |
| SYNGENIT | -9.4201 | -7.4480 | -1.9721 |
| TRONA | -20.4299 | -11.3840 | -9.0459 |

TOTAL MOLALITIES OF ELEMENTS

| ELEMENT | MOLALITY | LOG MOLALITY |
|---|---|---|
| CA | 1.096996D-02 | -1.9598 |
| MG | 5.811285D-01 | -0.2357 |
| NA | 5.176251D+00 | 0.7140 |
| K | 1.128079D-01 | -0.9477 |
| CL | 6.032687D+00 | 0.7805 |
| C | 1.620503D-04 | -3.7904 |
| S | 2.155373D-01 | -0.6665 |
| BR | 9.308121D-03 | -2.0311 |

----DESCRIPTION OF SOLUTION----

PH = 7.1144

ACTIVITY H2O = 0.7412
OSMOTIC COEFFICIENT = 1.3694
IONIC STRENGTH = 7.2808
TEMPERATURE = 25.0000
PRESSURE = 1.0000 ATM
DENSITY OF H2O = 0.9971 G/CC
ELECTRICAL BALANCE = -4.6020D-05
TOTAL ALKALINITY = 2.3239D-04
ITERATIONS = 14

DISTRIBUTION OF SPECIES

| I | SPECIES | Z | MOLALITY | LOG MOLAL | UNSCALED ACTIVITY | UNSCALED LOG ACT | UNSCALED GAMMA | UNSCALED LOG GAM |
|---|---|---|---|---|---|---|---|---|
| 1 | H+ | 1.0 | 1.815E-08 | -7.741 | 7.684E-08 | -7.114 | 4.234E+00 | 0.627 |
| 3 | H2O | 0.0 | 7.412E-01 | -0.130 | 7.412E-01 | -0.130 | 1.000E+00 | 0.000 |
| 4 | CA+2 | 2.0 | 1.097E-02 | -1.960 | 1.014E-02 | -1.994 | 9.248E-01 | -0.034 |
| 5 | MG+2 | 2.0 | 5.811E-01 | -0.236 | 1.006E+00 | 0.003 | 1.731E+00 | 0.238 |
| 6 | NA+ | 1.0 | 5.176E+00 | 0.714 | 4.773E+00 | 0.679 | 9.221E-01 | -0.035 |
| 7 | K+ | 1.0 | 1.128E-01 | -0.948 | 4.769E-02 | -1.322 | 4.228E-01 | -0.374 |
| 14 | CL- | -1.0 | 6.033E+00 | 0.781 | 7.784E+00 | 0.891 | 1.290E+00 | 0.111 |
| 15 | CO3-2 | -2.0 | 2.102E-06 | -5.677 | 2.845E-08 | -7.546 | 1.354E-02 | -1.869 |
| 16 | SO4-2 | -2.0 | 2.155E-01 | -0.666 | 4.714E-03 | -2.327 | 2.187E-02 | -1.660 |
| 22 | BR- | -1.0 | 9.308E-03 | -2.031 | 1.695E-02 | -1.771 | 1.821E+00 | 0.260 |
| 31 | OH- | -1.0 | 2.328E-07 | -6.633 | 9.690E-08 | -7.014 | 4.163E-01 | -0.381 |
| 34 | HCO3- | -1.0 | 1.322E-04 | -3.879 | 4.775E-05 | -4.321 | 3.612E-01 | -0.442 |
| 35 | H2CO3 | 0.0 | 3.100E-06 | -5.509 | 1.077E-05 | -4.968 | 3.473E+00 | 0.541 |
| 40 | HSO4- | -1.0 | 3.995E-08 | -7.398 | 3.451E-08 | -7.462 | 8.638E-01 | -0.064 |
| 76 | CACO3 | 0.0 | 4.089E-07 | -6.388 | 4.089E-07 | -6.388 | 1.000E+00 | 0.000 |
| 85 | MGOH+ | 1.0 | 4.644E-05 | -4.333 | 1.506E-05 | -4.822 | 3.243E-01 | -0.489 |
| 86 | MGCO3 | 0.0 | 2.425E-05 | -4.615 | 2.425E-05 | -4.615 | 1.000E+00 | 0.000 |

| SPECIES | TOTAL MOL | UNSCALED ACTIVITY | UNSCALED TOTAL GAMMA |
|---|---|---|---|
| H+ | 5.8098D-08 | 7.6843D-08 | 1.3226D+00 |
| CA+2 | 1.0970D-02 | 1.0145D-02 | 9.2479D-01 |
| MG+2 | 5.8113D-01 | 1.0060D+00 | 1.7311D+00 |
| NA+ | 5.1763D+00 | 4.7732D+00 | 9.2214D-01 |
| K+ | 1.1281D-01 | 4.7694D-02 | 4.2279D-01 |
| CL- | 6.0327D+00 | 7.7836D+00 | 1.2902D+00 |
| CO3-2 | 2.6764D-05 | 2.8450D-08 | 1.0630D-03 |
| SO4-2 | 2.1554D-01 | 4.7138D-03 | 2.1870D-02 |
| BR- | 9.3081D-03 | 1.6952D-02 | 1.8212D+00 |
| OH- | 4.6678D-05 | 9.6904D-08 | 2.0760D-03 |
| HCO3- | 1.3219D-04 | 4.7746D-05 | 3.6120D-01 |
| H2CO3 | 3.1002D-06 | 1.0766D-05 | 3.4727D+00 |

---- MEAN ACTIVITY COEFFICIENT ----

| FORMULA | MEAN GAMMA |
|---|---|
| CACL2 | 1.1547D+00 |
| CASO4 | 1.4221D-01 |
| CACO3 | 3.1353D-02 |
| CA(OH)2 | 1.5855D-02 |
| MGCL2 | 1.4231D+00 |
| MGSO4 | 1.9457D-01 |
| MGCO3 | 4.2897D-02 |
| MG(OH)2 | 1.9540D-02 |
| NACL | 1.0908D+00 |
| NA2SO4 | 2.6494D-01 |
| NAHCO3 | 5.7713D-01 |
| NA2CO3 | 9.6688D-02 |
| NAOH | 4.3754D-02 |
| KCL | 7.3858D-01 |
| K2SO4 | 1.5753D-01 |
| KHCO3 | 3.9079D-01 |
| K2CO3 | 5.7490D-02 |
| KOH | 2.9626D-02 |
| HCL | 1.3063D+00 |
| H2SO4 | 3.3696D-01 |
| HBR | 1.5520D+00 |

each new phase boundary to be reached in evaporation. Many more phase boundaries are encountered in the evaporation of sea water beyond halite saturation and are not considered here.

Table 17 (part b output) shows that an evaporation factor of 3.4878 is required to make sea water just saturated with gypsum (while maintaining equilibrium with dolomite in contact with air). Of the initial 1000 grams of water in the starting solution, 286.713 grams remain. Inspection of the LOOK MIN output shows that the modified sea water is saturated with gypsum and dolomite at a $PCO_2$ of $10^{-3.5}$ atm. and undersaturated with all other minerals in the Harvie and others (1984) data base. The modified sea water at completion of part b is stored in solution 1 (IOPT(7) = 1) to define the starting point in part c.

In part c we assume that the next phase encountered in evaporation will be halite. The starting solution is put back on a molal scale, that is moles per one kg of $H_2O$. An evaporation factor of 3.0572 is required to reach halite saturation. The cumulative evaporation factor over parts b and c is the product of both evaporation factors, that is, 3.4878 x 3.0572 = 10.6629 and the cumulative water remaining at the halite phase boundary is 1000/10.6629 = 93.78 grams $H_2O$.

Our problem becomes more complicated at the end of part c (Table 17) where inspection of the final saturation indices shows that at the halite phase boundary the solution is oversaturated with anhydrite and magnesite. If our goal is to follow rigorously the thermodynamic path, it would be necessary to back up and locate at least the magnesite phase boundary and evaluate again whether anhydrite saturation would be reached before halite saturation. At the magnesite phase boundary we could treat the system open or closed to re-reaction of dolomite previously formed, by inclusion or exclusion of dolomite in MINERALS input, respectively. In an open system it would be necessary to locate the point in evaporation where all the dolomite previously formed had reacted to form magnesite. After locating the magnesite phase boundary the point where dolomite vanishes is found by placing dolomite first in the MINERALS input with magnesite equilibrium included. Beyond this point in evaporation the solution will be undersaturated with dolomite and the mineral would be removed from the MINERALS input while maintaining equilibrium with magnesite. If for kinetic reasons it is assumed that magnesite would not precipitate in this environment, MINERALS input for magnesite would not be included and subsequent computed supersaturation with respect to magnesite in solution would be disregarded. Seawater evaporation reaction paths could also be more realistically examined if, for example, formation of magnesian calcites were considered rather than dolomite which is well known for its irreversible behavior in low-temperature environments. Diagenetic reaction paths responsible for dolomitization in marine evaporite sequences can be considered in subsequent simulations.

## PROGRAM SOURCE CODE

PHRQPITZ is written in FORTRAN 77 and currently runs on a Prime 850 minicomputer. The source code is listed in Attachment D along with the file COMMON.BLOCKS which is inserted in PHRQPITZ at the $INSERT statements. A machine-readable listing of PHRQPITZ, associated data files and test cases is written on a 360K 5 1/4 inch floppy disk (diskette 1) located in the back pocket of this report. The contents of this disk can be viewed on an IBM-compatible PC by typing the command "list". Although PHRQPITZ does not currently run on a PC, the floppy disk can be used to transport the code to other machines. In transporting to other machines, it may be necessary to insert the file COMMON.BLOCKS (listed at the end of Attachment D and on the floppy disk) at each $INSERT statement throughout the source code. Two data files are read internally by PHRQPITZ. These are PHRQPITZ.DATA (read from the main program as unit 11) and PITZER.DATA (read from SUBROUTINE INITPZ as unit 12). The file PHRQPITZ.DATA is listed in Attachment A and the file PITZER.DATA is listed in Attachment B. Both data files can be read from the floppy disk. The user is referred to Parkhurst and others (1980) for information on the construction and logic of PHREEQE. Comment statements in subroutines PITZER, BDK, PTEMP, and INITPZ define calculations based on the Pitzer model. References to equation numbers refer to equations in Harvie and Weare (1980), or to a lesser extent Harvie and others (1984). Subroutines BB, QQ, DFIND and Functions DW, BASE, PS, VLEST and DC are taken from Haar and others (1984) for calculation of the properties of water as a function of temperature and pressure.

## INTERACTIVE CONSTRUCTION OF INPUT FILES FOR THE COMPUTER PROGRAM

PITZINPT is a FORTRAN 77 program that facilitates formulation of input data files to PHRQPITZ. It is nearly identical to the code PHRQINPT (Fleming and Plummer, 1983) which is used interactively to construct input sets to PHREEQE (Parkhurst and others, 1980). The source code to PITZINPT is listed in Attachment E. PITZINPT reads two data files (PHRQPITZ.DATA, Attachment A, and MINERALS.2.DATA, Attachment F). Machine-readable copies of PHRQPITZ and associated data files are written on a 360K 5 1/4 inch floppy disk located in the back pocket of this report (diskette 2). Type the command "list" to view the contents of this disk on an IBM-compatible PC.

PITZINPT, written in Prime Fortran 77, interactively asks the user at the terminal for values of variables required by PHRQPITZ (see "Description of Input"), explains the meaning and significance of each variable when required, and internally checks to make sure that values entered are valid. In some cases, PITZINPT automatically assigns values to certain variables, based on values previously entered, and keeps track of additional required information. PITZINPT contains an editor which allows the user to make corrections after each line has been completed.

The file MINERALS.2.DATA (Attachment F) contains pre-constructed MINERALS input for the Harvie and others (1984) data base from which the user may select from the screen for inclusion under MINERALS input. The list of pre-constructed minerals may be displayed by entering the command LIST during MINERALS input.

Attachment G contains a listing of an interactive session in which PITZINPT was used to construct the input file to test problem 3 (table 10). The user is first asked to enter the name of the file to be created. The user may next enter a (optional) reference input file which can be edited to produce the new file. If no such pre-constructed input file exists, a carriage return should be entered (as was done in the example of Attachment G) signifying that all new data will be entered from the screen. PITZINPT then prompts for entry of a title and the option line; lines 1 and 2 of all PHRQPITZ input files. Following completion of entry for each line, the line is displayed and the user is given an opportunity to edit what has been entered. Following acceptance of lines 1 and 2 the user is then prompted for entry of a keyword. Allowable entries are ELEMENTS, SPECIES, SOLUTION, MINERALS, LOOK

MIN, TEMP, STEPS, REACTION, NEUTRAL, SUMS, and END. Under each keyword the user is prompted for necessary information defined under "Description of Input". See Fleming and Plummer (1983) for additional details.

## ACKNOWLEDGMENT

We benefited from discussions and correspondence with Charles E. Harvie and John H. Weare (University of California, San Diego) during code development. Eric C. Prestemon contributed computer calculations. The manuscript was improved by reviews from Eric J. Reardon (University of Waterloo), Ronald K. Stoessell (University of New Orleans) and Ronald J. Spencer (University of Calgary).

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Attachment A. -- Listing of the file PHRQPITZ.DATA

```
ELEMENTS
CA          4    40.08          CA+2
MG          5    24.305         MG+2
NA          6    22.9898        NA+
K           7    39.0983        K+
FE          8    55.847         FE+2
MN          9    54.9380        MN+2
BA         11    137.33         BA+2
SR         12    87.62          SR+2
CL         14    35.453         CL-
C          15    44.0098        CO2
S          16    96.06          SO4-2
LI         21     6.941         LI+
BR         22     79.904        BR-

SPECIES
  1
H+            100 1.0       0.0       9.0                          0.0
 0.0        0.0
  1 1.0
  2
E-            100 -1.0      0.0       0.0                          0.0
 0.0        0.0
  2 1.0
  3
H2O           100 0.0       0.0       0.0                          0.0
 0.0        0.0
  3 1.0
  4
CA+2          101 2.0       0.0       6.0       5.0      0.165     0.0
 0.0        0.0
  4 1.0
  5
MG+2          101 2.0       0.0       8.0       5.5      0.20      0.0
0.0        0.0
  5 1.0
  6
NA+           101 1.0       0.0       4.0       4.0      0.075     0.0
0.0        0.0
  6 1.0
  7
K+            101 1.0       0.0       3.0       3.5      0.015     0.0
0.0        0.0
  7 1.0
  8
FE+2          100 2.0       2.0       6.0                          0.0
0.0        0.0
  8 1.0
  9
MN+2          100 2.0       2.0       6.0                          0.0
 0.0        0.0
  9 1.0
 11
BA+2          100 2.0       0.0       5.0                          0.0
```

```
 0.0        0.0
 11 1.0
 12
SR+2          101 2.0        0.0        5.0              5.26       0.121 0.0
 0.0        0.0
 12 1.0
 14
CL-           101 -1.0       0.0        3.0        3.5         0.015      0.0
 0.0        0.0
 14 1.0
 15
CO3-2         101 -2.0       4.0        4.5        5.4         0.0        2.0
 0.0        0.0
 15 1.0
 16
SO4-2         101 -2.0       6.0        4.0        5.0         -0.04      0.0
 0.0        0.0
 16 1.0
 21
LI+           100 1.0        0.0        6.0                               0.0
0.0         0.0
 21 1.0
 22
BR-           100 -1.0       0.0        3.0                               0.0
0.0         0.0
 22 1.0
 31
OH-           200 -1.0       0.0        3.5                               1.0
-13.998    13.345
  3 1.0      1 -1.0
 34
HCO3-         211 -1.0       4.0        4.5        5.4         0.0        1.0
 10.3393    -3.561     107.8975     0.03252849  -5151.79     -38.92561    563713.9
 15 1.0      1 1.0
 35
H2CO3         310 0.0        4.0        0.0                               0.0
 16.6767    -5.738     464.1925     0.09344813  -26986.16    -165.75951   2248628.9
 15 1.0      1 2.0       3 -1.0
 40
HSO4-         210 -1.0       6.0        0.0                               0.0
 1.979      4.91       -5.3585      0.0183412   557.2461
 16 1.0      1 1.0
 76
CACO3         210 0.0        4.0        0.0                               2.0
3.151       3.547      -1228.806    -0.299440   35512.75      485.818
  4 1.0      15 1.0
 85
MGOH+         300 1.0        0.0        0.0                               1.0
-11.809    15.419
  5 1.0      3 1.0       1 -1.0
 86
MGCO3         210 0.0        4.0        0.0                               2.0
2.928       2.535      -32.225      0.0         1093.486     12.72433
  5 1.0      15 1.0

LOOK MIN
```

```
ANHYDRIT   2          6.00    -4.362                1
   4      1.000  16       1.000
422.950     0.0          -18431.      -147.708
ARAGONIT   2          4.00    -8.220                1
  15 1.0           4 1.0
-171.8607   -.077993    2903.293    71.595
ARCANITE   2          6.00    -1.776                1
   7      2.000  16       1.000
2.823       0.0          -1371.2
BISCHOFI   3          0.00     4.455                1
   5      1.000  14       2.000   3       6.000
3.524       0.0          277.6
BLOEDITE   4         12.00    -2.347                0
   6      2.000   5       1.000  16       2.000   3       4.000
BRUCITE    2          0.00   -10.884.85             0
   5      1.000  31       2.000
BURKEITE   3         16.00     -.772                0
   6      6.000  15       1.000  16       2.000
CALCITE    2          4.00    -8.406                1
  15 1.0           4 1.0
-171.8329   -.077993    2839.319    71.595
CARNALLI   4          0.00    4.330                 0
   7      1.000   5       1.000  14       3.000   3       6.000
DOLOMITE   3          8.00   -17.083 -9.436         0
   4 1.0           5 1.0           15 2.0
EPSOMITE   3          6.00    -1.881                1
   5      1.000  16       1.000   3       7.000
1.718       0.0          -1073.
GAYLUSSI   4          8.00    -9.421                0
   4      1.000   6       2.000  15       2.000   3       5.000
GLASERIT   3         24.00    -3.803                0
   6      1.000   7       3.000  16       2.000
GLAUBERI   3         12.00    -5.245                0
   6      2.000   4       1.000  16       2.000
GYPSUM     3          6.00    -4.581                1
   4 1.0           16 1.0           3 2.0
90.318      0.0          -4213.       -32.641
HALITE     2          0.00     1.570                1
   6      1.000  14       1.000
-713.4616   -.1201241   37302.21    262.4583    -2106915.
HEXAHYDR   3          6.00    -1.635                1
   5      1.000  16       1.000   3       6.000
-62.666     0.0          1828.        22.187
KAINITE    5          6.00    -0.193                0
   7      1.000   5       1.000  14       1.000  16       1.000   3       3.000
KALICINI   3          4.00   -10.058                0
   7      1.000   1       1.000  15       1.000
KIESERIT   3          6.00    -0.123                0
   5      1.000  16       1.000   3       1.000
LABILE S   4         18.00    -5.672                0
   6      4.000   4       1.000  16       3.000   3       2.000
LEONHARD   3          6.00    -0.887                0
   5      1.000  16       1.000   3       4.000
LEONITE    4         12.00    -3.979                0
   7      2.000   5       1.000  16       2.000   3       4.000
MAGNESIT   2          4.00    -7.834     -6.169     0
```

```
   5      1.000  15       1.000
MIRABIL    3   6.          -1.214                  1
   62.            161.             310.
-3862.234   -1.19856    93713.54    1577.756    0.
MISENITE   3        42.00  -10.806                  0
   7      8.000   1       6.000  16       7.000
NAHCOLIT   3          4.00  -10.742                  0
   6      1.000   1       1.000  15       1.000
NATRON     3          4.00   -0.825                  0
   6      2.000  15       1.000   3      10.000
NESQUEHO   3          4.00   -5.167                  0
   5      1.000  15       1.000   3       3.000
PCO2       1          4.0    -1.468     -4.776      1
  35  1.0
108.3865    0.01985076  -6919.53    -40.45154    669365.0
PENTAHYD   3          6.00   -1.285                  0
   5      1.000  16       1.000   3       5.000
PIRSSONI   4          8.00   -9.234                  0
   6      2.000   4       1.000  15       2.000   3       2.000
POLYHALI   5         24.00  -13.744                  0
   7      2.000   5       1.000   4       2.000  16       4.000   3       2.000
PORTLAND   2          0.00   -5.190                  0
   4      1.000  31       2.000
SCHOENIT   4         12.00   -4.328                  0
   7      2.000   5       1.000  16       2.000   3       6.000
SYLVITE    2          0.00     .900                  1
   7      1.000  14       1.000
3.984       0.0          -919.55
SYNGENIT   4         12.00   -7.448                  0
   7      2.000   4       1.000  16       2.000   3       1.000
TRONA      4          8.00  -11.384                  0
   6      3.000   1       1.000  15       2.000   3       2.000

MEAN GAM
CACL2     2   4   1.0  14   2.0
CASO4     2   4   1.0  16   1.0
CACO3     2   4   1.0  15   1.0
CA(OH)2   2   4   1.0  31   2.0
MGCL2     2   5   1.0  14   2.0
MGSO4     2   5   1.0  16   1.0
MGCO3     2   5   1.0  15   1.0
MG(OH)2   2   5   1.0  31   2.0
NACL      2   6   1.0  14   1.0
NA2SO4    2   6   2.0  16   1.0
NAHCO3    2   6   1.0  34   1.0
NA2CO3    2   6   2.0  15   1.0
NAOH      2   6   1.0  31   1.0
KCL       2   7   1.0  14   1.0
K2SO4     2   7   2.0  16   1.0
KHCO3     2   7   1.0  34   1.0
K2CO3     2   7   2.0  15   1.0
KOH       2   7   1.0  31   1.0
HCL       2   1   1.0  14   1.0
H2SO4     2   1   2.0  16   1.0
HBR       2   1   1.0  22   1.0
END
```

Attachment B. -- Listing of the file PITZER.DATA

```
SPECIES  21
  1  4  5  6  7  8  9 11 12 14 15 16 21 22 31 34 35 40 76 85 86
B0
  NA+       CL-       0.0765     -777.03     -4.4706      0.008946   -3.3158E-6
  K+        CL-       0.04835                             5.794E-4
  MG+2      CL-       0.35235                            -1.943E-4
  CA+2      CL-       0.3159                             -1.725E-4
  MGOH+     CL-      -0.1
  H+        CL-       0.1775                             -3.081E-4
  LI+       CL-       0.1494                             -1.685E-4
  SR+2      CL-       0.28575                             0.717E-3
  FE+2      CL-       0.335925
  MN+2      CL-       0.327225
  BA+2      CL-       0.2628                              0.6405E-3
  NA+       BR-       0.0973                              7.692E-4
  K+        BR-       0.0569                              7.39E-4
  H+        BR-       0.1960                             -2.049E-4
  MG+2      BR-       0.4327                             -5.625E-5
  CA+2      BR-       0.3816                             -5.2275E-4
  LI+       BR-       0.1748                             -1.819E-4
  SR+2      BR-       0.331125                           -0.32775E-3
  BA+2      BR-       0.31455                            -0.33825E-3
  NA+       SO4-2     0.01958                             2.367E-3
  K+        SO4-2     0.04995                             1.44E-3
  MG+2      SO4-2     0.221                              -0.69E-3
  CA+2      SO4-2     0.2
  H+        SO4-2     0.0298
  LI+       SO4-2     0.136275                            0.5055E-3
  SR+2      SO4-2     0.220                              -2.9E-3
  FE+2      SO4-2     0.2568
  MN+2      SO4-2     0.2065
  NA+       HSO4-     0.0454
  K+        HSO4-    -0.0003
  MG+2      HSO4-     0.4746
  CA+2      HSO4-     0.2145
  H+        HSO4-     0.2065
  FE+2      HSO4-     0.4273
  NA+       OH-       0.0864                              7.00E-4
  K+        OH-       0.1298
  CA+2      OH-      -0.1747
  LI+       OH-       0.015
  BA+2      OH-       0.17175
  NA+       HCO3-     0.0277                              1.00E-3
  K+        HCO3-     0.0296                              0.996E-3
  MG+2      HCO3-     0.329
  CA+2      HCO3-     0.4
  SR+2      HCO3-     0.12
  NA+       CO3-2     0.0399                              1.79E-3
  K+        CO3-2     0.1488                              1.788E-3
B1
  NA+       CL-       0.2664                              6.1608E-5  1.0715E-6
  K+        CL-       0.2122                              10.71E-4
  MG+2      CL-       1.6815                              3.6525E-3
  CA+2      CL-       1.614                               3.9E-3
```

| | | | | | |
|---|---|---|---|---|---|
| MGOH+ | CL- | 1.658 | | | |
| H+ | CL- | 0.2945 | | | 1.419E-4 |
| LI+ | CL- | 0.3074 | | | 5.366E-4 |
| SR+2 | CL- | 1.66725 | | | 2.8425E-3 |
| FE+2 | CL- | 1.53225 | | | |
| MN+2 | CL- | 1.55025 | | | |
| BA+2 | CL- | 1.49625 | | | 3.2325E-3 |
| NA+ | BR- | 0.2791 | | | 10.79E-4 |
| K+ | BR- | 0.2212 | | | 17.40E-4 |
| H+ | BR- | 0.3564 | | | 4.467E-4 |
| MG+2 | BR- | 1.753 | | | 3.8625E-3 |
| CA+2 | BR- | 1.613 | | | 6.0375E-3 |
| LI+ | BR- | 0.2547 | | | 6.636E-4 |
| SR+2 | BR- | 1.7115 | | | 6.5325E-3 |
| BA+2 | BR- | 1.56975 | | | 6.78E-3 |
| NA+ | SO4-2 | 1.113 | | | 5.6325E-3 |
| K+ | SO4-2 | 0.7793 | | | 6.6975E-3 |
| MG+2 | SO4-2 | 3.343 | | | 1.53E-2 |
| CA+2 | SO4-2 | 3.1973 | | | 5.46E-2 |
| LI+ | SO4-2 | 1.2705 | | | 1.41E-3 |
| SR+2 | SO4-2 | 2.88 | | | 27.0E-3 |
| FE+2 | SO4-2 | 3.063 | | | |
| MN+2 | SO4-2 | 2.9511 | | | |
| NA+ | HSO4- | 0.398 | | | |
| K+ | HSO4- | 0.1735 | | | |
| MG+2 | HSO4- | 1.729 | | | |
| CA+2 | HSO4- | 2.53 | | | |
| H+ | HSO4- | 0.5556 | | | |
| FE+2 | HSO4- | 3.48 | | | |
| NA+ | OH- | 0.253 | | | 1.34E-4 |
| K+ | OH- | 0.32 | | | |
| CA+2 | OH- | -0.2303 | | | |
| LI+ | OH- | 0.14 | | | |
| BA+2 | OH- | 1.2 | | | |
| NA+ | HCO3- | 0.0411 | | | 1.10E-3 |
| K+ | HCO3- | -0.013 | | | 1.104E-3 |
| MG+2 | HCO3- | 0.6072 | | | |
| CA+2 | HCO3- | 2.977 | | | |
| NA+ | CO3-2 | 1.389 | | | 2.05E-3 |
| K+ | CO3-2 | 1.43 | | | 2.051E-3 |
| B2 | | | | | |
| MG+2 | SO4-2 | -37.23 | | | -0.253 |
| CA+2 | SO4-2 | -54.24 | | | -0.516 |
| SR+2 | SO4-2 | -41.8 | | | -0.42 |
| FE+2 | SO4-2 | -42.0 | | | |
| MN+2 | SO4-2 | -40.0 | | | |
| CA+2 | OH- | -5.72 | | | |
| CO | | | | | |
| NA+ | CL- | 0.00127 | 33.317 | 0.09421 | -4.655E-5 |
| K+ | CL- | -0.00084 | | | -5.095E-5 |
| MG+2 | CL- | 0.00519 | | | -1.64933E-4 |
| CA+2 | CL- | -0.00034 | | | |
| H+ | CL- | 0.0008 | | | 6.213E-5 |
| LI+ | CL- | 0.00359 | | | -4.520E-5 |
| SR+2 | CL- | -0.00130461 | | | |
| FE+2 | CL- | -0.00860725 | | | |

| | | | | |
|---|---|---|---|---|
| | MN+2 | CL- | -0.0204972 | |
| | BA+2 | CL- | -0.0193782 | -1.53796E-4 |
| | NA+ | BR- | 0.00116 | -9.30E-5 |
| | K+ | BR- | -0.00180 | -7.004E-5 |
| | H+ | BR- | 0.00827 | -5.685E-5 |
| | MG+2 | BR- | 0.00312 | |
| | CA+2 | BR- | -0.00257 | |
| | LI+ | BR- | 0.0053 | -2.813E-5 |
| | SR+2 | BR- | 0.00122506 | |
| | BA+2 | BR- | -0.0159576 | |
| | NA+ | SO4-2 | 0.00497 | -4.87904E-4 |
| | MG+2 | SO4-2 | 0.025 | 0.523E-3 |
| | H+ | SO4-2 | 0.0438 | |
| | LI+ | SO4-2 | -0.00399338 | -2.33345E-4 |
| | SR+2 | SO4-2 | 0.019 | 3.0E-3 |
| | FE+2 | SO4-2 | 0.0209 | |
| | MN+2 | SO4-2 | 0.01636 | |
| | NA+ | OH- | 0.0044 | -18.94E-5 |
| | K+ | OH- | 0.0041 | |
| | K+ | HCO3- | -0.008 | |
| | NA+ | CO3-2 | 0.0044 | |
| | K+ | CO3-2 | -0.0015 | |
| THETA | | | | |
| | K+ | NA+ | -0.012 | |
| | MG+2 | NA+ | 0.07 | |
| | CA+2 | NA+ | 0.07 | |
| | H+ | NA+ | 0.036 | |
| | CA+2 | K+ | 0.032 | |
| | H+ | K+ | 0.005 | |
| | CA+2 | MG+2 | 0.007 | |
| | H+ | MG+2 | 0.1 | |
| | H+ | CA+2 | 0.092 | |
| | SO4-2 | CL- | 0.02 | |
| | HSO4- | CL- | -0.006 | |
| | OH- | CL- | -0.05 | |
| | HCO3- | CL- | 0.03 | |
| | CO3-2 | CL- | -0.02 | |
| | OH- | BR- | -0.065 | |
| | OH- | SO4-2 | -0.013 | |
| | HCO3- | SO4-2 | 0.01 | |
| | CO3-2 | SO4-2 | 0.02 | |
| | CO3-2 | OH- | 0.1 | |
| | CO3-2 | HCO3- | -0.04 | |
| LAMDA | | | | |
| | NA+ | H2CO3 | 0.1 | |
| | K+ | H2CO3 | 0.051 | |
| | MG+2 | H2CO3 | 0.183 | |
| | CA+2 | H2CO3 | 0.183 | |
| | CL- | H2CO3 | -0.005 | |
| | SO4-2 | H2CO3 | 0.097 | |
| | HSO4- | H2CO3 | -0.003 | |
| PSI | | | | |
| | NA+ | K+ | CL- | -0.0018 |
| | NA+ | K+ | BR- | -0.0022 |
| | NA+ | K+ | SO4-2 | -0.010 |
| | NA+ | K+ | HCO3- | -0.003 |

| | | | |
|---|---|---|---|
| NA+ | K+ | CO3-2 | 0.003 |
| NA+ | CA+2 | CL- | -0.007 |
| NA+ | CA+2 | SO4-2 | -0.055 |
| NA+ | MG+2 | CL- | -0.012 |
| NA+ | MG+2 | SO4-2 | -0.015 |
| NA+ | H+ | CL- | -0.004 |
| NA+ | H+ | BR- | -0.012 |
| NA+ | H+ | HSO4- | -0.0129 |
| K+ | CA+2 | CL- | -0.025 |
| K+ | MG+2 | CL- | -0.022 |
| K+ | MG+2 | SO4-2 | -0.048 |
| K+ | H+ | CL- | -0.011 |
| K+ | H+ | BR- | -0.021 |
| K+ | H+ | SO4-2 | 0.197 |
| K+ | H+ | HSO4- | -0.0265 |
| CA+2 | MG+2 | CL- | -0.012 |
| CA+2 | MG+2 | SO4-2 | 0.024 |
| CA+2 | H+ | CL- | -0.015 |
| MG+2 | MGOH+ | CL- | 0.028 |
| MG+2 | H+ | CL- | -0.011 |
| MG+2 | H+ | HSO4- | -0.0178 |
| CL- | BR- | K+ | 0.0000 |
| CL- | SO4-2 | NA+ | 0.0014 |
| CL- | SO4-2 | CA+2 | -0.018 |
| CL- | SO4-2 | MG+2 | -0.004 |
| CL- | HSO4- | NA+ | -0.006 |
| CL- | HSO4- | H+ | 0.013 |
| CL- | OH- | NA+ | -0.006 |
| CL- | OH- | K+ | -0.006 |
| CL- | OH- | CA+2 | -0.025 |
| CL- | HCO3- | NA+ | -0.015 |
| CL- | HCO3- | MG+2 | -0.096 |
| CL- | CO3-2 | NA+ | 0.0085 |
| CL- | CO3-2 | K+ | 0.004 |
| SO4-2 | HSO4- | NA+ | -0.0094 |
| SO4-2 | HSO4- | K+ | -0.0677 |
| SO4-2 | HSO4- | MG+2 | -0.0425 |
| SO4-2 | OH- | NA+ | -0.009 |
| SO4-2 | OH- | K+ | -0.050 |
| SO4-2 | HCO3- | NA+ | -0.005 |
| SO4-2 | HCO3- | MG+2 | -0.161 |
| SO4-2 | CO3-2 | NA+ | -0.005 |
| SO4-2 | CO3-2 | K+ | -0.009 |
| OH- | CO3-2 | NA+ | -0.017 |
| OH- | CO3-2 | K+ | -0.01 |
| OH- | BR- | NA+ | -0.018 |
| OH- | BR- | K+ | -0.014 |
| HCO3- | CO3-2 | NA+ | 0.002 |
| HCO3- | CO3-2 | K+ | 0.012 |

Attachment C. -- Summary of published Pitzer interaction parameters

Attachment C.1. -- List of references cited in Attachments C.2 through C.6

Attachment C.1 - List of References Cited in Attachments C.2 - C.6 *


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* Additional references are given in the text

Attachment C.2. -- Summary of literature values of Pitzer interaction parameters for single salts

Attachment C.2 - Summary of Literature Values of Pitzer Interaction Parameters for Single Salts

| INTERACTION | | B0 | B1 | C0 | B2 |
|---|---|---|---|---|---|
| Na+ | Cl- | .0765 (48) | .2644 (48) | .00127 (48) | |
| | | .07650 (49) | .2664 (49) | .00127 (49) | |
| | | .0765 (89) | .2664 (89) | .00127 (89) | |
| | | .07670 (83) | .26495 (83) | .00122 (83) | |
| | | .0754 (93) | .2770 (93) | .0014 (93) | |
| | | .0754 (85) | .2770 (85) | .0007 (85) | |
| | | .07669 (129) | .26461 (129) | .0012193 (129) | |
| | | .0757 (46) | .2795 (46) | .0014 (46) | |
| | | .08305 (5) | .21900 (5) | ----- | |
| | | .0765 (26) | .2665 (26) | .00062 (26) | |
| | | .0765 (25) | .2664 (25) | .00121 (25) | |
| | | .0765 (35) | .2664 (35) | .000126 (35) | |
| | | .10820 (10) | .03127 (10) | -.002469 (10) | |
| | | .0765 (24) | .2664 (24) | .00124 (24) | |
| K+ | Cl- | .04835 (48) | .2122 (48) | -.00084 (48) | |
| | | .04835 (49) | .2122 (49) | -.00084 (49) | .0 (49) |
| | | .04835 (89) | .2122 (89) | .00080 (89) | |
| | | .04827 (83) | .20887 (83) | .00082 (83) | |
| | | .0481 (85) | .2187 (85) | -.000394 (85) | |
| | | .0464 (46) | .2274 (46) | -.0004 (46) | |
| | | .04453 (5) | .22839 (5) | ----- | |
| | | .04808 (54) | .0476 (54) | -.000788 (54) | |
| | | .04626 (68) | .21844 (68) | -.000398 (68) | |
| | | .06577 (10) | .09351 (10) | -.002160 (10) | |
| | | .05041176 (123) | .195522 (123) | .001355442 (123) | |
| H+ | Cl- | .1775 (48) | .2945 (48) | .0008 (48) | |
| | | .1775 (89) | .2945 (89) | .00080 (89) | |
| | | .18352 (83) | .25503 (83) | -.00059 (83) | |
| | | .1775 (85) | .2945 (85) | .0004 (85) | |
| | | .18029 (5) | .27837 (5) | ----- | |
| | | .17527 (71) | .30197 (71) | .0014670 (71) | |
| | | .18104 (65) | .27779 (65) | -.00007307 (65) | |
| | | .3729 (61) | -.3886 (61) | .0008 (61) | |
| Li+ | Cl- | .1494 (89) | .3074 (89) | .00359 (89) | |
| | | .1485 (85) | .3070 (85) | .00186 (85) | |
| | | .16832 (5) | .17721 (5) | ----- | |
| | | .14847 (54) | .307 (54) | .003710 (54) | |
| MgB(OH)4+ | Cl- | .16 (18) | ----- | ----- | |
| | | .244 (50) | ----- | ----- | |
| CaB(OH)4+ | Cl- | .12 (18) | ----- | ----- | |
| | | .204 (50) | ----- | ----- | |
| Sr+2 | Cl- | .28575 (89) | 1.66725 (89) | -.00130461 (89) | |
| | | .2834 (85) | 1.626 (85) | -.000315 (85) | |
| | | .27967 (5) | 1.72429 (5) | ----- | |
| | | .28994 (72) | 1.5795 (72) | -.003755 (72) | |
| | | .27948 (72) | 1.6745 (72) | .0003532 (72) | |
| | | .28344 (99) | 1.625625 (99) | -.000890954 (99) | |
| Cs+ | Cl- | .0300 (89) | .0558 (89) | .00038 (89) | |
| | | .03449 (83) | .01336 (83) | -.00049 (83) | |
| | | .0335 (85) | .0429 (85) | -.000131 (85) | |
| | | .03352 (54) | .0429 (54) | -.000262 (54) | |
| | | .03478 (99) | .03974 (99) | -.000496 (99) | |
| | | .03917 (99) | -.002984 (99) | -.001183 (99) | |
| | | .03131 (4) | .065925 (4) | .00030705 (4) | |
| | | .03178 (5) | .02762 (5) | ----- | |
| NH4+ | Cl- | .0522 (89) | .1918 (89) | -.00301 (89) | |
| | | .03603 (5) | .29619 (5) | ----- | |
| | | .04568 (10) | .20431 (10) | -.001731 (10) | |

Attachment C.2 - continued

| INTERACTION | | B0 | B1 | C0 | B2 |
|---|---|---|---|---|---|
| Cu+2 | Cl- | .308025 (89) | 1.37625 (89) | -.0404323 (89) | |
| | | .2817 (26) | 1.4677 (26) | -.01395 (26) | .0023 (26) |
| | | .296625 (14) | 1.39125 (14) | .03602 (14) | |
| Cd+2 | Cl- | -.0169 (27) | .3468 (27) | .00747 (27) | -5.829 (27) |
| Fe+2 | Cl- | .335925 (89) | 1.53225 (89) | -.00860725 (89) | |
| | | .31583 (10) | 10.4224 (10) | -.010078 (10) | |
| Rb+ | Cl- | .0441 (89) | .1483 (89) | -.00101 (89) | |
| | | .03934 (5) | .17280 (5) | ----- | |
| UO+2 | Cl- | .42735 (89) | 1.644 (89) | -.0368632 (89) | |
| Zn+2 | Cl- | .260175 (89) | 1.6425 (89) | -.0879817 (89) | |
| Mn+2 | Cl- | .327225 (89) | 1.55025 (89) | -.0204972 (89) | |
| | | .3420 (35) | 1.4091 (35) | -.0298 (35) | .00102 (35) |
| | | .25811 (10) | 2.31108 (10) | -.010540 (10) | |
| Ba+2 | Cl- | .2628 (89) | 1.49625 (89) | -.0193782 (89) | |
| | | .21638 (5) | 1.84591 (5) | ----- | |
| | | 1.2556 (60) | -1.9783 (60) | -.01938 (60) | |
| Mg+2 | Cl- | .35235 (48) | 1.6815 (48) | .00519 (48) | |
| | | .35235 (49) | 1.6815 (49) | .00519 (49) | .0 (49) |
| | | .35235 (89) | 1.6815 (89) | .00519193 (89) | |
| | | .3509 (85) | 1.651 (85) | .002301 (85) | |
| | | .38110 (5) | 1.21197 (5) | ----- | |
| | | .35093 (98) | 1.65075 (98) | .006507 (98) | |
| | | .3509 (25) | 1.6508 (25) | .00610 (25) | |
| | | 1.4680 (58) | -2.2231 (58) | .0051919 (58) | |
| Ni+2 | Cl- | .347925 (89) | 1.581 (89) | -.00372291 (89) | |
| | | .4456 (26) | 2.4076 (26) | -.00784 (26) | .5680 (26) |
| | | .44104 (28) | 2.34470 (28) | -.02156 (28) | -.53354 (28) |
| | | 1.3969 (61) | -2.0903 (61) | -.0037 (61) | |
| Co+2 | Cl- | .364275 (89) | 1.47525 (89) | -.0152151 (89) | |
| | | .3454 (35) | 1.625 (35) | .00179 (35) | -.00329 (35) |
| | | .41908 (28) | 2.06641 (28) | -.02429 (28) | -.35136 (28) |
| | | .3582 (13) | 1.44975 (13) | .012537 (13) | |
| | | 1.3431 (62) | -1.9504 (62) | -.01522 (62) | |
| | | .4108 (24) | 2.0664 (24) | -.02430 (24) | -.0351 (24) |
| Ca+2 | Cl- | .3159 (48) | 1.614 (48) | -.00034 (48) | |
| | | .31590 (49) | 1.6140 (49) | -.00034 (49) | |
| | | .3159 (89) | 1.614 (89) | -.000339411 (89) | |
| | | .30534 (82) | 1.7083 (82) | .002153 (82) | |
| | | .3053 (85) | 1.708 (85) | .000761 (85) | |
| | | .31231 (5) | 1.64585 (5) | ----- | |
| | | .41328 (10) | .53043 (10) | -.014250 (10) | |
| MgOH+ | Cl- | -.10(48) | 1.658 (48) | ----- | |
| Al+3 | Cl- | .6993333 (89) | 5.8446667 (89) | .00273279 (89) | |
| | | .70632 (5) | 5.63756 (5) | ----- | |
| Cr+3 | Cl- | .7364 (89) | 5.2553333 (89) | -.0451103 (89) | |
| | | .65169 (5) | 6.14389 (5) | ----- | |
| Na+ | Br- | .0973 (89) | .2791 (89) | .00116 (89) | |
| | | .10164 (5) | .25274 (5) | ----- | |
| | | .13523 (10) | .02917 (10) | -.003478 (10) | |
| K+ | Br- | .0569 (89) | .2212 (89) | -.00180 (89) | |
| | | .04792 (5) | .27445 (5) | ----- | |
| | | .06292 (10) | .16046 (10) | -.001981 (10) | |
| H+ | Br- | .1960 (89) | .3564 (89) | .00827 (89) | |
| | | .22156 (5) | .23087 (5) | ----- | |
| | | .1905 (64) | .3975 (64) | .009687 (64) | |
| Mg+2 | Br- | .432675 (89) | 1.75275 (89) | .00312364 (89) | |
| | | .45016 (5) | 1.44995 (5) | ----- | |

Attachment C.2 - continued

| INTERACTION | | B0 | B1 | C0 | B2 |
|---|---|---|---|---|---|
| Ca+2 | Br- | .3816 (89) | 1.61325 (89) | -.0025721 (89) | |
| | | .40950 (5) | .84275 (5) | ----- | |
| | | .3648 (63) | 1.7269 (63) | -.004572 (63) | |
| | | .3562 (125) | 1.872 (125) | .005291 (125) | |
| Li+ | Br- | .1748 (89) | .2547 (89) | .0053 (89) | |
| | | .20243 (5) | .06713 (5) | ----- | |
| Rb+ | Br- | .0396 (89) | .1530 (89) | -.00144 (89) | |
| | | .03297 (5) | .18897 (5) | ----- | |
| Cs+ | Br- | .0279 (89) | .0139 (89) | .00004 (89) | |
| NH4+ | Br- | .0624 (89) | .1947 (89) | -.00436 (89) | |
| Ba+2 | Br- | .31455 (89) | 1.56975 (89) | -.0159576 (89) | |
| | | | | -.02257 (64) | |
| | | .3143 (64) | 1.5853 (64) | -.01579 (64) | |
| Sr+2 | Br- | .331125 (89) | 1.7115 (89) | .00122506 (89) | |
| | | .3303 (70) | 1.714 (70) | .001749 (70) | |
| Co+2 | Br- | .426975 (89) | 1.65975 (89) | -.000673519 (89) | |
| Zn+2 | Br- | .465975 (89) | 1.63425 (89) | -.1079221 (89) | |
| Na+ | SO4-2 | .01958 (48) | 1.113 (48) | .00497 (48) | |
| | | .01958 (49) | 1.113 (49) | .00497 (49) | |
| | | .019575 (89) | 1.113 (89) | .00497449 (89) | |
| | | .0148 (83) | 1.218 (83) | .00634 (83) | |
| | | .019575 (86) | 1.113 (86) | .00570104 (86) | |
| | | .0181 (85) | 1.0559 (85) | .00202 (85) | |
| | | .04210 (5) | .77712 (5) | ----- | |
| | | .01869 (106) | 1.0994 (106) | .005549 (106) | |
| | | .01869 (97) | 1.099425 (97) | .0055488 (97) | .0 (97) |
| | | .0187 (37) | 1.0094 (37) | .00550 (37) | |
| | | .01957 (45) | 1.113 (45) | .001758 (45) | |
| | | .0187 (40) | 1.0994 (40) | .00553 (40) | |
| | | .08610 (10) | .13037 (10) | -.003104 (10) | |
| K+ | SO4-2 | .04995 (48) | .7793 (48) | .0 (48) | |
| | | .04995 (49) | .7793 (49) | .0 (49) | .0 (49) |
| | | .0500 (89) | .77925 (89) | .0 (89) | |
| | | .000 (85) | 1.1023 (85) | .00665 (85) | |
| | | .04432 (68) | .7365 (68) | .00181 (68) | |
| | | .0927 (55) | .603 (55) | -.03661 (55) | |
| Mg+2 | SO4-2 | .2210 (48) | 3.343 (48) | .025 (48) | |
| | | .22100 (49) | 3.3430 (49) | .025 (49) | -37.25 (49) |
| | | .2150 (85) | 3.3636 (85) | .006993 (85) | -3.74 (85) |
| | | .21499 (97) | 3.3646 (97) | .02797 (97) | -32.743 (97) |
| | | | | | -37.23 (90) |
| | | | | | -39.23 (75) |
| Ca+2 | SO4-2 | .20 (48) | 3.1973 (48) | ----- | -54.24 (48) |
| | | .20000 (49) | 2.650 (49) | .0 (49) | -57.70 (49) |
| | | .20 (90) | 2.65 (90) | ----- | -55.7 (90) |
| | | .15 (77) | 3.0 (77) | .0 (77) | |
| H+ | SO4-2 | .0298 (48) | .0 (48) | .0438 (48) | |
| | | .0027 (94) | ----- | .0416 (94) | |
| | | -7.59 (66) | .0 (66) | 1.735 (66) | |
| | | -7.08 (66) | .0 (66) | 1.60 (66) | |
| Ni+ | SO4-2 | .1702 (90) | 2.907 (90) | .0366 (90) | -40.06 (90) |
| Cu+2 | SO4-2 | .2358 (90) | 2.485 (90) | -.0012 (90) | -47.35 (90) |
| | | .2340 (14) | 2.527 (14) | .0044 (14) | -48.33 (14) |
| | | .21757 (74) | 2.62597 (74) | .013756 (74) | -56.2413 (74) |
| Zn+2 | SO4-2 | .1949 (90) | 2.883 (90) | .02896 (90) | -32.81 (90) |
| Cd+2 | SO4-2 | .2053 (90) | 2.6170 (90) | .01140 (90) | -48.07 (90) |
| | | .2081 (20) | 2.6023 (20) | .01032 (20) | |

Attachment C.2 - continued

| INTERACTION | | B0 | B1 | C0 | B2 |
|---|---|---|---|---|---|
| Co+2 | SO4-2 | .20 (90) | 2.70 (90) | ----- | -30.7 (90) |
| | | .16310 (28,38) | 3.3458 (28,38) | .00926 (28,38) | |
| | | .1631 (38) | 3.3460 (38) | .03704 (38) | |
| Mn+2 | SO4-2 | .2010 (90) | 2.9511 (90) | .0182 (90) | |
| | | .2065 (40) | 2.9511 (40) | .01636 (40) | -40.0 (40) |
| | | .201 (86) | 2.980 (86) | .0182 (86) | |
| | | .33089 (10) | 3.14630 (10) | -.014731 (10) | |
| Be+ | SO4-2 | .3170 (90) | 2.914 (90) | .0062 (90) | |
| UO2+2 | SO4-2 | .3220 (90) | 1.827 (90) | -.0176 (90) | |
| Sr+2 | SO4-2 | .220 (102) | 2.88 (102) | .019 (102) | -41.8+/- 9.2 (102) |
| Fe+2 | SO4-2 | .2568 (103) | 3.063 (103) | .0209 (103) | -42.0+/- 9.2 (103) |
| Cs+ | SO4-2 | .0888 (89) | 1.11075 (89) | -.00599803 (89) | |
| | | .0882 (55) | 1.105 (55) | -.00795 (55) | |
| | | .0714 (44) | 1.2010 (44) | .00291 (44) | |
| Li+ | SO4-2 | .136275 (89) | 1.2705 (89) | .00399338 (89) | |
| | | .1308 (85) | 1.2913 (85) | -.000894 (85) | |
| | | .1339 (55) | 1.282 (55) | -.00333 (55) | |
| Rb+ | SO4-2 | .0579 (89) | 1.11075 (89) | -.000100762 (89) | |
| | | .05772 (20) | 1.1105 (20) | 0.0 (20) | |
| | | .0579 (34) | 1.1108 (34) | -.000036 (34) | |
| NH4+ | SO4-2 | .040875 (89) | .6585 (89) | -.00116142 (89) | |
| | | .03369 (5) | .74799 (5) | ----- | |
| | | .03905 (29) | .66379 (29) | -.00082 (29) | |
| | | .04888 (10) | .6585 (10) | -.00116 (10) | |
| | | .04763 (10) | .44459 (10) | -.001311 (10) | |
| Na+ | HSO4- | .0454 (48) | .398 (48) | ----- | |
| | | .0554 (94) | .2755 (94) | -.00118 (94) | |
| K+ | HSO4- | -.0003 (48) | .1735 (48) | ----- | |
| Mg+2 | HSO4- | .4746 (48) | 1.729 (48) | ----- | |
| Ca+2 | HSO4- | .2145 (48) | 2.53 (48) | ----- | |
| H+ | HSO4- | .2065 (48) | .5556 (48) | ----- | |
| | | .2103 (94) | .4711 (94) | ----- | |
| Fe+2 | HSO4- | .4273 (103) | 3.48 (103) | ----- | |
| Na+ | OH- | .0864 (48) | .253 (48) | .0044 (48) | |
| | | .0864 (89) | .253 (89) | .0044 (89) | |
| | | .0864 (85) | .2530 (85) | .00205 (85) | |
| | | .10691 (5) | .17653 (5) | ----- | |
| K+ | OH- | .1298 (48) | .320 (48) | .0041 (48) | |
| | | .1298 (89) | .32 (89) | .0041 (89) | |
| | | .14982 (5) | .22070 (5) | ----- | |
| Ca+2 | OH- | -.1747 (48) | -.2303 (48) | ----- | -5.72 (48) |
| Li+ | OH- | .015 (89) | .14 (89) | ----- | |
| Cs+ | OH- | .150 (89) | .30 (89) | ----- | |
| Mg+ | OH- | -7.6 (15) | ----- | ----- | |
| Ba+2 | OH- | .17175 (89) | 1.2 (89) | ----- | |
| Na+ | HCO3- | .0277 (48) | .0411 (48) | ----- | |
| | | .028 (81) | .044 (81) | ----- | |
| | | -.04096 (116) | .5062 (116) | .005250 (116) | |
| | | -.0490 (16) | ----- | ----- | |
| | | .0277 (92) | .0411 (92) | ----- | |
| K+ | HCO3- | .0296 (48) | -.013 (48) | -.008 (48) | |
| | | -.0005 (92) | -.013 (92) | ----- | |
| | | -.022 (113) | .09 (113) | ----- | |
| | | -.0107 (112) | .0478 (112) | ----- | |
| | | -.011 (114) | .049 (114) | ----- | |

Attachment C.2 - continued

| INTERACTION | | B0 | B1 | C0 | B2 |
|---|---|---|---|---|---|
| Mg+2 | HCO3- | .329 (48) | .6072 (48) | ----- | |
| | | .033 (91) | .85 (91) | ----- | |
| | | .46 (15) | ----- | ----- | |
| | | .019 (76) | .584 (76) | ----- | |
| | | .18 (127) | .49 (127) | ----- | |
| | | .49 (107) | 1.90 (107) | ----- | |
| | | .33 (96) | ----- | ----- | |
| Ca+2 | HCO3- | .4 (48) | 2.977 (48) | ----- | |
| | | .4 (91) | 3.0 (91) | ----- | |
| | | .28 (91) | .3 (91) | ----- | |
| | | .440 (107) | 1.70 (107) | ----- | |
| | | .12 (96) | ----- | ----- | |
| NH4+ | HCO3- | -.038 (114) | .070 (114) | ----- | |
| Sr+2 | HCO3- | .12 (75) | ----- | ----- | |
| Na+ | CO3-2 | .0399 (48) | 1.389 (48) | .0044 (48) | |
| | | .18975 (89) | .846 (89) | -.0480319 (89) | |
| | | .0362 (81) | 1.51 (81) | .0052 (81) | |
| | | .040822 (105) | 1.46790 (105) | .0042374 (105) | |
| K+ | CO3-2 | .1488 (48) | 1.43 (48) | -.0015 (48) | |
| | | .138 (113) | 1.481 (113) | ----- | |
| | | .1288 (112) | 1.433 (112) | .00050 (112) | |
| | | .075 (107) | .66 (107) | ----- | |
| Mg+2 | CO3-2 | -9.7 (15) | ----- | ----- | |
| | | 2.833 (76) | -15.069 (76) | -.970 (76) | -204.90 (76) |
| | | .180 (107) | 2.70 (107) | ----- | -46.0 (107) |
| | | -3.9 (96) | ----- | ----- | |
| | | -6.8 (75) | ----- | ----- | |
| Ca+2 | CO3-2 | .160 (107) | 2.10 (107) | ----- | -69.0 (107) |
| | | -11.9 (75) | ----- | ----- | |
| NH4+ | CO3-2 | .1288 (114) | 1.433 (114) | .00050 (114) | |
| Sr+2 | CO3-2 | -11.9 (75) | ----- | ----- | |
| Na+ | I- | .1195 (89) | .3439 (89) | .0018 (89) | |
| | | .1195 (85) | .3439 (85) | .0009 (85) | |
| | | .12549 (5) | .31106 (5) | ----- | |
| K+ | I- | .0746 (89) | .2517 (89) | -.00414 (89) | |
| | | .05708 (5) | .34662 (5) | ----- | |
| Mg+2 | I- | .4902 (89) | 1.804125 (89) | .00793373 (89) | |
| | | .53450 (5) | 1.80454 (5) | ----- | |
| Ca+2 | I- | .437925 (89) | 1.80675 (89) | -.000837921 (89) | |
| | | .43524 (5) | 1.81137 (5) | ----- | |
| H+ | I- | .2362 (89) | .392 (89) | .0011 (89) | |
| | | .23777 (5) | .39920 (5) | ----- | |
| Li+ | I- | .2104 (89) | .373 (89) | ----- | |
| | | .21024 (5) | .36981 (5) | ----- | |
| Rb+ | I- | .0397 (89) | .1330 (89) | -.00108 (89) | |
| | | .03461 (5) | .15964 (5) | ----- | |
| Cs+ | I- | .0244 (89) | .0262 (89) | -.00365 (89) | |
| | | .0244 (85) | .0262 (85) | -.00192 (85) | |
| Sr+2 | I- | .40125 (89) | 1.86 (89) | .00265695 (89) | |
| Ba+2 | I- | .421875 (89) | 1.68675 (89) | -.0174266 (89) | |
| Co+2 | I- | .52125 (89) | 1.6725 (89) | -.0046669 (89) | |
| Zn+2 | I- | .4821 (89) | 1.9455 (89) | -.0142658 (89) | |
| Na+2 | F- | .0215 (89) | .2107 (89) | ----- | |
| | | .02147 (5) | .20690 (5) | ----- | |
| K+ | F- | .08089 (89) | .2021 (89) | .00093 (89) | |
| Mg+2 | F- | -10.6 (75) | ----- | 10.0 (75) | |
| | | -10.6 (17) | ----- | 10.01 (17) | |

Attachment C.2 - continued

| INTERACTION | | B0 | B1 | C0 | B2 |
|---|---|---|---|---|---|
| Ca+2 | F- | -2.3 (75) | ----- | 1.9 (75) | |
| | | -2.3 (17) | ----- | 1.92 (17) | |
| | | -2.3 (17) | ----- | .81 (17) | |
| Cs+ | F- | .1306 (89) | .2570 (89) | -.0043 (89) | |
| | | .1306 (85) | .2570 (85) | -.00215 (85) | |
| Rb+ | F- | .1141 (89) | .2842 (89) | -.0105 (89) | |
| Sr+2 | F- | -2.3 (75) | ----- | 1.9 (75) | |
| Na+2 | ClO4- | .0554 (89) | .2755 (89) | -.00118 (89) | |
| K+ | ClO4- | -.040 (107) | .08 (107) | ----- | |
| Mg+2 | ClO4- | .496125 (89) | 2.0085 (89) | .00957776 (89) | |
| Ca+2 | ClO4- | .451125 (89) | 1.7565 (89) | -.005001 (89) | |
| H+ | ClO4- | .1747 (89) | .2931 (89) | .00819 (89) | |
| | | .1853 (126) | .2329 (126) | ----- | |
| | | .1998 (126) | .2695 (126) | ----- | |
| | | .1634 (6) | .3465 (6) | .0117 (6) | |
| | | .21795 (5) | -.00041 (5) | ----- | |
| Li+ | ClO4- | .1973 (89) | .3996 (89) | .0008 (89) | |
| NH4+ | ClO4- | -.0103 (89) | -.0194 (89) | ----- | |
| Sr+2 | ClO4- | .4269 (89) | 1.56675 (89) | -.0131097 (89) | |
| Ba+2 | ClO4- | .361425 (89) | 1.57575 (89) | -.0312576 (89) | |
| Zn+2 | ClO4- | .506025 (89) | 1.797 (89) | .0113172 (89) | |
| Pb+2 | ClO4- | .333225 (89) | 1.722 (89) | -.0088406 (89) | |
| | | .27386 (5) | 2.71678 (5) | ----- | |
| UO2+2 | ClO4- | .611325 (89) | 2.14425 (89) | .0216851 (89) | |
| | | .61785 (6) | 2.06175 (6) | .0153795 (6) | |
| Na+2 | ClO3- | .0249 (89) | .2455 (89) | .0004 (89) | |
| K+ | ClO3- | -.0960 (89) | .2481 (89) | ----- | |
| Mg+2 | ClO3- | .490 (107) | 1.804 (107) | ----- | |
| Ca+2 | ClO3- | .438 (107) | 1.76 (107) | ----- | |
| Na+2 | NO3- | .0068 (89) | .1783 (89) | -.00072 (89) | |
| | | .00661 (83) | .17939 (83) | -.00067 (83) | |
| | | .003 (46) | .2037 (46) | .00013 (46) | |
| | | .00351 (5) | .18642 (5) | ----- | |
| K+ | NO3- | -.08155 (83) | .04939 (83) | .00660 (89) | |
| | | -.0802 (46) | .0722 (46) | .0065 (46) | |
| | | -.05771 (5) | -.05759 (5) | ----- | |
| Mg+2 | NO3- | .367125 (89) | 1.58475 (89) | -.0206245 (89) | |
| | | .29978 (23) | 1.19260 (23) | -.00181 (23) | .30453 (23) |
| | | .3628425 (117) | 1.5944175 (117) | -.0166947 (117) | |
| Ca+2 | NO3- | .210825 (89) | 1.40925 (89) | -.0201419 (89) | |
| | | .12920 (23) | .79437 (23) | -.00263 (23) | .42877 (23) |
| H+ | NO3- | .1119 (89) | .3206 (89) | .0010 (89) | |
| | | .11477 (5) | .30437 (5) | ----- | |
| Li+ | NO3- | .1420 (89) | .2780 (89) | -.00551 (89) | |
| | | .12274 (5) | .36821 (5) | ----- | |
| | | .1421 (2) | .2772 (2) | -.0055 (2) | |
| Rb+ | NO3- | -.0789 (89) | -.0172 (89) | .00529 (89) | |
| | | -.07885 (83) | -.01736 (83) | .00528 (83) | |
| Cs+ | NO3- | -.0758 (89) | -.0669 (89) | ----- | |
| Ag+ | NO3- | -.0856 (89) | .0025 (89) | .00591 (89) | |
| | | -.05431 (5) | -.21042 (5) | ----- | |
| NH4+ | NO3- | -.0154 (89) | .1120 (89) | -.00003 (89) | |
| | | -.01561 (5) | .10898 (5) | ----- | |
| Cu+2 | NO3- | .3168 (89) | 1.43025 (89) | -.0219344 (89) | |
| | | .28076 (21) | 1.73230 (21) | -.008372 (21) | |
| | | .34782 (117) | 1.369185 (117) | -.0300697 (117) | |
| Sr+2 | NO3- | .134625 (89) | 1.38 (89) | -.0199245 (89) | |
| Ba+2 | NO3- | -.03225 (89) | .8025 (89) | ----- | |

