Calculation of Equilibria at Elevated Temperatures Using The MINTEQ Geochemical Code

December 1988

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**Pacific Northwest Laboratory
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CALCULATION OF EQUILIBRIA AT
ELEVATED TEMPERATURES USING
THE MINTEQ GEOCHEMICAL CODE

R. W. Smith

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Richland, Washington 99352

SUMMARY

Coefficients and equations for calculating mineral hydrolysis constants, solubility products and formation constants for 60 minerals and 57 aqueous species in the 13 component thermodynamic system K_2O - Na_2O - CaO - MgO - FeO - Al_2O_3 - SiO_2 - CO_2 - H_2O - HF - HCl - H_2S - H_2SO_4 are presented in a format suitable for inclusion in the MINTEQ computer code. The temperature functions presented for minerals are based on the MINTEQ data base at 25°C and the integration of analytical heat capacity power functions. This approach ensures that the temperature functions join smoothly with the low-temperature data base. Temperature functions for the formation constants of aqueous species were calculated by least-squares fit of power functions to available elevated temperature data. In cases where no data for elevated temperature could be identified, heat capacities or equilibrium constants were estimated.

A new subroutine, DEBYE, was added to MINTEQ that is used to calculate the theoretical Debye-Hückel parameters A and B as a function of temperature. In addition, this subroutine also calculates a universal value of the extended Debye-Hückel parameter, b_i , as a function of temperature.

The coefficients and equations provide the capability to use MINTEQ to more accurately calculate water/rock equilibrium for temperatures of up to 250°C, and in dilute, low-sulfate, near neutral groundwaters to 300°C.

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INTRODUCTION

Aquifer thermal energy storage (ATES) is a system of heat storage that is accomplished by pumping heated water into an aquifer during times of low energy demand (e.g., warm weather) and recovering the water and heat for use during times of higher energy demands (e.g., cold weather). The principal technical limitations of this process are scaling during heat extraction and potential plugging of the aquifer as a result of (thermal) water/rock interactions. In addition, biofouling and the precipitation of colloidal amorphous Fe(III) hydroxides as a result of oxidation of dissolved Fe(II) can be technical problems in some systems. The design and operation of a thermal energy storage system is greatly enhanced by the ability to predict the extent and type of reactions at ambient and elevated temperatures that lead to scaling and aquifer plugging.

Although the computer code MINTeq was developed to model geochemical equilibrium processes, it has previously been limited to systems at ambient temperatures. This report provides the thermodynamic data and the code changes in MINTeq to extend the temperature range for calculation to approximately 300°C. In addition, this report discusses the derivation of thermodynamic data (primarily, equilibrium constants, $K_r(T)$) for minerals and aqueous species in the 13-component thermodynamic system $K_2O-Na_2O-CaO-MgO-FeO-Al_2O_3-SiO_2-CO_2-H_2O-HF-HCl-H_2S-H_2SO_4$, which includes the major geochemical components of an ATES system. The incorporation of the high temperature thermodynamic data into MINTeq has been accomplished by calculating coefficients for the empirical relationship between equilibrium constants and temperature used by MINTeq for reactions involving 60 minerals and 57 aqueous species in the above 13-component thermodynamic system. These coefficients were calculated from measured and estimated heat capacities, equilibrium constants, enthalpies of reaction and theoretical and empirical relationships accounting for electrostatic behavior and temperature dependence of thermodynamic properties of aqueous ions and electrolytes. In addition, the MINTeq

code has been modified to calculate activity coefficients for elevated temperatures using the B* method (Helgeson 1969). The choice of reactions was governed by the availability of measured thermodynamic data and the need to model both laboratory data (McKinley, Jenne, and Smith 1988) and field results from the ATES Field Test Facility, University of Minnesota, St. Paul (Holm et al. 1987).

The computer code MINTEQ was developed by Felmy, Girvin, and Jenne (1984) by the integration of the "best" features of its two immediate predecessors, MINEQL and WATEQ. The computer code applies the principles of the thermodynamics of reversible reactions to the solution of a wide variety of geochemical equilibrium problems by using aqueous speciation-solubility-sorption submodels. The accurate modeling of equilibrium geochemical processes requires the availability of thermodynamic data that are

- complete (all relevant species and phases are included)
- accurate (the uncertainties in the thermodynamic data are known)
- internally consistent (the same values for ancillary data were used in the derivation of all the thermodynamic data)
- documented (the sources of data are established and available for inspection).

The data base for the computer code MINTEQ has been established considering the above requirements (e.g., Truesdell and Jones 1974; Ball, Nordstrom, and Jenne 1980; and Krupka and Jenne 1982), with particular emphasis placed on completeness and documentation.

MINTEQ (and its predecessor code WATEQ) was developed to model water/rock reactions at near-ambient temperatures. Calculations at temperatures other than 25°C use equilibrium constants ($\log K_{r,T}$) calculated from 25°C values of the equilibrium constants, the enthalpy of reaction ($\Delta H^\circ_{r,298}$), and the van't Hoff equation, or in limited instances from empirical $\log K_{r,T} = f(T)$ relationships. While the van't Hoff equation, as implemented in MINTEQ, is adequate for temperatures of typical surface and groundwaters, this method can introduce significant errors in the modeling of waters

with temperatures greater than approximately 80°C (Helgeson 1967). The current version of MINTEQA2 has the capability to use temperature functions of the form:

$$\log K_{r,T} = \frac{a_0}{T} + a_1 \ln T + a_2 T + \frac{a_3}{T^2} + a_4 + a_5 T^2 + \frac{a_6}{\sqrt{T}} \quad (1)$$

where a_0 , a_1 , a_2 , a_3 , a_4 , a_5 , and a_6 are empirical coefficients determined by the regression of Equation (1) with experimental results. However, coefficients are included in the data base for only a limited number of reactions. In addition, the upper temperature limits for the equations in the current data base are not specified. The ability of MINTEQA2 to accurately calculate thermodynamic properties of interest at elevated temperatures would be enhanced by the inclusion of a more extensive set of coefficients. A logical and practical approach for calculating these coefficients is presented in this report.

The number of terms used in the literature for regression equations of $\log K_{r,T}$ varies widely (cf., Nordstrom and Jenne 1977; Khodakovskiy, Ryzhenko, and Naumov 1968). Murray and Cobble (1980) point out that while a five-term power series can only approximate the heat capacity (seven terms for $\log K_{r,T}$) of an aqueous electrolyte, a three-term heat capacity power function (five terms for $\log K_{r,T}$) is accurate enough to reproduce the experimental equilibrium constants (twice-integrated heat capacities) to 300°C. For this reason, only the first five terms of Equation (1) were used in this report (i.e., a_5 and a_6 were set equal to 0).

This report discusses the thermodynamic relationships needed to calculate chemical equilibria in an ATE system. Initially, the relevant thermodynamic relationships are summarized. This is followed by the calculation of Equation (1) coefficients for mineral solubility and hydrolysis reactions. Next the derivation of coefficients for aqueous association reactions are discussed. The calculation of aqueous activity coefficients at elevated temperatures is discussed, and finally the

temperature and ionic strength limitation of the derived equations and coefficients are discussed. The changes to the MINTEQ computer code needed to implement the calculations described in this report are summarized in Appendix A.

SUMMARY OF THERMODYNAMIC RELATIONSHIPS

The calculation of equilibrium constants at elevated temperatures requires that the enthalpy and heat capacity of the reaction be known (or be estimated). The relationship among these thermodynamic quantities are given by^(a):

$$\left(\frac{\partial \ln K_{r,T}}{\partial T} \right)_p = \frac{\Delta H_r^\circ}{RT^2} \quad (2)$$

$$\left(\frac{\partial \Delta H_r^\circ}{\partial T} \right)_p = \Delta C_p^\circ \quad (3)$$

where ΔC_p° is the heat capacity of reaction, T is the temperature in Kelvin, and R is the gas constant ($1.98719 \text{ cal mol}^{-1} \text{ K}^{-1}$). Differentiating Equation (1) with respect to temperature and substituting the results into Equations (2) and (3), while setting a_5 and a_6 equal to 0, yields:

$$\Delta H_r^\circ = 2.303R \left[-a_0 + a_1T + a_2T^2 - \frac{2a_3}{T} \right] \quad (4)$$

$$\Delta C_p^\circ = 2.303R \left[a_1 + 2a_2T + \frac{2a_3}{T^2} \right] \quad (5)$$

Equation (5) is not adequate in most cases to represent the calorimetric heat capacity of

(a) Equations (2) and (3) are strictly true only at constant pressure. However, for convenience, the reference pressure has been defined as 1 bar for temperatures $\leq 100^\circ\text{C}$ and pressures of steam saturation water at temperature $> 100^\circ\text{C}$. The effects of the pressure differences between 1 bar and steam saturation are insignificant for temperatures $\leq 300^\circ\text{C}$ (Helgeson 1969).

aqueous species (e.g., Murray and Cobble 1980; Helgeson, Kirkham, and Flowers 1981). However, because the temperature dependence of equilibrium constants is not particularly sensitive to the analytical form of a heat capacity temperature function, Equation (1) can be used to calculate equilibrium constants for reactions involving aqueous species. If actual values for heat capacity are needed, equations such as those given by Tanger and Helgeson (1988) should be used rather than Equation (5).

The heat capacities of minerals at temperatures $\geq 298.15\text{K}$ can be closely represented by the Maier-Kelley power function (Maier and Kelley 1932), which can be written as:

$$C_p^0 = a + bT + \frac{c}{T^2} \quad (6)$$

where a , b , and c are temperature-independent coefficients characteristic of the mineral. Although alternate heat capacity expressions have been proposed (Haas and Fisher 1976, Berman and Brown 1985), Equation (6) is preferred for this exercise for three reasons:

- The values of a , b , and c for a large number of substances are available (Naumov, Ryzhenko, and Khodakovskiy 1974 and Helgeson et al. 1978).
- The accuracy (over the temperature range of 25° to 300°C) of equilibrium constants is not significantly improved by using expressions more complicated than Equation (6).
- The values of a_1 , a_2 , and a_3 can be calculated directly from values of Δa , Δb , and Δc (e.g., $\Delta a = a_1 2.303R$; $\Delta b = a_2 4.606R$; and $\Delta c = a_3 4.606R$).

Although the heat capacity of aqueous ions is a complex function of temperature and the dielectric constant of water (Tanger and Helgeson 1988), equilibrium constants (i.e., the twice-integrated heat capacity) can be represented by Equation (6) up to 300°C with very little loss of accuracy (Murray and Cobble 1980). Values of a , b , and c for

basis ions (MINTEQ "components") were determined from the following relationship:

$$\int_{T_r}^T C_p^{\circ} dT - T \int_{T_r}^T \frac{C_p^{\circ}}{T} dT = a \left[T - T_r - T \ln \frac{T}{T_r} \right] - b \frac{(T - T_r)^2}{2} - c \frac{(T - T_r)^2}{2TT_r^2} \quad (7)$$

where T_r is the reference temperature of 298.15K. Values for the left-hand side of Equation (7) were calculated in this study for 25° intervals (0° to 300°C) as described by Tanger and Helgeson (1988) using coefficients for ions given by Schock and Helgeson (1988). Values of a , b , and c were determined by regression of the right-hand side of Equation (7) to the calculated values. The derivation of Equation (7) is given in Appendix B.

CALCULATION OF COEFFICIENTS FOR MINERAL SOLUBILITY AND HYDROLYSIS REACTIONS

Values of a_0 to a_4 for minerals considered in this study are presented in Table 1. In addition, they are given in the format required for use by MINTEQA2 in Appendix A (Table A3). Values of a_1 , a_2 , and a_3 were calculated from the values of a , b , and c for minerals and aqueous species listed in Table 2. The value of a_0 was calculated from the enthalpy of reaction at 25°C given in the MINTEQA2 data file as listed in Peterson et al. (1987) and Equation (4). The value of a_4 was calculated from the room temperature equilibrium constant given in the MINTEQA2 data file and Equation (1) (with a_5 and a_6 set equal to 0). This procedure ensured that the temperature dependence for the equilibrium constants of reactions involving minerals are consistent with the equilibrium constants and enthalpies at 25°C currently in MINTEQA2.

