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Two modified versions of the speciation code PHREEQE for modelling macromolecule-proton/cation interaction

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PREFACE

This study has been carried out as part of the MIRAGE II research programme (MIgration of RAdionuclides in the GEosphere) funded by the Commission of the European Communities (CEC) and the UK Department of the Environment. The specific BGS research project is entitled "*In situ* determination of the effects of organics on the mobility of radionucliudes under controlled con-ditions of groundwater flow", which is centred around in situ radionuclide migration experiments carried out in a remote part of the Drigg Storage Depot, in Cumbria, operated by British Nuclear Fuels Plc.

The work involves the detailed geochemical and hydrogeological characterisation of a confined glacial sand aquifer, the laboratory scale investigation of radionuclide sorption processes and how these are affected by the presence of natural and anthropogenic organic compounds. Ultimately the results of field hydraulic testing and laboratory studies of radionuclide sorption will be used to predict the outcome of a field tracer experiment using conservative and reactive radionuclide species.

In parallel, an interlaboratory comparison excercise has been initiated by the CEC within the frame work of the COCO club (complexes and colloids), in which a reference humic material as well as site specific natural organic compounds are being characterised using a wide variety of techniques. In order predict the influence of heterogeneous, natural organic material on the speciation of radionuclides in solution a chemical speciation code (PHREEQE) has been extended to simulate organic matter–cation interaction with the electrostatic interaction approach.

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EXECUTIVE SUMMARY

There is a growing need to consider the influence of organic macromolecules on the speciation of ions in natural waters. It is recognised that a simple discrete ligand approach to binding of protons/cations to organic macromolecules is not appropriate to represent heterogeneities of binding site distributions. A more realistic approach has been incorporated into the speciation code PHREEQE which retains the discrete ligand approach but modifies the binding intensities using an electrostatic (surface complexation) model. To allow for different conformations of natural organic material two alternative concepts have been incorporated: it is assumed that a) the organic molecules form rigid, impenetrable spheres, and b) the organic molecules form flat-surfaces. The former concept will be more appropriate for molecules in the smaller size range, while the latter will be more representative for larger size molecules or organic surface coatings. The theoretical concept is discussed and the relevant changes to the standard PHREEQE code are explained. The modified codes are called PHREEQEO-RS and PHREEQEO-FS for the rigid-sphere and flat-surface model respectively. Improved output facilities for data transfer to other computers, e.g. the Macintosh, are introduced. Examples where the model is tested against literature data are shown and practical problems are discussed. Appendices contain listings of the modified subroutines GAMMA and PTOT, an example input file and an example command procedure to run the codes on VAX computers.

CONTENTS

1. INTRODUCTION

There is a growing need to consider the influence of organic macromolecules on the speciation of ions in natural waters. A recent review of models which describe the interaction between natural organic matter and cations/protons (FALCK, 1988) has shown that most models are conceptually incompatible with current speciation codes like PHREEQE. The major problem faced by all models is the need to describe adequately the heterogeneity in the distribution of binding sites. Various types of continuous distribution models have been suggested to represent binding site distribution curves (PERDUE and LYTLE, 1982; DZOMBAK et al. 1986; ALTMANN and BUFFLE, 1988). In contrast speciation codes require discrete binding sites with discrete properties. The discrete ligand approach does not allow *a priori* for variations in environmental conditions like ionic strength and pH, since the stability constants for complexes used are conditional rather than true thermodynamic ones, and non-specific binding (e.g. electrostatic interaction) and site interaction are not taken into account. These effects may have a strong influence on the binding behaviour of organic polyelectrolytes, as discussed in detail by BUFFLE (1988).

To solve these problems two modified versions of the speciation code PHREEQE (PARKHURST et al., 1980) have been produced. The two versions of the code allow for different conformational appearences of organic matter respectively. Version PHREEQEO-RS (**pH–RE**dox–**EQ**uilibrium–**E**quations–plus **O**rganics–**R**igid Sphere model) uses the diffuse layer–rigid sphere model (TANFORD, 1961) to describe the organic molecule. The binding takes place at discrete sites and the intrinsic association constant is modified to allow for electrostatic interaction using the Guy-Chapman diffuse layer model. The alternative version PHREEQEO-FS (**pH–RE**dox–**EQ**uilibrium–**E**quations–plus **O**rganics **–F**lat Surface model) uses the Guy-Chapman diffuse layer model as written for flat surface geometry. The former model may be appropriate for small organic molecules (e.g. fulvics, small humics), while the latter better represents large molecules or organic surface coatings.

2. THEORETICAL CONSIDERATIONS

The effect of unspecific electrostatic interaction on the binding between organic macromolecules and cations has been treated comprehensively by TANFORD (1961). He applied the Debye-Hückel theory to rigid, ion impenetrable macromolecules. An alternative concept is to treat macromolecules as planar, sorbing surfaces, using a diffuse double-layer model, which may be a good approximation for large, probably non-spherical molecules, where the organic molecules form rigid, cross-linked colloids or where they form coatings on the mineral matrix.

In both cases the free energy of formation for a complex ΔG° can be separated into two components, the intrinsic standard free energy of formation ΔG°_{int} and an arbitrary function ϕ which describes the change in free energy of formation due to varying charge Z on the macromolecule. For the sake of convience all associations between protons/ cations and the macromolecules will be called complexes here, regardless whether they are stricly speaking complexes:

$$\Delta G^\circ = \Delta G^\circ_{int} + RT \cdot \phi(\theta) \tag{1}$$

where θ is the degree of site occupation/dissociation. This can also be written in terms of association constants K:

$$K = K_{int} \cdot e^{-\phi(\theta)} \tag{2}$$

TANFORD (1961) relates ϕ to Z in the following way:

$$\phi(Z) = 2 \cdot z \cdot Z \cdot w \tag{3}$$

where z is the charge on the complexing cation and

$$w = W_{el} \cdot N \,/\, RT \cdot Z^2 \tag{4}$$

where N, R and T have their usual meaning. The free energy of electrostatic interaction W_{el} is a function of the (conformational) model chosen to represent the macromolecule. In the case of a spherical, rigid and impenetrable molecule it can be written as:

$$W_{el} = \frac{Z^2 \cdot e^2}{2 \cdot \varepsilon \cdot \varepsilon_0} \left[\frac{1}{b} - \frac{\kappa}{1 + \kappa \cdot a} \right] \tag{5}$$

where e = electronic charge; ε = relative permittivity; ε_0 = permittivity of the vacuum; a = radius of 'gyration' and b = radius of 'closest approach' (see TANFORD, 1961 and Figure 1). κ is the Debye-Hückel parameter or in its inverse form $1/\kappa$ the thickness of the double layer around spherical (macro-)ions:

$$\kappa = \sqrt{\frac{8 \cdot \pi \cdot N^2 \cdot e^2 \cdot I}{\varepsilon \cdot \varepsilon_0 \cdot R\, T}} = 1.17 \times 10^{10} \cdot I^{1/2} \ [\mathrm{m^{-1}}], \text{ at } 25^\circ\mathrm{C} \tag{6}$$

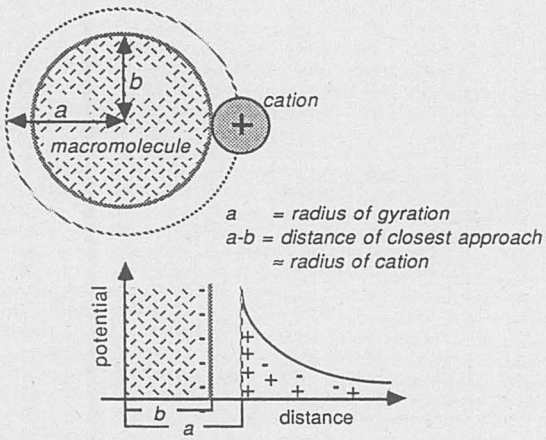

Figure 1: Rigid sphere model with diffuse layer for organic macromolecule (after TANFORD, 1961, and BUFFLE, 1988).

From equation (6) and (5) it can be seen that the free electrostatic energy and hence its contribution to the binding energy is an inverse function of the ionic strength I which diminishes with increasing I, i.e. W_{el} decreases with increasing I. For instance, in seawater the electric double layer is reduced almost to zero.

The phenomenological effect of electrostatic interaction is that as cations/protons dissociate the negative charge on the macromolecule increases and the remaining cations bind more strongly, i.e. the apparent stability constant K increases. It should be noted that in the case of amphoteric molecules/surfaces this is counteracted by anions associating and increasing the net charge on the molecule.

Assuming the organic macromolecules form rigid, cross linked colloids, a formulation similar to equation (3) is found for $\phi(Z)$:

$$\phi(Z) = z \cdot F \cdot \psi_0 / RT \qquad (7)$$

where ψ_0 is the surface potential, which is a function of the degree of site dissociation.

