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HYDROGEOCHEM: A Coupled Model of HYDROlogic Transport and
GEOCHEMical Equilibria in Reactive Multicomponent Systems

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* On floppy disks which will be sent to interested readers upon request.

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** Available on a 3 and 1/2 inch floppy disk. For further information, call Dr. G. T. Yeh at (814) 863-2931 or write to Prof. G. T. Yeh, Department of Civil Engineering, The Pennsylvania State University, University Park, PA 16802

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ABSTRACT

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This report presents the development of a hydrogeochemical transport model for multicomponent systems. The model is designed for applications to proper hydrological setting, accommodation of complete suite of geochemical equilibrium processes, easy extension to deal with chemical kinetics, and least constraints of computer resources. The hydrological environment to which the model can be applied is the heterogeneous, anisotropic, saturated-unsaturated subsurface media under either transient or steady state flow conditions. The geochemical equilibrium processes included in the model are aqueous complexation, adsorption-desorption, ion exchange, precipitation-dissolution, redox, and acid-base reactions. To achieve the inclusion of the full complement of these geochemical processes, total analytical concentrations of all chemical components are chosen as the primary dependent variables in the hydrological transport equations. Attendant benefits of this choice are to make the extension of the model to deal with kinetics of adsorption-desorption, ion exchange, precipitation-dissolution, and redox relatively easy. To make the negative concentrations during the iteration between the hydrological transport and geochemical equilibrium least likely, an implicit form of transport equations are proposed. To alleviate severe constraints of computer resources in terms of central processing unit (CPU) time and CPU memory, various optional numerical schemes are incorporated in the model.

The model consists of a hydrological transport module and a geochemical equilibrium module. Both modules were thoroughly tested in code consistency and were found to yield plausible results. The model is verified with ten examples ranging from the simple case of aqueous complexation only to the cases that simulates simultaneous processes of aqueous complexation, adsorption-desorption, ion exchange, precipitation-dissolution, redox, and acid-base reactions without fixing pH and pe.

1. INTRODUCTION

Subsurface contamination has become an environmental issue of national concern since the headline tragic news of the Love Canal case near Niagara Falls, New York, where a variety of discarded hazardous chemicals entered the basements of nearby homes after traveling through ambient groundwater (ABC News Close Up: The Killing Ground, March 29, 1979). Many federal Environmental Protection Agency-sponsored studies of hazardous waste disposal sites throughout the United States have shown that potentially dangerous situations are not rare, as thousands of similar sites in the United States are simply waiting for public discovery. Numerous new discoveries of hazardous disposal sites since then and public outcries on the severe environmental effects of these sites have forced the Congress to set up "SuperFund" to clean them up.

Increasing public concerns of groundwater contaminant problems have compelled the waste generators in industry, public sector, and private businesses to carefully formulate waste management plans and evaluate disposal sites. To comply with legal provisions of the Resource Conservation and Recovery Act of 1976 (RCRA), the 1974 Safe Drinking Water Act, the 1972 amendments to the Federal Pollution Control Act, and the Hazardous and Solid Waste Amendments of 1984 (HSWA), adequate techniques are needed to provide good estimates of the movement and attenuation of contaminants after they are released into the subsurface system to assess their environmental effects.

Once released into the subsurface system, contaminants will interact physically, chemically, and biologically with both the native water and granulated solid matrix. The major hydrological and physical processes of interaction include advection and convection, dispersion and diffusion, compaction and consolidation, and decay if the contaminant is radioactive.

The chemical reactions may include aqueous complexation, reduction-oxidation (Redox), acid-base reaction, adsorption-desorption, ion exchange, precipitation-dissolution, and volatilization. The biological processes involve uptake by biota and microorganism that may transform a chemical species into other species or simply use the species as their nutrient diet. A discussion of biological processes will not be included in this report, but will be the subject of another study.

Advection and convection are the hydrological processes of the flowing water that moves the mass and carries the contaminant with the mean velocity. Dispersion and diffusion are the processes that spread the mass about its mean position. Compaction and consolidation cause compression of the granular matrix, which in turn affects chemical concentration. Decay transforms the radionuclide from one isotope to another isotope, as characterized by a decay constants, which are known for practically all of the radionuclides. Advection and convection are determined by the stochastic mean fluid velocity, whereas dispersion depends on the variability of the velocity field. The processes of diffusion operates at the molecular level and is usually insignificant

relative to dispersion in most groundwater flow problems. For a velocity field with normal distribution, these hydrologic processes may be characterized by the diffusivities, molecular diffusion coefficient, and the moisture content. Compaction and consolidation depend on the pressure distribution and plastic-elastic properties of the granular matrix.

Aqueous complexation is the chemical process of homogeneous ionic association. This process is characterized by the stoichiometric coefficient and stability constant, which depends on the thermodynamic equilibrium constant, ionic strength, and the temperature. Redox is the chemical process involving either the homogeneous or heterogeneous ionic association and the change of oxidation states. This process determines the pe value in a system and is controlled by the stability constant and stoichiometric coefficient. Acid-base reaction is the chemical process involving transfer of protons. This process determines the pH in a system and is controlled by stability constants and stoichiometric coefficients of acid-base reactions (Stumm and Morgan 1981). Adsorption-desorption is the mechanism that transfers the dissolved chemicals to the matrix surface or vice versa. It is characterized by the abundance of adsorption-desorption sites, surface charge-potential, and stability constant. Ion exchange involves the exchange of aqueous species with surface species. It is characterized by the ion exchange capacity and selectivities. Precipitation is the mechanism that transforms the dissolved solutes into solids, which in a generalized sense may include gases. Dissolution is

the reverse process of the precipitation. Precipitation-dissolution process is controlled by the solubility product. By volatilization, solutes in the dissolved phase are transferred to the gaseous phase.

Any of these physical and chemical processes will contribute to the distribution and redistribution of chemical components after they are introduced into the subsurface system. The combined effect of all processes on the solute transport must satisfy the principle of mass balance. The statement of mass balance principle can be transformed into partial differential equations (PDEs) or integro-differential equations, one each for a component. In the past, such PDEs governing the subsurface solute transport often incorporated the effects of the hydrological and physical processes rigorously but frequently ignored the chemical interactions among the species and handled the heterogeneous interphase reactions with an empirical approach such as the linear isotherm (K_d approach) and/or the Langmuir and Freundlich nonlinear isotherms (Langmuir 1918; Freundlich 1926). On the other hand, there were sophisticated chemical equilibrium models that have incorporated the complete suite of the aforementioned chemical processes but which ignored completely the hydrological and physical transport processes (Morel and Morgan 1972; Mattigod and Sposito 1978; Garrels and Thompson 1962; Kharaka and Barnes 1973; Plummer et al. 1976; Parkhurst et al. 1980; Tripathi 1987). In other words, these chemical equilibrium models can only be applied to beaker systems. Recently, attempts have been made to account

for the complex physical and chemical processes in the hydrological transport modeling in subsurface systems (Valocchi et al. 1981; Jennings et al. 1982; Miller 1983; Cederberg 1985a, 1985b; Yeh and Tripathi 1987).

Although the modeling activity in coupling the hydrological transport and chemical equilibrium of reactive multi-components through the subsurface systems has been expanding rapidly, few of these models can really deal with practical problems. The difficulties arise mainly from the inappropriate adaptation of primary dependent variables (PDVs) in the transport equations and the misuse of numerical schemes to solve the equations. As a result, these models either cannot account for the complete suite of chemical processes, easily tumble into nonconvergency, or require excessive central process unit (CPU) memory and time. This report presents a model to overcome these problems.

Two basic ingredients are present in modeling the transport of reactive multicomponents: the transport is described by a set of partial differential equations (PDEs); the chemical reactions, under the assumption of local equilibrium, are described by a set of nonlinear algebraic equations (AEs). The problem can be formulated in three ways: (1) treating the system as a simultaneous mixed differential and algebraic equations (DAEs) and numerically solving the whole system of linear PDEs and nonlinear AEs simultaneously, (2) incorporating the nonlinear reaction as part of the transport equations and solving a reduced system of nonlinear PDEs simultaneously, (3) considering the system as a coupled

linear PDEs and nonlinear AEs and solving iteratively between two sequential systems of linear PDEs and nonlinear AEs. Each approach offers some advantages. An extremely important consideration in any approach is the choice of the PDVs in transport equations. Once the PDVs are obtained, the secondary dependent variables (SDVs) and/or all the partial derivatives of SDVs with respect to the PDVs are computed based directly or indirectly on the PDVs. For the DAE approach, molar concentrations of all species have been taken as the PDVs (Miller 1983). This approach would result in an excessive number of dependent variables and hence would require too much CPU storage and CPU time for realistic applications. It might provide a good research tool for one-dimensional (1-D) simulation with limited numbers of chemical species. The best aspect of this approach is the ease of extending it to deal with chemical kinetics. For the second (direct substitution) and third (coupled) approaches, either the component species concentrations and component activities, the total dissolved concentration, or the total analytical concentrations of the components may be chosen as the PDVs. Several models have used the total dissolved concentration as the PDVs (Rubin and James 1973; Valocchi 1981; Theis et al. 1982). This choice is inherently incapable of dealing with precipitation-dissolution processes. Other models have used the component activities or component species concentrations as the PDVs (Jennings et al. 1982), which not only fails to deal with precipitation-dissolution, but its applications are limited to a narrow class of sorption processes when the concentration of sorbed species can be expressed explicitly in terms of the activities. No matter which choice is made for the PDVs, the

direct substitution approach will not be practical because a system of substantial number of FDEs has to be solved simultaneously, such an operation would require excessive amounts of CPU storage and CPU time, even for a moderately sized two-dimensional (2-D) problem (Yeh 1985; Yeh 1986).

The equilibrium chemical reactions are generally posed as follows: given the total analytical concentration for each of all chemical components under consideration, find the concentrations of all chemical species (free, dissolved, adsorbed, ion-exchanged, and precipitated species). Considering this fact, one can easily see that the total analytical concentration for each chemical component would be a natural choice for PDVs in the transport equations. The total analytical concentrations obtained from the hydrologic transport equations are used in lieu of the measured total analytical concentration in the chemical equilibrium problems. To our knowledge, only one model has chosen the total concentration as the PDVs (Cederberg 1985a). Unfortunately, because the explicit iteration form of the transport equations was used in this case, two severe deficiencies have resulted. First, the solution can easily tumble into nonconvergence when the dissolved phase dominates in the chemical reaction even for a very simple linear case. Second, it cannot solve the steady-state problem in one step.

This report presents a model in which an implicit form of transport equations is proposed and solved for the total analytical concentration iterating between hydrological transport and chemical reactions. The model permits fast, nonnegative, convergent solutions and easily includes the full complement of chemical processes. Another unique feature of the model is its capability of solving steady-state problems in one step, without having to go through numerous time-step iterations. Several examples are used to demonstrate the flexibility and versatility of the model. Realistic applications of the models have been reported elsewhere (Tripathi and Yeh 1985; Tripathi and Yeh 1986).

2. MATHEMATICAL FORMULATION

2.1 FLOW EQUATIONS

The derivation of governing equations for flow through saturated-unsaturated media can be derived based on (1) continuity of fluid, (2) continuity of solid, (3) motion of fluid (Darcy's law), (4) consolidation of the media, and (5) compressibility of water (Yeh and Ward 1980; Yeh 1987). Neglecting the compressibility of the media and water, we can write these equations as (Yeh 1987):

$$\frac{\partial \theta}{\partial t} - \frac{d\theta}{dh} \frac{\partial h}{\partial t} = \nabla \cdot (K \cdot \nabla H) + Q, \quad (2.1)$$

$$H = h + z, \quad (2.2)$$

$$V = -K \cdot \nabla H, \quad (2.3)$$

where

- θ - moisture content (L^3/L^3),
- h - pressure head (L),
- t - time (T),
- K - hydraulic conductivity tensor (L/T),
- H - total head (L),
- Q - source or sink representing the artificial injection or withdrawal of water [$(L^3/L^3)/T$],
- $d\theta/dh$ - water capacity (1/L),
- z - potential head (L),
- V - Darcy's velocity (L/T).

Equations (2.1) through (2.3) and the constitutive relationships among the pressure head, moisture content, and hydraulic conductivity tensor, together with associated, appropriate initial and boundary conditions, can be used to compute the temporal-spatial distributions of the hydrological variables including pressure head, total head, moisture content, and the Darcy's velocity. These hydrological variables are necessary factors in determining the transport of solutes through saturated-unsaturated subsurface systems. Hence, the construction of a numerical model to solve Eqs. (2.1) through (2.3) is a necessary first step in the ultimate aim of building a model to simulate solute transport. A finite-element model has been constructed to achieve this purpose (Yeh 1987), and it will not be repeated here. Equations (2.1) through (2.3) are provided in this report because they are needed for deriving the advective form of the hydrological transport equations to be given in the next section.

2.2 HYDROLOGICAL TRANSPORT EQUATIONS

Two of the most frequently mentioned nomenclatures in chemical transport modeling are components and species. Definitions of these terms loosely follow those of Westall et al. (1976). Components are a set of linearly independent "basis" chemical entities such that every species can be uniquely represented as a combination of those components; and no component can be represented by other components than itself. For example, in a simple system containing water, carbon, and calcium, we can choose Ca^{2+} , CO_3^{2-} , and H^+ as the components, then all other species can

be considered as the products of these three basis chemical species; Ca^{2+} cannot be represented as a product of CO_3^{2-} and H^+ , CO_3^{2-} cannot be represented as a combination of Ca^{2+} and H^+ , and H^+ cannot be represented as a product of Ca^{2+} and CO_3^{2-} . In addition, we require that the global mass of a component be reaction invariant (Rubin 1983). A species is the product of a chemical reaction involving the components as reactants (Westall et al. 1976). For example, in the above simple system, the species HCO_3^- is the product of H^+ and CO_3^{2-} .

Let us consider a system of N chemical components. The N chemical components consist of N_a aqueous components (mobile components), N_s adsorbent components (immobile adsorbing sites), and one immobile ion exchange site. The N_a aqueous components will react with each other to form M_x complexed species and M_p precipitated species. In addition, any aqueous component has a species free from chemical reactions. This species is termed the aqueous component species. Thus, the total number of aqueous species, M_a , is the sum of N_a aqueous component species and M_x complexed species. The N_a aqueous components and N_s adsorbent components will react to form M_y adsorbed species for the case of sorption via surface complexation (adsorption). Any adsorbent component has a species free from adsorption reactions. This species is termed the adsorbent component species. In the meantime, some or all of N_a aqueous component species and M_x complexed species may compete with each other for the ion exchange site. Assume M_z species out of N_a aqueous component species and M_x complexed species are involved in ion exchange reactions. The total

number of sorbent species, M_s , is the sum of N_s adsorbent component species, M_y adsorbed species, and M_z ion-exchanged species. Thus, the total number of chemical species, M , is equal to the sum of N_s , M_s , and M_p . For the purpose of deriving the chemical transport equations, we assume that the aqueous component species and complexed species are subject to hydrological transport, whereas the precipitated species, adsorbent component species, adsorbed species, and ion-exchanged species are not subject to hydrological transport.

For clarity, when we speak of aqueous species, we mean aqueous component species and complexed species. Similarly, when we speak of adsorbent species, we mean to include adsorbent component species and adsorbed species, whereas when we speak of sorbent species, we mean to include adsorbent component species, adsorbed species, and ion-exchanged species. When we speak of sorbed species, we mean adsorbed species and ion-exchanged species.

The general transport equation governing the temporal-spatial distribution of any chemical species in a multicomponent system can be derived based on the principle of conservation of mass. Let c_j be the concentration of the j -th aqueous component species. The governing equation for c_j can be obtained by applying this principle in integral form as follows:

$$\frac{D}{Dt} \int_{\nu} \theta c_j d\nu = - \int_{\Gamma} \mathbf{n} \cdot \mathbf{J}_j d\Gamma + \int_{\nu} \theta r_j^a d\nu - \int_{\nu} \theta i_j^a d\nu + \int_{\nu} m_j^a d\nu, \quad j = 1, 2, \dots, N_a \quad (2.4)$$

where

- ν - material volume containing constant amount of media (L^3),
- c_j - concentration of the j -th aqueous component species, (M/L^3)
- Γ - surface enclosing the material volume ν (L^2),
- $\mathbf{n}$ - outward unit vector normal to the surface Γ ,
- $\mathbf{J}_j$ - $\theta c_j (\mathbf{V}_j - \mathbf{V}_f)$ is the surface flux of the j -th aqueous component species with respect to fluid velocity $\mathbf{V}_f$ [$(M/T)/L^2$],
- r_j^a - production rate of the j -th aqueous component species per unit fluid volume due to all chemical reactions [$(M/L^3)/T$],
- i_j^a - rate of decay of the j -th aqueous component species, [$(M/L^3)/T$],
- m_j^a - external source/sink rate of the j -th aqueous component species [$(M/L^3)/T$],
- N_a - number of aqueous component species.

By the Reynolds transport theorem (Owczarek, 1964), Eq. (2.4) can be written as

$$\int_{\nu} \frac{\partial \theta c_j}{\partial t} d\nu + \int_{\Gamma} \mathbf{n} \cdot (\theta c_j \mathbf{V}_f) d\Gamma + \int_{\Gamma} \mathbf{n} \cdot \mathbf{J}_j d\Gamma = \int_{\nu} \theta r_j^a d\nu - \int_{\nu} \theta i_j^a d\nu + \int_{\nu} m_j^a d\nu, \quad j = 1, 2, \dots, N_a \quad (2.5)$$

where

$\mathbf{V}_f$ - fluid velocity (L/T).

The fluid velocity V_f and Darcy velocity V are related to each other by

$$V = \theta V_f \quad (2.6)$$

Applying the Gaussian divergence theorem to Eq. (2.5) and using the fact that ν is arbitrary, one can obtain the following continuity equation for the j -th aqueous component species in differential form:

$$\frac{\partial \theta c_j}{\partial t} + \nabla \cdot (\theta c_j V_f) + \nabla \cdot J_j = \theta (r_j^a - i_j^a) + m_j^a, \quad j = 1, 2, \dots, N_a \quad (2.7)$$

The surface flux J_j has been postulated to be proportional to the gradient of c_j (Nguyen et al., 1982) as

$$J_j = -\theta D \cdot \nabla c_j, \quad j = 1, 2, \dots, N_a \quad (2.8a)$$

$$\theta D = a_T |V| \delta + (a_L - a_T) V V / |V| + a_m \theta \tau \delta \quad (2.8b)$$

where

a_T = transverse diffusivity (L),

δ = Kronecker delta tensor,

$|V|$ = the magnitude of the Darcy velocity V (L/T),

a_L = longitudinal diffusivity (L),

a_m = molecular diffusion coefficient (L^2/T),

τ = tortuosity.

Substitution of Eqs. (2.6) and (2.8) into Eq. (2.7) yields

$$\frac{\partial \theta c_j}{\partial t} + \nabla \cdot (c_j V) - \nabla \cdot (\theta D \cdot \nabla c_j) = \theta (r_j^a - i_j^a) + m_j^a, \quad j = 1, 2, \dots, N_a \quad (2.9)$$

Eq. (2.9) is simply the statement of mass balance over a differential volume. The first term represents the rate of mass accumulation, the second term represents the net rate of mass flux due to advection, the third term is the net mass flux due to dispersion and diffusion, the fourth term is the rate of mass production and reduction due to chemical reactions and radioactive decay, and the last term is source/sink term corresponding to artificial injection and or withdrawal.

Eq. (2.9) is written in conservative form. It has been suggested that using the advective form is sometimes more appropriate, especially if the finite element method is used to simulate the chemical transport equation (Huyakorn et al., 1985). More importantly, an advective form of transport equations allows one to use the mixed Lagrangian-Eulerian approach, which can better solve advection-dominant transport problems (Yeh and Tripathi, 1987). Therefore, an advective form of the transport equation is derived by expanding the advection term and using the continuity equation for water flow

$$\partial \theta / \partial t = - \nabla \cdot \mathbf{V} + Q \quad (2.10)$$

which is obtained by combining Eqs. (2.1) and (2.3). Performing the necessary manipulation, we obtain

$$\theta \frac{\partial c_j}{\partial t} + \mathbf{V} \cdot \nabla c_j - \nabla \cdot (\theta \mathbf{D} \cdot \nabla c_j) = \theta (r_j^a - \lambda_j^a) + m_j^a - Q c_j$$

$$j = 1, 2, \dots, N_a \quad (2.11)$$

To simplify the notation and for convenience of derivation, let us rewrite Eq. (2.11) in the following form:

$$\theta \frac{\partial c_j}{\partial t} = L(c_j) + \theta(r_j^a - \epsilon_j^a) + m_j^a - Qc_j, \quad j = 1, 2, \dots, N_a \quad (2.12)$$

in which L is the advection-dispersion operator denoting

$$L(c) = -V \cdot \nabla c + \nabla \cdot (\theta D \cdot \nabla c) \quad (2.13)$$

Since any complexed species is subject to the same hydrological transport mechanism as the aqueous component species, its governing transport equation would be identical in form to Eq. (2.12). If we let x_i denote the concentration of the i -th complexed species, we have the following transport equation:

$$\theta \frac{\partial x_i}{\partial t} = L(x_i) + \theta(r_i^x - \epsilon_i^x) + m_i^x - Qx_i, \quad i = 1, 2, \dots, M_x \quad (2.14)$$

where

- x_i = concentration of the i -th complexed species,
- r_i^x = production rate of i -th complexed species per unit fluid volume due to the i -th complexation reaction $[(M/T)/L^3]$,
- ϵ_i^x = rate of decay of the i -th complexed species, $[(M/L^3)/T]$,
- m_i^x = external source/sink rate of the i -th complexed species $[(M/L^3)/T]$,
- M_x = number of complexed species.

Because it is assumed that adsorbent component species, adsorbed species, ion-exchanged species, and precipitated species are not subject

to hydrological transport, their transport equations can be obtained by expanding the first term and by dropping the second and third terms on the left-hand side of Eq. (2.9):

$$\theta \frac{\partial s_j}{\partial t} + \frac{\partial \theta}{\partial t} s_j = \theta (r_j^s - \iota_j^s) + m_j^s, \quad j = 1, 2, \dots, N_s \quad (2.15)$$

$$\theta \frac{\partial y_i}{\partial t} + \frac{\partial \theta}{\partial t} y_i = \theta (r_i^y - \iota_i^y) + m_i^y, \quad i = 1, 2, \dots, M_y \quad (2.16)$$

$$\theta \frac{\partial z_i}{\partial t} + \frac{\partial \theta}{\partial t} z_i = \theta (r_i^z - \iota_i^z) + m_i^z, \quad i = 1, 2, \dots, M_z \quad (2.17)$$

and

$$\theta \frac{\partial p_i}{\partial t} + \frac{\partial \theta}{\partial t} p_i = \theta (r_i^p - \iota_i^p) + m_i^p, \quad i = 1, 2, \dots, M_p \quad (2.18)$$

where

- s_j - concentration of the j -th adsorbent component species, (M/L^3)
- r_j^s - production rate of the j -th adsorbent component species per unit fluid volume due to all sorption reactions $[(M/L^3)/T]$,
- m_j^s - external source/sink rate of the j -th adsorbent component species $[(M/L^3)/T]$,
- ι_j^s - rate of decay of the j -th adsorbent component species, $[(M/L^3)/T]$,
- N_s - number of adsorbent component species,
- y_i - concentration of the i -th adsorbed species (M/L^3) ,
- r_i^y - production rate of the i -th adsorbed species per unit fluid volume due the i -th adsorption reaction $[(M/T)/L^3]$,
- m_i^y - external source/sink rate of the i -th adsorbed species $[(M/L^3)/T]$,
- ι_i^y - rate of decay of the i -th adsorbed species, $[(M/L^3)/T]$,
- M_y - number of adsorbed species,
- z_i - concentration of the i -th ion-exchanged species (M/L^3) ,
- r_i^z - production rate of the i -th ion-exchanged species per unit fluid volume due the i -th ion-exchange reaction $[(M/T)/L^3]$,

- m_i^z - external source/sink rate of the i-th ion-exchanged species $[(M/L^3)/T]$,
 λ_i^z - rate of decay of the i-th ion-exchanged species, $[(M/L^3)/T]$,
 M_z - number of ion-exchanged species,
 p_i - concentration of the i-th precipitated species (M/L^3) ,
 r_i^p - production rate of the i-th precipitated species per unit fluid volume due to the i-th precipitation reaction $[(M/T)/L^3]$,
 m_i^p - external source/sink rate of the i-th precipitated species $[(M/L^3)/T]$,
 λ_i^p - rate of decay of the i-th precipitated species, $[(M/L^3)/T]$,
 M_p - number of precipitated species.

Equations (2.12) and (2.14) through (2.18) constitute six sets of equations for six sets of unknowns, c_j , x_i , s_j , y_i , z_i , and p_i . These equations form a closed system if the chemical production rates r_j^a , r_i^x , r_j^s , r_i^y , r_i^z , and r_i^p are known functions of c_j , x_i , s_j , y_i , z_i , and p_i . The functional relationships can be postulated from chemical reactions. Chemical reactions considered in this report are (1) aqueous complexation, (2) adsorption/desorption, (3) ion exchange, (4) precipitation-dissolution, (5) redox, and (6) acid-base reactions. Equations (2.12) and (2.14) through (2.18) can be further simplified regardless of whether the chemical reactions are in equilibrium or are controlled by kinetics. The simplification is demonstrated below.

As used in Eqs. (2.20) through (2.25), the superscripts x, y, z, and p in a^x , a^y , a^z , and a^p signify the stoichiometric constants of aqueous

components for the following reactions; complexation, adsorption, ion-exchange, and precipitation. Multiplying Eq. (2.14) by a_{ij}^x and summing over i from 1 to M_x , multiplying Eq. (2.16) by a_{ij}^y and summing over i from 1 to M_y , multiplying Eq. (2.17) by a_{ij}^z and summing over i from 1 to M_z , multiplying Eq. (2.18) by a_{ij}^p and summing over i from 1 to M_p , adding the results to Eq. (2.12), we obtain:

$$\theta \frac{\partial T_j}{\partial t} + \frac{\partial \theta}{\partial t} (S_j + P_j) - L(C_j) - \theta \Lambda_j^a + M_j^a - QC_j, \quad j = 1, 2, \dots, N_a \quad (2.19)$$

in which

$$C_j = c_j + \sum_{i=1}^{M_x} a_{ij}^x x_i, \quad j = 1, 2, \dots, N_a, \quad (2.20)$$

$$S_j = \sum_{i=1}^{M_y} a_{ij}^y y_i + \sum_{i=1}^{M_z} a_{ij}^z z_i, \quad j = 1, 2, \dots, N_a, \quad (2.21)$$

$$P_j = \sum_{i=1}^{M_p} a_{ij}^p p_i, \quad j = 1, 2, \dots, N_a, \quad (2.22)$$

$$T_j = c_j + \sum_{i=1}^{M_x} a_{ij}^x x_i + \sum_{i=1}^{M_y} a_{ij}^y y_i + \sum_{i=1}^{M_z} a_{ij}^z z_i + \sum_{i=1}^{M_p} a_{ij}^p p_i, \quad j = 1, 2, \dots, N_a, \quad (2.23)$$

$$M_j^a = m_j^a + \sum_{i=1}^{M_x} a_{ij}^x m_i^x + \sum_{i=1}^{M_y} a_{ij}^y m_i^y + \sum_{i=1}^{M_z} a_{ij}^z m_i^z + \sum_{i=1}^{M_p} a_{ij}^p m_i^p, \quad j = 1, 2, \dots, N_a, \quad (2.24)$$

$$\Lambda_j^a = r_j^a + \sum_{i=1}^{M_x} a_{ij}^x r_i^x + \sum_{i=1}^{M_y} a_{ij}^y r_i^y + \sum_{i=1}^{M_z} a_{ij}^z r_i^z + \sum_{i=1}^{M_p} a_{ij}^p r_i^p, \quad j = 1, 2, \dots, N_a, \quad (2.25)$$

where

- C_j - total dissolved concentration of the j-th aqueous component (M/L^3),
- S_j - total sorbed (adsorbed plus ion-exchanged) concentration of the j-th aqueous component (M/L^3),
- P_j - total precipitated concentration of the j-th aqueous component (M/L^3),
- T_j - total analytical concentration of the j-th aqueous component (M/L^3),
- M_j^a - total rate of source/sink of the j-th aqueous component ($M/L^3/T$),
- Λ_j^a - total decay rate of the j-th aqueous component ($M/L^3/T$),
- a_{ij}^x - stoichiometric coefficient of the j-th aqueous component in the i-th complexed species,
- a_{ij}^y - stoichiometric coefficient of the j-th aqueous component in the i-th adsorbed species,
- a_{ij}^z - stoichiometric coefficient of the j-th aqueous component in the i-th ion-exchanged species,
- a_{ij}^p - stoichiometric coefficient of j-th aqueous component in i-th precipitated species.

In deriving Eq. (2.19), we have used the following relationship,

$$r_j^a + \sum_{i=1}^{M_x} a_{ij}^x r_i^x + \sum_{i=1}^{M_y} a_{ij}^y r_i^y + \sum_{i=1}^{M_z} a_{ij}^z r_i^z + \sum_{i=1}^{M_p} a_{ij}^p r_i^p = 0, \quad j = 1, 2, \dots, N_a, \quad (2.26)$$

which results from the requirement that a component is reaction invariant.

The source/sink term M_j^a and decay term Λ_j^a can be defined by

$$M_j^a = QC_j^*, \quad j = 1, 2, \dots, N_a \quad (2.27)$$

and

$$\Lambda_j^a = \lambda_j^a T_j, \quad j = 1, 2, \dots, N_a \quad (2.28)$$

where

$$C_j^* = \begin{cases} \text{input concentration of the } j\text{-th aqueous component} \\ \text{if } Q \text{ is source (injection) (M/L)}, \\ -C_j \text{ if } Q \text{ is a sink (withdrawal) (M/L)}, \end{cases}$$

$$\lambda_j^a = \text{rate constant of the } j\text{-th aqueous component (1/T)}.$$

It is seen from the definition of C_j^* that the terms M_j^a and QC_j in Eq. (2.19) cancel each other for the cases of sink (withdrawal). Thus, another advantage of using the advection form of the transport equation is: one does not need to include the sink in the equation.

Similarly, we can derive the governing equations for the total analytical concentrations of adsorbent components and the number of equivalents occupying the ion-exchange site. However, it should be noted that for adsorbent components, the total analytical concentrations are the same as total adsorbed concentrations since the sum of total dissolved concentration and total precipitated concentration for any adsorbent component is zero. This is so because adsorbent components are not present in the aqueous species nor in the precipitated species. On the other hand, the total sorbed concentration of any aqueous component is not zero but is given by Eq. (2.21) because aqueous components are present in sorbed species either via surface complexation or via ion exchange. With these brief comments, we derive the governing equations for the total

analytical concentrations of all adsorbent components as follows.

Let b_{ij}^y signify the stoichiometric coefficients of the adsorbent components for adsorption reaction. Multiplying Eq. (2.16) by b_{ij}^y and summing over i from 1 to M_y , adding the results to Eq. (2.15), we obtain

$$\theta \frac{\partial W_j}{\partial t} + \frac{\partial \theta}{\partial t} W_j = -\theta \Lambda_j^s + M_j^s, \quad j = 1, 2, \dots, N_s \quad (2.29)$$

in which

$$W_j = s_j + \sum_{i=1}^{M_y} b_{ij}^y y_i, \quad j = 1, 2, \dots, N_s \quad (2.30)$$

$$M_j^s = m_j^s + \sum_{i=1}^{M_y} b_{ij}^y m_i^y, \quad j = 1, 2, \dots, N_s \quad (2.31)$$

$$\Lambda_j^s = \lambda_j^s + \sum_{i=1}^{M_y} b_{ij}^y \lambda_i^y, \quad j = 1, 2, \dots, N_s \quad (2.32)$$

where

W_j = total analytical concentration of the j -th adsorbent component (M/L^3),

b_{ij}^y = stoichiometric coefficient of the j -th adsorbent component in the i -th sorbed species,

M_j^s = total rate of source/sink of the j -th adsorbent component ($M/L^3/T$),

Λ_j^s = total decay rate of the j -th adsorbent component, ($M/L^3/T$).

The following relationship that results from the requirement that adsorption is reaction invariant with respect to any adsorbent component

$$r_j^s + \sum_{i=1}^{M_y} b_{ij}^y r_i^y = 0, \quad j = 1, 2, \dots, N_s \quad (2.33)$$

has been used in deriving Eq. (2.29). In addition, the source/sink term M_j^s is assumed to be zero,

$$M_j^s = 0, \quad j = 1, 2, \dots, N_s \quad (2.34)$$

The decay term Λ_j^s can be defined as

$$\Lambda_j^s = \lambda_j^s W_j, \quad j = 1, 2, \dots, N_s \quad (2.35)$$

where

$$\lambda_j^s = \text{rate constant of the } j\text{-th adsorbent component (1/T).}$$

The governing equation for the ion-exchange site is obtained similarly but with the exception that we have assumed the site is completely occupied. Multiplying Eq. (2.17) by ν_i and summing over i from 1 to M_z , we obtain

$$\theta \frac{\partial N_{eq}}{\partial t} + \frac{\partial \theta}{\partial t} N_{eq} = -\theta \Lambda_{eq} + M_{eq}, \quad (2.36)$$

in which

$$N_{eq} = \sum_{i=1}^{M_z} \nu_i z_i, \quad (2.37)$$

$$M_{eq} = \sum_{i=1}^{M_z} \nu_i m_i^z, \quad (2.38)$$

$$\Lambda_{eq} = \sum_{i=1}^{M_z} \nu_i i^z, \quad (2.39)$$

where

N_{eq} = number of equivalents of the ion-exchange site per unit volume of solution (M/L^3),

ν_i = charge of the i -th ion-exchanged species,

M_{eq} = total rate of source/sink of the ion-exchange site ($M/L^3/T$),

Λ_{eq} = total decay rate of the ion-exchange site, ($M/L^3/T$).

The following relationship that results from the requirement of invariability for the ion-exchange site

$$\sum_{i=1}^{M_z} \nu_i i^z = 0, \quad (2.40)$$

has been used in deriving Eq. (2.36). In addition, the source/sink term M_{eq} is assumed to be zero, that is,

$$M_{eq} = 0. \quad (2.41)$$

The decay term Λ_{eq} can be defined as

$$\Lambda_{eq} = \lambda_{eq} N_{eq}, \quad (2.42)$$

where

λ_{eq} = rate constant of the ion-exchange site ($1/T$).

Equations (2.19) through (2.23), (2.29), (2.30), (2.36), and (2.37) constitute 9 sets of equations in 12 sets of unknowns (T_j 's, C_j 's, S_j 's, P_j 's, c_j 's, W_j 's, N_{eq} , s_j 's, x_i 's, y_i 's, z_i 's, and p_i 's); hence, the

formulation is not complete. Three sets of constitutive relationships among those unknowns must be prescribed to complete the formulation. For hydrological transport modeling, the constitutive relationships are often posed empirically. For example, with the K_d concept, the relationship is given as follows:

$$T_j = R_{dj}C_j, \quad R_{dj} = 1 + \rho_b K_{dj}/\theta, \quad j = 1, 2, \dots, N_a, \quad (2.43a)$$

$$S_j = (\rho_b K_{dj}/\theta)C_j, \quad j = 1, 2, \dots, N_a, \quad (2.43b)$$

$$P_j = 0, \quad j = 1, 2, \dots, N_a, \quad (2.43c)$$

where

R_{dj} - retardation factor of the j -th component (dimensionless),

ρ_b - bulk density of the medium (M/L^3),

K_{dj} - distribution coefficient of the j -th aqueous component (L^3/M).

For coupled hydrological transport and geochemical equilibrium modeling, a chemical equilibrium model is normally adopted to give the implicit functional relationships among T_j 's, C_j 's, S_j 's, P_j 's, c_j 's, W_j 's, N_{eq} , s_j 's, x_i 's, y_i 's, z_i 's, and p_i 's, as described in the following section.

2.3 CHEMICAL EQUILIBRIUM EQUATIONS

Chemical equilibrium can be dealt with in essentially two ways: the ion association theory (Bjerrum 1926; Fuoss 1935) and the mixed electrolyte theory (Reilly et al. 1971). Nearly all computerized models

are based on the ion association theory (Nordstrom et al. 1979). Within this framework, the species distribution can be formulated in two distinct but thermodynamically related ways: the equilibrium constant approach and the Gibbs free-energy approach. In the Gibbs free-energy approach, the species distributions are obtained by minimizing the total Gibbs free-energy function of a given set of species subject to the constraints of mass balance equations. In the equilibrium constant approach, the set of nonlinear AEs is obtained based on the law of mass action and the principle of mole balance (Morel and Morgan 1972). This set of nonlinear AEs is then solved to yield the species distributions. In the latter approach, equilibrium constants are needed for the data base, whereas in the former approach, free-energy values are needed.

In the equilibrium constant approach, the formation of a complexed species x_i , an adsorbed species y_i , an ion-exchanged species z_i , or a precipitated (solid) species p_i is described at equilibrium by the law of mass action.

2.3.1 Complexation Reactions

The law of mass action for each complexation reaction is written as

$$A_i^x = K_i^x \prod_{k=1}^{N_a} X_k^{a_{ik}^x}, \quad i = 1, 2, \dots, M_x, \quad (2.44)$$

where

A_i^x - activity of the i -th complexed species,

K_i^x - equilibrium constant of the i -th complexed species,

X_k - activity of the k-th aqueous component species,
 a_{ik}^x - stoichiometric coefficient of the k-th aqueous
 component in the i-th complexed species.

The activities of all aqueous species are related to the species concentrations using the concept of activity coefficients. Thus,

$$A_i^x = \gamma_i^x x_i, \quad i = 1, 2, \dots, M_x, \quad (2.45a)$$

$$X_j = \gamma_j^a c_j, \quad j = 1, 2, \dots, N_a, \quad (2.45b)$$

where

γ_i^x - activity coefficient of the i-th complexed species (L^3/M),
 γ_j^a - activity coefficient of the j-th aqueous component species
 (L^3/M).

Substituting Eqs. (2.45a) and (2.45b) into Eq. (2.44), we obtain

$$x_i = \alpha_i^x \prod_{k=1}^{N_a} c_k^{a_{ik}^x}, \quad i = 1, 2, \dots, M_x, \quad (2.46)$$

in which

$$\alpha_i^x = K_i^x \prod_{k=1}^{N_a} (\gamma_k^a)^{a_{ik}^x} / \gamma_i^x, \quad i = 1, 2, \dots, M_x, \quad (2.47)$$

is the modified stability constant of the i-th complexed species. It is noted that the thermodynamic equilibrium constant K_i^x depends on the temperature and pressure of the system, whereas the activity coefficients γ_k^a 's and γ_i^x 's are functions of the ionic strength of the system. The ionic strength of the system is a function of the concentrations of all

aqueous species. Thus, the modified stability constants are functions of temperature, pressure, and concentrations of all aqueous species.

2.3.2 Adsorption/desorption Reactions

The law of mass action for each adsorption/desorption reaction is written as follows

$$B_i^y = K_i^y \left(\prod_{k=1}^{N_a} X_k^{a_{ik}^y} \right) \left(\prod_{k=1}^{N_s} Y_k^{b_{ik}^y} \right), \quad i = 1, 2, \dots, M_y, \quad (2.48)$$

where

- B_i^y - activity of the i -th adsorbed species of surface complexation,
- K_i^y - equilibrium constant of the i -th adsorbed species (dimensionless),
- a_{ik}^y - stoichiometric coefficient of the k -th aqueous component in the i -th adsorbed species of surface complexation,
- Y_k - activity of the k -th adsorbent component species,
- b_{ik}^y - stoichiometric coefficient of the k -th adsorbent component in the i -th adsorbed species of surface complexation.

Assuming that the activities of all adsorbent species are related to the species concentrations using the concept of activity coefficients, we obtain

$$B_i^y = \gamma_i^y y_i, \quad i = 1, 2, \dots, M_y, \quad (2.49a)$$

$$Y_j = \gamma_j^s s_j, \quad j = 1, 2, \dots, N_s, \quad (2.49b)$$

where

γ_i^y - activity coefficient of the i -th adsorbed species (L^3/M).

γ_j^s = activity coefficient of the j-th adsorbent component species (L^3/M).

Substitution of Eqs. (2.45b), (2.49a) and (2.49b) into Eq. (2.48) yields

$$y_i = \alpha_i^y \left(\prod_{k=1}^{N_a} c_k^{a_{ik}^y} \right) \left(\prod_{k=1}^{N_s} s_k^{b_{ik}^y} \right), \quad i = 1, 2, \dots, M_y, \quad (2.50)$$

in which

$$\alpha_i^y = K_i^y \left[\prod_{k=1}^{N_a} (\gamma_k^a)^{a_{ik}^y} \right] \left[\prod_{k=1}^{N_s} (\gamma_k^s)^{b_{ik}^y} \right] / \gamma_i^y, \quad i = 1, 2, \dots, M_y, \quad (2.51)$$

is the modified stability constant of the i-th adsorbed species.

2.3.3 Ion Exchange Reactions

The law of mass action for each ion exchange is written as follows

$$K_{iJ} = \left(\frac{B_i}{A_i} \right)^{\nu_J} \left(\frac{A_J}{B_J} \right)^{\nu_i}, \quad i = 1, 2, \dots, J-1, J+1, \dots, M_z, \quad (2.52)$$

where

K_{iJ} = selectivity coefficient of the i-th species with respect to the J-th species or the effective equilibrium constant of i-th ion-exchanged species (dimensionless),

A_i = activity of the i-th aqueous species denoting either A_i^x or X_j ,

B_i = activity of the i-th ion-exchanged species denoting either exchanged A_i^x or exchanged X_j ,

ν_i = charge of the i-th ion-exchanged species.

In the ion exchange model, the activities of aqueous species are related to species concentrations with activity coefficients. However, the

activity of any ion-exchanged species is assumed to be proportional to its molar concentration. Thus, we have

$$A_i = \gamma_i a_i, \quad (2.53a)$$

$$B_i = z_i/s_T, \quad (2.53b)$$

$$s_T = \sum_{i=1}^{M_z} z_i, \quad (2.53c)$$

where

γ_i = activity coefficient of the i -th aqueous species denoting either γ_i^a or γ_j^x , (L^3/M),

a_i = molar concentration of the i -th aqueous species denoting either c_j or x_i (M/L^3),

z_i = molar concentration of the i -th ion-exchanged species, denoting either exchanged c_j or x_i (M/L^3),

s_T = total concentration of all ion-exchanged species (M/L^3).

Substituting Eqs. (2.53a) and (2.53b) into Eq. (2.52), we obtain

$$\kappa_{iJ} = \frac{(z_i/s_T)^{\nu_J} a_J^{\nu_i}}{(z_J/s_T)^{\nu_i} a_i^{\nu_J}}, \quad i = 1, 2, \dots, J-1, J+1, \dots, M_z, \quad (2.54a)$$

where κ_{iJ} is the modified selectivity coefficient given by

$$\kappa_{iJ} = K_{iJ} \gamma_i^{\nu_J} / \gamma_J^{\nu_i} \quad (2.54b)$$

Equations (2.54a) and (2.37) constitute M_z equations for M_z unknown z_i 's. For homovalent exchange, substituting Eq. (2.46) into Eqs. (2.54a) and (2.37), and with adequate mathematical manipulation, we obtain equations in which the concentrations of every ion-exchanged species can be expressed as a function of aqueous component species concentrations and the ion-exchanged site as

$$z_i = f_i(c_1, c_2, \dots, c_{N_a}; N_{eq}), \quad i = 1, 2, \dots, M_z, \quad (2.54c)$$

For general heterovalent exchange, it is very difficult to derive such an analytical expression for the concentrations z_i 's, and numerical evaluations of z_i 's in terms of c_k 's via Eqs. (2.54a) and (2.37) are normally used.

2.3.4 Precipitation-dissolution Reactions

The law of mass action for each precipitation-dissolution reaction is written as

$$1 = K_i^P \prod_{k=1}^{N_a} X_k^{a_{ik}^P}, \quad i = 1, 2, \dots, M_p, \quad (2.55)$$

where

- K_i^P = equilibrium constant of the i -th precipitated species,
- a_{ik}^P = stoichiometric coefficient of the k -th aqueous component in the i -th precipitated species,
- M_p = number of precipitated species.

Substituting Eqs. (2.45b) into Eq. (2.55), one obtains

$$1 = \alpha_i^p \prod_{k=1}^{N_a} c_k^{a_{ik}^p}, \quad i = 1, 2, \dots, M_p, \quad (2.56)$$

in which

$$\alpha_i^p = K_i^p \prod_{k=1}^{N_a} (\gamma_k^a)^{a_{ik}^p}, \quad i = 1, 2, \dots, M_p, \quad (2.57)$$

is the modified stability constant of the i -th precipitated species.