Attachment C.2 - continued

| INTERACTION | | B0 | B1 | C0 | B2 |
|---|---|---|---|---|---|
| Co+2 | NO3- | .311925 (89) | 1.6905 (89) | -.00761554 (89) | |
| | | .356025 (117) | 1.577175 (117) | -.0195797 (117) | |
| Zn+2 | NO3- | .348075 (89) | 1.69125 (89) | -.0156712 (89) | |
| | | .3015 (21) | 1.2012 (21) | -.005798 (21) | .26536 (21) |
| | | .36915 (117) | 1.4663475 (117) | -.0241247 (117) | |
| Cd+2 | NO3- | .2865 (89) | 1.668 (89) | -.0256467 (89) | |
| Pb+2 | NO3- | -.03615 (89) | .285 (89) | .00532981 (89) | |
| UO2+2 | NO3- | .460725 (89) | 1.61325 (89) | -.031544 (89) | |
| Cr+5 | NO3- | .704 (89) | 5.1846667 (89) | -.0590051 (89) | |
| Mn+2 | NO3- | .337005 (117) | 1.54236 (117) | -.0155439 (117) | |
| Ni+2 | NO3- | .28790 (22) | 1.43724 (22) | -.00189 (22) | .30331 (22) |
| | | .353475 (117) | 1.60485 (117) | -.0194525 (117) | |
| Na+ | NO2- | .0641 (89) | .1015 (89) | -.0049 (89) | |
| | | .051 (46) | .1625 (46) | -.0023 (46) | |
| K+ | NO2- | .0151 (89) | .015 (89) | .0007 (89) | |
| Li+ | NO2- | .1336 (89) | .325 (89) | -.0053 (89) | |
| Rb+ | NO2- | .0269 (89) | -.1553 (89) | -.00366 (89) | |
| Cs+ | NO2- | .0427 (89) | .060 (89) | -.0051 (89) | |
| Na+ | H2PO4- | -.0533 (89) | .0396 (89) | .00795 (89) | |
| K+ | H2PO4- | -.0678 (89) | -.1042 (89) | ----- | |
| Mg+2 | H2PO4- | -.41 (3) | ----- | ----- | |
| Ca+2 | H2PO4- | -.29 (3) | ----- | ----- | |
| NH4+ | H2PO4- | -.07043 (29) | -.41564 (29) | .00669 (29) | |
| Na+ | HPO4-2 | -.058275 (89) | 1.4655 (89) | .0293802 (89) | |
| K+ | HPO4-2 | .02475 (89) | 1.27425 (89) | .0163872 (89) | |
| Mg+2 | HPO4-2 | -3.6 (3) | ----- | ----- | |
| | | -4.1 (57) | ----- | ----- | |
| Ca+2 | HPO4-2 | -1.6 (3) | ----- | ----- | |
| | | -2.0 (57) | ----- | ----- | |
| Na+ | PO4-3 | .1781333 (89) | 3.8513333 (89) | -.0515381 (89) | |
| K+ | PO4-3 | .3729333 (89) | 3.972 (89) | -.0867949 (89) | |
| Mg+2 | PO4-3 | -62.0 (3) | ----- | ----- | |
| | | -43.0 (57) | ----- | ----- | |
| Ca+2 | PO4-3 | -67.0 (3) | ----- | ----- | |
| | | -56.0 (57) | ----- | ----- | |
| Na+ | H2AsO4- | -.0442 (89) | .2895 (89) | ----- | |
| K+ | H2AsO4- | -.0584 (89) | .0626 (89) | ----- | |
| Na+ | HAsO4-2 | .030525 (89) | 1.62975 (89) | .00180312 (89) | |
| K+ | HAsO4-2 | .1296 (89) | 1.6485 (89) | -.017819 (89) | |
| Na+ | AsO4-3 | .2388 (89) | 3.93 (89) | -.0477276 (89) | |
| K+ | AsO4-3 | .4994 (89) | 4.3406667 (89) | .1299423 (89) | |
| Na+ | B(OH)4- | -.0526 (50) | .1104 (50) | .0154 (50) | |
| | | -.0427 (18) | .089 (18) | .0114 (18) | |
| K+ | B(OH)4- | .035 (18) | .14 (18) | ----- | |
| | | .20 (75) | ----- | ----- | |
| | | .19 (7) | ----- | ----- | |
| Mg+2 | B(OH)4- | -.21 (50) | -4.98 (50) | -.36 (50) | |
| | | -.93 (7) | ----- | ----- | |
| Ca+2 | B(OH)4- | -1.57 (50) | -4.49 (50) | -.17 (50) | |
| | | -2.35 (7) | ----- | ----- | |
| Sr+2 | B(OH)4- | -2.35 (75) | ----- | ----- | |
| Na+ | B3O3(OH)4 | -.056 (18) | -.910 (18) | ----- | |
| K+ | B3O3(OH)4 | -.13 (18) | ----- | ----- | |
| Na+ | B4O5(OH)4 | -.11 (18) | -.40 (18) | ----- | |
| K+ | B4O5(OH)4 | -.022 (18) | ----- | ----- | |
| Na+ | BrO3- | -.0205 (89) | .1910 (89) | .0059 (89) | |
| K+ | BrO3- | -.1290 (89) | .2565 (89) | ----- | |
| Na+ | BO2- | -.0526 (86) | .1104 (86) | .0154 (86) | |

Attachment C.2 - continued

| INTERACTION | | B0 | B1 | C0 | B2 |
|---|---|---|---|---|---|
| Na+ | CrO4-2 | .09375 (89) | 1.3695 (89) | -.00215844 (89) | |
| K+ | CrO4-2 | .075825 (89) | 1.239 (89) | -.000779585 (89) | |
| Na+ | HSO3- | .0249 (107) | .2455 (107) | .0004 (107) | |
| K+ | HSO3- | -.096 (107) | .2481 (107) | ----- | |
| Mg+2 | HSO3- | .490 (107) | 1.804 (107) | ----- | |
| Ca+2 | HSO3- | .438 (107) | 1.76 (107) | ----- | |
| Na+ | SO3-2 | .021 (108) | 1.0 (108) | ----- | |
| K+ | SO3-2 | .065 (108) | 1.0 (108) | ----- | |
| Mg+2 | SO3-2 | .200 (107) | 3.00 (107) | ----- | -41.0 (107) |
| | | .24 (108) | 3.60 (108) | ----- | -33.0 (108) |
| Ca+2 | SO3-2 | .180 (107) | 2.38 (107) | ----- | -61.3 (107) |
| | | .18 (108) | 2.38 (108) | ----- | -40.0 (108) |
| Na+ | S2O3-2 | .06615 (89) | 1.27575 (89) | .00373882 (89) | |
| Na+ | S2O5-2 | .07 (107) | .9 (107) | ----- | |
| K+ | S2O5-2 | .10 (107) | 1.1 (107) | ----- | |
| Mg+2 | S2O5-2 | .24 (107) | 3.7 (107) | ----- | -34.0 (107) |
| Ca+2 | S2O5-2 | .22 (107) | 3.0 (107) | ----- | -50.0 (107) |

Attachment C.3. -- Summary of literature values of Pitzer interaction parametes for mixed-salt solutions

Attachment C.3 - Summary of Literature Values of Pitzer Parameters for Mixed Salt Solutions

| INTERACTION | | | THETA | PSI | MEDIA | SINGLE SALT COMPATIBILITY DATA | BO | B1 | CO | B2 |
|---|---|---|---|---|---|---|---|---|---|---|
| Na+ | K+ | Cl- | -.012 (48) | -.0018 (48) | | | | | | |
| | | | -.012 (49) | -.0018 (49) | | | | | | |
| | | | -.012 (88) | -.0018 (88) | NaCl+KCl | | | | | |
| | | | -.0154 (51) | -.00078 (51) | NaCl+KCl | | | | | |
| | | | -.0203 (46) | -.004 (46) | NaCl+KCl | NaCl | .0757 | .2795 | .0014 | |
| | | | | | | KCl | .0464 | .2274 | -.0004 | |
| Na+ | K+ | Br- | -.012 (88) | -.0022 (88) | | | | | | |
| Na+ | K+ | SO4-2 | -.012 (48) | -.010 (48) | | | | | | |
| | | | -.012 (49) | -.010 (49) | | | | | | |
| | | | -.012 (88) | .010 (88) | Na2SO4+K2SO4 | | | | | |
| | | | .0 (47) | .0 (47) | | | | | | |
| | | | -.0303 (31) | -.0066 (31) | Na2SO4+K2SO4 | Na2SO4 | .0187 | 1.0994 | .0055 | |
| | | | | | | K2SO4 | .050 | .779 | .0 | |
| | | | -.0322 (31) | .0085 (31) | Na2SO4+K2SO4 | | | | | |
| Na+ | K+ | HCO3- | -.012 (48) | -.003 (48) | | | | | | |
| Na+ | K+ | CO3-2 | -.012 (48) | .003 (48) | | | | | | |
| Na+ | K+ | NO3-2 | -.012 (88) | -.0012 (88) | NaNO3+KNO3 | | | | | |
| Na+ | Ca+2 | Cl- | .07 (48) | -.007 (48) | | | | | | |
| | | | .07 (49) | -.014 (49) | | | | | | |
| | | | .0 (88)* | .0 (88) | NaCl+CaCl2 | | | | | |
| | | | -.0078 (52)* | .0029 (52) | NaCl+CaCl2 | | | | | |
| | | | .05 (77) | -.003 (77) | | | | | | |
| Na+ | Ca+2 | SO4-2 | .07 (48) | -.055 (48) | | | | | | |
| | | | .07 (49) | -.023 (49) | | | | | | |
| | | | .0 (47)* | .0 (47) | Na2SO4+CaSO4 | Na2SO4 | .01869 | 1.0994 | .0055488 | |
| | | | | | | CaSO4 | .15 | 3.0 | .0 | .0 |
| | | | .05 (77) | -.012 (77) | Na2SO4+CaSO4 | | | | | |
| Na+ | Mg+2 | Cl- | .07 (48) | -.0122 (48) | | | | | | |
| | | | .07 (49) | -.0122 (49) | | | | | | |
| | | | .07 (84) | -.010 (84) | NaCl+MgCl2 | | | | | |
| | | | .0 (88)* | .0 (88) | NaCl+MgCl2 | | | | | |
| | | | .050 (30)* | -.01 (30) | | | | | | |
| | | | .016130 (101)* | -.004633 (101) | NaCl+MgCl2 | NaCl | .0765 | .2664 | .00127 | |
| | | | | | | MgCl2 | .35093 | 1.65075 | .006507 | |
| Na+ | Mg+2 | SO4-2 | .07 (48) | -.015 (48) | | | | | | |
| | | | .07 (49) | -.015 (49) | | | | | | |
| | | | .07 (84) | -.023 (84) | Na2SO4+MgSO4 | | | | | |
| | | | .0 (88)* | .0 (88) | Na2SO4+MgSO4 | | | | | |
| | | | .0 (25)* | .00566 (25) | Na2SO4+MgSO4 | Na2SO4 | .0187 | 1.0994 | .00550 | |
| | | | | | | MgSO4 | .3150 | 3.3646 | .02797 | -32.74 |
| | | | .050 (30)* | .0224 (30) | Na2SO4+MgSO4 | Na2SO4 | .0187 | 1.0994 | .00550 | |
| | | | | | | MgSO4 | .2150 | 3.3646 | .02797 | -32.74 |
| Na+ | H+ | Cl- | .036 (48) | -.004 (48) | | | | | | |
| | | | .036 (88) | -.004 (88) | NaCl+HCl | | | | | |
| | | | .0279 (9) | .0105 (9) | HCl+NaCl | NaCl | .0765 | .2664 | .00127 | |
| | | | | | | HCl | .1775 | .2945 | .00080 | |
| Na+ | H+ | Br- | .036 (88) | -.012 (88) | | | | | | |
| Na+ | H+ | ClO4- | .036 (56) | .0 (56) | | | | | | |
| Na+ | H+ | HSO4- | .036 (48) | -.0129 (48) | | | | | | |
| Na+ | Cl- | NO3-2 | .016 (88) | -.006 (88) | NaCl+NaNO3 | | | | | |
| | | | -.0279 (46) | -.0035 (46) | NaCl+NaNO3 | NaCl | .0757 | .2795 | .0014 | |
| | | | | | | NaNO3 | .003 | .2037 | .00013 | |

Attachment C.3 - continued

| INTERACTION | | | THETA | PSI | MEDIA | SINGLE SALT COMPATIBILITY DATA | B0 | B1 | C0 | B2 |
|---|---|---|---|---|---|---|---|---|---|---|
| Na+ | Cl- | H2PO4- | .1004 (131) | .0 (131) | NaCl+NaH2PO4 | | | | | |
| Na+ | Cl- | H2AsO4- | .228 (75) | .0 (75) | NaCl+NaH2AsO4 | | | | | |
| Na+ | Cl- | HAsO4-2 | .122 (75)* | .0 (75) | NaCl+NaHAsO4 | | | | | |
| Na+ | Cl- | AsO4-3 | .060 (75)* | .0 (75) | NaCl+NaAsO4 | | | | | |
| Na+ | Cl- | Ac+ | -.017 (75) | .0 (75) | NaCl+NaAc | | | | | |
| Na+ | Cl- | B(OH)3- | .0 (75)* | .0 (75) | NaCl+NaB(OH)3 | | | | | |
| Na+ | Cl- | B(OH)4- | -.065 (18) | -.0073 (18) | NaCl+NaB(OH)4 | NaCl | | | | |
| | | | | | | NaB(OH)4 | -.0427 | .089 | .0114 | |
| Na+ | Cl- | B3O3(OH)4- | .12 (18) | -.024 (18) | NaCl+NaB3O3(OH)4 | NaCl | | | | |
| | | | | | | NaB3O3(OH)4 | -.056 | -.910 | .0 | |
| Na+ | Cl- | B4O5(OH)4-2 | .074 (18) | .026 (18) | NaCl+NaB4O5(OH)4 | NaCl | | | | |
| | | | | | | NaB4O5(OH)4 | -.11 | -.40 | | |
| Na+ | Br- | Cl- | .0 (88) | .0 (88) | NaCl+NaBr | | | | | |
| Na+ | Ba+2 | Cl- | -.003 (88)* | .0 (88) | NaCl+BaCl2 | | | | | |
| | | | .067 (84) | -.012 (84) | NaCl+BaCl2 | | | | | |
| Na+ | Cs+ | Cl- | -.033 (88) | -.003 (88) | NaCl+CsCl | | | | | |
| Na+ | Mn+2 | Cl- | .0 (88)* | -.003 (88) | NaCl+MnCl2 | | | | | |
| | | | .082 (84) | -.0174 (84) | NaCl+MnCl2 | | | | | |
| | | | .03687 (35)* | -.01275 (35) | NaCl+MnCl2 | NaCl | .0765 | .2664 | .000126 | |
| | | | | | | MnCl2 | .3420 | 1.4091 | -.0298 | .00102 |
| Na+ | Mn+2 | SO4-2 | .04320 (40)* | -.02155 (40) | | | | | | |
| Na+ | Co+2 | Cl- | -.016 (13)* | -.001 (13) | NaCl+CoCl2 | NaCl | Ref.(89) | | | |
| | | | | | | CoCl2 | .3582 | 1.44975 | -.012537 | |
| | | | -.01289 (35)* | -.0589 (35) | NaCl+CoCl2 | NaCl | .0765 | .2664 | .000126 | |
| | | | | | | CoCl2 | .3454 | 1.625 | .00179 | -.00329 |
| | | | -.01939 (24) | -.00845 (24) | NaCl+CoCl2 | | | | | |
| Na+ | Co+2 | SO4-2 | -.001413 (45)* | -.008986 (45) | Na2SO4+CoSO4 | Na2SO4 | .01957 | 1.113 | .001758 | |
| | | | | | | CoSO4 | .16310 | 3.3458 | .00926 | -30.7 |
| | | | -.01939 (24) | -.01738 (24) | Na2SO4+CoSO4 | | | | | |
| Na+ | Cu+2 | Cl- | .0 (14)* | -.014 (14) | NaCl+CuCl2 | NaCl | Ref.(89) | | | |
| | | | | | | CuCl2 | .2966 | 1.391 | -.03602 | |
| | | | .077 (14) | -.026 (14) | NaCl+CuCl2 | NaCl | Ref.(89) | | | |
| | | | | | | CuCl2 | .2966 | 1.391 | -.03602 | |
| | | | -.06404 (26)* | -.00358 (26) | NaCl+CuCl2 | NaCl | .0765 | .2665 | .00062 | .0 |
| | | | | | | CuCl2 | .2817 | 1.4677 | -.01395 | .0023 |
| Na+ | Cu+2 | SO4-2 | .0 (14)* | -.011 (14) | Na2SO4+CuSO4 | Na2SO4 | Ref.(89) | | | |
| | | | | | | CuSO4 | .2340 | 2.527 | .0044 | -48.33 |
| | | | .0031 (39)* | -.0125 (39) | Na2SO4+CuSO4 | | | | | |
| | | | .077 (14) | -.049 (14) | Na2SO4+CuSO4 | Na2SO4 | Ref.(89) | | | |
| | | | | | | CuSO4 | .2340 | 2.527 | .0044 | -48.33 |
| Na+ | Zn+2 | Br- | .0 (88)* | ----- (88) | NaBr+ZnBr2 | | | | | |
| Na+ | Zn+2 | SO4-2 | .05073 (41)* | -.03089 (41) | Na2SO4+ZnSO4 | Na2SO4 | .0187 | 1.0994 | .00553 | |
| | | | | | | ZnSO4 | .1949 | 2.8830 | .0290 | -32.81 |
| Na+ | Cd+2 | Cl- | -.00032 (27) | .14913 (27) | NaCl+CdCl2 | CdCl | -.0169 | .3468 | .00747 | -5.829 |
| Na+ | Cd+2 | SO4-2 | -.00032 (41)* | -.01521 (41) | Na2SO4+CdSO4 | Na2SO4 | .0187 | 1.0994 | .00553 | |
| | | | | | | CdSO4 | .2053 | 2.6170 | .01140 | -48.07 |
| Na+ | Ni+2 | Cl- | .05917 (26)* | .01152 (26) | NaCl+NiCl2 | NaCl | .0765 | .2665 | .00062 | .0 |
| | | | | | | NiCl2 | .4456 | 2.4076 | -.00784 | .5680 |
| Na+ | Cs+ | SO4-2 | -.0153 (37) | -.0035 (37) | Na2SO4+Cs2SO4 | Na2SO4 | .0187 | 1.0094 | .00550 | |
| | | | | | | Cs2SO4 | .0714 | 1.2010 | .00291 | |
| Na+ | Ni+2 | SO4-2 | .0027 (43)* | -.0128 (43) | Na2SO4+NiSO4 | Na2SO4 | .0187 | 1.0994 | .0053 | |
| | | | | | | NiSO4 | .1702 | 2.9070 | .03660 | -40.06 |

Attachment C.3 - continued

| INTERACTION | | | THETA | PSI | MEDIA | | SINGLE SALT COMPATIBILITY DATA B0 | B1 | C0 | B2 |
|---|---|---|---|---|---|---|---|---|---|---|
| Na+ | NO3- | NO2- | -.0144 (46) | -.0012 (46) | NaNO3+NaNO2 | NaNO3 | .003 | .2037 | .00013 | |
| | | | | | | NaNO2 | .051 | .1625 | -.0023 | |
| K+ | Ca+2 | Cl- | .032 (48) | -.025 (48) | | | | | | |
| | | | .032 (49) | -.025 (49) | | | | | | |
| | | | -.040 (88)* | -.015 (88) | KCl+CaCl2 | | | | | |
| K+ | Ca+2 | SO4-2 | .032 (49) | .0 (49) | K2SO4+CaSO4 | | | | | |
| | | | -.040 (47)* | .0 (47) | | | | | | |
| K+ | Mg+2 | Cl- | .0 (48) | -.022 (48) | | | | | | |
| | | | .0 (49) | -.022 (49) | | | | | | |
| | | | .0 (47)* | .0 (47) | KCl+MgCl2 | | | | | |
| | | | .0 (73)* | -.05 (73) | KCl+MgCl2 | | | | | |
| K+ | Mg+2 | SO4-2 | .0 (48) | -.048 (48) | | | | | | |
| | | | .0 (49) | -.048 (49) | | | | | | |
| | | | .0 (47)* | .0 (47) | K2SO4+MgSO4 | K2SO4 | .04995 | .7793 | .0 | |
| | | | | | | MgSO4 | .21499 | 3.3646 | .02797 | -32.743 |
| K+ | H+ | Cl- | .005 (48) | -.011 (48) | | | | | | |
| | | | .005 (88) | -.007 (88) | HCl+KCl | Ref.(88) | | | | |
| | | | .0049 (8) | -.0081 (8) | HCl+KCl | HCl | .1775 | .2945 | .00080 | |
| | | | | | | KCl | .04835 | .2122 | -.00084 | |
| | | | .0068 (8) | -.0106 (8) | HCl+KCl | HCl | .1775 | .2945 | .00080 | |
| | | | | | | KCl | .04835 | .2122 | -.00084 | |
| | | | .0074 (9) | -.0105 (9) | HCl+KCl | HCl | .1775 | .2945 | .00080 | |
| | | | | | | KCl | .04835 | .2122 | -.00084 | |
| | | | .0088 (9) | -.0131 (9) | HCl+KCl | HCl | .1775 | .2945 | .00080 | |
| | | | | | | KCl | .04835 | .2122 | -.00084 | |
| K+ | H+ | Br- | .005 (88) | -.021 (88) | | | | | | |
| K+ | H+ | SO4-2 | .005 (48) | .197 (48) | | | | | | |
| K+ | H+ | HSO4- | .005 (48) | -.0265 (48) | | | | | | |
| K+ | Cl- | NO3-2 | .016 (88) | -.006 (88) | KCl+KNO3 | | | | | |
| | | | -.000815 (46) | -.00023 (46) | KCl+KNO3 | KCl | .0464 | .2274 | -.0004 | |
| | | | | | | KNO3 | -.0802 | .0722 | .0065 | |
| K+ | Cl- | H2PO4- | .1004 (131) | .06 (131) | KCl+KH2PO4 | | | | | |
| | | | .1004 (95) | -.0105 (95) | KCl+KH2PO4 | Ref.(89) | | | | |
| | | | .10 (86) | -.01 (86) | KCl+KH2PO4 | KCl | .04835 | .2122 | -.00084 | |
| | | | | | | KH2PO4 | -.0678 | -.1042 | | |
| K+ | Br- | Cl- | .0 (88) | .0 (88) | KCl+KBr | | | | | |
| K+ | Ba+2 | Cl- | -.072 (88)* | .0 (88) | KCl+BaCl2 | | | | | |
| | | | .010 (84) | -.017 (84) | KCl+BaCl2 | | | | | |
| K+ | Cs+ | Cl- | .0 (88) | -.0013 (88) | KCl+CsCl | | | | | |
| K+ | Cs+ | SO4-2 | -.0049 (36) | -.0016 (36) | K2SO4+Cs2SO4 | K2SO4 | .0500 | .7790 | | |
| | | | | | | Cs2SO4 | .0714 | 1.2010 | .00291 | |
| K+ | Co+2 | SO4-2 | -.0982 (19)* | -.0328 (19) | | | | | | |
| | | | -.0819 (19)* | -.0411 (19) | | | | | | |
| Ca+2 | Mg+2 | Cl- | .007 (48) | -.012 (48) | | | | | | |
| | | | .007 (49) | -.012 (49) | | | | | | |
| | | | .010 (88) | .0 (88) | MgCl2+CaCl2 | | | | | |
| Ca+2 | Mg+2 | SO4-2 | .007 (48) | .024 (48) | | | | | | |
| | | | .007 (49) | .05 (49) | | | | | | |
| | | | .01 (47) | .0 (47) | Ca2SO4+Mg2SO4 | Ca2SO4 | .200 | 2.65 | .0 | -57.70 |
| | | | | | | MgSO4 | .21499 | 3.3646 | .02797 | -32.743 |
| Ca+2 | Cl- | NO3- | .016 (88) | -.017 (88) | CaCl2+Ca(NO3)2 | | | | | |

Attachment C.3 - continued

| INTERACTION | | | THETA | PSI | MEDIA | SINGLE SALT COMPATIBILITY DATA | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | B0 | B1 | C0 | B2 |
| Ca+2 | H+ | Cl- | .092 (48) | -.015 (48) | | | | | | |
| | | | -.0333 (110)* | .016 (110) | CaCl2+HCl | | | | | |
| | | | .0612 (110) | .0008 (110) | | | | | | |
| | | | .0600 (110) | .0163 (110) | | | | | | |
| | | | .0739 (61) | .0030 (61) | HCl+CaCl2 | | | | | |
| | | | .0628 (59)* | .0467 (59) | HCl+CaCl2 | | | | | |
| Ca+2 | Co+2 | Cl- | -.055 (9,76) | .013 (9,76) | CaCl2+CoCl2 | | | | | |
| Mg+2 | MgOH+ | Cl- | ----- | .028 (48) | | | | | | |
| Mg+2 | Cl- | NO3- | .016 (88) | .0 (88) | MgCl2+Mg(NO3)2 | | | | | |
| Mg+2 | H+ | Cl- | .10 (48) | -.011 (48) | | | | | | |
| | | | .062 (109) | .001 (109) | MgCl2+HCl | | | | | |
| | | | -.2257 (130) | .2775 (130) | HCl+MgCl2 | Ref.(89) but C0=0 | | | | |
| | | | -.024 (109)* | .0122 (109) | MgCl2+HCl | | | | | |
| | | | -.459 (58)* | .039 (58) | MgCl2+HCl | | | | | |
| | | | .0897 (61) | -.0014 (61) | HCl+MgCl2 | | | | | |
| | | | .0459 (58)* | .0396 (58) | HCl+MgCl2 | | | | | |
| | | | .0 (63)* | -.0298 (63) | | | | | | |
| Mg+2 | H+ | HSO4- | .10 (48) | -.0178 (48) | | | | | | |
| H+ | Na+ | ClO4- | .036 (88) | -.016 (88) | HClO4+NaClO4 | | | | | |
| | | | .107 (126) | -.113 (126) | HClO4+NaClO4 | HClO4 | 216 | | | |
| | | | | | | NaClO4 | Ref.(89) | | | |
| H+ | Mg+2 | Br- | .069 (110) | -.005 (110) | HBr+MgBr2 | | | | | |
| H+ | Ca+2 | Br- | .0600 (63) | .0163 (63) | HBr+CaBr2 | | | | | |
| | | | .073 (70) | .0 (70) | HBr+CaBr2 | | | | | |
| H+ | Ba+2 | Cl- | .072 (84) | .0 (84) | HCl+BaCl2 | | | | | |
| | | | -.036 (88)* | .024 (88) | HCl+BaCl2 | | | | | |
| | | | .074 (110) | .0137 (110) | HCl+BaCl2 | | | | | |
| | | | .0616 (61)* | .0424 (61) | HCl+BaCl2 | | | | | |
| | | | .0763 (61) | -.0001 (61) | HCl+BaCl2 | | | | | |
| H+ | Ba+2 | Br- | .0719 (64) | .0057 (64) | HBr+BaBr2 | | | | | |
| H+ | Br- | NH4+ | -.019 (86) | .0 (86) | HBr+NH4Br | HBr | .1960 | .3564 | .00827 | |
| | | | | | | NH4Br | .0624 | .1947 | -.00436 | |
| H+ | Co+2 | Cl- | .0787 (61) | .0064 (61) | HCl+CoCl2 | | | | | |
| | | | .0597 (61)* | .0493 (61) | | | | | | |
| H+ | Fe+2 | HSO4- | .0 (103) | .0143 (103) | H2SO4+FeHSO4 | | | | | |
| H+ | Li+ | Cl- | .015 (88) | .0 (88) | HCl+LiCl | | | | | |
| H+ | Li+ | Br- | .015 (88) | .0 (88) | HBr+LiBr | | | | | |
| H+ | Li+ | ClO4- | .015 (88) | -.0017 (88) | HClO4+LiClO4 | | | | | |
| H+ | Cs+ | Cl- | -.044 (88) | -.019 (88) | HCl+CsCl | | | | | |
| H+ | NH4+ | Cl- | -.016 (88) | .0 (88) | HCl+NH4Cl | | | | | |
| | | | -.0127 (9) | -.0091 (9) | HCl+NH4Cl | HCl | .1775 | .2945 | .00080 | |
| | | | | | | NH4Cl | .0522 | .1918 | -.00301 | |
| | | | -.005 (9) | -.0125 (9) | HCl+NH4Cl | HCl | .1775 | .2945 | .00080 | |
| | | | | | | NH4Cl | .0522 | .1918 | -.00301 | |
| H+ | Sr+2 | Cl- | -.020 (88)* | .018 (88) | HCl+SrCl2 | | | | | |
| | | | .065 (84) | .003 (84) | HCl+SrCl2 | | | | | |
| | | | .0311 (61)* | .0178 (61) | HCl+SrCl2 | | | | | |
| | | | .0720 (62) | .0007 (62) | HCl+SrCl2 | | | | | |

Attachment C.3 - continued

| INTERACTION | | | THETA | PSI | MEDIA | SINGLE SALT COMPATIBILITY DATA | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | B0 | B1 | C0 | B2 |
| H+ | Mn+2 | Cl- | .0 (88)* | .0 (88) | HCl+MnCl2 | | | | | |
| | | | .0834 (111) | -.0090 (111) | HCl+MnCl2 | | | | | |
| | | | .075 (84) | -.007 (84) | HCl+MnCl2 | | | | | |
| | | | .0694 (61) | -.0006 (61) | HCl+MnCl2 | | | | | |
| | | | .0666 (61)* | .0386 (61) | HCl+MnCl2 | | | | | |
| H+ | Ni+2 | Cl- | .0818 (61) | .0051 (61) | HCl+NiCl2 | | | | | |
| | | | .0559 (61) | .0475 (61) | | | | | | |
| H+ | UO2+2 | ClO4- | -.0732 (6)* | .0434 (6) | HClO4+UO2(ClO4)2 | HClO4 | .1634 | .3465 | .0117 | |
| | | | | | | UO2(ClO4)2 | .61785 | 2.06175 | .0153795 | |
| Cl- | Na+ | Sr+2 | .051 (102) | -.0021 (102) | NaCl+SrCl2 | NaCl | .0765 | .2664 | .00127 | |
| | | | | | | SrCl2 | .2858 | 1.667 | -.00130 | |
| | | | -.0084 (72)* | .0036 (72) | NaCl+SrCl2 | | | | | |
| | | | .00940 (100)* | -.00323 (100) | NaCl+SrCl2 | | | | | |
| Cl- | H+ | Al+3 | .185 (84) | .013 (84) | HCl+AlCl3 | HCl | | | | |
| | | | | | | AlCl3 | | | | |
| | | | .216 (2) | .004 (2) | HCl+AlCl3 | | | | | |
| Cl- | SO4-2 | Na+ | .02 (48) | .0014 (48) | | | | | | |
| | | | .02 (49) | .0014 (49) | | | | | | |
| | | | .030 (14) | .000 (14) | NaCl+Na2SO4 | | | | | |
| | | | -.02 (14)* | .004 (14) | NaCl+Na2SO4 | NaCl | Ref.(89) | | | |
| | | | | | | Na2SO4 | Ref.(89) | | | |
| | | | -.035 (88)* | .007 (88) | NaCl+Na2SO4 | | | | | |
| | | | -.045 (25)* | .007 (25) | NaCl+Na2SO4 | NaCl | .0765 | .2664 | .00127 | |
| | | | | | | Na2SO4 | .0187 | 1.0994 | .00550 | |
| | | | .030 (79) | .0 (79) | | | | | | |
| Cl- | SO4-2 | K+ | -.035 (88)* | .0 (88) | KCl+K2SO4 | | | | | |
| | | | .02 (84) | .0 (84) | | | | | | |
| | | | -.045 (25)* | .014 (25) | | | | | | |
| | | | -.045 (33)* | .018 (33) | KCl+K2SO4 | Pitz.Param. | | | | |
| | | | -.02 (86)* | -.007 (86) | KCl+K2SO4 | KCl | .04835 | .2122 | -.00084 | |
| | | | | | | K2SO4 | .04995 | .77925 | | |
| | | | .030 (14) | -.005 (14) | KCl+K2SO4 | Ref.(14) | | | | |
| | | | .030 (79) | -5.0 (79) | | | | | | |
| Cl- | SO4-2 | Ca+2 | .02 (48) | -.018 (48) | | | | | | |
| | | | .02 (49) | .0 (49) | | | | | | |
| | | | -.02 (47)* | .0 (47) | CaCl2+CaSO4 | CaCl2 | .3159 | 1.614 | -.00034 | |
| | | | | | | CaSO4 | .200 | 2.65 | .0 | -57.70 |
| Cl- | SO4-2 | Mg+2 | .02 (48) | -.004 (48) | | | | | | |
| | | | .02 (49) | -.004 (49) | | | | | | |
| | | | -.035 (88)* | .0 (88) | MgCl2+MgSO4 | | | | | |
| | | | -.02 (86)* | -.007 (86) | MgCl2+MgSO4 | MgCl2 | .35235 | 1.6815 | .00519193 | |
| | | | | | | MgSO4 | .2210 | 3.343 | .0250 | -37.23 |
| | | | .02 (84) | -.014 (84) | MgCl2+MgSO4 | | | | | |
| | | | -.056 (32)* | .0129 (32) | MgCl2+MgSO4 | MgCl2 | .3509 | 1.6508 | .00651 | |
| | | | | | | MgSO4 | .2150 | 3.3646 | .02797 | -32.74 |
| | | | .030 (14) | -.020 (14) | MgCl2+MgSO4 | Ref.(14) | | | | |
| | | | -.045 (20,27)* | .007 (20,27) | MgCl2+MgSO4 | MgCl2 | .3509 | 1.6508 | .00610 | |
| | | | | | | MgSO4 | .3150 | 3.3646 | .02797 | -32.74 |

| INTERACTION | | | THETA | PSI | MEDIA | | SINGLE SALT COMPATIBILITY DATA B0 | B1 | C0 | B2 |
|---|---|---|---|---|---|---|---|---|---|---|
| Cl- | SO4-2 | Cu+2 | .030 (14) | .031 (14) | CuCl2+CuSO4 | CuCl2 | .2966 | 1.391 | -.03602 | |
| | | | | | | CuSO4 | .2340 | 2.527 | .0044 | -48.33 |
| | | | -.02 (14)* | .043 (14) | CuCl2+CuSO4 | CuCl2 | .2966 | 1.391 | -.03602 | |
| | | | | | | CuSO4 | .2340 | 2.527 | .0044 | -48.33 |
| Cl- | HSO4- | Na+ | -.006 (48) | -.006 (48) | | | | | | |
| Cl- | HSO4- | H+ | -.006 (48) | .013 (48) | | | | | | |
| Cl- | OH- | Na+ | -.050 (88) | -.006 (88) | NaCl+NaOH | | | | | |
| Cl- | OH- | K+ | -.050 (48) | -.006 (48) | | | | | | |
| | | | -.050 (88) | -.008 (88) | KCl+KOH | | | | | |
| Cl- | OH- | Ca+2 | -.050 (48) | -.025 (48) | | | | | | |
| Cl- | HCO3- | Na+ | .03 (48) | -.015 (48) | | | | | | |
| | | | .0359 (81) | -.0143 (81) | NaCl+NaHCO3 | NaCl | .0765 | .2664 | .00127 | |
| | | | | | | NaHCO3 | .028 | .044 | | |
| | | | .030 (92) | ----- (92) | NaCl+NaHCO3 | NaCl | | | | |
| | | | | | | NaHCO3 | .0277 | .0411 | | |
| Cl- | HCO3- | K+ | -.063 (112) | -.0037 (112) | KCl+KHCO3 | KCl | .04835 | .2122 | -.00084 | |
| | | | | | | KHCO3 | -.0107 | .0478 | | |
| Cl- | HCO3- | Mg+2 | .03 (48) | -.096 (48) | | | | | | |
| Cl- | CO3-2 | Na+ | -.02 (48) | .0085 (48) | | | | | | |
| | | | -.1605 (129)* | .0503 (129) | NaCl+Na2CO3 | NaCl | .07669 | .026461 | .0012193 | |
| | | | | | | Na2CO3 | .040822 | 1.4679 | .0042374 | |
| | | | -.2343 (47)* | .0431 (47) | NaCl+Na2CO3 | NaCl | .07669 | .26461 | .0012193 | |
| | | | | | | Na2CO3 | .040822 | 1.4679 | .0042374 | |
| | | | -.053 (81) | .016 (81) | NaCl+Na2CO3 | NaCl | .0765 | .2664 | .00127 | |
| | | | | | | Na2CO3 | .0362 | 1.510 | .0052 | |
| | | | -.092 (81)* | .006 (81) | NaCl+Na2CO3 | NaCl | .0765 | .2664 | .00127 | |
| | | | | | | Na2CO3 | .0362 | 1.510 | .0052 | |
| Cl- | CO3-2 | K+ | -.02 (48) | .004 (48) | | | | | | |
| | | | -.053 (112) | .024 (112) | KCl+K2CO3 | KCl | .04835 | .2122 | -.00084 | |
| | | | | | | K2CO3 | .1288 | 1.433 | .00050 | |
| | | | -.092 (112)* | .0073 (112) | KCl+K2CO3 | KCl | .04835 | .2122 | -.00084 | |
| | | | | | | K2CO3 | .1288 | 1.433 | .00050 | |
| Cl- | Co+2 | SO4-2 | -.18140 (28)* | .08718 (28) | CoCl2+CoSO4 | CoCl2 | .41908 | 2.06641 | -.02429 | -.35136 |
| | | | -.045 (24) | .02911 (24) | | CoSO4 | Ref.(90) | | | |
| Cl- | Ni+2 | SO4-2 | -.16242 (28)* | .07202 (28) | NiCl2+Ni2SO4 | NiCl2 | .44104 | 2.34470 | -.02156 | -.53354 |
| | | | | | | NiSO4 | Ref.(90) | | | |
| SO4-2 | HSO4- | Na+ | .0 (48) | -.0094 (48) | | | | | | |
| SO4-2 | HSO4- | K+ | .0 (48) | -.0677 (48) | | | | | | |
| SO4-2 | HSO4- | Mg+2 | .0 (48) | -.0425 (48) | | | | | | |
| SO4-2 | OH- | Na+ | -.013 (48) | -.009 (48) | | | | | | |
| SO4-2 | OH- | K+ | -.013 (48) | -.050 (48) | | | | | | |
| SO4-2 | HCO3- | Na+ | .01 (48) | -.005 (48) | | | | | | |
| SO4-2 | HCO3- | Mg+2 | .01 (48) | -.161 (48) | | | | | | |
| SO4-2 | CO3-2 | Na+ | .02 (48) | -.005 (48) | | | | | | |
| SO4-2 | CO3-2 | K+ | .02 (48) | -.009 (48) | | | | | | |
| OH- | CO3-2 | Na+ | .10 (48) | -.017 (48) | | | | | | |
| | | | .0 (78)* | .0 (78) | NaOH+Na2CO3 | NaOH | .0864 | .253 | .0044 | |
| | | | | | | Na2CO3 | .0362 | 1.51 | .0052 | |
| OH- | CO3-2 | K+ | .10 (48) | -.01 (48) | | | | | | |
| OH- | Br- | Na+ | -.065 (88) | -.018 (88) | | | | | | |
| OH- | Br- | K+ | -.065 (88) | -.014 (88) | | | | | | |

| INTERACTION | | | THETA | PSI | MEDIA | | SINGLE SALT COMPATIBILITY DATA B0 | B1 | C0 | B2 |
|---|---|---|---|---|---|---|---|---|---|---|
| HCO3- | CO3-2 | Na+ | -.04 (48) | .002 (48) | | | | | | |
| HCO3- | CO3-2 | K+ | -.04 (48) | .012 (48) | | | | | | |
| | | | .089 (112) | -.036 (112) | KHCO3+K2CO3 | KHCO3 | -.0107 | .0478 | | |
| | | | | | | K2CO3 | .1288 | 1.433 | .00050 | |
| | | | -.063 (112)* | .013 (112) | KHCO3+K2CO3 | KHCO3 | -.0107 | .0478 | | |
| | | | | | | K2CO3 | .1288 | 1.433 | .00050 | |
| Li+ | Na+ | Cl- | .012 (88) | -.003 (88) | LiCl+NaCl | | | | | |
| Li+ | Na+ | NO3-2 | .012 (88) | -.0072 (88) | LiNO3+NaNO3 | | | | | |
| Li+ | Na+ | ClO4- | .012 (88) | -.0080 (88) | LiClO4+NaClO4 | | | | | |
| Li+ | K+ | Cl- | -.022 (88) | -.010 (88) | LiCl+KCl | | | | | |
| Li+ | Cl- | NO3-2 | .016 (88) | -.003 (88) | LiCl+LiNO3 | | | | | |
| Li+ | Ba+2 | Cl- | -.070 (88)* | .019 (88) | LiCl+BaCl2 | | | | | |
| | | | .0 (84) | .009 (84) | LiCl+BaCl2 | | | | | |
| Li+ | Cs+ | Cl- | -.095 (88) | -.0094 (88) | LiCl+CsCl | | | | | |
| Li+ | Cs+ | SO4-2 | -.1242 (37) | .0088 (37) | Li2SO4+Cs2SO4 | Li2SO4 | 1.1363 | 1.2705 | -.00399 | |
| | | | | | | Cs2SO4 | .0714 | 1.2010 | .00291 | |
| Li+ | Cd+2 | SO4-2 | .0 (42)* | .0 (42) | Li2SO4+CdSO4 | Li2SO4 | .1363 | 1.2705 | .00399 | |
| | | | | | | Cd2SO4 | .2053 | 2.6170 | .01140 | -48.07 |
| Li+ | Ni+2 | Cl- | -.059 (69)* | .047 (69) | LiCl+NiCl2 | Ref.(89) but C0=0 | | | | |
| Li+ | Mn+2 | SO4-2 | .0 (40)* | .0 (40) | Li2SO4+MnSO4 | Li2SO4 | .1363 | 1.2705 | -.00399 | |
| | | | | | | MnSO4 | .2065 | 2.9511 | .01636 | -40.0 |
| Cu+2 | Ni+2 | NO3-2 | .01314 (22) | -.003909 (22) | Cu(NO3)2+Ni(NO3)2 | Cu(NO3)2 | .28076 | 1.73230 | -.00838 | |
| | | | | | | Ni(NO3)2 | .28790 | 1.43724 | -.00189 | .30381 |
| Cu+2 | Zn+2 | NO3-2 | .00664 (21) | -.00141 (21) | Cu(NO3)2+Zn(NO3)2 | Cu(NO3)2 | .28076 | 1.73230 | -.008372 | |
| | | | | | | Zn(NO3)2 | .3015 | 1.2012 | -.005798 | .26536 |
| Cs+ | Ba+2 | Cl- | -.150 (88)* | .0 (88) | CsCl+BaCl2 | | | | | |
| | | | -.070 (84) | .015 (84) | CsCl+BaCl2 | | | | | |
| Rb+ | Cd+2 | SO4-2 | -.1226 (20)* | .3730 (20) | Rb2SO4+CdSO4 | Rb2SO4 | .05772 | 1.1105 | .0 | |
| | | | | | | CdSO4 | .2081 | 2.6023 | .01032 | -48.07 |
| Rb+ | Co+2 | SO4-2 | -.3058 (34)* | .0466 (34) | Rb2SO4+CoSO4 | Rb2SO4 | .0579 | 1.1108 | -.000036 | |
| | | | | | | CoSO4 | .1631 | 3.3458 | .00926 | -30.7 |
| NH4+ | SO4-2 | H2PO4- | .01837 (29)* | -.00427 (29) | NH4H2PO4+(NH4)2SO4 | NH4H2PO4 | -.07043 | -.41564 | .00669 | |
| | | | | | | (NH4)2SO4 | .03905 | .66379 | -.00082 | |

* - Higher order electrostatic terms not included. Values of theta and psi not consistent with PHRQPITZ.

Attachment C.4. -- Temperature dependence of single-salt parameters

Attachment C.4 - Temperature dependence of single salt parameters

| | | dB0/dT | dB1/dT | dC0/dT | dB2/dT |
|---|---|---|---|---|---|
| Na+ | Cl- | 7.159E-4 (121) | 7.005E-4 (121) | -10.54E-5 (121) | |
| | | .008946 (120) | 6.1608E-5 (120) | -4.655E-5 (120) | |
| Na+ | Br- | 7.692E-4 (121) | 10.79E-4 (121) | -9.30E-5 (121) | |
| Na+ | SO4-2 | 2.367E-3 (121) | 5.6325E-3 (121) | -4.879037 (121) | |
| | | .002349 (106) | .005958 (106) | -.00479 (106) | |
| Na+ | I- | 8.355E-4 (121) | 8.28E-4 (121) | -8.35E-5 (121) | |
| | | 9.163E-4 (118) | 9.964E-4 (118) | -5.58E-5 (118) | |
| Na+ | F- | 5.361E-4 (121) | 8.70E-4 (121) | | |
| Na+ | OH- | 7.00E-4 (121) | 1.34E-4 (121) | -18.94E-5 (121) | |
| Na+ | HCO3- | 1.00E-3 (81) | 1.10E-3 (81) | | |
| Na+ | CO3-2 | 1.79E-3 (81) | 2.05E-3 (81) | | |
| Na+ | ClO4- | 12.96E-4 (121) | 22.97E-4 (121) | -16.23E-5 (121) | |
| Na+ | NO3- | 12.66E-4 (121) | 20.60E-4 (121) | -23.16E-5 (121) | |
| Na+ | ClO3- | 10.35E-4 (121) | 19.07E-4 (121) | -9.29E-5 (121) | |
| Na+ | BrO3- | 5.59E-4 (121) | 34.37E-4 (121) | | |
| Na+ | IO3- | 20.66E-4 (121) | 60.57E-4 (121) | | |
| | | 11.79E-4 (118) | 59.38E-4 (118) | | |
| K+ | Cl- | 5.794E-4 (121) | 10.71E-4 (121) | -5.095E-5 (121) | |
| K+ | Br- | 7.39E-4 (121) | 17.40E-4 (121) | -7.004E-5 (121) | |
| K+ | SO4-2 | 1.44E-3 (121) | 6.6975E-3 (121) | | |
| K+ | I- | 9.914E-4 (121) | 11.86E-4 (121) | -9.44E-5 (121) | |
| K+ | F- | 2.14E-4 (121) | 5.44E-4 (121) | -5.95E-5 (121) | |
| K+ | HCO3- | .996E-3 (81) | 1.104E-3 (81) | | |
| K+ | CO3-2 | 1.1E-3 (112) | 4.36E-3 (112) | | |
| | | 1.788E-3 (81) | 2.051E-3 (81) | | |
| K+ | ClO4- | .60E-4 (121) | 10.07E-3 (121) | | |
| | | 4.98E-4 (118) | 95.19E-4 (118) | | |
| K+ | NO3- | 2.06E-4 (121) | 64.5E-4 (121) | 39.7E-5 (121) | |
| K+ | ClO3- | 19.87E-4 (121) | 31.8E-4 (121) | | |
| K+ | H2PO4- | 6.045E-4 (121) | 28.6E-4 (121) | -10.11E-5 (121) | |
| K+ | IO3- | 21.10E-4 (118) | 45.36E-4 (118) | | |
| H+ | Cl- | -3.081E-4 (121) | 1.419E-4 (121) | 6.213E-5 (121) | |
| | | -3.081E-4 (118) | 1.419E-4 (118) | 3.106E-5 (118) | |
| H+ | Br- | -2.049E-4 (121) | 4.467E-4 (121) | -5.685E-5 (121) | |
| H+ | I- | -.230E-4 (121) | 8.86E-4 (121) | -7.32E-5 (121) | |
| H+ | ClO4- | 4.905E-4 (121) | 19.31E-4 (121) | -11.77E-5 (121) | |
| Mg+2 | Cl- | -.19425E-3 (121) | 2.775E-3 (121) | -1.6493266 (121) | |
| | | -.429E-3 (86) | 3.6525E-3 (86) | | |
| Mg+2 | Br- | -.05625E-3 (121) | 3.8625E-3 (121) | | |
| Mg+2 | SO4-2 | -.69E-3 (121) | 1.53E-2 (121) | .523E-3 (121) | -2.53E-1 (121) |
| Mg+2 | ClO4- | .52275E-3 (121) | 4.5E-3 (121) | -3.5266952 (121) | |
| Mg+2 | NO3- | .51525E-3 (121) | 4.4925E-3 (121) | | |
| Ca+2 | Cl- | -.1725E-3 (121) | 3.9E-3 (121) | | |
| | | 1.049E-4 (82) | 3.54E-3 (82) | -1.565E-4 (82) | |
| Ca+2 | Br- | -.52275E-3 (121) | 6.0375E-3 (121) | | |
| Ca+2 | SO4-2 | ----- (121) | 5.46E-2 (121) | ----- (121) | -5.16E-1 (121) |
| Ca+2 | ClO4- | .8925E-3 (121) | 5.0775E-3 (121) | -3.0918245 (121) | |
| Ca+2 | NO3- | .5295E-3 (121) | 9.1875E-3 (121) | | |
| NH4+ | Cl- | .779E-4 (121) | 12.58E-4 (121) | 2.10E-5 (121) | |
| | | .5794E-3 (114) | 1.071E-3 (114) | -.05E-3 (114) | |
| NH4+ | CO3-2 | 1.1E-3 (114) | 4.36E-3 (114) | | |
| NH4+ | HCO3- | -12.6E-3 (114) | -1.75E-3 (114) | | |
| NH4+ | H2PO4- | 1.51E-4 (121) | 22.8E-4 (121) | -2.84E-5 (121) | |
| Rb+ | Cl- | 5.522E-4 (121) | 15.06E-4 (121) | | |
| Rb+ | Br- | 6.780E-4 (121) | 20.35E-4 (121) | | |
| Rb+ | SO4-2 | .9375E-3 (121) | 8.64E-3 (121) | | |
| Rb+ | I- | 8.578E-4 (121) | 23.83E-4 (121) | | |

Attachment C.4 - continued

| | | dB0/dT | dB1/dT | dC0/dT | dB2/dT |
|---|---|---|---|---|---|
| Rb+ | F- | -.76E-4 (121) | 14.7E-4 (121) | | |
| Cs+ | Cl- | 8.28E-4 (121) | 15.0E-4 (121) | -12.25E-5 (121) | |
| | | 7.030E-4 (118) | 21.07E-4 (118) | -4.06E-5 (118) | |
| Cs+ | Br- | 7.80E-4 (121) | 28.44E-4 (121) | | |
| Cs+ | SO4-2 | .8925E-3 (121) | 14.4825E-3 (121) | | |
| Cs+ | I- | 9.75E-4 (121) | 34.77E-4 (121) | | |
| Cs+ | F- | .95E-4 (121) | 5.97E-4 (121) | | |
| Ni+2 | ClO4- | .666E-3 (121) | 4.7625E-3 (121) | -3.8236801 (121) | |
| Cu+2 | Cl- | -2.715E-3 (121) | 8.475E-3 (121) | | |
| Cu+2 | SO4-2 | -4.4E-3 (121) | 2.38E-2 (121) | 4.80E-3 (121) | -4.73E-1 (121) |
| Zn+2 | SO4-2 | -3.66E-3 (121) | 2.33E-2 (121) | 3.97E-3 (121) | -3.33E-1 (121) |
| Zn+2 | ClO4- | .59625E-3 (121) | 5.0925E-3 (121) | -3.8554999 (121) | |
| Cd+2 | SO4-2 | -2.79E-3 (121) | 1.71E-2 (121) | 2.61E-3 (121) | -5.22E-1 (121) |
| Co+2 | ClO4- | .54525E-3 (121) | 5.3625E-3 (121) | -3.5903348 (121) | |
| Sr+2 | Cl- | .717E-3 (121) | 2.8425E-3 (121) | ----- (121) | |
| Sr+2 | Br- | -.32775E-3 (121) | 6.5325E-3 (121) | | |
| Sr+2 | SO4-2 | -2.9E-3 (102) | 27.0E-3 (102) | 3.0E-3 (102) | -.42 (102) |
| Sr+2 | ClO4- | 1.143E-3 (121) | 5.3925E-3 (121) | -3.1077344 (121) | |
| Sr+2 | NO3- | .177E-3 (121) | 12.4725E-3 (121) | | |
| Ba+2 | Cl- | .6405E-3 (121) | 3.2325E-3 (121) | -1.5379573 (121) | |
| Ba+2 | Br- | -.33825E-3 (121) | 6.78E-3 (121) | | |
| Ba+2 | NO3- | -2.91E-3 (121) | 29.1E-3 (121) | | |
| Mn+2 | ClO4- | .39675E-3 (121) | 5.025E-3 (121) | -3.3357764 (121) | |
| Li+2 | Cl- | -1.685E-4 (121) | 5.366E-4 (121) | -4.520E-5 (121) | |
| Li+2 | Br- | -1.819E-4 (121) | 6.636E-4 (121) | -2.813E-5 (121) | |
| Li+2 | SO4-2 | .5055E-3 (121) | 1.41E-3 (121) | -2.3334525 (121) | |
| Li+2 | ClO4- | .386E-4 (121) | 7.009E-4 (121) | -7.712E-5 (121) | |

Attachment C.5. -- Summary of analytical expressions for temperature (and pressure) dependence of selected single-salt Pitzer interaction parameters

Attachment C.5 - Summary of analytical expressions for temperature (and pressure) dependence of selected single salt Pitzer interaction parameters *

| Parameter Number | Solution NaCl (120,5) | CaCl2 (1,1) | Parameter Number | NaOH (80,3) |
|---|---|---|---|---|
| 1 | .0765 | 3.39701E-1 | 6 | -2.8131778E-3 |
| 2 | -777.03 | 5.10778E+3 | 7 | 3.7012540E-1 |
| 3 | -4.4706 | 4.64785E+1 | 8 | 7.1788733E-6 |
| 4 | .008946 | -1.38971E-1 | 9 | -5.8847404E-9 |
| 5 | -3.3158E-6 | 6.82557E-5 | 10 | -4.8217410E-3 |
| 6 | .2664 | 1.50481 | 11 | 4.0534778E-4 |
| 7 | ----- | -4.98241E+2 | 12 | -5.1714017E-2 |
| 8 | ----- | .0 | 13 | -1.0553037E-6 |
| 9 | 6.1608E-5 | -1.64685E-2 | 14 | 8.9893405E-10 |
| 10 | 1.0715E-6 | 2.34630E-5 | 17 | -4.9359970E+1 |
| 11 | .00127 | -2.67882E-2 | 20 | 1.1931122E+1 |
| 12 | 33.317 | -9.67633E+3 | 22 | 4.6286977E+2 |
| 13 | .09421 | -8.48338E+1 | 23 | -1.0294181E+4 |
| 14 | -4.655E-5 | 2.46219E-1 | 24 | -8.5960581E+1 |
| 15 | ----- | -1.18352E-4 | 25 | 2.3905969E-1 |
| 16 | 41587.11 | | 26 | -1.0795894E-4 |
| 17 | -315.90 | | 29 | 2.9680772E-0 |
| 18 | .8514 | | 32 | -6.8923899E-1 |
| 19 | -8.3637E-4 | | 33 | -8.1156286E-2 |
| | | | 34 | 2.7682478E+2 |
| | | | 35 | -7.3755443E+3 |
| | | | 36 | 1.0945106E-1 |
| | | | 37 | -4.0218506E-5 |
| | | | 38 | 2.4824963E-0 |
| | | | 39 | -1.6686897E+1 |
| | | | 40 | 4.5364961E+2 |
| | | | 41 | -6.5161667E-3 |
| | | | 42 | 2.3765786E-6 |

| | | KCl (54,2) | CsCl (54,2) | HCl (115,4) | LiCl (54,2) |
|---|---|---|---|---|---|
| B0 | 1 | .04808 | .03352 | .17416 | .14847 |
| | 2 | -758.48 | -1290.0 | -773.62 | .0 |
| | 3 | -4.7062 | -8.4279 | -4.5174 | .0 |
| | 4 | .010072 | .018502 | 8.1556E-3 | -1.546E-4 |
| | 5 | -3.7599E-6 | -6.7942E-6 | -2.8525E-6 | .0 |
| | 6 | .0 | .0 | | .0 |
| B1 | 1 | .0476 | .0429 | .28799 | .307 |
| | 2 | 303.9 | -38.0 | -374.50 | .0 |
| | 3 | 1.066 | .0 | -4.1319 | .0 |
| | 4 | .0 | .001306 | 1.0855E-2 | 6.36E-4 |
| | 5 | .0 | .0 | -9.2990E-7 | .0 |
| | 6 | .0470 | .0 | | .0 |
| C0 | 1 | -7.88E-4 | -2.62E-4 | | .003710 |
| | 2 | 91.270 | 157.13 | | 4.115 |
| | 3 | .58643 | 1.0860 | | .0 |
| | 4 | -.0012980 | -.0025242 | | .0 |
| | 5 | 4.9567E-7 | 9.840E-7 | | -3.71E-9 |
| | 6 | .0 | .0 | | .0 |

Attachment C.5 - continued

| | | MgSO4 (79,6) | Na2SO4 (79,10) | K2SO4 (79,7) | MgCl2 (79,9) |
|---|---|---|---|---|---|
| B0 | 1 | -1.0282 | -1.727E-2 | .0 | 5.93915E-7 |
| | 2 | 8.4790E-3 | 1.7828E-3 | 7.476E-4 | -9.31654E-4 |
| | 3 | -2.33667E-5 | 9.133E-6 | .0 | .576066 |
| | 4 | 2.1575E-8 | .0 | 4.265E-3 | ----- |
| | 5 | 6.8402E-4 | -6.552 | -3.088 | ----- |
| | 6 | .21499 | .0 | .0 | ----- |
| | 7 | ----- | -96.90 | .0 | ----- |
| B1 | 1 | -2.9596E-1 | .7534 | .6179 | 2.60169E-5 |
| | 2 | 9.4564E-1 | 5.61E-3 | 6.85E-3 | -1.09438E-2 |
| | 3 | .0 | -5.7513E-4 | 5.576E-5 | 2.60135 |
| | 4 | .0 | 1.11068 | -5.841E-2 | ----- |
| | 5 | 1.1028E-2 | -378.82 | .0 | ----- |
| | 6 | 3.3646 | .0 | -.90 | ----- |
| | 7 | ----- | 1861.3 | .0 | ----- |
| C0 | 1 | 1.0541E-1 | 1.1745E-2 | 9.1547E-3 | 2.41831E-7 |
| | 2 | -8.9316E-4 | -3.3038E-4 | .0 | -2.49949E-4 |
| | 3 | 2.51E-6 | 1.85794E-5 | .0 | 5.95320E-2 |
| | 4 | -2.3436E-9 | -3.9200E-2 | -1.81E-4 | ----- |
| | 5 | -8.7899E-5 | 14.2130 | .0 | ----- |
| | 6 | .006993 | .0 | .0 | ----- |
| | 7 | ----- | -24.950 | .0 | ----- |
| B2 | 1 | 1.0541E-1 | ----- | ----- | ----- |
| | 2 | 1.2121E-1 | ----- | ----- | ----- |
| | 3 | -2.7642E-4 | ----- | ----- | ----- |
| | 4 | .0 | ----- | ----- | ----- |
| | 5 | -2.1515E-1 | ----- | ----- | ----- |
| | 6 | -32.743 | ----- | ----- | ----- |

| | | MgCl2 (11) | HCl (53) |
|---|---|---|---|
| B0 | 1 | 5.93915E-7 | .17690 |
| | 2 | -9.31654E-4 | -9.140E-2 |
| | 3 | .576066 | .0 |
| | 4 | ----- | -4.034E-4 |
| | 5 | ----- | 6.02E-6 |
| B1 | 1 | 2.60169E-5 | .2973 |
| | 2 | -1.09438E-2 | 16.147 |
| | 3 | 2.60135 | -1.7631E-2 |
| | 4 | ----- | .0 |
| | 5 | ----- | 7.20E-5 |
| C0 | 1 | 2.41831E-7 (2**3/2C) | .362E-3 |
| | 2 | -2.49949E-4 (2**3/2C) | .0 |
| | 3 | 5.95320E-2 (2**3/2C) | .0 |
| | 4 | ----- | -3.036E-5 |
| | 5 | ----- | .0 |

| | NaCl (79,8) | | |
|---|---|---|---|
| | B0 | B1 | C0 |
| 1 | -656.81518 | 119.31966 | -6.1084589 |
| 2 | 24.86913 | -4.8309327E-1 | 4.0217793E-1 |
| 3 | 5.3812753E-5 | .0 | 2.2902837E-5 |
| 4 | -5.5887470E-8 | .0 | .0 |
| 5 | 6.589326E-12 | .0 | .0 |
| 6 | -4.4640952 | .0 | -7.5354649E-2 |
| 7 | 1.1109914E-2 | 1.4068095E-3 | 1.5317673E-8 |

Attachment C.5 - continued

NaCl (79,8)

| | B0 | B1 | C0 |
|---|---|---|---|
| 8 | -2.6573399E-7 | .0 | -9.0550901E-8 |
| 9 | 1.7460070E-10 | .0 | .0 |
| 10 | 1.0462619E-14 | .0 | .0 |
| 11 | -5.3070129E-6 | .0 | -1.5386008E-8 |
| 12 | 8.6340233E-10 | .0 | 8.6926600E-11 |
| 13 | -4.1785962E-13 | .0 | .0 |
| 14 | -1.579366 | -4.2345814 | 3.5310414E-1 |
| 15 | 2.2022821E-3 | .0 | -4.3314252E-4 |
| 16 | -1.3105503E-7 | .0 | .0 |
| 17 | -6.3813683E-11 | .0 | .0 |
| 18 | 9.7065780 | .0 | -9.1871455E-2 |
| 19 | -2.6860396E-2 | .0 | 5.1904777E-4 |
| 20 | 1.5344744E-5 | .0 | .0 |
| 21 | -3.2153983E-9 | .0 | .0 |

NaOH (79,11)

| | B0 | B1 | C0 |
|---|---|---|---|
| 1 | 2.7682478E+2 | 4.6286977E+2 | -1.6686897E+1 |
| 2 | -2.8131778E-3 | .0 | 4.0534778E-4 |
| 3 | -7.3755443E+3 | -1.0294181E+4 | 4.5364961E+2 |
| 4 | 3.7012540E-1 | .0 | -5.1714017E-2 |
| 5 | -4.9359970E+1 | -8.5960581E+1 | 2.9680772 |
| 6 | 1.0945106E-1 | 2.3905969E-1 | -6.5161667E-3 |
| 7 | 7.1788733E-6 | .0 | -1.05530373E-6 |
| 8 | -4.0218506E-5 | -1.079584E-4 | 2.3765786E-6 |
| 9 | -5.8847404E-9 | .0 | 8.9893405E-10 |
| 10 | 1.1931122E-1 | .0 | -6.8923899E-1 |
| 11 | 2.4824963 | .0 | -8.1156286E-2 |
| 12 | -4.8217410E-3 | .0 | .0 |

| | | NaCl (77) | Na2SO4 (77) | CaCl2 (77) | CaSO4 (77) |
|---|---|---|---|---|---|
| B0 | 1 | 1.43783204d+01 | 8.16920027d+01 | -9.41895832d+01 | .15d00 |
| | 2 | 5.60767406d-03 | 3.011049570d-02 | -4.04750026d-02 | .0 |
| | 3 | -4.22185236d+02 | -2.32193726d+03 | 2.34550368d+03 | .0 |
| | 4 | -2.51226677d00 | -1.43780207d+01 | 1.70912300d+01 | .0 |
| | 5 | .0 | -6.66496111d-01 | -9.22885841d-01 | .0 |
| | 6 | -2.61718135d-06 | -1.03923656d-05 | 1.51488122d-05 | .0 |
| | 7 | 4.43854508d00 | .0 | -1.39082000d00 | .0 |
| | 8 | -1.70502337d00 | .0 | .0 | .0 |
| B1 | 1 | -4.83060685d-01 | 1.00463018d+03 | 3.47870000d00 | 3.0d00 |
| | 2 | 1.40677479d-03 | 5.77453682d-01 | -1.54170000d-02 | .0 |
| | 3 | 1.19311989d+02 | -2.18434467d+04 | .0 | .0 |
| | 4 | .0 | -1.89110656d+02 | .0 | .0 |
| | 5 | .0 | -2.035505488-01 | .0 | .0 |
| | 6 | .0 | -3.23949532d-04 | 3.17910000d-05 | .0 |
| | 7 | .0 | 1.46772243d+03 | .0 | .0 |
| | 8 | -4.23433299d00 | .0 | .0 | .0 |

| | | NaCl (77) | Na2SO4 (77) | CaCl2 (77) | CaSO4 (77) |
|---|---|---|---|---|---|
| CO | 1 | -1.00588714d-01 | -8.07816886d+01 | -3.03578731d+01 | .0 |
| | 2 | -1.80529413d-05 | -3.54521126d-02 | -1.36264728d-02 | .0 |
| | 3 | 8.61185543d00 | 2.02438830d+03 | 7.64582238d+02 | .0 |
| | 4 | 1.24880954d-02 | 1.46197730d+01 | 5.50458061d00 | .0 |
| | 5 | .0 | -9.16974740d-02 | -3.27377782d-01 | .0 |
| | 6 | 3.41172108d-08 | 1.43946005d-05 | 5.69405869d-06 | .0 |
| | 7 | 6.83040995d-02 | -2.42272049d00 | -5.36231106d-01 | .0 |
| | 8 | 2.93922611d-01 | .0 | .0 | .0 |
| B2 | 1 | ----- | ----- | ----- | ----- |
| | 2 | ----- | ----- | ----- | ----- |
| | 3 | ----- | ----- | ----- | ----- |
| | 4 | ----- | ----- | ----- | ----- |
| | 5 | ----- | ----- | ----- | ----- |
| | 6 | ----- | ----- | ----- | ----- |
| | 7 | ----- | ----- | ----- | ----- |
| | 8 | ----- | ----- | ----- | ----- |

Equations

1) B(0)=q1+q2(1/T-1/Tr)+q3 ln(T/Tr)+q4(T-Tr)+q5(T**2-Tr**2)
   B(1)=q6+q7(1/T-1/Tr)+q9(T-Tr)+q10(T**2-Tr**2)
   CO=q11+q12(1/T-1/Tr)+q13 ln(T/Tr)+q14(T-Tr)+q15(T**2-Tr**2)
2) f(T)=p1+p2(1/T-1/Tr)+p3 ln(T/Tr)+p4(T-Tr)+p5(T**2-Tr**2)+p6 ln(T-260)
3) B(0)=U34+U6P+(U35+U7P)/T+U17 ln T+(U36+U8P)T+(U37+U9P)T**2+U20/(T-227)+(U38+U10P)/(647-T)
   B(1)=U22+U23/T+U24 ln T+U25T+U26T**2
   CO=U39+U11P+(U40+U12P)/T+U29 ln T+(U41+U13P)T+(U42+U14P)T**2+U32/(T-227)+U33/(647-T)
4) B*=Q1+Q2(1/T-1/Tr)+Q3 ln(T/Tr)+Q4(T-Tr)+Q5(T**2-Tr**2)
5) B(0)=q1+q2(1/T-1/Tr)+q3 ln(T/Tr)+q4(T-Tr)+q5(T**2-Tr**2)
   B(1)=q6+q9(T-Tr)+q10(T**2-Tr**2)
   CO=q11+q12(1/T-1/Tr)+q13 ln(T/Tr)+q14(T-Tr)
6) MgSO4
   f(T)=Q1(T/2+298**2/2T-298)+Q2(T**2/6+298**3/3T-298**2/2)+Q3(T**3/12+298**4/4T-298**3/3)
   +Q4(T**4/20+298**5/5T-298**4/4)+(298-298**2/T)Q5+Q6
7) K2SO4
   f(T)=Q1+Q2(Tr-Tr**2/T)+Q3(T**2+2Tr**3/T-3Tr**2)+Q4(T+Tr**2/T-2Tr)+Q5[ln(T/Tr)+Tr/T-1]
   +Q6{1/(T-263)+(263T-Tr**2)/[T(Tr-263)*2]}+Q7{1/(680-T)+(Tr**2-680T)/[T(680-Tr)**2]}
8) NaCl
   f(T)=Q1/T+Q2+Q3P+Q4P**2+Q5P**3+Q6ln(T)+(Q7+Q8P+Q9P**2+Q10P**3)T+(Q11+Q12P+Q13P**2)T**2
   +(Q14+Q15P+Q16P**2+Q17P**3)/(T-227)+(Q18+Q19P+Q20P**2+Q21P**3)/(630-T)
9) MgCl2
   f(T)=Q1T**2+Q2T+Q3
10) Na2SO4
   f(T)=Q1+Q2(Tr-Tr**2/T)+Q3(T**2+2Tr**3/T-3Tr**2)+Q4(T+Tr**2/T-2Tr)+Q5[ln(T/Tr)+Tr/T-1]
   +Q6{1/(T-263)+(263T-Tr**2)/[T(Tr-263)**2]}+Q7{1/(680-T)+(Tr**2-680T)/[T(680-Tr)**2]}
11) NaOH
   f(T)=Q1+Q2P+(Q3+Q4P)/T+Q5ln(T)+(Q6+Q7P)T+(Q8+Q9P)T**2+Q10/(T-227)+(Q11+Q12P)/(647-T)

* numbers in parentheses following designation of a salt correspond to reference number (Attachment C.1) and equation number given below.