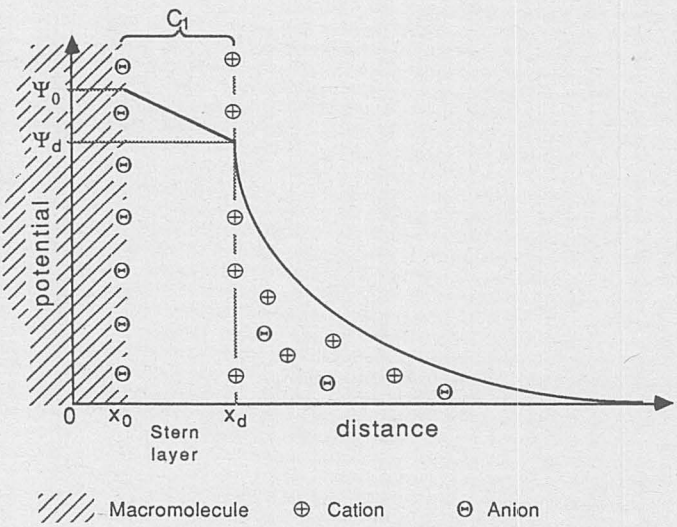

Figure 2: Stern-Guy-Chapman double layer model for flat surfaces.

The double-layer (Stern-Guy-Chapman) model (STERN, 1924) assumes that specific adsorption (i.e. of protons) takes place in the surface plane (at x_0), other ions sorb in the diffuse layer, i.e. at $x > x_d$ (Figure 2). Within the Stern layer ($x_0 < x < x_d$) there are no free charges and the layer can be characterised by a constant capacitance C_d. Therefore the surface potential ψ_0 can be written as:

$$\psi_0 = (\sigma_0 / C_d) + \psi_d \qquad (8)$$

σ_0 is the surface charge density which can evaluated from the degree of dissociation and the specific site density N_s [moles per surface area]:

$$\sigma_0 = N_s \cdot F \cdot \theta \qquad (9)$$

The potential at the Stern plane (x_d) can be calculated with equation (10):

$$\psi_d = \frac{2 \cdot R\,T}{F} \cdot arc\,sinh\left[\frac{\sigma_0 \cdot F}{2 \cdot \varepsilon \cdot \varepsilon_0 \cdot RT \cdot \kappa}\right] \tag{10}$$

where, being a flat-surface, a formulation for κ different from equation (6) has to be used:

$$\kappa = \sqrt{\frac{2 \cdot e^2 \cdot N^2 \cdot I}{\varepsilon \cdot \varepsilon_0 \cdot RT}} \tag{11}$$

Inserting equation (11), equation (10) can written as:

$$\psi_d = \frac{2 \cdot R\,T}{F} \cdot arc\,sinh\left[\frac{\sigma_0}{\sqrt{8 \cdot \varepsilon \cdot \varepsilon_0 \cdot R\,T \cdot I}}\right] \tag{12}$$

Again, it can be seen from equation (12) that increasing the ionic strength reduces the potential of the diffuse double layer, which will be close to zero in sea water conditions.

The problem of having to determine the capacitance C_d of the Stern layer is circumvented by assuming that for organic macromolecules and colloids surface plane and Stern plane fall together, since the relevant dissociable functional groups often protrude into the solution phase, creating a surface roughness in the dimension of the thickness of the Stern layer (DE WIT et al., 1988). Hence it is reasonable to assume that $C_d \rightarrow \infty$ and so the first term in equation (8) will disappear. The same reasoning, of course, would reduce a triple-layer model (DAVIES et al. 1978) to the above diffuse-layer (Guy-Chapman) model.

3. IMPLEMENTATION OF THE THEORY

In a comprehensive treatment of natural systems it is necessary to consider competition between different cations/protons for specific types of sites, and the competition between different sites for cations/protons. This is usually done by evaluating multi-component Stern-Langmuir equations (TANFORD, 1961, TIPPING et al., 1988, DE WIT et al., 1988)

which yield distribution ratios between bound and free ions. Since negatively charged organic ligands compete for cations with other small anions, e.g. sulphate, phosphate, hydroxide, it seems reasonable to develop one of the speciation codes (e.g. PHREEQE) for this task. Speciation codes solve simultaneously mass action equations for each species and mass balance equations for each chemcial element considered. Species are defined as being made up of 'elements' which do not necessarily have to be elements in a chemical sense (PARKHURST et al., 1980). For instance, the 'element' representing an organic ligand would be its fully discharged form. This concept has been used widely to model complexation with low molecular weight organic ligands, like EDTA. To represent heterogeneity in binding sites, a range of ligands had been used (SPOSITO and MATTIGOD, 1979).

Heterogeneity is introduced into the model considered here in two ways: a) by assuming that more than one type of ligand, each with different intrinsic stability constants are present, and b) by the introduction of electrostatic interaction, which effectively 'smears out' the stability constants of the discrete ligand model. However, assuming a uniform surface site density is an averaging procedure which reduces the degree of heterogeneity.

Examining equations (5) and (10) one finds that the major unkowns are the total charge on the macromolecule and the charge density respectively. These two parameters are conceptually similar, i.e. they relate the number of charges to a measure of the concentration of macromolecule/colloid in the sample.

In order to calculate W_{el} from equation (5) one has to know the charge Z on each molecule, but because of the heterogeneity of natural organic matter the charge on individual molecules cannot be determined. Only the total charge (Q) per mass of organic material, i.e. the titratable acidity, can be measured by experiment. If the molecular weight M_w of the natural organic material were known then Z could be determined using the relationship: $Z = M_w \cdot Q$. Molecular weight distributions can be estimated from size distribution experiments and used to calculate first estimates for average M_w's. M_w then is used, together with the related radius of gyration, as a fitting parameter.

Indeed, if one can calculate the volume/surface area of a macromolecule and can assume that all dissociable groups are exposed on the surface, the estimation of site densities is straightforward. TANFORD (1957a) has done this for a number of different proteins and gives a range of $0.6 - 1.5 \times 10^{-18}$ m^2 per dissociable site ($= 2.75 - 1.11 \times 10^{-6}$ mol·m^{-2}). This compares rather well with the 3.3×10^{-6} mol·m^{-2} used by DE WIT et al. (1988). Since the volume of a sphere increases faster than its surface area with increasing radius,

calculations show that with increasing molecular weight the ratio between 'back-bone' structure and functional groups exposed to the surface increases, otherwise the average density within the sphere would decrease and at the same time the surface site density would increase. This has three alternative consequences: (a) providing the spherical model is valid, not all functional groups can take part in binding, (b) a configuration with lower volume to surface ratio has to be assumed, or (c) the structure has to be penetrable by small ions. It seems likely from these considerations that fulvic acids, having comparatively low molecular weight, will behave more like impenetrable spheres, while high molecular weight humic substances have to be treated as either 'flat' surfaces or penetrable gels. TANFORD (1957b) has shown the distance of closest approach (a-b) does not vary appreciably from molecule to molecule and therefore a constant value of 10^{-10} m has been assumed.

The intrinsic stability constants for each type of sites are other unknowns in the model. It must be emphasised that the model presented here does not attempt to evaluate these constants from experimental data but is meant to be a predictive tool. To address the former problem some sort of fitting algorithm is needed to perform this task economically (compare TIPPING, 1988). A simple trial-and-error approach is possible, although time-consuming. The concentration of binding sites has to be determined experimentally, i.e. the concentration of carboxylic acids, dissociable OH-groups and the total acidity has to be known. Other experimental evidence can be used to estimate the likely nature of carboxylic and other dissociable groups to narrow the range of values for stability constants.

Once concentration and stability constants have been estimated it is a straightforward procedure using the speciation code to determine the actual charge Z on the organic macromolecules and consequently their degree of dissociation θ under given sample conditions. It is simply a book-keeping exercise, adding up all organic species and their charges.

4. THE NUMERICAL SCHEME WITHIN PHREEQE

Incorporation of a routine to calculate apparent stability constants, however, presents some numerical difficulties. In PHREEQE it is assumed that all species are made up from 'elements' which combine to form species according to the law of mass action. This requires the organic ligands to be introduced as free, e.g. L^-, species. In nature, of course, introduction of additional metals or protons into a system result in exchange reactions and a rearrangement of equilibria, while during simulations all components compete simultaneously. This gives rise to very large electrostatic interaction terms in the initial

iteration step which in the second iteration step cause equilibria to swing to complete neutralisation of macromolecules. In the following iteration step electrostatic interaction will be zero and the degree of dissociation θ is determined by intrinsic stability constants only. Ideally the iteration should converge to a stable value of θ, the apparent stability constant K being a function of θ which is in turn is a function K. However, rounding errors on the computer and the singularity at $\theta = 1$ can cause oscillations. This was found a problem particularly in weakly buffered solutions, as in *pH* titrations of humic acid in inert electrolytes (described below). Where strong *pH*-buffering species are present the problem of non-convergence seems less likely to occur.

This iteration procedure resembles the problem of calculating activity coefficients for small ions which are a function of the ionic strength, which in turn is a function of the activities of the dissolved species. Therefore it is appropriate to place the algorithm for the electrostatic model in the subroutine GAMMA of PHREEQE. As in the case of solids the activity coefficient for macromolecules is assumed to be unity.

