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Verification and Validation Studies of the Addition of Pitzer's Equations to the EQ3/6 Brine Model

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ABSTRACT

Recent modifications to the EQ3/6 geochemical modeling software package provide a new option which can be used to compute the activity of water and the activity coefficients of solute species in both brines and dilute solutions. This option is based on equations proposed by Pitzer (1973) which allow approximation of mean molal activity coefficients (γ_z) and osmotic coefficients (ϕ) up to high ionic strengths, and which, together with an appropriate ion-splitting convention, also afford calculation of individual ion activity coefficients (γ_i) in brines. Values of γ_z and ϕ generated by EQ3/6 for binary and compositionally higher order systems compare favorably with their experimental and hand-calculated counterparts. The addition of Pitzer's equations to EQ3/6 as an optional method for calculating activity coefficients represents a significant improvement over the previous versions of the codes, which were limited to the use of a simple extended form of the Debye-Hückel equation (the B-dot equation of Helgeson, 1969). Test runs using EQ3/6 to calculate solubility limits in simple binary and ternary systems ($NaCl-H_2O$, $KCl-H_2O$, and $KCl-NaCl-H_2O$) confirm the capability of the codes to accurately predict geochemical equilibria between brines and evaporite minerals in the sample systems. The test runs were sufficiently comprehensive to verify the accuracy of the calculational procedures and to partially validate the capability of the codes to dependably model the geochemical behavior of aqueous electrolyte solutions having ionic strengths as high as ~6 m, subject to the availability of the requisite thermodynamic data and activity coefficient parameters.

INTRODUCTION

Accurate evaluation of activity coefficients is necessary in order to relate the thermodynamic activities of electrolytes to their corresponding concentrations through the simple relationship

$$a = \gamma m \qquad (1)$$

where a, γ, and m stand for the thermodynamic activity, activity coefficient, and molality, respectively, of a given aqueous species or component. Although

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the standard state used for solutes requires their activity coefficients to approach unity in infinitely dilute solutions, values of activity coefficients frequently diverge significantly from unity even in quite dilute solutions. In addition, the activity of water, which also has a value of one in infinitely dilute solutions (i.e., pure water), can be shown to change appreciably as a function of ionic strength. It is the conversion from the activities of solute species or components used in chemical equilibrium and kinetics calculations into measurable concentrations that requires the use of some calculational method to accurately determine activity coefficient behavior.

Over the past half century there have been a number of algorithms proposed for the calculation of activity coefficients in aqueous electrolyte solutions, many of which have been summarized in recent works by Pitzer (1977, 1979) and Helgeson et al. (1981). Accurate results are obtained from many of the commonly used equations only when they are applied to quite dilute solutions (usually << 1 m). Recent developments, however, have yielded a variety of equations adapted for use in concentrated solutions. One of the most accurate and versatile of the available models for calculating activity coefficients in brines was developed by Pitzer (1973, 1975), Pitzer and Mayorga (1973, 1974), and Pitzer and Kim (1974), and subsequently modified and extended by Pitzer and others in several later papers (e.g., Pitzer, 1979, and references cited therein).

The set of equations suggested by Pitzer and co-workers and the requisite supporting ion interaction coefficients have been incorporated into the EQ3/6* geochemical modeling software package, and extend the range over

* The EQ3/6 software package is comprised of a family of computer codes and supporting data bases designed for calculation of the equilibrium distribution of species in an aqueous solution and to model the interaction of this fluid with mineral phases, a gas phase, or another aqueous solution. Included in this software package are two computer programs, EQ3NR and EQ6, which comprise the central features of the package. EQ3NR performs aqueous speciation and solubility calculations (Wolery, 1979, 1983), and EQ6 models reaction paths between aqueous solutions and specified geochemical systems (Wolery, 1979). Other components of the EQ3/6 package include several thermodynamic and activity coefficient data bases that support EQ3NR and EQ6 calculations. Also part of the EQ3/6 package are several codes and supporting data files that are designed to be used in conjunction with the construction and maintenance of the data files actually used by EQ3NR and EQ6 and a library of FORTRAN subroutines which support the EQ3/6 codes (EQLIB). Specific versions of the codes and data files used to generate the examples in this report are identified for each calculation.

which activity coefficients can be accurately calculated by EQ3/6 to significantly higher ionic strengths (Jackson and Wolery, 1985). The addition of Pitzer's equations to the coding is reflected by only minor changes to the input and output files of EQ3NR and EQ6 (which are illustrated by the sample input and output files in Appendices A and B), so their function is more or less transparent to the user. Their addition, however, allows the EQ3/6 user to model many geochemical processes that were previously inaccessible owing to the high ionic strengths of the solutions involved. For example, in order to calculate the concentrations of the major dissolved species in equilibrium with evaporite deposits made up of such highly soluble mineral phases as halite and sylvite, it is necessary to evaluate activity coefficients in solutions with ionic strengths as high as ~6 m (Eugster et al., 1980). EQ3/6 test runs outlined below document the capability of these codes to accurately approximate the activity coefficients of solute species as well as the activity of water in high ionic strength solutions. The extension of the range in salinity values over which accurate calculations can be made will allow application of these codes to problems necessitating the calculation of thermodynamic equilibria in systems involving brines, such as assessing quantitatively the geochemical environment that might be anticipated for nuclear waste canisters located in a salt repository, calculating mass transfer during diagenesis involving oil field brines, or modeling ore-forming processes for many hydrothermal ore deposits.

VERIFICATION AND VALIDATION STUDIES

Throughout this report, the words "verification" and "validation" are used to convey rather specific meanings. Verification of a computer code implies that the coding performs the specific task of correctly evaluating a given set of equations (Silling, 1983). In this case, the Pitzer brine modifications are said to be verified if it is shown that the coding faithfully follows Pitzer's activity coefficient expressions and conforms to various conventions described below. Validation consists of demonstrating that calculations made by the codes are realistic representations of various physically measurable parameters of aqueous solutions (Silling, 1983). The capability of the coding to predict such experimental data as the compositional dependence of the osmotic coefficient of an electrolyte solution

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is taken to be partial validation of the code. Precisely calculated values for mineral solubilities in brines are taken to be further evidence of partial validation, because such calculations depend on accurate computation of the activities of solute components and (in many cases) the activity of water.

The point at which the user should be satisfied that the coding has been completely validated necessarily depends upon the type of problem which is to be solved and the accuracy demanded by the code application being considered. That is, if the code has been thoroughly tested on problems reasonably similar to a particular application of the code, then the code has been validated for problems of that type. For calculations outside the realm of conditions for which analogous runs have been tested, however, the issue of whether or not the code has been validated for the case in question becomes a matter of careful judgment. Although verification and validation are defined differently and discussed individually in this report, it should be pointed out that many of the test runs detailed below contribute to both the verification and validation of the EQ3/6 Pitzer brine modifications. For example, a validation run which accurately reproduces experimentally determined values for the activity coefficients of aqueous species in brines necessarily contributes to the assurance that the equations in EQ3/6 are correctly implemented.

An additional feature of the EQ3/6 brine modifications which impacts the verification and validation studies outlined below is that they are highly modularized. In other words, the coding that does activity coefficient calculations is mostly external to both EQ3NR and EQ6, and resides in the companion EQLIB library routines. Therefore, examples in this report that were run using EQ3NR test many of the same code modifications as runs using EQ6. Duplicate runs using EQ3NR and EQ6 to solve the same problem yield identical results.

VERIFICATION

The results of sample calculations outlined below illustrate the capability of EQ3/6 to reproduce experimentally determined osmotic

coefficient* and mean molal activity coefficient data. Because the interaction parameters used in Pitzer's equations were, for the most part, fitted to this kind of experimental data, the fits described below serve to assure that the coding is in accordance with the formulation of $\gamma_{\pm}$ and ϕ as represented by Pitzer (e.g., 1973, 1975, and 1979). In addition, conformity of values calculated by EQ3/6 with values calculated by hand using alternate forms of the activity and osmotic coefficient expressions and comparison with published values of activity coefficients calculated using Pitzer's equations are used to verify the accuracy of the coding. Comparisons of values computed by EQ3/6 with experimental solubility data as well as with values computed using other activity coefficient expressions demonstrate that these codes are able to represent the compositional dependence of the activity coefficients of single and mixed electrolytes up to high ionic strengths.

The two different, but numerically equivalent, sets of expressions for the activity and osmotic coefficients of aqueous electrolyte solutions shown below are written either in terms of ion interaction parameters or in terms of observable combinations of those interaction parameters (Pitzer, 1973). The general form of the expression which describes the mean molal activity coefficient of a neutral electrolyte salt (MX) in terms of ion interaction parameters can be written as (Pitzer, 1979):

$$\ln \gamma_{\pm} = \frac{|z_M z_X|}{2} f' + \frac{2\nu_M}{\nu} \sum_j \lambda_{Mj} m_j \qquad (2)$$

$$+ \frac{2\nu_X}{\nu} \sum_j \lambda_{Xj} m_j + \frac{|z_M z_X|}{2} \sum_j \sum_k \lambda'_{jk} m_j m_k$$

$$+ \frac{3\nu_M}{\nu} \sum_j \sum_k \mu_{Mjk} m_j m_k$$

$$+ \frac{3\nu_X}{\nu} \sum_j \sum_k \mu_{Xjk} m_j m_k$$

*The osmotic coefficient (ϕ) can be related to the activity of water (a_w) by the expression

$$\phi = -(\Omega/\Sigma m) \ln a_w$$

where Ω is the number of moles of water in a kg of pure solvent (Ω = 55.51 moles.) and Σm represents the stoichiometric sum of the molalities of solute species. In high ionic strength brines the activity of water may differ substantially from unity and must be explicitly included in mass action expressions in order to accurately describe chemical equilibrium relationships.

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where λ and μ represent short range interaction parameters among the subscripted species; ν_M, ν_X, z_M, and z_X are the stoichiometric coefficients and charges of M and X in the salt; ν is the sum of ν_M and ν_X; and m stands for the molality of MX. The symbols λ_{jk} and f' designate the derivatives of λ_{jk} and a Debye-Hückel term (f) with respect to ionic strength (I). The Debye-Hückel term used in the Pitzer equations is defined by

$$f \equiv -A_\phi \frac{4I}{b} \ln (1 + bI^{1/2}) \quad . \tag{3}$$

The derivative of f with respect to I (denoted by f'), therefore, can be expressed as

$$f' = -4A_\phi I^{1/2}\left(\frac{1}{2(1+bI^{1/2})} + \frac{\ln (1+bI^{1/2})}{bI^{1/2}}\right) \quad . \tag{4}$$

A_ϕ is a Debye-Hückel constant defined by

$$A_\phi \equiv \left(\frac{e^3}{3(2.303)}\right)\left(\frac{2\pi N\rho_w}{1000}\right)^{1/2} \left(\frac{1}{\varepsilon kT}\right)^{3/2} \tag{5}$$

where N is Avogadro's number, ρ_w represents the density of water, e is the charge on an electron, ε designates the dielectric constant of water, k is Boltzmann's constant, and T stands for the temperature (in K). In these equations, the quantity 2.303 represents ln(10), and b is the product of an ion size parameter ($\dot{a}$) and another Debye-Hückel constant (B_γ), which can be written as

$$B_\gamma \equiv \left(\frac{8\pi N\rho_w e^2}{1000\varepsilon kT}\right)^{1/2} \quad . \tag{6}$$

Pitzer (1973) assigned a value of 1.2 to b for all solutions. This convention, which implies a single ion size value for each solute species corresponding to approximately 3.65 Å at 25°C, is used in all the computations shown below. At 25°C and 1 bar A_ϕ has a value of 0.391 $kg^{1/2}$ $mole^{-1/2}$ (Pitzer, 1979) and B_γ has a value of 0.3283 $kg^{1/2}$ $mole^{-1/2}$ $\dot{A}^{-1}$ (Helgeson and Kirkham, 1974).

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For a binary system composed of a single neutral electrolyte (MX) and water, eqn. 2 for mean molal activity coefficients simplifies to (Pitzer, 1973):

$$\ln \gamma_{\pm} = \frac{|z_M z_X|}{2} f' + \frac{m}{\nu} \Big[2\nu_M\nu_X(2\lambda_{MX} + I\lambda'_{MX}) + \nu_M^2(2\lambda_{MM} + I\lambda'_{MM}) + \nu_X^2(2\lambda_{XX} + I\lambda'_{XX})\Big] + \frac{9\nu_M\nu_X m^2}{\nu}(\nu_M\mu_{MMX} + \nu_X\mu_{MXX}) \quad (7)$$

An expression for the osmotic coefficient consistent with the activity coefficient expression in eqn. 2 was formulated by Pitzer (1973) as

$$\phi - 1 = \frac{1}{\Sigma m}\Big[(If' - f) + \sum_i \sum_j \lambda_{ij} + I\,\lambda'_{ij}\, m_i m_j + 2\sum_i \sum_j \sum_k \mu_{ijk}\, m_i m_j m_k\Big] \quad (8)$$

For binary solutions Eqn. 8 can be simplified to read

$$\phi - 1 = \frac{|z_M z_X|}{2}\left(f' - \frac{f}{I}\right) + \frac{m}{\nu}\,[2\nu_M\nu_X(\lambda_{MX} + I\lambda'_{MX}) + \nu_M^2(\lambda_{MM} + I\lambda'_{MM}) + \nu_X^2(\lambda_{XX} + I\lambda'_{XX})] + \frac{6\nu_M\nu_X m^2}{\nu}(\nu_M\mu_{MMX} + \nu_X\mu_{MXX}) \quad (9)$$

Equivalent forms of eqns. 7 and 9 can be written in terms of various observable combinations of the ion interaction parameters in binary solutions, which were defined by Pitzer (1973) and Pitzer and Kim (1974) as

$$B^{\phi}_{MX} = \lambda_{MX} + I\lambda'_{MX} + (\nu_M/2\nu_X)(\lambda_{MM} + I\lambda'_{MM}) + (\nu_X/2\nu_M)(\lambda_{XX} + I\lambda'_{XX}) \quad (10)$$

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$$B^{\gamma}_{MX} = 2\lambda_{MX} + I\lambda'_{MX} + (\nu_M/2\nu_X)(2\lambda_{MM} + I\lambda'_{MM}) \tag{11}$$

$$+ (\nu_X/2\nu_M)(2\lambda_{XX} + I\lambda'_{XX}) \quad ,$$

$$C^{\phi}_{MX} = [3/(\nu_M\nu_X)^{1/2}] \; [\nu_M\mu_{MMX} + \nu_X\mu_{MXX}] \quad , \tag{12}$$

and

$$C^{\gamma}_{MX} = \frac{3}{2} C^{\phi}_{MX} \quad . \tag{13}$$

Expressions for $\gamma_{\pm}$ and ϕ which can be derived by substituting eqns. 10-13 into eqns. 8 and 9 are given by

$$\ln \gamma_{\pm} = \frac{|z_M z_X|}{2} f' + m(2\nu_M\nu_X/\nu) \; B^{\gamma}_{MX} \tag{14}$$

$$+ m^2[2(\nu_M\nu_X)^{3/2}/\nu] \; C^{\gamma}_{MX}$$

and

$$\phi - 1 = \frac{|z_M z_X|}{2} (f' - f/I) + m(2\nu_M\nu_X/\nu) \; B^{\phi}_{MX} \tag{15}$$

$$+ m^2 \; [2(\nu_M\nu_X)^{3/2}/\nu] \; C^{\phi}_{MX} \; .$$

The modified version of the EQ3/6 software package uses coding based on forms of eqns. 2 and 8 for multicomponent systems. To assure that the coding calculates the activity and osmotic coefficients correctly, values for these quantities have been calculated by hand for the binary solutions discussed below using eqns. 7 and 9 and eqns. 14 and 15 in conjunction with data compiled by Pitzer (1979). By comparing the hand-computed values with results obtained from EQ3NR and EQ6, it is possible to assess the degree to which the program reliably evaluates eqns. 2 and 8.

