PB 220 464

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

WATEQ, A COMPUTER PROGRAM FOR CALCULATING CHEMICAL EQUILIBRIA OF NATURAL WATERS

By

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May 1973

Program Number:	C 737
Sponsor:	C. L. Christ, W. Back
Equipment:	IBM 360/65
Operating System:	IBM System 360
Language:	PL/1

BIBLIOGRAPHIC DATA SHEET	1. Report No. USGS-WRD-73-007	2.	3. Recipient's Accession No. PB-220 464

4. Title and Subtitle

WATEQ, a computer program for calculating chemical equilibria of natural waters

5. Report Date May 1973

6.

7. Author(s)
Alfred H. Truesdell and Blair F. Jones

8. Performing Organization Rept. No.

9. Performing Organization Name and Address

U.S. Geological Survey
19th and F Sts., N.W.
Washington, D.C. 20244

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Organization Name and Address

U.S. Geological Survey
19th and F Sts., N.W.
Washington, D.C. 20244

13. Type of Report & Period Covered

14.

15. Supplementary Notes

16. Abstracts

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17. Key Words and Document Analysis. 17a. Descriptors

Computer programs, Water chemistry, Equilibrium, temperature, hydrogen ion concentration, oxidation-reduction potential, thermodynamics, mineralogy, trace elements

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group 02K

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
No restriction on distribution	UNCLASSIFIED	
	20. Security Class (This Page) UNCLASSIFIED	22. Price

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WATEQ, a computer program for calculating chemical equilibria of natural waters

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Abstract. The computer program, WATEQ, calculates the equilibrium distribution of inorganic aqueous species of major and important minor elements in natural waters using the chemical analysis and in situ measurements of temperature, pH and redox potential. From this model, the states of reaction of the water with solid and gaseous phases are calculated. Thermodynamic stabilities of aqueous species, minerals and gases have been selected from a careful consideration of all available experimental data. The program is written in PL-1 for IBM 360 computers.

INTRODUCTION AND ACKNOWLEDGMENTS

The chemistry of water-rock interactions is determined in part by the states[1] of the water with regard to possible reactions. The reaction states may be calculated from an equilibrium chemical model of the water and from the stabilities of phases with which it may react. The examination of reaction states may suggest the origin of dissolved constituents and assist in the prediction of the chemical effects of ground water production, recharge and irrigation. Although the use of inorganic equilibrium models for the processes of mineral solution and precipitation cannot produce a complete description of these processes, an equilibrium model is a useful reference. It can indicate which processes are impossible for a given water-rock system and suggest which processes may control water compositions and which processes are so hindered by kinetic factors that the water compositions are indifferent to them.

Calculations of the states of saturation of natural waters with minerals are complicated by the necessity of considering all of the factors which affect the activity of the ions involved in the solution equilibria. One simple approach for multicomponent water solutions is to assume the existence of complexes whose formation is described by mass-action expressions and to assume that the activity coefficients of simple ions and complexes can be described by equations depending only on the temperature and a function of the water composition, the ionic strength. The number of possible ions, complexes, and minerals and the necessity of iteration for

[1] i.e., a description stating that a water is undersaturated or supersaturated with respect to a solid phase or to a gas at a certain pressure.

the solution of simultaneous equations and the calculation of activity coefficients makes the use of computer methods a near necessity.

This report is an attempt to provide a general computer program, for the calculation of chemical equilibria in natural waters at low temperatures, that may be expanded and updated by the user as additional stability data on complexes and minerals become available. Our thanks are extended to Ivan Barnes whose earlier program (Barnes and Clarke, 1969) suggested the format, and to C. L. Christ, J. Haas, G. M. Lafon, F. J. Pearson, Jr., Y. Karaka and E. A. Jenne for data and for corrections to the program. We are especially grateful to Manuel Nathenson for checking the thermodynamic data. The thermodynamic approach has been influenced by Garrels and Christ (1965), Sillen and Martell (1964), and Denbigh (1957). Many readers find the approach familiar and they may wish to omit the next sections in which the minimum thermodynamic theory necessary to explain the calculations is presented.

The study was financed in part by the Defense Advanced Research Projects Agency of the Department of Defense under Order no. 1813, Amendment no. 1.

MASS ACTION EQUILIBRIUM EQUATIONS

In a mixture at equilibrium, the activities of the chemical species present are related by a set of mass action equilibrium equations (Garrels and Christ, 1965, p. 6, 342; Denbigh, 1957, p. 138, 307). For each possible reaction of the form,

$$aA + bB = cC + dD, \qquad (1)$$

in which lower case letters are the stoichiometric coefficients of the chemical species represented by the upper case letters, there is a mass action equation of the form,

$$K = \frac{[C]^c \, [D]^d}{[A]^a \, [B]^b} \tag{2}$$

In this equation, K is the mass action or equilibrium constant and the brackets represent activities. For equilibria involving low pressure gases, the partial pressure of the gas may be used instead of activity and for gas-aqueous solution equilibria, activities and partial pressures may be used in the same equation.

The equilibrium constants may be derived from experimental measurement of concentrations in a series of equilibrium mixtures of different total concentration with extrapolation to infinite dilution. Alternatively, the experimental concentrations may be corrected to activities by means of calculated activity coefficients (see later discussion). Useful compilations of experimentally derived equilibrium constants have been made by Sillen and Martel (1964), Barnes, Helgeson, and Ellis (1966), Ellis (1967) and Helgeson (1969).

The equilibrium constant for a reaction may also be derived from the standard free energy change of that reaction. For the reaction given by equation 1, the sum of the standard free energies of formation, ΔG°_f, of the products times their stoichiometric coefficients less that of the reactants times their stoichiometric coefficients is the standard free energy change of reaction;

$$\Delta G^\circ_r = c \, \Delta G^\circ_{f,C} + d \, \Delta G^\circ_{f,D} - (a \, \Delta G^\circ_{f,A} + b \, \Delta G^\circ_{f,B}) \quad . \tag{3}$$

This is related to the equilibrium constant of the reaction by the equation,

$$\Delta G^\circ_r = -2.303 \, RT \log K \quad , \tag{4}$$

in which R is the gas constant and T the absolute temperature. By the use of these equations, experimental equilibrium data may be related to thermochemical data derived from calorimetric measurements. Useful compilations of standard free energies of formation (and other thermochemical data) have been made by the National Bureau of Standards (Rossini and others, 1952; Wagman and others, 1968 and 1969) and by Latimer (1952), Garrels and Christ (1965), Robie and Waldbaum (1968) and Helgeson (1969).

No single source of equilibrium constants or thermochemical data is of sufficient scope or of recent enough publication to include all of the data relevant to near-surface rock-water reactions. The data contained in WATEQ (Table 1) is from a compilation in preparation by the authors of this program and M. Nathenson.

TABLE 1 NEAR HERE

The effect of temperature and pressure on mass action equations will be considered in a later section.

ACTIVITY COEFFICIENTS

In the limit of infinite dilution, all ionic activities approach ionic concentrations, and activity coefficients (defined as the ratios of activities to concentrations) approach unity. This is a consequence of the definition of the standard state for ions in solution. This property is useful in experimental studies where mass action expressions written using concentrations may be extrapolated to infinite dilution to yield equilibrium constants but gives no clue to activity coefficients in real solutions of finite concentration. In real solutions of more than a few components, it is necessary to use single-ion activities and single ion activity coefficients. These are formally defined by the equation,

$$a_i = \gamma_i m_i, \qquad (5)$$

in which a_i, γ_i and m_i are respectively the activity, the activity coefficient and the molality of the i^{th} ion. The convention that activities are dimensionless requires that single ion activity coefficients have dimensions of molality^{-1}.

Single-ion activities and single-ion activity coefficients cannot be defined thermodynamically or exactly measured or calculated, because measurement of the activity (and therefore the chemical potential) of a single charged ion would require the measurement of the finite free energy change of the solution resulting from a finite change in concentration of the single charged ion while the concentrations of all other ions and the electrical potential of the phase are held constant. This is obviously impossible. We must, therefore, use non-thermodynamic models to evaluate single-ion activity coefficients. The reader should be aware of the additional uncertainties introduced by this approach.

Two models have been used in WATEQ for the calculation of single-ion activity coefficients, the Debye-Hückel equation and the MacInnes assumption. These are not the only models available but are perhaps the most widely used and are, in most cases, consistent with the functions used to correct experimental determinations to infinite dilution. The Debye-Hückel theory provides an equation which describes single-ion activity coefficient behavior of ions in dilute solutions and which can be extended with adjustable parameters to more concentrated solutions. The MacInnes assumption provides information on the behavior of single ion activities at higher concentrations with which to fit the parameters of the extended Debye-Hückel equation.

The Debye-Hückel theory

The Debye and Hückel theory considers the effect, on the free energy of a single ion, of electrical interactions with other ions by assuming that oppositely charged ions can be considered as forming a spherical shell around the ion. This assumption is valid only for very dilute solutions and activity coefficients derived from the theory deviate increasingly from experimental results as the concentration increases. The original equation (Robinson and Stokes, 1959, p. 229) states that

$$\log \gamma = - \frac{A z^2 \sqrt{I}}{1 + Ba \sqrt{I}} \qquad (6)$$

where A and B are constants depending only on the dielectric constant, density and temperature, z is the ionic charge, and I is the ionic strength (defined as half the sum of the products of the molality and the square of the charge of all ions in the solution), and contains one parameter, a, the "hydrated ion size" that must be estimated from experimental data. The extended form of the equation (Robinson and Stokes, 1959, p. 231),

$$\log \gamma = - \frac{A z^2 \sqrt{I}}{1 + Ba \sqrt{I}} + bI \ , \qquad (7)$$

adds a second adjustable parameter which allows for the effect of the decrease in concentration of solvent in concentrated solutions. This equation is used in WATEQ for major ions with a and b values calculated from experimental mean salt single-ion activity coefficients (see later) and for minor ions with values of a from Kielland (1936) and b set to zero. The constants A and B are calculated from the dielectric constant, density and temperature by the equations (Hamer, 1968),

$$A = \frac{1.82483 \times 10^6 \, d^{1/2}}{(\varepsilon T)^{3/2}} \quad \text{moles}^{-1/2} \; (10^3 \text{ g } H_2O)^{1/2} \tag{8}$$

$$B = \frac{50.2916 \times 10^8 \, d^{1/2}}{(\varepsilon T)^{1/2}} \quad \text{cm}^{-1} \; \text{mole}^{-1/2} \; (10^3 \text{ g } H_2O)^{1/2} \tag{9}$$

where d is the density of water (Keenan and Keyes, 1935); T is the absolute temperature and ε is the dielectric constant of water (Malmberg and Maryott, 1956, Akerlof and Oshery, 1950).