Appendices A and B give listings of the subroutine GAMMA for the spherical and flat-surface model respectively with the relevant changes and additions to the standard code highlighted. PARKHURST et al. (1982) give a full listing of the code and explanation of the variables. Variable GFLAG in data block SPECIES, which usually determines the option to calculate activity coefficients, is used to distinguish between inorganic and organic species, i.e. GFLAG=2 for organics. There is only one additional variable to the input data set of PHREEQE. In subroutine READ following lines have to be inserted just after the block which reads total concentrations, to read specific acidity (variable DSA) [eq/g]

```
      READ(IFILE,645) SUB,SUB,SUB,DSA
      WRITE(6,655) DSA
  645 FORMAT(3A8,E12.5)
  655 FORMAT(1X,'SPECIFIC ACIDITY [EQ/G]:',E12.5)
```

or site density (variable DNS) [eq/m^2]

```
      READ(IFILE,645) SUB,SUB,SUB,DNS
      WRITE(6,655) DNS
  645 FORMAT(3A8,E12.5)
  655 FORMAT(1X,'SITE DENSITY  [EQ/M^2]:',E12.5)
```

for the rigid-sphere or flat-surface model respectively. These variables have to be declared in other COMMON blocks as well. Other additional input data are conveyed via existing, but

in the case of organic species, unused variables. Since an activity of unity is assumed for organic ligands under all conditions, variable DHA has been used to read the radius of gyration (DRG). It is unlikely that data will be available for dependence of stability constants of organic complexes on temperature, therefore variable ASP(1) is used to read the charge z of the cation binding to the organic molecule from the input data-file. To avoid any interference in subroutine KTEMP the loop in which van't Hoff constants are calculated is left out for species where GFLAG=2. The average molecular weight is read as variable GFW (gramm formula weight). To avoid the conceptual problem of converting concentrations given in mass units to equivalent units, data input has been restricted in subroutine UNITS to mmol/l, i.e. if IUNITS.NE.1 an error message is displayed and the program stopped.

Caution is to be exercised when using the option NEUTRAL to balance the charge in a sample preceeding the actual computation. In nature, by necessity, the charge balance includes all species, whether dissolved, organic or solids. However, analyses may not comprise e.g. organics and therefore an apparent charge imbalance occurs. A conceptional problem arises in particular when beaker-type experiments of addition of (extracted) organics to other samples are to be modelled. The concept of PHREEQE requires the specification of organics as fully discharged species. Any counterions would have to be specified separately, which is impossible in the case of protons, for which only free activity can be defined. Therefore, when organics are added in the H-form, charge imbalance has to be maintained during the run.

It is recommended that thermodynamic data for organics are added via ELEMENTS and SPECIES data-blocks in input files rather than making additions to the actual thermodynamic database. A sample input file is given in Appendix C.

Other changes to GAMMA can be grouped in two blocks. For the rigid-sphere model in the first block the degree of dissociation DEGDISS of organic species is evaluated and the average charge is set on all organic species. In the second block the electrostatic interaction factor DPHI and finally the apparent stability constant LKSP is calculated. In the first block of changes in GAMMA for the flat-surface model again, the degree of dissociation of organic species is determined plus the electrostatic interaction factor DPHI. In the second block the apparent association constant LKSP is calculated from DPHI and the intrinsic association constant LKT0SP. Macromolecular species are not considered in the calculation of ionic strength.

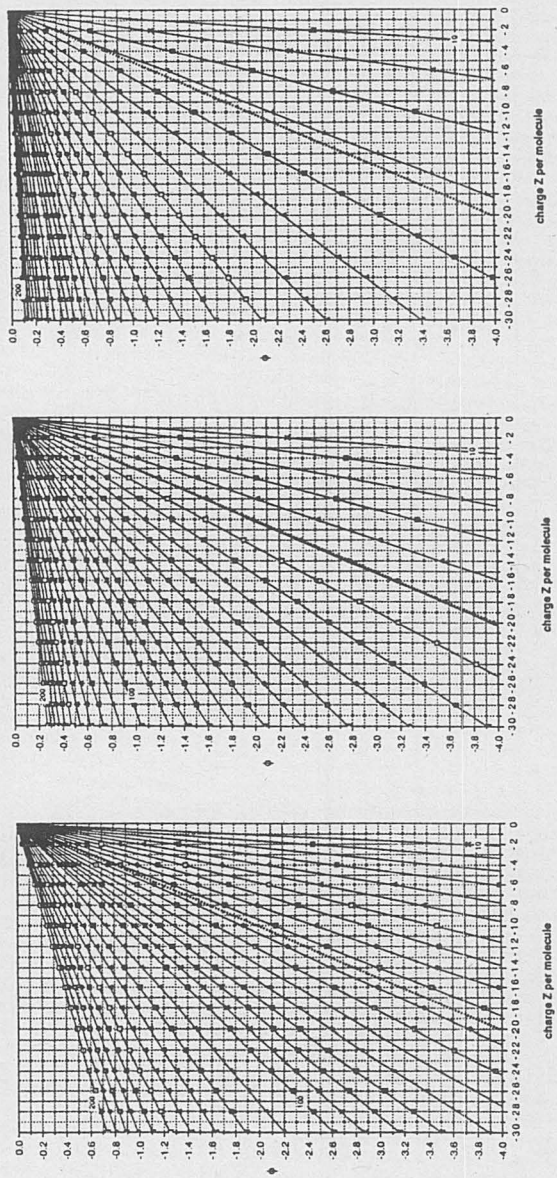

Figure 3: The electrostatic interaction factor $e^{-\phi}$ as a function of charge Z on the molecule and the radius of gyration a, given at three different ionic strength values. The broken line indicates the ratio between charge and $e^{-\phi}$ at which non-convergence is likely.

It was found that steep changes in LKSP due to steep changes in degree of dissociation from one iteration step to the next can cause the code not to converge. In the case of the flat-surface approach (Appendix B) this problem has been overcome by comparing LKSP with the value for LKSP from the previous iteration step and DPHI is cut down by a certain factor (e.g. 10) if the change in LKSP exceeds two log units between two iteration steps. To ensure convergence it was further found necessary to reduce the activity for organic master-species, i.e. for which GFLAG=2, to 0.01 in subroutine STEP which gives the initial estimates for the iteration. In particular the spherical model (Appendix A) caused serious problems with non-convergence. Figure 3 gives the electrostatic interaction factor $e^{-\phi}$ as a function of charge on the molecule and radius of gyration at three different ionic strength values. It appears that a ratio of less than 5:2 between charge and $e^{-\phi}$ causes non-convergence. Consequently there is a lower limit for the radius of gyration in any problem which is indicated in Figure 3. To obtain better convergence, in particular when modelling titration experiments, the final degree of dissociation from the previous STEP is conveyed via variable DISSDEG. To assist convergence further LKSP is kept constant when the change between two iterations is less then a predetermined threshold value (0.01%). However, with appropriate alterations to the iteration scheme in PHREEQE this problem could certainly be overcome.

To allow assessment of the progress of convergence relevant information is written into a separate output file in FORTRAN channel 9. It is suggested to identify this file by extension *.LGK. The information printed includes the degree of dissociation, apparent log K value, ϕ and other intermediate variables at each iteration step for all species designated to be be organic (i.e. for which GFLAG=2). See the listings in Appendices A and B for a full identification of variables printed. If no output is desired, the appropriate print lines can be commented out.

5. OTHER CHANGES TO THE STANDARD VERSION OF PHREEQE

It was found useful to have a summary output of the concentrations of aqueous species arranged in columns in order to faciliate datatransfer to other programs or computers, e.g. the Mackintosh. Subroutine PTOT (see Appendix E) therefore had a few lines added in order to write a file of concencentrations [molality] of all aqueous species into FORTRAN unit 7. Column 1 in this file identifies the species, while column 2 gives its concentration. It is suggested to identify these files by extension *.SUM, as it is shown in the command procedure in Appendix D.

Often plots of the distribution of aqueous species containing a particular element are desired. For this purpose the lists of all aqueous species in order of the elements they contain and the overall sum of that element is written as a two column file into unit 8. Again column 1 identifies the species and column 2 gives its concentration. It is suggested to identify these files by extension *.SPC.

The data can be TYPEd or EDIted with the full-screen editor of the *VAX* employing the *Macintosh™* computer as terminal. The terminal emulation software used here was *TextTerm+Graphics™*. Under *Multifinder™* database or wordprocessor software can be run in parallel and data can be cut as a whole or in sections of interest from the *TextTerm+ Graphics™* screen and pasted into database or wordprocessor documents. The examples and code listings below have been produced in this way, using *CricketGraph™* and *WriteNow™* respectively.

6. IMPLEMENTATION ON *VAX* COMPUTERS

The source codes are currently stored on the *VAX* in the directory K_WEF[PHREEQE] under names PHREEQEO-RS.FOR and PHREEQEO-SF.FOR respectively, plus connected object and executable files. When linking the object file no reference to other object files or system routines is necessary. Appendix D gives a sample command file used to run the codes. The input data file is identified by the problem name and extension *.DAT. The standard PHREEQE output is directed to file *.RES. The remaining extension have been explained previously.

7. EXAMPLES

The models have been tested against published results for pH-titration experiments with humic/fulvic acids (TIPPING et al., 1988, RHEA and YOUNG, 1987). NaCl had to be substituted in the calculations where $NaNO_3$ had been used as supporting electrolyte in experiments. Depending on the redox potential chosen, thermodynamic equilibrium models predict that substantial amounts of total nitrogen would be present as $N_{2(aq)}$ and the system NO_3^-—NH_4^+ acts as an additional *pH*-buffer. This has repercussions on calculated ionic strength and *pH*. In nature, however, these redox-reactions are slow and are probably far from equilibrium.