Equation (2.56) represents a chemical action expression: the solubility product equation. As in all other solubility product equations of physical chemistry, it does not contain the precipitated molar concentration p_i because it assumes that the activity of the solids is constant (Pauling 1956). The absence of p_i 's from the chemical action expressions characterizes the chemical reaction of precipitation-dissolution and distinguishes it from other heterogeneous classes of chemical reactions, such as adsorption and ion exchange, and from homogeneous reaction of soluble complexation. This implies that models developed specifically for dealing with complexation and sorption are not necessarily capable of handling precipitation-dissolution.

2.3.5 Redox Reactions and Electron Activity

Redox reactions are a class of chemical reactions involving a transfer of electrons. Hence, when redox reactions are present in a system, we must invoke the principle of conservation of electrons to ensure that all electrons donated by chemical species are accepted by another species. This is equivalent to the statement that oxidation

numbers must be conserved in a chemical reaction.

In nonredox systems, the total analytical concentrations of all components and the number of equivalents of the ion-exchange site must be known before one can calculate the concentrations of all species. In redox systems, the unknowns are not only the concentrations of all species but also a redox parameter that describes the oxidation state of the system. To be consistent with the approach that uses concentrations or activities as unknowns, the "activity of electrons," designated by the symbol X_e in this report, is normally used as the redox parameter. Hence in redox systems, both the total analytical concentrations of all components and the number of equivalents of the ion exchange site and the total concentration of the "operational electrons" must be known before the concentrations of all species and the activity of electrons (or the p_e value) can be computed (Walsh et al. 1984). Total analytical concentrations of all components are determined by solving the transport equations [Eq. (2.19)] for aqueous components and the mass balance equations [Eq. (2.29)] for adsorbent components, respectively. The number of equivalents of the ion exchange site is obtained by solving the transport equation, Eq. (2.36). A transport equation for operational electron is needed to determine the total concentration of "operational electrons."

Multiplying Eq. (2.12) by a_{je}^a and summing over j from 1 to N_a , multiplying Eq. (2.14) by a_{ie}^x and summing over i from 1 to M_y , multiplying

Eq. (2.15) by a_{je}^s and summing over j from 1 to N_s , multiplying Eq. (2.16) by a_{ie}^y and summing over i from 1 to M_y , multiplying Eq. (2.17) by a_{ie}^z and summing over i from 1 to M_z , multiplying Eq. (2.18) by a_{ie}^p and summing over i from 1 to M_p , adding the results to the transport equation of the free electron species [this transport equation is identical in form to Eq. (2.12) with the subscript j replaced by e], and invoking the principle of conservation of electrons, one obtains an equation identical in form to Eq. (2.19) for describing the transport of operational electron, but with C_e , S_e , P_e , T_e , M_e^a , and Λ_e^a replacing C_j , S_j , P_j , T_j , M_j^a , and Λ_j^a , respectively (Walsh et al. 1984). [Walsh et al. use the term "available electron". We think the term "operational electron" is more appropriate.] However, the definitions of C_e , S_e , P_e , T_e , M_e^a , and Λ_e^a are slightly different from those of C_j , S_j , P_j , T_j , M_j^a , and Λ_j^a . The quantities C_e , S_e , P_e , T_e , M_e^a , and Λ_e^a are given by

$$C_e = c_e + \sum_{j=1}^{N_a} a_{je}^a c_j + \sum_{i=1}^{M_x} a_{ie}^x x_i, \quad (2.58)$$

$$S_e = \sum_{j=1}^{N_s} a_{je}^s s_j + \sum_{i=1}^{M_y} a_{ie}^y y_i + \sum_{i=1}^{M_z} a_{ie}^z z_i, \quad (2.59)$$

$$P_e = \sum_{i=1}^{M_p} a_{ie}^p p_i, \quad (2.60)$$

$$T_e = c_e + \sum_{j=1}^{N_a} a_{je}^a c_j + \sum_{i=1}^{M_x} a_{ie}^x x_i + \sum_{i=1}^{M_z} a_{ie}^z z_i +$$

$$\sum_{j=1}^{N_s} a_{je}^s s_j + \sum_{i=1}^{M_y} a_{ie}^y y_i + \sum_{i=1}^{M_p} a_{ie}^p p_i, \quad (2.61)$$

$$M_e^a = m_e^a + \sum_{j=1}^{N_a} a_{je}^a m_j^a + \sum_{i=1}^{M_x} a_{ie}^x m_i^x + \sum_{i=1}^{M_z} a_{ie}^z m_i^z +$$

$$\sum_{j=1}^{N_s} a_{je}^s m_j^s + \sum_{i=1}^{M_y} a_{ie}^y m_i^y + \sum_{i=1}^{M_p} a_{ie}^p m_i^p, \quad (2.62)$$

$$\Lambda_e^a = \iota_e^a + \sum_{j=1}^{N_a} a_{je}^a \iota_j^a + \sum_{i=1}^{M_x} a_{ie}^x \iota_i^x + \sum_{i=1}^{M_z} a_{ie}^z \iota_i^z +$$

$$\sum_{j=1}^{N_s} a_{je}^s \iota_j^s + \sum_{i=1}^{M_y} a_{ie}^y \iota_i^y + \sum_{i=1}^{M_p} a_{ie}^p \iota_i^p, \quad (2.63)$$

where

- C_e - concentration of operational electrons in aqueous phase (M/L^3),
- S_e - concentration of operational electrons in sorbent phase (M/L^3),
- P_e - concentration of operational electrons in solid phase (M/L^3),
- T_e - total concentration of operational electrons (M/L^3),
- c_e - concentration of the free electrons in solution (M/L^3),
- a_{je}^a - stoichiometric coefficient of the electron in the j-th aqueous component species (dimensionless),
- a_{ie}^x - stoichiometric coefficient of the electron in the i-th complexed species (dimensionless),
- a_{je}^s - stoichiometric coefficient of the electron in the j-th adsorbent component species (dimensionless),
- a_{ie}^y - stoichiometric coefficient of the electron in the i-th adsorbed species (dimensionless),

a_{ie}^z - stoichiometric coefficient of the electron in the i-th ion-exchanged species (dimensionless),

a_{ie}^p - stoichiometric coefficient of the electron in the i-th precipitated species (dimensionless),

m_e^a - external source/sink rate of the free electron species $[(M/L^3)/T]$,

M_e^a - total rate of source/sink of the operational electron $[(M/L^3)/T]$,

λ_e^a - rate of decay of the free electron species $[(M/L^3)/T]$,

Λ_e^a - total rate of decay of the operational electron $[(M/L^3)/T]$.

These stoichiometric coefficients are given (Walsh et al. 1984) by

$$a_{je}^a = \sum_{k=1}^{N_e} h_{jk}^a (v_{mk} - v_{jk}^a), \quad j = 1, 2, \dots, N_a, \quad (2.64a)$$

$$a_{ie}^x = \sum_{k=1}^{N_e} h_{ik}^x (v_{mk} - v_{ik}^x), \quad i = 1, 2, \dots, M_x, \quad (2.64b)$$

$$a_{je}^s = \sum_{k=1}^{N_e} h_{jk}^s (v_{mk} - v_{jk}^s), \quad j = 1, 2, \dots, N_s, \quad (2.64c)$$

$$a_{ie}^y = \sum_{k=1}^{N_e} h_{ik}^y (v_{mk} - v_{ik}^y), \quad i = 1, 2, \dots, M_y, \quad (2.64d)$$

$$a_{ie}^z = \sum_{k=1}^{N_e} h_{ik}^z (v_{mk} - v_{ik}^z), \quad i = 1, 2, \dots, M_z, \quad (2.64e)$$

$$a_{ie}^p = \sum_{k=1}^{N_e} h_{ik}^p (v_{mk} - v_{ik}^p), \quad i = 1, 2, \dots, M_p, \quad (2.64f)$$

where

h_{jk}^a - stoichiometric coefficient of the k-th chemical element in the j-th aqueous component species,

h_{ik}^x - stoichiometric coefficient of the k-th chemical element in the i-th complexed component species,

h_{jk}^s - stoichiometric coefficient of the k-th chemical element in the j-th adsorbent component species,

h_{ik}^y - stoichiometric coefficient of the k-th chemical element in the i-th adsorbed species,

h_{ik}^z - stoichiometric coefficient of the k-th chemical element in the i-th ion-exchanged species,

h_{ik}^p - stoichiometric coefficient of the k-th chemical element in the i-th precipitated component species,

v_{jk}^a - valence of the k-th chemical element in the j-th aqueous component species,

v_{ik}^x - valence of the k-th chemical element in the i-th complexed species,

v_{jk}^s - valence of the k-th chemical element in the j-th adsorbent component species,

v_{ik}^y - valence of the k-th chemical element in the i-th adsorbed species,

v_{ik}^z - valence of the k-th chemical element in the i-th ion-exchanged species,

v_{ik}^p - valence of the k-th chemical element in the i-th precipitated species,

v_{mk} - valence of the k-th chemical element in its maximum oxidation state, except for oxygen in which $v_{mk} = -2$,

N_e - number of chemical elements considered in the system.

If component species are chosen such that they contain only chemical elements in their maximum oxidation state, then $a_{j_e}^g$'s and $a_{j_e}^s$'s are equal to zero and Eqs. (2.58) through (2.63) are identical in form to Eqs. (2.20) through (2.25), respectively. Choosing such components is especially useful for describing coupled transport and chemical equilibria problems involving redox reactions because the operational electron can be considered computationally an aqueous component. Nevertheless, even without such a choice, the operational electron can still be considered an aqueous component, but the possibility exists of having a negative total concentration.

When redox reactions occur in the system under consideration, the mass action equation for any species involving chemical elements of changing oxidation states must be modified to include the activity of electrons. For example, Eq. (2.46) for complexation reactions is modified by multiplying its right-hand side by X_e raised to the $a_{i_e}^x$ power. In the meantime, chemical components are chosen such that their chemical formulae contain only elements in maximum oxidation states. Under such circumstances, the electron is considered an aqueous component, and computationally no special treatment is needed for redox reactions (Reed 1982) except for one minor adjustment. This minor adjustment is to exclude the first term on the right-hand sides of Eqs. (2.58) and (2.61) through (2.63) in actual computations because free electrons do not exist in appreciable amount in solution.

2.3.6 Acid-Base Reactions and Proton Activity

Acid-base reactions are defined as a class of chemical reactions involving a transfer of protons. Acid-base reactions are among the simplest types of chemical reactions (Stumm and Morgan 1981). In a system involving acid-base reactions, an additional parameter describing the acidity of the system is needed. This additional parameter is the proton activity (or the pH value). The pH value may be simulated by using either the electroneutrality or proton condition. These two approaches can be shown to be mathematically equivalent but not computationally equivalent. In coupling the hydrological transport and chemical equilibria, it is preferable to use the proton-condition approach. In the proton-condition approach, the total concentration of the excess protons ($H^+ - OH^-$) must be known before activity of protons can be computed. A transport equation for excess proton is, therefore, needed to determine the total concentration of excess protons.

Applying the principle of conservation of mass to both oxygen and hydrogen, one obtains an equation identical in form to Eq. (2.19) describing the transport of excess protons, but with C_H , S_H , P_H , T_H , M_H^a , and Λ_H^a replacing C_j , S_j , P_j , T_j , M_j^a , and Λ_j^a , respectively. The algebraic equations defining C_H , S_H , P_H , T_H , M_H^a , and Λ_H^a are identical in form to Eqs. (2.20) through (2.25). However, if hydroxides appear in a species, the stoichiometric coefficient of the proton term in that species is negative. On the other hand, if hydrogens appear in a species, the stoichiometric coefficient of the proton term in that species is positive.

After this slight difference is considered and the mass action equation for any species involving hydrogen and/or hydroxide is modified to include the activity of protons, the proton can be considered an aqueous component. Thus, the computation of pH requires no special treatment; it can be simulated just as the activity of any other aqueous component. The only difference between the proton as an aqueous component and all other regular aqueous components is that the former can have a negative total analytical concentration (i.e., T_H may be negative), but the latter cannot have negative total analytical concentrations (i.e., T_j 's are always positive).

Because the simulation of pH and/or pe uses transport equations identical in form to Eq. (2.19), we can treat the proton and/or electron as aqueous components, and special consideration to distinguish proton and/or electron from other regular aqueous components is no longer needed. The only things we must keep in mind are that (1) the stoichiometric coefficient of the proton term in a species may be negative, resulting in a possibility of negative total analytical concentration of excess protons, and (2) when a chemical element is present at several oxidation states, only one of these can be considered to be a component and the others must be treated as species. For example, if Fe^{2+} and Fe^{3+} are present simultaneously in a system, we may consider Fe^{3+} to be a component species. Then Fe^{2+} shall be considered a complexed species, which is a product of Fe^{3+} and e^- . A mole of Fe^{2+} will contribute a mole of operational electrons to T_e and C_e . Of course, if we have not chosen the

stoichiometric coefficient of the electron term with respect to maximum oxidation state, a negative total analytical concentration of operational electron may result.

Although the full complement of geochemical reactions considered here include complexation, sorption, precipitation-dissolution, redox, and acid-base reactions, the term "full complement" is meant to include only the first three types of reactions because the latter two reactions require no special treatment as discussed previously. If only aqueous components are involved, a redox reaction can be treated as a complexation reaction when the resulting species is in aqueous phase or as a precipitation reaction when the resulting species is in solid phase. If aqueous components, adsorbent components, and the ion exchanged site are involved, it is treated as a sorption reaction. Similar treatment is given for acid-base reactions.

Equations (2.20) through (2.23), (2.30), (2.46), (2.50), (2.54), and (2.56) form 9 sets of equations and contain 12 sets of unknowns (C_j 's, S_j 's, P_j 's, T_j 's, W_j 's, N_{eq} , x_i 's, c_i 's, y_i 's, z_i 's, s_i 's, and p_i 's); the system is not closed. Three sets of equations are needed to close the chemical equilibrium model. For chemical equilibrium computations, it is generally assumed that the total analytical concentrations of all components and the ion-exchange site are given from measurements (Morel and Morgan 1972; Westall et al. 1976; Sposito and Mattigod 1980; Garrels and Thompson 1962; Kharaka and Barnes 1973; Plummer et al. 1976; Parkhurst

et al., 1980):

$$T_j = T_{jm} ; \quad j = 1, 2, \dots, N_a , \quad (2.65)$$

$$W_j = W_{jm} ; \quad j = 1, 2, \dots, N_a , \quad (2.66)$$

$$N_{eq} = CEC \quad (2.67)$$

where

T_{jm} - measured total analytical concentration of the j -th aqueous component (M/L^3),

W_{jm} - measured total analytical concentration of the j -th sorbent component (M/L^3),

CEC - cation exchange capacity.

For the coupled modeling of hydrological transport and geochemical equilibrium of multicomponent systems, these three sets of equations are given by Eqs. (2.19), (2.29), and (2.36), respectively.

2.4 INITIAL AND BOUNDARY CONDITIONS

To complete the description of the hydrological transport as given by Eqs. (2.19), (2.29), and (2.36), initial and boundary conditions must be specified in accordance with dynamic and physical consideration. It will be assumed that initially the total analytical concentrations for all components and the number of equivalents of the ion exchange site are known throughout the region of interest, that is,

$$T_j = T_{j0} \quad \text{at } t = 0 , \quad j = 1, 2, \dots, N_a , \quad (2.68)$$

$$W_j = W_{j0} \quad \text{at } t = 0, \quad j = 1, 2, \dots, N_s, \quad (2.69)$$

$$N_{eq} = N_{eq0} \quad \text{at } t = 0 \quad (2.70)$$

where

T_{j0} = Initial total analytical concentration of j-th aqueous component (M/L^3),

W_{j0} = Initial total analytical concentration of j-th adsorbent component (M/L^3),

N_{eq0} = Initial number of equivalents of the ion exchange site (M/L^3).

Initial concentrations for aqueous components may be obtained from field measurements or by solving the steady state version of Eq. (2.19) with time invariant boundary conditions.

The specification of boundary conditions is the most difficult and intricate task in multicomponent transport modeling. From the dynamic point of view, a boundary segment may be classified as either flow-through impervious. From physical point of view, it is a soil-air interface, or soil-soil interface, or soil-water interface. From the mathematical point of view, it may be treated as Dirichlet boundary on which the total analytical concentration is prescribed, Neumann boundary on which the flux due to the gradient of total analytical concentration is known, or Cauchy boundary on which the total flux is given. An even more difficult mathematical boundary is the variable conditions on which the boundary conditions are not known a priori but are themselves the solution to be sought. In other words, on the mathematically variable boundary, either

Neumann or Cauchy conditions may prevail and change with time. Which condition prevails at a particular time can be determined only in the cyclic processes of solving the governing equations (Freeze 1972a, 1972b; Yeh and Ward 1980; Yeh and Ward 1981).

Whatever point of view is chosen, all boundary conditions eventually must be transformed into mathematical equations for quantitative simulations. Thus, we will specify the boundary conditions from the mathematical point of view in concert with dynamic and physical considerations. The boundary conditions imposed on any segment of the boundary are taken to be either Dirichlet, Neumann, Cauchy, or variable for T_j with $j = 1, 2, \dots, N_a$ independently of each other. Thus, for any T_j , the global boundary may be split into four parts, B_D , B_N , B_C , and B_V (Fig. 2.1), denoting Dirichlet, Neumann, Cauchy, and variable boundaries, respectively. The conditions imposed on the first three types of boundaries are given as:

$$T_j = T_{jD} \quad \text{on} \quad B_D, \quad j = 1, 2, \dots, N_a, \quad (2.71)$$

$$-n \cdot \theta D \cdot \nabla C_j = q_{jN} \quad \text{on} \quad B_N, \quad j = 1, 2, \dots, N_a, \quad (2.72)$$

and

$$n \cdot (\nabla C_j - \theta D \cdot \nabla C_j) = q_{jC} \quad \text{on} \quad B_C, \quad j = 1, 2, \dots, N_a, \quad (2.73)$$

where

$$T_{jD} = \text{prescribed Dirichlet total analytical concentration (M/L}^3\text{)},$$

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Fig. 2. 1 Region of interest and its boundaries.

q_{jN} - normal Neumann flux ($M/L^2/T$),

q_{jC} - normal Cauchy flux ($M/L^2/T$),

n - an outward unit vector normal to the boundary.

The conditions imposed on the variable-type boundary, which is normally the soil-air interface or soil-water interface, are either the Neumann with zero gradient flux or the Cauchy with given total flux. The former is specified when the water flow is directed out of the region from the far away boundary, whereas the latter is specified when the water flow is directed into the region. This type of variable condition would normally occur at flow-through boundaries. Written mathematically, the variable boundary condition is given by

$$-n \cdot \theta D \cdot \nabla C_j = q_{jV} \quad \text{if } V \cdot n > 0 \quad \text{on } B_V, \quad j = 1, 2, \dots, N_a, \quad (2.74)$$

and

$$n \cdot (VC_j - \theta D \cdot \nabla C_j) = q_{jV} \quad \text{if } V \cdot n < 0 \quad \text{on } B_V, \quad j = 1, 2, \dots, N_a \quad (2.75)$$

3. MODEL CONSIDERATIONS

Equations (2.19) through (2.23), (2.29), (2.30), (2.46), (2.50), (2.54), and (2.56) form a closed system for the unknowns T_j 's, C_j 's, S_j 's, P_j 's, c_k 's, W_j 's, s_k 's, x_i 's, y_i 's, z_i 's, and p_i 's. This system of equations represents the processes of hydrological transport and chemical equilibrium of complexation, redox, acid-base reactions, sorption, and precipitation-dissolution. Depending on the processes of chemical equilibrium considered, there may be many ways to mathematically reduce the system of equations and thereby simplify the analysis.

Rubin has presented an excellent review on how such simplifications can be made (Rubin 1983). According to Rubin (1983), for sufficiently fast and reversible chemical reactions, local equilibrium assumption (LEA) can be made, and the reaction can be classified as Class I homogeneous, Class II surface heterogeneous, or Class III classical heterogeneous. In fact, Class I reactions are aqueous complexation, Class II reactions are sorption via either ion exchange or surface complexation, and class III reactions refer to precipitation-dissolution. Although mathematical analyses according to these classifications can be simplified greatly, they offer limited value for practical applications. Nevertheless, they may provide an invaluable research tool for controlled environments in which only the designated chemical reactions are allowed to occur. For example, if one wants to investigate precipitation-dissolution, the

researcher must design the experiment such that only precipitation-dissolution reactions are allowed to occur. Then the Class III models can be used to analyze the experimental data. In reality, some chemical reactions may be occurring in one region while other types of reactions are occurring in adjacent regions. Thus, for the ultimate purpose of application, any hydrogeochemical model must be designed to accommodate simultaneous reactions of complexation, redox, acid-base reaction, sorption, and precipitation-dissolution.

3.1 MATHEMATICAL STRATEGIES

Currently, there are basically three approaches to modeling coupled hydrological transport and geochemical equilibrium reactions: (1) the differential and algebraic equations (DAE) approach, (2) the direct substitution approach (DSA), and (3) the sequential iteration approach (SIA) between hydrological transport and chemical equilibrium computations. An extremely important consideration in any approach is the choice of the primary dependent variables (PDVs), which determines whether the approach can deal with the complete suite of chemical reactions, how practically it can be used for realistic two- and three-dimensional (2- and 3-D) applications, and how easily it can be extended to handle chemical kinetics, if necessary. PDVs are defined in this paper as the variables that are solved via primary governing equations, rather than via secondary governing equations. Any variable that is solved via a secondary governing equation is termed a secondary dependent variable (SDV). Thus, how one chooses the PDVs and SDVs from among all variables

(T_j 's, C_j 's, S_j 's, P_j 's, c_k 's, W_j 's, s_k 's, x_i 's, y_i 's, z_i 's, and p_i 's) is equivalent to how one divides and reduces the system of equations [Eqs. (2.19) through (2.23), (2.29), (2.30), (2.46), (2.50), (2.54), and (2.56)] into two subsystems. One subsystem consists of primary governing equations (PGEs), which are mainly hydrological transport equations, and the other consists of secondary governing equations (SGEs), which are made mainly chemical reaction equations.

3.1.1 Differential and Algebraic Equations Approach (DAE)

For the DAE approach, PDVs are either (1) the concentrations of all species (Miller 1983) or (2) the concentrations of all component and precipitated species (Lichtner 1985).

3.1.1.1 DAE-1: Concentrations of all species as PDVs

When the concentrations of all species are considered as PDVs, the total number of PDVs is equal to $(N_a + M_x + M_p + N_s + M_y + M_z)$. Using the definitions of total analytical concentrations as given by Eqs. (2.23) and (2.30) and total dissolved, total sorbed, and total precipitated concentrations as given by Eq. (2.20), (2.21), and (2.22), respectively, we may rewrite Eqs. (2.19) and (2.29) in the following form under the conditions of steady-state flow (Miller and Benson 1983):

$$\theta \left[\frac{\partial c_j}{\partial t} + \sum_{i=1}^{M_x} a_{ij}^x \frac{\partial x_i}{\partial t} + \sum_{i=1}^{M_y} a_{ij}^y \frac{\partial y_i}{\partial t} + \sum_{i=1}^{M_z} a_{ij}^z \frac{\partial z_i}{\partial t} + \sum_{i=1}^{M_p} a_{ij}^p \frac{\partial p_i}{\partial t} \right] -$$

$$L(c_j) - \sum_{i=1}^{M_x} a_{ij}^x L(x_i) = 0, \text{ for } j = 1, 2, \dots, N_a \quad (3.1)$$

$$\theta \left[\frac{\partial s_j}{\partial t} + \sum_{i=1}^{M_y} b_{ij}^y \frac{\partial y_i}{\partial t} \right] = 0, \text{ for } j = 1, 2, \dots, N_s \quad (3.2)$$

Equations (3.1), (3.2), (2.46), (2.50), (2.54), and (2.56) constitute the subsystem of PGEs for the PDVs c_j 's, s_j 's, x_i 's, y_i 's, z_i 's and p_i 's whereas Eqs. (2.20) through (2.23) and (2.30) form the subsystem of SGEs for the SDVs T_j 's, C_j 's, S_j 's, P_j 's, and W_j 's. The partial differential equations (PDEs), Eq. (3.1), are discretized in space, leading to a set of ordinary differential equations (ODEs) governing the concentrations of all species at all nodes. In the meantime, the ODEs [Eq. (3.2)] and the nonlinear algebraic equations (AEs) [Eqs. (2.46), (2.50), (2.54), and (2.56)] are also applied to all spatial nodes. These manipulations result in a set of mixed DAEs:

$$G(m, t) \frac{dm}{dt} + F(m, t) = 0 \quad (3.3)$$

where m is a vector which contains all the unknowns (c_j , s_j , x_i , y_i , z_i , and p_i) at all the spatial nodes. Equation (3.3) has been solved simultaneously by some DAE solvers (Hindmarsh 1980; Petzold 1981; Miller 1983). Once all PDVs are obtained by solving Eq. (3.3), the computation of SDVs (C_j , S_j , P_j , T_j , and W_j) is straightforward.

3.1.1.2 DAE-2: Concentrations of component and precipitated species as PDVs.

Using the concentrations of all species as the PDVs, one must solve $(N_a + M_x + M_p + N_s + M_y + M_z)$ simultaneous equations for the same number of unknowns. To reduce the number of simultaneous equations, one can substitute Eqs. (2.46), (2.50), and (2.54) into Eqs. (3.1) and (3.2) to yield (Grove and Wood 1979; Lichtner 1985):

$$\theta \left[\frac{\partial c_j}{\partial t} + \sum_{i=1}^{M_x} a_{ij}^x \frac{\partial f_i}{\partial t} + \sum_{i=1}^{M_y} a_{ij}^y \frac{\partial g_i}{\partial t} + \sum_{i=1}^{M_z} a_{ij}^z \frac{\partial h_i}{\partial t} + \sum_{i=1}^{M_p} a_{ij}^p \frac{\partial p_i}{\partial t} \right] =$$

$$L(c_j) + \sum_{i=1}^{M_x} a_{ij}^x L(f_i) = 0, \quad \text{for } j = 1, 2, \dots, N_a \quad (3.4)$$

$$\theta \left[\frac{\partial s_j}{\partial t} + \sum_{i=1}^{M_y} b_{ij}^y \frac{\partial g_i}{\partial t} \right] = 0, \quad \text{for } j = 1, 2, \dots, N_s \quad (3.5)$$

where

$f_i = f_i(c_1, c_2, \dots, c_N)$ is an explicit function of the concentrations of aqueous component species,

$g_i = g_i(c_1, c_2, \dots, c_N; s_1, s_2, \dots, s_N)$ is an explicit function of the concentrations of component species,

$h_i = h_i(c_1, c_2, \dots, c_N; N_{eq})$ is an explicit function of the concentrations of aqueous component species.

Equations (3.4), (3.5), and (2.56) constitute the subsystem of PGEs and are solved for the PDVs, c_j 's, s_j 's, p_i 's. Equations (2.20) through (2.23), (2.30), (2.46), (2.50), and (2.54) form the subsystem of SGEs and

are used for computing the SDVs, C_j 's, S_j 's, P_j 's, T_j 's, W_j 's, x_i 's, y_i 's and z_i 's. The two subsystems are solved iteratively. For the first subsystem system, $(N_a + N_s + M_p)$ equations are solved simultaneously (Lichtner 1985). An iteration scheme was used to solve the precipitation-dissolution front (Grove and Wood 1979; Lichtner 1985).

The advantage of this DAE approach is that it is easy to include the complete suite of chemical processes simultaneously. However, the DAE approach will require excessive central process unit (CPU) storage and possibly CPU time beyond present-day computer capacity for any realistic 2- and 3-D problems. These points are discussed later.

3.1.2 Direct Substitution Approach (DSA)

In the direct substitution approach, the chemical equilibrium equations are substituted into the hydrological transport equations to result in a set of N nonlinear PDEs which are subsequently solved simultaneously for the N PDVs. Several models have been proposed, each using a different set of variables as the PDVs (Rubin and James 1973; Valocchi et al. 1981; Jennings et al. 1982; Rubin 1983; Lewis et al. 1987).

3.1.2.1 DSA-1: Concentrations of aqueous component species as PDVs

A few investigators have used c_j 's as the PDVs (Jennings et al. 1982). Substituting Eqs. (2.20) through (2.23), (2.46), (2.50), and (2.54) into Eq. (2.19), excluding precipitation-dissolution reactions,

ignoring source/sink and decay, and assuming steady state saturated flow, one obtains (Jennings et al. 1982)

$$\theta \left(\sum_{i=1}^{N_a} \frac{\partial C_j}{\partial c_i} \frac{\partial c_i}{\partial t} + \sum_{i=1}^{N_a} \frac{\partial S_j}{\partial c_i} \frac{\partial c_i}{\partial t} \right) - \sum_{i=1}^{N_a} \mathbf{V} \cdot \frac{\partial C_j}{\partial c_i} \nabla c_i - \sum_{i=1}^{N_a} \nabla \cdot \left(\theta \mathbf{D} \frac{\partial C_j}{\partial c_i} \nabla c_i \right) = 0, \quad j = 1, 2, \dots, N_a. \quad (3.6)$$

Equations (3.6) constitute the subsystem of PGEs for the PDVs c_j 's and Eqs. (2.20), (2.21), (2.29), (2.30), (2.46), (2.50), and (2.54) form the subsystem of SGEs for the SDVs C_i 's, S_i 's, W_j 's, s_j 's, x_i 's, y_i 's, and z_i 's. Equations (2.22), (2.23), and (2.56) are not included in this type of formulation because using the concentrations of aqueous component species c_j 's as PDVs cannot deal with precipitation-dissolution reactions. The first subsystem of equations was solved simultaneously, not one by one sequentially (Jennings et al. 1982). Because Jennings et al. (1982) only considered the sorption of aqueous component species, assumed fixed pH, and specified activity coefficients of all species to be 1, $\partial C_j / \partial c_i$'s and $\partial S_j / \partial c_i$'s can be derived analytically in terms of c_j 's. Thus, the first subsystem can be solved independently of the second subsystem. For general cases, both $\partial C_j / \partial c_i$'s and $\partial T_j / \partial c_i$'s have to be computed numerically. Under such circumstances, the two subsystems must be solved iteratively. In any event, because of the simultaneous solution of N_a PDEs in the first subsystem, there will be N_a degrees of freedom at each node, which makes the application of this type of formulation impractical

for realistic 2- and 3-D problems. These points are discussed in subsequent sections.

3.1.2.2 DSA-2: Total dissolved concentrations of aqueous components as PDVs

Several investigators have attempted to adapt the total dissolved concentrations, C_j 's, as the PDVs (Rubin and James 1973; Valocchi et al. 1981). Rubin and James (1973) and Valocchi et al. (1981) considered only the process of sorption via ion exchange under steady-state saturated flow conditions. In other words, the processes of aqueous complexation, sorption via surface complexation, and precipitation-dissolution were not included. Thus, these models give limited practical applications. Nevertheless, the adaption of C_j 's as the PDV can be extended to include aqueous complexation and sorption via surface complexation but not the precipitation-dissolution. Substituting Eqs. (2.20) and (2.21) into Eq. (2.19), assuming steady state saturated flow, and ignoring source/sink and decay, one obtains

$$\theta \left(\frac{\partial C_j}{\partial t} + \sum_{i=1}^{N_a} \frac{\partial S_i}{\partial C_i} \frac{\partial C_i}{\partial t} \right) - \nabla \cdot \nabla C_j - \nabla \cdot (\theta D \cdot \nabla C_j) = 0, \quad j = 1, 2, \dots, N_a. \quad (3.7)$$

Equation (3.7) constitutes the subsystem of PGEs for the PDVs C_j 's whereas Eqs. (2.20), (2.21), (2.29), (2.30), (2.46), (2.50), and (2.54) form the subsystem of SGEs for the SDVs c_j 's, S_j 's, W_j 's, s_j 's, x_1 's,

y_i 's, and z_i 's. Just as in the case of using concentrations of aqueous component species as PDVs, Eqs. (2.22), (2.23), and (2.56) are not included in this type of formulation because using total dissolved concentrations of aqueous components as PDVs cannot deal with precipitation-dissolution reactions either. Equation (3.7) contains N_a simultaneous nonlinear PDEs which necessitate the simultaneous solution of the subsystem. For a very simple problem, $\partial S_j / \partial C_i$'s can be derived analytically in terms of C_j 's (Kirkner et al. 1984). This makes it possible to solve the first subsystem independent of the second subsystem. For general cases, the two systems must be solved iteratively. This formulation is impractical for realistic 2- and 3-D problems, the same as the case of using the concentrations of all aqueous component species as PDVs.

3.1.2.3 DSA-3: Total analytical concentrations of aqueous Components as PDVs

One may also use the total analytical concentrations of aqueous components, T_j 's, as the PDVs (Yeh and Tripathi 1989). Ignoring the decay term and assuming $M_j^a = QC_j^*$, we may write the hydrological transport equation, Eq. (2.19), as follows

$$\begin{aligned} \theta \frac{\partial T_j}{\partial t} + \frac{\partial \theta}{\partial t} T_j + \sum_{i=1}^{N_a} V \cdot \frac{\partial C_j}{\partial T_i} \nabla T_i - \sum_{i=1}^{N_a} \nabla \cdot (\theta D \cdot \frac{\partial C_j}{\partial T_i} \nabla T_i) - \sum_{i=1}^{N_s} V \cdot \frac{\partial C_j}{\partial W_i} \nabla W_i \\ + \sum_{i=1}^{N_s} \nabla \cdot (\theta D \cdot \frac{\partial C_j}{\partial W_i} \nabla W_i) + \frac{\partial \theta}{\partial t} C_j + Q(C_j^* - C_j), j = 1, 2, \dots, N_a. \quad (3.8) \end{aligned}$$

Equation (3.8) constitutes the subsystem of PGEs for the PDVs T_j 's whereas Eqs. (2.20) through (2.23), (2.29), (2.30), (2.46), (2.50), (2.54), and (2.56) form the subsystem of SGEs for the SDVs C_j 's, S_j 's, P_j 's, c_j 's, W_j 's, s_j 's, x_i 's, y_i 's, z_i 's, and p_i 's. The two systems are solved iteratively (Yeh and Tripathi 1989). In any iteration, N_a simultaneous nonlinear PDEs given by Eq. (3.8) are solved simultaneously to yield N_a PDVs, T_j 's. As a result, this formulation is also impractical for realistic 2- and 3-D applications. However, this formulation can deal with precipitation-dissolution simultaneously with complexation and sorption.

3.1.2.4 Hybrid PDVs

Most of the investigators have used natural PDVs that do not require algebraic manipulations. These natural variables include the concentrations of all species, concentrations and/or activities of aqueous component species and/or all component species, total dissolved concentrations of aqueous components, and total analytical concentrations of all components. A few investigators have used hybrid PDVs that are linear combinations of species concentrations (Rubin 1983; Lewis et al. 1987). One then attempts to formulate transport equations so that they have a single variable whenever possible (Lewis 1987). This approach requires algebraic manipulations to attain the hybrid PDVs and to derive the linear and quasi-linear transport equations. This is a problem-specific approach and requires that the type of chemical reactions be known *a priori*. For example, in a system of two aqueous components under

the conditions of only Class III reactions, a hybrid PDV, namely the difference in concentrations of two aqueous component species, is defined; this hybrid PDV is governed by the advection-dispersion equation with moving boundary conditions (Rubin 1983). Other examples involving Class I and Class II reactions can be found elsewhere (Lewis et al., 1987). In the latter cases, the hybrid PDVs are attained as the linear combinations of species concentration, and the corresponding transport equations are formulated as quasi-linear equations in which the highest order of derivatives is the first power and all nonlinear coefficients are expressed analytically (Lewis et al. 1987). This approach of attaining hybrid PDVs and deriving corresponding transport equations works well for extremely simple systems. However, for realistic problems, several difficulties arise. First, it is almost impossible to write a general-purpose computer program for this approach because one must know specific chemical reactions *a priori* in order to derive the PDVs; furthermore, for a large number of components, a significant algebraic manipulation is required for each new problem to obtain PDVs (equal to the number of components in the case of Class I/Class II reactions or equal to the number of components minus the number of minerals in the case of Class 3 reactions). Second, for Class III reactions, if different minerals are present as a function of space and time, a moving-boundary-value problem with multiple moving interfaces would result. It would be extremely difficult to solve such a problem. Third, when all three classes of reactions are present in a problem, the derivation of hybrid PDVs requires even more strenuous efforts. Fourth, for each given problem, after

deriving the hybrid PDVs, one still has to develop the transport equations using analytical nonlinear coefficients, one for each of the hybrid PDVs. The derivation of analytical nonlinear coefficients may be done for simple systems (Lewis et al. 1987). For complex systems, it is almost insurmountable to attain analytical nonlinear coefficients; hence, the evaluation of nonlinear coefficients requires geochemical models, which makes the approach impractical. Fifth, the derivation of appropriate boundary conditions for the hybrid PDVs is not an easy task, especially for the interfacial moving boundary conditions (Rubin 1983). Due to these reasons, only models using the natural PDVs will be evaluated for their practicality and flexibility.

3.1.3 Sequential Iteration Approach (SIA)

Neither the DAE nor the direct substitution approach is practical for realistic 2- and 3-D applications because both approaches require the simultaneous solution of a significant number of field equations (equations include spatial derivatives, hence transport), which demand excessive CPU memory and CPU time as shall be discussed later. To find a way to circumvent the difficulty, we observe that only the PDEs governing the chemical transport are the field equations. The ODEs governing the change of total adsorbent concentrations and the nonlinear AEs governing chemical equilibrium reactions are point equations (equations do not include spatial derivatives, hence applicable to batch systems only). Furthermore, each transport equation for a component is identical in form.

This suggests that once the PDVs are chosen for the set of transport equations, they can be solved one by one independently of each other, each for the associated PDV. All other SDVs can be obtained from the set of chemical-equilibrium and molar-balance equations. This approach of iterating between sequentially (not simultaneously as done in DSA models) solving transport equations and solving geochemical equilibria equations provides perhaps the best hope for realistic, practical 2- and 3-D applications in terms of the CPU memory and CPU time requirements.

3.1.3.1 SIA-1: Concentrations of aqueous component species as PDVs

Using c_j 's as the PDVs and excluding precipitation-dissolution reactions, one can substitute Eqs. (2.20) and (2.21) into (2.19) to result in:

$$\theta \frac{\partial c_j}{\partial t} - L(c_j) = - \theta \left[\sum_{i=1}^{M_x} a_{ij}^x \frac{\partial x_i}{\partial t} + \frac{\partial S_i}{\partial t} \right] - \frac{\partial \theta}{\partial t} S_j$$

$$+ \sum_{i=1}^{M_x} a_{ij}^x L(x_i) = 0, \text{ for } j = 1, 2, \dots, N_a. \quad (3.9)$$

Equations (3.9) constitute the subsystem of PGEs for the PDVs c_j 's, whereas Eqs. (2.20), (2.21), (2.29), (2.30), (2.46), (2.50), and (2.54) constitute the subsystem of SGEs for the SDVs C_i 's, S_i 's, W_j 's, s_j 's, x_i 's, y_i 's, and z_i 's.

If all terms on the right-hand side of Eq. (3.13) are considered as source/sink terms, then Eq. (3.19) consists of N_a linear advection-dispersion equations one for each aqueous component. Furthermore, each equation can be solved independently, provided the source/sink terms are given. The nonlinearity of Eq. (3.9) arises through the source/sink terms via chemical reactions described by the second subsystem of equations. Thus, the two subsystems must be solved iteratively. This formulation has not been previously reported to the knowledge of the authors. In general, c_j may be much smaller than S_j or the sum of $(a_{ij}^x x_i)$ over i from 1 to M_x . Under such circumstances, a small error in computing the source/sink on the right-hand side of Eq. (3.13) can easily render negative concentrations for c_j . Once some of c_j 's become negative, the solution is prone to nonconvergent solutions. Perhaps this is why this formulation was not adapted in the modeling of multicomponent systems.

3.1.3.2 SIA-2: Total dissolved concentrations of aqueous components as PDVs

For the models that employ C_j 's as the PDV, the hydrological transport equations under steady-state saturated-flow conditions (Theis et al. 1982; Kirkner et al. 1984; Kirkner et al. 1985) can be written as:

$$\theta \left(\frac{\partial C_j}{\partial t} + \frac{\partial S_j}{\partial t} \right) = L(C_j) \quad , \quad j = 1, 2, \dots, N_a \quad (3.10)$$

Equations (3.10) constitute the subsystem of PGEs for the PDVs C_j 's whereas Eqs. (2.20), (2.21), (2.29), (2.30), (2.46), (2.50), and (2.54) constitute the subsystem of SGEs for the SDVs c_j 's, S_j 's, W_j 's, s_j 's,

x_i 's, y_i 's, and z_i 's. The two subsystems must be solved iteratively, and the procedure of doing so has been reported elsewhere (Theis et al. 1982). The N_a PDEs in Eq. (3.10) could be solved one by one, considering $\partial S_j / \partial t$ as a source/sink term. However, having to circumvent the convergence problem for some situations because of the inappropriate numerical scheme used, Kirkner et al. (1984, 1985) solved N_a PDEs in Eq. (3.14) simultaneously, which would demand as much excessive CPU storage for realistic 2- and 3-D problems as DSA-2 models.

As with the direct substitution, it is not possible to treat the process of precipitation-dissolution when C_j 's are chosen as the PDVs. Therefore, the term $\partial P_j / \partial t$ was not included in Eq. (3.10) (Theis et al. 1982). If one wants to add the term $\partial P_j / \partial t$ in Eq. (3.10), then this equation must be coupled with Eq. (2.56) to form a set of $(N_a + M_p)$ simultaneous equations (Kirkner et al. 1987), which would then become impractical, just as in the case of DAE models.

3.1.3.3 SIA-3: Total analytical concentrations of aqueous components as PDVs

For the models that use T_j 's as PDVs, the hydrologic transport equations without the decay term can be written in the explicit form (Walsh et al. 1984; Cederberg 1985b; Bryant et al. 1986) as

$$\theta \frac{\partial T_j}{\partial t} + \frac{\partial \theta}{\partial t} T_j = L(C_j) + \frac{\partial \theta}{\partial t} C_j + Q(C_j^* - C_j), \quad j = 1, 2, \dots, N_a \quad (3.11)$$

or in the implicit form (Yeh and Tripathi 1989):

$$\theta \frac{\partial T_j}{\partial t} + \frac{\partial \theta}{\partial t} T_j - L(T_j) = -L(S_j + P_j) + QC_j^*, \quad j = 1, 2, \dots, N_a \quad (3.12a)$$

in which

$$L(!) = (-V \cdot \nabla + \nabla \cdot \theta D \cdot \nabla - Q + \frac{\partial \theta}{\partial t})(!) \quad (3.12b)$$

Equations (3.11) or (3.12) constitute the subsystem of PGEs for the PDVs T_j 's, whereas Eqs. (2.20) through (2.23), (2.29), (2.30), (2.46), (2.50), (2.54), and (2.56) constitute the subsystem of SGEs for the SDVs C_j 's, S_j 's, P_j 's, c_j 's, w_j 's, s_j 's, x_i 's, y_i 's, z_i 's, and p_i 's.

The sequences of iterating the PGEs [Eq. (3.11)] and the SGEs [Eqs. (2.20) through (2.23), (2.29), (2.30), (2.46), (2.50), (2.54), and (2.56)] have been well documented (Walsh et al. 1984, Cederberg 1985b, Bryant et al. 1986) and will not be repeated here. Using the implicit form of hydrological transport equation, we can perform a similar iteration procedure (Yeh and Tripathi 1989).

In solving Eq. (3.11) or (3.12), one substitutes the known values of previous iteration C_j^k 's or S_j^k 's and P_j^k 's for the terms on the right-hand side and solve for the unknown values of the present iteration $T_j^{(k+1)}$'s for the terms on the left-hand side. Thus, it can be seen that $T_j^{(k+1)}$'s computed with Eq. (3.11) are prone to negative concentrations if $L(C_j^k)$ on the right-hand side is negative. On the other hand, even if $-L(S_j^k + P_j^k)$ on the right-hand side of Eq. (3.12) is negative, $T_j^{(k+1)}$'s obtained with Eq. (3.12) are not necessarily negative because the term $-L(T_j^{(k+1)})$ can yield a larger negative value than that resulting

from the operation of $-L$ on $(S_j^k + P_j^k)$ and can make the solution $T_j^{(k+1)}$'s positive. This intuitive observation has been confirmed elsewhere (Yeh and Tripathi 1986).

