A COMPUTER PROGRAM FOR GEOCHEMICAL

ANALYSIS OF ACID-RAIN AND OTHER

LOW-IONIC-STRENGTH, ACIDIC WATERS

By Patricia A. Johnsson and Deborah G. Lord

U. S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 87-4095A

CONTENTS

TABLES

A COMPUTER PROGRAM FOR
GEOCHEMICAL ANALYSIS OF ACID-RAIN AND OTHER
LOW-IONIC-STRENGTH, ACIDIC WATERS

By Patricia A. Johnsson and Deborah G. Lord

ABSTRACT

This paper describes ARCHEM, a computer program written in FORTRAN 77[1], which is designed primarily for use in the routine geochemical interpretation of low-ionic-strength, acidic waters. On the basis of chemical analyses of the water and either laboratory or field determinations of pH, temperature, and dissolved oxygen, the program calculates the equilibrium distribution of major inorganic aqueous species and of inorganic aluminum complexes. The concentration of the organic anion is estimated from the dissolved organic carbon concentration, and the ratio of ferric to ferrous iron is calculated from the dissolved oxygen concentration. Ionic balances and comparisons of computed with measured specific conductance are performed as checks on the analytical accuracy of chemical analyses. ARCHEM may be tailored easily to fit different sampling protocols, and may be run on multiple sample analyses.

INTRODUCTION

Researchers of acidic deposition (acid rain) are commonly confronted with unique geochemical problems in data interpretation because of the low pH and low ionic strength of precipitation. In areas affected by acid rain, surface and ground waters are commonly acidified, and may even display some interesting geochemical properties such as negative alkalinities. Surface-water geochemistry can be particularly complex in areas such as the New Jersey Pinelands (Means and others, 1981), the North Carolina Sandhills region (J.K. Crawford, U.S. Geological Survey, Raleigh, N.C., oral commun., 1986), and the Bickford watershed, in Massachusetts (Eshleman and Hemond, 1985), where organic materials are present in high concentrations. Although there is a substantial library of geochemical computer models, including WATEQ[2] (Truesdell and Jones, 1974), SOLMENEQ[3] (Kharaka and Barnes, 1973), and MINEQL[4] (Westall and others, 1976), among others (see Nordstrom, 1979, for a review), the peculiarities of many low-ionic-strength waters require special modeling techniques.

ARCHEM[5], a FORTRAN 77 computer program, was designed specifically to deal with geochemical factors such as: pH, alkalinity, organic-anion concentration, and aluminum speciation in a manner rigorous enough for use

with low-ionic-strength waters. ARCHEM is not intended to be as sophisticated a model as WATEQ, SOLMENEQ, and MINEQL, nor does it give as detailed information on solution-mineral equilibria. The number of reactions considered by the model is limited, and a number of simplifications and estimation techniques are employed. However, the model may be used simply and effectively in the routine geochemical interpretation of low-ionic-strength, acidic water samples, and in the evaluation of their analytical accuracy. ARCHEM may be most useful for precipitation samples, which generally do not warrant calculations of mineral saturation indexes; for samples containing dissolved organics that can greatly complicate the geochemistry through interactions which are at present not well understood; and for performing checks on the analytical accuracy of large numbers of samples.

Like many existing geochemical computer programs, ARCHEM is based on an equilibrium model that uses both mass balance and mass action equations. The equations are solved through the method of successive iterations (Garrels and Thompson, 1962; Truesdell and Jones, 1974). The main body of the program calculates: (1) equilibrium molarities and activities of major aqueous species (see table 1), including an estimation of the organic-anion concentration; (2) equilibrium concentrations of major aluminum species (see table 2); and (3) ionic strength.

Purpose and Scope

This paper describes (1) the geochemical equations used to perform these calculations, (2) the iterative method for solving these equations, and (3) a number of calculations that aid in the interpretation of water chemistry. These calculations include (1) ion ratios, including a ferric to ferrous iron ratio computed from oxidation-reduction equations; (2) cation/anion balances based on analytical and computed data and inclusion of the organic-anion concentration as a component; and (3) specific conductance.

Acknowledgments

GEOCHEMICAL BASIS FOR COMPUTER PROGRAM

Major Equilibrium Equations

Table 1 is a list of the major, non-aluminum equilibrium relations considered in ARCHEM. Both the equations and their corresponding thermodynamic values are from Truesdell and Jones (1974, p. 234-240). For the major reactions in table 1, the equilibrium constants (K_t) are calculated for input temperatures from 0° to 30°C. These calculations are based on the Van't Hoff equation at constant pressure:

$$dlnK/dT = \Delta H/RT^2 \qquad (1)$$

2

Table 1.--Major equilibrium relations considered
by computer program
[Adapted from Truesdell and Jones, 1974]

Reaction	log K*	H_r*
$H_2CO_3 = HCO_3^- + H^+$	-6.379	1,976
$HCO_3^- = H^+ + CO_3^{-2}$	-10.330	3,550
$Mg^{+2} + HCO_3^- = MgHCO_3^+$	0.928	1.037
$Ca^{+2} + HCO_3^- = CaHCO_3^+$	1.260	6,331
$Mg^{+2} + SO_4^{-2} = MgSO_4^o$	2.238	4,920
$Ca^{+2} + SO_4^{-2} = CaSO_4^o$	2.309	1,650
$Mg^{+2} + CO_3^{-2} = MgCO_3^o$	3.398	58
$Ca^{+2} + CO_3^{-2} = CaCO_3^o$	3.200	3,130
$H_2O = H^+ + OH^-$	-13.998	13,345

* K is the equilibrium constant at 25°C. H_r is
the heat of reaction at 25°C (298°K).

where K is the equilibrium constant, T is the absolute temperature (degrees Kelvin), R is the ideal gas constant (1.99 calories/mole), and ΔH is the change in enthalpy of a reaction. From this equation, the expression for K at temperatures other than 25° Celsius can be derived:

$$K_t = K_{25} \times 10^{((\Delta H /(2.303 \times R)) \times ((T_2 - 298°K)/(T_2 \times 298°K)))} \qquad (2)$$

where K_{25} is the value of the equilibrium constant at 25°C (298°K) and K_t is the value of the equilibrium constant at the sample temperature, T_2, in degrees Kelvin.

The Van't Hoff equation, as presented above, assumes that the enthalpy change is independent of temperature. This assumption is not, in fact, correct for all of the reactions considered by ARCHEM. Although corrections for enthalpy changes can be made (see Stumm and Morgan, 1981, p. 69-71), ARCHEM uses the more simple equation presented above. According to Hem (1985), the use of the Van't Hoff equation as an approximation "is applicable over temperature ranges to be expected in most natural waters." The program is intended and designed for use on samples approaching standard pressure and temperature conditions, so that this approximation does not present additional limitations.

<u>Aluminum Equilibria</u>

ARCHEM also calculates the equilibrium concentrations of inorganic aluminum species (see table 2), because (1) aluminum species can act as the predominant buffering agents in low-ionic-strength waters (see, for example, Johnson and others, 1981), and (2) certain aluminum species may be toxic to fish populations (Driscoll and others, 1980) and may adversely affect tree growth (Ulrich and others, 1980). Table 2 is a list of the aluminum equilibrium equations and thermodynamic values utilized by ARCHEM. These values were chosen on the basis of (1) values prevalent in the recent acid-rain literature (see, for example, Johnson and others, 1981; Driscoll, 1984; and Cosby and others, 1985a) and (2) suggestions in Nordstrom and others (1984). An effort was made to maintain internal consistency within any one set of complexes (fluoride versus sulfate versus hydroxide) by choosing logK data from only one source for each of these sets (aluminum-fluoride complexes from Hem, 1968; aluminum-sulfate complexes from Behr and Wendt, 1962; and aluminum-hydroxide complexes from May and others, 1979). However, no attempt was made to maintain consistency between the sets of complexes.

Cozzarelli (U.S. Geological Survey, Reston, Va., written commun., 1987) cautions that the use of inconsistent thermodynamic data in the program may cause problems in the calculation of species' equilibrium distributions. The authors, therefore, strongly recommend that users perform a careful review of the recent literature before using the program. Nordstrom and others (1984), which is an excellent reference for such a review, provides a compilation of aluminum thermodynamic data along with recommendations for use, and a discussion of problems involving thermodynamic inconsistency. The responsibility for selection of thermodynamic data, for all of the species in the program, ultimately rests with the user. The thermodynamic values may be altered easily within the source code.

Table 2.--Aluminum equilibrium relations considered by computer program

Reaction	log K	H_r	Data source[*]
Fluoride Complexes			
$Al^{+3} + F^- = AlF^{+2}$	7.01	1.10	1;2
$Al^{+3} + 2F^- = AlF_2^+$	12.75	2.00	1;2
$Al^{+3} + 3F^- = AlF_3^o$	17.02	2.50	1;2
$Al^{+3} + 4F^- = AlF_4^-$	19.72	2.20	1;2
$Al^{+3} + 5F^- = AlF_5^{-2}$	20.91	1.80	1;2
$Al^{+3} + 6F^- = AlF_6^{-3}$	20.86	0.10	1;3
Sulfate Complexes			
$Al^{+3} + SO_4^{-2} = AlSO_4^+$	3.20	2.29	4;5
$Al^{+3} + 2SO_4^{-2} = Al(SO_4)_2^-$	5.10	3.07	4;5
Hydroxide Complexes			
$Al^{+3} + H_2O = Al(OH)^{+2} + H^+$	-4.99	14.775	6;7
$Al^{+3} + 2H_2O = Al(OH)_2^+ + 2H^+$	-10.13	22.0	6;3
$AL^{+3} + 3H_2O = AL(OH)_3^o + 3H^+$	-16.76	33.0	6;3
$Al^{+3} + 4H_2O = Al(OH)_4^- + 4H^+$	-22.16	42.22	6;7

Total inorganic Aluminum = $[Al^{+3}] + [Al(OH)^{+2}] + [Al(OH)_2^+] + [Al(OH)_4^-] + [Al(SO_4)^+] + [Al(SO_4)_2^-] + [AlF^{+2}] + [AlF_2^+] + [AlF_3^o] + [AlF_4^-] + [AlF_5^{-2}] + [AlF_6^{-3}]$

[*]Data Sources:
1 Hem, 1968.
2 Smith and Martell, 1976.
3 Nordstrom and others, 1984.
4 Behr and Wendt, 1962.
5 Izatt and others, 1969.
6 May and others, 1979.
7 Plummer and others, 1976.

If dissolved aluminum has been analytically fractionated into nonlabile monomeric aluminum (monomeric alumino-organic complexes) and labile monomeric aluminum (free aluminum and alumino-sulfate, fluoride, and hydroxide complexes), then the program will subtract out organically bound aluminum before calculating concentrations of inorganic species. Otherwise, the programmer may choose between two options: (1) to calculate aluminum speciation treating the input value of aluminum as the total of all inorganic aluminum, or (2) to set the concentration of Al^3 equal to the input value of aluminum, disregarding speciation entirely. In many instances, option (1) may give a better value for the computed ion balance, because AlF^2 is generally the dominant inorganic aluminum species (LaZerte, 1984). Aluminum fractionation by analytical means is strongly recommended, however, because the concentrations of dissolved inorganic aluminum species may be overestimated in waters containing organically-bound aluminum. A potential method for estimating the maximum quantity of aluminum that may be bound to organics is discussed below.

Organic-anion Concentration

Oliver and others (1983) showed that calculation of the concentration of the 'organic anion', which results from the dissociation of aquatic humic substances, can greatly improve ion balances for highly-colored natural waters. ARCHEM, therefore, performs an estimation of the organic-anion concentration, based on the equations derived by Oliver and others (1983) for "highly colored natural waters, where most of the organic carbon is humic material." First, an empirical expression is used to calculate the negative logarithm of the mass action quotient of humic and fulvic acids (the pK) from the pH:

$$pK = 0.96 + (0.90 \times pH) - (0.039 \times pH^2) \tag{3}$$

(Oliver and others, 1983, p.2033). Next, the concentration of organic acid (C_t) is calculated by multiplying the dissolved organic carbon concentration (DOC) in milligrams per liter by 10 $\mu eq/mg$ C (microequivalents per milligram carbon)--the factor that Oliver and others (1983) found to be representative of humic substances from a variety of surface and ground waters in North America and Hawaii. This factor can be changed easily within the body of ARCHEM (see documentation in the source code) in instances where 10 $\mu eq/mg$ C is not a representative value. Finally, the values thus calculated are substituted into the following equation to determine the organic-anion concentration [OA]:

$$[OA] = K \times [C_t]/(K + [H^+]) \quad \text{(Oliver and others, 1983, p. 2034).} \tag{4}$$

Alkalinity Equations

The equation for alkalinity can be used along with mass action and mass balance equations in solving for the equilibrium concentrations of species. The equation for alkalinity must, however, be defined according to the specific chemical characteristics of any given system. A generalized

alkalinity equation was synthesized from the recent acid-rain literature. This equation is applicable to a wide range of conditions, including waters with negative values of alkalinity.

In ARCHEM, the concentrations of phosphate ion, of the organic anion, and of the major aluminum species as defined by Cosby and others (1985b, p. 1594) have been added to the standard form of the alkalinity equation (Stumm and Morgan, 1981, p. 188):

$$Alk = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-] - [H^+] \tag{5}$$

to yield:

$$Alk = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-] + [OA^-] - 3[Al^{+3}] + [Al(OH)_4^-] + 3[PO_4^{-3}] \tag{6}$$
$$- [H^+] - 2[AlOH^{+2}] - [Al(OH)_2^+] - 3[AlF^{+2}] - 3[AlF_2^+] - 3[AlF_3^0]$$
$$- 3[AlF_4^-] - 3[AlF_5^{-2}] - 3[AlF_6^{-3}] - 3[Al(SO_4^+)] - 3[Al(SO_4)_2^-].$$

This equation can be rearranged and used to solve for the concentrations of the bicarbonate ($[HCO_3^-]$) and carbonate ($[CO_3^{-2}]$) ions. In these and future equations, [ ] represents molar concentrations.

