

Attn: M. Knapp / J. Starmer MS 62355

UPGRADED PARENT CODE FOR RADIONUCLIDE RETARDATION MODELING

(Letter Report on Milestone A, Task 3)

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To: M Knapp & John Starmer From: R. Cook

John R. Morrey

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INTRODUCTION

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A number of sophisticated computer codes have been written to model complex aqueous geochemical equilibria. To varying degrees of success, they can be used to predict what will happen when aqueous fluids interact with geological media, e.g. how the pH, Eh or gas pressures will change when certain elements are added to the aqueous or solid phases. They may also be used to understand what will happen when the pH is altered by external means or the effect of a change in oxygen or carbon dioxide pressure.

Just as importantly, geochemical codes can provide valuable inferential insight while interpreting laboratory or field data. Using these codes to test models of the actual physical processes can help distinguish important from unimportant factors affecting the complex chemistry. Thereby they can help to develop a cohesive understanding of important mechanisms. For example, modeling can be used to test the hypothesis that a certain chemical equilibrium has been attained, or conversely, determine which minerals are not in thermodynamic equilibrium. They can help to distinguish the relative importance of adsorption and precipitation and can, in the absence of some experimental data, identify the redox state of the system.

An improved and expanded parent geochemical code is being generated as part of the Radionuclide Retardation Modeling Program. This code, also referred to as the "baseline geochemical code", will satisfy three major functions during studies of hydrogeochemical migration of radionuclides at specific sites. Its likely first use for a specific problem will be to help the investigator identify the critical geochemical elements of the problem. By so doing, it will alert him to crucial and desired field measurements required to make adequate predictions

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about contamination of groundwaters at the site under study. The second use will be to prepare a site-specific data base for use by the coupled geochemical code currently being developed (see letter report "DEVELOPMENT OF A COMPACT GEOCHEMICAL CODE FOR COUPLING TO A TRANSPORT CODE", C. J. Hostetler, August 30, 1983). The third will be to initialize the geochemistry of the hydrogeological problem to be studied.

One of our previous tasks in this program was to select from a number of existing geochemical codes the best one for application to radionuclide retardation problems at Hanford. This code was chosen after an examination of several extant codes (see Letter Report "SELECTION OF A BASELINE CODE FOR RADIOUNUCLIDE RETARDATION MODELING", J. R. Morrey, July 30, 1983).

We now briefly outline our accomplishments in the subsequent task to modify and update the chosen code, MINTEQ, to meet DOE needs and standards. Below we will briefly describe the code chosen for modification then will briefly describe the modifications so far accomplished and will identify those that remain to be made.

BRIEF DESCRIPTION OF CHOSEN BASELINE CODE

MINTEQ was developed at the Pacific Northwest Laboratory by Felmy, Girvin and Jenne (1983). They combined the code MINEQL, authored by Westall, Zachary, and Morel (1976), with the data base of WATEQ3, authored by Ball, Nordstrom and Jenne (1981). MINTEQ now includes the most complete set of algorithms for adsorption of any of the codes we have considered. It also has the most completely documented data base for radionuclides and has been extended to model finite quantities of solids.

MINTEQ has demonstrated some limitations. The major one is its inability to solve a problem when starting estimates are far from equilibrium. It also is not easily and appropriately used by the those not familiar with the code. Nevertheless, based on our assessment of its strengths in adsorption capability and its data base, along with its capability to at least partially successfully model closed solid systems, we have selected MINTEQ as the baseline code.

MINTEQ is an equilibrium geochemical code designed to accept an

assemblage of gaseous and solid phases in contact with but not in equilibrium with an aqueous phase. The code then adjusts concentrations in the aqueous phase to conform to an equilibrium state between the gaseous, aqueous and solid phases. Figure 1 outlines in simple block form the modeling capability of MINTEQ and the updated code, MINTEQ2. The valves sketched in Figure 1 can be either open, indicating an open chemical system with respect to the solid or gas (infinite quantity), or closed, indicating a closed system (finite quantity). The valves in dashed lines represent modeling capability available to the updated code that were not previously available.