The explicit form, Eq. (3.11), cannot be used to solve for the steady-state concentration distribution in a one-step iteration. For a one-step solution, one simply sets the time derivative term equal to zero. If this is done, the PDVs disappear from Eq. (3.11) and one is left with nothing to solve for. To reach a steady state solution with the explicit modeling, one has to proceed with many time-step iterations. On the other hand, for the implicit form, Eq. (3.12), we simply set the time derivative term on the left-hand side equal to zero and iterate between the simplified Eq. (3.12) and the chemical reaction equations, Eqs. (2.20) through (2.23), (2.29), (2.30), (2.46), (2.50), (2.54), and (2.56). Our experience has shown that the number of iterations required for a one-step iteration is approximately equal to, if not smaller than, that required for the iteration in the first time-step of the many time-steps.

A possible alternative formulation to Eqs. (3.11) or (3.12) is to modify the direct substitution approach so that the N_a PDEs do not have to be solved simultaneously (Yeh and Tripathi 1989). For example, we can rewrite Eq. (3.8) in the following form:

$$\theta \frac{\partial T_j}{\partial t} + \frac{\partial \theta}{\partial t} T_j + Q T_j + \mathcal{L}(C_j, T_j) = - \sum_{i=1}^{N_a} \mathcal{L}(C_j, T_i) - \sum_{k=1}^{N_s} \mathcal{L}(C_j, W_k) + \frac{\partial \theta}{\partial t} C_j +$$

$$Q(S_j + P_j) + Q C_j^*, \quad i \neq j, \quad j = 1, 2, 3, \dots, N_a \quad (3.13)$$

in which $\mathcal{L}(C_j, T_i)$ is the operator denoting

$$\mathcal{L}(C_j, T_i) = V \cdot \frac{\partial C_j}{\partial T_i} \nabla T_i - \nabla \cdot (\theta D \cdot \frac{\partial C_j}{\partial T_i} \nabla T_i) \quad (3.14)$$

In the iteration solution of Eq. (3.13), if we compute C_j 's, ∇T_i 's, and $\partial C_j / \partial T_i$'s ($i \neq j$) using the previous iterate T_i^k 's, we can solve Eq. (3.14) for each component, one at a time. The effectiveness of this approach has yet to be evaluated further. However, it can be surmised that, if geochemical reactions are such that

$$\left| \frac{\partial C_j}{\partial T_j} \right| > \left(\sum_{i=1}^{N_a} \left| \frac{\partial C_j}{\partial T_i} \right| + \sum_{k=1}^{N_s} \left| \frac{\partial C_j}{\partial W_k} \right| \right); \quad i \neq j, \quad j = 1, 2, \dots, N_a \quad (3.15)$$

this modified direct substitution approach may be superior to either the explicit or implicit coupled approach given by Eq. (3.11) or (3.12).

Other categories of models include the reaction path approach (Helgeson 1968; Helgeson 1979; Helgeson and Murphy 1983) and the mixing cell approach (Schulz and Reardon 1983; Narasimhan et al. 1986). Provision for fluid flow in reaction path models is necessarily *ad hoc*. Mixing cell models do not treat fluid flow and chemical reactions rigorously. For these reasons, both reaction path models and mixing cell

models are not discussed further in this report.

3.2 COMPUTER RESOURCE REQUIREMENTS

One of the most important considerations in evaluating a model for practical applications is the requirement of computer resources in terms of CPU memory and CPU time. If a model requires excessive CPU memory and CPU time beyond the reach of even mainframe computers for realistic field problems, it would remain in the ivory tower as a research tool for small problems when demands for computer resources are much restricted. It cannot be used for routine applications.

The requirements for CPU storage depend on the number of grid points used to discretize the region, the number of chemical components and chemical species included in the simulation, and the method used to solve resulting matrix equations. Let I , J , and K denote the number of grid points in three directions, respectively, with $I > J > K$. Let F denote the degree of freedom (number of unknowns) at each grid point. The total number of algebraic equations is $NEQ = F \times (I \times J \times K)$. This set of algebraic equations can be solved either by direct elimination methods (Lapidus and Pinder 1982) or by iteration methods (Hageman and Young 1981). The most widely used direct solution method is the banded matrix solver; however, other direct elimination methods can also be used (Yeh 1986). Iteration methods require less CPU storage than direct methods for 2- and 3-D problems. Table 3.1 lists the formulae to compute CPU storage requirements for storing the coefficient matrix when various methods are

used to solve the matrix equation. In Table 3.1 BWD is the band width of the coefficient matrix, $BWD = [2(J \times K + K + ND - 1) \times F - 1]$ (where ND is the number of dimension); NZO is the maximum number of non-zero entries in any row of the coefficient matrix, $NZO = F \times NC$ (where NC is the maximum number of nodes connected to any node point including the node point itself); and FIF is the fill-in factor for the sparse matrix solver. For 2-D problems, FIF ranges from 2 to 4 (Duff 1977), and NC is normally 9, although it may be greater or less depending on the discretization. It is very unlikely that NC will vary over a factor of 2. For 3-D problems, FIF may increase slightly, and NC is normally 27 with very little chance of varying over a factor of 2. For 1-D problems, FIF will not be large enough to make the size of the fill-in matrix greater than the banded matrix, and NC is equal to 3.

Table 3.1 CPU memory requirements of the coefficient matrix with different solvers (units - words)

Full Matrix	Band Matrix	Sparse Matrix	Iteration Method	Frontal Method
NEQ x NEQ	NEQ x BWD	NEQ x NZO x FIF	NEQ x NZO	BWD x BWD

Let us use a simple example to illustrate how we can compute the CPU storage requirements using various mathematical strategies in the preceding. Consider a moderately sized 2-D problem with 60 by 50 node discretization (Yeh 1985; Yeh 1986), we have $I = 60$, $J = 50$, and $K = 1$.

For a simulation with ten aqueous components and two sorbent components, we can easily end up with 30 species. For the DAE-1 models, $F = 30$ because concentrations of all species are the PDVs. For DAE-2 models, $F = 15$, assuming there are three species undergoing precipitation/dissolution. For DSA-1, DSA-2, and DSA-3 models, $F = 10$ because the number of unknowns at each grid point is equal to the number of aqueous components. All unknowns appear in each of the governing equations, hence they are solved simultaneously. For SIA-1, SIA-2, and SIA-3 models, although the degree of freedom at each grid node is also ten, each PDV is associated with a governing equation. Hence the PDV's are normally solved one by one, resulting in $F = 1$. Table 3.2 lists the CPU memory requirements for storing the coefficient matrix, assuming we need a double precision representation in the computation. In computing the CPU memory requirement with the sparse matrix solver, we have assumed a fill-in factor of 3 because it has been reported that a fill-in factor of from 2 to 4 are normally encountered for 2-D problems (Duff 1977). For comparison purposes, the CPU storage capacities in megabytes (MB) of IBM 3033, CRAY-1, CRAY-XMP, CRAY-2, and VAX-8600 are 8.8, 16.0, 64.0, 32.0, and 32.0, respectively.

From Table 3.2, it can be seen that for DAE-1 models, if a full matrix solver is used to solve the problem, we would need 1,013 CRAY-XMP supercomputers just to store the coefficient matrix. Of course, no practitioners would ever employ a full matrix solver to solve the transport problems. Full-matrix solvers remain in textbooks for teaching

Table 3.2 CPU memory requirements in MB of the coefficient matrix with various mathematical strategies using different solvers for the moderately sized 2-D problem

Solvers Models	Full Matrix	Band Matrix	Sparse Matrix	Iteration Method	Frontal Method
DAE-1	64,800	2,245.92	583.20	194.40	77.81
DAE-2	16,200	561.24	145.80	48.60	19.44
DSA-1	7,200	249.36	64.80	21.60	8.64
DSA-2					
DSA-3					
SIA-1	72	2.47	0.65	0.22	0.09
SIA-2					
SIA-3					

purposes (Wang and Anderson 1982). The most widely used band matrix solver is also far from being able to handle this moderately sized 2-D problem no matter which mainframe computer is used. Even the specialized sparse matrix solver and the iteration method, which would normally encounter convergent problem, cannot be used to solve the problem. Only the frontal method can be used to solve the problem in conjunction with a CRAY-XMP computer. The application of the frontal method to transport problems is lacking, but it has been widely used in structural engineering problems. Similarly, for DAE-2 models or the direct substitution approach (DSA-1, DSA-2, and DSA-3) models, one cannot use the band matrix solver or even the specialized sparse matrix solver to solve this moderately sized problem. Only the iteration method or frontal method can be used to solve this type of models in conjunction with using super computers. Most of

the existing DSA models (Rubin and James 1973; Valocchi et al. 1981; Jennings et al. 1982; Kirkner et al. 1984; Kirkner et al. 1985; Lewis et al. 1987) use the band matrix solver. Hence, these models cannot address this moderately sized 2-D problem. However, for the models using the sequential iteration approach, all practical matrix solution methods can be used to solve this problem on mainframe computers with plenty of storage to spare.

For 3-D problems, the requirements on the CPU storage are more severe. For example, consider a small problem of $30 \times 20 \times 10$ discretization, we have $I = 30$, $J = 20$, and $K = 10$. Table 3.3 lists the CPU memory requirements for storing the coefficient matrix for this small 3-D problem. For this small 3-D problem, only the sequential iteration approach is feasible in terms of CPU storage requirement. The CPU storage requirement for a 1-D problem having a 500-node discretization is listed in Table 3.4. It is seen that even with this 1-D problem, any practical solver can be used.

From the preceding discussion, it can be said that the DAE and DSA approaches are not practical in dealing with realistic 2- and 3-D problems in terms of CPU memory requirements. For the near future, they are useful only as research tools for 1-D investigations. On the other hand, the SIA models in conjunction with appropriate practical matrix solution methods do offer perhaps the only hope for solving realistic 2- and 3-D problems.

Table 3.3 CPU memory requirements in MB of the coefficient matrix with various mathematical strategies using different solvers for the small 3-D problem

Solvers Models	Full Matrix	Band Matrix	Sparse Matrix	Iteration Method	Frontal Method
DAE-1	259,200	1,8315.36	3,499.20	1,164.40	1,186.62
DAE-2	64,800	4,578.48	874.80	291.60	323.50
DSA-1	28,800	2,034.72	388.80	129.60	143.75
DSA-2					
DSA-3					
SIA-1	288	20.30	3.89	1.30	1.43
SIA-2					
SIA-3					

Table 3.4 CPU memory requirements in MB of the coefficient matrix with various mathematical strategies using different solvers for the large 1-D problem

Solvers Models	Full Matrix	Band Matrix	Sparse Matrix	Iteration Method	Frontal Method
DAE-1	1800	14.28	14.28	10.80	0.11
DAE-2	450	3.54	3.54	2.70	0.03
DSA-1	200	1.56	1.56	1.20	0.01
DSA-2					
DSA-3					
SIA-1	2	0.012	0.012	0.012	0.000
SIA-2					
SIA-3					

Evaluating the CPU time requirements is much more involved than evaluating the CPU storage. In addition to dependence on the number of grid points, the number of chemical components and chemical species, and the method used to solve the matrix equation, CPU time also greatly depends on the skill of programmers and the level of computer compilers. To actually compare the CPU time requirements of various models, one has to run those models for a wide range of problems on various computers with various versions of compilers. Although this type of direct comparison is beyond the scope of this report, there is an objective means that can be used to evaluate the CPU time requirement that is independent of the skill of programmers and the level of computer compilers. Operational count (mainly the multiplication, division, and recording of numbers) can be used to evaluate the CPU time requirements for various model approaches. Table 3.5 lists the formulae to compute the number of operations required for solving a matrix equation with various solvers. Because the full matrix solver is not practical based on memory requirements, it is not included for the evaluation of CPU time requirements. In Table 3.5, NIN is the number of iterations required to solve the nonlinear equations, and NIL is the number of iterations required to solve the linearized matrix equation iteratively.

Using the same examples given, we can compute the number of operations needed for solving the moderately sized 2-D, small 3-D, and large 1-D problems. These requirements are given in Tables 3.6, 3.7, and 3.8, respectively. It is noted that, for SIA models, NEQ is computed with

Table 3.5 CPU time in operational counts needed to solve a nonlinear matrix equation with different solvers

Band Matrix and Frontal Method	Sparse Matrix	Iteration Method
$[(NEQ \times BWD^2 \times NIN)]/3$ $[NEQ \times (NZO \times FIF)^2 \times NIN]/3$ $[(NEQ \times NZO \times NIL) \times NIN]$		

the actual degrees of freedom F, but BWD and NZO are computed with $F = 1$. This is because F sets of NEQ equations are solved one by one. It is also noted that the frontal method and the sparse matrix solver will actually require more operations than those given in the tables because "bookkeeping" and "index-locking" operations were not included in these tables.

Table 3.6 CPU time in mega-operations needed to solve the moderately sized 2-D problem using various matrix solvers

Solvers Models	Band Matrix and Frontal Method	Sparse Matrix	Iteration Method
DAE-1	2.9×10^5 NIN	2.0×10^4 NIN	2.4×10^1 NIL x NIN
DAE-2	3.6×10^4 NIN	2.1×10^3 NIN	6.1×10^0 NIL x NIN
DSA-1 DSA-2 DSA-3	1.1×10^4 NIN	7.3×10^2 NIN	2.7×10^0 NIL x NIN
SIA-1 SIA-2 SIA-3	1.1×10^2 NIN	7.3×10^0 NIN	2.7×10^{-1} NIL x NIN

Table 3.7 CPU time in megaoperations needed to solve the small 3-D problem using various matrix solvers

Solvers Models	Band Matrix and Frontal Method	Sparse Matrix	Iteration Method
DAE-1	9.7×10^6 NIN	3.5×10^5 NIN	1.5×10^2 NIL x NIN
DAE-2	1.2×10^6 NIN	4.4×10^4 NIN	3.6×10^1 NIL x NIN
DSA-1 DSA-2 DSA-3	3.6×10^5 NIN	1.3×10^4 NIN	1.6×10^1 NIL x NIN
SIA-1 SIA-2 SIA-3	3.6×10^3 NIN	1.3×10^2 NIN	1.6×10^0 NIL x NIN

Table 3.8 CPU time in megaoperations needed to solve the large 1-D problem using various matrix solvers

Solvers Models	Band Matrix and Frontal Method	Sparse Matrix	Iteration Method
DAE-1	7.1×10^1 NIN	7.1×10^1 NIN	1.4×10^0 NIL x NIN
DAE-2	8.7×10^0 NIN	8.7×10^0 NIN	3.4×10^{-1} NIL x NIN
DSA-1 DSA-2 DSA-3	2.5×10^0 NIN	2.5×10^0 NIN	1.5×10^{-1} NIL x NIN
SIA-1 SIA-2 SIA-3	1.5×10^{-2} NIN	1.5×10^{-2} NIN	1.5×10^{-2} NIL x NIN

For the moderately sized 2-D problem, experience has indicated that the number of iterations needed to solve the nonlinear algebraic equations resulting from reactive multicomponent transport, NIN, is on the order of 20. The number of iterations used to solve the linearized matrix equation, NIL, is on the order of 50 (Yeh 1985). One of the fastest computers in the United States is the CRAY-XMP, which can perform about 200 mega-floating-point operations per seconds (MFLOPS) at its maximum efficiency. Substituting these numbers into Tables 3.6, 3.7, and 3.8, we can estimate the minimum amount of time required to perform one-time-step computations. The results are given in Tables 3.9, 3.10, and 3.11, respectively, for the moderately sized 2-D, small 3-D, and large 1-D problems.

Table 3.9 Estimated minimum CPU time in seconds needed for one-time step computation using CRAY-XMP computers for the moderately sized 2-D problem

Solvers Models	Band Matrix and Frontal Method	Sparse Matrix	Iteration Method
DAE-1	2.9×10^4	2.0×10^3	1.2×10^1
DAE-2	3.6×10^3	2.5×10^2	3.1×10^0
DSA-1 DSA-2 DSA-3	1.1×10^3	7.3×10^1	1.4×10^0
SIA-1 SIA-2 SIA-3	1.1×10^1	7.3×10^{-1}	1.4×10^{-1}

Table 3.10 Estimated minimum CPU time in seconds needed for one-time step computation using CRAY-XMP computers for the small 3-D problem

Solvers Models	Band Matrix and Frontal Method	Sparse Matrix	Iteration Method
DAE-1	9.7×10^5	3.5×10^4	7.5×10^1
DAE-2	1.2×10^5	4.4×10^3	1.8×10^1
DSA-1	3.6×10^4	1.3×10^3	8.0×10^0
DSA-2			
DSA-3			
SIA-1	3.6×10^2	1.3×10^1	8.0×10^{-1}
SIA-2			
SIA-3			

Table 3.11 Estimated minimum CPU time in seconds needed for one-time step computation using CRAY-XMP computers for the large 1-D problem

Solvers Models	Band Matrix and Frontal Method	Sparse Matrix	Iteration Method
DAE-1	7.1×10^0	7.1×10^0	7.0×10^{-1}
DAE-2	8.7×10^{-1}	8.7×10^{-1}	1.7×10^{-1}
DSA-1	2.5×10^{-1}	2.5×10^{-1}	7.5×10^{-2}
DSA-2			
DSA-3			
SIA-1	1.5×10^{-3}	1.5×10^{-3}	7.5×10^{-3}
SIA-2			
SIA-3			

Tables 3.9 and 3.10 suggest that the DAE and DSA models using the band matrix solver require excessive CPU time. Hence, these models are probably not suitable for addressing realistic 2- and 3-D problems. However, if iteration methods are used to solve the resulting matrix equation, the DAE and DSA models may be used to solve for moderately sized 2-D and small 3-D problems. Unfortunately, most of the DAE and DSA model developers (Rubin and James 1973; Grove and Wood 1979; Valocchi et al. 1981; Jennings et al. 1982; Kirkner et al. 1984; Lichtner 1985; Kirkner et al. 1985; Lewis et al. 1987) have used the band matrix solver. Tables 3.9 and 3.10 also indicate that the SIA models using the band matrix solver (Theis et al. 1982; Walsh et al. 1984; Cederberg 1985a; Bryant et al. 1986; Yeh and Tripathi 1987) are suitable for applications to 2-D problems in terms of CPU time requirements. If an iteration method is included as an option to solve the matrix equation (Yeh and Tripathi 1987), then the SIA model may be suitable for application to realistic 2- and 3-D problems. Table 3.11 shows that whatever approach is taken, all models can deal with 1-D problems without requiring an excessive amount of CPU time. Thus, in terms of CPU time requirement, DAE and DSA models can only be used as a research tool for 1-D problems such as column experiments. They cannot be applied to realistic 2- and 3-D problems. Only the SIA models can be applied to realistic 2-D problems without excessive demand on CPU time. For 3-D problems, SIA models using the iteration method to solve the matrix equation provides perhaps the only hope for realistic applications.

3.3 CHEMICAL EQUILIBRIUM PROCESSES

A realistic model must be flexible enough to deal with as many reaction processes as possible. These reaction processes include aqueous complexation, adsorption and ion-exchange, and precipitation-dissolution. [If a model can deal with these three processes, it can handle redox and acid-base reactions as well because no special consideration is required for dealing with redox and acid-base reactions as stated previously.] Whether a model can deal with the complete suite of these chemical reaction processes simultaneously depends on what PDVs are chosen for solving the PGEs (which usually include the complete set of transport equations and/or partial set of chemical reaction equations). In this section, we examine the capability of various models presented in the previous section to deal with complete suite of chemical reactions. As shown herein, some models cannot be used to for precipitation-dissolution.

A simple criterion can be used to determine the number of chemical processes that can be included in a model. We simply ask the question: after the PDVs are obtained by solving the PGEs, can we compute the SDVs from the SGEs? Using this criterion, we evaluate in the following how various choices of PDVs can affect the number of chemical reaction processes that can be included in a model. We recall in a reactive multi-chemical component system, there are N_a T_j 's, N_a C_j 's, N_a S_j 's, N_a P_j 's, N_a c_j 's, N_s W_j 's, N_s s_j 's, M_x x_i 's, M_y y_i 's, M_z z_i 's, and M_p p_i 's, variables. Some of these variables are chosen as the PDVs and the remaining are designated as the SDVs.

For the DAE-1 models, $N_a c_j$'s, $N_s s_j$'s, $M_x x_i$'s, $M_y y_i$'s, $M_z z_i$'s, and $M_p p_i$'s are chosen as the PDVs. Once these PDVs are obtained by solving the mixed DAE set of equations, $N_a C_j$'s, $N_a S_j$'s, $N_a P_j$'s, $N_a T_j$'s, and $N_s W_j$'s can be computed in a straightforward manner from Eqs. (2.20) through (2.23) and (2.30), respectively. It can be shown that $N_a c_j$'s from DAE-1 models will satisfy the solubility condition given by Eq. (2.56) because Eq. (2.56) is included as one of the governing equations in solving for the PDVs. Therefore, the DAE-1 models can include the complete suite of chemical reaction processes discussed in this paper. For DAE-2 models, $N_a c_j$'s, $N_s s_j$'s, and $M_p p_i$'s are chosen as the PDVs and are obtained by solving Eqs. (3.4), (3.5), and (2.56). Having obtained $N_a c_j$'s and $N_s s_j$'s, we can use Eqs. (2.46), (2.50), and (2.54) to compute the SDVs, $M_x x_i$'s, $M_y y_i$'s, and $M_z z_i$'s, respectively. Finally, the remaining SDVs, $N_a C_j$'s, $N_a S_j$'s, $N_a P_j$'s, $N_a T_j$'s, and $N_s W_j$'s, can then be computed using Eqs. (2.20) through (2.23) and (2.30), respectively. Again, the $N_a c_j$'s can be shown to satisfy the solubility condition specified by Eq. (2.56) because it has been utilized in solving for the PDVs. Hence, the DAE-2 models can treat the complete suite of the chemical reactions, too.

For DSA-1 and SIA-1 models, $N_a c_j$'s are chosen as the PDVs. They are obtained by solving Eq. (3.6) in the case of DSA-1 models and by Eq. (3.9) in the case of SIA-1 models, respectively. $N_s W_j$'s are obtained by solving Eq. (2.29). Having obtained $N_a c_j$'s, one can compute $M_x x_i$'s with Eq. (2.46). Given $N_s W_j$'s and $N_a c_j$'s, Eqs. (2.30), (2.50), and (2.54)

can be solved simultaneously to yield N_s s_j 's, M_y y_i 's, and M_z z_j 's. The SDVs, N_a C_j 's and N_a S_j 's, can be computed using Eqs. (2.20) and (2.21), respectively. However, it is not possible to obtain the remaining SDVs, N_a T_j 's, N_a P_j 's and M_p p_i 's, because M_p p_i 's cannot be obtained from the solubility condition given by Eq. (2.56), which does involve the concentration of precipitated species. Furthermore, N_a c_j 's do not necessarily satisfy the solubility condition even if precipitation reactions do occur. Therefore, it is obvious that DSA-1 and SIA-1 models cannot treat precipitation-dissolution reactions simultaneously with aqueous complexation and sorption reactions. Hence, the model of Jennings et al. (1982) is not applicable if precipitation-dissolution reactions are present.

For DSA-2 and SIA-2 models, N_a C_j 's are chosen as the PDVs. They are obtained by solving Eq. (3.7) in the case of DSA-2 models and by Eq. (3.10) in the case of SIA-2 models. For both models, N_s W_j 's are obtained by solving Eq. (2.29). Then, one substitutes Eqs. (2.46) into Eq. (2.20) to yield N_a equations relating C_j 's to the concentrations of aqueous components, c_j 's. These N_a equations are then solved for N_a c_j 's. With N_a c_j 's and N_s W_j 's known, one substitutes Eq. (2.50) into Eq. (2.30) to result in N_s equations relating W_j 's as functions of s_j 's and solves the resulting equations for N_s s_j 's. Then Eqs. (2.46), (2.50), and (2.54) are used to compute M_x x_i 's, M_y y_i 's, and M_z z_i 's, respectively. Finally, Eq. (2.21) is used to compute N_a S_j 's. However, as in the case of DSA-1 and SIA-1 models, it is not possible to obtain the remaining SDVs' N_a T_j 's, N_a

P_j 's, and $M_p p_i$'s. The $N_a c_j$'s obtained in the manner outlined here do not, as in the case of DSA-1 and SIA-1 models, necessarily satisfy the solubility condition even if the precipitation reactions do happen in the system. Therefore, it can be concluded that DSA-2 and SIA-2 models cannot handle precipitation-dissolution reactions. Hence, these types of models (Rubin and James 1973, Valocchi et al. 1981, Kirkner et al. 1984, Kirkner et al. 1985) have to ignore the precipitation-dissolution reactions.

For DSA-3 and SIA-3 models, $N_a T_j$'s are chosen as the PDVs. They are obtained by solving Eqs. (3.8) in the case of DSA-3 models and by Eq. (3.11), (3.12), or (3.13) in the case of SIA-3 models. $N_s W_j$'s are obtained by solving Eq. (2.29). Substituting Eqs. (2.46), (2.50), and (2.54) into Eq. (2.23), one obtains N_a equations relating T_j 's to the concentrations of aqueous components, c_j 's, and the concentrations of precipitated species p_i 's. In the meantime, substituting Eq. (2.50) into Eq. (2.39), one obtains N_s equations relating W_j 's to the component species concentrations c_j 's and s_j 's. These newly obtained N_a and N_s equations along with M_p equations given by Eq. (2.56) are solved simultaneously for $N_a c_j$'s, $N_s s_j$'s and $M_p p_i$'s. Next, $M_x x_i$'s, $M_y y_i$'s, and $M_z z_i$'s are computed in a straightforward manner from Eqs. (2.46), (2.50), and (2.54), respectively. Finally, Eqs. (2.20) through (2.22) are used to compute $N_a C_j$'s, $N_a S_j$'s, and $N_a P_j$'s, respectively. Thus, it is seen that once the PDVs, $N_a T_j$'s, are obtained, the remaining variables ($N_a C_j$'s, $N_a S_j$'s, $N_a P_j$'s, $N_s W_j$'s, $N_a c_j$'s, $N_s s_j$'s, $M_x x_i$'s, $M_y y_i$'s, $M_z z_i$'s and $M_p p_i$'s) can all be computed. Hence, DSA-3 and SIA-3 models can

include the full complement of chemical reactions just as the DAE-1 and DAE-2 models do.

3.4 MIXED EQUILIBRIUM AND KINETIC REACTIONS

The transport of chemicals through soil matrix under various chemical reactions has mostly been modelled with the assumption of geochemical equilibria. However, experimental evidence has shown that many chemical reactions, in particular, the sorption, precipitation-dissolution, and redox, are very slow in comparison with the physical and hydrological transport of chemicals. Thus, ideally, one would like to have a generic hydrogeochemical transport model that can treat every reaction as equilibrium or kinetic, as one desires. Here, we will briefly describe how easily the various types of models evaluated in this paper can be modified and extended to treat mixed chemical kinetics and equilibrium.

If any chemical reaction resulting in a species is kinetic rather than in equilibrium, two adjustments to the governing equations must be made. First, the mass action equation for that species is replaced by a transport equation in the case of complexation reactions or by a rate balance equation in the case of sorption and precipitation reactions. Second, the rate of the reaction must be specified in terms of the species concentration and activities of all components. For the complexation reactions, Eq. (2.46) is replaced by:

$$\theta \frac{\partial x_i}{\partial t} = -L(x_i) + \theta r_i^x, \quad i = 1, 2, \dots, K_x \quad (3.16)$$

where

K_x = number of complexed species of kinetic reactions.

The specification of the reaction rate depends on the kinetic models used. For demonstration and without loss of generality, the collision theory assumptions for writing the reaction rate are utilized to yield

$$r_i^x = -k_i^{bx} x_i + k_i^{fx} \prod_{k=1}^{N_a} c_k^{a_{ik}^x}, \quad i = 1, 2, \dots, K_x \quad (3.17)$$

where

k_i^{bx} = modified backward reaction rate constant for the i -th complexation reaction,

k_i^{fx} = modified forward reaction rate constant for the i -th complexation reaction.

For the sorption reaction via surface complexation, Eq. (2.50) is replaced by

$$\theta \frac{\partial y_i}{\partial t} + \frac{\partial \theta}{\partial t} y_i = \theta r_i^y, \quad i = 1, 2, \dots, K_y \quad (3.18)$$

and the reaction rate is given by

$$r_i^y = -k_i^{by} y_i + k_i^{fy} \prod_{k=1}^{N_a} c_k^{a_{ik}^y} \prod_{k=1}^{N_s} s_k^{b_{ik}^y}, \quad i = 1, 2, \dots, K_y \quad (3.19)$$

where

K_y = number of adsorbed species of kinetic reactions,

k_i^{by} = modified backward reaction rate constant for the i -th adsorption reaction,

k_i^{fy} - modified forward reaction rate constant for the i -th adsorption reaction.

For the sorption reaction via ion-exchange, Eq. (2.54) is replaced by

$$\theta \frac{\partial z_i}{\partial t} + \frac{\partial \theta}{\partial t} z_i = \theta r_i^z, \quad i = 1, 2, \dots, K_z \quad (3.20)$$

and the reaction rate is given by

$$r_i^z = -k_i^{bz} y_i + k_i^{fz} f_i(c_1, c_2, \dots, c_{N_a}; N_{eq}), \quad i = 1, 2, \dots, K_z \quad (3.21)$$

where

K_z - number of ion-exchanged species of kinetic reactions,

k_i^{bz} - modified backward reaction rate constant for the i -th ion-exchange reaction,

k_i^{fz} - modified forward reaction rate constant for the i -th ion-exchange reaction.

For precipitation reaction, Eq. (2.56) is replaced by

$$\theta \frac{\partial p_i}{\partial t} + \frac{\partial \theta}{\partial t} p_i = \theta r_i^p, \quad i = 1, 2, \dots, K_p \quad (3.22)$$

and the reaction rate is given by

$$r_i^p = -k_i^{lp} + k_i^{fp} \prod_{k=1}^{N_a} x_k^{a_{ik}^p}, \quad i = 1, 2, \dots, K_p \quad (3.23)$$

where

K_p - number of precipitated species of kinetic reactions,

k_i^{bp} - modified backward reaction rate constant for the i-th precipitation reaction,

k_i^{fp} - modified forward reaction rate constant for the i-th precipitation reaction.

How easily a model can be modified to treat the mixed equilibrium and chemical kinetics reactions can be stated as two questions: (1) how easily can one use Eqs. (3.16), (3.18), (3.20), and (3.22) for solving additional PDVs without excessive complications and (2) how easily can one compute the reaction rates specified by Eqs. (3.17), (3.19), (3.21), and (3.23) once the PDVs are given. As far as the second question is concerned, all the comments regarding the ability of a model to consider the full complement of equilibrium reactions also apply to mixed equilibrium and kinetic reactions (i.e., SIA-3, DSA-3, DAE-2, and DAE-1 models can encompass full complement of complexation, redox, acid-base reactions, sorption, and precipitation-dissolution reactions either in equilibrium or kinetically). DSA-1, DSA-2, SIA-1, and SIA-2 models cannot deal with cases in which both equilibrium and kinetic precipitation reactions occur simultaneously.

For DAE-1 models, no additional PDVs are needed. One can simply replace K_x equations of Eq. (2.46) by Eq. (3.16), K_y equations of Eq. (2.50) by Eq. (3.18), K_z equations of Eq. (2.54) by Eq. (3.20), and K_p equations of Eq. (2.56) by Eq. (3.22). Then, one proceeds to discretize Eq. (3.16) along with Eq. (3.1) in space to result in a set of $(N_a + K_x)$ ODEs. This set of ODEs coupled with N_s ODEs given by Eq. (2.29), K_y ODEs

given by Eq. (3.18), K_z ODEs given by Eq. (3.20), and K_p ODEs given by Eq. (3.22), $(M_x - K_x)$ AEs given by Eq. (2.46), $(M_y - K_y)$ AEs given by Eq. (2.50), $(M_z - K_z)$ AEs given by Eq. (2.54), and $(M_p - K_p)$ AEs given by Eq. (2.56) form a set of mixed differential and algebraic equations. Thus, it is seen that DAE-1 models can be easily modified to deal with mixed kinetic and equilibrium reactions without much effort.

For DAE-2, DSA, and SIA models, additional K_x PDVs are needed. These are the concentrations of K_x complexed species, x_i 's ($i = 1, 2, \dots, K_x$), resulting from complexation kinetics. Because these variables are subject to hydrological transport, they are considered as the PDVs rather than the SDVs. On the other hand, K_y y_i 's, K_z z_i 's, and K_p p_i 's can be treated as the SDVs because spatial derivatives do not appear in their governing equations. Thus, K_x equations of Eq. (3.16) should be solved simultaneously with Eqs. (3.4), (3.5), and (2.56) for DAE-2 models, with Eq. (3.6) for DSA-1 models, with Eq. (3.7) for DSA-2 models, with Eq. (3.8) for DSA-3 models, with Eq. (3.9) for SIA-1 models, with Eq. (3.10) for SIA-2 models, and with Eq. (3.11) or (3.12) for SIA-3 models, respectively. In the case of DAE-2 and SIA models, no modification is needed to alter the governing equations. However, for DSA-1 models, Eq. (3.6) must be modified to include terms associated with terms $\partial C_j / \partial x_i$'s and $\partial S_j / \partial x_i$'s ($j = 1, 2, \dots, N_a$ and $i = 1, 2, \dots, K_x$). Similarly, for DSA-2 models, Eq. (3.7) must be modified to include terms associated with $\partial S_j / \partial x_i$'s. For DSA-3 models, Eq. (3.8) must be modified to include terms

associated with $\partial C_j / \partial x_i$'s ($j = 1, 2, \dots, N_a$ and $i = 1, 2, \dots, K_x$). Hence, for DAE-2 and SIA models, the modification to treat chemical kinetics can be done with reasonable ease by simply adding K_x equations to the primary governing equations for K_x PDVs. For DSA models, the modification requires extra strenuous efforts to altering the governing equations.

From these discussions, it is obvious that very little effort is required to modify DAE-1 models for dealing with complete suite of mixed equilibrium and chemical kinetic reactions. The SIA-3 models can also be modified to treat complete suite of mixed equilibrium and chemical kinetic reactions with reasonable ease. SIA-1 and SIA-2 models can be modified to treat equilibrium and chemical kinetic reactions with reasonable ease if precipitation equilibria do not occur. DSA models are not appropriate candidates for modification to deal with mixed equilibrium and chemical kinetic reactions.

4. HYDROLOGIC TRANSPORT MODULE

Equations. (2.19) through (2.23), (2.29), (2.30), (2.46), (2.50), (2.54), and (2.56) constitute a coupled system of hydrological transport and chemical equilibrium reactions. Analytical solution to the system in general is beyond the capability of present-day applied mathematics. Numerical methods are the only tool that can be used to achieve a solution. A large number of numerical approximations can be used to reduce the partial differential equations (PDEs) governing the hydrologic transport to a system of algebraic equations (AEs). The most common numerical methods used to approximate Eq. (2.19) are finite-difference methods (FDMs) and finite-element methods (FEMs) (Forsythe and Wasaw 1960; Huebner 1975; Lapidus and Pinder 1982). Many other numerical techniques such as the integrated finite-difference method (IFDM) (Narasimhan and Witherspoon 1977), the integrated compartment method (ICM) (Yeh and Luxmoore 1983), or the method of characteristics (MOC) (Koniknow and Bredehoeft 1978) have been employed to deal with special cases of the hydrologic transport equations. Only the finite differences and finite elements can be applied to the most generalized form of the transport equations. The advantages of FEMs are their inherent ability to discretize complex boundaries, ease to deal with flux-type boundary conditions, and flexibility to include cross-derivative terms. Disadvantages of FEM include the requirements of central process unit (CPU) time to obtain element matrices and the inflexibility of using iteration methods to solve the resulting matrix equation. On the other

hand, the FDM offers great economy because of simple interpolation for the derivatives and provides flexibility of solving the resulting matrix equation with various iteration methods. However, it suffers from the following aspects: the regular rectangular grid system has to be used, the flux-type boundary conditions have to be extrapolated, and the cross-derivative terms cannot be consistently approximated. The most severe limitations of the IFDM are its inability to treat anisotropic media and its usage of the Jacobian iteration method in which the rate of convergency is extremely slow; however, it offers even more flexibility than the FEMs in discretizing the complex boundaries, and the physical representation of the method is clearly understood. The ICM, while retaining the advantage of the IFDM, can deal with anisotropic media by defining new variables but at the expense of having to solve a large number of simultaneous field equations (Yeh and Luxmoore 1983). In addition, ICM provides options of using the direct elimination method and iteration methods with the Gauss-Seidel or successive over-relaxation schemes to solve the matrix equation (Yeh and Luxmoore 1983). The MOC is best used to solve advection dominant transport problems. The main limitations of the MOC lies in the fact that computer codes based on the method are problem specific and are very difficult to modify for generic applications.

In light of these discussions, FEMs are the preferred numerical method. In addition, there has been recent, significant progress in using iteration methods to solve finite element equations (Yeh 1985; Yeh 1986)

and influence coefficient methods have been proposed to analytically and thus economically, compute the element matrices (Huyakorn 1984).

The hydrologic transport module is used to solve the transport equation specified by Eqs. (3.11), (3.12), or (3.13) and (2.29).

4.1 SPATIAL FINITE-ELEMENT DISCRETIZATION

Rearranging Eq. (3.12) in the implicit form, disregarding the decay term, and dropping the subscript to simplify the notation, we obtain

$$\theta \frac{\partial T}{\partial t} + V \cdot \nabla T + K(T) + \frac{\partial \theta}{\partial t} T = V \cdot \nabla (S+P) + K(S+P) + QC^* \quad (4.1)$$

where K is an operator denoting

$$K(!) = (-\nabla \cdot \theta D \cdot \nabla + Q - \frac{\partial \theta}{\partial t})(!) \quad (4.2)$$

4.1.1 Weighted-Residual Finite-Element Method

Equation (4.1) is integrated in the spatial dimensions by the weighted residual method in conjunction with finite elements. Because of the formulation and use of the finite-element method has been well documented, the theoretical basis will not be presented here. Only the numerical procedures are summarized in the following discussion. The region of interest is subdivided into an assemblage of smaller subdomains call elements interconnected by nodes that may be either on the vertices or the boundaries of the elements. Following the procedure of the finite-

element weighted-residual method, approximate formulation of the distribution of the total analytical concentration T in Eq. (4.1) is obtained. Thus, let the variable T be approximated by

$$T = \sum_{j=1}^n T_j(t) N_j \quad (4.3)$$

where

N_j - the basis function of the spatial coordinate
for j -th node,

T_j - the value of T at node j ,

n - number of nodes in the region.

Upon substituting Eq. (4.3) into Eq. (4.1) and applying the principle of weighted-residual, we obtain the following matrix equation

$$[M] \left(\frac{dT}{dt} \right) + ([A] + [K] + [E])(T) = ([A] + [K])(S + P) + (Q) + (B) \quad (4.4)$$

where (dT/dt) , (T) , (S) , and (P) are the column vectors containing the values of dT/dt , T , S , and P , respectively, at all nodes; $[M]$ is the mass matrix resulting from the storage term; $[A]$ is the advection matrix representing the velocity term; $[K]$ is the modified stiff matrix resulting from the action of dispersion, source of water, and the rate of change of moisture content; $[E]$ is the growth matrix representing the effect of the rate of change of moisture content; and (Q) and (B) are the load vectors from the internal and boundary sources, respectively. The matrices, $[M]$, $[A]$, $[K]$, and $[E]$, are given by

$$M_{ij} = \sum_{e \in M_e} \int_{R_e} N_{\alpha}^e \theta N_{\beta}^e dR \quad (4.5)$$

$$A_{ij} = \sum_{e \in M_e} \int_{R_e} W_{\alpha}^e (V \cdot \nabla N_{\beta}^e) dR \quad (4.6)$$

$$K_{ij} = \sum_{e \in M_e} \int_{R_e} [(\nabla N_{\alpha}^e) \cdot \theta D \cdot (\nabla N_{\beta}^e) + N_{\alpha}^e (Q - \frac{\partial \theta}{\partial t}) N_{\beta}^e] dR \quad (4.7)$$

$$E_{ij} = \sum_{e \in M_e} \int_{R_e} N_{\alpha}^e \frac{\partial \theta}{\partial t} N_{\beta}^e dR \quad (4.8)$$

where

R_e - the region of element e ,

M_e - the set of elements that have a local side α - β coinciding with the global side i - j ,

W_{α}^e - the α -th local weighting function of element e ,

N_{α}^e - the α -th local basis function of element e .

Similarly the load vectors (Q) and (B) are given by

$$Q_i = \sum_{e \in M_e} \int_{R_e} N_{\alpha}^e Q C^* dR \quad (4.9)$$

and

$$B_i = - \sum_{e \in N_{se}} \int_{B_e} N_{\alpha}^e n \cdot (- \theta D \cdot \nabla C) dB \quad (4.10)$$

where

B_e - the length of boundary segment e ,

N_{se} - the set of boundary segments that have a local node coinciding with the global node i .

It should be noted that in applying the weighted-residual finite element method to Eq. (4.1), we have used the set of basis functions as the set of weighting functions for all terms in Eq. (4.1) except for the velocity term. For the velocity term, we may use either the set of basis functions or a set of different functions, which will be described subsequently.

The reduction of the partial differential equation (PDE), Eq. (4.1), to the set of ordinary differential equations (ODE), Eq. (4.4), simplifies to the evaluation of integrals on the right-hand side of Eqs. (4.5) through (4.10) for every element or boundary segment e . The major task that remains is the specification of basis and weighting functions and the performance of integration to yield the element matrices. This will be carried out for both the quadrilateral and triangular elements because both types of elements are employed in this report.

4.1.2 Base and Weighting Functions

For a quadrilateral element having four corner nodes, a bilinear polynomial base function for the α -th node may be written in terms of local normalized coordinate as

$$N_{\alpha}^e = (1 + \xi_{\alpha}\xi)(1 + \eta_{\alpha}\eta)/4, \quad \alpha = 1, 2, 3, 4 \quad (4.11)$$

where ξ_α and η_α are the local coordinates of the corner nodes, which are numbered 1 to 4 progressing around the element in a counterclock direction as shown in Fig. 4.1. The transformation from local coordinate (ξ, η) to the global coordinate (x, z) is achieved by

$$x = \sum_{\alpha=1}^4 x_\alpha N_\alpha^e(\xi, \eta) \quad \text{and} \quad z = \sum_{\alpha=1}^4 z_\alpha N_\alpha^e(\xi, \eta) \quad (4.12)$$

When the advection terms in Eq. (4.1) are much more important than other terms, it is sometimes advantageous to use a weighting function different from the base function. For example, upstream weighting functions have been shown to be adequate (Huyakorn and Pinder 1977). In this report, two options are provided: the Galerkin finite-element option and the upstream weighting finite-element option. The function W^e for the former will be set equal to the base function N^e , that is,

$$W_\alpha^e = N_\alpha^e, \quad \alpha = 1, 2, 3, 4 \quad (4.13)$$

The weighting function for the latter case can be derived as follows:

$$W_1^e = [(2-3\alpha_1) - 2\xi + 3\alpha_1\xi^2][(2-3\beta_2) - 2\eta + 3\beta_2\eta^2]/16 \quad (4.14a)$$

$$W_2^e = [(2+3\alpha_1) + 2\xi - 3\alpha_1\xi^2][(2-3\beta_1) - 2\eta + 3\beta_1\eta^2]/16 \quad (4.14b)$$

$$W_3^e = [(2+3\alpha_2) + 2\xi - 3\alpha_2\xi^2][(2+3\beta_1) + 2\eta - 3\beta_1\eta^2]/16 \quad (4.14c)$$

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LOCAL COORDINATES

GLOBAL COORDINATES

Fig. 4.1 Global coordinate vs local coordinate for a typical quadrilateral element

$$w_4^e = [(2-3\alpha_2) - 2\xi + 3\alpha_2\xi^2][(2+3\beta_2) + 2\eta - 3\beta_2\eta^2]/16 \quad (4.14d)$$

where α_1 , α_2 , β_1 , and β_2 are the weighting factors assigned to the sides 12, 43, 23, and 14, respectively, of the element e as shown in Fig. 4.2.

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Fig. 4.2 Location and direction of upstream weighting function along the edge of a transformed element

The exact solution of the original differential equation can be obtained at the nodal points if (Christie et al. 1976)

$$\alpha = \coth[(UL)/(2D)] - [(2D)/(UL)] \quad (4.15)$$

where α may denote α_1 , α_2 , β_1 , or β_2 ; and U , L , and D are the velocity component, length, and dispersion coefficient component, respectively, along the corresponding side (Fig. 4.2). It should be noted that α in Eq. (4.15) was derived for steady state transport. For the transient transport, dimensional analysis would yield the dependence of α on the mesh Courant number $U\Delta t/L$ as well as the mesh Peclet number UL/D (Zienkiewicz and Parekh, 1970). The relationship between α and the Courant and Peclet numbers has to be a further topic of research.