All reactions involving minerals are written in terms of MINTEQA2 "components" or basis species (Peterson et al. 1987). For the thermodynamic system considered in this study, these basis species and their identification numbers are: e^- (001), H_2O (002), Al^{3+} (003), CO_3^{2-} (140), Ca^{2+} (150), Cl^- (180), F^- (270), Fe^{2+} (280), Fe^{3+} (281), H^+ (330), K^+ (410), Mg^{2+} (460), Na^+ (500), HS^- (730), SO_4^{2-} (732) and H_4SiO_4 (770). The inclusion of three additional "components" (above the 13 required by the Gibbs phase rule) allows for redox disequilibrium and greater flexibility in adjusting charge balance for modeling measured water compositions.

The minerals included in Table 1 are minerals in the thermodynamic system of interest for which both $\log K_{r,298}$ and $\Delta H_{r,298}^\circ$ values are available in the current data base. This constraint resulted in the exclusion of several (especially iron) minerals. In addition, soluble salts (e.g., halite and epsomite) and some aluminum and ferric sulfates were excluded as not being relevant to heated, dilute near-neutral groundwaters. The temperature limit of 300°C is from the heat capacity expression for the ions. However,

TABLE 1. Coefficients for Equation (1) to Calculate Hydrolysis Constants and Solubility Products of Minerals for Temperatures of 0° to 300°C

ID No.	Mineral	a_0	a_1	a_2	a_3	a_4
8015005	AKERMINITE	-6.0939E+04	-133.0062	1.3512E-01	2.4734E+06	846.6236
2003000	AlOH ₃ (A)	-1.6836E+04	-38.2210	4.3446E-02	5.0579E+05	245.2116
8450003	ANALBITE	-3.8791E+04	-102.2816	1.0687E-01	2.0015E+06	654.9809
8450001	ANALCIME	-3.4202E+04	-88.1805	9.0984E-02	1.6411E+06	564.8244
6015000	ANHYDRITE	-8.3368E+04	-234.7851	2.4132E-01	5.0679E+06	1493.0070
8641001	ANNITE	-7.9785E+04	-198.6774	2.0647E-01	3.6588E+06	1273.5773
8415001	ANORTHITE	-5.5985E+04	-128.5914	1.4545E-01	2.2564E+06	826.2554
5015000	ARAGONITE	-8.0884E+04	-229.4150	2.3798E-01	4.9294E+06	1460.3533
2003001	BOEHMITE	-1.5907E+04	-32.9831	3.8987E-02	5.0579E+05	215.3866
2046000	BRUCITE	-1.7140E+04	-36.3214	3.4694E-02	5.5882E+05	231.0087
5015001	CALCITE	-8.0400E+04	-228.3551	2.3743E-01	4.8982E+06	1453.3214
2077000	CHALCEDONY	-5.2681E+03	-17.4168	1.7836E-02	3.9790E+05	110.6320
2077001	CHISTOBALITE	-4.2223E+03	-16.0683	1.6974E-02	3.1933E+05	100.6464
8646000	CHRYSOTILE	-5.8973E+04	-143.9899	1.4017E-01	2.5395E+06	915.6477
2003002	DIASPORE	-1.5143E+04	-32.9831	3.8987E-02	5.0579E+05	214.5266
5015002	DOLOMITE	-1.6336E+05	-461.7837	4.7782E-01	9.8907E+06	2942.2582
4215000	FLUORITE	-7.8930E+04	-229.9078	2.3622E-01	4.8316E+06	1460.8337
8046000	FORSTERITE	-3.9590E+04	-87.2929	8.6297E-02	1.5855E+06	558.2815
8015006	GEHLENITE	-6.9777E+04	-143.0168	1.6061E-01	2.3913E+06	917.2774
2003003	GIBBSITE (C)	-1.5908E+04	-38.2210	4.3446E-02	5.0579E+05	243.7107
2028102	GOETHITE	-1.6738E+04	-42.0312	4.6194E-02	7.6751E+05	272.7081
6015001	GYPSUM	-8.4030E+04	-241.6264	2.4692E-01	5.0679E+06	1532.7479
8441003	H SANIDINE	-3.4924E+04	-95.1526	1.0238E-01	1.8696E+06	606.6599
8603000	HALLOYSITE	-3.9324E+04	-100.0834	1.1406E-01	1.6312E+06	640.7753
2028105	HEMATITE	-3.2226E+04	-80.3926	9.1843E-02	1.4433E+06	526.5203
5015003	HUNTITE	-3.2995E+05	-926.5738	9.5657E-01	1.9841E+07	5907.4600
5046001	HYDROMAGNESITE	-3.5128E+05	-974.7832	9.9450E-01	2.0520E+07	6213.5493
8441000	KALSILITE	-2.6617E+04	-62.9329	6.8986E-02	1.1430E+06	401.5756
8603001	KAOLINITE	-3.8351E+04	-100.0834	1.1406E-01	1.6312E+06	640.7822
8015002	LARNITE	-4.5224E+04	-96.9193	1.0068E-01	1.9040E+06	613.3129
8415002	LAUMONTITE	-6.6638E+04	-171.1349	1.8232E-01	3.1004E+06	1094.8665
8415000	LEONHARDITE	-1.2943E+05	-340.7876	3.6470E-01	6.2009E+06	2180.8092
8441001	LEUCITE	-3.1955E+04	-81.6675	8.7683E-02	1.5765E+06	522.1871
2015000	LIME	-2.0306E+04	-31.8375	3.2955E-02	5.4173E+05	200.7857
8450002	LOW ALBITE	-3.8223E+04	-102.2816	1.0687E-01	2.0015E+06	653.9895

TABLE 1. (contd)

ID No.	Mineral	a_0	a_1	a_2	a_3	a_4
5046002	MAGNESITE	-8.2842E+04	-232.7394	2.3971E-01	4.9809E+06	1484.4357
3025000	MAGNETITE	-4.8433E+04	-117.0316	1.2918E-01	2.0868E+06	763.5169
8015004	MERWINITE	-7.7654E+04	-164.5793	1.6802E-01	2.9989E+06	1045.7845
8441002	MICROCLINE	-3.4500E+04	-95.1526	1.0238E-01	1.8696E+06	605.6820
8015003	MONTICELLITE	-4.4586E+04	-99.7303	1.0169E-01	1.9518E+06	635.2195
8641000	MUSCOVITE	-6.3317E+04	-160.0568	1.8091E-01	2.7895E+06	1025.9976
8450004	NEPHELINE	-2.9422E+04	-68.1806	7.2177E-02	1.2306E+06	437.5664
8215003	P-WOLLASTONITE	-2.0722E+04	-48.4347	5.0170E-02	9.1493E+05	306.3656
2046001	PERICLASE	-1.9470E+04	-35.4003	3.4511E-02	6.0941E+05	228.3445
8646001	PHLOGOPITE	-8.6084E+04	-203.9633	2.0701E-01	3.6977E+06	1281.2080
2015001	PORTLANDITE	-1.7631E+04	-34.1938	3.3952E-02	5.5877E+05	214.8725
1028003	PYRITE	-7.6831E+04	-227.6001	2.3258E-01	4.7877E+06	1449.7437
8603002	PYROPHYLLITE	-4.8434E+04	-134.3916	1.4910E-01	2.5324E+06	856.8136
2077002	QUARTZ	-4.9174E+03	-17.4168	1.7836E-02	3.9790E+05	109.9388
8646003	SEPIOLITE(C)	-5.0371E+04	-131.5078	1.2493E-01	2.4313E+06	837.7095
5028000	SIDERITE	-8.2876E+04	-233.1718	2.4105E-01	5.0118E+06	1488.7856
2077003	SiO ₂ (A, GL)	-3.8003E+03	-18.5729	2.2098E-02	1.7848E+05	112.9888
2077004	SiO ₂ (A, PT)	-3.9161E+03	-18.5729	2.2098E-02	1.7848E+05	113.0692
8646002	TALC	-6.8313E+04	-178.2985	1.7520E-01	3.4406E+06	1131.0000
6050002	THENARDITE	-8.6770E+04	-244.8092	2.4363E-01	5.2641E+06	1554.1762
5050001	THERMONATR	-8.5770E+04	-239.8110	2.3590E-01	5.1622E+06	1525.4921
8215001	TREMOLITE	-1.4846E+05	-378.6905	3.7899E-01	7.1749E+06	2405.2929
8415003	WAIRAKITE	-6.8518E+04	-168.1706	1.8245E-01	3.1004E+06	1079.8327
8215002	WOLLASTONITE	-2.0379E+04	-48.4347	5.0170E-02	9.1493E+05	306.0651
2028000	WUSTITE	-1.5879E+04	-32.0262	3.2511E-02	5.6527E+05	207.9928

TABLE 2 . Coefficients to Calculate C_p° (cal mol⁻¹ K⁻¹) for Minerals and Aqueous Species Using Equation (6)

ID No.	Mineral	a	b x 10 ³	c x 10 ⁻⁵	Source
8015005	AKERMINITE	60.09	11.40	-11.40	Helgeson et al. (1978)
2003000	Al(OH) ₃ (A)	8.65	45.60	0.00	Helgeson et al. (1978)(a)
8450003	ANALBITE	61.70	13.90	-15.01	Helgeson et al. (1978)
8450001	ANALCIME	53.49	24.14	-8.88	Helgeson et al. (1978)
6015000	ANHYDRITE	16.78	23.60	0.00	Helgeson et al. (1978)
8641001	ANNITE	106.43	29.77	-19.31	Helgeson et al. (1978)
8415001	ANORTHITE	63.31	14.79	-15.44	Helgeson et al. (1978)
5015000	ARAGONITE	20.13	10.24	-3.34	Helgeson et al. (1978)
2003001	BOEHMITE	14.44	4.20	0.00	Helgeson et al. (1978)
2046000	BRUCITE	24.15	4.01	-6.11	Helgeson et al. (1978)
5015001	CALCITE	24.98	5.24	-6.20	Helgeson et al. (1978)
2077000	CHALCEDONY	11.22	8.20	-2.70	Helgeson et al. (1978)
2077001	CHISTOBALITE	17.39	0.31	-9.89	Helgeson et al. (1978)
8646000	CHRYSTOTILE	75.82	31.60	-17.58	Helgeson et al. (1978)
2003002	DIASPORE	14.44	4.20	0.00	Helgeson et al. (1978)
5015002	DOLOMITE	41.56	23.95	-9.88	Helgeson et al. (1978)
4215000	FLUORITE	14.30	7.28	0.47	Helgeson et al. (1978)
8046000	FORSTERITE	35.81	6.54	-8.52	Helgeson et al. (1978)
8015006	GEHLENITE	63.74	8.00	-15.12	Helgeson et al. (1978)
2003003	GIBBSITE (C)	8.65	45.60	0.00	Helgeson et al. (1978)
2028102	GOETHITE	12.44	12.09	2.42	Helgeson et al. (1978)(b)
6015001	GYPSUM	21.84	76.00	0.00	Naumov, Ryzhenko, and Khodakovskiy (1974)
8441003	H SANIDINE	63.83	12.90	-17.05	Helgeson et al. (1978)
8603000	HALLOYSITE	72.77	29.20	-21.52	Helgeson et al. (1978)
2028105	HEMATITE	23.49	18.60	-3.55	Helgeson et al. (1978)
5015003	HUNTITE	84.17	42.86	-20.44	Helgeson et al. (1978)
5046001	HYDROMAGNESITE	141.46	65.28	-21.67	Helgeson et al. (1978)
8441000	KALSILITE	29.43	17.36	-5.32	Helgeson et al. (1978)
8603001	KAOLINITE	72.77	29.20	-21.52	Helgeson et al. (1978)
8015002	LARNITE	34.87	9.74	-6.26	Naumov, Ryzhenko, and Khodakovskiy (1974)
8415002	LAUMONTITE	123.20	44.47	-16.43	Helgeson et al. (1978)
8415000	LEONHARDITE	235.00	88.94	-32.86	Helgeson et al. (1978)
8441001	LEUCITE	34.62	33.44	-4.76	Naumov, Ryzhenko, and Khodakovskiy (1974)
2015000	LIME	11.67	1.08	-1.56	Helgeson et al. (1978)
8450002	LOW ALBITE	61.70	13.90	-15.01	Helgeson et al. (1978)