Alkalinity can also be defined as the sum of base cations (C_b) minus the sum of strong acid anions (C_a) (Stumm and Morgan, 1981, p. 182). ARCHEM, therefore, performs a second calculation of alkalinity according to the equation:

$$Alk = C_b - C_a = [Na^+] + [K^+] + [NH_4^+] + 2[Ca^{+2}] + 2[Mg^{+2}] \tag{7}$$
$$- [Cl^-] - [NO_3^-] - 2[SO_4^{-2}] - [F^-].$$

The value of alkalinity thus computed is reported in the output file but is not utilized in further equilibrium calculations. This value of alkalinity can, however, be used as a rough check on the analytical value of alkalinity, and can be used in future runs of the program as an estimate of the alkalinity when no analytical value is available.

Fluoride Concentrations

Fluoride is a particularly important component of the equations considered by ARCHEM because of the role fluoride plays in complexing aluminum (see table 2). The program's treatment of fluoride depends on the method of analysis. If an ion-specific electrode was used, then the activity of the fluoride ion ((F^-)) is set equal to the input value for fluoride. However, if only the concentration of total dissolved fluoride was determined, then an extra set of equations must be added to the equilibrium equations described above in order to solve for free fluoride, $[F^-]$. In this case, the assumption:

$$[Total\ Fluoride] = [HF] + [F^-] + [AlF^{+2}], \tag{8}$$

7

where

$$H^+ + F^- = HF; \quad \log_{10}K = 3.17 \quad \text{(Roberson and Hem, 1969, p. C3)} \qquad (9)$$
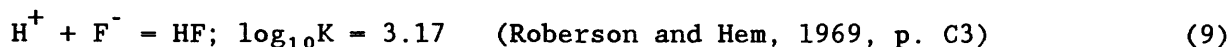
is a necessary simplification (LaZerte, 1984) that yields a linear expression and first approximation for $[F^-]$. The value of $[F^-]$ determined from this equation is then substituted into the other equilibrium equations in order to solve for the concentrations of the various aluminum-fluoride components. The value of $[F^-]$ is refined by the iterative procedure.

Activity Coefficients and Ionic Strength

The reactions presented in tables 1 and 2 and equation 9 have corresponding mass action equations which may be used in solving for the concentrations of species at equilibrium. For a generalized reaction:

$$aA + bB = cC + dD, \qquad (10)$$

with an equilibrium constant K, the mass action equation would be:

$$\frac{\{A\}^a \{B\}^b}{\{C\}^c \{D\}^d} = K, \qquad (11)$$

where $\{\ \}$ symbolizes an activity. In order to utilize these mass action equations, ARCHEM must calculate the activity coefficients (γ_is) of the various ionic species (where $\{A\} = \gamma_a \times [A]$). The activity coefficients are dependent, in turn, on the ionic strength of the sample solution. The ionic strength (I) is calculated using the standard equation:

$$I = 1/2 \sum_{n=1}^{i} m_i z_i^2 \quad , \qquad (12)$$

where n is the total number of ions in solution, m_i is the molarity of the i-th ion in the solution, and z_i is the ion's charge (Garrels and Christ, 1965, p. 56).

The following extended form of the Debye-Hückel expression, accurate for ionic strengths of less than 0.1 (Stumm and Morgan, 1981, p. 135), is used to calculate the ion activity coefficients (γ_i) :

$$\log \gamma_i = -Az_i^2 I^{\frac{1}{2}}/(1 + å_i B I^{\frac{1}{2}}) \qquad (13)$$

Here, $å_i$ is a constant related to the 'effective hydrated diameter' of the ion in solution (Garrels and Christ, 1965, p. 61), and A and B are constants whose values depend on temperature and pressure. The values of $å_i$ used by ARCHEM are listed in table 3. Values of A and B were calculated using empirical expressions designed to duplicate the values reported in Garrels and Christ (1965, p. 61). The equations, along with their results compared to the Garrels and Christ values, are reported in table 4. The calculated values agree well with the values from Garrels and Christ over the temperature range considered (0 to 30°C).

8

Table 3.--Values of $\mathring{a}_i$ in the Debye-Hückel Equation

[Values from Klotz and Rosenberg, 1972.]

Species	$\mathring{a}_i \times 10^8$
NH_4^+	2.5
K^+ Cl^- Br^- I^- NO_3^-	3.0
SO_4^{-2} PO_4^{-3}	4.0
HCO_3^- Na^+	4.0-4.5
CO_3^{-2}	4.5
Ca^{+2} Mn^{+2} Fe^{+2}	6.0
Mg^{+2}	8.0
H^+ Al^{+3} Fe^{+3}	9.0

Table 4.--Values of A and B in Debye-Hückel Equation *

Temperature degrees C	Garrels and Christ A	Calculated A	Garrels and Christ B	Calculated B
0	0.4883	0.4880	0.3241	0.3241
5	0.4921	0.4921	0.3249	0.3249
10	0.4960	0.4962	0.3258	0.3257
15	0.5000	0.5003	0.3262	0.3265
20	0.5042	0.5044	0.3273	0.3273
25	0.5085	0.5085	0.3281	0.3281
30	0.5130	0.5126	0.3290	0.3289

* Equations used to calculate A and B values:

$$A = 0.0082(T-5) + 0.4291$$
$$B = 0.3421 + 0.0008(T/5)$$

where T is the temperature in degrees Celsius.

The activity coefficients of the ionic aluminum species are calculated in the manner of Johnson and others (1981) by taking the average of the activity coefficients of other species with the same charge.

ARCHEM treats pH as the negative logarithm of the hydrogen-ion activity. For any individual sample, the hydrogen-ion activity remains constant throughout the program.

Activity coefficients of all non-ionic species, including water, are taken to be 1.

STRUCTURE OF COMPUTER PROGRAM

The equilibrium relations (mass-action equations, and the organic-anion, alkalinity, and fluoride equations), along with various mass-balance relationships, represent a group of simultaneous equations which can be solved through successive approximations. The equations are solved first using a carefully-chosen array of simplifications: the activity coefficients are set equal to 1, the sulfate concentration, $[SO_4^{-2}]$ is set equal to 10 percent of the total sulfate, and bicarbonate is set equal to the alkalinity. The value, $[SO_4^{-2}] = 0.10$ x total sulfate, is an arbitrary value that is refined by the program in future iterations. The molarity of free calcium, $[Ca^{+2}]$ is then calculated from the expression:

$$[Ca^{+2}] = [Total\ calcium]/ (1 + X + Y + Z) , \qquad (14)$$

where $X = (\gamma Ca \times \gamma SO_4 \times [SO_4^{-2}])/K_{CaSO_4}^o,$

$Y = (\gamma HCO_3 \times \gamma Ca \times [HCO_3^-])/(K_{CaHCO_3}^o \times \gamma_{CaHCO_3}),$

$Z = (\gamma Ca \times \gamma CO_3 \times [CO_3^{-2}])/KCaCO_3^o,$

and γ represents the appropriate activity coefficient.

Equation 14 is derived by substituting equilibrium mass action equations such as:

$$K_{CaSO_4}^o = \frac{\{Ca^{+2}\} \times \{SO_4^{-2}\}}{\{CaSO_4^o\}} , \qquad (15)$$

where { } symbolizes an activity, into the mass-balance equation for calcium:

$$[Total\ calcium] = [CaSO_4^o] + [CaCO_3^o] + [CaHCO_3^+] + [Ca^{+2}] \qquad (16)$$

and solving for $[Ca^{+2}]$.

Free magnesium, $[Mg^{+2}]$ and free aluminum, $[Al^{+3}]$ are both calculated in a similar fashion. Although equilibrium concentrations are normally written in terms of molalities, ARCHEM uses molarities. This

simplification is valid because for dilute waters, the differences between molality and molarity are small and generally can be neglected (Garrels and Christ, 1965; Hem, 1985).

The $[Ca^{+2}]$, $[Mg^{+2}]$, and $[Al^{+3}]$ values determined from equations similar to equation 14, are substituted back into mass-action equations such as equation 15 to calculate the concentrations of the various complexes. The ionic strength is calculated next, and is used to recalculate the activity coefficients of the separate ions (see equations 12 and 13). The bicarbonate concentration is recalculated from the alkalinity equation (see equation 6). The sulfate-ion concentration (old SO_4) used in these calculations (where $[SO_4^{-2}] = 0.10$ x total sulfate) is then compared to the sulfate-ion concentration (new SO_4) calculated from the mass-balance equation:

$$[SO_4^{-2}] = [\text{total sulfate}] - [CaSO_4] - [MgSO_4] - ([AlSO_4^{+}] + 2[Al(SO_4)_2^{-}]), \quad (17)$$

where the components in parentheses have values only if aluminum speciation is selected as an option. If these two sulfate values (old SO_4 and new SO_4) differ by less than 0.1 percent, then the iterations are halted and the various calculated concentrations are taken to be representative of the water sample, under equilibrium conditions. Otherwise, the sulfate ion concentration is increased by the amount (old SO_4 - new SO_4)/2, the calculations are performed again using the various refined values, and the loop is repeated until sulfate values converge. This convergence generally occurs within six iterations.

SPECIAL INTERPRETIVE FEATURES OF COMPUTER PROGRAM

After solving for equilibrium concentrations and activities, as described above, ARCHEM performs a series of calculations to assist in the interpretation of analytical and computed data. These calculations include ion ratios, cation/anion balances, and specific conductance. Ion ratios can be used to classify waters, to compare waters from similar or different geohydrologic sources, and in some instances, to determine the mineralogic sources of ions in solution (see Hem, 1985). Cation/anion balances and specific-conductance calculations can be used to evaluate the accuracy of water analyses. The analytical accuracy in turn limits the accuracy of all of the calculations performed by ARCHEM. As a further aid in the interpretation of water analyses, the input file for ARCHEM includes a section for identifying input values that are below the detection limit, estimated, or otherwise noteworthy. These 'flags,' which do not alter program functions, are included in the output file.

Ion Ratios

ARCHEM calculates the following ratios of analytical molarities: Na/Cl, Ca/Cl, Mg/Cl, K/Cl, Al/Cl, SO_4/Cl, Ca/Mg, SO_4/NO_3, H+/SO_4, H+/NO_3, and H+/($SO_4 + NO_3$); and of computed molarities: Ca/Cl, Mg/Cl, SO_4/Cl, and Al/Cl. The ratio of the logarithm of $[Al^{+3}]$ to the pH is also calculated, because this ratio may be used in acid-rain studies to determine whether or not aluminum is in equilibrium with an $Al(OH)_3$ mineral (Johnson and others,

12

1981, p. 1430-1431; Hooper and Shoemaker, 1985, p 463). Lastly, the ratio of ferric to ferrous iron is calculated from the dissolved oxygen concentration (DO) using oxidation-reduction equations. The DO, in mg/L (milligrams per liter), is first converted to the partial pressure of oxygen (pO_2) using the equation:

$$pO_2 = DO/32000. \tag{18}$$

The value of pO_2, thus calculated, is then substituted into the equation for electron activity (Sato, 1960) to determine the electron activity (pE):

$$pE = 11.385 - pH + 1/4\log(pO_2), \tag{19}$$

where 11.385 is the value of $-\log K_{O_2}$ from Truesdell and Jones (1974, p. 239). This equation has been simplified by assuming that the activity of water is 1.

The ratio of ferric to ferrous iron is then calculated from the redox relation (Stumm and Morgan, 1981, p. 447):

$$pE = 13.01 + \log(Fe^{+3})/(Fe^{+2}) \tag{20}.$$

Cation/anion Balances

ARCHEM performs two cation/anion balances; one based on analytical data, and the other on computed data. The formula used to calculate percent difference is:

$$\text{Percent difference} = \frac{\text{Sum of cations (eq/L) - sum of anions (eq/L)}}{\text{Sum of cations (eq/L) + sum of anions (eq/L)}} \times 100, \tag{19}$$

where eq/L represents equivalents per liter. The cation/anion balances have a few special features: (1) both balances include the organic anion concentration, which is computed as outlined above; (2) the analytical ion balance treats all iron present as Fe^{+3}, whereas the computed ion balance uses either Fe^{+3} or Fe^{+2} according to the pE computed above; (3) for positive alkalinity, the analytical ion balance sets the bicarbonate-ion concentration equal to the alkalinity; for negative alkalinity, the bicarbonate-ion concentration is set to zero; and (4) in instances where aluminum speciation is not calculated, the computed ion balance treats all aluminum as Al^{+3}. An error statement is printed if the analytical ion balance is off by more than 5 percent but less than 10 percent. A separate message flags imbalances greater than 10 percent.

Specific Conductance

The specific conductance of a water sample depends on the types and concentrations of dissolved ionic substances, and on the sample temperature. Along with cation/anion balances, specific-conductance (SC) calculations can thus serve as data-quality checks in aqueous geochemical systems (American Public Health Association and others, 1975). Calculations of equivalent conductances were first incorporated into an equilibrium computer model by

13

Reynolds (1978, p. 589-590), and his approach is utilized here. The specific conductance of a solution at 25°C can be calculated using the Onsager Limiting Law (Harned and Owen, 1958):

$$SC = 1000 \sum_i m_i \, z_i \, (\, \lambda_o i - (.634 \, \lambda_o i \, |z_i| \, I \,)^{\frac{1}{2}}, \tag{22}$$

where m_i is the molarity of the i-th species in solution, z_i is the ion's charge, and I is the ionic strength of the solution. The values of $\lambda_o i$ used by ARCHEM are presented in table 5.

For conductances measured on a meter that does not correct the reading to 25°C, the following equation is needed in order to compare calculated with measured conductance:

$$SCT = SC25/\exp(0.02x[25-T]), \tag{23},$$

where SC25 is the calculated conductance at 25°C and SCT is the conductance at the sample temperature, T (°C). This equation is based on the observation that conductance increases with temperature at a rate of about 2 percent per degree Celsius. Instructions for incorporating this equation are provided in the source code.

ARCHEM computes the percent difference between calculated and observed conductances according to the equation:

$$SC \text{ difference } (\%) = (SCcalc - SCobser)/(SCcalc + SCobser) \text{ x100 } \% \tag{24}.$$

An error flag is printed if the value of SC difference is greater than 5 percent, and a separate message is printed for a SC difference of more than 10 percent.