Attachment C.6. -- Sources of data in the file PITZER.DATA

Attachment C.6 - Sources of data in file PITZER.DATA

```
SPECIES  21
  1  4  5  6  7  8  9  11 12 14 15 16 21 22 31 34 35 40 76 85 86
B0
  NA+       CL-       0.0765 (48)    -777.03 (120)    -4.4706 (120)    0.008946 (120) -3.3158E-6 (120)
  K+        CL-       0.04835 (48)                                     5.794E-4 (121)
  MG+2      CL-       0.35235 (48)                                    -1.943E-4 (121)
  CA+2      CL-       0.3159 (48)                                     -1.725E-4 (121)
  MGOH+     CL-      -0.1 (48)
  H+        CL-       0.1775 (48)                                     -3.081E-4 (121)
  LI+       CL-       0.1494 (89)                                     -1.685E-4 (121)
  SR+2      CL-       0.28575 (89)                                     0.717E-3 (121)
  FE+2      CL-       0.335925 (89)
  MN+2      CL-       0.327225 (89)
  BA+2      CL-       0.2628 (89)                                      0.6405E-3 (121)
  NA+       BR-       0.0973 (89)                                      7.692E-4 (121)
  K+        BR-       0.0569 (89)                                      7.39E-4 (121)
  H+        BR-       0.1960 (89)                                     -2.049E-4 (121)
  MG+2      BR-       0.43268 (89)                                    -5.625E-5 (121)
  CA+2      BR-       0.3816 (89)                                     -5.2275E-4 (121)
  LI+       BR-       0.1748 (89)                                     -1.819E-4 (121)
  SR+       BR-       0.331125 (89)                                   -0.32775E-3 (121)
  BA+       BR-       0.31455 (89)                                    -0.33825E-3 (121)
  NA+       SO4-2     0.01958 (48)                                     2.367E-3 (121)
  K+        SO4-2     0.04995 (48)                                     1.44E-3 (121)
  MG+2      SO4-2     0.221 (48)                                      -0.69E-3 (121)
  CA+2      SO4-2     0.2 (48)
  H+        SO4-2     0.0298 (48)
  LI+       SO4-2     0.136275 (89)                                    0.5055E-3 (121)
  SR+2      SO4-2     0.220 (102)                                     -2.9E-3 (102)
  FE+2      SO4-2     0.2568 (103)
  MN+2      SO4-2     0.2065 (40)
  NA+       HSO4-     0.0454 (48)
  K+        HSO4-    -0.0003 (48)
  MG+2      HSO4-     0.4746 (48)
  CA+2      HSO4-     0.2145 (48)
  H+        HSO4-     0.2065 (48)
  FE+2      HSO4-     0.4273 (103)
  NA+       OH-       0.0864 (48)                                      7.00E-4 (121)
  K+        OH-       0.1298 (48)
  CA+2      OH-      -0.1747 (48)
  LI+       OH-       0.015 (89)
  BA+2      OH-       0.17175 (89)
  NA+       HCO3-     0.0277 (48)                                      1.00E-3 (81)
  K+        HCO3-     0.0296 (48)                                      0.996E-3 (81)
  MG+2      HCO3-     0.329 (48)
  CA+2      HCO3-     0.4 (48)
  SR+2      HCO3-     0.12 (75)
  NA+       CO3-2     0.0399 (48)                                      1.79E-3 (81)
  K+        CO3-2     0.1488 (48)                                      1.788E-3 (81)
  SR+2      CO3-2   -11.9 (75)
B1
  NA+       CL-       0.2664 (49)                                      6.1608E-5 (120) 1.0715E-6 (120)
  K+        CL-       0.2122 (48)                                     10.71E-4 (121)
  MG+2      CL-       1.6815 (48)                                      3.6525E-3 (86)
```

| | | | | | |
|---|---|---|---|---|---|
| CA+2 | CL- | 1.614 (48) | | | 3.9E-3 (121) |
| MGOH+ | CL- | 1.658 (48) | | | |
| H+ | CL- | 0.2945 (48) | | | 1.419E-4 (121) |
| LI+ | CL- | 0.3074 (89) | | | 5.366E-4 (121) |
| SR+2 | CL- | 1.66725 (89) | | | 2.8425E-3 (121) |
| FE+2 | CL- | 1.53225 (89) | | | |
| MN+2 | CL- | 1.55025 (89) | | | |
| BA+2 | CL- | 1.49625 (89) | | | 3.2325E-3 (121) |
| NA+ | BR- | 0.2791 (89) | | | 10.79E-4 (121) |
| K+ | BR- | 0.2212 (89) | | | 17.40E-4 (121) |
| H+ | BR- | 0.3564 (89) | | | 4.467E-4 (121) |
| MG+2 | BR- | 1.75275 (89) | | | 3.8625E-3 (121) |
| CA+2 | BR- | 1.613 (89) | | | 6.0375E-3 (121) |
| LI+ | BR- | 0.2547 (89) | | | 6.636E-4 (121) |
| SR+2 | BR- | 1.7115 (89) | | | 6.5325E-3 (121) |
| BA+2 | BR- | 1.56975 (89) | | | 6.78E-3 (121) |
| NA+ | SO4-2 | 1.113 (48) | | | 5.6325E-3 (121) |
| K+ | SO4-2 | 0.77925 (48) | | | 6.6975E-3 (121) |
| MG+2 | SO4-2 | 3.343 (48) | | | 1.53E-2 (121) |
| CA+2 | SO4-2 | 3.1973 (48) | | | 5.46E-2 (121) |
| LI+ | SO4-2 | 1.2705 (89) | | | 1.41E-3 (121) |
| SR+2 | SO4-2 | 2.88 (102) | | | 27.0 (102) |
| FE+2 | SO4-2 | 3.063 (103) | | | |
| MN+2 | SO4-2 | 2.9511 (40) | | | |
| NA+ | HSO4- | 0.398 (48) | | | |
| K+ | HSO4- | 0.1735 (48) | | | |
| MG+2 | HSO4- | 1.729 (48) | | | |
| CA+2 | HSO4- | 2.53 (48) | | | |
| H+ | HSO4- | 0.5556 (48) | | | |
| FE+2 | HSO4- | 3.48 (103) | | | |
| NA+ | OH- | 0.253 (48) | | | 1.34E-4 (121) |
| K+ | OH- | 0.32 (48) | | | |
| CA+2 | OH- | -0.2303 (48) | | | |
| LI+ | OH- | 0.14 (89) | | | |
| BA+2 | OH- | 1.2 (89) | | | |
| NA+ | HCO3- | 0.0411 (48) | | | 1.10E-3 (81) |
| K+ | HCO3- | -0.013 (48) | | | 1.104E-3 (81) |
| MG+2 | HCO3- | 0.6072 (48) | | | |
| CA+2 | HCO3- | 2.977 (48) | | | |
| NA+ | CO3-2 | 1.389 (48) | | | 2.05E-3 (81) |
| K+ | CO3-2 | 1.43 (48) | | | 2.051E-3 (81) |
| B2 | | | | | |
| MG+2 | SO4-2 | -37.23 (48) | | | -0.253 (121) |
| CA+2 | SO4-2 | -54.24 (48) | | | -0.516 (121) |
| SR+2 | SO4-2 | -41.8 (48) | | | -0.42 (102) |
| FE+2 | SO4-2 | -42.0 (103) | | | |
| MN+2 | SO4-2 | -40.0 (40) | | | |
| CA+2 | OH- | -5.72 (48) | | | |
| CO | | | | | |
| NA+ | CL- | 0.00127 (48) | 33.317 (120) | 0.09421 (120) | -4.655E-5 (120) |
| K+ | CL- | -0.00084 (48) | | | -5.095E-5 (121) |
| MG+2 | CL- | 0.00519 (48) | | | -1.6493266 (121) |
| CA+2 | CL- | -0.00034 (48) | | | |
| H+ | CL- | 0.0008 (48) | | | 6.213E-5 (121) |
| LI+ | CL- | 0.00359 (89) | | | -4.520E-5 (121) |

| | | | |
|---|---|---|---|
| SR+2 | CL- | -0.00130461 (89) | |
| FE+2 | CL- | -0.00860725 (89) | |
| MN+2 | CL- | -0.0204972 (89) | |
| BA+2 | CL- | -0.0193782 (89) | -1.5379573 (121) |
| NA+ | BR- | 0.00116 (89) | -9.30E-5 (121) |
| K+ | BR- | -0.00180 (89) | -7.004E-5 (121) |
| H+ | BR- | 0.00827 (89) | -5.685E-5 (121) |
| MG+2 | BR- | 0.00312 (89) | |
| CA+2 | BR- | -0.00257 (89) | |
| LI+ | BR- | 0.0053 (89) | -2.813E-5 (121) |
| SR+2 | BR- | 0.00122506 (89) | |
| BA+2 | BR- | -0.0159576 (89) | |
| NA+ | SO4-2 | 0.00497 (48) | -4.879037E-4 (121) |
| MG+2 | SO4-2 | 0.025 (48) | 0.523E-3 (121) |
| H+ | SO4-2 | 0.0438 (48) | |
| LI+ | SO4-2 | 0.0039933B (89) | -2.3334525 (121) |
| SR+2 | SO4-2 | 0.019 (102) | 3.0E-3 (102) |
| FE+2 | SO4-2 | 0.0209 (103) | |
| MN+2 | SO4-2 | 0.01636 (40) | |
| NA+ | OH- | 0.0044 (48) | -18.94E-5 (121) |
| K+ | OH- | 0.0041 (48) | |
| K+ | HCO3- | -0.008 (48) | |
| NA+ | CO3-2 | 0.0044 (48) | |
| K+ | CO3-2 | -0.0015 (48) | |
| THETA | | | |
| K+ | NA+ | -0.012 (48) | |
| MG+2 | NA+ | 0.07 (48) | |
| CA+2 | NA+ | 0.07 (48) | |
| H+ | NA+ | 0.036 (48) | |
| CA+2 | K+ | 0.032 (48) | |
| H+ | K+ | 0.005 (48) | |
| CA+2 | MG+2 | 0.007 (48) | |
| H+ | MG+2 | 0.1 (48) | |
| H+ | CA+2 | 0.092 (48) | |
| SO4-2 | CL- | 0.02 (48) | |
| HSO4- | CL- | -0.006 (48) | |
| OH- | CL- | -0.05 (48) | |
| HCO3- | CL- | 0.03 (48) | |
| CO3-2 | CL- | -0.02 (48) | |
| OH- | BR- | -0.065 (88) | |
| OH- | SO4-2 | -0.013 (48) | |
| HCO3- | SO4-2 | 0.01 (48) | |
| CO3-2 | SO4-2 | 0.02 (48) | |
| CO3-2 | OH- | 0.1 (48) | |
| CO3-2 | HCO3- | -0.04 (48) | |
| LAMDA | | | |
| NA+ | H2CO3 | 0.1 (48) | |
| K+ | H2CO3 | 0.051 (48) | |
| MG+2 | H2CO3 | 0.183 (48) | |
| CA+2 | H2CO3 | 0.183 (48) | |
| CL- | H2CO3 | -0.005 (48) | |
| SO4-2 | H2CO3 | 0.097 (48) | |
| HSO4- | H2CO3 | -0.003 (48) | |
| PSI | | | |
| NA+ | K+ | CL- -0.0018 (48) | |

Attachment C.6 - continued

| | | | |
|---|---|---|---|
| NA+ | K+ | BR- | -0.0022 (88) |
| NA+ | K+ | SO4-2 | -0.010 (48) |
| NA+ | K+ | HCO3- | -0.003 (48) |
| NA+ | K+ | CO3-2 | 0.003 (48) |
| NA+ | CA+2 | CL- | -0.007 (48) |
| NA+ | CA+2 | SO4-2 | -0.055 (48) |
| NA+ | MG+2 | CL- | -0.012 (48) |
| NA+ | MG+2 | SO4-2 | -0.015 (48) |
| NA+ | H+ | CL- | -0.004 (48) |
| NA+ | H+ | BR- | -0.012 (88) |
| NA+ | H+ | HSO4- | -0.0129 (48) |
| K+ | CA+2 | CL- | -0.025 (48) |
| K+ | MG+2 | CL- | -0.022 (48) |
| K+ | MG+2 | SO4-2 | -0.048 (48) |
| K+ | H+ | CL- | -0.011 (48) |
| K+ | H+ | BR- | -0.021 (88) |
| K+ | H+ | SO4-2 | 0.197 (48) |
| K+ | H+ | HSO4- | -0.0265 (48) |
| CA+2 | MG+2 | CL- | -0.012 (48) |
| CA+2 | MG+2 | SO4-2 | 0.024 (48) |
| CA+2 | H+ | CL- | -0.015 (48) |
| MG+2 | MGOH+ | CL- | 0.028 (48) |
| MG+2 | H+ | CL- | -0.011 (48) |
| MG+2 | H+ | HSO4- | -0.0178 (48) |
| CL- | BR- | K+ | 0.0000 (88) |
| CL- | SO4-2 | NA+ | 0.0014 (48) |
| CL- | SO4-2 | CA+2 | -0.018 (48) |
| CL- | SO4-2 | MG+2 | -0.004 (48) |
| CL- | HSO4- | NA+ | -0.006 (48) |
| CL- | HSO4- | H+ | 0.013 (48) |
| CL- | OH- | NA+ | -0.006 (48) |
| CL- | OH- | K+ | -0.006 (48) |
| CL- | OH- | CA+2 | -0.025 (48) |
| CL- | HCO3- | NA+ | -0.015 (48) |
| CL- | HCO3- | MG+2 | -0.096 (48) |
| CL- | CO3-2 | NA+ | 0.0085 (48) |
| CL- | CO3-2 | K+ | 0.004 (48) |
| SO4-2 | HSO4- | NA+ | -0.0094 (48) |
| SO4-2 | HSO4- | K+ | -0.0677 (48) |
| SO4-2 | HSO4- | MG+2 | -0.0425 (48) |
| SO4-2 | OH- | NA+ | -0.009 (48) |
| SO4-2 | OH- | K+ | -0.050 (48) |
| SO4-2 | HCO3- | NA+ | -0.005 (48) |
| SO4-2 | HCO3- | MG+2 | -0.161 (48) |
| SO4-2 | CO3-2 | NA+ | -0.005 (48) |
| SO4-2 | CO3-2 | K+ | -0.009 (48) |
| OH- | CO3-2 | NA+ | -0.017 (48) |
| OH- | CO3-2 | K+ | -0.01 (48) |
| OH- | BR- | NA+ | -0.018 (88) |
| OH- | BR- | K+ | -0.014 (88) |
| HCO3- | CO3-2 | NA+ | 0.002 (48) |
| HCO3- | CO3-2 | K+ | 0.012 (48) |

Attachment D. -- Listing of the source code to program PHRQPITZ

```
      PROGRAM PHRQPITZ                                                  00010
C          ************************************************           00020
C                                                                     00030
C                          PROGRAM PHRQPITZ                           00040
C                                                                     00050
C     L.N. PLUMMER, D.L. PARKHURST, G.W. FLEMING, AND S.A. DUNKLE     00060
C                                                                     00070
C                 VERSION CURRENT - NOVEMBER, 1988                    00080
C                                                                     00090
C          ************************************************           00100
C                                                                     00110
C                                                                     00120
$INSERT COMMON.BLOCKS                                                 00130
      OPEN (UNIT=11,FILE='PHRQPITZ.DATA',STATUS='OLD')                00140
      MAXT=30                                                         00150
      MAXS=250                                                        00160
      MAXT1=31                                                        00170
      MAXM=20                                                         00180
      MAXEQ=50                                                        00190
      DO 10 I=1,MAXS                                                  00200
      NSP(I)=0                                                        00210
   10 CONTINUE                                                        00220
      IFILE=11                                                        00230
      CALL RDATA(IFILE)                                               00240
      CALL INITPZ                                                     00250
   20 CONTINUE                                                        00260
C          SINGLE SIMULATION LOOP                                     00270
      CALL READ                                                       00280
      CLOSE (UNIT=11)                                                 00290
      ISTEP=0                                                         00300
C          SOLVE INITIAL SOLUTIONS                                    00310
      DO 40 ISOL=1,2                                                  00320
      IF (ISOLV(ISOL).EQ.0) GO TO 40                                  00330
      JSOL=ISOL                                                       00340
      CALL SOLN(JSOL)                                                 00350
      IESPEC=IOPT(2)                                                  00360
      IF (IOPT(2).GE.2) IESPEC=0                                      00370
      CALL PICK1                                                      00380
      CALL PTOT                                                       00390
      CALL KTEMP                                                      00400
      CALL MODEL                                                      00410
      IF (IOPT(2).LT.2) GO TO 30                                      00420
      IESPEC=LNEG                                                     00430
      IF (ELECT.LT.0D0) IESPEC=LPOS                                   00440
      CALL PICK1                                                      00450
      CALL KTEMP                                                      00460
      CALL MODEL                                                      00470
      TOTAL(ISOL,IESPEC)=TOT(IESPEC)                                  00480
   30 CONTINUE                                                        00490
      IF (IASPEC.GT.0) TOTAL(ISOL,IASPEC)=TOT(IASPEC)                 00500
      CALL THORIT(T)                                                  00510
      TH(ISOL)=T                                                      00520
      THOR=T                                                          00530
      DIFFZ(ISOL)=ELECT                                               00540
```

```
      CALL PSPEC                                                        00550
      CALL PLOOK                                                        00560
   40 CONTINUE                                                          00570
      IF (IOPT(3).EQ.0) GO TO 20                                        00580
C          TAKE REACTION STEPS                                          00590
      DO 50 ISTEP=1,MAXO(1,NSTEPS)                                      00600
      CALL STEP                                                         00610
      CALL PTOT                                                         00620
      CALL PICK2                                                        00630
      CALL KTEMP                                                        00640
      CALL KMINO                                                        00650
      CALL MODEL                                                        00660
      CALL PPHASE                                                       00670
      CALL PLOOK                                                        00680
      CALL PTOT                                                         00690
      CALL PSPEC                                                        00700
   50 CONTINUE                                                          00710
      CALL SAVE                                                         00720
      GO TO 20                                                          00730
      END                                                               00740
C     ----------                                                        00750
      BLOCK DATA                                                        00760
C     ----------                                                        00770
C                                                                       00780
C     SEE SUBROUTINE PITZER                                             00790
C                                                                       00800
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               00810
      INTEGER TRANS(40),IN(20)                                          00820
      LOGICAL LELEM(4:30)                                               00830
      DOUBLE PRECISION LAM(40,20),BCX(4,20,21:40)                       00840
      DOUBLE PRECISION PSI(40,40,40),BC(4,20,21:40,5),THETA(40,40)      00850
      COMMON / MX1 / BC                                                 00860
      COMMON / MX3 / BCX,OTEMP                                          00870
      COMMON / MX6 / LAM,TRANS,PSI,IN                                   00880
      COMMON / MX7 / THETA                                              00890
      COMMON / MX8 / AK,BK,DK                                           00900
      COMMON / MX9 / ALPHA                                              00910
      COMMON / MXO / B                                                  00920
      COMMON / PI1C / SPECS,NEUTRL                                      00930
      COMMON / PI1 / M1,M2,M3                                           00940
      COMMON / PEL / LELEM                                              00950
      CHARACTER *8 SPECS(40),NEUTRL(20)                                 00960
      DIMENSION ALPHA(5),Z(40)                                          00970
      DIMENSION AK(0:20,2),BK(0:22),DK(0:22)                            00980
C                                                                       00990
C     LINES 01020-01300 FROM HAAR, GALLAGHER, AND KELL (1984)           01000
C                                                                       01010
      COMMON /ACONST/ GASCON,TZ,AA,ZB,DZB,YB                            01020
      COMMON /NCONST/ G(40),II(40),JJ(40),NC                            01030
      COMMON /ELLCON/ G1,G2,GF,B1,B2,B1T,B2T,B1TT,B2TT                  01040
      COMMON /BCONST/ P(10),Q(10)                                       01050
      COMMON /ADDCON/ ATZ(4),ADZ(4),AAT(4),AAD(4)                       01060
      DATA ATZ/2*64.D1,641.6D0,27.D1/,ADZ/3*.319D0,1.55D0/,AAT/2*2.D4   01070
     1,4.D4,25.D0/,AAD/34.D0,4.D1,3.D1,1.05D3/                          01080
      DATA GASCON/.461522D0/,TZ/647.073D0/,AA/1.D0/,NC/36/              01090
      DATA G1,G2,GF/11.D0,44.333333333333D0,3.5D0/                      01100
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      DATA P/.7478629D0,-.3540782D0,2*0.D0,.007159876D0,0.D0,-.003528426 01110
     1D0,3*0.D0/                                                         01120
      DATA Q/1.1278334D0,0.D0,-.5944001D0,-5.010996D0,0.D0,.63684256D0,  01130
     1  4*0.D0/                                                          01140
      DATA G/-.53062968529023D3,.22744901424408D4,.78779333020687D3      01150
     1,-.69830527374994D2,.17863832875422D5,-.39514731563338D5           01160
     2,.33803884280753D5,-.13855050202703D5,-.2563743661326OD6           01170
     3,.48212575981415D6,-.34183016969660D6, .12223156417448D6          01180
     4,.11797433655832D7,-.21734810110373D7, .10829952168620D7          01190
     5,-.25441998064049D6,-.31377774947767D7,.52911910757704D7          01200
     6,-.13802577177877D7,-.25109914369001D6, .46561826115608D7         01210
     7,-.72752773275387D7,.41774246148294D6,.14016358244614D7           01220
     8,-.31555231392127D7,.47929666384584D7,.40912664781209D6           01230
     9,-.13626369388386D7, .69625220862664D6,-.10834900096447D7         01240
     A,-.22722827401688D6,.38365486000660D6,.68833257944332D4           01250
     B,.21757245522644D5,-.26627944829770D4,-.70730418082074D5          01260
     C,-.225D0,-1.68D0,.055D0,-93.0D0/                                  01270
      DATA II/4*0,4*1,4*2,4*3,4*4,4*5,4*6,4*8,2*2,0,4,3*2,4/            01280
      DATA JJ/2,3,5,7,2,3,5,7,2,3,5,7,2,3,5,7,2,3,5,7,2,3,5,7           01290
     1,2,3,5,7,1,3*4,0,2,0,0/                                           01300
      DATA M1,M3,M2 / 2*0,20 /, LELEM / 27*.FALSE. /                    01310
      DATA BK,DK / 46*0.0D0 /                                           01320
      DATA BC,LAM,THETA / 10400*0.0D0 /                                 01330
      DATA BCX / 1600*0.0 /, OTEMP / 0.0 /                              01340
      DATA B / 1.2D0 /                                                  01350
C                                                                       01360
C     AK IS USED TO CALCULATE HIGHER ORDER ELECTROSTATIC TERMS IN       01370
C     SUBROUTINE PITZER                                                 01380
C                                                                       01390
      DATA AK  / 1.925154014814667,-.060076477753119,-.029779077456514  01400
     1,          -.007299499690937,0.000388260636404,0.000636874599598  01410
     2,          0.000036583601823,-.000045036975204,-.000004537895710  01420
     3,          0.000002937706971,0.000000396566462,-.000000202099617  01430
     4,          -.000000025267769,0.000000013522610,0.000000001229405  01440
     5,          -.000000000821969,-.000000000050847,0.000000000046333  01450
     6,          0.000000000001943,-.000000000002563,-.000000000010991  01460
     7,          0.628023320520852,0.462762985338493,0.150044637187895  01470
     8,          -.028796057604906,-.036552745910311,-.001668087945272  01480
     9,          0.006519840398744,0.001130378079086,-.000887171310131  01490
     A,          -.000242107641309,0.000087294451594,0.000034682122751  01500
     B,          -.000004583768938,-.000003548684306,-.000000250453880  01510
     C,          0.000000216991779,0.000000080779570,0.000000004558555  01520
     D,          -.000000006944757,-.000000002849257,0.000000000237816/ 01530
      DATA ALPHA / 2.0D0, 1.4D0, 12.0D0, 2.0D0, 50.0D0 /                01540
      END                                                               01550
      SUBROUTINE MODEL                                                  01560
$INSERT COMMON.BLOCKS                                                   01570
      CALL SET                                                          01580
      ITER=1                                                            01590
      ITER1=0                                                           01600
   10 CONTINUE                                                          01610
      ITER1=ITER1+1                                                     01620
      IF (IOPT(8).EQ.1) WRITE (6,25) ITER,ITER1                         01630
   25 FORMAT(/' BEGINNING OF ITERATION ',I4,'  SUB-ITERATION ',I4,'.')  01640
      DO 20 N=1,LASTS                                                   01650
      LG(N)=0.0D0                                                       01660
```

```
   20 CONTINUE                                                          01670
      CALL PITZER(M,LG,AW,MU,IOPT(10))                                  01680
      TOT(3)=AW                                                         01690
      LA(3)=DLOG10(AW)                                                  01700
      IF (IOPT(8).EQ.1) WRITE (6,15) MU,AW                              01710
   15 FORMAT (' AFTER SUBROUTINE PITZER ',                              01720
     1   '   MU  =',1PD15.7,'   AW',0PF15.7)                            01730
      CALL ZEROAR                                                       01740
      CALL AQMOD                                                        01750
      CALL CHECK(ISTAT)                                                 01760
      IF (ISTAT.EQ.0) THEN                                              01770
         RETURN                                                         01780
      ELSE IF (ISTAT.EQ.1) THEN                                         01790
         KMIN=NMINS                                                     01800
         CALL SOLVE                                                     01810
         CALL RESET                                                     01820
         ITER=ITER+1                                                    01830
         ITER1=0                                                        01840
         GO TO 10                                                       01850
      ELSE IF (ISTAT.EQ.2) THEN                                         01860
         CALL RESET                                                     01870
         GO TO 10                                                       01880
      END IF                                                            01890
      STOP 'SUBROUTINE MODEL, UNKNOWN STATUS'                           01900
      END                                                               01910
      SUBROUTINE SET                                                    01920
$INSERT COMMON.BLOCKS                                                   01930
      LA(1)=DLOG10(TOT(1))                                              01940
      LA(2)=DLOG10(TOT(2))                                              01950
      LA(3)=0.0D0                                                       01960
      PH=-LA(1)                                                         01970
      IF(LA(1).GT.-1.0D0) LA(1)=-1.0D0                                  01980
      M(1)=1D1**(LA(1))                                                 01990
      LG(1)=0.0                                                         02000
      DO 20 I=4,MAXS                                                    02010
      M(I)=0.0D0                                                        02020
      LG(I)=0.0                                                         02030
   20 CONTINUE                                                          02040
      MU=0D0                                                            02050
      DO 10 I=4,LASTT                                                   02060
      IF (IIN(I).LE.0) GO TO 10                                         02070
      IF (TOT(I).LE.0.0D0) TOT(I)=1D-10                                 02080
      IF (I.EQ.IASPEC) THEN                                             02090
C            SET CARBON SPECIES                                         02100
         M(15)=TOT(I)*1D-3                                              02110
         IF (PH.LT.6.3) M(35)=TOT(I)*0.8                                02120
         IF (PH.LT.10.3.AND.PH.GE.6.3) THEN                             02130
            M(34)=TOT(I)*0.8                                            02140
            MU=MU+0.5*M(34)                                             02150
         END IF                                                         02160
         IF (PH.GE.10.3) M(15)=TOT(I)*0.8                               02170
      ELSE                                                              02180
         M(I)=TOT(I)                                                    02190
      END IF                                                            02200
      MU=MU+M(I)*ZSP(I)*ZSP(I)*0.5D0                                    02210
      LA(I)=DLOG10(M(I))                                                02220
```

```
   10 CONTINUE                                                          02230
      RETURN                                                            02240
      END                                                               02250
      SUBROUTINE GAMMA                                                  02260
$INSERT COMMON.BLOCKS                                                   02270
C                                                                       02280
C             THIS SUBROUTINE IS NOT USED                               02290
C                                                                       02300
      SAVE DSUM                                                         02310
C          CALCULATE IONIC STRENGTH                                     02320
      DOLDMU=MU                                                         02330
      SUM=M(1)                                                          02340
      MU=M(1)                                                           02350
      DO 10 I=4,LASTS                                                   02360
      IF (SFLAG(I).EQ.0) GO TO 10                                       02370
      SUM=SUM+M(I)                                                      02380
      MU=MU+M(I)*ZSP(I)*ZSP(I)                                          02390
   10 CONTINUE                                                          02400
      IF (ITER.EQ.1) GO TO 20                                           02410
      IF (SUM-DSUM.LT.1D0) GO TO 20                                     02420
      SUM=DSUM+1D0                                                      02430
   20 CONTINUE                                                          02440
      DSUM=SUM                                                          02450
      MU=MU*0.5                                                         02460
      MU=DMIN1(MU,1D1)                                                  02470
      IF (ITER.EQ.1) GO TO 30                                           02480
      IF (DABS(DOLDMU-MU).LE.0.75D0) GO TO 30                           02490
      MU=DOLDMU+((MU-DOLDMU)/DABS(MU-DOLDMU))*0.5D0                     02500
   30 CONTINUE                                                          02510
      MUHALF=DSQRT(MU)                                                  02520
C          ACTIVITY OF WATER                                            02530
      AH2O=1.0-SUM*0.017                                                02540
      IF (SUM.GT.40.0D0) AH2O=0.32                                      02550
      LA(3)=DLOG10(AH2O)                                                02560
      TOT(3)=AH2O                                                       02570
C          CALCULATE ACTIVITY COEFFICIENTS                              02580
      AMU=-A*MUHALF                                                     02590
      BMU=B*MUHALF                                                      02600
      CMU=-A*(MUHALF/(1.0+MUHALF)-0.3*MU)                               02610
      ZCHRG=0.1*MU                                                      02620
      LG(1)=AMU/(1.0+DHA(1)*BMU)                                        02630
      IF (IOPT(6).EQ.1) LG(1)=CMU                                       02640
      LG(2)=0.0D0                                                       02650
      LG(3)=0.0D0                                                       02660
      DO 70 I=4,LASTS                                                   02670
      IF (SFLAG(I).EQ.0) GO TO 70                                       02680
      IF (DABS(ZSP(I)).LE.1.0D-40) GO TO 40                             02690
      IF (GFLAG(I).EQ.1) GO TO 50                                       02700
      IF (DHA(I).LE.0D0) GOTO 60                                        02710
      IF (IOPT(6).EQ.1) GO TO 60                                        02720
      LG(I)=AMU*ZSP(I)*ZSP(I)/(1.0+DHA(I)*BMU)                          02730
      GO TO 70                                                          02740
   40 LG(I)=ZCHRG                                                       02750
      GO TO 70                                                          02760
   50 LG(I)=AMU*ZSP(I)*ZSP(I)/(1.0+ADHSP(I,1)*BMU)+ADHSP(I,2)*MU        02770
      GO TO 70                                                          02780
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   60 LG(I)=CMU*ZSP(I)*ZSP(I)                                          02790
   70 CONTINUE                                                         02800
C          LG FOR CARBONIC ACID                                        02810
      RETURN                                                           02820
      END                                                              02830
      SUBROUTINE AQMOD                                                 02840
$INSERT COMMON.BLOCKS                                                  02850
      DIMENSION OLDG(250),GAMMA(250),DELGAM(250)                       02860
      COMMON /GBLOCK/ OLDG,OLDMU,OLDAW,GAMMA,DELGAM                    02870
      DIMENSION DM2(30)                                                02880
C                                                                      02890
C             INITIALIZE VARIABLES FOR THIS ITERATION                  02900
C                                                                      02910
      ELECT=0.0D0                                                      02920
      THSOLN=0.0D0                                                     02930
      DALKS=0D0                                                        02940
      IF(ITER.LE.1) THEN                                               02950
         OLDMU=0.0D0                                                   02960
         DO 7 I=1,LASTS                                                02970
         OLDG(I)=0.99D0                                                02980
    7    CONTINUE                                                      02990
      END IF                                                           03000
      DMU=MU-OLDMU                                                     03010
      IF(DABS(DMU).LE.1.0D-40) DMU=1.0D0                               03020
C             SET GAMMA ARRAY                                          03030
      DO 8 I=1,LASTS                                                   03040
      GAMMA(I)=1D1**LG(I)                                              03050
    8 CONTINUE                                                         03060
      SUM=M(1)                                                         03070
C             CALCULATE DELTA ACTIVITY OF WATER PER MOLE SOLUTE        03080
      DO 9 I=4,LASTS                                                   03090
      IF (SFLAG(I).EQ.0) GO TO 9                                       03100
      SUM=SUM+M(I)                                                     03110
    9 CONTINUE                                                         03120
      DAW=-(1D0-TOT(3))/SUM                                            03130
      IF (IOPT(8).GT.0) WRITE(6,4) DAW                                 03140
    4 FORMAT(' DELTA ACTIVITY WATER PER MOLE SOLUTE ',1PD12.4)         03150
      DAW=DAW/TOT(3)                                                   03160
C             INITIALIZE ACTIVITY OF WATER AND IONIC STRENGTH ARRAYS    03170
      DO 2 I=1,50                                                      03180
      AR(50,I)=0D0                                                     03190
      AR(30,I)=0D0                                                     03200
      AR(I,30)=0D0                                                     03210
    2 CONTINUE                                                         03220
C                                                                      03230
C             SET ACTIVITY OF MASTER SPECIES USING MOLALITY AND GAMMA   03240
C                                                                      03250
      IF(IESPEC.NE.1) M(1)=1D1**(LA(1)-LG(1))                          03260
C             HOLD HYDROXIDE CONSTANT FOR ENTIRE ITERATION IF PH > 12   03270
      IF(M(1).GT.1D-12.AND.M(31).LT.5D-3) THEN                         03280
         LA(1)=DLOG10(M(1))+LG(1)                                      03290
         LM(31)=LKSP(31)+LA(3)-LG(31)-LA(1)                            03300
         M(31)=1D1**LM(31)                                             03310
      ELSE                                                             03320
         IF(IESPEC.EQ.1) THEN                                          03330
            LA(1)=LKSP(31)+LA(3)-LM(31)-LG(31)                         03340
```

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            LM(1)=LA(1)-LG(1)                                          03350
            M(1)=1D1**LM(1)                                            03360
         END IF                                                        03370
      END IF                                                           03380
      DO 5 I=4,30                                                      03390
      IF(SFLAG(I).GT.0) LA(I)=DLOG10(M(I))+LG(I)                       03400
    5 CONTINUE                                                         03410
C                                                                      03420
C             RECALCULATE MOLALITIES OF MASTER SPECIES TO OBTAIN       03430
C             MASS BALANCE.  UPDATE CATIONS THEN ANIONS.               03440
C                                                                      03450
      DO 80 IZ=1,2                                                     03460
      DO 10 I=1,MAXT                                                   03470
      DM2(I)=0D0                                                       03480
   10 CONTINUE                                                         03490
C             CALCULATE MOLALITIES WITH NEW GAMMAS, NEW ACTIVITIES.    03500
      DO 40 I=1,LASTS                                                  03510
      IF (SFLAG(I).EQ.0) GO TO 40                                      03520
      K=NSP(I)                                                         03530
      DM=LKSP(I)-LG(I)                                                 03540
      DO 20 J=1,K                                                      03550
      DM=DM+LA(LSP(I,J))*CSP(I,J)                                      03560
   20 CONTINUE                                                         03570
      IF (I.NE.31) THEN                                                03580
         LM(I)=DM                                                      03590
         M(I)=UNDER(DM)                                                03600
      END IF                                                           03610
      IF (DABS(M(I)).LE.1.0D-40) GO TO 40                              03620
C             SUM MOLALITIES FOR EACH ELEMENT                          03630
      DO 30 I1=1,K                                                     03640
      DM=M(I)*CSP(I,I1)                                                03650
      K2=LSP(I,I1)                                                     03660
      IF (K2.LT.4) GO TO 30                                            03670
      AR(K2,K2)=AR(K2,K2)+DM                                           03680
   30 CONTINUE                                                         03690
   40 CONTINUE                                                         03700
C             CALCULATE NEW MOLALITIES OF MASTER SPECIES               03710
      DO 70 K=4,LASTT                                                  03720
      IF (IIN(K).EQ.0) GO TO 70                                        03730
      IF (IESPEC.EQ.K) GO TO 60                                        03740
      IF (IASPEC.EQ.K) GO TO 60                                        03750
      IF (ZSP(K).LE.0.0.AND.IZ.EQ.1) GO TO 60                          03760
      IF (ZSP(K).GT.0.0.AND.IZ.EQ.2) GO TO 60                          03770
      IF (AR(K,K).LE.0D0) AR(K,K)=1D-35                                03780
      LM(K)=LM(K)+(DLOG10(TOT(K))-DLOG10(AR(K,K)))                     03790
      LA(K)=LM(K)+LG(K)                                                03800
   60 CONTINUE                                                         03810
      AR(K,K)=0D0                                                      03820
   70 CONTINUE                                                         03830
   80 CONTINUE                                                         03840
      ZSP(2)=0.0D0                                                     03850
C                                                                      03860
C          SET UP ARRAYS FOR SUBROUTINE SOLVE                          03870
C                                                                      03880
      DO 120 I=1,LASTS                                                 03890
      IF (SFLAG(I).EQ.0) GO TO 120                                     03900
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      IF (I.EQ.2.OR.I.EQ.3) GO TO 120                                   03910
      K=NSP(I)                                                          03920
      DM=LKSP(I)-LG(I)                                                  03930
C          CALCULATE MOLALITY                                           03940
      DO 90 J=1,K                                                       03950
      DM=DM+LA(LSP(I,J))*CSP(I,J)                                       03960
   90 CONTINUE                                                          03970
      IF (I.NE.31) THEN                                                 03980
         LM(I)=DM                                                       03990
         M(I)=UNDER(DM)                                                 04000
      END IF                                                            04010
      IF (DABS(M(I)).LE.1.0D-40) GO TO 120                              04020
C             CALCULATE EFFECT OF IONIC STRENGTH ON GAMMA              04030
      DGI=0D0                                                           04040
      IF(DABS(DMU).GT.1D-11)                                            04050
     1   DGI=(GAMMA(I)-OLDG(I))/DMU/GAMMA(I)*M(I)                       04060
      DELGAM(I)=(GAMMA(I)-OLDG(I))/DMU                                  04070
C             ELECT, THOR, ALK, MU, AND H2O EQNS.                      04080
      AR(1,30)=AR(1,30)-DGI*ZSP(I)                                      04090
      AR(2,30)=AR(2,30)-DGI*THSP(I)                                     04100
      AR(3,30)=AR(3,30)-DGI*ALKSP(I)                                    04110
      AR(30,30)=AR(30,30)-DGI*0.5D0*ZSP(I)*ZSP(I)                       04120
      AR(50,30)=AR(50,30)-DGI*DAW                                       04130
C             MORE TERMS FOR MATRIX                                    04140
      DO 110 I1=1,K                                                     04150
      DM=M(I)*CSP(I,I1)                                                 04160
      K2=LSP(I,I1)                                                      04170
      DG=0D0                                                            04180
      IF(DABS(DMU).GT.1D-11)                                            04190
     1   DG=(GAMMA(K2)-OLDG(K2))/DMU/GAMMA(K2)*DM                       04200
C             EFFECT ON MOLALITY FROM CHANGE IN IONIC STRENGTH          04210
      IF(K2.GT.3) AR(K2,30)=AR(K2,30)-DGI*CSP(I,I1)                     04220
C                   MASS BALANCE                                       04230
      DO 100 J1=1,K                                                     04240
      K1=LSP(I,J1)                                                      04250
      IF (K1.LT.4) GO TO 100                                            04260
      AR(K1,K2)=AR(K1,K2)+DM*CSP(I,J1)                                  04270
      AR(K1,30)=AR(K1,30)+DG*CSP(I,J1)                                  04280
  100 CONTINUE                                                          04290
C                   IONIC STRENGTH                                     04300
      AR(30,K2)=AR(30,K2)+DM*0.5D0*ZSP(I)*ZSP(I)                        04310
      AR(30,30)=AR(30,30)+DG*0.5D0*ZSP(I)*ZSP(I)                        04320
C                   ELECTRICAL BALANCE                                 04330
      AR(1,K2)=AR(1,K2)+DM*ZSP(I)                                       04340
      AR(1,30)=AR(1,30)+DG*ZSP(I)                                       04350
C                   THOR BALANCE                                       04360
      AR(2,K2)=AR(2,K2)+DM*THSP(I)                                      04370
      AR(2,30)=AR(2,30)+DG*THSP(I)                                      04380
C                   ALKALINITY EQUATION                                04390
      AR(3,K2)=AR(3,K2)+DM*ALKSP(I)                                     04400
      AR(3,30)=AR(3,30)+DG*ALKSP(I)                                     04410
C                   H2O DERIVATIVE                                     04420
      AR(50,K2)=AR(50,K2)+DM*DAW                                        04430
      AR(50,30)=AR(50,30)+DG*DAW                                        04440
  110 CONTINUE                                                          04450
      THSOLN=THSOLN+M(I)*THSP(I)                                        04460
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      ELECT=ELECT+M(I)*ZSP(I)                                          04470
      DALKS=DALKS+M(I)*ALKSP(I)                                        04480
  120 CONTINUE                                                         04490
      ZSP(2)=-1.0                                                      04500
C                                                                      04510
C                    H2O EQUATION                                      04520
C                                                                      04530
      AR(50,3)=AR(50,3)-1.0D0                                          04540
      AR(30,30)=AR(30,30)-1.0D0                                        04550
C     *****                                                            04560
      ENTRY SI                                                         04570
C     *****                                                            04580
      IF (NMINS.NE.0) THEN                                             04590
         DO 140 I=1,NMINS                                              04600
         J=MAXT+I                                                      04610
         K=NMIN(I)                                                     04620
C          CALCULATE INVERSE SATURATION INDEX                         04630
         DSI=LKMIN(I)                                                  04640
         DO 130 I1=1,K                                                 04650
         K1=LMIN(I,I1)                                                 04660
         IF(DABS(DMU).GT.1D-11) THEN                                   04670
            AR(J,30)=AR(J,30)+(GAMMA(K1)-OLDG(K1))/DMU/GAMMA(K1)       04680
     1      *CMIN(I,I1)                                                04690
            DG=(GAMMA(K1)-OLDG(K1))/DMU/GAMMA(K1)*CMIN(I,I1)           04700
         END IF                                                        04710
         DSI=DSI-LA(LMIN(I,I1))*CMIN(I,I1)                             04720
  130    CONTINUE                                                      04730
         CR(J)=DSI*DLOG(1D1)                                           04740
  140    CONTINUE                                                      04750
      END IF                                                           04760
      IF(IOPT(8).GT.0) THEN                                            04770
         WRITE(6,107)                                                  04780
  107    FORMAT(/'  I   SPECIES  DEL MU      GAMMA     ,              04790
     1   '  OLD GAMMA  ',' MOLALITY ')                                 04800
         DO 105 I=1,LASTS                                              04810
         IF (SFLAG(I).EQ.0) GO TO 105                                  04820
         D=(GAMMA(I)-OLDG(I))/DMU/GAMMA(I)                             04830
         DM=D*M(I)                                                     04840
         WRITE(6,106) I,SNAME(I),DMU,GAMMA(I),OLDG(I),M(I)             04850
  106    FORMAT(I4,1X,A8,1PD10.3,1P2D13.4,3D10.3)                      04860
  105    CONTINUE                                                      04870
      END IF                                                           04880
      RETURN                                                           04890
C                                                                      04900
      END                                                              04910
      SUBROUTINE CHECK(ISTAT)                                          04920
$INSERT COMMON.BLOCKS                                                  04930
      DIMENSION OLDG(250),GAMMA(250),DELGAM(250)                       04940
      COMMON /GBLOCK/ OLDG,OLDMU,OLDAW,GAMMA,DELGAM                    04950
      DOUBLE PRECISION MCLOSE                                          04960
      SAVE OLDMU1                                                      04970
      DATA ECLOSE,TCLOSE,THCLOS,MCLOSE /5D-9,1D-7,1D-7,1D-5/           04980
      DATA CHKMU /1D-3/                                                04990
      ICHECK=0                                                         05000
      JCHECK=0                                                         05010
C                                                                      05020
```

```
C             CALCULATE RESIDUAL ERROR                                  05030
C                                                                       05040
      CR(1)=DZOFF-ELECT                                                 05050
      CR(2)=THOR-THSOLN                                                 05060
      CR(3)=DALKT-DALKS                                                 05070
C          CALCULATE MASS BALANCE                                       05080
      THTOT=DABS(THOR)                                                  05090
      DO 10 I=4,LASTT                                                   05100
      IF (IIN(I).LE.0) GO TO 10                                         05110
      CR(I)=TOT(I)-AR(I,I)                                              05120
      THTOT=DABS(THSP(I))*TOT(I)+THTOT                                  05130
   10 CONTINUE                                                          05140
C                                                                       05150
C             CHECK IONIC STRENGTH                                      05160
C                                                                       05170
      IF(ITER1.GT.1) THEN                                               05180
         IF(DABS(MU-OLDMU1).GT.CHKMU) THEN                              05190
            JCHECK=1                                                    05200
            IF(IOPT(8).EQ.1) WRITE(6,18) DABS(MU-OLDMU1),CHKMU          05210
   18       FORMAT(' FAILED IONIC STRENGTH CHECK.  MU-ERROR ',1PD11.3,  05220
     1      ' TOLER ',1PD11.3)                                          05230
         END IF                                                         05240
      END IF                                                            05250
      OLDMU1=MU                                                         05260
C                                                                       05270
C             CHECK ELECTRICAL BALANCE                                  05280
C                                                                       05290
      DCHECK=1D1**(DABS(PH-7D0))*ECLOSE                                 05300
      DCHECK=DMIN1(DCHECK,1D-5)                                         05310
      IF (IESPEC.GT.0.AND.DABS(CR(1)).GT.DCHECK) THEN                   05320
         ICHECK=1                                                       05330
         IF (IOPT(8).EQ.1) THEN                                         05340
            WRITE (6,12) IESPEC,CR(1),DCHECK                            05350
   12       FORMAT(1X,'FAILED ELECTRICAL BALANCE. '                     05360
     1      ' E-SPECIES',I3,' E-ERROR',1PD11.3,' TOLER',D11.3)          05370
         END IF                                                         05380
      END IF                                                            05390
C                                                                       05400
C             CHECK THOR BALANCE                                        05410
C                                                                       05420
      IF (IIN(2).GT.0.AND.DABS(CR(2)).GT.THCLOS*THTOT) THEN             05430
         ICHECK=1                                                       05440
         IF (IOPT(8).EQ.1) THEN                                         05450
            WRITE (6,13) CR(2),THCLOS*THTOT                             05460
   13       FORMAT(1X,'FAILED THOR BALANCE. '                           05470
     1      ' THOR ERROR',1PD11.3,' THOR TOLERANCE',D11.3)              05480
         END IF                                                         05490
      END IF                                                            05500
C                                                                       05510
C             CHECK ALKALINITY                                          05520
C                                                                       05530
      IF (IASPEC.GT.0) THEN                                             05540
         IF(DABS(CR(3)).GT.TCLOSE*DALKT) THEN                           05550
            ICHECK=1                                                    05560
            IF (IOPT(8).EQ.1) THEN                                      05570
               WRITE (6,14) IASPEC,CR(3),TCLOSE*DALKT                   05580
```

```
   14          FORMAT(1X,'FAILED ALKALINITY BALANCE. '                    05590
     1         ' A-SPECIES',I3,' A-ERROR',1PD11.3,' TOLER',D11.3)         05600
            END IF                                                        05610
         END IF                                                           05620
      END IF                                                              05630
C                                                                         05640
C          CHECK MASS BALANCES                                            05650
C                                                                         05660
      DO 20 I=4,LASTT                                                     05670
      IF (IIN(I).GT.0.AND.I.NE.IESPEC.AND.I.NE.IASPEC) THEN               05680
         IF (DABS(CR(I)).GT.TCLOSE*TOT(I)) THEN                           05690
            ICHECK=1                                                      05700
            IF(IOPT(8).EQ.1) WRITE (6,25) I                               05710
   25       FORMAT(' FAILED MASS BALANCE.  SPECIES',I4)                   05720
            IF(DABS(CR(I)).GT.1D-4*TOT(I)) THEN                           05730
               JCHECK=1                                                   05740
               IF(IOPT(8).EQ.1) WRITE(6,16)                               05750
   16          FORMAT('    MASS-BALANCE-ONLY FLAG SET.')                  05760
            END IF                                                        05770
         END IF                                                           05780
      END IF                                                              05790
   20 CONTINUE                                                            05800
C                                                                         05810
C          CHECK MINERAL EQUILIBRIA                                       05820
C                                                                         05830
      IF (NMINS.GT.0) THEN                                                05840
         DO 30 I=1,NMINS                                                  05850
         K=MAXT+I                                                         05860
         IF (DABS(CR(K)).GT.MCLOSE) THEN                                  05870
            ICHECK=1                                                      05880
            IF (IOPT(8).GT.0) THEN                                        05890
               WRITE(6,35) MNAME(I),CR(K),MCLOSE                          05900
   35          FORMAT(' FAILED SATURATION TEST. ',A12,' SI-ERROR ',       05910
     1         1PD11.3,' SI-TOLER ',1PD10.2)                              05920
            END IF                                                        05930
         END IF                                                           05940
   30    CONTINUE                                                         05950
      END IF                                                              05960
C                                                                         05970
C            STOP ON MAX ITERATIONS                                       05980
C                                                                         05990
      IF (ITER.GT.100.OR.ITER1.GT.50) THEN                                06000
         WRITE (6,70) ITER, ITER1                                         06010
   70    FORMAT(1H1,80('*')//' CALCULATIONS TERMINATED ',/,               06020
     1   ' ITER  ',I5,' ITER1 ',I5)                                       06030
         F=0.0D0                                                          06040
         CALL PBUG(F,F)                                                   06050
         CALL PTOT                                                        06060
         CALL PSPEC                                                       06070
         CALL PPHASE                                                      06080
         CALL PLOOK                                                       06090
         ENDFILE (UNIT=6)                                                 06100
         STOP 'SUBROUTINE CHECK, MAXIMUM ITERATIONS'                      06110
      END IF                                                              06120
C                                                                         06130
C            SET ISTAT TO BRANCH ON CONVERGENCE CRITERIA                  06140
```

```
C                                                                       06150
      DO 50 I=1,NEQ+1                                                   06160
      DELTA(I)=0D0                                                      06170
   50 CONTINUE                                                          06180
      IF (JCHECK.GT.0.OR.ITER1.LE.1) THEN                               06190
C             POOR MASS BALANCE, BACK TO AQMOD                          06200
         ISTAT=2                                                        06210
         RETURN                                                         06220
      ELSE IF (ICHECK.GT.0.OR.ITER.LT.5) THEN                           06230
C             GOOD MASS BALANCE, GO TO SOLVE                            06240
         DO 107 I=1,LASTS                                               06250
         OLDG(I)=GAMMA(I)                                               06260
  107    CONTINUE                                                       06270
         OLDMU=MU                                                       06280
         OLDAW=TOT(3)                                                   06290
         ISTAT=1                                                        06300
         RETURN                                                         06310
      ELSE IF (ICHECK.EQ.0.AND.JCHECK.EQ.0.AND.ITER.GT.4) THEN          06320
C             CONVERGED                                                 06330
         ISTAT=0                                                        06340
         RETURN                                                         06350
      ELSE                                                              06360
         WRITE(6,80) ICHECK, JCHECK, ITER, ITER1                        06370
   80 FORMAT(' UNKNOWN STATUS IN SUBROUTINE CHECK.'/                    06380
     1   ' ICHECK = ',I4,/                                              06390
     1   ' JCHECK = ',I4,/                                              06400
     1   ' ITER   = ',I4,/                                              06410
     1   ' ITER1  = ',I4)                                               06420
      END IF                                                            06430
      STOP 'SUBROUTINE CHECK, UNKNOWN STATUS'                           06440
C                                                                       06450
      END                                                               06460
      SUBROUTINE SOLVE                                                  06470
$INSERT COMMON.BLOCKS                                                   06480
      DIMENSION OLDG(250),GAMMA(250),DELGAM(250)                        06490
      COMMON /GBLOCK/ OLDG,OLDMU,OLDAW,GAMMA,DELGAM                     06500
      COMMON / FLAGMU / INMU                                            06510
C                                                                       06520
C          COPY ROWS OF AR INTO MATRIX AS WHICH IS INVERTED IN SLNQ      06530
C                                                                       06540
      IF (NEQ.EQ.0) RETURN                                              06550
C                                                                       06560
C          SWITCH OUT DELTA MU CALCULATIONS FOR MASTER SPECIES           06570
C                                                                       06580
      INMU=0                                                            06590
      DMU=DABS(MU-OLDMU)                                                06600
C             NO MU EQN IF ELECT > 1 OR DEL MU > 1 OR SI > 0.5          06610
      IF(DABS(CR(1)).GT.1D0.AND.IIN(1).GT.0) INMU=1                     06620
      IF(DMU.GT.0.1D0.AND.IIN(1).GT.0) INMU=1                           06630
      IF(NMINS.GT.0) THEN                                               06640
         DO 6 I=1,NMINS                                                 06650
         J=MAXT+I                                                       06660
         IF(DABS(CR(J)).GT.5D0) INMU=1                                  06670
    6    CONTINUE                                                       06680
      END IF                                                            06690
      IF (INMU.GT.0) THEN                                               06700
```

```
      AR(1,30)=0D0                                                      06710
      AR(3,30)=0D0                                                      06720
      DO 5 I=4,49                                                       06730
      IF(I.NE.30) AR(I,30)=0D0                                          06740
    5 CONTINUE                                                          06750
      AR(30,30)=-1.0D0                                                  06760
      END IF                                                            06770
C                                                                       06780
C          PUT ELECTRICAL BALANCE EQUATION IN PLACE OF A MASS BALANCE    06790
C                                                                       06800
      LASTTX=LASTT                                                      06810
      LASTT=30                                                          06820
      IIN(30)=ILT+1                                                     06830
      IF (IESPEC.LT.2) GO TO 30                                         06840
      TOT(IESPEC)=AR(IESPEC,IESPEC)                                     06850
      DO 10 I=1,LASTT                                                   06860
      IF (IIN(I).EQ.0) GO TO 10                                         06870
      AR(IESPEC,I)=AR(1,I)                                              06880
   10 CONTINUE                                                          06890
      CR(IESPEC)=-ELECT                                                 06900
   30 CONTINUE                                                          06910
C                                                                       06920
C          PUT ALKALINITY EQUATION IN PLACE OF MASS BALANCE             06930
C                                                                       06940
      IF (IASPEC.EQ.0) GO TO 50                                         06950
      TOT(IASPEC)=AR(IASPEC,IASPEC)                                     06960
      DO 40 I=1,LASTT                                                   06970
      AR(IASPEC,I)=AR(3,I)                                              06980
   40 CONTINUE                                                          06990
      CR(IASPEC)=CR(3)                                                  07000
   50 CONTINUE                                                          07010
C                                                                       07020
C          FIX AH2O EQUATION.                                           07030
C                                                                       07040
      IF(IIN(3).GT.0) THEN                                              07050
         DO 65 I=1,50                                                   07060
         AR(3,I)=AR(50,I)                                               07070
   65    CONTINUE                                                       07080
         CR(3)=0D0                                                      07090
      END IF                                                            07100
C                                                                       07110
C          COPY EQUATIONS INTO ARRAY AS.                                07120
C                                                                       07130
      DO 80 I=1,LASTT                                                   07140
      IF (IIN(I).EQ.0) GO TO 80                                         07150
      K1=IIN(I)                                                         07160
      DO 60 J=1,LASTT                                                   07170
      K2=IIN(J)                                                         07180
      IF (K2.EQ.0) GO TO 60                                             07190
      AS(K1,K2)=AR(I,J)                                                 07200
   60 CONTINUE                                                          07210
      AS(K1,NEQ1+1)=CR(I)                                               07220
      IF(NMINS.EQ.0) GO TO 80                                           07230
      DO 70 J=1,NMINS                                                   07240
      AS(K1,ILT+1+J)=AR(I,MAXT+J)                                       07250
   70 CONTINUE                                                          07260
```

```
   80 CONTINUE                                                          07270
C                                                                       07280
C          COPY MINERAL EQUATIONS                                       07290
C                                                                       07300
      IF (NMINS.EQ.0) GO TO 120                                         07310
      DO 110 I=1,NMINS                                                  07320
      K=MAXT+I                                                          07330
      L=ILT+I+1                                                         07340
      DO 90 J=1,LASTT                                                   07350
      IF (IIN(J).LE.0) GO TO 90                                         07360
      AS(L,IIN(J))=AR(K,J)                                              07370
   90 CONTINUE                                                          07380
      DO 100 J=1,NMINS                                                  07390
      AS(L,ILT+J+1)=AR(K,MAXT+J)                                        07400
  100 CONTINUE                                                          07410
      AS(L,NEQ1+1)=CR(K)                                                07420
  110 CONTINUE                                                          07430
  120 CONTINUE                                                          07440
C                                                                       07450
C          INVERT MATRIX.  (DX/X VALUES IN DELTA)                       07460
C                                                                       07470
      CALL SLNQ                                                         07480
      LASTT=LASTTX                                                      07490
      IIN(30)=0                                                         07500
      RETURN                                                            07510
      END                                                               07520
      SUBROUTINE SLNQ                                                   07530
      IMPLICIT DOUBLE PRECISION(A-H,O-Z),INTEGER(I-N)                   07540
      CHARACTER *12 SNAME,TNAME,MNAME                                   07550
      DOUBLE PRECISION LM,LA,LG,LKSP,LKMIN,MU                           07560
      COMMON /REAL8/ LM(250),E(250),LA(250),LG(250),LKSP(250),          07570
     1       TOT(50),    DELTA(50),DELTOT(50),AR(50,50),                07580
     2       AS(50,50),CR(50),CS(50),LKMIN(20),                         07590
     3       THOR,ELECT,THSOLN,PH,PE,G,H,MU,TOTAL(2,30),                07600
     4       DALKT,DALKS,DIFFZ(2),DZOFF                                 07610
      INTEGER GFLAG,SFLAG                                               07620
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),          07630
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,           07640
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),        07650
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),      07660
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,       07670
     5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,        07680
     6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)             07690
C                                                                       07700
C     SOLUTION OF N LINEAR EQUATIONS IN N UNKNOWNS BY GAUSSIAN          07710
C     ELIMINATION OR DETERMINANT EVALUTAION.                            07720
C     A CONTAINS THE MATRIX OF THE COEFFICIENTS AND N INDICATES THE     07730
C     ORDER OF THE MATRIX. IF J EQUALS ZERO, D CONTAINS THE VALUE OF THE 07740
C     DETERMINANT. IF J DOES NOT EQUAL ZERO, X CONTAINS THE N VALUES OF 07750
C     THE UNKNOWNS.                                                     07760
C                                                                       07770
      J=1                                                               07780
      N=NEQ+1                                                           07790
      D=0.0D0                                                           07800
      NP1=N+1                                                           07810
      NM1=N-1                                                           07820
```

```
      IF (IOPT(9).NE.1) GO TO 20                                        07830
      DO 10 II=1,N                                                      07840
      WRITE (6,240) (AS(II,JJ),JJ=1,NP1)                                07850
   10 CONTINUE                                                          07860
   20 CONTINUE                                                          07870
      IF (N.EQ.1) GO TO 210                                             07880
      DO 120 I=1,NM1                                                    07890
      M=I                                                               07900
      K=I+1                                                             07910
      B=AS(I,I)                                                         07920
      DO 40 L=K,N                                                       07930
      IF (DABS(B)-DABS(AS(L,I))) 30,40,40                               07940
   30 M=L                                                               07950
      B=AS(L,I)                                                         07960
   40 CONTINUE                                                          07970
      IF (B) 50,160,50                                                  07980
   50 CC=AS(M,I)                                                        07990
      IF (I-M) 60,80,60                                                 08000
   60 D=-D                                                              08010
      IF (DABS(CC).LE.1.0D-40) GO TO 300                                08020
      DO 70 L=I,NP1                                                     08030
      B=AS(I,L)                                                         08040
      AS(I,L)=AS(M,L)/CC                                                08050
   70 AS(M,L)=B                                                         08060
      GO TO 100                                                         08070
   80 CONTINUE                                                          08080
      IF (DABS(CC).LE.1.0D-40) GO TO 300                                08090
      DO 90 L=I,NP1                                                     08100
   90 AS(I,L)=AS(I,L)/CC                                                08110
  100 D=D*CC                                                            08120
      DO 110 M=K,N                                                      08130
      B=AS(M,I)                                                         08140
      DO 110 L=I,NP1                                                    08150
  110 AS(M,L)=AS(M,L)-B*AS(I,L)                                         08160
  120 CONTINUE                                                          08170
      D=D*AS(N,N)                                                       08180
      IF (J) 130,200,130                                                08190
  130 CONTINUE                                                          08200
      IF(DABS(AS(N,N)).GE.1.0D-40) GO TO 135                            08210
      WRITE (6,320)N                                                    08220
  320 FORMAT(1X,'AS(N,N)=0D0.  N=',I3)                                  08230
      DELTA(N)=0D0                                                      08240
      GO TO 145                                                         08250
  135 DELTA(N)=AS(N,NP1)/AS(N,N)                                        08260
  145 CONTINUE                                                          08270
      K=NM1                                                             08280
  140 M=K+1                                                             08290
      B=0.0D0                                                           08300
      DO 150 L=M,N                                                      08310
  150 B=B+AS(K,L)*DELTA(L)                                              08320
      DELTA(K)=AS(K,NP1)-B                                              08330
      K=K-1                                                             08340
      IF (K) 160,180,140                                                08350
  160 IF (J) 170,180,170                                                08360
  170 WRITE (6,260)                                                     08370
      ENDFILE (UNIT=6)                                                  08380
```