Three binary solutions of $MgCl_2$-H_2O, $MgSO_4$-H_2O, and $AlCl_3$-H_2O were selected for hand calculations. The $MgCl_2$ and $AlCl_3$ solutions were

chosen because they illustrate the capability of calculating $\gamma_{\pm}$ and ϕ for asymmetric (i.e., not 1:1 or 2:2) electrolytes. This is potentially more diagnostic than for symmetric electrolytes because in the case of symmetric electrolytes, several of the factors in the equations are either equal to one or cancel out, and possible errors in the use of these factors might be overlooked. In addition, the capability of EQ3NR and EQ6 to correctly calculate activity coefficients for symmetric electrolytes for binary solutions containing $KCl-H_2O$ (1:1), $NaCl-H_2O$ (1:1), and $MgSO_4-H_2O$ (2:2) is illustrated below for $MgSO_4$ and discussed in the section on mineral solubilities for the systems $KCl-H_2O$, $NaCl-H_2O$, and $NaCl-KCl-H_2O$. Another reason for concentrating on asymmetric electrolytes is that it is commonly more difficult to model their activity and osmotic coefficient behavior, so they potentially represent a more diagnostic test of the coding.

Calculated values of the mean activity coefficient of $MgCl_2$ are listed in Table 1-a along with experimental data from Robinson and Stokes (1965) for

Table 1-a

Mean molal activity coefficients of $MgCl_2$ at 25°C as a function of the molality of dissolved $MgCl_2$. $\gamma^{obs}_{\pm,MgCl_2}$ values are experimental data of Robinson and Stokes (1965), $\gamma^{a}_{\pm,MgCl_2}$ are values calculated by hand using eqn. 14, $\gamma^{b}_{\pm,MgCl_2}$ designates values calculated by hand using eqn. 7, and $\gamma^{c}_{\pm,MgCl_2}$ represents results from EQ3NRU14 and EQLIBU08. Values with the superscript d are outside Pitzer's (1979) fit region.

m_{MgCl_2}	$\gamma^{obs}_{\pm,MgCl_2}$	$\gamma^{a}_{\pm,MgCl_2}$	$\gamma^{b}_{\pm,MgCl_2}$	$\gamma^{c}_{\pm,MgCl_2}$
0.1	0.528	0.529	0.529	0.530
0.5	0.480	0.480	0.480	0.481
1.0	0.569	0.572	0.572	0.572
1.6	0.802	0.805	0.805	0.805
2.0	1.051	1.057	1.057	1.058
3.0	2.32	2.31	2.31	2.31
4.0	5.53	5.53	5.53	5.53
4.5	8.72	8.79	8.78	8.79
5.0^{d}	13.92	14.17^{d}	14.15^{d}	14.16^{d}

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compositions ranging from 0.1 to 5 m. Neglecting small differences due to round-off errors in the hand calculations, all three methods of calculation yield identical values at each composition. Furthermore, the differences between calculated values and the experimental data represent less than one percent of the experimental value at each concentration except for the case of 5.0 m, which is outside the region to which the virial coefficients of Pitzer's equations were fit. Similar calculations for osmotic coefficients of $MgCl_2$ solutions are illustrated in Table 1-b. Good agreement between the results computed by EQ3NR and hand calculations using eqns. 14 and 15 is also demonstrated for $AlCl_3$ in Table 2-a and for $MgSO_4$ in Table 2-b. Again, neglecting round-off differences, both methods of calculation yield identical results which are in agreement with the experimental determinations reported by Robinson and Stokes (1965) for $AlCl_3$ and by Rard and Miller (1981) for $MgSO_4$.

The agreement between values of $\gamma_\pm$ and ϕ calculated by EQ3NR and the results of the two different methods of hand calculations discussed above for

Table 1-b

Osmotic coefficients of $MgCl_2$ solutions at 25°C as a function of the molality of $MgCl_2$. Values in the column labeled ϕ^{obs} are experimental data of Robinson and Stokes (1965), ϕ^a and ϕ^b designate values calculated by hand (using eqns. 15 and 9, respectively), and ϕ^c represents values calculated by EQ3NRU14 and EQLIBU08. Values with the superscript d are outside Pitzer's (1979) fit region.

m_{MgCl_2}	ϕ^{obs}	ϕ^a	ϕ^b	ϕ^c
0.1	0.861	0.864	0.864	0.864
0.5	0.947	0.945	0.946	0.946
1.0	1.108	1.110	1.110	1.110
1.6	1.347	1.350	1.350	1.350
2.0	1.523	1.526	1.526	1.526
3.0	2.010	2.005	2.004	2.004
4.0	2.521	2.519	2.520	2.519
4.5	2.783	2.788	2.788	2.788
5.0[d]	3.048	3.063[d]	3.063[d]	3.062[d]

2:1, 3:1, and 2:2 electrolytes is ample evidence that the coding in EQ3NR is verifiably conformable with eqns. 2, 8, 14, and 15. The capability of the coding to accurately reproduce the experimental data discussed in the following section is additional evidence of verification as well as evidence of partial validation.

VALIDATION

The capability of the modified EQ3/6 coding to accurately reproduce experimentally determined activity and osmotic coefficient properties of electrolyte solutions is a useful yardstick by which validation of the coding can be gauged. Additional evidence of validation is obtained from predicting the measured concentrations of solutes in an aqueous solution in equilibrium with highly soluble evaporite minerals, because solubility data were not used

Table 2-a

Mean molal activity coefficients and osmotic coefficients of $AlCl_3$ solutions at 25°C as a function of the molality of $AlCl_3$. Values in the columns labeled $\gamma^{obs}_{\pm,AlCl_3}$ and ϕ^{obs} are experimentally determined values listed in Robinson and Stokes (1965); $\gamma^{a}_{\pm,AlCl_3}$ and ϕ^{a} are values calculated by hand using eqns. 14 and 15, and $\gamma^{b}_{\pm,AlCl_3}$ and ϕ^{b} are values calculated by EQ3NRU14 and EQLIBU08. The superscript c represents values outside Pitzer's (1979) fit region.

m_{AlCl_3}	$\gamma^{obs}_{\pm,AlCl_3}$	$\gamma^{a}_{\pm,AlCl_3}$	$\gamma^{b}_{\pm,AlCl_3}$	ϕ^{obs}	ϕ^{a}	ϕ^{b}
0.2	0.305	0.330	0.330	0.841	0.851	0.851
0.5	0.331	0.353	0.354	1.008	1.004	1.004
1.0	0.539	0.584	0.585	1.382	1.392	1.392
1.2	0.701	0.764	0.765	1.560	1.572	1.573
1.4	0.936	1.021	1.023	1.749	1.760	1.761
1.6	1.284	1.390	1.393	1.951	1.955	1.955
1.8^{c}	1.819	1.919^{c}	1.923^{c}	2.175	2.154^{c}	2.154^{c}

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to regress the Pitzer interaction coefficients used in this report. As was pointed out in the section on verification, the capability of EQ3NR to successfully model $\gamma_\pm$ and ϕ for binary solutions (e.g., $MgCl_2$-H_2O, $AlCl_3$-H_2O, and $MgSO_4$-H_2O) is evidence which contributes to validation of the EQ3/6 brine model as well as to assuring that the codes have been verified. The capability to accurately determine the activity coefficients and osmotic coefficient behavior of binary solutions over a wide range of ionic strength is shown by Figs. 1-3. In Fig. 1(a) and (b) the mean molal activity coefficients of $SrCl_2$, and the corresponding osmotic coefficients of $SrCl_2$ solutions are plotted as a function of molality. The solid curves represent values of $\gamma_\pm$ or ϕ calculated by EQ3NR for $SrCl_2$, and the symbols are data from Robinson and Stokes (1965). It can be seen from Fig. 1(a) and (b) that agreement between the computed values and experimental data is quite good. Similarly faithful fits to the $\gamma_\pm$ and ϕ data discussed above for $MgSO_4$ and $AlCl_3$ are apparent in Figs. 2 and 3, respectively. Because the activity coefficient and osmotic coefficient behavior of $MgSO_4$ as a function of composition is notoriously difficult to model (Helgeson et al., 1981) owing

Table 2-b

Mean molal activity coefficients and osmotic coefficients of $MgSO_4$ solutions at 25°C as a function of the molality of dissolved $MgSO_4$. Values in the columns labeled $\gamma^{obs}_{\pm,MgSO_4}$ and ϕ^{obs} are experimental data from Rard and Miller (1981), $\gamma^{a}_{\pm,MgSO_4}$ and ϕ^{a} designate values calculated by hand using eqns. 14 and 15 respectively, while $\gamma^{b}_{\pm,MgSO_4}$ and ϕ^{b} designate values calculated by EQ3NRU14 and EQLIB08.

m_{MgSO_4}	$\gamma^{obs}_{\pm,MgSO_4}$	$\gamma^{a}_{\pm,MgSO_4}$	$\gamma^{b}_{\pm,MgSO_4}$	ϕ^{obs}	ϕ^{a}	ϕ^{b}
0.2	0.1160	0.120	0.120	0.5578	0.5614	0.5618
0.8	0.0583	0.0607	0.0608	0.5199	0.5222	0.5226
1.2	0.0494	0.0512	0.0514	0.5448	0.5439	0.5442
2.0	0 0451	0.0468	0.0470	0.6616	0.6626	0.6633
3.0	0.0532	0.0550	0.0552	0.9193	0.9158	0.9166

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to its large deviation from the Debye-Hückel limiting law even at very low concentrations, the fit to the data provided by eqns. 2 and 8 as calculated by EQ3NR is particularly encouraging.

The Pitzer activity coefficient option in EQ3NR and EQ6 can also be used to accurately predict activity coefficients in more complicated compositional

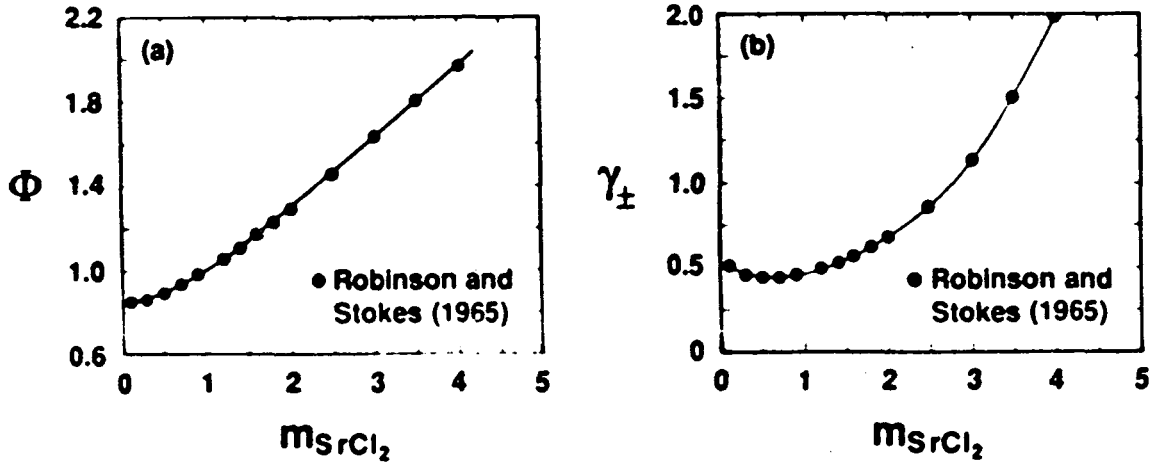

Figure 1. Osmotic coefficient (ϕ) of $SrCl_2$ solutions and mean molal activity coefficient ($\gamma_\pm$) of $SrCl_2$ at 25°C as functions of molality. The curves represent values calculated by EQ3/6. EQ3/6 calculations in Figs. 1-4 were performed using EQ3NR and EQLIBU08.

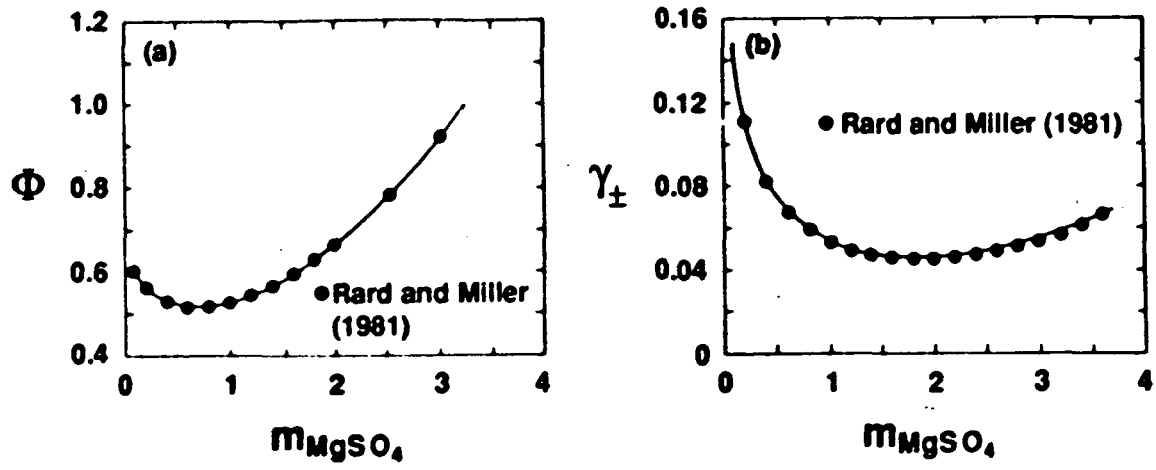

Figure 2. Osmotic coefficient (ϕ) of $MgSO_4$ solutions and mean molal activity coefficient ($\gamma_\pm$) of $MgSO_4$ at 25°C as functions of molality. The curves represent values calculated by EQ3/6.

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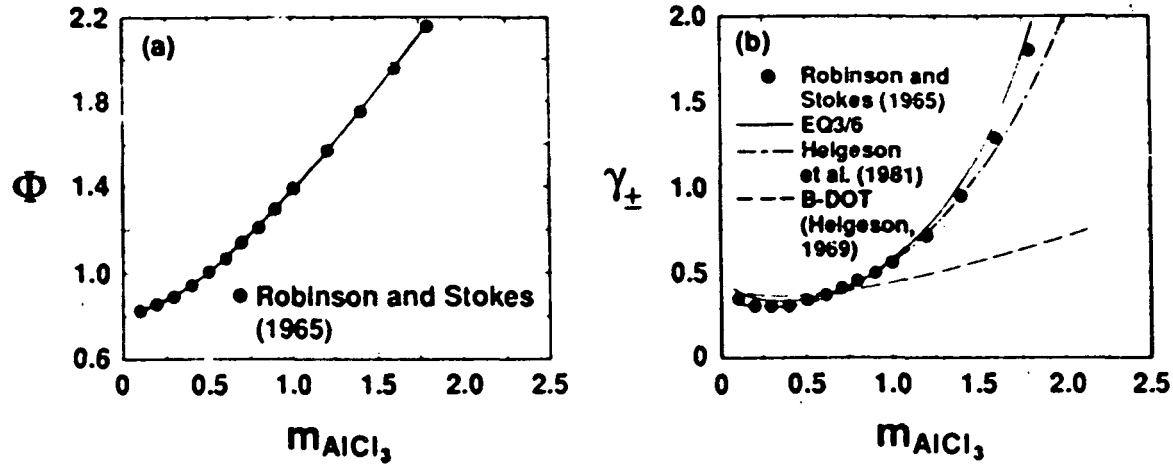

Figure 3. Osmotic coefficient (ϕ) of $AlCl_3$ solutions and mean molal activity coefficient ($\gamma_\pm$) of $AlCl_3$ at 25°C as functions of molality. Solid curves were calculated by EQ3/6 using eqns. 1 and 4.

systems. For example, the mean molal activity coefficient of HCl ($\gamma_{\pm,HCl}$) in the quaternary systems HCl-NaCl-KCl-H_2O and HCl-NH_4Cl-KCl-H_2O were measured by Chan et al. (1979) using the electromotive force method. Their results, together with values calculated by EQ3NR, are listed in Tables 3-a and b. For the system HCl-NaCl-KCl-H_2O the maximum difference between the experimental and calculated log $\gamma_\pm$ values is 7.2×10^{-4}, and it is 4.49×10^{-3} for the system HCl-NH_4Cl-KCl-H_2O. These differences represent less than about 0.5% and 3.1% of the experimental values, respectively, and in most cases the agreement is considerably better than these limits. Although the ionic strength of these solutions is only about 1 m, much less accurate results would be expected using the B-dot equations.