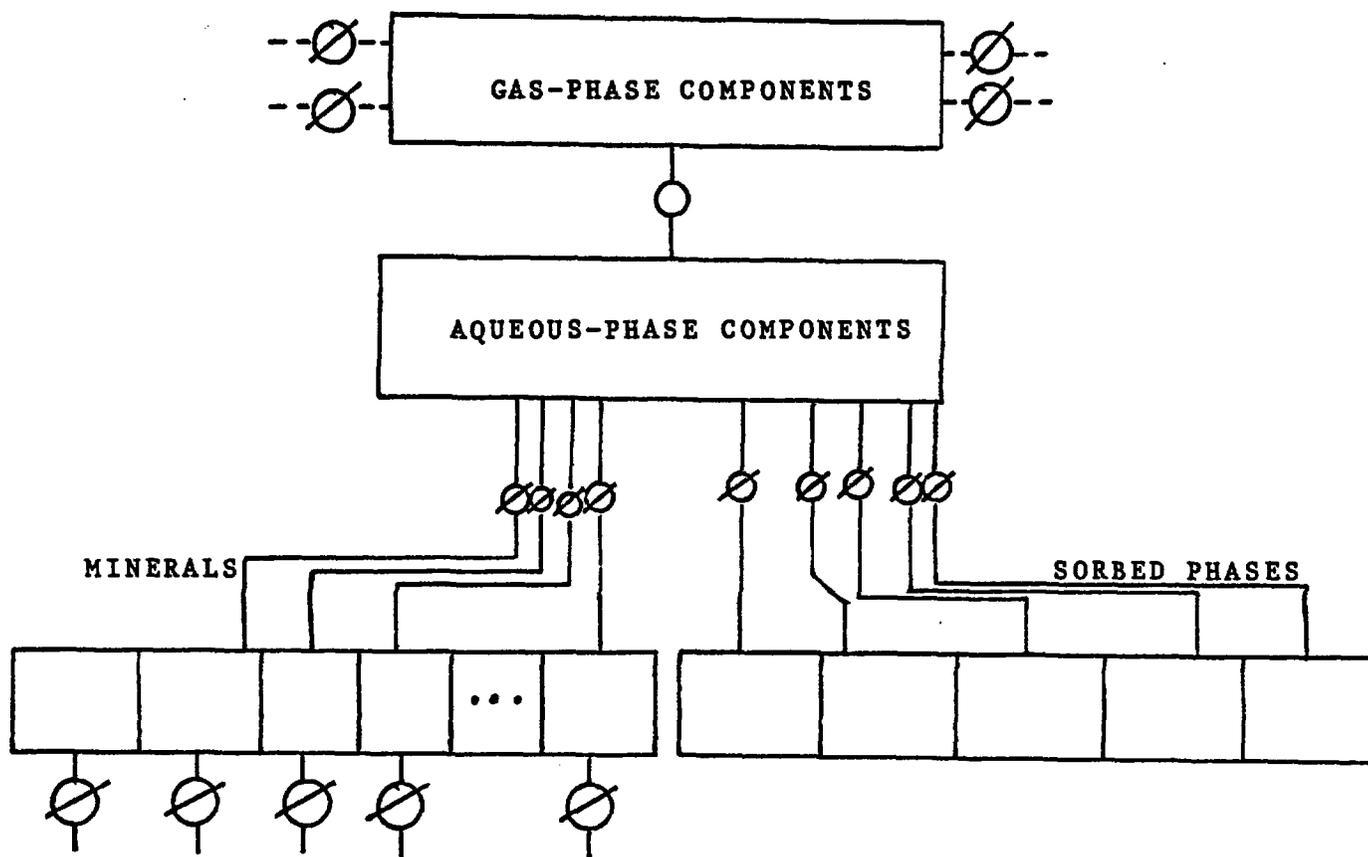


Figure 1: Schematic of Geochemical Modeling Capabilities Available Through MINTEQ or its Successor, MINTEQ2.

REQUIRED MODIFICATIONS TO MINTEQ

MINTEQ required several modifications to be acceptable as a parent or baseline DOE code:

- o Its convergence reliability required improvement. The Newton Raphson technique it uses has the advantage of being very efficient when estimates are not too far from the solution. However, often this is not the case, causing the code to terminate in an error mode.
- o Preparation of problems had to be facilitated. The hand-construction of the problem data file required a knowledge of formats, definitions of flags, and index numbers for all chemical species to be incorporated into the problem. In addition, it was easy to construct problems that would not execute because required initial estimates of activities were often out of the range of convergence and it was easy to create conflicting requests of the code. Experience amply verified that the user had to contend with a large number of aborted runs caused by errors in defining problems. A large fraction could be avoided by constructing a problem-defining preprocessor or interactive subroutine.
- o Improved algorithms were required to calculate activity coefficients for solutions with high ionic strengths. Additional algorithms were needed for neutral species, water and ions at high ionic strength. The Pitzer model therefore also needed to be added.
- o MINTEQ needed the capability to calculate equilibria at temperatures above 100° C. Though high-temperature competency probably will not be needed for most applications, the code could be modified easily to provide this capability.
- o MINTEQ required modification to reliably model solid systems with finite quantities of soluble materials. In some cases, the code failed to give answers because it artificially dissolved enough soluble salt to saturate the aqueous phase with respect to that salt, causing the ionic strength to exceed values which

the code could handle.