Component Flags

As a final interpretive feature, the program is designed to read an extra line of input containing single-digit, real numbers which can be used to 'flag' important information about any particular component. For example, '1.' may be used to symbolize a concentration below the detection limit; '2.' may represent an estimated value. These flags appear in a column of the output file, and can serve as useful indicators of the significance of values. The flags do not play an active role in determining program functions; the program uses whatever value is input, regardless of the flag. The treatment of detection-limit values and of missing values must be determined by the individual user.

LIMITATIONS OF COMPUTER PROGRAM

A number of factors limit the types of water samples that should be run on ARCHEM. The water temperature should be greater than 0° but less than 30°C (a temperature of 0.0° will cause mathematical problems), and the pH should be less than 10. Additionally, the ionic strength of the water should be less than 0.1, the maximum value permitted by the equation for the ion-activity coefficients (see equation 11). Lastly, the user should

14

Table 5.--Limiting ion conductances at 25°Celsius   *

Ion	λ_o
H^+	349.82
K^+	73.52
Na^+	50.11
½ Ca^{+2}	59.50
½ Mg^{+2}	53.06
**$CaHCO_3^+$	45.
**$MgHCO_3^+$	45.
Cl^-	76.34
Br^-	78.4
NO_3^-	71.44
HCO_3^-	44.48
***½ CO_3^{-2}	97.
OH^-	198.
½ SO_4^{-2}	79.8

*   Data from MacInnes, 1961, unless otherwise indicated.
** Values estimated by Reynolds, 1978.
***Value from the Handbook of Physics.

evaluate whether the chemical equations considered by ARCHEM and the constants such as those associated with complexing by organic material adequately describe the geochemical system and whether the species considered are likely to encompass the major species in solution.

Another important program limitation arises because the user must choose between laboratory and field data (pH, SC, and temperature) for use in calculating the equilibrium distribution of species and the value of SC difference. The program, therefore, must be run twice in order to compare equilibrium distribution of species under both field and laboratory conditions.

The following cautionary notes concern the use of the program: (1) the program assumes equilibrium conditions, and thus may yield results that are not representative of the water if nonequilibrium conditions exist; (2) the 10 μeq/mg C conversion factor used in the organic-anion calculation may not be correct for a particular water sample and at best will yield only an estimate of the organic-anion concentration; (3) the treatment of iron is fairly crude, although the ferric to ferrous iron ratio should serve as an aid in detecting errors caused by this treatment; (4) although the program may be run on an incomplete data set, the results may be misleading; and (5) for samples that fail the analytical ion balance by greater than 10 percent, the calculated equilibrium concentrations may be erroneous due to analytical errors. Furthermore, the chemistry of the water sample may limit the usefulness of the specific conductance calculation. As the pH decreases, the utility of the specific conductance calculation decreases. At low pH, the hydrogen ion dominates the sample conductance, so that the calculated specific conductance provides less information about the other ions in solution, but is an excellent check on the pH measurement.

The use of specific conductance calculations also may be limited by the presence of ions such as aluminum and iron, for which the limiting ion conductances are not known (Cronan, 1978). ARCHEM has been tested on more than 200 surface- and ground-water samples from McDonalds Branch basin in Lebanon State Forest, N.J., where the surface and ground waters often have high concentrations of dissolved aluminum and iron. In spite of the high aluminum and iron concentrations, the calculated specific conductances, generally, were within 5 percent of the measured values. Furthermore, the sample with the highest combined aluminum and iron values, 10,000 and 370 μg/L (D.G. Lord, U.S. Geological Survey, West Trenton, N.J., written commun., 1986), respectively, had a calculated specific conductance that differed from the measured value by only 6.4 percent.

ARCHEM may be run on data files containing from 1 to 50 sample analyses. The maximum number of samples may be reset using an available editor. Instructions for this procedure are outlined in the source code.

DATA INPUT

The format of sample input files is presented in Attachment A. In addition to the information contained in the input files, the program prompts the user for: (1) the name of the input file (up to 10 characters), (2) the name of the output file (up to 10 characters), (3) the date of the program run (up to 12 characters), and (4) the number of samples to be run

(up to 50 from any one file, in integer format). The maximum number of data
files may be reset using an available editor. Instructions for this
procedure are outlined in the source code.

TEST CASE

A sample output file is shown in Attachment B. This sample is from
McDonalds Branch in Lebanon State Forest, N.J., and was obtained as part of
a U.S. Geological Survey study of acidic deposition in McDonalds Branch
basin. The waters of McDonalds Branch commonly have low pH, low alkalinity,
and high concentrations of DOC, aluminum, and iron. The analytical ion
balance for this sample has been improved significantly by the addition of
the organic-anion concentration to the sum of anions. Without the organic-
anion concentration, the percent difference in cations and anions would have
been 13.2; with the organic-anion concentration, the percent difference is
only 7.2. Despite the high concentrations of aluminum and iron (1,300 and
290 μg/L, respectively) the percent difference in measured versus
calculated specific conductance is only 3.1. Although aluminum
fractionation was not performed on this sample, the equilibrium distribution
of aluminum species has been calculated for display purposes. In some
instances, ARCHEM may be used to estimate the maximum concentration of
organically bound aluminum, by assuming that all of the calculated organic
anion is balanced by aluminum (Thurman, E. M., U.S. Geological Survey
Denver, Colo., oral commun., 1986). This approach is being evaluated
presently by the authors.

SUMMARY

The computer program ARCHEM was designed for the routine geochemical
interpretation of low-ionic-strength, acidic waters, as are commonly
encountered in acid-rain studies. ARCHEM calculates equilibrium speciation,
ionic strength, ion ratios, cation/anion balances, and specific conductance.
The program has a number of special features, including a calculation of the
organic-anion concentration, which can greatly improve cation/anion balances
in some waters. Furthermore, the program allows for the input of negative
alkalinity values. Lastly, ARCHEM may be run on files of multiple sample
analyses.

REFERENCES CITED

American Public Health Association and others, 1976, Standard methods for
    the examination of water and wastewater (14th ed.): Washington D.C.,
    American Public Health Association, 1193 p.

Behr, Barbara, and Wendt, H., 1962, Fast ion reactions in solutions, (I)
    formation of the aluminum sulfate complex: Zeitschr. Elekrochemie,
    v. 66, p. 223-228.

Condon, E.U., and Odishaw, Hugh, editors, 1967, Handbook of physics (2nd
    ed.): New York, McGraw-Hill Book Company.

Cosby, B.J., Hornberger, G.M., and Galloway, J.N., 1985a, Modeling the
    effects of acid deposition: Assessment of a lumped parameter model of
    soil water and streamwater chemistry: Water Resources Research, v. 21,
    no. 11, p. 51-63.

Cosby, B.J., Hornberger, G.M., Galloway, J.N., and Wright, R.F., 1985b,
    Modeling the effects of acid deposition: Estimation of long-term water
    quality responses in a small forested catchment: Water Resources
    Research, v. 21, no. 11, p. 1591-1601.

Cronan, C.S., 1978, Solution chemistry of a New Hampshire subalpine
    ecosystem: Biogeochemical patterns and processes: unpublished Ph.D.
    thesis, Dartmouth College, Hanover, New Hampshire. 248 p.

Driscoll, C.T., 1984, A procedure for the fractionation of aqueous aluminum
    in dilute acidic waters: International Journal of Environmental
    Analytical Chemistry, v. 16, p. 267-283.

Driscoll, C.T., Jr., Baker, J.P., Biscogni, J.J., Jr., and Schofield, C.L.,
    1980, Effect of aluminum speciation on fish in dilute acidified waters:
    Nature, v. 284, p. 161-164.

Eshleman, K.N., and Hemond, H.F., 1985, The role of organic acids in the
    acid-base status of surface waters at Bickford Watershed,
    Massachusetts: Water Resources Research, v. 21, no. 10, p. 1503-1510.

Garrels, R.M. and Christ, C.L., 1965, Solutions, Minerals, and Equilibria:
    San Francisco, California, Freeman Cooper and Company, 450 p.

Garrels, R.M. and Thompson, M.E., 1962, A chemical model for sea water at
    25°C and one atmosphere total pressure: American Journal of Science,
    v. 260, p. 57-66.

Harned, H.S., and Owen, B.B., 1958, The physical chemistry of electrolytic
    solutions: New York, Reinhold, 450 p.

Hem, J.D., 1968, Graphical methods for studies of aqueous aluminum
    hydroxide, fluoride, and sulfate complexes: U.S. Geological
    Survey Water-Supply Paper 1827-B, 33 p.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water (3rd ed.): U.S. Geological Survey Water-Supply Paper 2254, 263 p.

Hooper, R.P., and Shoemaker, C.A., 1985, Aluminum mobilization in an acidic headwater stream: Temporal variation and mineral dissolution disequilibria: Science, v. 229, p. 463-465.

Johnson, N.M., Driscoll, C.T., Eaton, J.S., Likens, G.E., and McDowell, W.H., 1981, 'Acid rain', dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire: Geochimica et Cosmochimica Acta, 45, 1421-1437.

Kharaka, Y.K., and Barnes, Ivan, 1973, SOLMENEQ: Solution-mineral equilibrium computations, NTIS #PB215899, 75 p.

Klotz, I.M., and Rosenberg, R.M., 1972, Chemical thermodynamics: Menlo Park, California, W.A. Benjamin, Incorporated, 444 p.

LaZerte, Bruce D., 1984, Forms of aqueous aluminum in acidified catchments of central Ontario: A Methodological Analysis: Canadian Journal of Fisheries and Aquatic Science, v. 41, p. 766-776.

MacInnes, D.A., 1961, The principles of electrochemistry: New York, Dover Publishers, Incorporated, 478 p.

May, H.M., Helmke, P.A., and Jackson, M.L., 1979, Gibbsite solubility and thermodynamic properties of hydroxy-aluminum ions in aqueous solution at 25°C: Geochimica et Cosmochimica Acta, v. 43, p. 861-868.

Means, J.L., Yuretich, R.F., Crerar, D.A., Kinsman, D.J.J., and Borcsik, M.P., 1981, Hydrogeochemistry of the New Jersey Pine Barrens: New Jersey Department of Environmental Protection Bulletin 76, 107 p.

Nordstrom, D.K., compiler, 1979, A comparison of computerized chemical models for equilibrium calculations in aqueous systems, in E.A. Jenne, ed., Chemical modeling in aqueous systems: Washington D.C., American Chemical Society, p. 856-892.

Nordstrom, D.K., Valentine, S.D., Ball, J.W., Plummer, L.N., and Jones, B.F., 1984, Partial compilation and revision of basic data in the WATEQ programs: U.S. Geological Survey Water-Resources Investigations 84-4186, 40 p.

Oliver, B.G., Thurman, E.M., and Malcolm, R.L., 1983, The contribution of humic substances to the acidity of colored natural waters: Geochimica et Cosmochimica Acta., v. 47, p. 2031-2035.

Plummer, L.N., Jones, B.F., and Truesdell, A.H., 1976, WATEQF - A FORTRAN IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters: U.S. Geological Survey Water-Resources Investigations 76-13, 61 p.

19

REFERENCES CITED--Continued

Reynolds, R.C., Jr., 1978, Polyphenol inhibition of calcite precipitation in Lake Powell: Limnology and Oceanography, v. 23, no. 4, p. 585-597.

Roberson, C.E., and Hem, J.D., 1969, Solubility of aluminum in the presence of hydroxide, fluoride, and sulphate: U.S. Geological Survey Water - Supply Paper 1827-C, 37 p.

Sato, M., 1960, Oxidation of sulfide ore bodies, 1. Geochemical environments in terms of Eh and pH: Economic Geology, v. 55, p. 928-961.

Smith, R.M., and Martell, A.E., 1976, Critical stability constants Vol. 4: Inorganic Complexes, New York, Plenum Press, 257 p.

Stumm, W. and Morgan, J.J., 1981, Aquatic chemistry: An introduction emphasizing chemical equilibria in natural waters (2nd ed.): New York, John Wiley and Sons, Incorporated, 780 p.

Truesdell, A.H., and Jones, B.F., 1974, WATEQ, a computer program for calculating chemical equilibria of natural waters: Journal of Research U.S. Geological Survey, v. 2, no. 2, p. 233-248.

Ulrich, Bernhard, Mayer, R., and Khanna, P.K., 1980, Chemical changes due to acid precipitation in a loess-derived soil in central Europe: Soil Science, v. 130, p. 193-199.

Westall, J.C., Zachary, J.L., and Morel, F.M.M., 1976, MINEQL, A computer program for the calculation of chemical equilibrium of aqueous systems: Technical Note 18, Department of Civil Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, 91 p.

```
     S-7        ' ' 2/19/1986'       3.7000    134.0000         0.0000    124.0000    0.5
   290.0000       0.0887      4.6000       0.1000      0.0100      18.0000
  1300.0000       1.6000      1.0000      55.0000      2.8000       0.3100
     0.0000       0.0031     -0.2E-3      14.0000     10.50         3.9000   2.4791
0.  2.  2.  2. 1.
0. 0. 0. 0. 1. 0. 0. 0. 0. 0. 0. 0. 3. 0. 2. 0. 0.
```

Description of Format

CARD 1   A17,1X,A12,1X,5(G10.4E2,1X) SITE ID,DATE,FIELD PH,FIELD

SPECIFIC CONDUCTANCE(UMHOS),LAB PH, LAB SPECIFIC CONDUCT-

AND(UMHOS),FIELD TEMPERATURE(DEGREES CELSIUS)

CARD 2   6(G10.4E2,1X) IRON(UG/L),AMMONIUM(MG/L),CHLORIDE(MG/L),

FLUORIDE(MG/L),BROMIDE(MG/L),SULFATE(MG/L)

CARD 3   6(G10.4E2,1X) ALUMINUM(UG/L),CALCIUM(MG/L),MAGNESIUM(MG/L),

MANGANESE(UG/L),SODIUM(MG/L),POTASSIUM(MG/L)

CARD 4   5(G10.4E2,1X) NITRATE(MG/L),PHOSPHATE(MG/L),ALAKLINITY(EQ/L),

DOC(MG/L),DO(MG/L)

CARD 5   G10.4E2,4(1X,F1) CONCENTRATION OF ORGANICALLY-BOUND ALUM-

INUM(UG/L),FLAG FOR LAB/FIELD DATA(1. OR 2.),FLAG FOR

CALCULATION OF ALUMINUM SPECIATION(1. OR 2.),FLAG FOR

FLUORIDE INPUT AS [F-] OR TOTAL FLUORIDE(1. OR 2.),FLAG

TO INPUT CARD 1-5 DATA IN EQ/L INSTEAD OF MG/L OR UG/L

(2. OR 1.).