TABLE 2. (contd)

ID No.	Mineral	a	b x 10 ³	c x 10 ⁻⁵	Source
5046002	MAGNESITE	19.73	12.54	-4.75	Helgeson et al. (1978)
3025000	MAGNETITE	21.88	48.20	0.00	Helgeson et al. (1978)
8015004	MERWINITE	72.97	11.96	-14.44	Helgeson et al. (1978)
8441002	MICROCLINE	63.83	12.90	-17.05	Helgeson et al. (1978)
8015003	MONTICELLITE	36.82	5.34	-8.00	Helgeson et al. (1978)
8641000	MUSCOVITE	97.56	26.38	-25.44	Helgeson et al. (1978)
8450004	NEPHELINE	35.91	6.46	-7.33	Helgeson et al. (1978)
8215003	P-WOLLASTONITE	26.64	3.60	-6.52	Helgeson et al. (1978)(c)
2046001	PERICLASE	10.18	1.74	-1.48	Helgeson et al. (1978)
8646001	PHLOGOPITE	100.61	28.78	-21.50	Helgeson et al. (1978)
2015001	PORTLANDITE	19.07	10.80	0.00	Naumov, Ryzhenko, and Khodakovskiy (1974)
1028003	PYRITE	17.88	1.32	-3.05	Helgeson et al. (1978)
8603002	PYROPHYLLITE	79.43	39.21	-17.28	Helgeson et al. (1978)
2077002	QUARTZ	11.22	8.20	-2.70	Helgeson et al. (1978)
8646003	SEPIOLITE(C)	78.96	52.15	-9.34	Helgeson et al. (1978)(d)
5028000	SIDERITE	11.63	26.80	0.00	Helgeson et al. (1978)
2077003	SiO ₂ (A, GL)	5.93	47.20	-22.78	Helgeson et al. (1978)(e)
2077004	SiO ₂ (A, PT)	5.93	47.20	-22.78	Helgeson et al. (1978)
8646002	TALC	82.48	41.61	-13.34	Helgeson et al. (1978)
6050002	THENARDITE	14.97	52.90	0.00	Naumov, Ryzhenko, and Khodakovskiy (1974)
5050001	THERMONATR	34.80	0.00	0.00	Naumov, Ryzhenko, and Khodakovskiy (1974)
8215001	TREMOLITE	188.22	57.29	-44.82	Helgeson et al. (1978)
8415003	WAIRAKITE	100.40	44.47	-16.43	Helgeson et al. (1978)
8215002	WOLLASTONITE	26.64	3.60	-6.52	Helgeson et al. (1978)
2028000	WUSTITE	11.66	2.00	-0.67	Naumov, Ryzhenko, and Khodakovskiy (1974)
001	e-	3.26	0.39	0.06	Helgeson et al. (1981)(f)
002	H ₂ O	18.18	0.60	0.00	Present Study(g)
003	Al ³⁺	128.99	-353.77	-46.29	Present Study(g)
140	CO ₃ ²⁻	930.69	-1866.47	-403.31	Present Study(g)
150	Ca ²⁺	139.17	-301.10	-51.14	Present Study(g)
270	F-	463.56	-926.67	-195.28	Present Study(g)
280	Fe ²⁺	147.86	-312.68	-55.33	Present Study(g)
281	Fe ³⁺	168.40	-411.84	-67.82	Present Study(g)
330	H+	0.00	0.00	0.00	Present Study(g)
410	K+	61.12	-106.35	-24.52	Present Study(g)

TABLE 2. (contd)

ID No.	Mineral	a	b x 10 ³	c x 10 ⁻⁵	Source
460	Mg ²⁺	153.98	-314.68	-57.25	Present Study(g)
500	Na ⁺	91.61	-146.45	-34.55	Present Study(g)
730	HS ⁻	458.98	-906.82	-192.87	Present Study(g)
732	SO ₄ ²⁻	951.91	-1883.70	-412.64	Present Study(g)
770	SiO _{2,aq} ^(h)	90.91	-155.02	-39.11	Present Study(g)

(a) C_p same as for gibbsite.

(b) Estimated, assuming that ΔC_p for the reaction $2\text{AlOOH} + \text{Fe}_2\text{O}_3 = 2\text{FeOOH} + \text{Al}_2\text{O}_3$ is equal to zero.

(c) C_p same as for wollastonite.

(d) The MINTEQ formula for sepiolite is one-half that of Helgeson et al. (1978). Therefore these values are one-half the values given by Helgeson et al. (1978).

(e) C_p same as for amorphous silica.

(f) C_p, by definition is one-half that of H₂ gas.

(g) Calculated for this report using Equation (7) and Helgeson and Kirkham (1974a); Shock and Helgeson. (1988); and Shock, E. L., H. C. Helgeson, and D. A. Sverjensky. 1988. "Calculation of the Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures: Standard Partial Molal Properties of Inorganic Neutral Species." Geochim. Cosmochim. Acta Submitted.

(h) The thermodynamic properties for the MINTEQ basis species, H₄SiO₄⁰, are identical to the sum of the properties for SiO_{2,aq} and 2 H₂O. Mass balance constraints result in values of log K_{r,T} that are independent of the choice of SiO_{2,aq} or H₄SiO₄⁰ as the representation of monomeric neutral silica species.

in some instances, minerals (such as gibbsite) decompose at temperatures less than this limit. In using MINTEQ for calculations at elevated temperatures, the user must be aware of this limitation when interpreting the results of saturation calculations and evaluating possible solubility constraints on groundwater compositions.

The coefficients for minerals presented in Table 2 were taken from Helgeson et al. (1978). If values for a particular mineral were not found in Helgeson et al. (1978), values from Naumov, Ryzhenko, and Khodakovskiy (1974) were used. Comparison calculations for selected reactions using more accurate heat capacities from Robie, Hemingway, and Fisher (1978) typically resulted in differences of < 0.05 log units for $\log K_{r,573}$. Given the uncertainties in the heat capacities for the ions and those inherent generally in geochemical calculations, these differences are probably insignificant.

CALCULATION OF COEFFICIENTS FOR AQUEOUS ASSOCIATION REACTIONS

Values of a_0 through a_4 for aqueous speciation reactions are reported in Table 3. In addition, they are given in the format required for use by MINTEQA2 in Appendix A (Table A3). The lack of published or estimated heat capacities for many of the complexes precludes a treatment similar to that given minerals. In addition, values of $\Delta H^\circ_{r,298}$ for many potentially significant complexes are not in the current MINTEQA2 data base. As a result, experimentally determined values of equilibrium constants as a function of temperature were used to determine the coefficients in Equation (1) by least-squares methods. In many cases, the values for $\log K_{r,298}$ and $\Delta H^\circ_{r,298}$ calculated from Equations (1) and (4) and given in Table 4 differ slightly from the corresponding values in MINTEQA2 (also given in Table 4). These differences result from the use of different sources for the equilibrium constants, and/or the requirement that the Equation (1) be a best fit of all available data.

For a limited number of cases, values for a_0 through a_4 were taken directly from sources in the literature. However, for most reactions, these values were determined by regression of Equation (1) to experimentally determined equilibrium constants, to constants calculated using estimated heat capacities, or to both. The number of terms of Equation (1) used was the minimum needed to reproduce the experimental results. For most reactions, the values of equilibrium constants could be reproduced using Equation (1) with a_1 , a_3 , a_5 , and a_6 set equal to 0. The criterion to establish the number of terms was the use of stepwise linear regression with Equation (1) truncated after the fifth term. The linear regression identified the combination of terms that resulted in the smallest standard error and simultaneously had regression coefficients significantly ($p > 0.05$) different than zero. This set of terms typically resulted in the standard error of

TABLE 3. Coefficients for Equation (1) to Calculate Formation Constants for Temperatures of 0° to 300°C

ID No.	Species	a_0	a_1	a_2	a_3	a_4
3300020	OH ⁻	3.1286E+04	94.9734	-9.7611E-02	-2.1709E+06	-606.5220(a)
3307700	H ₃ SiO ₄ ⁻	3.3633E+04	97.5532	-9.7611E-02	-2.1709E+06	-624.9234(b)
3307701	H ₂ SiO ₄ ²⁻	3.3633E+04	111.2423	-1.2946E-01	-2.1709E+06	-706.4820(b)
3301400	HCO ₃ ²⁻	3.1402E+03	13.3115	-5.7100E-03	1.6191E+05	-76.1578(c)
3301401	H ₂ CO ₃ ⁰	-2.6548E+04	-68.5286	8.3939E-02	2.2087E+06	446.3032(c)
3302700	HF ⁰	-2.9282E+03	-17.8144	3.5952E-02	0.0	103.7800(d)
3302701	HF ₂ ⁻	-2.9282E+03	-17.8144	3.7765E-02	0.0	103.7800(d)
3307320	HSO ₄ ⁻	-4.9516E+04	-131.9470	1.3008E-01	3.0629E+06	846.6010(e)
3301800	HCl ⁰	-2.0455E+03	-17.5051	3.5302E-02	0.0	95.3540(f)
3307300	H ₂ S ⁰	-3.9295E+04	-110.7982	1.1357E-01	2.6156E+06	706.7778(g)
0303300	AlOH ₂ ⁺	1.0158E+03	11.5130	0.0	0.0	-74.0110(h)
0303301	Al(OH) ₂ ⁺	-6.0533E+03	0.0	0.0	0.0	10.1270(h)
0303303	Al(OH) ₃ ⁰	-1.9670E+04	-28.6830	0.0	0.0	212.6480(h)
0303302	Al(OH) ₄ ⁻	7.1264E+03	89.9620	-1.2311E-01	0.0	-521.9790(h)
0302700	AlF ₂ ⁺	1.8166E+03	0.0	2.1112E-02	0.0	-5.3776(i)
0302701	AlF ₂ ⁺	2.9934E+03	0.0	3.4891E-02	0.0	-7.6925(i)
0307202	AlF ₃ ⁰	3.8066E+03	0.0	4.2905E-02	0.0	-8.5394(i)
0307203	AlF ₄ ⁻	4.3655E+03	0.0	4.9667E-02	0.0	-9.7300(i)
0307320	AlSO ₄ ⁺	-1.4096E+03	0.0	4.2260E-03	0.0	6.1060(j)
0307321	Al(SO ₄) ₂ ⁻	4.1313E+03	0.0	7.3161E-02	0.0	-32.0030(j)
1503300	CaOH ⁺	3.1854E+04	94.9734	-8.8362E-02	-2.1709E+06	-610.0479(k)
1502700	CaF ⁺	2.4447E+02	0.0	9.1070E-03	0.0	-2.3266(l)
1501400	CaHCO ₃ ⁺	3.6121E+03	13.3115	3.3570E-03	1.6191E+05	-79.3834(m)
1501401	CaCO ₃ ⁰	-2.4890E+03	0.0	1.4995E-02	4.6341E+05	1.9142(m)
1507320	CaSO ₄ ⁰	6.1742E+02	0.0	1.0871E-02	0.0	-3.0127(n)
2803300	FeOH ⁺	-2.1576E+03	0.0	0.0	0.0	-2.9946(o)
2803302	Fe(OH) ₂ ⁰	-5.4119E+03	0.0	0.0	0.0	-2.6493(o)
2803301	Fe(OH) ₃ ⁻	-7.8178E+03	0.0	0.0	0.0	-7.1602(o)
2802700	FeF ⁺	2.5248E+02	0.0	9.1070E-03	0.0	-2.1521(p)
2801400	FeHCO ₃ ⁺	5.7924E+02	-0.1987	5.7100E-03	-1.6191E+05	-9.5889(q)
2807320	FeSO ₄ ⁰	6.1669E+02	0.0	1.0871E-02	0.0	-3.1096(r)
2813300	FeOH ₂ ⁺	1.1597E+03	11.5130	0.0	0.0	-71.6761(s)
2813301	Fe(OH) ₂ ⁺	-3.7026E+03	0.0	0.0	0.0	6.7487(s)
2813302	Fe(OH) ₃ ⁰	-7.5756E+03	-4.3930	0.0	0.0	38.4920(o)
2813303	Fe(OH) ₄ ⁻	-7.9647E+03	-2.9201	0.0	0.0	21.7962(o)