```
      STOP 'SINGULAR MATRIX IN SUBROUTINE SLNQ'                          08390
  180 D=0.0D0                                                            08400
      IF (IOPT(9).LT.1) GO TO 190                                        08410
      WRITE (6,220)                                                      08420
      WRITE (6,230) (DELTA(I),I=1,N)                                     08430
      WRITE (6,250)                                                      08440
  190 CONTINUE                                                           08450
  200 RETURN                                                             08460
  210 CONTINUE                                                           08470
      IF (DABS(AS(1,1)).LE.1.0D-40) GO TO 170                            08480
      DELTA(1)=AS(1,2)/AS(1,1)                                           08490
      GO TO 180                                                          08500
  300 CONTINUE                                                           08510
      WRITE (6,310)I,L,M,ITER                                            08520
  310 FORMAT(1X,'CC=0',' I=',I3,' L=',I3,' M=',I3,' ITER=',I3)           08530
      ENDFILE (UNIT=6)                                                   08540
      STOP                                                               08550
C                                                                        08560
C                                                                        08570
C                                                                        08580
  220 FORMAT (1X,'DELTA VALUES')                                         08590
  230 FORMAT (3X,1P6D12.3)                                               08600
  240 FORMAT (/(3X,1P6D12.3))                                            08610
  250 FORMAT (1X)                                                        08620
  260 FORMAT (1H1,'THE PHASE RULE HAS BEEN VIOLATED')                    08630
      END                                                                08640
      SUBROUTINE RESET                                                   08650
$INSERT COMMON.BLOCKS                                                    08660
      DIMENSION OLDG(250),GAMMA(250),DELGAM(250)                         08670
      COMMON /GBLOCK/ OLDG,OLDMU,OLDAW,GAMMA,DELGAM                      08680
      COMMON / FLAGMU / INMU                                             08690
C             INITIALIZE                                                 08700
      DMIN=0.6D0                                                         08710
      DMAX=3.0D0                                                         08720
      F=1D0                                                              08730
      DPHPE=1D0                                                          08740
      DO 20 I=1,LASTT                                                    08750
      DELTOT(I)=0.0D0                                                    08760
   20 CONTINUE                                                           08770
C                                                                        08780
C          CALCULATE DELTA TOTALS IN MASSES                              08790
C                                                                        08800
      DELMU=DELTA(ILT+1)                                                 08810
      IF (NMINS.GT.0) THEN                                               08820
         DO 25 I=IFM,ILM                                                 08830
         DELTA(I)=DELTA(I+1)                                             08840
   25    CONTINUE                                                        08850
         DO 40 I=IFT,ILT                                                 08860
         DT=0.0D0                                                        08870
         DO 30 J=IFM,ILM                                                 08880
         K=MAXT+J-ILT                                                    08890
         DT=DT-DELTA(J)*AR(IOUT(I),K)                                    08900
   30    CONTINUE                                                        08910
         DELTOT(I)=DT                                                    08920
   40    CONTINUE                                                        08930
C            MAKE SURE DELTA MINERALS IS SMALL                           08940
```

```
      DO 510 I=IFM,ILM                                                  08950
      IF (DELTA(I).GT.0.5D0) THEN                                       08960
C                MAXIMUM INCREASE                                       08970
         DF=0.5D0/DELTA(I)                                              08980
         F=DMIN1(DF,F)                                                  08990
      ELSE IF (DELTA(I).LT.-0.7D0) THEN                                 09000
C                MAXIMUM DECREASE                                       09010
         DF=0.7D0/DABS(DELTA(I))                                        09020
         F=DMIN1(DF,F)                                                  09030
      END IF                                                            09040
  510 CONTINUE                                                          09050
      DO 50 I=IFT,ILT                                                   09060
C                MAXIMUM INCREASE IN ELEMENT CONCENTRATION              09070
      IF (DABS(DELTOT(I)).GT.5.0D0) THEN                                09080
         DF=5.0D0/DABS(DELTOT(I))                                       09090
         F=DMIN1(F,DF)                                                  09100
      END IF                                                            09110
C                MAKE SURE NO NEGATIVE CONCENTRATIONS RESULT            09120
      IF (TOT(IOUT(I))+DELTOT(I).LE.0.0D0) THEN                         09130
         DF=-0.9D0*TOT(IOUT(I))/DELTOT(I)                               09140
         F=DMIN1(F,DF)                                                  09150
      END IF                                                            09160
   50 CONTINUE                                                          09170
   END IF                                                               09180
C                                                                       09190
C            ENSURE DECREASE OR INCREASE IN ACTIVITY IS NOT TOO LARGE   09200
C                                                                       09210
   DO 55 I=IFT,ILT                                                      09220
   IF (DELTA(I).LT.-0.9D0) THEN                                         09230
      DF=-0.9D0/DELTA(I)                                                09240
      F=DMIN1(F,DF)                                                     09250
   END IF                                                               09260
   IF (DELTA(I).GT.3.0D0) THEN                                          09270
      DF=3.0D0/DELTA(I)                                                 09280
      F=DMIN1(F,DF)                                                     09290
   END IF                                                               09300
55 CONTINUE                                                             09310
C                                                                       09320
C                ENSURE DELTA IONIC STRENGTH IS SMALL                   09330
C                                                                       09340
   DMU=MU+DELMU                                                         09350
   IF (INMU.GT.0) DELMU=0D0                                             09360
   IF(DELMU.GT.0.5D0) THEN                                              09370
C            MAXIMUM INCREASE ABSOLUTE                                  09380
      DF=0.5D0/DELMU                                                    09390
      F=DMIN1(F,DF)                                                     09400
   ELSE IF (DELMU.LE.-MU*.4D0) THEN                                     09410
C            MAXIMUM DECREASE BY FRACTION                               09420
      DF=MU*0.4/DABS(DELMU)                                             09430
      F=DMIN1(F,DF)                                                     09440
   END IF                                                               09450
   IF (DELMU.LT.-0.4D0) THEN                                            09460
C            MAXIMUM DECREASE ABSOLUTE                                  09470
      DF=0.4D0/DABS(DELMU)                                              09480
      F=DMIN1(F,DF)                                                     09490
   END IF                                                               09500
```

```
C                                                                       09510
C          ENSURE PH CHANGE REASONABLE                                  09520
C                                                                       09530
      IF (IIN(1).GT.0) THEN                                             09540
         IF (DELTA(1).LT.-DMIN.OR.DELTA(1).GT.DMAX) THEN                09550
            DF=DABS(DMIN/DELTA(1))                                      09560
            IF (DELTA(1).GT.0D0) DF=DMAX/DELTA(1)                       09570
            DPHPE=DF                                                    09580
         END IF                                                         09590
      END IF                                                            09600
C                                                                       09610
C          ENSURE PE CHANGE REASONABLE.                                 09620
C                                                                       09630
      IF (IFTH.GT.0) THEN                                               09640
         IF (DELTA(IFTH).LT.-DMIN.OR.DELTA(IFTH).GT.DMAX) THEN          09650
            DF=DABS(DMIN/DELTA(IFTH))                                   09660
            IF (DELTA(IFTH).GT.0D0) DF=DMAX/DELTA(IFTH)                 09670
            DPHPE=DMIN1(DF,DPHPE)                                       09680
         END IF                                                         09690
      END IF                                                            09700
C                                                                       09710
C          ENSURE ALKALINITY CHANGE IS REASONABLE.                      09720
C                                                                       09730
      IF (IASPEC.GT.0.AND.IOPT(2).NE.1) THEN                            09740
         I=IIN(IASPEC)                                                  09750
         IF (DELTA(I).LT.-DMIN.OR.DELTA(I).GT.DMAX) THEN                09760
            DF=DABS(DMIN/DELTA(I))                                      09770
            IF (DELTA(I).GT.0D0)DF=DMAX/DELTA(I)                        09780
            DPHPE=DMIN1(DF,DPHPE)                                       09790
         END IF                                                         09800
      END IF                                                            09810
      F=DMIN1(DPHPE,F)                                                  09820
      DPHPE=F                                                           09830
C                                                                       09840
C          SCALE DELTAS                                                 09850
C                                                                       09860
      IF(DABS(1D0-F).GT.1D-8) THEN                                      09870
         DO 95 I=IFT,ILT                                                09880
         DELTA(I)=DELTA(I)*F                                            09890
   95    CONTINUE                                                       09900
         DELMU=DELMU*F                                                  09910
      END IF                                                            09920
      IF(DABS(1D0-F).GT.1D-8.AND.NMINS.GT.0) THEN                       09930
         DO 90 I=IFT,ILT                                                09940
         DELTOT(I)=DELTOT(I)*F                                          09950
   90    CONTINUE                                                       09960
         DO 100 I=IFM,ILM                                               09970
         DELTA(I)=DELTA(I)*F                                            09980
  100    CONTINUE                                                       09990
      END IF                                                            10000
      IF (IIN(1).GT.0) DELTA(1)=DELTA(1)*DPHPE                          10010
      IF (IIN(2).GT.0) DELTA(IIN(2))=DELTA(IIN(2))*DPHPE                10020
C                                                                       10030
C             CALL DEBUG PRINT                                          10040
C                                                                       10050
      IF (IOPT(8).GT.0) WRITE(6,97) DELMU                               10060
```

```
   97 FORMAT(' CALCULATED DELTA MU, SCALED = ',1PD10.2)                  10070
      IF (ITER.GT.190.OR.IOPT(8).EQ.1.OR.ITER1.GT.40) CALL PBUG(F,DPHPE) 10080
C                                                                        10090
C          RESET ELECTRICAL BALANCE SPECIES                              10100
C                                                                        10110
      IF (IESPEC.GT.0) THEN                                              10120
         D=DELTA(IIN(IESPEC))                                            10130
         LM(IESPEC)=LM(IESPEC)+DLOG10(1D0+D)                             10140
         M(IESPEC)=1D1**LM(IESPEC)                                       10150
         DGI=GAMMA(IESPEC)+DELGAM(IESPEC)*DELMU                          10160
         IF (DGI.LE.0) THEN                                              10170
            DGI=LG(IESPEC)                                               10180
         ELSE                                                            10190
            DGI=DLOG10(DGI)                                              10200
         END IF                                                          10210
         LA(IESPEC)=LM(IESPEC)+DGI                                       10220
         TOT(1)=1D1**LA(1)                                               10230
         PH=-LA(1)                                                       10240
      END IF                                                             10250
C                                                                        10260
C          RESET ALKALINITY SPECIES                                      10270
C                                                                        10280
      IF (IASPEC.GT.0) THEN                                              10290
         D=DELTA(IIN(IASPEC))*DPHPE                                      10300
         IF (IOPT(2).NE.1) THEN                                          10310
            LM(IASPEC)=LM(IASPEC)+DLOG10(1D0+D)                          10320
            M(IASPEC)=1.0D1**LM(IASPEC)                                  10330
            DGI=GAMMA(IASPEC)+DELGAM(IASPEC)*DELMU                       10340
            IF (DGI.LE.0) THEN                                           10350
               DGI=LG(IASPEC)                                            10360
            ELSE                                                         10370
               DGI=DLOG10(DGI)                                           10380
            END IF                                                       10390
            LA(IASPEC)=LM(IASPEC)+DGI                                    10400
         END IF                                                          10410
      END IF                                                             10420
C                                                                        10430
C          RESET ACTIVITY OF ELECTRON                                    10440
C                                                                        10450
      IF (IFTH.GT.0) THEN                                                10460
         TOT(2)=TOT(2)*(1D0+DELTA(IFTH))                                 10470
         LA(2)=DLOG10(TOT(2))                                            10480
         PE=-LA(2)                                                       10490
      END IF                                                             10500
C                                                                        10510
C          ESTIMATE NEW ACTIVITY OF WATER                                10520
C                                                                        10530
      IF(DELMU.GT.0D0.AND.IIN(3).GT.0.AND.INMU.LE.0) THEN                10540
         DAW=DELTA(IIN(3))*F                                             10550
         IF(DABS(DAW).GT.0D0) THEN                                       10560
            LA(3)=LA(3)+DLOG10(1D0+DAW)                                  10570
         END IF                                                          10580
      END IF                                                             10590
      M(3)=1D1**LA(3)                                                    10600
C                                                                        10610
C          RESET MASTER SPECIES                                          10620
```

```
C                                                                       10630
      DO 165 I=IFT,ILT                                                  10640
      K=IOUT(I)                                                         10650
      IF(K.EQ.IASPEC) GO TO 165                                         10660
      IF(K.EQ.IESPEC) GO TO 165                                         10670
      LM(K)=LM(K)+DLOG10(1D0+DELTA(I))                                  10680
      M(K)=UNDER(LM(K))                                                 10690
      DGI=GAMMA(K)+DELGAM(K)*DELMU                                      10700
      IF (DGI.LE.0) THEN                                                10710
         DGI=LG(K)                                                      10720
      ELSE                                                              10730
         DGI=DLOG10(DGI)                                                10740
      END IF                                                            10750
      LA(K)=LM(K)+DGI                                                   10760
  165 CONTINUE                                                          10770
      DO 122 I=4,LASTS                                                  10780
      IF (SFLAG(I).EQ.0) GO TO 122                                      10790
      DGI=GAMMA(I)+DELGAM(I)*DELMU                                      10800
      IF (DGI.LE.0) THEN                                                10810
         DGI=LG(I)                                                      10820
      ELSE                                                              10830
         DGI=DLOG10(DGI)                                                10840
      END IF                                                            10850
      DM=LKSP(I)-DGI                                                    10860
      K=NSP(I)                                                          10870
C          CALCULATE MOLALITY                                           10880
      DO 92 J=1,K                                                       10890
      DM=DM+LA(LSP(I,J))*CSP(I,J)                                       10900
   92 CONTINUE                                                          10910
         LM(I)=DM                                                       10920
         M(I)=UNDER(DM)                                                 10930
  122 CONTINUE                                                          10940
      IF(IOPT(8).GT.0) THEN                                             10950
         WRITE(6,107)                                                   10960
  107    FORMAT('PRINTED IN RESET AFTER RECALCULATION OF M(I).',        10970
     1          /,'    I  GAMMA    MOLALITY')                          10980
         DO 105 I=1,LASTS                                               10990
         IF (SFLAG(I).EQ.0) GO TO 105                                   11000
         D=1D1**LG(I)                                                   11010
         WRITE(6,106) I,D,M(I)                                          11020
  106    FORMAT(I5,1P2D10.3)                                            11030
  105    CONTINUE                                                       11040
      END IF                                                            11050
C          RESET TOTALS                                                 11060
      IF (NMINS.EQ.0) GO TO 180                                         11070
      DO 160 I=IFT,ILT                                                  11080
      K=IOUT(I)                                                         11090
      TOT(K)=TOT(K)+DELTOT(I)                                           11100
      IF (TOT(K).LE.1D-30) TOT(K)=1D-30                                 11110
  160 CONTINUE                                                          11120
C          RESET TOTAL MINERALS ADDED OR REMOVED AND THE THOR.          11130
      DO 170 I=IFM,ILM                                                  11140
      K=MAXT+I-ILT                                                      11150
      TOT(K)=TOT(K)+DELTA(I)                                            11160
      IF(IOPT(3).EQ.6.AND.I.EQ.IFM) THEN                                11170
         THOR=THOR+DELTA(I)*THREAC                                      11180
```

```
      ELSE                                                              11190
         THOR=THOR+THMIN(I-ILT)*DELTA(I)                                11200
      END IF                                                            11210
  170 CONTINUE                                                          11220
  180 CONTINUE                                                          11230
      RETURN                                                            11240
      END                                                               11250
      FUNCTION UNDER(D)                                                 11260
      DOUBLE PRECISION D,UNDER                                          11270
      UNDER=0D0                                                         11280
      IF (D.LT.-33.0D0) GO TO 10                                        11290
      UNDER=1D2                                                         11300
      IF (D.GT.2D0) GO TO 10                                            11310
      UNDER=1D1**D                                                      11320
   10 CONTINUE                                                          11330
      RETURN                                                            11340
      END                                                               11350
      SUBROUTINE PTOT                                                   11360
$INSERT COMMON.BLOCKS                                                   11370
      LOGICAL EVAP                                                      11380
      COMMON /EVAP/ EVAP                                                11390
      COMMON / MX10 / VP,DW0                                            11400
      CHARACTER *12 DALK,DN,DN1,DN2,DN3,DNAME                           11410
      CHARACTER *80 CARD                                                11420
      DIMENSION DA0(250),DM(250),COR(1:34),DG0(40)                      11430
      LOGICAL LHSP,LNHSP                                                11440
      COMMON / COS / COSMOT                                             11450
      DATA IDATA /0/, DALK/'TOT ALK'/                                   11460
      DATA DN1/'O2'/,DN2/'H2'/,DN3/'CHARGE'/                            11470
      WRITE (6,220)                                                     11480
      WRITE (6,230)                                                     11490
      KK=0                                                              11500
      DO 10 I=4,MAXT                                                    11510
      IF (DABS(TOT(I)).LE.1.0D-40) GO TO 10                             11520
      KK=1                                                              11530
      DLT=DLOG10(TOT(I))                                                11540
      DNAME=TNAME(I)                                                    11550
      IF (IASPEC.EQ.I) DNAME=DALK                                       11560
      WRITE (6,240) DNAME,TOT(I),DLT                                    11570
   10 CONTINUE                                                          11580
      IF (KK.EQ.0) WRITE (6,250)                                        11590
      WRITE (6,260)                                                     11600
      RETURN                                                            11610
C     *****                                                             11620
      ENTRY PSPEC                                                       11630
C     *****                                                             11640
      WRITE (6,270)                                                     11650
      WRITE (6,280) PH,TOT(3),COSMOT,MU,TC,VP,DW0,ELECT,DALKS,ITER      11660
      IF (IASPEC.LE.0) GO TO 20                                         11670
      WRITE (6,290) TOTAL(ISOL,IASPEC)                                  11680
   20 CONTINUE                                                          11690
      IF (IESPEC.LE.1) GO TO 30                                         11700
      DD=TOT(IESPEC)-DNEUT                                              11710
      WRITE (6,300) TNAME(IESPEC),DD                                    11720
   30 CONTINUE                                                          11730
      WRITE (6,310)                                                     11740
```

```
      IF(IOPT(10).EQ.0) THEN                                            11750
         WRITE(6,312)                                                   11760
      ELSE                                                              11770
         WRITE(6,311)                                                   11780
      END IF                                                            11790
      WRITE (6,313)                                                     11800
      LM(1)=LA(1)-LG(1)                                                 11810
      LG(2)=0.0D0                                                       11820
      LM(2)=LA(2)                                                       11830
      LG(3)=0.0D0                                                       11840
      LM(3)=LA(3)                                                       11850
      DO 40 I=1,LASTS                                                   11860
      IF (SFLAG(I).EQ.0) GO TO 40                                       11870
      DAO(I)=0D0                                                        11880
      DM(I)=0D0                                                         11890
      IF (LM(I).LT.-30D0.AND.I.GT.30) GO TO 40                          11900
      IF (LM(I).GE.-60D0) DM(I)=1D1**LM(I)                              11910
      DLA=LM(I)+LG(I)                                                   11920
      IF (DLA.GE.-60D0) DAO(I)=1D1**DLA                                 11930
      DG=1D1**LG(I)                                                     11940
      IF (I.NE.2) WRITE (6,320) I,SNAME(I),ZSP(I),DM(I),LM(I),DAO(I)    11950
     1,DLA,DG,LG(I)                                                     11960
   40 CONTINUE                                                          11970
      DO 41 I=1,34                                                      11980
      DGO(I)=0.0D0                                                      11990
      COR(I)=0.0D0                                                      12000
   41 CONTINUE                                                          12010
      DO 52 I=35,LASTS                                                  12020
      IF (SFLAG(I).EQ.0) GO TO 52                                       12030
      LHSP=.FALSE.                                                      12040
      LNHSP=.FALSE.                                                     12050
      DO 45 J=1,NSP(I)                                                  12060
      IF (LSP(I,J).NE.1) GO TO 45                                       12070
      LHSP=.TRUE.                                                       12080
      IF (CSP(I,J).GT.0.0D0) LNHSP=.TRUE.                               12090
      ITH=J                                                             12100
   45 CONTINUE                                                          12110
      DO 42 J=1,NSP(I)                                                  12120
      IF (LSP(I,J).EQ.3.AND.LHSP) GO TO 47                              12130
      IF (LSP(I,J).EQ.3.OR.LSP(I,J).EQ.2) GO TO 42                      12140
      IF (LSP(I,J).EQ.15.AND.LNHSP) GO TO 48                            12150
      IF (LSP(I,J).EQ.16.AND.LNHSP) GO TO 42                            12160
      IF (LSP(I,J).NE.1) GO TO 49                                       12170
      IF (.NOT.LNHSP) GO TO 42                                          12180
      DO 46 N=1,NSP(I)                                                  12190
      IF (LSP(I,N).EQ.15) GO TO 42                                      12200
   46 CONTINUE                                                          12210
   49 COR(LSP(I,J))=COR(LSP(I,J))+CSP(I,J)*DM(I)                        12220
      GO TO 42                                                          12230
   47 DCSP=DABS(CSP(I,J)-DABS(CSP(I,ITH)))                              12240
      IF (DCSP.GT.0.1D0) GO TO 42                                       12250
      COR(31)=COR(31)+CSP(I,J)*DM(I)                                    12260
      GO TO 42                                                          12270
   48 IF (CSP(I,ITH).GT.1.1D0) GO TO 42                                 12280
      COR(34)=COR(34)+CSP(I,J)*DM(I)                                    12290
   42 CONTINUE                                                          12300
```

```
   52 CONTINUE                                                          12310
C                                                                       12320
      IF(IOPT(10).EQ.0) THEN                                            12330
         WRITE(6,36)                                                    12340
   36    FORMAT(//39X,'UNSCALED    UNSCALED')                          12350
      ELSE                                                              12360
         WRITE(6,35)                                                    12370
   35    FORMAT(//39X,'MACINNES    MACINNES')                          12380
      END IF                                                            12390
      WRITE (6,31)                                                      12400
   31 FORMAT (14X,'SPECIES',4X,'TOTAL MOL',5X,'ACTIVITY',3X,            12410
     1'TOTAL GAMMA'/)                                                   12420
      DO 43 I=1,35                                                      12430
      IF (SFLAG(I).EQ.0) GO TO 43                                       12440
      IF (I.EQ.2.OR.I.EQ.3) GO TO 43                                    12450
      IF (I.EQ.35) GO TO 32                                             12460
      DM(I)=DM(I)+COR(I)                                                12470
   32 DGO(I)=DAO(I)/DM(I)                                               12480
      WRITE (6,44) SNAME(I),DM(I),DAO(I),DGO(I)                         12490
   44 FORMAT (14X,A8,3(3X,1PD10.4))                                     12500
   43 CONTINUE                                                          12510
C                                                                       12520
      IF (NMGS.EQ.0) GO TO 700                                          12530
      STOT=0.0D0                                                        12540
      DO 590 I=4,30                                                     12550
      STOT=STOT+TOT(I)                                                  12560
  590 CONTINUE                                                          12570
      IF (STOT.LT.1.0D-20) GO TO 700                                    12580
  600 WRITE (6,610)                                                     12590
  610 FORMAT (//22X,'---- MEAN ACTIVITY COEFFICIENT ----',//            12600
     1,27X,'FORMULA',7X,'MEAN GAMMA',/)                                 12610
      DO 620 I=1,NMGS                                                   12620
      EG=0.0D0                                                          12630
      GG=1.0D0                                                          12640
      DO 630 J=1,IMEANG(I)                                              12650
      GG=GG*DGO(LMEANG(I,J))**CMEANG(I,J)                               12660
      EG=EG+CMEANG(I,J)                                                 12670
  630 CONTINUE                                                          12680
      IF (GG.LT.1.0D-30) GO TO 620                                      12690
      GG=GG**(1.0D0/EG)                                                 12700
      WRITE (6,640) NMEANG(I),GG                                        12710
  640 FORMAT (27X,A8,6X,1PD10.4)                                        12720
  620 CONTINUE                                                          12730
C     *****                                                             12740
      ENTRY PSUM                                                        12750
C     *****                                                             12760
  700 IF (NSUMS.EQ.0) GO TO 80                                          12770
      KK=0                                                              12780
      DO 70 I=1,NSUMS                                                   12790
      LL=0                                                              12800
      DSUM=0D0                                                          12810
      K=NSUM(I)                                                         12820
      DO 50 J=1,K                                                       12830
      IF (SFLAG(LSUM(I,J)).LE.0) GO TO 50                               12840
      LL=1                                                              12850
      DSUM=DSUM+M(LSUM(I,J))                                            12860
```

```
   50 CONTINUE                                                          12870
      IF (LL.EQ.0) GO TO 70                                             12880
      IF (LL.EQ.0.OR.KK.NE.0) GO TO 60                                  12890
      WRITE (6,330)                                                     12900
      KK=1                                                              12910
   60 CONTINUE                                                          12920
      WRITE (6,340) SUNAME(I),DSUM                                      12930
   70 CONTINUE                                                          12940
   80 CONTINUE                                                          12950
      RETURN                                                            12960
C     *****                                                            12970
      ENTRY PBUG(D,DPHPE)                                               12980
C     *****                                                            12990
      WRITE (6,350) D,CR(1),DPHPE                                       13000
C          PRINT CHANGES IN PH AND PE                                   13010
      IF (IIN(1).LE.0) GO TO 90                                         13020
      DPH=-DLOG10(1D0+DELTA(1))                                         13030
      WRITE (6,360) PH,DPH                                              13040
   90 CONTINUE                                                          13050
      IF (IIN(2).LE.0) GO TO 100                                        13060
      DPE=-DLOG10(1D0+DELTA(IIN(2)))                                    13070
      WRITE (6,370) PE,DPE,CR(2)                                        13080
  100 CONTINUE                                                          13090
C          PRINT TOTALS AND ACTIVITIES                                  13100
      WRITE(6,105)                                                      13110
  105 FORMAT('    ERROR     EQN      TOT      DELTOT  FRAC TOT '       13120
     1 'SPECIES   MOLALITY   DELTA MOL')                                13130
      DO 110 K=4,LASTT                                                  13140
      I=IIN(K)                                                          13150
      IF (I.LE.0) GO TO 110                                             13160
      DRT=DELTOT(I)/TOT(K)                                              13170
      TEMPM=1D1**LM(K)                                                  13180
      DRA=DELTA(I)*DA                                                   13190
      WRITE (6,380) CR(K),TNAME(K),TOT(K),DELTOT(I),DRT,SNAME(K),TEMPM  13200
     1,DELTA(I)                                                         13210
  110 CONTINUE                                                          13220
C          PRINT MINERAL TOTALS AND DELTAS                              13230
      IF (NMINS.LE.0) GO TO 130                                         13240
      DO 120 I=1,NMINS                                                  13250
      K=MAXT+I                                                          13260
      J=ILT+I                                                           13270
      WRITE (6,390) CR(K),MNAME(I),TOT(K),DELTA(J)                      13280
  120 CONTINUE                                                          13290
  130 CONTINUE                                                          13300
      RETURN                                                            13310
C     *****                                                            13320
      ENTRY PPHASE                                                      13330
C     *****                                                            13340
C                                                                       13350
C             PRINT MASS TRANFER FOR MINERAL PHASES                     13360
C                                                                       13370
      IF (NMINS.EQ.0) RETURN                                            13380
      IF (EVAP) THEN                                                    13390
         FACTOR=TOT(MAXT+1)+1D0                                         13400
         WRITE (6,401)                                                  13410
  401 FORMAT (27X,'----PHASE BOUNDARIES----'/                           13420
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     1 /12X,' MASS PRECIPITATED/DISSOLVED FROM INITIAL KILOGRAM WATER'   13430
     2 //,9X,'PHASE',5X,'DELTA PHASE*',6X,'LOG IAP',6X,'LOG KT',         13440
     3 6X,'LOG IAP/KT'/)                                                13450
      ELSE                                                              13460
         FACTOR=1D0                                                     13470
         WRITE (6,400)                                                  13480
      END IF                                                            13490
      DO 150 I=1,NMINS                                                  13500
      K=NMINO(I)                                                        13510
      DIAP=0.0D0                                                        13520
      DO 140 J=1,K                                                      13530
      DIAP=DIAP+(LG(LMINO(I,J))+LM(LMINO(I,J)))*CMINO(I,J)              13540
  140 CONTINUE                                                          13550
      DSI=DIAP-LKMINO(I)                                                13560
      K=MAXT+I                                                          13570
      D1=TOT(K)/FACTOR                                                  13580
      IF (IOPT(3).EQ.6.AND.I.EQ.1) D1=0D0                               13590
      WRITE (6,410) MNAME(I),D1,DIAP,LKMINO(I),DSI                      13600
      IF (IOPT(3).EQ.6.AND.I.EQ.1) WRITE (6,420)                        13610
  150 CONTINUE                                                          13620
      WRITE (6,430)                                                     13630
C                                                                       13640
C             PRINT IF ADDING REACTION TO A PHASE BOUNDARY              13650
C                                                                       13660
      IF (IOPT(3).EQ.6) THEN                                            13670
         IF (EVAP) THEN                                                 13680
            FACTOR=TOT(MAXT+1)+1D0                                      13690
            WRITE (6,445) FACTOR, MNAME(1)                              13700
  445 FORMAT (/,1X,'** ',1PD13.6,' IS THE EVAPORATION FACTOR NECESSARY'  13710
     1  ,' TO REACH THE ',/4X,14X,A8,'   PHASE BOUNDARY.')               13720
            WRITE (6,221)                                               13730
  221 FORMAT(///17X,'MOLES OF ELEMENTS REMAINING AFTER REACTION'        13740
     1        /,17X,'----- -- -------- --------- ----- --------')       13750
            WRITE (6,231)                                               13760
  231 FORMAT (/16X,'ELEMENT',10X,' MOLES  ',9X,' LOG MOLES'/)           13770
            DO 11 I=4,MAXT                                              13780
            IF (DABS(TOT(I)).LE.1.0D-40) GO TO 11                       13790
            DMT=TOT(I)/FACTOR                                           13800
            DLT=DLOG10(DMT)                                             13810
            DNAME=TNAME(I)                                              13820
            WRITE (6,240) DNAME,DMT,DLT                                 13830
   11       CONTINUE                                                    13840
            WRITE (6,242) 1D0/FACTOR                                    13850
  242       FORMAT(/15X,1PD13.6, ' KILOGRAMS OF WATER REMAINING')       13860
            WRITE (6,260)                                               13870
         ELSE                                                           13880
            WRITE (6,440) TOT(MAXT+1),MNAME(1)                          13890
         END IF                                                         13900
      END IF                                                            13910
      IF (IOPT(3).NE.6.OR.EVAP) RETURN                                  13920
C     *****                                                             13930
      ENTRY PREAC                                                       13940
C     *****                                                             13950
      WRITE (6,450)                                                     13960
      DO 160 I=1,NCOMPS                                                 13970
      L=LREAC(I)                                                        13980
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      IF (L.EQ.0) DN=DN3                                                14000
      IF (L.LT.31) DN=TNAME(L)                                          14010
      IF (L.GT.30) DN=DN1                                               14020
      IF (L.GT.30.AND.THMEAN(I).LT.0) DN=DN2                            14030
      WRITE (6,460) CREAC(I),DN,THMEAN(I)                               14040
  160 CONTINUE                                                          14050
      RETURN                                                            14060
C     *****                                                             14070
      ENTRY PLOOK                                                       14080
C     *****                                                             14090
      IF (NLOOKS.EQ.0) RETURN                                           14100
      KK=0                                                              14110
      DO 190 I=1,NLOOKS                                                 14120
      K=NLOOK(I)                                                        14130
      DIAP=0D0                                                          14140
      DO 170 J=1,K                                                      14150
      LL=LLOOK(I,J)                                                     14160
      IF (SFLAG(LL).LE.0) GO TO 190                                     14170
      DIAP=DIAP+(LG(LL)+LM(LL))*CLOOK(I,J)                              14180
  170 CONTINUE                                                          14190
      IF (KK.NE.0) GO TO 180                                            14200
      KK=1                                                              14210
      WRITE (6,470)                                                     14220
  180 CONTINUE                                                          14230
      DSI=DIAP-LKLOOK(I)                                                14240
      WRITE (6,480) NAMELK(I),DIAP,LKLOOK(I),DSI                        14250
  190 CONTINUE                                                          14260
      RETURN                                                            14270
C     *****                                                             14280
      ENTRY PDATA                                                       14290
C     *****                                                             14300
      IF (IOPT(1).NE.1) RETURN                                          14310
      IF (IDATA.GT.0) RETURN                                            14320
      IDATA=1                                                           14330
      REWIND (UNIT=11)                                                  14340
      WRITE (6,490)                                                     14350
  200 CONTINUE                                                          14360
      READ (11,500,END=210) CARD                                        14370
      WRITE (6,510) CARD                                                14380
      GO TO 200                                                         14390
  210 CONTINUE                                                          14400
      RETURN                                                            14410
C                                                                       14420
  220 FORMAT (///24X,'TOTAL MOLALITIES OF ELEMENTS'/,24X,'----- -------- 14430
     1-- -- --------')                                                  14440
  230 FORMAT (/16X,'ELEMENT',10X,'MOLALITY',9X,'LOG MOLALITY'/)         14450
  240 FORMAT (16X,A8,6X,1PD13.6,8X,0PF9.4)                              14460
  250 FORMAT (16X,'PURE WATER')                                         14470
  260 FORMAT (//)                                                       14480
  270 FORMAT (//,24X,'----DESCRIPTION OF SOLUTION----')                 14490
  280 FORMAT (/,39X,'PH = ',F8.4/29X,'ACTIVITY H2O = ',F8.4/22X         14500
     1,'OSMOTIC COEFFICIENT = ',F8.4/,27X,'IONIC STRENGTH = ',F8.4/30X  14510
     2,'TEMPERATURE = ',F8.4/33X,'PRESSURE = ',F8.4,' ATM',/27X         14520
     3,'DENSITY OF H2O = ',F8.4,' G/CC',/23X,'ELECTRICAL BALANCE = '    14530
     4,1PD12.4/25X,'TOTAL ALKALINITY = ',D12.4/31X,'ITERATIONS = ',0PI3) 14540
  290 FORMAT (29X,'TOTAL CARBON = ',1PD12.4)                            14550
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  300 FORMAT (20X,'MOLES OF ',A8,' ADDED = ',D12.4)                          14550
  310 FORMAT (///,26X,23('-')/26X,'DISTRIBUTION OF SPECIES'/26X,23('-'))     14560
  311 FORMAT (43X,'MACINNES SCALE      MACINNES SCALE ')                     14570
  312 FORMAT (43X,'   UNSCALED            UNSCALED')                        14580
  313 FORMAT (2X,'I',2X,'SPECIES',4X,'Z',3X,'MOLALITY',2X,'LOG MOLAL',       14590
     1 3X,'ACTIVITY',2X,'LOG ACT',4X,'GAMMA',3X,'LOG GAM'/)                  14600
  320 FORMAT (1X,I3,1X,A8,1X,F4.1,1X,1PE10.3,2X,0PF7.3,2X,2(1PE10.3,1X,      14610
     10PF7.3,1X))                                                           14620
  330 FORMAT (///25X,'SUMS OF SPECIES'/)                                    14630
  340 FORMAT (22X,A8,' = ',1PD13.6)                                         14640
  350 FORMAT (/1X,'REDUCTION FACTOR: ',1PD12.5,3X,'ELECT: ',D12.5,3X,       14650
     1'DPHPE: ',D12.5)                                                      14660
  360 FORMAT (1X,'PH = ',F8.4,5X,'DPH = ',F8.4)                             14670
  370 FORMAT (1X,'PE = ',F8.4,5X,'DPE = ',F8.4,5X,'DTHOR = ',1PD12.5)       14680
  380 FORMAT (1X,1PD12.5,1X,A4,1X,D11.4,2(1X,D8.1),1X,A8,1X,D11.4,1X,       14690
     1D8.1)                                                                 14700
  390 FORMAT (1X,1PD12.5,1X,A4,1X,D11.4,2(1X,D8.1))                         14710
  400 FORMAT (27X,'----PHASE BOUNDARIES----'//,9X,'PHASE',5X,'DELTA PHAS    14720
     1E*',6X,'LOG IAP',6X,'LOG KT',6X,'LOG IAP/KT'/)                        14730
  410 FORMAT (8X,A8,2X,1PD13.6,3(4X,0PF9.4))                                14740
  420 FORMAT (1H+,5X,'**')                                                  14750
  430 FORMAT (/,1X,'* NEGATIVE DELTA PHASE INDICATES PRECIPITATION',/,3X    14760
     1,'AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.')                   14770
  440 FORMAT (/,1X,'** ',1PD13.6,' MOLES OF REACTION',' HAVE BEEN ADDED     14780
     1TO THE SOLUTION',/,4X,'TO REACH THE ',A8,' PHASE BOUNDARY.')          14790
  450 FORMAT (/,6X,'REACTION IS:')                                          14800
  460 FORMAT (15X,F12.6,' MOLES OF ',A8,'  VALENCE =  ',F6.3)               14810
  470 FORMAT (//28X,'---- LOOK MIN IAP ----'//15X,'PHASE',8X,'LOG IAP',6    14820
     1X,'LOG KT',6X,'LOG IAP/KT'/)                                          14830
  480 FORMAT (14X,A8,3(4X,F9.4))                                            14840
  490 FORMAT (1H1,25X,'DATA:  CARD IMAGES FROM DISK'/)                      14850
  500 FORMAT (A80)                                                          14860
  510 FORMAT (1X,A80)                                                       14870
      END                                                                   14880
      SUBROUTINE READ                                                       14890
$INSERT COMMON.BLOCKS                                                       14900
      CHARACTER *12 SUBS,SUB,TNAM,DELETE                                    14910
      LOGICAL LELEM(4:30)                                                   14920
      DIMENSION ISUB(12),SUBS(12),LT(30),DTOT(30)                           14930
      LOGICAL EVAP                                                          14940
      COMMON /EVAP/ EVAP                                                    14950
      COMMON / PEL / LELEM                                                  14960
      DATA SUBS /'TEMP     ','MINERALS ','SOLUTION ','REACTION ',           14970
     1           'STEPS    ','ELEMENTS ','SPECIES  ','END      ',          14980
     2           'LOOK MIN ','SUMS     ','NEUTRAL  ','MEAN GAM '/          14990
      DATA NLKS,NSMS,NMG /3*0/                                              15000
      DATA DELETE /'DELETE   '/                                             15010
   10 CONTINUE                                                              15020
      IERR=0                                                                15030
      ISOLV(1)=0                                                            15040
      ISOLV(2)=0                                                            15050
      NRMINS=0                                                              15060
      NLOOKS=NLKS                                                           15070
      NSUMS=NSMS                                                            15080
      EVAP=.FALSE.                                                          15090
      DO 20 I=1,11                                                          15100
```

```
      ISUB(I)=0                                                          15110
   20 CONTINUE                                                           15120
C          READ TITLE CARD                                             15130
      READ (5,420,END=410) (TITLE(I),I=1,20)                           15140
C          READ OPTION CARD                                            15150
      READ (5,430) (IOPT(I),I=1,10),NSTEPS,NCOMPS,VO                   15160
C             SET MANDATORY OPTION                                     15170
      IOPT(5)=0                                                        15180
      IOPT(6)=2                                                        15190
      IF (IOPT(1).EQ.1) CALL PDATA                                     15200
      WRITE (6,440) (TITLE(I),I=1,20)                                  15210
      WRITE (6,450) (IOPT(I),I=1,10),NSTEPS,NCOMPS,VO                  15220
      IREAD=0                                                          15230
      IFILE=5                                                          15240
      GO TO 30                                                         15250
C     *****                                                            15260
      ENTRY RDATA (KFILE)                                              15270
C     *****                                                            15280
      JFILE=6                                                          15290
      WRITE (JFILE,460)                                                15300
      IREAD=1                                                          15310
      IFILE=KFILE                                                      15320
   30 CONTINUE                                                         15330
C          READ SUBROUTINE CARD AND BRANCH                             15340
   40 CONTINUE                                                         15350
      READ (IFILE,470) SUB,ISOLN                                       15360
      DO 50 I=1,12                                                     15370
      IF (SUB.NE.SUBS(I)) GO TO 50                                     15380
      GO TO (60,70,110,150,170,180,220,400,260,350,390,1000), I        15390
   50 CONTINUE                                                         15400
      WRITE (6,480) SUB                                                15410
      GO TO 40                                                         15420
C                                                                      15430
C          READ TEMP DATA                                              15440
C                                                                      15450
   60 CONTINUE                                                         15460
      WRITE (6,490)                                                    15470
      IF (IOPT(4).EQ.0) GO TO 40                                       15480
      NTEMP=IOPT(4)                                                    15490
      IF (NTEMP.EQ.3) NTEMP=NSTEPS                                     15500
      READ (5,500) (TSTEP(I),I=1,NTEMP)                                15510
      WRITE (6,510) (TSTEP(I),I=1,NTEMP)                               15520
      ISUB(1)=1                                                        15530
      GO TO 40                                                         15540
C                                                                      15550
C          READ MINERAL DATA                                           15560
C                                                                      15570
   70 CONTINUE                                                         15580
      WRITE (6,520)                                                    15590
      I=0                                                              15600
   80 CONTINUE                                                         15610
      I=I+1                                                            15620
C          READ NAME ETC. FOR MINERAL                                  15630
      READ (5,530) MNAME(I),NMINO(I),THMIN(I),LKTOM(I),DHMIN(I),MFLAG(I) 15640
     1,SIMIN(I)                                                        15650
      WRITE (6,540) MNAME(I),NMINO(I),THMIN(I),LKTOM(I),DHMIN(I),MFLAG 15660
```

```
     1(I),SIMIN(I)                                                      15670
      IF (NMINO(I).EQ.0) GO TO 100                                      15680
      NRMINS=I                                                          15690
C          READ COEFFICIENTS FOR MINERAL                              15700
      K=NMINO(I)                                                        15710
      READ (5,550) (LMINO(I,J),CMINO(I,J),J=1,K)                        15720
      WRITE (6,560) (LMINO(I,J),CMINO(I,J),J=1,K)                       15730
C          READ ANALYTIC EXPRESSION COEFFICIENTS                      15740
      IF (MFLAG(I).EQ.0) GO TO 90                                       15750
      READ (5,570) (AMIN(I,J),J=1,5)                                    15760
      WRITE (6,580) (AMIN(I,J),J=1,5)                                   15770
   90 CONTINUE                                                          15780
      GO TO 80                                                          15790
  100 CONTINUE                                                          15800
      CALL MINCON                                                       15810
      CALL CHKMIN(IERR)                                                 15820
      ISUB(2)=1                                                         15830
      GO TO 40                                                          15840
C                                                                       15850
C          READ A SOLUTION                                            15860
C                                                                       15870
  110 CONTINUE                                                          15880
      WRITE (6,590) ISOLN                                               15890
C          READ SOLUTION TITLE                                        15900
      READ (5,600) (HEAD(ISOLN,J),J=1,20)                               15910
      WRITE (6,610) (HEAD(ISOLN,J),J=1,20)                              15920
C          READ NTOTS,PH,EH                                           15930
      READ (5,620) NTOTS,IALK(ISOLN),IUNITS(ISOLN),PH,PE,TEMP(ISOLN),   15940
     1SDENS(ISOLN)                                                      15950
C             FIX PE AT 4.0                                           15960
      PE=4.0                                                            15970
      IF (DABS(SDENS(ISOLN)).LE.1.0D-40) SDENS(ISOLN)=1.0               15980
      WRITE (6,630) NTOTS,IALK(ISOLN),IUNITS(ISOLN),PH,PE,TEMP(ISOLN),  15990
     1SDENS(ISOLN)                                                      16000
C          READ TOTALS                                                16010
      DO 120 I=1,MAXT                                                   16020
      TOTAL(ISOLN,I)=0D0                                                16030
  120 CONTINUE                                                          16040
      IF (NTOTS.EQ.0) GO TO 140                                         16050
      READ (5,640) (LT(J),DTOT(J),J=1,NTOTS)                            16060
      WRITE (6,650) (LT(J),DTOT(J),J=1,NTOTS)                           16070
C          ZERO TOTAL AND INSERT VALUES                               16080
      NTOTM=0                                                           16090
      DO 130 I=1,NTOTS                                                  16100
C          THROW OUT ELEMENTS NOT IN PITZER'S MODEL                   16110
      IF (LELEM(LT(I))) GO TO 125                                       16120
      NTOTM=NTOTM+1                                                     16130
      GO TO 130                                                         16140
  125 TOTAL(ISOLN,LT(I))=DTOT(I)                                        16150
  130 CONTINUE                                                          16160
      NTOTS=NTOTS-NTOTM                                                 16170
C                                                                       16180
      CALL UNITS(ISOLN)                                                 16190
  140 CONTINUE                                                          16200
      TOTAL(ISOLN,1)=1D1**(-PH)                                         16210
      TOTAL(ISOLN,2)=1D1**(-PE)                                         16220
```