CARD 6   17(F1) FLAGS USED TO SIGNAL IMPORTANCE OF INPUT VALUE, IN

FOLLOWING ORDER: AL,CA,MG,MN,NA,K,FE,NH4,CL,F,BR,SO4,NO3,

PO4,ALKALINITY,DOC,DO

(REPEAT CARDS 1-6 FOR REMAINING SAMPLES)

1***

SITE ID =   S-7   DATE: 2/19/1986
DATE RUN ON ARCHEM.F77: 4/12/87

PHFLD= 3.700   TEMP= 0.500   SCFLD= 134.000
PHLAB= 0.000   TEMP= 25.000   SCLAB= 124.000

RATIO OF H+ ACTIVITY FIELD TO H+ ACTIVITY LAB= 0.0000
RATIO OF SC FIELD TO SC LAB=   1.08

FIELD DATA WERE USED

INPUT PARAMETERS   CALCULATED PARAMETERS

	MG/L	MOLARITY	EQ/L	ACTIVITY	GAMMA	1.=<
H=		0.2058E-03	0.2058E-03	0.1995E-03	0.9695	
CA=	1.600	0.3992E-04	0.7984E-04	0.3438E-04	0.8804	0.
MG=	1.000	0.4113E-04	0.8226E-04	0.3590E-04	0.8825	0.
NA=	2.800	0.1218E-03	0.1218E-03	0.1179E-03	0.9682	1.
K=	0.3100	0.7927E-05	0.7927E-05	0.7671E-05	0.9678	0.
NH4=	0.8870E-01	0.4918E-05	0.4918E-05	0.4758E-05	0.9676	0.
CL=	4.600	0.1298E-03	0.1298E-03	0.1256E-03	0.9678	0.
F=	0.1000	0.5264E-05	0.5264E-05	0.1886E-07	0.9679	0.
BR=	0.1000E-01	0.1251E-06	0.1251E-06	0.1211E-06	0.9678	0.
SO4=	18.00	0.1874E-03	0.3748E-03	0.1589E-03	0.8786	0.
NO3=	0.0000	0.0000	0.0000	0.0000	0.9678	3.
PO4=	0.3100E-02	0.3264E-07	0.9793E-07	0.2440E-07	0.7474	0.
ALK=		-.2000E-03	-.2000E-03			2.
DOC=	14.00					0.
DO=	10.50					0.

	UG/L	MOLARITY	EQ/L	ACTIVITY	GAMMA	1.=<
AL=	1300.	0.4829E-04	0.1449E-03	0.2851E-04	0.7567	0.
MN=	55.00	0.1001E-05	0.2002E-05	0.8813E-06	0.8804	0.
FE=	290.0	0.5194E-05	0.1039E-04	0.4573E-05	0.8804	0.

ALL FE ASSIGNED TO +2 VALENCE AS FE+3/FE+2 RATIO
COMPUTED BELOW IS LESS THAN 1.

MOLARITIES CALCULATED
FROM EQUILIBRIUM SPECIATION EQUATIONS

CA=   0.3905E-04
MG=   0.4068E-04
SO4=   0.1808E-03
F=   0.1949E-07
HF=   0.5565E-08
OH=   0.6111E-11

SULFATE SPECIES

CASO4=   0.8534E-06
MGSO4=   0.4468E-06

CARBONATE SPECIES

CAHCO3= 0.1928E-07
MGHCO3= 0.4829E-08
CO3=   0.1242E-10
HCO3=   0.5358E-04
H2CO3=   0.5361E-01
CACO3=   0.3609E-12
MGCO3=   0.9711E-12

ALUMINUM SPECIES

```
AL3+=      0.3768E-04
ALOH=      0.1554E-06
ALOH2=     0.1618E-08
ALOH3=     0.3167E-12
ALOH4=     0.1490E-14
ALF=       0.5238E-05
ALF2=      0.4273E-07
ALF3=      0.1341E-10
ALF4=      0.1374E-15
ALF5=      0.4814E-22
ALF6=      0.0000
ALSO4=     0.5119E-05
ALSO42=    0.5718E-07
```

```
ION RATIOS FROM ANALYTICAL MOLARITIES=
NA/CL= 0.9386
CA/CL= 0.3076
MG/CL= 0.3170
K/CL= 0.6108E-01
AL/CL= 0.3722
SO4/CL=  1.444
CA/MG= 0.9706
SO4/NO3 = 0.0000
H/SO4= 1.065
H/NO3= 0.0000
H/(SO4+NO3)= 0.0000
```

```
ION RATIOS FROM COMPUTED MOLARITIES
CA/CL= 0.3009
MG/CL= 0.3135
SO4/CL=  1.394
AL/CL= 0.2904
```

```
FE+3/FE+2=     0.6368E-06
PE=      6.814
```

RATIO (LOG ACTIVITY AL3+)/(LOG ACTIVITY OF H+)= 1.228

```
RECALCULATED TOTAL ALUMINUM, MOLES/L  = 0.4830E-04
SATURATION INDEX FOR BASIC ALUMINUM SULFATE= 0.4550E-02
```

ORGANIC ANION CONC, EQ/L =   0.6549E-04

```
MEASURED ALKALINITY, EQ/L = -.2000E-03
NEWALK, ALKALINITY CALCULATED FROM Cb-Ca= -.1970E-03
```

IONIC STRENGTH= 0.8978E-03

```
SUM CATION EQ/L = 0.6587E-03
SUM ANION EQ/L = 0.5703E-03
ANALYTICAL PERCENT DIFFERENCE IN CATIONS VS ANIONS=   7.200
```

*** FAILS IONBAL AT 5% ***

```
SUM OF CATIONS=  0.6257E-03
SUM OF ANIONS=  0.6108E-03
COMPUTED PERCENT DIFFERENCE IN CATIONS VS ANIONS=   1.206
```

```
PREDICTED  SC = 125.997
PERCENT DIFFERENCE IN SC MEASURED VS PREDICTED=   3.078
```

(Copies of this source code on diskette can be purchased from
the address given in the front of the book)

```
C       ARCHEM.F77, A FORTRAN 77 PROGRAM WRITTEN BY P.A. JOHNSSON, WITH      1
C       D.G.LORD AT THE U.S. GEOL. SURVEY WRD TRENTON, NJ. THIS PROGRAM      2
C       TAKES CHEMICAL DATA IN MG/L AND UG/L AND CALCULATES MOLARITIES,      3
C       EQ/L, ORGANIC ANION CONCENTRATION, IONIC STRENGTH, CATION/ANION      4
C       BALANCE, AND PREDICTED SPECIFIC CONDUCTANCE.                         5
C       CALCULATION OF ALUMINUM SPECIATION IS OPTIONAL.                      6
C       ARCHEM.F77 WAS SPECIFICALLY FORMULATED FOR USE WITH LOW-PH, LOW      7
C       IONIC STRENGTH, ORGANIC-RICH WATERS, AS OCCUR IN THE NEW JERSEY      8
C       PINELANDS.                                                          9
C       PLEASE NOTE THAT THE CHEMICAL DATA MAY ALSO BE INPUT AS UEQ/L.      10
C       SEE EQGRAM(M), BELOW, AND LOOP FOLLOWING READ STATEMENTS.           11
C       SAMPLE INPUT FILE:                                                 12
C       CARD 1   A17,1X,A12,1X,5(G10.4E2,1X) SITE ID,DATE,FIELD PH,FIELD    13
C                SPECIFIC CONDUCTANCE(UMHOS),LAB PH, LAB SPECIFIC CONDUCT-   14
C                AND(UMHOS),FIELD TEMPERATURE(DEGREES CELSIUS)              15
C       CARD 2   6(G10.4E2,1X) IRON(UG/L),AMMONIUM(MG/L),CHLORIDE(MG/L),    16
C                FLUORIDE(MG/L),BROMIDE(MG/L),SULFATE(MG/L)                 17
C       CARD 3   6(G10.4E2,1X) ALUMINUM(UG/L),CALCIUM(MG/L),MAGNESIUM(MG/L),18
C                MANGANESE(UG/L),SODIUM(MG/L),POTASSIUM(MG/L)               19
C       CARD 4   5(G10.4E2,1X) NITRATE(MG/L),PHOSPHATE(MG/L),ALAKLINITY(EQ/L),20
C                DOC(MG/L),DO(MG/L)                                         21
C       CARD 5   G10.4E2,4(1X,F1) CONCENTRATION OF ORGANICALLY-BOUND ALUM-  22
C                INUM(UG/L),FLAG FOR LAB/FIELD DATA(1. OR 2.),FLAG FOR      23
C                CALCULATION OF ALUMINUM SPECIATION(1. OR 2.),FLAG FOR      24
C                FLUORIDE INPUT AS [F-] OR TOTAL FLUORIDE,FLAG FOR INPUT    25
C                AS MILLIGRAMS OR MICROEQUIVALENTS PER LITER (1. OR 2.).    26
C       CARD 6   17(F1) FLAGS USED TO SIGNAL IMPORTANCE OF INPUT VALUE, IN  27
C                FOLLOWING ORDER:  AL,CA,MG,MN,NA,K,FE,NH4,CL,F,BR,SO4,NO3, 28
C                PO4,ALKALINITY,DOC,DO                                      29
C                                                                          30
C                (REPEAT CARDS 1-6 FOR REMAINING SAMPLES)                   31
C                                                                          32
C       ****************************************************************    33
C       PARAMETER STATEMENT-- CHANGE M MANUALLY TO ALTER MAXIMUM           34
C       NUMBER OF SAMPLES THAT CAN BE RUN AT ONE TIME.  PRESENT MAXIMUM    35
C       IS 50.                                                            36
C       ****************************************************************    37
        PARAMETER (M = 50)                                                38
C       ****************************************************************    39
C                                                                          40
C......INPUT FLAGS FOR LESS THAN VALUES (CARD 6 DATA)                       41
        REAL AZ1(M),AZ2(M),AZ3(M),AZ4(M),AZ5(M),AZ6(M),AZ7(M),            42
     *       AZ8(M),AZ9(M),AZ10(M),AZ11(M),AZ12(M),AZ13(M),AZ14(M),       43
     *       AZ15(M),AZ16(M),AZ17(M)                                      44
```

```
C......INPUT PARAMETERS, IN MG/L                                        45
      REAL TCA(M),TMG(M),TSO4(M),NO3(M),NH4(M),NA(M),K(M),CL(M),        46
     *      BR(M),F(M),DOC(M),PO4(M)                                    47
C......INPUT PARAMETERS, IN UG/L                                        48
      REAL FE(M),MN(M),AL(M)                                            49
C                                                                       50
C......INPUT PARAMETERS, IN EQ/L                                        51
      REAL ALK1(M)                                                      52
C                                                                       53
C......OTHER INPUT PARAMETERS-- DISSOLVED OXYGEN, FIELD SPECIFIC        54
C......CONDUCTANCE, LAB SPECIFIC CONDUCTANCE, FIELD PH, LAB PH,         55
C      FIELD TEMPERATURE (DEG. CELSIUS).                                56
C      CTEMP2 IS LAB TEMPERATURE AND IS AUTOMATICALLY PUT IN BY         57
C      ARCHEM AS 25 DEGREES CELSIUS.                                    58
      REAL DO(M),SCFLD(M),SCLAB(M),PH(M),PH2(M),CTEMP(M),               59
     *      CTEMP2,SI(M)                                                60
C......CHARACTER INPUT SITE (17 CHARACTERS), DATE (12 CHARACTERS).      61
C......INPUT SHOULD INCLUDE SINGLE QUOTES.                              62
      CHARACTER*17 SITE(M)                                              63
      CHARACTER*12 DATE(M)                                              64
C......CHARACTER INPUT CALLED FOR BY PROMPT.  NAME OF INPUT FILE HAS    65
C      TEN CHARACTERS, NAME OF OUTPUT FILE HAS TEN CHARACTERS, TODAY'S  66
C      DATE HAS 12 CHARACTERS.  NO SINGLE QUOTES NEEDED.                67
      CHARACTER INFILE*10, OUTFILE*10, TODAY*12                         68
C......CALCULATED SPECIES, MOLARITIES                                   69
      REAL OH,CO3,ORG,HCO3,CA,MG,SO4,CASO4,MGSO4,CAHCO3,MGHCO3,         70
     *      H2CO3,CACO3,MGCO3,HF                                        71
C......A PARAMETERS ARE ACTIVITIES.  ACTIVITIES OF UNCHARGED SPECIES ARE 72
C      TAKEN AS EQUAL TO 1.                                             73
      REAL ACA,AMG,ASO4,ANO3,ANH4,ANA,AK,ACL,ABR,AF,APO4,              74
     *      AFE,AMN,AAL,ACO3,AHCO3,AOH                                  75
C......Z PARAMETERS ARE MOLARITIES                                      76
      REAL TCAZ,TMGZ,TSO4Z,NO3Z,NH4Z,NAZ,KZ,CLZ,BRZ,FZ,DOCZ,PO4Z,      77
     *      FEZ,MNZ,ALZ,ALKZ                                            78
C......E PARAMETERS ARE EQ/L  (FOR DI- AND TRI-VALENT SPECIES).         79
      REAL CAE,MGE,SO4E,PO4E,FEE,MNE,ALE                               80
C......E2 PARAMETERS ARE UEQ/L                                          81
      REAL CAE2,MGE2,SO4E2,NO3E2,NH4E2,NAE2,KE2,CLE2,BRE2,FE2,          82
     *      PO4E2,FEE2,MNE2,ALE2,OHE2,ORGE2,                            83
     *      EF                                                          84
C......G PARAMETERS ARE ACTIVITY COEFFICIENTS, GAMMAS                   85
      REAL GCA,GMG,GSO4,GHCO3,GCAHCO3,GMGHCO3,GOH,GH,GAL,GMN,           86
     *      GFE,GPO4,GNA,GF,GK,GCL,GBR,GNO3,GNH4                        87
C......SC PARAMETERS ARE EQUIVALENT CONDUCTANCES                        88
      REAL SCCA,SCMG,SCH,SCNA,SCK,SCCAHCO3,SCMGHCO3,SCCO3,SCHCO3,       89
     *      SCOH,SCCL,SCSO4,SCNH4,SCNO3,SCBR                            90
```

```
C......K VALUES ARE EQUILIBRIUM EXPRESSIONS CORRECTED FOR TEMPERATURE.      91
      REAL K1,K2,K3,K4,K5,K6,KW,K9,K10                                      92
C......VALUES FOR ORGANIC ANION CALCULATION                                 93
      REAL PK,KBAR,CBAR                                                     94
C                                                                          95
C......PARAMETERS FOR REDOX IRON CALCULATIONS (FROM STUMM AND              96
C      MORGAN)                                                             97
      REAL PO2,PE,FER,FEV2,FE3                                             98
C......NEWALK IS THE ALKALINITY CALCULATED FROM THE ALTERNATIVE            99
C......EQUATION FOR ALKALINITY:                                            100
C...... ALK = Cb-Ca                                                        101
C...... WHERE Cb= 2*CA + 2*MG + NA + K + NH4                               102
C...... AND Ca= NO3 + 2*SO4 + CL + F                                       103
C...... THE VALUE OF NEWALK CAN BE COMPARED TO THE MEASURED                104
C...... VALUE OF ALKALINITY.                                               105
      REAL NEWALK                                                          106
C......VALUES FOR SPECIFIC CONDUCTANCE CALCULATION                         107
      REAL SCT,SC25,SC25T,SCDIF                                            108
C......VARIOUS CONSTANTS                                                   109
      REAL A,B,C,D,Z,KTEMP                                                 110
C......VALUES FOR LOOP                                                     111
      REAL L,MSO4,GMSO4,T,FZ2,FZM                                          112
C......IONIC STRENGTH                                                      113
      REAL MU,MU2,MUF                                                      114
C......ION BALANCE                                                         115
      REAL CAT2,AN2,CATAN2,CAT,AN,CATAN                                    116
C......R VALUES ARE ANALYTICAL ION RATIOS OF MOLARITIES                    117
      REAL RCA,RMG,RNA,RK,RAL,RSO4,RSO4NO3,RHSO4,RHNO3,RHSN                118
C......R2 VALUES ARE COMPUTED ION RATIOS OF MOLARITIES                     119
      REAL R2CA,R2MG,R2AL,R2SO4                                            120
C......VALUE OF LOG (ACTIVITY AL3+)/LOG(ACTIVITY H+)                       121
      REAL LRAL                                                            122
C......RATIO OF TDS TO SC.                                                 123
      REAL TDSRAT                                                          124
C......VALUES FOR LAB VERSUS FIELD DATA                                    125
      REAL RATPH,RATSC,RPH1,RPH2                                           126
C......FLAG FOR USE OF LAB OR FIELD DATA                                   127
C......INPUT I=1. USES LAB DATA.  INPUT I = 2.                             128
C......USES FIELD DATA.                                                    129
      REAL LFI(M)                                                          130
C......FLAG FOR FLUORIDE INPUT.  FI(M) = 1. FOR ION-SPECIFIC ELECTRODE     131
C......VALUE, WHERE FLUORIDE = {F-}.  FI(M) = 2. FOR FLUORIDE = TOTAL      132
C......DISSOLVED FLUORIDE.                                                 133
      REAL FI(M)                                                           134
```