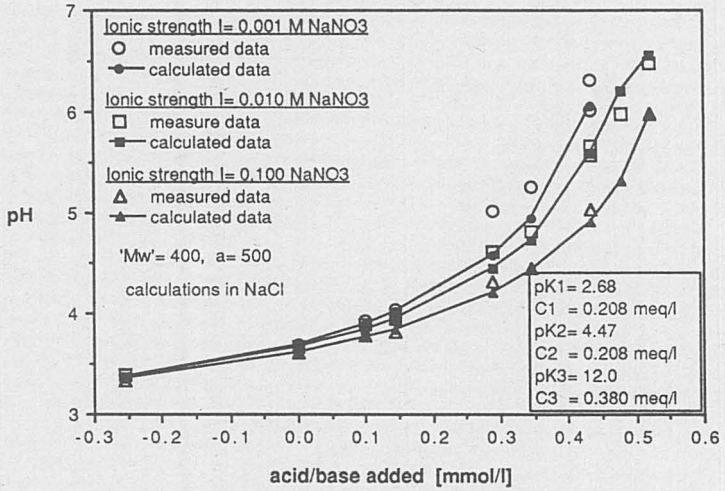

Figure 4: Titration of lake sediment humic acid and curves calculated with the rigid-sphere model (sample MBHA, from TIPPING et al., 1988).

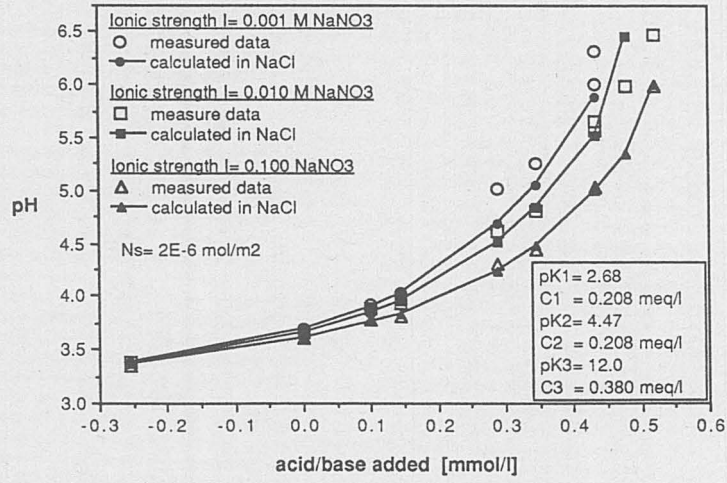

Figure 5: Titration of lake sediment humic acid and curves calculated with the flat-surface model (sample MBHA, from TIPPING et al., 1988).

Variables for both models are: total acidity and acidity associated with the various functional groups. Fitting parameters are the respective stability constants and, in the case of a spherical model the molecular weight, which is used together with the specific acidity to calculate the average charge Z on organic molecules, and the radius of gyration. The flat-surface model uses the site density as fitting parameter.

In Figure 4 and 5 calculated results from both models are compared with measured data from TIPPING et al. (1988). The original pK-values calculated by these authors have been used. These pK-values were derived by non-linear least-square fitting using the electrostatic model of equations 2 and 3 with an empirical expression for w, which contains two arbitrary, adjustable parameters P and Q:

$$w = P \cdot log\ I \cdot exp(Q \cdot |Z|) \qquad (13)$$

pK-values around 2.5 and 4.5 or 6.5 account for two dissociation steps analogous to small organic acids containing carboxylic functional groups. The difference between carboxylic and total acidity of a sample is attributed to a type of functional group containing (phenolic) OH-groups with pK values >10. As in TIPPING et al. (op.cit.) a three pK-value model was choosen here. The K value attributed to OH-groups can be varied in some cases over several orders of magnitude, i.e. from 10^{-10} to 10^{-12}, without perceptible change in the numerical result. Choosing a three ligand model sometimes ensures convergence and is probably more realistic. In fact, to reproduce titration curves one class of pK-value is necessary for every 2 to 3 pH-unit covered as previously noted by DZOMBAK et al. (1986). The measured data can be represented reasonably well with both models. This is not surprising, considering the relative large radius of gyration a needed for a good fit. A constant value for a at all ionic strengths was assumed.

Figures 6 and 7 present calculations for a different sample from TIPPING et al. (1988). The calculations were attempted at two different ionic strengths and at two concentrations of humic material. At I= 0.1 the rigid-sphere model reproduces the measured data rather well for both concentrations of organics, while at I= 0.01 the buffering is overestimated in the high-concentration sample. Assuming less expansion at higher concentration, i.e. smaller value for a, probably would give a better fit, however, a= 35 Å was the smallest value at which the code converged. No reasonable fit with the flat-surface model could be obtained. Comparing the radii of gyration a at different ionic strengths shows an increase in a with decreasing ionic strength which seems reasonable. It was found that varying the site density in the flat-surface model over orders of magnitude did not have any perceptible

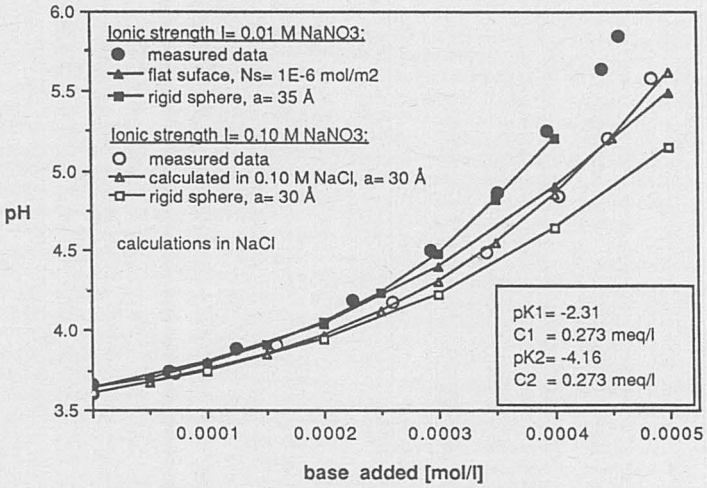

Figure 6: Titration of lake humic acid and comparison of calculations with the flat-surface and the rigid-sphere model (sample LFHS, 100 mg/l, from TIPPING et al., 1988).

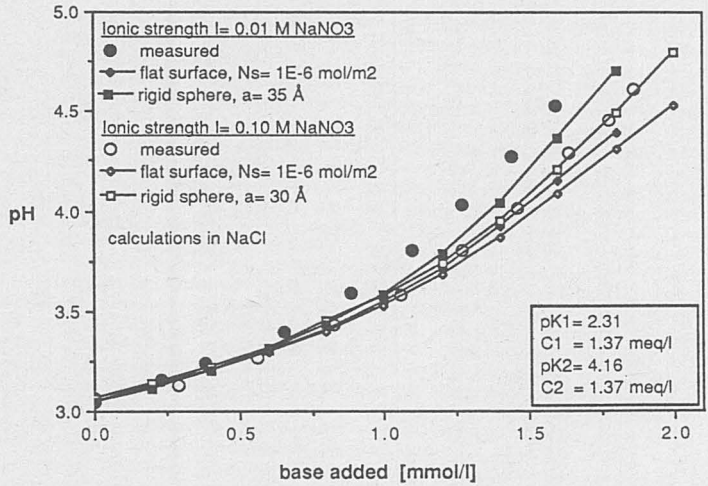

Figure 7: Titration of lake humic acid and comparison of calculations with the flat-surface and the rigid-sphere model (sample LFHS, 500 mg/l, from TIPPING et al., 1988).

effect on the calculated curves. This suggests that sample LFHS is made up of smaller entities than sample MBHA. Indeed, TIPPING et al. (1988) suggest that this is the case.

RHEA and YOUNG (1987) estimated their parameters with a continuous-distribution model; however, doubt has to be cast onto the lowest, pK_1 value, which cannot be determined unambiguously from their experiments. To obtain a reasonable fit using the spherical model, pK-values and respective amounts of acidities slightly different from their values had to be assumed (Figure 8). The flat-surface model reproduces the trend of the measured values, but could not be brought to coincide with them.

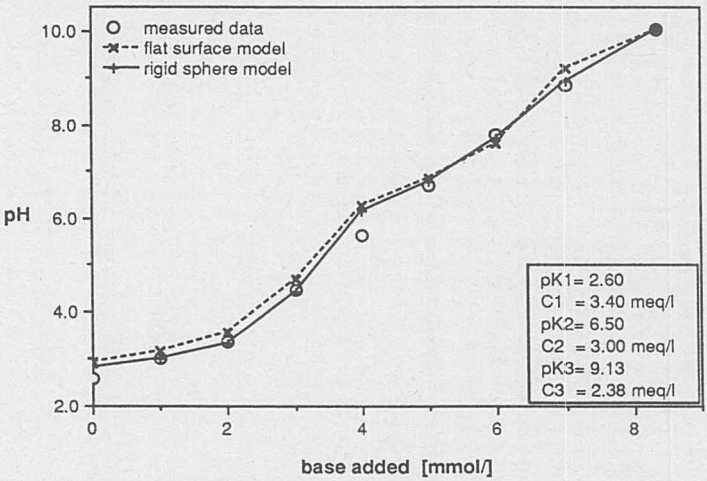

Figure 8: Titration of lake sediment humic acid from RHEA and YOUNG (1987) and comparison of calculations with the flat-surface and the rigid-sphere model.