The MacInnes Assumption

In order to assign the adjustable parameters in equation 7, it is necessary to know the variation of single ion activity coefficients with ionic strength in a single solution. Experimental values are available for the mean molal activity coefficients, $\gamma\pm$, of many salts and if the activity coefficient of one ion can be calculated then others may be derived from it. The MacInnes assumption (MacInnes, 1939) that the single ion activity coefficients of K^+ and Cl^- are equal to each other and to the mean activity coefficient of KCl allows this to be done. By definition,

$$\gamma_+ \; \gamma_- \equiv \gamma_\pm^2 \tag{10}$$

If

$$\gamma_{\pm\,KCl} = \gamma_{K^+} = \gamma_{Cl^-} \tag{11}$$

Then

$$\gamma_{Na^+} = \frac{\gamma^2_{\pm\,NaCl}}{\gamma_{\pm\,KCl}} \tag{12}$$

$$\gamma_{Ca^{++}} = \frac{\gamma^3_{\pm\,CaCl_2}}{\gamma^2_{\pm\,KCl}} \tag{13}$$

and

$$\gamma_{Br^-} = \frac{\gamma^2_{\pm\,KBr}}{\gamma_{\pm\,KCl}} \quad \text{and so forth.} \tag{14}$$

In deriving these "mean salt" activity coefficients one must be careful to avoid solutions in which the ions are highly associated. In calculating $\gamma_{SO_4^{--}}$, for example, $\gamma_{\pm K_2SO_4}$ cannot be used because of the formation of the KSO_4^- ion pair. In this case, the most reasonable values of $\gamma_{SO_4^{--}}$ can be obtained from $\gamma_{\pm Cs_2SO_4}$, $\gamma_{\pm CsCl}$, and $\gamma_{\pm KCl}$ by the relation,

$$\gamma_{SO_4^{--}} = \frac{\gamma^3_{\pm Cs_2SO_4} \quad \gamma^2_{\pm KCl}}{\gamma^4_{\pm CsCl}} \tag{15}$$

Even here, the results must be used with caution because Cs^+ and Cl^- may be weakly associated and $\gamma_{SO_4^{--}}$ values derived in this way may be somewhat too high at high ionic strengths.

Values of a and b for major ions obtained from computer fitting of calculated mean salt activity coefficients as well as values of a for minor ions derived from Kielland (1936) are shown in Table 2.

Single-ion activity coefficients have been calculated for concentrated single-salt solutions by use of the Stokes-Robinson equation (Bates and others, 1970). Where comparisons are possible, these values agree reasonably with activity coefficients based on mean salt calculations. In Table 2, values of single-ion activity coefficients used in WATEQ are compared with mean salt coefficients and those calculated by Bates and others (1970).

TABLE 2 NEAR HERE

The use of any model of single-ion activity coefficients based on experimental measurements made on single salt solutions requires the assumption that at a given temperature activity coefficients in simple solution are equal to those in complex solutions of the same ionic strength. This is reasonable in dilute solutions but limited experimental work in concentrated (>1 molal) mixed electrolyte solutions indicates that it is not always true. The extent of deviation from ionic strength dependence is small except for ions that differ greatly in size and hydration such as H^+ and Cs^+. It is encouraging, however, that for models in which all ion associations are considered (as in WATEQ) these deviations have proved to be insignificant (Pytkowicz and Kester, 1969; Yeatts and Marshall, 1970). For further discussion and comparison of activity coefficient equations, see Truesdell and Jones (1969).

SOLUTION OF MASS ACTION AND MASS BALANCE EQUATIONS

Computation of solution species distribution is accomplished by means of a chemical model (Garrels and Thompson, 1962) using analytical concentrations, experimental solution equilibrium constants, mass balance equations, and the measured pH. The distribution of anionic weak acid species is calculated first from total analyzed concentrations, the pH and activity coefficients of individual species, as illustrated by silicate equilibria,

$$H_4SiO_4 = H^+ + H_3SiO_4^- \quad (16)$$

and

$$H_3SiO_4^- = H^+ + H_2SiO_4^{--} \quad (17)$$

The concentration of each species is calculated from the total or analytical concentration, the pH and the activity coefficients of the species. From the preceding equations,

$$K_1 = \frac{m_{H_3SiO_4^-} \gamma_{H_3SiO_4^-} 10^{-pH}}{m_{H_4SiO_4} \gamma_{H_4SiO_4}} \quad (18)$$

$$K_2 = \frac{m_{H_2SiO_4^{--}} \quad \gamma_{H_2SiO_4^{--}} \quad 10^{-pH}}{m_{H_3SiO_4^-} \quad \gamma_{H_3SiO_4^-}} \tag{19}$$

The mass balance equation for total silica (silicic acid and silicate ions) is

$$m_{Si\ total} = m_{H_4SiO_4} + m_{H_3SiO_4^-} + m_{H_2SiO_4^{--}} \tag{20}$$

The mass action equations can be combined with the mass balance equation to solve for $m_{H_4SiO_4}$,

$$m_{H_4SiO_4} = \frac{m_{Si\ total}}{1 + \gamma_{H_4SiO_4}\left(\frac{K_1\ 10^{pH}}{\gamma_{H_3SiO_4^-}} + \frac{K_1\ K_2\ 10^{2pH}}{\gamma_{H_2SiO_4^{--}}}\right)} \tag{21}$$

$m_{H_4SiO_4}$ is then substituted into the mass action equations to solve for $m_{H_3SiO_4^-}$ and $m_{H_2SiO_4^{--}}$. The activity coefficients are calculated from the ionic strength by an iterative procedure. The same method is employed for phosphate, borate and sulfide species, and to obtain the carbonate-bicarbonate distribution from pH and the alkalinity determination, after correction for other weak acid radicals (if the alkalinity has been corrected during the chemical analysis, this step may be bypassed in the program). The concentration of H_2CO_3 is calculated from the re-computed bicarbonate molality and the first dissociation constant of carbonic acid.

Calculation of the concentrations of ion pairs is accomplished by a procedure similar to that for weak acid species, but utilizing the analyzed or computed values for the anion concentrations in place of the pH, and employing equilibrium association constants. The calculations may be illustrated for the calcium ion species. The major ion pairing reactions are

$$Ca^{++} + OH^{--} = CaOH^{+} \quad (22)$$

$$Ca^{++} + HCO_3^{-} = CaHCO_3^{+} \quad (23)$$

$$Ca^{++} + CO_3^{--} = CaCO_3^{\circ} \quad (24)$$

$$Ca^{++} + SO_4^{--} = CaSO_4^{\circ} \quad . \quad (25)$$

From equations 22-25, equilibrium constants for the association reactions are

$$K_1 = \frac{a_{CaOH^+}}{a_{Ca^{++}}\, a_{OH^-}} \quad (26)$$

$$K_2 = \frac{a_{CaHCO_3^+}}{a_{Ca^{++}}\, a_{HCO_3^-}} \quad (27)$$

$$K_3 = \frac{a_{CaCO_3^\circ}}{a_{Ca^{++}}\, a_{CO_3^{--}}} \quad (28)$$

$$K_4 = \frac{a_{CaSO_4^\circ}}{a_{Ca^{++}}\, a_{SO_4^{--}}} \quad (29)$$

From these equations the expressions,

$$m_{CaOH^+} = \frac{K_1\; a_{OH^-}\; m_{Ca^{++}}\; \gamma_{Ca^{++}}}{\gamma_{CaOH^+}} \quad (30)$$

$$m_{CaHCO_3^+} \frac{K_2\; a_{HCO_3^-}\; m_{Ca^{++}}\; \gamma_{Ca^{++}}}{\gamma_{CaHCO_3^{++}}} \quad (31)$$

$$m_{CaCO_3^\circ} = \frac{K_3\; a_{CO_3^{--}}\; m_{Ca^{++}}\; \gamma_{Ca^{++}}}{\gamma_{CaCO_3^\circ}} \quad (32)$$

$$m_{CaSO_4^\circ} = \frac{K_4\; a_{SO_4^{--}}\; m_{Ca^{++}}\; \gamma_{Ca^{++}}}{\gamma_{CaSO_4^\circ}} \quad (33)$$

may be substituted into the mass balance for calcium

$$m_{Ca\ total} = m_{Ca^{++}} + m_{CaOH^+} + m_{CaHCO_3^+} + m_{CaCO_3^\circ} + m_{CaSO_4^\circ}$$

to obtain an expression for free (uncomplexed) Ca^{++} ion,

$$m_{Ca^{++}} = \frac{m_{Ca\ total}}{1 + \gamma_{Ca^{++}}\left(\frac{K_1 a_{OH^-}}{\gamma_{CaOH^+}} + \frac{K_2\ a_{HCO_3^-}}{\gamma_{CaHCO_3^+}} + \frac{K_3\ a_{CO_3^{--}}}{\gamma_{CaCO_3^\circ}} + \frac{K_4\ a_{SO_4^{--}}}{\gamma_{CaSO_4}}\right)} \quad (34)$$

In actuality, these computations in WATEQ also include phosphate species. The computed concentration of free calcium ion, $m_{Ca^{++}}$, is substituted back into the mass action expressions to solve for the concentrations of ion pairs. The concentrations assigned to ion pairs and weak acids reduce the concentrations of the free ions and change the ionic strength and therefore the activity coefficients. The corrected values are calculated by iteration. In each iteration, the program reduces if necessary the molalities of the free anions, HCO_3^-, CO_3^{--}, SO_4^{--}, Cl^-, F^-, and PO_4^{---} and recalculates the ionic strength and the activity coefficients. Then the calculations of free Ca^{++} and Ca complexes along with similar calculations for Na, K, Mg, Fe, and H complexes are repeated. When the sums of all weak acids, complex ions and free ions for all anions agree with the analytical values within 0.5 percent the iteration is stopped.

ION RATIOS

When the chemical model is complete, it is useful to calculate molal concentration ratios and ion activity ratios for plotting on water composition and mineral stability diagrams, respectively. Comparison of these ratios with those of related waters can suggest possible origins of dissolved constituents and possible controls by mineral reactions. A number of these ratios are calculated in WATEQ.

ACTIVITY PRODUCTS AND SOLUBILITY PRODUCTS

The equilibrium of a solid phase with an aqueous solution can be characterized by a mass action equation. For a solid of formula AX which dissolves to form ions A^+ and X^-, this expression is

$$K = \frac{a_{A^+} \, a_{X^-}}{a_{AX}} , \qquad (35)$$

where K is the equilibrium constant of solubility. If the solid is a pure substance, not a solid solution, its activity is equal to one because it is in its standard state (Garrels and Christ, 1965, p. 5) and the expression for the equilibrium constant reduces to the "solubility product",

$$K_{SP} = a_{A^+} \, a_{X^-} \quad . \qquad (36)$$

In hydrolysis reactions, water is considered explicitly as part of the reaction. In the solution of quartz to form silicic acid, for example,

$$SiO_{2\ quartz} + 2H_2O = H_4SiO_4 \qquad (37)$$

the water is written as part of the reaction and its activity appears in the equilibrium expression.