For a linear triangular element e (Fig. 4.3), the basis functions for its three nodes are given by

$$N_1^e = L_1, \quad N_2^e = L_2, \quad \text{and} \quad N_3^e = L_3 \quad (4.16)$$

where N_α^e ($\alpha = 1, 2, \text{ or } 3$) is the base function of node α in terms of local coordinate (L_1, L_2, L_3) (Fig. 4.3). The local coordinates are also called area coordinates for a reason to be explained later. The global coordinate (x, z) and the area coordinates (L_1, L_2, L_3) are related by

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(a)

(b)

Fig. 4.3 Global coordinate vs area coordinate for a typical triangular element

$$L_1 = (a_1 + b_1x + c_1z)/(2A) \quad (4.17a)$$

$$L_2 = (a_2 + b_2x + c_2z)/(2A) \quad (4.17b)$$

$$L_3 = (a_3 + b_3x + c_3z)/(2A) \quad (4.17c)$$

where

$$a_1 = x_2z_3 - x_3z_2, \quad b_1 = z_2 - z_3, \quad c_1 = x_3 - x_2 \quad (4.17d)$$

$$a_2 = x_3z_1 - x_1z_3, \quad b_2 = z_3 - z_1, \quad c_2 = x_1 - x_3 \quad (4.17e)$$

$$a_3 = x_1z_2 - x_2z_1, \quad b_3 = z_1 - z_2, \quad c_3 = x_2 - x_1 \quad (4.17f)$$

and A is the area of the triangle. It is seen from Eqs. (4.17a) through (4.17f) that

$$L_1 + L_2 + L_3 = 0 \quad (4.18)$$

Thus, it is clear that only two of the area coordinates can be independent, just as in the original coordinate system, where there are only two independent coordinates, x and z. Furthermore, a little algebraic manipulation will reveal that the coordinates L_1 , L_2 , and L_3 are in fact the ratios of the areas A_1 , A_2 , and A_3 , respectively, to the triangular area A (Fig. 4.3). This is why they are called area coordinates.

Again for the advection dominant transport, two options of weighting functions are given for the linear triangular elements. For the Galerkin weighting, the function is given by

$$W_{\alpha}^e = N_{\alpha}^e = L, \quad \alpha = 1, 2, 3 \quad (4.19)$$

For the upstream weighting, the function can be derived based on the conditions of compatibility, completeness, total unit weight, and upstream weighting:

$$W_1^e = L_1 - 3\alpha_3 L_2 L_1 + 3\alpha_2 L_3 L_1 \quad (4.20a)$$

$$W_2^e = L_2 - 3\alpha_1 L_3 L_2 + 3\alpha_3 L_1 L_2 \quad (4.20b)$$

$$W_3^e = L_3 - 3\alpha_2 L_1 L_3 + 3\alpha_1 L_2 L_3 \quad (4.20c)$$

where α_1 , α_2 , and α_3 are the weighting factors associated with the element sides opposite to nodes 1, 2, and 3, respectively (Fig. 4.4).

4.1.3 Evaluation of Element Matrices

To complete the reduction of the PDE [Eq. (4.1)] to the ODE [Eq. (4.4)], one has to evaluate the integrals on the right-hand sides of Eqs. (4.5) through (4.9) for every element to yield the element mass matrix $[M^e]$, advection matrix $[A^e]$, dispersion matrix $[D^e]$, fluid source matrix $[F^e]$, growth matrix $[E^e]$, and the element column vector (Q^e) as

Fig. 4.4 Location and direction of upstream weighting function along the edge of a triangular element

$$M_{\alpha\beta}^e = \int_{R_e} N_{\alpha}^e \theta N_{\beta}^e dR \quad (4.21)$$

$$A_{\alpha\beta}^e = \int_{R_e} W_{\alpha}^e (V \cdot \nabla N_{\beta}^e) dR \quad (4.22)$$

$$D_{\alpha\beta}^e = \int_{R_e} (\nabla N_{\alpha}^e) \cdot \theta D \cdot (\nabla N_{\beta}^e) dR \quad (4.23)$$

$$F_{\alpha\beta}^e = \int_{R_e} W_{\alpha}^e Q N_{\beta}^e dR \quad (4.24)$$

$$E_{\alpha\beta}^e = \int_{R_e} N_{\alpha}^e \frac{\partial \theta}{\partial t} N_{\beta}^e dR \quad (4.25)$$

and

$$Q^e = \int_{R_e} N_{\alpha}^e Q C^* dR \quad (4.26)$$

where the superscript or subscript e denotes the element and $\alpha, \beta = 1, 2, 3$, or 4 for linear quadrilateral elements or $\alpha, \beta = 1, 2$, or 3 for linear triangular elements.

For a quadrilateral element, Eqs. (4.21) through (4.26) are computed by Gaussian quadrature (Conte 1965) because it is not easy to solve Eq. (4.12) for ρ and θ in terms of x and z . On the other hand, for a triangular element, the transformation from the global coordinate (x, z) to

the local coordinate (L_1, L_2, L_3) is already given explicitly by Eqs. (4.17a) through (4.17f). This fact and the following integration identity,

$$\int_{R_e} L_1^n L_2^m L_3^k dR = 2A \frac{n! m! k!}{(n+m+k+2)!} \quad (4.27)$$

make the evaluation of Eqs. (4.21) through (4.26) analytically possible for triangular elements. With the element matrices $[M^e]$, $[A^e]$, $[D^e]$, $[F^e]$, and $[E^e]$ and the element column vector (Q^e) computed, the global matrices $[M]$, $[A]$, $[K]$, and $[E]$ and the global column vector (Q) are then assembled element by element.

4.1.4 Mass Lumping Option

Referring to the element mass matrix $[M^e]$, fluid source matrix $[F^e]$, and growth matrix $[E^e]$, one may note that these are the unit matrix if the finite-difference formulation is adopted in the spatial discretization. Hence, by proper scaling, these matrices can be reduced to the finite difference equivalent by lumping (Clough 1971). In many cases, the lumped mass, fluid source, and growth matrices would result in better solution. Furthermore, with these lumped element matrices, the problem can be reduced to a beaker system when advection and dispersion-diffusion terms are not involved in the transport equation. Under such circumstances, they are preferred to the non-lumped mass, fluid source, and growth matrices. Therefore, an option is provided in this report for the lumping

of these matrices. A systematic and mathematically acceptable procedure for such lumping has been well established (Zienkiewicz 1977). For example, the element mass matrix can be lumped according to the following:

$$M_{\alpha\alpha}^e = \sum_{\beta=1}^4 \int_{R_e} N_a^e \theta N_b^e dR \quad (4.28a)$$

$$M_{\alpha\beta}^e = 0 \quad \text{if } \beta \neq \alpha \quad (4.28b)$$

4.2 TIME INTEGRATION

An important advantage in finite-element approximation over the finite difference approximation is the inherent ability to handle complex boundaries and obtain the normal derivatives therein. In the time dimension, such advantages are not evident. Thus, finite difference methods are typically used in the approximation of the time derivative. Using a time weighting factor w_v for the advection term and w for all other terms, we obtain from Eq. (4.4) the following matrix equation:

$$[G](T)_{t+\Delta t} = [H]((S)_{t+\Delta t} + (P)_{t+\Delta t}) + (L) + (B) \quad (4.29)$$

where $(T)_{t+\Delta t}$, $(S)_{t+\Delta t}$, and $(P)_{t+\Delta t}$ are column vectors representing the values of (T) , (S) , and (P) , respectively, at time $(t + \Delta t)$ with Δt being the time step size and the matrices $[G]$ and $[H]$ and the load vector (L) are given as

$$[G] = [M]/\Delta t + w_v[A] + w([K] + [E]) \quad (4.30)$$

$$[H] = w_v[A] + w[K] \quad (4.31)$$

and

$$\{L\} = \{Q\} + ([M]/\Delta t - (1-w)[E])(T)_t - ((1-w_v)[A] + (1-w)[K])(C)_t \quad (4.32)$$

in which w_v is the time weighting factor for the velocity term, w is the time weighting factor for all other terms, and $(T)_t$ and $(C)_t$ are the values of (T) and (C) , respectively, at time t . When $w_v = 0$ and $w = 0$, the time integration is explicit. When $w_v = 0.5$ and $w = 0.5$, it is the Crank-Nicolson central difference. For the implicit (or backward) difference, both w_v and w are equal to 1.0.

4.3 BOUNDARY CONDITIONS

To incorporate the boundary conditions, we have to evaluate the right-hand side of Eq. (4.10) for every boundary segment B_e to yield the load vector $\{B^e\}$:

$$B_{\alpha}^e = - \int_{B_e} N_a^e n \cdot (-\theta D \cdot \nabla C) \, dB, \quad \alpha = 1, 2 \quad (4.33)$$

For the Neumann boundary condition given by Eq. (2.54), we simply substitute Eq. (2.54) into Eq. (4.33) to yield a boundary-element column vector $\{B_n^e\}$ for a Neumann segment:

$$\{B_n^e\} = \{q_n^e\} \quad (4.34)$$

where $\{q_n^e\}$ is the Neumann boundary flux vector given by

$$q_{n\alpha}^e = - \int_{B_e} N_a^e q_N dB, \quad \alpha = 1, 2 \quad (4.35)$$

This Neumann boundary flux vector represents the normal fluxes through the two nodal points of the segment B_e on B_N .

For the Cauchy boundary condition given by Eq. (2.55), we may rewrite Eq. (4.33) in the following form:

$$B_\alpha^e = - \int_{B_e} N_a^e n \cdot (VC - \theta D \cdot \nabla C) dB + \int_{B_e} N_a^e n \cdot \nabla T dB - \int_{B_e} N_a^e n \cdot \nabla (S+P) dB, \quad \alpha = 1, 2 \quad (4.36)$$

The total analytical concentration on the boundary segment B_e can be approximated by

$$T = \sum_{\beta=1}^2 T_\beta N_\beta^e, \quad (4.37a)$$

Similarly, the total sorbed concentration S and the total precipitated concentration on the same boundary segment can be approximated by

$$S = \sum_{\beta=1}^2 S_{\beta} N_{\beta}^e, \quad (4.37b)$$

and

$$P = \sum_{\beta=1}^2 P_{\beta} N_{\beta}^e, \quad (4.37c)$$

Substituting Eqs. (2.55) and (4.37) into Eq. (4.36), we obtain boundary-

element column vector (B_c^e) for a Cauchy segment:

$$(B_c^e) = (q_c^e) + [V_c^e](T) - [V_c^e]((S)+(P)) \quad (4.38)$$

in which the Cauchy boundary flux vector (q_c^e) and the Cauchy boundary matrix $[V_c^e]$ from the normal velocity component are given by

$$q_{c\alpha}^e = - \int_{B_e} N_{\alpha}^e q_c \, dB, \quad \alpha = 1, 2 \quad (4.39a)$$

and

$$v_{c\alpha\beta}^e = \int_{B_e} N_{\alpha}^e n \cdot \nabla N_{\beta}^e \, dB, \quad \alpha = 1, 2 \text{ and } \beta = 1, 2 \quad (4.39b)$$

Segments on which the variable boundary conditions are imposed are the flow-through boundaries on which the flow direction is not known a priori. When the flow is directed into the region, Cauchy boundary conditions will be used. The boundary-element column vector (B_v^e) for a

variable-boundary segment can be obtained similar to (B_C^e) :

$$(B_V^e) = (q_V^e) + [V_V^e](T) - [V_V^e]((S)+(P)) \quad (4.40)$$

in which the variable-boundary flux vector (q_V^e) and the variable-boundary matrix $[V_V^e]$ from the normal velocity component are given by:

$$q_{V\alpha}^e = - \int_{B_e} N_\alpha^e (n \cdot V) C_{in} dB, \quad \alpha = 1, 2 \quad (4.41a)$$

and

$$V_{V\alpha\beta}^e = \int_{B_e} N_a^e n \cdot V N_b^e dB, \quad \alpha = 1, 2 \text{ and } \beta = 1, 2 \quad (4.41b)$$

where C_{in} is the total dissolved concentration of the incoming fluid.

When the flow is directed out from the region, both (q_V^e) and $[V_V^e]$ are set equal to 0.

Assembling over all Neumann, Cauchy, and variable boundary segments, we obtain the global boundary column vector (B) as:

$$(B) = (q) + [V](T) - [V]((S)+(P)) \quad (4.42)$$

in which

$$(q) = \sum_{e \in N_{ne}} (q_n^e) + \sum_{e \in N_{ce}} (q_c^e) + \sum_{e \in N_{ve}} (q_v^e) \quad (4.43a)$$

$$[V] = \sum_{e \in N_{ce}} [V_c^e] + \sum_{e \in N_{ve}} [V_v^e] \quad (4.43b)$$

where N_{ne} , N_{ce} , and N_{ve} are the number of Neumann, Cauchy, and variable-boundary segments, respectively.

Substituting Eq. (4.42) into Eq. (4.29) and dropping the subscript $(t + \Delta t)$ to simplify the notation, we obtain

$$[U](T) = [W]([S] + [P]) + [R] \quad (4.44)$$

where $[U]$, $[W]$, and $[R]$ after using Eqs. (4.30) through (4.32) are given by the following equations:

$$[U] = [G] - w_v[V] \quad (4.45)$$

$$[W] = [H] - w_v[V] \quad (4.46)$$

and

$$[R] = [L] + [q] + (1-w_v)[C]_t \quad (4.47)$$

At nodes where Dirichlet boundary conditions are applied, an identity equation is generated for each node and included in the matrices of Eq. (4.44). The detailed method of applying this type of boundary condition can be found elsewhere (Wang and Connor 1975).

Equation (4.44) after modified for the Dirichlet boundary condition is solved iteratively and in sequence with the chemical equilibrium problem specified by Eqs. (2.19) through (2.22), (2.28), (2.29), (2.36), (2.38), (2.39), (2.41) and (2.42) to yield (T) , (C) , (S) , (P) , (W) , (p) , (X) , (Y) , (c) , (s) , (x) , and (y) for all chemical components.

4.4 SOLUTION OF MATRIX EQUATIONS

Although both the matrices $[U]$ and $[W]$ are not functions of the unknown (T) , Eq. (4.44) still represents a system of nonlinear algebraic equations because both (S) and (P) are functions of (T) . This requires some type of iterative procedure to obtain the solution. The approach taken here is to make an initial estimate of the unknown (T) . Using this estimate, we then compute the total sorbed concentration (S) and total precipitated concentration (P) from the chemical equilibrium reactions. Substituting these computed (S) and (P) into the right-hand side of Eq. (4.44) and combining $[W]((S)+(P))$ with (R) to form a new right-hand side load vector, we linearize the matrix equation, which is then solved by the method of linear algebra. The new estimate is now obtained by the weighted average of the new solution and the previous estimate

$$(T^{(k+1)}) = \omega(T) + (1-\omega)(T^k) \quad (4.48)$$

where $(T^{(k+1)})$ is the new estimate, (T^k) is the previous estimate, (T) is the new solution, and ω is the iteration parameter. The procedure is repeated until the new solution (T) is within a tolerance error. When the iteration parameter is greater than or equal to 0 but is less than 1, the

iteration is termed under-relaxation. If $\omega = 1$, the method is the exact relaxation. For the cases when ω is greater than 1 but less than or equal to 2, the iteration is termed over-relaxation.

Two options are employed to solve the linearized matrix equation: the direct elimination method and the pointwise iteration method. When the direct elimination method is used to solve the matrix equation, a single iteration loop is employed to iterate the nonlinearity. However, when the pointwise iterations are used, a double loop is required: the inner loop to solve the linearized equation and the outer loop to iterate the nonlinearity. Three options have been employed when the pointwise iteration method is used to solve the linearized matrix equation. These are the successive under-relaxation (SUR), Gauss-Seidel (G-S) iteration, and successive over-relaxation (SOR). These three methods are unified by a relaxation parameter, Ω . When Ω is less than 1 but greater than or equal to 0, the method is termed SUR iteration. When Ω is equal to 1, the method is termed Gauss-Seidel iteration. If Ω is greater than 1 but less than or equal to 2, the method is termed SOR iteration.

4.5 SOLUTION FOR TOTAL ANALYTICAL CONCENTRATIONS OF ADSORBENT COMPONENTS

Equation (2.29) governs the mass balance of adsorbent components. It does not involve spatial derivatives and its solution can, thus, be obtained by simple integration of the equation with respect to time. Furthermore, the solution of Eq. (2.29) can be achieved independently of the solutions of Eq. (2.19). The solution is performed only once during

any iteration between the hydrologic transport module and chemical equilibrium module. An implicit scheme can be used to integrate Eq. (2.29) to yield

$$\left(\theta + \Delta t \frac{\partial \theta}{\partial t}\right) (W_j)_{t+\Delta t} - \theta (W_j)_t, \quad j = 1, 2, \dots, N_s \quad (4.49)$$

where $(W_j)_{t+\Delta t}$ and $(W_j)_t$ are the value of W_j at time $(t+\Delta t)$ and t , respectively. Equation (4.49) is applicable to all nodes in the region of interest.

5. CHEMICAL EQUILIBRIUM MODULE

Equations (3.11), (3.12), or (3.13) form the primary governing equations (PGEs) whereas Equations (2.20) through (2.23), (2.29), (2.30), (2.46), (2.50), (2.54), and (2.56) constitute the secondary governing equations (SGEs). Numerical solutions of the PGEs [Eq. (3.12)] for the primary dependent variables (PDVs) T_j 's, and the SGEs [Eq. (2.29)] for the secondary dependent variables (SDVs) W_j 's are discussed in Chapter 4. This chapter describes the numerical solution of the SGEs [Eqs. (2.20) through (2.23), (2.30), (2.46), (2.50), (2.54), and (2.56)] for the SDVs C_j 's, S_j 's, P 's, c_j 's, s_j 's, x_i 's, y_i 's, z_i 's, and p_i 's, respectively.

5.1 REDUCTION AND RECAPTURE OF THE SECONDARY GOVERNING EQUATIONS

Given the total analytical concentrations (T_j 's and W_j 's) of all components, the SGEs [Eqs. (2.20) through (2.23), (2.30), (2.46), (2.50), (2.54), and (2.56)] contain nine sets of unknowns ($N_a C_j$'s, $N_a S_j$'s, $N_a P_j$'s, $N_a c_k$'s, $N_s s_k$'s, $M_x x_i$'s, $M_y y_i$'s, $M_z z_i$'s, and $M_p p_i$'s) in nine sets of algebraic equations. Simultaneous solution of these nine sets of algebraic equations should yield nine sets of unknowns. However, simplifications can be made to reduce the number of simultaneous equations to be solved.

Substitution of Eqs. (2.46) and (2.50) into Eqs. (2.23) and (2.30) yield the following mole balance equations

$$T_j = c_j + \sum_{i=1}^{M_x} a_{ij}^x (\alpha_i^x \prod_{k=1}^{N_a} c_k^{a_{ik}^x}) + \sum_{i=1}^{M_y} a_{ij}^y [\alpha_i^y (\prod_{k=1}^{N_a} c_k^{a_{ik}^y}) (\prod_{k=1}^{N_s} s_k^{b_{ik}^y})] +$$

$$\sum_{i=1}^{M_z} a_{ij}^z z_i + \sum_{i=1}^{M_p} a_{ij}^p p_i, \quad j = 1, 2, \dots, N_a, \quad (5.1)$$

$$W_j = s_j + \sum_{i=1}^{M_y} b_{ij}^y [\alpha_i^y (\prod_{k=1}^{N_a} c_k^{a_{ik}^y}) (\prod_{k=1}^{N_s} s_k^{b_{ik}^y})],$$

$$j = 1, 2, \dots, N_s, \quad (5.2)$$

To turn our attention to the chemical model, let us repeat the mass action equations [Eqs. (2.54), (2.56), (2.46) and (2.50)] and other mole balance equations [Eqs. (2.20), (2.21), and (2.22)] in the following:

$$z_i = f_i(c_1, c_2, \dots, c_N; N_{eq}) , \quad i = 1, 2, \dots, M_z, \quad (5.3)$$

$$1 = \alpha_i^p \prod_{k=1}^{N_a} c_k^{a_{ik}^p}, \quad i = 1, 2, \dots, M_p \quad (5.4)$$

$$x_i = \alpha_i^x \prod_{k=1}^{N_a} c_k^{a_{ik}^x}, \quad i = 1, 2, \dots, M_x \quad (5.5)$$

$$y_i = \alpha_i^y (\prod_{k=1}^{N_a} c_k^{a_{ik}^y}) (\prod_{k=1}^{N_s} s_k^{b_{ik}^y}), \quad i = 1, 2, \dots, M_y, \quad (5.6)$$

$$C_j = c_j + \sum_{i=1}^{M_x} a_{ij}^x x_i, \quad j = 1, 2, \dots, N_a \quad (5.7)$$

$$S_j = \sum_{i=1}^{M_y} a_{ij}^y y_i + \sum_{i=1}^{M_z} a_{ij}^z z_i, \quad j = 1, 2, \dots, N_a \quad (5.8)$$

$$P_j = \sum_{i=1}^{M_p} a_{ij}^p p_i, \quad j = 1, 2, \dots, N_a \quad (5.9)$$

5.2 ACTIVITY COEFFICIENTS AND THERMODYNAMIC EQUILIBRIUM CONSTANTS.

Because the activity coefficients of all aqueous species are functions of the ionic strength of the system, the ionic strength must be known before one can compute the activity coefficients. Let I denote the ionic strength, then I is given by

$$I = \frac{1}{2} \sum_{i=1}^{M_a} a_i Z_i^2 \quad (5.10)$$

where a_i and Z_i are the molality and charge of the i -th aqueous species, respectively, M_a is the number of aqueous species equal to the number of aqueous component species plus the number of complexed species.

Many semi-empirical formulae, usually based on the Debye-Huckel theory of ion clustering, have been proposed to calculate activity coefficients. All these semi-empirical formulae have the same generalized form (Kincad et al. 1984)

$$\log(\gamma_i) = -AZ_i^2 \left(\frac{\sqrt{I}}{1 + a_i B \sqrt{I}} + B' I \right) + b_i I + B_i I^2 \quad (5.11)$$

where A, B, and B' are constants depending only on the dielectric constant and density of water and the temperature of the solution and a_i , b_i , and B_i are species dependent, adjustable parameters. For example, for the Davies Formula b_i and B_i are equal to 0; for the Debye-Huckel Formula B', b_i , and B_i are equal to 0; and the for the extended Debye-Huckel Formula used in WATEQ (Truesdell and Jones 1974) B' and B_i are equal to zero.

The thermodynamic equilibrium constants K_X^Y , K_Y^X , $K_{i,j}$, and K_P^Q are normally given for conditions at temperature equal to 25 °C and pressure equal to 1 atm. Under other conditions, the thermodynamic equilibrium constants must be corrected for temperature and pressure (Truesdell and Jones 1974).

Activity coefficients of all adsorbed species are assumed to be 1.

5.3 SOLUTION OF NONLINEAR ALGEBRAIC EQUATIONS

Equations (5.1) through (5.9) involve nine sets of unknowns given the T_j 's and W_j 's in nine sets of algebraic equations: $N_a c_k$'s, $N_s s_k$'s, $M_p p_i$'s, $M_x x_i$'s, $M_y y_i$'s, $M_z z_i$'s, $N_a C_j$'s, $N_a S_j$'s, and $N_a P_j$'s. These sets of equations can be solved by methods of nonlinear algebra, and in the proposed model, Newton-Raphson iterative technique (Westall et. al. 1976) is used. It is summarized as follows.

Consider a system of algebraic equations given by

$$y(x) = 0 \quad (5.12)$$

Taylor expansion of Eq. (5.12) about the previous iterates yield

$$y^n + \frac{dy}{dx} (x^{n+1} - x^n) = 0 \quad (5.13)$$

where y^n is the value of $y(x)$ evaluated at x^n , x^n is the value of x from previous iteration, and x^{n+1} is the value of x at new iteration. Written in matrix notation, Eq. (5.13) becomes

$$Z^n(X^n - X^{n+1}) = Y^n \quad (5.14)$$

where Y is the residues, Z is the Jacobian of Y with respect the X , the superscript n denotes the value to be evaluated at previous iteration, and the superscript $n+1$ denotes the value to be evaluated at the new iteration. Thus, the solution of Eq. (5.12) involves the following steps. First, knowing X^n , one computes the residue Y^n via the function $y(x)$. Second, one computes the Jacobian Z^n . Third one solves equation (5.14) to obtain the values ΔX (where ΔX denotes $X^n - X^{n+1}$). Finally, one obtains the new iterate by

$$X^{n+1} = \Delta X - X^n \quad (5.15)$$

The above steps are repeated until a convergent solution is obtained. The application of Newton-Raphson method to chemical equilibrium model is straightforward. The residues are computed from Eqs. (5.1) through (5.9)

(or their reduced sets). The Jacobian is computed by taking the partial differential of Eqs. (5.1) through (5.9) (or their reduced sets) with respect the species concentrations (or the reduced set of species concentrations). The derivation of the Jacobian has been reported elsewhere and will not be repeated here except for the modification for adsorption models to be given in Sect. 5.5.

5.4 TREATMENT OF PRECIPITATION-DISSOLUTION

Precipitation-dissolution can be computed with two different approaches. The first one is to consider the concentrations of all precipitated species as independent unknowns in addition to the component species concentrations. Thus, the basic independent unknowns will include N_a c_k 's, N_s s_k 's, M_z z_i 's, and M_p p_i 's, and the reduced sets of governing equations would be Eqs. (5.1) through (5.4). This approach has been used in several geochemical equilibrium models such as EQ3/EQ6 (Wolery 1979) and PHREEQE (Parkhurst et al. 1980) and in some multi-species transport models such as THCC (Carnahan 1986). The second approach is to substitute Eq. (5.4) into Eqs. (5.1), (5.2), and (5.3) to eliminate M_p c_k 's out of N_a c_k 's and M_p p_i 's from Eqs. (5.1) through (5.3). Thus, the basic independent unknowns will include $(N_a - M_p)$ c_k 's, N_s s_k 's, and M_z z_i 's, and the reduced sets of governing equations would be $(N_a - M_p)$ equations out of the N_a equations in Eq. (5.1), and Eq. (5.2) and (5.3). The detailed procedure of substituting Eq. (5.4) into Eq. (5.1) and the subsequent reduction of the number of equations can be found on pages 56 through 63 in MINEQL (Westall et al. 1976). Using the first approach,

one can modify the code to treat mixed chemical equilibrium and chemical kinetics with ease. Thus, this report uses the first approach to treat precipitation-dissolution reactions because of its simplicity.

5.5 TREATMENT OF SORPTION

Two sorption models are used in the chemical equilibrium module in this report: one is the surface complexation or adsorption model and the other is ion-exchange model. The treatment of adsorption can be dealt with as were the cases of aqueous complexation because Eqs. (5.2) and (5.6) are similar in form to Eqs. (5.1) and (5.5), respectively. However, if the double layer theory (Stumm and Morgan 1981; Davis and Leckie 1978) is used to model the adsorption process, two additional unknowns, c_o and c_b , are introduced in the adsorption reaction equations in Eq. (2.50). These two additional unknowns are defined as

$$c_o = \exp\left(-\frac{e\psi_o}{kT}\right) \quad (5.16)$$

and

$$c_b = \exp\left(-\frac{e\psi_b}{kT}\right) \quad (5.17)$$

where k is the Boltzman constant, (Joule/ $^{\circ}$ K); T is the absolute temperature, ($^{\circ}$ K); e is the electronic charge, (Columb); ψ_o is the electric potential at the surface, (Volt); and ψ_b is the electric potential at the beta layer, (volt). These two additional unknowns can be obtained by assuming that the total charge calculated by summing over the

charges of all surface species is equal to the total charge calculated by electro-static theory. Written mathematically, these two governing equations are

$$C_1(\psi_o - \psi_b)B - \sigma_o = 0 \quad (5.18a)$$

$$\sigma_o = \sum_{i=1}^M a_{io}^y y_i \quad (5.18b)$$

and

$$C_1(\psi_b - \psi_o)B + C_2(\psi_b - \psi_d)B - \sigma_b = 0 \quad (5.19a)$$

$$\sigma_b = \sum_{i=1}^M a_{ib}^y y_i \quad (5.19b)$$

where C_1 is the capacitance of the region between the "o" plane and "b" plane, B is a conversion factor from charge per unit area to moles per unit volume, σ_o is the charge density in moles per unit volume on the "o" plane, a_{io}^y is the stoichiometric coefficient of c_o in the i -th adsorbed species y_i , C_2 is the capacitance of the region between the "b" plane and "d" plane, σ_b is the charge density in moles per unit volume on the "b" plane, and a_{ib}^y is the stoichiometric coefficient of c_b in the i -th adsorbed species y_i .

Electroneutrality requires that the following relationship must be satisfied

$$\sigma_o + \sigma_b + \sigma_d = 0 \quad (5.20)$$

and the Gouy-Chapman diffuse layer theory yields the following equation

$$\sigma_d/B = - (8\epsilon\epsilon_o RT)^{1/2} \sinh\left(\frac{ze\psi_d}{2kT}\right) \quad (5.21)$$

where σ_d is the charge density in moles per unit volume in the diffusive layer "d", R is the universal gas constant, ϵ is the relative dielectric constant, ϵ_o is the permittivity of the free space, and z is valence of the ion. It should be noted that Eq. (5.21) is valid only for the cases of a symmetrical electrolyte. The charge potential relationship gives

$$C_2(\psi_d - \psi_b)B = \sigma_d \quad (5.22)$$

Combining Eqs. (5.21) and (5.22), we relate the unknowns ψ_d to ψ_b implicitly as follows

$$C_2(\psi_d - \psi_b) = - (8\epsilon\epsilon_o RT)^{1/2} \sinh\left(\frac{ze\psi_d}{2kT}\right) \quad (5.23)$$

To solve Eqs. (5.18) and (5.19) with Newton-Raphson method, we need to evaluate σ_o , σ_b , ψ_o , ψ_b , and ψ_d , and their partial derivatives with respect to c_o and c_b ($\partial\sigma_o/\partial c_o$, $\partial\sigma_o/\partial c_b$, $\partial\sigma_b/\partial c_o$, $\partial\sigma_b/\partial c_b$, $\partial\psi_o/\partial c_o$, $\partial\psi_o/\partial c_b$, $\partial\psi_b/\partial c_o$, $\partial\psi_b/\partial c_b$, $\partial\psi_d/\partial c_o$, and $\partial\psi_d/\partial c_b$). The evaluation of σ_o and σ_b , and $\partial\sigma_o/\partial c_o$, $\partial\sigma_o/\partial c_b$, $\partial\sigma_b/\partial c_o$, and $\partial\sigma_b/\partial c_b$ can be performed similarly to the evaluation for other aqueous components. The evaluation of ψ_o , ψ_b , and ψ_d , and $\partial\psi_o/\partial c_o$, $\partial\psi_o/\partial c_b$, $\partial\psi_b/\partial c_o$, $\partial\psi_b/\partial c_b$, $\partial\psi_d/\partial c_o$, and $\partial\psi_d/\partial c_b$ requires a little further elaboration. Knowing c_o and c_b from a

previous iteration, we compute ψ_o and ψ_b by inverting Eqs. (5.16) and (5.17) as

$$\psi_o = -\frac{kT}{e} \ln(c_o) \quad (5.24)$$

and

$$\psi_b = -\frac{kT}{e} \ln(c_b) \quad (5.25)$$

respectively. Having computed σ_o and σ_b from Eqs. (5.18b) and (5.19b), respectively, we compute σ_d from Eq. (5.20) and then invert Eq. (5.21) to obtain ψ_d as

$$\psi_d = \frac{2kT}{ze} \sinh^{-1} [-(\sigma_d/B)/(8\epsilon\epsilon_o RIT)^{1/2}] \quad (5.26)$$

Taking the differentiation of Eq. (5.16) with respect to c_o and c_b , respectively, we obtain

$$\frac{\partial \psi_o}{\partial c_o} = (-\frac{kT}{e})/c_o \quad (5.27a)$$

and

$$\frac{\partial \psi_o}{\partial c_b} = 0 \quad (5.27b)$$

Similarly, taking the differentiation of Eq. (5.17) with respect to c_o and c_b , respectively, we obtain

$$\frac{\partial \psi_b}{\partial c_o} = 0 \quad (5.28a)$$

and

$$\frac{\partial \psi_b}{\partial c_b} = (-\frac{kT}{e})/c_b \quad (5.28b)$$

Finally, taking the differentiation of Eq. (5.23) with respect to c_o and c_b , respectively, and substituting Eq. (5.28) into the resulting equation, we obtain

$$\frac{\partial \psi_d}{\partial c_o} = 0 \quad (5.29a)$$

and

$$\frac{\partial \psi_d}{\partial c_b} = [(-\frac{kT}{e})/c_b] / [1 + (\frac{e}{2kT})(8\epsilon\epsilon_o RIT)^{1/2} \cosh(\frac{ze\psi_d}{2kT})/C_2] \quad (5.29b)$$

For sorption via ion-exchange, Eq. (5.3) can easily be written explicitly in terms of component species concentration if the ion-exchange involves only homovalent exchange. Under such circumstances, the computation of the Jacobian of Eq. (5.3) is relatively easy and can be performed analytically. However, when ion-exchanges involve hetrovalent exchange, it is very difficult, if not impossible, to express the concentration of ion-exchanged species in terms of component species concentrations. In other word, the computation of the Jacobian can no longer be done analytically. Therefore, for generality, numerical evaluations of the Jacobian involving ion-exchange reactions are used in this report.

5.6 TREATMENT OF OXIDATION-REDUCTION

Oxidation-reduction reactions are treated by defining electron activity as a component species, and the "operational" electron is subject to transport as are other aqueous components. For multivalent chemical elements, a species in the highest oxidation state is chosen as the component species. Reduction to a lower oxidation state is described by a half-cell reaction which is analogous to complexation. The total "operational" electron is obtained by solving the transport equation, Eq. (2.19) with index j replaced by index e . The mole balance equation for the "operational" electron is different from those for other aqueous components in that the first term on the right hand side of Eq. (5.1) is set to zero and c_e (i.e., set $k = e$ in c_k) in all other terms is interpreted as the activity of the electron rather than the concentration of free electron.

Although mathematically the "operational electron" can be treated just as other aqueous components; numerically, this component requires special attention. Because the electron activity can span over at least 40 orders of magnitude, the solution of the balance equation of "operational" electron often renders the Newton-Raphson matrix ill-conditioned when this equation is solved simultaneously with other mole balance equations with the Newton-Raphson method. To circumvent this difficulty, a split scheme is used in the proposed model. In this split scheme, the mole balance equation for the "operational" electron is solved with a modified bisection method (Forsythe et al. 1977), whereas all other

mole balance equations are solved simultaneously with the Newton-Raphson method. This split scheme significantly reduced convergence problems.

5.7 TREATMENT OF ACID-BASE REACTIONS

Acid-base reactions are treated by defining hydrogen activity as a component species, and the "excess" hydrogen is subject to transport as are other aqueous components. The mole balance equation for the "excess" hydrogen is different from those for other aqueous components in that the first term on the right-hand side of Eq. (5.1) is written as c_H/γ_H , and c_H (i.e., set $k = H$ in c_k) in all other terms is interpreted as the activity of hydrogen rather than the concentration of free hydrogen, where γ_H is the activity coefficient of the free hydrogen ion. Another point one should bear in mind is that if an hydroxyl (OH) appears in any species, the stoichiometric coefficient of the hydrogen in that species must be set to -1. If n (OH)s appear in any species, the stoichiometric coefficient of hydrogen in that species must be set to $-n$.

6. DESCRIPTION OF THE COMPUTER PROGRAM

HYDROGEOCHEM is a general computer program written in FORTRAN 77 to solve coupled hydrologic transport and chemical equilibrium problems. It consists of two major modules: the hydrologic transport module and chemical equilibrium module. The former solves the primary governing equations (PGEs), whereas the latter solves the secondary governing equations (SGEs). Numerical implementations of these two modules are described in Chapters 4 and 5, respectively. In this chapter, program organization is discussed.

HYDROGEOCHEM consists of a MAIN program, a section of BLOCK DATA, and 43 subroutines. The MAIN is utilized to specify the sizes of all arrays. The control and coordinate activity are performed by the subroutine GM2DXZ. The linkage between the hydrologic module and chemical equilibrium module is performed by the subroutine OCSPIT. The remaining 41 subroutines can be classified into three major categories: (a) 11 subroutines making up the hydrologic module, (b) 16 subroutines making up the chemical equilibrium module, and (c) 14 subroutines performing utility functions. Figure 6.1 shows the structure of the program. The functions of these subroutine are described below.

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Fig. 6.1 Program structure of HYDROGEOCHEM

6.1 SUBROUTINE GM2DXZ

The subroutine GM2DXZ controls the entire sequence of operations, a function generally performed by the MAIN program. It is, however, preferable to keep a short MAIN and several subroutines with variable storage allocation. This makes it possible to place most of the FORTRAN deck on a permanent file and to deal with a site-specific problem without making changes in array dimensions throughout all subroutines.

The subroutine GM2DXZ will perform either the steady-state computation alone ($KSS = 0$ and $NTI = 0$), a transient state computation using the steady-state solution as the initial conditions ($KSS = 0$, $NTI > 0$), or a transient computation using user-supplied initial conditions ($KSS = 1$, $NTI > 0$).

GM2DXZ calls to subroutine DATAHT to read and print input data required for hydrologic transport computation and subroutine DATACS to read and print input data required for chemical equilibrium computation; subroutine LNDGEN to generate the relationship between node number and equation number when pointwise iteration solution strategies are used; subroutine AFABTA to compute upstream weighting factor; subroutine INTERP to obtain sources/sinks and boundary values; subroutine OCSPIT to obtain total dissolved concentrations, total sorbed concentrations, and total precipitated concentrations of all components at all nodes given the total analytical concentrations; subroutine TACADC to compute the total analytical concentrations of all adsorbent components; subroutine ASEMBL

to assemble the element matrices and load vectors over all elements to form a compressed global matrix and global load vectors; subroutine HYDROT to perform hydrologic transport computation; subroutine SFLOW to compute net rate of chemicals through open boundaries; subroutine CALKD to compute equivalent K_d ; subroutine PRINTT to print out the results; subroutine PRITER to print the intermediate results between hydrologic transport and chemical equilibrium iterations; and subroutine STORE to store the results for plotting.

6.2 SUBROUTINE OCSFIT

This subroutine calculates the total dissolved concentrations, total sorbed concentrations, and total precipitated concentrations of all components and the values of the negative logarithm of the concentrations of all component species by calling the subroutine EQMOD. The input to this subroutine is the total analytical concentrations of all components and their identification numbers.

6.3 UTILITY SUBROUTINES

A total of 14 subroutines are used to perform utility computations and to print the results either via line printer or auxiliary storage devices. These 14 subroutines are described in the following.

Subroutine DATAHT

Subroutine DATAHT reads Data Sets 2 through 15 as described in Appendix A, Section A.2. It also prints all the input information and calls subroutine SURF to identify the boundary segments and boundary nodes and subroutines READR and READN, respectively, to automatically generate real and integer numbers.

Subroutine SURF

Subroutine SURF identifies the boundary sides, sequences the boundary nodes, and computes the directional cosine of the surface sides. The mapping from boundary nodes to global nodes are stored in NPB(I), where NPB(I) is the global node number of i-th boundary node. The element number associated with the boundary sides are stored in NBE. The length and directional cosines for each side are stored in DLB and DCOSXB and DCOSZB, respectively. The local and global nodal number of two nodes of each side are stored in ISB. The information containing in NPB, NBE, ISB, DCOSXB, and DCOSZB, along with the number of boundary nodes and the number of boundary sides, are returned to subroutine DATAHT for use by other subroutines.

Subroutine READR

This subroutine is called by the subroutine DATAHT to generate real numbers for Data Sets 7 and 11 in Appendix A, Sect. A.2. Automatic generation of regularly patterned data is built into this subroutine.

Subroutine READN

This subroutine is also called by the subroutine DATAHT to generate integers Data Sets 5(2), 9, 13(1)(c), 13(2)(c), 14(b), 14(c), 15(b), and 15(c) in Appendix A, Sect. A.2.

Subroutine DATACS

This subroutine reads Data Sets 16 through 22 as described in Appendix A, Sect. A.2 and print out all input information.

Subroutine LNDGEN

This subroutine is called by the controlling subroutine GM2DXZ to preprocess the pointer array that is needed to assemble the global matrix in compressed form when pointwise solution methods are used. The pointer array automatically generated in this subroutine is the global node connectivity (stencil) GNOJCN(J,N). Here GNOJCN(J,N) is the global node number of J-th node connected to the global node N. This pointer array is generated based on the element connectivity IE(M,J), which is the global node number of J-th node of element M.

Subroutine AFABTA

Subroutine AFABTA is called to compute the optimum weighting factors for all sides of an element. The results are stored in array WETAB(M,J), where $M = 1, 2, \dots, NEL$ and $J = 1, 2, 3, 4$ for quadrilateral elements and $J = 1, 2, 3$ for triangular elements.

Subroutine INTERP

This subroutine is called by the subroutine GM2DXZ to compute the functional values (such as the Dirichlet concentrations, element source/sink, point source/sink, incoming concentrations of fluids through variable boundary segment) at a particular time for all profiles. It uses the linear interpolation of the tabular data.

Subroutine SFLOW

This subroutine is called by the subroutine GM2DXZ to compute mass fluxes through all open boundary nodes.

Subroutine CALKD

This subroutine is called by the subroutine GM2DXZ to calculate the equivalent K_d for all components.

Subroutine PRINTT

This subroutine is used to line-print the transport variables. These include the total analytical concentrations, total dissolved concentrations, total sorbed concentrations, total precipitated concentrations of all components, and the values of negative logarithm of the concentrations of all component species.

Subroutine PRITER

This subroutine is used to line-print the intermediate total analytical concentrations of all components between hydrologic transport and chemical equilibrium iterations.

Subroutine STORE

This subroutine is used to store the transport variables on Logical Unit 2. It is intended for use for plotting. The information stored includes region geometry and transport variables.

Subroutine LPOUT

This subroutine is called by the subroutine EQMOD to line print chemical species distribution at desired nodes at desired time interval. The information printed included concentrations, modified equilibrium constants, and stoichiometric coefficients of all species.

6.4 HYDROLOGIC MODULE

The hydrologic module consists of 11 subroutines that simulate the transport of all aqueous components [Eq. (3.12)] and compute the mass balance of adsorbent components [Eq. (2.29)]. The function of these 11 subroutines are described in the following.

Subroutine TACADC

This subroutine is called by GM2DXZ to compute total concentrations of all adsorbent components. The computation is based on Eq. (4.49) in Sect. 4.5.

Subroutine ASEMBL

This subroutine calls Q4 and Q3 to evaluate the element matrices. It then sums over all element matrices to form the compressed global matrices MMTRX, SMTRX, VMTRX, and DMTRX and the global load vector RLD.

Subroutines Q4 and Q3

This subroutine is called by the subroutine ASEMBL to compute the element matrix given by

$$QA(I,J) = \int_{R_e} N_i^e \theta N_j^e dR, \quad (6.1a)$$

$$QB(I,J) = \int_{R_e} (\nabla N_i^e) \cdot \theta D \cdot (\nabla N_j^e) dR, \quad (6.1b)$$

$$QV(I,J) = \int_{R_e} W_i^e V \cdot (\nabla N_j^e) dR, \quad (6.1c)$$

$$QQ(I,J) = \int_{R_e} N_i^e Q N_j^e dR, \quad (6.1d)$$

$$QC(I,J) = \int_{R_e} N_i^e \frac{\partial \theta}{\partial t} N_j^e dR, \quad (6.1e)$$

Q4 computes the integration in Eq. (6.1) for quadrilateral elements, whereas Q3 computes those for triangular elements. Subroutines Q4 and Q3 also calculate the element load vector given by

$$QR(I,K) = \int_{R_e} N_i^e QC_k^* dR, \quad k = 1, 2, \dots, N_k \quad (6.1f)$$

where C_k^* is the source concentration of the k-th aqueous component.

Subroutine SHAPE

This subroutine is called by the subroutines Q4 to evaluate the value of the base and weighting functions and the derivatives of the base functions at a Gaussian point. The computation is straightforward.