It should be noted that solutions are not necessarily unambiguous since various parameters have opposing effects on the calculated curves and different combinations of parameters may lead to nearly the same result. The rigid-sphere model contains $2 \cdot n+2$ adjustable parameters, i.e. radius of gyration, average molecular weight, n stability constants and n ligand concentrations, while the flat-surface model contains only $2 \cdot n+1$ parameters, i.e. surface site density, n stability constants and n ligand concentrations. In the above examples stability constants and ligand concentrations were taken from the references (with exception of the last example). However, choosing different values for the stability

constant would probably lead to a better fit. In both variations of the model a least-squares optimisation for the variables should be adopted.

The degree of dissociation θ and its dependence on the amount of base added and ionic strength is illustrated in Figure 9. It should be noted that θ is invariant with respect to ionic strength if no electrostatic interaction were considered. However, θ will vary slightly in calculations as a result of changes in activity coefficients of other constituents with ionic strength. Figure 10 serves to illustrate the dependence of the apparent pK-value on ionic strength and pH. As should be expected, extrapolation to zero ionic strength leads to the intrinsic pK-values.

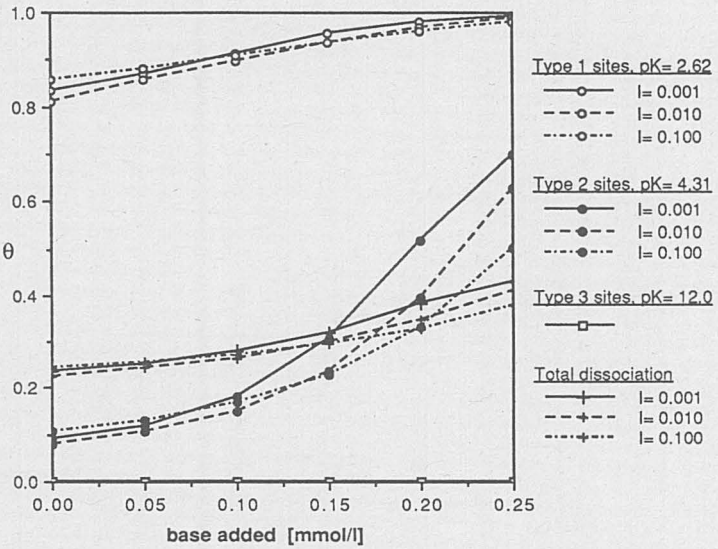

Figure 9: Degree of dissociation θ as function of base added and ionic strength (sample from TIPPING et al., 1988).

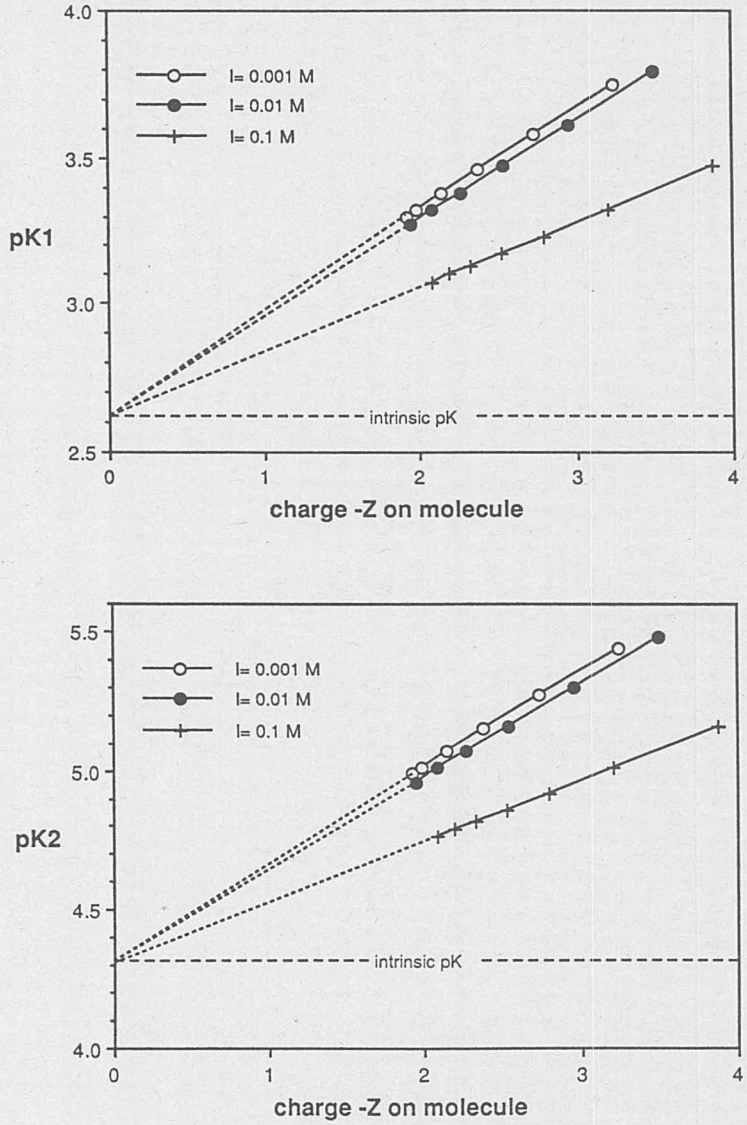

Figure 10: Apparent *pK*-values for two types of sites as function of ionic strength and *pH*, i.e. base added (sample PRHS-A, from TIPPING et a., 1988).