It should be noted that the addition of Pitzer's equations to EQ3/6 as an optional method for calculating activity coefficient values represents a significant improvement over the previous versions of the codes, which were limited to the use of an extended form of the Debye-Hückel equation (the B-dot equation of Helgeson, 1969). The B-dot equation for estimating $\gamma_\pm$, however, is not likely to be dependable at high ionic strengths (Helgeson, 1969; Wolery, 1983), as is illustrated by the dashed curve in Figure 3-b. In fact, for some electrolytes the B-dot equation predicts values that diverge from the data even in relatively dilute solutions.

Table 3-a

Mean molal activity coefficients of HCl at 25°C in the quaternary system HCl-NaCl-KCl-H_2O. Experimental values of log $\gamma_{\pm,HCl}$ are from Chan et al. (1979), whereas calculated values are computed by EQ3NRU14 and EQLIBU08. Δ log $\gamma_{\pm,HCl}$ represents the absolute value of the differences between experimental and calculated values of log $\gamma_{\pm,HCl}$.

m_{HCl}	m_{NaCl}	m_{KCl}	log $\gamma_{\pm,HCl}$ Experimental	log $\gamma_{\pm,HCl}$ Calculated	Δ log $\gamma_{\pm,HCl}$
0.79956	0.05011	0.15033	-0.10145	-0.10114	0.00031
0.59972	0.10007	0.30021	-0.11245	-0.11192	0.00053
0.29979	0.17505	0.52516	-0.12819	-0.12792	0.00027
0.09977	0.22506	0.67517	-0.13865	-0.13846	0.00019
0.05000	0.23750	0.71250	-0.14135	-0.14106	0.00029
0.01000	0.24750	0.74250	-0.14314	-0.14315	0.00001
0.79992	0.10004	0.10004	-0.09969	-0.09957	0.00012
0.59913	0.20043	0.20043	-0.10894	-0.10887	0.00007
0.30035	0.34983	0.34983	-0.12279	-0.12254	0.00025
0.10062	0.44969	0.44969	-0.13229	-0.13157	0.00072
0.05000	0.47500	0.47500	-0.13443	-0.13384	0.00062
0.01000	0.49500	0.49500	-0.13604	-0.13563	0.00041
0.79922	0.15059	0.05020	-0.09806	-0.09805	0.00001
0.59966	0.30026	0.10009	-0.10634	-0.10575	0.00059
0.29983	0.52513	0.17504	-0.11743	-0.11718	0.00025
0.09993	0.67505	0.22502	-0.12505	-0.12471	0.00034
0.05110	0.71168	0.23723	-0.12697	-0.12653	0.00044
0.01000	0.74250	0.24750	-0.12801	-0.12807	0.00006

For purposes of comparison, results from an alternate expression for $\gamma_{\pm}$ suitable for use in high ionic strength solutions have been shown in Figure 3-b. The curve defined by the dash-dot-dash pattern in this figure describes the array of values predicted by equations and parameters suggested by Helgeson et al. (1981). These equations use an extended form of the

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Table 3-b

Mean molal activity coefficients of HCl at 25°C in the quaternary system $HCl-NH_4Cl-KCl-H_2O$. The code versions, symbols, and source of data are the same as those described in the caption to Table 3-a.

m_{HCl}	m_{NH_4Cl}	m_{KCl}	$\log \gamma_{\pm, HCl}$ Experimental	$\log \gamma_{\pm, HCl}$ Calculated	$\Delta \log \gamma_{\pm, HCl}$
0.86612	0.033477	0.10041	-0.09996	-0.09879	0.00117
0.57756	0.10562	0.31679	-0.11956	-0.11710	0.00245
0.30937	0.17268	0.51789	-0.13723	-0.13394	0.00329
0.14117	0.21472	0.64401	-0.14833	-0.14441	0.00392
0.062377	0.23442	0.70310	-0.15327	-0.14929	0.00398
0.84641	0.076805	0.076797	-0.10097	-0.10030	0.00067
0.58335	0.20834	0.20831	-0.11835	-0.11747	0.00088
0.28711	0.35645	0.35641	-0.13760	-0.13667	0.00093
0.14265	0.42852	0.42848	-0.14622	-0.14597	0.00025
0.065350	0.46735	0.46731	-0.15142	-0.15094	0.00048
0.84710	0.11469	0.038216	-0.10013	-0.10051	0.00038
0.57350	0.31988	0.10659	-0.11736	-0.11888	0.00152
0.27674	0.54244	0.18075	-0.13560	-0.13873	0.00313
0.14613	0.64040	0.21340	-0.14322	-0.14744	0.00422
0.082647	0.68801	0.22926	-0.14718	-0.15167	0.00449

Debye-Hückel model for $\gamma_{\pm}$ which is modified to take explicit account of the actual speciation of the electrolyte in solution and which incorporates ion size and interaction parameters fitted to the properties of individual electrolytes. As can be seen in Fig. 3-b, values calculated by EQ3NR using Pitzer's equations and values calculated by hand using the method of Helgeson et al. (1981) agree rather well with the data up to the limit of their respective fit regions (m_{AlCl_3} = 1.6 and m_{AlCl_3} = 1.4).

Because both methods commonly yield similarly accurate fits of the experimental data, the method of Helgeson and co-workers offers an additional tool which could be used to evaluate the dependability of results obtained using Pitzer's method. For example, when EQ3/6 is used to calculate activity

coefficients in a compositional system for which extensive experimental data are not available, it might be useful to make an alternate set of calculations using the equations of Helgeson et al. (1981) for the purpose of comparison. Although agreement between values calculated using both methods in such cases will not assure the accuracy of the calculations, it does lend some degree of confidence to their reliability.

Test runs performed using EQ6 to calculate activity coefficients in simple binary systems ($NaCl-H_2O$ and $KCl-H_2O$) over the entire compositional range, defined by saturation with respect to halite (NaCl) and sylvite (KCl), confirm the accuracy of the brine modifications within the compositional ranges defined by these solubility limits. These runs simulate successive additions of the salt components (NaCl or KCl) to a dilute solution until saturation with respect to halite or sylvite is reached. Values of $\gamma_{\pm}$ calculated by EQ6 during these runs agree with the published values of Robinson and Stokes (1965) to within a maximum deviation of 0.003 over the entire concentration range. EQ6 computes values for the solubility limits of halite and sylvite equal to ~6.25 and ~4.80 m, respectively, which are acceptably close to experimentally determined solubilities of these minerals. For example, Linke (1965) reports the solubility of crystalline NaCl and KCl in water as 6.15 molal and 4.84 molal, respectively. The accuracy of these values is comparable to those calculated by Harvie and Weare (1980) and Harvie (1981), who report* similar solubilities for halite (~6.1 m) and sylvite (~4.8 m). Results of a test run in the $NaCl-H_2O$ system are shown in Fig. 4, in which $\gamma_{\pm,NaCl}$ is plotted against the total molality of dissolved NaCl. The solid symbols represent experimental data (Robinson and Stokes, 1965) and illustrate the excellent agreement between calculated and measured values. This agreement is especially impressive considering that solubility data were not used to determine any of the interaction coefficients used in the calculations.

The capability of EQ3/6 to use Pitzer's equations to calculate the thermodynamic properties of a brine at slightly elevated temperatures and to model the interaction of such a solution with evaporite minerals is demonstrated by the following example. Results of EQ6 runs defining the solubility limits as a function of composition in the ternary system

*These values were taken from figures in Harvie and Weare (1980) and Harvie (1981) and, therefore, represent approximations of their results.

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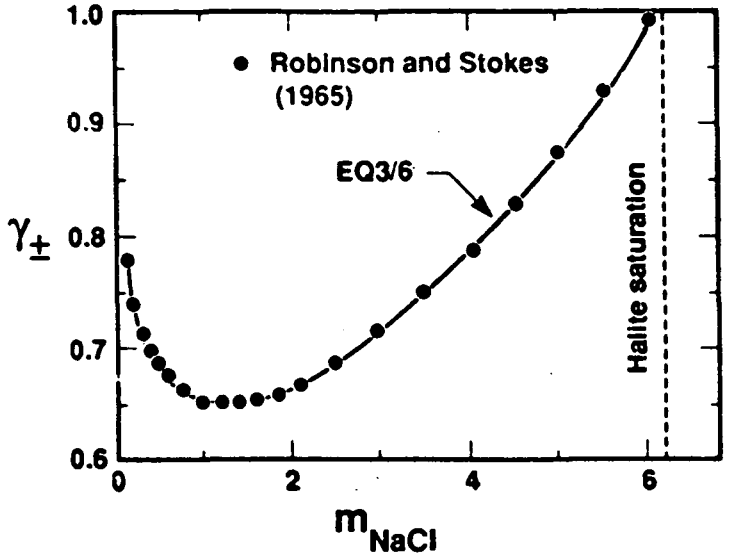

Figure 4. Mean molal activity coefficient ($\gamma_{\pm}$) of NaCl at 25°C as a function of solution composition in the system NaCl-H_2O. Experimental data points are from Robinson and Stokes (1965), the solid curve represents the values computed by EQ3/6, and the dashed line designates the NaCl concentration at which the solution is saturated with respect to halite.

NaCl-KCl-H_2O at 40°C are depicted in Fig. 5. The solid curves in this figure represent the equilibrium solubility limits of halite and sylvite as indicated, whereas the dashed curves represent metastable extensions of their solid counterparts. The data points are from experimental determinations reported by Linke (1965). Although calculations for a few salts can be made at temperatures up to ~300°C, it should be noted that the temperature range over which the properties of other electrolytes can be modeled is commonly restricted by the lack of requisite data to values <100°C.

Harvie and co-workers (Harvie, 1981; Harvie and Weare, 1980; Harvie et al., 1980; Harvie et al., 1984) have successfully used Pitzer's equations to calculate geochemical equilibria in systems involving solutions with up to eight components. These components represent the major constituents of many naturally occurring brines and were used to model the geochemical evolution of the aqueous phase during formation of evaporite minerals and to predict the sequence of mineral deposition during formation of evaporite sequences with impressive accuracy.

Because the EQ3/6 brine modifications use equations compatible with the data and equations used by Harvie and co-workers, it is reasonable to expect

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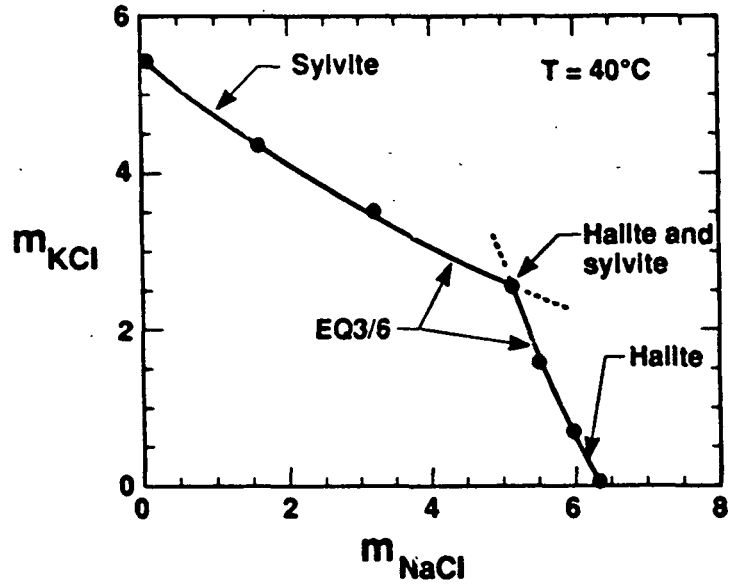

Figure 5. Solubility limits of halite and sylvite in the system NaCl-KCl-H_2O at 40°C. Experimentally determined solubilities (Linke, 1965) are represented by data points, values calculated by EQ3/6 using the Pitzer activity coefficient option are represented by the solid curves, and the dashed curves designate metastable extensions of the solid curves.

EQ3/6 calculations to yield similar results. For example, Harvie et al. (1984) list a set of individual ion activity coefficients (γ_i) for the components of an "artificial sea water" composition. Their calculated values for γ_i together with values generated using EQ3NR for the same solution composition are plotted in Fig. 6. Small differences between the values calculated by EQ3NR and those tabulated by Harvie and co-workers are due to different choices of ion splitting conventions used in the two models. (Note that all values of γ_i for cations calculated by Harvie et al. are slightly larger than the corresponding values resulting from the EQ3NR run, whereas the opposite is true for anionic species shown in Fig. 6.) If corrections are made accounting for the differences in ion splitting conventions, the EQ3NR results are identical to those tabulated by Harvie et al. Mean molal activity coefficients calculated by both models for neutral electrolytes are the same.

The degree to which these test runs represent validation of the brine modeling capability of EQ3/6 depends on several considerations. It has been demonstrated in the examples outlined above that the EQ3/6 codes evaluate activity coefficients of electrolyte species in aqueous solutions to the

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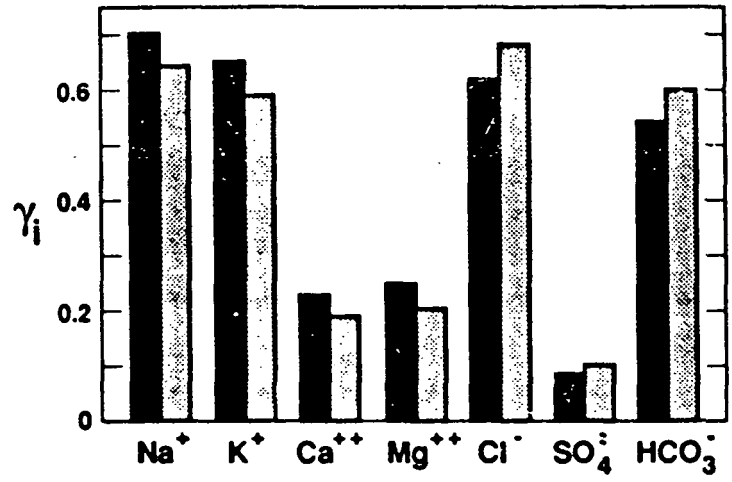

Figure 6. Comparison between individual ion activity coefficients calculated using the Pitzer's equation option in EQ3NR (shaded bars) and values tabulated by Harvie et al. (1984) (solid bars). Ion interaction parameters used in the EQ3NR calculations are from Harvie et al.(1984). The solution composition corresponds to an "artificial seawater" model having 3.5 wt% total dissolved solids with the following stoichiometric molal concentrations: m_{Na} = 0.48695; m_{Cl} = 0.56817; m_K = 0.01063; m_{Ca} = 0.001073; m_{Mg} = 0.05516; m_{SO_4} = 0.02939; and $m_{CO_{2(aq)}}$ = 0.00213. pH is fixed at 8.31. The C49 stage of the 3245 version of the EQ3NR was used in conjunction with EQLIBC40 to make these calculations.

accuracy afforded by Pitzer's equations. That these equations can be used to model the activity-composition relationships in binary, ternary, and some higher order systems is well established, but their use is obviously constrained by the availability of the appropriate interaction parameters, a limitation especially evident at higher temperatures.

SUMMARY

Major modifications have been made to the EQ3/6 codes that enable them to use Pitzer's equations to calculate activity and osmotic coefficients in aqueous solutions. These code modifications make it possible to use EQ3NR and EQ6 in conjunction with data files containing aqueous species interaction

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parameters that are generated with various commonly used data regression conventions [e.g., the Harvie et al. (1984) data base or the Pitzer (1979) data base] by making appropriate choices of option switch settings. Activity coefficient and activity of water values generated using the Pitzer activity coefficient option improve the accuracy of activity coefficient calculations made by these codes and greatly expand the range of ionic strengths over which accurate geochemical modeling calculations can be made, thereby increasing the capability of the modeling codes to include calculations of a diverse class of geochemical problems involving high ionic strength aqueous solutions.