```
      ISOLV(ISOLN)=1                                                    16230
      ISUB(3)=1                                                         16240
      GO TO 40                                                          16250
C                                                                       16260
C          READ REACTION DATA                                           16270
C                                                                       16280
  150 CONTINUE                                                          16290
      IF (NCOMPS.EQ.0) GO TO 40                                         16300
      WRITE(6,660)                                                      16310
C          READ COEFFICIENTS OF REACTION                                16320
      READ (5,670) (LREAC(I),CREAC(I),THMEAN(I),I=1,NCOMPS)             16330
      WRITE (6,680) (LREAC(I),CREAC(I),THMEAN(I),I=1,NCOMPS)            16340
      THREAC=0D0                                                        16350
      DO 160 I=1,NCOMPS                                                 16360
      THREAC=THREAC+THMEAN(I)*CREAC(I)                                  16370
  160 CONTINUE                                                          16380
      IF(IOPT(3).EQ.6.AND.NCOMPS.EQ.1.AND.LREAC(1).EQ.3) THEN           16390
         EVAP=.TRUE.                                                    16400
      END IF                                                            16410
      ISUB(4)=1                                                         16420
      GO TO 40                                                          16430
C                                                                       16440
C          READ STEPS DATA                                              16450
C                                                                       16460
  170 CONTINUE                                                          16470
      IF (NSTEPS.EQ.0.OR.IOPT(3).EQ.5) GO TO 40                         16480
      WRITE(6,690)                                                      16490
      K=NSTEPS                                                          16500
      IF (IOPT(3).EQ.4) K=1                                             16510
      READ (5,700) (XSTEP(I),I=1,K)                                     16520
      WRITE (6,710) (XSTEP(I),I=1,K)                                    16530
      ISUB(5)=1                                                         16540
      GO TO 40                                                          16550
C                                                                       16560
C          READ ELEMENT CARDS                                           16570
C                                                                       16580
  180 CONTINUE                                                          16590
      WRITE(6,720)                                                      16600
C          READ ELEMENTS UNTIL BLANK CARD                               16610
  190 CONTINUE                                                          16620
      READ (IFILE,730) TNAM,NELT,TGFW                                   16630
      IF (IREAD.EQ.0) WRITE (6,740) TNAM,NELT,TGFW                      16640
      IF (NELT.EQ.0) GO TO 210                                          16650
      IF (NELT.GT.3.AND.NELT.LE.29) GO TO 200                           16660
      WRITE (6,750) NELT,TNAM,SUBS(6)                                   16670
      ENDFILE (UNIT=6)                                                  16680
      STOP 'INDEX ERROR IN SUBROUTINE READ'                             16690
  200 CONTINUE                                                          16700
      IF (IREAD.EQ.1) LELEM(NELT)=.TRUE.                                16710
      TNAME(NELT)=TNAM                                                  16720
      GFW(NELT)=TGFW                                                    16730
      GO TO 190                                                         16740
  210 CONTINUE                                                          16750
      ISUB(6)=1                                                         16760
      GO TO 40                                                          16770
C                                                                       16780
```

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C          READ SPECIES CARDS                                                   16790
C                                                                               16800
  220 CONTINUE                                                                  16810
      WRITE (6,760)                                                             16820
C          READ SPECIES CARDS UNTIL BLANK CARD                                  16830
  230 CONTINUE                                                                  16840
      READ (IFILE,770) I                                                        16850
      IF (IREAD.EQ.0) WRITE (6,780) I                                           16860
C          READ SPECIES NAME ETC.                                               16870
      IF (I.EQ.0) GO TO 250                                                     16880
      IF (I.GT.0.AND.I.LE.MAXS) GO TO 240                                       16890
      READ (IFILE,790) TNAM                                                     16900
      WRITE (6,750) I,TNAM,SUBS(7)                                              16910
      ENDFILE (UNIT=6)                                                          16920
      STOP 'INDEX ERROR IN SUBROUTINE READ'                                     16930
  240 CONTINUE                                                                  16940
      READ (IFILE,790) SNAME(I),NSP(I),KFLAG(I),GFLAG(I),ZSP(I),THSP(I),        16950
     1DHA(I),(ADHSP(I,J),J=1,2),ALKSP(I)                                        16960
      IF (IREAD.EQ.0) WRITE (6,800)SNAME(I),NSP(I),KFLAG(I),GFLAG(I)            16970
     1,ZSP(I),THSP(I),DHA(I),(ADHSP(I,J),J=1,2),ALKSP(I)                        16980
      IF (NSP(I).EQ.0) GO TO 230                                                16990
C          READ LOG K DATA FOR SPECIES                                          17000
      READ (IFILE,810) LKTOSP(I),DHSP(I),(ASP(I,J),J=1,5)                       17010
      IF (IREAD.EQ.0) WRITE (6,820) LKTOSP(I),DHSP(I),(ASP(I,J),J=1,5)          17020
C          READ COEFFICIENTS                                                    17030
      K=NSP(I)                                                                  17040
      READ (IFILE,830) (LSP(I,J),CSP(I,J),J=1,K)                                17050
      IF (IREAD.EQ.0) WRITE (6,840) (LSP(I,J),CSP(I,J),J=1,K)                   17060
      GO TO 230                                                                 17070
  250 CONTINUE                                                                  17080
      ISUB(7)=1                                                                 17090
      CALL CHKSPE(IERR)                                                         17100
      GO TO 40                                                                  17110
C                                                                               17120
C          READ MINERALS TO LOOK AT                                             17130
C                                                                               17140
  260 CONTINUE                                                                  17150
      WRITE (6,850)                                                             17160
      I=NLKS                                                                    17170
  270 CONTINUE                                                                  17180
      I=I+1                                                                     17190
      IF (I.LT.41) GO TO 280                                                    17200
      WRITE (6,860)                                                             17210
      I=40                                                                      17220
  280 CONTINUE                                                                  17230
C          READ NAME ETC.                                                       17240
      READ (IFILE,870) NAMELK(I),NLOOK(I),LKOLK(I),DHLOOK(I),LOOKFL(I)          17250
      IF (IREAD.EQ.0) WRITE (6,880) NAMELK(I),NLOOK(I),LKOLK(I),DHLOOK          17260
     1(I),LOOKFL(I)                                                             17270
      IF (NAMELK(I).NE.DELETE) GO TO 290                                        17280
      I=0                                                                       17290
      NLOOKS=I                                                                  17300
      GO TO 270                                                                 17310
  290 CONTINUE                                                                  17320
      IF (NLOOK(I).EQ.0) GO TO 340                                              17330
C          CHECK TO SEE IF MINERAL IS ALREADY IN THE LIST                       17340
```

```
      IF (I.LE.1) GO TO 310                                              17350
      L=I-1                                                              17360
      DO 300 N=1,L                                                       17370
      IF (NAMELK(I).NE.NAMELK(N)) GO TO 300                              17380
      NLOOK(N)=NLOOK(I)                                                  17390
      LKOLK(N)=LKOLK(I)                                                  17400
      DHLOOK(N)=DHLOOK(I)                                                17410
      LOOKFL(N)=LOOKFL(I)                                                17420
      I=I-1                                                              17430
      GO TO 320                                                          17440
  300 CONTINUE                                                           17450
  310 CONTINUE                                                           17460
      N=I                                                                17470
      NLOOKS=I                                                           17480
C          N IS THE NUMBER FOR THE MINERAL BEING READ.                   17490
  320 CONTINUE                                                           17500
C          READ COEFFICIENTS                                             17510
      K=NLOOK(N)                                                         17520
      READ (IFILE,550) (LLOOK(N,J),CLOOK(N,J),J=1,K)                     17530
      IF (IREAD.EQ.0) WRITE (6,560) (LLOOK(N,J),CLOOK(N,J),J=1,K)        17540
C          READ ANALYTIC EXPRESSION                                      17550
      IF (LOOKFL(N).EQ.0) GO TO 330                                      17560
      READ (IFILE,570) (ALOOK(N,J),J=1,5)                                17570
      IF (IREAD.EQ.0) WRITE (6,580) (ALOOK(N,J),J=1,5)                   17580
  330 CONTINUE                                                           17590
      GO TO 270                                                          17600
  340 CONTINUE                                                           17610
      NLKS=NLOOKS                                                        17620
      CALL CHKLK                                                         17630
      ISUB(9)=1                                                          17640
      GO TO 40                                                           17650
C                                                                        17660
C          READ LISTS FOR SUMS OF SPECIES                                17670
C                                                                        17680
  350 CONTINUE                                                           17690
      WRITE (6,890)                                                      17700
      I=NSMS                                                             17710
  360 CONTINUE                                                           17720
      I=I+1                                                              17730
      READ (IFILE,900) SUNAME(I),K                                       17740
      IF (IREAD.EQ.0) WRITE (6,910) SUNAME(I),K                          17750
      IF (SUNAME(I).NE.DELETE) GO TO 370                                 17760
      I=0                                                                17770
      NSUMS=0                                                            17780
      GO TO 360                                                          17790
  370 CONTINUE                                                           17800
      IF (K.EQ.0) GO TO 380                                              17810
      NSUM(I)=K                                                          17820
      NSUMS=I                                                            17830
      READ (IFILE,920) (LSUM(I,J),J=1,K)                                 17840
      IF (IREAD.EQ.0) WRITE (6,930) (LSUM(I,J),J=1,K)                    17850
      GO TO 360                                                          17860
  380 CONTINUE                                                           17870
      NSMS=NSUMS                                                         17880
      ISUB(10)=1                                                         17890
      GO TO 40                                                           17900
```

```
C                                                                       17910
C          READ SPECIES TO ADJUST FOR ELECTRICAL NEUTRALITY             17920
C                                                                       17930
  390 CONTINUE                                                          17940
      WRITE (6,940)                                                     17950
      READ (5,950) LPOS,LNEG                                            17960
      WRITE (6,960) LPOS,LNEG                                           17970
      ISUB(11)=1                                                        17980
      GO TO 40                                                          17990
C                                                                       18000
C          END DATA ENTRY FOR THIS SIMULATION                           18010
C                                                                       18020
  400 CONTINUE                                                          18030
      IF (IREAD.EQ.1) RETURN                                            18040
      IF (IERR.LE.0) GO TO 405                                          18050
      ENDFILE (UNIT=6)                                                  18060
      STOP 'ERROR IN SPECIES OR MINERAL EQUATIONS'                      18070
  405 IF (IOPT(4).GT.0.AND.ISUB(1).EQ.0) IERR=1                         18080
      IF (IOPT(3).GT.0.AND.IOPT(3).LT.5.AND.ISUB(5).EQ.0) IERR=5        18090
      IF (IOPT(3).GE.3.AND.IOPT(3).LT.5.AND.ISUB(4).EQ.0) IERR=4        18100
      IF (IOPT(3).EQ.5.AND.ISUB(2).EQ.0) IERR=2                         18110
      IF (IOPT(3).EQ.6.AND.ISUB(2).EQ.0) IERR=2                         18120
      IF (IOPT(3).EQ.6.AND.ISUB(4).EQ.0) IERR=4                         18130
      IF (IOPT(2).EQ.2.AND.ISUB(11).EQ.0) IERR=11                       18140
      IF (IERR.EQ.0) RETURN                                             18150
      WRITE (6,970) SUBS(IERR)                                          18160
      IF (IOPT(7).EQ.0) GO TO 10                                        18170
  410 CONTINUE                                                          18180
      ENDFILE (UNIT=6)                                                  18190
      STOP 'NORMAL TERMINATION'                                         18200
C                                                                       18210
C     READ MEAN GAMMAS                                                  18220
C                                                                       18230
 1000 WRITE (6,980)                                                     18240
 1005 NMG=NMG+1                                                         18250
      IF (NMG.LE.40) GO TO 1100                                         18260
      WRITE (6,990)                                                     18270
 1010 READ (IFILE,1020) NM                                              18280
 1020 FORMAT (8X,I2)                                                    18290
      IF (NM.EQ.0) GO TO 40                                             18300
      GO TO 1010                                                        18310
 1100 READ (IFILE,995) NMEANG(NMG),IMEANG(NMG),(LMEANG(NMG,J)           18320
     1,CMEANG(NMG,J),J=1,3)                                             18330
      IF (IREAD.EQ.0) WRITE (6,996) NMEANG(NMG),IMEANG(NMG)             18340
     1,(LMEANG(NMG,J),CMEANG(NMG,J),J=1,IMEANG(NMG))                    18350
      IF (NMEANG(NMG).EQ.DELETE) GO TO 1150                             18360
      IF (IMEANG(NMG).NE.0) GO TO 1110                                  18370
      NMG=NMG-1                                                         18380
      GO TO 1200                                                        18390
 1110 DO 1120 J=1,NMG-1                                                 18400
      IF (NMEANG(J).EQ.NMEANG(NMG)) GO TO 1130                          18410
 1120 CONTINUE                                                          18420
      GO TO 1005                                                        18430
 1130 IMEANG(J)=IMEANG(NMG)                                             18440
      DO 1140 I=1,IMEANG(J)                                             18450
      LMEANG(J,I)=LMEANG(NMG,I)                                         18460
```

```
      CMEANG(J,I)=CMEANG(NMG,I)                                          18470
 1140 CONTINUE                                                           18480
      NMG=NMG-1                                                          18490
      GO TO 1005                                                         18500
 1150 NMG=0                                                              18510
      GO TO 1005                                                         18520
 1200 NMGS=NMG                                                           18530
      GO TO 40                                                           18540
C                                                                        18550
  420 FORMAT (20A4)                                                      18560
  430 FORMAT (10I1,I2,I2,6X,F10.5)                                       18570
  440 FORMAT (1H1,20A4)                                                  18580
  450 FORMAT (1X,10I1,I2,I2,6X,F10.5)                                    18590
  460 FORMAT (10X,'DATA READ FROM DISK'/)                                18600
  470 FORMAT (A8,1X,I1)                                                  18610
  480 FORMAT (1X,'** ',A8,' **  INPUT UNKNOWN')                          18620
  490 FORMAT (1X,'TEMP')                                                 18630
  500 FORMAT (8F10.1)                                                    18640
  510 FORMAT (1X,8G10.3)                                                 18650
  520 FORMAT (1X,'MINERALS')                                             18660
  530 FORMAT (A8,2X,I2,3X,3F10.2,5X,I1,9X,F10.3)                         18670
  540 FORMAT (1X,A8,2X,I2,3X,3G10.2,5X,I1,9X,F10.3)                      18680
  550 FORMAT ((5(I4,F11.3)))                                             18690
  560 FORMAT ((1X,5(I4,G11.3)))                                          18700
  570 FORMAT (5E12.5)                                                    18710
  580 FORMAT (1X,1P5E12.4)                                               18720
  590 FORMAT (1X,'SOLUTION ',I1)                                         18730
  600 FORMAT (20A4)                                                      18740
  610 FORMAT (1X,20A4)                                                   18750
  620 FORMAT (I2,I3,I2,3X,4F10.0)                                        18760
  630 FORMAT (1X,I2,I3,I2,3X,4G10.3)                                     18770
  640 FORMAT ((5(I4,D11.3)))                                             18780
  650 FORMAT ((1X,5(I4,1PD11.3)))                                        18790
  660 FORMAT (1X,'REACTION')                                             18800
  670 FORMAT ((4(I4,2F8.3)))                                             18810
  680 FORMAT ((1X,4(I4,2F8.3)))                                          18820
  690 FORMAT (1X,'STEPS')                                                18830
  700 FORMAT (8F10.3)                                                    18840
  710 FORMAT (1X,8G10.3)                                                 18850
  720 FORMAT (1X,'ELEMENTS')                                             18860
  730 FORMAT (A9,1X,I2,3X,F10.0)                                         18870
  740 FORMAT (1X,A9,2X,I2,3X,E16.5)                                      18880
  750 FORMAT (1X,I4,2X,A8,5X,A8,' INDEX NUMBER IS OUT OF RANGE.'//1X,'CA 18890
     1LCULATION TERMINATED.')                                            18900
  760 FORMAT (1X,'SPECIES')                                              18910
  770 FORMAT (I3)                                                        18920
  780 FORMAT (1X,I3)                                                     18930
  790 FORMAT (A8,2X,I3,I1,I1,6F10.3)                                     18940
  800 FORMAT (1X,A8,2X,I3,I1,I1,6F10.3)                                  18950
  810 FORMAT (2F10.3,5E12.5)                                             18960
  820 FORMAT (1X,2F10.3,5G12.5)                                          18970
  830 FORMAT (6(I3,F7.3))                                                18980
  840 FORMAT ((1X,6(I3,F7.3)))                                           18990
  850 FORMAT (1X,'LOOK MIN')                                             19000
  860 FORMAT (1X,'***** LOOK MIN ARRAY ALREADY HAS 40 MINERALS. *****')  19010
  870 FORMAT (A8,2X,I2,13X,2F10.2,5X,I1)                                 19020
```

```
  880 FORMAT (1X,A8,2X,I2,13X,2G10.3,5X,I1)                                 19030
  890 FORMAT (1X,'SUMS')                                                    19040
  900 FORMAT (A8,2X,I2)                                                     19050
  910 FORMAT (1X,A8,2X,I2)                                                  19060
  920 FORMAT (20I4)                                                         19070
  930 FORMAT (1X,20I4)                                                      19080
  940 FORMAT (1X,'NEUTRAL')                                                 19090
  950 FORMAT (2I5)                                                          19100
  960 FORMAT (1X,2I5)                                                       19110
  970 FORMAT (//1X,14('*')/1X,'TERMINAL ERROR  INPUT LACKED ',A8,' CARDS    19120
     1'/1X,14('*'))                                                         19130
  980 FORMAT (1X,'MEAN GAM')                                                19140
  990 FORMAT (1X,'***** MEAN GAM ARRARY ALREADY HAS 40 SALTS. *****')       19150
  995 FORMAT (A8,I2,3(I4,F6.0))                                             19160
  996 FORMAT (1X,A8,I2,3(I4,F6.2))                                          19170
      END                                                                   19180
      SUBROUTINE INOUT                                                      19190
$INSERT COMMON.BLOCKS                                                       19200
C                                                                           19210
C          DETERMINE TOTALS TO BE INCLUDED AS EQUATIONS IN MATRIX.          19220
C                                                                           19230
      DO 10 I=4,MAXT                                                        19240
      IIN(I)=0                                                              19250
      IF (TOT(I).LE.0.0D0) GO TO 10                                         19260
      IIN(I)=1                                                              19270
   10 CONTINUE                                                              19280
      LAST=0                                                                19290
      LASTT=0                                                               19300
      DO 20 I=1,MAXT                                                        19310
      IF (IIN(I).EQ.0) GO TO 20                                             19320
      LAST=LAST+1                                                           19330
      IIN(I)=LAST                                                           19340
      LASTT=I                                                               19350
      IOUT(LAST)=I                                                          19360
   20 CONTINUE                                                              19370
      ILT=LAST                                                              19380
C          PICK SPECIES TO BE INCLUDED                                      19390
      IF (LASTT.LT.4) LASTT=4                                               19400
      SFLAG(1)=1                                                            19410
      SFLAG(2)=1                                                            19420
      SFLAG(3)=1                                                            19430
      DO 30 I=4,MAXT                                                        19440
      SFLAG(I)=0                                                            19450
      IF (IIN(I).GT.0) SFLAG(I)=1                                           19460
   30 CONTINUE                                                              19470
      DO 50 I=MAXT1,MAXS                                                    19480
      SFLAG(I)=0                                                            19490
      K=NSP(I)                                                              19500
      IF (K.EQ.0) GO TO 50                                                  19510
      DO 40 J=1,K                                                           19520
      IF (SFLAG(LSP(I,J)).LE.0) GO TO 50                                    19530
   40 CONTINUE                                                              19540
      SFLAG(I)=1                                                            19550
      LASTS=I                                                               19560
   50 CONTINUE                                                              19570
C          ZERO ARRAY AR                                                    19580
```

```
      DO 70 I=1,MAXEQ                                                   19590
      DO 60 J=1,MAXEQ                                                   19600
      AR(I,J)=0D0                                                       19610
   60 CONTINUE                                                          19620
   70 CONTINUE                                                          19630
C          PUT MINERAL COEFFICIENTS INTO FULL ARRAY                     19640
      IF (NMINS.LE.0) GO TO 120                                         19650
      DO 90 I=1,NMINS                                                   19660
      K=NMIN(I)                                                         19670
      L=MAXT+I                                                          19680
      DO 80 J=1,K                                                       19690
      K1=LMIN(I,J)                                                      19700
      AR(K1,L)=-CMIN(I,J)                                               19710
      AR(L,K1)=CMIN(I,J)                                                19720
   80 CONTINUE                                                          19730
      AR(1,L)=0D0                                                       19740
      AR(2,L)=-THMIN(I)                                                 19750
   90 CONTINUE                                                          19760
      IF (IOPT(3).NE.6) GO TO 120                                       19770
C          ADD REACTION TO EQUILBRATE WITH MINERAL # 1.                 19780
      L=MAXT+1                                                          19790
      DO 100 I=1,MAXT                                                   19800
      AR(I,L)=0D0                                                       19810
  100 CONTINUE                                                          19820
      DO 110 I=1,NCOMPS                                                 19830
      J=LREAC(I)                                                        19840
      AR(J,L)=AR(J,L)-CREAC(I)                                          19850
      AR(2,L)=AR(2,L)-CREAC(I)*THMEAN(I)                                19860
  110 CONTINUE                                                          19870
  120 CONTINUE                                                          19880
      RETURN                                                            19890
      END                                                               19900
      SUBROUTINE KTEMP                                                  19910
$INSERT COMMON.BLOCKS                                                   19920
      DATA C/2.302585092/,R/1.98719D-3/                                 19930
C                                                                       19940
C          COMPUTE TEMPERATURE DEPENDENCE OF A AND B FOR DEBYE-HUCKEL   19950
C                                                                       19960
      S1=374.11-TC                                                      19970
      S2=S1**0.33333333                                                 19980
      S3=1.0+0.1342489*S2-3.946263E-03*S1                               19990
      S3=S3/(3.1975-0.3151548*S2-1.203374E-03*S1+7.48908E-13*S1**4.0)   20000
      S3=DSQRT(S3)                                                      20010
      IF (TK.LT.373.15) GO TO 10                                        20020
      C1=5321.0/TK+233.76-TK*(TK*(8.292E-07*TK-1.417E-03)+0.9297)       20030
      GO TO 20                                                          20040
   10 C1=87.74-TC*(TC*(1.41E-06*TC-9.398E-04)+0.4008)                   20050
   20 CONTINUE                                                          20060
      C1=DSQRT(C1*TK)                                                   20070
      A=1824600.0*S3/C1**3.0                                            20080
      B=50.29*S3/C1                                                     20090
C                                                                       20100
C          COMPUTE VANT HOFF CONSTANTS                                  20110
C                                                                       20120
      C1=(298.15-TK)/(298.15*TK*C*R)                                    20130
      DO 30 I=1,LASTS                                                   20140
```

```
      IF (SFLAG(I).EQ.0) GO TO 30                                       20150
      IF (KFLAG(I).EQ.1) LKSP(I)=ASP(I,1)+ASP(I,2)*TK+ASP(I,3)/TK+ASP(I, 20160
     14)*DLOG10(TK)+ASP(I,5)/TK**2D0                                    20170
      IF (KFLAG(I).EQ.0) LKSP(I)=LKTOSP(I)-DHSP(I)*C1                   20180
   30 CONTINUE                                                          20190
      IF (NLOOKS.EQ.0) GO TO 50                                         20200
      DO 40 I=1,NLOOKS                                                  20210
      IF (LOOKFL(I).EQ.0) LKLOOK(I)=LKOLK(I)-DHLOOK(I)*C1               20220
      IF (LOOKFL(I).EQ.1) LKLOOK(I)=ALOOK(I,1)+ALOOK(I,2)*TK+ALOOK(I,3)/ 20230
     1TK+ALOOK(I,4)*DLOG10(TK)+ALOOK(I,5)/TK**2D0                       20240
   40 CONTINUE                                                          20250
   50 CONTINUE                                                          20260
      RETURN                                                            20270
C     *****                                                             20280
      ENTRY KMINO                                                       20290
C     *****                                                             20300
      IF (NMINS.EQ.0) GO TO 80                                          20310
      DO 70 I=1,NMINS                                                   20320
      IF (MFLAG(I).EQ.0) LKMINO(I)=LKTOM(I)-DHMIN(I)*C1                 20330
      IF (MFLAG(I).EQ.1) LKMINO(I)=AMIN(I,1)+AMIN(I,2)*TK+AMIN(I,3)/TK+A 20340
     1MIN(I,4)*DLOG10(TK)+AMIN(I,5)/TK**2D0                             20350
C          CONVERT K TO MASTER SPECIES                                  20360
      LKMIN(I)=LKMINO(I)+SIMIN(I)                                       20370
      IF (NMCON(I).EQ.0) GO TO 70                                       20380
      K=NMCON(I)                                                        20390
      DO 60 J=1,K                                                       20400
      LKMIN(I)=CMCON(I,J)*LKSP(LMCON(I,J))+LKMIN(I)                     20410
   60 CONTINUE                                                          20420
   70 CONTINUE                                                          20430
   80 CONTINUE                                                          20440
      RETURN                                                            20450
      END                                                               20460
      SUBROUTINE MINCON                                                 20470
$INSERT COMMON.BLOCKS                                                   20480
C          LOOP ON NUMBER OF MINERALS                                   20490
      DO 100 I=1,NRMINS                                                 20500
      K=NMINO(I)                                                        20510
      ICOMP=0                                                           20520
      NONMAS=0                                                          20530
C          LOOP ON INDIVIDUAL MINERAL                                   20540
      DO 90 J=1,K                                                       20550
      IF (LMINO(I,J).GT.MAXT) GO TO 40                                  20560
      IF (ICOMP.EQ.0) GO TO 20                                          20570
C          CHECK TO SEE IF COMPONENT IS ALREADY IN LIST                 20580
      DO 10 I1=1,ICOMP                                                  20590
      IF (LMIN(I,I1).EQ.LMINO(I,J)) GO TO 30                            20600
   10 CONTINUE                                                          20610
   20 CONTINUE                                                          20620
C          COMPONENT NOT IN LIST                                        20630
      ICOMP=ICOMP+1                                                     20640
      LMIN(I,ICOMP)=LMINO(I,J)                                          20650
      CMIN(I,ICOMP)=CMINO(I,J)                                          20660
      GO TO 90                                                          20670
C         COMPONENT ALREADY IN LIST                                     20680
   30 CONTINUE                                                          20690
      CMIN(I,I1)=CMIN(I,I1)+CMINO(I,J)                                  20700
```

```
      GO TO 90                                                          20710
C           COMPONENT MUST BE REDUCED TO MASTER SPECIES                 20720
   40 CONTINUE                                                          20730
      J1=LMINO(I,J)                                                     20740
      K1=NSP(J1)                                                        20750
      NONMAS=NONMAS+1                                                   20760
      LMCON(I,NONMAS)=J1                                                20770
      CMCON(I,NONMAS)=-CMINO(I,J)                                       20780
C           LOOP THROUGH MASTER SPECIES OF NON-MASTER SPECIES COMPONENT  20790
      DO 80 I1=1,K1                                                     20800
      IF (ICOMP.EQ.0) GO TO 60                                          20810
      DO 50 L1=1,ICOMP                                                  20820
      IF (LSP(J1,I1).EQ.LMIN(I,L1)) GO TO 70                            20830
   50 CONTINUE                                                          20840
C           MASTER SPECIES NOT IN LIST                                  20850
   60 CONTINUE                                                          20860
      ICOMP=ICOMP+1                                                     20870
      LMIN(I,ICOMP)=LSP(J1,I1)                                          20880
      CMIN(I,ICOMP)=CMINO(I,J)*CSP(J1,I1)                               20890
      GO TO 80                                                          20900
C           MASTER SPECIES IN LIST                                      20910
   70 CONTINUE                                                          20920
      CMIN(I,L1)=CMIN(I,L1)+CMINO(I,J)*CSP(J1,I1)                       20930
   80 CONTINUE                                                          20940
C           END LOOP MASTER SPECIES OF NON MASTER SPECIES COMPONENT     20950
   90 CONTINUE                                                          20960
      NMIN(I)=ICOMP                                                     20970
      NMCON(I)=NONMAS                                                   20980
C           END LOOP ON SINGLE MINERAL                                  20990
  100 CONTINUE                                                          21000
C           END ALL MINERALS                                            21010
      RETURN                                                            21020
      END                                                               21030
      SUBROUTINE PICK1                                                  21040
$INSERT COMMON.BLOCKS                                                   21050
C                                                                       21060
C           THIS SUBROUTINE CHOOSES THE MODEL FOR THE INITIAL SOLUTIONS 21070
C                                                                       21080
      DZOFF=0D0                                                         21090
      IIN(1)=1                                                          21100
      IIN(2)=0                                                          21110
      IIN(3)=0                                                          21120
      NMINS=0                                                           21130
      IFE=1                                                             21140
      ILE=1                                                             21150
      IF (IESPEC.EQ.1) GO TO 10                                         21160
      IIN(1)=0                                                          21170
      IFE=0                                                             21180
      ILE=0                                                             21190
   10 CONTINUE                                                          21200
C           CHECK ALKALINITY TOTAL                                      21210
      DALKT=0D0                                                         21220
      IASPEC=IALK(ISOL)                                                 21230
      IF (IASPEC.EQ.0) GO TO 30                                         21240
      IF (TOTAL(ISOL,IASPEC).GT.0D0) GO TO 20                           21250
      WRITE (6,140)                                                     21260
```

```
      ENDFILE (UNIT=6)                                                  21270
      STOP 'ERROR IN ALKALINITY OPTIONS'                                21280
   20 CONTINUE                                                          21290
      DALKT=TOTAL(ISOL,IASPEC)                                          21300
      IF (IESPEC.EQ.0.OR.IESPEC.NE.IASPEC) GO TO 30                     21310
      WRITE (6,150)                                                     21320
      ENDFILE (UNIT=6)                                                  21330
      STOP 'ERROR IN ALKALINITY/NEUTRAL OPTIONS'                        21340
   30 CONTINUE                                                          21350
      IF (IOPT(2).EQ.1.AND.IASPEC.GT.0) THEN                            21360
         WRITE(6,146)                                                   21370
  146    FORMAT(' CAN NOT ADJUST PH AND ALKALINITY SIMULTANEOUSLY')     21380
         ENDFILE (UNIT=6)                                               21390
         STOP 'ERROR IN ALKALINITY/ELECTRICAL BALANCE OPTIONS'          21400
      END IF                                                            21410
      DNEUT=0.0D0                                                       21420
      IF (IESPEC.LT.4) GO TO 40                                         21430
C          MAKE SURE NEUTRAL SPECIES .GT. 0                           21440
      DNEUT=TOT(IESPEC)                                                 21450
      IF (TOT(IESPEC).LE.0D0) TOT(IESPEC)=1D-3                          21460
   40 CONTINUE                                                          21470
      CALL INOUT                                                        21480
C          SET COUNTERS ON THE ARRAY                                  21490
      IFTH=0                                                            21500
      ILTH=0                                                            21510
      IFT=ILE+1                                                         21520
      ILT=ILT                                                           21530
      IFM=0                                                             21540
      ILM=0                                                             21550
      NEQ=ILT                                                           21560
      NEQ1=NEQ+1                                                        21570
      RETURN                                                            21580
C     *****                                                             21590
      ENTRY PICK2                                                       21600
C     *****                                                             21610
C                                                                       21620
C          THIS SUBROUTINE CHOOSES THE MODEL FOR THE REACTION SOLUTIONS 21630
C                                                                       21640
      IIN(1)=1                                                          21650
      IIN(2)=0                                                          21660
      IF (IOPT(5).GT.0) IIN(2)=1                                        21670
      IIN(3)=1                                                          21680
      IESPEC=1                                                          21690
      IASPEC=0                                                          21700
      NMINS=NRMINS                                                      21710
C          ADD IN ANY MINERALS NOT INCLUDED IN TOTALS                 21720
      IF (NMINS.EQ.0) GO TO 110                                         21730
      TOT(3)=1D0                                                        21740
      ICK=0                                                             21750
      DO 50 I=1,NMINS                                                   21760
      TOT(MAXT+I)=0D0                                                   21770
   50 CONTINUE                                                          21780
   55 CONTINUE                                                          21790
C          CHECK TO MAKE SURE NECESSARY TOTALS > 0.                   21800
      JCK=0                                                             21810
      ICK=ICK+1                                                         21820
```

```
      DO 70 I=1,NMINS                                                   21830
      IF (IOPT(3).EQ.6.AND.I.EQ.1) GO TO 70                             21840
      K=NMIN(I)                                                         21850
C          IF TOTALS > 0 NEXT MINERAL                                   21860
      DO 60 J=1,K                                                       21870
      IF (LMIN(I,J).LT.4) GO TO 60                                      21880
      IF(TOT(LMIN(I,J)).GT.0D0) GO TO 60                                21890
      GO TO 65                                                          21900
   60 CONTINUE                                                          21910
      GO TO 70                                                          21920
   65 CONTINUE                                                          21930
C          SOME TOTAL <= 0.  IF ALL CMIN > 0 ADD MINERAL.               21940
      DO 75 J=1,K                                                       21950
      IF (LMIN(I,J).LT.4) GO TO 75                                      21960
      IF (CMIN(I,J).GT.0) GO TO 75                                      21970
      GO TO 85                                                          21980
   75 CONTINUE                                                          21990
      D=1D-6                                                            22000
C          ADD D OF MINERAL # I.                                        22010
   95 CONTINUE                                                          22020
      TOT(MAXT+I)=D                                                     22030
      THOR=THOR+THMIN(I)*D                                              22040
      DO 105 J=1,K                                                      22050
      K1=LMIN(I,J)                                                      22060
      IF(K1.LT.4)GO TO 105                                              22070
      TOT(K1)=TOT(K1)+D*CMIN(I,J)                                       22080
  105 CONTINUE                                                          22090
      GO TO 70                                                          22100
C          SOME TOTAL <= 0.  CHECK IF TOTALS <= 0 HAVE SAME SIGN FOR CMI 22110
   85 CONTINUE                                                          22120
      NCNEG=0                                                           22130
      NCPOS=0                                                           22140
      D=1D1                                                             22150
      DO 115 J=1,K                                                      22160
      K1=LMIN(I,J)                                                      22170
      D1=TOT(K1)                                                        22180
      IF (D1.LE.0D0) GO TO 125                                          22190
      IF (D1.LT.D) D=D1                                                 22200
      GO TO 115                                                         22210
  125 CONTINUE                                                          22220
      IF(CMIN(I,J).LE.0D0) NCNEG=1                                      22230
      IF(CMIN(I,J).GT.0D0) NCPOS=1                                      22240
  115 CONTINUE                                                          22250
      IF(NCNEG.GT.0.AND.NCPOS.GT.0) GO TO 135                           22260
      D=D/5D1                                                           22270
      IF(NCNEG.EQ.1) D=-D                                               22280
      GO TO 95                                                          22290
  135 CONTINUE                                                          22300
      JCK=1                                                             22310
   70 CONTINUE                                                          22320
      IF(JCK.EQ.0) GO TO 145                                            22330
      IF(ICK.LE.NMINS+1) GO TO 55                                       22340
      WRITE (6,155)                                                     22350
  155 FORMAT(1H1,90('*')/'I HAD TROUBLE ADDING MINERALS SO THAT',       22360
     1       ' ALL THE NECESSARY ELEMENTS HAD POSITIVE CONCENTRATIONS.'/ 22370
     2       'PLEASE ADJUST INITIAL CONCENTRATIONS TO SOME SMALL ',     22380
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     3      'POSITIVE QUANTITY.'/90('*'))                                    22390
      ENDFILE (UNIT=6)                                                       22400
      STOP                                                                   22410
  145 CONTINUE                                                               22420
C           ADD ANY REACTION ELEMENTS IF IOPT(3)=6.                          22430
      IF (IOPT(3).NE.6) GO TO 100                                            22440
      DO 90 I=1,NCOMPS                                                       22450
      IF (TOT(LREAC(I)).GT.0D0) GO TO 90                                     22460
      D=DSIGN(1D-6,CREAC(I))                                                 22470
      TOT(MAXT1)=D                                                           22480
      DO 80 J=1,NCOMPS                                                       22490
      THOR=THOR+CREAC(J)*THMEAN(J)*D                                         22500
      TOT(LREAC(J))=TOT(LREAC(J))+CREAC(J)*D                                 22510
   80 CONTINUE                                                               22520
      GO TO 100                                                              22530
   90 CONTINUE                                                               22540
  100 CONTINUE                                                               22550
      TOT(1)=1D1**(-PH)                                                      22560
      TOT(2)=1D1**(-PE)                                                      22570
      TOT(3)=1D0                                                             22580
  110 CONTINUE                                                               22590
      CALL INOUT                                                             22600
C           SET COUNTERS FOR ARRAY                                           22610
      IFE=1                                                                  22620
      ILE=1                                                                  22630
      LAST=1                                                                 22640
      IFTH=0                                                                 22650
      ILTH=0                                                                 22660
      IF (IIN(2).LE.0) GO TO 120                                             22670
      IFTH=2                                                                 22680
      ILTH=2                                                                 22690
      LAST=2                                                                 22700
  120 CONTINUE                                                               22710
      LAST=LAST+1                                                            22720
C           THIS IS FOR H2O EQUATION.                                        22730
      IFT=LAST+1                                                             22740
      ILT=ILT                                                                22750
      IFM=0                                                                  22760
      ILM=0                                                                  22770
      NEQ=ILT                                                                22780
      IF (NMINS.EQ.0) GO TO 130                                              22790
      IFM=ILT+1                                                              22800
      ILM=ILT+NMINS                                                          22810
      NEQ=ILM                                                                22820
  130 CONTINUE                                                               22830
      NEQ1=NEQ+1                                                             22840
      RETURN                                                                 22850
C                                                                            22860
  140 FORMAT (1X,'CARBON WAS SPECIFIED AS ALKALINITY BUT WAS LESS ','THA     22870
     1N OR EQUAL 0.0.'/1X,'CALCULATIONS TERMINATED')                         22880
  150 FORMAT (1X,'ALKALINITY SPECIES CAN NOT BE THE SAME AS THE ','NEUTR    22890
     1AL SPECIES'/1X,'CALCULATIONS TERMINATED')                              22900
      END                                                                    22910
      SUBROUTINE STEP                                                        22920
$INSERT COMMON.BLOCKS                                                        22930
      LOGICAL EVAP                                                           22940
```

```
      COMMON /EVAP/ EVAP                                                22950
      IF (IOPT(3).EQ.0) GO TO 120                                       22960
      I=IOPT(3)                                                         22970
      WRITE (6,140) ISTEP                                               22980
      GO TO (10,30,50,60,100,100), I                                    22990
      GO TO 100                                                         23000
C          MIX SOLUTION 1 WITH SOLUTION 2                               23010
   10 CONTINUE                                                          23020
      X1=XSTEP(ISTEP)                                                   23030
      X2=1.0-X1                                                         23040
      DO 15 I=1,3                                                       23050
      TOT(I)=(TOTAL(1,I)*TOTAL(2,I))**0.5                               23060
   15 CONTINUE                                                          23070
      DO 20 I=4,MAXT                                                    23080
      TOT(I)=X1*TOTAL(1,I)+X2*TOTAL(2,I)                                23090
   20 CONTINUE                                                          23100
      THOR=TH(1)*X1+TH(2)*X2                                            23110
      TC=X1*TEMP(1)+X2*TEMP(2)                                          23120
      DZOFF=X1*DIFFZ(1)+X2*DIFFZ(2)                                     23130
      WRITE (6,150) X1,X2                                               23140
      GO TO 120                                                         23150
C          TITRATE                                                      23160
   30 CONTINUE                                                          23170
      X1=XSTEP(ISTEP)                                                   23180
      VTOT=VO+X1                                                        23190
      DO 40 I=1,MAXT                                                    23200
      TOT(I)=(TOTAL(1,I)*VO+TOTAL(2,I)*X1)/VTOT                         23210
   40 CONTINUE                                                          23220
      TC=(TEMP(1)*VO+TEMP(2)*X1)/VTOT                                   23230
      THOR=(TH(1)*VO+TH(2)*X1)/VTOT                                     23240
      DZOFF=(DIFFZ(1)*VO+DIFFZ(2)*X1)/VTOT                              23250
      WRITE (6,160) X1                                                  23260
      GO TO 120                                                         23270
C          ADD REACTION IN INCREMENTS                                   23280
   50 CONTINUE                                                          23290
      X1=XSTEP(ISTEP)                                                   23300
      GO TO 70                                                          23310
C            ADD REACTION LINEARLY                                      23320
   60 CONTINUE                                                          23330
      X1=(ISTEP*XSTEP(1))/NSTEPS                                        23340
   70 CONTINUE                                                          23350
      DZOFF=DIFFZ(1)                                                    23360
      DO 80 I=1,MAXT                                                    23370
      TOT(I)=TOTAL(1,I)                                                 23380
   80 CONTINUE                                                          23390
      DO 90 I=1,NCOMPS                                                  23400
      K=LREAC(I)                                                        23410
      IF (K.EQ.0) DZOFF=DIFFZ(1)+X1*CREAC(I)                            23420
      IF (K.LT.4.OR.K.GT.MAXT) GO TO 90                                 23430
      TOT(K)=TOT(K)+X1*CREAC(I)                                         23440
   90 CONTINUE                                                          23450
      THOR=TH(1)+THREAC*X1                                              23460
      TC=TEMP(1)                                                        23470
      IF (ISTEP.GT.1) TOT(1)=1D1**LA(1)                                 23480
      WRITE (6,170) X1                                                  23490
      CALL PREAC                                                        23500
```

```
      GO TO 120                                                          23510
C          FOLLOW PHASE BOUNDARIES ONLY                                  23520
  100 CONTINUE                                                           23530
C                                                                        23540
C             SPECIAL CASE OF EVAPORATION                                23550
C                                                                        23560
      IF (EVAP) THEN                                                     23570
         NCOMPS=0                                                        23580
         THREAC=0D0                                                      23590
         DO 115 I=4,29                                                   23600
         IF (TOTAL(1,I).GT.0.0D0) THEN                                   23610
            NCOMPS=NCOMPS+1                                              23620
            LREAC(NCOMPS)=I                                              23630
            CREAC(NCOMPS)=TOTAL(1,I)                                     23640
C             EVAPORATION DOES NOT CONSIDER REDOX                        23650
            THMEAN(I)=0D0                                                23660
         END IF                                                          23670
  115    CONTINUE                                                        23680
      END IF                                                             23690
      DO 110 I=1,MAXT                                                    23700
      TOT(I)=TOTAL(1,I)                                                  23710
  110 CONTINUE                                                           23720
      THOR=TH(1)                                                         23730
      TC=TEMP(1)                                                         23740
      DZOFF=DIFFZ(1)                                                     23750
      WRITE (6,180)                                                      23760
  120 CONTINUE                                                           23770
C          TEMPERATURE                                                   23780
      IF (IOPT(4).EQ.0) GO TO 130                                        23790
      IF (IOPT(4).EQ.1) TC=TSTEP(1)                                      23800
      IF (IOPT(4).EQ.2) TC=(ISTEP*(TSTEP(2)-TSTEP(1)))/NSTEPS+TSTEP(1)   23810
      IF (IOPT(4).EQ.3) TC=TSTEP(ISTEP)                                  23820
      WRITE (6,190) TC                                                   23830
  130 CONTINUE                                                           23840
      TK=TC+273.15                                                       23850
      RETURN                                                             23860
C                                                                        23870
  140 FORMAT (/1H1,'STEP NUMBER',I3,/1H0,14('-'))                        23880
  150 FORMAT (1H0,F10.3,' = FRACTION OF SOLUTION 1.',3X,F10.3,' = FR',   23890
     1'ACTION OF SOLUTION 2.'//)                                         23900
  160 FORMAT (1H0,F10.3,' VOLUME UNITS OF SOLUTION 2 HAVE BEEN ',        23910
     1'ADDED.'//)                                                        23920
  170 FORMAT (1H0,1PD10.3,' MOLES OF REACTION HAVE BEEN ADDED.'//)       23930
  180 FORMAT (//)                                                        23940
  190 FORMAT (23X,F10.2,' = NEW TEMPERATURE (C).'//)                     23950
      END                                                                23960
      SUBROUTINE THORIT(T)                                               23970
$INSERT COMMON.BLOCKS                                                    23980
      T=0.0D0                                                            23990
      DALKS=0D0                                                          24000
      DO 10 I=1,LASTS                                                    24010
      IF (SFLAG(I).EQ.0) GO TO 10                                        24020
      DALKS=DALKS+M(I)*ALKSP(I)                                          24030
      T=T+M(I)*THSP(I)                                                   24040
   10 CONTINUE                                                           24050
      RETURN                                                             24060
```

```
C     *****                                                          24070
      ENTRY SOLN(J1)                                                 24080
C     *****                                                          24090
      WRITE (6,260) J1,(HEAD(J1,I),I=1,20)                           24100
      DO 20 I=1,MAXT                                                 24110
      TOT(I)=TOTAL(J1,I)                                             24120
   20 CONTINUE                                                       24130
      THOR=0.0D0                                                     24140
      TC=TEMP(J1)                                                    24150
      TK=TC+273.15                                                   24160
      IF (DABS(TC-25.0).GT.30.0) WRITE (6,265)                       24170
      PH=-DLOG10(TOT(1))                                             24180
      PE=-DLOG10(TOT(2))                                             24190
      RETURN                                                         24200
C     *****                                                          24210
      ENTRY SAVE                                                     24220
C     *****                                                          24230
      IF (IOPT(7).EQ.0) RETURN                                       24240
      K=IOPT(7)                                                      24250
      DO 30 I=1,MAXT                                                 24260
      TOTAL(K,I)=TOT(I)                                              24270
   30 CONTINUE                                                       24280
      TEMP(K)=TC                                                     24290
      TH(K)=THOR                                                     24300
      DIFFZ(K)=DZOFF                                                 24310
      RETURN                                                         24320
C     *****                                                          24330
      ENTRY CHKSPE (IERR1)                                           24340
C     *****                                                          24350
C          CHECK MASTER SPECIES IN AQUEOUS SPECIES                   24360
      DO 80 I=1,MAXS                                                 24370
      IF (NSP(I).LE.0) GO TO 80                                      24380
      K=NSP(I)                                                       24390
      DO 70 J=1,K                                                    24400
      L=LSP(I,J)                                                     24410
      IF (L.GE.1.AND.L.LE.MAXT) GO TO 70                             24420
      WRITE (6,270) I,SNAME(I)                                       24430
      IERR1=1                                                        24440
   70 CONTINUE                                                       24450
   80 CONTINUE                                                       24460
C          CHECK SPECIES                                             24470
      DO 100 I=MAXT1,MAXS                                            24480
      K=NSP(I)                                                       24490
      IF (K.EQ.0) GO TO 100                                          24500
      Z=0.0D0                                                        24510
      DO 90 J=1,K                                                    24520
      Z=Z+ZSP(LSP(I,J))*CSP(I,J)                                     24530
   90 CONTINUE                                                       24540
      IF (DABS(ZSP(I)-Z).LT.1D-5) GO TO 100                          24550
      IERR1=1                                                        24560
      WRITE (6,280) I,SNAME(I)                                       24570
  100 CONTINUE                                                       24580
      RETURN                                                         24590
C     *****                                                          24600
      ENTRY CHKMIN (IERR2)                                           24610
C     *****                                                          24620
```

```
C          CHECK MINERALS FOR CHARGE AND VALENCE                        24630
      IF (NRMINS.EQ.0) GO TO 140                                        24640
      THSP(2)=-1D0                                                      24650
      DO 130 I=1,NRMINS                                                 24660
      K=NMINO(I)                                                        24670
      Z=0.0D0                                                           24680
      THR=0.0D0                                                         24690
      DO 110 J=1,K                                                      24700
      Z=Z+ZSP(LMINO(I,J))*CMINO(I,J)                                    24710
      THR=THR+THSP(LMINO(I,J))*CMINO(I,J)                               24720
  110 CONTINUE                                                          24730
      IF (DABS(Z).LT.1D-5) GO TO 120                                    24740
      IERR2=2                                                           24750
      WRITE (6,290) I,MNAME(I)                                          24760
  120 CONTINUE                                                          24770
      IF (DABS(THR-THMIN(I)).LT.1D-5) GO TO 130                         24780
      IERR2=3                                                           24790
      WRITE (6,300) I,MNAME(I)                                          24800
  130 CONTINUE                                                          24810
      THSP(2)=0D0                                                       24820
  140 CONTINUE                                                          24830
      RETURN                                                            24840
C     *****                                                             24850
      ENTRY CHKLK                                                       24860
C     *****                                                             24870
C          CHECK LOOK MINERALS                                          24880
      IF (NLOOKS.EQ.0) GO TO 170                                        24890
      DO 160 I=1,NLOOKS                                                 24900
      K=NLOOK(I)                                                        24910
      Z=0.0D0                                                           24920
      DO 150 J=1,K                                                      24930
      Z=Z+ZSP(LLOOK(I,J))*CLOOK(I,J)                                    24940
  150 CONTINUE                                                          24950
      IF (DABS(Z).LT.1D-5) GO TO 160                                    24960
      WRITE (6,310) I,NAMELK(I)                                         24970
  160 CONTINUE                                                          24980
  170 CONTINUE                                                          24990
      RETURN                                                            25000
C     *****                                                             25010
      ENTRY UNITS(ISOLN)                                                25020
C     *****                                                             25030
      IASPEC=IALK(ISOLN)                                                25040
      IF (IUNITS(ISOLN).EQ.0) GO TO 250                                 25050
      IF (IUNITS(ISOLN).NE.1) GO TO 190                                 25060
C          MMOLES/L                                                     25070
      DO 180 I=4,MAXT                                                   25080
      TOTAL(ISOLN,I)=TOTAL(ISOLN,I)*GFW(I)                              25090
  180 CONTINUE                                                          25100
      IUNITS(ISOLN)=2                                                   25110
  190 CONTINUE                                                          25120
      IF (IUNITS(ISOLN).NE.2) GO TO 210                                 25130
C          MG/L                                                         25140
      DO 200 I=4,MAXT                                                   25150
      TOTAL(ISOLN,I)=TOTAL(ISOLN,I)/SDENS(ISOLN)                        25160
  200 CONTINUE                                                          25170
      IUNITS(ISOLN)=3                                                   25180
```

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  210 CONTINUE                                                          25190
      IF (IUNITS(ISOLN).NE.3) GO TO 256                                 25200
C          PPM                                                        25210
      TOTMG=0.0D0                                                       25220
      DO 220 I=4,MAXT                                                   25230
      TOTMG=TOTMG+TOTAL(ISOLN,I)                                        25240
  220 CONTINUE                                                          25250
      C=1.0-TOTMG*1E-06                                                 25260
      IF (C.GT.0.0) GO TO 230                                           25270
      WRITE (6,320)                                                     25280
      ENDFILE (UNIT=6)                                                  25290
      STOP                                                              25300
  230 CONTINUE                                                          25310
      C=1.0/(C*1E+03)                                                   25320
      DO 240 I=4,MAXT                                                   25330
      IF (TOTAL(ISOLN,I).LE.0.0D0) GO TO 240                            25340
      TOTAL(ISOLN,I)=C*TOTAL(ISOLN,I)/GFW(I)                            25350
  240 CONTINUE                                                          25360
      GO TO 250                                                         25370
  256 CONTINUE                                                          25380
      IF(IUNITS(ISOLN).NE.4) GO TO 400                                  25390
C     MMOL/KG SOLN                                                    25400
      DO 257 I=4,MAXT                                                   25410
      IF(TOTAL(ISOLN,I).LE.0.0D0) GO TO 257                             25420
      TOTAL(ISOLN,I) = TOTAL(ISOLN,I)*GFW(I)                            25430
  257 CONTINUE                                                          25440
C     NOW IN PPM                                                      25450
      IUNITS(ISOLN)=3                                                   25460
      GO TO 210                                                         25470
  400 WRITE(6,410)                                                      25480
      ENDFILE (UNIT=6)                                                  25490
      STOP                                                              25500
  250 CONTINUE                                                          25510
C          UNITS ARE NOW MOLALITY                                     25520
      RETURN                                                            25530
C                                                                       25540
  260 FORMAT (1H1,'SOLUTION NUMBER ',I1,/,1X,20A4/)                     25550
  265 FORMAT (/' WARNING -- TEMPERATURE IS MORE THAN 30 DEGREES FROM '  25560
     1,'THE REFERENCE',/,12X,'TEMPERATURE (25C); LARGE ERRORS IN '      25570
     2,'PITZER PARAMETERS',/,12X,'CAN BE EXPECTED IN THE CALCULATIONS ' 25580
     3,'THAT FOLLOW.',/)                                                25590
  270 FORMAT (1X,I4,2X,A8,5X,'SPECIES HAS A MASTER SPECIES NUMBER OUT OF 25600
     1        RANGE')                                                   25610
  280 FORMAT (1H ,'***** ERROR IN SPECIES NUMBER',I4,'  ',A8,'REACTION D 25620
     1OES NOT CHARGE BALANCE.')                                         25630
  290 FORMAT (1H ,'***** ERROR IN MINERAL NUMBER',I4,2X,A8,' REACTION DO 25640
     1ES NOT CHARGE BALANCE.')                                          25650
  300 FORMAT (1H ,'***** ERROR IN MINERAL NUMBER',I4,2X,A8,' REACTION',  25660
     1/,7X,'DOES NOT BALANCE THE SPECIFIED VALENCE.')                   25670
  310 FORMAT (1H ,'***** WARNING:  LOOK MINERAL NUMBER',I4,2X,A8,' REACT 25680
     1ION',/,7X,'DOES NOT CHARGE BALANCE.')                             25690
  320 FORMAT (1H1,80('*')//'TERMINAL ERROR'/'TOTAL SALT PPM GREATER ','T 25700
     1HAN 1 MILLION.'/'CHECK CONCENTRATION UNITS AND ELEMENT',' GRAM FOR 25710
     2MULA WEIGHT INPUT',//,1X,80('*'))                                 25720
  410 FORMAT(///,10X,'*** TERMINAL ERROR **** UNITS OF CONCENTRATION UNK 25730
     1NOWN',///)                                                        25740
```

```
      END                                                               25750
      SUBROUTINE ZEROAR                                                 25760
$INSERT COMMON.BLOCKS                                                   25770
C                                                                       25780
      DO 60 I=1,30                                                      25790
      DO 40 J=1,30                                                      25800
      AR(I,J)=0.0D0                                                     25810
   40 CONTINUE                                                          25820
   60 CONTINUE                                                          25830
      RETURN                                                            25840
      END                                                               25850
C                                                                       25860
      SUBROUTINE PITZER (MO,LG,AW,MU,ICON)                              25870
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               25880
      CHARACTER *8 SPECS(40),NEUTRL(20)                                 25890
      INTEGER TRANS(40),IN(20)                                          25900
      DOUBLE PRECISION MU,MO(250),LG(250),LAM(40,20),MN(20),LGN(20),I   25910
     1,LGAMMA(40),Z(40),PSI(40,40,40),BCX(4,20,21:40),M(40)             25920
      LOGICAL IPRSNT(40),LNEUT                                          25930
      COMMON / MX2 / I,J,K                                              25940
      COMMON / MX3 / BCX,OTEMP                                          25950
      COMMON / MX4 / AO                                                 25960
      COMMON / MX5 / Z                                                  25970
      COMMON / MX6 / LAM,TRANS,PSI,IN                                   25980
      COMMON / MXO / B                                                  25990
      COMMON / PI1C / SPECS,NEUTRL                                      26000
      COMMON / PI1 / M1,M2,M3                                           26010
      COMMON / COS / COSMOT                                             26020
      DATA CONV / 0.4342944819D0 /                                      26030
C                                                                       26040
C     THIS IS THE MAIN ROUTINE FOR CALCULATING GAMMAS USING HARVIE AND  26050
C     WEARE (1980) MODEL.  VALUES OF CONCENTRATION ARE PASSED INTO      26060
C     SUBROUTINE PITZER VIA THE VARIABLE 'MO'.  'MO' CONTAINS MOLALITY  26070
C     OF SPECIES, NUMBERED BY PHREEQE'S CONVENTION.  ONCE INSIDE PITZER, 26080
C     VALUES OF CONCENTRATION OF SPECIES USED IN PITZER'S MODEL ARE     26090
C     TRANSFERED TO THE VARIABLES 'M' AND 'MN'. FOR A LIST OF SPECIES,  26100
C     SEE SPECIES INPUT IN 'PITZER.DATA'.                               26110
C                                                                       26120
C     THE VARIABLE 'M' CONTAINS CONCENTRATIONS OF IONIZED SPECIES:      26130
C                   M(1:20)  => CATIONS                                 26140
C                   M(21:40) => ANIONS                                  26150
C     'MN' CONTAINS CONCENTRATION OF NEUTRAL SPECIES                    26160
C                                                                       26170
C     VARIABLES 'SPECIES' AND 'NEUT' CONTAIN NAMES OF IONIZED AND       26180
C     NEUTRAL SPECIES RESPECTIVELY, USING THE SAME NUMBERING SYSTEM AS  26190
C     'M' AND 'MN'.                                                     26200
C                                                                       26210
C     OTHER IMPORTANT VARIABLES:                                        26220
C          M1 => MAX INDEX # FOR CATIONS (<21)                          26230
C          M2 => MAX INDEX # FOR ANIONS (20 < M2 < 41)                  26240
C          M3 => MAX INDEX # FOR NEUTRALS (<21)                         26250
C          IPRESENT,NEUTRAL => LOGICAL VARIABLE ARRAYS TO INDICATE      26260
C                              WHICH SPECIES HAVE NON-ZERO              26270
C                              CONCENTRATION.                           26280
C          I => IONIC STRENGTH                                          26290
C          BCX(1,-,-) => BETA (0)  |  SECOND SUBSCRIPT IS FOR CATION    26300
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```
C           BCX(2,-,-) => BETA (1)  |  INDEX;                                  26310
C           BCX(3,-,-) => BETA (2)  |  THIRD SUBSCRIPT IS FOR ANION            26320
C           BCX(4,-,-) => C PHI     |  INDEX.                                  26330
C           LAM => LAMBDA, IONIZED-NEUTRAL INTERACTION PARAMETER              26340
C           PSI => PSI, 1 CATION - 2 ANION INTERACTION OR 2 CATION -           26350
C                  1 ANION INTERACTION PARAMETER.                             26360
C           CONV => CONVERSION FACTOR FROM LOG BASE E TO LOG BASE 10          26370
C           LGAMMA => LOG OF GAMMAS                                           26380
C           PHIMAC => CONVERSION FACTOR FOR MACINNES CONVENTION               26390
C           COSMOTIC => OSMOTIC COEFFICIENT                                   26400
C           AW => ACTIVITY OF WATER                                           26410
C           GAMCLM => LOG GAMMA OF KCL SYSTEM AT SAME IONIC STRENGTH          26420
C                     AND TEMPERATURE.  USED BY 'PHIMAC'                      26430
C           Z => CHANGE OF SPECIES                                            26440
C                                                                             26450
C     EQUATION NUMBERS REFER TO HARVIE AND WEARE (1980)                       26460
C                                                                             26470
C     INITIALIZE                                                              26480
C                                                                             26490
      XI=0.0D0                                                                26500
      XX=0.0D0                                                                26510
      OSUM=0.0D0                                                              26520
      LNEUT=.FALSE.                                                           26530
C                                                                             26540
C     TRANSFER DATA FROM MO TO M                                              26550
C                                                                             26560
      DO 20 N=1,M2                                                            26570
      M(N)=0.0D0                                                              26580
      IF (N.GT.M1.AND.N.LT.21) GO TO 20                                       26590
      M(N)=MO(TRANS(N))                                                       26600
   20 CONTINUE                                                                26610
      DO 30 N=1,M3                                                            26620
      MN(N)=MO(IN(N))                                                         26630
      IF (MN(N).GT.1.0D-40) LNEUT=.TRUE.                                      26640
   30 CONTINUE                                                                26650
C                                                                             26660
      DO 40 N=1,M2                                                            26670
      IF (M(N).GT.1.0D-40) GO TO 50                                           26680
      IPRSNT(N)=.FALSE.                                                       26690
      GO TO 40                                                                26700
   50 IPRSNT(N)=.TRUE.                                                        26710
   40 CONTINUE                                                                26720
C                                                                             26730
C     COMPUTE PITZER COEFFICIENTS' TEMPERATURE DEPENDENCE                     26740
C                                                                             26750
      CALL PTEMP                                                              26760
C                                                                             26770
      DO 10 N=1,M2                                                            26780
      IF (.NOT.IPRSNT(N)) GO TO 10                                            26790
      XX=XX+M(N)*DABS(Z(N))                                                   26800
      XI=XI+M(N)*Z(N)*Z(N)                                                    26810
      OSUM=OSUM+M(N)                                                          26820
   10 CONTINUE                                                                26830
      DO 15 N=1,M3                                                            26840
      OSUM=OSUM+MN(N)                                                         26850
   15 CONTINUE                                                                26860
```

```
      I=XI/2.0D0                                                        26870
C                                                                       26880
C     EQUATION (8)                                                      26890
C                                                                       26900
      BIGZ=XX                                                           26910
      DI=DSQRT(I)                                                       26920
C                                                                       26930
C     CALCULATE F & GAMCLM                                              26940
C                                                                       26950
      F=-A0*(DI/(1.0D0+B*DI)+2.0D0*DLOG(1.0D0+B*DI)/B)                  26960
      XXX=2.0D0*DI                                                      26970
      XXX=(1.0D0-(1.0D0+XXX-XXX*XXX*0.5D0)*DEXP(-XXX))/(XXX*XXX)        26980
      IK=ISPEC('K+      ')                                              26990
      IC=ISPEC('CL-     ')                                              27000
      GAMCLM=F+I*2.0D0*(BCX(1,IK,IC)+BCX(2,IK,IC)*XXX)+1.5D0            27010
     1*BCX(4,IK,IC)*I*I                                                 27020
      DO 75 J=1,M1                                                      27030
      IF (.NOT.IPRSNT(J)) GO TO 75                                      27040
      DO 70 K=21,M2                                                     27050
      IF (.NOT.IPRSNT(K)) GO TO 70                                      27060
C                                                                       27070
C     EQUATION (3) PART 1                                               27080
C                                                                       27090
      F=F+M(J)*M(K)*BMXP()                                              27100
   70 CONTINUE                                                          27110
   75 CONTINUE                                                          27120
      DO 85 J=1,M1-1                                                    27130
      IF (.NOT.IPRSNT(J)) GO TO 85                                      27140
      DO 80 K=J+1,M1                                                    27150
      IF (.NOT.IPRSNT(K)) GO TO 80                                      27160
C                                                                       27170
C     EQUATION (3) PART 2                                               27180
C                                                                       27190
      F=F+M(J)*M(K)*ETHEAP()                                            27200
   80 CONTINUE                                                          27210
   85 CONTINUE                                                          27220
      DO 90 J=21,M2-1                                                   27230
      IF (.NOT.IPRSNT(J)) GO TO 90                                      27240
      DO 110 K=J+1,M2                                                   27250
      IF (.NOT.IPRSNT(K)) GO TO 110                                     27260
C                                                                       27270
C     EQUATION (3) PART 3                                               27280
C                                                                       27290
      F=F+M(J)*M(K)*ETHEAP()                                            27300
  110 CONTINUE                                                          27310
   90 CONTINUE                                                          27320
C                                                                       27330
      CSUM=0.0D0                                                        27340
      DO 125 J=1,M1                                                     27350
      IF (.NOT.IPRSNT(J)) GO TO 125                                     27360
      DO 120 K=21,M2                                                    27370
      IF (.NOT.IPRSNT(K)) GO TO 120                                     27380
C                                                                       27390
C     EQUATION (2B) PART 4                                              27400
C                                                                       27410
      CSUM=CSUM+M(J)*M(K)*CMX()                                         27420
```

```
  120 CONTINUE                                                          27430
  125 CONTINUE                                                          27440
C                                                                       27450
C     CALCULATE LGAMMA FOR CATIONS                                      27460
C                                                                       27470
      DO 130 J=1,M1                                                     27480
      LGAMMA(J)=Z(J)*Z(J)*F+DABS(Z(J))*CSUM                             27490
      DO 140 K=21,M2                                                    27500
      IF (.NOT.IPRSNT(K)) GO TO 140                                     27510
C                                                                       27520
C     EQUATION (2B) PART 3                                              27530
C                                                                       27540
      LGAMMA(J)=LGAMMA(J)+M(K)*(2.0D0*BMX()+BIGZ*CMX())                 27550
  140 CONTINUE                                                          27560
      DO 150 K=1,M1                                                     27570
      IF (.NOT.IPRSNT(K)) GO TO 150                                     27580
      LGAMMA(J)=LGAMMA(J)+2.0D0*M(K)*PHI()                              27590
      DO 160 KK=21,M2                                                   27600
      IF (.NOT.IPRSNT(KK)) GO TO 160                                    27610
C                                                                       27620
C     EQUATION (2B) PART 2                                              27630
C                                                                       27640
      LGAMMA(J)=LGAMMA(J)+M(KK)*M(K)*PSI(J,K,KK)                        27650
  160 CONTINUE                                                          27660
  150 CONTINUE                                                          27670
      DO 170 K=21,M2-1                                                  27680
      IF (.NOT.IPRSNT(K)) GO TO 170                                     27690
      DO 180 KK=K+1,M2                                                  27700
      IF (.NOT.IPRSNT(KK)) GO TO 180                                    27710
C                                                                       27720
C     EQUATION (2B) PART 3                                              27730
C                                                                       27740
      LGAMMA(J)=LGAMMA(J)+M(K)*M(KK)*PSI(K,KK,J)                        27750
  180 CONTINUE                                                          27760
  170 CONTINUE                                                          27770
      IF (.NOT.LNEUT) GO TO 130                                         27780
      DO 190 K=1,M3                                                     27790
      LGAMMA(J)=LGAMMA(J)+2.0D0*MN(K)*LAM(J,K)                          27800
  190 CONTINUE                                                          27810
  130 CONTINUE                                                          27820
C                                                                       27830
C     CALCULATE LGAMMA OF ANIONS                                        27840
C                                                                       27850
      DO 230 K=21,M2                                                    27860
C                                                                       27870
C     EQUATION (2C) PART 1                                              27880
C                                                                       27890
      LGAMMA(K)=Z(K)*Z(K)*F+DABS(Z(K))*CSUM                             27900
      DO 240 J=1,M1                                                     27910
      IF (.NOT.IPRSNT(J)) GO TO 240                                     27920
C                                                                       27930
C     EQUATION (2C) PART 2                                              27940
C                                                                       27950
      LGAMMA(K)=LGAMMA(K)+M(J)*(2.0D0*BMX()+BIGZ*CMX())                 27960
  240 CONTINUE                                                          27970
      DO 250 J=21,M2                                                    27980
```

```
      IF (.NOT.IPRSNT(J)) GO TO 250                                     27990
      LGAMMA(K)=LGAMMA(K)+2.0D0*M(J)*PHI()                              28000
      DO 260 KK=1,M1                                                    28010
      IF (.NOT.IPRSNT(KK)) GO TO 260                                    28020
C                                                                       28030
C     EQUATION (2C) PART 3                                              28040
C                                                                       28050
      LGAMMA(K)=LGAMMA(K)+M(KK)*M(J)*PSI(K,J,KK)                        28060
  260 CONTINUE                                                          28070
  250 CONTINUE                                                          28080
      DO 270 J=1,M1-1                                                   28090
      IF (.NOT.IPRSNT(J)) GO TO 270                                     28100
      DO 280 KK=J+1,M1                                                  28110
      IF (.NOT.IPRSNT(KK)) GO TO 280                                    28120
C                                                                       28130
C     EQUATION (2C) PART 4                                              28140
C                                                                       28150
      LGAMMA(K)=LGAMMA(K)+M(J)*M(KK)*PSI(J,KK,K)                        28160
  280 CONTINUE                                                          28170
  270 CONTINUE                                                          28180
      IF (.NOT.LNEUT) GO TO 230                                         28190
      DO 290 J=1,M3                                                     28200
      LGAMMA(K)=LGAMMA(K)+2.0D0*MN(J)*LAM(K,J)                          28210
  290 CONTINUE                                                          28220
  230 CONTINUE                                                          28230
C                                                                       28240
C     CONVERT TO MACINNES CONVENTION                                    28250
C                                                                       28260
      IF (ICON.EQ.0) GO TO 300                                          28270
      PHIMAC=GAMCLM-LGAMMA(IC)                                          28280
      DO 220 K=1,M2                                                     28290
      IF (.NOT.IPRSNT(K)) GO TO 220                                     28300
      LGAMMA(K)=LGAMMA(K)+Z(K)*PHIMAC                                   28310
  220 CONTINUE                                                          28320
C                                                                       28330
  300 IF (.NOT.LNEUT) GO TO 860                                         28340
C                                                                       28350
C     CALCULATE THE GAMMA OF NEUTRAL IONS                               28360
C                                                                       28370
      DO 800 K=1,M3                                                     28380
      LGN(K)=0.0D0                                                      28390
      DO 870 J=1,M2                                                     28400
      IF (.NOT.IPRSNT(J)) GO TO 870                                     28410
      LGN(K)=LGN(K)+2.0D0*M(J)*LAM(J,K)                                 28420
  870 CONTINUE                                                          28430
  800 CONTINUE                                                          28440
C                                                                       28450
C     CALCULATE THE OSMOTIC COEFFICIENT                                 28460
C                                                                       28470
C     EQUATION (2A) PART 1                                              28480
C                                                                       28490
  860 OSMOT=-(A0)*I**1.5D0/(1.0D0+B*DI)                                 28500
      DO 420 J=1,M1                                                     28510
      IF (.NOT.IPRSNT(J)) GO TO 420                                     28520
      DO 430 K=21,M2                                                    28530
      IF (.NOT.IPRSNT(K)) GO TO 430                                     28540
```

```
C                                                                       28550
C     EQUATION (2A) PART 2                                              28560
C                                                                       28570
      OSMOT=OSMOT+M(J)*M(K)*(BMXPHI()+BIGZ*CMX())                       28580
  430 CONTINUE                                                          28590
  420 CONTINUE                                                          28600
      DO 440 J=1,M1-1                                                   28610
      IF (.NOT.IPRSNT(J)) GO TO 440                                     28620
      DO 450 K=J+1,M1                                                   28630
      IF (.NOT.IPRSNT(K)) GO TO 450                                     28640
      OSMOT=OSMOT+M(J)*M(K)*PHIPHI()                                    28650
      DO 460 KK=21,M2                                                   28660
      IF (.NOT.IPRSNT(KK)) GO TO 460                                    28670
C                                                                       28680
C     EQUATION (2A) PART 3                                              28690
C                                                                       28700
      OSMOT=OSMOT+M(J)*M(K)*M(KK)*PSI(J,K,KK)                           28710
  460 CONTINUE                                                          28720
  450 CONTINUE                                                          28730
  440 CONTINUE                                                          28740
      DO 470 J=21,M2-1                                                  28750
      IF (.NOT.IPRSNT(J)) GO TO 470                                     28760
      DO 480 K=J+1,M2                                                   28770
      IF (.NOT.IPRSNT(K)) GO TO 480                                     28780
      OSMOT=OSMOT+M(J)*M(K)*PHIPHI()                                    28790
      DO 490 KK=1,M1                                                    28800
      IF (.NOT.IPRSNT(KK)) GO TO 490                                    28810
C                                                                       28820
C     EQUATION (2A) PART 4                                              28830
C                                                                       28840
      OSMOT=OSMOT+M(J)*M(K)*M(KK)*PSI(J,K,KK)                           28850
  490 CONTINUE                                                          28860
  480 CONTINUE                                                          28870
  470 CONTINUE                                                          28880
      IF (.NOT.LNEUT) GO TO 850                                         28890
      DO 810 K=1,M3                                                     28900
      DO 820 J=1,M2                                                     28910
      IF (.NOT.IPRSNT(J)) GO TO 820                                     28920
C                                                                       28930
C     EQUATION (A.3A) PART 5  HARVIE, MOLLER, WEARE (1984)              28940
C                                                                       28950
      OSMOT=OSMOT+MN(K)*M(J)*LAM(J,K)                                   28960
  820 CONTINUE                                                          28970
  810 CONTINUE                                                          28980
  850 COSMOT=1.0D0+2.0D0*OSMOT/OSUM                                     28990
C                                                                       29000
C     CALCULATE THE ACTIVITY OF WATER                                   29010
C                                                                       29020
      AW=DEXP(-OSUM*COSMOT/55.50837D0)                                  29030
C                                                                       29040
C     SET APPROPRIATE VALUES FOR RETURN                                 29050
C                                                                       29060
      MU=I                                                              29070
      DO 900 N=1,M2                                                     29080
      IF (.NOT.IPRSNT(N)) GO TO 900                                     29090
      LG(TRANS(N))=LGAMMA(N)*CONV                                       29100
```

```
  900 CONTINUE                                                          29110
      IF (.NOT.LNEUT) RETURN                                            29120
      DO 910 N=1,M3                                                     29130
      LG(IN(N))=LGN(N)*CONV                                             29140
  910 CONTINUE                                                          29150
      RETURN                                                            29160
      END                                                               29170
C                                                                       29180
C     THESE FUNCTIONS CALCULATE THE BM'S                                29190
C                                                                       29200
      DOUBLE PRECISION FUNCTION BMXPHI()                                29210
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               29220
      COMMON / MX2 / I,J,K                                              29230
      COMMON / MX3 / BCX,OTEMP                                          29240
C                                                                       29250
C     ALPHA DEFINED IN BLOCK DATA                                       29260
C                                                                       29270
      COMMON / MX9 / ALPHA                                              29280
      DIMENSION ALPHA (5),BCX(4,20,21:40)                               29290
      DOUBLE PRECISION I                                                29300
      LOGICAL TWOTWO,ONEANY                                             29310
C                                                                       29320
C     STATEMENT FUNCTIONS                                               29330
C                                                                       29340
C     EQUATION (5)                                                      29350
C                                                                       29360
      G(Y)=2.0D0*(1.0D0-(1.0D0+Y)*DEXP(-Y))/Y**2.0D0                    29370
C                                                                       29380
C     EQUATION (6)                                                      29390
C                                                                       29400
      GP(Y)=-2.0D0*(1.0D0-(1.0D0+Y+Y**2.0D0/2.0D0)*DEXP(-Y))/           29410
     1 Y**2.0D0                                                         29420
C                                                                       29430
      IF (ONEANY()) GO TO 40                                            29440
      IF (TWOTWO()) GO TO 50                                            29450
C                                                                       29460
C     EQUATION (7A)                                                     29470
C                                                                       29480
      BMXPHI=BCX(1,J,K)+BCX(2,J,K)*DEXP(-ALPHA(4)*DSQRT(I))+BCX(3,J,K)* 29490
     1 DEXP(-ALPHA(5)*DSQRT(I))                                         29500
      RETURN                                                            29510
C                                                                       29520
C     EQUATION (4A)                                                     29530
C                                                                       29540
   40 BMXPHI=BCX(1,J,K)+BCX(2,J,K)*DEXP(-ALPHA(1)*DSQRT(I))             29550
      RETURN                                                            29560
C                                                                       29570
C     EQUATION (7A)                                                     29580
C                                                                       29590
   50 BMXPHI=BCX(1,J,K)+BCX(2,J,K)*DEXP(-ALPHA(2)*DSQRT(I))+BCX(3,J,K)* 29600
     1 DEXP(-ALPHA(3)*DSQRT(I))                                         29610
      RETURN                                                            29620
C     **********                                                        29630
      ENTRY BMX                                                         29640
C     **********                                                        29650
      IF (ONEANY()) GO TO 55                                            29660
```

```
      IF (TWOTWO()) GO TO 60                                            29670
C                                                                       29680
C     EQUATION (7B)                                                     29690
C                                                                       29700
      BMX=BCX(1,J,K)+BCX(2,J,K)*G(ALPHA(4)*DSQRT(I))+BCX(3,J,K)*        29710
     1 G(ALPHA(5)*DSQRT(I))                                             29720
      RETURN                                                            29730
C                                                                       29740
C     EQUATION (4B)                                                     29750
C                                                                       29760
   55 BMX=BCX(1,J,K)+BCX(2,J,K)*G(ALPHA(1)*DSQRT(I))                    29770
      RETURN                                                            29780
C                                                                       29790
C     EQUATION (7B)                                                     29800
C                                                                       29810
   60 BMX=BCX(1,J,K)+BCX(2,J,K)*G(ALPHA(2)*DSQRT(I))+BCX(3,J,K)*        29820
     1 G(ALPHA(3)*DSQRT(I))                                             29830
      RETURN                                                            29840
C     **********                                                        29850
      ENTRY BMXP                                                        29860
C     **********                                                        29870
      IF (ONEANY()) GO TO 65                                            29880
      IF (TWOTWO()) GO TO 70                                            29890
C                                                                       29900
C     EQUATION (7C)                                                     29910
C                                                                       29920
      BMXP=(BCX(2,J,K)*GP(ALPHA(4)*DSQRT(I))+BCX(3,J,K)*GP(ALPHA(5)*    29930
     1 DSQRT(I)))/I                                                     29940
      RETURN                                                            29950
C                                                                       29960
C     EQUATION (4C)                                                     29970
C                                                                       29980
   65 BMXP=BCX(2,J,K)*GP(ALPHA(1)*DSQRT(I))/I                           29990
      RETURN                                                            30000
C                                                                       30010
C     EQUATION (7C)                                                     30020
C                                                                       30030
   70 BMXP=(BCX(2,J,K)*GP(ALPHA(2)*DSQRT(I))+BCX(3,J,K)*GP(ALPHA(3)*    30040
     1 DSQRT(I)))/I                                                     30050
      RETURN                                                            30060
      END                                                               30070
C                                                                       30080
C     SUBROUTINE TO DETERMINE ONE-ANY ELECTROLYTES                      30090
C                                                                       30100
C     ONEANY = .TRUE.  IF EITHER ION IS UNIVALENT                       30110
C                                                                       30120
      LOGICAL FUNCTION ONEANY()                                         30130
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               30140
      COMMON / MX2 / I,J,K                                              30150
      COMMON / MX5 / Z                                                  30160
      DOUBLE PRECISION I                                                30170
      DIMENSION Z(40)                                                   30180
      ONEANY=.FALSE.                                                    30190
      IF (DABS(Z(J)).LT.2.0D0.AND.DABS(Z(J)).GT.0.0D0) ONEANY=.TRUE.    30200
      IF (DABS(Z(K)).LT.2.0D0.AND.DABS(Z(K)).GT.0.0D0) ONEANY=.TRUE.    30210
      RETURN                                                            30220
```

```
      END                                                               30230
C                                                                       30240
C     SUBROUTINE TO DETERMINE TWO-TWO ELECTROLYTES                      30250
C                                                                       30260
C     TWOTWO = .TRUE.  IF BOTH IONS ARE DOUBLY CHARGED                  30270
C                                                                       30280
      LOGICAL FUNCTION TWOTWO()                                         30290
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               30300
      COMMON / MX2 / I,J,K                                              30310
      COMMON / MX5 / Z                                                  30320
      DOUBLE PRECISION I                                                30330
      DIMENSION Z(40)                                                   30340
      TWOTWO=.FALSE.                                                    30350
      ZDIF=DABS(DABS(Z(J)*Z(K))-4.0D0)                                  30360
      IF (ZDIF.LT.1.0D0) TWOTWO=.TRUE.                                  30370
      RETURN                                                            30380
      END                                                               30390
C                                                                       30400
C     FUNCTION TO CALCULATE C(MX)                                       30410
C                                                                       30420
      DOUBLE PRECISION FUNCTION CMX()                                   30430
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               30440
      COMMON / MX2 / I,J,K                                              30450
      COMMON / MX3 / BCX,OTEMP                                          30460
      COMMON / MX5 / Z                                                  30470
      DOUBLE PRECISION I,Z(40),BCX(4,20,21:40)                          30480
C                                                                       30490
C     EQUATION (9)                                                      30500
C                                                                       30510
      CMX=BCX(4,J,K)/(2.0D0*DSQRT(DABS(Z(J)*Z(K))))                     30520
      RETURN                                                            30530
      END                                                               30540
C                                                                       30550
C     FUNCTIONS TO CALCULATE ETHETA AND ETHEAP                          30560
C                                                                       30570
      DOUBLE PRECISION FUNCTION ETHETA()                                30580
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               30590
      COMMON / MX2 / I,J,K                                              30600
      COMMON / MX4 / A0                                                 30610
      COMMON / MX5 / Z                                                  30620
      DIMENSION Z(40)                                                   30630
      DOUBLE PRECISION I,JAY,JPRIME                                     30640
      IFLAG=1                                                           30650
      ETHETA=0.0D0                                                      30660
      GO TO 10                                                          30670
C     **************                                                    30680
      ENTRY ETHEAP                                                      30690
C     **************                                                    30700
      IFLAG=2                                                           30710
      ETHEAP=0.0D0                                                      30720
   10 XCON=6.0D0*A0*DSQRT(I)                                            30730
      IF (DABS(Z(J)-Z(K)).LE.1.0D-40) RETURN                            30740
      ZZ=Z(J)*Z(K)                                                      30750
C                                                                       30760
C     NEXT 3 ARE EQUATION (A1)                                          30770
C                                                                       30780
```