- o Conservation of water needed to be built into the code. Dissolution and precipitation of quantities of water-containing minerals can sometimes significantly modify the amount of water in the aqueous phase.
- o Solid-solution competency needed to be added. This is a lower priority addition because it can only be useful after an extensive collection of thermodynamic data for solid solutions becomes available sometime in the future. Nevertheless the code should be capable of using such data as soon as they become available.

IMPROVEMENTS IN CONVERGENCE BEHAVIOR

The solution of a complex problem in chemical equilibrium is dependent on the simultaneous satisfaction of m mass-action expressions and n mass-balance expressions, where m is the number of dependent chemical species needed to describe the chemistry and n is the number of components in the system. The number of independent variables that must be determined to solve the problem is equal to the number of degrees of freedom, f , of the system which is equal to the number of components minus the number of separate phases, as defined by the Gibb's Phase rule; (temperature and pressure are assumed to be constant).

MINTEQ, like nearly all other modern geochemical codes, relies on the Newton-Raphson formulation to solve these f equations. At the outset, the concentrations of the derived species, C^0_i , are calculated from the activities, X^0_j , of f independent components as given in equation (1):

$$\log(C^0_i) = \log(K_i) - \sum_j a_{ij} \log(X^0_j) - \log(\gamma_i) \quad (1)$$

where K_i is the equilibrium constant for the derived species, a_{ij} is the stoichiometric coefficient for the j th component in the i th reaction, X^0_j is the initial guess for the activity of the j th independent component and γ_i is the activity coefficient for the i th derived species.

After the concentrations of all of the derived species have been calculated, a variance function is calculated according to equation (2):

$$Y_j = \sum_i a_{ij} C^0_i - T^0_j \quad (2)$$

This same function is expressed as a Taylor Series:

$$Y_j = Y^0_j + \sum_k (\partial Y^0_j / \partial X^0_k) \delta X_k$$

It is desired to set the new variance, Y_j , to zero. Thus, a series of f equations of the form

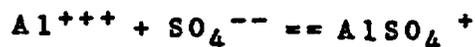
$$\sum_k (\partial Y_j / \partial X_k) \delta X_k = - Y_j$$

remain to be solved to obtain the change vector, δX_k . Since the partial derivative $(\partial Y^0_j / \partial X^0_k)$ can be calculated in terms of the mass action equations above, the equations can be solved simultaneously for f new activities:

$$X_k = X^0_k + \delta X_k$$

This process is repeated until all Y_j are sufficiently small to meet the criterion of convergence.

If bad estimates for component activities are given to MINTEQ, the calculation of the derived species C_i by equation 1 may be so far in error as to cause the code to terminate in the error mode. For example, if the reaction



were being used to calculate the derived species $AlSO_4^+$ and the initial activity of Al^{+++} and SO_4^{--} respectively were estimated to be 1 molal, by substitution, the calculated value for the activity of $AlSO_4^+$ would be 870. Since it has a charge, it would cause the ionic strength to be at

least 870, way beyond the range of well defined behavior for the activity algorithms, and would cause the code to terminate. Calculating activities, hence concentrations, of derived species under the assumption that the formation of the derived species does not affect the concentrations and activities of the reactants often causes very large errors.