26

```
C......FLAG ALSP CALCULATES ALUMINUM SPECIATION.  USE THIS OPTION          135
C......ONLY WHEN TEMP - 25 DEG C.  IF YOU HAVE DATA FOR ORGANICALLY         136
C......BOUND ALUMINUM, INPUT THIS CONCENTRATION AS ORGAL.  THIS VALUE IS    137
C......SUBTRACTED FROM TOTAL ALUMINUM IN THE SUBSEQUENT CALCULATIONS.       138
C......ALSP - 1. TO DELETE ALUMINUM SPECIATION.  ALSP - 2. TO CALCULATE     139
C......ALUMINUM SPECIATION.                                                 140
      REAL ALSP(M)                                                         141
      REAL ORGAL(M)                                                        142
C......FLAG FOR INPUT AS MILLIGRAMS PER LITER (1.) OR MICROEQUIVALENTS      143
C......PER LITER (2.)                                                       144
      REAL EQGRAM(M)                                                       145
C......MOLARITIES OF ALUMINUM SPECIES (AL3 IS ACTIVITY)                     146
      REAL AL3,ALOH,ALOH2,ALOH3,ALOH4,ALF,ALF2,ALF3,ALF4,ALF5,ALF6,        147
     *      ALSO4,ALSO42,TAL,AL3M                                          148
C......ACTIVITY COEFFICIENTS FOR ALUMINUM SPECIES, TAKEN AS THE            149
C......AVERAGE VALUE FOR MONO-, DI-, AND TRI- VALENT SPECIES IN            150
C......SOLUTION, AS IN JOHNSON ET. AL., 1981.                              151
      REAL G1,G2,G3                                                        152
C......EQUIVALENTS/LITER OF ALUMINUM SPECIES                               153
      REAL AL3E,ALOHE,ALOH2E,ALOH4E,ALFE,ALF2E,ALF3E,ALF4E,ALF5E,          154
     *      ALF6E,ALSO4E,ALSO42E,ALOH3E                                    155
C......SATURATION INDEX FOR BASIC ALUMINUM SULFATE (ALOHSO4)               156
      REAL ALSULF                                                          157
C......VALUES OF EQUILIBRIUM CONSTANTS FOR ALUMINUM SPECIATION EQNS.,      158
C......AT 25C. VALUES FROM HEM, 1968; BEHR AND WENDT, 1962,                159
C......OR MAY ET. AL., 1968.                                               160
C......KSO IS FOR NATURAL GIBBSITE (MAY, ET AL., 1979)                     161
      REAL KOH1,KOH2,KOH3,KOH4,KF1,KF2,KF3,KF4,KF5,KF6,KS1,KS2,KSO         162
      REAL DOH1,DOH4,DF1,DF2,DF3,DF4,DF5,DS1,DS2                           163
      DATA KOH1/1.02E-05/,                                                 164
     *      KOH2/7.41E-11/,                                                165
     *      KOH3/1.74E-17/,                                                166
     *      KOH4/6.92E-23/,                                                167
     *      KF1/1.023E+07/,                                                168
     *      KF2/5.62E+12/,                                                 169
     *      KF3/1.047E+17/,                                                170
     *      KF4/5.25E+19/,                                                 171
     *      KF5/8.32E+20/,                                                 172
     *      KF6/7.49E+20/,                                                 173
     *      KS1/1.58E+03/,                                                 174
     *      KS2/1.26E+05/,                                                 175
     *      KSO/5.89E+08/                                                  176
C......VALUES OF DELTA H FOR AL-FLOURIDE SPECIES ARE FROM SMITH AND        177
C      MARTELL, 1976.  VALUES FOR ALUMINUM SULFATE SPECIES ARE            178
C      FROM IZATT ET. AL., 1969.  VALUES FOR ALUMINUM HYDROXIDES          179
C      ARE FROM NORDSTROM ET. AL., 1984 OR PLUMMER ET. AL., 1976.         180
```

```
        DATA DOH1/14.775/,                                              181
     *      DOH2/22.0/,                                                 182
     *      DOH3/33.0/,                                                 183
     *      DOH4/42.22/,                                                184
     *      DF1/1.100/,                                                 185
     *      DF2/2.000/,                                                 186
     *      DF3/2.500/,                                                 187
     *      DF4/2.200/,                                                 188
     *      DF5/1.800/,                                                 189
     *      DF6/0.10/,                                                  190
     *      DS1/2.290/,                                                 191
     *      DS2/3.070/                                                  192
        CTEMP2 = 25.                                                    193
C        ****************************************************************  194
C        THIS PORTION OF THE PROGRAM READS IN DATA FROM KEYBOARD AND FILES.  195
C        ****************************************************************  196
C......PROMPT FOR TODAY'S DATE, NAME OF INPUT FILE, NAME OF OUTPUT FILE  197
        PRINT*,'WELCOME TO ARCHEM.F77. PLEASE TYPE IN THE DATE'         198
        READ '(A)',TODAY                                                199
        PRINT*,'TYPE IN NAME OF INPUT FILE'                             200
        READ '(A)',INFILE                                               201
        PRINT*,'TYPE IN NAME OF OUTPUT FILE'                            202
        READ '(A)',OUTFILE                                              203
        PRINT*,'TYPE IN NUMBER OF DATA FILES (UP TO 50)'               204
        READ (1,*) NDAT                                                 205
        OPEN (20,FILE=INFILE)                                           206
        OPEN (61,FILE=OUTFILE)                                          207
        DO 500 IL = 1,NDAT                                              208
C        READS DATA FROM INPUT FILE, CARDS 1-6 AS DESCRIBED ABOVE       209
        READ (20,*)SITE(IL),DATE(IL),PH(IL),SCFLD(IL),                 210
     * PH2(IL),SCLAB(IL),CTEMP(IL),FE(IL),NH4(IL),CL(IL),F(IL),        211
     * BR(IL),TSO4(IL),AL(IL),TCA(IL),TMG(IL),MN(IL),NA(IL),K(IL),     212
     * NO3(IL),PO4(IL),ALK1(IL),DOC(IL),DO(IL)                         213
        READ(20,*) ORGAL(IL),LFI(IL),ALSP(IL),FI(IL),EQGRAM(IL)        214
        READ (20,*)AZ1(IL),AZ2(IL),AZ3(IL),AZ4(IL),AZ5(IL),           215
     * AZ6(IL),AZ7(IL),AZ8(IL),AZ9(IL),AZ10(IL),AZ11(IL),             216
     * AZ12(IL),AZ13(IL),AZ14(IL),AZ15(IL),AZ16(IL),AZ17(IL)          217
C        ****************************************************************  218
C        CHANGE FOR INPUTTING DATA AS UEQ/LITER.  NOTE FE IS            219
C        ASSUMED TO BE AS FE+3 IN DATA SET.                            220
        IF (EQGRAM(IL) .EQ. 2.) THEN                                   221
           FE(IL) = FE(IL)/.05372                                      222
           NH4(IL) = NH4(IL)*.001/.05544                               223
           CL(IL) = CL(IL)*.001/.02821                                 224
           F(IL) = F(IL)*.001/.05264                                   225
           BR(IL) = BR(IL)*.001/.01251                                 226
```

```
        TSO4(IL) = TSO4(IL)*.001/.02082                            227
        AL(IL) = AL(IL)/.11119                                     228
        TCA(IL) = TCA(IL)*0.001/.04990                             229
        TMG(IL) = TMG(IL)*.001/.08226                              230
        MN(IL) = MN(IL)/.03640                                     231
        NA(IL) = NA(IL)*.001/.04350                                232
        K(IL) = K(IL)*.001/.02557                                  233
        NO3(IL) = NO3(IL)*.001/.01613                              234
        PO4(IL) = PO4(IL)*.001/.03159                              235
        ELSE                                                       236
        CONTINUE                                                   237
      END IF                                                       238
C......COMPUTATION OF RATIOS: 1) HYDROGEN ION FROM FIELD DATA OVER  239
C      HYDROGEN ION FROM LAB DATA AND 2) SCFIELD VERSUS SCLAB.      240
      IF (PH(IL) .GT. 0. .AND. PH2(IL) .GT. 0.) THEN               241
        RPH1 = 10.**(-(PH(IL)))                                    242
        RPH2 = 10.**(-(PH2(IL)))                                   243
        RATPH = RPH1/RPH2                                          244
        ELSE                                                       245
        CONTINUE                                                   246
      END IF                                                       247
        RATSC = SCFLD(IL)/SCLAB(IL)                                248
      CTEMP2 = 25.                                                 249
      WRITE (61,1) SITE(IL),DATE(IL),TODAY                         250
      WRITE (61,2) PH(IL),CTEMP(IL),SCFLD(IL)                      251
      WRITE (61,3) PH2(IL),CTEMP2,SCLAB(IL)                        252
      IF (LFI(IL) .EQ. 2.) THEN                                    253
        SCLAB(IL) = SCFLD(IL)                                      254
        CTEMP2 = CTEMP(IL)                                         255
        PH2(IL) = PH(IL)                                           256
      END IF                                                       257
      IF (PH2(IL) .GE. 10.0) THEN                                  258
        WRITE (61,4)                                               259
        WRITE (*,4)                                                260
      END IF                                                       261
      IF (CTEMP2 .LE. .1 .OR. CTEMP2 .GE. 100.0) THEN             262
        WRITE (61,5)                                               263
        WRITE (*,5)                                                264
      END IF                                                       265
      WRITE(61,6) RATPH,RATSC                                      266
C......CALCULATES TDS/S.C RATIO                                    267
      TDSRAT=((.001*AL(IL))+TCA(IL)+TMG(IL)+(.001*MN(IL))+NA(IL)+K(IL)  268
     * +(.001*FE(IL))+NH4(IL)+CL(IL)+F(IL)+BR(IL)+TSO4(IL)+NO3(IL)+    269
     * PO4(IL)+DOC(IL)+DO(IL))/SCLAB(IL)                          270
```

```
C......CALCULATES VALUES OF FE+2 AND FE+3 FROM REDOX (STUMM AND MORGAN)      271
       IF (DO(IL) .NE. 0.) THEN                                             272
           PO2 = DO(IL)/32000                                              273
           PE = 11.385-PH2(IL) +(.25*LOG10(PO2))                          274
           FER = 10.**(PE-13.01)                                          275
           ELSE                                                            276
           PE = 0.                                                        277
           FER = 1.                                                       278
       END IF                                                             279
C......Z PARAMETERS ARE MOLARITIES                                         280
C......CONVERSION FACTORS ARE FROM USGS WATER SUPPLY PAPER 1473            281
       PO4Z = PO4(IL)*.001*.01053                                        282
       DOCZ = DOC(IL)                                                    283
       TCAZ = TCA(IL)*.001*.02495                                        284
       TMGZ = TMG(IL)*.001*.04113                                        285
       TSO4Z = TSO4(IL)*.001*.01041                                      286
       NAZ = .001*NA(IL)*.04350                                          287
       CLZ = .001*CL(IL)*.02821                                          288
       NO3Z = .001*NO3(IL)*.01613                                        289
       FZ = .001*F(IL)*.05264                                            290
       FZ2 = FZ                                                          291
       MNZ = MN(IL)*.001*.01820*.001                                     292
       KZ = K(IL)*.001*.02557                                            293
       BRZ = .001*BR(IL)*.01251                                          294
       ALKZ = ALK1(IL)                                                   295
       FEZ = FE(IL)*.001*.01791*.001                                     296
       ALZ = AL(IL)*.001*.03715*.001                                     297
       NH4Z = NH4(IL)*.001*.05544                                        298
       ORGAL(IL) = ORGAL(IL)*.001*.03715*.001                            299
C......E PARAMETERS ARE EQ/LI                                              300
       ALE = ALZ*3.                                                      301
       MNE = MNZ*2.                                                      302
       IF (FER .GE. 1.) THEN                                             303
           FEE = FEZ*3.                                                  304
           ELSE                                                          305
           FEE = FEZ*2.                                                  306
       END IF                                                            307
       CAE =TCAZ*2.                                                      308
       MGE = TMGZ*2.                                                     309
       SO4E = TSO4Z*2.                                                   310
       PO4E = PO4Z*3.                                                    311
C......SETS TEMPERATURE-DEPENDENT EQM. CONSTANTS.   THERMODYNAMIC          312
C......DATA FROM TRUESDELL AND JONES, 1974.                                313
       KTEMP = CTEMP2 + 273.15                                          314
       C = ((1/KTEMP)-(3.35D-3))                                        315
```

```
      D = (1.9D-3)*2.303                                         316
      K1 = (4.909D-3)*(10.**((1.65/D)*C))                        317
      K2 =(5.495*10.**(-2.))*(10.**((6.331/D)*C))                318
      K3 =(5.8*10.**(-3.))*(10.**((4.92/D)*C))                   319
      K4 =(1.2*10.**(-1.))*(10.**((10.37/D)*C))                  320
      K5 =(6.3*10.**(-4.))*(10.**((3.13/D)*C))                   321
      K6 =(3.999*10.**(-4.))*(10.**((.058/D)*C))                 322
      KW =(1.0*10.**(-14.))*(10.**((-13.345/D)*C))               323
      K9 =(4.677*10.**(-11.))*(10.**((-3.55/D)*C))               324
      K10=(4.2*10.**(-7.))*(10.**((-1.976/D)*C))                 325
      C = (3.35D-3)-(1/KTEMP)                                    326
      KOH1 = KOH1*(10.**((DOH1/D)*C))                            327
      KOH2 = KOH2*(10.**((DOH2/D)*C))                            328
      KOH3 = KOH3*(10.**((DOH3/D)*C))                            329
      KOH4 = KOH4*(10.**((DOH4/D)*C))                            330
      KF1 = KF1*(10.**((DF1/D)*C))                               331
      KF2 = KF2*(10.**((DF2/D)*C))                               332
      KF3 = KF3*(10.**((DF3/D)*C))                               333
      KF4 = KF4*(10.**((DF4/D)*C))                               334
      KF5 = KF5*(10.**((DF5/D)*C))                               335
      KS1 = KS1*(10.**((DS1/D)*C))                               336
      KS2 = KS2*(10.**((DS2/D)*C))                               337
      HCO3 = ALKZ                                                338
C......SETS ACTIVITY COEFFICIENTS TO 1                           339
      GH = 1.                                                    340
      GOH = 1.                                                   341
      GSO4 = 1.                                                  342
      GCA = 1.                                                   343
      GMG = 1.                                                   344
      GCO3 = 1.                                                  345
      GHCO3 = 1.                                                 346
      GCAHCO3 = 1.                                               347
      GMGHCO3 = 1.                                               348
      GF = 1.                                                    349
      GAL = 1.                                                   350
      GMN = 1.                                                   351
      GFE = 1.                                                   352
      GPO4 = 1.                                                  353
      GNA = 1.                                                   354
      GK = 1.                                                    355
      GCL = 1.                                                   356
      GBR = 1.                                                   357
      GNO3 = 1.                                                  358
      GNH4 = 1.                                                  359
C     INITIALIZES [SO4] AS .1 X TSO4                             360
      L = 1.*(10.**(-1.))                                        361
        SO4 = L*TSO4Z                                            362
```

```
C      INITIALIZES HYDROGEN, HYDROXIDE, AND CARBONATE CONCENTRATIONS        363
   63  HY =(10.**(-PH2(IL)))/GH                                              364
       H = HY*GH                                                            365
       HE2 = H*1000.*1000.                                                  366
       CO3 = K9*GHCO3*HCO3/(HY*GH*GCO3)                                     367