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APPENDIX A: New subroutine GAMMA of PHREEQEO-RS (rigid-sphere model).

```
      SUBROUTINE GAMMA
      IMPLICIT REAL*8(D),INTEGER*2(I-N)
      REAL*8 SUM,MUHALF,AMU,BMU,CMU,ZCHRG
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,
     >       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
     >               SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
     >               AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
     >               MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,DISSDEG,
     >               TOTAL(2,30),DALKT,DALKS,DIFFZ(2),DZOFF,DSUM
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),DSA,
     >               DHSP(250),ASP(250,6),ADHSP(250,2),TH(2),
     >               TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
     >               DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
     >               LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,
     >               XSTEP(50),TSTEP(50),CREAC(30),THREAC,TITLE(18),
     >               THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     >              SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     >              IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     >              NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20)
     >             ,LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     >              NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     >              MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
C
C -------CALCULATE IONIC STRENGTH
C
      DOLDMU=MU
      SUM=M(1)
      MU=M(1)
      DO 10 I=4,LASTS
      IF(GFLAG(I).EQ.2) GO TO 10
      IF(SFLAG(I).EQ.0) GO TO 10
      SUM=SUM+M(I)
      MU=MU+M(I)*ZSP(I)*ZSP(I)
   10 CONTINUE
      IF(ITER.EQ.1) GO TO 20
      IF(SUM-DSUM.LT.1.0D0) GO TO 20
      SUM=DSUM+1.0D0
   20 CONTINUE
      DSUM=SUM
      MU=MU*0.5D0
      MU=DMIN1(MU,1.0D1)
      IF(ITER.EQ.1) GO TO 30
      IF(DABS(DOLDMU-MU).LE.0.75D0) GO TO 30
      MU=DOLDMU+((MU-DOLDMU)/DABS(MU-DOLDMU))*0.5D0
   30 CONTINUE
      MUHALF=DSQRT(MU)
C
C  --------DEBYE-HUECKEL  PARAMETER
C
       DKAPPA=DSQRT(4.0748E+19*1000*MU/TK)
C--------KAPPA=  SQRT((8*PI*NL*I*e^2)/(E*E0*k*T))
C          NL=6.02217E+23 mol-1;  e=1.602192E-19 Cb;  k=1.38062E-23 J/K
C          E=78.0;  E0=8.8542E-12 Cb/Vm
C
C --------ACTIVITY OF WATER
C
      AH20=1.0-SUM*0.017
      IF(SUM.GT.40.0D0) AH20=0.32
      LA(3)=ALOG10(AH20)
      TOT(3)=AH20
C
```

```
C ---------CALCULATE OVERALL CHARGE ON ORGANIC SPECIES
C
      IF (DSA.EQ.0.0D0) GO TO 100
C----SUM BY ORGANIC LIGAND
      DZORG=0.0D0
      DZTOT=0.0D0
      DO 110 I=4,LASTS
      IF (GFLAG(I).NE.2) GO TO 110
       DZORG=DZORG+(M(I)*ZSP(I))
       IF  (I.LT.31)  DZTOT=DZTOT+TOT(I)*ZSP(I)
C       WRITE(9,145)  I,SNAME(I),DZORG,M(I),DZTOT,TOT(I)
 110   CONTINUE
      DEGDISS=DZORG/DZTOT
      IF  (ITER.EQ.1)  DEGDISS=DISSDEG
C
C----------SET CHARGES ON ALL MACROMOLECULAR SPECIES
C           ADHSP(I,1)= MAXIMUM CHARGE ON ORGANIC SPECIES
C           ADHSP(I,2)= ACTUAL  CHARGE ON ORGANIC SPECIES
C
      DO 120 I=4,LASTT
       IF  (GFLAG(I).NE.2)  GO TO 120
       IF  (ITER.EQ.1)  ADHSP(I,1)=DSA*GFW(I)
       DO 130 J=31,LASTS
          IF  (GFLAG(I).NE.2)  GO TO 130
          DO 140 K=1,NSP(J)
            IF  (LSP(J,K).NE.I)  GO TO 140
            ADHSP(J,1)=ADHSP(I,1)
            ADHSP(J,2)=ADHSP(I,1)*DEGDISS
            GO TO 130
 140       CONTINUE
 130     CONTINUE
       ADHSP(I,2)=ADHSP(I,1)*DEGDISS
C       WRITE(9,145)  I,SNAME(I),DZORG,DZTOT,DEGDISS,ADHSP(I,2),GFW(I)
 120     CONTINUE
C 145   FORMAT(1X,1I3,1X,1A8,5E12.3)
 100   CONTINUE
C
C ---------CALCULATE ACTIVITY COEFFICIENTS
C
      AMU=-A*MUHALF
      BMU=B*MUHALF
      CMU=-A*(MUHALF/(1.0+MUHALF)-0.3*MU)
      ZCHRG=0.1*MU
      LG(1)=AMU/(1.0+DHA(1)*BMU)
      IF(IOPT(6).EQ.1) LG(1)=CMU
      LG(2)=0.0D0
      LG(3)=0.0D0
C
      DO 70 I=4,LASTS
       IF(GFLAG(I).EQ.2)  GO TO 80
      IF(SFLAG(I).EQ.0) GO TO 70
      IF(ZSP(I).EQ.0.0) GO TO 40
      IF(GFLAG(I).EQ.1) GO TO 50
      IF(DHA(I).LE.0.0D0) GO TO 60
      IF(IOPT(6).EQ.1) GO TO 60
C
C--------EXTENDED DEBYE-HUECKEL EQUATION
      LG(I)=AMU*ZSP(I)*ZSP(I)/(1.0+DHA(I)*BMU)
      GO TO 70
C--------UNCHARGED SPECIES
   40 LG(I)=ZCHRG
      GO TO 70
C--------WATEQ DEBYE-HUECKEL EQUATION
   50 LG(I)=AMU*ZSP(I)*ZSP(I)/(1.0+ADHSP(I,1)*BMU)+ADHSP(I,2)*MU
      GO TO 70
C--------DAVIES EQUATION
   60 LG(I)=CMU*ZSP(I)*ZSP(I)
```

```
      GO TO 70
C
C--------ELECTROSTATIC MODEL FOR ORGANIC SPECIES
  80  IF (I.LT.31) GO TO 90
      DRG=DHA(I)
      DRG=DRG*1.0D-10
      DRCA=DRG-1.0D-10
C          DHA=   'RADIUS OF GYRATION' [ANGSTROEM] IF GFLAG=2
C          DRG=   'RADIUS OF GYRATION' [M]
C          DRCA=  'RADIUS OF CLOSEST APPROACH' [M]
      DUMMY1=DKAPPA*(DRCA)/(1+DKAPPA*DRG)
      DUMMY2=ADHSP(I,2)*ASP(I,1)*2.69223E-06/(TK*DRCA)
C--------DUMMY2=  (e^2*N*ASP*ADHSP)/(E*E0*R*T*DRCA)
C          ASP(I,1)= CHARGE ON COMPLEXING ION; R= 8.3143 J K-1 mol-1
C           (e^2*N)/(E*E0*R)= 2.69223E-06
      DPHI=(DUMMY2-DUMMY2*DUMMY1)/2.3025851
      ASP(I,2)=LKSP(I)
      LKSP(I)=LKTOSP(I)-DPHI
      DUMMY=DABS(LKSP(I)-ASP(I,2))
      IF (DUMMY.LT.1.0E-05) LKSP(I)=ASP(I,2)
       WRITE (9,1411) I,SNAME(I),LKSP(I),
     >ADHSP(I,2),MU,DRG,DUMMY1,DUMMY2,DPHI
 141   FORMAT (1X,1I3,1X,1A7,1E10.3,1F7.1,1F8.5,4E10.3)
 142   FORMAT (80('-'))
C--------SET ACTIVITY COEFFICIENT FOR MACROMOLECULES TO 1.0
  90   LG(I)=0.0
C
  70  CONTINUE
      WRITE (9,82)
      DISSDEG=DEGDISS
C
      RETURN
      END
```

APPENDIX B: New subroutine GAMMA of PHREEQEO-FS (flat-surface model).

```
      SUBROUTINE GAMMA
        IMPLICIT REAL*8(D),INTEGER*2(I-N)
        REAL*8 SUM,MUHALF,AMU,BMU,CMU,ZCHRG
        REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,
       >       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL
        COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
       >               SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
       >               AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
       >               MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,
       >               TOTAL(2,30),DALKT,DALKS,DIFFZ(2),DZOFF,DSUM
        REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
        COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),DNS,
       >               DHSP(250),ASP(250,6),ADHSP(250,2),TH(2),
       >               TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
       >               DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
       >               LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,
       >               XSTEP(50),TSTEP(50),CREAC(30),THREAC,TITLE(18),
       >               THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
        INTEGER*2 GFLAG,SFLAG
        COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
       >              SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
       >              IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
       >              NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20)
       >             ,LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
       >              NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
       >              MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
C
C -------CALCULATE IONIC STRENGTH
C
        DOLDMU=MU
        SUM=M(1)
        MU=M(1)
        DO 10 I=4,LASTS
         IF(GFLAG(I).EQ.2) GO TO 10
        IF(SFLAG(I).EQ.0) GO TO 10
        SUM=SUM+M(I)
        MU=MU+M(I)*ZSP(I)*ZSP(I)
   10   CONTINUE
        IF(ITER.EQ.1) GO TO 20
        IF(SUM-DSUM.LT.1.0D0) GO TO 20
        SUM=DSUM+1.0D0
   20   CONTINUE
        DSUM=SUM
        MU=MU*0.5D0
        MU=DMIN1(MU,1.0D1)
        IF(ITER.EQ.1) GO TO 30
        IF(DABS(DOLDMU-MU).LE.0.75D0) GO TO 30
        MU=DOLDMU+((MU-DOLDMU)/DABS(MU-DOLDMU))*0.5D0
   30   CONTINUE
        MUHALF=DSQRT(MU)
C
C --------ACTIVITY OF WATER
C
        AH20=1.0-SUM*0.017
        IF(SUM.GT.40.0D0) AH20=0.32
        LA(3)=ALOG10(AH20)
        TOT(3)=AH20
C
C ---------CALCULATE DEGREE OF DISSOCIATION OF MACROMOLECULAR SPECIES
C
         IF (DNS.EQ.0.0D0) GO TO 100
         DZORG=0.0D0
         DEGDISS=0.0D0
C----SUM CHARGE ON ORGANIC SPECIES
         DO 110 I=4,LASTS
```

```
C----SKIP  ALL  INORGANIC  SPECIES
       IF (GFLAG(I).NE.2) GO TO 110
        DZORG=DZORG+(M(I)*ZSP(I))
 110   CONTINUE
C----SUM MAXIMUM CHARGE ON ORGANIC MASTERSPECIES
       DZTOT=0.0D0
       DO 120 I=4,LASTT
C----SKIP  ALL  INORGANIC  MASTERSPECIES
       IF (GFLAG(I).NE.2) GO TO 120
       DZTOT=DZTOT+(TOT(I)*ZSP(I))
 120   CONTINUE
       DEGDISS=DZORG/DZTOT
C
C--------CALCULATE  ELECTROSTATIC  INTERACTION  FACTOR
            DUMMY1=DNS*(-DEGDISS)*4.5018E+08/DSQRT(TK*MU)
C--------DUMMY1=DNS*(DEGDISS-1)*F/SQRT((8*E*E0*R*T*I)
C          DNS=SITE DENSITY [MOL/M^2]
C          F=9.64867E+4 Cb/mol; R= 8.3143 J K-1 mol-1
C          E= 78.0; E0= 8.8542E-12 Cb/Vm
           DPHI=DLOG(DUMMY1+DSQRT(DUMMY1*DUMMY1+1.0D0))/1.1512925
  100   CONTINUE
C
C ---------CALCULATE ACTIVITY COEFFICIENTS
C
      AMU=-A*MUHALF
      BMU=B*MUHALF
      CMU=-A*(MUHALF/(1.0+MUHALF)-0.3*MU)
      ZCHRG=0.1*MU
      LG(1)=AMU/(1.0+DHA(1)*BMU)
      IF(IOPT(6).EQ.1) LG(1)=CMU
      LG(2)=0.0D0
      LG(3)=0.0D0
C
      DO 70 I=4,LASTS
       IF(GFLAG(I).EQ.2) GO TO 80
      IF(SFLAG(I).EQ.0) GO TO 70
      IF(ZSP(I).EQ.0.0) GO TO 40
      IF(GFLAG(I).EQ.1) GO TO 50
      IF(DHA(I).LE.0.0D0) GO TO 60
      IF(IOPT(6).EQ.1) GO TO 60
C---------EXTENDED DEBYE-HUECKEL EQUATION
      LG(I)=AMU*ZSP(I)*ZSP(I)/(1.0+DHA(I)*BMU)
      GO TO 70
C---------UNCHARGED SPECIES
  40  LG(I)=ZCHRG
      GO TO 70
C---------WATEQ DEBYE-HUECKEL EQUATION
  50  LG(I)=AMU*ZSP(I)*ZSP(I)/(1.0+ADHSP(I,1)*BMU)+ADHSP(I,2)*MU
      GO TO 70
C---------DAVIES EQUATION
  60  LG(I)=CMU*ZSP(I)*ZSP(I)
      GO TO 70
C--------ELECTROSTATIC MODEL FOR MACROMOLECULAR SPECIES
  80   IF (I.LT.31) GO TO 90
       DUMMY2=LKSP(I)
       LKSP(I)=LKTOSP(I)-DPHI
       DUMMY2=DABS(DUMMY2-LKSP(I))
C-------RESTRAIN CHANGES IN LOG K IN ANY ITERATION STEP
       IF  (DUMMY2.GT.2.0D0)  LKSP(I)=LKTOSP(I)-(DPHI/1.0D+01)
  90   LG(I)=0.0
C
  70  CONTINUE
C
      RETURN
      END
```