To correct this difficulty, which occurs rather frequently in the operation of MINTEQ, we have created a subroutine EQUADS, which shifts the equilibrium to simultaneously adjust all components. This was accomplished in the following fashion. Consider equation 1 again. If we define the superscripted components as the initial guesses (which do not satisfy the equation) and the non-superscripted components as the adjusted values that do satisfy equation 1, and further relate the initial and final values by a parameter, called the deDonder parameter, then we can write

$$X_j = \gamma_j C_j = \gamma_j [C_j^0 + \delta a_{ij}] = X_j^0 (1 + a_{ij} \delta / C_j^0).$$

Substituting into equation 1 and rearranging, we obtain

$$\log(1 - \delta / C_i^0) = \log(K_i) - \log(C_i^0) + \sum_j a_{ij} \log(X_j^0) + \sum_j a_{ij} \log(1 + a_{ij} \delta / X_j^0).$$

In this fashion, we arrive at an equation with only one unknown (δ). The subroutine EQUADS solves this equation by a halving procedure after first placing limits on the range of δ by consideration of the total masses present. The subroutine calculates the concentrations of all derived species, including solids or gases in finite supply, as an initialization step before proceeding to solve the problem by conventional means. This obviates the need to make any guesses on initial activities.

The subroutine is also used during the iteration procedure in a somewhat complicated way, taking into account the chemical mass-action equations that have been transformed to exclude components when finite or infinite solids or gases are present.

While investigating mathematical methods of increasing convergence efficiency, we determined that the Newton-Raphson technique is at best slow and at worst divergent if starting estimates are too far from the

mathematical solution. As an empirical guide, if the mass balance is in error by more than about 20%, then it is better to use a back-substitution method for convergence. This employs a simple equation:

$$X_j = X_j^0 T_j^0 / [\sum_i a_{ij} C_i^0]$$

It is readily apparent that when the weighted sum of all species made up of the jth component equals the total analytical quantity, T_j^0 , then X_j will not change from iteration to iteration. It will have arrived at the final solution.

MINTEQ2 has been structured to use the back-substitution method until the mass balance of all components is within 20%. At this point, the code chooses the Newton-Raphson method and uses it until a mathematical solution has been obtained or until 10 iterative steps have been executed. If at this time, convergence is not proceeding well, the code reverts to the back-substitution method again for a maximum of 10 iterations.

Marquardt (1963) outlined a method for constraining the size of the change vector δX_j obtained by the Newton-Raphson method. If an arbitrary parameter is added to the diagonal of the Jacobian matrix used by Newton-Raphson, it can be made to proportionately scale down the change vector. Since the Newton-Raphson method often fails because it has been linearized and does not accurately represent the curvature of the hypersurface, divergence or slow convergence often is caused by the calculated change vector being too large. Yet the correct direction of the change is generally indicated. Thus we have added a parameter to the diagonal of the Jacobian matrix and caused it to vary from iteration to iteration. If an iteration is bad, the parameter is increased by a factor of 10; if the iteration is good, the parameter is decreased by a factor of 10. In this fashion, the code automatically seeks the optimum scaled change vector.

In actuality, with the addition of EQUADS and the back substitution algorithm, we have not yet seen a case where the Marquardt addition was needed.

IMPROVEMENTS IN EASE OF PROBLEM FORMULATION

To use MINTEQ, the user is first required to construct a sample file that describes the problem to be solved. Figure 2 illustrates such a file. Several common problems arise when a user constructs this file: 1) he can easily make a mistake in formatting input; 2) he must know the indices for all of the elements and special derived species that he wants to model, and 3) he can easily and unknowingly formulate problems that violate the phase rule. Additionally, he is required to use chemical intuition in choosing initial activities for all of the components. When the problem being modeled is complex, chemical intuition is not sufficient.

To correct these problems, we have written a code called PRODEF (PROblem DEFINition) to improve the ease of usage by minimizing logical and formatting errors and minimizing failures because of ill-defined problems. The code allows for quick recovery if a mistake is made as the problem is being constructed and releases the user from the tedium of dealing with index numbers instead of his traditional symbols.

PRODEF is an interactive program that prompts the user for information needed to completely define the problem and checks for logical errors that would cause MINTEQ2 to fail. It also calculates appropriate starting values for the activities of the components, though the new version of MINTEQ now obviates this feature.

PRODEF, having undergone a number of evolutionary changes, is maturing into a reliable software package. However, as the final changes are made on MINTEQ2, they will likely require some associated changes in PRODEF. Therefore, we intend to release both PRODEF and MINTEQ2 simultaneously after documentation has been completed.

Figure 3, illustrating the dialogue prompted by PRODEF, should give the reader a reasonably accurate idea of the usefulness of the program. Responses required by the user are circled

Figure 4 illustrates the problem definition file created by PRODEF. Comparing it with Figure 1, one finds a slightly modified form to insert the number of allowed iterations and the "debug" options. He also notices that the species are all labeled when PRODEF creates the file.