TABLE 3. (Contd)

ID No.	Species	a_0	a_1	a_2	a_3	a_4
2811800	FeCl ₂ ⁺	1.4570E+02	0.0	2.1500E-02	0.0	-5.4275(l)
2811801	FeCl ₂ ⁺	1.9579E+02	0.0	2.2739E-02	0.0	-5.3184(l)
2811802	FeCl ₃ ⁰	1.2753E+02	0.0	2.6633E-02	0.0	-7.2396(l)
2811803	FeCl ₄ ⁻	0.0	0.0	3.2054E-02	0.0	-10.3300(l)
2812700	FeF ₂ ⁺	1.3032E+03	0.0	2.1298E-02	0.0	-4.5209(i)
2812701	FeF ₂ ⁺	1.8057E+03	0.0	3.2114E-02	0.0	-4.8311(i)
2812702	FeF ₃ ⁰	1.8658E+03	0.0	3.4265E-02	0.0	-2.4740(i)
2817320	FeSO ₄ ⁺	-4.7886E+02	0.0	4.2260E-03	0.0	4.2661(u)
2817321	Fe(SO ₄) ₂ ⁻	5.4981E+03	0.0	7.3161E-02	0.0	-34.8335(u)
4107320	KSO ₄ ⁻	1.8200E+02	0.0	7.5770E-03	0.0	-2.0106(v)
4603300	MgOH ⁺	3.1753E+04	94.9734	-8.8427E-02	-2.1709E+06	-608.5988(w)
4602700	MgF ⁺	3.0204E+02	0.0	9.1070E-03	0.0	-1.8368(l)
4601401	MgHCO ₃ ⁺	4.1747E+03	13.3115	7.9520E-03	1.6191E+05	-82.6283(x)
4601400	MgCO ₃ ⁰	1.9463E+02	0.0	8.4370E-03	0.0	-0.1865(x)
4607320	MgSO ₄ ⁰	6.6046E+02	0.0	1.0871E-02	0.0	-3.2264(r)
5001800	NaCl ⁰	-1.3910E+04	-37.3677	4.5379E-02	1.0919E+06	232.8184(y)
5002700	NaF ⁰	2.9559E+03	10.0830	0.0	0.0	-68.3130(l)
5001401	NaHCO ₃ ⁰	5.5302E+03	23.3945	-5.7100E-03	1.6191E+05	-141.4428(z)
5001400	NaCO ₃ ⁻	1.6483E+03	0.0	7.5770E-03	0.0	-7.2474(z)
5007320	NaSO ₄ ⁻	4.2877E+02	0.0	7.5770E-03	0.0	-2.9972(z)
2812800	Fe ³⁺ /Fe ²⁺	2.8477E+03	0.0	6.6240E-03	0.0	1.5276(g)
7307320	HS ⁻ /SO ₄ ²⁻	-2.5771E+04	-105.3407	1.1254E-01	2.5972E+06	657.5363(g)
3301403	CO ₂ ,gas	-1.9628E+04	-50.9607	6.4088E-02	1.5393E+06	337.9167(aa)

(a) Sweeton, Mesmer and Baes (1974).

(b) Busey and Mesmer (1977) give values for neutralization reactions. These have been combined with the dissociation of water. In addition, for H₂SiO₄²⁻ results are given at ionic strength of 1. The values were used to estimate the value of ΔH_f° which was combined with the room-temperature dissociation constant from Baes and Mesmer (1976) and heat capacities from Smith, Popp and Norman (1986).

(c) Patterson et al. (1982) and Patterson, Busey, and Mesmer (1984).

(d) Ellis (1963).

(e) Smith, Popp, and Norman (1986).

(f) Ruaya and Seward (1987). Only the authors' measurements are used.

(g) Shock and Helgeson (1988) and Shock, E. L., H. C. Helgeson, and D. A. Sverjensky. 1988.

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(h) Based on values reported by May, Helmke, and Jackson (1979); Baes and Mesmer (1976); and Bourcier, Knauss, and Jackson (1987).

TABLE 3. (Contd)

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- (i) Room temperature values for aluminum and ferric fluoride complexes are from Smith (1983) and Nordstrom and Jenne (1977). Higher temperature values were calculated as described in the text.
 - (j) Based on the results (extrapolated to zero ionic strength) of Lo, Meites, and Matijevic (1982).
 - (k) Based on values given by Baes and Mesmer (1976), assuming the heat capacity of $\text{Ca}^{2+} + \text{OH}^- = \text{CaOH}^+$ is the same as for the formation of CaF^+ .
 - (l) Richardson and Holland (1979).
 - (m) Based on Plummer and Busenberg (1982), assuming the heat capacity for the reactions $\text{CaF}^+ + \text{HCO}_3^- = \text{CaHCO}_3^+ + \text{F}^-$ and $\text{CaCO}_3^\circ + \text{H}^+ = \text{CaHCO}_3^+$ are constants.
 - (n) Based on reevaluation of the values reported by Yeatts and Marshall (1969) using the model for activity coefficients of Helgeson, Kirkham, and Flowers (1981).
 - (o) Tremaine and LeBlanc (1980) and the equilibrium constant for the ferric/ferrous couple given here.
 - (p) Based on room temperature data given by Smith (1983), assuming the heat capacity of reaction is the same as for the formation of MgF^+ .
 - (q) Cobble et al. (1982).
 - (r) Smith and Martell (1976), assuming the same heat capacity of reaction as CaSO_4° .
 - (s) Calculated from hydrolysis constants given in Baes and Mesmer (1976), assuming the heat capacity for hydrolysis is the same as for aluminum. The entropy for $\text{Fe}(\text{OH})_2^+$ is estimated.
 - (t) Helgeson (1969).
 - (u) MINTEO, assuming the same heat capacity of reactions as for $\text{Al}(\text{SO}_4)_n^{3-2n}$.
 - (v) Calculated from values at 25° (Smith and Martell 1976), 39°, 100°, and 200°C (Sillen and Martell 1971).
 - (w) Based on McGee and Hostettler (1975), assuming the heat capacity of $\text{Mg}^{2+} + \text{OH}^- = \text{MgOH}^+$ is the same as for the formation of MgF^+ .
 - (x) Based on Siebert and Hostettler (1977 a,b), assuming the heat capacity for the reactions $\text{MgF}^+ + \text{HCO}_3^- = \text{MgHCO}_3^+ + \text{F}^-$ and $\text{MgCO}_3^\circ + \text{H}^+ = \text{MgHCO}_3^+$ are constants.
 - (y) Helgeson, Kirkham, and Flowers (1981).
 - (z) Wagman et al. (1982), assuming that the heat capacity of reaction for NaHCO_3° is the same as for NaF° and that the heat capacity of reaction for NaSO_4^- and NaCO_3^- are the same as for KSO_4^- .
 - (aa) Plummer and Busenberg (1982).

TABLE 4. Values of $\log K_{r,298}^\circ$ and $\Delta H_{r,298}^\circ$ for Formation Constants From the MINTEQ Data Base^(a) and Derived by the Present Study

ID No.	Species	$\Delta H_{r,298}^\circ$ (kcal)			$\log K_{r,298}^\circ$		
		Present Study	MINTEQ	Δ	Present Study	MINTEQ	Δ
3300020	OH ⁻	13.34	13.35	-0.01	-13.99	-14.00	0.01
3307700	H ₃ SiO ₄ ⁻	6.12	8.94	-2.82	-9.82	-9.93	0.11
3307701	H ₂ SiO ₄ ²⁻	11.84	29.71	-17.87	-22.88	-21.62	-1.26
3301400	HCO ₃ ⁻	-3.50	-3.62	0.12	10.34	10.33	0.01
3301401	H ₂ CO ₃ ⁰	-5.67	-2.25	-3.42	16.69	13.68	0.01
3302700	HF ⁰	3.72	3.46	0.26	3.18	3.17	0.01
3302701	HF ₂ ⁻	4.46	4.55	-0.09	3.72	3.75	-0.03
3307320	HSO ₄ ⁻	5.46	4.91	0.55	1.98	1.99	-0.01
3301800	HCl ⁰	-0.16	new		-0.72	new	
3307300	H ₂ S ⁰	-5.44	-5.30	-0.14	6.98	6.99	-0.01
0303300	Al(OH) ₂ ⁺	11.06	11.90	-0.84	-5.01	-4.99	-0.02
0303301	Al(OH) ₂ ⁺	27.70	no value		-10.18	-10.10	-0.08
0303303	Al(OH) ₃ ⁰	50.87	no value		-16.75	-16.00	-0.75
0303302	Al(OH) ₄ ⁻	40.05	44.06	-4.01	-22.21	-23.00	0.79
0302700	AlF ₂ ⁺	0.27	no value		7.01	7.01	0.00
0302701	AlF ₂ ⁺	0.50	20.00	-19.50	12.75	12.75	0.00
0307202	AlF ₃ ⁰	0.03	2.50	-1.18	17.02	17.02	0.00
0307203	AlF ₄ ⁻	0.23	no value		19.72	19.72	0.00
0307320	AlSO ₄ ⁺	8.17	2.15	6.02	2.64	3.02	-0.38
0307321	Al(SO ₄) ₂ ⁻	10.85	2.84	8.01	3.67	4.92	-1.25
1503300	CaOH ⁺	14.50	14.54	-0.04	-12.85	-12.60	-0.25
1502700	CaF ⁺	2.59	3.80	-1.21	1.21	0.94	0.27
1501400	CaHCO ₃ ⁺	-1.97	1.79	-3.76	11.40	11.33	0.07
1501401	CaCO ₃ ⁰	3.26	4.03	-0.77	3.25	3.15	0.10
1507320	CaSO ₄ ⁰	1.60	1.47	0.13	2.30	2.31	-0.01
2803300	FeOH ⁺	9.87	13.20	-3.33	-10.23	-9.50	-0.73
2803302	Fe(OH) ₂ ⁰	24.76	28.57	-3.81	-20.80	-20.57	-0.23
2803301	Fe(OH) ₃ ⁻	35.77	30.30	5.47	-33.38	-31.00	-2.38
2802700	FeF ⁺	2.55	new		1.41	new	
2801400	FeHCO ₃ ⁺	4.37	new		-8.90	new	
2807320	FeSO ₄ ⁰	1.60	3.23	-1.63	2.20	2.25	-0.05

(a) MINTEQ data reported in Peterson et al. (1987).