       OH = KW/(HY*GH*GOH)                                                  368
       OHE2 = OH*1000.*1000.                                                369
C......CALCULATES ORGANIC ANION(ORG) CONC.                                  370
C......EQUATIONS FROM OLIVER, ET. AL., 1983.                                371
C      TO CHANGE THE CONVERSION FACTOR FROM 10 UEG/MG DOC TO                372
C      A VALUE APPROPRIATE FOR YOUR PARTICULAR WATERS,                      373
C      REPLACE THE 10. IN THE CBAR = LINE WITH THIS VALUE.                  374
       PK = .96 + (.9*PH2(IL))-(.039*(PH2(IL)**2.))                         375
       KBAR = 10.**(-PK)                                                    376
       CBAR = DOCZ*(10.*(1.E-6))                                            377
       ORG = (KBAR*CBAR)/(KBAR + H)                                         378
       ORGE2 = ORG*(10.**6)                                                 379
C                                                                          380
C******LOOP TO CALCULATE IONIC STRENGTH AND CARBONATE SPECIES               381
C                                                                          382
C      A AND B ARE FACTORS USED IN THE DEBYE-HUCKEL EQUATION.               383
       A =(.00082*((Ctemp2)-5.))+.4921                                      384
       B=(.3241+(.0008*(ctemp2/5.)))*(10.**(-8))                            385
       CA = TCAZ/(1.+(GCA*GSO4*SO4/K1)+(GHCO3*HCO3*GCA/(K2*GCAHCO3))+       386
     * (GCA*GCO3*CO3/K5))                                                   387
       MG = TMGZ/(1.+(GMG*GSO4*SO4/K3)+(GHCO3*HCO3*GMG/(K4*GMGHCO3))+       388
     * (GMG*GCO3*CO3/K6))                                                   389
       CASO4 = (CA*GCA*GSO4*SO4)/K1                                         390
       MGSO4 = (MG*GMG*GSO4*SO4)/K3                                         391
       CAHCO3 = (CA*GCA*GHCO3*HCO3)/(K2*GCAHCO3)                            392
       MGHCO3 = (MG*HCO3*GMG*GHCO3)/(K4*GMGHCO3)                            393
       CACO3 = GCA*CA*GCO3*CO3/K5                                           394
       MGCO3 = GMG*MG*GCO3*CO3/K6                                           395
C......OPTIONAL AL SPECIATION CALCULATIONS                                  396
       IF (ALSP(IL) .EQ. 2.) THEN                                           397
          G1 = (GH+GNA+GK+GNH4+GCL+GF+GBR+GNO3)/8.                          398
          G2 = (GCA+GMG+GSO4+GMN)/4.                                        399
          G3 = (GPO4+GAL)/2.                                               400
          AL3 = (ALZ-(ORGAL(IL)))/((1./GAL)+(KOH1/(GH*HY*G2))+             401
     *    (KOH2/(GH*GH*HY*HY*G1)) + (KOH3/(GH*GH*GH*HY*HY*HY))+            402
     *    (KOH4/(HY*HY*HY*HY*GH*GH*GH*GH*G1))+(FZ*GF*KF1/G2)+             403
     *    (FZ*FZ*GF*GF*KF2/G1)+(FZ*FZ*FZ*GF*GF*GF*KF3) + (FZ*FZ*FZ*FZ*     404
     *    GF*GF*GF*GF*KF4/G1)+(FZ*FZ*FZ*FZ*FZ*GF*GF*GF*GF*GF*KF5/G2)       405
     *    + ((FZ**6)*(GF**6)*KF6/G3)+(SO4*GSO4*KS1/G1)+                    406
     *    ((SO4**2)*(GSO4**2)*(KS2/G1)))                                   407
```

```
          AL3M = AL3/GAL                                                     408
          ALOH = (AL3*KOH1)/(HY*GH*G2)                                       409
          ALOH2 = (AL3*KOH2)/(HY*HY*GH*GH*G1)                                410
          ALOH3 = (AL3*KOH3)/(HY*HY*HY*GH*GH*GH)                             411
          ALOH4 = (AL3*KOH4)/((HY**4.)*(GH**4.)*G1)                          412
          ALF = (AL3*FZ*GF*KF1)/G2                                           413
          ALF2 = (AL3*FZ*FZ*GF*GF*KF2)/G1                                    414
          ALF3 = (AL3*FZ*FZ*FZ*GF*GF*GF*KF3)                                 415
          ALF4 = (AL3*FZ*FZ*FZ*FZ*GF*GF*GF*GF*KF4)/G1                        416
          ALF5 = (AL3*FZ*FZ*FZ*FZ*FZ*GF*GF*GF*GF*GF*KF5)/G2                  417
          ALF6 = (AL3*(FZ**6.)*(GF**6.)*KF6)/G3                             418
          ALSO4 = (AL3*SO4*GSO4*KS1)/G1                                      419
          ALSO42 = (AL3*SO4*SO4*GSO4*GSO4*KS2)/G1                            420
C     RECALCULATES [F-]                                                      421
          IF (FI(IL) .EQ. 2.) THEN                                           422
            FZM =FZ2/(1.+(AL3*GF*KF1/G2)+(H*GF/(10.**(-3.17))))              423
            HF = H*GF*FZ/(10.**(-3.17))                                      424
            FZ = FZM                                                         425
            FZM = FZM+HF+ALF+(2.*ALF2)+(3.*ALF3)+(4.*ALF4)+(5.*ALF5)+        426
     *      (6.*ALF6)                                                        427
          ELSE                                                              428
            FZ = FZ                                                          429
          END IF                                                            430
 65       TAL =AL3M+ALOH+ALOH2+ALOH3+ALOH4+ALF+ALF2+ALF3+ALF4+ALF5+ALF6+    431
     *    ALSO4+ALSO42                                                       432
        ELSE                                                                433
          CONTINUE                                                          434
        END IF                                                             435
C   CALCULATES IONIC STRENGTH                                               436
        MU=.5*((CA*4.)+(MG*4.)+(CO3*4.)+SO4*4.+CAHCO3+MGHCO3+FZ+PO4Z*9.+    437
     * HCO3)                                                               438
        IF (FER .GE. 1.) THEN                                               439
          MU = MU+(FEZ*9.)                                                  440
        ELSE                                                               441
          MU = MU+(FEZ*4.)                                                  442
        END IF                                                             443
        MU2=MU+0.5*(BRZ+NAZ+(MNZ*4.)+KZ+HY+OH+NO3Z+NH4Z+CLZ+ORG)           444
        IF (ALSP(IL) .EQ. 1. ) THEN                                        445
          MU2 = MU2+(.05*(ALZ*9.))                                         446
        ELSE                                                               447
          MU2 = MU2+(.05*(AL3M*9.)+(ALOH*4.)+ALOH2+ALOH4+(ALF*4.)+         448
     *    ALF2+ALF4+(ALF5*4.)+(ALF6*9.)+ALSO4+ALSO42)                      449
        END IF                                                             450
C   CHECKS FOR CONVERGENCE OF SULFATE VALUES                               451
        IF (SO4.GE.TSO4Z) THEN                                             452
          GO TO 64                                                         453
```

```
        ELSE                                                         454
            MSO4 = TSO4Z - CASO4 - MGSO4-ALSO4-(2.*ALSO42)           455
        END IF                                                       456
        IF(ABS((MSO4-SO4)/(MSO4+SO4)) .LE. .001) THEN               457
            GO TO 64                                                 458
        ELSE                                                         459
            SO4 = ((MSO4 - SO4)/2.)+ SO4                             460
C......DEBYE-HUCKEL EQUATION USED TO COMPUTE ACTIVITY COEFFICIENTS.  461
C       AN EXTENDED FORM OF THE DEBYE-HUCKEL EQUATION, GOOD FOR MU < 462
C       .1 (STUMM AND MORGAN) IS USED:                               463
C       LOGF = -A*(Z**2)*(MU**.5)/(1.+B*a*(MU**.5))                  464
C       A AND B ARE COMPUTED ACCORDING TO CHANGES WITH TEMPERATURE.  465
        MUF = MU2**.5                                                466
        Z= (-A*(MUF))/(1.0+((9.0E+8)*B*(MUF)))                       467
        GH = 10.**Z                                                  468
        GOH = 10.**((-A*(MUF))/(1.0+(3.5E+8)*B*(MUF)))              469
        GCA = 10.**((-A*4.*(MUF))/(1.0+(6.0E+8)*B*(MUF)))          470
        GMG = 10.**((-A*4.*(MUF))/(1.0+(8.0E+8)*B*(MUF)))          471
        GCAHCO3 = 10.**((-A*(MUF))/(1.0+(4.25E+8)*B*(MUF)))        472
        GMGHCO3=GCAHCO3                                              473
        GCO3 = 10.**((-A*4.*(MUF))/(1.0+(4.5E+8)*B*(MUF)))         474
        GSO4 = 10.**((-A*4.*(MUF))/(1.0+(4.25E+8)*B*(MUF)))        475
        GHCO3 = GCAHCO3                                              476
        GAL = 10.**((-A*9.*(MUF))/(1.0+(9.0E+8)*B*(MUF)))         477
        GMN = GCA                                                    478
        GPO4 = 10.**((-A*9.*(MUF))/(1.0+(4.25E+8)*B*(MUF)))       479
        IF (FER .GE. 1.) THEN                                        480
            GFE = GPO4                                               481
            ELSE                                                     482
            GFE = GCA                                                483
        END IF                                                       484
        GNA = GHCO3                                                  485
        GF = GOH                                                     486
        GK = 10.**((-A*(MUF))/(1.0+(3.0E+8)*B*(MUF)))             487
        GCL = GK                                                     488
        GBR = GK                                                     489
        GNO3 = GK                                                    490
        GNH4 = 10.**(-A*(MUF)/(1.0+(2.5E+8)*B*(MUF)))             491
C       CALCULATES HCO3 FROM ALKALINITY EQUATION                    492
        IF (ALSP(IL) .EQ. 1.) THEN                                   493
            HCO3 = ALKZ-(2.*CO3)+HY-ORG-(3.*PO4Z)-OH+(3.*ALZ)       494
        ELSE                                                         495
            HCO3 = ALKZ-(2.*CO3) + HY-ORG-(3.*PO4Z)-OH+(3.*AL3M)+   496
     *      (2.*(ALOH))+(ALOH2)-ALOH4+(3.*ALF)+(3.*ALF2)+(3.*ALF3)+ 497
     *      (3.*ALF4)+(3.*ALF5)+(3.*ALF6)+(3.*ALSO4)+(3.*ALSO42)    498
```

```
        END IF                                                        499
        H2CO3 = GH*HY*GHCO3*HCO3/K10                                  500
        GO TO 63                                                      501
        END IF                                                        502
C       CALCULATES ALKALINITY USING ALTERNATIVE METHOD Cb-Ca.        503
   64   NEWALK =(2.*CA)+(2.*MG)+NAZ+KZ+NH4Z-(NO3Z+(2.*SO4)+FZ+CLZ)   504
        IF (ALSP(IL) .EQ. 1.) THEN                                   505
            HCO3 = ALKZ-(2.*CO3)+HY-ORG-(3.*PO4Z)-OH+(3.*ALZ)        506
            ELSE                                                     507
            HCO3 = ALKZ-(2.*CO3) + HY-ORG-(3.*PO4Z)-OH+(3.*AL3M)+    508
     *              (2.*(ALOH))+(ALOH2)-ALOH4                        509
        END IF                                                       510
        SO4 = MSO4                                                   511
C                                                                    512
C******END OF LOOP TO CALCULATE IONIC STRENGTH AND CARBONATE SPECIES. 513
C                                                                    514
C......CALCULATION OF SPECIFIC CONDUCTANCE USING METHOD OF           515
C......R.C. REYNOLDS (1978).                                         516
        SCCA=CA*2.*(59.5-(59.5*.634*2.*MUF))                         517
        SCMG=MG*2.*(53.06-(53.06*.634*2.*MUF))                       518
        SCH=HY*(349.82-(349.82*.634*MUF))                            519
        SCNA=NAZ*(50.11-(50.11*.634*MUF))                            520
        SCK =KZ*(73.52-(73.52*.634*MUF))                             521
        SCCAHCO3=CAHCO3*(45.-(45.*.634*MUF))                         522
        SCMGHCO3=MGHCO3*(45.-(45.*.634*MUF))                         523
        SCCO3=CO3*2.*(97.-(97.*.634*2.*MUF))                         524
        SCHCO3=HCO3*(44.48-(44.48*.634*MUF))                         525
        SCOH=OH*(198-(198*.634*MUF))                                 526
        SCCL=CLZ*(76.34-(76.34*.634*MUF))                            527
        SCSO4=SO4*2.*(79.8-(79.8*.634*2.*MUF))                       528
        SCNH4=NH4Z*(73.4-(73.4*.634*MUF))                            529
        SCNO3Z=NO3Z*(71.44-(71.44*.634*MUF))                         530
        SCBR=BRZ*(78.4-(78.4*.634*MUF))                              531
        SC25 = 1000.*(SCCA+SCMG+SCH+SCNA+SCK+SCCAHCO3+SCMGHCO3+SCBR) 532
        SC25T = SC25 +(1000.*(SCCO3+SCHCO3+SCOH+SCCL+SCSO4+SCNH4+SCNO3)) 533
C......FOR SOME SC METERS, THE FOLLOWING TEMPERATURE CORRECTION MAY BE 534
C      NEEDED.                                                       535
C         SC25T = SC25T/(EXP(0.02*(25-CTEMP2)))                      536
        SCDIF = ((ABS(SC25T-SCLAB(IL)))/(SC25T+SCLAB(IL)))*100.      537
C......E2 PARAMETERS ARE UEQ/L (USED FOR GRAPHING)                   538
        EF = 10.**6.                                                 539
        CAE2 = CAE*EF                                                540
        MGE2 = MGE*EF                                                541
        NAE2 = NAZ*EF                                                542
        KE2 = KZ*EF                                                  543
        NH4E2 = NH4Z*EF                                              544
```

```
       ALE2 = ALE*EF                                                      545
       MNE2 = MNE*EF                                                      546
       FEE2 = FEE*EF                                                      547
       PO4E2 = PO4E*EF                                                    548
       SO4E2 = SO4E*EF                                                    549
       BRE2 = BRZ*EF                                                      550
       IF (FI(IL) .EQ. 2.) THEN                                          551
          FE2 = FZ2*EF                                                    552
          ELSE                                                           553
          FE2 = FZ*EF                                                     554
       END IF                                                            555
       CLE2 = CLZ*EF                                                      556
       NO3E2 = NO3Z*EF                                                    557
C......CALCULATES ACTIVITIES                                             558
       ACA = CA*GCA                                                       559
       AMG = MG*GMG                                                       560
       ASO4 = SO4*GSO4                                                    561
       ANO3 = NO3Z*GNO3                                                   562
       ANH4 = NH4Z*GNH4                                                   563
       ANA = NAZ*GNA                                                      564
       AK = KZ*GK                                                         565
       ACL = CLZ*GCL                                                      566
       ABR = BRZ*GBR                                                      567
       AF = FZ*GF                                                         568
       APO4 = PO4Z*GPO4                                                   569
       AFE = FEZ*GFE                                                      570
       AMN = MNZ*GMN                                                      571
       AAL = AL3M*GAL                                                     572
       ACO3 = CO3*GCO3                                                    573
       AHCO3 = HCO3*GHCO3                                                 574
       AOH = GOH*OH                                                       575
C......CALCULATES ION RATIOS                                             576
       RNA = NAZ/CLZ                                                      577
       RCA = TCAZ/CLZ                                                     578
       RMG = TMGZ/CLZ                                                     579
       RK = KZ/CLZ                                                        580
       RAL = ALZ/CLZ                                                      581
       RSO4 = TSO4Z/CLZ                                                   582
       IF (TSO4Z .NE. 0.0 .AND. NO3Z .NE. 0.0) THEN                      583
          RSO4NO3 = TSO4Z/NO3Z                                           584
          RHNO3 = H/NO3Z                                                 585
          RHSN = H/(TSO4Z+NO3Z)                                          586
          ELSE RHNO3 = 0.0                                               587
       END IF                                                            588
       IF (TSO4Z .NE. 0.0) THEN                                          589
          RHSO4 = H/TSO4Z                                                590
```

```
      END IF                                                       591
      R2CA = CA/CLZ                                                592
      R2MG = MG/CLZ                                                593
      R2SO4 = SO4/CLZ                                              594