TEST OF MINTEQ WITH SEVERAL FIXED MINERALS
FORMAT REQUIRED FOR OLD MINTEQ

```
11.00 'MOLAL' 0.0
0 1 0 2 0 0 0 0
0.00 0.00 0.00 0.00
1 0.393E-12 -12.41
140 0.100E-05 -5.00
281 0.794E-24 -24.10
280 0.100E-34 -35.00
150 0.377E-02 -2.42
732 0.377E-02 -2.42
30 0.148E-15 -15.83
600 0.741E-13 -13.13
330 6.309E-09 -8.20

3 10
2 0.000E+00 0.00
330 0.820E+01 0.00
2028102 -.500E+00 14.48
3300023 -.824E+02 136.63
3301403 0.210E+02 -0.53
2812800 0.130E+02 -10.00
6015001 0.485E+01 -0.26
2003003 -.877E+01 22.80
2028102 -.500E+00 14.48
```

FIGURE 2 - Problem Definition File for MINTEQ. To construct, the user must know the definition of each input field, know the index representing elements, minerals or gases, the format for each input field, and an estimate of each starting value.

```

ENTER THE FIRST SIX CHARACTERS OF THE NEW, SAMPLE FILE. TESTAA.DAT
THE NEW QUESTION FILE IS NAMED TESTAA.QUE
WILL THE TESTAA FILE BE MODIFIED FROM AN OLD FILE? (Y/N) (Y)
ENTER NAME OF OLD SAMPLE FILE: SAMPLE.DAT
1-TITLE= TEST OF MINTEQ2
2-TITLE= TEST OF PRODEF VERSION ON 4/12/84
3-DEGREES C= 11.00; 4-CONCEN°N UNITS='MOLAL'; 5-IONIC STNGTH
OPTION FLAGS:
6-ALKALINITY=0; 7-DEBUG -NNNNNNNNYYNNNN; 8-CHARGE BAL=1;
10-ITERATION =100; 11-PH VARY =0; 12-ION STNGTH=0; 13-MODHIS
14-ACT°Y COEF=0; 15-THERMOLIST=0; 16-ADSORPT°N =0
ENTER INDEX NUMBER TO MODIFY ANY OF ABOVE. (0=NONE) (7)
WANT TO RUN A DEBUG CASE (ADDITIONAL OUTPUT)? (Y/N) (Y)
PRINT NAME, IDY, GAMMA, C, Y, X, T IN "ACTVTY"? (Y/N) (Y)
PRINT ALKALINITY VALUES IN "ALKCOR"? (Y/N) (N)
PRINT ADDITIONAL ALKALINITY VALUES IN "ALKCOR"? (Y/N) (N)
PRINT DETAILS OF Y(J) CALCN IN "SOLVE" (Y/N) (Y)
PRINT AQUEOUS COMPOS°N BETWEEN SOLIDS ITERATN? (Y/N) (Y)
PRINT VALUES FOR ALL SPECIES IN "PREP?" (Y/N) (Y)
PRINT DETAILED EQN CHANGES IN "SOLID" AND "SOLIDX"? (Y/N) (Y)
PRINT NAME, IDY, GAMMA, C, Y, X, T IN "OUTPC" (Z AMTS)? (Y/N) (Y)
PRINT PROGRESSION DURING AQUEOUS SPECIATION? (Y/N) (Y)
PRINT PRINT C, GC, X, GX, T IN "EQUADS" (Y/N) (Y)
PRINT MODIFICATION HISTORY AT START? (Y/N) (N)
1-TITLE= TEST OF MINTEQ2
2-TITLE= TEST OF PRODEF VERSION ON 4/12/84
3-DEGREES C= 11.00; 4-CONCEN°N UNITS='MOLAL'; 5-IONIC STNGTH
OPTION FLAGS:
6-ALKALINITY=0; 7-DEBUG -YNNYYYYYYNNNNN; 8-CHARGE BAL=1;
10-ITERATION =100; 11-PH VARY =0; 12-ION STNGTH=0; 13-MODHIS
14-ACT°Y COEF=0; 15-THERMOLIST=0; 16-ADSORPT°N =0
ENTER INDEX NUMBER TO MODIFY ANY OF ABOVE. (0=NONE) (0)

```

Figure 3 - Example of Interactive Dialogue between PRODEF and User; File Being Modified.