A water sample when collected is usually no longer in contact with mineral phases and these phases may not be accessible to observation. It is of interest then to determine with what mineral phases the water is saturated or nearly so. The calculated activities of the dissolved ions in a water may be combined to produce the appropriate activity product which may be compared with the solubility equilibrium constant to show the degree of saturation of the water with each mineral considered.

This comparison may be made by means of the ratio of the activity product to the equilibrium solubility product which is given in the program as "AP/K" and "LOG AP/K" and by means of the free energy change of the reaction, ΔG_R (which is zero at equilibrium). This is given as "DELGR" in the program. These quantities are related by the expression

$$\Delta G_R = 2.303RT \log(AP/K) \quad . \tag{38}$$

Some mineral formulas contain a relatively large number of atoms and the ΔG_R values for these minerals will deviate from zero more rapidly with dilution or concentration than will those for minerals with simple formulas. This can be illustrated by comparing the activity product of dolomite, $a_{Ca^{++}} a_{Mg^{++}} a^2_{CO_3^{--}}$, with that of calcite, $a_{Ca^{++}} a_{CO_3^{--}}$. If a water initially saturated with both minerals is diluted with pure water, ΔG_R dolomite will be twice ΔG_R calcite. To correct this, ΔG_R values are divided by the number of negative charges in the formula of the mineral and presented as (for want of a better label) "PER EQUIV" ΔG_R.

The compilation of a consistent set of stability constants for minerals suffers from several uncertainties. The standard enthalpy of formation and standard entropy of most minerals have been measured by calorimetric methods, and the standard free energy of formation calculated from these quantities is often referenced to the free energies of formation of the elements rather than the ions formed on solution of the mineral. The combination of such values with those for solution species involving aqueous ions may lead to erroneous stability constants. The use of experimental solubility products or resulting free energy values is free from this inconsistency. The main uncertainty in the use of these data lies in the precise definition of reactants and products involved in the experiment, and in the difficulty of reversing the equilibrium.

Because of these uncertainties, the logarithms of the maximum and minimum solubility products are calculated in WATEQ and presented in addition to the logarithm of the most probable value for visual comparison with the logarithm of the activity product. Because of space limitations only the most probable solubility product is used in calculating values of AP/K, log (AP/K), ΔG_R, and ΔG_R per equivalent. Enthalpy values and solubility products used in the program, together with the sources of all data, are given in table 1.

EFFECTS OF TEMPERATURE AND PRESSURE

In the relationships developed in the previous sections temperature and pressure have been assumed constant and their effect on the equilibria has not been discussed. The great majority of experimental determinations of equilibrium constants and free energy values have been made at 25°C and, particularly for solution equilibria, data at other temperatures may be entirely lacking. If experiments have been made over a wide range of temperatures or if complete thermochemical data are available for all species of a reaction then the equilibrium constant may be expressed as a power function of the absolute temperature

$$\log K = A + BT + C/T + D \log T, \qquad (39)$$

in which one or more coefficients may be zero. Where this type of expression was available in the literature it has been used in WATEQ (Table 4). If experimental determinations at only two or three temperatures

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TABLE 4 NEAR HERE

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are available a linear dependence of log K with the reciprocal of the absolute temperature may be indicated (i.e., B and D are zero in eq. 39) which is equivalent to a constant value of the enthalpy (heat content) change of the reaction, ΔH. This is expressed by the Van't Hoff relation,

$$\log K = \log K_{Tr} - \frac{\Delta H_{Tr}}{2.3\ R}\left(\frac{1}{T} - \frac{1}{T_r}\right) , \tag{40}$$

in which Tr is the reference temperature(298.15° K (= 25°C) in WATEQ) and the constants A and C in eq. 39 are equal to

$$\log K_{Tr} + \frac{\Delta H_{Tr}}{2.3RT} \quad \text{and} \quad \frac{\Delta H_{Tr}}{2.3R}$$

respectively.

The enthalpy change of reaction can be obtained by determining the slope of a plot of experimental values of log K versus (1/T), from tabulated values of the standard enthalpy of formation of the species in the reaction using a relation analogous to eq. 3, or from direct measurements. The enthalpy of reaction at 25°C has been calculated for most of the equilibria used in WATEQ (Table 1) and eq. 40 is used to calculate the value of the equilibrium constant for the temperature of the water. For a few reactions in which data at temperatures other than 25°C was not available the 25°C value of the equilibrium constant is used at all temperatures.

The effect of pressure has not been calculated in WATEQ because the necessity of inputing a measured pH value virtually limits WATEQ to surface and near surface waters and because much necessary data is not available for ion pairs. Correlations suggested by Ellis and McFadden (1972) allow the calculation of the pressure effect on equilibria involving only minerals and simple ions (not ion pairs) to be made for temperatures to 250°C. These calculations suggest that for pressures less than a few hundred atmosphere, pressure effects are not large.

REDOX REACTIONS

Oxidation-reduction equilibria have been treated in the same manner as other reactions in WATEQ. To achieve this, the measured Eh value or the Eh value calculated from the measured concentration of dissolved oxygen is converted to the negative logarithm of the conventional activity of the electron (or pE) by the relation,

$$pE \equiv Eh/(2.303RT/F), \quad (41)$$

in which (2.303RT/F) is the Nernst slope. pE is related to the conventional activity of the electron by

$$a_{e^-} = 10^{-pE} \quad (42)$$

This equation is similar to that assumed for pH and because both measurements have an unknown liquid junction potential, the relations of pE to electron activity and of pH to hydrogen ion activity are equally uncertain. It is necessary, however, to use these relations despite the uncertainty. The standard free energy and enthalpy of the hydrated electron in aqueous solution are zero by convention. The conventional electron activity thus ranges from 10^{-20} to 10^{+20} while the actual electron activity is about 10^{-60} to 10^{-100}. These conventions are discussed by Sillen and Martell (1964) and by Truesdell (1968)

An advantage of the use of electron activity is it is not necessary to set up separate redox equilibrium expressions. For example, the equilibrium between Fe^{++} and Fe^{+++} is expressed by a conventional equilibrium constant,

$$K = \frac{a_{Fe^{+++}} \, a_{e^-}}{a_{Fe^{++}}} \tag{43}$$

and the value of the equilibrium constant may be calculated from G°_f,Fe^{+++} and G°_f,Fe^{++} (G°_f,electron = 0 by convention). Other redox equilibria are treated similarly and the method of calculation of the concentration of ion pairs involving iron is the same as for non redox-active metals.

In natural waters that contact the atmosphere the dissolved oxygen (DOX) content may have been measured in addition to or in place of the Eh. If the dissolved oxygen has been measured it is read into the program after the normal data as a statement, "DOX = (ppm dissolved oxygen),". Two values of pE are calculated in WATEQ from the relation,

$$pE = -\log K - pH - 0.5 \log a_{H_2O} + 0.25 \log a_{DOX} \tag{44}$$

in which log K values are from thermodynamic data ("PE CALC O") and from the empirical Eh-pH relation for waters in contact with the atmosphere cited by Garrels and Christ (1965, p. 137) ("EMPIR PE O") and DOX activities are on a molal scale. If a DOX measurement is given without an Eh value, the value of PE CALC O is used through the program. If instead, EMPIR PE O is to be adopted, the statement "EMPOX = 1 " is added to the optional data.

Separate analyses of reduced and oxidized species allow the calculation of pE values which may be compared with each other or the measured pE to estimate the degree of internal redox equilibrium. Two such pairs are sulfide-sulfate and ammonia-nitrate. The equilibrium between sulfide and sulfate can be written,

$$H_2S + 4\ H_2O = SO_4^{--} + 10\ H^+ + 8\ e^-, \qquad (45)$$

and the mass action expression can be rearranged to give

$$pE = (\log K + \log a_{SO_4^{--}} - \log a_{H_2S} - 10\ pH - 4 \log a_{H_2O})/8. \qquad (46)$$

Similarly, the equilibrium between ammonium and nitrate yields the expression

$$pE = (- \log K + \log a_{NO_3^-} - \log a_{NH_4^+} - 10\ pH - 3 \log a_{H_2O})/8. \qquad (47)$$

These quantities, PE CALC S and PE CALC N are calculated in WATEQ.

GAS PARTIAL PRESSURES

Although gas partial pressures are seldom measured in natural waters, in some cases they may be calculated from the gas solubility constants and the water analysis. The partial pressure of CO_2, O_2, and CH_4 are calculated from the following equations,

$$\log P_{CO_2} = \log K + \log a_{HCO_3} + \log a_{H^+} - \log a_{H_2O}, \qquad (48)$$

$$\log P_{O_2} = \log K' + 2 \log a_{H_2O} + 4\ pH + 4\ pE, \quad \text{and} \qquad (49)$$

$$\log P_{CH_4} = \log K'' + \log a_{HCO_3^-} - 9\ pH - 9\ pE - 3 \log a_{H_2O}. \qquad (50)$$

ACTIVITY OF WATER

The activity of water is calculated in WATEQ by the approximate relation (Garrels and Christ, 1965, p. 66)

$$a_{H_2O} = 1 - 0.017\Sigma\ m_i. \qquad (51)$$

where Σm_i is the sum of the molalities of dissolved anions, cations and neutral species. The equation yields reasonable values if Σm_i is less than 4m.

INPUT

Input to WATEQ consists of a complete chemical analysis of the water sample and field measurements of its temperature and pH. If available, measurements of Eh, dissolved oxygen as well as some trace element analyses may be included. In order to allow the inclusion of optional data, the last space on the first card is coded with ISTDATA which is the number of cards containing the necessary data including the normal chemical analysis and the sample description. Cards after the chemical analysis are used for optional data. A blank card must be included after each data set to separate data sets. The required data is coded in free field (i.e., one space between each number) in the following order. See list of identifiers for detailed descriptions.

Card 1	SAMPLE DESCRIPTION (79 spaces) ISTDATA (Space 80)
Card 2	TEMP, PH, EHM (in volts, code 9.9 if data is not available), FLAG (= 'PPM', 'MG/L', 'MEQ/L' or 'MOL/L')
Card 3	Chemical analysis in PPM, MG/L, MEQ/L or MOL/L (set FLAG) in the order Ca, Mg, Na, K, Cl, SO_4, HCO_3, Fe, H_2S, CO_3, SiO_2, NH_4, B, PO_4, Al, F, NO_3.
Succeeding Cards	Other data (identifier, equality sign, numerical value and comma) including: "DENS = ," (if not specified, density is set equal to one); if alkalinity is corrected for

non-carbonate alkalinity "CORALK = 1," (omitted if not corrected); electrical potential (volts) of the Eh cell including the calomel reference electrode "EHMC = ,"; electrical potential (volts) of the Eh cell with Zobell's solution for calibration, "EMFZSCE = ,"; ppm of dissolved oxygen, "DOX = ,"; and certain trace elements including Li (I = 80), Sr (I = 87), Ba (I = 89) in the form, "CUNITS(I) = ,". A semicolon in place of a comma follows the last data statement.