      R2AL = AL3M/CLZ                                              595
      IF (AL(IL) .NE. 0. .AND. AL3 .NE. 0.) THEN                   596
         LRAL =(LOG10(AL3))/(LOG10(H))                             597
      END IF                                                       598
C......CALCULATES SATURATION INDEX FOR BASIC ALUMINUM SULFATE      599
      ALSULF = (AL3*AOH*ASO4)/(5.89E-18)                           600
C......CALCULATES ION BALANCE FROM COMPUTED DATA, USING ORG. ANION AND 601
C......CARBONATE SPECIES.                                          602
      IF (ALSP(IL) .EQ. 2.) THEN                                   603
         CAT =(CA*2.)+(MG*2.)+HY+(NAZ)+(NH4Z)+                     604
     *   (KZ)+                                                     605
     *   (CAHCO3)+                                                 606
     *   (MGHCO3)+((MNZ*2.))+                                      607
     *   (AL3M*3.)+(2.*ALOH) + (ALOH2)                             608
         IF (FER .GE. 1.) THEN                                     609
            CAT = CAT+(FEZ*3.)                                     610
            ELSE                                                   611
            CAT = CAT+(FEZ*2.)                                     612
         END IF                                                    613
         AN =(CO3*2.)+(HCO3)+(OH)+(SO4*2.)+(PO4Z*3.)               614
     *   +(FZ)+(BRZ)+(NO3Z)+ORG+(CLZ)+ALOH4                        615
         CATAN =((ABS(CAT-AN))/(CAT+AN))*100.                      616
         ELSE                                                      617
         CAT =(CA*2.)+(MG*2.)+HY+(NAZ)+(NH4Z)+                     618
     *   (KZ)+(CAHCO3)+(MGHCO3)+((MNZ*2.))+(ALZ*3.)                619
         IF (FER .GE. 1.) THEN                                     620
            CAT = CAT+(FEZ*3.)                                     621
            ELSE                                                   622
            CAT = CAT+(FEZ*2.)                                     623
         END IF                                                    624
         AN =(CO3*2.)+(HCO3)+(OH)+(SO4*2.)+(PO4Z*3.)+              625
     *   (FZ)+(BRZ)+(NO3Z)+ORG+(CLZ)                               626
         CATAN =((ABS(CAT-AN))/(CAT+AN))*100.                      627
      END IF                                                       628
C......CALCULATES ION BALANCE FROM ANALYTICAL DATA, USING ORG. ANION, AND 629
C      BICARBONATE                                                 630
      CAT2=(TCAZ*2.)+(TMGZ*2.)+H+NAZ+KZ+(FEZ*3.)+(MNZ*2.)+ALZ*3.+NH4Z 631
      AN2=OH+(TSO4Z*2.)+(PO4Z*3.)+FZ+BRZ+NO3Z+CLZ+ORG+ALK1(IL)    632
      IF (ALK1(IL) .LE. 0. ) THEN                                 633
         AN2 = AN2 - ALK1(IL)                                     634
         ELSE                                                      635
         AN2 = AN2                                                636
```

```
        END IF                                                        637
        CATAN2 = ((ABS(CAT2-AN2))/(CAT2+AN2))*100.                    638
C                                                                     639
C......WRITES OUTPUT FOR CREATING BAR GRAPHS                          640
C......OF UEQ/L FOR EACH CONSTITUENT.                                 641
C                                                                     642
C       WRITE (62,130)SITE(IL),DATE(IL)                              643
C       WRITE (62,131) HE2,NAE2,CAE2,MGE2,KE2,NH4E2                  644
C       WRITE (62,132)                                                645
C       WRITE (62,133) ALE2,MNE2,FEE2                                 646
C       WRITE (62,132)                                                647
C       WRITE (62,134) OHE2,NO3E2,PO4E2,ORGE2,SO4E2,CLE2,BRE2,FE2    648
C                                                                     649
C......GENERATES OUTPUT TO SCREEN AND OUTPUT FILE                     650
C                                                                     651
        IF (LFI(IL) .EQ. 2.) THEN                                     652
           WRITE(61,7)                                                653
           ELSE                                                       654
           WRITE(61,8)                                                655
        END IF                                                        656
        WRITE (61,9)                                                  657
        WRITE (61,10) HY,HY,H,GH                                      658
        WRITE(61,11) TCA(IL),TCAZ,CAE,ACA,GCA,AZ2(IL)                659
        WRITE (61,12) TMG(IL),TMGZ,MGE,AMG,GMG,AZ3(IL)               660
        WRITE (61,13) NA(IL),NAZ,NAZ,ANA,GNA,AZ5(IL)                 661
        WRITE(61,14) K(IL),KZ,KZ,AK,GK,AZ6(IL)                       662
        WRITE(61,15) NH4(IL),NH4Z,NH4Z,ANH4,GNH4,AZ8(IL)            663
        WRITE(61,16) CL(IL),CLZ,CLZ,ACL,GCL,AZ9(IL)                 664
        IF (FI(IL) .EQ. 2.) THEN                                      665
           WRITE (61,17) F(IL),FZ2,FZ2,AF,GF,AZ10(IL)               666
           ELSE                                                       667
           WRITE (61,18) F(IL),FZ,FZ,AF,GF,AZ10(IL)                 668
        END IF                                                        669
        WRITE(61,19) BR(IL),BRZ,BRZ,ABR,GBR,AZ11(IL)                670
        WRITE (61,20) TSO4(IL),TSO4Z,SO4E,ASO4,GSO4,AZ12(IL)        671
        WRITE (61,21) NO3(IL),NO3Z,NO3Z,ANO3,GNO3,AZ13(IL)          672
        WRITE (61,22) PO4(IL),PO4Z,PO4E,APO4,GPO4,AZ14(IL)          673
        WRITE (61,23) ALK1(IL),ALKZ,AZ15(IL)                        674
        WRITE (61,24) DOC(IL),AZ16(IL)                              675
        WRITE (61,25) DO(IL),AZ17(IL)                               676
        WRITE(61,26)                                                 677
        WRITE (61,27) AL(IL),ALZ,ALE,AAL,GAL,AZ1(IL)               678
        WRITE (61,28) MN(IL),MNZ,MNE,AMN,GMN,AZ4(IL)               679
        WRITE (61,29) FE(IL),FEZ,FEE,AFE,GFE,AZ7(IL)               680
        IF (DO(IL) .EQ. 0.) THEN                                     681
           WRITE (61,30)                                             682
```

```
          FER = 0.                                                          683
          ELSE IF (FER .GE. 1.) THEN                                        684
          WRITE(61,31)                                                      685
          ELSE                                                              686
          WRITE(61,32)                                                      687
      END IF                                                                688
      WRITE (61,33)                                                         689
      WRITE (61,34) CA,MG,SO4                                               690
      IF (FI(IL) .EQ. 2.) THEN                                             691
          WRITE (61,35) FZ,HF                                               692
          ELSE                                                             693
          CONTINUE                                                          694
      END IF                                                                695
      WRITE (61,36) OH,CASO4,MGSO4                                          696
      WRITE (61,37) CAHCO3,MGHCO3                                           697
      WRITE (61,38) CO3,HCO3,H2CO3,CACO3,MGCO3                              698
      WRITE (61,39) AL3M,ALOH,ALOH2,ALOH3,ALOH4                            699
      WRITE (61,40) ALF,ALF2,ALF3,ALF4,ALF5,ALF6,ALSO4,ALSO42              700
      WRITE (61,41) RNA,RCA,RMG,RK,RAL,RSO4,RSO4NO3,RHSO4,RHNO3,            701
     *              RHSN                                                    702
      WRITE (61,42) R2CA,R2MG,R2SO4,R2AL                                    703
      WRITE (61,43) FER,PE                                                  704
      WRITE (61,44) LRAL                                                    705
      WRITE (61,45) TAL,ALSULF                                             706
      WRITE (61,46) ORG                                                     707
      WRITE (61,47)ALKZ,NEWALK                                              708
      WRITE (61,48) MU2                                                     709
      WRITE (61,49) TDSRAT                                                  710
      WRITE(61,50)CAT2,AN2                                                  711
      WRITE(61,51)CATAN2                                                    712
      IF (CATAN2 .GE. 10.) THEN                                            713
          WRITE (61,52)                                                     714
          ELSE IF (CATAN2 .LE. 10. .AND. CATAN2 .GE. 5.) THEN              715
          WRITE (61,53)                                                     716
      END IF                                                                717
      WRITE (61,54)CAT,AN                                                   718
      WRITE(61,55)CATAN                                                     719
      WRITE (61,56) SC25T                                                   720
      WRITE (61,57)SCDIF                                                    721
      IF (SCDIF .GE. 10.) THEN                                             722
          WRITE (61,58)                                                     723
          ELSE IF (SCDIF .LE. 10. .AND. SCDIF .GE. 5.) THEN                724
          WRITE (61,59)                                                     725
      END IF                                                                726
  500 CONTINUE                                                              727
  800 FORMAT (G10.4E2)                                                      728
```

```
     66  FORMAT (G10.4E2,G10.4E2,G10.4E2)                                      729
    600  FORMAT (G10.4E2,G10.4E2)                                              730
C    130  FORMAT (A15,A15,'$',/,'0.0')                                         731
C    131  FORMAT (5(F7.2),/)                                                   732
C    132  FORMAT ('0.0',/)                                                     733
C    133  FORMAT (3(F7.2,/))                                                   734
C    134  FORMAT (7(F7.2,/))                                                   735
      1  FORMAT ('1',98('*'),//,' SITE ID = ',A15,3X,'DATE:  ',A12,/,          736
     * ' DATE RUN ON ARCHEM.F77:  ',A12,//)                                    737
      2  FORMAT(1X,'PHFLD= ',F6.3,5X,' TEMP= ',F6.3,5X,' SCFLD= ',F7.3)        738
      3  FORMAT(1X,'PHLAB= ',F6.3,5X,' TEMP= ',F6.3,5X,' SCLAB= ',F7.3,/)      739
      4  FORMAT ('***WARNING: THIS PROGRAM SHOULD ONLY BE USED FOR',/,         740
     * 'SAMPLES WITH PH LESS THAN 10.0***')                                    741
      5  FORMAT ('***WARNING: THIS PROGRAM SHOULD ONLY BE USED FOR',/,         742
     * 'TEMPERATURES IN THE RANGE OF 0.1 TO 100 DEGREES CENTIGRADE***')        743
      6  FORMAT(' RATIO OF H+ ACTIVITY FIELD TO H+ ACTIVITY LAB=  ',           744
     * G10.4E2,/,' RATIO OF SC FIELD TO SC LAB=  ',F5.2,/)                     745
      7  FORMAT (' FIELD DATA WERE USED',/,98('_'),/,/)                        746
      8  FORMAT (' LAB DATA WERE USED',/,98('_'),/,/)                          747
      9  FORMAT (1X,'INPUT PARAMETERS',47X,'CALCULATED PARAMETERS',            748
     * /,/,10X,'MG/L ',9X,'MOLARITY',                                          749
     * 7X,'EQ/L ',20X,'ACTIVITY',7X,'GAMMA',9X,'1.=<')                         750
     10  FORMAT (1X,'H= ',20X,G10.4E2,5X,G10.4E2,15X,G10.4E2,5X,G10.4E2)       751
     11  FORMAT (' CA=',3(5X,G10.4E2),10X,2(5X,G10.4E2),6X,F2.0)               752
     12  FORMAT (' MG=',3(5X,G10.4E2),10X,2(5X,G10.4E2),6X,F2.0)               753
     13  FORMAT (' NA=',3(5X,G10.4E2),10X,2(5X,G10.4E2),6X,F2.0)               754
     14  FORMAT (' K= ',3(5X,G10.4E2),10X,2(5X,G10.4E2),6X,F2.0)               755
     15  FORMAT (' NH4=',4X,G10.4E2,2(5X,G10.4E2),10X,2(5X,G10.4E2),           756
     * 6X,F2.0)                                                                757
     16  FORMAT (' CL=',3(5X,G10.4E2),10X,2(5X,G10.4E2),6X,F2.0)               758
     17  FORMAT (' F= ',3(5X,G10.4E2),10X,2(5X,G10.4E2),6X,F2.0)               759
     18  FORMAT (' F= ',3(5X,G10.4E2),10X,2(5X,G10.4E2),6X,F2.0)               760
     19  FORMAT (' BR=',3(5X,G10.4E2),10X,2(5X,G10.4E2),6X,F2.0)               761
     20  FORMAT (' SO4=',4X,G10.4E2,2(5X,G10.4E2),10X,2(5X,G10.4E2),           762
     * 6X,F2.0)                                                                763
     21  FORMAT (' NO3=',4X,G10.4E2,2(5X,G10.4E2),10X,2(5X,G10.4E2),           764
     * 6X,F2.0)                                                                765
     22  FORMAT (' PO4=',4X,G10.4E2,2(5X,G10.4E2),10X,2(5X,G10.4E2),           766
     * 6X,F2.0)                                                                767
     23  FORMAT (' ALK=',4X,15X,G10.4E2,5X,G10.4E2,46X,F2.0)                   768
     24  FORMAT (' DOC=',4X,G10.4E2,76X,F2.0)                                  769
     25  FORMAT (' DO=',5X,G10.4E2,76X,F2.0,/)                                 770
     26  FORMAT (10X,'UG/L ',9X,'MOLARITY',7X,'EQ/L ',20X,                     771
     * 'ACTIVITY',7X,'GAMMA',9X,'1.=<')                                        772
     27  FORMAT (' AL=',3(5X,G10.4E2),10X,2(5X,G10.4E2),6X,F2.0)               773
     28  FORMAT (' MN=',3(5X,G10.4E2),10X,2(5X,G10.4E2),6X,F2.0)               774
```

```
29   FORMAT (' FE=',3(5X,G10.4E2),10X,2(5X,G10.4E2),6X,F2.0,/,          775
   *  98('_'),/)                                                        776
30   FORMAT (/,' ALL FE ASSIGNED TO +3 VALENCE AND RATIO FE+3/FE+2'/,   777
   *  ' SET EQUAL TO 1 (SEE BELOW) AS INPUT VALUE OF DOX WAS 0.',/)     778
31   FORMAT (/,' ALL FE ]ASSIGNED TO +3 VALENCE AS FE+3/FE+2 RATIO',/,  779
   *  ' COMPUTED BELOW IS GREATER THAN 1.',/)                           780
32   FORMAT (/,' ALL FE ASSIGNED TO +2 VALENCE AS FE+3/FE+2 RATIO',/,   781
   *  ' COMPUTED BELOW IS LESS THAN 1.',/)                              782
33   FORMAT(1X,70('_'),//,1X,'MOLARITIES CALCULATED',/                  783
   *  ' FROM EQUILIBRIUM SPECIATION EQUATIONS',/)                       784
34   FORMAT (' CA= ',8X,G10.4E2,/,' MG= ',8X,G10.4E2,/,' SO4= ',7X,     785
   *  G10.4E2)                                                          786
35   FORMAT (' F= ',9X,G10.4E2,/,' HF= ',8X,G10.4E2)                    787
36   FORMAT (' OH= ',8X,G10.4E2,/,/,' SULFATE SPECIES',/,/' CASO4= ',   788
   *  5X,G10.4E2,/,' MGSO4= ',5X,G10.4E2)                               789
37   FORMAT (/,' CARBONATE SPECIES',/,/' CAHCO3= ',4X,G10.4E2,          790
   *  /' MGHCO3= ',4X,G10.4E2)                                          791
38   FORMAT (' CO3= ',7X,G10.4E2,3X,                                    792
   *  /' HCO3= ',6X,G10.4E2,/,1X,'H2CO3= ',5X,G10.4E2,/,                793
   *  ' CACO3= ',5X,G10.4E2,/,' MGCO3= ',5X,G10.4E2)                    794
39   FORMAT (/,' ALUMINUM SPECIES',/,/,                                 795
   *  ' AL3+= ',6X,G10.4E2,/' ALOH= ',6X,G10.4E2,/' ALOH2= ',5X,G10.4E2, 796
   *  /,' ALOH3= ',5X,G10.4E2,/,' ALOH4= ',5X,G10.4E2)                  797
40   FORMAT (' ALF= ',7X,G10.4E2,/' ALF2= ',6X,G10.4E2,/' ALF3= ',6X,   798
   *  G10.4E2,                                                          799
   *  /' ALF4= ',6X,G10.4E2,/' ALF5= ',6X,G10.4E2,/' ALF6= ',6X,        800
   *  G10.4E2,/,' ALSO4= ',5X,G10.4E2,/' ALSO42= ',4X,G10.4E2)          801
41   FORMAT(/,1X,70('_'),//,' ION RATIOS FROM ANALYTICAL MOLARITIES=',  802
   *  1X,/,' NA/CL= ',G10.4E2,/,' CA/CL= ',G10.4E2,/,' MG/CL= ',        803
   *  G10.4E2,/,' K/CL= ',G10.4E2,/,' AL/CL= ',G10.4E2,/,' SO4/CL= ',   804
   *  G10.4E2,/,' CA/MG= ',G10.4E2,/,' SO4/NO3= ',G10.4E2,/,            805
   *  ' H/SO4= ',G10.4E2,/,' H/NO3= ',G10.4E2,/,' H/(SO4+NO3)= ',       806
   *  G10.4E2,/)                                                        807
42   FORMAT (/,' ION RATIOS FROM COMPUTED MOLARITIES',/,' CA/CL= ',     808
   *  G10.4E2,/,' MG/CL= ',G10.4E2,/,' SO4/CL= ',G10.4E2,/,' AL/CL= ',  809
   *  G10.4E2,/)                                                        810
43   FORMAT (/,' FE+3/FE+2= ',5X,G10.4E2,/,' PE=',                      811
   *  5X,G10.4E2,/)                                                     812
44   FORMAT (' RATIO (LOG ACTIVITY AL3+)/(LOG ACTIVITY OF H+)= ',       813
   *  G10.4E2,/,1X,70('_'),/)                                           814
45   FORMAT (/,' RECALCULATED TOTAL ALUMINUM, MOLES/L  = ',G10.4E2,     815
   *  /,' SATURATION INDEX FOR BASIC ALUMINUM SULFATE= ',G10.4E2)       816
46   FORMAT (/,' ORGANIC ANION CONC, EQ/L =    ',G10.4E2,/)             817
47   FORMAT (' MEASURED ALKALINITY, EQ/L = ',G10.4E2,/,                 818
   *  ' NEWALK, ALKALINITY CALCULATED FROM Cb-Ca= ',G10.4E2,/)          819
48   FORMAT (' IONIC STRENGTH= ',G10.4E2,/)                             820
```