LISTING OF COMPONENT FOLLOWS FOR VERIFICATION OR CHANGE

	INDEX	TOTAL CONC°N	LOG10(ACT)
1	2	0.00000E+00	0.00000E+00
2	330	0.00000E+00	-0.82000E+01
3	1	0.39300E-12	-0.12410E+02
4	140	0.10000E-05	-0.50000E+01
5	281	0.79400E-24	-0.24100E+02
6	280	0.10000E-34	-0.35000E+02
7	231	0.16200E-10	-0.10790E+02
8	150	0.37700E-02	-0.24200E+01
9	732	0.37700E-02	-0.24200E+01
10	30	0.14800E-15	-0.15830E+02
11	600	0.74100E-13	-0.13130E+02

ENTER LINE # TO CHANGE, ADD OR DELETE (0=DONE) 0
 NO TYPE 2 SPECIES EXIST.

LISTING OF FIXED SPECIES FOLLOWS FOR VERIFICATION OR CHANGE

	INDEX	LOG10(KEQ)	DELTA H REAC
1	2	0.00000E+00	0.00000E+00
2	330	0.82000E+01	0.00000E+00
3	3300023	-0.82400E+02	0.13663E+03
4	3301403	0.21000E+02	-0.53000E+00
6	5023101	0.51800E+01	0.15610E+02
7	6015001	0.48500E+01	-0.26000E+02
8	2003003	-0.87700E+01	0.22800E+02
9	5060000	0.13100E+02	-0.48600E+01
10	2028102	-0.50000E+01	0.22800E+02

NO TYPE 4 SPECIES EXIST.
 NO TYPE 5 SPECIES EXIST.
 NO TYPE 6 SPECIES EXIST.
 NO TYPE 7 SPECIES EXIST.

ARE ALL CORRECTIONS COMPLETED?(Y/N) Y

Figure 3 Continued - Example of Interactive Dialogue between PRODEF and User; File Being Modified.

```

1      TEST OF MINTEQ2
2      TEST OF PRODEF VERSION ON 4/12/84
3      15 0 1 0 0 0 0 0 0 0
4      YNNYYYYYYYNNNNN
5      0      0.00      0.00      0.00      0.00
6          2 0.000E+00      0.00      /H2 0
7          330 0.000E+00      -8.20      /H
8          140 0.100E-05      -5.00      /CO 3
9          281 0.794E-24      -24.10      /FE+3
10         280 0.100E-34      -35.00      /FE+2
11         231 0.162E-10      -10.79      /CU+1
12         150 0.377E-02      -2.42      /CA+2
13         732 0.377E-02      -2.42      /S 04
14         30 0.148E-15      -15.83      /AL
15
16         3      9
17             2 0.000E+00      0.00      /H2 0
18             330 0.820E+01      0.00      /H
19         3300023 -.824E+02  136.63      /O2(GAS)
20         3301403 0.210E+02   -0.53      /CO2(GAS)
21         2812800 0.130E+02  -10.00      /FE+3/FE+2
22         5023101 0.518E+01   15.61      /GIBBSITE
23         6015001 0.485E+01   -0.26      /GOETHITE
24         2003003 -.877E+01   22.80      /GYPSUM
25         2028102 -.500E+00   14.48      /MALACHITE

```

Figure 4 - Example of Problem Definition File Created by PRODEF. Compare with Figure 1. Lines 1 & 2 are an arbitrary title. Line 3 is slightly modified from the comparable line in figure 1 in that the actual number of iterations is the first entry. Line 4 is new with MINTEQ2, providing a number of debug options. Line 5, unaltered from the comparable line in MINTEQ, provides adsorption parameters when adsorption is to be modeled. Lines 6 through 14 provide the aqueous input. The first column of these lines lists the index number of the component; the second column, the concentration; the third column, the initial log(activity) and the fourth column, the name. Line 15 is blank. Line 16 signal that 9 species of type 3 follow. Type 3 species are in infinite supply. The first column for lines 17 to 25 lists the index number of the species. The second column is the $\log(K_{eq})$ for the reaction and the third column is the H for the reaction at 25°C.

IMPROVEMENTS IN HIGH IONIC STRENGTH COMPETENCY

MINTEQ uses ion-pair formation to calculate aqueous speciation. Since this is an attempt to describe solutions in microscopic detail, we designate it the "microdescriptive approach". Justification for this approach lies in the ample evidence that a large number of aqueous species have been spectroscopically verified. Others have been strongly inferred from measurements of solution properties such as vapor pressure, conductivity and solubility. Furthermore, there is ample evidence that some of these species are important in aqueous systems because they preferentially respond to sorption and uptake by biological systems.