Last Card BLANK

Sample sets of data are given with the resulting printout after the program.

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Table 1. Reactions and thermodynamic data

Reaction Number	Mineral or Species Name	Reaction	log K	ΔH_R
0	Fe^{++}	$Fe^{++} = Fe^{+++} + e^-$	-13.013	9700
1	$FeOH^{++}$	$Fe^{++} + H_2O = FeOH^{++} + e^- + H^+$	-15.473	20115
2	$FeOH^+$	$Fe^{++} + H_2O = FeOH^+ + H^+$	-9.319	13218
3	$Fe(OH)_3^-$	$Fe^{++} + 3\ H_2O = Fe(OH)_3^- + 3\ H^+$	-29.458	32995
4	$FeSO_4^+$	$Fe^{++} + SO_4^{--} = FeSO_4^+ + e^-$	- 8.886	15920
5	$FeCl^{++}$	$Fe^{++} + Cl^- = FeCl^{++} + e^-$	-11.600	18152
6	$FeCl_2^+$	$Fe^{++} + 2\ Cl^- = FeCl_2^+ + e^-$	-10.919	
7	$FeCl_3^\circ$	$Fe^{++} + 3\ Cl^- = FeCl_3^\circ + e^-$	-11.925	
8	$FeSO_4^\circ$	$Fe^{++} + SO_4^{--} = FeSO_4^\circ$	2.200	560
9	Siderite	$FeCO_3 = Fe^{++} + CO_3^{--}$	-11.738	-5328
10	Magnesite	$MgCO_3 = Mg^{++} + CO_3^{--}$	- 8.029	-6169
11	Dolomite	$CaMg(CO_3)_2 = Ca^{++} + Mg^{++} + 2\ CO_3^{--}$	-17.000	-8290
12	Calcite	$CaCO_3 = Ca^{++} + CO_3^{--}$	-8.370	-3190
13	$H_3SiO_4^-$	$H_4SiO_4^\circ = H_3SiO_4^- + H^+$	-9.930	8935
14	$H_2SiO_4^{--}$	$H_4SiO_4^\circ = 2\ H^+ + H_2SiO_4^{--}$	-21.619	29714
15	HPO_4^{--}	$H^+ + PO_4^{---} = HPO_4^{--}$	12.346	-3530
16	$H_2PO_4^-$	$2\ H^+ + PO_4^{---} = H_2PO_4^-$	19.553	-4520
17	Anhydrite	$CaSO_4 = Ca^{++} + SO_4^{--}$	-4.637	-3769
18	Gypsum	$CaSO_4 . 2H_2O = Ca^{++} + SO_4^{--} + 2\ H_2O$	-4.848	261
19	Brucite	$Mg(OH)_2 = Mg^{++} + 2\ OH^-$	-11.204	850
20	Chrysotile	$Mg_3Si_2O_5(OH)_4 + 5\ H_2O = 3\ Mg^{++} + 2\ H_4SiO_4^\circ + 6\ OH^-$	-51.800	27585
21	Aragonite	$CaCO_3 = Ca^{++} + CO_3^{--}$	-8.305	-2959
22	MgF^+	$Mg^{++} + F^- = MgF^+$	1.820	4674
23	$CaSO_4^\circ$	$Ca^{++} + SO_4^{--} = CaSO_4^\circ$	2.309	1650
24	$MgOH^+$	$Mg^{++} + OH^- = MgOH^+$	2.600	2140

25	$H_2BO_3^-$	$H_3BO_3^\circ = H^+ + H_2BO_3^-$	-9.240	3224
26	NH_3°	$NH_4^+ = NH_3^\circ + H^+$	-9.252	12480
27	Forsterite	$Mg_2SiO_4 + 4\ H_2O = 2\ Mg^{++} + H_4SiO_4^\circ + 4\ OH^-$	-27.694	4870
28	Diopside	$CaMgSi_2O_6 + 6\ H_2O = Ca^{++} + Mg^{++} + 2\ H_4SiO_4^\circ + 4\ OH^-$	-36.106	21100
29	Clinoenstatite	$MgSiO_3 + 3\ H_2O = Mg^{++} + H_4SiO_4^\circ + 2\ OH^-$	-16.658	6675
30	$NaHPO_4^-$	$Na^+ + HPO_4^{--} = NaHPO_4^-$	1.200	
31	Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2 + 22\ H_2O = 2\ Ca^{++} + 5\ Mg^{++} + 8\ H_4SiO_4^\circ + 14\ OH^-$	-139.426	90215
32	$KHPO_4^-$	$K^+ + HPO_4^{--} = KHPO_4^-$	1.090	
33	$MgHPO_4^\circ$	$Mg^{++} + HPO_4^{--} = MgHPO_4^\circ$	2.870	3300
34	$CaHPO_4^\circ$	$Ca^{++} + HPO_4^{--} = CaHPO_4^\circ$	2.739	3300
35	HCO_3^-	$H_2CO_3^\circ = HCO_3^- + H^+$	-6.379	1976
36	Sepiolite	$Mg_2Si_3O_{7.5}OH\cdot 3H_2O + 4.5\ H_2O = 2Mg^{++} + 3\ H_4SiO_4^\circ + 4\ OH^-$	-40.079	26532
37	Talc	$Mg_3Si_4O_{10}(OH)_2 + 10\ H_2O = 3\ Mg^{++} + 4\ H_4SiO_4^\circ + 6\ OH^-$	-60.933	45065
38	Hydromagnesite	$Mg_5(CO_3)_4(OH)_2\cdot 4H_2O = 5Mg^{++} + 4\ CO_3^{--} + 2\ OH^- + 4\ H_2O$	-36.762	-25520
39	Adularia	$KAlSi_3O_8 + 8\ H_2O = K^+ + Al(OH)_4^- + 3\ H_4SiO_4^\circ$	-20.573	30820
40	Albite	$NaAlSi_3O_8 + 8\ H_2O = Na^+ + Al(OH)_4^- + 3\ H_4SiO_4^\circ$	-18.002	25896
41	Anorthite	$CaAl_2Si_2O_8 + 8\ H_2O = Ca^{++} + 2\ Al(OH)_4^- + 2\ H_4SiO_4^\circ$	-19.424	17530
42	Analcime	$NaAlSi_2O_6\cdot H_2O + 5\ H_2O = Na^+ + Al(OH)_4^- + 2\ H_4SiO_4^\circ$	-12.701	18206
43	K Mica	$KAl_3Si_3O_{10}(OH)_2 + 12\ H_2O = K^+ + 3\ Al(OH)_4^- + 3\ H_4SiO_4^\circ + 2\ H^+$	-49.102	67860
44	Phlogopite	$KMg_3AlSi_3O_{10}(OH)_2 + 10\ H_2O = K^+ + 3\ Mg^{++} + Al(OH)_4^- + 3\ H_4SiO_4^\circ + 6\ OH^-$	No Data	

45	Illite	$K_{.6}Mg_{.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2 + 11.2\ H_2O = .6\ K^+ + .25\ Mg^{++} + 2.3\ Al(OH)_4^- + 3.5\ H_4SiO_4^\circ + 1.2\ H^+$	−40.267	54684
46	Kaolinite	$Al_2Si_2O_5(OH)_4 + 7\ H_2O = 2\ Al(OH)_4^- + 2\ H_4SiO_4^\circ + 2\ H^+$	−36.921	49150
47	Halloysite	$Al_2Si_2O_5(OH)_4 + 7\ H_2O = 2\ Al(OH)_4^- + 2\ H_4SiO_4^\circ + 2\ H^+$	−32.830	44680
48	Beidellite	$(Na,K,\frac{1}{2}Mg)_{.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 12\ H_2O = .33\ (Na,K,\frac{1}{2}Mg)^+ + 2.33\ Al(OH)_4^- + 3.67\ H_4SiO_4^\circ + 2\ H^+$	−45.272	60355
49	Chlorite	$Mg_5Al_2Si_3O_{10}(OH)_8 + 10\ H_2O = 5\ Mg^{++} + 2\ Al(OH)_4^- + 3\ H_4SiO_4^\circ + 8\ OH^-$	−89.563	54760
50	Alunite	$KAl_3(SO_4)_2(OH)_6 = K^+ + 3\ Al^{+++} + 2\ SO_4^{--} + 6\ OH^-$	−85.334	29820
51	Gibbsite (crystalline)	$Al(OH)_3 = Al^{+++} + 3\ OH^-$	−32.774	14470
52	Boehmite	$AlO(OH) + H_2O = Al^{+++} + 3\ OH^-$	−33.416	11905
53	Pyrophylite	$Al_2Si_4O_{10}(OH)_2 + 12\ H_2O = 2\ Al(OH)_4^- + 4\ H_4SiO_4^\circ + 2\ H^+$	−48.314	
54	Phillipsite	$Na_{.5}K_{.5}AlSi_3O_8 \cdot H_2O + 7\ H_2O + .5\ Na^+ + .5\ K^+ + Al(OH)_4^- + 3\ H_4SiO_4^\circ$	−19.874	
55	Erionite	$NaAlSi_{3.5}O_9 . 3H_2O + 6\ H_2O = Na^+ + Al(OH)_4^- + 3.5\ H_4SiO_4^\circ$	No Data	
56	Clinoptilolite	$(K,Na)\ AlSi_5O_{12} \cdot 3.5\ H_2O + 8.5\ H_2O = (K,Na)^+ + Al(OH)_4^- + 5\ H_4SiO_4^\circ$	No Data	
57	Mordenite	$(Na,K)\ AlSi_{4.5}O_{11} \cdot 3\ H_2O + 8\ H_2O = (Na,K)^+ + Al(OH)_4^- + 4.5\ H_4SiO_4^\circ$	No Data	
58	Nahcolite	$NaHCO_3 = Na^+ + HCO_3^-$	− 0.548	3720
59	Trona	$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O = 2\ H_2O + 3\ Na^+ + CO_3^{--} + HCO_3^-$	− 0.795	−18000