Subroutine HYDROT

This subroutine is called by GM2DXZ to perform hydrologic transport computations. Two additional entries are called by GM2DXZ: HYTRNI and HYTRNC. When the subroutine HYDROT is called, it simulates the transport of conservative chemical components. At entry point HYTRNI, it makes an initial guess of all nonconservative chemical components by solving the transport equations. At entry point HYTRNC, it simulates the transport of nonconservative chemical components for the new iterates. This subroutine

calls to subroutine EQNGEN to obtain the matrix equation out of the compressed matrix and load vector for each chemical component; subroutine BC to implement the boundary conditions; subroutine SOLVT or subroutine PISS to solve the resulting matrix equations with direct elimination method or pointwise iteration methods.

Subroutine EQNGEN

This subroutine generates the matrix equation for an aqueous component out of the compressed global matrices and the global load vectors. It utilizes the array of the node connectivity produced in the subroutine LNDGEN to form a banded matrix and load vector for all aqueous components.

Subroutine BC

This subroutine incorporates Dirichlet and variable-boundary conditions. For a Dirichlet boundary condition, an identity algebraic equation is generated for each Dirichlet nodal point. Any other equation having this nodal variable is modified accordingly to simplify the computation. The subroutine BC also implements the variable-boundary conditions. It calls the subroutine Q2VB to compute the contributions of a variable-boundary segment to the global matrix equation.

Subroutine Q2VB

This subroutine is called by the subroutine BC to compute a 2 by 2 matrix BQ and a load vector RQ for each variable boundary segment as follows:

$$BQ(I,J) = - \int_{R_e} N_i^e (n \cdot V) N_j^e dB, \quad \text{if } (n \cdot V) < 0 \quad (6.2a)$$

$$BQ(I,J) = 0, \quad \text{if } (n \cdot V) \geq 0 \quad (6.2b)$$

$$RQ(I) = \int_{R_e} N_i^e (n \cdot V) C_{IN} dB, \quad \text{if } (n \cdot V) < 0 \quad (6.2c)$$

$$RQ(I) = 0, \quad \text{if } (n \cdot V) \geq 0 \quad (6.2b)$$

Subroutine SOVLT

This subroutine is called by the subroutine GM2DXZ to solve for the matrix equation of the type

$$[C](x) = (y), \quad (6.3)$$

where [C] is the coefficient matrix and (x) and (y) are two vectors. (x) is the unknown to be solved, and (y) is the known load vector. The computer returns the solution (y) and stores it in (y). The computation is a standard banded Gaussian direct-elimination procedure.

Subroutine PISS

This subroutine is called by the subroutine HYDROT to solve Eq. (6.3) with point iteration solution strategies if desired by setting IPNTS = 1 in Data Set 2 (Appendix A, Sect. A.2).

6.5 CHEMICAL EQUILIBRIUM MODULE

Sixteen subroutines consist of the chemical equilibrium module to solve chemical equilibrium problem posed by Eqs. (5.1) through (5.9). The function of these 16 subroutines are described in the following.

Subroutine EQMOD

Subroutine EQMOD is called by the subroutine OCSPIT to schedule the chemical equilibrium computation. It initiates the concentrations of all product species, given the guess of component species concentrations from subroutine OCSPIT. It then calls to subroutine EQUIL to solve a set of algebraic equations governing mole balance and chemical equilibrium reactions. Finally, it calls to subroutine TOTDSP to compute the log of free species concentrations and total dissolved, total sorbed, and total precipitated concentrations of all components after concentrations of all species have been found.

Subroutine EQUIL

This subroutine solves the system of nonlinear algebraic equations specified by Eqs. (5.1) through (5.9) and Eqs. (5.18) and (5.19) if adsorption is treated with double-layer theory. The method of solution is

done with Newton-Raphson iteration. For each iteration, subroutine EQUIL calls subroutine ACOEF to compute the activity coefficients for all species; subroutine MODIFK to calculate the modified equilibrium constants for all product species; subroutine RESIDU to evaluate residuals of all governing equations; subroutine JACOBI to compute the Jacobian of all governing equations; subroutine DECOMP to decompose the Jacobian matrix with partial pivoting; and subroutine SOLVE for back substitution to obtain the differences between new iteration and previous iterations of all unknowns. New iterations are obtained by adding these differences to the old iterations.

Subroutine ACOEF

This subroutine is called by subroutine EQUIL to compute ionic strength and activity coefficients of all species.

Subroutine MODIFK

This subroutine is called by subroutine EQUIL to calculate the modified equilibrium constants for all product species.

Subroutine INDEXX

This subroutine is used to index the saturation value among all potential species that are subject to precipitation-dissolution reactions.

Subroutine NPPT

This subroutine is used to determine the number of species allowed to precipitate without violating the phase rule.

Subroutine BISEC

This subroutine is used to solve with modified bisection method any mole balance equation that is not solved by the Newton-Raphson method in conjunction with other mole balance equations. The electron mole balance equation is often solved using this subroutine. Although any mole balance equation also can be solved with this subroutine, it is seldom used because the modified bisection method is very slow to compute. This subroutine should be used for a mole balance equation only when the solution fails to converge if this mole balance equation is included in the Newton-Raphson method.

Subroutine RESIDU

This subroutine is called to evaluate residuals of nonlinear algebraic equations governing chemical equilibrium. Residuals are evaluated in the subroutine RESIDU for the following equations: (1) mole balance equations for aqueous components and adsorbent components and (2) precipitation-dissolution reaction equations. Residuals for equations governing the balance of c_o and c_b are obtained by calling subroutines RADC. Residuals for the ion-exchanged reactions are obtained by calling subroutines RIES.

Subroutine RADC

This subroutine is called by subroutine RESIDU to evaluate residuals for equations governing the charge balance on the "o" and "b" plane.

Subroutine RIES

This subroutine is called by subroutine RESIDU to evaluate residuals for ion-exchange reactions and cation ion exchange capacity constraint.

Subroutine JACOBI

This subroutine is called to evaluate Jacobians of nonlinear algebraic equations governing chemical equilibrium. Jacobians are evaluated in the subroutine JACOBI for the following equations: (1) mole balance equations for aqueous components and adsorbent components and (2) precipitation-dissolution reaction equations. Jacobians for equations governing the balance of the c_o and c_b are obtained by calling subroutines JADC. Jacobians for the ion-exchanged reactions are obtained by calling subroutines JIES.

Subroutine JADC

This subroutine is called by subroutine JACOBI to compute the Jacobian for Eqs. (5.18) and (5.19).

Subroutine JIES

This subroutine is called by subroutine JACOBI to compute the Jacobian for ion-exchange reactions and cation ion exchange capacity constraint.

Subroutine DECOMP

This subroutine is called by subroutine EQUIL to solve the Jacobian matrix equation. Gaussian elimination with partial pivoting is used in the algorithm.

Subroutine SOLVE

This subroutine is called by subroutine EQUIL for the back substitution step in solving the Jacobian matrix equation after the matrix has been decomposed in subroutine DECOMP.

Subroutine TOTDSP

This subroutine is called by subroutine EQMOD to evaluate the log of free species concentrations and total dissolved concentrations, total sorbed concentrations, and total precipitated concentrations of all components.

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7. SAMPLE PROBLEMS

Ten example problems are used to test and verify HYDROGEOCHEM. Problem No. 1 is used to verify the hydrologic transport module of HYDROGEOCHEM. Problems Nos. 2 through 7 are used to test the chemical equilibrium module of HYDROGEOCHEM. Problems Nos. 8 through 10 are used to test and demonstrate the coupling of the hydrologic transport and geochemical equilibria. Only one example problem is used to test the hydrologic transport module because this module is adapted from FEMWASTE (Yeh 1989), which has been well tested. Thus, extensive testing of the hydrologic transport module is not needed. On the other hand, the chemical equilibrium module is adapted from EQMOD (Yeh et al. 1990, manuscript in preparation), which has not undergone extensive testing. The complexity of tests range from simple aqueous complexation to more complicated adsorption, precipitation, and redox and acid-base reactions. The last three problems are selected to represent meaningful hydrogeochemical problems, not just test cases. The ability of HYDROGEOCHEM to solve classes of hydrologic transport and geochemical equilibrium problems are demonstrated in the first seven examples, and the last three examples are provided to illustrate the model's ability to solve complex hydrogeochemical interactions. Each example includes a description of the problem, chemical species/minerals considered, thermodynamic data used, and, for the last three examples, program output in graphical form. The input data files are provided in Appendix B. The output files are given in Appendix C.

7.1 TEST OF HYDROLOGIC TRANSPORT MODULE

7.1.1 Problem No. 1 - Test of Hydrologic Transport Module

This problem deals with transport in a 1-D column, which is 1 dm long; the flow velocity from the bottom to top is $2 \cdot 10^{-2}$ dm/h, the effective porosity was 0.3, the bulk density was 1.2 g/cm^3 , and the dispersivity was $3 \cdot 10^{-3}$ dm. The transport involves four chemical components. The initial conditions are as follows: total analytical concentrations are 10^{-4} M for all four chemical components. The boundary conditions are as follows: at $z = 0.0$ dm, total analytical concentrations are 10^{-3} M; at $z = 1.0$ dm, variable boundary conditions with zero concentration gradient fluxes are specified for all four components.

To mimic the hydrologic transport without interaction among four chemical components, we assume that each chemical component has two species: one, a free species and the other, an adsorbed species. The ratios of the adsorbed species to the free species are assumed to be 0, $1/9$, 1, and 9, respectively, for chemical components 1, 2, 3, and 4. In other words, there was a 0%, 10%, 50%, and 90% adsorption, respectively, for chemicals 1, 2, 3, and 4. In terms of geochemical equilibrium constants, the four formation constants for the four adsorbed species are 0, $1/9$, 1, and 9, respectively. To mimic no-interaction scenario among four components, the adsorbent component is not considered (i.e., the adsorbing site is not a constraint for the equilibrium between free species and adsorbed species for each component).

For numerical simulation, the column is discretized by 1 x 40 elements of size 0.025 dm by 0.025 dm, which results in 82 nodes. The simulation was conducted for three time-steps only because the purpose of this simulation is simply to verify the hydrologic module. The time-step size was 0.5 h.

The input data set was prepared according to Appendix A, Sect. A.2 and is given in Appendix B, Sect. B.1. The output (Appendix C, Sect. C.1) is on a floppy disk, which will be sent to interested readers on request. The agreement between the simulations with HYDROGEOCHEM and FEMWASTE (Yeh 1989) is almost perfect for all four chemical components.

7.2 TEST OF CHEMICAL EQUILIBRIUM MODULE

Six example problems are used to test the chemical equilibrium module of HYDROGEOCHEM. The first problem is to test for simple aqueous complexation, the second problem for adsorption, the third problem for ion-exchange, the fourth problem for aqueous complexation and precipitation-dissolution, the fifth problem for aqueous complexation and adsorption-desorption, and the sixth problem for aqueous complexation and oxidation-reduction as well as acid-base reactions. To test the chemical equilibrium module in HYDROGEOCHEM, a vertical soil column of two elements (6 nodes) with size of 1 dm by 1 dm is used. A velocity of 0.0 dm/s, an effective porosity of 0.2, a dispersivity of 0.002 dm, an effective diffusion coefficient of 0.0 dm²/s, and a bulk density of 1.0 g/cm³ are assumed for the medium in the soil column. This transport scenario is

equivalent to a six batch simulation, each batch should yield identical results if the initial conditions for all six nodes are identical.

7.2.1 Problem No. 2 - Test of Equilibrium Module: Complexation

To test simple aqueous complexation reactions, four chemical components (sodium, lead, hydrogen, and chloride) are considered. The initial total analytical concentrations of sodium, lead, and chloride are 10^{-1} , $2.9 \cdot 10^{-4}$, and 10^{-1} , respectively, and the activity of hydrogen ion is fixed at $\text{pH} = 7.10535$. In addition to four free species, two aqueous complexed species, OH^- and $\text{Pb}(\text{OH})^+$, are considered. The input data set for this simple problem is given in Appendix B, Sect. B.2, and floppy-disk output data set can be requested (Appendix C, Sect C.2). Table 7.1 lists

Table 7.1. List of geochemical data and species concentrations at equilibrium at Node 1 for Problem No. 2

Species	Components				Log K	Log C
	<u>Stoichiometric Coefficient</u>					
	Na ⁺	Pb ⁺⁺	H ⁺	Cl ⁻		
Na ⁺	1	0	0	0	0.00	-1.0
Pb ⁺⁺	0	1	0	0	0.00	-3.59
H ⁺	0	0	1	0	0.00	-7.11
Cl ⁻	0	0	0	1	0.00	-1.0
OH ⁻	0	0	-1	0	-13.99	-6.78
Pb(OH) ⁺	0	1	-1	0	-7.71	-4.51

the geochemical data and the simulated logarithm of species concentrations (last column) at equilibrium for Node 1. The species concentrations at equilibrium for all other five nodes are identical as expected because this problem is equivalent to six identical batch simulations. It is seen that the free concentrations of free species Na^+ and Cl^- are the same as their respective total analytical concentrations as expected because these two components do not form other complexes. Simulation results indicate that to maintain a fixed pH of 7.10535 at equilibrium, a total excess hydronium of $-3.11 \cdot 10^{-5}$ M must be supplied. The concentrations of all species are in agreement with hand calculations using Davies Formula for ionic strength correction.

7.2.2 Problem No. 3 - Test of Equilibrium Module: Adsorption

To test adsorption reactions, an adsorbent component, SOH, is specified as a sorbing site, and two fictitious adsorbent components, SIGO and SIGB, are specified because the double-layer model was used for treating adsorption. In addition, the same four aqueous components used in Problem No. 2 (sodium, lead, hydrogen, and chloride) are also included. Thus, the total number of components is seven. The concentrations of free species, Na^+ , Pb^{++} , and Cl^- , are fixed at 10^{-1} , $2.9 \cdot 10^{-4}$, and 10^{-1} M, respectively, and the activity of hydrogen ion is fixed at pH = 7.10535 as in Problem No. 1. The total analytical concentration of the adsorbent component SOH is assumed to be $1.7 \cdot 10^{-2}$ molar. In addition to seven free species, two aqueous complexed species [OH^- and $\text{Pb}(\text{OH})^+$] and six adsorbed species [SO^- , SOH_2^+ , SONa , SOPb^+ , SOH_2Cl , and SOPbOH] are included for the

simulation. The species concentrations of OH^- and $\text{Pb}(\text{OH})^+$ are fixed at $1.662 \cdot 10^{-7}$ and $3.107 \cdot 10^{-5}$ M, respectively. The input data set for this simple adsorption problem is prepared according to input data guide in Appendix A, Sect. A.2, and is given in Appendix B, Sect. B.3. Floppy-diske output (Appendix C, Sect. C.3) is available on request. Table 7.2 lists the geochemical data and the simulated logarithm of species concentrations at equilibrium for Node 1. The species concentrations at

Table 7.2. List of geochemical data and species concentrations at equilibrium at Node 1 for Problem No. 3

Species	Components Stoichiometric Coefficients							Log K	Log C
	Na^+	Pb^{++}	H^+	Cl^-	SOH	SIGO	SIGB		
Na^+	1	0	0	0	0	0	0	0.00	-1.0
Pb^{++}	0	1	0	0	0	0	0	0.00	-3.59
H^+	0	0	1	0	0	0	0	0.00	-7.11
Cl^-	0	0	0	1	0	0	0	0.00	-1.00
SOH	0	0	0	0	1	0	0	0.00	-5.72
SIGO	0	0	0	0	0	1	0	0.00	-1.49
SIGB	0	0	0	0	0	0	1	0.00	-5.45
OH^-	0	0	-1	0	0	0	0	-13.99	-6.78
$\text{Pb}(\text{OH})^+$	0	1	-1	0	0	0	0	-7.71	-4.51
SO^-	0	0	-1	0	1	-1	0	-11.50	-8.62
SOH^{2+}	0	0	1	0	1	1	0	5.70	-8.62
SONA	1	0	-1	0	1	-1	1	-9.20	-12.87
SOPb^+	0	1	-1	0	1	-1	2	-5.00	-17.03
SOH_2Cl	0	0	1	1	1	1	-1	7.90	-2.07
SOPbOH	0	1	-2	0	1	-1	1	-2.60	-2.07

equilibrium for all other five nodes are identical, as expected. Simulation results indicate that the total analytical concentrations of the four components (Na^+ , Pb^{++} , H^+ , and Cl^-) required to maintain equilibrium condition are $1.0 \cdot 10^{-1}$, $8.789 \cdot 10^{-3}$, $-8.53 \cdot 10^{-3}$, and $1.7 \cdot 10^{-1}$, respectively. These total analytical concentrations must be provided via external sources in order to maintain the fixed concentrations of free species at equilibrium. The simulated concentrations (on last column in Table 7.2) of all species are in agreement with hand calculations using Davies Formula (1962) for ionic strength correction.

7.2.3 Problem No. 4 - Test of Equilibrium Module: Ion-Exchange

To test ion-exchange reactions, four chemical components, sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), and chloride (Cl^-), are considered. The initial total analytical concentrations of sodium, magnesium, calcium, and chloride are 0.217, 0.1463, 0.1562, and 0.1600 M, respectively. Ion-exchange reactions occur among sodium, magnesium, and calcium. Thus, in addition to four free species, there are three ion-exchanged species: sorbed sodium, sorbed magnesium, and sorbed calcium. The selectivities of magnesium and calcium with respect to sodium are 2.24 and 3.98, respectively. The cation-ion exchange capacity is 0.6701 equivalents per gram of soil. The input data set for this simple ion-exchange problem is given in Appendix B, Sect. B.4, and the output data set is available on floppy disk (Appendix C, Sect. C.4). Table 7.3 lists the geochemical data and the simulated logarithm of species concentrations

(last column) at equilibrium for Node 1. It is seen that the free concentration of Cl^- is the same as its total analytical concentrations as expected because chloride does not involve in ion-exchange reactions. The concentrations of all species are in agreement with those obtained by CHEMTRAN (Miller 1983).

Table 7.3. List of geochemical data and species concentrations at equilibrium at Node 1 for Problem No. 4

Species	Components <u>Stoichiometric Coefficient</u>				Log K	Log C
	Na^+	Mg^{++}	Ca^{++}	Cl^-		
Na^+	1	0	0	0	0.00	-1.05
Mg^{++}	0	1	0	0	0.00	-1.72
Ca^{++}	0	0	1	0	0.00	-1.91
Cl^-	0	0	0	1	0.00	-0.796
Sorbed Na^+	1	0	0	0	0.00	-0.892
Sorbed Mg^{++}	0	1	0	0	0.35	-0.896
Sorbed Ca^{++}	0	0	1	0	0.60	-0.842
Given						
Total, (M)	.2173	.1463	.1562	.1600		

7.2.4 Problem No. 5 - Test of Equilibrium Module: Complexation and Precipitation

To test complexation as well as precipitation-dissolution reactions, six aqueous components (sodium, uranium, hydrogen, carbonate, sulfate, and chloride) are considered. The initial total analytical concentrations of sodium, uranium, carbonate, sulfate, and chloride are $3.6 \cdot 10^{-1}$, $3.0 \cdot 10^{-3}$, $5.0 \cdot 10^{-3}$, 10^{-2} , and $4.8 \cdot 10^{-1}$ M, respectively, and the activity of hydrogen is fixed at pH = 7.0. In addition to six free species, nineteen aqueous complexed species and two minerals are included for equilibrium simulations. Thus, a total of twenty-seven species resulting from chemical reactions of six components are involved. These species are given in Table 7.4. The input data set for this problem of complexation and precipitation-dissolution reaction was prepared according input data guide in Appendix A, Sect. A.2, and is given in Appendix B, Sect. B.5. The output data is available on floppy disk (Appendix C, Sect. C.5). Table 7.4 lists geochemical data, and the logarithm of species concentrations (last column) at equilibrium for Node 1. Computer output shows that to maintain a fixed pH of 7.0 at equilibrium, a total excess hydronium of $-4.6574 \cdot 10^{-4}$ must be supplied from external source. The concentrations of all species are in agreement with those computed using MINEQL (Westall et al. 1976).

Table 7.4. List of geochemical data and species concentrations at equilibrium at Node 1 for Problem No. 5

Species	Components						Log K	Log C
	Stoichiometric Coefficient							
	Na ⁺	UO ₂ ⁺⁺	H ⁺	CO ₃ ⁻⁻	SO ₄ ⁻⁻	Cl ⁻		
Na ⁺	1	0	0	0	0	0	0.00	-0.452
UO ₂ ⁺⁺	0	1	0	0	0	0	0.00	-8.600
H ⁺	0	0	1	0	0	0	0.00	-7.000
CO ₃ ⁻⁻	0	0	0	1	0	0	0.00	-5.923
SO ₄ ⁻⁻	0	0	0	0	1	0	0.00	-2.442
Cl ⁻	0	0	0	0	0	1	0.00	-0.319
NaCO ₃ ⁻	1	0	0	1	0	0	1.27	-5.106
NaHCO ₃	1	0	1	1	0	0	10.08	-3.297
NaSO ₄ ⁻	1	0	0	0	1	0	0.70	-2.195
UO ₂ (OH) ⁺	0	1	-1	0	0	0	-5.30	-6.900
(UO ₂) ₂ (OH) ₂ ⁺⁺	0	2	-2	0	0	0	-5.68	-8.880
(UO ₂) ₃ (OH) ₄ ⁺⁺	0	3	-4	0	0	0	-11.88	-9.680
(UO ₂) ₃ (OH) ₅ ⁺	0	3	-5	0	0	0	-15.82	-6.620
(UO ₂) ₄ (OH) ₇ ⁺	0	4	-7	0	0	0	-21.90	-7.300
(UO ₂) ₃ (OH) ₇ ⁻	0	3	-7	0	0	0	-28.34	-5.140
UO ₂ CO ₃	0	1	0	1	0	0	9.65	-4.874
UO ₂ (CO ₃) ₂ ⁻⁻	0	1	0	2	0	0	17.08	-3.367
UO ₂ (CO ₃) ₃ ⁴⁻	0	1	0	3	0	0	21.70	-4.670
(UO ₂) ₂ CO ₃ (OH) ₃	0	2	-3	1	0	0	-1.18	-3.303
UO ₂ Cl ⁺	0	1	0	0	0	1	-0.21	-9.129

Table 7.4. List of geochemical data and species concentrations at equilibrium at Node 1 for Problem No. 5 (Continued).

Species	Components Stoichiometric Coefficient						Log K	Log C
	Na ⁺	UO ₂ ⁺⁺	H ⁺	CO ₃ ⁻⁻	SO ₄ ⁻⁻	Cl ⁻		
UO ₂ SO ₄	0	1	0	0	1	0	2.95	-8.092
UO ₂ (SO ₄) ₂ ⁻⁻	0	1	0	0	2	0	4.00	-9.485
HCO ₃ ⁻	0	0	1	1	0	0	10.32	-2.603
H ₂ CO ₃	0	0	2	1	0	0	16.67	-3.253
HSO ₄ ⁻	0	0	1	0	1	0	1.99	-7.452
UO ₂ (OH) ₂	0	1	-2	0	0	0	-5.40	-2.819
UO ₂ CO ₃	0	1	0	1	0	0	13.03	-infinity

7.2.5 Problem No. 6 - Test of Equilibrium Module: Complexation and Adsorption

To test adsorption reactions, the same four aqueous components, one adsorbent component, and two fictitious components used in Problem No. 3, are considered. The total analytical concentrations of Na⁺, Pb⁺⁺, Cl⁻, and SOH are $1.00004186 \cdot 10^{-1}$, $5.50099 \cdot 10^{-3}$, $1.05158 \cdot 10^{-1}$, and $1.7 \cdot 10^{-2}$, M, respectively, and the activity of the hydrogen ion is fixed at pH = 7.1054. In addition to seven free species, two aqueous complexed species, OH⁻ and Pb(OH)⁺, and 6 adsorbed species, SO⁻, SOH₂⁺, SONa, SOPb⁺, SOH₂Cl, and SOPbOH, are included for the simulation. Thermodynamic data base for

these eight product species are given in Table 7.5, from which the input data set for this problem was prepared and is given in Appendix B, Sect. B.6. The output data is available on floppy disk (Appendix C, Sect.C.6). Table 7.5 lists geochemical data and simulated logarithm of species concentration (last column) at equilibrium for Node 1. Computer printout shows that to maintain a fixed pH of 7.1054 at equilibrium, a total excess hydronium of $-5.501 \cdot 10^{-3}$ must be supplied to each node of the system. The concentrations of all species are in agreement with calculations from CHEMTRAN (Miller 1983).

Table 7.5. List of geochemical data and species concentrations at equilibrium at Node 1 for Problem No. 6

Species	Components							Log K	Log C
	<u>Stoichiometric Coefficient</u>								
	Na ⁺	Pb ⁺⁺	H ⁺	Cl ⁻	SOH	SIGO	SIGB		
Na ⁺	1	0	0	0	0	0	0	0.00	-1.000
Pb ⁺⁺	0	1	0	0	0	0	0	0.00	-10.950
H ⁺	0	0	1	0	0	0	0	0.00	-7.105
Cl ⁻	0	0	0	1	0	0	0	0.00	-1.000
SOH	0	0	0	0	1	0	0	0.00	-2.223
SIGO	0	0	0	0	0	1	0	0.00	-1.495
SIGB	0	0	0	0	0	0	1	0.00	-1.771
OH ⁻	0	0	-1	0	0	0	0	-13.99	-6.799
Pb(OH) ⁺	0	1	-1	0	0	0	0	-7.71	-11.870
SO ⁻	0	0	-1	0	1	-1	0	-11.50	-5.123

Table 7.5. List of geochemical data and species concentrations
at equilibrium at Node 1 for Problem No. 6
(Continued)

Species	Components Stoichiometric Coefficient							Log K	Log C
	Na ⁺	Pb ⁺⁺	H ⁺	Cl ⁻	SOH	SIGD	SIGB		
SOH ₂ ⁺	0	0	1	0	1	1	0	5.70	-5.123
SONA	1	0	-1	0	1	-1	1	-9.20	-5.699
SOPb ⁺	0	1	-1	0	1	-1	2	-5.00	-13.536
SOH2Cl	0	0	1	1	1	1	-1	7.90	-2.259
SOPbOH	0	1	-2	0	1	-1	1	-2.60	-2.260

7.2.6 Problem No. 7 - Test of Equilibrium Module: Redox and Acid-Base Reactions

To test oxidation-reduction and acid-base reactions, four chemical components, ferric, sulfate, hydrogen, and electron, are considered. The initial total analytical concentrations of ferric, sulfate, excess proton, and "operational" electron are $2.0000001 \cdot 10^{-1}$, $3.000000002 \cdot 10^{-1}$, 10^{-2} , and $1.3 \cdot 10^{-8}$ M, respectively. In addition to four free species, nineteen aqueous complexes are included for equilibrium simulations. Thermodynamic data for these 19 species are given in Table 7.6, from which the input data set for this problem was prepared as in Appendix B, Sect. B.7. The output data set is given in Appendix C, Sect. C.7, on a floppy disk. Table 7.6 lists the geochemical data, and the simulated logarithm of species concentrations at equilibrium for Node 1. Exact agreement was obtained between results from HYDROGEOCHEM and MINEQUL.

Table 7.6. List of geochemical data and species concentrations at equilibrium at Node 1 for Problem No. 7

Species	Components				Log K	Log C
	Stoichiometric Coefficient					
	Fe ⁺⁺⁺	SO ₄ ⁻⁻	H ⁺	e ⁻		
Fe ⁺⁺⁺	1	0	0	0	0.00	-3.186
SO ₄ ⁻⁻	0	1	0	0	0.00	-1.668
H ⁺	0	0	1	0	0.00	-2.787
e ⁻	0	0	0	1	0.00	-18.354
OH ⁻	0	0	-1	0	-13.99	-11.203
FeSO ₄ ⁺	1	1	0	0	3.92	-0.933
Fe(SO ₄) ₂ ⁻	1	2	0	0	5.42	-1.101
FE(OH) ⁺⁺	1	0	-1	0	-2.19	-2.589
FE(OH) ₂ ⁺	1	0	-2	0	-5.67	-3.281
Fe(OH) ₃	1	0	-3	0	-13.60	-8.424
Fe(OH) ₄ ⁻	1	0	-4	0	-21.60	-13.637
Fe ₂ (OH) ₂ ⁴⁺	2	0	-2	0	-2.95	-3.747
Fe ₃ (OH) ₄ ⁵⁺	3	0	-4	0	-6.31	-4.718
Fe(SO ₄)	1	1	0	1	15.21	-7.998
Fe(OH) ⁺	1	0	-1	1	3.51	-15.243
Fe(OH) ₂	1	0	-2	1	-7.56	-23.526
Fe(OH) ₃ ⁻	1	0	-3	1	-17.99	-31.169
Fe(OH) ₄ ⁻⁻	1	0	-4	1	-32.99	-43.381
H(SO ₄) ⁻	0	1	1	0	1.99	-2.465
H ₉ (SO ₄) ⁻	0	1	9	8	33.64	-139.948
H ₁₀ (SO ₄)	0	1	10	8	40.63	-135.746
Fe ⁺⁺	1	0	0	1	13.01	-8.530
Hg(SO ₄) ⁻⁻	0	1	8	8	20.72	-150.081
Given						
total, (M)	2.0D-1	3.0D-1	1.0D-3	1.3D-8		

7.3 TEST OF COUPLED HYDROLOGIC TRANSPORT AND CHEMICAL EQUILIBRIUM

The ability of HYDROGEOCHEM to solve classes of hydrologic and geochemical problems was demonstrated in the preceding sections, and the following examples are provided to illustrate the program's ability to solve complex hydrogeochemical interactions. Each example includes a description of the problem, chemical species/minerals considered, a program output in graphical form, and the thermodynamic data used in computations. The input data are provided in Appendix B, while the output are given in Appendix C on floppy disks.

7.3.1 Problem No. 8 - One-Dimensional Multifront Precipitation

Problem No. 8 considers transport and reaction in a 1-D horizontal column; the flow velocity (from right to left) is 0.5 dm/day, the porosity is 0.3, and the dispersivity is 5 dm. The material density is 1.2 g/cc. The reactions involve calcium, carbonate, magnesium, sulfate, and hydronium in water. A total of 12 aqueous species and 1 mineral were considered in computations.

Appendix B, Sect. B.8 contains program inputs and Appendix C, Sect. C.8 contains part of the program output. The simulation was conducted for 150 days with a time-step size of 0.5 day. The region is made up of 100 elements of size 1 dm by 1 dm. The pH is fixed and held steady with nonuniform distribution throughout the column; the pH was 7.7 at the left end of the column and monotonically increased at equal steps to become 8.0 at the right end of the column. The initial calcium concentration in the

column is uniform at 10^{-4} M. The initial carbonate concentration linearly increased from $2 \cdot 10^{-3}$ M at the left end to $8 \cdot 10^{-3}$ M at the right end of the column. The initial magnesium concentration at the left end is $5 \cdot 10^{-3}$ M and decreased linearly to 10^{-3} M at the right end. The initial concentration of sulfate at the left end was set to $2 \cdot 10^{-3}$ M and decreased linearly to 10^{-4} M at the right end.

The pH of the water entering at the right end of the column was fixed at 8.0. The carbonate concentration in the incoming water was held constant at $2 \cdot 10^{-3}$ M. The concentration of calcium in incoming water was 10^{-4} M at time 0 through time 0.99 days, $6 \cdot 10^{-3}$ M at time 1 through 3.5 days, and 10^{-4} M at time 3.5 days and after respectively. The concentrations of magnesium and sulfate in incoming water were held at constant values of 10^{-3} and 10^{-4} M, respectively.

The reactions in the column were driven by the increase in the initial carbonate concentration in the column and the pulse in the calcium concentration of the incoming water. Figure 7.1a shows the precipitation of calcite in the column as a function of time and distance. Because of the short peak in calcium concentration of the incoming water, there is significant precipitation of calcite. As the new solution moves into the column, the extent of calcite precipitation decreases. Figures 7.1b and 7.1c show the total calcium (dissolved plus precipitated) and the total dissolved calcium in the column, respectively. An interesting feature of

Fig. 7.1 Precipitation-dissolution dynamics of four chemical components in a 1-D column

the simulation is that there are two areas (regions) of calcite precipitation (three interfaces of calcite dissolution-precipitation). Some other models of solute transport specifically seek to solve for the solid-solution interfaces; these models have considerable difficulties when the number of such interfaces is greater than one and when the number of interfaces cannot be determined a priori. HYDROGEOCHEM, on the other hand, simply solves for the equilibrium, and if any minerals are present, the solid-solution interfaces are automatically defined. Therefore, HYDROGEOCHEM has no difficulty associated with the complexity of dissolution-precipitation interfaces. This problem demonstrates HYDROGEOCHEM's ability to compute transport with aqueous complexation and mineral precipitation and dissolution.

7.3.2 Problem No. 9 - One-dimensional Bimodal Adsorption

This example considers the transport and interaction of 8 chemical components: calcium, carbonate, uranium (VI), sulfate, neptunium (V), plutonium (IV), hydronium (H^+), and SOH (adsorbing site). The flow velocity (from left to right) was 3 dm/day; the porosity was 0.3, and the dispersivity was 1 dm. A total of 500 days (500 time-steps of size 1 day) was simulated. The region is made up of 50 elements of 20 dm x 20 dm.

Appendix B, Sect. B.9 and Appendix C, Sect. C.9 provide the input data and part of the program output, respectively. A total of eight components is included, three of which, uranium (VI), neptunium (V), and plutonium (IV), are radioelements. Twenty-three aqueous complexes and

five surface species were considered (Appendix B, Sect. B.9). The initial pH was fixed within a narrow range between 7.6 and 7.9. The initial concentration of total calcium, carbonate and sulfate in the column was 10^{-4} M. The goethite surface area was specified for each node so that the site density of surface sites (available to 1 L of the solution) was 10^{-4} M everywhere except for a region 10 to 30 dm from the left end of the column; in this region the site density was $2.5 \cdot 10^{-2}$ M, or 250 times the background value. The higher concentration of the adsorbent was chosen to facilitate adsorption of uranium and neptunium in the region. The initial (background) concentration of uranium (VI), Neptunium (V) and Plutonium (IV) in the column was 10^{-8} , 10^{-16} , and 10^{-16} M, respectively.

The boundary condition (composition of the groundwater entering the column at the left end) was set differently for different components. The calcium concentration was held constant at 10^{-3} M through the period. The sulfate concentration was set to a low value of 10^{-4} M to signify near-absence of sulfate. The boundary concentrations of U, Np and Pu were set at 10^{-6} , $2.5 \cdot 10^{-10}$, and 10^{-9} M respectively. The pH value of the incoming water was held constant at a value of 3.0. The boundary concentration of carbonate was set to vary with time; for the first 198 days of the simulation, the total concentration of incoming carbonate was set to a low value of 10^{-4} M; at 202 days, it was set to 10^{-2} M; and at 498 days, it was set to 10^{-3} M.

The time-dependent gradient on carbonate concentration was imposed to permit a buildup of uranium and neptunium during the first 198 days of simulation due to adsorption and to facilitate desorption of the adsorbed elements after 200 days. Of the 8 chemical components considered, uranium forms strong carbonate complexes and adsorbs strongly onto goethite, the model adsorbent used in this simulation; neptunium forms weaker carbonate complexes and adsorbs less strongly than uranium onto goethite. The adsorption of plutonium onto goethite and complex formation between plutonium and carbonate was deliberately ignored; thus, plutonium was forced to behave as a totally conservative element.

The transport dynamics of the three radioelements is described in detail in the following. Uranium transport dynamics (a plot of total uranium vs distance in the column) at various times (180 to 300 days) is shown in Fig. 7.2. Adsorption of uranium onto goethite creates a peak in total uranium concentration; the peak is especially pronounced in the goethite-rich zone (Figs. 7.2a through 7.2c). Figure 7.2c shows a buildup of 50 times over the concentration of uranium in incoming groundwater, and an examination of the computational results indicates that nearly all of the uranium (in the peak) is present in the adsorbed phase on the goethite surface (surface coverage = 0.04%). The first impact of the carbonate pulse is visible at 200 days (Fig. 7.2d), when the most interesting observation is the presence of a bimodal peak in total uranium concentrations (Figs. 7.2d through 7.2h); the peak in dissolved uranium

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Fig. 7.2 Adsorption dynamics of uranium in the transport
of eight chemical components (1 of 3)

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Fig. 7.2 Adsorption dynamics of uranium in the transport of eight chemical components (2 of 3)

Fig. 7.2 Adsorption dynamics of uranium in the transport of eight chemical components (3 of 3)

concentration is created by desorption of uranium adsorbed onto goethite due to an increase in carbonate complexation. At 220 days (Fig. 7.2j) the carbonate pulse reaches the goethite-rich zone in the column, and a large peak in total dissolved uranium (more than 50 times the concentration in the incoming groundwater). The formation of the peak indicates that the adsorption-desorption processes can lead to higher concentrations of solutes and contaminants away from the source than near the source. This result is in sharp contrast to the prediction of the K_d -based models, which always project a monotonic decrease in the solute-contaminant concentration away from the source. The sharp peak in dissolved uranium concentration, of course, is created as a result of the assumption of instantaneous desorption (an assumption also common to the K_d -based models). In real-world situations, both adsorption and desorption processes are slower, and therefore, the peak would be distributed over a longer time-space region. However, given the longer times for chemical reactions in natural systems, the formations of such peaks is a distinct possibility.

Neptunium transport dynamics (a plot of total neptunium vs distance in the column) at various times (100 to 239 days) is shown in Figure 7.3. Adsorption of neptunium onto goethite creates a peak in total neptunium concentration; the peak is especially pronounced in the goethite-rich zone (Figs. 7.3a- 7.3c). Figure 7.3c shows a buildup of approximately 64-fold

Fig. 7.3 Adsorption dynamics of neptunium in the transport of eight chemical components (1 of 2)

Fig. 7.3 Adsorption dynamics of neptunium in the transport of eight chemical components (2 of 2)

over the incoming neptunium concentration; the extent of the buildup is smaller than that for uranium. The impact of the incoming carbonate pulse is visible at 200 days (Fig. 7.3d), however, it is much less noticeable than the similar increase in uranium. At 239 days (Fig. 7.3g), the extent of neptunium remobilization resulting from desorption is markedly less compared to the extent in uranium remobilization (Fig. 7.2j).

7.3.3 Problem No. 10 - Two-dimensional Uranium Tailing

The problem considers a simplified hypothetical scenario of uranium mill-tailing disposal and the release and migration of uranium from the tailings. A 2-D vertical cross section is considered. The region is discretized with 152 elements and 192 nodes (Fig. 7.4a). The vertical left edge of the region is a no-flow boundary; the horizontal bottom is also an impermeable no-flow boundary. The sloping region on the top right has variable boundary with either zero ponding depth or a net rainfall rate of 0.0139 dm/day. The horizontal region on the top of the mill tailing is a Cauchy boundary with an infiltration rate of 0.139 dm/day. The five nodes on the vertical line on the right side and the two nodes on the river bottom are specified as known-head conditions (Dirichlet boundary conditions). The total head for the five vertical nodes was given as 39 dm. The total head on the left and right nodes of the river bottom are specified as 44 dm and 40 dm, respectively. The flow was simulated using the HYDROGEOFLOW program (a simplified version of FEMWATER, Yeh, 1987) and the flow field is shown in Figure 7.4b.

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Fig. 7.4 Finite element discretization and flow field of infiltration from a uranium mill tailing

The input data for HYDROGEOCHEM simulation is provided in Appendix B, Sect. B.10, and part of the output is provided in Appendix C, Sect. C.10 on a floppy disk. The problem considered seven components, namely calcium, carbonate, uranium (VI), sulfate, phosphate, ferrous iron, and H^+ (pH). The redox processes were not considered. The pH was computed for each point on the basis of the total excess hydronium ions designated by TOT H (total analytical excess or deficit of protons, a concept similar to the proton condition). A total of 35 species and 14 minerals were considered. The initial conditions were specified for the various regions. The mill-tailing itself, for the problem, was considered to be a boundary in the sense that the total concentration of the chemical components was set at fixed values; these values were not allowed to decrease during the course of the simulation.

The composition of the pore water in tailings was 10^{-2} M for calcium, 10^{-2} M for carbonate, $5 \cdot 10^{-4}$ M for uranium (VI), 10^{-6} M for phosphate, $2 \cdot 10^{-1}$ M for sulfate, $3.5 \cdot 10^{-2}$ M for ferrous, and $2 \cdot 10^{-1}$ M for excess hydronium (H^+). The initial condition (concentration) of components outside of the tailing pond was 10^{-2} , $1.5 \cdot 10^{-3}$, 10^{-7} , 10^{-6} , $2 \cdot 10^{-2}$, 10^{-7} , and 10^{-3} M for calcium, carbonate, uranium (VI), phosphate, sulfate, ferrous, and hydronium (H^+), respectively. For this hypothetical problem, the recharge water was assumed to have the following composition: 10^{-3} M for calcium, $1.5 \cdot 10^{-3}$ M for carbonate, 10^{-8} M for uranium (VI), 10^{-6} M for phosphate, 10^{-4} M for sulfate, 10^{-7} M for ferrous, and 10^{-3} M for excess hydronium (H^+).

At the start of the simulation, the computed pH in the tailing pond was 1.3 and the tailing pile was supersaturated with gypsum. Outside of the tailing pile, calcite was supersaturated, and the computed pH was 7.6.

The results of HYDROGEOCHEM computations at each finite-element node were interpolated with the algorithm described elsewhere (1974; Transactions on Mathematical Software 526, Association of Computing Machinery) over a uniform grid. The interpolated results were plotted with the DISSPLA package. The contour plots are used to describe and discuss simulation results. For brevity, only the behavior of pH, calcium, sulfate, and uranium is presented.

Figs. 7.5a-7.5d show contour plots of computed pH at 0, 300, 700 and 1000 days, respectively. Initially (Fig. 7.5a), the acidity is confined to the tailings pond, and the pH is greater than 7 outside. Simulation at 300 and 1000 days illustrate transport of the acidity outside the tailings, however, due to reaction with CaCO_3 the pH is neutralized rapidly in the reaction zone as indicated by closely spaced contours.

Figs 7.6a-7.6d describe the initial (time 0) distribution of total calcium, total dissolved calcium, total precipitated calcium, and free Ca^{2+} , respectively. The CaSO_4 and CaCO_3 accounted for precipitated calcium. The contours essentially mark the boundary of the tailings pond. Figs. 7.7a - 7.7d show the total calcium, total dissolved calcium, total

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Fig. 7.5 Dynamics of pH plume from a uranium mill tailing

Time	log of Total Concentration of CA at Time	0.0 days
0.0	0.0	0.0
0.5	0.5	0.5
1.0	1.0	1.0
1.5	1.5	1.5
2.0	2.0	2.0
2.5	2.5	2.5
3.0	3.0	3.0
3.5	3.5	3.5
4.0	4.0	4.0
4.5	4.5	4.5
5.0	5.0	5.0
5.5	5.5	5.5
6.0	6.0	6.0
6.5	6.5	6.5
7.0	7.0	7.0
7.5	7.5	7.5
8.0	8.0	8.0
8.5	8.5	8.5
9.0	9.0	9.0
9.5	9.5	9.5
10.0	10.0	10.0
10.5	10.5	10.5
11.0	11.0	11.0
11.5	11.5	11.5
12.0	12.0	12.0
12.5	12.5	12.5
13.0	13.0	13.0
13.5	13.5	13.5
14.0	14.0	14.0
14.5	14.5	14.5
15.0	15.0	15.0
15.5	15.5	15.5
16.0	16.0	16.0
16.5	16.5	16.5
17.0	17.0	17.0
17.5	17.5	17.5
18.0	18.0	18.0
18.5	18.5	18.5
19.0	19.0	19.0
19.5	19.5	19.5
20.0	20.0	20.0
20.5	20.5	20.5
21.0	21.0	21.0
21.5	21.5	21.5
22.0	22.0	22.0
22.5	22.5	22.5
23.0	23.0	23.0
23.5	23.5	23.5
24.0	24.0	24.0
24.5	24.5	24.5
25.0	25.0	25.0
25.5	25.5	25.5
26.0	26.0	26.0
26.5	26.5	26.5
27.0	27.0	27.0
27.5	27.5	27.5
28.0	28.0	28.0
28.5	28.5	28.5
29.0	29.0	29.0
29.5	29.5	29.5
30.0	30.0	30.0
30.5	30.5	30.5
31.0	31.0	31.0
31.5	31.5	31.5
32.0	32.0	32.0
32.5	32.5	32.5
33.0	33.0	33.0
33.5	33.5	33.5
34.0	34.0	34.0
34.5	34.5	34.5
35.0	35.0	35.0
35.5	35.5	35.5
36.0	36.0	36.0
36.5	36.5	36.5
37.0	37.0	37.0
37.5	37.5	37.5
38.0	38.0	38.0
38.5	38.5	38.5
39.0	39.0	39.0
39.5	39.5	39.5
40.0	40.0	40.0
40.5	40.5	40.5
41.0	41.0	41.0
41.5	41.5	41.5
42.0	42.0	42.0
42.5	42.5	42.5
43.0	43.0	43.0
43.5	43.5	43.5
44.0	44.0	44.0
44.5	44.5	44.5
45.0	45.0	45.0
45.5	45.5	45.5
46.0	46.0	46.0
46.5	46.5	46.5
47.0	47.0	47.0
47.5	47.5	47.5
48.0	48.0	48.0
48.5	48.5	48.5
49.0	49.0	49.0
49.5	49.5	49.5
50.0	50.0	50.0
50.5	50.5	50.5
51.0	51.0	51.0
51.5	51.5	51.5
52.0	52.0	52.0
52.5	52.5	52.5
53.0	53.0	53.0
53.5	53.5	53.5
54.0	54.0	54.0
54.5	54.5	54.5
55.0	55.0	55.0

-Log of Total Dissolved CA at Time 0.0 days

Log of Total Precipitated CA at Time 0.0 days

log of Free CA at Time 0.0 days

Fig. 7.6 Initial distribution of calcium in a uranium mill tailing

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Fig. 7.7 Distribution of calcium in a uranium mill tailing at 300 days

precipitated calcium, and free Ca^{2+} at 300 days. The diagrams highlight the high calcium concentration, and the same trend is continued after 700 and 100 days as shown in Figs. 7.8 and 7.9, respectively.