Though the microdescriptive approach is justified, models incorporating it have not been very successful in predicting activities of solutions with ionic strengths much above 0.5 molal. The reason is that their algorithms universally compute activity coefficients on the assumption that they are dependent on only one solution-variant parameter, the ionic strength, I:

$$a_i = f(I),$$

whereas in concentrated solutions the activity is dependent on the interactions between individual neighboring ions and complexes:

$$a_i = f(C_j).$$

The alternative thermodynamic formulation of Pitzer (1981), a pseudo-theoretical, accounting of the longer range interactions between ions, has proven to be more successful for high ionic strengths. Instead of describing the detailed thermodynamics of aqueous species, this formulation deals with dissolved salts as components, ignoring the details of the structure of the aqueous phase.

The advantages of Pitzer's macrodescriptive approach are that fewer

components are needed to calculate aqueous-solid equilibria and the parameters can be directly measured. This approach works best for systems where strong aqueous complexes are not formed; it has worked successfully for concentrated brines that could not be modeled reliably by microdescriptive speciation models.

We have added Pitzer's formulation to MINTEQ, thus allowing it to be useful for high ionic strength solutions. At the same time, we have retained the original formulation as an option because it is unwise to disregard the preponderance of evidence of thermodynamic data already obtained for important aqueous species. It seems prudent to retain both the micro and macro formulations.

As MINTEQ2 is now structured, it has either modified or additional activity algorithms for water, neutral aqueous species, and charged species.

Water

MINTEQ makes no corrections for the activity of water. In other words, it was always assumed to be unity. We have incorporated into MINTEQ2 an algorithm described by Helgeson et. al. (1970). The expression used is

$$\ln(a_{H_2O}) = -0.018 Z\phi$$

where the quantity Z is a sum of the concentrations of all aqueous salts times the number of ions that they will produce at full ionization:

$$Z = \sum_i |Z_i| \times C_i$$

and the osmotic coefficient, ϕ , is expressed as a series function in the stoichiometric ionic strength of the solution:

$$\phi = 1 - D_e J_e + FH2O_2 \times I/2 + FH2O_3 \times I^{2/3}$$

where

$$D_e = 2.303 A \times Z^2 / FH2O_1^3$$

and

$$J_e = 1 + FH2O_1 I^{1/2} - 2 \ln(1 + FH2O_1 I^{1/2}) - 1/(1 + FH2O_1 I^{1/2})$$

The coefficients $FH2O_i$, obtained from Lietzke and Stoughton (1974), are temperature dependent. MINTEQ2 calculates the dependence on the specified temperature.

Neutral Aqueous Species

MINTEQ used the simple relationship

$$\log(\gamma) = 0.1 \times I$$

for neutral species. The new version has incorporated experimental data for neutral CO_2 and assumes that all neutral aqueous species will behave like CO_2 . We have incorporated coefficients $CO2_i$ as given by Helgeson et. al. in the original code PATRI and fitted to temperature polynomials by Morrey (1978). The form of the equation is

$$\log(\gamma_{CO2}) = \log(CO2_1 + CO2_2 \times Z + CO2_3 \times Z^2)$$

Charged Species

MINTEQ contains two algorithms for charged species. The Davies algorithm (Davies, 1962) is still used under default by MINTEQ2 when insufficient data are available to use other more precise algorithms. The form of the Davies equation is

$$\log(\gamma_i) = -Z_i^2 [I^{1/2}/(1+I^{1/2}) - 0.3 \times I].$$

The extended Debye-Huckel equation requires parameters for individual species and is expressed in the form

$$\log(\gamma_i) = -A \times Z_i^2 I^{1/2} / (1 + B \times DHA_i I^{1/2}) + DHB_i I.$$

Temperature dependencies for the ion-specific terms, DHA_i and DHB_i , have

been included in both MINTEQ and MINTEQ2.