60	Natron	$Na_2CO_3 \cdot 10\ H_2O = 2\ Na^+ + CO_3^{--} + 10\ H_2O$	- 1.311	15745
61	Thermonatrite	$Na_2CO_3 \cdot H_2O = 2\ Na^+ + CO_3^{--} + H_2O$	0.125	-2802
62	Fluorite	$CaF_2 = Ca^{++} + 2\ F^-$	- 9.046	1530
63	Ca Montmorillonite	$Ca_{.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 12\ H_2O = .17\ Ca^{++} + 2.33\ Al(OH)_4^- + 3.67\ H_4SiO_4^\circ + 2\ H^+$	-45.027	58373
64	Halite	$NaCl = Na^+ + Cl^-$	1.582	918
65	Thenardite	$Na_2SO_4 = 2\ Na^+ + SO_4^{--}$	- 0.179	-572
66	Mirabilite	$Na_2SO_4 \cdot 10H_2O = 2\ Na^+ + SO_4^{--} + 10\ H_2O$	- 1.114	18987
67	Mackinawite	$FeS + H^+ = Fe^{++} + HS^-$	- 4.648	
68	CO_3^{--}	$HCO_3^- = H^+ + CO_3^{--}$	-10.330	3550
69	$NaCO_3^-$	$Na^+ + CO_3^{--} = NaCO_3^-$	1.268	8911
70	$NaHCO_3^\circ$	$Na^+ + HCO_3^- = NaHCO_3^\circ$	- 0.250	
71	$NaSO_4^-$	$Na^+ + SO_4^{--} = NaSO_4^-$	0.226	2229
72	KSO_4^-	$K^+ + SO_4^{--} = KSO_4^-$	0.847	3082
73	$MgCO_3^\circ$	$Mg^{++} + CO_3^{--} = MgCO_3^\circ$	3.398	58
74	$MgHCO_3^+$	$Mg^{++} + HCO_3^- = MgHCO_3^+$	0.928	10370
75	$MgSO_4^\circ$	$Mg^{++} + SO_4^{--} = MgSO_4^\circ$	2.238	4920
76	$CaOH^+$	$Ca^{++} + OH^- = CaOH^+$	1.400	1190
77	$CaHCO_3^+$	$Ca^{++} + HCO_3^- = CaHCO_3^+$	1.260	6331
78	$CaCO_3^\circ$	$Ca^{++} + CO_3^{--} = CaCO_3^\circ$	3.200	3130
79	$Na_2CO_3^\circ$	$2Na^+ + CO_3^{--} = Na_2CO_3^\circ$	0.672	
80	$AlOH^{++}$	$Al^{+++} + OH^- = AlOH^{++}$	8.998	1990
81	$Al(OH)_2^+$	$Al^{+++} + 2\ OH^- = Al(OH)_2^+$	18.235	
82	$Al(OH)_4^-$	$Al^{+++} + 4\ OH^- = Al(OH)_4^-$	33.938	-9320
83	AlF^{++}	$Al^{+++} + F^- = AlF^{++}$	7.010	
84	AlF_2^+	$Al^{+++} + 2F^- = AlF_2^+$	12.750	20000

85	AlF_3°	$Al^{+++} + 3F^- = AlF_3^\circ$	17.020	2500
86	AlF_4^-	$Al^{+++} + 4F^- = AlF_4^-$	19.720	
87	$AlSO_4^+$	$Al^{+++} + SO_4^{--} = AlSO_4^+$	3.200	2290
88	$Al(SO_4)_2^-$	$Al^{+++} + 2\ SO_4^{--} = Al(SO_4)_2^-$	5.100	3070
89	HSO_4^-	$H^+ + SO_4^{--} = HSO_4^-$	1.987	4910
90	SO_4^{--}/H_2S	$SO_4^{--} + 10\ H^+ + 8\ e^- = H_2S + 4\ H_2O$	40.644	-65440
91	HS^-	$H_2S = H^+ + HS^-$	-6.994	5300
92	S^{--}	$HS^- = H^+ + S^{--}$	-12.918	12100
93	$H_2O/O_2(g)$	$.5\ H_2O = .25\ O_2(g) + H^+ + e^-$	-20.780	34157
94	$HCO_3^-/CH_4(g)$	$HCO_3^- + 8\ e^- + 9\ H^+ = CH_4 + 3\ H_2O$	30.741	-57435
95	OH Apatite	$Ca_5(PO_4)_3(OH) + 3\ H_2O = 5\ Ca^{++} + 3\ HPO_4^{--} + 4\ OH^-$	-59.421	17225
96	F Apatite	$Ca_5(PO_4)_3\ F + 3\ H_2O = 5\ Ca^{++} + 3\ HPO_4^{--} + 3\ OH^- + F^-$	-67.243	19695
97	Chalcedony	$SiO_2 + 2\ H_2O = H_4SiO_4^\circ$	-3.523	4615
98	Magadiite	$NaSi_7O_{13}(OH)_3 \cdot 3\ H_2O + H^+ + 9\ H_2O = Na^+ + 7\ H_4SiO_4^\circ$	-14.300	
99	Christobalite	$SiO_2 + 2\ H_2O = H_4SiO_4^\circ$	-3.587	5500
100	Silica Gel	$SiO_2 + 2\ H_2O = H_4SiO_4^\circ$	-3.018	4440
101	Quartz	$SiO_2 + 2\ H_2O = H_4SiO_4^\circ$	-4.006	6220
102	$Fe(OH)_2^+$	$Fe^{++} + 2\ H_2O = Fe(OH)_2^+ + 2\ H^+ + e^-$	-20.173	
103	$Fe(OH)_3^\circ$	$Fe^{++} + 3\ H_2O = Fe(OH)_3^\circ + 3\ H^+ + e^-$	-26.571	
104	$Fe(OH)_4^-$	$Fe^{++} + 4\ H_2O = Fe(OH)_4^- + 4\ H^+ + e^-$	-34.894	
105	$Fe(OH)_2^\circ$	$Fe^{++} + 2\ H_2O = Fe(OH)_2^\circ + 2\ H^+$	-20.570	28565
106	Vivianite	$Fe_3(PO_4)_2 \cdot 8H_2O = 3\ Fe^{++} + 2\ PO_4^{---} + 8\ H_2O$	-36.000	
107	Magnetite	$Fe_3O_4 + 8H^+ = 3\ Fe^{+++} + 4\ H_2O + e^-$	-9.565	-40660
108	Hematite	$Fe_2O_3 + 6H^+ = 2\ Fe^{+++} + 3\ H_2O$	- 4.008	-30845
109	Maghemite	$Fe_2O_3 + 6H^+ = 2\ Fe^{+++} + 3\ H_2O$	6.386	
110	Goethite	$FeO(OH) + H_2O = Fe^{+++} + 3\ OH^-$	-44.197	25555
111	Greenalite	$Fe_3Si_2O_5(OH)_4 + 5\ H_2O = 3\ Fe^{++} + 2\ H_4SiO_4^\circ + 6\ OH^-$	No Data	
112	$Fe(OH)_3$ Amorph.	$Fe(OH)_3 + 3H^+ = Fe^{+++} + 3\ H_2O$	4.891	
113	Annite	$KFe_3AlSi_3O_{10}(OH)_2 + 10\ H_2O = K^+ + 3Fe^{++} + Al(OH)_4^- + 3\ H_4SiO_4^\circ + 6\ OH^-$	-85.645	62480

114	Pyrite	$FeS_2 + 2\ H^+ + 2\ e^- = Fe^{++} + 2\ HS^-$	-18.479	11300
115	Montmorillonite Belle Fourche	$(H,Na,K)_{.28}Mg_{.29}Fe^{+++}_{.23}Al_{1.58}Si_{3.93}O_{10}(OH)_2 + 10.04\ H_2O = .28(H,Na,K)^+ + .29\ Mg^{++} + .23\ Fe^{+++} + 1.58\ Al(OH)_4^- + 3.93\ H_4SiO_4^\circ + .04\ H^+$	-34.913	
116	Montmorillonite Aberdeen	$(H,Na,K)_{.42}Mg_{.45}Fe^{+++}_{.34}\ Al_{1.47}Si_{3.82}O_{10}(OH)_2 + 9.16\ H_2O + .84\ H^+ = .42\ (H,Na,K)^+ + .45\ Mg^{++} + .34\ Fe^{+++} + 1.47\ Al(OH)_4^- + 3.82\ H_4SiO_4^\circ$	-29.688	
117	Huntite	$CaMg(CO_3)_4 = 3\ Mg^{++} + Ca^{++} + 4\ CO_3^{--}$	-29.968	-25760
118	Gregite	$Fe_3S_4\ + 4\ H^+ + 2\ e^- = 3\ Fe^{++} + 4\ HS^-$	-18.959	
119	FeS ppt	$FeS + H^+ = Fe^{++} + HS^-$	- 3.915	
120	$FeH_2PO_4^+$	$Fe^{++} + H_2PO_4^- = FeH_2PO_4^+$	2.700	
121	$CaPO_4^-$	$Ca^{++} + PO_4^{---} = CaPO_4^-$	6.459	3100
122	$CaH_2PO_4^+$	$Ca^{++} + H_2PO_4^- = CaH_2PO_4^+$	1.408	3400
123	$MgPO_4^-$	$Mg^{++} + PO_4^{---} = MgPO_4^-$	6.589	3100
124	$MgH_2PO_4^+$	$Mg^{++} + H_2PO_4^- = MgH_2PO_4^+$	1.513	3400
125	$LiOH^\circ$	$Li^+ + OH^- = LiOH^\circ$	0.200	4832
126	$LiSO_4^-$	$Li^+ + SO_4^{--} = LiSO_4^-$	0.640	
127	NO_3^-/NH_4^+	$NO_3^- + 10\ H^+ + 8\ e^- = NH_4^+ + 3\ H_2O$	119.077	-187055
128	Laumontite	$CaAl_2Si_4O_{12}\cdot 4H_2O\ + 8\ H_2O = Ca^{++} + 2\ Al(OH)_4^- + 4\ H_4SiO_4^\circ$	-31.053	39610
129	$SrOH^+$	$Sr^{++} + OH^- = SrOH^+$	0.820	1150
130	$BaOH^+$	$Ba^{++} + OH^- = BaOH^+$	0.640	1750
131	$NH_4SO_4^-$	$NH_4^+ + SO_4^{--} = NH_4SO_4^-$	1.110	
132	HCl°	$H^+ + Cl^- = HCl^\circ$	-6.100	18630
133	$NaCl^\circ$	$Na^+ + Cl^- = NaCl^\circ$	-1.602	
134	KCl°	$K^+ + Cl^- = KCl^\circ$	-1.585	
135	$H_2SO_4^\circ$	$2H^+ + SO_4^{--} = H_2SO_4^\circ$	-1.000	
136	$H_2O/O_2(aq)$	$.5\ H_2O = .25\ O_2(aq) + H^+ + e^-$	-11.385	
137	$H_2CO_3^\circ$	$CO_2(g) + H_2O = H_2CO_3^\circ$	-1.452	-5000
138	$FeHPO_4^\circ$	$Fe^{++} + HPO_4^{--} = FeHPO_4^\circ$	3.600	
139	$FeHPO_4^+$	$Fe^{++} + HPO_4^{--} = FeHPO_4^+ + e^-$	-7.613	
140	$Al(OH)_3$ Amorph.	$Al(OH)_3 = Al^{+++} + 3\ OH^-$	-31.611	12990