```
      XJK=XCON*ZZ                                                       30790
      XJJ=XCON*Z(J)*Z(J)                                                30800
      XKK=XCON*Z(K)*Z(K)                                                30810
C                                                                       30820
C     EQUATION (A2)                                                     30830
C                                                                       30840
      ETHETA=ZZ*(JAY(XJK)-JAY(XJJ)/2.0D0-JAY(XKK)/2.0D0)/(4.0D0*I)      30850
      IF (IFLAG.EQ.1) RETURN                                            30860
C                                                                       30870
C     EQUATION (A3)                                                     30880
C                                                                       30890
      ETHEAP=ZZ*(JPRIME(XJK)-JPRIME(XJJ)/2.0D0-JPRIME(XKK)/             30900
     1 2.0D0)/(8.0D0*I**2.0D0) - ETHETA/I                               30910
      RETURN                                                            30920
      END                                                               30930
C                                                                       30940
C     FUNCTION TO CALCULATE JAY AND JPRIME                              30950
C                                                                       30960
C     J0 AND J1, USED IN CALCULATION OF ETHETA AND ETHEAP               30970
C                                                                       30980
      DOUBLE PRECISION FUNCTION JAY(X)                                  30990
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               31000
      COMMON / MX8 / AK,BK,DK                                           31010
      DIMENSION AK(0:20,2),BK(0:22),DK(0:22)                            31020
      DOUBLE PRECISION JPRIME                                           31030
      CALL BDK (X)                                                      31040
      JAY=X/4.0D0-1.0D0+0.5D0*(BK(0)-BK(2))                             31050
      RETURN                                                            31060
C     ***************                                                   31070
      ENTRY JPRIME(Y)                                                   31080
C     ***************                                                   31090
      CALL BDK (Y)                                                      31100
      IF (Y.GT.1.0D0) GO TO 10                                          31110
      DZ=0.8D0*Y**(-0.8D0)                                              31120
      GO TO 20                                                          31130
   10 DZ=-4.0D0*Y**(-1.1D0)/9.0D0                                       31140
   20 JPRIME=Y*(.25D0+DZ*(DK(0)-DK(2))/2.0D0)                           31150
      RETURN                                                            31160
      END                                                               31170
C                                                                       31180
      SUBROUTINE BDK (X)                                                31190
C                                                                       31200
C     NUMERICAL APPROXIMATION TO THE INTEGRALS IN THE EXPRESSIONS FOR J0 31210
C     AND J1.  CHEBYSHEV APPROXIMATION IS USED.  THE CONSTANTS 'AK' ARE 31220
C     DEFINED IN BLOCK COMMON.                                          31230
C                                                                       31240
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               31250
      COMMON / MX8 / AK,BK,DK                                           31260
      DIMENSION AK(0:20,2),BK(0:22),DK(0:22)                            31270
      II=1                                                              31280
      IF (X.LE.1.0D0) GO TO 10                                          31290
      II=2                                                              31300
      Z=40.0*X**(-1.0D-1)/9.0D0-22.0D0/9.0D0                            31310
      GO TO 20                                                          31320
   10 Z=4.0D0*X**(0.2D0)-2.0D0                                          31330
   20 DO 30 M=20,0,-1                                                   31340
```

```
      BK(M)=Z*BK(M+1)-BK(M+2)+AK(M,II)                                  31350
      DK(M)=BK(M+1)+Z*DK(M+1)-DK(M+2)                                   31360
   30 CONTINUE                                                          31370
      RETURN                                                            31380
      END                                                               31390
C                                                                       31400
C     FUNCTION TO CALCULATE PHI   (PHI' IS EQUAL TO ETHEAP)             31410
C                                                                       31420
      DOUBLE PRECISION FUNCTION PHI()                                   31430
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               31440
      COMMON / MX2 / I,J,K                                              31450
      COMMON / MX7 / THETA                                              31460
      DIMENSION THETA(40,40)                                            31470
      DOUBLE PRECISION I                                                31480
C                                                                       31490
C     EQUATION (10B)                                                    31500
C                                                                       31510
      PHI=THETA(J,K)+ETHETA()                                           31520
      RETURN                                                            31530
C     *************                                                     31540
      ENTRY PHIPHI                                                      31550
C     *************                                                     31560
C                                                                       31570
C     EQUATION (10A)                                                    31580
C                                                                       31590
      PHIPHI=THETA(J,K)+ETHETA()+I*ETHEAP()                             31600
      RETURN                                                            31610
      END                                                               31620
C                                                                       31630
C     SUBROUTINE TO CALUCLATE TEMPERATURE DEPENDENCE OF PITZER PARAMETER 31640
C                                                                       31650
      SUBROUTINE PTEMP                                                  31660
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               31670
$INSERT COMMON.BLOCKS                                                   31680
      DOUBLE PRECISION BC(4,20,21:40,5),BCX(4,20,21:40)                 31690
      CHARACTER *8 SPECS(40),NEUTRL(20)                                 31700
      COMMON / MX1 / BC                                                 31710
      COMMON / MX3 / BCX,OTEMP                                          31720
      COMMON / MX4 / AO                                                 31730
      COMMON / MX10 / VP,DWO                                            31740
      COMMON / PI1C / SPECS,NEUTRL                                      31750
      COMMON / PI1 / M1,M2,M3                                           31760
      DATA TR /298.15/                                                  31770
C                                                                       31780
      IF (DABS(TK-OTEMP).LT.0.01) RETURN                                31790
      OTEMP=TK                                                          31800
      DWO=DW(TK)                                                        31810
      IF (DABS(TK-TR).LT.0.01) GO TO 10                                 31820
      DCO=DC(TK)                                                        31830
      AO=1.400684D6*(DWO/(DCO*TK)**3.0D0)**0.5D0                        31840
      DO 30 L=1,4                                                       31850
      DO 40 K=1,M1                                                      31860
      DO 50 N=21,M2                                                     31870
      BCX(L,K,N)=BC(L,K,N,1)+BC(L,K,N,2)*(1.0/TK-1.0/TR)+BC(L,K,N,3)    31880
     1*DLOG(TK/TR)+BC(L,K,N,4)*(TK-TR)+BC(L,K,N,5)*(TK*TK-TR*TR)        31890
   50 CONTINUE                                                          31900
```

```
   40 CONTINUE                                                          31910
   30 CONTINUE                                                          31920
      RETURN                                                            31930
   10 DO 20 L=1,4                                                       31940
      DO 60 K=1,M1                                                      31950
      DO 70 N=21,M2                                                     31960
      BCX(L,K,N)=BC(L,K,N,1)                                            31970
   70 CONTINUE                                                          31980
   60 CONTINUE                                                          31990
   20 CONTINUE                                                          32000
      A0=0.392D0                                                        32010
      RETURN                                                            32020
      END                                                               32030
C                                                                       32040
C     SUBROUTINE TO INITIALIZE DATA                                     32050
C                                                                       32060
      SUBROUTINE INITPZ                                                 32070
C                                                                       32080
C     'PITZER.DATA' IS READ IN THIS SUBROUTINE.                         32090
C                                                                       32100
C     SOME VARIABLES:                                                   32110
C         IS => TOTAL NUMBER OF SPECIES USED IN PITZER'S MODEL          32120
C         NS => INDIVIDUAL SPECIES NUMBERS (IN PHREEQE'S NUMBERING      32130
C               SYSTEM) USED IN PITZER'S MODEL.                         32140
C         TRANS,IN => ARRAYS TO TRANSLATE PHREEQE'S NUMBERING SYSTEM    32150
C                     INTO NUMBERING SYSTEM USED IN SUBROUTINE PITZER.  32160
C                                                                       32170
      PARAMETER (IF=12)                                                 32180
$INSERT COMMON.BLOCKS                                                   32190
      INTEGER TRANS(40),IN(20),NS(40)                                   32200
      CHARACTER *8 SPEC1,SPEC2,SPEC3,NEUTRL(20),SPECS(40)               32210
      DOUBLE PRECISION PSI(40,40,40),BC(4,20,21:40,5),THETA(40,40),Z(40) 32220
     1,LAM(40,20),VALUE(5)                                              32230
      COMMON / MX1 / BC                                                 32240
      COMMON / MX5 / Z                                                  32250
      COMMON / MX6 / LAM,TRANS,PSI,IN                                   32260
      COMMON / MX7 / THETA                                              32270
      COMMON / PI1C / SPECS,NEUTRL                                      32280
      COMMON / PI1 / M1,M2,M3                                           32290
      OPEN (UNIT=IF,FILE='PITZER.DATA')                                 32300
      READ (IF,10) SPEC1,IS                                             32310
   10 FORMAT (A8,I3)                                                    32320
      READ (IF,20) (NS(J),J=1,IS)                                       32330
   20 FORMAT (25(I3))                                                   32340
      DO 90 J=1,IS                                                      32350
      IF (NS(J).GT.0.AND.NS(J).LT.251) GO TO 40                         32360
      WRITE (6,30)                                                      32370
   30 FORMAT (//,' PITZER DATA FILE ERROR.')                            32380
      STOP                                                              32390
   40 IF (DABS(ZSP(NS(J))).LE.1.0D-40) GO TO 80                         32400
      IF (ZSP(NS(J)).LT.-1.0D-5) GO TO 60                               32410
C                                                                       32420
C     CATIONS (UP TO 20)                                                32430
C                                                                       32440
      M1=M1+1                                                           32450
      IF (M1.LE.20) GO TO 58                                            32460
```

```
   53 WRITE (6,55)                                                          32470
   55 FORMAT (' ***** ERROR:  ONLY 20 IONS OF EACH TYPE ARE ALLOWED.')      32480
      STOP                                                                  32490
   58 TRANS(M1)=NS(J)                                                       32500
      SPECS(M1)=SNAME(NS(J))                                                32510
      Z(M1)=ZSP(NS(J))                                                      32520
      GO TO 90                                                              32530
C                                                                           32540
C     ANIONS (UP TO 20)                                                     32550
C                                                                           32560
   60 M2=M2+1                                                               32570
      IF (M2.GT.40) GO TO 53                                                32580
      TRANS(M2)=NS(J)                                                       32590
      SPECS(M2)=SNAME(NS(J))                                                32600
      Z(M2)=ZSP(NS(J))                                                      32610
      GO TO 90                                                              32620
C                                                                           32630
C     NEUTRAL SPECIES (UP TO 20)                                            32640
C                                                                           32650
   80 M3=M3+1                                                               32660
      IF (M3.GT.20) GO TO 53                                                32670
      IN(M3)=NS(J)                                                          32680
      NEUTRL(M3)=SNAME(NS(J))                                               32690
   90 CONTINUE                                                              32700
C                                                                           32710
      READ (IF,95)                                                          32720
   95 FORMAT (1X)                                                           32730
      K=1                                                                   32740
C                                                                           32750
C     READ IN BETA(0), BETA(1), BETA(2), AND C(PHI)                         32760
C                                                                           32770
  100 READ (IF,105) SPEC1,SPEC2,(VALUE(J),J=1,5)                            32780
  105 FORMAT (2(2X,A8),5(1X,F11.0))                                         32790
      IF (DABS(VALUE(1)).GT.1.0D-30) GO TO 107                              32800
      K=K+1                                                                 32810
      IF (K.GT.4) GO TO 120                                                 32820
      GO TO 100                                                             32830
  107 K1=ISPEC(SPEC1)                                                       32840
      K2=ISPEC(SPEC2)                                                       32850
      DO 110 J=1,5                                                          32860
      BC(K,K1,K2,J)=VALUE(J)                                                32870
  110 CONTINUE                                                              32880
      GO TO 100                                                             32890
  120 READ (IF,105) SPEC1,SPEC2,VALUE(1)                                    32900
      IF (DABS(VALUE(1)).LE.1.0D-40) GO TO 130                              32910
      I1=ISPEC(SPEC1)                                                       32920
      I2=ISPEC(SPEC2)                                                       32930
      THETA(I1,I2)=VALUE(1)                                                 32940
      THETA(I2,I1)=VALUE(1)                                                 32950
      GO TO 120                                                             32960
C                                                                           32970
C     READ IN LAMBDA                                                        32980
C                                                                           32990
  130 READ (IF,105) SPEC1,SPEC2,VALUE(1)                                    33000
      IF (DABS(VALUE(1)).LE.1.0D-40) GO TO 140                              33010
      LAM(ISPEC(SPEC1),ISPEC(SPEC2))=VALUE(1)                               33020
```

```
      GO TO 130                                                          33030
C        INITIALIZE PSI (TOO BIG TO DO IT IN BLOCK DATA)                 33040
  140 I1=1                                                               33050
      I2=1                                                               33060
      I3=1                                                               33070
  142 PSI(I1,I2,I3)=0.0D0                                                33080
      I1=I1+1                                                            33090
      IF (I1.GT.M2) GO TO 143                                            33100
      IF (I1.GT.M1.AND.I1.LT.21) I1=21                                   33110
      GO TO 142                                                          33120
  143 I1=1                                                               33130
      I2=I2+1                                                            33140
      IF (I2.GT.M2) GO TO 144                                            33150
      IF (I2.GT.M1.AND.I2.LT.21) I2=21                                   33160
      GO TO 142                                                          33170
  144 I2=1                                                               33180
      I3=I3+1                                                            33190
      IF (I3.GT.M2) GO TO 145                                            33200
      IF (I3.GT.M1.AND.I3.LT.21) I3=21                                   33210
      GO TO 142                                                          33220
C                                                                        33230
C     READ IN PSI                                                        33240
C                                                                        33250
  145 READ (IF,150,END=160) SPEC1,SPEC2,SPEC3,VALUE(1)                   33260
  150 FORMAT (3(2X,A8),2X,F10.0)                                         33270
      I1=ISPEC(SPEC1)                                                    33280
      I2=ISPEC(SPEC2)                                                    33290
      I3=ISPEC(SPEC3)                                                    33300
      PSI(I1,I2,I3)=VALUE(1)                                             33310
      PSI(I1,I3,I2)=VALUE(1)                                             33320
      PSI(I2,I1,I3)=VALUE(1)                                             33330
      PSI(I2,I3,I1)=VALUE(1)                                             33340
      PSI(I3,I1,I2)=VALUE(1)                                             33350
      PSI(I3,I2,I1)=VALUE(1)                                             33360
      GO TO 145                                                          33370
  160 CLOSE (UNIT=IF)                                                    33380
      RETURN                                                             33390
      END                                                                33400
C                                                                        33410
C     FUNCTION TO TRANSFORM SPECIES NAME INTO SPECIES NUMBER             33420
C                                                                        33430
      FUNCTION ISPEC(SPEC)                                               33440
      CHARACTER *8 SPEC,SPECS(40),NEUTRL(20)                             33450
      COMMON / PI1C / SPECS,NEUTRL                                       33460
      COMMON / PI1 / M1,M2,M3                                            33470
      DO 10 I=1,M2                                                       33480
      IF (I.GT.M1.AND.I.LT.21) GO TO 10                                  33490
      IF (SPEC.EQ.SPECS(I)) GO TO 20                                     33500
   10 CONTINUE                                                           33510
      DO 40 I=1,M3                                                       33520
      IF (SPEC.EQ.NEUTRL(I)) GO TO 20                                    33530
   40 CONTINUE                                                           33540
      WRITE (6,30) SPEC                                                  33550
   30 FORMAT (' ******* ERROR IN DATA BASE ******   ',A8,' IS NOT A '    33560
     1,'VALID ION.')                                                     33570
      STOP                                                               33580
```

```
   20 ISPEC=I                                                          33590
      RETURN                                                           33600
      END                                                              33610
C                                                                      33620
C      SUBROUTINE TO CALCULATE THE DENSITY OF WATER AS A FUNCTION OF   33630
C      TEMPERATURE.  T IS IN KELVIN, P IS IN PASCALS, DW IS IN G/CM^3  33640
C                                                                      33650
C      FROM L. HAAR, J. S. GALLAGHER, AND G. S. KELL, (1984)           33660
C                                                                      33670
      DOUBLE PRECISION FUNCTION DW (T)                                 33680
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                              33690
      COMMON / MX10 / VP,DWO                                           33700
      COMMON /ACONST/ GASCON,TZ,AA,Z,DZ,Y                              33710
      DATA FP / 9.869232667D0 /                                        33720
      CALL BB (T)                                                      33730
      P=1.0D0/FP                                                       33740
      IF (T.GT.373.149D0) P=PS(T)                                      33750
      DGSS=P/T/.4D0                                                    33760
      IF (T.GE.TZ) GO TO 10                                            33770
      DGSS=1.0D0/(VLEST(T))                                            33780
   10 CALL DFIND (D,P,DGSS,T)                                          33790
      DW=D                                                             33800
      VP=P*FP                                                          33810
      RETURN                                                           33820
      END                                                              33830
C                                                                      33840
C      THIS SUBROUTINE CALCULATES THE B'S NEEDED FOR FUNCTION DW.      33850
C      THE B'S CALCULATED HERE ARE IN CM3/G.                           33860
C                                                                      33870
C      FROM L. HAAR, J. S. GALLAGHER, AND G. S. KELL, (1984)           33880
C                                                                      33890
      SUBROUTINE BB(T)                                                 33900
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                              33910
      COMMON /ELLCON/ G1,G2,GF,B1,B2,B1T,B2T,B1TT,B2TT                 33920
      COMMON /ACONST/ GASCON,TZ,AA,Z,DZ,Y                              33930
      COMMON /BCONST/ P(10),Q(10)                                      33940
      DIMENSION V(10)                                                  33950
      V(1)=1.D0                                                        33960
      DO 2 I=2,10                                                      33970
   2  V(I)=V(I-1)*TZ/T                                                 33980
      B1=P(1)+P(2)*DLOG(1.D0/V(2))                                     33990
      B2=Q(1)                                                          34000
      B1T=P(2)*V(2)/TZ                                                 34010
      B2T=0.D0                                                         34020
      B1TT=0.D0                                                        34030
      B2TT=0.D0                                                        34040
      DO 4 I=3,10                                                      34050
      B1=B1+P(I)*V(I-1)                                                34060
      B2=B2+Q(I)*V(I-1)                                                34070
      B1T=B1T-(I-2)*P(I)*V(I-1)/T                                      34080
      B2T=B2T-(I-2)*Q(I)*V(I-1)/T                                      34090
      B1TT=B1TT+P(I)*(I-2)**2*V(I-1)/T/T                               34100
   4  B2TT=B2TT+Q(I)*(I-2)**2*V(I-1)/T/T                               34110
      B1TT=B1TT-B1T/T                                                  34120
      B2TT=B2TT-B2T/T                                                  34130
      RETURN                                                           34140
```

```
      END                                                               34150
C                                                                       34160
C     THIS FUNCTION CALCULATES THE Z (=PBASE/(DRT)) NEEDED FOR FUNCTION 34170
C                                                                       34180
C     FROM L. HAAR, J. S. GALLAGHER, AND G. S. KELL, (1984)             34190
C                                                                       34200
      FUNCTION BASE(D,T)                                                34210
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               34220
      COMMON /ELLCON/ G1,G2,GF,B1,B2,B1T,B2T,B1TT,B2TT                  34230
C                                                                       34240
C     G1,G2 AND GF ARE THE ALPHA, BETA AND GAMMA FOR DENSITY OF WATER   34250
C     CALCULATIONS.  B1 AND B2 ARE THE 'EXCLUDED VOLUME' AND '2ND VIRIAL 34260
C     SUPPLIED BY THE SUBROUTINE BB(T), WHICH ALSO SUPPLIES THE 1ST AND 34270
C     2ND DERIVATIVES WITH RESPECT TO T (B1T,B2T,B1TT,B2TT).            34280
C                                                                       34290
      COMMON /ACONST/ GASCON,TZ,A,Z,DZ,Y                                34300
      Y=.25D0*B1*D                                                      34310
      X=1.D0-Y                                                          34320
      Z0=(1.D0+G1*Y+G2*Y*Y)/X**3                                        34330
      Z=Z0+4.D0*Y*(B2/B1-GF)                                            34340
      DZ0=(G1+2.D0*G2*Y)/X**3 + 3.D0*(1.D0+G1*Y+G2*Y*Y)/X**4            34350
      DZ=DZ0+4.D0*(B2/B1-GF)                                            34360
      BASE=Z                                                            34370
      RETURN                                                            34380
      END                                                               34390
C                                                                       34400
C     THIS ROUTINE CALCULATES, FOR A GIVEN T(K) AND D(G/CM3), THE RESIDU 34410
C     CONTRIBUTIONS TO: PRESSURE (Q), DP/DRHO (Q5)                      34420
C     THIS SUBROUTINE IS USED IN DENSITY OF WATER CALCULATION.          34430
C                                                                       34440
C     FROM L. HAAR, J. S. GALLAGHER, AND G. S. KELL, (1984)             34450
C                                                                       34460
      SUBROUTINE QQ(T,D)                                                34470
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               34480
      COMMON /QQQQ/ Q,Q5                                                34490
      DIMENSION QR(11),QT(10),QZR(9),QZT(9)                             34500
      EQUIVALENCE (QR(3),QZR(1)),(QT(2),QZT(1))                         34510
      COMMON /NCONST/ G(40),II(40),JJ(40),N                             34520
      COMMON /ACONST/ GASCON,TZ,AA,Z,DZ,Y                               34530
      COMMON /ADDCON/ ATZ(4),ADZ(4),AAT(4),AAD(4)                       34540
      RT=GASCON*T                                                       34550
      QR(1)=0.D0                                                        34560
      Q5=0.D0                                                           34570
      Q=0.D0                                                            34580
      E=DEXP(-AA*D)                                                     34590
      Q10=D*D*E                                                         34600
      Q20=1.D0-E                                                        34610
      QR(2)=Q10                                                         34620
      V=TZ/T                                                            34630
      QT(1)=T/TZ                                                        34640
      DO 4 I=2,10                                                       34650
      QR(I+1)=QR(I)*Q20                                                 34660
    4 QT(I)=QT(I-1)*V                                                   34670
      DO 10 I=1,N                                                       34680
      K=II(I)+1                                                         34690
      L=JJ(I)                                                           34700
```

```
      ZZ=K                                                              34710
      QP=G(I)*AA*QR(K+1)*QZT(L)                                         34720
      Q=Q+QP                                                            34730
   10 Q5 = Q5 + AA*(2.D0/D-AA*(1.D0-E*(K-1)/Q20))*QP                    34740
      QP=0.D0                                                           34750
C                                                                       34760
      DO 20 J=37,40                                                     34770
      IF(DABS(G(J)).LT.1.0D-20) GO TO 20                                34780
      K=II(J)                                                           34790
      KM=JJ(J)                                                          34800
      DDZ = ADZ(J-36)                                                   34810
      DEL = D/DDZ - 1.D0                                                34820
      IF(DABS(DEL).LT.1.D-10) DEL=1.D-10                                34830
      EX1 = -AAD(J-36)*DEL**K                                           34840
      IF(EX1.GT.-88.028D0)  GO TO 5                                     34850
      DEX=0.D0                                                          34860
      GO TO 6                                                           34870
    5 CONTINUE                                                          34880
       DEX=DEXP(EX1)*DEL**KM                                            34890
    6 CONTINUE                                                          34900
      ATT = AAT(J-36)                                                   34910
      TX = ATZ(J-36)                                                    34920
      TAU = T/TX-1.D0                                                   34930
      EX2 = -ATT*TAU*TAU                                                34940
      IF(EX2.GT.-88.028D0)  GO TO 7                                     34950
      TEX=0.D0                                                          34960
      GO TO 8                                                           34970
    7 CONTINUE                                                          34980
      TEX = DEXP(EX2)                                                   34990
    8 CONTINUE                                                          35000
      Q10 = DEX*TEX                                                     35010
      QM = KM/DEL - K*AAD(J-36)*DEL**(K-1)                              35020
      FCT=QM*D**2*Q10/DDZ                                               35030
      Q5T = FCT*(2.D0/D+QM/DDZ)-(D/DDZ)**2*Q10*(KM/DEL/DEL+             35040
     1  K*(K-1)*AAD(J-36)*DEL**(K-2))                                   35050
      Q5 = Q5 + Q5T*G(J)                                                35060
      QP = QP + G(J)*FCT                                                35070
   20 CONTINUE                                                          35080
      Q=Q+QP                                                            35090
      RETURN                                                            35100
      END                                                               35110
C                                                                       35120
C     ROUTINE TO FIND DENSITY CORRESPONDING TO INPUT PRESSURE P(MPA), AN 35130
C     TEMPERATURE T(K), USING INITIAL GUESS DENSITY D(G/CM3). THE OUTPUT 35140
C     DENSITY IS IN G/CM3.                                              35150
C                                                                       35160
C     FROM L. HAAR, J. S. GALLAGHER, AND G. S. KELL, (1984)             35170
C                                                                       35180
      SUBROUTINE DFIND(DOUT,P,D,T)                                      35190
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               35200
      COMMON /QQQQ/ Q0,Q5                                               35210
      COMMON /ACONST/ GASCON,TZ,AA,Z,DZ,Y                               35220
      DD=D                                                              35230
      RT=GASCON*T                                                       35240
      IF(DD.LE.0.D0) DD=1.D-8                                           35250
      IF(DD.GT.1.9D0) DD=1.9D0                                          35260
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```
      L=0                                                               35270
    9 L=L+1                                                             35280
      IF(DD.LE.0.D0) DD=1.D-8                                           35290
      IF(DD.GT.1.9D0) DD=1.9D0                                          35300
      CALL QQ(T,DD)                                                     35310
      PP = RT*DD*BASE(DD,T)+Q0                                          35320
      DPD=RT*(Z+Y*DZ)+Q5                                                35330
C                                                                       35340
C  THE FOLLOWING 3 LINES CHECK FOR NEGATIVE DP/DRHO, AND IF SO ASSUME   35350
C    GUESS TO BE IN 2-PHASE REGION, AND CORRECT GUESS ACCORDINGLY.      35360
C                                                                       35370
      IF(DPD.GT.0.D0) GO TO 13                                          35380
      IF(D.GE..2967D0) DD=DD*1.02D0                                     35390
      IF(D.LT..2967D0) DD=DD*.98D0                                      35400
      IF(L.LE.10) GO TO 9                                               35410
   13 DPDX=DPD*1.1D0                                                    35420
      IF(DPDX.LT..1D0) DPDX=.1D0                                        35430
      DP=DABS(1.D0-PP/P)                                                35440
      IF(DP.LT.1.D-8) GO TO 20                                          35450
      IF(D.GT..3D0 .AND. DP.LT.1.D-7) GO TO 20                          35460
      IF(D.GT..7D0 .AND. DP.LT.1.D-6) GO TO 20                          35470
      X=(P-PP)/DPDX                                                     35480
      IF(DABS(X).GT..1D0) X=X*.1D0/DABS(X)                              35490
      DD=DD+X                                                           35500
      IF(DD.LE.0.D0) DD=1.D-8                                           35510
      IF(L.LE.30) GO TO 9                                               35520
      STOP 1                                                            35530
   20 CONTINUE                                                          35540
      DOUT=DD                                                           35550
      RETURN                                                            35560
      END                                                               35570
C                                                                       35580
C     THIS FUNCTION CALCULATES AN APPROXIMATION TO THE VAPOR PRESSURE, P 35590
C     AS A FUNCTION OF THE INPUT TEMPERATURE. THE VAPOR PRESSURE        35600
C     CALCULATED AGREES WITH THE VAPOR PRESSURE PREDICTED BY THE SURFACE 35610
C     TO WITHIN .02% TO WITHIN A DEGREE OR SO OF THE CRITICAL TEMPERATUR 35620
C     AND CAN SERVE AS AN INITIAL GUESS FOR FURTHER REFINEMENT BY       35630
C     IMPOSING THE CONDITION THAT GL=GV.                                35640
C                                                                       35650
C     FROM L. HAAR, J. S. GALLAGHER, AND G. S. KELL, (1984)             35660
C                                                                       35670
      FUNCTION PS(T)                                                    35680
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               35690
      DIMENSION A(8)                                                    35700
      DATA A/-7.8889166D0,2.5514255D0,-6.716169D0                       35710
     1,33.239495D0,-105.38479D0,174.35319D0,-148.39348D0                35720
     2,48.631602D0/                                                     35730
      IF(T.GT.314.D0) GO TO 2                                           35740
      PL=6.3573118D0-8858.843D0/T+607.56335D0*T**(-.6)                  35750
      PS=.1*DEXP(PL)                                                    35760
      RETURN                                                            35770
    2 V=T/647.25D0                                                      35780
      W=DABS(1.D0-V)                                                    35790
      B=0.D0                                                            35800
      DO 4 I=1,8                                                        35810
      Z=I                                                               35820
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```
    4  B=B+A(I)*W**((Z+1.D0)/2.D0)                                          35830
       Q=B/V                                                                35840
       PS=22.093D0*DEXP(Q)                                                  35850
       RETURN                                                               35860
       END                                                                  35870
C                                                                           35880
       FUNCTION VLEST (T)                                                   35890
C                                                                           35900
C      FROM L. HAAR, J. S. GALLAGHER, AND G. S. KELL, (1984)                35910
C                                                                           35920
       IMPLICIT DOUBLE PRECISION (A-H,O-Z)                                  35930
       DATA A,B,C,D,E,F,G/-1.59259D1,6.57886D-2,-1.12666D-4,7.33191D-8,     35940
      1                   1.60229D3,2.88572D0,650.0D0/                      35950
       VLEST=A+B*T+C*T*T+D*T**3+E/T+F/(G-T)                                 35960
       RETURN                                                               35970
       END                                                                  35980
C                                                                           35990
C      THIS FUNCTION CALCULATES THE RELATIVE DIELECTRIC CONSTANT AS A       36000
C      FUNCTION OF TEMPERATURE, ASSUMING ONE ATMOSPHERE PRESSURE            36010
C      ACCORDING TO D. J. BRADLEY AND K. S. PITZER, (1979)                  36020
C                                                                           36030
       DOUBLE PRECISION FUNCTION DC (T)                                     36040
       IMPLICIT DOUBLE PRECISION (A-H,O-Z)                                  36050
       COMMON / MX10 / VP,DW0                                               36060
       DIMENSION U(9)                                                       36070
       DATA U / 3.4279D2, -5.0866D-3, 9.4690E-7, -2.0525D0, 3.1159D3        36080
      1, -1.8289D2, -8.0325D3, 4.2142D6, 2.1417D0 /                         36090
       D1000=U(1)*DEXP(U(2)*T+U(3)*T*T)                                     36100
       C=U(4)+U(5)/(U(6)+T)                                                 36110
       B=U(7)+U(8)/T+U(9)*T                                                 36120
       DC=D1000+C*DLOG((B+VP*1.01325)/(B+1000.0D0))                         36130
       RETURN                                                               36140
       END                                                                  36150
```

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C                                                                       00010
C     THE FILE COMMON.BLOCKS TO BE INSERTED IN PHRQPITZ AT $INSERT      00020
C     STATEMENTS.                                                       00030
C                                                                       00040
      IMPLICIT DOUBLE PRECISION(A-H,O-Z),INTEGER(I-N)                   00050
      CHARACTER *4 TITLE,HEAD                                           00060
      CHARACTER *12 SNAME,TNAME,MNAME,NAMELK,NMEANG,SUNAME              00070
      COMMON /CHARS/ TITLE(20),HEAD(2,20),SNAME(250),TNAME(30),         00080
     1       MNAME(20),NAMELK(40),NMEANG(40),SUNAME(10)                 00090
      DOUBLE PRECISION LM,M,LA,LG,LKSP,LKMIN,MU                         00100
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),          00110
     1       TOT(50),DELTA(50),DELTOT(50),AR(50,50),                    00120
     2       AS(50,50),CR(50),CS(50),LKMIN(20),                         00130
     3       THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),                00140
     4       DALKT,DALKS,DIFFZ(2),DZOFF                                 00150
      DOUBLE PRECISION LKTOSP,LKTOM,LKMINO                              00160
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),         00170
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),                   00180
     2       TEMP(2),CMIN(20,10),THMIN(20),LKTOM(20),                   00190
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),             00200
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),       00210
     5       TSTEP(50),CREAC(30),THREAC,                                00220
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30),           00230
     7       IMEANG(40),LMEANG(40,3),CMEANG(40,3),NMGS                  00240
      INTEGER GFLAG,SFLAG                                               00250
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),          00260
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,           00270
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),        00280
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),      00290
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,       00300
     5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,        00310
     6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)             00320
      DOUBLE PRECISION LKLOOK,LKOLK                                     00330
      COMMON /LOOK/ LKOLK(40),LKLOOK(40),DHLOOK(40),                    00340
     1       ALOOK(40,5),CLOOK(40,10),LLOOK(40,10),NLOOK(40),           00350
     2       LOOKFL(40),NLOOKS                                          00360
      COMMON /OFFSET/ SIMIN(20)                                         00370
      COMMON /CHKIT/ JCHECK,ICHECK                                      00380
      COMMON /H2O/ ICKH2O,ITER1                                         00390
      COMMON /NEUT/ DNEUT,NSUM(10),NSUMS,LSUM(10,50),LPOS,LNEG          00400
      COMMON / PMIN / KMIN                                              00410
```

Attachment E. -- Listing of the source code to the interactive input program PITZINPT

```
      PROGRAM PITZINPT                                                  00010
C                                                                       00020
C                                                                       00030
C             **PROGRAM TO FORMAT INPUT-DATA FOR PHRQPITZ**              00040
C                                                                       00050
C       THIS INTERACTIVE PROGRAM WILL SET UP THE INPUT FILE OF          00060
C       PHRQPITZ BY ASKING THE USER VALUES OF THE VARIABLES.  ALL       00070
C       QUESTIONS SHOULD BE SELF-EXPLANATORY.  IF YOU DON'T             00080
C       UNDERSTAND THE USE OF A CERTAIN VARIABLE, A SHORT EXPLANATION   00090
C       OF THAT VARIABLE IS AVAILABLE BY ENTERING A "?".  IN SOME       00100
C       CASES, HELP IS ALSO OBTAINABLE BY ENTERING SOMETHING THAT IS    00110
C       INCOMPATIBLE WITH THE VARIABLE OR JUST A <CR>.  TO BE ON THE    00120
C       SAFE SIDE, HOWEVER, A "?" IS RECOMMENDED.                       00130
C                                                                       00140
C       AFTER EACH RECORD, OR CARD, IS COMPLETED, IT WILL BE PRINTED    00150
C       ON THE SCREEN AND YOU WILL BE ASKED WHETHER THIS CARD IS ALL    00160
C       RIGHT.  IF YOU ANSWER 'NO', THE PROGRAM WILL TAKE THE           00170
C       VARIABLES ON THE CARD, PRINT THEM INDIVIDUALLY, AND YOU WILL    00180
C       BE GIVEN THE CHANCE OF CORRECTING ANY OF THEM.  IF YOU ANSWER   00190
C       'YES', THE PROGRAM WILL GO ON TO THE NEXT CARD AND YOU WILL     00200
C       NOT HAVE ANY MORE CHANCE OF CORRECTING ANY VARIABLES ON THAT    00210
C       CARD.                                                           00220
C                                                                       00230
C                                                                       00240
C          -WRITTEN BY GEORGE W. FLEMING  AND  L. NIEL PLUMMER-         00250
C                                SUMMER, 1980.                          00260
C                     LAST UPDATE--NOVEMBER, 1987                       00270
C                                                                       00280
C                                                                       00290
      COMMON / PHRQ1 / ADHSP(250,2),ALKSP(250),AMIN(2,100,5),ASP(250,5) 00300
     1,CMIN(2,100,10),CREAC(30),CSP(250,6),DHA(250),DHMIN(2,100)        00310
     2,DHSP(250),DTOT(2,30),GFLAG(250),HEAD(2),IALK(2),IOPT(10)         00320
     3,ISDEL(250),IUNITS(2),KFLAG(250),LKTOM(2,100),LKTOSP(250)         00330
     4,LMIN(2,100,10),LNEG,LPOS,LREAC(30),LSP(250,6),LSUM(10,50)        00340
      COMMON / PHRQ2 / LT(2,30),MFLAG(2,100),MNAME(2,100),NCOMPS        00350
     1,NELT(30),NI(250),NMINO(2,100),NSOLUTION(2),NSP(250),NSTEPS       00360
     2,NSUM(10),PE(2),PH(2),SDENS(2),SIMIN(2,100),SNAME(250),SUNAME(10) 00370
     3,TEMP(2),TGFW(30),THMEAN(30),THMIN(2,100),THSP(250),TITLE         00380
     4,TNAME(30),VO,XSTEP(50),XTEMP(50),ZSP(250)                        00390
      DIMENSION JSUB(11),IMINERAL(2),IMORE(11),NTOTS(2),IREQUIRED(11)   00400
     2,ICHECK(2,4:30),MUSED(100),IORDER(11),IMAX(10)                    00410
      COMMON /IUNIT/ J                                                  00420
      COMMON /REFF/ JOPTION,IOPEN,JLINE                                 00430
      COMMON /REFF1/ I                                                  00440
      COMMON /PN/ NFLAG                                                 00450
      COMMON /EE/ EXIT,LIST,LINE,JFLAG                                  00460
      COMMON /PT/ MNAMEO,NMINOO(100),THMINO,LKTOMO,DHMINO,MFLAGO(100)   00470
     1,SIMINO,LMINO(100,10),CMINO,AMINO,IMINO,SUB,ICOL1,ICOL2(0:30)     00480
     2,ICOL3,ICOL4,SPEC,OPV(30)                                         00490
      PARAMETER (IOUT=10)                                               00500
      REAL ICOL3(0:30)                                                  00510
      LOGICAL YN,EXIT,LIST,STOP,OK                                      00520
      INTEGER GFLAG,OUT                                                 00530
      CHARACTER *80 TITLE,LINE,HEAD,JLINE(3)                            00540
```

```
      CHARACTER *72 TFILE                                                   00550
      CHARACTER *8 SUB(11),KEYWORD(20),TNAME,SNAME,MNAME,SUNAME,DELETE      00560
     1,ICOL1(0:30),ICOL4(0:30),CSP,MNAMEO(100),SPEC(30),CREAC,THMEAN        00570
     2,EQUIVWT,SUBO(11)                                                     00580
      CHARACTER *12 OPTION,VO,PH,PE,TEMP,SDENS,TGFW,ZSP,THSP,DHA            00590
     1,ADHSP,ALKSP,LKTOSP,THMIN,LKTOM,DHMIN,SIMIN                           00600
     2,XTEMP,XSTEP,DTOT,CMIN,DHSP,AMIN,ASP,BLANK,CMINO(100,10)              00610
     3,THMINO(100),LKTOMO(100),DHMINO(100),SIMINO(100),AMINO(100,5)         00620
      DATA SUB/'SOLUTION','ELEMENTS','SPECIES ','MINERALS','LOOK MIN',      00630
     1'TEMP    ','STEPS   ','REACTION','NEUTRAL ','SUMS    ','END     '/ 00640
     2SUBO/'solution','elements','species ','minerals','look min',          00650
     3'temp    ','steps   ','reaction','neutral ','sums    ','end     '/ 00660
      DATA OPTION/'OPTION CARD'/BLANK/'    0.0     '/                       00670
      DATA IMAX/ 1,2,6,3,0,2,2,1,1,1 /IORDER/2,3,1,4,5,6,7,8,9,10,11/       00680
     1IMORE/1,1,1,1,1,0,0,0,0,1,0/DELETE/'DELETE  '/                        00690
C                                                                           00700
C         READ NECESSARY DATA AND INITIALIZE VARIABLES.                     00710
C                                                                           00720
      CALL READFILE                                                         00730
      WRITE (J,1)                                                           00740
    1 FORMAT ('ENTER OUTPUT FILE NAME')                                     00750
      READ (J,20) TFILE                                                     00760
   20 FORMAT (A72)                                                          00770
      OPEN (UNIT=IOUT,FILE=TFILE,STATUS='UNKNOWN')                          00780
C                                                                           00790
      ITIME=0                                                               00800
    2 CALL OPEN (ITIME)                                                     00810
    3 JOPEN=IOPEN                                                           00820
C                                                                           00830
      DO 101 K=1,11                                                         00840
      IREQUIRED(K)=0                                                        00850
  101 JSUB(K)=0                                                             00860
      DO 103 K=1,100                                                        00870
  103 MUSED(K)=0                                                            00880
      DO 104 K=1,250                                                        00890
  104 ISDEL(K)=0                                                            00900
      DO 105 K=4,30                                                         00910
      DO 105 K2=1,2                                                         00920
  105 ICHECK(K2,K)=0                                                        00930
      DO 106 K=1,50                                                         00940
      XSTEP(K)=BLANK                                                        00950
  106 XTEMP(K)=BLANK                                                        00960
      DO 102 K=1,30                                                         00970
      LREAC(K)=0                                                            00980
      CREAC(K)=BLANK                                                        00990
  102 THMEAN(K)=BLANK                                                       01000
      ISUB=0                                                                01010
      IELEMENT=0                                                            01020
      IMINERAL(1)=0                                                         01030
      IDELETE=0                                                             01040
      JDELETE=0                                                             01050
      IMINERAL(2)=0                                                         01060
      ISPECIE=0                                                             01070
      ISUM=0                                                                01080
      NSTART=1                                                              01090
      OUT=IOUT                                                              01100
```

```
      I=0                                                               01110
      ISOL=0                                                            01120
      IERROR=0                                                          01130
      JOPTION=0                                                         01140
C                                                                       01150
      IF (IOPEN.EQ.0)GO TO 10                                           01160
C                                                                       01170
C         EXPLANATION OF SOME FLAGS:                                    01180
C                                                                       01190
C         ICHECK      -->MAKE SURE THAT FOR EVERY MASTER SPECIES        01200
C                         ENTERED, THERE IS A CORRESPONDING ELEMENT.    01210
C         IERROR      -->FLAG TO SEE IF IT IS OK TO END THE             01220
C                         SIMULATION.                                   01230
C         JSUB        -->KEEPS TRACK OF WHICH DATA BLOCK IS USED,       01240
C                         AND WHICH ISN'T.                              01250
C         MUSED       -->KEEPS TRACK OF WHICH MINERAL DATA HAS BEEN     01260
C                         CALLED.                                       01270
C         ISDEL       -->SPECIES TO BE DELETED.                         01280
C         IELEMENT    -->NUMBER OF ELEMENTS.                            01290
C         IMINERAL(1)-->NUMBER OF MINERALS.                             01300
C         IMINERAL(2)-->NUMBER OF LOOK MINS.                            01310
C         IMINO       -->NUMBER OF PRE-CONSTRUCTED MINERAL DATA.        01320
C         ISPECIE     -->NUMBER OF SPECIES.                             01330
C         ISUM        -->NUMBER OF SUMS.                                01340
C         IDELETE     -->SET TO 1 IF ALL MINERALS ARE TO BE DELETED.    01350
C         JDELETE     -->SET TO 1 IF ALL OLD SUMS ARE TO BE DELETED.    01360
C         I           -->WHICH DATA BLOCK IS THE USER USING.            01370
C         NFLAG       -->SET TO 1 IF THE VARIABLE IS SEEN BY THE USER   01380
C                         THE SECOND TIME.                              01390
C         JFLAG       -->USER'S RESPONSE FLAG                           01400
C         IREQUIRED   -->WHICH DATA BLOCKS ARE REQUIRED.                01410
C         IMASTER     -->IS THE SPECIES OR ELEMENT ENTERED 'MASTER'?    01420
C         IOPEN       -->IF IT IS > 0, A REFERENCE FILE IS USED.        01430
C         JOPTION     -->IF IOPEN > 0, WHAT DOES THE USER WANT TO DO    01440
C                         WITH EACH CARD.                               01450
C         ITIME       -->NUMBER OF TIMES SUBROUTINE OPEN IS CALLED.     01460
C         ILINE       -->NUMBER OF LINES TO BE READ FROM THE REFERENCE  01470
C                         FILE.                                         01480
C         IMAX        -->MAXIMUM VALUES PERMITTED FOR EACH OPTION.      01490
C         IORDER      -->THE ORDER THAT THE DATA BLOCKS ARE TO BE       01500
C                         PRINTED.                                      01510
C         IMORE       -->IS IT OK TO CALL A CERTAIN DATA BLOCK MORE     01520
C                         THAN ONCE.                                    01530
C                                                                       01540
C                                                                       01550
C       *** THE TITLE ***                                               01560
C                                                                       01570
      WRITE (J,94)                                                      01580
   94 FORMAT (/'TITLE CARD:')                                           01590
      CALL REF (1,1,4)                                                  01600
      TITLE=JLINE(1)                                                    01610
      IF (IOPEN.EQ.0.OR.JOPTION.NE.1)GO TO 10                           01620
      GO TO 90                                                          01630
   10 NFLAG=0                                                           01640
      CALL QUESTA (*1000,0,'THE TITLE',9,TITLE,'A80 ',0,0)              01650
      WRITE (J,9110)                                                    01660
```

```
      WRITE (J,1731) TITLE                                                  01670
      IF (.NOT.OK()) GO TO 10                                               01680
C                                                                           01690
C       *** OPTIONS ***                                                     01700
C                                                                           01710
   90 IF (IOPEN.EQ.0)GO TO 91                                               01720
      WRITE (J,95) OPTION                                                   01730
   95 FORMAT (/,A11,':')                                                    01740
      CALL REF (1,1,1)                                                      01750
      READ (JLINE(1),9991)(IOPT(N),N=1,10),NSTEPS,NCOMPS,VO                 01760
      IOPT03=IOPT(3)                                                        01770
      IOPT04=IOPT(4)                                                        01780
      NSTEPS0=NSTEPS                                                        01790
      NCOMPS0=NCOMPS                                                        01800
      IF (JOPTION.EQ.3.OR.IOPEN.EQ.0)GO TO 91                               01810
      IF (JOPTION.EQ.1)GO TO 92                                             01820
      GO TO 91                                                              01830
   91 IOPT(5)=0                                                             01840
      IOPT(6)=2                                                             01850
   93 DO 200 N=NSTART,10                                                    01860
      IF (N.EQ.5.OR.N.EQ.6) GO TO 200                                       01870
      CALL QUESTB (*290,N,'IOPT',4,IOPT(N),'I2  ',0,IMAX(N),0)              01880
  200 CONTINUE                                                              01890
      IF ((IOPT(3).LE.4.AND.IOPT(3).GE.1).OR.IOPT(4).GE.2) GO TO 250        01900
      NSTEPS=0                                                              01910
      GO TO 300                                                             01920
C                                                                           01930
C       *** NSTEPS ***                                                      01940
C                                                                           01950
  250 CALL QUESTB (*2200,0,'NSTEPS',6,NSTEPS,'I2  ',1,50,0)                 01960
  300 IF (IOPT(3).EQ.3.OR.IOPT(3).EQ.4.OR.IOPT(3).EQ.6)GO TO 301            01970
      NCOMPS=0                                                              01980
      GO TO 400                                                             01990
C                                                                           02000
C       *** NCOMPS ***                                                      02010
C                                                                           02020
  301 CALL QUESTB (*2300,0,'NCOMPS',6,NCOMPS,'I2  ',1,100,0)                02030
  400 IF (IOPT(3).EQ.2) GO TO 430                                           02040
      VO=' 0.0'                                                             02050
      GO TO 500                                                             02060
C                                                                           02070
C       *** VO ***                                                          02080
C                                                                           02090
  430 CALL QUESTA (*2400,0,'VO',2,VO,'A10 ',1,0)                            02100
  500 WRITE (J,9110)                                                        02110
      WRITE (J,9991) (IOPT(I),I=1,10),NSTEPS,NCOMPS,VO                      02120
      IF (OK()) GO TO 92                                                    02130
      NSTART=1                                                              02140
      GO TO 91                                                              02150
C                                                                           02160
C         SET FLAGS FOR THE DATA BLOCKS THAT ARE REQUIRED.                  02170
C                                                                           02180
   92 IF (IOPT(3).EQ.5.OR.IOPT(3).EQ.6)IREQUIRED(4)=1                       02190
      IF (IOPT(2).EQ.2)IREQUIRED(9)=1                                       02200
      IF (IOPT(3).GE.1.AND.IOPT(3).LE.4)IREQUIRED(7)=1                      02210
      IF (IOPT(3).EQ.3.OR.IOPT(3).EQ.4.OR.IOPT(3).EQ.6)IREQUIRED(8)=1       02220
```

```
      IF (IOPT(4).NE.0)IREQUIRED(6)=1                                   02230
C                                                                       02240
C         KEYWORD DATA BLOCKS.                                          02250
C         THE PROGRAM IS DESIGNED SO THAT THE DATA BLOCKS CAN BE        02260
C         ENTERED IN ANY ORDER.  CERTAIN DATA BLOCKS, SUCH AS           02270
C         'ELEMENTS', 'SPECIES', 'MINERALS', ETC., CAN BE CALLED        02280
C         UPON MORE THAN ONCE.  IN THAT CASE, NEW ELEMENTS, SPECIES,    02290
C         MINERALS, ETC., WILL JUST BE ATTACHED TO THE END OF THE       02300
C         DATA BLOCK.  AT THE END OF THE SIMULATION, THE PROGRAM        02310
C         RE-ARRANGES THE DATA BLOCKS AND PRINTS THEM IN A PREFERRED    02320
C         ORDER.                                                        02330
C                                                                       02340
C         IF YOU ACCIDENTALLY ENTERED A DATA BLOCK THAT YOU DO NOT      02350
C         WISH TO USE, ENTER 'EXIT' AS THE FIRST COMMAND AFTER YOU'VE   02360
C         ENTERED THE DATA BLOCK NAME.                                  02370
C                                                                       02380
  531 ISUB=1                                                            02390
  621 WRITE (J,601)                                                     02400
  601 FORMAT (/,19('*'),/,'KEYWORD DATA BLOCKS',/,19('*'),//)           02410
      IF (IOPEN.EQ.0)GO TO 604                                          02420
  612 READ (13,9001,END=608,ERR=650) KEYWORD(ISUB),NSOL                 02430
      DO 609 I=1,11                                                     02440
  609 IF (KEYWORD(ISUB).EQ.SUB(I))GO TO 615                             02450
  650 GO TO 612                                                         02460
C                                                                       02470
C         IF THE KEYWORD DATA BLOCKS ARE NOT ALLOWED, DON'T BOTHER      02480
C         TO ASK THE USER.                                              02490
C                                                                       02500
  615 IF (I.EQ.6.AND.IOPT(4).EQ.0)GO TO 612                             02510
      IF (I.EQ.7.AND.(IOPT(3).EQ.0.OR.IOPT(3).EQ.5.OR.IOPT(3).EQ.6))    02520
     1GO TO 612                                                         02530
      IF (I.EQ.8.AND.NCOMPS.EQ.0)GO TO 612                              02540
      IF (I.EQ.9.AND.IOPT(2).NE.2)GO TO 612                             02550
      WRITE (J,613)                                                     02560
  613 FORMAT (/,'KEYWORD:')                                             02570
      IF (I.EQ.1)GO TO 660                                              02580
      WRITE (J,9050)KEYWORD(ISUB)                                       02590
      GO TO 670                                                         02600
  660 WRITE (J,9001)KEYWORD(ISUB),NSOL                                  02610
  670 CALL REF (0,1,2)                                                  02620
      IF (I.NE.11)GO TO 120                                             02630
      IOPEN=0                                                           02640
  120 IF (JOPTION.EQ.1)GO TO 620                                        02650
      JOPTION=0                                                         02660
      IF (I.EQ.11) GO TO 604                                            02670
      GO TO 621                                                         02680
  608 IOPEN=0                                                           02690
      GO TO 531                                                         02700
  604 WRITE (J,603)                                                     02710
  603 FORMAT (/,'ENTER KEYWORD.')                                       02720
      READ (J,20) LINE                                                  02730
      READ (LINE,*,ERR=622) IHELP                                       02740
      IF (IHELP.GT.11.OR.IHELP.LT.1)GO TO 4200                          02750
C                                                                       02760
C         HE ASKED FOR HELP..                                           02770
C                                                                       02780
```

```
      GO TO (4148,4150,4146,4152,4154,4156,4158,4160,4162,4164,4166),     02790
     1IHELP                                                               02800
  622 READ (LINE,9050,ERR=4200) KEYWORD(ISUB)                             02810
      READ (LINE,810,ERR=820) NSOL                                        02820
  810 FORMAT (9X,I1)                                                      02830
      GO TO 830                                                           02840
  820 NSOL=0                                                              02850
  830 DO 610 I=1,11                                                       02860
      IF (KEYWORD(ISUB).EQ.SUBO(I)) GO TO 620                             02870
      IF (KEYWORD(ISUB).EQ.SUB(I)) GO TO 620                              02880
  610 CONTINUE                                                            02890
      GO TO 4200                                                          02900
C                                                                         02910
C         AH, A LEGITIMATE KEYWORD...                                     02920
C                                                                         02930
  620 IF(JSUB(I).EQ.1.AND.IMORE(I).EQ.0)GO TO 630                         02940
      JSUB(I)=1                                                           02950
      GO TO 640                                                           02960
  630 WRITE (J,635)                                                       02970
  635 FORMAT (/,'YOU HAVE ALREADY USED IT ONCE'/)                         02980
      GO TO 621                                                           02990
  640 WRITE (J,639) KEYWORD(ISUB)                                         03000
  639 FORMAT (//,8('-'),/,A8,/,8('-'),//)                                 03010
      II=I-3                                                              03020
      GO TO (1700,1725,1750,3260,3250,3270,3280,3900,6000,7000,950), I    03030
      STOP                                                                03040
C                                                                         03050
C  -------------------                                                    03060
C  SOLUTION DATA BLOCK                                                    03070
C  -------------------                                                    03080
C                                                                         03090
 1700 CONTINUE                                                            03100
      ISOL=ISOL+1                                                         03110
      IF (ISOL.LE.2) GO TO 1510                                           03120
      WRITE (J,1300)                                                      03130
 1300 FORMAT ('ONLY 2 SOLUTIONS ARE ALLOWED. ')                           03140
      ISOL=2                                                              03150
      GO TO 531                                                           03160
 1510 IF (IOPEN.EQ.0.AND.NSOL.EQ.0)GO TO 1739                             03170
      IF (NSOL.EQ.1.OR.NSOL.EQ.2) GO TO 1500                              03180
      JOPTION=0                                                           03190
      GO TO 1492                                                          03200
 1500 IF (ISOL.NE.2.OR.NSOL.NE.NSOLUTION(1)) GO TO 1501                   03210
      WRITE (J,1502) NSOL                                                 03220
 1502 FORMAT ('SOLUTION #',I1,' HAS ALREADY BEEN ENTERED.')               03230
      ISOL=1                                                              03240
      GO TO 531                                                           03250
 1501 NSOLUTION(ISOL)=NSOL                                                03260
      IF (IOPEN.EQ.0) GO TO 1400                                          03270
      WRITE (J,1736) SUB(I)                                               03280
 1736 FORMAT (/,A8,' CARD:')                                              03290
      CALL REF (2,1,0)                                                    03300
      READ (JLINE(1),1731) HEAD(ISOL)                                     03310
 1731 FORMAT (A80)                                                        03320
      READ (JLINE(2),9003) NTOTS(ISOL),IALK(ISOL),IUNITS(ISOL),PH         03330
     1 (ISOL),PE(ISOL),TEMP(ISOL),SDENS(ISOL)                             03340
```

```
      IF (NTOTS(ISOL).EQ.0)GO TO 1734                                   03350
      CALL REF(1,1,0)                                                   03360
      READ (JLINE(1),9004) (LT(ISOL,M),DTOT(ISOL,M),M=1,5)              03370
      IF (NTOTS(ISOL).LE.5)GO TO 1734                                   03380
      LLINE=INT((NTOTS(ISOL)-1)/5)                                      03390
      DO 1738 KLINE=1,LLINE                                             03400
      CALL REF (1,1,0)                                                  03410
 1738 READ (JLINE(1),9004) (LT(ISOL,M),DTOT(ISOL,M),M=KLINE*5+1,        03420
     1 (KLINE+1)*5)                                                     03430
 1734 CALL REF (0,1,1)                                                  03440
      IF (JOPTION.EQ.1.AND.IALK(ISOL).GT.0)GO TO 1752                   03450
      IF (JOPTION.EQ.1)GO TO 531                                        03460
C                                                                       03470
C       *** SOLUTION NUMBER ***                                         03480
C                                                                       03490
 1739 CALL QUESTB (*1492,0,'SOLUTION NUMBER',15,NSOLUTION(ISOL),'I1     03500
     1,1,2,1)                                                           03510
      IF (.NOT.EXIT)GO TO 1730                                          03520
      JSUB(1)=0                                                         03530
 1753 GO TO 531                                                         03540
 1730 IF (ISOL.NE.2.OR.NSOLUTION(2).NE.NSOLUTION(1)) GO TO 1732         03550
      WRITE (J,1502) NSOLUTION(2)                                       03560
      GO TO 1739                                                        03570
 1732 WRITE (J,1001) NSOLUTION(ISOL)                                    03580
 1001 FORMAT (/,'SOLUTION',1X,I1)                                       03590
      IF (.NOT.OK()) GO TO 1739                                         03600
 1400 IREQUIRED(1)=0                                                    03610
C                                                                       03620
C       *** HEAD ***                                                    03630
C                                                                       03640
      IF (JOPTION.EQ.2) NFLAG=1                                         03650
 1488 CALL QUESTA (*4300,0,'HEAD',4,HEAD(ISOL),'A80 ',0,0)              03660
      IF (HEAD(ISOL).EQ.'*') HEAD(ISOL)='Pure water'                    03670
      WRITE (J,9110)                                                    03680
      WRITE (J,1731)HEAD(ISOL)                                          03690
      IF (.NOT.OK()) GO TO 1488                                         03700
      IF (HEAD(ISOL).NE.'Pure water') GO TO 1713                        03710
      NTOTS(ISOL)=0                                                     03720
      IALK(ISOL)=0                                                      03730
      IUNITS(ISOL)=0                                                    03740
      PH(ISOL)=' 7.0'                                                   03750
      PE(ISOL)=' 4.0'                                                   03760
      TEMP(ISOL)=' 25.0'                                                03770
      GO TO 1719                                                        03780
C                                                                       03790
C       *** NTOTS ***                                                   03800
C                                                                       03810
 1713 CALL QUESTB (*4320,0,'NTOTS',5,NTOTS(ISOL),'I2  ',0,100,0)        03820
 1714 IF (NTOTS(ISOL).NE.0)GO TO 1727                                   03830
      IALK(ISOL)=0                                                      03840
      IUNITS(ISOL)=0                                                    03850
      GO TO 1718                                                        03860
C                                                                       03870
C       *** IALK ***                                                    03880
C                                                                       03890
 1727 CALL QUESTB (*4340,0,'IALK',4,IALK(ISOL),'I3  ',0,0,0)            03900
```

```
      JUMP=0                                                            03910
      IF (IALK(ISOL)) 4340,1715,1708                                    03920
 1708 IF (IALK(ISOL).GT.30.OR.IALK(ISOL).LT.4) GO TO 4340               03930
C                                                                       03940
C       *** IUNITS ***                                                  03950
C                                                                       03960
 1715 CALL QUESTB (*4360,0,'IUNITS',6,IUNITS(ISOL),'I2  ',0,4,0)        03970
C                                                                       03980
C       *** PH ***                                                      03990
C                                                                       04000
 1718 CALL QUESTA (*4380,0,'PH',2,PH(ISOL),'A10 ',1,0)                  04010
C                                                                       04020
C       *** PE ***                                                      04030
C                                                                       04040
 1723 PE(ISOL)=' 4.0                                                    04050
C                                                                       04060
C       *** TEMP ***                                                    04070
C                                                                       04080
 1724 CALL QUESTA (*4420,0,'TEMP',4,TEMP(ISOL),'A10 ',1,0)              04090
      IF (IUNITS(ISOL).EQ.1.OR.IUNITS(ISOL).EQ.2) GO TO 1482            04100
 1719 SDENS(ISOL)=' 1.0'                                                04110
      GO TO 1490                                                        04120
C                                                                       04130
C       *** SDENS ***                                                   04140
C                                                                       04150
 1482 CALL QUESTA (*4440,0,'SDENS',5,SDENS(ISOL),'A10 ',1,0)            04160
 1490 WRITE (J,9110)                                                    04170
      WRITE (J,9003) NTOTS(ISOL),IALK(ISOL),IUNITS(ISOL),PH(ISOL)       04180
     1,PE(ISOL),TEMP(ISOL),SDENS(ISOL)                                  04190
      IF (.NOT.OK()) GO TO 1713                                         04200
      IF (IALK(ISOL).EQ.0)GO TO 1726                                    04210
 1752 WRITE (J,1006)                                                    04220
 1006 FORMAT (/,'HAS THE APPROPRIATE CARBON ELEMENT-CARD BEEN',         04230
     1' CONSTRUCTED?')                                                  04240
      JUMP=1                                                            04250
      IF (.NOT.YN()) GO TO 1728                                         04260
      GO TO (1726,1753,1726,1726),JOPTION+1                             04270
C                                                                       04280
C         ADD AN EXTRA ELEMENT CARD FOR HIM...                          04290
C                                                                       04300
 1728 WRITE (J,1709)                                                    04310
 1709 FORMAT (/,'WHAT IS THE GRAM EQUIVALENT WEIGHT (GRAMS/EQUIVALENT'  04320
     1,') OF THE',/,'CHEMICAL SPECIES IN WHICH THE ALKALINITY IS',      04330
     2' REPORTED?')                                                     04340
      WRITE (J,1710)                                                    04350
 1710 FORMAT (//,'FOR EXAMPLE:',/,19X,'CACO3     50.0446 G/EQ',/,19X    04360
     1,'HCO3-     61.0171 G/EQ',/,19X,'CO3--     30.0046 G/EQ.',//)     04370
      READ (J,1731) LINE                                                04380
      READ (LINE,*,ERR=1728) EQ                                         04390
      EQUIVWT=LINE(1:8)                                                 04400
      JSUB(2)=2                                                         04410
      WRITE (J,1712)                                                    04420
 1712 FORMAT (//,'ELEMENTS DATA BLOCK WILL BE CONSTRUCTED AUTOMATICALLY' 04430
     1,//)                                                              04440
      IF (IELEMENT.LT.27)GO TO 1004                                     04450
      WRITE (J,1002)                                                    04460
```

```
 1002 FORMAT (1X,52('*'),/,1X,'WARNING:  NUMBER OF ELEMENTS EXCEEDS ',   04470
     1'MAXIMUM POSSIBLE.',/,1X,'CARBON CARD IS DELETED.',/,1X,52('*')/)  04480
      GO TO (1726,1753),JOPTION+1                                        04490
 1004 IELEMENT=IELEMENT+1                                                04500
      TNAME(IELEMENT)='C'                                                04510
      NELT(IELEMENT)=IALK(ISOL)                                          04520
      TGFW(IELEMENT)=EQUIVWT                                             04530
      GO TO 1600                                                         04540
 1601 IF (JOPTION.EQ.1)GO TO 1753                                        04550
 1726 IF (IUNITS(ISOL).GE.2.AND.IUNITS(ISOL).LE.3.AND.IELEMENT.EQ.0)     04560
     1 IREQUIRED(2)=1                                                    04570
      IF (NTOTS(ISOL).EQ.0)GO TO 531                                     04580
 1320 M=1                                                                04590
 1310 N2=1                                                               04600
C                                                                        04610
C       *** LT ***                                                       04620
C                                                                        04630
 1326 CALL QUESTB (*4100,M,'LT',2,LT(ISOL,M),'I4  ',1,10000,2)           04640
      IF (.NOT.LIST)GO TO 1057                                           04650
 1361 CALL LISTM                                                         04660
      GO TO (1326,1356),N2                                               04670
 1057 N2=2                                                               04680
C                                                                        04690
C       *** DTOT ***                                                     04700
C                                                                        04710
 1356 CALL QUESTA (*4100,M,'DTOT',4,DTOT(ISOL,M),'A11 ',1,2)             04720
      IF (LIST)GO TO 1361                                                04730
      M=M+1                                                              04740
      IF (M.LE.NTOTS(ISOL)) GO TO 1310                                   04750
      WRITE (J,9110)                                                     04760
      WRITE (J,9004) (LT(ISOL,M),DTOT(ISOL,M),M=1,NTOTS(ISOL))           04770
      IF (.NOT.OK())GO TO 1320                                           04780
      GO TO 531                                                          04790
 1725 CONTINUE                                                           04800
C                                                                        04810
C   --------------------                                                 04820
C    ELEMENTS DATA BLOCK                                                 04830
C   --------------------                                                 04840
C                                                                        04850
      IELEMENT=IELEMENT+1                                                04860
      IF (IOPEN.EQ.0)GO TO 1729                                          04870
 1536 CALL REF (1,0,0)                                                   04880
      IF (JOPTION.EQ.0)GO TO 1530                                        04890
      WRITE (J,1736) SUB(I)                                              04900
      WRITE (J,1731)JLINE(1)                                             04910
      CALL REF (0,0,3)                                                   04920
      GO TO (1530,1531,1531,1536), JOPTION+1                             04930
 1531 READ (JLINE(1),9102) TNAME(IELEMENT),NELT(IELEMENT),TGFW(IELEMENT) 04940
      IREQUIRED(2)=0                                                     04950
      IF (JOPTION.EQ.1) GO TO 1600                                       04960
C                                                                        04970
C       *** TNAME ***                                                    04980
C                                                                        04990
 1729 CALL QUESTA (*4102,0,'TNAME',5,TNAME(IELEMENT),'A8  ',0,3)         05000
      IF (.NOT.LIST)GO TO 1549                                           05010
      CALL LISTM                                                         05020
```

```
      GO TO 1729                                                        05030
 1549 IF (.NOT.EXIT)GO TO 1550                                          05040
 1530 IELEMENT=IELEMENT-1                                               05050
      IF (IELEMENT.EQ.0)JSUB(2)=0                                       05060
      GO TO 531                                                         05070
 1550 IREQUIRED(2)=0                                                    05080
C                                                                       05090
C       *** NELT ***                                                    05100
C                                                                       05110
      CALL QUESTB (*4104,0,'NELT',4,NELT(IELEMENT),'I2  ',4,30,2)       05120
      IF (.NOT.LIST) GO TO 1558                                         05130
      CALL LISTM                                                        05140
      GO TO 1550                                                        05150
 1558 DO 1547 M=1,IELEMENT-1                                            05160
 1547 IF (NELT(IELEMENT).EQ.NELT(M))GO TO 1548                          05170
      GO TO 1570                                                        05180
 1548 WRITE (J,1551) NELT(M)                                            05190
 1551 FORMAT (/,'WARNING:  ELEMENT #',I2,' IS ALREADY ENTERED.'/)       05200
C                                                                       05210
C       *** TGFW ***                                                    05220
C                                                                       05230
 1570 CALL QUESTA (*4106,0,'TGFW',4,TGFW(IELEMENT),'A10 ',1,2)          05240
      IF (.NOT.LIST) GO TO 1580                                         05250
      CALL LISTM                                                        05260
      GO TO 1570                                                        05270
 1580 WRITE (J,9110)                                                    05280
      WRITE (J,9102) TNAME(IELEMENT),NELT(IELEMENT),TGFW(IELEMENT)      05290
      IF (.NOT.OK()) GO TO 1729                                         05300
C                                                                       05310
C         KEEP TRACK OF ELEMENTS AND SPECIES                            05320
C                                                                       05330
 1600 IF(ICHECK(2,NELT(IELEMENT)).EQ.1)GO TO 1557                       05340
      ICHECK(1,NELT(IELEMENT))=1                                        05350
      GO TO 1575                                                        05360
 1557 ICHECK(2,NELT(IELEMENT))=0                                        05370
 1575 IF (I.EQ.1)GO TO 1601                                             05380
      IF (IELEMENT.EQ.27) GO TO 531                                     05390
      IF (IOPEN.NE.0)GO TO 1725                                         05400
      WRITE (J,1573)                                                    05410
 1573 FORMAT (/,'MORE ELEMENTS?')                                       05420
      IF (YN()) GO TO 1725                                              05430
      GO TO 531                                                         05440
 1750 CONTINUE                                                          05450
C                                                                       05460
C  -----------------                                                    05470
C  SPECIES DATA BLOCK                                                   05480
C  -----------------                                                    05490
C                                                                       05500
      ISPECIE=ISPECIE+1                                                 05510
      IF (IOPEN.EQ.0)GO TO 1590                                         05520
 1523 CALL REF (1,0,0)                                                  05530
      IF (JOPTION.EQ.0)GO TO 1529                                       05540
      WRITE (J,1736)SUB(I)                                              05550
      WRITE (J,1731)JLINE(1)                                            05560
      READ (JLINE(1),9202) NI(ISPECIE)                                  05570
      CALL REF (3,1,3)                                                  05580
```

```
      GO TO (1521,1521,1523),JOPTION                                    05590
      CALL REF (0,0,2)                                                  05600
      IF (JOPTION.EQ.2) GO TO 1523                                      05610
      ISDEL(ISPECIE)=1                                                  05620
      GO TO 1750                                                        05630
 1521 READ (JLINE(1),9203) SNAME(ISPECIE),NSP(ISPECIE),KFLAG            05640
     1(ISPECIE),GFLAG(ISPECIE),ZSP(ISPECIE),THSP(ISPECIE),DHA(ISPECIE)  05650
     2,ADHSP(ISPECIE,1),ADHSP(ISPECIE,2),ALKSP(ISPECIE)                 05660
      READ (JLINE(2),9204) LKTOSP(ISPECIE),DHSP(ISPECIE),               05670
     1(ASP(ISPECIE,MMM),MMM=1,5)                                        05680
      READ (JLINE(3),9205) (LSP(ISPECIE,MMM),CSP(ISPECIE,MMM),          05690
     1MMM=1,NSP(ISPECIE))                                               05700
      IF (JOPTION.EQ.1) GO TO 1670                                      05710
C                                                                       05720
C       *** I ***                                                       05730
C                                                                       05740
 1590 CALL QUESTB (*4110,0,'I',1,NI(ISPECIE),'I3  ',4,250,1)            05750
      IF (.NOT.EXIT) GO TO 1654                                         05760
 1529 ISPECIE=ISPECIE-1                                                 05770
      IF (ISPECIE.EQ.0)JSUB(3)=0                                        05780
      IF (IOPEN.NE.0)GO TO 531                                          05790
      GO TO 1933                                                        05800
 1654 WRITE (J,9110)                                                    05810
      WRITE (J,9202) NI (ISPECIE)                                       05820
      IF (.NOT.OK()) GO TO 1590                                         05830
      IF(ISDEL(ISPECIE).NE.1) GO TO 1660                                05840
      IF (JOPTION.EQ.2)GO TO 1750                                       05850
      GO TO 1934                                                        05860
C                                                                       05870
C       *** SNAME ***                                                   05880
C                                                                       05890
 1660 CALL QUESTA (*4112,0,'SNAME',5,SNAME(ISPECIE),'A8  ',0,0)         05900
C                                                                       05910
C         IS IT A MASTER SPECIE....                                     05920
C                                                                       05930
 1670 IMASTER=0                                                         05940
      IF (NI(ISPECIE).LE.30.AND.NI(ISPECIE).GT.3.AND.ISDEL(ISPECIE)     05950
     1.NE.1)IMASTER=1                                                   05960
      IF (JOPTION.EQ.1.AND.IMASTER.EQ.0)GO TO 1750                      05970
      IF (IMASTER.EQ.0.OR.(NFLAG.EQ.1.AND.JOPTION.NE.2))GO TO 1676      05980
C                                                                       05990
C         KEEP TRACK OF ELEMENTS AND SPECIES...                         06000
C                                                                       06010
      IF (ICHECK(1,NI(ISPECIE)).EQ.1)GO TO 1679                         06020
      ICHECK(2,NI(ISPECIE))=1                                           06030
      GO TO 1595                                                        06040
 1679 ICHECK(1,NI(ISPECIE))=0                                           06050
 1595 IF (JOPTION.EQ.1)GO TO 1750                                       06060
C                                                                       06070
C         IF IT IS A MASTER SPECIES, A LOT OF VARIABLES CAN BE          06080
C         DETERMINED WITHOUT ASKING THE USER...                         06090
C                                                                       06100
      NSP(ISPECIE)=1                                                    06110
      KFLAG(ISPECIE)=0                                                  06120
      CSP(ISPECIE,1)=' 1.0'                                             06130
      LSP(ISPECIE,1)=NI(ISPECIE)                                        06140
```

```
      LKTOSP(ISPECIE)=' 0.0'                                              06150
      DHSP(ISPECIE)=' 0.0'                                                06160
      DO 1678 NII=1,5                                                     06170
 1678 ASP(ISPECIE,NII)=' 0.0'                                             06180
      GO TO 1690                                                          06190
C                                                                         06200
C       *** NSP ***                                                       06210
C                                                                         06220
 1676 CALL QUESTB (*4114,0,'NSP',3,NSP(ISPECIE),'I3  ',0,6,0)            06230
C                                                                         06240
C       *** KFLAG ***                                                     06250
C                                                                         06260
 1680 CALL QUESTB (*4116,0,'KFLAG',5,KFLAG(ISPECIE),'I2  ',0,1,0)        06270
C                                                                         06280
C       *** GFLAG ***                                                     06290
C                                                                         06300
 1690 CALL QUESTB (*4118,0,'GFLAG',5,GFLAG(ISPECIE),'I2  ',0,1,0)        06310
C                                                                         06320
C       *** ZSP ***                                                       06330
C                                                                         06340
 1780 CALL QUESTA (*4120,0,'ZSP',3,ZSP(ISPECIE),'A10 ',1,0)              06350
C                                                                         06360
C       *** THSP ***                                                      06370
C                                                                         06380
 1790 CALL QUESTA (*4122,0,'THSP',4,THSP(ISPECIE),'A10 ',1,0)            06390
C                                                                         06400
C       *** DHA ***                                                       06410
C                                                                         06420
 1880 CALL QUESTA (*4124,0,'DHA',3,DHA(ISPECIE),'A10 ',1,0)              06430
      IF (GFLAG(ISPECIE).EQ.1)GO TO 1891                                  06440
      ADHSP(ISPECIE,1)=' 0.0'                                             06450
      ADHSP(ISPECIE,2)=' 0.0'                                             06460
      GO TO 1740                                                          06470
C                                                                         06480
C       *** ADHSP ***                                                     06490
C                                                                         06500
 1891 M=1                                                                 06510
 1892 CALL QUESTA (*1897,M,'ADHSP',5,ADHSP(ISPECIE,M),'A10 ',1,0)        06520
      M=M+1                                                               06530
      IF (M.EQ.3)GO TO 1740                                               06540
      GO TO 1892                                                          06550
 1897 GO TO (4126,4128), M                                                06560
C                                                                         06570
C       *** ALKSP ***                                                     06580
C                                                                         06590
 1740 CALL QUESTA (*4130,0,'ALKSP',5,ALKSP(ISPECIE),'A10 ',1,0)          06600
      WRITE (J,9110)                                                      06610
      WRITE (J,9203)SNAME(ISPECIE),NSP(ISPECIE),KFLAG(ISPECIE),           06620
     1GFLAG(ISPECIE),ZSP(ISPECIE),THSP(ISPECIE),DHA(ISPECIE),             06630
     2ADHSP(ISPECIE,1),ADHSP(ISPECIE,2),ALKSP(ISPECIE)                    06640
      IF (.NOT.OK()) GO TO 1660                                           06650
 1960 IF(IMASTER.EQ.0)GO TO 1967                                          06660
      GO TO 1930                                                          06670
C                                                                         06680
C       *** LKTOSP ***                                                    06690
C                                                                         06700
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 1967 CALL QUESTA (*4132,0,'LKTOSP',6,LKTOSP(ISPECIE),'A10 ',1,0)          06710
C                                                                          06720
C        *** DHSP ***                                                      06730
C                                                                          06740
 1970 CALL QUESTA (*4136,0,'DHSP',4,DHSP(ISPECIE),'A10 ',1,0)              06750
      IF (KFLAG(ISPECIE).EQ.1)GO TO 1986                                   06760
C                                                                          06770
C       *** ASP ***                                                        06780
C                                                                          06790
      DO 1988 K=1,5                                                        06800
 1988 ASP(ISPECIE,K)=' 0.0'                                                06810
      GO TO 1990                                                           06820
 1986 K=1                                                                  06830
 1987 CALL QUESTA (*4138,K,'ASP',3,ASP(ISPECIE,K),'A12 ',1,0)              06840
      K=K+1                                                                06850
      IF (K.LT.6)GO TO 1987                                                06860
 1990 WRITE (J,9110)                                                       06870
      WRITE (J,9204) LKTOSP(ISPECIE),DHSP(ISPECIE),(ASP(ISPECIE,I8),       06880
     1I8=1,5)                                                              06890
      IF (.NOT.OK()) GO TO 1960                                            06900
 1910 K=1                                                                  06910
      IF (NSP(ISPECIE).EQ.0)GO TO 1930                                     06920
 1912 K2=1                                                                 06930
C                                                                          06940
C       *** LSP, CSP ***                                                   06950
C                                                                          06960
 1915 IF (K2.EQ.1) CALL QUESTB (*4142,K,'LSP',3,LSP(ISPECIE,K),'I3  ',1    06970
     1,30,2)                                                               06980
      IF (K2.EQ.2) CALL QUESTA (*4144,K,'CSP',3,CSP(ISPECIE,K),'A7  ',1    06990
     1,2)                                                                  07000
      IF (.NOT.LIST)GO TO 1922                                             07010
      CALL LISTM                                                           07020
      GO TO 1915                                                           07030
 1922 IF (K2.EQ.2) GO TO 1923                                              07040
      K2=2                                                                 07050
      GO TO 1915                                                           07060
 1923 K=K+1                                                                07070
      IF (K.GT.NSP(ISPECIE)) GO TO 1940                                    07080
      GO TO 1912                                                           07090
 1940 WRITE (J,9110)                                                       07100
      WRITE (J,9205)(LSP(ISPECIE,MM),CSP(ISPECIE,MM),MM=1,NSP(ISPECIE))    07110
      IF (.NOT.OK())GO TO 1910                                             07120
 1930 IF (IOPEN.NE.0)GO TO 1750                                            07130
      WRITE (J,1931)                                                       07140
 1931 FORMAT (/,'MORE SPECIES?')                                           07150
      IF (YN())GO TO 1750                                                  07160
 1933 WRITE (J,1932)                                                       07170
 1932 FORMAT (/,'ANY SPECIES TO DELETE?')                                  07180
 1936 IF (.NOT.YN())GO TO 531                                              07190
      ISDEL(ISPECIE+1)=1                                                   07200
      JSUB(3)=1                                                            07210
      GO TO 1750                                                           07220
 1934 WRITE (J,1935)                                                       07230
 1935 FORMAT (/,'MORE SPECIES TO DELETE?')                                 07240
      GO TO 1936                                                           07250
C                                                                          07260
```