TABLE 4. (contd)

ID No.	Species	$\Delta H^\circ_{r,298}$ (kcal)			$\log K^\circ_{r,298}$		
		Present Study	MINTEQ	Δ	Present Study	MINTEQ	Δ
2813300	FeOH ²⁺	10.40	10.34	0.06	-2.19	-2.19	0.00
2813301	Fe(OH) ₂ ⁺	16.94	no value		-5.67	-5.67	0.00
2813302	Fe(OH) ₃ ⁰	28.67	no value		-11.95	-13.60	1.65
2813303	Fe(OH) ₄ ⁻	32.46	no value		-21.56	-21.60	0.04
2811800	FeCl ₂ ⁺	8.08	5.60	2.48	1.47	1.48	-0.01
2811801	FeCl ₂ ⁺	8.35	no value		2.12	2.13	-0.01
2811802	FeCl ₃ ⁰	10.25	no value		1.13	1.13	0.00
2811803	FeCl ₄ ⁻	13.04	new		-0.77	new	
2812700	FeF ₂ ⁺	2.70	2.70	0.00	6.20	6.20	0.00
2812701	FeF ₂ ⁺	4.80	4.80	0.00	10.80	10.80	0.00
2812702	FeF ₃ ⁰	5.40	5.40	0.00	14.00	14.00	0.00
2817320	FeSO ₄ ⁺	3.91	3.91	0.00	3.92	3.92	0.00
2817321	Fe(SO ₄) ₂ ⁻	4.60	4.60	0.00	5.42	5.42	0.00
4107320	KSO ₄ ⁻	2.25	2.25	0.00	0.86	0.85	0.01
4603300	MgOH ⁺	14.94	15.94	-1.00	-11.76	-11.79	0.03
4602700	MgF ⁺	2.32	4.67	-2.35	1.89	1.82	0.07
4601401	MgHCO ₃ ⁺	-2.68	-2.43	-0.25	11.41	11.40	0.01
4601400	MgCO ₃ ⁰	2.54	2.02	0.52	2.98	2.98	0.00
4607320	MgSO ₄ ⁰	1.40	1.40	0.00	2.23	2.25	-0.02
5001800	NaCl ⁰	-2.39	new		-0.93	new	
5002700	NaF ⁰	0.23	no value		-0.95	-0.79	-0.16
5001401	NaHCO ₃ ⁰	-0.68	no value		10.52	10.08	0.44
5001400	NaCO ₃ ⁻	-4.46	8.91	-13.37	0.54	1.27	-0.73
5007320	NaSO ₄ ⁻	1.12	1.12	0.00	0.70	0.70	0.00
2812800	Fe ³⁺ /Fe ²⁺	-10.34	-10.00	-0.34	13.05	13.03	0.02
7307320	HS ⁻ /SO ₄ ⁻²	-59.74	-60.14	0.40	33.68	33.66	0.02
3301403	CO _{2,gas}	-0.89	-0.53	-0.36	18.15	18.16	-0.01

estimate being the same (or smaller) than the stated (or estimated) experimental uncertainties. The reactions where the standard error of estimate was larger than the reported experimental uncertainties were the result of underestimating experimental uncertainties or using equilibrium constants from multiple sources that disagree. In the first case, new error estimates were made. In the latter case, methods used to approximate the heat capacity for aqueous association reactions such as described below were used to identify data sets (or individual measurements) that disagreed.

ESTIMATION OF TEMPERATURE DEPENDENCE

The heat capacity for ions and many dissociation reactions are strongly dependent on temperature (cf., Helgeson, Kirkham, and Flowers 1981). Typically, the heat capacity increases rapidly as temperature is increased above 0°, pass through a maximum at about 60 to 70°C and then plunging to negative infinity as the critical temperature (374.14°C) of water is approached (Helgeson, Kirkham, and Flowers 1981). However, recent work by Tanger and Helgeson (1988) suggests that the heat capacity for cations passes through a minimum and climbs to positive infinity at the critical point. In order to minimize the magnitude of the change of heat capacity with temperature, chemical reactions were rewritten using the Principle of Balance of Identical Like Charges (Murray and Cobble 1980; Cobble et al. 1982). These authors suggest that the heat capacity for a reaction involving aqueous ions can be treated as being constant over a large range of temperatures if the reaction is written such that there is a balance of similar species having the same ionic charge on both sides of the equilibrium reaction. For example, Cobble et al. (1982) point out that for the reaction:

ΔC_p° varies between -43 and -218 cal mol⁻¹ K⁻¹ for temperatures of 25° and 300°C, respectively. However, rewriting the reaction using the Principle of Balance of Identical

Like Charges, Reaction (8) becomes:

For Reaction (9), values of $\log K_{r,T}$ between 0° and 300°C can be represented within experimental uncertainties using a constant value of 12 cal mole⁻¹ K⁻¹ for ΔC_p° . This approach was used extensively in this study to calculate values of equilibrium constants for aqueous association reactions for temperatures of up to 300°C by using equilibrium measurements for temperatures of 0° to 90°C.

Smith, Popp, and Norman (1986) found that, for dissociation of oxy-acids, ΔC_p° could be treated as acid-independent. This is equivalent to the heat capacity of reaction $\Delta C_p^\circ = 0$ for reactions of the form:

In the present study it was assumed that, for complexes of mono- and divalent cations with fluoride, hydroxide, and sulfate, the heat capacity for reaction written in the form of Reaction (10) was zero. For example, equilibrium constants for temperatures of 0° to 260°C are reported (Richardson and Holland 1979) for:

McGee and Hostetler (1975) report equilibrium constant for temperatures of 10° to 90°C for:

Combining Reactions (11) and (12) yields:

Equilibrium constants for Reaction (13) in the temperature range of 10° to 90°C can be calculated from smoothed experimental values of $\log K_{r,T}$ for Reactions (11) and (12). These values can be used along with the assumption that $\Delta C_p^\circ = 0$ to estimate values of $\log K_{r,T}$ for Reaction (13) for elevated temperatures. Values of $\log K_{r,T}$ for Reaction (12) can be estimated by subtracting the $\log K_{r,T}$ values for Reaction (11). Using this approach, the heat capacity of species such as MgOH^+ , CaOH^+ , and NaSO_4^- could be estimated from MgF^+ , CaF^+ , and KSO_4^- , respectively.

In many cases, there were not enough low-temperature equilibrium data to use the Principle of Balance of Identical Like Charges. In these cases, the method described by Jackson and Helgeson (1985) to estimate values of $\log K_{r,T}$ was used. Helgeson (1967) found that the dissociation constant of an aqueous complex for the temperature range of 0° to 150°C can be closely approximated by:

$$\log K_{r,T} = \frac{\Delta S_{Tr}^\circ}{2.303RT} \left\{ Tr - \frac{\theta}{\omega} \left(1 - \exp \left[\exp(b + aT) - c + \frac{T - Tr}{\theta} \right] \right) \right\} - \frac{\Delta H_{r,Tr}^\circ}{2.303RT} \quad (14)$$

where ΔS_{Tr}° and $\Delta H_{r,Tr}^\circ$ are the entropy and enthalpy of reaction, respectively, at temperature Tr (298.15); and a , b , c , θ and ω are temperature-independent constants characteristic of the solvent (water) with values of 0.01875, -12.741, 7.84×10^{-4} , 219 and 1.00322, respectively (Helgeson 1967). Equation (14) was used in the present study to estimate dissociation constants for reaction (primarily Al^{3+} and Fe^{3+} fluoride complexes and Fe^{3+} chloride complexes) at 25° intervals from 0° to 150°C. These estimated constants and the principle of balance of identical charges were used to calculate equilibrium constants to temperatures of 250°C. Consider, for example, the

reaction:

Values of the equilibrium constant for Reaction (15) were calculated at 25° intervals between 0° and 150°C (Figure 2) using the method of Helgeson (1967) and values of $\Delta S^{\circ}_{\text{Tr}}$ and $\Delta H^{\circ}_{\text{r,Tr}}$ taken or calculated from the MINTEQA data file. These calculated values were combined with dissociation constants for AlOH^{2+} (these have been measured from 0° to 250°C, as in Table 3) to provide equilibrium constants for the reaction:

Variation of the equilibrium constants with temperature for Reactions (15) and (16) is illustrated in Figure 1. The substantial curvature for Reaction (13) requires that at least three terms of Equation (1) are required to represent the temperature dependence of Reaction (15). However, the temperature dependence of Reaction (14) can be represented to ± 0.2 (error bars, Figure 1) by just two terms of Equation (1). Equation (1), with a_2 and a_3 set equal to zero, was fit to the calculated values of $\log K_{\text{r,T}}$ for Reaction (16) and the resulting equation used to calculate equilibrium constants up to 250°C. Subtraction of dissociation constants for AlOH^{2+} provides calculated equilibrium constants for Reaction (13) from 0° to 250°C. These results were used in regression analysis to derive the coefficients given in Table 3. In addition, the regression was constrained so that $\log K_{\text{r,298}}$ and/or $\Delta H^{\circ}_{\text{r,298}}$ agreed with the current MINTEQA values.

FIGURE 1. Equilibrium Constants for reactions (15) and (16)

ACTIVITY COEFFICIENTS

Various extended forms of the Debye-Hückel equation can be used to approximate the activity coefficient of an individual ion as a function of ionic strength (I). The current MINTEQA2 code uses two such extended forms: the Davies equation,

$$\log \gamma_i = -A z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right) \quad (17)$$

or an extended Debye-Hückel equation (Peterson et al. 1987; Truesdell and Jones 1974) of the form

$$\log \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + a_i B \sqrt{I}} + b_i I \quad (18)$$

where γ_i , z_i , a_i and b_i are the activity coefficient, the charge, the ion size, and extended parameter for the i th ion, respectively. A and B are constants that depend on the temperature, the density, and the dielectric constant of water (see below). Values of a_i and b_i for major ions were calculated from experimental mean salt single-ion activity coefficients (Truesdell and Jones 1974). For other ions considered in this study, only values of a_i are in the current data base.

Calculation of activity coefficient at elevated temperatures requires that A , B , a_i , and b_i be known as a function of temperature. In principle, the procedure used by Truesdell and Jones (1974) to calculate a_i and b_i could be repeated at elevated temperatures. However, a simpler approach is that proposed by Helgeson (1969) in which a_i is assumed to be independent of temperature and b_i (B° in Helgeson's formulation) is a function of temperature but the same for all ions. Helgeson (1969) calculated values of B° for temperatures of up to 270°C from NaCl mean activity

coefficient. Least squares fit of Equation (1) to the B^* values of Helgeson (1969) results in:

$$B^* = \frac{15698.4}{T} + 41.8088 \ln T - 0.0367626 T - \frac{974169}{T^2} - 268.902 \quad (20)$$

Values of A and B are calculated from (Helgeson and Kirkham 1974b):

$$A = \frac{1.8248229238 \times 10^6 \rho^{1/2}}{(\epsilon T)^{3/2}} \quad (21)$$

and [for $\hat{A}_i$ in cm, Equation (18)]:

$$B = \frac{50.29158649 \times 10^8 \rho^{1/2}}{(\epsilon T)^{1/2}} \quad (22)$$

The temperature is given by T , ρ is the density of water, and ϵ is the static dielectric constant of water.

The density of steam saturated water can be represent by (Saul and Wagner 1987):

$$\frac{\rho}{\rho_c} = b_1 \tau^{1/3} + b_2 \tau^{2/3} + b_3 \tau^{5/3} + b_4 \tau^{16/3} + b_5 \tau^{43/3} + b_6 \tau^{110/3} \quad (23)$$

where $\tau = 1 - T / T_c$ and c refers to the corresponding value at the critical point ($\rho_c = 0.322 \text{ g cm}^{-3}$ and $T_c = 647.14\text{K}$). The numerical values of the coefficients b_1 through b_6 are 1.99206, 1.10123, -0.512506, -1.75263 -45.4485, and -675615, respectively.