The initial and boundary conditions set for the simulation are such that CaSO_4 is supersaturated throughout the system. However, CaCO_3 , which was initially present everywhere outside of the tailings, disappears as the acidity is transported out of the tailings. The progressive dissolution of CaCO_3 with time is shown in Figs. 7.10. At 20 days (Fig. 7.10a) CaCO_3 is present close to the tailings, whereas at 1000 days (Fig. 7.10d) CaCO_3 is present only in a small zone near the right edge of the cross section.

The behavior of sulfate is controlled to a large degree by precipitation of CaSO_4 , and Fig. 7.11 shows total sulfate, total dissolved sulfate, precipitated sulfate (zone of most CaSO_4 precipitation are readily apparent from the contours), and free SO_4^{2-} concentration at 300 days.

The distribution of uranium is significantly different from that of calcium and sulfate. Unlike calcium and sulfate that are present in high concentrations throughout the cross section, there is a difference of more than three orders of magnitude between the uranium concentration within

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-Log of Total Dissolved CA at Time 700.0 days

-Log of Free CA at Time 700.0 days

-Log of Total Concentration of CA at Time 700.0 days

-Log of Total Precipitated CA at Time 700.0 days

Fig. 7.8 Distribution of calcium in a uranium mill tailing at 700 days

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Fig. 7.9 Distribution of calcium in a uranium mill tailing at 1,000 days

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Fig. 7.10 Dissolution dynamics of calcite in a
uranium mill tailing

ORNL-DWG 90-17760

-Log of Total Dissolved SO_4 at Time 300.0 days

-Log of Total Concentration of SO_4 at Time 300.0 days

-Log of Free SO_4 at Time 300.0 days

-Log of Total Precipitated SO_4 at Time 300.0 days

Fig. 7.11 Distribution of sulfate in a uranium mill tailing at 300 days

and outside of the tailings. As a result, uranium is mobilized, and its concentration steadily increases with time in the region surrounding the tailings. The adsorption of uranium is not considered; therefore, the only process that can retard uranium migration is precipitation of uranium bearing minerals. The presence of high carbonate concentration further facilitates the migration of uranium. Figure 7.12 shows total uranium, total dissolved uranium, total precipitated uranium, and free UO_2^{2+} at time 0. The contours show the high uranium concentrations within the tailings, and Fig 7.12c shows the absence of any uranium minerals. At 300 days, Fig. 7.13c shows small zones of uranium precipitation $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2]$. The precipitation zone is limited principally due to low pH and high carbonate. Similar behavior is exhibited at 700 days (Fig. 7.14). Naturally, the concentration of uranium is greater at 700 days, and the zone of precipitation of calcium uranyl phosphate is pushed further away from the tailings in response to pH changes. At 1000 days, the same trend is continued (see Figs. 7.15a - d); the increased uranium concentration, however, created a wider zone of calcium uranyl phosphate precipitation in areas where the pH was less acidic.

This hypothetical example illustrates that HYDROGEOCHEM is capable of simulating the complex interactions between the flow, transport, and chemical reactions. The patterns in concentrations of various chemical constituents are created by the aforementioned interactions. The simulation results also indicates that an a priori selected distribution

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- Log of Total Concentration of UO₂ at Time 0.0 days

- Log of Total Dissolved UO₂ at Time 0.0 days

- Log of Total Precipitated UO₂ at Time 0.0 days

- Log of Free UO₂ at Time 0.0 days

Fig. 7.12 Initial distribution of uranium in a uranium mill tailing

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Fig. 7.13 Distribution of uranium in a uranium mill tailing at 300 days

ORNL-DWG 90-17763

- Log of Total Dissolved UO₂ at Time 7000.0 days

- Log of Free UO₂ at Time 7000.0 days

- Log of Total Concentration of UO₂ at Time 7000.0 days

- Log of Total Precipitated UO₂ at Time 7000.0 days

Fig. 7.14 Distribution of uranium in a uranium mill tailing at 700 days

ORNL-DWG 90-17764

Fig. 7.15 Distribution of uranium in a uranium mill tailing at 1,000 days

coefficient or a retardation factor cannot accurately simulate the behavior patterns that arise from complex nonlinear chemical reactions and fluid flow.

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APPENDIX A: USERS' MANUAL

This appendix describes information required for using HYDROGEOCHEM.

A.1 Specifications of Array Dimensions

The subscripted variable arrays have to be dimensioned for each site-specific problem in the MAIN program. One hundred and two (102) arrays variables contained between lines MAIN 150 and MAIN 370 in the source code should be dimensioned according to the indicated subscripts (a total of 29). The listing and definitions of these parameters and their associated subscripts (maximum-control numbers) are given below:

Arrays for Node Coordinates and Element and Node Connectivities

X(MAXNP), Z(MAXNP), IE(MAXEL,5), LRN(JBAND,MAXNP);

MAXEL - maximum number of elements,

MAXNP - maximum number of nodes;

JBAND - maximum number of non-zero elements in any row of the matrix,

X(NP) - x-coordinate of NP-th nodal point,

Z(NP) - z-coordinate of NP-th nodal point,

IE(M,I) - global node number of the I-th node of the M-th element if I is between 1 and 4, integer to indicate the material type of the M-th element if I is equal to 5.

LRN(I,NP) - global node number of I-th node connected to node NP,

Arrays for Boundary Surfaces

DLB(MAXBES), DCOSXB(MAXBES), DCOSZB(MAXBES),

MBES(MAXBES), ISB(4,MAXBES), NPB(4,MAXBNP),

MAXBES - maximum number of boundary-element sides,

MAXBNP - maximum number of boundary nodal points;

DLB(I) - length of the I-th boundary element side,

DCOSXB(I) - x-directional cosine of I-th boundary element side,

DCOSZB(I) - z-directional cosine of I-th boundary element side,

MBES(I) - element number to which the I-th boundary element-side belong,

ISB(1,I) - global node number of the first node of I-th
 boundary element surface,
 ISB(2,I) - global node number of the second node of I-th
 boundary element surface,
 ISB(3,I) - element NBE(I)'s local node number of the first node
 of the I-th boundary element side,
 ISB(4,I) - element NBE(I)'s local node number of the second node
 of the I-th boundary element side,
 NPBB(I) - global node number of I-th boundary node.

Arrays to Store Compressed Global Matrices and Global Load Vectors

SMTRX(MAXNP,JBAND), VMTRX(MAXNP,JBAND), DMTRX(MAXNP,JBAND),
 MMTRX(MAXNP,JBAND), RLD(MAXNP,MXNCC)
 SMTRX(N,I) - compressed global matrix from dispersion terms,
 source terms, and moisture change terms,
 - sum of QB + QQ - QC [cf. Eqs. (6.7b), (6.7d), and
 and (6.7e)],
 VMTRX(N,I) - compressed global matrix from velocity term,
 - sum of QV [cf. Eq. (6.7b)],
 DMTRX(N,I) - compressed global matrix from moisture change terms,
 - sum of QC [cf. Eq. (6.7e)],
 MMTRX(N,I) - compressed global matrix from moisture terms,
 - sum of QA [cf. Eq. (6.7a)],
 RLD(N,K) - compressed global load vector of the N-th node for
 the K-th component - sum of QR [cf. eq. (6.f)].

Arrays to Store the Global Matrix and Global Load Vector

CMATRX(MAXNP,MAXBHP), RVCTR(MAXNP), RI(MAXNP), RL(MAXNP)
 MAXBHP - maximum number of half bandwidth plus 1.
 CMATRX(NP,I) - an array to store the assembled global matrix,
 RVCTR(NP) - an array to store the assembled global load vector,
 RI(NP) - concentration iterate in subroutine PISS,
 RL(NP) - a working array to contain final solution for the
 concentration in subroutine PISS.

Arrays to store Chemical Component Variables

T(MAXNP,MAXN), TP(MAXNP,MAXN), TW(MAXNP,MAXN), C(MAXNP,MAXN),
 CP(MAXNP,MAXN), S(MAXNP,MAXN), P(MAXNP,MAXN), XLOG(MAXNP,MAXN),
 CNAM(MAXN), INDC(MAXN), IDN(MAXN), TMC(MAXN), DMC(MAXN),
 SMC(MAXN), PMC(MAXN), XMC(MAXN)

MAXN - Maximum number of chemical components,

T(N,K) - total analytical concentration at the N-th node for the K-th chemical component,
 TP(N,K) - value of T(N,K) at previous time step,
 TW(N,K) - value of T(N,K) for the previous iteration,
 C(N,K) - total dissolved concentration at the N-th node for the K-th chemical component,
 CP(N,K) - value of C(N,K) at the previous time-step,
 S(N,K) - total sorbed concentration at the N-th node for the K-th chemical component,
 P(N,K) - total precipitated concentration at the N-th node for the K-th chemical component,
 XLOG(N,K) - negative logarithm of free ion concentration at the N-th node for the K-th chemical components,
 CNAM(K) - name of the K-th chemical component,
 INDC(K) - index of the type of the K-th chemical components,
 0 - mobile conservative chemical (aqueous component),
 1 - mobile non-conservative chemical (aqueous components),
 2 - immobile non-conservative chemical (sorbing sites),
 3 - mobile chemical component with activity specified,
 IDN(K) - identification number of the K-th chemical (cf. A.4)
 TMC(K) - total molar concentration of the K-th chemical component at any given node,
 DMC(K) - total dissolved molar concentration of the K-th chemical component at any given node,
 SMC(K) - total sorbed molar concentration of the K-th chemical component at any given node,
 PMC(K) - total precipitated molar concentration of the K-th chemical component at any given node,
 XMCLOG(K) - negative logarithm of the free ion molar concentration of the K-th chemical component at any given node.

Arrays to store Variables Related to Equilibrium Computation

ZM(MAXEQ,MAXEQ), RE(MAXEQ), RR(MAXEQ), WORK(MAXEQ), IPVT(MAXEQ),
 SPECN(MAXM), CNMOL(MAXM), CWMOL(MAXM), ISCN(MAXM), GAMA(MAXM),
 VJ(MAXM), AXYZP(MAXPD,MAXN), EQK(MAXPD), EQKM(MAXPD),
 LOCZ(MAXMZ), INDPS(MAXMP), ITCPS(MAXMP), RIAP(MAXMP), IAP(MAXMP),
 INDTB(MAXMP), GXW(MAXN), ICELI(MAXN), GEK(MAXN)

MAXEQ - maximum number of Newton-Ralsphson equations,
 MAXPD - maximum number of product species,
 MAXMZ - maximum number of ion-exchanged species,
 MAXMP - maximum number of species allowed for precipitation-dissolution.

ZM(I,J) - Jacobian matrix - $\partial RE(I)/\partial CW(J)$,
 RE(I) - residue of the I-th equation,
 RR(I) - residue of the I-th equation,
 WORK(I) - an array used to the equation solver
 IPVT(I) - index of the I-th pivot,

SPECN(I) - species name of the I-th species,
 CNMOL(I) - concentration of the I-th species,
 CWMOL(I) - concentration of the iterate of the I-th species,
 ISCN(I) - indicator of species concentration of the I-th species:
 3 - concentration is specified for dissolved species,
 activity is fixed for solid species,
 1 - mole balance equation of the I-th component is to
 be solved with a modified bisection method,
 GAMA(I) - activity of the I-th species,
 VJ(I) - charge of the I-th species,
 XYZP(I,J) - stoichiometric coefficient of the J-th component in
 the I-th product species,
 EQK(I) - equilibrium constant of the I-th product species,
 EQKM(I) - modified equilibrium constant of the I-th product
 species,
 LOCZ(I) - location of the I-th ion exchanging species in the
 species list,
 INDPS(I) - index of the I-th potentially precipitated species:
 0 - the I-th species is not allowed to precipitate,
 1 - the I-th species is allowed to precipitate,
 ITCPS(I) - values of INDPS(I) of the previous cycle,
 RIAP(I) - saturation value of the I-th potentially precipitated
 species,
 IAP(I) - rank of the saturation value of the I-th potentially
 precipitated species; the larger the rank, the larger
 the saturation value,
 INDTB(I) - the INDTB(I)-th potentially precipitated species has
 the I-th lowest saturation value,
 GXW(J) - Log10 of CW(J),
 ICELI(J) - indicator of the J-th component legimitatable for
 elimination in determining the number of species
 allowed for precipitation;
 0 - not legitimate, 1 - legitimate,
 GEK(I) - Log10 of EQKM(I).

Arrays for Hydrological Variables and Nonconvergent Nodes

VX(MAXNP), VZ(MAXNP), TH(4,MAXEL), THP(4,MAXEL),
 DTH(4,MAXEL), WETAB(4,MAXEL)
 VX(NP) - x-component velocity at NP-th node,
 VZ(NP) - z-component velocity at NP-th node,
 TH(I,M) - water content at I-th Gaussian point of M-th element,
 THP(I,M) - value of TH(I,M) at previous time step,
 DTH(I,M) - dTH/dt at the I-th Gaussian node of the M-th element,
 WETAB(I,M) - weighting factor for the I-th side of the M-th element.

Arrays for Element (Distributed) and Well (Point) Sources/Sinks

SOSF(MXSDP,MXSPR,MAXN1), TSOSF(MXSDP,MXSPR,MAXN1),
 SOS(MXSPR,MAXN1), ISTYP(MXSEL,MAXN1), LES(MXSEL),
 WSSF(MXWDP,MXWPR,MAXN1), TWSSF(MXWDP,MXWPR,MAXN1),
 WSS(MXWPR,MAXN1), IWTYP(MXWNP,MAXN1), NPW(MXWNP);

MAXN1 - maximum number of chemical components plus 1,
 MXSEL - maximum number of source elements,
 MXSPR - maximum number of source profiles,
 MXSDP - maximum number of data points on each well-source
 profile,
 MXWNP - maximum number of well nodal points,
 MXWPR - maximum number of well-source profiles,
 MXWDP - maximum number of data point on each well source
 profile;

SOSF(I,J,K) - source concentration of I-th data point in J-th
 element-source vs time profile for the K-th chemical,
 component; when K = NCC + 1, SOSF(I,J,K) is the
 source flow rate,
 TSOSF(I,J,K) - time of I-th data point in J-th element-source
 vs time profile for the K-th chemical component,
 SOS(I,K) - value of I-th element-source profile for the K-th
 chemical component; when K = NCC + 1, SOS(I,K) is
 the source flow rate,
 ISTYP(M,K) - source type assigned to M-th source-element for
 the K-th chemical component,
 LES(M) - element number of the M-th source-element,
 WSSF(I,J,K) - source concentration of the I-th data point in the
 J-th well-source vs time profile for the K-th
 chemical component; when K = NCC + 1, WSSF(I,J,K)
 is the source flow rate,
 TWSSF(I,J,K) - time of the I-th data point in the J-th well-source
 vs time profile for the K-th chemical component,
 WSS(I,K) - value of I-th well-source profile for the K-th
 chemical component; when K = NCC + 1, WSS(I,K) is
 the source flow rate,
 IWTYP(N,K) - source type assigned to the N-th well-source node for
 the K-th chemical component,
 NPW(N) - global node number of the N-th well-source node,

Arrays for Dirichlet Boundary Conditions

CDBF(MXDDP,MXDPR,MAXN), TCDBF(MXDDP,MXDPR,MAXN),
 CDB(MXDPR,MAXN), IDTYP(MXDNP,MAXN), NPDB(MXDNP);

MXDNP - maximum number of Dirichlet nodal points,
 MXDPR - maximum number of Dirichlet total head profiles,
 MXDDP - maximum number of data points on each Dirichlet profile;

CDBF(I,J,K) - total concentration of the I-th data point in the J-th Dirichlet total concentration vs time profile for the K-th chemical,
 TCDBF(I,,K) - time of the I-th data point in the J-th Dirichlet total concentration vs time profile for the K-th chemical component,

 CDB(I,K) - value of total concentration at the present time of the I-th total concentration vs time profile for K-th chemical component,
 IDTYP(NP,K) - type of Dirichlet total concentration vs time profile assigned to the NP-th Dirichlet node for the K-th chemical component,
 NPDB(NP) - global node number of NP-th Dirichlet node,

Arrays for Variable Boundary Conditions

DLV(MXVES), DCOSXV(MXVES), DCOSZV(MXVES), MVES(MXVES),
 ISV(4,MXVES), IVFTYP(MXVES,MXNCC), NPVB(MXVNP),
 CVBF(MXVDP,MXVPR,MAXN), TCVBF(MXVDP,MXVPR,MAXN),
 CVB(MXVPR,MAXN);

 MXVES - maximum number of variable boundary element sides,
 MXVNP - maximum number of variable boundary nodal points,
 MXVPR - maximum number of variable boundary profiles,
 MXVDP - maximum number of data point on each variable profile;

 DLV(MP) - length of the MP-th variable boundary element side,
 DCOSXV(MP) - x-directional cosine of the MP-th VB element side,
 DCOSZV(MP) - z-directional cosine of the MP-th VB element side,
 MVES(MP) - element number to which the MP-th variable boundary element-side belong,
 IS(1,MP) - Compressed VB node number of the first node of the MP-th VB element side,
 IS(2,MP) - Compressed VB node number of the second node of the MP-th VB element side,
 IS(3,MP) - Element MVES(MP)'s local node number of the first node of the MP-th VB element side,
 IS(4,MP) - Element MVES(MP)'s local node number of the second node of the MP-th VB element side,
 IVTYP(MP,K) - type of incoming-fluid-concentration profile assigned to MP-th VB boundary side for the K-th chemical component,
 NPVB(NP) - global node number of the NP-th VB node,
 CVBF(I,J,K) - concentration of incoming fluid of the I-th data point J-th concentration vs time profile for the K-th chemical component,
 TCVBF(I,J,K) - time of the I-th data point in the J-th incoming concentration vs time profile for the K-th chemical component,

CVB(I,K) - concentration of the I-th profile for the K-th chemical component.

Arrays for Material Property Array and node indicator

PROP(MXMPPM,MAXMAT), NODEP(MAXNP,2)

MAXMAT - maximum number of material types (medium formations),

MXMPPM - maximum number of material properties per material;

PROP(J,I) - J-th material property of I-th materials

J - 1 - longitudinal dispersivity (L),

J - 2 - lateral dispersivity (L),

J - 3 - effective molecular diffusion coefficient (L^2/T),

J - 4 - bulk density of the medium, (M/L^3),

J - 5 - cation ion exchange capacity, (Equivalent/ L^3),

J - 6 - capacitance between the surface and the "o" plane, (Farady/ L^2),

J - 7 - capacitance between the "o" plane and diffuse layer, (Farady/ L^2),

J - 8 - surface area of adsorption site, (L^2/L^3).

NODEP(NP,1) - are chemical equilibrium results at the NP-th node to be printed? 1 - yes, 0 - no,

NODEP(NP,2) - chemical property type assigned to node NP.

Arrays for Output Control and Time Step Size Change

KPR(MAXNTI), KDSK(MAXNTI), TDTCH(MXNDTC);

MAXNTI - maximum number of time steps,

MXNDTC - maximum number of DELT changes;

KPR(I) - line print for I-th time step? 1 - yes, 0 - no,

KDSK(I) - storage results on unit 2 for the I-th time step?
1 - yes, 0 - no,

TDTCH(I) - time of I-th time to reset time step size - DELT0.

Arrays for Required for Other Computations

RKD(MAXNP,MAXN), IWRK(MAXNP), THN(MAXNP), DTHN(MAXNP),

THOBN(MAXNP)

FRATE(MXVNP,MAXN), FLOW(MXVNP,MAXN), TFLOW(MXVNP,MAXN),

RKD(N,K) - computed equivalent Kd at the N-th node for the K-th chemical component,

IWRK(N) - a working array for computing THN(N) and DTHN(N),

THN(N) - moisture content at the N-th node,
DTHN(N) - dTH/dt at the N-th node,
RHOBN(N) - bulk density at the N-th node,
FRATE(I,K) - rate of material flux at the I-th variable node for
the K-th chemical component,
FLOW(I,K) - $FRATE(I,K) * DELT$
TFLOW(I,K) - accumulated amount of material per unit area
going through the I-th variable node for the
K-th chemical component.

The subscripts (maximum-control numbers) of the above 102 arrays should be specified in the BLOCK DATA in the source program. One should always assign correct numbers to these subscripts so that the program can function properly. If the program fails to function, it is most likely that either the arrays mentioned above are not properly dimensioned or the numbers assigned in the BLOCK DATA to these specification numbers of the arrays are not correct. In the following, we will demonstrate how to dimension the above 102 arrays in the MAIN and how to specify the maximum-control numbers in the BLOCK DATA with an example.

Let us assume that a region of interest is discretized by 15 by 89 nodes and 14 by 88 elements. In other words, we are discretizing the region with 89 nodes along the longitudinal, or x-direction, and 15 nodes along the vertical, or z-direction. Because we have a total of $15 \times 89 = 1,335$ nodes, the maximum number of nodes is MAXNP = 1335. The total number of elements is $14 \times 88 = 1,232$, i.e. MAXEL = 1232. For this simple discretization problem, the maximum connecting number to any of the 1,335 nodes in the region of interest is 9 (i.e., JBAND = 9). There will be 14 element-sides each on the right and left sides and 88 element-sides each

on the top and bottom sides of the region. Thus, there will be a total of 204 element-sides (i.e., MAXBES = 204). Similarly, we can compute the boundary nodes to be 220 (i.e., MAXBNP = 204). The bandwidth is equal to 33 (i.e., MAXBW = 33). We further assume that we are dealing with 12 chemical components, i.e. (MAXN = 12). Among these 12 components, there will be chemical reactions to result in a maximum of 78 product species, of which a maximum number of 10 species involve in ion-exchange and a maximum number of 38 is potentially precipitated species. Thus, we have MAXPD = 78, MAXMZ = 10, MAXMP = 38, and MAXM = 90. Of course, the maximum number of equations will be MAXEQ = MAXN + MAXMZ + MAXMP = 60. With these maximum-control numbers specified, the arrays related to the global region, global boundary, and hydrologic variables can be dimensioned as:

```
DIMENSION X(1335),Z(1335),IE(1232,5),LRN(9,1335)
```

```
DIMENSION DLB(204),DCOSXB(204),DCOSZB(204),MVES(4,204),ISB(4,204)
DIMENSION NPBB(204)
```

```
DIMENSION SMTRX(1335,9),VMTRX(1335,9),DMTRX(1335,9),MMTRX(1335,9)
DIMENSION RLD(1335,12)
DIMENSION CMATRX(1335,33),RVCTR(1335)
DIMENSION RI(1335),RL(1335)
```

```
DIMENSION T(1335,12),TP(1335,12),TW(1335,12)
DIMENSION C(1335,12),CP(1335,12)
DIMENSION S(1335,12),P(1335,12),XLOG(1335,12)
```

```
DIMENSION CNAM(12),INDC(12),IDN(12)
DIMENSION TMC(12),DMC(12),SMC(12),PMC(12),XMCLOG(12)
```

```
DIMENSION ZM(60,60),RE(60),RR(60),WORK(60),IPVY(60)
DIMENSION SPECN(90),CNOML(90),CWMOL(90),ISCN(90),GAMA(90),VJ(90)
DIMENSION XYZP(78,12),EQK(78),EQKM(78),LOCZ(10)
DIMENSION INDPS(38),ITCPS(38),RIAP(38),IAP(38),INDTB(38)
DIMENSION GXW(12),ICELI(12),GEK(78)
```

```
DIMENSION VX(1335),VZ(1335),TH(3,1232),THP(4,1232),DTH(4,1232)
DIMENSION WETAB(4,1232)
```


We will assume that there will be a maximum of 11 elements that have the distributed sources/sinks (i.e., MXSEL = 11) and a maximum of 10 nodal points that can be considered as well sources/sinks (i.e. MXWNP = 10). We will also assume that there will be three different distributed source/sink profiles and five distinguish point source/sink profiles. Then we will have MXSPR = 3 and MXWPR = 5. Let us further assume four data points are needed to describe the distributed source/sink profiles as function of time and 8 data points are required to described point source/sink profiles, i.e., MXSDP = 4 and MXWDP = 8. With these assumptions, we can now dimension the arrays related to source/sink conditions:

```
DIMENSION SOSF(4,3,12),TSOSF(4,3,12),SOS(3,12)
DIMENSION ISTYP(11,12),LES(11)
DIMENSION WSSF(8,5,12),TWSSF(8,5,12),WSS(5,12)
DIMENSION IWTYP(10,12),NPW(10)
```

To specify arrays for boundary conditions, let us assume that the total analytical concentrations on the left side and the left half of the top side are known. The right half of the top side, bottom side, and right side are specified as variable boundaries.

On the left side there are 15 nodes, and on the left half of the top side there are 44 nodes. Thus, we have a total of 59 Dirichlet nodes. Let us assume that the middle 9 nodes on the left side have a specified total analytical concentration, the bottom 3 nodes on the left side have a

different specified concentration, and the other 47 nodes have a another specified total analytical concentration. We further assume that both total analytical concentrations can be described by 8 data points as functions of time. We then have MXDNP = 59, MXDPR = 3, and MXDDP = 8; and the Dirichlet boundary condition arrays can be dimensioned as:

```
DIMENSION CDBF(8,3,11),THDBF(8,3,11),CDB(3,11)
DIMENSION IDTYP(59,11),NPDB(59)
```

There are 147 nodes and 146 element-sides on the right half of the top side, bottom side, and right side; thus MXVNP = 147 and MXVES = 146. It is further assumed that there three different incomping fluid concentrations going into the region through the top, bottom, and right sides, respectively, and each of these three concentration is function of time and can be described by 8 data points. With these descriptions, we have MXVPR = 3 and MXVDP = 8. The variable boundary condition arrays can be specified as:

```
DIMENSION DLB(146),DCOSXB(146),DCOSZB(146),MVES(4,146),ISV(4,146)
DIMENSION IVTYP(146,11),NPVB(147)
DIMENSION CVBF(8,3,11),TCVBF(8,3,11),CVB(3,11)
```

In this report, we have 8 material properties per material. We will assume that the whole region of interest is composed of three different kinds of materials. We then have MAXMAT = 3 and MXMPPM = 8. The material property and node-output indicator arrays can be dimensioned as:

```
DIMENSION PROP(8,3),NODEP(1335)
```

If we assume that we will make a 500 time step-simulation and we will re-initiate the change on the time step size for 20 times during our simulation, then we have MAXNTI = 500 and MXNDTC = 20. With this assumption, arrays related to time can be dimensioned as:

```
DIMENSION KPR(500),KDSK(500),TDTCH(20)
```

Other miscellaneous arrays can be dimensioned as:

```
DIMENSION RKD(1335,12),IWRK(1335),THN(1335),DTHN(1335),RHOWB(1335)  
DIMENSION FRATE(147,12),FLOW(146,12),TFLOW(147,12)
```

Corresponding to the above dimension specifications, the following data statements must be made in BLOCK DATA to specify the maximum-control integers:

```
DATA MAXEL,MAXNP,MAXBES,MAXBNP,MAXBW,JBAND/1232,1335,204,204,33,9/  
DATA MAXNTI,MXNDTC/500,20/  
DATA MXSEL,MXSPR,MXSDP/11,3,4/  
DATA MXWNP,MXWPR,MXWDP/10,5,8/  
DATA MXDNP,MXDPR,MXDDP/59,3,4/  
DATA MXVES,MXVNPR,MXVPR,MXVDP/146,147,3,4/  
DATA MAXMAT,MXMPPM/3,8/  
DATA MAXN,MAXM,MAXMZ,MAXMP,MAXPD,MAXEQ/12,90,10,38,78,60/
```

If we use the point iteration method to solve the matrix equation instead of the direct band matrix solver, we should set MAXBW equal to JBAND.

A.2 Data Input Guide

All data sets except for data set 1 must be preceded by a data set name.

1. DATA SET 1: TITLE - One line per problem.

FORMAT(I5,7A10,3I1,I2)

1. NPROB - Problem number.
2. TITLE - Array for the title of the problem. It may contain up to 70 characters from column 6 to column 75.
3. IITR - Integer indicating if iteration table of convergence information to be printed?
0 - no, 1 - transport iteration table be printed,
2 - both transport and chemical iteration tables printed
4. INTER - Integer indicating if concentration field to be printed for each hydrological-chemical interaction? 1 - yes, 0 - no.
5. ICOND - Integer indicating if the condition number of the Jacobian matrix in chemical equilibrium computation to be printed? 1 - yes, 0 - no.
6. NHGCI - Integer indicating if chemical equilibrium information to be printed? 0 - no, > 0 - every NHGC inter-hydro-geochem iterations print once.

2. DATA SET 2: BASIC INTEGER PARAMETERS

Unformatted input contains 18 integers as follows:

1. NNP - Number of nodal points.
2. NEL - Number of elements.
3. NMAT - Number of material types.
4. NCM - Number of elements with material property correction.
5. NTI - Number of time steps or time increments.
6. KSS - steady-state simulation control,
0 - steady-state solution desired,
1 - no steady-state solution is wanted.

7. NMPPM - No. of material properties per material
EQ. 8 in the present program.
8. KVI - Velocity input control,
 - 1 - card input for velocity and moisture content,
1 - steady state velocity and moisture content
input via logical unit 1,
 - 2 - transient velocity and moisture content
input via auxiliary storage logical unit 1.
9. ILUMP - Mass matrix lumping control, 0 - no lump, 1 - lump.
10. IMID - Mid difference control,
 - 0 - no mid-difference,
 - 1 - mid-difference and W in DATA SET 3 should be 1.
11. IWET - Weighting function control,
 - 0 - Galerkin weighting,
 - 1 - Upstream weighting.
12. IOPTIM - Optimization factor computing indicator,
 - 1 - optimization factor is to be computed,
 - 0 - optimization factor is set to 1.0, 0.0, or -1.0
13. NITER - No. of iterations between hydrological-chemical
iterations allowed.
14. NDTCHG - No. of times to reset initial time step size.
15. NPITER - No. of iterations allowed for solving the
linear matrix equation with pointwise iteration.
16. IPNTS - Is pointwise iteration method to be used to
solve the matrix equations? 0 - no, 1 - yes.
17. KSTR - Auxiliary storage output control;
 - 0 - no storage,
 - 1 - output stored in logical unit 2.
18. NSTR - Number of logical records to be read via
Logical Unit 3 for restarting calculation;
0 - no restart.

*** NOTE: NTI can be computed by $NTI = I1 + 1 + I2 + 1$,
where $I1$ - largest integer not exceeding
 $\text{Log}(\text{DELMAX}/\text{DELT})/\text{LOG}(1+\text{CHNG})$,
 $I2$ - largest integer not exceeding
 $(\text{RTIME}-\text{DELT}*((1+\text{CHNG})^{**}(I1+1)-1))/\text{CHNG})/\text{DELMAX}$,
 RTIME - real simulation time,
 DELMAX , DELT , and CHNG are defined in Data Set 3.

3. DATA SET 3: BASIC REAL PARAMETERS

Unformatted input contains 10 real numbers as follows.

1. DELT - Initial time-step size, (T).
2. CHNG - Percentage of change in time step size in each of the subsequent time increment, (dimensionless in decimal point).
3. DELMAX - Maximum value of DELT, (T).
4. TMAX - Maximum simulation time, (T).
5. W - Time derivative weighting factor for all terms except for the velocity terms;
0.5 - Crank-Nicolson central,
1.0 - backward difference and mid-difference.
6. WV - Time integration factor for the velocity terms, 0.0 - forward difference (explicit),
0.5 - central difference, 1.0 - backward difference (complete implicit).
7. OME - Iteration parameter for solving nonlinear equation. 0.0 - 1.0 - under-relaxation, 1.0 - exact relaxation, 1.0 - 2.0 - over-relaxation.
8. OMI - Relaxation parameter for pointwise solving the matrix equation; 0.0 - 1.0 - under-relaxation, 1.0 - exact relaxation, 1.0-2.0 - over-relaxation.
9. TOLA - Error tolerance for solving the nonlinear equations. Half of its value is used as the tolerance for solving the linearized matrix equation with pointwise iteration
10. APHAG - Upstream weighting factor if IOPTIM = 0, Values are between 0.0 and 1.50 when advection form of the equation is used. If APHAG .GE. 1.34D0, the program will choose appropriate values of weighting factor. When conservative form of equations is used or when IOPTIM = 1, this value is not used by the program.

4. DATA SET 4: PRINTER OUTPUT AND DISK STORAGE CONTROL, AND TIMES FOR STEP SIZE RESETTING

The number of lines here depends on the number of time increments NTI and the times of resetting step size NDTCHG. The number of lines is $[(NTI/80+1)*2] + NLINE$. $(NTI/80+1)$ lines for printer output control, $(NTI/80+1)$ lines for storage control, and NLINE lines for time-step-size resetting control, which depends on NDTCHG.

Line 1 to Line $[(NTI/80+1)]$ - FORMAT(80I1)

```
-----
KPRO  KPR(1)  KPR(2)  ---  KPR(I)  ---  KPR(NTI)
-----
      1      2      3                               80
```

KPRO - Printer control for steady-state and initial conditions;
 0 - print nothing,
 1 - print FLOW, FRATE, and TFLOW,
 2 - print above (1) plus concentration,
 3 - print above (2) plus material flux.

KPR(I) - Printer control for I-th time-step similar to KPRO.

Line $[(NTI/80+1)+1]$ to Line $[(NTI/80+1)*2]$ - FORMAT(80I1)

```
-----
KDSK0 KDSK(1) KDSK(2)  ---  KDSK(I)  ---  KDSK(NTI)
-----
      1      2      3                               80
```

KDSK0 - Auxiliary storage control for steady-state and initial condition;
 0 - no storage,
 1 - store on logical unit 2.

KDSK(I) - Auxiliary storage control for I-th time-step similar to KDSK0.

Line greater than line $(NTI/80+1)*2$ - Unformatted input contains NDTCHG real number as follows.

1. TDTCH(1) - Time when the first time to reset time-step size,
2. TDTCH(2) - Time when the second time to reset time-step size,
- ...
- N. TDTCH(N) - Time when the N-th time to reset time-step size.

5. DATA SET 5: CHEMICAL PRINTOUT AND CHEMICAL PROPPERTY INDICATOR
Two groups of data are needed. The first group reads detail chemical printout indicator and the second group reads type of chemical property assigned to each node.

- (1) Group 1 - The number of lines depends on NCPRT. Normally, two lines should be sufficient.

Line 1 - Unformatted contains one integer.

1. NCPRT - Number of nodes where detailed chemical equilibrium information will be printed.

Line 2 - Unformatted input contains NCPRT integers.

1. IWRK(1) - Global node number of the first node where detail chemical equilibrium information will be printed.
2. IWRK(2) - Global node number of the second node where detail chemical equilibrium information will be printed.
- .
- .
- .
- N. IWRK(N) - Global node number of the N-th node where detail chemical equilibrium information will be printed.

**** NOTE: IWRK(I), I=1, NCPRT is used temporary to store the node numbers where detailed chemical information is be printed. These nodes numbers are then used to set NODEP(NP) = 1 or 0.

- (2) Group 2 - The number of lines required is in general equal to NNP. However, automatic generation may be made.

Line 1 to Line NNP - Each line is an unformatted input containing

1. NI - Node number of the first node in the sequence.
2. NSEQ - NSEQ subsequent nodes will be automatically generated.
3. NAD - Increment of node number for each of the NSEQ subsequent nodes.
4. NITYP - Type of chemical property assigned to node NI,

5. NTYPAD - Increment of NITYP for each of the NSEQ subsequent nodes.

**** NOTE: A line containing 5 zeros must be used to signal the end of this data set.

6. DATA SET 6: MATERIAL PROPERTIES

A total of NMAT lines are required for this data set.

Each line is an unformatted input contains the following information.

1. PROP(1,I) - Longitudinal dispersivity, (L).
2. PROP(2,I) - Lateral dispersivity, (L).
3. PROP(3,I) - effective molecular diffusion coefficient of I-th medium, (L^2/T).
4. PROP(4,I) - Bulk density of medium I, (M/L^3).
5. PROP(5,I) - Cation ion-exchange capacity of medium I, (Equivalents/M of Solids).
6. PROP(6,I) - Capacitance between the surface and "b" plane of medium I, ($Farady/L^2$)
7. PROP(7,I) - Capacitance between the "b" plane and diffuse layer of medium I, ($Farady/L^2$).
8. PROP(8,I) - Surface area of adsorption site of medium I, (L^2/M of Solids Medium).

NOTE: DATA SETS 7 and 8 TO BE DESCRIBED BELOW ARE NEEDED
IF AND ONLY IF KVI IS LESS THAN ZERO.

7. DATA SET 7: NODAL POINT COORDINATE

Usually a total of $2 \times \text{NNP}$ lines are required, NNP lines for the x-coordinate and NNP lines for the z-coordinate. However, if a group of cards appears in regular pattern, automatic generation may be made.

Line 1 to Line NNP - Each line is an unformatted input containing.

1. NI - Node number of the first node in the sequence.
2. NSEQ - NSEQ subsequent nodes will be automatically generated.
3. NAD - Increment of node number for each of the NSEQ subsequent nodes.
4. XNI - x-coordinate of node NI, (L).
5. XAD - Increment of x-coordinate for each of the NSEQ subsequent nodes, (L).
6. XRD - Percentage of increase of the increment over its preceding increment, (Decimal point);
If XRD .EQ. 0, all increments XAD's are the same.
If XRD .GT. 0, the first increment is $\text{XAD} \times (1 + \text{XRD})$, the second increment is $\text{XAD} \times (1 + \text{XRD})^2$, the third increment is $\text{XAD} \times (1 + \text{XRD})^3$, and so on.

**** NOTE: A line containing 6 zeros must be used to signal the end of this data set.

Line (NNP+1) to Line $2 \times \text{NNP}$ are input similarly but for the z-coordinate.

8. DATA SET 8: ELEMENT INCIDENCES

Usually a total of NEL lines are needed, one for each element. However, if a group of elements appears in regular pattern, automatic generation is made.

Unformatted input for each line containing the following information

1. MI - Global element number.
2. IE(MI,1) - Global node number of the first node of element MI.
3. IE(MI,2) - Global node number of the second node of element MI.

4. IE(MI,3) - Global node number of the third node of element MI.
5. IE(MI,4) - Global node number of the fourth node of element MI.
6. IE(MI,5) - Material type to be applied to element MI.
7. MODL - Number of elements in the direction of most rapidly numbered nodes.
8. NLAY - Number of elements in the direction of least rapidly numbered nodes.