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C     ------------------                                                07270
C     MINERALS DATA BLOCK                                               07280
C     ------------------                                                07290
C                                                                       07300
 3260 CONTINUE                                                          07310
      IF (IMINO.EQ.0.OR.IOPEN.NE.0)GO TO 3100                           07320
C                                                                       07330
C         MINERAL DATA AVAILABLE...                                     07340
C                                                                       07350
      WRITE (J,3002)                                                    07360
 3002 FORMAT (/,'PRE-CONSTRUCTED MINERAL DATA ARE AVAILABLE.'/,         07370
     1'DO YOU WISH TO HAVE ANY OF THEM?')                               07380
      IF (.NOT.YN())GO TO 3100                                          07390
C                                                                       07400
C         PRINT THE LIST OF MINERALS.....                               07410
C                                                                       07420
 3004 WRITE (J,3003)(K,MNAMEO(K),K=1,IMINO)                             07430
 3003 FORMAT (/20(1X,5(I3,1X,A8,2X,:)/))                                07440
 3021 WRITE (J,3005)                                                    07450
 3005 FORMAT (/,'ENTER THE INDEX NUMBER OF MINERAL. (TYPE <STOP> TO'    07460
     1,' EXIT)')                                                        07470
      READ (J,1731) LINE                                                07480
      IF (LINE(1:4).EQ.'STOP'.OR.LINE(1:4).EQ.'stop') GO TO 3010        07490
      READ (LINE,*,ERR=3004) INDEX                                      07500
      IF (INDEX.GT.IMINO.OR.INDEX.LT.1)GO TO 3004                       07510
      IF (MUSED(INDEX).EQ.1)GO TO 3012                                  07520
      MUSED(INDEX)=1                                                    07530
      GO TO 3013                                                        07540
 3012 WRITE (J,3014) INDEX                                              07550
 3014 FORMAT (//,'MINERAL # ',I3,' HAS ALREADY BEEN ENTERED.'//)        07560
      GO TO 3021                                                        07570
 3013 IMINERAL(1)=IMINERAL(1)+1                                         07580
      IM=IMINERAL(1)                                                    07590
      IREQUIRED(4)=0                                                    07600
      MNAME(1,IM)=MNAMEO(INDEX)                                         07610
      NMINO(1,IM)=NMINOO(INDEX)                                         07620
      THMIN(1,IM)=THMINO(INDEX)                                         07630
      LKTOM(1,IM)=LKTOMO(INDEX)                                         07640
      DHMIN(1,IM)=DHMINO(INDEX)                                         07650
      MFLAG(1,IM)=MFLAGO(INDEX)                                         07660
      SIMIN(1,IM)=SIMINO(INDEX)                                         07670
      DO 3006 K2=1,NMINO(1,IM)                                          07680
      LMIN(1,IM,K2)=LMINO(INDEX,K2)                                     07690
 3006 CMIN(1,IM,K2)=CMINO(INDEX,K2)                                     07700
 3015 LFLAG=1                                                           07710
      GO TO 3032                                                        07720
 3020 DO 3008 K2=1,5                                                    07730
 3008 AMIN(1,IM,K2)=AMINO(INDEX,K2)                                     07740
      GO TO 3210                                                        07750
 3024 IF (MFLAG(II,IM).EQ.1) GO TO 3020                                 07760
      DO 3001 K2=1,5                                                    07770
 3001 AMIN(1,IM,K2)=BLANK                                               07780
 3000 IF (OK()) GO TO 3016                                              07790
      WRITE (J,3017)                                                    07800
 3017 FORMAT ('DO YOU WISH TO CHANGE SIMIN?')                           07810
      IF (.NOT.YN())GO TO 3019                                          07820
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      LFLAG=3                                                          07830
      GO TO 3167                                                       07840
 3009 WRITE (J,3022)                                                   07850
 3022 FORMAT ('DO YOU WISH TO CHANGE ANYTHING ELSE?')                  07860
      IF (.NOT.YN())GO TO 3015                                         07870
 3019 LFLAG=2                                                          07880
      GO TO 3102                                                       07890
 3016 LFLAG=0                                                          07900
      GO TO 3021                                                       07910
 3010 WRITE (J,3011)                                                   07920
 3011 FORMAT (/,'MORE MINERALS TO BE TYPED IN FROM THE TERMINAL?')     07930
      IF (.NOT.YN()) GO TO 3061                                        07940
 3100 IF (IOPEN.EQ.0)GO TO 3221                                        07950
      IMINERAL(II)=IMINERAL(II)+1                                      07960
      IM=IMINERAL(II)                                                  07970
 3062 CALL REF (1,0,0)                                                 07980
      IF (JOPTION.NE.0)GO TO 3056                                      07990
 3059 IMINERAL(II)=IMINERAL(II)-1                                      08000
 3061 IF (IMINERAL(II).EQ.0)JSUB(I)=0                                  08010
      GO TO 531                                                        08020
 3056 WRITE (J,1736) SUB(I)                                            08030
      WRITE (J,1731)JLINE(1)                                           08040
       READ (JLINE(1),9302)MNAME(II,IM),NMINO(II,IM),THMIN(II,IM)      08050
     1,LKTOM(II,IM),DHMIN(II,IM),MFLAG(II,IM),SIMIN(II,IM)             08060
      IF (MNAME(II,IM).NE.DELETE)GO TO 3051                            08070
      CALL REF (0,0,2)                                                 08080
      GO TO (3063,3062),JOPTION                                        08090
 3063 IDELETE=1                                                        08100
      GO TO 3062                                                       08110
 3051 NLINE=2                                                          08120
      IF (NMINO(II,IM).GT.5)NLINE=3                                    08130
      IF (MFLAG(II,IM).NE.1)NLINE=NLINE-1                              08140
      CALL REF (NLINE,1,3)                                             08150
      READ (JLINE(1),9303)(LMIN(II,IM,MMM),CMIN(II,IM,MMM),MMM=1,5)    08160
      IF (NMINO(II,IM).LE.5)GO TO 3054                                 08170
      READ (JLINE(2),9303)(LMIN(II,IM,MMM),CMIN(II,IM,MMM),MMM=6       08180
     1,NMINO(II,IM))                                                   08190
 3054 IF (MFLAG(II,IM).NE.1)GO TO 3057                                 08200
      READ (JLINE(NLINE),9304) (AMIN(II,IM,MMM),MMM=1,5)               08210
 3057 GO TO (3102,3062), JOPTION-1                                     08220
      IREQUIRED(I)=0                                                   08230
      GO TO 3100                                                       08240
C                                                                      08250
C       *** MNAME ***                                                  08260
C                                                                      08270
 3221 IMINERAL(II)=IMINERAL(II)+1                                      08280
      IM=IMINERAL(II)                                                  08290
      LFLAG=0                                                          08300
 3102 CALL QUESTA (*8000,0,'MNAME',5,MNAME(II,IM),'A8  ',0,1)          08310
      IF (EXIT) GO TO 3059                                             08320
 3106 IREQUIRED(I)=0                                                   08330
C                                                                      08340
C       *** NMINO ***                                                  08350
C                                                                      08360
 3110 CALL QUESTB (*8002,0,'NMINO',5,NMINO(II,IM),'I2  ',1,10,0)       08370
C                                                                      08380
```

```
C       *** THMIN ***                                                          08390
C                                                                              08400
 3120 CALL QUESTA (*8004,0,'THMIN',5,THMIN(II,IM),'A10 ',1,0)                  08410
C                                                                              08420
C       *** LKTOM ***                                                          08430
C                                                                              08440
 3130 CALL QUESTA (*8006,0,'LKTOM',5,LKTOM(II,IM),'A10 ',1,0)                  08450
C                                                                              08460
C       *** DHMIN ***                                                          08470
C                                                                              08480
 3140 CALL QUESTA (*8008,0,'DHMIN',5,DHMIN(II,IM),'A10 ',1,0)                  08490
C                                                                              08500
C       *** MFLAG ***                                                          08510
C                                                                              08520
 3150 CALL QUESTB (*8010,0,'MFLAG',5,MFLAG(II,IM),'I1  ',0,1,0)                08530
      IF (LFLAG.EQ.2) GO TO 3032                                               08540
C                                                                              08550
C       *** SIMIN ***                                                          08560
C                                                                              08570
 3167 CALL QUESTA (*8012,0,'SIMIN',5,SIMIN(II,IM),'A10 ',1,0)                  08580
      IF (LFLAG.EQ.3)GO TO 3009                                                08590
 3032 WRITE (J,9110)                                                           08600
      WRITE (J,9302) MNAME(II,IM),NMINO(II,IM),THMIN(II,IM),LKTOM(II,IM)       08610
     1,DHMIN(II,IM),MFLAG(II,IM),SIMIN(II,IM)                                  08620
      IF (LFLAG.EQ.1)GO TO 3187                                                08630
      IF (LFLAG.EQ.2) LFLAG=4                                                  08640
      IF (.NOT.OK()) GO TO 3102                                                08650
      IF (LFLAG.EQ.4) NFLAG=1                                                  08660
C                                                                              08670
C       *** LMIN, CMIN ***                                                     08680
C                                                                              08690
 3190 K=1                                                                      08700
 3192 K2=1                                                                     08710
 3195 IF (K2.EQ.1) CALL QUESTB (*8014,K,'LMIN',4,LMIN(II,IM,K),'I4  ',0        08720
     1,0,2)                                                                   08730
      IF (K2.EQ.2) CALL QUESTA (*8016,K,'CMIN',4,CMIN(II,IM,K),'A11 ',1        08740
     1,2)                                                                     08750
      IF (.NOT.LIST)GO TO 3191                                                 08760
      CALL LISTM                                                               08770
      GO TO 3195                                                               08780
 3191 IF (K2.EQ.2) GO TO 3186                                                  08790
      K2=2                                                                     08800
      GO TO 3195                                                               08810
 3186 K=K+1                                                                    08820
      IF (K.LE.NMINO(II,IM)) GO TO 3192                                        08830
      WRITE (J,9110)                                                           08840
 3187 WRITE (J,9303) (LMIN(II,IM,K),CMIN(II,IM,K),K=1,NMINO(II,IM))            08850
      IF (LFLAG.EQ.1) GO TO 3024                                               08860
      IF (.NOT.OK()) GO TO 3190                                                08870
      IF(MFLAG(II,IM).EQ.1)GO TO 3201                                          08880
      IF (LFLAG.EQ.4) GO TO 3016                                               08890
      IF (IOPEN.NE.0)GO TO 3100                                                08900
      GO TO 3010                                                               08910
C                                                                              08920
C       *** AMIN ***                                                           08930
C                                                                              08940
```

```
 3201 IF (LFLAG.EQ.4) NFLAG=1                                          08950
 3200 K=1                                                              08960
 3207 CALL QUESTA (*8018,K,'AMIN',4,AMIN(II,IM,K),'A12 ',1,0)          08970
      K=K+1                                                            08980
      IF (K.LT.6)GO TO 3207                                            08990
      WRITE (J,9110)                                                   09000
 3210 WRITE (J,9304)(AMIN(II,IM,K),K=1,5)                              09010
      IF (LFLAG.EQ.1) GO TO 3000                                       09020
      IF (.NOT.OK()) GO TO 3200                                        09030
      IF (LFLAG.EQ.4) GO TO 3016                                       09040
      IF (IOPEN.NE.0)GO TO 3100                                        09050
      GO TO 3010                                                       09060
 3250 CONTINUE                                                         09070
C                                                                      09080
C     ------------------                                               09090
C     LOOK MIN DATA BLOCK                                              09100
C     ------------------                                               09110
C                                                                      09120
      IF(IMINERAL(2).NE.0.OR.IOPEN.NE.0)GO TO 3100                     09130
      WRITE (J,3251)                                                   09140
 3251 FORMAT (/,'DO YOU WANT TO DELETE ALL OLD MINERALS?')             09150
      IF (YN())IDELETE=1                                               09160
      IF (IDELETE.EQ.1) JSUB(I)=1                                      09170
C                                                                      09180
C         SINCE LOOK MIN IS ALMOST IDENTICAL TO MINERAL,               09190
C         WHY NOT USE MINERAL SECTION AND SAVE SOME SPACE?             09200
C                                                                      09210
      GO TO 3100                                                       09220
 3270 CONTINUE                                                         09230
C                                                                      09240
C     ---------------                                                  09250
C     TEMP DATA BLOCK                                                  09260
C     ---------------                                                  09270
C                                                                      09280
      IF(IOPT(4).EQ.0)GO TO 3320                                       09290
      NTEMP=IOPT(4)                                                    09300
      IF (IOPT(4).EQ.3)NTEMP=NSTEPS                                    09310
      IF (IOPEN.EQ.0)GO TO 3308                                        09320
      NSTEPS2=IOPT04                                                   09330
      IF (IOPT04.EQ.3) NSTEPS2=NSTEPS0                                 09340
      READ (13,9501)(XTEMP(K3),K3=1,NSTEPS2)                           09350
      WRITE (J,1736) SUB(I)                                            09360
      WRITE (J,9501)(XTEMP(K3),K3=1,NTEMP)                             09370
      CALL REF (0,0,1)                                                 09380
      IF (JOPTION.NE.1) GO TO 3308                                     09390
      IREQUIRED(6)=0                                                   09400
      GO TO 531                                                        09410
C                                                                      09420
C       *** XTEMP ***                                                  09430
C                                                                      09440
 3308 K=1                                                              09450
 3307 CALL QUESTA (*8020,K,'XTEMP',5,XTEMP(K),'A10 ',1,1)              09460
      IF (.NOT.EXIT)GO TO 3312                                         09470
      JSUB(6)=0                                                        09480
      GO TO 531                                                        09490
 3312 K=K+1                                                            09500
```

```
      IF (K.LE.NTEMP)GO TO 3307                                          09510
      IREQUIRED(6)=0                                                     09520
      WRITE (J,9110)                                                     09530
      WRITE (J,9501)(XTEMP(K),K=1,NTEMP)                                 09540
      IF (OK())GO TO 531                                                 09550
      GO TO 3308                                                         09560
 3320 WRITE (J,3321)                                                     09570
 3321 FORMAT (/,'ERROR:  TEMP DATA BLOCK NOT REQUIRED WHEN IOPT(4) ='    09580
     1,' 0',//)                                                          09590
      JSUB(6)=0                                                          09600
      GO TO 531                                                          09610
 3280 CONTINUE                                                           09620
C                                                                        09630
C     ---------------                                                    09640
C     STEPS DATA BLOCK                                                   09650
C     ---------------                                                    09660
C                                                                        09670
      IF(IOPT(3).EQ.0.OR.IOPT(3).EQ.5.OR.IOPT(3).EQ.6)GO TO 3630         09680
      NSTEP=NSTEPS                                                       09690
      IF (IOPT(3).EQ.4)NSTEP=1                                           09700
      IF (IOPEN.EQ.0)GO TO 3608                                          09710
      NSTEPS1=NSTEPS0                                                    09720
      IF (IOPT03.EQ.4) NSTEPS1=1                                         09730
      READ (13,9501)(XSTEP(K3),K3=1,NSTEPS1)                             09740
      WRITE (J,1736) SUB(I)                                              09750
      WRITE (J,9501)(XSTEP(K3),K3=1,NSTEP)                               09760
      CALL REF (0,0,1)                                                   09770
      GO TO (3801,3801,3608), JOPTION                                    09780
 3801 IREQUIRED(7)=0                                                     09790
      IF (JOPTION.NE.2) GO TO 531                                        09800
C                                                                        09810
C       *** XSTEP ***                                                    09820
C                                                                        09830
 3608 K=1                                                                09840
 3607 CALL QUESTA (*3620,K,'XSTEP',5,XSTEP(K),'A10 ',1,1)                09850
      IF (.NOT.EXIT)GO TO 3606                                           09860
      JSUB(7)=0                                                          09870
      GO TO 531                                                          09880
 3606 K=K+1                                                              09890
      IF (K.LE.NSTEP)GO TO 3607                                          09900
      IREQUIRED(7)=0                                                     09910
      WRITE (J,9110)                                                     09920
      WRITE (J,9501)(XSTEP(K),K=1,NSTEP)                                 09930
      IF (OK())GO TO 531                                                 09940
      GO TO 3608                                                         09950
 3620 GO TO (8022,8024,8026,8028),IOPT(3)                                09960
 3630 WRITE (J,3631) IOPT(3)                                             09970
 3631 FORMAT (/,'ERROR:  STEPS DATA BLOCK NOT ALLOWED WHEN IOPT(3) ='    09980
     1,1X,I1,//)                                                         09990
      JSUB(7)=0                                                          10000
      GO TO 531                                                          10010
 3900 CONTINUE                                                           10020
C                                                                        10030
C     ------------------                                                 10040
C     REACTION DATA BLOCK                                                10050
C     ------------------                                                 10060
```

```
C                                                                       10070
      IF (NCOMPS.NE.0)GO TO 3902                                        10080
      WRITE (J,3901)                                                    10090
 3901 FORMAT (//,'ERROR:   REACTION DATA BLOCK NOT ALLOWED WHEN',       10100
     1' NCOMPS = 0',//)                                                 10110
      JSUB(8)=0                                                         10120
      GO TO 531                                                         10130
 3902 IF (IOPEN.EQ.0)GO TO 5010                                         10140
      READ (13,9701)(LREAC(K3),CREAC(K3),THMEAN(K3),K3=1,NCOMPS0)       10150
      WRITE (J,1736) SUB(I)                                             10160
      WRITE (J,9701)(LREAC(K3),CREAC(K3),THMEAN(K3),K3=1,NCOMPS)        10170
      CALL REF (0,0,1)                                                  10180
      IF (JOPTION.EQ.2) GO TO 5010                                      10190
      IREQUIRED(8)=0                                                    10200
      IF (JOPTION.EQ.1) GO TO 531                                       10210
C                                                                       10220
C       *** THMEAN, LREAC, CREAC ***                                    10230
C                                                                       10240
 5010 K=1                                                               10250
 5012 K2=1                                                              10260
 5015 IF (K2.EQ.1) CALL QUESTB (*8032,K,'LREAC',5,LREAC(K),'I4  ',0,0,3) 10270
      IF (K2.EQ.2) CALL QUESTA (*8034,K,'CREAC',5,CREAC(K),'A8  ',1,3)  10280
      IF (K2.EQ.3) CALL QUESTA (*8036,K,'THMEAN',6,THMEAN(K),'A8  ',1,3) 10290
      IF (.NOT.EXIT)GO TO 5023                                          10300
 5300 JSUB(8)=0                                                         10310
      GO TO 531                                                         10320
 5023 IF (.NOT.LIST) GO TO 5025                                         10330
      CALL LISTM                                                        10340
      GO TO 5015                                                        10350
 5025 IF (K2.EQ.3) GO TO 5026                                           10360
      K2=K2+1                                                           10370
      IREQUIRED(8)=0                                                    10380
      GO TO 5015                                                        10390
 5026 K=K+1                                                             10400
      IF (K.GT.NCOMPS) GO TO 5027                                       10410
      GO TO 5012                                                        10420
 5027 WRITE (J,9110)                                                    10430
      WRITE (J,9701) (LREAC(K),CREAC(K),THMEAN(K),K=1,NCOMPS)           10440
      IF (OK()) GO TO 531                                               10450
      GO TO 5010                                                        10460
 6000 CONTINUE                                                          10470
C                                                                       10480
C     ------------------                                                10490
C     NEUTRAL DATA BLOCK                                                10500
C     ------------------                                                10510
C                                                                       10520
      IF(IOPT(2).NE.2)GO TO 6040                                        10530
      IF (IOPEN.EQ.0)GO TO 6010                                         10540
      CALL REF (1,1,1)                                                  10550
      GO TO (6100,6110,6110,6010),JOPTION+1                             10560
 6100 JSUB(9)=0                                                         10570
      GO TO 531                                                         10580
 6110 READ(JLINE(1),9801)LPOS,LNEG                                      10590
      IREQUIRED(9)=0                                                    10600
      IF (JOPTION.EQ.1)GO TO 531                                        10610
C                                                                       10620
```

```
C       *** LPOS ***                                                    10630
C                                                                       10640
 6010 CALL QUESTB (*8038,0,'LPOS',4,LPOS,'I5  ',0,0,3)                  10650
      IF (.NOT.EXIT)GO TO 6016                                          10660
      JSUB(9)=0                                                         10670
      GO TO 531                                                         10680
 6016 IF (.NOT.LIST)GO TO 6017                                          10690
      CALL LISTM                                                        10700
      GO TO 6010                                                        10710
 6017 IREQUIRED(9)=0                                                    10720
C                                                                       10730
C       *** LNEG ***                                                    10740
C                                                                       10750
 6020 CALL QUESTB (*8040,0,'LNEG',4,LNEG,'I5  ',0,0,2)                  10760
      IF (.NOT.LIST)GO TO 6030                                          10770
      CALL LISTM                                                        10780
      GO TO 6020                                                        10790
 6030 WRITE (J,9110)                                                    10800
      WRITE (J,9801)LPOS,LNEG                                           10810
      IF (OK()) GO TO 531                                               10820
      GO TO 6000                                                        10830
 6040 WRITE (J,6041)                                                    10840
 6041 FORMAT (/,'ERROR:  NEUTRAL DATA BLOCK IS REQUIRED ONLY IF IOPT'   10850
     1,'(2) = 2',//)                                                    10860
      JSUB(9)=0                                                         10870
      GO TO 531                                                         10880
 7000 CONTINUE                                                          10890
C                                                                       10900
C     ---------------                                                   10910
C     SUMS DATA BLOCK                                                   10920
C     ---------------                                                   10930
C                                                                       10940
      IF(ISUM.NE.0.OR.IOPEN.NE.0)GO TO 7001                             10950
C                                                                       10960
C         DELETE ALL OLD SUMS....                                       10970
C                                                                       10980
      WRITE (J,7003)                                                    10990
 7003 FORMAT (/,'DO YOU WANT TO DELETE ALL OLD SUMS?')                  11000
      IF (YN())JDELETE=1                                                11010
 7001 ISUM=ISUM+1                                                       11020
      IF (IOPEN.EQ.0)GO TO 7010                                         11030
 7116 CALL REF (1,0,0)                                                  11040
      IF (JOPTION.EQ.0)GO TO 7111                                       11050
      WRITE (J,1736) SUB(I)                                             11060
      WRITE (J,1731)JLINE(1)                                            11070
      READ (JLINE(1),9901) SUNAME(ISUM),NSUM(ISUM)                      11080
      IF (SUNAME(ISUM).NE.DELETE)GO TO 7120                             11090
      CALL REF (0,0,2)                                                  11100
      GO TO (7111,7117,7116),JOPTION+1                                  11110
 7117 JDELETE=1                                                         11120
      GO TO 7116                                                        11130
 7120 READ (13,9902)(LSUM(ISUM,M3),M3=1,NSUM(ISUM))                     11140
      WRITE (J,9902) (LSUM(ISUM,M3),M3=1,NSUM(ISUM))                    11150
      CALL REF (0,0,3)                                                  11160
      GO TO (7111,7001,7010,7116),JOPTION+1                             11170
C                                                                       11180
```

```
C       *** SUNAME ***                                                  11190
C                                                                       11200
 7010 CALL QUESTA (*8042,0,'SUNAME',6,SUNAME(ISUM),'A8  ',0,1)          11210
      IF (.NOT.EXIT)GO TO 7020                                          11220
 7111 ISUM=ISUM-1                                                       11230
      IF (ISUM.EQ.0)JSUB(10)=0                                          11240
      GO TO 531                                                         11250
C                                                                       11260
C       *** NSUM ***                                                    11270
C                                                                       11280
 7020 CALL QUESTB (*8044,0,'NSUM',4,NSUM(ISUM),'I2  ',0,50,0)           11290
      WRITE (J,9110)                                                    11300
      WRITE (J,9901) SUNAME(ISUM),NSUM(ISUM)                            11310
      IF (.NOT.OK())GO TO 7010                                          11320
C                                                                       11330
C       *** LSUM ***                                                    11340
C                                                                       11350
 7030 K=1                                                               11360
 7037 CALL QUESTB (*8046,K,'LSUM',4,LSUM(ISUM,K),'I4  ',0,10000,0)      11370
      K=K+1                                                             11380
      IF (K.LE.NSUM(ISUM))GO TO 7037                                    11390
      WRITE (J,9110)                                                    11400
      WRITE (J,9902) (LSUM(ISUM,K),K=1,NSUM(ISUM))                      11410
      IF (.NOT.OK())GO TO 7030                                          11420
      IF (JOPTION.EQ.2)GO TO 7001                                       11430
      WRITE (J,7051)                                                    11440
 7051 FORMAT (/,'MORE SUMS?')                                           11450
      IF (YN())GO TO 7000                                               11460
      GO TO 531                                                         11470
C                                                                       11480
C  --------------                                                       11490
C  END DATA BLOCK                                                       11500
C  --------------                                                       11510
C                                                                       11520
  950 CONTINUE                                                          11530
      JOPTION=0                                                         11540
      KKK=1                                                             11550
  954 IF (IREQUIRED(KKK).EQ.1)GO TO 952                                 11560
  953 KKK=KKK+1                                                         11570
      IF (KKK.EQ.11)GO TO 958                                           11580
      GO TO 954                                                         11590
C                                                                       11600
C         OOPS!!   HE LEFT OUT A DATA BLOCK.                            11610
C                                                                       11620
  952 WRITE (J,955)SUB(KKK)                                             11630
  955 FORMAT (/,'ERROR:  ',A8,' DATA BLOCK IS REQUIRED'/)               11640
      IERROR=1                                                          11650
      GO TO 953                                                         11660
  958 IF (IERROR.EQ.0)GO TO 957                                         11670
      JSUB(11)=0                                                        11680
      IERROR=0                                                          11690
      GO TO 531                                                         11700
C                                                                       11710
C         EXCLUDE ELEMENTS OR SPECIES THAT ARE ALREADY IN PHRQPITZ'S    11720
C         THERMODYNAMIC DATA.                                           11730
C                                                                       11740
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```
  957 DO 951 JL=4,30                                                    11750
      IF (ICOL2(JL).EQ.0)GO TO 951                                      11760
      ICHECK(1,ICOL2(JL))=0                                             11770
      ICHECK(2,ICOL2(JL))=0                                             11780
  951 CONTINUE                                                          11790
      JJ=1                                                              11800
  943 JJJ=4                                                             11810
  942 IF (ICHECK(JJ,JJJ).EQ.1)GO TO (944,945),JJ                        11820
  949 JJJ=JJJ+1                                                         11830
      IF (JJJ.EQ.31)GO TO 946                                           11840
      GO TO 942                                                         11850
  946 JJ=JJ+1                                                           11860
      IF (JJ.EQ.3)GO TO 947                                             11870
      GO TO 943                                                         11880
  944 WRITE (J,948)JJJ                                                  11890
  948 FORMAT ('ERROR:  SPECIES #',I2,' WAS NOT ENTERED.')               11900
  938 IERROR=1                                                          11910
      GO TO 949                                                         11920
  945 WRITE (J,937)JJJ                                                  11930
  937 FORMAT ('ERROR:  ELEMENT #',I2,' WAS NOT ENTERED.')               11940
      GO TO 938                                                         11950
  947 IF (IERROR.EQ.0)GO TO 959                                         11960
C                                                                       11970
C         HE ISN'T ALLOWED TO END.                                      11980
C                                                                       11990
      IERROR=0                                                          12000
      JSUB(11)=0                                                        12010
      GO TO 531                                                         12020
C                                                                       12030
C         EVERYTHING NEEDED IS PRESENT.                                 12040
C                                                                       12050
  959 GO TO 9010                                                        12060
 5001 WRITE (J,5000)                                                    12070
 5000 FORMAT ('MORE SIMULATIONS?')                                      12080
      IF (.NOT.YN())GO TO 50                                            12090
      IF (JOPEN.EQ.0)GO TO 5003                                         12100
 5006 READ (13,1731,END=5003)LINE                                       12110
      WRITE (J,5005)                                                    12120
 5005 FORMAT(/,'DO YOU WISH TO USE THE NEXT SIMULATION IN YOUR',        12130
     1' REFERENCE?')                                                    12140
      IF (.NOT.YN())GO TO 5008                                          12150
      BACKSPACE 13                                                      12160
      IOPEN=1                                                           12170
      GO TO 3                                                           12180
 5008 READ (13,5009,END=5003)LINE                                       12190
 5009 FORMAT (A3)                                                       12200
      IF (LINE(1:3).EQ.'END')GO TO 5006                                 12210
      GO TO 5008                                                        12220
 5003 WRITE (J,5002)                                                    12230
 5002 FORMAT (/,'DO YOU WISH TO DEFINE THE PREVIOUS OUTPUT AS '         12240
     1,/,1X,'YOUR NEW REFERENCE?')                                      12250
      IF (.NOT.YN())GO TO 2                                             12260
C                                                                       12270
C         WRITE THE OUTPUT ONTO THE REFERENCE FILE.■                    12280
C                                                                       12290
      OUT=13                                                            12300
```

```
      CLOSE (UNIT=OUT)                                                  12310
      OPEN (UNIT=OUT,STATUS='SCRATCH')                                  12320
      REWIND OUT                                                        12330
      GO TO 9010                                                        12340
  999 ENDFILE (UNIT=OUT)                                                12350
      REWIND OUT                                                        12360
      IOPEN=1                                                           12370
C                                                                       12380
C         LET'S TRY AGAIN...                                            12390
C                                                                       12400
      GO TO 3                                                           12410
   50 ENDFILE (UNIT=10)                                                 12420
      STOP                                                              12430
C                                                                       12440
 9010 CONTINUE                                                          12450
C                                                                       12460
C         WRITE TO FILE.....                                            12470
C                                                                       12480
      ITER=1                                                            12490
C                                                                       12500
C          PRINT TITLE CARD.                                            12510
C                                                                       12520
      WRITE (OUT,1731)TITLE                                             12530
C                                                                       12540
C         PRINT OPTION CARD.                                            12550
C                                                                       12560
      WRITE (OUT,9991) (IOPT(I),I=1,10),NSTEPS,NCOMPS,VO                12570
 9991 FORMAT (10I1,2I2,6X,A10)                                          12580
      DO 9999 L=1,11                                                    12590
      IF (JSUB(IORDER(L)).LT.1) GO TO 9999                              12600
      IF (IORDER(L).EQ.1)GO TO 9000                                     12610
      WRITE (OUT,9050)SUB(IORDER(L))                                    12620
 9050 FORMAT (A8)                                                       12630
      GO TO (9100,9200,9300,9300,9500,9600,9700,9800,9900,9999),IORDER(L 12640
     1)-1                                                               12650
C                                                                       12660
C         PRINT SOLUTION DATA BLOCK.                                    12670
C                                                                       12680
 9000 WRITE (OUT,9001) SUB(1),NSOLUTION(ITER)                           12690
 9001 FORMAT (A8,1X,I1)                                                 12700
      WRITE (OUT,1731) HEAD(ITER)                                       12710
      WRITE (OUT,9003) NTOTS(ITER),IALK(ITER),IUNITS(ITER),PH(ITER)     12720
     1, PE(ITER),TEMP(ITER),SDENS(ITER)                                 12730
 9003 FORMAT(I2,I3,I2,3X,4A10)                                          12740
      IF (NTOTS(ITER).EQ.0)GO TO 9005                                   12750
      WRITE (OUT,9004)(LT(ITER,M),DTOT(ITER,M),M=1,NTOTS(ITER))         12760
 9004 FORMAT (6(5(I4,A11),:,/))                                         12770
 9005 IF (ISOL.EQ.ITER) GO TO 9999                                      12780
      ITER=2                                                            12790
      GO TO 9000                                                        12800
C                                                                       12810
C         PRINT ELEMENTS DATA BLOCK.                                    12820
C                                                                       12830
 9100 DO 9103 MM=1,IELEMENT                                             12840
 9103 WRITE (OUT,9102) TNAME(MM),NELT(MM),TGFW(MM)                      12850
 9102 FORMAT(A8,2X,I2,3X,A10)                                           12860
```