The value of the static dielectric constants of water as a function of density and temperature (Uematsu and Franck 1980) can be represented by:

$$\varepsilon = 1 + \sum_{j=1}^4 \sum_{k=1}^3 A_{j,k} T^{\theta_{j,k}} \rho^j \quad (24)$$

where $T^* = T / 298.15$ and the numerical values of the coefficients of $A_{j,k}$ and $e_{j,k}$ are given in Table 5.

TABLE 5. Values for $A_{j,k}$ (Upper Matrix) and $e_{j,k}$ (Lower Matrix) for Calculation of the Dielectric Constant of Water Using Equation (24)

j	k		
	1	2	3
1	7.62571	0	0
2	244.003	-140.569	27.7841
3	-96.2805	41.7909	-10.2099
4	-45.2059	84.6395	-35.8644

j	k		
	1	2	3
1	-1	0	0
2	-1	0	1
3	-1	1	2
4	-2	-1	0

Equations (18) through (24) provide a simple means by which individual ion activity coefficients can be calculated for elevated temperatures. However, it is important to note that the extended Debye-Hückel equation, the Davies equation used in MINTEQA2, and the B⁺ method of Helgeson (1969) will not yield identical values for activity coefficients at 25°C. The difference between these methods as a function of ionic strength is given in Table 6.

Appendix A presents the modifications to the MINTEQA2 computer code that allow it to calculate activity coefficients at elevated temperatures, as discussed in this report.

TABLE 6. Comparison of Activity Coefficient Calculated for 25°C From the MINTEQA2 Extended Debye-Hückel Equation^(a), the B⁺ Method^(b), and the Davies Equation^(c)

		Ionic Strength			
		0.01	0.10	0.30	0.50
γ_{Na^+}	MINTEQA2	0.903	0.783	0.725	0.709
	B ⁺	0.902	0.777	0.708	0.682
	Davies	0.902	0.781	0.734	0.733
γ_{Cl^-}	MINTEQA2	0.900	0.765	0.681	0.644
	B ⁺	0.901	0.769	0.694	0.664
	Davies	0.902	0.781	0.734	0.733
$\gamma_{\text{Ca}^{2+}}$	MINTEQA2	0.671	0.391	0.290	0.261
	B ⁺	0.669	0.380	0.266	0.226
	Davies	0.662	0.373	0.290	0.289
$\gamma_{\text{SO}_4^{2-}}$	MINTEQA2	0.668	0.373	0.252	0.206
	B ⁺	0.669	0.380	0.266	0.226
	Davies	0.662	0.373	0.290	0.289

(a) Equation (18) and the values of $\hat{a}_i$ and b_i given by Truesdell and Jones (1974).

(b) Helgeson (1969) and values of $\hat{a}_i$ given by Truesdell and Jones (1974).

(c) Equation (17).

TEMPERATURE AND IONIC STRENGTH LIMITATIONS OF EQUATIONS AND COEFFICIENTS

The equilibrium constants calculated from the equations and coefficients presented in this report are useful for the equilibrium modeling of water/rock systems. Equations presented for mineral solubility and hydrolysis reactions are valid for temperatures of up to 300°C. Equations for the formation constant for aqueous complexes are also valid for temperatures of up to 300°C, with some exceptions. The equations for sulfate, fluoride and chloride complexes of Al^{3+} and Fe^{3+} are valid to temperatures of 250°C. Fortunately, these complexes do not significantly contribute to the speciation of most heated groundwater. The equations and coefficients present here should not be used for temperatures >300°C. If higher temperature calculations are needed, the equation of state of Tanger and Helgeson (1988) should be used. Because of the use of extrapolation techniques, the uncertainties associated with modeling results are proportional, to the temperature with calculations for 300°C having larger uncertainties than those at 200°C^(a).

The goal of this study was to produce temperature functions for MINTEQ that joined smoothly with the current room temperature data base (Peterson et al. 1987) wherever possible. This has been accomplished for mineral hydrolysis and solubility reactions. For many aqueous complexes, this goal has not been realized. However, the differences between the temperature functions presented here and the current MINTEQ data base are documented in Table 4. No attempt was made in this study to perform a complete evaluation of the 25°C data base. As a result, the existence of any inconsistencies or errors in the current data base has been implicitly incorporated into the temperature functions.

(a) The definition of the absolute magnitude of the uncertainties associated with such calculations is outside the scope of this report.

The equations presented here and used by MINTEQ provide estimates of the values of individual ion activity coefficients. The models used are based on the behavior of a single salt in water and these values are assumed to represent the behavior of ions in mixed electrolyte. In dilute solutions the uncertainties introduced by this assumption are less significant than in concentrated solutions (cf., Helgeson, Kirkham, and Flowers 1981). The MINTEQ User's Manual (Peterson et al. 1987) recommends that the activity coefficients calculation in MINTEQ be limited to ionic strengths of less than 0.5 molal. For more concentrated brines, a more elaborate model of mixed electrolyte activity coefficients, such as that presented by Helgeson, Kirkham, and Flowers (1981) should be incorporated into the code.^(a)

(a) An alternate approach is to use Pitzer's (1973) model of aqueous electrolytes. However, this approach (summarized by Pitzer, 1987) is not compatible with the conceptual aqueous speciation model upon which MINTEQ is based in that the formation of aqueous complexes is implicitly accounted for by double and triple ion interaction terms in the activity coefficient expression. Geological application of models based on Pitzer's equations are reviewed by Weare (1987).

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APPENDIX A

CODE CHANGES IN MINTEQ AND ANALYT.DAT

APPENDIX A

CODE CHANGES IN MINTEQ AND ANALYT.DAT

Several changes have been made to the MINTEQ code (the IBM Personal Computer™ version, MINTEQP2) to incorporate the calculations in this report. These changes include:

- a new subroutine (DEBYE) to calculate the dielectric constant, the Debye-Hückel A and B, and B° as a function of temperature.
- changes to calculate activity coefficients using the B° method of Helgeson (1969) – Calculations by the B° method are invoked by setting $KDAV = 2$.
- a new ANALYT.DAT file containing the coefficients given in Tables 1 and 3 (a_1 in Tables 1 and 3 by 2.30258509 to convert from natural to base 10 logarithms).

To facilitate these modifications by MINTEQ users the changes in code and data files are documented in Tables A.1 through A.3. In addition, MAIN is a reserved symbol in the Microsoft™ version 4.0 FORTRAN compiler for the IBM Personal Computer™. Therefore, the subroutine MAIN was renamed START.

TABLE A.1. Subroutine DEBYE

```

SUBROUTINE DEBYE (TEMP, DIE, DHA, DHB, BDOT)
C
C This Subroutine calculates the dielectric constant of water as a
C function of temperature and density using the equation of Uematsu
C and Franck (1980, J. Phys. Chem. Ref. Data, 9, 1291-1306). This
C equation is valid from 0 to 550 C and 0 to 5 kbars. The
C density of water is calculated at saturation pressures from the
C equation of Saul and Wagner (1987, J. Phys. Chem. Ref. DATA, 16,
C 893-901). The A and B Debye-Huckel values are calculated from
C the dielectric constants and the density. The temperature
C dependence of the Bdot values (Helgeson 1969, Am. J. Sci., 267,
C 729-804.) are also calculated for use with the extended
C Debye-Huckel equation.
C
C
C WRITTEN BY: R.W. SMITH
C           PACIFIC NORTHWEST LABORATORY
C           JULY 1988
C
C VARIABLES:
C           TEMP = TEMPERATURE IN C (FROM CALLING ROUTINE)
C
C           DIE  = DIELECTRIC CONSTANT AT TEMPERATURE TEMP
C                 (RETURNED)
C
C           DHA  = DEBYE-HUCKEL A AT TEMPERATURE TEMP
C                 (RETURNED)
C
C           DHB  = DEBYE-HUCKEL B AT TEMPERATURE TEMP
C                 (RETURNED)
C
C           BDOT = HELGESON BDOT PARAMETER AT TEMPERATURE TEMP
C                 (RETURNED)
C
C           DIMENSION A(4,3), IAE(4,3), B(6), BE(6)
C
C LOAD COEFFICIENTS (B) AND EXPONENTS (IBE) FOR DENSITY POLY
C
C           B(1) =      1.99206
C           B(2) =      1.10123
C           B(3) =     -0.512506
C           B(4) =     -1.75263
C           B(5) =    -45.4485
C           B(6) = -675615.0
C           BE(1) =    1.0/3.0
C           BE(2) =    2.0/3.0
C           BE(3) =    5.0/3.0
C           BE(4) =   16.0/3.0
C           BE(5) =   43.0/3.0
C           BE(6) =  110.0/3.0
C
C CRITICAL TEMPERATURE AND DENSITY FOR WATER

```

```

C
      TCRIT = 647.14
      RHOCRIT = 0.322
C
C REFERENCE TEMPERATURE FOR DIELECTRIC CONSTANT
C
      TO = 298.15
C
C COEFFICIENTS (A) AND EXPONENTS (IAE) FOR DIELECTRIC POLY
C
      A(1,1) = 7.62571
      A(1,2) = 0.00
      A(1,3) = 0.00
      A(2,1) = 244.003
      A(2,2) = -140.569
      A(2,3) = 27.7841
      A(3,1) = -96.2805
      A(3,2) = 41.7909
      A(3,3) = -10.2099
      A(4,1) = -45.2059
      A(4,2) = 84.6395
      A(4,3) = -35.8644
      IAE(1,1) = -1
      IAE(1,2) = 0
      IAE(1,3) = 0
      IAE(2,1) = -1
      IAE(2,2) = 0
      IAE(2,3) = 1
      IAE(3,1) = -1
      IAE(3,2) = 1
      IAE(3,3) = 2
      IAE(4,1) = -2
      IAE(4,2) = -1
      IAE(4,3) = 0
C
      T = TEMP + 273.15
C
C CALCULATE THE DENSITY OF WATER (RHO)
C
      RHO = 1
      DO 100 I = 1,6
          RHO = RHO + B(I)*(1 - T/TCRIT)**BE(I)
100  CONTINUE
      RHO = RHO*RHOCRIT
C
      TT = T/TO
      DIE = 1
      DO 120 J = 1,4
          DO 110 I = 1,3
              DIE = DIE + A(J,I)*TT**IAE(J,I)*RHO**J
110  CONTINUE
120  CONTINUE
C
C CALCULATE DEBYE-HUCKEL A AND B VALUES
C
      DHA = 1824829.238*SQRT(RHO/(DIE*T)**3)
      DHB = 50.29158649*SQRT(RHO/(DIE*T))
C

```

C CALCULATE VALUE OF BDOT

C

BDOT = 15698.4/T + 41.8088*ALOG(T) - 0.0367626*T

1 - 974169./T**2 - 268.902

RETURN

END

TABLE A.2. Changes to MINTEQP2

Changes to the subroutine ACTVTY:

Present:

```

      SUBROUTINE ACTVTY
C
C *****
C
C ACTVTY
C
C THIS SUBROUTINE CALCULATES
C   1. ACTIVITY COEFFICIENTS FOR ALL SPECIES BY BOTH
C      THE DAVIES AND DEBYE-HUCKEL EQUATIONS
C   2. THE IONIC STRENGTH(MU)
C   3. THE IONIC STRENGTH CORRECTION FOR THE EQUILIBRIUM
C      CONSTANTS BY CALLING KCORR
C
C *****
C

```

new:

```

      SUBROUTINE ACTVTY
C
C *****
C
C ACTVTY
C
C THIS SUBROUTINE CALCULATES
C   1. ACTIVITY COEFFICIENTS FOR ALL SPECIES BY BOTH
C      THE DAVIES AND DEBYE-HUCKEL EQUATIONS
C   2. THE IONIC STRENGTH(MU)
C   3. THE IONIC STRENGTH CORRECTION FOR THE EQUILIBRIUM
C      CONSTANTS BY CALLING KCORR
C7/88 4. ACTIVITY COEFFICIENTS BY THE BDOT METHOD
C
C *****
C