41

```
     49  FORMAT(' RATIO TDS TO SC (GENERALLY .55 TO .75. USE WITH CAUTION          821
        * FOR VERY LOW I.S. SAMPLES)- ',2X,G10.4E2,/)                             822
     50  FORMAT(' SUM CATION EQ/L - ',G10.4E2,/' SUM ANION EQ/L = ',              823
        * G10.4E2)                                                               824
     51  FORMAT (' ANALYTICAL PERCENT DIFFERENCE IN CATIONS VS ANIONS= ',         825
        * F7.3,/)                                                                826
     52  FORMAT (' *** FAILS IONBAL AT 10% ***',/)                               827
     53  FORMAT (' *** FAILS IONBAL AT 5% ***',/)                                828
     54  FORMAT (' SUM OF CATIONS-  ',G10.4E2,/' SUM OF ANIONS=  ',              829
        * G10.4E2)                                                               830
     55  FORMAT (' COMPUTED PERCENT DIFFERENCE IN CATIONS VS ANIONS= ',          831
        * F7.3,/,/)                                                              832
     56  FORMAT (' PREDICTED  SC -',F8.3)                                        833
     57  FORMAT(' PERCENT DIFFERENCE IN SC MEASURED VS PREDICTED= ',F7.3)        834
     58  FORMAT (/,' *** FAILS SC TEST AT 10% ***',/)                           835
     59  FORMAT (/,' *** FAILS SC TEST AT 5% ***',/)                            836
C    65  FORMAT (/,' H/SC- ',G10.4E2,/,' H/SCDIF- ',G10.4E2,/,                   837
C       * ' ORG/H- ',G10.4E2,/,' ORG/SCDIF= ',G10.4E2,/,' ORG/SC- ',            838
C       * G10.4E2,/)                                                            839
         GO TO 62                                                               840
     60  WRITE (*,61)                                                           841
     61  FORMAT (' ERROR')                                                      842
     62  STOP                                                                   843
         END                                                                   844
```