```
      WRITE (OUT,9110)                                                  12870
 9110 FORMAT (1X)                                                       12880
      GO TO 9999                                                        12890
C                                                                       12900
C         PRINT SPECIES DATA BLOCK.                                     12910
C                                                                       12920
 9200 DO 9206 MM=1,ISPECIE                                              12930
      WRITE (OUT,9202) NI(MM)                                           12940
 9202 FORMAT (I3)                                                       12950
      IF(ISDEL(MM).EQ.0)GO TO 9207                                      12960
      WRITE (OUT,9110)                                                  12970
      GO TO 9206                                                        12980
 9207 WRITE (OUT,9203) SNAME(MM),NSP(MM),KFLAG(MM),GFLAG(MM),ZSP(MM)    12990
     1,THSP(MM),DHA(MM),ADHSP(MM,1),ADHSP(MM,2),ALKSP(MM)               13000
 9203 FORMAT (A8,2X,I3,2I1,6A10)                                        13010
      WRITE (OUT,9204) LKTOSP(MM),DHSP(MM),(ASP(MM,M),M=1,5)            13020
 9204 FORMAT (2A10,5A12)                                                13030
      WRITE (OUT,9205)(LSP(MM,M),CSP(MM,M),M=1,NSP(MM))                 13040
 9205 FORMAT (6(I3,A7))                                                 13050
 9206 CONTINUE                                                          13060
      WRITE (OUT,9110)                                                  13070
      GO TO 9999                                                        13080
C                                                                       13090
C         PRINT MINERALS OR LOOK MIN DATA BLOCK.                        13100
C                                                                       13110
 9300 NM=IORDER(L)-3                                                    13120
      IF (NM.NE.2.OR.IDELETE.NE.1)GO TO 9301                            13130
      WRITE (OUT,9050) DELETE                                           13140
 9301 IM=IMINERAL(NM)                                                   13150
      DO 9305 MM=1,IM                                                   13160
      WRITE (OUT,9302) MNAME(NM,MM),NMINO(NM,MM),THMIN(NM,MM),LKTOM(NM  13170
     1,MM),DHMIN(NM,MM),MFLAG(NM,MM),SIMIN(NM,MM)                       13180
 9302 FORMAT (A8,2X,I2,3X,3A10,5X,I1,9X,A10)                            13190
      WRITE (OUT,9303) (LMIN(NM,MM,M),CMIN(NM,MM,M),M=1,NMINO(NM,MM))   13200
 9303 FORMAT (2(5(I4,A11,:),/))                                         13210
      IF(MFLAG(NM,MM).NE.1)GO TO 9305                                   13220
      WRITE (OUT,9304) (AMIN(NM,MM,M),M=1,5)                            13230
 9305 CONTINUE                                                          13240
      WRITE (OUT,9110)                                                  13250
 9304 FORMAT (5A12)                                                     13260
      GO TO 9999                                                        13270
C                                                                       13280
C         PRINT TEMP DATA BLOCK.                                        13290
C                                                                       13300
 9500 WRITE (OUT,9501) (XTEMP(IF),IF=1,NTEMP)                           13310
 9501 FORMAT (7(8(A10,:),/))                                            13320
      GO TO 9999                                                        13330
C                                                                       13340
C         PRINT STEP DATA BLOCK.                                        13350
C                                                                       13360
 9600 WRITE (OUT,9501) (XSTEP(IF),IF=1,NSTEP)                           13370
      GO TO 9999                                                        13380
C                                                                       13390
C         PRINT REACTION DATA BLOCK.                                    13400
C                                                                       13410
 9700 WRITE (OUT,9701)(LREAC(M),CREAC(M),THMEAN(M),M=1,NCOMPS)          13420
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 9701 FORMAT (8(4(I4,2A8,:),/))                                          13430
      GO TO 9999                                                         13440
C                                                                        13450
C         PRINT NEUTRAL DATA BLOCK.                                      13460
C                                                                        13470
 9800 WRITE (OUT,9801)LPOS,LNEG                                          13480
 9801 FORMAT (2I5)                                                       13490
      GO TO 9999                                                         13500
C                                                                        13510
C         PRINT SUMS DATA BLOCK.                                         13520
C                                                                        13530
 9900 IF (JDELETE.NE.1)GO TO 9904                                        13540
      WRITE (OUT,9302) DELETE                                            13550
 9904 DO 9903 MM=1,ISUM                                                  13560
      WRITE (OUT,9901)SUNAME(MM),NSUM(MM)                                13570
 9901 FORMAT (A8,2X,I2)                                                  13580
 9903 WRITE (OUT,9902) (LSUM(MM,M),M=1,NSUM(MM))                         13590
 9902 FORMAT(20I4)                                                       13600
      WRITE (OUT,9110)                                                   13610
 9999 CONTINUE                                                           13620
C                                                                        13630
      IF (OUT.EQ.10) GO TO 5001                                          13640
      GO TO 999                                                          13650
C                                                                        13660
C        HELP MESSAGES....                                               13670
C                                                                        13680
  290 NSTART=N                                                           13690
      GO TO (2000,2020,2040,2060,2080,2080,2120,2140,2160,2180),N        13700
 1000 WRITE (J,1010)                                                     13710
 1010 FORMAT (/1X,'TITLE CARD',2X,'TITLE',/,1X,'FORMAT (A80)',           13720
     1/,1X,'EIGHTY CHARACTERS OF TITLES OR COMMENTS.'//)                 13730
      GO TO 10                                                           13740
 2000 WRITE (J,2010) OPTION                                              13750
 2010 FORMAT (/1X,A11,/,13X,'IOPT(1) = 0, NO PRINT OF',                  13760
     1' THERMODYNAMIC DATA OR COEFFICIENTS',/,26X,'OF AQUEOUS',          13770
     2' SPECIES.',//,21X,'= 1, PRINT THE AQUEOUS MODEL DATA',            13780
     3' (WHICH ARE STORED',/26X,'ON DISK) ONCE DURING THE ENTIRE',       13790
     4' COMPUTER RUN.',/,1X,'FORMAT (I1)',//)                            13800
      GO TO 93                                                           13810
 2020 WRITE (J,2030) OPTION                                              13820
 2030 FORMAT(/1X,A11,/,13X,'IOPT(2) = 0, INITIAL SOLUTIONS',             13830
     1' ARE NOT TO BE CHARGE BALANCED.',/,26X,'REACTION SOLUTIONS',      13840
     2' MAINTAIN THE INITIAL CHARGE',/,26X,'IMBALANCE.',//,21X,'= 1,',   13850
     3' PH IS ADJUSTED IN INITIAL SOLUTION(S) TO',/,26X,'OBTAIN CHARGE', 13860
     4' BALANCE.',//,21X,'= 2, THE TOTAL CONCENTRATION OF ONE OF THE',   13870
     5' ELEMENTS',/,26X,'(EXCEPT H OR O) IS ADJUSTED TO OBTAIN',         13880
     6' ELECTRICAL',/,26X,'BALANCE.  NEUTRAL INPUT IS REQUIRED.',/,1X,'F 13890
     7ORMAT (I1)',//)                                                    13900
      GO TO 93                                                           13910
 2040 WRITE (J,2050) OPTION                                              13920
 2050 FORMAT (/1X,A11,/,13X,'IOPT(3) = 0, NO REACTIONS ARE',             13930
     1' MODELED.  ONLY THE INITIAL',/,26X,'SOLUTIONS ARE SOLVED.'//,     13940
     221X,'= 1, SOLUTION 1 IS MIXED (A HYPOTHETICAL CONSTANT',/,26X,     13950
     3'VOLUME PROCESS) WITH SOLUTION 2 IN SPECIFIED',/,26X,'REACTION',   13960
     4' STEPS.  STEPS INPUT AND A VALUE FOR',/,26X,'NSTEPS ARE REQUIRED' 13970
     5,'.  MINERALS INPUT MAY BE',/,26X,'INCLUDED.',//,21X,'= 2,',       13980
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     6' SOLUTION 1 IS TITRATED WITH SOLUTION 2 IN SPECI-',/,26X,          13990
     7'FIED REACTION STEPS.  STEPS INPUT, A VALUE FOR',/,26X,'NSTEPS,',   14000
     8' AND A VALUE FOR VO ARE REQUIRED.',/,26X,'MINERALS INPUT MAY',     14010
     9' BE INCLUDED.',//,21X,'= 3, A',                                    14020
     !' STOICHIOMETRIC REACTION IS ADDED IN SPECIFIED',/,26X,'REACTION',  14030
     @' STEPS.  REACTION  INPUT, STEPS INPUT,',/,26X,'A VALUE FOR',       14040
     #' NSTEPS, AND A VALUE FOR NCOMPS ARE',/,26X,'REQUIRED.  MINERALS',  14050
     $' INPUT MAY BE INCLUDED.'///' HIT <RETURN> FOR MORE INFORMATION.')  14060
      READ (J,20) LINE                                                    14070
      WRITE (J,2055)                                                      14080
2055  FORMAT(21X,'= 4, A NET STOICHIOMETRIC',                             14090
     ^' REACTION IS ADDED IN NSTEPS',/,26X,'EQUAL INCREMENTS.  REACTION'  14100
     &,' INPUT, STEPS INPUT,',/,26X,'A VALUE FOR NSTEPS, AND A VALUE FOR  14110
     * NCOMPS ARE',/,26X,'REQUIRED.  MINERALS INPUT MAY BE INCLUDED.',    14120
     ('  ONLY',/,26X,'ONE VALUE FOR THE TOTAL REACTION IS READ IN STEPS.  14130
     )',//,21X,'= 5, SOLUTION NUMBER 1 IS EQUILIBRATED WITH MINERAL',     14140
     -/,26X,'PHASES ONLY.  NO OTHER REACTION IS PERFORMED.',/,26X,        14150
     ='MINERALS INPUT IS REQUIRED.',//,21X,'= 6, A REACTION IS ADDED',    14160
     +' TO SOLUTION 1 UNTIL EQUI-',/,26X,'LIBRIUM IS ATTAINED WITH THE',  14170
     |' FIRST PHASE IN',/,26X,'MINERAL INPUT (EQUILIBRIUM WITH OTHER',    14180
     :' MINERALS',/,26X,'PHASES IS MAINTAINED THROUGHOUT THE REACTION)',  14190
     /'.',/,26X,'REACTION INPUT, A VALUE FOR NCOMPS, AND MINERALS',/,     14200
     ]26X,'INPUT ARE REQUIRED.  NO STEPS INPUT IS REQUIRED.',/,26X,       14210
     ['NOTE:  THERE SHOULD BE A COMMON ELEMENT IN THE',/,26X,'REACTION',  14220
     ~' AND THE FIRST PHASE IN MINERALS INPUT.',/,1X,'FORMAT (I1)',//)    14230
      GO TO 93                                                            14240
2060  WRITE (J,2070) OPTION                                               14250
2070  FORMAT (/1X,A11,/,13X,'IOPT(4) = 0, THE TEMPERATURE OF',            14260
     1' THE REACTION SOLUTION IS',/,26X,'A) THE SAME AS THE INITIAL',     14270
     2' SOLUTION IF ADDING',/,26X,'A REACTION, OR B) CALCULATED LINEARLY  14280
     3 FROM THE',/,26X,'END MEMBERS IF MIXING OR TITRATING.  NO TEMP',    14290
     4/,26X,'INPUT IS REQUIRED.',//,21X,'= 1, THE TEMPERATURE IS',        14300
     5' CONSTANT DURING THE REACTION',/,26X,'STEPS AND DIFFERS FROM THAT  14310
     6 OF THE INITIAL SOL-',/,26X,'UTION(S).  ONE VALUE IS READ IN THE',  14320
     7' TEMP INPUT.'//,21X,'= 2, THE TEMPERATURE IS VARIED FROM T(O) TO'  14330
     8,' T(F) IN',/,26X,'NSTEPS EQUAL INCREMENTS, DURING THE REACTION',/  14340
     9,26X,'STEPS.',//,21X,'= 3, THE TEMPERATURE',                        14350
     $' OF EACH REACTION STEP IS SPEC-',/,26X,'IFIED IN TEMP INPUT, IN'   14360
     %,' ORDER.  NSTEPS VALUES',/,26X,'ARE READ.',/,1X,'FORMAT (I1)',//)  14370
2080  GO TO 93                                                            14380
2120  WRITE (J,2130) OPTION                                               14390
2130  FORMAT (/1X,A11,/,13X,'IOPT(7) = 0, DO NOT SAVE THE',               14400
     1' AQUEOUS PHASE COMPOSITION AT',/,26X,'THE END OF A REACTION FOR',  14410
     2' ADDITIONAL SIMU-',/,26X,'LATIONS.',//,21X,'= 1, SAVE THE FINAL',  14420
     3' REACTION SOLUTION IN SOLUTION',/,26X,'NUMBER 1.',//,21X,'= 2,',   14430
     4' SAVE THE FINAL REACTION SOLUTION IN SOLUTION',/,26X,'NUMBER 2.'   14440
     5,/,1X,'FORMAT (I1)',//)                                             14450
      GO TO 93                                                            14460
2140  WRITE (J,2150) OPTION                                               14470
2150  FORMAT (/1X,A11,/,13X,'IOPT(8) = 0, THE DEBUGGING PRINT'            14480
     1,' ROUTINE IS NOT CALLED.',//,21X,'= 1, A LONG PRINTOUT IS OUTPUT'  14490
     2,' AT EACH ITERATION IN',/,26X,'EACH PROBLEM.  THIS PRINT IS TO BE  14500
     3 USED ONLY',/,26X,'IF THERE ARE CONVERGENCE PROBLEM WITH THE',      14510
     4/,26X,'PROGRAM.  (SEE SUBROUTINE PBUG)',/,1X,'FORMAT (I1)',//)      14520
      GO TO 93                                                            14530
2160  WRITE (J,2170) OPTION                                               14540
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2170 FORMAT (/1X,A11,/,13X,'IOPT(9) = 0, NO PRINTOUT OF EACH',          14550
    1' ARRAY INVERTED.',//,21X,'= 1, A LONG PRINTOUT OCCURS OF THE',    14560
    2' ENTIRE ARRAY TO',/,26X,'BE INVERTED AT EACH ITERATION.  THIS',   14570
    3' PRINT IS',/,26X,'USED ONLY IF THERE ARE CONVERGENCE PROBLEMS.',  14580
    4/,26X,'(SEE SUBROUTINE SLNQ)',/,1X,'FORMAT (I1)',//)               14590
     GO TO 93                                                           14600
2180 WRITE (J,2190) OPTION                                              14610
2190 FORMAT (/1X,A11,/,13X,'IOPT(10) = 0, NO CONVENTION'                14620
    1,' FOR ACTIVITY',/,27X,'COEFFICIENT IS USED.',//,22X,'= 1,'        14630
    2,' MACINNES CONVENTION IS USED.',/,1X,'FORMAT (I1)',//)            14640
     GO TO 93                                                           14650
2200 WRITE (J,2210) OPTION                                              14660
2210 FORMAT (/1X,A11,/,13X,'NSTEPS',7X,'THE NUMBER OF'                  14670
    1,' STEPS.  A VALUE IS',/,26X,'REQUIRED IF IOPT(3) = 1, 2, 3,',     14680
    2'OR 4, OR IF',/,26X,'IOPT(4) = 2 OR 3.',/,1X,'FORMAT (I2)',//)     14690
     GO TO 250                                                          14700
2300 WRITE (J,2310) OPTION                                              14710
2310 FORMAT (/1X,A11,/,13X,'NCOMPS',7X,'THE NUMBER OF CONSTIT',         14720
    1'UENTS IN A NET STOICHIO-',/26X,'METRIC REACTION.  A CONSTITUENT M 14730
    2AY BE ANY',/,26X,'ELEMENT WITH AN INDEX NUMBER BETWEEN 4 AND',     14740
    3/,26X,'30 INCLUSIVE.  NO AQUEOUS SPECIES WITH INDEX',/,26X,'NUMBER 14750
    4S GREATER THAN 30 MAY BE INCLUDED AS',/,26X,'REACTION CONSTITUENTS 14760
    5 EXCEPT H2 AND O2.  ANY',/,26X,'CONSTITUENT WITH AN INDEX NUMBER G 14770
    6REATER THAN',/,26X,'30 IS ASSUMED TO BE EITHER H2 OR O2 AND HAS',/ 14780
    7,26X,'THE EFFECT OF RAISING OR LOWERING THE REDOX',/,26X,'STATE OF 14790
    8 THE SOLUTION DEPENDING ON THE AS-',/,26X,'SIGNED VALENCE (THMEAN) 14800
    9.  A VALUE FOR NCOMPS',/,26X,'IS REQUIRED IF IOPT(3) = 3, 4, OR 6. 14810
    !',/,1X,'FORMAT (I2)',//)                                           14820
     GO TO 301                                                          14830
2400 WRITE (J,2410) OPTION                                              14840
2410 FORMAT (/1X,A11,/,13X,'VO',11X,'THE INITIAL VOLUME OF SO',         14850
    1'LUTION NUMBER 1 WHEN',/26X,'MODELING A TITRATION.  THIS UNIT OF V 14860
    2O MUST',/,26X,'BE THE SAME AS THAT OF XSTEP (SEE STEPS INPUT)',/,2 14870
    36X,'IF IOPT(3) = 2.  OTHERWISE, VO IS NOT REQUIRED',/,1X,'FORMAT ( 14880
    4F10.5)',//)                                                        14890
     GO TO 430                                                          14900
4146 WRITE (J,4147) SUB(1)                                              14910
4147 FORMAT (/1X,A8,10X,'THIS INPUT IS USED TO DEFINE A STARTING'       14920
    1,' SOLU-',/,19X,'TION.',//)                                        14930
     GO TO 621                                                          14940
4148 WRITE (J,4149) SUB(2)                                              14950
4149 FORMAT (/1X,A8,10X,'THIS INPUT DEFINES THE NAMES AND INDICES',     14960
    1' OF ALL',/,19X,'ELEMENTS IN THE AQUEOUS MODEL DATA BASE.',//)     14970
     GO TO 621                                                          14980
4150 WRITE (J,4151) SUB(3)                                              14990
4151 FORMAT (/1X,A8,10X,'THIS INPUT DEFINES THE NAMES, INDEX NUMB'      15000
    1'ERS AND',/,19X,'COMPOSITION OF ALL AQUEOUS SPECIES IN THE',       15010
    2' AQUEOUS',/,19X,'MODEL DATA BASE.',//)                            15020
     GO TO 621                                                          15030
4152 WRITE (J,4153) SUB(4)                                              15040
4153 FORMAT (/1X,A8,10X,'THIS INPUT DEFINES THE PHASES WHICH WILL'      15050
    1,' BE MAIN-',/,19X,'TAINED AT EQUILIBRIUM WITH EACH OF THE'        15060
    2,' REACTION',/,19X,'SOLUTIONS',//)                                 15070
     GO TO 621                                                          15080
4154 WRITE (J,4155) SUB(5)                                              15090
4155 FORMAT (/1X,A8,10X,'THE PURPOSE OF THIS INPUT IS SIMPLY TO         15100
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     1,'PROVIDE',/,19X,'INFORMATION ON THE SATURATION STATE OF THE'      15110
     2,' AQUEOUS',/,19X,'PHASE WITH RESPECT TO DESIRED MINERALS.  '      15120
     3,'THE',/,19X,'MINERALS IN THIS BLOCK OF INPUT DO NOT AFFECT'       15130
     4,' THE',/,19X,'CALCULATIONS OF THE INITIAL SOLUTION OR ANY '       15140
     5,'OF THE',/,19X,'REACTION SOLUTIONS.  THIS INPUT IS NEVER'         15150
     6,' MANDATORY.',//)                                                 15160
      GO TO 621                                                          15170
4156 WRITE (J,4157) SUB(6)                                              15180
4157 FORMAT (/1X,A8,10X,'THIS INPUT VARIES THE TEMPERATURE DURING'      15190
     1,' THE',/,19X,'REACTION STEPS.',//)                               15200
      GO TO 621                                                         15210
4158 WRITE (J,4159) SUB(7)                                              15220
4159 FORMAT (/1X,A8,10X,'THIS INPUT DEFINES THE STEPS OF THE '          15230
     1,'REACTION PROCESS.',//)                                          15240
      GO TO 621                                                         15250
4160 WRITE (J,4161) SUB(8)                                              15260
4161 FORMAT (/1X,A8,10X,'THIS INPUT DESCRIBES THE STOICHIOMETRY'        15270
     1,' AND VALENCE',/,19X,'OF THE ELEMENTS TO BE ADDED AS A'          15280
     2,' REACTION.',//)                                                 15290
      GO TO 621                                                         15300
4162 WRITE (J,4163) SUB(9)                                              15310
4163 FORMAT (/1X,A8,10X,'THIS INPUT DEFINES THE ELEMENTS TO BE '        15320
     1,'USED TO',/,19X,'ADJUST THE INITIAL SOLUTION(S) TO ELECTRI'      15330
     2,'CAL',/,19X,'NEUTRALITY.',//)                                    15340
      GO TO 621                                                         15350
4164 WRITE (J,4165) SUB(10)                                             15360
4165 FORMAT (/1X,A8,10X,'THIS INPUT SUMS MOLALITIES OF AQUEOUS'         15370
     1,' SPECIES WHICH',/,19X,'ARE THEN PRINTED IN THE OUTPUT OF THE'   15380
     2,' RUN.  THESE',/,19X,'SUMS DO NOT AFFECT THE CALCULATIONS IN'    15390
     3,' ANY WAY AND',/,19X,'ARE NEVER MANDATORY.',//)                  15400
      GO TO 621                                                         15410
4166 WRITE (J,4167) SUB(11)                                             15420
4167 FORMAT (/1X,A8,10X,'THIS CARD TERMINATES INPUT OPERATIONS'         15430
     1,' FOR A',/,19X,'SINGLE SIMULATION.  ANY COMPUTER RUN HAS '       15440
     2,'AT LEAST ONE',/,19X,'END CARD.',//)                             15450
      GO TO 621                                                         15460
4200 WRITE (J,4210)                                                     15470
4210 FORMAT (/1X,'POSSIBLE KEYWORDS:',//1X,'(1)ELEMENTS, (2)SPECIES'    15480
     1,', (3)SOLUTION, (4)MINERALS, (5)LOOK MIN,',/,1X,'(6)TEMP, '      15490
     2,'(7)STEPS, (8)REACTION, (9)NEUTRAL, (10)SUMS, (11)END',//,1X     15500
     3,'FORMAT (A8)',//,' FOR MORE INFORMATION ON ANY OF THE DATA'       15510
     4,' BLOCK, ENTER THE',/,1X,'NUMBER ASSOCIATED WITH IT.',/)         15520
      GO TO 621                                                         15530
1492 WRITE (J,1493)SUB(1)                                               15540
1493 FORMAT (/1X,A8,/,13X,'N',12X,'A NUMBER OF EITHER 1 OR 2 INDICAT'   15550
     1,'ING THE',/,26X,'SOLUTION NUMBER OF THE FOLLOWING DATA.',/,1X    15560
     2,'FORMAT (I1)'//)                                                 15570
      GO TO 1739                                                        15580
4300 WRITE (J,4310) SUB(1)                                              15590
4310 FORMAT (/1X,A8,/,13X,'HEAD',/,13X,'FORMAT (A80)',/,13X,            15600
     1'TITLE OR COMMENTS ABOUT THE SOLUTION.',//)                       15610
      GO TO 1488                                                        15620
4320 WRITE (J,4330) SUB(1)                                              15630
4330 FORMAT (/1X,A8,/,13X,'NTOTS',8X,'THE NUMBER OF TOTAL CONCENTRATION 15640
     1S TO BE',/,26X,'READ FROM CARD INPUT.  FOR EXAMPLE, IF THE',/,26X, 15650
     2'STARTING SOLUTION IS MGCL2-NAHCO3 SOLUTION',/,26X,'NTOTS = 4 (FOR 15660
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    3 MG, CL, NA, AND C)',/,1X,'FORMAT (I2)',//)                          15670
     GO TO 1713                                                           15680
4340 WRITE (J,4350) SUB(1)                                                15690
4350 FORMAT (/1X,A8,/,13X,'IALK',9X,'FLAG WHICH INDICATES WHETHER TOTAL   15700
    1 CARBON OR',/,26X,'TOTAL ALKALINITY IS TO BE INPUT.',//,21X,'= 0,    15710
    2INDICATES THE TOTAL CONCENTRATION OF CARBON',/,26X,'(NOT ALKALINIT   15720
    3Y) IS INPUT IN THE UNITS',/,26X,'SPECIFIED BY IUNITS.',//,21X,'= N   15730
    4, 4<=N<=30, WHERE N IS THE INDEX NUMBER FOR',/,26X,'THE ELEMENT CA   15740
    5RBON, (IN OUR DATA BASE N=15)',/,26X,'INDICATES TOTAL ALKALINITY I   15750
    6S BEING ENTERED.',/,26X,'ELEMENTS INPUT MAY BE REQUIRED.  THE UNIT   15760
    7S OF',/,26X,'ALKALINITY ARE SPECIFIED BY IUNITS',/,26X,'AND IF ',    15770
    9'IUNITS > 0, THE GRAM FORMULA WEIGHT (GFW)',/,26X,'OF THE ELEMENT'   15780
    !,' CARBON IS CRITICALLY IMPORTANT.',/,26X,'THE GFW IN THE CASE OF'   15790
    @,' ALKALINITY MUST BE THE',/,26X,'GRAM EQUIVALENT WEIGHT (GRAMS/EQ   15800
    #UIVALENT) OF',/,26X,'THE CHEMICAL SPECIES IN WHICH THE ALKALINTY',   15810
    $/,26X,'IS REPORTED.  THE FOLLOWING IS A LIST OF',///,' HIT <RETURN   15820
    /> FOR MORE EXPLANATION')                                             15830
     READ (J,1731) LINE                                                   15840
     WRITE (J,4355)                                                       15850
4355 FORMAT(//26X,'SPECIES ',                                             15860
    %'COMMONLY USED FOR REPORTING ALKA-',/,26X,'LINITY AND THEIR CORRES   15870
    ^PONDING EQUIVALENT',/,26X,'WEIGHTS:',//,31X,'CACO3',4X,'50.0446 G/   15880
    &EQ',//,31X,'HCO3-',4X,'61.0171 G/EQ',//,31X,'CO3--',4X,'30.0046 G/   15890
    *EQ',//,26X,'IN OUR DATA BASE 44.010 IS THE GFW OF CARBON',/,26X,'W   15900
    (HICH IS SUITABLE FOR ENTERING CARBON AS',/,26X,'TOTAL CO2.  THIS G   15910
    )FW MUST BE CHANGED VIA',/,26X,'ELEMENTS INPUT IF ALKALINITY IS TO'   15920
    -,' BE ENTERED',/,26X,'AS MG/L OR PPM (IUNITS = 2 OR 3).  IF IUNITS   15930
    =',/,26X,'= 0 ALKALINITY MUST BE INPUT AS EQ/KG H2O AND',/,26X,'IN'   15940
    +,' THIS CASE THE GFW NEED NOT BE CHANGED SINCE',/,26X,'NO CONVERSI   15950
    :ON IS NECESSARY.',/,1X,'FORMAT (I3)',//)                             15960
     GO TO (1714,1752),JUMP+1                                             15970
4360 WRITE (J,4370) SUB(1)                                                15980
4370 FORMAT (/1X,A8,/,13X,'IUNITS',7X,'FLAG DESCRIBING UNITS OF INPUT C   15990
    1ONCENTRATIONS.',/,26X,'THE PROGRAM MAKES ALL OF ITS CALCULATIONS'    16000
    2,/,26X,'IN TERMS OF MOLALITY AND ANY OTHER ALLOWED',/,26X,'CONCEN'   16010
    3,'TRATION UNITS (MMOLES/L, MG/L,',/26X,'PPM OR MMOL/KG) MUST BE'     16020
    4,' CONVERTED TO MOLALITY',/26X,'BEFORE THE CALCULATION MAY BEGIN.'   16030
    5,'  TO MAKE',/26X,'THE CONVERSIONS IT IS NECESSARY TO KNOW THE'      16040
    6,/26X,'GRAM FORMULA WEIGHT (GFW), IN G/MOLE, OF THE',/26X            16050
    7,'CHEMICAL FORMULA IN WHICH ELEMENTAL ANALYSES',/,26X,'ARE'          16060
    8,' REPORTED.  THE GFW IS AN INPUT PARAMETER',/,26X,'UNDER'           16070
    9,' ELEMENTS INPUT AND MUST BE IN AGREEMENT',/,26X,'WITH THE'         16080
    !,' ANALYTICAL UNITS FOR EACH SOLUTION',/,26X,'DATA SET.  (IF THE'    16090
    @,' UNITS ARE MOLALITY, NO',/,26X,'CONVERSION IS NECESSARY AND THE'   16100
    #,' GFWS ARE NOT',/,26X,'USED.)  NOTE:  ALL ELEMENTS MUST HAVE',/     16110
    $,26X,'THE SAME UNITS.  IT IS NOT POSSIBLE TO ENTER MG/L',/,26X       16120
    /,'OF ONE ELEMENT AND MOLALITY OF ANOTHER.',///,' HIT <RETURN> FOR'   16130
    *,' MORE EXPLANATION')                                                16140
     READ (J,1731) LINE                                                   16150
     WRITE (J,4375)                                                       16160
4375 FORMAT (/21X,'= 0, CONCENTRATION ',                                  16170
    %'OF ELEMENTS ENTERED AS MOLALITY',/,26X,'OF EACH ELEMENT, OR FO','   16180
    ^R ALKALINITY, EQUIV-',/,26X,'ALENTS/KG H2O.',//,21X,'= 1, CONCENTR   16190
    &ATION OF ELEMENTS ENTERED AS MMOLES/L',/,26X,'OF EACH ELEMENT, OR'   16200
    *,' FOR ALKALINITY, MEQ/L.',//,21X,'= 2, CONCENTRATION OF ELEMENTS    16210
    (ENTERED AS MG/L',/,26X,'OF THE SPECIES WHICH HAS A GRAM FORMULA',    16220
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    )/,26X,'WEIGHT GIVEN IN ELEMENTS INPUT.  (ELEMENTS',/,26X,'INPUT MA 16230
    -Y BE REQUIRED.)',//,21X,'= 3, CONCENTRATION OF ELEMENTS ENTERED AS 16240
    = PPM',/,26X,'OF THE SPECIES WHICH HAS A GRAM FORMULA',/,26X,'WEIGH 16250
    +T GIVEN IN ELEMENTS INPUT.  (ELEMENTS',/,26X,'INPUT MAY BE REQUIRE 16260
    :D.)',//,21X,'= 4, CONCENTRATION OF ELEMENTS ENTERED AS MMOL/KG',/, 16270
    !26X,'SOLUTION.',/,1X,'FORMAT (I1)')                                16280
     GO TO 1715                                                         16290
4380 WRITE (J,4390) SUB(1)                                              16300
4390 FORMAT (/1X,A8,/,13X,'PH',11X,'THE PH OF THE SOLUTION (THE APPROXI 16310
    1MATE PH',/,26X,'IF IOPT(2) = 1)',/,1X,'FORMAT (F10.3)',//)         16320
     GO TO 1718                                                         16330
4420 WRITE (J,4430) SUB(1)                                              16340
4430 FORMAT (/1X,A8,/,13X,'TEMP',9X,'THE TEMPERATURE OF THE SOLUTION IN 16350
    1 DEGREES',/,26X,'CELCIUS.',/,1X,'FORMAT (F10.3)',//)               16360
     GO TO 1724                                                         16370
4440 WRITE (J,4450) SUB(1)                                              16380
4450 FORMAT (/1X,A8,/,13X,'SDENS',8X,'THE DENSITY OF THE SOLUTION.',/,1 16390
    1X,'FORMAT (F10.3)',//)                                             16400
     GO TO 1482                                                         16410
4100 WRITE (J,4101) SUB(1)                                              16420
4101 FORMAT (/1X,A8,/,13X,'LT,DTOT',6X,'TOTAL CONCENTRATIONS OF ELEMENT 16430
    1S.',/,26X,'LT',8X,'INDEX NUMBER OF THE ELEMENT.',//,26X,'DTOT',    16440
    26X,'TOTAL CONCENTRATION OF THE ELEMENT IN',/,36X,'MOLALITY, MMOLES 16450
    3/L, MG/L, OR',/,36X,'PPM ACCORDING TO IUNITS.',/,1X,'FORMAT (I4'   16460
    4,',1X,F11.4)')                                                     16470
     WRITE (J,4000)                                                     16480
     GO TO (1326,1356),N2                                               16490
4102 WRITE (J,4103) SUB(2)                                              16500
4103 FORMAT (/1X,A8,/,13X,'TNAME',8X,'ALPHANUMERIC NAME OF ELEMENT.',   16510
    1/,1X,'FORMAT (A8)')                                                16520
     WRITE (J,4000)                                                     16530
4000 FORMAT (' NOTE:  FOR A LISTING OF MASTER SPECIES AND ELEMENTS,'    16540
    1,/,8X,'ENTER <LIST>.',//)                                          16550
     GO TO 1729                                                         16560
4104 WRITE (J,4105) SUB(2)                                              16570
4105 FORMAT (/1X,A8,/,13X,'NELT',9X,'INDEX NUMBER ASSIGNED TO THE ELEME 16580
    1NT.  NUMBER',/,26X,'MUST BE BETWEEN 4 AND 30, INCLUSIVE.',/,1X,    16590
    2'FORMAT (I2)')                                                     16600
     WRITE (J,4000)                                                     16610
     GO TO 1550                                                         16620
4106 WRITE (J,4107) SUB(2)                                              16630
4107 FORMAT (/1X,A8,/,13X,'TGFW',9X,'GRAM FORMULA WEIGHT OF THE SPECIES 16640
    1 USED TO',/,26X,'REPORT THE ANALYTICAL DATA.  IF SOLUTION DATA'    16650
    2,/,26X,'IS TO INCLUDE ALKALINITY, TGFW FOR THE ELEMENT',/,26X,'CAR 16660
    3BON MUST BE THE EQUIVALENT WEIGHT OF THE',/,26X,'REPORTED ALKALINI 16670
    4TY SPEC  S.',/,1X,'FORMAT (F10.4)')                                16680
     WRITE (J,4000)                                                     16690
     GO TO 1570                                                         16700
4110 WRITE (J,4111) SUB(3)                                              16710
4111 FORMAT (/1X,A8,/,13X,'I',12X,'THE INDEX NUMBER ASSIGNED TO THE AQU 16720
    1EOUS',/,26X,'SPECIES.  NUMBER 4 THROUGH 30 ARE RESERVED',/,26X,    16730
    2'FOR MASTER SPECIES.  250 IS THE MAXIMUM INDEX',/,26X,'NUMBER FOR  16740
    3AN AQUEOUS SPECIES.',/,1X,'FORMAT (I3)',//)                        16750
     GO TO 1590                                                         16760
4112 WRITE (J,4113) SUB(3)                                              16770
4113 FORMAT (/1X,A8,/,13X,'SNAME',8X,'ALPHANUMERIC SPECIES NAME.',/,1X, 16780
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     1'FORMAT (A8)',//)                                                  16790
      GO TO 1660                                                        16800
4114 WRITE (J,4115) SUB(3)                                             16810
4115 FORMAT (/1X,A8,/,13X,'NSP',10X,'THE TOTAL NUMBER OF MASTER SPECIES 16820
     1 IN THE',/,26X,'ASSOCIATION REACTION THAT FORMS THIS SPECIES;',/,2 16830
     26X,'DO NOT COUNT THE SPECIES ITSELF UNLESS THE',/,26X,'SPECIES IS  16840
     3A MASTER SPECIES.',/,1X,'FORMAT (I3)',//)                         16850
      GO TO 1676                                                        16860
4116 WRITE (J,4117) SUB(3)                                             16870
4117 FORMAT (/1X,A8/,13X,'KFLAG',3X,'= 0, THE VAN''T HOFF EXPRESSION IS 16880
     1 USED TO CALCU-',/,26X,'LATE TEMPERATURE DEPENDENCE OF THE ASSOCIA 16890
     2TION',/,26X,'CONSTANT FOR THIS SPECIES.',//,21X,'= 1, AN ANALYTICA 16900
     3L EXPRESSION IS USED TO CALCU-',/,26X,'LATE TEMPERATURE DEPENDENCE 16910
     4 OF THE ASSOCIATION',/,26X,'CONSTANT.',/,1X,'FORMAT (I1)',//)     16920
      GO TO 1680                                                        16930
4118 WRITE (J,4119) SUB(3)                                             16940
4119 FORMAT (/1X,A8,/,13X,'GFLAG',3X,'= 0, THE EXTENDED DEBYE-HUCKEL OR 16950
     1 DAVIS EXPRES-',/,26X,'SION (ACCORDING TO IOPT(6)) IS USED TO CALC 16960
     2ULATE',/,26X,'THE ACTIVITY COEFFICIENT FOR THIS SPECIES.',//,21X,  16970
     3'= 1, THE WATEQ DEBYE-HUCKEL EXPRESSION IS USED',/,26X,'TO CALCULA 16980
     4TE THE ACTIVITY COEFFICIENT OF THIS',/,26X,'SPECIES REGARDLESS OF  16990
     5THE VALUE OF IOPT(6)',/,1X,'FORMAT (I1)',//)                      17000
      GO TO 1690                                                        17010
4120 WRITE (J,4121) SUB(3)                                             17020
4121 FORMAT (/1X,A8,/,13X,'ZSP',10X,'THE CHARGE ON THIS AQUEOUS SPECIES 17030
     1.',/,1X,'FORMAT (F10.3)',//)                                      17040
      GO TO 1780                                                        17050
4122 WRITE (J,4123) SUB(3)                                             17060
4123 FORMAT (/1X,A8,/,13X,'THSP',9X,'THE SUM OF THE FORMAL VALENCE OF T 17070
     1HE REDOX',/,26X,'SPECIES IN THIS SPECIES.  (E.G. FESO4 HAS',/,26X, 17080
     2'A THSP = 2 + 6 = 8.)',/,1X,'FORMAT (F10.3)',//)                  17090
      GO TO 1790                                                        17100
4124 WRITE (J,4125) SUB(3)                                             17110
4125 FORMAT (/1X,A8,/,13X,'DHA',10X,'THE EXTENDED DEBYE-HUCKEL A 0 TERM 17120
     1.',/,1X,'FORMAT (F10.3)'//)                                       17130
      GO TO 1880                                                        17140
4126 WRITE (J,4127) SUB(3)                                             17150
4127 FORMAT (/1X,A8,/,13X,'ADHSP(1)',5X,'THE A(I) TERM FOR THE WATEQ DE 17160
     1BYE-HUCKEL EXPRESSION.',/,1X,'FORMAT (F10.3)',//)                 17170
      GO TO 1892                                                        17180
4128 WRITE (J,4129) SUB(3)                                             17190
4129 FORMAT (/1X,A8,/,13X,'ADHSP(2)',5X,'THE B(I) TERM FOR THE WATEQ DE 17200
     1BYE-HUCKEL EXPRESSION.',/,1X,'FORMAT (F10.3)',//)                 17210
      GO TO 1892                                                        17220
4130 WRITE (J,4131) SUB(3)                                             17230
4131 FORMAT (/1X,A8,/,13X,'ALKSP',8X,'THE ALKALINITY ASSIGNED TO THIS A 17240
     1QUEOUS SPECIES.',/,1X,'FORMAT (F10.3)',//)                        17250
      GO TO 1740                                                        17260
4132 WRITE (J,4133) SUB(3)                                             17270
4133 FORMAT (/1X,A8,/,13X,'LKTOSP',7X,'LOG (K) AT 25 DEGREES CELCIUS',  17280
     1', WHERE',/)                                                      17290
      WRITE (J,4134)                                                    17300
4134 FORMAT (24X,'LOG K = A1 + A2*T + A3/T + A4*LOG(T) + A5/T^2 ')      17310
      WRITE (J,4135)                                                    17320
4135 FORMAT (/1X,'FORMAT (F10.3)'//)                                   17330
      GO TO 1960                                                        17340
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4136 WRITE (J,4137) SUB(3)                                              17350
4137 FORMAT (/1X,A8,/,13X,'DHSP',9X,'STANDARD ENTHALPY OF THE ASSOCIAT' 17360
    1,'ION REACTION AT',/,26X,'25 DEGREES CELCIUS ( H(R), IN KCAL/'     17370
    2,'MOLE ).',/,1X,'FORMAT (F10.3)',//)                               17380
     GO TO 1970                                                         17390
4138 WRITE (J,4139) SUB(3),K,K                                          17400
4139 FORMAT (/1X,A8,/,13X,'ASP(',I1,')',7X,'A',I1,' OF THE FOLLOWING',  17410
    1' EQUATION:',/)                                                    17420
     WRITE (J,4134)                                                     17430
     WRITE (J,4140)                                                     17440
4140 FORMAT (/1X,'FORMAT (F12.5)')                                      17450
     GO TO 1987                                                         17460
4142 WRITE (J,4143) SUB(3)                                              17470
4143 FORMAT (/1X,A8,/,13X,'LSP',10X,'INDEX NUMBER OF MASTER SPECIES.'   17480
    1,/,1X,'FORMAT (I3)')                                               17490
     WRITE (J,4000)                                                     17500
     GO TO 1915                                                         17510
4144 WRITE (J,4145) SUB(3)                                              17520
4145 FORMAT (/1X,A8,/,13X,'CSP',10X,'STOICHIOMETRIC COEFFICIENT OF',    17530
    1' MASTER SPECIES',/,26X,'IN THIS AQUEOUS SPECIES.',/,1X,'FORMAT'   17540
    2,' (F7.3)')                                                        17550
     WRITE (J,4000)                                                     17560
     GO TO 1915                                                         17570
8000 WRITE (J,8001) SUB(I)                                              17580
8001 FORMAT (/1X,A8,/,13X,'MNAME',8X,'ALPHANUMERIC NAME OF MINERAL',/,  17590
    11X,'FORMAT (A8)',//)                                               17600
     GO TO 3102                                                         17610
8002 WRITE (J,8003) SUB(I)                                              17620
8003 FORMAT (/1X,A8,/,13X,'NMINO',8X,'NUMBER OF DIFFERENT SPECIES IN TH 17630
    1E MINERAL',/,26X,'DISSOCIATION REACTION (INCLUDING H+, E-, AND',/  17640
    2,26X,'H2O).  NMINO MUST BE LESS THAN OR EQUAL TO 10.',/,1X,        17650
    3'FORMAT (I2)',//)                                                  17660
     GO TO 3110                                                         17670
8004 WRITE (J,8005) SUB(I)                                              17680
8005 FORMAT (/1X,A8,/,13X,'THMIN',8X,'THE SUM OF THE VALENCES OF THE RE 17690
    1DOX SPECIES',/,26X,'IN THE MINERAL DISSOCIATION REACTION.',/,1X,   17700
    2'FORMAT (F10.3)',//)                                               17710
     GO TO 3120                                                         17720
8006 WRITE (J,8007)SUB(I)                                               17730
8007 FORMAT (/1X,A8,/,13X,'LKTOM',8X,'LOG OF THE EQUILIBRIUM CONSTANT'  17740
    1,' AT 25 DEGREES',/,26X,'CELCIUS FOR THE REACTION',/,1X,'FORM AT'  17750
    2,' (F10.3)',//)                                                    17760
     GO TO 3130                                                         17770
8008 WRITE (J,8009) SUB(I)                                              17780
8009 FORMAT (/1X,A8,/,13X,'DHMIN',8X,'DELTA H(R) (KCAL/MOLE) FOR THE '  17790
    1,'VANT HOFF',/,26X,'EXPRESSION.',/,1X,'FORMAT (F10.3)'//)          17800
     GO TO 3140                                                         17810
8010 WRITE (J,8011) SUB(I)                                              17820
8011 FORMAT (/1X,A8,/,13X,'MFLAG',3X,'= 0, THE VANT HOFF EXPRESSION IS' 17830
    1,' USED TO CALCU-',/,26X,'LATE THE TEMPERATURE DEPENDENCE OF THE', 17840
    2' EQUIL-',/,26X,'IBRIUM CONSTANT',//,21X,'= 1, THE ANALYTICAL EXP' 17850
    3,'RESSION IS USED TO CALCU-'/,26X,'LATE THE TEMPERATURE DEPENDENCE 17860
    4 OF THE EQUIL-',/,26X,'IBRIUM CONSTANT.',/,1X,'FORMAT (I1)'//)     17870
     GO TO 3150                                                         17880
8012 WRITE (J,8013) SUB(I)                                              17890
8013 FORMAT (/1X,A8,/,13X,'SIMIN',8X,'SATURATION INDEX (LOG(ION ACTIVI' 17900
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    1,'TY PRODUCT/K(SP)))',/,26X,'DESIRED IN THE FINAL SOLUTION.  SIMIN 17910
    2 = 0.0',/,26X,'WOULD PRODUCE EQUILIBRIUM WITH THE MINERAL',/,26X,  17920
    3'WHILE 1.0 WOULD PRODUCE A SOLUTION 10 TIMES',/,26X,'SUPERSATURATE 17930
    4D (SI = 1.0).  THIS VARIABLE IS',/,26X,'USEFUL IN SPECIFYING THE ' 17940
    5,'PARTIAL PRESSURE OF',/,26X,'A GAS.  THE HENRY(S) LAW CONSTANT ', 17950
    6'FOR THE GAS',/,26X,'WOULD BE ENTERED USING THE VANT HOFF (LKTOM)  17960
    7'/,26X,'OR ANALYTICAL EXPRESSION (AMIN) AND THE LOG OF'/,25X,' THE 17970
    8 PARTIAL PRESSURE WOULD BE ENTERED FOR SIMIN.',/,1X,'FORMAT (F10.3 17980
    9)',//)                                                             17990
     GO TO 3167                                                         18000
8014 WRITE (J,8015) SUB(I)                                              18010
8015 FORMAT (/1X,A8,/,13X,'LMIN',9X,'INDEX NUMBER OF SPECIES (NOT NECE' 18020
    1,'SSARILY MASTER',/,26X,'SPECIES) IN THE DISSOCIATION REACTION ',  18030
    2'FOR',/,26X,'THIS MINERAL',/,1X,'FORMAT (I4)')                     18040
     WRITE (J,3800)                                                     18050
     GO TO 3195                                                         18060
8016 WRITE (J,8017) SUB(I)                                              18070
8017 FORMAT (/1X,A8,/,13X,'CMIN',9X,'STOICHIOMETRIC COEFFICIENT OF ',   18080
    1'SPECIES IN',/,26X,'DISSOCIATION REACTION.',/,1X,'FORMAT (F11.3)') 18090
     WRITE (J,3800)                                                     18100
     GO TO 3195                                                         18110
8018 WRITE (J,8019) SUB(I),K,K                                          18120
8019 FORMAT (/1X,A8,/,9X,'AMIN(',I1,')',6X,'A',I1,1X,'OF THE FOLLOWING  18130
    1 MINERAL DISSOCIATION',/,22X,'REACTION:',//,22X,'LOG K = A1 +'     18140
    2,' A2*T + A3/T + A4*LOG(T) + A5/T^2 ',//,22X,'WHERE T IS'          18150
    3,' IN DEGREES KELVIN',/,1X,'FORMAT (F12.5)',//)                    18160
     GO TO 3207                                                         18170
8020 WRITE (J,8021) SUB(6)                                              18180
8021 FORMAT (/1X,A8,/,13X,'XTEMP',8X,'TEMPERATURE IN DEGREES CELSIUS.'  18190
    1,/,1X,'FORMAT (F10.3)',//)                                         18200
     GO TO 3307                                                         18210
8022 WRITE (J,8023) SUB(7)                                              18220
8023 FORMAT (/1X,A8,/,13X,'XSTEP',8X,'THE FRACTION OF SOLUTION 1 TO BE' 18230
    1,/,26X,'MIXED WITH SOLUTION 2.')                                   18240
8030 WRITE (J,8029)                                                     18250
8029 FORMAT (1X,'FORMAT (F10.9)',//)                                    18260
     GO TO 3607                                                         18270
8024 WRITE (J,8025) SUB(7)                                              18280
8025 FORMAT (/1X,A8,/,13X,'XSTEP',8X,'THE VOLUME OF SOLUTION 2 TO',     18290
    1' BE',/,26X,'TITRATED INTO SOLUTION 1.  XSTEP MUST',/,26X,'HAVE'   18300
    2,' THE SAME UNITS AS VO.')                                         18310
     GO TO 8030                                                         18320
8026 WRITE (J,8027) SUB(7)                                              18330
8027 FORMAT (/1X,A8,/,13X,'XSTEP',8X,'THE MOLES OF REACTION TO BE ',    18340
    1'ADDED',/,26X,'TO SOLUTION 1')                                     18350
     GO TO 8030                                                         18360
8028 WRITE (J,8031) SUB(7)                                              18370
8031 FORMAT (/1X,A8,/,13X,'XSTEP',8X,'THE TOTAL NUMBER OF MOLES OF'     18380
    1,/,26X,'REACTION TO BE ADDED IN NSTEPS',/,26X,'STEPS.  NSTEPS'     18390
    2,' REACTION SOLUTIONS'/,26X,'WILL BE CALCULATED.  THE I(TH) SOLU-' 18400
    3,/,26X,'TION WILL HAVE I*XSTEP/NSTEPS MOLES',/,26X,'OF REACTION'   18410
    4,' ADDED TO SOLUTION 1.')                                          18420
     GO TO 8030                                                         18430
8032 WRITE (J,8033) SUB(8)                                              18440
8033 FORMAT (/1X,A8,/,13X,'LREAC',8X,'INDEX NUMBER OF ELEMENT FOR THE'  18450
    1,' REACTION.',/,26X,'LREAC MUST BE BETWEEN 4 AND 30 INCLUSIVE.',/, 18460
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     226X,'IF LREAC IS GREATER THAN 30 THE PROGRAM',/,26X,'CONSIDERS',    18470
     3' THIS CONSTITUENT TO BE H2 OR ',/,26X,'O2 AND ONLY USES CREAC',    18480
     4' AND THMEAN',/,26X,'TO CHANGE THE OXIDATION STATE OF THE',/,26X    18490
     5,'REACTION SOLUTION.',/,1X,'FORMAT (I4)')                           18500
      WRITE (J,3800)                                                      18510
      GO TO 5015                                                          18520
 8034 WRITE (J,8035) SUB(8)                                               18530
 8035 FORMAT (/1X,A8,/,13X,'CREAC',8X,'STOICHIOMETRIC COEFFICIENT OF'     18540
     1,' THE ELEMENT',/,26X,'IN THE REACTION',/,1X,'FORMAT (F8.3)')       18550
      WRITE (J,3800)                                                      18560
      GO TO 5015                                                          18570
 8036 WRITE (J,8037) SUB(8)                                               18580
 8037 FORMAT (/1X,A8,/,13X,'THMEAN',7X,'THE VALENCE OF THE ELEMENT IN'    18590
     1,' THE REACTION.',/,26X,'AN ELEMENT MAY BE INCLUDED MORE THAN',     18600
     2' ONCE IN',/,26X,'A REACTION TO ACCOMODATE DIFFERENT VALENCE',/,    18610
     326X,'STATES OF THE ELEMENT.',/,1X,'FORMAT (F8.3)')                  18620
      WRITE (J,3800)                                                      18630
      GO TO 5015                                                          18640
 8038 WRITE (J,8039) SUB(9)                                               18650
 8039 FORMAT (/1X,A8,/,13X,'LPOS',9X,'INDEX NUMBER OF AN ELEMENT WITH'    18660
     1,' A CATION',/,26X,'MASTER SPECIES.',/,1X,'FORMAT (I5)')            18670
      WRITE (J,3800)                                                      18680
      GO TO 6010                                                          18690
 8040 WRITE (J,8041) SUB(9)                                               18700
 8041 FORMAT (/1X,A8,/,13X,'LNEG',9X,'INDEX NUMBER OF AN ELEMENT WITH'    18710
     1,' AN ANION',/,26X,'MASTER SPECIES.',/,1X,'FORMAT (I5)')            18720
      WRITE (J,3800)                                                      18730
 3800 FORMAT (1X,'NOTE:  FOR A LISTING OF MASTER SPECIES AND ELEMENTS,'   18740
     1,/,8X,'ENTER <LIST>.',//)                                           18750
      GO TO 6020                                                          18760
 8042 WRITE (J,8043) SUB(10)                                              18770
 8043 FORMAT (/1X,A8,/,13X,'SUNAME',7X,'ALPHANUMERIC NAME TO BE PRINT'    18780
     1'ED TO IDENTIFY',/,26X,'THE SUM.',/,1X,'FORMAT (A8)'//)             18790
      GO TO 7010                                                          18800
 8044 WRITE (J,8045) SUB(10)                                              18810
 8045 FORMAT (/1X,A8,/,13X,'NSUM',9X,'THE NUMBER OF INDEX NUMBER TO BE'   18820
     1,' READ.',/,26X,'NSUM<=50.',/,1X,'FORMAT (I2)'//)                   18830
      GO TO 7020                                                          18840
 8046 WRITE (J,8047) SUB (10)                                             18850
 8047 FORMAT (/1X,A8,/,13X,'LSUM',9X,'INDEX NUMBERS OF SPECIES IN '       18860
     1,'SUM.',/,1X,'FORMAT (I4)'//)                                       18870
      GO TO 7037                                                          18880
      END                                                                 18890
      SUBROUTINE READFILE                                                 18900
C                                                                         18910
C         THIS SUBROUTINE READS FROM LOGICAL FILE #11,                    18920
C         PRE-CONSTRUCTED MINERAL CARDS; AND FROM LOGICAL FILE #12,       18930
C         THE THERMODYNAMIC DATA OF PHREEQE, THE NECESSARY INFORMATIONS   18940
C         TO CONSTRUCT A MASTER SPECIES AND ELEMENTS TABLE.               18950
C                                                                         18960
      PARAMETER (IU1=11,IU2=12)                                           18970
      REAL ICOL3(0:30),NOUSE6                                             18980
      CHARACTER *12 THMIN(100),LKTOM(100),DHMIN(100),SIMIN(100)           18990
     1,CMIN(100,10),AMIN(100,5)                                           19000
      CHARACTER *8 NONE,MNAME(100),SUB(11),ICOL1(0:30),ICOL4(0:30)        19010
     1,SPEC(30),KEYWORD,NOUSE2                                            19020
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      COMMON /IUNIT/ J                                                  19030
      COMMON /PT/ MNAME,NMINO(100),THMIN,LKTOM,DHMIN,MFLAG(100)         19040
     1,SIMIN,LMIN(100,10),CMIN,AMIN,IMINERAL,SUB,ICOL1,ICOL2(0:30)      19050
     2,ICOL3,ICOL4,SPEC,OPV(30)                                         19060
      DATA NONE/'********'/                                             19070
C                                                                       19080
      LREAD=0                                                           19090
      J=1                                                               19100
      DO 40 M=1,30                                                      19110
   40 ICOL2(M)=0                                                        19120
      NUM=1                                                             19130
C                                                                       19140
C         READ MINERAL CARDS.                                           19150
C         NOTE:  MAXIMUM NUMBER OF MINERALS IS 100.                     19160
C                                                                       19170
      OPEN (UNIT=IU1,FILE='RATEMOD>PITZ>INPUT>MINERALS.2.DATA',STATUS=  19180
     1'OLD')                                                            19190
      DO 26 M=1,100                                                     19200
      READ (IU1,27,END=7)MNAME(M),NMINO(M),THMIN(M),LKTOM(M),DHMIN(M)   19210
     1,MFLAG(M),SIMIN(M)                                                19220
   27 FORMAT (A8,2X,I2,3X,3A10,5X,I1,9X,A10)                            19230
      NO2=NMINO(M)                                                      19240
      IF (NO2.LE.5) GO TO 29                                            19250
      NO2=5                                                             19260
   29 READ (IU1,28) (LMIN(M,MO),CMIN(M,MO),MO=NUM,NO2)                  19270
   28 FORMAT (5(I4,A11))                                                19280
      IF (NMINO(M).LE.5.OR.NUM.EQ.6) GO TO 30                           19290
      NUM=6                                                             19300
      NO2=NMINO(M)                                                      19310
      GO TO 29                                                          19320
   30 IF (MFLAG(M).EQ.0) GO TO 26                                       19330
   10 READ (IU1,31) (AMIN(M,MO),MO=1,5)                                 19340
   31 FORMAT (5A12)                                                     19350
   26 CONTINUE                                                          19360
    7 IMINERAL=M-1                                                      19370
C                                                                       19380
C            READ THERMODYNAMIC DATA OF PHREEQE.                        19390
C         NOTE: THE DATA BLOCKS OF PHREEQE DATA CAN BE ARRNAGED         19400
C               IN ANY ORDER.                                           19410
C                                                                       19420
      CLOSE (UNIT=IU1)                                                  19430
      OPEN (UNIT=IU2,FILE='RATEMOD>PITZ>LATEST>PHRQPITZ.DATA'           19440
     1,STATUS='OLD')                                                    19450
   48 READ (IU2,11,END=50) KEYWORD                                      19460
   11 FORMAT (A8)                                                       19470
C                                                                       19480
C         READ IS REPEATED UNTIL A KEYWORD IS FOUND.                    19490
C                                                                       19500
      IF (KEYWORD.EQ.SUB(2))GO TO 42                                    19510
      IF (KEYWORD.EQ.SUB(3))GO TO 44                                    19520
      GO TO 48                                                          19530
   46 LREAD=LREAD+1                                                     19540
      IF (LREAD.NE.2) GO TO 48                                          19550
      CLOSE (UNIT=IU2)                                                  19560
      RETURN                                                            19570
C                                                                       19580
```

```
C         READ SPECIES DATA BLOCK.                                      19590
C                                                                       19600
   44 DO 80 JL=1,250                                                    19610
      READ (IU2,51) NOUSE1                                              19620
      IF (NOUSE1.EQ.0)GO TO 46                                          19630
      READ (IU2,52)NOUSE2,NOUSE3,NOUSE6                                 19640
   51 FORMAT (I3)                                                       19650
   52 FORMAT (A8,2X,I3,12X,F10.3,//)                                    19660
      IF (NOUSE3.GT.6)READ (22,53)                                      19670
   53 FORMAT (1X)                                                       19680
      IF (NOUSE1.GT.30)GO TO 80                                         19690
      SPEC(NOUSE1)=NOUSE2                                               19700
      OPV(NOUSE1)=NOUSE6                                                19710
   80 CONTINUE                                                          19720
      GO TO 46                                                          19730
C                                                                       19740
C         READ ELEMENTS DATA BLOCK.                                     19750
C                                                                       19760
   42 DO 8 JL=1,50                                                      19770
      READ (IU2,9)ICOL1(0),ICOL2(0),ICOL3(0),ICOL4(0)                   19780
    9 FORMAT (A8,2X,I2,3X,F10.0,5X,A8)                                  19790
      IF (ICOL2(0).GT.30)GO TO 8                                        19800
      IF (ICOL2(0).NE.0)GO TO 100                                       19810
      JCOL=JL-1                                                         19820
      GO TO 46                                                          19830
  100 ICOL1(ICOL2(0))=ICOL1(0)                                          19840
      ICOL2(ICOL2(0))=ICOL2(0)                                          19850
      ICOL3(ICOL2(0))=ICOL3(0)                                          19860
      ICOL4(ICOL2(0))=ICOL4(0)                                          19870
    8 CONTINUE                                                          19880
   50 STOP                                                              19890
C     ***********                                                       19900
      ENTRY LISTM                                                       19910
C     ***********                                                       19920
C                                                                       19930
C         THIS SUBROUTINE FORMATS AND PRINTS A TABLE OF MASTER          19940
C         SPECIES AND ELEMENTS.                                         19950
C                                                                       19960
      DO 200 MO=1,3                                                     19970
      ICOL1(MO)=NONE                                                    19980
      ICOL2(MO)=MO                                                      19990
      ICOL3(MO)=0.0                                                     20000
      ICOL4(MO)=NONE                                                    20010
      OPV(MO)=0.0                                                       20020
  200 CONTINUE                                                          20030
      ICOL3(3)=18.0152                                                  20040
      SPEC(1)='H+       '                                               20050
      SPEC(2)='E-       '                                               20060
      SPEC(3)='H2O      '                                               20070
      WRITE (J,201)                                                     20080
  201 FORMAT (/34X,'INPUT FORMULA',/,34X,'CORRESPONDING',5X,'MASTER',/  20090
     1,1X,'ELEMENTS',5X,'#',9X,'GFW',10X,'TO GFW',9X,'SPECIES',6X,'OPV' 20100
     2,/,1X,8('-'),4X,3('-'),4X,10('-'),4X,14('-'),4X,8('-'),4X,5('-')  20110
     3,/)                                                               20120
      DO 203 MO=1,30                                                    20130
      IF (ICOL2(MO).EQ.0)GO TO 203                                      20140
```

```
      WRITE(J,202)ICOL1(MO),ICOL2(MO),ICOL3(MO),ICOL4(MO),SPEC(MO)      20150
     1,OPV(MO)                                                          20160
  203 CONTINUE                                                          20170
  202 FORMAT (1X,A8,4X,I2,5X,F10.4,8X,A8,6X,A8,4X,SP,F4.1,SS)           20180
      RETURN                                                            20190
      END                                                               20200
C                                                                       20210
      SUBROUTINE REF (ILINE,JOPT,JOPEN)                                 20220
C                                                                       20230
C         THIS SUBROUTINE READS CERTAIN NUMBER OF LINES--ACCORDING      20240
C         TO THE VALUE OF ILINE--FROM THE REFERENCE FILE, PRINTS        20250
C         IT(THEM) ON THE SCREEN, AND, DEPENDING ON THE VALUE OF        20260
C         IOPEN, ASKS A QUESTION CONCERNING THE FATE OF THE LINE(S).    20270
C                                                                       20280
C         JOPT:  0 = NO PRINT OF LINES                                  20290
C                1 = PRINT THE LINES                                    20300
C         JOPEN: 0 = NO QUESTION ASKED                                  20310
C                > 0 = QUESTION ASKED                                   20320
C                                                                       20330
      COMMON /IUNIT/ J                                                  20340
      COMMON /REFF/ JOPTION,IOPEN,JLINE                                 20350
      COMMON /REFF1/ I                                                  20360
      CHARACTER *80 JLINE(3),LINE                                       20370
C                                                                       20380
      DO 310 II=1,ILINE                                                 20390
      READ (13,10,END=99) JLINE(II)                                     20400
   10 FORMAT (A80)                                                      20410
      IF (JLINE(II)(1:10).NE.'          ')GO TO 311                     20420
      IF (II.NE.1) GO TO 311                                            20430
      JOPTION=0                                                         20440
      RETURN                                                            20450
  311 IF (JOPT.EQ.0) GO TO 310                                          20460
      WRITE (J,300) JLINE(II)                                           20470
  300 FORMAT (A80)                                                      20480
  310 CONTINUE                                                          20490
      IF (JOPEN.EQ.0)RETURN                                             20500
  402 GO TO (303,400,500,600), JOPEN                                    20510
  303 WRITE (J,301)                                                     20520
  301 FORMAT ('ENTER OPTION.  (1=KEEP, 2=MODIFY, 3=REPLACE)')           20530
  305 READ (J,300) LINE                                                 20540
      READ (LINE,*,ERR=402) JOPTION                                     20550
      IF (JOPTION.LE.0.OR.JOPTION.GT.3)GO TO 402                        20560
      IF ((JOPTION.EQ.3).AND.(JOPEN.EQ.2.OR.JOPEN.EQ.4))GO TO 402       20570
      RETURN                                                            20580
   99 IOPEN=0                                                           20590
      RETURN                                                            20600
  400 WRITE (J,401)                                                     20610
  401 FORMAT ('ENTER OPTION.  (1=KEEP, 2=ELIMINATE)')                   20620
      GO TO 305                                                         20630
  500 WRITE (J,501)                                                     20640
  501 FORMAT ('ENTER OPTION.  (1=KEEP, 2=MODIFY, 3=ELIMINATE)')         20650
      GO TO 305                                                         20660
  600 WRITE (J,601)                                                     20670
  601 FORMAT ('ENTER OPTION.  (1=KEEP, 2=REPLACE)')                     20680
      GO TO 305                                                         20690
      END                                                               20700
```

```
C                                                                       20710
      SUBROUTINE SPECL(I)                                               20720
C                                                                       20730
C       THIS SUBROUTINE CHECKS FOR SPECIAL CHARACTERS 'EXIT' AND 'LIST' 20740
C                                                                       20750
      COMMON /EE/ EXIT,LIST,LINE,JFLAG                                  20760
      LOGICAL EXIT,LIST                                                 20770
      CHARACTER *80 LINE                                                20780
      CHARACTER *4 QUIT(6)                                              20790
      DATA QUIT /'EXIT','exit','STOP','stop','QUIT','quit'/             20800
C                                                                       20810
      EXIT=.FALSE.                                                      20820
      LIST=.FALSE.                                                      20830
      IF (I.EQ.0) RETURN                                                20840
      IF ((LINE(1:4).EQ.'LIST'.OR.LINE(1:4).EQ.'list').AND.(I.EQ.2.OR.  20850
     11.EQ.3)) LIST=.TRUE.                                              20860
      DO 10 N=1,6                                                       20870
      IF (LINE(1:4).EQ.QUIT(N).AND.(I.EQ.1.OR.I.EQ.3)) EXIT=.TRUE.      20880
   10 CONTINUE                                                          20890
      RETURN                                                            20900
      END                                                               20910
C                                                                       20920
      LOGICAL FUNCTION OK()                                             20930
C                                                                       20940
C         THIS SUBROUTINE ASKS WHETHER IT IS O.K.                       20950
C                                                                       20960
      COMMON /IUNIT/ J                                                  20970
      COMMON /PN/ NFLAG                                                 20980
      LOGICAL ANSWER,YN                                                 20990
C                                                                       21000
      WRITE (J,10)                                                      21010
   10 FORMAT ('O.K.?')                                                  21020
      NFLAG=0                                                           21030
      OK=.TRUE.                                                         21040
      ANSWER=YN()                                                       21050
      IF (ANSWER) RETURN                                                21060
      NFLAG=1                                                           21070
      OK=.FALSE.                                                        21080
      RETURN                                                            21090
      END                                                               21100
C                                                                       21110
C     THIS SUBROUTINE READS VALUES FROM THE TERMINAL AND CHECKS TO MAKE  21120
C        SURE THAT IT IS PROPER                                         21130
C                                                                       21140
      SUBROUTINE QUESTA (*,J1,CHAR1,L1,STRING,F1,K1,M1)                 21150
      COMMON /REFF/ JOPTION,IOPEN,JLINE                                 21160
      COMMON /PN/ NFLAG                                                 21170
      COMMON /EE/ EXIT,LIST,LINE,JFLAG                                  21180
      COMMON /IUNIT/ N                                                  21190
      CHARACTER *(*) STRING                                             21200
      CHARACTER *80 LINE,JLINE(3)                                       21210
      CHARACTER *72 QUESTION                                            21220
      CHARACTER *40 FMT                                                 21230
      CHARACTER *16 CHAR,CHAR1,CHAR2                                    21240
      CHARACTER *4 F,F1,F2,FF                                           21250
      CHARACTER *2 FO(16)                                               21260
```

```
      LOGICAL EXIT,LIST,NONB                                            21270
      DATA FO/'1 ','2 ','3 ','4 ','5 ','6 ','7 ','8 ','9 ','10','11'   21280
     1,'12','13','14','15','16' /                                       21290
      DATA QUESTION /'KEEP THE OLD VALUE? (HIT <RETURN> IF YOU DO; IF NO 21300
     1T, REENTER THE DATA)'/                                            21310
C                                                                       21320
C        K=0 ==> STRING                                                 21330
C        K=1 ==> REAL                                                   21340
C        K=2 ==> INTEGER                                                21350
C                                                                       21360
      FF=F1                                                             21370
      IF (F1.EQ.'A80') FF='/A80'                                        21380
      F1=FF                                                             21390
      J=J1                                                              21400
      CHAR=CHAR1                                                        21410
      F=F1                                                              21420
      K=K1                                                              21430
      L=L1                                                              21440
      M=M1                                                              21450
      GO TO 100                                                         21460
C     ************************************************                  21470
      ENTRY QUESTB (*,J2,CHAR2,L2,IVAL,F2,IMIN,IMAX,M2)                 21480
C     ************************************************                  21490
      K=2                                                               21500
      J=J2                                                              21510
      CHAR=CHAR2                                                        21520
      F=F2                                                              21530
      L=L2                                                              21540
      M=M2                                                              21550
C                                                                       21560
  100 IF (J.GT.0.AND.J.LT.10) I 1                                       21570
      IF (J.GE.10.AND.J.LT.100) I=2                                     21580
      IF (J.GE.100) I=3                                                 21590
      IF (NFLAG.GT.0.OR.JOPTION.EQ.2) GO TO 30                          21600
      IF (J.GT.0) GO TO 10                                              21610
      FMT='(/,''INPUT '',A'//FO(L)//')'                                 21620
      WRITE (N,FMT) CHAR                                                21630
      GO TO 300                                                         21640
   10 FMT='(/,''INPUT '',A'//FO(L)//','''('',I'//FO(I)//','')''')'      21650
      WRITE (N,FMT) CHAR,J                                              21660
      GO TO 300                                                         21670
   30 IF (J.GT.0) GO TO 40                                              21680
      FMT='(/,''OLD '',A'//FO(L)//','''='','//F//',/,A72)'              21690
      IF (K.EQ.2) WRITE (N,FMT) CHAR,IVAL,QUESTION                      21700
      IF (K.NE.2) WRITE (N,FMT) CHAR,STRING,QUESTION                    21710
      GO TO 300                                                         21720
   40 FMT='(/,''OLD '',A'//FO(L)//','''('',I'//FO(I)//','')='','//F//', 21730
     1/,A72)'                                                           21740
      IF (K.EQ.2) WRITE (N,FMT) CHAR,J,IVAL,QUESTION                    21750
      IF (K.NE.2) WRITE (N,FMT) CHAR,J,STRING,QUESTION                  21760
C                                                                       21770
C     READ RESPONSE                                                     21780
C                                                                       21790
  300 JFLAG=0                                                           21800
      READ (N,105) LINE                                                 21810
  105 FORMAT(A80)                                                       21820
```

```
C                                                                       21830
C         JFLAG=0 ---> PROPER ENTRY                                     21840
C         JFLAG=1 ---> EXPLANATION IS ASKED                             21850
C         JFLAG=2 ---> A NULL ANSWER                                    21860
C         JFLAG=3 ---> ANSWER OF WRONG TYPE                             21870
C         JFLAG=4 ---> SPECIAL CHARACTERS                               21880
C                                                                       21890
      IF (LINE(1:1).NE.'') GO TO 110                                    21900
      JFLAG=2                                                           21910
      IF (K.EQ.2) IVALO=IVAL                                            21920
  110 IF (LINE(1:1).EQ.'?') JFLAG=1                                     21930
      CALL SPECL (M)                                                    21940
      IF (EXIT.OR.LIST) JFLAG=4                                         21950
      IF (JFLAG.NE.0) GO TO 200                                         21960
      GO TO (140,150,120), K+1                                          21970
  140 STRING=LINE                                                       21980
      RETURN                                                            21990
  120 READ (LINE,*,ERR=130) IVALO                                       22000
      GO TO 170                                                         22010
  150 READ (LINE,*,ERR=130) G                                           22020
C                                                                       22030
C     MAKE SURE THAT DECIMAL POINT IS PRESENT                           22040
C                                                                       22050
      NONB=.FALSE.                                                      22060
      DO 155 I2=1,80                                                    22070
      IF (LINE(I2:I2).NE.' ') NONB=.TRUE.                               22080
      IF (NONB.AND.LINE(I2:I2).EQ.' ') GO TO 130                        22090
      IF (LINE(I2:I2).EQ.'.') GO TO 156                                 22100
  155 CONTINUE                                                          22110
      GO TO 130                                                         22120
  156 STRING=LINE                                                       22130
      GO TO 200                                                         22140
C                                                                       22150
  130 JFLAG=3                                                           22160
  200 IF (JFLAG.EQ.2.AND.(NFLAG.NE.0.OR.JOPTION.EQ.2)) GO TO 170        22170
      IF (JFLAG.EQ.4) RETURN                                            22180
      IF (JFLAG.NE.0) RETURN 1                                          22190
  170 IF (K.NE.2) RETURN                                                22200
      IF (IMAX.GT.IMIN) GO TO 180                                       22210
      GO TO 190                                                         22220
  180 IF (IVALO.GT.IMAX.OR.IVALO.LT.IMIN) RETURN 1                      22230
  190 IVAL=IVALO                                                        22240
      RETURN                                                            22250
      END                                                               22260
C                                                                       22270
      LOGICAL FUNCTION YN()                                             22280
C                                                                       22290
C          THIS FUNCTION CHECKS FOR YES OR NO ANSWER                    22300
C                                                                       22310
      CHARACTER *1 YESNO                                                22320
      COMMON /IUNIT/ J                                                  22330
C                                                                       22340
    5 READ (J,10) YESNO                                                 22350
   10 FORMAT (A1)                                                       22360
      YN=.FALSE.                                                        22370
      IF (YESNO.EQ.'Y'.OR.YESNO.EQ.'y') GO TO 20                        22380
```

```
      IF (YESNO.EQ.'N'.OR.YESNO.EQ.'n') RETURN                          22390
      WRITE (J,30)                                                      22400
   30 FORMAT ('PLEASE ANSWER ''Y'' OR ''N''.')                          22410
      GO TO 5                                                           22420
   20 YN=.TRUE.                                                         22430
      RETURN                                                            22440
      END                                                               22450
C                                                                       22460
      SUBROUTINE OPEN(ITIME)                                            22470
C                                                                       22480
C         THIS SUBROUTINE GIVES THE USER A CHOICE OF CHOOSING A         22490
C         REFERENCE FILE OR NOT TO USE IT AT ALL.  IF THE               22500
C         REFERENCE FILE IS DESIRED, IT OPENS THE FILE AND              22510
C         POSITION THE POINTER SO THAT THE PROGRAM CAN USE IT;          22520
C         IF REFERENCE FILE IS NOT WANTED, IT SETS IOPEN TO ZERO        22530
C         AND RETURN TO 'MAIN.                                          22540
C                                                                       22550
      COMMON /REFF/ JOPTION,IOPEN,JLINE                                 22560
      COMMON /IUNIT/ J                                                  22570
      CHARACTER *36 TREAD                                               22580
      CHARACTER *80 LINE,JLINE(3)                                       22590
      SAVE TREAD,KOPEN                                                  22600
      LOGICAL YN                                                        22610
C                                                                       22620
      ITIME=ITIME+1                                                     22630
      IF (ITIME.EQ.1.OR.KOPEN.EQ.0)GO TO 100                            22640
  120 WRITE (J,110)                                                     22650
  110 FORMAT (/,'DO YOU WISH TO USE THE SAME REFERENCE FILE?')          22660
      IF (.NOT.YN()) GO TO 100                                          22670
      CLOSE (UNIT=13)                                                   22680
      GO TO 25                                                          22690
  100 WRITE (J,10)                                                      22700
   10 FORMAT (/,'ENTER REFERENCE FILE NAME:  (HIT <CR> TO OMIT)')       22710
      READ (J,20) TREAD                                                 22720
   20 FORMAT (A36)                                                      22730
      IF (TREAD(1:1).NE.'')GO TO 25                                     22740
      IOPEN=0                                                           22750
      GO TO 30                                                          22760
   25 OPEN (UNIT=13,FILE=TREAD,STATUS='OLD')                            22770
      IOPEN=1                                                           22780
   30 KOPEN=IOPEN                                                       22790
      RETURN                                                            22800
      END                                                               22810
```

Attachment F. -- Listing of the file MINERALS.2.DATA read by the interactive input program PITZINPT

```
ANHYDRIT   2          6.00    -4.362                1
   4      1.000  16       1.000
422.950     0.0          -18431.      -147.708
ARAGONIT   2          4.00    -8.220                1
  15 1.0           4 1.0
-171.8607   -.077993    2903.293    71.595
ARCANITE   2          6.00    -1.776                1
   7      2.000  16       1.000
2.823       0.0          -1371.2
BISCHOFI   3          0.00     4.455                1
   5      1.000  14       2.000   3       6.000
3.524       0.0          277.6
BLOEDITE   4         12.00    -2.347                0
   6      2.000   5       1.000  16       2.000   3       4.000
BRUCITE    2          0.00   -10.884.85             0
   5      1.000  31       2.000
BURKEITE   3         16.00     -.772                0
   6      6.000  15       1.000  16       2.000
CALCITE    2          4.00    -8.406                1
  15 1.0           4 1.0
-171.8329   -.077993    2839.319    71.595
CARNALLI   4          0.00    4.330                 0
   7      1.000   5       1.000  14       3.000   3       6.000
DOLOMITE   3          8.00  -17.083 -9.436          0
   4 1.0           5 1.0           15 2.0
EPSOMITE   3          6.00    -1.881                1
   5      1.000  16       1.000   3       7.000
1.718       0.0          -1073.
GAYLUSSI   4          8.00    -9.421                0
   4      1.000   6       2.000  15       2.000   3       5.000
GLASERIT   3         24.00    -3.803                0
   6      1.000   7       3.000  16       2.000
GLAUBERI   3         12.00    -5.245                0
   6      2.000   4       1.000  16       2.000
GYPSUM     3          6.00    -4.581                1
   4 1.0           16 1.0           3 2.0
90.318      0.0          -4213.       -32.641
HALITE     2          0.00     1.570                1
   6      1.000  14       1.000
-713.4616   -.1201241   37302.21    262.4583    -2106915.
HEXAHYDR   3          6.00    -1.635                1
   5      1.000  16       1.000   3       6.000
-62.666     0.0          1828.        22.187
KAINITE    5          6.00    -0.193                0
   7      1.000   5       1.000  14       1.000  16       1.000   3       3.000
KALICINI   3          4.00   -10.058                0
   7      1.000   1       1.000  15       1.000
KIESERIT   3          6.00    -0.123                0
   5      1.000  16       1.000   3       1.000
LABILE S   4         18.00    -5.672                0
   6      4.000   4       1.000  16       3.000   3       2.000
LEONHARD   3          6.00    -0.887                0
   5      1.000  16       1.000   3       4.000
LEONITE    4         12.00    -3.979                0
```

```
   7      2.000   5       1.000  16       2.000   3       4.000
MAGNESIT   2          4.00   -7.834      -6.169      0
   5      1.000  15       1.000
MIRABILI   3          6.00-1.214                      1
   6      2.000  16       1.000   3      10.000
-3862.234    -1.19856     93713.54     1577.756
MISENITE   3         42.00  -10.806                   0
   7      8.000   1       6.000  16       7.000
NAHCOLIT   3          4.00  -10.742                   0
   6      1.000   1       1.000  15       1.000
NATRON     3          4.00   -0.825                   0
   6      2.000  15       1.000   3      10.000
NESQUEHO   3          4.00   -5.167                   0
   5      1.000  15       1.000   3       3.000
PCO2       1          4.0    -1.468      -4.776      1
  35  1.0
108.3865     0.01985076  -6919.53     -40.45154     669365.0
PENTAHYD   3          6.00   -1.285                   0
   5      1.000  16       1.000   3       5.000
PIRSSONI   4          8.00   -9.234                   0
   6      2.000   4       1.000  15       2.000   3       2.000
POLYHALI   5         24.00  -13.744                   0
   7      2.000   5       1.000   4       2.000  16       4.000   3       2.000
PORTLAND   2          0.00   -5.190                   0
   4      1.000  31       2.000
SCHOENIT   4         12.00   -4.328                   0
   7      2.000   5       1.000  16       2.000   3       6.000
SYLVITE    2          0.00     .900                   1
   7      1.000  14       1.000
3.984        0.0          -919.55
SYNGENIT   4         12.00   -7.448                   0
   7      2.000   4       1.000  16       2.000   3       1.000
TRONA      4          8.00  -11.384                   0
   6      3.000   1       1.000  15       2.000   3       2.000
```

Attachment G. -- Example of use of the interactive input program PITZINPT to construct the input file for test problem 3

```
ENTER OUTPUT FILE NAME
TEST.3

ENTER REFERENCE FILE NAME:  (HIT <CR> TO OMIT)


INPUT THE TITLE
Test Problem 3: Find the anhydrite-gypsum phase boundary with NaCl addition.

Test Problem 3: Find the anhydrite-gypsum phase boundary with NaCl addition.
O.K.?
Y

INPUT IOPT(1)
0

INPUT IOPT(2)
0

INPUT IOPT(3)
6

INPUT IOPT(4)
0

INPUT IOPT(7)
0

INPUT IOPT(8)
0

INPUT IOPT(9)
0

INPUT IOPT(10)
0

INPUT NCOMPS
2

0060020000 0 2       0.0
O.K.?
Y

********************
KEYWORD DATA BLOCKS
********************



ENTER KEYWORD.
SOLUTION 1
```

```
--------
SOLUTION
--------


INPUT HEAD
*

Pure water
O.K.?
Y

 0  0 0    7.0       4.0       25.0      1.0
O.K.?
Y

********************
KEYWORD DATA BLOCKS
********************


ENTER KEYWORD.
MINERALS


--------
MINERALS
--------


PRE-CONSTRUCTED MINERAL DATA ARE AVAILABLE.
DO YOU WISH TO HAVE ANY OF THEM?
Y

   1 ANHYDRIT    2 ARAGONIT    3 ARCANITE    4 BISCHOFI    5 BLOEDITE
   6 BRUCITE     7 BURKEITE    8 CALCITE     9 CARNALLI   10 DOLOMITE
  11 EPSOMITE   12 GAYLUSSI   13 GLASERIT   14 GLAUBERI   15 GYPSUM
  16 HALITE     17 HEXAHYDR   18 KAINITE    19 KALICINI   20 KIESERIT
  21 LABILE S   22 LEONHARD   23 LEONITE    24 MAGNESIT   25 MIRABILI
  26 MISENITE   27 NAHCOLIT   28 NATRON     29 NESQUEHO   30 PCO2
  31 PENTAHYD   32 PIRSSONI   33 POLYHALI   34 PORTLAND   35 SCHOENIT
  36 SYLVITE    37 SYNGENIT   38 TRONA

ENTER THE INDEX NUMBER OF MINERAL. (TYPE <STOP> TO EXIT)
1

ANHYDRIT   2          6.00    -4.362                1
   4      1.000  16       1.000
422.950     0.0          -18431.      -147.708
O.K.?
Y

ENTER THE INDEX NUMBER OF MINERAL. (TYPE <STOP> TO EXIT)
```

```
15

GYPSUM      3          6.00    -4.581                  1
   4 1.0          16 1.0           3 2.0
90.318       0.0          -4213.       -32.641
O.K.?
Y

ENTER THE INDEX NUMBER OF MINERAL. (TYPE <STOP> TO EXIT)
STOP

MORE MINERALS TO BE TYPED IN FROM THE TERMINAL?
N

********************
KEYWORD DATA BLOCKS
********************



ENTER KEYWORD.
REACTION


--------
REACTION
--------



INPUT LREAC(1)
6

INPUT CREAC(1)
1.

INPUT THMEAN(1)
0.

INPUT LREAC(2)
14

INPUT CREAC(2)
1.

INPUT THMEAN(2)
0.

   61.       0.         141.       0.
O.K.?
Y

********************
KEYWORD DATA BLOCKS
********************
```