```

Present:

```

C
C NOW USE THE DEBYE HUCKEL IF DHA IS NOT EQUAL TO 0
C
      DO 120 I=1,I3
      IF(I.EQ.INDE.OR.DHA(I).EQ.0.0) GO TO 120
      GAMMA(I)=-1.0*AA*SPCZ(I)*SPCZ(I)*MUHALF/(1.0
1          +BB*DHA(I)*MUHALF)+DHB(I)*MU

```


120 CONTINUE

New:

```
C
C NOW USE THE DEBYE HUCKEL IF DHA IS NOT EQUAL TO 0
C
C7/88
C7/88 IF KDAV=2, GAMMAS FOR SPECIES WITH NONZERO DHA ARE
C7/88 CALCULATED USING THE BDOT METHOD OF HELGESON (1969)
C7/88 BDOT IS CALCULATED AS A FUNCTION OF TEMPERATURE IN
C7/88 THE SUBROUTINE DEBYE
C7/88
      DO 120 I=1,I3
      IF (I.EQ.INDE.OR.DHA(I).EQ.0.0) GO TO 120
      IF (KKDAV.EQ.2) DHB(I) = BDOT
      GAMMA(I)=-1.0*AA*SPCZ(I)*SPCZ(I)*MUHALF/(1.0
1      +BB*DHA(I)*MUHALF)+DHB(I)*MU
120 CONTINUE
```

Changes to the subroutine IAP

Present:

```
      DIMENSION AT(10),IDT(10),ID(20),TA(20),TB(20),TC(20),
1TD(20),TE(20),TF(20),TG(20)
      REAL*4 MINGKT,MAXGKT,NEWPK,KO
      CHARACTER*12 MINNAM
      CHARACTER*2 MATCH,MATCHE
```

New:

```
      DIMENSION AT(10),IDT(10),ID(100),TA(100),TB(100),TC(100),
1TD(100),TE(100),TF(100),TG(100)
      REAL*4 MINGKT,MAXGKT,NEWPK,KO
      CHARACTER*12 MINNAM
      CHARACTER*2 MATCH,MATCHE
```

Changes to the subroutine INPUT

Present:

```
      WRITE(LUN0,6006)
6006 FORMAT(15X,'23. 9/28/84 C. CCWAN REMOVED HUMATE AND
1FULVATE COMPLEXES FROM THERMO DATA'/
215X,'24. 11/19/84 C. COWAN CORRECTED ERROR IN ID NUMBER
3 FOR FE(OH)3-SOIL'/)
```

C2345678901234567890123456789012345678901234567890123456789012

New:

```
        WRITE(LUNO,6006)
6006  FORMAT(15X,'23.  9/28/84 C. COWAN REMOVED HUMATE AND
        1FULVATE COMPLEXES FROM THERMO DATA'/
        215X,'24.  11/19/84 C. COWAN CORRECTED ERROR IN ID NUMBER
        3 FOR FE(OH)3-SOIL'/)
C2345678901234567890123456789012345678901234567890123456789012
        WRITE(LUNO,6007)
6007  FORMAT(15X,'25.  7/26/88 R.W. SMITH ADDED SUBROUTINE DEBYE TO
        1CALCULATE THE DIELECTRIC CONSTANT AND DEBYE-HUCKEL PARAMETERS'/
        215X,'26.  7/26/88 R.W. SMITH ADDED BDOT METHOD TO CALCULATE
        3ACTIVITY COEFFICIENTS'/15X,'27  R.W. SMITH EXPANDED ANALYT.DAT
        4 TO INCLUDE 120+ MINERALS AND SPECIES (PNL-XXXX).')
```

Changes to the subroutine PREP

Present:

```
C
C
C THE NEXT SECTION OF CODE WHICH COMPUTES THE DEBYE-HUCKEL
C CONSTANTS AS A FUNCTION OF TEMPERATURE WAS TAKEN DIRECTLY
C FROM WATEQ2(BALL ET AL. 1979). THE MATHEMATICS IS DOCUMENTED
C IN TRUESDELL AND JONES(1974).
C
      S1=374.11-TEMP
      S2=S1**0.333333
      S3=SQRT((1+0.1342489*S2-3.946263E-3*S1)/
      1      (3.1975-0.3151548*S2-1.203374E-3*S1+7.48908E-13*S1**4))
      IF (TEMPK.LT.373.16) THEN
        CC1=87.74-TEMP*(TEMP*(1.41E-6*TEMP-9.398E-4)+0.4008)
      ELSE
        CC1=5321/TEMPK+233.76-TEMPK*(TEMPK*(8.29E-7*TEMPK-1.417E-3)+.9297)
      ENDIF
C INITIALIZE ADSORPTION CONSTANTS WHICH DEPEND UPON CC1
      E0=8.876E-09
      EE=SQRT(8*CC1*E0*RJ*TEMPK)
C
      CC1=SQRT(CC1*TEMPK)
      AA=18246E2*S3/CC1**3
      BB=50.29*S3/CC1
C
```

New:

```
C
C
C THE NEXT SECTION OF CODE WHICH COMPUTES THE DEBYE-HUCKEL
```

```

C CONSTANTS AS A FUNCTION OF TEMPERATURE WAS TAKEN DIRECTLY
C FROM WATEQ2(BALL ET AL. 1979). THE MATHEMATICS IS DOCUMENTED
C IN TRUESDELL AND JONES(1974).
C
C7/88 S1=374.11-TEMP
C7/88 S2=S1**0.333333
C7/88 S3=SQRT((1+0.1342489*S2-3.946263E-3*S1)/
C7/881      (3.1975-0.3151548*S2-1.203374E-3*S1+7.48908E-13*S1**4))
C7/88 IF (TEMPK.LT.373.16) THEN
C7/88 CC1=87.74-TEMP*(TEMP*(1.41E-6*TEMP-9.398E-4)+0.4008)
C7/88 ELSE
C7/88 CC1=5321/TEMPK+233.76-TEMPK*(TEMPK*(8.29E-7*TEMPK-1.417E-3)+.9297)
C7/88 ENDIF
C7/88
C7/88 THE NEXT SECTION OF CODE CALCULATES THE DEBYE-HUCKEL CONSTANTS
C7/88 BY CALLING THE SUBROUTINE DEBYE. IN ADDITION, THE VALUE OF
C7/88 DIELECTRIC CONSTANT (CC1) IS ALSO RETURNED, AS WELL AS, AN
C7/88 UNIVERSAL DEBYE-HUCKEL EXTENDED TERM PARAMETER (BDOT, HELGESON
C7/88 1969). THIS SUBROUTINE REPLACES THE ORIGINAL CODING OF TRUESDELL
C7/88 AND JONES (1974) WITH MODERN EXPRESSIONS FOR BOTH THE DENSITY OF
C7/88 WATER AND THE DIELECTRIC CONSTANT.
      CALL DEBYE (TEMP, CC1, AA, BB, BDOT)
C INITIALIZE ADSORPTION CONSTANTS WHICH DEPEND UPON CC1
      E0=8.876E-09
      EE=SQRT(8*CC1*E0*RJ*TEMPK)
C
C7/88 CC1=SQRT(CC1*TEMPK)
C7/88 AA=18246E2*S3/CC1**3
C7/88 BB=50.29*S3/CC1
C

```

Changes to the file COMMON.DAT

Present:

```

COMMON/PARM/NXDIM,NYDIM,ITMAX,ITER,IADS,EPS,PSID,NN(6),EE,RJ,SSA,
1NNN,TEMP,TEMPK,VH,R,VHC,CORALK,SOLCON,CAP2,CAP1,PSIO,PSIB,
2IPRINT,IDEBUG,KOUNT,AA,BB,DENS,MU,MUHALF,NONCRB,MAXSIZ,ICHARG,
3LUN0,LUN1,LUN2,LUN3,LUN4,LUN5,NITER,FCC,TIS,FIONS,ISOPT,IPRDT,
4IPHVR,LUN6,LUN7,KKDAV,KKTHR

```

New:

```

COMMON/PARM/NXDIM,NYDIM,ITMAX,ITER,IADS,EPS,PSID,NN(6),EE,RJ,SSA,
1NNN,TEMP,TEMPK,VH,R,VHC,CORALK,SOLCON,CAP2,CAP1,PSIO,PSIB,
2IPRINT,IDEBUG,KOUNT,AA,BB,DENS,MU,MUHALF,NONCRB,MAXSIZ,ICHARG,
3LUN0,LUN1,LUN2,LUN3,LUN4,LUN5,NITER,FCC,TIS,FIONS,ISOPT,IPRDT,
4IPHVR,LUN6,LUN7,KKDAV,KKTHR,BDOT

```

TABLE A.3. The MINTEQ Data File, ANALYT.DAT, Containing the Coefficients Used by MINTEQ to Calculate Equilibrium Constants for Elevated Temperatures.

8015005	846.6236	0.1351200	-60939.00	-306.2581	0.	2473400.	0.
2003000	245.2116	0.0434460	-16836.00	-88.0071	0.	505790.	0.
8450003	654.9809	0.1068700	-38791.00	-235.5121	0.	2001500.	0.
8450001	564.8244	0.0909840	-34202.00	-203.0431	0.	1641100.	0.
6015000	1493.0070	0.2413200	-83368.00	-540.6127	0.	5067900.	0.
8641001	1273.5773	0.2064700	-79785.00	-457.4716	0.	3658800.	0.
8415001	826.2554	0.1454500	-55985.00	-296.0927	0.	2256400.	0.
5015000	1460.3533	0.2379800	-80884.00	-528.2476	0.	4929400.	0.
2003001	215.3866	0.0389870	-15907.00	-75.9464	0.	505790.	0.
2046000	231.0087	0.0346940	-17140.00	-83.6331	0.	558820.	0.
5015001	1453.3214	0.2374300	-80400.00	-525.8071	0.	4898200.	0.
2077000	110.6320	0.0178360	-5268.10	-40.1037	0.	397900.	0.
2077001	100.6464	0.0169740	-4222.30	-36.9986	0.	319330.	0.
8646000	915.6477	0.1401700	-58973.00	-331.5490	0.	2539500.	0.
2003002	214.5266	0.0389870	-15143.00	-75.9464	0.	505790.	0.
5015002	2942.2583	0.4778200	-163360.00	-1063.2963	0.	9890700.	0.
4215000	1460.8337	0.2362200	-78930.00	-529.3823	0.	4831600.	0.
8046000	558.2815	0.0862970	-39590.00	-200.9993	0.	1585500.	0.
8015006	917.2774	0.1606100	-69777.00	-329.3083	0.	2391300.	0.
2003003	243.7107	0.0434460	-15908.00	-88.0071	0.	505790.	0.
2028102	272.7081	0.0461940	-16738.00	-96.7804	0.	767510.	0.
6015001	1532.7479	0.2469200	-84030.00	-556.3654	0.	5067900.	0.
8441003	606.6599	0.1023800	-34924.00	-219.0970	0.	1869600.	0.
8603000	640.7753	0.1140600	-39324.00	-230.4505	0.	1631200.	0.
2028105	526.5203	0.0918430	-32226.00	-185.1108	0.	1443300.	0.
5015003	5907.4600	0.9565700	-329950.00	-2133.5151	0.	19841000.	0.
5046001	6213.5493	0.9945000	-351280.00	-2244.5212	0.	20520000.	0.
8441000	401.5756	0.0689860	-26617.00	-144.9084	0.	1143000.	0.
8603001	640.7822	0.1140600	-38351.00	-230.4505	0.	1631200.	0.
8015002	613.3129	0.1006800	-45224.00	-223.1649	0.	1904000.	0.
8415002	1094.8665	0.1823200	-66638.00	-394.0527	0.	3100400.	0.
8415000	2180.8091	0.3647000	-129430.00	-784.6924	0.	6200900.	0.
8441001	522.1871	0.0876830	-31955.00	-188.0464	0.	1576500.	0.
2015000	200.7857	0.0329550	-20306.00	-73.3086	0.	541730.	0.
8450002	653.9895	0.1068700	-38223.00	-235.5121	0.	2001500.	0.
5046002	1484.4357	0.2397100	-82842.00	-535.9023	0.	4980900.	0.
3025000	763.5169	0.1291800	-48433.00	-269.4752	0.	2086800.	0.
8015004	1045.7845	0.1680200	-77654.00	-378.9579	0.	2998900.	0.
8441002	605.6820	0.1023800	-34500.00	-219.0970	0.	1869600.	0.
8015003	635.2195	0.1016900	-44586.00	-229.6375	0.	1951800.	0.
8641000	1025.9976	0.1809100	-63317.00	-368.5444	0.	2789500.	0.
8450004	437.5664	0.0721770	-29422.00	-156.9916	0.	1230600.	0.
8215003	306.3656	0.0501700	-20722.00	-111.5250	0.	914930.	0.
2046001	228.3445	0.0345110	-19470.00	-81.5122	0.	609410.	0.
8646001	1281.2080	0.2070100	-86084.00	-469.6429	0.	3697700.	0.
2015001	214.8725	0.0339520	-17631.00	-78.7341	0.	558770.	0.
1028003	1449.7437	0.2325800	-76831.00	-524.0686	0.	4787700.	0.
8603002	856.8136	0.1491000	-48434.00	-309.4481	0.	2532400.	0.
2077002	109.9388	0.0178360	-4917.40	-40.1037	0.	397900.	0.
8646003	837.7095	0.1249300	-50371.00	-302.8079	0.	2431300.	0.
5028000	1488.7856	0.2410500	-82876.00	-536.8979	0.	5011800.	0.
2077003	112.9888	0.0220980	-3800.30	-42.7657	0.	178480.	0.
2077004	113.0692	0.0220980	-3916.10	-42.7657	0.	178480.	0.