APPENDIX C: Sample input file.

```
TEST CASE ELECTROSTATIC MODEL
003000000  6 1              0.0
ELEMENTS
L1-1        21      1450.000
L2-1        22      1450.000
L3-1        23      1450.000

SPECIES
 21
L1-1          122     -1.000      0.000     44.000      0.000      0.000      0.000
     0.000      0.000          0.0      0.00000      0.00000
 21  1.000
 22
L2-1          122     -1.000      0.000     44.000      0.000      0.000      0.000
     0.000      0.000          0.0      0.00000      0.00000
 22  1.000
 23
L3-1          122     -1.000      0.000     44.000      0.000      0.000      0.000
     0.000      0.000          0.0      0.00000      0.00000
 23  1.000
127
HL1           222      0.000      0.000     44.000      0.000      0.000      0.000
     2.620      0.000     1.00000      0.00000      0.00000
 21  1.000  1  1.000
128
HL2           222      0.000      0.000     44.000      0.000      0.000      0.000
     4.310      0.000     1.00000      0.00000      0.00000
 22  1.000  1  1.000
129
HL3           222      0.000      0.000     44.000      0.000      0.000      0.000
    12.000      0.000     1.00000      0.00000      0.00000
 23  1.000  1  1.000

SOLUTION 1
TITRATE WITH NAOH
 5  0 1          4.000     12.000      25.0           1
   6  1.000E-00  13  1.000E-00  21  1.730E-01  22  1.743E-01  23  3.330E-01
SPECIFIC ACIDITY [eq/g]:   -5.85E-03
STEPS
  1.00E-12  0.50E-04  1.00E-04  1.50E-04  2.00E-04  2.36E-04
REACTION
   6     1.0      0.0
END
```

APPENDIX D: Command procedure to run PHREEQEO-RS or PHREEQEO-FS on a VAX computer.

```
$ WRITE SYS$OUTPUT ""
$ WRITE SYS$OUTPUT ""
$ DIR/EXCL=(*DB*.DAT,*PICK*.DAT) *.DAT
$ READ/PROMPT="Enter file name (without extension): " SYS$COMMAND FILE
$ ASSIGN [K_WEF.PHREEQE.HUMICS]'FILE'.DAT FOR005
$ ASSIGN [K_WEF.PHREEQE.HUMICS]'FILE'.RES FOR006
$ ASSIGN [K_WEF.PHREEQE.HUMICS]'FILE'.SPC FOR007
$ ASSIGN [K_WEF.PHREEQE.HUMICS]'FILE'.SUM FOR008
$ ASSIGN [K_WEF.PHREEQE.HUMICS]'FILE'.LGK FOR009
$ ASSIGN [K_WEF.PHREEQE.HUMICS]DBHUMICS.DAT FOR010
$ R [K_WEF.PHREEQE]PHREEQEO-RS
$ DEASSIGN FOR005
$ DEASSIGN FOR006
$ DEASSIGN FOR007
$ DEASSIGN FOR008
$ DEASSIGN FOR009
$ DEASSIGN FOR010
```