The accuracy of the implementation of the Pitzer activity coefficient option has been demonstrated by a variety of modeling calculations using EQ3/6 to generate accurate activity coefficient and osmotic coefficient values. Other computations that involve calculating the solubility of evaporite minerals in concentrated aqueous solutions further illustrate that the Pitzer activity coefficient option has been verifiably implemented and that values generated using this option can be validated for simple compositional systems. Validation for complex geochemical modeling codes remains problematic, but for all the systems discussed in this report, the EQ3/6 codes dependably predict the observed values of activity/composition variables to the accuracy expected for experimental errors, and the new code versions represent a considerable improvement in the ability to dependably model geochemical equilibria involving brines.

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APPENDIX A: INPUT AND OUTPUT FILE MODIFICATIONS*

The implementation of Pitzer's equations in EQ3/6 is evidenced by minor changes to the input files for EQ3NR and EQ6. In addition, there are a few modifications to the output files produced by the codes. Sample input and output files for EQ3NR and a sample input file for EQ6 are described below which illustrate these changes. Upper case letters are used in the text below to designate names of computer codes, files, and variables in order to set them apart.

EQ3NR

I3SALT, listed in Table A-1, is an input file for EQ3NR which instructs the code to calculate the equilibrium distribution of aqueous species in a dilute [illegible] m, NaCl solution saturated with respect to sylvite (KCl). Differences in format between this input file and the examples listed in the EQ3NR user's manual (Wolery, 1983) include changes to two of the print option switches (IOPR6 and IOPR9) and the addition of an input line which is used to set the IOPG (activity coefficient) options. Other changes are reflected in the format of the lines used to define the composition of the aqueous phase; these changes have been made independently of the activity coefficient updates and will not be discussed further in this report.

IOPR6 now functions as a toggle switch which, if set to IOPR6 = 1, prints a table of mean molal activity coefficients (and their logarithms) for pairs of aqueous species in the compositional system defined by the run. If IOPR6=0, the table is not printed. An example of a table produced by turning on the IOPR6 option is illustrated by the O3SALT listing in Table A-2. O3SALT is the output file created by an EQ3NR run using I3SALT as input. The function of the IOPR9 print option is to produce tables of ion interaction parameters that have been read from the data files. Its use is described in Appendix B.

*The information in Appendices A and B is not intended to serve as a formal user's manual but should be considered an interim description of the use of the Pitzer option and a set of examples which show what the INPUT and OUTPUT files should look like.

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Only a few of the nine IOPG activity coefficient option switches labeled on the INPUT file are currently used. Several of these option switches are dedicated to various debugging functions, which are outside the scope of this report. These will be described in detail elsewhere (Wolery, in preparation). It is sufficient, for the purpose of this report, to point out the IOPG options that are commonly useful in running the Pitzer activity coefficient option and to describe their functions. IOPG1 controls the selection of a choice among the available activity coefficient algorithms, one of which is to be activated in a given run. By setting the IOPG1 switch to IOPG1 = 1, the user instructs the code to use Pitzer's equations to calculate activity coefficients and the activity of water.* IOPG2 is used to designate whether or not the electrostatic contributions to the interaction parameters in Pitzer's equations (Pitzer, 1975) are to be considered, and IOPG3 allows the user to choose which of two available approximations is to be used for the electrostatic function [J(x)] in the activity coefficient calculations. In all of the examples given in this report, the ion interaction parameters are consistent with ignoring the electrostatic contributions in Pitzer's equations (i.e., IOPG2 = 0).

In addition to the tabulation option for $\gamma_{\pm}$ and log $\gamma_{\pm}$ described above, the EQ3NR and EQ6 output file now includes various informational messages and prints the osmotic coefficient and stoichiometric sum of solute molalities of the solution. These changes are illustrated in the listing of the O3SALT file in Table A-2.

*IOPG1=0 selects the B-dot equation (Helgeson, 1969) for calculating activity coefficients, whereas settings of 2, 3, 4, and 5 designate various other activity coefficient options that are not yet fully implemented.

Table A-1

Sample input file for EQ3NR excercising the Pitzer activity coefficient option (IOPG1 = 1). The corresponding output file (O3SALT) is listed in Table A-2.

```
input file name= i3salt     created= 04/16/87     creator= k.j. jackson

the problem:
            calculate the equilibrium speciation in
            a solution containing a trace amount of
            nacl and in equilibrium with sylvite at
            40 degrees c.

note:
            activity coefficients and the activity of
            water are computed using pitzer's equations
            (i.e., iopg1 = 1)



endit.
     tempc=          40.
       rho=           1.    tdspkg=          0.    tdspl=          0.
       fep=       -1.000    uredox=
     tolbt=           0.     toldl=          0.   tolsat=          0.
    itermx=
•                 1    2    3    4    5    6    7    8    9   10
  iopt1-10=       0    0    0    0    0    0    0    0    0    0
  iopg1-10=       1    0    0    0    0    0    0    0    0    0
  iopr1-10=       0    0    0    0    0    1    0    0    0    0
  iodb1-10=       0    0    0    0    0    0    0    0    0    0
     uebal= cl-
    uacion=
     nxmod=  0
data file master species= h+
   switch with species=
   jflag= 16   csp= -7.0
data file master species= na+
   switch with species=
   jflag=  0   csp= .00001
data file master species= k+
   switch with species=
   jflag= 19   csp= 4.8
   phase=  sylvite
data file master species= cl-
   switch with species=
   jflag=  0   csp= 4.8
endit.
```


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Table A-2

Sample output file from EQ3NR (version 3245, stage number R95, supported by the R116 stage of the EQLIB library) which illustrates the results obtained by invoking Pitzer's equations to calculate activity coefficients. The I3SALT file illustrated in Table A-1 was used as input to EQ3NR to produce these results.

```
eq3nr.3245R95  run  10:46     17Apr87
  supported by eqlib.3245R116


----- reading the input file -----
input file name= i3salt     created= 04/16/87     creator= k.j. jackson

the problem:
             calculate the equilibrium speciation in
             a solution containing a trace amount of
             nacl and in equilibrium with sylvite at
             40 degrees c.

note:
             activity coefficients and the activity of
             water are computed using pitzer's equations
             (i.e., iopgl = 1)


endit.
      tempc=  0.40000E+02
        rho=  0.10000E+01    tdspkg=  0.00000E+00     tdspl=  0.00000E+00
        fep= -0.10000E+01    uredox=
      tolbt=  0.00000E+00     toldl=  0.00000E+00    tolsat=  0.00000E+00
    itermx=  0
                 1    2    3    4    5    6    7    8    9   10
  ioptl-10=      0    0    0    0    0    0    0    0    0    0
  iopgl-10=      1    0    0    0    0    0    0    0    0    0
  ioprl-10=      0    0    0    0    0    1    0    0    0    0
  iodbl-10=      0    0    0    0    0    0    0    0    0    0
     uebal= cl-
    uacion=
     nxmod=  0
data file master species= h+
   switch with species=
   jflag= 16   csp= -0.70000E+01
data file master species= na+
   switch with species=
   jflag=  0   csp=  0.10000E-04
data file master species= k+
   switch with species=
   jflag= 19   csp=  0.48000E+01
           uphas1= sylvite                    uphas2=
data file master species= cl-
   switch with species=
   jflag=  0   csp=  0.48000E+01
endit.

----- the input file has been read -----


----- file datal has been successfully read -----

--- pitzer data has been successfully read from file datal ---
```

```
eeee   qqq   33333  n   n  rrrr
e     q   q      3  nn  n  r   r
eeee  q   q    33   n n n  rrrr
e     q q q      3  n  nn  r  r
eeee   qqq   3333   n   n  r   r
          q
```

eq3nr.3245R95
supported by eqlib.3245R116

input file name= i3salt created= 04/16/87 creator= k.j. jackson

the problem:
calculate the equilibrium speciation in
a solution containing a trace amount of
nacl and in equilibrium with sylvite at
40 degrees c.

note:
activity coefficients and the activity of
water are computed using pitzer's equations
(i.e., iopg1 = 1)

data file data0.3245R47
1 atm steam saturation curve data
last modified 13Aug86 (da0r)

the activity coefficients of aqueous solute species
and the activity of water are calculated according to
pitzer
dpt0a.3245R16, last revised 6jun84 kjj
this file contains pitzer coefficient data consistent with
1. no higher-order electrostatic (e-lambda or e-theta) terms
2. no ion pairs or complexes, except acid-base species

uelam= off

temperature= 40.00 degrees celsius
pressure= 1.0134 bars

29 elements are in the data base
50 elements can be loaded into memory
5 elements are active in this problem

38 aqueous species are in the data base
35 aqueous species were loaded into memory
750 aqueous species can be loaded into memory
7 aqueous species are active in this problem
8 aqueous reactions are in the data base
5 aqueous reactions were loaded into memory
699 aqueous reactions can be loaded into memory

000032

```
207 minerals are in the data base
  2 minerals were loaded into memory
750 minerals can be loaded into memory
  2 minerals are active in this problem

  7 solid solutions are in the data base
 20 solid solutions can be loaded into memory

  4 gases are in the data base
  3 gases were loaded into memory
 15 gases can be loaded into memory
  3 gases are active in this problem


iopt1  =  0 (redox option switch)
iopt2  =  0 (automatic basis switching switch)
iopt3  =  0 (interfacing output control switch)
iopt4  =  0 (turn-on solid solutions switch)
iopt5  =  0 (not used)
iopt6  =  0 (conv. test criteria switch)
iopt7  =  0 (0/1 3245/post-3245 pickup file)
iopt8  =  0 (not used)
iopt9  =  0 (not used)
iopt10 =  0 (not used)


iopg1  =  1 (act. coeff. choice)
iopg2  =  0 (approx. of j(x) function)
iopg3  =  0 (iopg1=3 - 0/1 uelam= on/onplus)
iopg4  =  0 (iopg1=3 or 4 - f switch - 0/1 dhoa/dhca)
iopg5  =  0 (not used)
iopg6  =  0 (not used)
iopg7  =  0 (not used)
iopg8  =  0 (not used)
iopg9  =  0 (not used)
iopg10 =  0 (not used)


ioprl  =  0 (list loading of species)
iopr2  =  0 (list reactions and log k values)
iopr3  =  0 (aqueous species print order control)
iopr4  =  0 (aqueous species print cut-off control)
iopr5  =  0 (mass balance percentages print control)
iopr6  =  1 (mean ionic act coeff print control)
iopr7  =  0 (mineral affinity print control)
iopr8  =  0 (ion size and hydr. no. print control)
iopr9  =  0 (pitzer coefficients tabulation)
iopr10 =  0 (not used)


iodb1  =  0 (print info. messages switch)
iodb2  =  0 (print adat1 read info. switch)
iodb3  =  0 (request iteration variables to kill)
iodb4  =  0 (print newton-raphson iterations switch)
iodb5  =  0 (list stoichiometric equivalences)
iodb6  =  0 (controls iodb5 level of detail,
iodb7  =  0 (write reactions on file rlist switch)
iodb8  =  0 (s-lambda turn-off switch)
iodb9  =  0 (mu turn-off switch)
iodb10 =  0 (f turn-off switch)
```

the default redox state is constrained by log fo2 = -1.0000 (log bars)

solution density = 1.00000 g/ml

total dissolved salts = 0. mg/kg solution
total dissolved salts = 0. mg/l

tolbt = 0.10000E-09 (convergence tolerance on residual functions)
toldl = 0.10000E-09 (convergence tolerance on correction terms)
tolsat = 0.50000E+00 (phase saturation tolerance, does not affect convergence)

----- input constraints -----

species	csp	jflag	type of input	controlling phase
h+	-0.70000E+01	16	log activity	
na+	0.10000E-04	0	tot conc, molal	
k+	0.48000E+01	19	mineral equilibrium	sylvite

1.000 sylvite
==
1.000 cl-
+ 1.000 k+
log k = 1.0940

cl-	0.48000E+01	0	tot conc, molal	

electrical balance will be achieved by adjusting the concentration of cl-

--- inactive aqueous species ---

--- modified input constraints ---

species	csp	jflag	type of input	controlling phase
cl-	0.48000E+01	0	tot conc, molal	
h+	-0.70000E+01	16	log activity	
k+	0.48000E+01	19	mineral equilibrium	sylvite

1.000 sylvite
==
1.000 cl-
+ 1.000 k+
log k = 1.0940

na+	0.10000E-04	0	tot conc, molal	
oh-	0.00000E+00	30	eliminated species	
clo4-	0.00000E+00	30	eliminated species	

```
iter =   0   delmax =  0.000E+00   delfnc =  0.000E+00
             del(              ) =  0.000E+00   beta(conc  cl-    ) =  0.276E+00
iter =   1   delmax =  0.202E+00   delfnc =  0.000E+00
             del(gamma oh-     ) = -0.506E-01   beta(conc  cl-    ) =  0.211E+00
iter =   2   delmax =  0.151E+00   delfnc =  0.254E+00
             del(gamma oh-     ) = -0.151E+00   beta(gamma h+     ) =  0.583E-02
```


000034

```
iter =   3   delmax =  0.429E-02   delfnc =  0.972E+00
             del(conc  h+     ) = -0.429E-02   beta(act   h2o    ) = -0.158E-02
iter =   4   delmax =  0.158E-02   delfnc =  0.631E+00
             del(act   h2o    ) = -0.158E-02   beta(act   h2o    ) =  0.186E-03
iter =   5   delmax =  0.186E-03   delfnc =  0.882E+00
             del(act   h2o    ) =  0.186E-03   beta(act   h2o    ) = -0.185E-06
iter =   6   delmax =  0.185E-06   delfnc =  0.999E+00
             del(act   h2o    ) = -0.185E-06   beta(act   h2o    ) = -0.140E-11
iter =   7   delmax =  0.140E-11   delfnc =  0.100E+01
             del(act   h2o    ) = -0.140E-11   beta(act   h2o    ) = -0.753E-13

newton-raphson iteration converged in   7 steps
```

----- Summary of the Aqueous Phase -----

----- Elemental composition of the aqueous phase -----

element	mg/l	mg/kg	moles/kg
o	888105.6044	888105.6044	0.5550868185E+02
cl	198864.6489	198864.6489	0.5609247424E+01
h	111894.4006	111894.4006	0.1110173635E+03
k	219311.6573	219311.6573	0.5609237673E+01
na	0.2299	0.2299	0.1000000000E-04

----- elemental composition as strict basis species -----

species	mg/l	mg/kg	moles/kg
h2o	1000000.0053	1000000.0053	0.5550868185E+02
cl-	198864.6489	198864.6489	0.5609247424E+01
h+	111894.4006	111894.4006	0.1110173635E+03
k+	219311.6573	219311.6573	0.5609237673E+01
na+	0.2299	0.2299	0.1000000000E-04

----- equivalent composition of the aqueous phase (cte balances) -----

original basis		existing basis	
species	moles/kg h2o	species	moles/kg h2o
h2o	0.5550868185E+02	h2o	0.5550868185E+02
cl-	0.5609247424E+01	cl-	0.5609247424E+01
h+	0.1110173635E+03	h+	0.1110173635E+03
k+	0.5609237673E+01	k+	0.5609237673E+01
na+	0.1000000000E-04	na+	0.1000000000E-04

```
                                   ph =    7.00000
                   activity of water =    0.81159
               log activity of water =   -0.09066
                 osmotic coefficient =    1.03295
                   stoichiometric sum of molalities =   11.2184950972299
               titration alkalinity =    0.0000002916326 eq/kg h2o
                     ionic strength =    5.6092477159959
```

----- electrical balance totals -----

	equiv/kg
sigma(mz) cations =	0.5609247716E+01
sigma(mz) anions =	-0.5609247716E+01
total charge =	0.1121849543E+02
mean charge =	0.5609247716E+01
charge imbalance =	-0.2664535259E-14

total charge = sigma(mz) cations + abs (sigma(mz) anions)
mean charge = 1/2 total charge

the electrical imbalance is

0.00 per cent of the total charge
0.00 per cent of the mean charge
0.00 per cent of sigma(mz) cations
0.00 per cent of abs (sigma(mz) anions)