141	Prehnite	$Ca_2Al_2Si_3O_{10}(OH)_2 + 8\ H_2O + 2\ H^+ =$ $2\ Ca^{++} + 2\ Al(OH)_4^- + 3\ H_4SiO_4^\circ$	-11.695	10390
142	Strontianite	$SrCO_3 = Sr^{++} + CO_3^{--}$	-11.789	2361
143	Celestite	$SrSO_4 = Sr^{++} + SO_4^{--}$	- 6.349	-1054
144	Barite	$BaSO_4 = Ba^{++} + SO_4^{--}$	- 9.773	6141
145	Witherite	$BaCO_3 = Ba^{++} + CO_3^{--}$	- 13.335	6950
146	Strengite	$FePO_4.2H_2O = Fe^{+++} + PO_4^{---} + 2\ H_2O$	-26.400	-2030
147	Leonhardite	$Ca_2Al_4Si_8O_{24}.7H_2O + 17\ H_2O =$ $2\ Ca^{++} + 4\ Al(OH)_4^- + 8\ H_4SiO_4^\circ$	-69.756	90070
148	$Na_2SO_4^\circ$	$2\ Na^+ + SO_4^{--} = Na_2SO_4^\circ$	1.512	-2642
149	Nesquehonite	$MgCO_3.3H_2O = Mg^{++} + CO_3^{--} + 3\ H_2O$	4.999	-4619
150	Artinite	$MgCO_3 \cdot Mg(OH)_2.3H_2O = 2\ Mg^{++} + CO_3^{--} + 2\ OH^-$ $+ 3\ H_2O$	-17.980	498
151	$H_2O/O_2(aq)$	$.5\ H_2O = .25\ O_2(aq) + H^+ + e^-$	-21.495	33457
152	H_2O	$H_2O = H^+ + OH^-$	-13.998	13345
153	Sepiolite (ppt)	$Mg_2Si_3O_{7.5}(OH).3\ H_2O + 4.5\ H_2O =$ $2\ Mg^{++} + 3\ H_4SiO_4^\circ + 4\ OH^-$	-37.212	
154	Diaspore	$AlOOH + H_2O = Al^{+++} + 3\ OH^-$	-35.121	15405
155	Wairakite	$CaAl_2Si_4O_{12}.2\ H_2O + 10\ H_2O = Ca^{++}$ $+ 2\ Al(OH)_4^- + 4\ H_4SiO_4^\circ$	-26.708	26140
156	$FeH_2PO_4^{++}$	$Fe^{++} + H_2PO_4^- = FeH_2PO_4^{++} + e^-$	-7.583	

Table 1a. Notes. Log K_{298} and $\Delta H_{R,298}$ of reactions unless otherwise noted, are calculated from free energies and enthalpies. The sources of thermodynamic data on minerals, gases and species in solution are given below. R and W refer to Robie and Waldbaum (1968). 270-3 and 270-4 refer to Wagman and others (1968) and (1969) respectively.

Al^{+++}:	ΔG_f and ΔH_f from 270-3
Ba^{++}:	ΔG_f and ΔH_f from Latimer (1952)
Ca^{++}:	ΔG_f and ΔH_f from Latimer (1952)
Cl^-:	ΔG_f and ΔH_f from 270-3
CO_3^{--}:	ΔG_f and ΔH_f from 270-3
e^-:	definition
F^-:	ΔG_f and ΔH_f from 270-3
Fe^{++}:	ΔG_f and ΔH_f from 270-4
H^+:	definition
H_2O:	ΔG_f and ΔH_f from 270-3
HS^-:	ΔG_f and ΔH_f from 270-3
$H_2BO_3^-$:	ΔG_f and ΔH_f from 270-3
$H_4SiO_4^\circ$:	ΔG_f and ΔH_f from Helgeson (1969)
K^+:	ΔG_f and ΔH_f from 270-3
Li^+:	ΔG_f and ΔH_f from Latimer (1952)
Mg^{++}:	ΔG_f and ΔH_f from Latimer (1952)
Na^+:	ΔG_f and ΔH_f from 270-3
NH_3°:	ΔG_f and ΔH_f from 270-3
OH^-:	ΔG_f and ΔH_f from 270-3

PO_4^{---}: ΔG_f and ΔH_f from 270-3.

SO_4^{--}: ΔG_f and ΔH_f from 270-3.

Sr^{++}: ΔG_f and ΔH_f from Latimer (1952).

0 Fe^{+++}: ΔG_f and ΔH_f from 270-4.

1 $FeOH^{++}$: $Fe^{+++} + H_2O = FeOH^{+} + H^{+}$, log K = -2.46; Lamb and Jacques as quoted in Langmuir (1969), ΔH_f from 270-4.

2 $FeOH^{+}$: from ΔH_R and ΔS_R of magnetite hydrolysis (Sweeton and Baes, 1970).

3 $Fe(OH)_3^{-}$: from ΔH_R and ΔS_R of magnetite hydrolysis (Sweeton and Baes, 1970).

4 $FeSO_4^{+}$: ΔG_f and ΔH_f from 270-4.

5 $FeCl^{+}$: ΔG_f and ΔH_f from 270-4.

6 $FeCl_2^{+}$: ΔG_f from 270-4.

7 $FeCl_3^{\circ}$: ΔG_f from 270-4.

8 $FeSO_4^{\circ}$: log K = 2.20, ΔH_R = 560 (Izatt et al., 1969).

9 Siderite: ΔG_f and ΔH_f from R and W.

10 Magnesite: ΔG_f and ΔH_f from R and W .

11 Dolomite: log K_{298} = -17.0 (Berner, 1967), ΔH_R = -8290 (Helgeson, 1969).

12 Calcite: log K_{298} = -8.37 (Berner, 1967), ΔH_R = -3190 (Helgeson, 1969).

13 $H_3SiO_4^{-}$: log K = -9.929, ΔH_R = 8935, from log K(T) expression (Ryzhenko, 1967).

14 $H_2SiO_4^{--}$: log K = -21.617, ΔH_R = 29714 from log K(T) expression (Ryzhenko, 1967).

15 HPO_4^{--}: ΔG_f and ΔH_f from 270-3.

16 $H_2PO_4^{-}$: ΔG_f and ΔH_f from 270-3.

17 Anhydrite: ΔG_f and ΔH_f from R and W.

18 Gypsum: ΔG_f and ΔH_f from R and W.

19 Brucite: ΔG_f and ΔH_f from H_f from R and W.

20 Chrysotile: log K = −51.8 (Hostetler and Christ, 1968), ΔH_f from R and W.

21 Aragonite: ΔG_f and ΔH_f from R and W.

22 MgF^+: log K = 1.82, ΔS_R = 24 (Sillen, 1964).

23 $CaSO_4^\circ$: log K = 2.309, ΔH_R = 1650 (Bell and George, 1953).

24 $MgOH^+$: log K = 2.6 (Hostetler, 1963); ΔH_R = 2140 (Helgeson, 1969).

25 $H_3BO_3^\circ$: log K = 4.757−log KW, ΔH_R = −10121 −$(\Delta H_R)_{KW}$ from log K(T) expression (Mesmer, Baes, and Sweeton, 1972).

26 NH_4^+: ΔG_f and ΔH_f from 270-3.

27 Forsterite: ΔG_f and ΔH_f from R and W.

28 Diopside: ΔG_f and ΔH_f from R and W.

29 Clinoenstatite: ΔG_f and ΔH_f from R and W.

30 $NaHPO_4^-$: log K = 1.20 obtained by calculation from data of Smith and Alberty (1956) (using $K_{equi} = \gamma NaHPO_4^- / (\gamma Na^+ \ \gamma HPO_4^{--})$. K_{app} and assuming $\gamma_{HPO_4^{--}} = \gamma_{SO_4^{--}} = .25$, $\gamma_{Na^+} = 0.75$, and $\gamma_{NaHPO_4^-} = \gamma_{Na^+}$)

31 Tremolite: ΔG_f and ΔH_f from R and W.

32 $KHPO_4^-$: log K = 1.09 obtained by calculation from data of Smith and Alberty (1956) in a similar manner to $NaHPO_4^-$.

33 $MgHPO_4^\circ$: log K = 2.87 (Sillen, 1964), ΔH_R = 3300 by analogy to $CaHPO_4^\circ$ data of Chughtai, Marshall, and Nancollas (1968).

34 $CaHPO_4^\circ$: log K = 2.739, ΔH_R = 3300 (Chughtai, Marshall, and Nancollas, 1968).

35 $H_2CO_3^\circ$: log K = −6.379, ΔH_R = 1976 from log K(T) expression (Ryzhenko, 1963).

36 Sepiolite: ΔG_f = -1 105 600, S° = 90.1 (Christ, Hostetler and Siebert, in press).

37 Talc: ΔG_f from Hostetler et al., (1971); ΔH_f from R and W.

38 Hydromagnesite: ΔG_f from ΔH_f from Robie and Hemingway (1972).

39 Adularia: ΔG_f and ΔH_f from R and W.

40 Albite-low: ΔG_f and ΔH_f from R and W.

41 Anorthite: ΔG_f and ΔH_f from R and W.

42 Analcime: ΔG_f and ΔH_f from R and W.

43 Muscovite: ΔG_f and ΔH_f from R and W.

45 Illite: ΔG_f and ΔH_f from Helgeson (1969).

46 Kaolinite: Kaolinite + 6 H^+ = 2 Al^{+++} + 2 $H_4SiO_4^\circ$ + H_2O; log K = 7.185 (Kittrick, 1966); ΔH_f from R and W.

47 Halloysite: ΔG_f and ΔH_f from R and W.

48 Beidellite: ΔG_f and ΔH_f from Helgeson (1969) for Na end member.

49 Chlorite: ΔG_f and ΔH_f taken as average of Helgeson (1969) and Zen (1972).

50 Alunite: ΔG_f and ΔH_f from Hemley (1969).

51 Gibbsite: ΔG_f and ΔH_f from R and W.

52 Boehmite: ΔG_f and ΔH_f from R and W.

53 Pyrophyllite: ΔG_R = 65 900 from data in Tables 4 and 5 in Reesman and Keller (1968).

54 Phillipsite: Log K = .7 for reaction Phillipsite + 0.5 K^+ = K - feldspar + 0.5 Na^+ + H_2O; ΔG_f of K-feldspar from Robie and Waldbaum (1968), (Hess, 1966).