IE(MI,1) - IE(MI,4) are numbered beginning with the lower left corner and progressing around the element in a counterclockwise direction. For a rectangular block of elements, it is only necessary to specify the first element, the width MODL and the length NLAY, where MODL and NLAY are measured in elements. Element numbering proceeds most rapidly along MODL dimension and least rapidly along the NLAY dimension. The following figure provides an example. The object is considered to be rectangular, since it has width MODL = 3 on two opposite sides and length NLAY = 5 on the other two opposite sides. To generate definitions of elements 2 through 15 automatically, including the both the incidence and material type, only one card is necessary:

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```

-----
1   1   5   6   2   1   3   5
-----

```

Although all elements of this example will be assumed to contain the same material type, MTYP = 1, this situation can easily be changed by using material-correction facility.

9. DATA SET 9: MATERIAL TYPE CORRECTION

This data set is required only if NCM .GT. 0. Normally NCM lines are required. However, if the elements to be corrected with different material properties appear in regular patterns, automatic generation may be made.

Unformatted input for each line containing the following information

1. MI - Global element number of the first element in the sequence.
2. NSEQ - NSEQ subsequent elements will be generated automatically.
3. MAD - Increment of element number for each of the NSEQ subsequent elements.
4. MITYP - Type of material made up of element MI.
5. MTYPAD - Increment of the type of material for each of subsequent NSEQ elements.

*** NOTE: A line containing five zeros must be used to signal the end of this data set.

10. DATA SET 10: CHEMICAL COMPONENT INFORMATION

Line 1 - Unformatted input contains one integer

1. NON - Number of components.

Line 2 through Line (NON + 1) - FORMAT(A10,2I5)

Each line containing the following information

1. CNAM(I) - component name of the I-th component
2. IDN(I) - identification number of the I-th component
3. INDC(I) - indicator of the I-th component,
0 - conservative component
1 - nonconservative mobile component
2 - immobile component
3 - component whose activity is fixed.

11. DATA SET 11: BATCH INPUT FOR INITIAL OR PRE-INITIAL CONDITIONS
This data set is needed only if NSTR .EQ. 0. When this data set is needed, normally a total of NNP lines are required for each chemical component, one each for a node. However, if the initial or pre-initial conditions appear in a regular pattern, automatic generation may be made. The following set of lines should be repeated for each of the NON components.

Each line is an unformatted input containing the following information

1. NI - Global node number of the first node in the sequence.
2. NSEQ - NSEQ subsequent nodes will be generated automatically.
3. NAD - Increment of node number for each of the NSEQ nodes.
4. RNI - Initial or pre-initial total concentration at node NI, (M/L**3).
5. RAD - Increment of initial or pre-initial total concentration for each of the NSEQ nodes, (M/L**3).

**** NOTE: A line with five zeros must be used to signal end of this data set for each chemical component.

**** NOTE: For any chemical component, if its INDC is equal to 3, then the Log10 of its activity should be the input for initial values or pre-initial values.

NOTE ON INITIAL CONDITIONS: The initial conditions for a transient calculation may be obtained in three different ways: from batch input, auxiliary storage input, or steady-state calculation using time-invariant boundary conditions. In the latter case a batch input of the pre-initial conditions is required as the zero-th order iterate of the steady state solution. Auxiliary storage input is necessary whenever the restarting facility is being used. That is, concentration distribution for NSTR different times have been generated and written on disk or magnetic tape. If NSTR .GT. 0, these distributions will be read from Logical Unit 3, and NSTR-th distribution will be used as the initial condition for current calculation. If KSTR is greater than zero, the concentration values will be written on a different device as they are read out from Logical Unit 3 so that a complete record of calculations may be kept on one device, Logical Unit 2. If either the first (card input) or the last (steady-state) options are used, then NSTR = 0

NOTE ON AUXILIARY UNITS: Logical Unit 1 is used to input hydrodynamic variables to HYDROGEOCHEM if KVI .GT. 0. Logical Unit 2 is used to store output of HYDROGEOCHEM if KSTR .GT. 0. Logical Unit 3 is used to input initial condition if NSTR .GT. 0. Proper identification of these three units must be made in the JCL if either of these options are used. It

can be seen that the DSNAM for Logical Unit 3 of the current job should be the same as that for Logical Unit 2 of the previous job.

NOTE ON STEADY-STATE INPUT: A steady-state option may be used to provide either the final state of a system under study or the initial conditions for a transient state calculation. In former case KSS = 0 and NTI = 0, and in the latter case KSS = 0 and NTI.GT.0. If KSS.GT.0, there will be no steady-state calculation.

12. DATA SET 12: INTEGER PARAMETERS for SOURCES and BOUNDARY CONDITIONS.

Unformatted input contains 13 integers as follows

1. NSEL - No. of source/sink elements
2. NSPR - No. of source/sink profiles.
3. NSDP - No. of data points in each source/sink profile.
4. NWNP - No. of well or point source/sink nodes.
5. NWPR - No. of well or point source/sink strength profiles.
6. NWDP - No. of data points in each of the NWPR profiles.
7. NDNP - No. of Dirichlet nodes, should be .GE. 1.
8. NDPR - No. of Dirichlet profiles, should be .GE. 1.
9. NDDP - No. of data points in each of the NDPR profiles, should be .GE. 2.
10. NVNP - No. of variable-boundary nodes
11. NVES - No. of variable-boundary sides.
12. NVPR - No. of incoming fluid concentration profiles to be applied to variable-boundary element sides.
13. NVDP - No. of data points in each of the NVPR profiles.

13. DATA SET 13: ELEMENT (DISTRIBUTED) AND WELL (POINT) SOURCE/SINK

- (1) Element Source/Sink: Subdata sets (a) through (c) are needed if and only if NSEL .GT. 0. When NSEL .GT. 0, subdata sets (b) and (c) should be repeated for (NON+1) times.
- (a) Global element number of compressed source/sink element number: Unformatted input containing the following information.
1. LES(1) - Global element number of the first distributed source/sink element.
 2. LES(2) - Global element number of the second distributed source/sink element.
 - .
 - .
 - .
 - N. LES(N) - Global element number of the N-th distributed source/sink element.

For K =1, NON+1

- (b) Element Source/sink Profile: Number of lines depends on NSPR, NSDP, and NON. This sub-data set is read in NSPR-wisely. Each line contains a number of data points. Each line is an unformatted input.

First profile

```
-----
TSOSF(1,1,K) SOSF(1,1,K) TSOSF(2,1,K) SOSF(2,1,K)
-----
```

```
-----
--- TSOSF(NSDP,1,K) SOSF(NSDP,1,K)
-----
```

80

Second profile

```
-----
TSOSF(1,2,K) SOSF(1,2,K) TSOSF(2,2,K) SOSF(2,2,K) ---
-----
```

```

-----
--- TSOSF(NSDP,2,K)   SOS(NSDP,2,K)
-----
80

```

I-th profile

```

-----
TSOSF(1,I,K) SOSF(1,I,K) TSOSF(2,I,K) SOSF(2,I,K) ---
-----
.
.
.
-----
--- TSOSF(NSDP,I,K)   SOSF(NSDP,I,K)
-----
80

```

NSPR-th profile

```

-----
TSOSF(1,NSPR,K) SOSF(1,NSPR,K) TSOSF(2,NSPR,K) SOSF(2,NSPR,K) .
-----
.
.
.
-----
--- TSOSF(NSDP,NSPR,K) SOSF(NSDP,NSPR,K)
-----
80

```

TSOSF(J,I,K) - Time of J-th data point in I-th profile for K-th component, (T).

SOSF(J,I,K) - Source/sink value of J-th data point in I-th profile for K-th component,
(M/T/L**3) if K. LE. NON
(L**3/T/L**3) if K. EQ. (NON+1).

- (c) Source/sink Type in Each Source/sink Element: Usually one line per element. However, automatic generation can be made.

Each line is an unformatted input containing the following

1. MI - Compressed source/sink element number of first element in the sequence.

2. NSEQ - NSEQ source/sink elements will have type MITYP.
3. MAD - Increment of MI for each of the NSEQ elements.
4. MITYP - Source/sink type for element MI.
5. MTYPAD - Increment of source type in each of the NSEQ subsequent elements.

*** NOTE: A line containing 5 zeros must be used to end this data set.

- (2) Point Source/Sink: Subdata sets (a) through (c) are needed if and only if $NWNP > 0$. When $NWNP > 0$, subdata sets (b) and (c) should be repeated for $(NON+1)$ times.

- (a) Global node number of compressed point source/sink number: Unformatted input containing the following information.

1. NPW(1) - Global node number of the first source/sink node.
2. NPW(2) - Global node number of the second source/sink node.
- .
- .
- N. NPW(N) - Global node number of the N-th source/sink node.

For $K = 1, NON+1$

- (b) Point source/sink profile:
Number of lines depends on NWPR, NWDP, and NON. This sub-data set is read in NWPR-wisely. Each card contains a number of data points.

First profile

TWSSF(1,1,K) WSSF(1,1,K) TWSSF(2,1,K) WSSF(2,1,K)

--- TWSSF(NWDP,1,K) WSSF(NWDP,1,K)

Second profile

```

-----
TWSSF(1,2,K) WSSF(1,2,K) TWSSF(2,2,K) WSSF(2,2,K) ---
-----
.
.
-----
--- TWSSF(NWDP,2,K) WSSF(NWDP,2,K)
-----
80

```

I-th profile

```

-----
TWSSF(1,I,K) WSSF(1,I,K) TWSSF(2,I,K) WSSF(2,I,K) ---
-----
.
.
-----
--- TWSSF(NWDP,I,K) WSSF(NWDP,I,K)
-----
80

```

NWPR-th profile

```

-----
TWSSF(1,NWPR,K) WSSF(1,NWPR,K) TWSSF(2,NWPR,K) WSSF(2,NWPR,K) .
-----
.
.
-----
--- TWSSF(NWDP,NWPR,K) WSSF(NWDP,NWPR,K)
-----
80

```

TWSSF(J,I,K) - Time of J-th data point in I-th
profile for K-th component, (T).

WSSF(J,I,K) - Source/sink value of J-th data point
in I-th profile for K-th component,
(M/T/L**3) if K. LE. NON
(L**3/T) if K. EQ. (NON+1).

- (c) Type of point source/sink nodes
Normally one line per well node. However, automatic generation may be made.

Each line is an unformatted input containing the following

1. NI - Compressed well node number of the first node in a sequence.
2. NSEQ - NSEQ subsequent well nodes will be generated automatically for the source type.
3. NIAD - Increment of compressed well node number for each of the NSEQ subsequent nodes.
4. NITYP - Type of well source/sink profile assigned to NI-th well node
5. NITYPA - Increment of NITYP for each of the NSEQ subsequent nodes.

**** NOTE: A line containing five zeros must be used to signal the end of this subdata set.

14. DATA SET 14: VARIABLE BOUNDARY CONDITIONS

Four groups of cards are required for this data set if and only if NVES .GT. 0. The first group is used to specify the incoming concentration profiles, the second group is used to assign the type of incoming concentration profile to each of the NVES boundary sides, the third group is used to read the global nodal number of NVNP flowing-in and flowing-out nodes, and the fourth group is used to specify the information of the NVES element sides. The first group and the second group should be repeated NON times, for each one of the NON chemical components.

- (a) Incoming concentration profiles:

This subdata set is read in similar to that of 13 (b).

First profile

TCVBF(1,1,K) CVBF(1,1,K) TCVBF(2,1,K) CVBF(2,1,K) ...

... TCVBF(NVDP,1,K) CVBF(NVDP,1,K)

Second profile

```
-----
TCVBF(1,2,K) CVBF(1,2,K)   TCVBF(2,2,K) CVBF(2,2,K) ...
-----
```

```
-----
... TCVBF(NVDP,2,K)   CVBF(NVDP,2,K)
-----
```

80

I-th profile

```
-----
TCVBF(1,I,K) CVBF(1,I,K)   TCVBF(2,I,K) CVBF(2,I,K) ...
-----
```

```
-----
... TCVBF(NVDP,I,K)   CVBF(NVDP,I,K)
-----
```

80

NVPR-th profile

```
-----
TCVBF(1,NVPR,K) CVBF(1,NVPR,K) TCVBF(2,NVPR,K) CVBF(2,NVPR,K) .
-----
```

```
-----
...TCVBF(NVDP,NVPR,K) CVBF(NVDP,NVPR,K)
-----
```

80

TCVBF(J,I,K) - Time of the J-th data point on I-th
incoming-concentration vs time
profile for K-th component, (T).

CVBF(J,I,K) - Concentration of the J-th data point on
I-th incoming-concentration vs time
profile for K-th component, (M/L**3).

- (b) Incoming concentration type assigned to variable-boundary sides. This subdata set is read in similarly to that in 13 (c).

1. MI - Compressed variable-boundary side number of the first side in a sequence.
2. NSEQ - NSEQ subsequent sides will be generated automatically.
3. MIAD - Increment of the compressed variable-boundary element side number for each of the NSEQ subsequent sides.
4. MITYP - Type of incoming concentration profile assigned to side MI.
5. MTYPAD - Increment of the type of incoming concentration profile for each of the NSEQ subsequent sides.

*** NOTE: A line containing five zeros is used to end the input of this subdata set.

- (c) Global nodal number of NVNP variable-boundary condition nodes. Normally NVNP lines are needed. However, automatic generation can be made.

Each line is an unformatted input containing the following

1. NI - Compressed variable-boundary node number of the first node in a sequence.
2. NSEQ - NSEQ subsequent nodes will be generated automatically.
3. NIAD - Increment of the compressed variable-boundary node number for each of the NSEQ subsequent sides.
4. NODE - Global node of the compressed node NI.
5. NODEAD - Increment of NODE for each of the NSEQ subsequent nodes.

*** NOTE: A line containing five zeros is used to end the input of this subdata set.

(d) Specification of variable-boundary sides:

Normally, NVES lines are required, one each for a variable-boundary element side. However, if a group of variable-boundary element sides appears in a regular pattern, automatic generation may be made.

Each line is an unformatted input containing the following

1. MI - Compressed variable boundary element-side number of the first element side in a sequence.
2. NSEQ - NSEQ subsequent variable-boundary element sides will be generated automatically.
3. M - Global element number to which MI-th element-side belong to.
4. IS1 - Compressed variable-boundary nodal number of the first node of element side MI.
5. IS2 - Compressed variable-boundary nodal number of the second node of element side MI.
6. MIAD - Increment of MI for each of the NSEQ subsequent variable-boundary element sides.
7. MAD - Increment of M for each of the NSEQ subsequent variable-boundary element sides.
8. IS1AD - Increment of IS1 for each of the NSEQ subsequent variable-boundary element sides.
9. IS2AD - Increment of IS2 for each of the NSEQ subsequent variable boundary element-sides.

*** NOTE: A line with 9 zeros is used to end the input of this subdata set.

15. DATA SET 15: DIRICHLET BOUNDARY CONDITIONS

This data set is required if and only if $NDNP > 0$. Subdata sets (a) and (b) should be repeated NON times, one for each of the NON components.

(a) Dirichlet concentration profile:

This subdata set is read in similar to that in 13 (b).

First Profile