----- electrical balancing on cl- -----

	mg/l	mg/kg	moles/kg
input	170174.4000	170174.4000	0.4800000000E+01
final	198864.6489	198864.6489	0.5609247424E+01
adj	28690.2489	28690.2489	0.8092474244E+00

----- activity ratios of ions -----

log (act(cl-	) x act(h+)xx 1) =	-6.4530
log (act(k+	) / act(h+)xx 1) =	7.5470
log (act(na+	) / act(h+)xx 1) =	1.9242
log (act(oh-	) x act(h+)xx 1) =	-13.6195
log (act(clo4-	) x act(h+)xx 1) =	-29.6425

----- distribution of aqueous species -----

species	molal conc	log conc	log g	activity	log act
cl-	0.5609E+01	0.7489	-0.2019	0.3524E+01	0.5470
k+	0.5609E+01	0.7489	-0.2019	0.3524E+01	0.5470
na+	0.1000E-04	-5.0000	-0.0758	0.8399E-05	-5.0758
oh-	0.2916E-06	-6.5352	-0.0843	0.2402E-06	-6.6195
h+	0.4313E-07	-7.3652	0.3652	0.1000E-06	-7.0000
clo4-	0.7913E-22	-22.1017	-0.5408	0.2278E-22	-22.6425

----- mean ionic properties -----

					true (a)		stoichiometric (b)	
species	species	log a(+/-)	a(+/-)	m(+/-)	g(+/-)	m(+/-)	g(+/-)
h+	cl-	-3.22649	5.936E-04	4.919E-04	1.207E+00	1.765E+01	3.364E-05
h+	clo4-	-14.82125	1.509E-15	1.847E-15	9.170E-01		
k+	cl-	0.54702	3.524E+00	5.609E+00	6.282E-01	5.609E+00	6.282E-01
k+	oh-	-3.03622	9.200E-04	1.279E-03	7.193E-01	1.279E-03	7.193E-01
k+	clo4-	-11.04774	8.959E-12	2.107E-11	4.253E-01		

na+	cl-	-2.26437	5.440E-03	7.489E-03	7.264E-01	7.489E-03	7.264E-01
na+	oh-	-5.84761	1.420E-06	1.708E-06	8.317E-01	1.708E-06	8.317E-01
na+	clo4-	-13.85913	1.383E-14	2.813E-14	4.917E-01		

(a) true quantities consistent with the speciation model
(b) stoichiometric quantities consistent with the cte mass balance lumpings, except that
1. effective cte(h+) = cte(h+) - conc(h2o)
2. effective cte(oh-) = cte(h2o) - conc(h2o)

----- major aqueous species contributing to mass balances -----

aqueous species accounting for 99% or more of cl-

species	molal conc	per cent
cl-	0.5609E+01	100.00
total		100.00

aqueous species accounting for 99% or more of k+

species	molal conc	per cent
k+	0.5609E+01	100.00
total		100.00

aqueous species accounting for 99% or more of na+

species	molal conc	per cent
na+	0.1000E-04	100.00
total		100.00

----- summary of aqueous redox reactions -----

couple	eh, volts	pe-	log fo2	ah, kcal
default	0.779	0.1254E+02	-1.000	17.962
clo4- /cl-	0.779	0.1254E+02	-1.000	17.962

----- summary of aqueous non-equilibrium non-redox reactions -----

couple	affinity, kcal
none	

----- summary of stoichiometric mineral saturation states -----

(minerals with affinities .lt. -10 kcal are not listed)

mineral	log q/k	aff, kcal	state	mineral	log q/k	aff, kcal	state
halite	-6.147	-8.808		sylvite	0.	0.	satc

```
1 approx. saturated pure minerals
0 approx. saturated end-members of specified solid solutions
0 saturated end-members of hypothetical solid solutions


0 supersaturated pure minerals
0 supersatd. end-members of specified solid solutions
0 supersatd. hypothetical solid solution phases


                    ----- summary of gases -----

     gas                        fugacity     log fugacity

  h2(g)                      0.181135E-38     -38.74200
  o2(g)                      0.100000E+00      -1.00000
  steam                      0.592057E-01      -1.22764

 ----- end of output -----
 ----- pickup file successfully written -----
 ----- reading the input file -----
 ----- end of input file -----

          start time = 10:46:10
            end time = 10:47:15
 normal exit
```

EQ6

Changes to the input and output files for EQ6 closely parallel those described above for the corresponding EQ3NR files. Additional modifications related to the "Pitzer Tabulation Option" are described in Appendix B. For illustration, however, a sample EQ6 input file (I6SALT) is listed in Table A-3 which invokes the use of Pitzer's equations in a simple problem. The problem defined by I6SALT, is to "titrate" halite (NaCl) into a solution defined by the EQ3NR run shown in Tables A-1 and A-2. Using the I6SALT file as input, EQ6 calculates the thermodynamic properties of a sylvite-saturated solution into which successive aliquots of a NaCl component are added until the solution is also saturated with halite.* Note that the bottom half of this file comes from the pickup file generated by EQ3NR using I3SALT as input. A table of mean molal activity coefficients is produced when IOPR6=1, and the activity coefficient options are controlled by the IOPG switches in a manner directly analogous to that described above for EQ3NR. No sample EQ6 output file is included in this report because the changes to this file are very similar to those which are illustrated by the O3SALT file listed above.

*Results of this run constitute part of the calculations shown in Fig. 5.

000038

Table A-3

Sample input file for EQ6 which calls on the Pitzer activity coefficient option. Note that the IOPG1 option is automatically set to one in this file by an earlier EQ3NR run or a previous EQ6 run to assure consistency in the use of activity coefficient options.

```
input file name= i6salt      revised= 04/17/87     revisor= k.j. jackson

the problem:
        the initial solution is saturated with respect
        to sylvite (kcl).  halite (nacl) is added to this
        solution until equilibrium with both halite and
        sylvite is achieved.  the temperature is 40 deg c.

note:
        pitzer's equations are used to calculate the
        activity coefficients and the activity of water

endit.
    nmodl1=  1              nmodl2=  0
    tempc0=  4.00000E+01     jtemp=  0
       tk1=  0.00000E+00       tk2=  0.00000E+00       tk3=  0.00000E+00
    zistrt=  0.00000E+00     zimax=  1.00000E+02
     tstrt=  0.00000E+00    timemx=  0.0
    kstpmx=          550     cplim=  0.0
    dzprnt=  1.00000E-01    dzprlg=  1.00000E+01    ksppmx= 1000
    dzplot=  1.00000E+38    dzpllg=  1.00000E+38    ksplmx=10000
     ifile= 60
*
*              1    2    3    4    5    6    7    8    9   10
*
  iopt1-10=    0    0    0    0    0    0    0    0    0    0
 iopt11-20=    0    1    0    0    0    0    0    0    0    0
  iopr1-10=    0    0    0    0    0    0    0    0    1    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
  iodb1-10=    0    0    0    0    0    0    0    0    0    0
     11-20=    0    0    0    0    0    0    0    0    0    0
*
     nxopt=  0
      nffg=  0
      nrct=  2
* ------------------------------------------------------------------
  reactant= halite
     jcode= 0                jreac= 0
      morr=       7.          modr=      0.
       nsk=  0                  sk=          0.        fk=          0.
       nrk=  1                nrpk= 0
       rk1=         2.0        rk2=          0.       rk3=          0.
* ------------------------------------------------------------------
  reactant= sylvite
     jcode= 0                jreac= 0
      morr=       7.          modr=      0.
       nsk=  0                  sk=          0.        fk=          0.
       nrk=  1                nrpk= 0
       rk1=         1.0        rk2=          0.       rk3=          0.
* ------------------------------------------------------------------
```

```
    dlzidp=  0.10000E+39
     tolbt=  1.00000E-06     toldl=  1.00000E-06      tolx=  1.00000E-06
    tolsat=  5.00000E-05    tclsst=  1.00000E-04
    screw1=  1.00000E-05    screw2=  5.00000E-01    screw3=  1.00000E-05
    screw4=  1.00000E-04    screw5=  2.00000E+00    screw6=  2.00000E+00
    zklogu= -8.00000E+00    zklogl=  2.00000E+00
    dlzmx1=  1.00000E-04    dlzmx2=  1.00000E+38


    itermx= 30              ntrymx= 15
    npslmx=  3              nsslmx=  3              ioscan=  0
* pickup file written by eq3nr.3245R95
*  supported by eqlib.3245R1i6
input file name= i3salt     created= 04/16/87     creator= k.j. jackson

the problem:
             calculate the equilibrium speciation in
             a solution containing a trace amount of
             nacl and in equilibrium with sylvite at
             40 degrees c.

note:
             activity coefficients and the activity of
             water are computed using pitzer's equations
             (i.e., iopgl = 1)



endit.
    uacion= none
    tempci=  0.40000E+02
     nxmod=  0
     iopg1=  1              iopg2=  0              iopg3=  0
     iopg4=  0              iopg5=  0              iopg6=  0
     iopg7=  0              iopg8=  0              iopg9=  0
    iopg10=  0
       kct=  5                ksq=  6               kgmt= 14
       kmt= 16                kxt= 16               kdim= 16
      kprs=  0
   o                  0.555086818494281E+02
   cl                 0.560924742436330E+01
   h                  0.111017363450353E+03
   k                  0.560923767286663E+01
   na                 0.100000000000000E-04
   electr            -0.266453525910038E-14
   h2o                h2o                    0.174436091209183E+01
   cl-                cl-                    0.748904597197199E+00
   h+                 h+                    -0.736522809286058E+01
   k+                 k+                     0.748903842189521E+00
   na+                na+                   -0.500000000000000E+01
   o2(g)              o2(g)                 -0.100000000000000E+01
   act                h2o                   -0.906642269310798E-01
   gamma              cl-                   -0.201884283028009E+00
   gamma              h+                     0.365228092860578E+00
   gamma              k+                    -0.201884727787282E+00
   gamma              na+                   -0.757573813022236E-01
   gamma              o2(g)                  0.000000000000000E+00
   gamma              oh-                   -0.842905523018552E-01
   gamma              clo4-                 -0.540817846160329E+00
   xisteq                                    0.000000000000000E+00
   xi                                        0.748904619776773E+00
```


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APPENDIX B: PITZER TABULATION OPTION

The numerical values for activity coefficients calculated using Pitzer's equations depend on two-ion and three-ion interaction parameters regressed from various experimental data. Pitzer's equations can be used to calculate accurate values for activity coefficients over a wide range of ionic strengths and in multicomponent solutions only if the appropriate interaction parameters are available. It is critical, therefore, to determine whether the data file that contains the interaction parameters adequately describes the compositional system defined by the problem being modeled. It is deceptively easy, however, to lose track of whether or not the aqueous components necessary to describe a system are adequately covered by the data set being used. In order to make it more convenient to evaluate the "completeness" of the Pitzer parameters, and to insure against accidental misuse of the Pitzer activity coefficient option, an additional input/output option was added to the EQ3NR and EQ6 codes. These code modifications are referred to in this report as the Pitzer Tabulation Option.

OPERATION

The Pitzer Tabulation Option is controlled by turning print options on or off in the EQ3NR and EQ6 input files. There are two levels of detail with which the codes may be required to tabulate interaction coefficient information. Alternatively, the tabulation may be turned off entirely. In EQ3NR, the Pitzer Tabulation Option is activated by the IOPR9 switch. This switch has three legitimate settings which determine whether the option will be invoked, and, if so, which of the two available levels of detail will be printed. If IOPR9 = 1, the number of two-ion (λ) interaction terms and three-ion (μ) interaction terms that appear in the data files is tabulated for each of the aqueous components in the model.* If IOPR9 is set to a value of 2, a detailed table is printed on the output file specifying which ion interaction parameters are covered in the data base. Table B-2 shows an

*Eqns. 2 and 7 illustrate how the two-ion and three-ion interaction parameters are used to calculate the activity coefficient and osmotic coefficient values.

example of an output file created using IOPR9 = 1, and Table B-4 illustrates the results of setting IOPR9 = 2. Values of IOPR9 less than zero default to zero, and values of IOPR9 greater than 2 result in IOPR9 being reset to 2.

The Pitzer Tabulation Option is invoked in EQ6 in a way analogous to that used in EQ3NR. The only difference is that the appropriate print switch in EQ6 is IOPR10. Numerical values for the settings are the same as those used in EQ3NR.

CODE MODIFICATIONS

Aside from minor modifications to the subroutines that read the input files for EQ3NR and EQ6 (READZ and READX, respectively), the code modifications which account for the installation of the Pitzer Tabulation Option in EQ3/6 are confined to changes in subroutines SCRIPX and SCRIPZ, which write the output files for EQ3NR and EQ6, and the addition of a new subroutine (PTZTAB) which tabulates the ion interaction parameters after they have been read from the DATA1 or DATA2 file. Subroutine PTZTAB resides in the EQLIB library.

Table B-1

Sample input file for the EQ3NR code which illustrates how to set up an EQ3NR run with the Pitzer Tabulation Option invoked. This input file is used to generate the output file shown in Table B-2. Note that the IOPR9 variable is set to a value of 1, which produces only summary tables of the Pitzer interaction terms read from the data files for the aqueous species present in the model.

```
input file name= tab.tst    created= 04/21/87    creator= k.j. jackson

the problem:
            this is a sample input file designed to
            to illustrate the use of the pitzer tabulation
            option in the eq3nr code.

            the model is of a sodium chloride brine with
            trace amounts of several other solutes common
            in geologic waters.

            the temperature is 25 degrees c.

note:
            activity coefficients and the activity of
            water are computed using pitzer's equations
            (i.e., iopgl = 1)


endit.
     tempc=          25.
       rho=           1.    tdspkg=          0.    tdspl=          0.
       fep=       -0.700    uredox=
     tolbt=           0.     toldl=          0.   tolsat=          0.
    itermx=
*                1    2    3    4    5    6    7    8    9   10
  iopt1-10=      0    0    0    0    0    0    0    0    0    0
  iopg1-10=      1    0    0    0    0    0    0    0    0    0
  iopr1-10=      0    0    0    0    0    1    0    0    1    0
  iodb1-10=      0    0    0    0    0    0    0    0    0    0
     uebal= na+
    uacion=
     nxmod=  0
data file master species= h+
   switch with species=
   jflag= 16   csp= -6.6
data file master species= na+
   switch with species=
   jflag=  0   csp= 3.9
data file master species= k+
   switch with species=
   jflag=  2   csp= 75.11
data file master species= ca++
   switch with species=
   jflag=  2   csp= 12.5
data file master species= mg++
   switch with species=
   jflag=  2   csp= 1.92
```

```
data file master species= no3-
   switch with species=
   jflag=  2   csp= 9.6
data file master species= f-
   switch with species=
   jflag=  2   csp= 2.2
data file master species= cl-
   switch with species=
   jflag=  0   csp= 3.9
endit.
```