58 Nahcolite: ΔG_f and ΔH_f from Latimer (1952).

59 Trona: from data on natron (this study), nahcolite (Latimer, 1952), and trona-nahcolite-soda being in equilibrium at 21.1°C (Linke and Seidell, 1965, p. 925).

60 Natron: $Na_2CO_3 \cdot 10\ H_2O = Na_2CO_3 \cdot H_2O + 9\ H_2O$ (g) $\Delta G_R = 20435$, $\Delta H_R = 113\ 218$ (Waterfield, et al., 1968), ΔG_f and ΔH_f of thermonatrite computed in this study.

61 Thermonatrite: $Na_2CO_3 \cdot H_2O = Na_2CO_3 + H_2O(g)$, $\Delta G_R = 2944$, $\Delta H_R = 14037$, Waterfield, et al. (1968); ΔG_f of Na_2CO_3 from ΔH_f of Latimer (1952) and S° of Waterfield, et al. (1968).

62 Fluorite: ΔG_f and ΔH_f from R and W.

63 Ca Montmorillonite: ΔG_f and ΔH_f from Helgeson (1969).

64 Halite: ΔG_f and ΔH_f from R and W.

65 Thenardite: ΔG_f and ΔH_f from R and W.

66 Mirabilite: ΔG_f and ΔH_f from R and W.

67 Mackinawite: log K = -17.566 (Berner, 1967).

68 HCO_3^-: ΔG_f and ΔH_f from 270-3.

69 $NaCO_3^-$: log K = -1.268 (Garrels, Thompson, and Siever, 1961), $\Delta H_R = -8911$ (Lafon, 1969).

70 $NaHCO_3^\circ$: log K = 0.25 (Garrels and Thompson, 1962).

71 $NaSO_4^-$: log K = 0.226, $\Delta H_R = 308$ from log K(T) expression (Lafon and Truesdell, 1971).

72 KSO_4^-: log K = 0.847, $\Delta H_R = 3082$ from log K(T) expression (Truesdell and Hostetler, 1968).

73 $MgCO_3^\circ$: log K = 3.398 (Garrels, Thompson, and Siever, 1961), $\Delta H_R = 58$ (Lafon, 1969).

74 $MgHCO_3^+$: $MgHCO_3^+ = MgCO_3^\circ + H^+$ log K = -7.86 (Hostetler, 1963), $\Delta H_R = +10370$ (Lafon, 1969).

75 $MgSO_4^\circ$: log K = -2.238 (Hanna, Pethybridge, and Prue, 1971), $\Delta H_R = -4920$ (Helgeson, 1969).

76 $CaOH^+$: log K = 1.40; ΔH_R = 1190 (Sillen and Martell, 1964).

77 $CaHCO_3^+$: log K = -1.26 (Garrels and Thompson, 1962), ΔH_R = -6331 (Lafon, 1969).

78 $CaCO_3^\circ$: log K = -3.2 (Garrels and Thompson, 1962), ΔH_R = -3130 (Helgeson, 1969).

79 $Na_2CO_3^\circ$: log K = -.672 (Garrels and Christ, 1965, p. 109).

80 $AlOH^{++}$: $Al^{+++} + H_2O = AlOH^{++} + H^+$; log K = -5.00 (Hem, Roberson, Lind, and Polzer, 1972), ΔH_R = 1990 (Helgeson, 1969).

81 $Al(OH)_2^+$: $Al^{+++} + 2\ H_2O = Al(OH)_2^+ + 2\ H^+$; log K = -9.76 (Hem, Roberson, Lind and Polzer, 1972).

82 $Al(OH)_4^-$: $Al(OH)_3$ (microxl.) = $Al^{+++} + 3\ OH^-$; log K = 32.65, $Al(OH)_3$ (microxl.) + $H_2O = Al(OH)_4^- + H^+$; log K = -12.71 (Hem and Roberson, 1967), ΔH_f from 270-3.

83 AlF^{++}: log K = 7.01 (Hem, 1968).

84 AlF_2^+: log K = 12.75 (Hem, 1968), ΔH_f from 270-3.

85 AlF_3°: log K = 17.02 (Hem, 1968), ΔH_f from 270-3.

86 AlF_4^-: log K = 19.72 (Hem, 1968).

87 $AlSO_4^+$: log K = 3.2 (Hem, 1968), ΔH_R = 2290 (Izatt, Eatough, Christensen, and Bartholomew, 1969).

88 $Al(SO_4)_2^-$: log K = 5.1 (Hem, 1968), ΔH_R 3070 (Izatt, Eatough, Christensen, and Bartholomew, 1969).

89 HSO_4^-: log K = -1.987, ΔH_R = -4910 from log K(T) expression (Lietzke, Stoughton, and Young, 1961).

90, 91 H_2S (aq): ΔG_f and ΔH_f from 270-3.

92 S^{--}: ΔG_f and ΔH_f from 270-3.

93 $O_2(g)$: definition

94 $CH_4(g)$: ΔG_f and ΔH_f from 270-3.

95 OH Apatite: OH apatite = 5 Ca^{++} + 3 PO_4^{---} + OH^-; log K = -54.408 (Brown, 1960). ΔH_f from R and W.

96 F Apatite: ΔG_f and ΔH_f from Roberson (1966).

97 Chalcedony: log K and ΔH_R obtained from data of Fournier and Rowe (1962).

98 Magadiite: log K = -14.3 (Bricker, 1969).

99 Christobalite: ΔG_f and ΔH_f from R and W.

100 Silica gel: ΔG_f and ΔH_f from R and W.

101 Quartz: ΔG_f and ΔH_f from R and W.

102 $Fe(OH)_2^+$: $FeOH^{++}$ + H_2O = $Fe(OH)_2^+$ + H^+; log K = -4.7, Lamb and Jacques as quoted in quoted in Langmuir (1969).

103 $Fe(OH)_3^o$: $Fe(OH)_3^o$ = $Fe(OH)_2^+$ + OH^-; log K = -7.6, Hem and Cropper as quoted in Langmuir (1969).

104 $Fe(OH)_4^-$: Rough estimate from Fe^{+++} + 4 OH^- = $Fe(OH)_4^-$; log K = 34.11 in 3M $NaClO_4$ solution (Langmuir, 1969).

105 $Fe(OH)_2^o$ from ΔH_R and ΔS_R of magnetite hydrolysis (Sweeton and Baes, 1970)

106 Vivianite: Vivianite = 3 Fe^{++} + 2 PO_4^{---} + 8 H_2O; log K = -36 (Nriagu, 1972b).

107 Magnetite: ΔG_f and ΔH_f from R and W.

108 Hematite: ΔG_f and ΔH_f from R and W.

109 Maghemite: Maghemite + 3 H_2O = 2 Fe^{+++} + 6 OH^-; log K = -77.6 (Doyle as quoted in Langmuir, 1969).

110 Geothite: 2 geothite = hematite + H_2O; ΔG_R = 545 (Langmuir, 1971), ΔH_f from R and W.

112 $Fe(OH)_3$ amor.: $Fe(OH)_3$ amor. = Fe^{+++} + 3 OH^-; log K = -37.1 (Langmuir, 1969).

113 Annite: ΔG_f and ΔH_f from Helgeson (1969).

114 Pyrite: ΔG_f and ΔH_f from R and W.

115 Montmorillonite BF (Belle Fourche): recalculated from data in Table 2 of Kittrick (1971) assuming hydrogen montmorillonite was dissolved in equilibrium with $Fe(OH)_3$ amorph. rather than hematite.

116 Montmorillonite Ab (Aberdeen): recalculated from data in Table 2 of Kittrick (1971) assuming hydrogen montmorillonite was dissolved in equilibrium with $Fe(OH)_3$ amorph. rather than hematite.

117 Huntite: ΔG_f and ΔH_f from Hemingway and Robie (1972).

118 Gregite: log K = -70.63 (Berner, 1967).

119 FeS ppt.: log K = -16.833 (Berner, 1967).

120 $FeH_2PO_4^+$: log K = -2.7 (Nriagu, 1972b).

121 $CaPO_4^-$: log K = 6.459; ΔH_R = 3100 (Chughtai, Marshall, and Nancollas, 1968).

122 $CaH_2PO_4^+$: log K = 1.408; ΔH_R = 3400 (Chughtai, Marshall and Nancollas, 1968).

123 $MgPO_4^-$: log K adjusted from $CaPO_4^-$ by using analogy between $CaHPO_4^\circ$ and $MgHPO_4^\circ$, i.e., log K = 6.459 + (2.87 - 2.74) = 6.589, ΔH_R = 3100 by analogy with $CaPO_4^-$.

124 $MgH_2PO_4^+$: log K adjusted from $CaH_2PO_4^-$ by using analogy between $CaHPO_4^-$ and $MgHPO_4^\circ$, i.e., log K = 1.408 + (2.87 - 2.774) = 1.513, ΔH_R = 3400 by analogy with $MgH_2PO_4^-$.

125 $LiOH^\circ$: ΔG_R = -273, ΔH_R = 4832 obtained by fitting best straight line in log K vs. 1/T plot of data in Sillen and Martell (1964).

126 $LiSO_4^-$: log K = 0.64 (Sillen and Martell, 1964).

127 NO_3^-: ΔG_f and ΔH_f from 270-3.

128 Laumontite: ΔG_f and ΔH_f from Zen (1972).

129 $SrOH^+$: log K = 0.82, ΔH_R = 1150 (Sillen and Martell, 1964).

130 $BaOH^+$: log K = 0.64, ΔH_R = 1750 (Sillen and Martell, 1964).

131 $NH_4SO_4^-$: log K = 1.110 (Sillen and Martell, 1964).

132 HCl°: log K = -6.1, ΔH_R = 18630 (Helgeson, 1969).

133 $NaCl°$: log K = −1.602 (Hanna, Pethybridge, Prue, 1971).

134 $KCl°$: log K = −1.585 (Hanna, Pethybridge, Prue, 1971).

135 $H_2SO_4°$: $H^+ + HSO_4^- = H_2SO_4°$; log K = −3, (Sillen and Martell, 1964).

136 $O_2(aq)$: Eh = 0.70 from Eq (5.26) of Garrels and Christ (1965) for systems exposted to air.

137 $CO_2(g)$: ΔG_f and ΔH_f from 270-3.

138 $FeHPO_4°$: log K = −3.6 (Nriagu, 1972b).

139 $FeHPO_4^+$: $Fe^{+++} + HPO_4^{--} = FeHPO_4^+$; log K = 5.4 (Nriagu, 1971).

140 $Al(OH)_3$ amor.: ΔG_f and ΔH_f from Latimer (1952).