APPENDIX E: Listing of improved subroutine PTOT.

```
      SUBROUTINE PTOT
        IMPLICIT REAL*8(D), INTEGER*2(I-N)
        REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,
       >       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL,DISSDEG
        COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
       >               SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
       >               AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
       >               MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,DISSDEG,
       >               TOTAL(2,30),DALKT,DALKS,DIFFZ(2),DZOFF,DSUM
        REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
        COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),DSA,
       >               DHSP(250),ASP(250,6),ADHSP(250,2),TH(2),
       >               TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
       >               DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
       >               LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,
       >               XSTEP(50),TSTEP(50),CREAC(30),THREAC,TITLE(18),
       >               THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
        INTEGER*2 GFLAG,SFLAG
        COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
       >              SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
       >              IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
       >              NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20)
       >             ,LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
       >              NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
       >              MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
        REAL*8 NAMELK
        REAL*4 LKLOOK,LKOLK
        COMMON /LOOK/ NAMELK(40),LKOLK(40),LKLOOK(40),DHLOOK(40),
       >              ALOOK(40,10),CLOOK(40,10),LLOOK(40,10),NLOOK(40),
       >              LOOKFL(40),NLOOKS
        REAL*8 SUNAME(10)
        COMMON /NEUT/ SUNAME,DNEUT,NSUM(10),NSUMS,LSUM(10,50),LPOS,LNEG
        DIMENSION CARD(20)
C
        DATA IDATA/0/,DALK/'TOT ALK'/
        DATA DN1/'02'/,DN2/'H2'/,DN3/'CHARGE'/
C
C
        WRITE(6,220)
        WRITE(6,230)
        KK=0
        DO 10 I=4,MAXT
        IF(TOT(I).EQ.0.0D0) GO TO 10
        KK=1
        DLT=DLOG10(TOT(I))
        DNAME=TNAME(I)
        IF(IASPEC.EQ.I) DNAME=DALK
        WRITE(6,240) DNAME,TOT(I),DLT
   10   CONTINUE
        IF(KK.EQ.0) WRITE(6,250)
        WRITE(6,260)
        RETURN
C******************
        ENTRY PSPEC
C******************
        WRITE(6,270)
         EH=PE*(273.16+TC)*1.979E-04
        WRITE(6,280) PH,PE,EH,TOT(3),MU,TC,ELECT,THSOLN,DALKS,ITER
        IF(IASPEC.LE.0) GO TO 20
        WRITE(6,290) TOTAL(ISOL,IASPEC)
   20   CONTINUE
        IF(IESPEC.LE.1) GO TO 30
        D=TOT(IESPEC)-DNEUT
        WRITE(6,300) TNAME(IESPEC),D
```

```
  30  CONTINUE
      WRITE(6,310)
      LM(1)=LA(1)-LG(1)
      LG(2)=0.0D0
      LM(2)=LA(2)
      LG(3)=0.0D0
      LM(3)=LA(3)
      DO 40 I=1,LASTS
      IF(SFLAG(I).EQ.0) GO TO 40
      DA=0.0D0
      DM=0.0D0
      IF(LM(I).LT.-30.0D0.AND.I.GT.30) GO TO 40
      IF(LM(I).GE.-60.0D0) DM=1D1**LM(I)
      DLA=LM(I)+LG(I)
      IF(DLA.GE.-60.0D0) DA=1.0D1**DLA
      DG=1.0D1**LG(I)
      WRITE(6,320) I,SNAME(I),ZSP(I),DM,LM(I),DA,DLA,DG,LG(I)
  40  CONTINUE
C
C----- WRITE SEPARATE FILE WITH ALL SPECIES ON UNIT 7
C
       WRITE(7,314)ISTEP,(HEAD(ISOLN,J),J=1,20)
       WRITE(7,315)
       DO 45 I=1,LASTS
       IF(SFLAG(I).EQ.0) GO TO 45
       DM=0.0D0
       DM=1D1**LM(I)
       WRITE(7,325) SNAME(I),DM
  45   CONTINUE
C
C----- WRITE SEPARATE FILE WITH SPECIES SORTED
C       IN ORDER OF ELEMENTS ON UNIT 8
C
       WRITE(8,314)ISTEP,(HEAD(ISOLN,J),J=1,20)
       WRITE(8,326)
       DO 46 I=4,LASTT
       WRITE(8,327) TNAME(I)
       DSUM=0.0D0
       DO 47 J=4,LASTS
       DO 48 K=1,NSP(J)
       IF (LSP(J,K).NE.I) GO TO 48
       IF(SFLAG(J).EQ.0) GO TO 47
       DM=0.0D0
       DM=1.0D1**LM(J)
       DSUM=DSUM+DM*CSP(J,K)
       WRITE(8,325) SNAME(J),DM
       GOTO 47
  48   CONTINUE
  47   CONTINUE
       WRITE(8,328) TNAME(I),DSUM
  46   CONTINUE
C*****************
      ENTRY PSUM
C*****************
      IF(NSUMS.EQ.0) GO TO 80
      KK=0
      DO 70 I=1,NSUMS
      LL=0
      DSUM=0.0D0
      K=NSUM(I)
      DO 50 J=1,K
      IF(SFLAG(LSUM(I,J)).LE.0) GO TO 50
      LL=1
      DSUM=DSUM+M(LSUM(I,J))
  50  CONTINUE
      IF(LL.EQ.0) GO TO 70
      IF(LL.EQ.0.OR.KK.NE.0) GO TO 60
      WRITE(6,330)
```

```
      KK=1
   60 CONTINUE
      WRITE(6,340) SUNAME(I),DSUM
   70 CONTINUE
   80 CONTINUE
      RETURN
C*************************
      ENTRY PBUG(DARG,DPHPE)
C*************************
      D=DARG
      WRITE(6,350) D,CR(1),DPHPE
C
C -------- PRINT CHANGES IN PH AND PE
C
      IF(IIN(1).LE.0) GO TO 90
      DPH=-DLOG10(1D0+DELTA(1))
      WRITE(6,360) PH,DPH
   90 CONTINUE
      IF(IIN(2).LE.0) GO TO 100
      DPE=-DLOG10(1D0+DELTA(IIN(2)))
      WRITE(6,370) PE,DPE,CR(2)
  100 CONTINUE
C
C -------- PRINT TOTALS AND ACTIVITIES
C
      DO 110 K=4,LASTT
      I=IIN(K)
      IF(I.LE.0) GO TO 110
      DRT=DELTOT(I)/TOT(K)
      DA=UNDER(LA(K))
      DRA=DELTA(I)*DA
      WRITE(6,380) CR(K),TNAME(K),TOT(K),DELTOT(I),DRT,SNAME(K),DA,
     >             DELTA(I),DRA
  110 CONTINUE
C
C ------- PRINT MINERAL TOTALS AND DELTAS
C
      IF(NMINS.LE.0) GO TO 130
      DO 120 I=1,NMINS
      K=MAXT+I
      J=ILT+I
      WRITE(6,390) CR(K),MNAME(I),TOT(K),DELTA(J)
  120 CONTINUE
  130 CONTINUE
      RETURN
C*******************
      ENTRY PPHASE
C*******************
      IF(NMINS.EQ.0) RETURN
      WRITE(6,400)
      DO 150 I=1,NMINS
      K=NMIN0(I)
      DIAP=0.0D0
      DO 140 J=1,K
  140 DIAP=DIAP+(LG(LMIN0(I,J))+LM(LMIN0(I,J)))*CMIN0(I,J)
      DSI=DIAP-LKMIN0(I)
      K=MAXT+I
      D1=TOT(K)
      IF(IOPT(3).EQ.6.AND.I.EQ.1) D1=0.0D0
      WRITE(6,410) MNAME(I),D1,DIAP,LKMIN0(I),DSI
      IF(IOPT(3).EQ.6.AND.I.EQ.1) WRITE(6,420)
  150 CONTINUE
      WRITE(6,430)
      IF(IOPT(3).EQ.6) WRITE(6,440) TOT(MAXT+1),MNAME(1)
      IF(IOPT(3).NE.6) RETURN
C*****************
      ENTRY PREAC
C*****************
```

```
      WRITE(6,450)
      DO 160 I=1,NCOMPS
      L=LREAC(I)
      IF(L.EQ.0) DN=DN3
      IF(L.LT.31) DN=TNAME(L)
      IF(L.GT.30) DN=DN1
      IF(L.GT.30.AND.THMEAN(I).LT.0) DN=DN2
      WRITE(6,460) CREAC(I),DN,THMEAN(I)
 160  CONTINUE
      RETURN
C******************
      ENTRY PLOOK
C******************
      IF(NLOOKS.EQ.0) RETURN
      KK=0
      DO 190 I=1,NLOOKS
      K=NLOOK(I)
      DIAP=0.0D0
      DO 170 J=1,K
      LL=LLOOK(I,J)
      IF(SFLAG(LL).LE.0) GO TO 190
 170  DIAP=DIAP+(LG(LL)+LM(LL))*CLOOK(I,J)
      IF(KK.NE.0) GO TO 180
      KK=1
      WRITE(6,470)
 180  CONTINUE
      DSI=DIAP-LKLOOK(I)
      WRITE(6,480) NAMELK(I),DIAP,LKLOOK(I),DSI
 190  CONTINUE
      RETURN
C******************
      ENTRY PDATA
C******************
      IF(IOPT(1).NE.1) RETURN
      IF(IDATA.GT.0) RETURN
      IDATA=1
      REWIND 10
      WRITE(6,490)
 200  CONTINUE
      READ(10,500,END=210) CARD
      WRITE(6,510) CARD
      GO TO 200
 210  CONTINUE
      RETURN
C
 220  FORMAT(//40X,'TOTAL MOLALITIES OF ELEMENTS'/40X,
     >           '----- ---------- -- --------')
 230  FORMAT(/32X,'ELEMENT',10X,'MOLALITY',9X,'LOG MOLALITY'/)
 240  FORMAT(32X,A8,6X,1PD13.6,8X,0PF9.4)
 250  FORMAT(32X,'PURE WATER')
 260  FORMAT(//)
 270  FORMAT(//40X,'---- DESCRIPTION OF SOLUTION ----')
 280  FORMAT(/55X,'PH= ',F8.4/55X,'PE= ',F8.4/55X,'EH= ',F8.4/45X,
     >       'ACTIVITY H2O= ',F8.4/43X,'IONIC STRENGTH= ',F8.4/46X,
     >       'TEMPERATURE= ',F8.4/39X,'ELECTRICAL BALANCE= ',
     >       1PD12.4/53X,'THOR= ',D12.4/41X,'TOTAL ALKALINITY= ',
     >       D12.4/47X,'ITERATIONS= ',I3)
 290  FORMAT(45X,'TOTAL CARBON =',1PD12.4)
 300  FORMAT(34X,'MOLES OF ',A8,' ADDED =',D12.4)
 310  FORMAT(//44X,23('-')/44X,'DISTRIBUTION OF SPECIES'/44X,23('-')//
     >       9X,'I',3X,'SPECIES',4X,'Z',6X,'MOLALITY',4X,'LOG MOLALITY',
     >       4X,'ACTIVITY',4X,'LOG ACTIVITY',5X,'GAMMA',8X,'LOG GAMMA'/)
 314    FORMAT(/,80('-'),/,1X,'STEP',I2,3X,20A4)
 315    FORMAT(1X,'DISTRIBUTION OF SPECIES'/1X,'SPECIES',4X,'MOLALITY')
 320  FORMAT(8X,I3,2X,A8,1X,F4.1,3X,3(1PD12.5,4X,0PF8.4,4X))
 325    FORMAT(1X,A8,1E12.5)
 326    FORMAT(1X,'DISTRIBUTION OF SPECIES, IN ORDER OF ELEMENTS')
 327    FORMAT(80('-'),/,' SPECIES CONTAINING ',1A8)
```

```
328   FORMAT(1X,'SUM (MOLALITY) OF SPECIES CONTAINING ',
     > 1A8,'=',1PE12.5)
330   FORMAT(//48X,'SUMS OF SPECIES'/)
340   FORMAT(45X,A8,' = ',1PD13.6)
350   FORMAT(/10X,'REDUCTION FACTOR: ',1PD12.5,10X,'ELECT: ',D12.5,
     >        10X,'DPHPE: ',D12.5)
360   FORMAT(10X,'PH= ',F8.4,5X,'DPH= ',F8.4)
370   FORMAT(10X,'PE= ',F8.4,5X,'DPE= ',F8.4,5X,'DTHOR= ',1PD12.5)
380   FORMAT(1X,1PD12.5,2X,A8,3(3X,D12.5),2X,A8,3(3X,D12.5))
390   FORMAT(1X,1PD12.5,2X,A8,3(3X,D12.5))
400   FORMAT(42X,'---- PHASE BOUNDARIES ----'//24X,'PHASE',5X,'DELTA ',
     >       'PHASE*',6X,'LOG IAP',6X,'LOG KT',6X,'LOG IAP/KT'/)
410   FORMAT(23X,A8,2X,1PD13.6,3(4X,0PF9.4))
420   FORMAT(1H+,20X,'**')
430   FORMAT(/4X,'* NEGATIVE DELTA PHASE INDICATES PRECIPITATION AND '
     >       ,'POSITIVE DELTA PHASE INDICATES DISSOLUTION.')
440   FORMAT(/3X,'** ',1PD12.6,' MOLES OF REACTION HAVE BEEN ADDED ',
     >       'TO THE SOLUTION TO REACH THE ',A8,' PHASE BOUNDARY.')
450   FORMAT(/25X,'REACTION IS:')
460   FORMAT(39X,F6.2,' MOLES OF ',A8,' VALENCE= ',F6.3)
470   FORMAT(//45X,'---- LOOK MIN IAP ----'//30X,'PHASE',8X,'LOG IAP',
     >       6X,'LOG KT',6X,'LOG IAP/KT'/)
480   FORMAT(29X,A8,3(4X,F9.4))
490   FORMAT(1H1,30X,'DATA: CARD IMAGES FROM DISK'/)
500   FORMAT(20A4)
510   FORMAT(1X,20A4)
      END
```