000044

Table B-2

Sample output file from the EQ3NR code (version 3245, stage number R95, supported by stage number R116 of EQLIB) which illustrates the results obtained by using the file in Table B-1 as input. Note that the IOPR9 variable is set to a value of 1, which produces only summary tables of the Pitzer interaction terms.

```
eq3nr.3245R95  run  10:16     21Apr87
  supported by eqlib.3245R116


----- reading the input file -----
input file name= tab.tst    created= 04/21/87     creator= k.j. jackson

the problem:
             this is a sample input file designed to
            to illustrate the use of the pitzer tabulation
            option in the eq3nr code.

            the model is of a sodium chloride brine with
            trace amounts of several other solutes common
            in geologic waters.

            the temperature is 25 degrees c.

note:
             activity coefficients and the activity of
             water are computed using pitzer's equations
             (i.e., iopgl = 1)


endit.
      tempc=  0.25000E+02
        rho=  0.10000E+01    tdspkg=  0.00000E+00     tdspl=  0.00000E+00
        fep= -0.70000E+00    uredox=
      tolbt=  0.00000E+00     toldl=  0.00000E+00    tolsat=  0.00000E+00
    itermx=  0
                 1    2    3    4    5    6    7    8    9   10
  iopt1-10=      0    0    0    0    0    0    0    0    0    0
  iopg1-10=      1    0    0    0    0    0    0    0    0    0
  iopr1-10=      0    0    0    0    0    1    0    0    1    0
  iodb1-10=      0    0    0    0    0    0    0    0    0    0
     uebal= na+
    uacion=
     nxmod=  0
data file master species= h+
   switch with species=
   jflag= 16   csp= -0.66000E+01
data file master species= na+
   switch with species=
   jflag=  0   csp=  0.39000E+01
data file master species= k+
   switch with species=
   jflag=  2   csp=  0.75110E+02
data file master species= ca++
   switch with species=
   jflag=  2   csp=  0.12500E+02
```

```
 data file master species= mg++
    switch with species=
    jflag=  2   csp=  0.19200E+01
 data file master species= no3-
    switch with species=
    jflag=  2   csp=  0.96000E+01
 data file master species= f-
    switch with species=
    jflag=  2   csp=  0.22000E+01
 data file master species= cl-
    switch with species=
    jflag=  0   csp=  0.39000E+01
endit.

 ----- the input file has been read -----


 ----- file datal has been successfully read -----


 species        lamda pairs                        mu triplets

 ca++               6                                  10
 cl-                8                                  26
 f-                 2                                   4
 h+                 6                                  10
 k+                 8                                  16
 mg++               5                                   9
 na+               10                                  20
 no3-               7                                  17
 no2-               2                                   4
 nh4+               4                                   7
 oh-                3                                   6
 clo4-              5                                  11
 --- pitzer data has been successfully read from file datal ---


 eeee   qqq   33333  n   n  rrrr
 e     q   q      3  nn  n  r   r
 eeee  q   q    33   n n n  rrrr
 e     q q q      3  n  nn  r  r
 eeee   qqq   3333   n   n  r   r
           q


 eq3nr.3245R95
  supported by eqlib.3245R116


 input file name= tab.tst    created= 04/21/87    creator= k.j. jackson
 the problem:
              this is a sample input file designed to
              to illustrate the use of the pitzer tabulation
              option in the eq3nr code.

              the model is of a sodium chloride brine with
              trace amounts of several other solutes common
              in geologic waters.

              the temperature is 25 degrees c.
```


000046

```
note:
            activity coefficients and the activity of
            water are computed using pitzer's equations
            (i.e., iopg1 = 1)


data file data0.3245R47
         1 atm steam saturation curve data
last modified  13Aug86   (da0r)


  the activity coefficients of aqueous solute species
and the activity of water are calculated according to
pitzer
dpt0a.3245R16, last revised  6jun84    kjj
this file contains pitzer coefficient data consistent with
  1. no higher-order electrostatic (e-lambda or e-theta) terms
  2. no ion pairs or complexes, except acid-base species

  uelam= off


temperature=  25.00 degrees celsius
pressure=    1.0134 bars


        29 elements are in the data base
        50 elements can be loaded into memory
         9 elements are active in this problem


        38 aqueous species are in the data base
        35 aqueous species were loaded into memory
       750 aqueous species can be loaded into memory
        13 aqueous species are active in this problem

         8 aqueous reactions are in the data base
         5 aqueous reactions were loaded into memory
       699 aqueous reactions can be loaded into memory


           207 minerals are in the data base
            27 minerals were loaded into memory
           750 minerals can be loaded into memory
            26 minerals are active in this problem

             7 solid solutions are in the data base
            20 solid solutions can be loaded into memory

             4 gases are in the data base
             4 gases were loaded into memory
            15 gases can be loaded into memory
             4 gases are active in this problem


     iopt1  =  0 (redox option switch)
     iopt2  =  0 (automatic basis switching switch)
     iopt3  =  0 (interfacing output control switch)
     iopt4  =  0 (turn-on solid solutions switch)
     iopt5  =  0 (not used)
     iopt6  =  0 (conv. test criteria switch)
     iopt7  =  0 (0/1 3245/post-3245 pickup file)
     iopt8  =  0 (not used)
```

```
iopt9  =  0 (not used)
iopt10 =  0 (not used)


     iopg1  =  1 (act. coeff. choice)
     iopg2  =  0 (approx. of j(x) function)
     iopg3  =  0 (iopg1=3 - 0/1 uelam= on/onplus)
     iopg4  =  0 (iopg1=3 or 4 - f switch - 0/1 dhoa/dhca)
     iopg5  =  0 (not used)
     iopg6  =  0 (not used)
     iopg7  =  0 (not used)
     iopg8  =  0 (not used)
     iopg9  =  0 (not used)
     iopg10 =  0 (not used)


          iopr1  =  0 (list loading of species)
          iopr2  =  0 (list reactions and log k values)
          iopr3  =  0 (aqueous species print order control)
          iopr4  =  0 (aqueous species print cut-off control)
          iopr5  =  0 (mass balance percentages print control)
          iopr6  =  1 (mean ionic act coeff print control)
          iopr7  =  0 (mineral affinity print control)
          iopr8  =  0 (ion size and hydr. no. print control)
          iopr9  =  1 (pitzer coefficients tabulation)
          iopr10 =  0 (not used)


               iodb1  =  0 (print info. messages switch)
               iodb2  =  0 (print adat1 read info. switch)
               iodb3  =  0 (request iteration variables to kill)
               iodb4  =  0 (print newton-raphson iterations switch)
               iodb5  =  0 (list stoichiometric equivalences)
               iodb6  =  0 (controls iodb5 level of detail)
               iodb7  =  0 (write reactions on file rlist switch)
               iodb8  =  0 (s-lambda turn-off switch)
               iodb9  =  0 (mu turn-off switch)
               iodb10 =  0 (f turn-off switch)

the default redox state is constrained by log fo2 =      -0.7000 (log bars)

          solution density =  1.00000 g/ml

          total dissolved salts =       0.   mg/kg solution
          total dissolved salts =       0.   mg/l

     tolbt  =  0.10000E-09 (convergence tolerance on residual functions)
     toldl  =  0.10000E-09 (convergence tolerance on correction terms)
     tolsat =  0.50000E+00 (phase saturation tolerance, does not affect
                            convergence)


                                  ----- input constraints -----

  species          csp        jflag  type of input      controlling phase

h+                         -0.66000E+01   16   log activity
na+                         0.39000E+01    0   tot conc, molal
k+                          0.75110E+02    2   tot conc, mg/l
```


000048

ca++	0.12500E+02	2	tot conc, mg/l
mg++	0.19200E+01	2	tot conc, mg/l
no3-	0.96000E+01	2	tot conc, mg/l
f-	0.22000E+01	2	tot conc, mg/l
cl-	0.39000E+01	0	tot conc, molal

electrical balance will be achieved by adjusting
the concentration of na+

--- inactive aqueous species ---

--- modified input constraints ---

species	csp	jflag	type of input	controlling phase
ca++	0.31188E-03	0	tot conc, molal	
cl-	0.39000E+01	0	tot conc, molal	
f-	0.11580E-03	0	tot conc, molal	
h+	-0.66000E+01	16	log activity	
k+	0.19211E-02	0	tot conc, molal	
mg++	0.78996E-04	0	tot conc, molal	
na+	0.39000E+01	0	tot conc, molal	
no3-	0.15483E-03	0	tot conc, molal	
no2-	0.00000E+00	30	eliminated species	
nh4+	0.00000E+00	30	eliminated species	
oh-	0.00000E+00	30	eliminated species	
clo4-	0.00000E+00	30	eliminated species	

```
iter =   0   delmax =  0.000E+00   delfnc =  0.000E+00
             del(              ) =  0.000E+00   beta(conc   na+    ) =  0.623E-03
iter =   1   delmax =  0.612E-03   delfnc =  0.000E+00
             del(gamma mg++   ) =  0.612E-03   beta(gamma mg++   ) = -0.628E-04
iter =   2   delmax =  0.626E-04   delfnc =  0.898E+00
             del(gamma mg++   ) = -0.626E-04   beta(act    h2o    ) =  0.207E-04
iter =   3   delmax =  0.207E-04   delfnc =  0.669E+00
             del(act    h2o    ) =  0.104E-04   beta(act    h2o    ) =  0.104E-04
iter =   4   delmax =  0.104E-04   delfnc =  0.500E+00
             del(act    h2o    ) =  0.104E-04   beta(gamma mg++   ) =  0.835E-13
iter =   5   delmax =  0.837E-13   delfnc =  0.100E+01
             del(gamma mg++   ) =  0.837E-13   beta(act    h2o    ) = -0.294E-13
```

newton-raphson iteration converged in 5 steps

----- Summary of the Aqueous Phase -----

----- Elemental composition of the aqueous phase -----

element	mg/l	mg/kg	moles/kg
o	888113.0322	888113.0322	0.5550914610E+02
ca	12.5000	12.5000	0.3118762475E-03
cl	138266.7000	138266.7000	0.3900000000E+01
f	2.2000	2.2000	0.1157992252E-03

h	111894.4005	111894.4005	0.1110173633E+03
k	75.1100	75.1100	0.1921055391E-02
mg	1.9200	1.9200	0.7899609134E-04
na	89604.1867	89604.1867	0.3897567775E+01
n	2.1686	2.1686	0.1548264734E-03

----- elemental composition as strict basis species -----

species	mg/l	mg/kg	moles/kg
h2o	1000008.3689	1000008.3689	0.5550914610E+02
ca++	12.5000	12.5000	0.3118762475E-03
cl-	138266.7000	138266.7000	0.3900000000E+01
f-	2.2000	2.2000	0.1157992252E-03
h+	111894.4005	111894.4005	0.1110173633E+03
k+	75.1100	75.1100	0.1921055391E-02
mg++	1.9200	1.9200	0.7899609134E-04
na+	89604.1867	89604.1867	0.3897567775E+01
no3-	9.6000	9.6000	0.1548264734E-03

----- equivalent composition of the aqueous phase (cte balances) -----

original basis		existing basis	
species	moles/kg h2o	species	moles/kg h2o
h2o	0.5550914610E+02	h2o	0.5550914610E+02
ca++	0.3118762475E-03	ca++	0.3118762475E-03
cl-	0.3900000000E+01	cl-	0.3900000000E+01
f-	0.1157992252E-03	f-	0.1157992252E-03
h+	0.1110173633E+03	h+	0.1110173633E+03
k+	0.1921055391E-02	k+	0.1921055391E-02
mg++	0.7899609134E-04	mg++	0.7899609134E-04
na+	0.3897567775E+01	na+	0.3897567775E+01
no3-	0.1548264734E-03	no3-	0.1548264734E-03

ph = 6.60000
activity of water = 0.85575
log activity of water = -0.06765
osmotic coefficient = 1.10858
stoichiometric sum of molalities = 7.8001503284109
titration alkalinity = 0.0000000654679 eq/kg h2o
ionic strength = 3.9006615635053

----- electrical balance totals -----

	equiv/kg
sigma(mz) cations =	0.3900270691E+01
sigma(mz) anions =	-0.3900270691E+01
total charge =	0.7800541382E+01
mean charge =	0.3900270691E+01
charge imbalance =	-0.4440892099E-15

total charge = sigma(mz) cations + abs (sigma(mz) anions)
mean charge = 1/2 total charge

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the electrical imbalance is

0.00 per cent of the total charge
0.00 per cent of the mean charge
0.00 per cent of sigma(mz) cations
0.00 per cent of abs (sigma(mz) anions)

----- electrical balancing on na+ -----

	mg/l	mg/kg	moles/kg
input	89660.1030	89660.1030	0.3900000000E+01
final	89604.1867	89604.1867	0.3897567775E+01
adj	-55.9163	-55.9163	-0.2432225018E-02

----- activity ratios of ions -----

log (act(ca++) / act(h+)xx 2) =	9.4576
log (act(cl-) x act(h+)xx 1) =	-6.1193
log (act(f-) x act(h+)xx 1) =	-10.8674
log (act(k+) / act(h+)xx 1) =	3.5898
log (act(mg++) / act(h+)xx 2) =	9.0372
log (act(na+) / act(h+)xx 1) =	7.0803
log (act(no3-) x act(h+)xx 1) =	-10.7899
log (act(no2-) x act(h+)xx 1) =	-24.3036
log (act(nh4+) / act(h+)xx 1) =	-56.5922
log (act(oh-) x act(h+)xx 1) =	-14.0545
log (act(clo4-) x act(h+)xx 1) =	-29.0280

----- distribution of aqueous species -----

species	molal conc	log conc	log g	activity	log act
cl-	0.3900E+01	0.5911	-0.1104	0.3025E+01	0.4807
na+	0.3898E+01	0.5908	-0.1105	0.3022E+01	0.4803
k+	0.1921E-02	-2.7165	-0.2937	0.9768E-03	-3.0102
ca++	0.3119E-03	-3.5060	-0.2364	0.1810E-03	-3.7424
no3-	0.1548E-03	-3.8102	-0.3798	0.6458E-04	-4.1899
f-	0.1158E-03	-3.9363	-0.3311	0.5402E-04	-4.2674
mg++	0.7900E-04	-4.1024	-0.0604	0.6874E-04	-4.1628
h+	0.1161E-06	-6.9351	0.3351	0.2512E-06	-6.6000
oh-	0.6547E-07	-7.1840	-0.2705	0.3512E-07	-7.4545
no2-	0.3487E-17	-17.4575	-0.2461	0.1979E-17	-17.7036
clo4-	0.5845E-22	-22.2332	-0.1948	0.3732E-22	-22.4280
nh4+	0.11[illegible]8E-62	-62.9476	-0.2446	0.6424E-63	-63.1922

----- mean ionic properties -----

				true (a)		stoichiometric (b)	
species	species	log a(+/-)	a(+/-)	m(+/-)	g(+/-)	m(+/-)	g(+/-)
ca++	cl-	-0.92700	1.183E-01	1.680E-01	7.041E-01	1.680E-01	7.041E-01
ca++	f-	-4.09241	8.083E-05	1.611E-04	5.017E-01	1.611E-04	5.017E-01
[illegible]	no3-	-4.04074	9.105E-05	1.955E-04	4.656E-01	1.955E-04	4.656E-01
ca++	no2-	-13.04987	8.915E-14	1.559E-13	5.717E-01		
ca++	oh-	-6.21710	6.066E-07	1.102E-06	5.507E-01	4.068E-04	1.491E-03
ca++	clo4-	-16.19947	6.317E-17	1.021E-16	6.185E-01		
h+	cl-	-3.05966	8.717E-04	6.729E-04	1.295E+00	1.471E+01	5.924E-05
h+	f-	-5.43371	3.684E-06	3.667E-06	1.005E+00	8.017E-02	4.595E-05
h+	no3-	-5.39496	4.028E-06	4.240E-06	9.499E-01	9.270E-02	4.344E-05
h+	no2-	-12.15181	7.050E-13	6.363E-13	1.108E+00		

h+	clo4-	-14.51401	3.062E-15	2.605E-15	1.175E+00		
k+	cl-	-1.26475	5.436E-02	8.656E-02	6.280E-01	8.656E-02	6.280E-01
k+	f-	-3.63880	2.297E-04	4.717E-04	4.871E-01	4.717E-04	4.871E-01
k+	no3-	-3.60005	2.512E-04	5.454E-04	4.605E-01	5.454E-04	4.605E-01
k+	no2-	-10.35690	4.396E-11	8.185E-11	5.371E-01		
k+	oh-	-5.23232	5.857E-06	1.121E-05	5.223E-01	9.447E-04	6.200E-03
k+	clo4-	-12.71910	1.909E-13	3.351E-13	5.698E-01		
mg++	cl-	-1.06714	8.568E-02	1.063E-01	8.059E-01	1.063E-01	8.059E-01
mg++	f-	-4.23254	5.854E-05	1.019E-04	5.743E-01	1.019E-04	5.743E-01
mg++	no3-	-4.18087	6.594E-05	1.237E-04	5.330E-01	1.237E-04	5.330E-01
mg++	no2-	-13.19001	6.456E-14	9.867E-14	6.543E-01		
mg++	oh-	-6.35723	4.393E-07	6.970E-07	6.303E-01	2.574E-04	1.707E-03
mg++	clo4-	-16.33960	4.575E-17	6.462E-17	7.080E-01		
na+	cl-	0.48051	3.024E+00	3.899E+00	7.755E-01	3.899E+00	7.755E-01
na+	f-	-1.89354	1.278E-02	2.124E-02	6.015E-01	2.124E-02	6.015E-01
na+	no3-	-1.85479	1.397E-02	2.457E-02	5.687E-01	2.457E-02	5.687E-01
na+	no2-	-8.61164	2.445E-09	3.687E-09	6.633E-01		
na+	oh-	-3.48706	3.258E-04	5.051E-04	6.450E-01	4.255E-02	7.657E-03
na+	clo4-	-10.97384	1.062E-11	1.509E-11	7.037E-01		
nh4+	cl-	-31.35574	4.408E-32	6.633E-32	6.645E-01		
nh4+	f-	-33.72980	1.863E-34	3.615E-34	5.154E-01		
nh4+	no3-	-33.69105	2.037E-34	4.180E-34	4.873E-01		
nh4+	no2-	-40.44790	3.565E-41	6.272E-41	5.684E-01		
nh4+	oh-	-35.32331	4.750E-36	8.594E-36	5.527E-01		
nh4+	clo4-	-42.81009	1.548E-43	2.568E-43	6.030E-01		