141 Prehnite: ΔG_f and ΔH_f from Zen (1972).

142 Strontianite: ΔG_f and ΔH_f from R and W.

143 Celestite: ΔG_f and ΔH_f from R and W.

144 Barite: ΔG_g and ΔH_f from R and W.

145 Witherite: ΔG_f and ΔH_f from R and W.

146 Strengite: log K = −26.4 (Nriagu, 1972), ΔH_f from R and W.

147 Leonhardite: ΔG_f and ΔH_f from R and W.

148 $Na_2SO_4°$: log K = 1.512, ΔH_R = 2642 from log K(T) expression in Lafon and Truesdell (1971).

149 Nesquehonite: ΔG_f and ΔH_f from Robie and Hemingway (1972).

150 Artinite: ΔG_f and ΔH_f from Hemingway and Robie (1972).

151 $O_2(aq)$: ΔG_f and ΔH_f from 270-3.

152 H_2O: ΔG_f and ΔH_f from 270-3.

153 Sepiolite (ppt): log K = −37.212 (Wollast, et al., 1968).

154 Diaspore: ΔG_f and ΔH_f from 270-3.

155 Wairakite: ΔG_f and ΔH_f from Zen (1972).

156 $FeH_2PO_4^{++}$: $Fe^{+++} + H_2PO_4^- = FeH_2PO_4^{++}$; log K = −5.43 Nriagu (1972).

Table 2. Parameters of the Debye-Huckel equation

I. Major Ions

Ion	a	b
Ca^{++}	5.0	0.165
Mg^{++}	5.5	0.20
Na^{+}	4.0	0.075
K^{+}	3.5	0.015
Cl^{-}	3.5	0.015
SO_4^{--}	5.0	-0.04
HCO_3^{-}	5.4	0.0
CO_3^{--}	5.4	0.0

II. Minor Ions

a = 2.5

$H_2BO_3^{-}$, NH_4^{+}

a = 3.0

NO_3^{-}

a = 3.5

OH^{-}, F^{-}, HS^{-} .

a = 4.0

$MgHCO_3^{+}$, $H_3SiO_4^{-}$, Br^{-}.

a = 4.5

MgF^{+}, $Al(OH)_4^{-}$, AlF_4^{-}, $AlSO_4^{+}$, $Al(SO_4)_2^{-}$, HSO_4^{-}.

Table 2. Parameters of the Debye-Hückel equation (Continued)

a = 5.0

$FeOH^{++}$, $FeOH^{+}$, $FeSO_4^{+}$, $FeCl^{++}$, $FeCl_2^{+}$, PO_4^{---}, HPO_4^{--}, S^{--}, $LiSO_4^{-}$, Sr^{++}, $SrOH^{+}$, Ba^{++}, $BaOH^{+}$, NH_4SO_4

a = 5.4

$H_2SiO_4^{--}$, $CaPO_4^{-}$, $CaH_2PO_4^{+}$, $MgPO_4^{-}$, $MgH_2PO_4^{+}$, $NaCO_3^{-}$, $NaSO_4^{-}$, KSO_4^{-}, $H_2PO_4^{-}$, $NaHPO_4^{-}$, $KHPO_4^{-}$, $AlOH^{++}$, $Al(OH)_2^{+}$, AlF^{++}, AlF_2^{+}, $Fe(OH)_4^{-}$, $FeHPO_4^{+}$, $FeH_2PO_4^{+}$.

a = 6.0

Fe^{++}, $CaOH^{+}$, $CaHCO_3^{+}$, Li^{+}.

a = 9.0

Fe^{+++}, Al^{+++}, H^{+}.

Table 3. Single ion activity coefficients at 25°C from a 2 parameter (table) Debye-Hückel type equation (DH) used in WATEQ compared with mean salt (MS), Stokes-Robinson (SR) and other single ion activity coefficient

	Ionic Strength	0.01	0.1	0.5	1.0	2.0	3.0	4.0
γ_{Na^+}	DH	0.903	0.782	0.708	0.715	0.789	0.901	1.043
	MS	0.904	0.786	0.713	0.716	0.779	0.896	1.062
	SR*	-	0.783	0.701	0.697	0.756	0.870	1.038
γ_{K^+}	DH	0.900	0.763	0.642	0.600	0.570	0.562	0.563
	MS	0.901	0.770	0.649	0.604	0.573	0.569	0.577
	SR*	-	0.773	0.659	0.623	0.610	0.626	0.659
$\gamma_{Ca^{++}}$	DH	0.670	0.389	0.266	0.247	0.289	0.376	0.509
	MS	0.680	0.382	0.266	0.251	0.291	0.385	0.553
	SR*	-	0.380	0.234	0.210	0.220	0.265	0.340
	Davies**	0.661	0.372	0.288				
$\gamma_{Mg^{++}}$	DH	0.674	0.406	0.292	0.297	0.389	0.554	0.822
	MS	0.685	0.400	0.289	0.293	0.380	0.567	0.945
	SR*	-	0.390	0.247	0.230	0.265	0.350	0.470
γ_{Cl^-}	DH	0.900	0.763	0.642	0.600	0.570	0.562	0.563
	MS	0.901	0.770	0.649	0.604	0.573	0.569	0.577
	SR*	-	0.773	0.661	0.620	0.590	0.586	0.591
$\gamma_{SO_4^{--}}$	DH	0.667	0.371	0.205	0.155	0.112	0.091	0.077
	MS	0.653	0.368	0.214	0.155	0.108	0.085	0.070
$\gamma_{HCO_3^-}$	DH	0.905	0.788	0.692	0.654	0.623	0.606	0.596
	WBJ***	0.904	0.790	0.692	0.654	0.627	0.600	0.580
$\gamma_{CO_3^{--}}$	DH	0.671	0.386	0.229	0.184	0.150	0.135	0.126
	WBJ***	0.668	0.388	0.230	0.183	0.154	-	-

*In chloride solutions from Bates, et al.(1970). γ_{Cl^-} from NaCl solutions.

**No adjustable parameters, Davies (1962).

***From Walker, Bray, and Johnson (1927)

Table 4. Analytical expressions for log K(T) used in WATEQ

Identifier	Reaction	Expression (T in °K)	Reference
		[illegible] - 0.0[illegible] T - 4470.99/T	[illegible] (1939, [illegible])
KT(13)	$H_4SiO_4^\circ = H_3SiO_4^- + H^+$	log K(T) = 6.368 - 0.016346 T - 3405.9/T	Ryzhenko (1967)
KT(14)	$H_4SiO_4^\circ = H_2SiO_4^{--} + 2H^+$	log K(T) = 39.478 - 0.065927 T - 12355.1/T	Ryzhenko (1967)
KT(25)	$H_3BO_3^\circ = H_2BO_3^- + H^+$	log K(T) = 1573.21/T + 28.6059 + 0.012078 T - 13.2258 log T + log KW	Mesmer Baes, and Sweeton (1972)
KT(26)	$NH_4^+ = NH_3^\circ + H^+$	log K(T) = 0.6322 - 0.001225 T - 2835.76/T	Wright, Lindsay, and Druga (1961)
KT(35)	$H_2CO_3^\circ = HCO_3^- + H^+$	log K(T) = 8.153 - 0.02194 T - 2382.3/T	Ryzhenko (1963)
KT(68)	$HCO_3^- = H^+ + CO_3^{--}$	log K(T) = 5.388 - 0.02199 T - 2730.7/T	Ryzhenko (1963)
KT(72)	$K^+ + SO_4^{--} = KSO_4^-$	log K(T) = 3.106 - 673.6/T	Truesdell and Hostetl (1968)
KT(89)	$H^+ + SO_4^{--} = HSO_4^-$	log K(T) = -5.3505 + 0.0183412 T + 557.2461/T	Lietzke, Stoughton, and Young (1961)
KT(91)	$H_2S^\circ = H^+ + HS^-$	log K(T) = 11.17 - 0.02386 T - 3279/T	D'yachkova and Khodakovskiy (1968)

Appendix 1. Glossary of Identifiers

A,	Debye-Hückel constant for activity coefficient calculation. See text eq. 8.
AH20,	Activity of water. Approximated from total molality in eq. 51.
ALFA (0:D),	Activities of dissolved species (D+1 in number) used in the activity product calculations. Also used from statement 4570 as $\log_{10}$ (activity).
ALTOT,	Total dissolved aluminum species in molal units.
ANALCO3,	Total analytical CO_2 species. Equal to titrated $HCO_3^- + CO_3^{--}$ less non-carbonate.
ANALMI (0:D)	Molalities of analysed constituents.
AP (0:E),	Activity products of solid phases. Reactions are given in Table 1.
B,	Debye-Hückel constant, defined in text eq. 9.
BATOT,	The total dissolved barium species (molal).
BTOT,	The total molal concentration of boron species.
CARBONIC,	The sum of calculated $m_{HCO_3^-}$ and $m_{CO_3^{--}}$.
CATOT,	The total molal concentration of calcium containing species.
CLTOT,	The total molal concentration of chloride species.
CO2TIT,	The total alkalinity computed from the analytical molalities of $HCO_3^- + CO_3^{--}$.
CO3CALC,	The molal concentration of carbonate ion calculated from the analytical bicarbonate concentration using the measured pH and the dissociation constants of carbonic acid.
CORALK,	A flag to indicate if the analytical values of HCO_3^- and CO_3^{--} have been corrected for non-carbonate alkalinity.

CUNITS (0:D),	The analytical concentration of solution constituents in parts per million or milliequivalents per liter.
D,	The number of dissolved species.
DATE,	The date of calculation.
DENS,	The density of the solution, equal to one unless set otherwise.
DH (O:E),	The enthalpy changes of reaction for the calculation of log K values at temperatures other than 25°C.
DHA (O:D),	The ion size parameters, å; in the Debye-Hückel equation for activity coefficients.
DOX,	The concentration of dissolved oxygen in ppm.
E,	The number of reactions.
EHDO,	The redox potential (Eh) calculated from the dissolved oxygen.
EHM,	The potential of the Pt half-cell in the sample solution.
EHMC,	The EMF of the cell consisting of a Pt electrode, the sample solution and a saturated calomel reference electrode.
EMFZSCE,	The EMF of the above cell containing Zobel's solution for calibration.
EMPOX,	A flag to indicate that an empirical relation of pE to DOX is to be used.
EPMAN,	The sum of milliequivalents of anions per kilogram of H_2O.
EPMCAT,	The sum of milliequivalents of cations per kilogram of H_2O.
F,	The Faraday constant used in eq. 41.
FETOTAL,	The total molal concentration of ion containing species.
FLAG,	The units in which the analysis is given, "PPM" (parts per million parts by weight), "MG/L" (milligrams per liter solution) "MEQ/L" (milliequivalents per liter solution), or "MOL" (moles per 1000 grams H_2O).

```
 50.0 1.60 9.9 SPRING
264.4 222.0 2095.0 265.0 5145.2 1683.4 0.0 103.6 0.0 0.0 326.0 0.0
16.0 0.0 88.8 0.0  0
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