8646002	1131.0000	0.1752000	-68313.00	-410.5475	0.	3440600.	0.
6050002	1554.1761	0.2436300	-86770.00	-563.6940	0.	5264100.	0.
5050001	1525.4921	0.2359000	-85770.00	-552.1852	0.	5162200.	0.
8215001	2405.2930	0.3789900	-148460.00	-871.9671	0.	7174900.	0.
8415003	1079.8326	0.1824500	-68518.00	-387.2271	0.	3100400.	0.
8215002	306.0651	0.0501700	-20379.00	-111.5250	0.	914930.	0.
2028000	207.9928	0.0325110	-15879.00	-73.7430	0.	565270.	0.
0							
3300020	-606.5220	-0.0976110	31286.00	218.6843	0.	-2170900.	0.
3307700	-624.9234	-0.0976110	33633.00	224.6245	0.	-2170900.	0.
3307701	-706.4820	-0.1294600	33633.00	256.1449	0.	-2170900.	0.
3301400	-76.1578	-0.0057100	3140.20	30.6509	0.	161910.	0.
3301401	446.3032	0.0839390	-26548.00	-157.7929	0.	2208700.	0.
3302700	103.7800	0.0359520	-2928.20	-41.0192	0.	0.	0.
3302701	103.7800	0.0377650	-2928.20	-41.0192	0.	0.	0.
3307320	846.6010	0.1300800	-49516.00	-303.8192	0.	3062900.	0.
3301800	95.3540	0.0353020	-2045.50	-40.3070	0.	0.	0.
3307300	706.7778	0.1135700	-39295.00	-255.1223	0.	2615600.	0.
303300	-74.0110	0.	1015.80	26.5097	0.	0.	0.
303301	10.1270	0.	-6053.30	0.	0.	0.	0.
303303	212.6480	0.	-19670.00	-66.0451	0.	0.	0.
303302	-521.9790	-0.1231100	7126.40	207.1452	0.	0.	0.
302700	-5.3776	0.0211120	1816.60	0.	0.	0.	0.
302701	-7.6925	0.0348910	2993.40	0.	0.	0.	0.
307202	-8.5394	0.0429050	3806.60	0.	0.	0.	0.
307203	-9.7300	0.0496670	4365.50	0.	0.	0.	0.
307320	6.1060	0.0042260	-1409.60	0.	0.	0.	0.
307321	-32.0030	0.0731610	4131.30	0.	0.	0.	0.
1503300	-610.0479	-0.0883620	31854.00	218.6843	0.	-2170900.	0.
1502700	-2.3266	0.0091070	244.47	0.	0.	0.	0.
1501400	-79.3834	0.0033570	3612.10	30.6509	0.	161910.	0.
1501401	1.9142	0.0149950	-2489.00	0.	0.	463410.	0.
1507320	-3.0127	0.0108710	617.42	0.	0.	0.	0.
2803300	-2.9946	0.	-2157.60	0.	0.	0.	0.
2803302	-2.6493	0.	-5411.90	0.	0.	0.	0.
2803301	-7.1602	0.	-7817.80	0.	0.	0.	0.
2802700	-2.1521	0.0091070	252.48	0.	0.	0.	0.
2801400	-9.5889	0.0057100	579.24	-0.4575	0.	-161910.	0.
2807320	-3.1096	0.0108710	616.69	0.	0.	0.	0.
2813300	-71.6761	0.	1159.70	26.5097	0.	0.	0.
2813301	6.7487	0.	-3702.60	0.	0.	0.	0.
2813302	38.4920	0.	-7575.60	-10.1153	0.	0.	0.
2813303	21.7962	0.	-7964.70	-6.7238	0.	0.	0.
2811800	-5.4275	0.0215000	145.70	0.	0.	0.	0.
2811801	-5.3184	0.0227390	195.79	0.	0.	0.	0.
2811802	-7.2396	0.0266330	127.53	0.	0.	0.	0.
2811803	-10.3300	0.0320540	0.00	0.	0.	0.	0.
2812700	-4.5209	0.0212980	1303.20	0.	0.	0.	0.
2812701	-4.8311	0.0321140	1805.70	0.	0.	0.	0.
2812702	-2.4740	0.0342650	1865.80	0.	0.	0.	0.
2817320	4.2661	0.0042260	-478.86	0.	0.	0.	0.
2817321	-34.8335	0.0731610	5498.10	0.	0.	0.	0.
4107320	-2.0106	0.0075770	182.00	0.	0.	0.	0.
4603300	-608.5988	-0.0884270	31753.00	218.6843	0.	-2170900.	0.
4602700	-1.8368	0.0091070	302.04	0.	0.	0.	0.
4601401	-82.6283	0.0079520	4174.70	30.6509	0.	161910.	0.
4601400	-0.1865	0.0084370	194.63	0.	0.	0.	0.
4607320	-3.2264	0.0108710	660.46	0.	0.	0.	0.

5001800	232.8184	0.0453790	-13910.00	-86.0423	0.	1091900.	0.
5002700	-68.3130	0.	2955.90	23.2170	0.	0.	0.
5001401	-141.4428	-0.0057100	5530.20	53.8678	0.	161910.	0.
5001400	-7.2474	0.0075770	1648.30	0.	0.	0.	0.
5007320	-2.9972	0.0075770	428.77	0.	0.	0.	0.
2812800	1.5276	0.0066240	2847.70	0.	0.	0.	0.
7307320	657.5363	0.1125400	-25771.00	-242.5559	0.	2597200.	0.
3301403	337.9167	0.0640880	-19628.00	-117.3414	0.	1539300.	0.

0

APPENDIX B

DERIVATION OF EQUATION (7)

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DERIVATION OF EQUATION (7)

The Equilibrium constants for a reaction at temperature T ($\log K_{r,T}$) is related to $\Delta G^\circ_{r,T}$ by:

$$\Delta G^\circ_{r,T} = -2.303 R T \log K_{r,T} \quad (\text{B.1})$$

where R is the gas constant and 2.303 represents the value of the natural logarithm of 10. $\Delta G^\circ_{r,T}$ is given by:

$$\Delta G^\circ_{r,T} = \Delta H^\circ_{r,T} - T \Delta S^\circ_T \quad (\text{B.2})$$

where $\Delta H^\circ_{r,T}$ and ΔS°_T are the enthalpy and entropy of reaction, respectively. Values of $\Delta H^\circ_{r,T}$ and ΔS°_T can be calculated from $\Delta H^\circ_{r,T_r}$ and $\Delta S^\circ_{T_r}$ (where T_r is a reference temperature) using:

$$\Delta H^\circ_{r,T} = \Delta H^\circ_{r,T_r} + \int_{T_r}^T \Delta C_p^\circ dT \quad (\text{B.3})$$

$$\Delta S^\circ_T = \Delta S^\circ_{T_r} + \int_{T_r}^T \frac{\Delta C_p^\circ}{T} dT \quad (\text{B.4})$$

Substituting Equations (B.3) and (B.4) into (B.2) yields:

$$\Delta G^\circ_{r,T} = \Delta H^\circ_{r,T_r} - T \Delta S^\circ_{T_r} + \int_{T_r}^T \Delta C_p^\circ dT - T \int_{T_r}^T \frac{\Delta C_p^\circ}{T} dT \quad (\text{B.5})$$

Because Equation (B.2) is true at any temperature, Equation (B.2) for temperature T_r can be subtracted from Equation (B.5) to yield:

$$\Delta G_{r,T}^{\circ} - \Delta G_{r,T_r}^{\circ} = -\Delta S_r^{\circ} (T - T_r) + \int_{T_r}^T \Delta C_p^{\circ} dT - T \int_{T_r}^T \frac{\Delta C_p^{\circ}}{T} dT \quad (B.6)$$

The change in $\Delta G_{r,T}^{\circ}$ resulting from a change in temperature from T_r to T is dependent on the entropy of reaction (at T_r) and the heat capacity of the reactions. Since the thermodynamic properties discussed here are additive, an expression equivalent to (B.6) can be written for individual minerals or aqueous species in a chemical reaction:

$$G_T^{\circ} - G_{T_r}^{\circ} = -S_{T_r}^{\circ} (T - T_r) + \int_{T_r}^T C_p^{\circ} dT - T \int_{T_r}^T \frac{C_p^{\circ}}{T} dT \quad (B.7)$$

The *apparent* Gibbs free energy of formation of an aqueous species, mineral or gas from its elements at temperature T (ΔG_T°) is given by (Helgeson, Kirkham, and Flowers 1981):

$$\Delta G_T^{\circ} \equiv \Delta G_f^{\circ} + (G_T^{\circ} - G_{T_r}^{\circ}) \quad (B.8)$$

where ΔG_f° is the standard molal Gibbs free energy of formation at temperature T_r . The contribution of the heat capacity to the *apparent* Gibbs free energy of formation of an aqueous species, mineral, or gas is:

$$\Delta G_T^{\circ} - \Delta G_f^{\circ} + S_{T_r}^{\circ} (T - T_r) = \int_{T_r}^T C_p^{\circ} dT - T \int_{T_r}^T \frac{C_p^{\circ}}{T} dT \quad (B.9)$$

If the heat capacity is represented by the Maier-Kelley power function (Maier and Kelley 1932):

$$C_p^o = a + bT + \frac{c}{T^2} \quad (6)$$

then substituting Equation (6) into Equation (B.9) and integrating the results gives Equation (7):

$$\int_{T_r}^T C_p^o dT - T \int_{T_r}^T \frac{C_p^o}{T} dT = a \left[T - T_r - T \ln \frac{T}{T_r} \right] - b \frac{(T - T_r)^2}{2} - c \frac{(T - T_r)^2}{2TT_r^2} \quad (7)$$

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