(a) true quantities consistent with the speciation model
(b) stoichiometric quantities consistent with the cte mass balance lumpings, except that
1. effective cte(h+) = cte(h+) - conc(h2o)
2. effective cte(oh-) = cte(h2o) - conc(h2o)

----- major aqueous species contributing to mass balances -----

aqueous species accounting for 99% or more of ca++

species	molal conc	per cent
ca++	0.3119E-03	100.00
total		100.00

aqueous species accounting for 99% or more of cl-

species	molal conc	per cent
cl-	0.3900E+01	100.00
total		100.00

aqueous species accounting for 99% or more of f-

species	molal conc	per cent
f-	0.1158E-03	100.00
total		100.00

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aqueous species accounting for 99% or more of k+

species	molal conc	per cent
k+	0.1921E-02	100.00
total		100.00

aqueous species accounting for 99% or more of mg++

species	molal conc	per cent
mg++	0.7900E-04	100.00
total		100.00

aqueous species accounting for 99% or more of na+

species	molal conc	per cent
na+	0.3898E+01	100.00
total		100.00

aqueous species accounting for 99% or more of no3-

species	molal conc	per cent
no3-	0.1548E-03	100.00
total		100.00

----- summary of aqueous redox reactions -----

couple		eh, volts	pe-	log fo2	ah, kcal
default		0.830	0.1403E+02	-0.700	19.147
no2-	/no3-	0.830	0.1403E+02	-0.700	19.147
nh4+	/no3-	0.830	0.1403E+02	-0.700	19.147
clo4-	/cl-	0.830	0.1403E+02	-0.700	19.147

----- summary of aqueous non-equilibrium non-redox reactions -----

couple	affinity, kcal
none	

----- summary of stoichiometric mineral saturation states -----

(minerals with affinities .lt. -10 kcal are not listed)

mineral	log q/k	aff, kcal	state	mineral	log q/k	aff, kcal	state
antarcticite	-7.300	-9.959		fluorite	-1.318	-1.799	
halite	-0.632	-0.862		mgf2(c)	-4.519	-6.165	
sylvite	-3.489	-4.760					

0 approx. saturated pure minerals
0 approx. saturated end-members of specified solid solutions
0 saturated end-members of hypothetical solid solutions

0 supersaturated pure minerals
0 supersatd. end-members of specified solid solutions
0 supersatd. hypothetical solid solution phases

----- summary of gases -----

gas	fugacity	log fugacity
h2(g)	0.538203E-41	-41.26905
n2(g)	0.585084E-17	-17.23278
o2(g)	0.199526E+00	-0.70000
steam	0.267945E-01	-1.57195

----- end of output -----
----- pickup file successfully written -----
----- reading the input file -----
----- end of input file -----

start time = 10:16:58
end time = 10:17:21
normal exit

000054

Table B-3

Sample input file for the EQ3NR code which illustrates how to set up an EQ3NR run with the detailed Pitzer Tabulation Option invoked. This input file is used to generate the output file shown in Table B-4. The Pitzer Tabulation Option is set to produce the full complement of tabulated values by setting IOPR9 to a value of 2, but the file is otherwise identical to the file in Table B-1.

```
input file name= tab.tst2   created= 04/21/87     creator= k.j. jackson

the problem:
             this is a sample input file designed to
             to illustrate the use of the pitzer tabulation
             option in the eq3nr code.

             the model is of a sodium chloride brine with
             trace amounts of several other solutes common
             in geologic waters.

             the temperature is 25 degrees c.

note:
             activity coefficients and the activity of
             water are computed using pitzer's equations
             (i.e., icpgl = 1)


endit.
     tempc=          25.
       rho=           1.    tdspkg=          0.     tdspl=          0.
       fep=       -0.700    uredox=
     tolbt=           0.     toldl=          0.    tolsat=          0.
    itermx=
*                 1    2    3    4    5    6    7    8    9   10
  iopt1-10=       0    0    0    0    0    0    0    0    0    0
  iopg1-10=       1    0    0    0    0    0    0    0    0    0
  iopr1-10=       0    0    0    0    0    1    0    0    2    0
  iodb1-10=       0    0    0    0    0    0    0    0    0    0
     uebal= na+
    uacion=
     nxmod=  0
data file master species= h+
   switch with species=
   jflag= 16   csp= -6.6
data file master species= na+
   switch with species=
   jflag=  0   csp= 3.9
data file master species= k+
   switch with species=
   jflag=  2   csp= 75.11
data file master species= ca++
   switch with species=
   jflag=  2   csp= 12.5
data file master species= mg++
   switch with species=
   jflag=  2   csp= 1.92
```


000055

```
data file master species= no3-
   switch with species=
   flag=  2   csp= 5.6
data file master species= f-
   switch with species=
   flag=  2   csp= 2.2
data file master species= cl-
   switch with species=
   flag=  0   csp= 3.9
endit.
```


000096

Table B-4

Sample output file from the EQ3NR code (version 3245, stage number R95, supported by stage number R116 of EQLIB) which illustrates the results obtained by using the file in Table B-3 as input. Note that the IOPR9 variable is set to a value of 2, which produces the expanded summary tables of Pitzer interaction terms.

```
eq3nr.3245R95  run  11:21     21Apr87
  supported by eqlib.3245R116

----- reading the input file -----
input file name= tab.tst2   created= 04/21/87     creator= k.j. jackson

the problem:
             this is a sample input file designed to
            to illustrate the use of the pitzer tabulation
            option in the eq3nr code.

            the model is of a sodium chloride brine with
            trace amounts of several other solutes common
            in geologic waters.

            the temperature is 25 degrees c.

note:
             activity coefficients and the activity of
             water are computed using pitzer's equations
             (i.e., iopg1 = 1)

endit.
      tempc=  0.25000E+02
        rho=  0.10000E+01    tdspkg=  0.00000E+00     tdspl=  0.00000E+00
        fep= -0.70000E+00    uredox=
      tolbt=  0.00000E+00     toldl=  0.00000E+00    tolsat=  0.00000E+00
    itermx=  0
                 1    2    3    4    5    6    7    8    9   10
  iopt1-10=      0    0    0    0    0    0    0    0    0    0
  iopg1-10=      1    0    0    0    0    0    0    0    0    0
  iopr1-10=      0    0    0    0    0    1    0    0    2    0
  iodb1-10=      0    0    0    0    0    0    0    0    0    0
     uebal= na+
    uacion=
     nxmod=  0
data file master species= h+
   switch with species=
   jflag= 16   csp= -0.66000E+01
data file master species= na+
   switch with species=
   jflag=  0   csp=  0.39000E+01
data file master species= k+
   switch with species=
   jflag=  2   csp=  0.75110E+02
data file master species= ca++
   switch with species=
   jflag=  2   csp=  0.12500E+02
data file master species= mg++
   switch with species=
   jflag=  2   csp=  0.19200E+01
data file master species= no3-
   switch with species=
   jflag=  2   csp=  0.96000E+01
```

```
data file master species= f-
   switch with species=
   jflag=  2   csp=  0.22000E+01
data file master species= cl-
   switch with species=
   jflag=  0   csp=  0.39000E+01
endit.
```

----- the input file has been read -----

----- file datal has been successfully read -----

species	lamda pairs		mu triplets		
ca++					
	ca++	cl-	ca++	cl-	ca++
	ca++	clo4-	ca++	cl-	cl-
	ca++	no3-	ca++	clo4-	ca++
	ca++	na+	ca++	clo4-	clo4-
	ca++	k+	ca++	no3-	ca++
	ca++	mg++	ca++	no3-	no3-
			ca++	na+	cl-
			ca++	k+	cl-
			ca++	mg++	cl-
			cl-	no3-	ca++
cl-					
	h+	cl-	h+	cl-	h+
	na+	cl-	h+	cl-	cl-
	k+	cl-	na+	cl-	na+
	nh4+	cl-	na+	cl-	cl-
	mg++	cl-	k+	cl-	k+
	ca++	cl-	k+	cl-	cl-
	cl-	oh-	nh4+	cl-	nh4+
	cl-	no3-	nh4+	cl-	cl-
			mg++	cl-	mg++
			mg++	cl-	cl-
			ca++	cl-	ca++
			ca++	cl-	cl-
			h+	na+	cl-
			h+	k+	cl-
			h+	nh4+	cl-
			k+	na+	cl-
			mg++	na+	cl-
			ca++	na+	cl-
			ca++	k+	cl-
			ca++	mg++	cl-
			cl-	oh-	na+
			cl-	oh-	k+
			cl-	no3-	na+
			cl-	no3-	k+
			cl-	no3-	mg++
			cl-	no3-	ca++
f-					
	na+	f-	na+	f-	na+
	k+	f-	na+	f-	f-
			k+	f-	k+
			k+	f-	f-

000058

h+

h+	cl-	h+	cl-	h+
h+	clo4-	h+	cl-	cl-
h+	no3-	h+	clo4-	h+
h+	na+	h+	clo4-	clo4-
h+	k+	h+	no3-	h+
h+	nh4+	h+	no3-	no3-
		h+	na+	cl-
		h+	na+	clo4-
		h+	k+	cl-
		h+	nh4+	cl-

k+

k+	f-	k+	f-	k+
k+	cl-	k+	f-	f-
k+	oh-	k+	cl-	k+
k+	no2-	k+	cl-	cl-
k+	no3-	k+	oh-	k+
h+	k+	k+	oh-	oh-
k+	na+	k+	no2-	k+
ca++	k+	k+	no2-	no2-
		k+	no3-	k+
		k+	no3-	no3-
		h+	k+	cl-
		k+	na+	cl-
		k+	na+	no3-
		ca++	k+	cl-
		cl-	oh-	k+
		cl-	no3-	k+

mg++

mg++	cl-	mg++	cl-	mg++
mg++	clo4-	mg++	cl-	cl-
mg++	no3-	mg++	clo4-	mg++
mg++	na+	mg++	clo4-	clo4-
ca++	mg++	mg++	no3-	mg++
		mg++	no3-	no3-
		mg++	na+	cl-
		ca++	mg++	cl-
		cl-	no3-	mg++

na+

na+	f-	na+	f-	na+
na+	cl-	na+	f-	f-
na+	oh-	na+	cl-	na+
na+	clo4-	na+	cl-	cl-
na+	no2-	na+	oh-	na+
na+	no3-	na+	oh-	oh-
h+	na+	na+	clo4-	na+
k+	na+	na+	clo4-	clo4-
mg++	na+	na+	no2-	na+
ca++	na+	na+	no2-	no2-
		na+	no3-	na+
		na+	no3-	no3-
		h+	na+	cl-
		h+	na+	clo4-
		k+	na+	cl-
		k+	na+	no3-
		mg++	na+	cl-
		ca++	na+	cl-
		cl-	oh-	na+
		cl-	no3-	na+

no3-

h+	no3-	h+	no3-	h+
na+	no3-	h+	no3-	no3-
k+	no3-	na+	no3-	na+
nh4+	no3-	na+	no3-	no3-
mg++	no3-	k+	no3-	k+
ca++	no3-	k+	no3-	no3-
cl-	no3-	nh4+	no3-	nh4+
		nh4+	no3-	no3-
		mg++	no3-	mg++
		mg++	no3-	no3-
		ca++	no3-	ca++
		ca++	no3-	no3-
		k+	na+	no3-
		cl-	no3-	na+
		cl-	no3-	k+
		cl-	no3-	mg++
		cl-	no3-	ca++

---

no2-

na+	no2-	na+	no2-	na+
k+	no2-	na+	no2-	no2-
		k+	no2-	k+
		k+	no2-	no2-

---

nh4+

nh4+	cl-	nh4+	cl-	nh4+
nh4+	clo4-	nh4+	cl-	cl-
nh4+	no3-	nh4+	clo4-	nh4+
h+	nh4+	nh4+	clo4-	clo4-
		nh4+	no3-	nh4+
		nh4+	no3-	no3-
		h+	nh4+	cl-

---

oh-

na+	oh-	na+	oh-	na+
k+	oh-	na+	oh-	oh-
cl-	oh-	k+	oh-	k+
		k+	oh-	oh-
		cl-	oh-	na+
		cl-	oh-	k+

---

clo4-

h+	clo4-	h+	clo4-	h+
na+	clo4-	h+	clo4-	clo4-
nh4+	clo4-	na+	clo4-	na+
mg++	clo4-	na+	clo4-	clo4-
ca++	clo4-	nh4+	clo4-	nh4+
		nh4+	clo4-	clo4-
		mg++	clo4-	mg++
		mg++	clo4-	clo4-
		ca++	clo4-	ca++
		ca++	clo4-	clo4-
		h+	na+	clo4-

--- pitzer data has been successfully read from file data1 ---

```
eeee   qqq   33333  n   n  rrrr
e     q   q      3  nn  n  r   r
eeee  q   q    33   n n n  rrrr
e     q q q      3  n  nn  r  r
eeee   qqq   3333   n   n  r   r
          q
```


000060

```
eq3nr.3245R95
 supported by eqlib.3245R116


input file name= tab.tst2   created= 04/21/87     creator= k.j. jackson

the problem:
             this is a sample input file designed to
            to illustrate the use of the pitzer tabulation
            option in the eq3nr code.

            the model is of a sodium chloride brine with
            trace amounts of several other solutes common
            in geologic waters.

            the temperature is 25 degrees c.

note:
             activity coefficients and the activity of
             water are computed using pitzer's equations
             (i.e., iopgl = 1)


data file data0.3245R47
         1 atm steam saturation curve data
last modified  13Aug86   (da0r)


  the activity coefficients of aqueous solute species
and the activity of water are calculated according to
pitzer


dpt0a.3245R16, last revised  6jun84    kjj
this file contains pitzer coefficient data consistent with
  1. no higher-order electrostatic (e-lambda or e-theta) terms
  2. no ion pairs or complexes, except acid-base species

  uelam= off


temperature=  25.00 degrees celsius
pressure=    1.0134 bars


        29 elements are in the data base
        50 elements can be loaded into memory
         9 elements are active in this problem


        38 aqueous species are in the data base
        35 aqueous species were loaded into memory
       750 aqueous species can be loaded into memory
        13 aqueous species are active in this problem

         8 aqueous reactions are in the data base
         5 aqueous reactions were loaded into memory
       699 aqueous reactions can be loaded into memory


            207 minerals are in the data base
             27 minerals were loaded into memory
            750 minerals can be loaded into memory
             26 minerals are active in this problem
```

```
 7 solid solutions are in the data base
20 solid solutions can be loaded into memory

 4 gases are in the data base
 4 gases were loaded into memory
15 gases can be loaded into memory
 4 gases are active in this problem


iopt1  =  0 (redox option switch)
iopt2  =  0 (automatic basis switching switch)
iopt3  =  0 (interfacing output control switch)
iopt4  =  0 (turn-on solid solutions switch)
iopt5  =  0 (not used)
iopt6  =  0 (conv. test criteria switch)
iopt7  =  0 (0/1 3245/post-3245 pickup file)
iopt8  =  0 (not used)
iopt9  =  0 (not used)
iopt10 =  0 (not used)


iopg1  =  1 (act. coeff. choice)
iopg2  =  0 (approx. of j(x) function)
iopg3  =  0 (iopg1=3 - 0/1 uelam= on/onplus)
iopg4  =  0 (iopg1=3 or 4 - f switch - 0/1 dhoa/dhca)
iopg5  =  0 (not used)
iopg6  =  0 (not used)
iopg7  =  0 (not used)
iopg8  =  0 (not used)
iopg9  =  0 (not used)
iopg10 =  0 (not used)


iopr1  =  0 (list loading of species)
iopr2  =  0 (list reactions and log k values)
iopr3  =  0 (aqueous species print order control)
iopr4  =  0 (aqueous species print cut-off control)
iopr5  =  0 (mass balance percentages print control)
iopr6  =  1 (mean ionic act coeff print control)
iopr7  =  0 (mineral affinity print control)
iopr8  =  0 (ion size and hydr. no. print control)
iopr9  =  2 (pitzer coefficients tabulation)
iopr10 =  0 (not used)


iodb1  =  0 (print info. messages switch)
iodb2  =  0 (print adat1 read info. switch)
iodb3  =  0 (request iteration variables to kill)
iodb4  =  0 (print newton-raphson iterations switch)
iodb5  =  0 (list stoichiometric equivalences)
iodb6  =  0 (controls iodb5 level of detail)
iodb7  =  0 (write reactions on file rlist switch)
iodb8  =  0 (s-lambda turn-off switch)
iodb9  =  0 (mu turn-off switch)
iodb10 =  0 (f turn-off switch)

the default redox state is constrained by log fo2 =      -0.7000 (log bars)
```