The Pitzer formulation is based on the demonstrated very good approximation that interactions between ion pairs are the same in pure and in mixed electrolytes, that short-range electrically repulsive forces give rise to only small terms and that for complex mixtures, all important terms are obtainable from experimental measurements on single and binary mixtures of aqueous electrolytes. The equation now incorporated into MINTEQ2 can be optionally used. The excess Gibbs energy from which the activity coefficient can be obtained is

$$G^{ex}/n_w RT = f(I) + \sum_i \sum_j \lambda_{ij}(I) C_i C_j + \sum_i \sum_j \sum_k \mu_{ijk} C_i C_j C_k$$

where R, n_w , T and I are respectively the gas constant, the number of moles of water, the absolute temperature and the ionic strength. The parameter λ_{ij} is the binary virial coefficient and μ_{ijk} is the ternary virial coefficient. The function f(I) is

$$f(I) = -3.33A I \ln(1 + bI^{1/2}).$$

A is the Debye limiting parameter and $b=1.2$.

The activity coefficient for the kth ion, either positive or negative, is then expressed as

$$\begin{aligned} \log(\gamma_k) = & -Z_k^2 F + \sum_a C_a (2B_{ka} + ZQ_{ka}) + \sum_c C_c (2\theta_{kc} + \sum_a C_a \psi_{kca}) \\ & + 0.5 \sum_a \sum_{a'} C_a C_{a'} \psi_{aa'k} + |Z_k| \sum_c \sum_a C_c C_a Q_{ca} \end{aligned}$$

where B_{ka} and θ_{kc} are measurable combinations of λ . The parameters Q_{ka} and ψ_{kca} are measurable combinations of μ_{kca} . The function F is given by

$$F = -A [I^{1/2}/U + (2/b) \log(U)] + \sum_c \sum_a C_c C_a B_{ca} + 0.5 [\sum_a \sum_{c'} C_a C_{c'} \theta_{cc'} + \sum_a \sum_{a'} C_a C_{a'} \psi_{aa'}]$$

In the latter equation, $U = 1 + bI^{1/2}$, c represents cations, and a represents anions.

Several computer-coded functions, included to calculate the various parameters of the above equations, are listed in table I.

Table I--COMPUTER FUNCTIONS AND SYMBOLS FOR THE PITZER FORMULATION

<u>SYMBOL</u>	<u>COMPUTER FUNCTION</u>	<u>DATA FILE</u>
B _{ca}	BPFUN	PSIPIT.DAT
Q _{ka}	CIJ	BCP.DAT
Θ _{kca}	PSI	THEPIT.DAT
Ψ _{kc}	THE	NEUPIT.DAT
A	APHI(T,P)	
F	FG	BCP.DAT

We have not yet carefully and thoroughly verified that the code properly calculates activity coefficients according to the various added algorithms.

IMPROVEMENTS IN HIGH TEMPERATURE COMPETENCY

Improvements in the parent code to calculate equilibria at high temperatures are categorized in three parts: 1) providing temperature dependence to the calculation of activity coefficients, 2) modifying MINTEQ to read polynomial functions with which to calculate equilibrium constants, and 3) generating a data base of polynomials for these constants. The first and second parts have been essentially completed and await verification. The third, the generation of the high temperature data base has been deferred until FY 85 because funding for FY 84 was reduced.

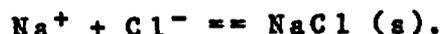
IMPROVEMENTS IN MODELING FINITE INITIAL QUANTITIES OF SOLIDS AND GASES

MINTEQ has no option of modeling cases where gases may be in finite supply. Furthermore, although it is the only one of the MINEQL based codes that can model finite solids, it cannot model small quantities of very soluble solids because it first calculates the saturated quantity that would dissolve into the aqueous phase if there were an infinite supply available then precipitates back out sufficient of the salt to bring the total concentration in aqueous and solid phase back to the original concentration. When the salt is very soluble, the first step,

will cause the aqueous phase to be extremely concentrated and will cause the code to terminate in the error mode.

MINTEQ2, has provision to model both finite solids and gases. It treats finite quantities of gases in exactly the same fashion as it treats aqueous species.

EQUADS is initially employed to adjust the equilibrium of finite quantities of solids. Thus for example, if one started with 0.02 moles of NaCl, EQUADS would adjust the reaction



It can only dissolve as much NaCl(s) as is present originally, thus avoiding the problems created by oversaturation.

REMAINING MODIFICATIONS

Most of the required modifications to MINTEQ have now been made. Three major tasks remain to be accomplished: 1) adding a subroutine to update species concentrations when the water mass in the aqueous phase changes, 2) adding a capability to create a selected thermodata file to be used by the coupled code, and 3) adding a solid solution capability.

The remaining efforts on MINTEQ2 primarily will be to verify the code under a wide range of options and to document MINTEQ2 and PRODEF, to be completed during the last quarter of FY 85.

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