000062

solution density = 1.00000 g/ml

total dissolved salts = 0. mg/kg solution
total dissolved salts = 0. mg/l

tolbt = 0.10000E-09 (convergence tolerance on residual functions)
toldl = 0.10000E-09 (convergence tolerance on correction terms)
tolsat = 0.50000E+00 (phase saturation tolerance, does not affect convergence)

----- input constraints -----

species	csp	jflag	type of input	controlling phase
h+	-0.66000E+01	16	log activity	
na+	0.39000E+01	0	tot conc, molal	
k+	0.75110E+02	2	tot conc, mg/l	
ca++	0.12500E+02	2	tot conc, mg/l	
mg++	0.19200E+01	2	tot conc, mg/l	
no3-	0.96000E+01	2	tot conc, mg/l	
f-	0.22000E+01	2	tot conc, mg/l	
cl-	0.39000E+01	0	tot conc, molal	

electrical balance will be achieved by adjusting
the concentration of na+

--- inactive aqueous species ---

--- modified input constraints ---

species	csp	jflag	type of input	controlling phase
ca++	0.31188E-03	0	tot conc, molal	
cl-	0.39000E+01	0	tot conc, molal	
f-	0.11580E-03	0	tot conc, molal	
h+	-0.66000E+01	16	log activity	
k+	0.19211E-02	0	tot conc, molal	
mg++	0.78996E-04	0	tot conc, molal	
na+	0.39000E+01	0	tot conc, molal	
no3-	0.15483E-03	0	tot conc, molal	
no2-	0.00000E+00	30	eliminated species	
nh4+	0.00000E+00	30	eliminated species	
oh-	0.00000E+00	30	eliminated species	
clo4-	0.00000E+00	30	eliminated species	

```
iter =   0   delmax =  0.000E+00   delfnc =  0.000E+00
             del(            ) =  0.000E+00   beta(conc   na+    ) =  0.623E-03
iter =   1   delmax =  0.612E-03   delfnc =  0.000E+00
             del(gamma mg++  ) =  0.612E-03   beta(gamma mg++   ) = -0.628E-04
iter =   2   delmax =  0.626E-04   delfnc =  0.898E+00
             del(gamma mg++  ) = -0.626E-04   beta(act    h2o   ) =  0.207E-04
iter =   3   delmax =  0.207E-04   delfnc =  0.669E+00
             del(act   h2o   ) =  0.104E-04   beta(act    h2o   ) =  0.104E-04
iter =   4   delmax =  0.104E-04   delfnc =  0.500E+00
             del(act   h2o   ) =  0.104E-04   beta(gamma mg++   ) =  0.835E-13
```

iter = 5 delmax = 0.837E-13 delfnc = 0.100E+01
del(gamma mg++) = 0.837E-13 beta(act h2o) = -0.294E-13

newton-raphson iteration converged in 5 steps

----- Summary of the Aqueous Phase -----

----- Elemental composition of the aqueous phase -----

element	mg/l	mg/kg	moles/kg
o	888113.0322	888113.0322	0.5550914610E+02
ca	12.5000	12.5000	0.3118762475E-03
cl	138266.7000	138266.7000	0.3900000000E+01
f	2.2000	2.2000	0.1157992252E-03
h	111894.4005	111894.4005	0.1110173633E+03
k	75.1100	75.1100	0.1921055391E-02
mg	1.9200	1.9200	0.7899609134E-04
na	89604.1867	89604.1867	0.3897567775E+01
n	2.1686	2.1686	0.1548264734E-03

----- elemental composition as strict basis species -----

species	mg/l	mg/kg	moles/kg
h2o	1000008.3689	1000008.3689	0.5550914610E+02
ca++	12.5000	12.5000	0.3118762475E-03
cl-	138266.7000	138266.7000	0.3900000000E+01
f-	2.2000	2.2000	0.1157992252E-03
h+	111894.4005	111894.4005	0.1110173633E+03
k+	75.1100	75.1100	0.1921055391E-02
mg++	1.9200	1.9200	0.7899609134E-04
na+	89604.1867	89604.1867	0.3897567775E+01
no3-	9.6000	9.6000	0.1548264734E-03

----- equivalent composition of the aqueous phase (cte balances) -----

original basis		existing basis	
species	moles/kg h2o	species	moles/kg h2o
h2o	0.5550914610E+02	h2o	0.5550914610E+02
ca++	0.3118762475E-03	ca++	0.3118762475E-03
cl-	0.3900000000E+01	cl-	0.3900000000E+01
f-	0.1157992252E-03	f-	0.1157992252E-03
h+	0.1110173633E+03	h+	0.1110173633E+03
k+	0.1921055391E-02	k+	0.1921055391E-02
mg++	0.7899609134E-04	mg++	0.7899609134E-04
na+	0.3897567775E+01	na+	0.3897567775E+01
no3-	0.1548264734E-03	no3-	0.1548264734E-03

ph = 6.60000
activity of water = 0.85575
log activity of water = -0.06765
osmotic coefficient = 1.10858
stoichiometric sum of molalities = 7.8001503284109

titration alkalinity = 0.0000000654679 eq/kg h2o
ionic strength = 3.9006615635053

----- electrical balance totals -----

	equiv/kg
sigma(mz) cations =	0.3900270691E+01
sigma(mz) anions =	-0.3900270691E+01
total charge =	0.7800541382E+01
mean charge =	0.3900270691E+01
charge imbalance =	-0.4440892099E-15

total charge = sigma(mz) cations + abs (sigma(mz) anions)
mean charge = 1/2 total charge

the electrical imbalance is

0.00 per cent of the total charge
0.00 per cent of the mean charge
0.00 per cent of sigma(mz) cations
0.00 per cent of abs (sigma(mz) anions)

----- electrical balancing on na+ -----

	mg/l	mg/kg	moles/kg
input	89660.1030	89660.1030	0.3900000000E+01
final	89604.1867	89604.1867	0.3897567775E+01
adj	-55.9163	-55.9163	-0.2432225018E-02

----- activity ratios of ions -----

log (act(ca++) / act(h+)xx 2) =	9.4576
log (act(cl-) x act(h+)xx 1) =	-6.1193
log (act(f-) x act(h+)xx 1) =	-10.8674
log (act(k+) / act(h+)xx 1) =	3.5898
log (act(mg++) / act(h+)xx 2) =	9.0372
log (act(na+) / act(h+)xx 1) =	7.0803
log (act(no3-) x act(h+)xx 1) =	-10.7899
log (act(no2-) x act(h+)xx 1) =	-24.3036
log (act(nh4+) / act(h+)xx 1) =	-56.5922
log (act(oh-) x act(h+)xx 1) =	-14.0545
log (act(clo4-) x act(h+)xx 1) =	-29.0280

----- distribution of aqueous species -----

species	molal conc	log conc	log g	activity	log act
cl-	0.3900E+01	0.5911	-0.1104	0.3025E+01	0.4807
na+	0.3898E+01	0.5908	-0.1105	0.3022E+01	0.4803
k+	0.1921E-02	-2.7165	-0.2937	0.9768E-03	-3.0102
ca++	0.3119E-03	-3.5060	-0.2364	0.1810E-03	-3.7424
no3-	0.1548E-03	-3.8102	-0.3798	0.6458E-04	-4.1899
f-	0.1158E-03	-3.9363	-0.3311	0.5402E-04	-4.2674
mg++	0.7900E-04	-4.1024	-0.0604	0.6874E-04	-4.1628
h+	0.1161E-06	-6.9351	0.3351	0.2512E-06	-6.6000
oh-	0.6547E-07	-7.1840	-0.2705	0.3512E-07	-7.4545
no2-	0.3487E-17	-17.4575	-0.2461	0.1979E-17	-17.7036

clo4-	0.5845E-22	-22.2332	-0.1948	0.3732E-22	-22.4280
nh4+	0.1128E-62	-62.9476	-0.2446	0.6424E-63	-63.1922

----- mean ionic properties -----

				true (a)		stoichiometric (b)	
species	species	log a(+/-)	a(+/-)	m(+/-)	g(+/-)	m(+/-)	g(+/-)
ca++	cl-	-0.92700	1.183E-01	1.680E-01	7.041E-01	1.680E-01	7.041E-01
ca++	f-	-4.09241	8.083E-05	1.611E-04	5.017E-01	1.611E-04	5.017E-01
ca++	no3-	-4.04074	9.105E-05	1.955E-04	4.656E-01	1.955E-04	4.656E-01
ca++	no2-	-13.04987	8.915E-14	1.559E-13	5.717E-01		
ca++	oh-	-6.21710	6.066E-07	1.102E-06	5.507E-01	4.068E-04	1.[illegible]91E-03
ca++	clo4-	-16.19947	6.317E-17	1.021E-16	6.185E-01		
h+	cl-	-3.05966	8.717E-04	6.729E-04	1.295E+00	1.471E+01	5.924E-05
h+	f-	-5.43371	3.684E-06	3.667E-06	1.005E+00	8.017E-02	4.595E-05
h+	no3-	-5.39496	4.028E-06	4.240E-06	9.499E-01	9.270E-02	4.344E-05
h+	no2-	-12.15181	7.050E-13	6.363E-13	1.108E+00		
h+	clo4-	-14.51401	3.062E-15	2.605E-15	1.175E+00		
k+	cl-	-1.26475	5.436E-02	8.656E-02	6.280E-01	8.656E-02	6.280E-01
k+	f-	-3.63880	2.297E-04	4.717E-04	4.871E-01	4.717E-04	4.871E-01
k+	no3-	-3.60005	2.512E-04	5.454E-04	4.605E-01	5.454E-04	4.605E-01
k+	no2-	-10.35690	4.396E-11	8.185E-11	5.371E-01		
k+	oh-	-5.23232	5.857E-06	1.121E-05	5.223E-01	9.447E-04	6.200E-03
k+	clo4-	-12.71910	1.909E-13	3.351E-13	5.698E-01		
mg++	cl-	-1.06714	8.568E-02	1.063E-01	8.059E-01	1.063E-01	8.059E-01
mg++	f-	-4.23254	5.854E-05	1.019E-04	5.743E-01	1.019E-04	5.743E-01
mg++	no3-	-4.18087	6.594E-05	1.237E-04	5.330E-01	1.237E-04	5.330E-01
mg++	no2-	-13.19001	6.456E-14	9.867E-14	6.543E-01		
mg++	oh-	-6.35723	4.393E-07	6.970E-07	6.303E-01	2.574E-04	1.707E-03
mg++	clo4-	-16.33960	4.575E-17	6.462E-17	7.080E-01		
na+	cl-	0.48051	3.024E+00	3.899E+00	7.755E-01	3.899E+00	7.755E-01
na+	f-	-1.89[illegible]	1.278E-02	2.124[illegible]-02	6.015E-01	2.124E-0[illegible]	6.015E-01
na+	no3-	-1.85479	1.397E-02	2.45[illegible]-02	5.687E-01	2.457E-02	5.687E-01
na+	no2-	-8.61164	2.445E-09	3.68[illegible]-9	6.633E-01		
na+	oh-	-3.48706	3.258E-04	5.051E[illegible]1	6.450E-01	4.255E-02	7.657E-03
na+	clo4-	-10.97384	1.062E-11	1.509E-11	7.037E-01		
nh4+	cl-	-31.35574	4.408E-32	6.633E-32	6.645E-01		
nh4+	f-	-33.72980	1.863E-34	3.615E-34	5.154E-01		
nh4+	no3-	-33.69105	2.037E-34	4.180E-34	4.873E-01		
nh4+	no2-	-40.44790	3.565E-41	6.272E-41	5.684E-01		
nh4+	oh-	-35.32331	4.750E-36	8.594E-36	5.527E-01		
nh4+	clo4-	-42.81009	1.548E-43	2.568E-43	6.030E-01		

(a) true quantities consistent with the speciation model
(b) stoichiometric quantities consistent with the cte mass balance lumpings, except that
1. effective cte(h+) = cte(h+) - conc(h2o)
2. effective cte(oh-) = cte(h2o) - conc(h2o)

----- major aqueous species contributing to mass balances -----

aqueous species accounting for 99% or more of ca++

species	molal conc	per cent
ca++	0.3119E-03	100.00
total		100.00

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aqueous species accounting for 99% or more of cl-

species	molal conc	per cent
cl-	0.3900E+01	100.00
total		100.00

aqueous species accounting for 99% or more of f-

species	molal conc	per cent
f-	0.1158E-03	100.00
total		100.00

aqueous species accounting for 99% or more of k+

species	molal conc	per cent
k+	0.1921E-02	100.00
total		100.00

aqueous species accounting for 99% or more of mg++

species	molal conc	per cent
mg++	0.7900E-04	100.00
total		100.00

aqueous species accounting for 99% or more of na+

species	molal conc	per cent
na+	0.3898E+01	100.00
total		100.00

aqueous species accounting for 99% or more of no3-

species	molal conc	per cent
no3-	0.1548E-03	100.00
total		100.00

----- summary of aqueous redox reactions -----

couple		eh, volts	pe-	log fo2	ah, kcal
default		0.830	0.1403E+02	-0.700	19.147
no2-	/no3-	0.830	0.1403E+02	-0.700	19.147
nh4+	/no3-	0.830	0.1403E+02	-0.700	19.147
clo4-	/cl-	0.830	0.1403E+02	-0.700	19.147

```
----- summary of aqueous non-equilibrium non-redox reactions -----

couple        affinity, kcal

none

----- summary of stoichiometric mineral saturation states -----

(minerals with affinities .lt. -10 kcal are not listed)

mineral      log q/k   aff, kcal  state   mineral      log q/k   aff, kcal  state

antarcticite -7.300    -9.959             fluorite     -1.318    -1.799
halite       -0.632    -0.862             mg.2(c)      -4.519    -6.165
sylvite      -3.489    -4.750

0 approx. saturated pure minerals
0 approx. saturated end-members of specified solid solutions
0 saturated end-members of hypothetical solid solutions

0 supersaturated pure minerals
0 supersatd. e.d-members of specified solid solutions
0 supersatd. hypothetical solid solution phases

----- summary of gases -----

      gas                    fugacity    log fugacity

  h2(g)                   0.538203E-41    -41.26905
  n2(g)                   0.585084E-17    -17.23278
  o2(g)                   0.199526E+00     -0.70000
  steam                   0.267945E-01     -1.57195

----- end of output -----
----- pickup file successfully written -----
----- reading the input file -----
----- end of input file -----

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          end time = 11:22:14
normal exit
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