```
-----
TCDBF(1,1,K) CDBF(1,1,K) TCDBF(2,1,K) CDBF(2,1,K) ---
-----
```

```
-----
--- TCDBF(NDDP,1,K) CDBF(NDDP,1,K)
-----
```

80

Second profile

```
-----
TCDBF(1,2,K) CDBF(1,2,K) TCDBF(2,2,K) CDBF(2,2,K) ---
-----
```

```
-----
--- TCDBF(NDDP,2,K) CDBF(NDDP,2,K)
-----
```

80

I-th profile

```
-----
TCDBF(1,I,K) CDBF(1,I,K) TCDBF(2,I,K) CDBF(2,I,K) ---
-----
```

```
-----
--- TCDBF(NDDP,I,K) CDBF(NDDP,I,K)
-----
```

80

NDPR-th profile

```
-----
TCDBF(1,NDPR,K) CDBF(1,NDPR,K) TCDBF(2,NDPR,K) CDBF(2,NDPR,K) ...
-----
```

```

-----
... TCDBF(NDDP,NDPR,K)  CDBF(NDDP,NDPR,K)
-----

```

80

TCDBF(J,I,K) - Time of J-th data point in I-th
Dirichlet-concentration profile
for K-th component, (T).

CDBF(J,I,K) - Dirichlet concentration of J-th data
point in I-th Dirichlet concentration vs
time profile for K-th component,
(M/L**3).

(b) Type of Dirichlet node:

This subdata set is read in similar to DATA SET 14 (b).

Each line is an unformatted input containing five integers

1. NI - Compressed Dirichlet node number of
the first node in the sequence.
2. NSEQ - NSEQ subsequent Dirichlet nodes will
be generated automatically.
3. NAD - Increment of compressed Dirichlet
node number for each of the NSEQ nodes.
4. NITYP - Type of Dirichlet concentration profile for
node NI and the NSEQ subsequent nodes.
5. NTYPAD - Increment of NITYP for each of the NSEQ
subsequent nodes.

***** NOTE: A line with 5 zeros must be used to signal the
end of this sub-data set.

(c) Dirichlet nodes:

This sub-data set is read in similar to DATA SET 14 (c).

Each line is an unformatted input containing five integers

1. NI - Compressed Dirichlet boundary node number of
the first node in a sequence.
2. NSEQ - NSEQ subsequent nodes will be generated
automatically.

3. NIAD - Increment of the compressed Dirichlet boundary node number for each of the NSEQ subsequent sides.
4. NODE - Global node of the compressed node NI.
5. NODEAD - Increment of NODE for each of the NSEQ subsequent nodes.

*** NOTE: A line containing five zeros is used to end the input of this subdata set.

16. DATA SET 16: VELOCITY AND MOISTURE CONTENT

If KVI .GT. 0, this data set is not needed because these will be read via Logical Unit 1.

(a) Velocity field

Normally, one line per node is needed. However, automatic generation can be made.

Each line is an unformatted input containing 7 variables as

1. NI - Node number of the first node in the sequence.
2. NSEQ - NSEQ subsequent nodes will be automatically generated.
3. NAD - Increment of node number in each of the NSEQ subsequent nodes.
4. VXNI - x-velocity component of node NI, (L/T).
5. VZNI - z-velocity component of node NI, (L/T).
6. VXAD - Increment of x-velocity for each of the NSEQ subsequent nodes, (L/T).
7. VZAD - Increment of z-velocity for each of the NSEQ subsequent nodes, (L/T).

**** NOTE: A line with 7 zeros is used to signal the end of this sub-data set.

(b) Moisture content field

Normally, one line per element. However, automatic generation can be made.

Each line is an unformatted input containing five variables as

1. NI - Element number of the first element in the sequence.
2. NSEQ - NSEQ subsequent elements will have the moisture content automatically generated.
3. NAD - Increment of element number for each of the NSEQ subsequent elements.
4. THNI - Moisture content of node element NI, (decimal point).
5. THNIAD - Increment of moisture content for each of the NSEQ subsequent elements, (decimal point).

**** NOTE: A line with 5 zeros signals the end of this sub-data set.

17. DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES

Unformatted input contains 10 variables as follows:

1. NONA - Number of aqueous components.
2. NONS - Number of adsorbent components.
3. NOMX - Number of complexed species.
4. NOMY - Number of adsorbed species.
5. NOMZ - Number of ion-exchanged species.
6. NOMP - Number of precipitated species.
7. NITERC - Number of iterations allowed to solve chemical equilibrium problems.
8. EPSC - Error tolerance used in solving chemical equilibrium problems.
9. TOLS - Error tolerance for switching to Newton-Ralphson iteration on the electron balance equation.
10. TOL - Error tolerance for solving the electron balance equation with the modified bisection method.

18. DATA SET 18: H+, e-, IONIC STRENGTH AND SORPTION INFORMATION

Line 1 unformatted input containing the following 4 variables

1. SICOR - User's specified ionic strength for computing activity coefficient
2. ICOR - Is ionic strength used to correct activity coefficient?
0 - no
1 - constant ionic strength is used
2 - variable ionic strength is used
3. LNH - Location of the component H among component list.
4. LNE - Location of the component e among component list.

Line 2 unformatted input containing the following 6 variables

1. TEMP - Absolute temperature in Kelvin.
2. PRESU - Pressure in ATM.
3. IADS - Adsorption model index:
0 - simple surface complexation
1 - constant capacitance model
2 - double layer model
4. LNO - Location of the $\exp(-e\psi_{sio}/kt)$ component in the component list.
5. LNB - Location of the $\exp(-e\psi_{sib}/kt)$ component in the component list.
6. LNI - Location of the referenced ion-exchanging species in the ion-exchanging species list.

Line 3 unformatted input containing the following 4 variables

1. PEMN - Expected minimum pe.
2. PEMX - Expected maximum pe.
3. PHMN - Expected minimum pH.
4. PHMX - Expected maximum pH.

19. DATA SET 19: COMPONENT SPECIES AND THEIR ION-EXCHANGED SPECIES
For each component species, either two lines or four lines are needed depending on whether the species participates in ion-exchange reaction. If the species does not participate in ion-exchange reaction, two lines are needed for the species. If the species is involved in ion-exchanged reaction, four lines are needed for the species.

Line 1 - FORMAT(A20,I5)

1. SPECN(I) - Name of the I-th component species
2. ISCN(I) - Indicator of the I-th species concentration
3 - species concentration or activity is fixed.

Line 2 - Unformatted input containing two variables

1. CW(I) - Initial guess of the I-th component species concentration, (M/L**3).
2. VJ(I) - Charge of the I-th component species
3. IONEX - Integer indicating if the species is involved in ion-exchange reaction, 0 - no, 1 - yes.

Line 3 - FORMAT(A20,I5): This line is needed if and only if IONEX is not equal to zero.

1. SPECN(II) - Name of the ion-exchanged species resulted from the I-th component species.
2. ISCN(II) - indicator of the ion-exchanged species concentration
3 - species concentration is fixed.

Line 4 - Unformatted input containing one variable: This line is needed if and only if IONEX is not equal to zero.

1. CW(II) - Initial guess of the ion-exchanged species concentration, (M/L**3).
2. PKIPD - Log10 of the selectivity of the ion-exchanged species resulted from the I-th component species.

20. DATA SET 20: COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES
This data set is read in similar to DATA SET 19.

Line 1 - FORMAT(A20,I5)

1. SPECN(II) - Name of the II-th species or the I-th complexed species
2. ISCN(II) - Indicator of the II-th species concentration
3 - species concentration is fixed.

Line 2 - Unformatted input containing the following variables

1. CW(II) - Initial guess of the complexed species concentration, (M/L**3).
2. PKIPD - Log10 of the equilibrium constant of the I-th complexed species.
3. AXYZP(I,1) - Stoichiometric coefficient of the first component in the I-th complexed species.
4. AXYZP(I,2) - Stoichiometric coefficient of the second component in the I-th complexed species.
5. AXYZP(I,3) - Stoichiometric coefficient of the third component in the I-th complexed species.
- .
- .
- .
- NON+2. AXYZP(I, NON) - Stoichiometric coefficient of the NON-th component in the I-th complexed species.
- NON+3. IONEX - Integer indicating if the I-th complexed species is involved in ion-exchange reaction:
0 - no, 1 - yes.

Line 3 - FORMAT(A20,I5): This line is needed if and only if IONEX is not equal to zero.

1. SPECN(II) - Name of the II-th species resulted from the I-th complexed species.
2. ISCN(II) - Indicator of the II-th species concentration
3 - species concentration is fixed.

Line 4 - Unformatted input containing one variable: This line is needed if and only if IONEX is not equal to zero.

1. CW(II) - Initial guess of the ion-exchanged species concentration, (M/L**3).
2. PKIPD - Log10 of the selectivity of the ion-exchanged species resulted from the I-th complexed species.

21. DATA SET 21: ADSORBED SPECIES

Two lines per adsorbed species are needed.

Line 1 - FORMAT(A20,I5)

1. SPECN(II) - Name of the II-th species or the I-th adsorbed species.
2. ISCN(II) - Indicator of the II-th species concentration
3 - species concentration is fixed.

Line 2 - Unformatted input containing the following variables

1. CW(II) - Initial guess of the adsorbed species concentration, (M/L**3).
2. PKIPD - Log10 of the equilibrium constant of the I-th adsorbed species.
3. XYZP(II,1) - Stoichiometric coefficient of the first component in the II-th species or in the I-th adsorbed species.
4. XYZP(II,2) - Stoichiometric coefficient of the second component in the II-th species or in the I-th adsorbed species.
5. XYZP(II,3) - Stoichiometric coefficient of the third component in the II-th species or in the I-th adsorbed species.

NON+2. XYZP(II, NON) - Stoichiometric coefficient of the NON-th component in the II-th species or in the I-th adsorbed species.

22. DATA SET 22: PRECIPITATED/DISSOLVED SPECIES

Two lines per adsorbed species are needed.

Line 1 - FORMAT(A20,I5)

1. SPECN(II) - Name of the II-th species or the I-th precipitated-dissolved species.
2. ISCN(II) - Indicator of the II-th species concentration
3 - species concentration is fixed.

Line 2 - Unformatted input containing the following variables

1. CW(II) - Initial guess of the precipitated species concentration, (M/L**3).
2. PKIPD - Log10 of the equilibrium constant of the I-th precipitated-dissolved species.
3. XYZP(II,1) - Stoichiometric coefficient of the first component in the II-th species or in the I-th precipitated-dissolved species.
4. XYZP(II,2) - Stoichiometric coefficient of the second component in the II-th species or in the I-th precipitated-dissolved species.
5. XYZP(II,3) - Stoichiometric coefficient of the third component in the II-th species or in the I-th precipitated-dissolved species.
- .
- .
- .
- NON+2. XYZP(II, NON) - Stoichiometric coefficient of the NON-th component in the II-th species or in the I-th precipitated-dissolved species.

23. DATA SET 23: END-OF-JOB CARD

A blank line must be used to signal the end of the job.

A.3 Input and Output Devices

Five logical units are needed to execute HYDROGEOCHEM. Logical Unit 15 is used for batch file input, whereas Logical Unit 16 is used for line printer output. Logical Unit 11 is used to read hydrological parameters, including flow velocity and moisture contents, as functions of time. Logical Unit 12 is used to store output from HYDROGEOCHEM simulation in binary form, which can then be used for plotting purposes. Logical Unit 13 is needed if restart simulation is to be done.

A.4 Thermodynamic Data

The chemical module, EQMOD, of HYDROGEOCHEM requires information about the identity of chemical complexes, minerals-solids, and surface species, as well as the formation constants and the selectivity coefficients if ion-exchange reactions are considered. The chemical complexes and other species must be represented in terms of certain basis chemicals called components (Westall et al. 1976), and the formation constants (equilibrium constant for a reaction written to form the species from the components) and the stoichiometric coefficients for each species must be known accurately. The formation constants as well as stoichiometric coefficients of all species and the total analytical concentrations of components are used to calculate solution-mineral equilibria.

In any application of geochemical/hydrogeochemical models, an internally consistent and accurate set of species and formation constants and stoichiometric coefficients of all species is required for reliable results. The processes of critical review and selection of formation constants is complex. For this report, we have taken the liberty of listing the thermodynamic data distributed with the computer program MUNEQL (Westall et. al. 1976). Sect. A.4.1 lists component data and Sect. A.4.2 lists species data. We only enclose the data as a starting point for the convenience of potential users and highly recommend that the users select their own set of species, stoichiometric coefficients, and formation constants for their application. An expert system is being developed to aid in this process by Tripathi, Yeh, and colleagues and will be available in the future to provide assistance.

A.4.1 Component Data Base

<u>Component ID</u>	<u>Component Name</u>	<u>Component Charge</u>
1	Ca++	2
2	Mg++	2
3	Sr++	2
4	K+	1
5	Na+	1
6	Fe+++	3
7	Fe++	2
8	Mn++	2
9	Cu++	2
10	Ba++	2
11	Cd++	2
12	Zn++	2
13	Ni++	2
14	Hg++	2

<u>Component ID</u>	<u>Component Name</u>	<u>Component Charge</u>
15	Pb++	2
16	Co++	2
17	Co+++	3
18	Ag+	1
19	Cr+++	3
20	Al+++	3
21	Cs+	1
22	Li+	1
23	Be+++	3
24	Sc+++	3
25	TiO++	2
26	Sn++	2
27	Sn++++	4
28	La+++	3
29	Ce+++	3
30	Au+++	3
31	Th++++	4
32	UO2++	2
33	Cu+	1
34	X34++++	4
35	X35++	2
36	X36	0
50	H+	1
99	E-	-1
101	CO3--	-2
102	SO4--	-2
103	CL-	-1
104	F-	-1
105	Br-	-1
106	I-	-1
107	NH3	0
108	S--	-2
109	PO4---	-3
110	P2O7----	-4
111	PO10-----	-5
112	SiO3--	-2
113	S2O3--	-2
114	Cn-	-1
115	Ag-	-1
116	ACAC-	-1
117	CIT---	-3
118	OX-	-1
119	SAL--	-2
120	TART--	-2
121	EN	0

<u>Component ID</u>	<u>Component Name</u>	<u>Component Charge</u>
122	DIP	0
123	SUSA---	-3
124	GLY-	-1
125	GLU--	-2
126	PIC-	-1
127	NTA---	-3
128	EDTA----	-4
129	DCTA----	-4
130	CYST--	-2
131	NOR---	-3
132	PTH--	-2
133	ARG-	-1
134	ORN-	-1
135	LYS-	-1
136	HIS-	-1
137	ASP-	-1
138	SER-	-1
139	ALA-	-1
140	TYR--	-2
141	MET-	-1
142	VAL-	-1
143	THR-	-1
144	PHE-	-1
145	ISO-	-1
146	LEU-	-1
147	PRO-	-1
148	BOH4-	-1
149	SO3--	-2
150	SCN-	-1
151	NHOH	0
152	MoO4--	-2
153	WO4--	-2
154	AsO4---	-3
155	VO4---	-3
156	SeO4--	-2
157	NO3-	-1
158	TRIS-	-1
159	SOH	0
160	PSIB	0
161	PSIO	0
162	PCCA---	-3
163	PDCA--	-2
164	SYR-	-1

A.4.2 Species Data Base

<u>Species</u>	<u>Four Pairs of Component ID and</u>									
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								<u>Comment</u>
1286	Complexed Species									
1000	3.00	1	1	101	1	0	0	0	0	0.0000
1010	11.60	1	1	50	1	101	1	0	0	0.0000
1020	2.30	1	1	102	1	0	0	0	0	0.0000
1030	1.10	1	1	104	1	0	0	0	0	0.0000
1040	-0.10	1	1	107	1	0	0	0	0	0.0000
1050	-0.70	1	1	107	2	0	0	0	0	0.0000
1060	-1.50	1	1	107	3	0	0	0	0	0.0000
1070	-2.60	1	1	107	4	0	0	0	0	0.0000
1080	14.60	1	1	50	1	109	1	0	0	0.0000
1090	7.50	1	1	110	1	0	0	0	0	0.0000
1100	13.80	1	1	50	1	110	1	0	0	0.0000
1110	14.80	1	1	50	1	111	1	0	0	0.0000
1120	8.40	1	1	111	1	0	0	0	0	0.0000
1130	1.90	1	1	113	1	0	0	0	0	0.0000
1140	1.10	1	1	115	1	0	0	0	0	0.0000
1150	21.60	1	1	50	1	117	1	0	0	0.0000
1160	26.30	1	1	50	2	117	1	0	0	0.0000
1170	28.40	1	1	50	3	117	1	0	0	0.0000
1180	3.60	1	1	118	1	0	0	0	0	0.0000
1190	14.80	1	1	50	1	119	1	0	0	0.0000
1200	5.80	1	1	50	1	120	1	0	0	0.0000
1210	2.80	1	1	120	1	0	0	0	0	0.0000
1220	1.80	1	1	124	1	0	0	0	0	0.0000
1230	2.50	1	1	125	1	0	0	0	0	0.0000
1240	2.30	1	1	126	1	0	0	0	0	0.0000
1250	8.20	1	1	127	1	0	0	0	0	0.0000
1260	12.50	1	1	128	1	0	0	0	0	0.0000
1270	16.00	1	1	50	1	128	1	0	0	0.0000
1280	15.00	1	1	129	1	0	0	0	0	0.0000
1290	13.10	1	1	131	1	0	0	0	0	0.0000
1300	2.70	1	1	132	1	0	0	0	0	0.0000
1310	2.10	1	1	137	1	0	0	0	0	0.0000
1320	1.90	1	1	138	1	0	0	0	0	0.0000
1330	1.70	1	1	139	1	0	0	0	0	0.0000
1340	2.70	1	1	140	1	0	0	0	0	0.0000
1350	-12.20	1	1	50	-1	0	0	0	0	0.0000
1360	3.20	2	1	101	1	0	0	0	0	0.0000
1370	11.60	2	1	50	1	101	1	0	0	0.0000
1380	2.40	2	1	102	1	0	0	0	0	0.0000
1390	1.80	2	1	104	1	0	0	0	0	0.0000
1400	0.10	2	1	107	1	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>							<u>Comment</u>	
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								
1410	0.00	2	1	107	2	0	0	0	0	0.0000
1420	-0.30	2	1	107	3	0	0	0	0	0.0000
1430	-1.00	2	1	107	4	0	0	0	0	0.0000
1440	15.10	2	1	50	1	109	1	0	0	0.0000
1450	7.00	2	1	110	1	0	0	0	0	0.0000
1460	15.50	2	1	50	1	111	1	0	0	0.0000
1470	8.70	2	1	111	1	0	0	0	0	0.0000
1480	1.80	2	1	113	1	0	0	0	0	0.0000
1490	1.10	2	1	115	1	0	0	0	0	0.0000
1500	3.70	2	1	116	1	0	0	0	0	0.0000
1510	6.40	2	1	116	2	0	0	0	0	0.0000
1520	20.80	2	1	50	1	117	1	0	0	0.0000
1530	25.00	2	1	50	2	117	1	0	0	0.0000
1540	2.90	2	1	118	1	0	0	0	0	0.0000
1550	2.30	2	1	120	1	0	0	0	0	0.0000
1560	5.60	2	1	50	1	120	1	0	0	0.0000
1570	0.30	2	1	121	1	0	0	0	0	0.0000
1580	0.50	2	1	122	1	0	0	0	0	0.0000
1590	3.90	2	1	124	1	0	0	0	0	0.0000
1600	7.40	2	1	124	2	0	0	0	0	0.0000
1610	3.00	2	1	125	1	0	0	0	0	0.0000
1620	2.70	2	1	126	1	0	0	0	0	0.0000
1630	7.20	2	1	127	1	0	0	0	0	0.0000
1640	10.50	2	1	128	1	0	0	0	0	0.0000
1650	14.80	2	1	50	1	128	1	0	0	0.0000
1660	12.70	2	1	129	1	0	0	0	0	0.0000
1670	4.20	2	1	130	1	0	0	0	0	0.0000
1680	15.90	2	1	131	1	0	0	0	0	0.0000
1690	1.80	2	1	133	1	0	0	0	0	0.0000
1700	4.90	2	1	137	2	0	0	0	0	0.0000
1710	2.60	2	1	139	1	0	0	0	0	0.0000
1720	3.20	2	1	140	1	0	0	0	0	0.0000
1730	4.90	2	1	147	2	0	0	0	0	0.0000
1740	-11.20	2	1	50	-1	0	0	0	0	0.0000
1750	14.10	3	1	50	1	109	1	0	0	0.0000
1760	6.00	3	1	109	1	0	0	0	0	0.0000
1770	5.70	3	1	110	1	0	0	0	0	0.0000
1780	15.60	3	1	50	1	111	1	0	0	0.0000
1790	6.80	3	1	111	1	0	0	0	0	0.0000
1800	2.00	3	1	113	1	0	0	0	0	0.0000
1810	0.90	3	1	115	1	0	0	0	0	0.0000
1820	20.80	3	1	50	1	117	1	0	0	0.0000
1830	1.90	3	1	118	1	0	0	0	0	0.0000
1840	1.40	3	1	124	1	0	0	0	0	0.0000
1850	1.80	3	1	125	1	0	0	0	0	0.0000
1860	2.20	3	1	126	1	0	0	0	0	0.0000
1870	6.90	3	1	127	1	0	0	0	0	0.0000

<u>Species</u> <u>ID</u>	<u>Log K</u>	<u>Four Pairs of Component ID and</u> <u>Stoichiometric Coefficient</u>							<u>Comment</u>
1880	10.40	3	1 128	1	0	0	0	0	0.0000
1890	14.70	3	1 50	1 128	1	0	0	0	0.0000
1900	12.50	3	1 129	1	0	0	0	0	0.0000
1910	13.70	3	1 131	1	0	0	0	0	0.0000
1920	2.10	3	1 137	1	0	0	0	0	0.0000
1930	0.90	3	1 138	1	0	0	0	0	0.0000
1940	1.20	3	1 139	1	0	0	0	0	0.0000
1950	-12.60	3	1 50	-1	0	0	0	0	0.0000
1960	1.10	4	1 102	1	0	0	0	0	0.0000
1970	3.40	4	1 110	1	0	0	0	0	0.0000
1980	4.20	4	1 111	1	0	0	0	0	0.0000
1990	0.90	4	1 113	1	0	0	0	0	0.0000
2000	1.20	5	1 101	1	0	0	0	0	0.0000
2010	0.70	5	1 102	1	0	0	0	0	0.0000
2020	3.80	5	1 110	1	0	0	0	0	0.0000
2030	4.20	5	1 111	1	0	0	0	0	0.0000
2040	0.60	5	1 113	1	0	0	0	0	0.0000
2050	2.40	5	1 127	1	0	0	0	0	0.0000
2060	2.60	5	1 128	1	0	0	0	0	0.0000
2070	4.20	6	1 102	1	0	0	0	0	0.0000
2080	5.60	6	1 102	2	0	0	0	0	0.0000
2090	1.40	6	1 103	1	0	0	0	0	0.0000
2100	2.10	6	1 103	2	0	0	0	0	0.0000
2110	1.30	6	1 103	3	0	0	0	0	0.0000
2120	6.00	6	1 104	1	0	0	0	0	0.0000
2130	10.60	6	1 104	2	0	0	0	0	0.0000
2140	12.90	6	1 104	3	0	0	0	0	0.0000
2150	0.70	6	1 105	1	0	0	0	0	0.0000
2160	2.10	6	1 106	1	0	0	0	0	0.0000
2170	20.70	6	1 50	1 109	1	0	0	0	0.0000
2180	26.00	6	1 50	2 110	1	0	0	0	0.0000
2190	23.50	6	1 50	1 112	1	0	0	0	0.0000
2200	3.90	6	1 113	1	0	0	0	0	0.0000
2210	43.60	6	1 114	6	0	0	0	0	0.0000
2220	4.20	6	1 115	1	0	0	0	0	0.0000
2230	7.50	6	1 115	2	0	0	0	0	0.0000
2240	10.50	6	1 115	3	0	0	0	0	0.0000
2250	10.10	6	1 116	1	0	0	0	0	0.0000
2260	19.30	6	1 116	2	0	0	0	0	0.0000
2270	26.90	6	1 116	3	0	0	0	0	0.0000
2280	27.80	6	1 117	1	0	0	0	0	0.0000
2290	29.50	6	1 50	1 117	1	0	0	0	0.0000
2300	30.40	6	1 50	2 117	1	0	0	0	0.0000
2310	8.90	6	1 118	1	0	0	0	0	0.0000
2320	15.70	6	1 118	2	0	0	0	0	0.0000
2330	20.40	6	1 118	3	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>							<u>Comment</u>	
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								
2340	18.20	6	1	119	1	0	0	0	0	0.0000
2350	30.70	6	1	119	2	0	0	0	0	0.0000
2360	17.10	6	1	123	1	0	0	0	0	0.0000
2370	27.90	6	1	123	2	0	0	0	0	0.0000
2380	32.00	6	1	123	3	0	0	0	0	0.0000
2390	10.90	6	1	124	1	0	0	0	0	0.0000
2400	18.60	6	1	127	1	0	0	0	0	0.0000
2410	27.10	6	1	127	2	0	0	0	0	0.0000
2420	14.60	6	1	50	-1	127	1	0	0	0.0000
2430	6.30	6	1	50	-2	127	1	0	0	0.0000
2440	27.80	6	1	128	1	0	0	0	0	0.0000
2450	29.40	6	1	50	1	128	1	0	0	0.0000
2460	20.90	6	1	50	-1	128	1	0	0	0.0000
2470	10.10	6	1	50	-2	128	1	0	0	0.0000
2480	33.00	6	1	129	1	0	0	0	0	0.0000
2490	23.40	6	1	50	-1	129	1	0	0	0.0000
2500	33.60	6	1	130	2	0	0	0	0	0.0000
2510	35.30	6	1	131	1	0	0	0	0	0.0000
2520	9.50	6	1	133	1	0	0	0	0	0.0000
2530	9.50	6	1	134	1	0	0	0	0	0.0000
2540	5.50	6	1	136	1	0	0	0	0	0.0000
2550	12.20	6	1	137	1	0	0	0	0	0.0000
2560	10.00	6	1	138	1	0	0	0	0	0.0000
2570	11.20	6	1	139	1	0	0	0	0	0.0000
2580	10.40	6	1	142	1	0	0	0	0	0.0000
2590	9.40	6	1	143	1	0	0	0	0	0.0000
2600	9.70	6	1	144	1	0	0	0	0	0.0000
2610	10.70	6	1	145	1	0	0	0	0	0.0000
2620	10.70	6	1	146	1	0	0	0	0	0.0000
2630	10.90	6	1	147	1	0	0	0	0	0.0000
2640	8.90	6	1	148	1	0	0	0	0	0.0000
2650	15.80	6	1	148	2	0	0	0	0	0.0000
2660	3.10	6	1	150	1	0	0	0	0	0.0000
2670	-1.70	6	1	50	-1	0	0	0	0	0.0000
2680	-4.70	6	1	50	-2	0	0	0	0	0.0000
2690	-20.10	6	1	50	-3	0	0	0	0	0.0000
2700	-21.50	6	1	50	-4	0	0	0	0	0.0000
2710	-2.30	6	2	50	-2	0	0	0	0	0.0000
2720	2.30	7	1	102	1	0	0	0	0	0.0000
2730	0.90	7	1	103	1	0	0	0	0	0.0000
2740	1.30	7	1	107	1	0	0	0	0	0.0000
2750	2.10	7	1	107	2	0	0	0	0	0.0000
2760	3.60	7	1	107	4	0	0	0	0	0.0000
2770	35.40	7	1	114	6	0	0	0	0	0.0000
2780	3.70	7	1	115	1	0	0	0	0	0.0000
2790	5.20	7	1	116	1	0	0	0	0	0.0000
2800	8.90	7	1	116	2	0	0	0	0	0.0000

Species		Four Pairs of Component ID and							
ID	Log K	Stoichiometric Coefficient							Comment
2810	17.40	7	1	117	1	0	0	0	0.0000
2820	20.60	7	1	50	1	117	1	0	0.0000
2830	24.70	7	1	50	2	117	1	0	0.0000
2840	7.70	7	1	119	1	0	0	0	0.0000
2850	12.40	7	1	119	2	0	0	0	0.0000
2860	4.20	7	1	121	1	0	0	0	0.0000
2870	7.50	7	1	121	2	0	0	0	0.0000
2880	9.50	7	1	121	3	0	0	0	0.0000
2890	4.30	7	1	122	1	0	0	0	0.0000
2900	8.00	7	1	122	2	0	0	0	0.0000
2910	17.50	7	1	122	3	0	0	0	0.0000
2920	7.70	7	1	123	1	0	0	0	0.0000
2930	10.90	7	1	123	2	0	0	0	0.0000
2940	4.30	7	1	124	1	0	0	0	0.0000
2950	4.70	7	1	125	1	0	0	0	0.0000
2960	5.40	7	1	126	1	0	0	0	0.0000
2970	9.90	7	1	126	2	0	0	0	0.0000
2980	13.10	7	1	126	3	0	0	0	0.0000
2990	10.60	7	1	127	1	0	0	0	0.0000
3000	-0.10	7	1	50	-1	127	1	0	0.0000
3010	16.70	7	1	128	1	0	0	0	0.0000
3020	20.10	7	1	50	1	128	1	0	0.0000
3030	20.60	7	1	129	1	0	0	0	0.0000
3040	12.20	7	1	130	1	0	0	0	0.0000
3050	3.80	7	1	133	1	0	0	0	0.0000
3060	3.60	7	1	134	1	0	0	0	0.0000
3070	5.10	7	1	135	1	0	0	0	0.0000
3080	6.30	7	1	136	1	0	0	0	0.0000
3090	10.90	7	1	136	2	0	0	0	0.0000
3100	4.80	7	1	137	1	0	0	0	0.0000
3110	9.40	7	1	137	2	0	0	0	0.0000
3120	7.90	7	1	138	2	0	0	0	0.0000
3130	3.90	7	1	138	1	0	0	0	0.0000
3140	4.10	7	1	139	1	0	0	0	0.0000
3150	8.10	7	1	139	2	0	0	0	0.0000
3160	8.20	7	1	140	2	0	0	0	0.0000
3170	3.70	7	1	141	1	0	0	0	0.0000
3180	7.50	7	1	141	2	0	0	0	0.0000
3190	3.90	7	1	142	1	0	0	0	0.0000
3200	7.60	7	1	142	2	0	0	0	0.0000
3210	3.80	7	1	143	1	0	0	0	0.0000
3220	3.80	7	1	144	1	0	0	0	0.0000
3230	7.10	7	1	144	2	0	0	0	0.0000
3240	3.90	7	1	145	1	0	0	0	0.0000
3250	3.90	7	1	146	1	0	0	0	0.0000
3260	4.60	7	1	147	1	0	0	0	0.0000
3270	9.10	7	1	147	2	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>								
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								<u>Comment</u>
3280	-8.60	7	1	50	-1	0	0	0	0	0.0000
3290	12.10	8	1	50	1	101	1	0	0	0.0000
3300	2.30	8	1	102	1	0	0	0	0	0.0000
3310	1.10	8	1	103	1	0	0	0	0	0.0000
3320	1.10	8	1	103	2	0	0	0	0	0.0000
3330	0.60	8	1	103	3	0	0	0	0	0.0000
3340	0.70	8	1	107	1	0	0	0	0	0.0000
3350	1.20	8	1	107	2	0	0	0	0	0.0000
3360	16.20	8	1	50	1	109	1	0	0	0.0000
3370	6.00	8	1	110	1	0	0	0	0	0.0000
3380	1.90	8	1	113	1	0	0	0	0	0.0000
3390	1.10	8	1	115	1	0	0	0	0	0.0000
3400	2.20	8	1	115	2	0	0	0	0	0.0000
3410	4.30	8	1	116	1	0	0	0	0	0.0000
3420	7.40	8	1	116	2	0	0	0	0	0.0000
3430	21.40	8	1	50	1	117	1	0	0	0.0000
3440	26.00	8	1	50	2	117	1	0	0	0.0000
3450	3.20	8	1	118	1	0	0	0	0	0.0000
3460	4.90	8	1	118	2	0	0	0	0	0.0000
3470	7.00	8	1	119	1	0	0	0	0	0.0000
3480	10.90	8	1	119	2	0	0	0	0	0.0000
3490	2.60	8	1	121	1	0	0	0	0	0.0000
3500	4.70	8	1	121	2	0	0	0	0	0.0000
3510	5.60	8	1	121	3	0	0	0	0	0.0000
3520	2.50	8	1	122	1	0	0	0	0	0.0000
3530	4.50	8	1	122	2	0	0	0	0	0.0000
3540	6.20	8	1	122	3	0	0	0	0	0.0000
3550	7.00	8	1	123	1	0	0	0	0	0.0000
3560	9.00	8	1	123	2	0	0	0	0	0.0000
3570	3.70	8	1	124	1	0	0	0	0	0.0000
3580	6.40	8	1	124	2	0	0	0	0	0.0000
3590	4.30	8	1	125	1	0	0	0	0	0.0000
3600	4.10	8	1	126	1	0	0	0	0	0.0000
3610	7.10	8	1	126	2	0	0	0	0	0.0000
3620	8.90	8	1	126	3	0	0	0	0	0.0000
3630	9.20	8	1	127	1	0	0	0	0	0.0000
3640	15.80	8	1	128	1	0	0	0	0	0.0000
3650	19.30	8	1	50	1	128	1	0	0	0.0000
3660	19.20	8	1	129	1	0	0	0	0	0.0000
3670	22.60	8	1	50	1	129	1	0	0	0.0000
3680	4.70	8	1	130	1	0	0	0	0	0.0000
3690	13.70	8	1	131	1	0	0	0	0	0.0000
3700	20.30	8	1	50	1	131	1	0	0	0.0000
3710	2.60	8	1	133	1	0	0	0	0	0.0000
3720	4.70	8	1	133	2	0	0	0	0	0.0000
3730	2.70	8	1	135	1	0	0	0	0	0.0000
3740	4.10	8	1	136	1	0	0	0	0	0.0000

Species	Four Pairs of Component ID and								Comment
ID	Log K	Stoichiometric Coefficient							
3750	8.50	8	1 136	2	0	0	0	0	0.0000
3760	4.60	8	1 137	1	0	0	0	0	0.0000
3770	3.70	8	1 139	1	0	0	0	0	0.0000
3780	6.90	8	1 139	2	0	0	0	0	0.0000
3790	3.50	8	1 140	1	0	0	0	0	0.0000
3800	3.30	8	1 142	1	0	0	0	0	0.0000
3810	6.40	8	1 142	2	0	0	0	0	0.0000
3820	3.30	8	1 145	1	0	0	0	0	0.0000
3830	6.20	8	1 145	2	0	0	0	0	0.0000
3840	3.30	8	1 146	1	0	0	0	0	0.0000
3850	6.20	8	1 146	2	0	0	0	0	0.0000
3860	3.80	8	1 147	1	0	0	0	0	0.0000
3870	6.40	8	1 147	2	0	0	0	0	0.0000
3880	1.40	8	1 150	1	0	0	0	0	0.0000
3890	0.50	8	1 151	1	0	0	0	0	0.0000
3900	-10.10	8	1 50	-1	0	0	0	0	0.0000
3910	-34.20	8	1 50	-3	0	0	0	0	0.0000
3920	6.80	9	1 101	1	0	0	0	0	0.0000
3930	10.00	9	1 101	2	0	0	0	0	0.0000
3940	2.30	9	1 102	1	0	0	0	0	0.0000
3950	0.60	9	1 103	1	0	0	0	0	0.0000
3960	0.40	9	1 103	2	0	0	0	0	0.0000
3970	1.30	9	1 104	1	0	0	0	0	0.0000
3980	1.10	9	1 105	1	0	0	0	0	0.0000
3990	5.80	9	1 107	1	0	0	0	0	0.0000
4000	10.70	9	1 107	2	0	0	0	0	0.0000
4010	16.60	9	1 50	1 109	1	0	0	0	0.0000
4020	9.10	9	1 110	1	0	0	0	0	0.0000
4030	9.10	9	1 110	2	0	0	0	0	0.0000
4040	16.50	9	1 50	1 111	1	0	0	0	0.0000
4050	10.30	9	1 111	1	0	0	0	0	0.0000
4060	2.20	9	1 115	1	0	0	0	0	0.0000
4070	3.50	9	1 115	2	0	0	0	0	0.0000
4080	3.90	9	1 115	3	0	0	0	0	0.0000
4090	3.40	9	1 115	4	0	0	0	0	0.0000
4100	8.30	9	1 116	1	0	0	0	0	0.0000
4110	15.10	9	1 116	2	0	0	0	0	0.0000
4120	19.90	9	1 117	1	0	0	0	0	0.0000
4130	24.10	9	1 50	1 117	1	0	0	0	0.0000
4140	29.60	9	1 50	3 117	1	0	0	0	0.0000
4150	6.40	9	1 50	1 118	1	0	0	0	0.0000
4160	5.10	9	1 118	1	0	0	0	0	0.0000
4170	9.70	9	1 118	2	0	0	0	0	0.0000
4180	10.30	9	1 119	1	0	0	0	0	0.0000
4190	19.00	9	1 119	2	0	0	0	0	0.0000
4191	1.90	9	1 119	1 50	1	0	0	0	0.0000
4200	4.30	9	1 120	1	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>								
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								<u>Comment</u>
4210	6.20	9	1	120	2	0	0	0	0	0.0000
4220	4.60	9	1	120	3	0	0	0	0	0.0000
4230	3.90	9	1	120	4	0	0	0	0	0.0000
4240	10.50	9	1	121	1	0	0	0	0	0.0000
4250	19.50	9	1	121	2	0	0	0	0	0.0000
4260	8.00	9	1	122	1	0	0	0	0	0.0000
4270	13.50	9	1	122	2	0	0	0	0	0.0000
4280	17.00	9	1	122	3	0	0	0	0	0.0000
4290	11.40	9	1	123	1	0	0	0	0	0.0000
4300	17.40	9	1	123	2	0	0	0	0	0.0000
4310	8.70	9	1	124	1	0	0	0	0	0.0000
4320	16.00	9	1	124	2	0	0	0	0	0.0000
4330	7.85	9	1	125	1	0	0	0	0	0.0000
4340	14.40	9	1	125	2	0	0	0	0	0.0000
4350	7.60	9	1	126	1	0	0	0	0	0.0000
4360	14.20	9	1	126	2	0	0	0	0	0.0000
4370	14.50	9	1	127	1	0	0	0	0	0.0000
4380	17.10	9	1	127	2	0	0	0	0	0.0000
4390	4.90	9	1	50	-1	127	1	0	0	0.0000
4400	20.60	9	1	128	1	0	0	0	0	0.0000
4410	24.00	9	1	50	1	128	1	0	0	0.0000
4420	8.70	9	1	50	-1	128	1	0	0	0.0000
4430	23.70	9	1	129	1	0	0	0	0	0.0000
4440	27.40	9	1	50	1	129	1	0	0	0.0000
4450	15.50	9	1	131	1	0	0	0	0	0.0000
4460	24.60	9	1	50	1	131	1	0	0	0.0000
4470	4.20	9	1	132	1	0	0	0	0	0.0000
4480	5.50	9	1	132	2	0	0	0	0	0.0000
4490	8.10	9	1	133	1	0	0	0	0	0.0000
4500	14.90	9	1	133	2	0	0	0	0	0.0000
4510	7.40	9	1	134	1	0	0	0	0	0.0000
4520	13.20	9	1	134	2	0	0	0	0	0.0000
4530	14.40	9	1	135	2	0	0	0	0	0.0000
4540	10.60	9	1	136	1	0	0	0	0	0.0000
4550	18.60	9	1	136	2	0	0	0	0	0.0000
4560	8.90	9	1	137	1	0	0	0	0	0.0000
4570	16.00	9	1	137	2	0	0	0	0	0.0000
4580	15.40	9	1	138	2	0	0	0	0	0.0000
4590	8.70	9	1	139	1	0	0	0	0	0.0000
4600	15.90	9	1	139	2	0	0	0	0	0.0000
4610	16.20	9	1	140	2	0	0	0	0	0.0000
4620	15.50	9	1	141	2	0	0	0	0	0.0000
4630	8.40	9	1	142	1	0	0	0	0	0.0000
4640	15.20	9	1	142	2	0	0	0	0	0.0000
4650	15.40	9	1	143	2	0	0	0	0	0.0000
4660	8.20	9	1	144	1	0	0	0	0	0.0000
4670	15.40	9	1	144	2	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>							<u>Comment</u>	
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								
4680	8.60	9	1	145	1	0	0	0	0	0.0000
4690	16.60	9	1	145	2	0	0	0	0	0.0000
4700	8.60	9	1	146	1	0	0	0	0	0.0000
4710	16.60	9	1	146	2	0	0	0	0	0.0000
4720	17.60	9	1	147	2	0	0	0	0	0.0000
4730	7.10	9	1	148	1	0	0	0	0	0.0000
4740	12.40	9	1	148	2	0	0	0	0	0.0000
4750	2.40	9	1	150	1	0	0	0	0	0.0000
4760	2.40	9	1	151	1	0	0	0	0	0.0000
4770	4.10	9	1	151	2	0	0	0	0	0.0000
4780	4.00	9	1	158	1	0	0	0	0	0.0000
4790	7.60	9	1	158	2	0	0	0	0	0.0000
4800	11.10	9	1	158	3	0	0	0	0	0.0000
4810	14.10	9	1	158	4	0	0	0	0	0.0000
4820	1.30	9	1	50	-1	158	2	0	0	0.0000
4830	-6.60	9	1	50	2	158	2	0	0	0.0000
4831	12.80	9	1	162	1	0	0	0	0	0.0000
4832	22.60	9	1	162	2	0	0	0	0	0.0000
4833	7.60	9	1	163	1	0	0	0	0	0.0000
4844	14.20	9	1	163	2	0	0	0	0	0.0000
4840	-8.00	9	1	50	-1	0	0	0	0	0.0000
4841	-13.70	9	1	50	-2	0	0	0	0	0.0000
4850	-10.30	9	2	50	-2	0	0	0	0	0.0000
4842	-26.30	9	1	50	-3	0	0	0	0	0.0000
4843	-39.40	9	1	50	-4	0	0	0	0	0.0000
4860	7.00	10	1	110	1	0	0	0	0	0.0000
4870	9.30	10	1	111	1	0	0	0	0	0.0000
4880	2.30	10	1	113	1	0	0	0	0	0.0000
4890	0.90	10	1	115	1	0	0	0	0	0.0000
4900	4.40	10	1	50	1	117	1	0	0	0.0000
4910	1.70	10	1	118	1	0	0	0	0	0.0000
4920	1.40	10	1	119	1	0	0	0	0	0.0000
4930	5.60	10	1	50	1	120	1	0	0	0.0000
4940	2.70	10	1	120	1	0	0	0	0	0.0000
4950	1.30	10	1	124	1	0	0	0	0	0.0000
4960	2.40	10	1	125	1	0	0	0	0	0.0000
4970	2.20	10	1	126	1	0	0	0	0	0.0000
4980	6.50	10	1	127	1	0	0	0	0	0.0000
4990	10.20	10	1	128	1	0	0	0	0	0.0000
5000	15.40	10	1	50	1	128	1	0	0	0.0000
5010	10.50	10	1	129	1	0	0	0	0	0.0000
5020	17.70	10	1	50	1	129	1	0	0	0.0000
5030	2.70	10	1	132	1	0	0	0	0	0.0000
5040	1.60	10	1	137	1	0	0	0	0	0.0000
5050	1.30	10	1	139	1	0	0	0	0	0.0000
5060	-12.80	10	1	50	-1	0	0	0	0	0.0000
5070	3.20	11	1	101	1	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>							<u>Comment</u>	
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								
5080	2.30	11	1	102	1	0	0	0	0	0.0000
5081	3.50	11	1	102	2	0	0	0	0	0.0000
5090	2.00	11	1	103	1	0	0	0	0	0.0000
5100	2.70	11	1	103	2	0	0	0	0	0.0000
5110	2.70	11	1	103	3	0	0	0	0	0.0000
5120	1.10	11	1	104	1	0	0	0	0	0.0000
5130	2.10	11	1	105	1	0	0	0	0	0.0000
5140	2.90	11	1	105	2	0	0	0	0	0.0000
5150	3.00	11	1	105	3	0	0	0	0	0.0000
5160	3.10	11	1	105	4	0	0	0	0	0.0000
5170	2.90	11	1	106	1	0	0	0	0	0.0000
5180	4.20	11	1	106	2	0	0	0	0	0.0000
5190	5.90	11	1	106	3	0	0	0	0	0.0000
5200	6.60	11	1	106	4	0	0	0	0	0.0000
5210	2.50	11	1	107	1	0	0	0	0	0.0000
5220	4.50	11	1	107	2	0	0	0	0	0.0000
5230	6.00	11	1	107	3	0	0	0	0	0.0000
5240	6.80	11	1	107	4	0	0	0	0	0.0000
5250	6.50	11	1	107	5	0	0	0	0	0.0000
5260	4.80	11	1	107	6	0	0	0	0	0.0000
5270	3.90	11	1	109	1	0	0	0	0	0.0000
5280	9.60	11	1	110	1	0	0	0	0	0.0000
5290	11.20	11	1	111	1	0	0	0	0	0.0000
5300	-0.80	11	1	50	-1	111	1	0	0	0.0000
5310	3.90	11	1	113	1	0	0	0	0	0.0000
5311	6.20	11	1	113	2	0	0	0	0	0.0000
5320	6.10	11	1	114	1	0	0	0	0	0.0000
5330	11.40	11	1	114	2	0	0	0	0	0.0000
5340	16.10	11	1	114	3	0	0	0	0	0.0000
5350	19.40	11	1	114	4	0	0	0	0	0.0000
5360	1.60	11	1	115	1	0	0	0	0	0.0000
5370	2.70	11	1	115	2	0	0	0	0	0.0000
5380	2.60	11	1	115	3	0	0	0	0	0.0000
5390	1.80	11	1	115	4	0	0	0	0	0.0000
5400	3.90	11	1	116	1	0	0	0	0	0.0000
5410	6.90	11	1	116	2	0	0	0	0	0.0000
5420	13.10	11	1	117	1	0	0	0	0	0.0000
5430	22.60	11	1	50	1	117	1	0	0	0.0000
5440	26.60	11	1	50	2	117	1	0	0	0.0000
5450	3.40	11	1	118	1	0	0	0	0	0.0000
5460	5.50	11	1	118	2	0	0	0	0	0.0000
5470	6.70	11	1	119	1	0	0	0	0	0.0000
5480	3.90	11	1	120	1	0	0	0	0	0.0000
5490	5.50	11	1	121	1	0	0	0	0	0.0000
5500	10.00	11	1	121	2	0	0	0	0	0.0000
5510	12.00	11	1	121	3	0	0	0	0	0.0000
5520	4.50	11	1	122	1	0	0	0	0	0.0000

<u>Species</u> <u>ID</u>	<u>Log K</u>	<u>Four Pairs of Component ID and</u> <u>Stoichiometric Coefficient</u>							<u>Comment</u>
5530	8.00	11	1 122	2	0	0	0	0	0.0000
5540	10.50	11	1 122	3	0	0	0	0	0.0000
5550	6.50	11	1 123	1	0	0	0	0	0.0000
5560	4.40	11	1 124	1	0	0	0	0	0.0000
5570	7.90	11	1 124	2	0	0	0	0	0.0000
5580	5.80	11	1 125	1	0	0	0	0	0.0000
5590	8.50	11	1 125	2	0	0	0	0	0.0000
5600	5.10	11	1 126	1	0	0	0	0	0.0000
5610	9.00	11	1 126	2	0	0	0	0	0.0000
5620	11.60	11	1 126	3	0	0	0	0	0.0000
5630	11.90	11	1 127	1	0	0	0	0	0.0000
5640	15.40	11	1 127	2	0	0	0	0	0.0000
5650	19.00	11	1 128	1	0	0	0	0	0.0000
5660	22.40	11	1 50	1 128	1	0	0	0	0.0000
5670	21.60	11	1 129	1	0	0	0	0	0.0000
5680	25.20	11	1 50	1 129	1	0	0	0	0.0000
5690	10.60	11	1 131	1	0	0	0	0	0.0000
5700	18.10	11	1 50	1 131	1	0	0	0	0.0000
5710	3.70	11	1 132	1	0	0	0	0	0.0000
5720	3.80	11	1 133	1	0	0	0	0	0.0000
5730	7.40	11	1 133	2	0	0	0	0	0.0000
5740	4.20	11	1 134	1	0	0	0	0	0.0000
5750	7.20	11	1 134	2	0	0	0	0	0.0000
5760	6.10	11	1 136	1	0	0	0	0	0.0000
5770	10.60	11	1 136	2	0	0	0	0	0.0000
5780	4.90	11	1 137	1	0	0	0	0	0.0000
5790	8.40	11	1 137	2	0	0	0	0	0.0000
5800	6.60	11	1 139	1	0	0	0	0	0.0000
5810	8.60	11	1 139	2	0	0	0	0	0.0000
5820	10.00	11	1 139	3	0	0	0	0	0.0000
5830	4.40	11	1 141	1	0	0	0	0	0.0000
5840	7.90	11	1 141	2	0	0	0	0	0.0000
5850	5.20	11	1 142	1	0	0	0	0	0.0000
5860	9.20	11	1 142	2	0	0	0	0	0.0000
5870	4.60	11	1 145	1	0	0	0	0	0.0000
5880	8.20	11	1 145	2	0	0	0	0	0.0000
5890	4.60	11	1 146	1	0	0	0	0	0.0000
5900	8.20	11	1 146	2	0	0	0	0	0.0000
5910	9.50	11	1 147	2	0	0	0	0	0.0000
5920	5.40	11	1 149	2	0	0	0	0	0.0000
5930	-9.00	11	1 50	-1	0	0	0	0	0.0000
5940	-19.10	11	1 50	-2	0	0	0	0	0.0000
5950	-30.40	11	1 50	-3	0	0	0	0	0.0000
5960	2.30	12	1 102	1	0	0	0	0	0.0000
5970	-0.50	12	1 103	1	0	0	0	0	0.0000
5980	-1.00	12	1 103	2	0	0	0	0	0.0000
5990	0.00	12	1 103	3	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>							<u>Comment</u>
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>							
6000	1.30	12	1	104	1	0	0	0	0.0000
6010	0.10	12	1	105	1	0	0	0	0.0000
6020	2.20	12	1	107	1	0	0	0	0.0000
6030	4.50	12	1	107	2	0	0	0	0.0000
6040	7.00	12	1	107	3	0	0	0	0.0000
6050	9.00	12	1	107	4	0	0	0	0.0000
6060	15.70	12	1	50	1	109	1	0	0.0000
6070	11.10	12	1	110	1	0	0	0	0.0000
6080	11.00	12	1	110	2	0	0	0	0.0000
6090	1.00	12	1	50	-1	110	1	0	0.0000
6100	16.10	12	1	50	1	111	1	0	0.0000
6110	9.90	12	1	111	1	0	0	0	0.0000
6120	2.30	12	1	113	1	0	0	0	0.0000
6130	17.20	12	1	114	4	0	0	0	0.0000
6140	1.80	12	1	115	1	0	0	0	0.0000
6150	2.90	12	1	115	2	0	0	0	0.0000
6160	5.10	12	1	116	1	0	0	0	0.0000
6170	9.10	12	1	116	2	0	0	0	0.0000
6180	13.20	12	1	117	1	0	0	0	0.0000
6190	4.20	12	1	118	1	0	0	0	0.0000
6200	6.90	12	1	118	2	0	0	0	0.0000
6210	5.70	12	1	50	1	118	1	0	0.0000
6220	11.10	12	1	50	2	118	2	0	0.0000
6230	8.00	12	1	119	1	0	0	0	0.0000
6240	5.60	12	1	50	1	120	1	0	0.0000
6250	3.50	12	1	120	1	0	0	0	0.0000
6260	5.60	12	1	121	1	0	0	0	0.0000
6270	10.30	12	1	121	2	0	0	0	0.0000
6280	12.00	12	1	121	3	0	0	0	0.0000
6290	5.30	12	1	122	1	0	0	0	0.0000
6300	9.70	12	1	122	2	0	0	0	0.0000
6310	13.50	12	1	122	3	0	0	0	0.0000
6320	7.90	12	1	123	1	0	0	0	0.0000
6330	11.40	12	1	123	2	0	0	0	0.0000
6340	5.30	12	1	124	1	0	0	0	0.0000
6350	9.70	12	1	124	2	0	0	0	0.0000
6360	6.50	12	1	125	1	0	0	0	0.0000
6370	10.70	12	1	125	2	0	0	0	0.0000
6380	5.80	12	1	126	1	0	0	0	0.0000
6390	10.40	12	1	126	2	0	0	0	0.0000
6400	13.70	12	1	126	3	0	0	0	0.0000
6410	12.40	12	1	127	1	0	0	0	0.0000
6420	14.20	12	1	127	2	0	0	0	0.0000
6430	18.30	12	1	128	1	0	0	0	0.0000
6440	21.70	12	1	50	1	128	1	0	0.0000
6450	21.10	12	1	129	1	0	0	0	0.0000
6460	24.70	12	1	50	1	129	1	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>							<u>Comment</u>	
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								
6470	11.00	12	1	130	1	0	0	0	0	0.0000
6480	19.80	12	1	130	2	0	0	0	0	0.0000
6490	14.00	12	1	131	1	0	0	0	0	0.0000
6500	20.40	12	1	50	1	131	1	0	0	0.0000
6510	3.30	12	1	132	1	0	0	0	0	0.0000
6520	4.70	12	1	133	1	0	0	0	0	0.0000
6530	9.00	12	1	133	2	0	0	0	0	0.0000
6540	4.60	12	1	134	1	0	0	0	0	0.0000
6550	8.10	12	1	134	2	0	0	0	0	0.0000
6560	8.40	12	1	135	2	0	0	0	0	0.0000
6570	7.30	12	1	136	1	0	0	0	0	0.0000
6580	13.00	12	1	136	2	0	0	0	0	0.0000
6590	6.30	12	1	137	1	0	0	0	0	0.0000
6600	11.20	12	1	137	2	0	0	0	0	0.0000
6610	5.70	12	1	139	1	0	0	0	0	0.0000
6620	10.40	12	1	139	2	0	0	0	0	0.0000
6630	10.20	12	1	140	2	0	0	0	0	0.0000
6640	4.90	12	1	141	1	0	0	0	0	0.0000
6650	9.40	12	1	141	2	0	0	0	0	0.0000
6660	5.10	12	1	142	1	0	0	0	0	0.0000
6670	9.90	12	1	142	2	0	0	0	0	0.0000
6680	4.60	12	1	145	1	0	0	0	0	0.0000
6690	8.20	12	1	145	2	0	0	0	0	0.0000
6700	4.60	12	1	146	1	0	0	0	0	0.0000
6710	8.20	12	1	146	2	0	0	0	0	0.0000
6720	11.00	12	1	147	2	0	0	0	0	0.0000
6730	0.50	12	1	151	1	0	0	0	0	0.0000
6740	-9.10	12	1	50	-1	0	0	0	0	0.0000
6741	-16.50	12	1	50	-2	0	0	0	0	0.0000
6750	-28.00	12	1	50	-3	0	0	0	0	0.0000
6760	-40.70	12	1	50	-4	0	0	0	0	0.0000
6770	2.30	13	1	102	1	0	0	0	0	0.0000
6780	0.50	13	1	103	1	0	0	0	0	0.0000
6790	1.10	13	1	104	1	0	0	0	0	0.0000
6800	0.60	13	1	105	1	0	0	0	0	0.0000
6810	2.70	13	1	107	1	0	0	0	0	0.0000
6820	4.80	13	1	107	2	0	0	0	0	0.0000
6830	6.50	13	1	107	3	0	0	0	0	0.0000
6840	7.70	13	1	107	4	0	0	0	0	0.0000
6850	8.50	13	1	107	5	0	0	0	0	0.0000
6860	8.50	13	1	107	6	0	0	0	0	0.0000
6870	8.20	13	1	110	1	0	0	0	0	0.0000
6880	7.10	13	1	110	2	0	0	0	0	0.0000
6890	2.20	13	1	113	1	0	0	0	0	0.0000
6900	31.80	13	1	114	4	0	0	0	0	0.0000
6910	1.20	13	1	115	1	0	0	0	0	0.0000
6920	2.10	13	1	115	2	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>							<u>Comment</u>	
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6930	6.10	13	1	116	1	0	0	0	0	0.0000
6940	10.60	13	1	116	2	0	0	0	0	0.0000
6950	12.70	13	1	116	3	0	0	0	0	0.0000
6960	16.10	13	1	117	1	0	0	0	0	0.0000
6970	22.80	13	1	50	1	117	1	0	0	0.0000
6980	27.00	13	1	50	2	117	1	0	0	0.0000
6990	4.60	13	1	118	1	0	0	0	0	0.0000
7000	8.00	13	1	118	2	0	0	0	0	0.0000
7010	9.40	13	1	118	3	0	0	0	0	0.0000
7020	8.20	13	1	119	1	0	0	0	0	0.0000
7030	12.90	13	1	119	2	0	0	0	0	0.0000
7040	7.60	13	1	121	1	0	0	0	0	0.0000
7050	14.00	13	1	121	2	0	0	0	0	0.0000
7060	18.50	13	1	121	3	0	0	0	0	0.0000
7070	7.00	13	1	122	1	0	0	0	0	0.0000
7080	13.80	13	1	122	2	0	0	0	0	0.0000
7090	20.00	13	1	122	3	0	0	0	0	0.0000
7100	8.20	13	1	123	1	0	0	0	0	0.0000
7110	11.00	13	1	123	2	0	0	0	0	0.0000
7120	6.30	13	1	124	1	0	0	0	0	0.0000
7130	11.40	13	1	124	2	0	0	0	0	0.0000
7140	7.00	13	1	125	1	0	0	0	0	0.0000
7150	11.40	13	1	125	2	0	0	0	0	0.0000
7160	7.30	13	1	126	1	0	0	0	0	0.0000
7170	13.40	13	1	126	2	0	0	0	0	0.0000
7180	18.00	13	1	126	3	0	0	0	0	0.0000
7190	13.10	13	1	127	1	0	0	0	0	0.0000
7200	21.00	13	1	128	1	0	0	0	0	0.0000
7210	24.80	13	1	50	1	128	1	0	0	0.0000
7220	21.80	13	1	129	1	0	0	0	0	0.0000
7230	19.90	13	1	130	2	0	0	0	0	0.0000
7240	14.00	13	1	131	1	0	0	0	0	0.0000
7250	20.60	13	1	50	1	131	1	0	0	0.0000
7260	3.20	13	1	132	1	0	0	0	0	0.0000
7270	5.60	13	1	133	1	0	0	0	0	0.0000
7280	10.10	13	1	133	2	0	0	0	0	0.0000
7290	13.40	13	1	133	3	0	0	0	0	0.0000
7300	5.30	13	1	134	1	0	0	0	0	0.0000
7310	9.50	13	1	134	2	0	0	0	0	0.0000
7320	9.60	13	1	135	2	0	0	0	0	0.0000
7330	9.30	13	1	136	1	0	0	0	0	0.0000
7340	16.60	13	1	136	2	0	0	0	0	0.0000
7350	7.60	13	1	137	1	0	0	0	0	0.0000
7360	13.50	13	1	137	2	0	0	0	0	0.0000
7370	6.10	13	1	138	1	0	0	0	0	0.0000
7380	10.90	13	1	138	2	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>								
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								<u>Comment</u>
7390	14.00	13	1	138	3	0	0	0	0	0.0000
7400	6.60	13	1	139	1	0	0	0	0	0.0000
7410	11.50	13	1	139	2	0	0	0	0	0.0000
7420	11.20	13	1	140	2	0	0	0	0	0.0000
7430	6.20	13	1	141	1	0	0	0	0	0.0000
7440	11.40	13	1	141	2	0	0	0	0	0.0000
7450	14.00	13	1	141	3	0	0	0	0	0.0000
7460	5.90	13	1	142	1	0	0	0	0	0.0000
7470	10.50	13	1	142	2	0	0	0	0	0.0000
7480	13.00	13	1	142	3	0	0	0	0	0.0000
7490	6.10	13	1	145	1	0	0	0	0	0.0000
7500	10.90	13	1	145	2	0	0	0	0	0.0000
7510	6.10	13	1	146	1	0	0	0	0	0.0000
7520	10.90	13	1	146	2	0	0	0	0	0.0000
7530	12.10	13	1	147	2	0	0	0	0	0.0000
7540	1.70	13	1	150	1	0	0	0	0	0.0000
7550	1.50	13	1	151	1	0	0	0	0	0.0000
7560	9.70	13	1	151	2	0	0	0	0	0.0000
7570	2.60	13	1	158	1	0	0	0	0	0.0000
7580	4.50	13	1	158	2	0	0	0	0	0.0000
7590	-8.70	13	1	50	-1	0	0	0	0	0.0000
7600	2.40	14	1	102	1	0	0	0	0	0.0000
7610	3.50	14	1	102	2	0	0	0	0	0.0000
7620	6.70	14	1	103	1	0	0	0	0	0.0000
7630	13.20	14	1	103	2	0	0	0	0	0.0000
7640	14.20	14	1	103	3	0	0	0	0	0.0000
7650	15.20	14	1	103	4	0	0	0	0	0.0000
7651	3.60	14	1	50	-1	103	1	0	0	0.0000
7660	1.60	14	1	104	1	0	0	0	0	0.0000
7670	9.60	14	1	105	1	0	0	0	0	0.0000
7680	18.10	14	1	105	2	0	0	0	0	0.0000
7690	20.50	14	1	105	3	0	0	0	0	0.0000
7700	21.60	14	1	105	4	0	0	0	0	0.0000
7710	13.40	14	1	106	1	0	0	0	0	0.0000
7720	24.60	14	1	106	2	0	0	0	0	0.0000
7730	28.40	14	1	106	3	0	0	0	0	0.0000
7740	30.30	14	1	106	4	0	0	0	0	0.0000
7750	8.70	14	1	107	1	0	0	0	0	0.0000
7760	17.50	14	1	107	2	0	0	0	0	0.0000
7770	18.50	14	1	107	3	0	0	0	0	0.0000
7780	19.30	14	1	107	4	0	0	0	0	0.0000
7790	68.00	14	1	50	2	108	2	0	0	0.0000
7800	54.20	14	1	108	2	0	0	0	0	0.0000
7810	5.20	14	1	50	-1	110	1	0	0	0.0000
7820	29.90	14	1	113	1	0	0	0	0	0.0000
7830	32.80	14	1	113	2	0	0	0	0	0.0000
7840	18.60	14	1	114	1	0	0	0	0	0.0000

<u>Species</u> <u>ID</u>	<u>Log K</u>	<u>Four Pairs of Component ID and</u> <u>Stoichiometric Coefficient</u>							<u>Comment</u>
7850	35.50	14	1 114	2	0	0	0	0	0.0000
7860	39.40	14	1 114	3	0	0	0	0	0.0000
7870	42.10	14	1 114	4	0	0	0	0	0.0000
7880	23.30	14	1 121	2	0	0	0	0	0.0000
7890	10.80	14	1 124	1	0	0	0	0	0.0000
7900	20.00	14	1 124	2	0	0	0	0	0.0000
7910	8.20	14	1 126	1	0	0	0	0	0.0000
7920	16.40	14	1 126	2	0	0	0	0	0.0000
7930	14.50	14	1 127	1	0	0	0	0	0.0000
7940	8.80	14	1 50	-1 127	1	0	0	0	0.0000
7950	24.20	14	1 128	1	0	0	0	0	0.0000
7960	27.90	14	1 50	1 128	1	0	0	0	0.0000
7970	14.50	14	1 50	-1 128	1	0	0	0	0.0000
7980	26.70	14	1 129	1	0	0	0	0	0.0000
7990	30.40	14	1 50	1 129	1	0	0	0	0.0000
8000	15.60	14	1 50	-1 129	1	0	0	0	0.0000
8010	45.20	14	1 130	2	0	0	0	0	0.0000
8020	7.80	14	1 136	1	0	0	0	0	0.0000
8030	13.10	14	1 136	2	0	0	0	0	0.0000
8040	-3.40	14	1 50	-1	0	0	0	0	0.0000
8050	-6.00	14	1 50	-2	0	0	0	0	0.0000
8060	7.40	15	1 101	1	0	0	0	0	0.0000
8070	10.80	15	1 101	2	0	0	0	0	0.0000
8080	2.70	15	1 102	1	0	0	0	0	0.0000
8090	1.70	15	1 103	1	0	0	0	0	0.0000
8100	2.60	15	1 103	2	0	0	0	0	0.0000
8110	3.90	15	1 103	3	0	0	0	0	0.0000
8120	1.60	15	1 105	1	0	0	0	0	0.0000
8130	2.20	15	1 105	2	0	0	0	0	0.0000
8140	3.00	15	1 105	3	0	0	0	0	0.0000
8150	1.80	15	1 106	1	0	0	0	0	0.0000
8160	3.60	15	1 106	2	0	0	0	0	0.0000
8170	4.20	15	1 106	3	0	0	0	0	0.0000
8180	4.40	15	1 106	4	0	0	0	0	0.0000
8190	5.20	15	1 110	2	0	0	0	0	0.0000
8200	6.20	15	1 113	1	0	0	0	0	0.0000
8210	7.50	15	1 113	2	0	0	0	0	0.0000
8220	10.60	15	1 114	4	0	0	0	0	0.0000
8230	2.40	15	1 115	1	0	0	0	0	0.0000
8240	4.10	15	1 115	2	0	0	0	0	0.0000
8250	4.70	15	1 116	1	0	0	0	0	0.0000
8260	7.40	15	1 116	2	0	0	0	0	0.0000
8270	29.10	15	1 50	2 117	1	0	0	0	0.0000
8280	23.20	15	1 50	1 117	1	0	0	0	0.0000
8290	14.10	15	1 117	1	0	0	0	0	0.0000
8300	4.90	15	1 120	1	0	0	0	0	0.0000
8310	3.00	15	1 122	1	0	0	0	0	0.0000

Species	Four Pairs of Component ID and								
ID	Log K	Stoichiometric Coefficient							Comment
8320	6.10	15	1 124	1	0	0	0	0	0.0000
8330	10.60	15	1 124	2	0	0	0	0	0.0000
8340	5.10	15	1 126	1	0	0	0	0	0.0000
8350	8.70	15	1 126	2	0	0	0	0	0.0000
8360	13.60	15	1 127	1	0	0	0	0	0.0000
8370	20.50	15	1 128	1	0	0	0	0	0.0000
8380	23.80	15	1 50	1 128	1	0	0	0	0.0000
8390	22.10	15	1 129	1	0	0	0	0	0.0000
8400	25.60	15	1 50	1 129	1	0	0	0	0.0000
8410	13.40	15	1 130	1	0	0	0	0	0.0000
8420	4.50	15	1 132	1	0	0	0	0	0.0000
8430	4.50	15	1 132	2	0	0	0	0	0.0000
8440	5.10	15	1 133	1	0	0	0	0	0.0000
8450	9.50	15	1 133	2	0	0	0	0	0.0000
8460	7.30	15	1 136	1	0	0	0	0	0.0000
8470	5.60	15	1 139	1	0	0	0	0	0.0000
8480	9.00	15	1 139	2	0	0	0	0	0.0000
8490	4.90	15	1 141	1	0	0	0	0	0.0000
8500	5.20	15	1 148	1	0	0	0	0	0.0000
8510	11.10	15	1 148	2	0	0	0	0	0.0000
8520	-7.80	15	1 50	-1	0	0	0	0	0.0000
8530	-17.20	15	1 50	-2	0	0	0	0	0.0000
8540	-27.40	15	1 50	-3	0	0	0	0	0.0000
8550	-6.30	15	2 50	-1	0	0	0	0	0.0000
8560	2.50	16	1 102	1	0	0	0	0	0.0000
8570	0.50	16	1 103	1	0	0	0	0	0.0000
8580	0.60	16	1 105	1	0	0	0	0	0.0000
8590	2.00	16	1 107	1	0	0	0	0	0.0000
8600	3.50	16	1 107	2	0	0	0	0	0.0000
8610	4.50	16	1 107	3	0	0	0	0	0.0000
8620	5.20	16	1 107	4	0	0	0	0	0.0000
8630	5.30	16	1 107	5	0	0	0	0	0.0000
8640	6.50	16	1 107	6	0	0	0	0	0.0000
8650	16.00	16	1 50	1 111	1	0	0	0	0.0000
8660	9.60	16	1 111	1	0	0	0	0	0.0000
8670	2.00	16	1 113	1	0	0	0	0	0.0000
8680	1.60	16	1 115	1	0	0	0	0	0.0000
8690	2.40	16	1 115	2	0	0	0	0	0.0000
8700	5.60	16	1 116	1	0	0	0	0	0.0000
8710	9.70	16	1 116	2	0	0	0	0	0.0000
8720	6.80	16	1 50	1 117	1	0	0	0	0.0000
8730	5.10	16	1 50	2 117	1	0	0	0	0.0000
8740	4.10	16	1 118	1	0	0	0	0	0.0000
8750	6.60	16	1 118	2	0	0	0	0	0.0000
8760	5.70	16	1 50	1 118	1	0	0	0	0.0000
8770	10.90	16	1 50	2 118	2	0	0	0	0.0000
8780	7.90	16	1 119	1	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>								
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8790	12.70	16	1	119	2	0	0	0	0	0.0000
8800	3.20	16	1	120	1	0	0	0	0	0.0000
8810	5.80	16	1	121	1	0	0	0	0	0.0000
8820	10.60	16	1	121	2	0	0	0	0	0.0000
8830	13.70	16	1	121	3	0	0	0	0	0.0000
8840	5.60	16	1	122	1	0	0	0	0	0.0000
8850	11.10	16	1	122	2	0	0	0	0	0.0000
8860	16.00	16	1	122	3	0	0	0	0	0.0000
8870	7.90	16	1	123	1	0	0	0	0	0.0000
8880	10.60	16	1	123	2	0	0	0	0	0.0000
8890	5.10	16	1	124	1	0	0	0	0	0.0000
8900	9.20	16	1	124	2	0	0	0	0	0.0000
8910	11.70	16	1	124	3	0	0	0	0	0.0000
8920	6.20	16	1	125	1	0	0	0	0	0.0000
8930	9.70	16	1	125	2	0	0	0	0	0.0000
8940	6.20	16	1	126	1	0	0	0	0	0.0000
8950	11.20	16	1	126	2	0	0	0	0	0.0000
8960	14.90	16	1	126	3	0	0	0	0	0.0000
8970	12.40	16	1	127	1	0	0	0	0	0.0000
8980	18.10	16	1	128	1	0	0	0	0	0.0000
8990	21.60	16	1	50	1	128	1	0	0	0.0000
9000	21.30	16	1	129	1	0	0	0	0	0.0000
9010	24.80	16	1	50	1	129	1	0	0	0.0000
9020	10.20	16	1	130	1	0	0	0	0	0.0000
9030	17.50	16	1	130	2	0	0	0	0	0.0000
9040	13.60	16	1	131	1	0	0	0	0	0.0000
9050	20.30	16	1	50	1	131	1	0	0	0.0000
9060	26.00	16	1	50	2	131	1	0	0	0.0000
9070	5.20	16	1	132	2	0	0	0	0	0.0000
9080	4.30	16	1	133	1	0	0	0	0	0.0000
9090	7.70	16	1	133	2	0	0	0	0	0.0000
9100	4.60	16	1	134	1	0	0	0	0	0.0000
9110	7.70	16	1	134	2	0	0	0	0	0.0000
9120	7.60	16	1	135	2	0	0	0	0	0.0000
9130	7.40	16	1	136	1	0	0	0	0	0.0000
9140	13.20	16	1	136	2	0	0	0	0	0.0000
9150	6.40	16	1	137	1	0	0	0	0	0.0000
9160	11.00	16	1	137	2	0	0	0	0	0.0000
9170	8.90	16	1	138	2	0	0	0	0	0.0000
9180	4.80	16	1	139	1	0	0	0	0	0.0000
9190	8.50	16	1	139	2	0	0	0	0	0.0000
9200	10.40	16	1	139	3	0	0	0	0	0.0000
9210	9.20	16	1	140	2	0	0	0	0	0.0000
9220	8.70	16	1	141	2	0	0	0	0	0.0000
9230	8.70	16	1	144	2	0	0	0	0	0.0000
9240	5.10	16	1	145	1	0	0	0	0	0.0000
9250	8.90	16	1	145	2	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>							<u>Comment</u>
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9260	5.10	16	1 146	1	0	0	0	0	0.0000
9270	8.90	16	1 146	2	0	0	0	0	0.0000
9280	10.10	16	1 147	2	0	0	0	0	0.0000
9290	1.60	16	1 150	1	0	0	0	0	0.0000
9300	-9.20	16	1 50	-1	0	0	0	0	0.0000
9310	-18.30	16	1 50	-2	0	0	0	0	0.0000
9320	-31.20	16	1 50	-3	0	0	0	0	0.0000
9330	5.20	17	1 104	1	0	0	0	0	0.0000
9340	9.10	17	1 104	2	0	0	0	0	0.0000
9350	12.00	17	1 104	3	0	0	0	0	0.0000
9360	7.10	17	1 107	1	0	0	0	0	0.0000
9370	13.90	17	1 107	2	0	0	0	0	0.0000
9380	19.90	17	1 107	3	0	0	0	0	0.0000
9390	25.50	17	1 107	4	0	0	0	0	0.0000
9400	30.60	17	1 107	5	0	0	0	0	0.0000
9410	35.00	17	1 107	6	0	0	0	0	0.0000
9420	46.70	17	1 121	3	0	0	0	0	0.0000
9430	39.80	17	1 128	1	0	0	0	0	0.0000
9440	41.20	17	1 50	1 128	1	0	0	0	0.0000
9450	1.30	18	1 102	1	0	0	0	0	0.0000
9460	3.30	18	1 103	1	0	0	0	0	0.0000
9470	5.30	18	1 103	2	0	0	0	0	0.0000
9480	5.30	18	1 103	3	0	0	0	0	0.0000
9490	6.10	18	1 103	4	0	0	0	0	0.0000
9500	4.30	18	1 105	1	0	0	0	0	0.0000
9510	7.30	18	1 105	2	0	0	0	0	0.0000
9520	7.70	18	1 105	3	0	0	0	0	0.0000
9530	8.10	18	1 105	4	0	0	0	0	0.0000
9540	14.00	18	1 106	1	0	0	0	0	0.0000
9550	13.90	18	1 106	2	0	0	0	0	0.0000
9560	3.20	18	1 107	1	0	0	0	0	0.0000
9570	7.20	18	1 107	2	0	0	0	0	0.0000
9580	14.00	18	1 50	1 108	1	0	0	0	0.0000
9590	19.00	18	1 50	2 108	2	0	0	0	0.0000
9600	17.30	18	1 108	1	0	0	0	0	0.0000
9610	8.90	18	1 113	1	0	0	0	0	0.0000
9620	13.20	18	1 113	2	0	0	0	0	0.0000
9630	20.40	18	1 114	2	0	0	0	0	0.0000
9640	21.40	18	1 114	3	0	0	0	0	0.0000
9650	0.60	18	1 115	1	0	0	0	0	0.0000
9660	24.80	18	2 50	1 117	1	0	0	0	0.0000
9670	2.60	18	1 118	1	0	0	0	0	0.0000
9680	4.70	18	1 121	1	0	0	0	0	0.0000
9690	7.70	18	1 121	2	0	0	0	0	0.0000
9691	2.35	18	1 121	1 50	1	0	0	0	0.0000
9700	6.60	18	1 122	2	0	0	0	0	0.0000
9710	3.90	18	1 124	1	0	0	0	0	0.0000

Species	Four Pairs of Component ID and								Comment
ID	Log K	Stoichiometric Coefficient							
9720	7.30	18	1 124	2	0	0	0	0	0.0000
9721	3.50	18	1 125	1	0	0	0	0	0.0000
9722	6.90	18	1 125	2	0	0	0	0	0.0000
9730	3.60	18	1 126	1	0	0	0	0	0.0000
9740	6.10	18	1 126	2	0	0	0	0	0.0000
9750	8.40	18	1 128	1	0	0	0	0	0.0000
9760	15.30	18	1 50	1 128	1	0	0	0	0.0000
9770	3.60	18	1 133	1	0	0	0	0	0.0000
9780	7.40	18	1 133	2	0	0	0	0	0.0000
9790	6.50	18	1 136	1	0	0	0	0	0.0000
9800	14.30	18	1 136	2	0	0	0	0	0.0000
9820	3.80	18	1 139	1	0	0	0	0	0.0000
9830	7.40	18	1 139	2	0	0	0	0	0.0000
9840	5.60	18	1 149	1	0	0	0	0	0.0000
9850	7.90	18	1 149	2	0	0	0	0	0.0000
9860	3.10	18	1 158	1	0	0	0	0	0.0000
9870	6.60	18	1 158	2	0	0	0	0	0.0000
9880	-11.90	18	1 50	-1	0	0	0	0	0.0000
9881	-24.00	18	1 50	-2	0	0	0	0	0.0000
9890	4.90	19	1 102	1	0	0	0	0	0.0000
9900	5.20	19	1 104	1	0	0	0	0	0.0000
9910	9.10	19	1 104	2	0	0	0	0	0.0000
9920	6.40	19	1 118	1	0	0	0	0	0.0000
9930	12.30	19	1 123	1	0	0	0	0	0.0000
9940	26.80	19	1 128	1	0	0	0	0	0.0000
9950	29.20	19	1 50	1 128	1	0	0	0	0.0000
9960	19.00	19	1 50	-1 128	1	0	0	0	0.0000
9970	4.40	19	1 137	1	0	0	0	0	0.0000
9980	2.80	19	1 150	1	0	0	0	0	0.0000
9990	4.50	19	1 150	2	0	0	0	0	0.0000
10000	-3.30	19	1 50	-1	0	0	0	0	0.0000
10010	-8.80	19	1 50	-2	0	0	0	0	0.0000
10020	-23.80	19	1 50	-4	0	0	0	0	0.0000
10030	3.20	20	1 102	1	0	0	0	0	0.0000
10040	4.80	20	1 102	2	0	0	0	0	0.0000
10050	6.90	20	1 104	1	0	0	0	0	0.0000
10060	13.00	20	1 104	2	0	0	0	0	0.0000
10070	16.90	20	1 104	3	0	0	0	0	0.0000
10080	19.50	20	1 104	4	0	0	0	0	0.0000
10090	20.80	20	1 104	5	0	0	0	0	0.0000
10100	20.50	20	1 104	6	0	0	0	0	0.0000
10110	8.90	20	1 116	1	0	0	0	0	0.0000
10120	17.10	20	1 116	2	0	0	0	0	0.0000
10130	23.00	20	1 116	3	0	0	0	0	0.0000
10140	25.70	20	1 50	1 117	1	0	0	0	0.0000
10150	22.80	20	1 117	1	0	0	0	0	0.0000
10160	19.40	20	1 50	-1 117	1	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>							<u>Comment</u>
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10170	12.50	20	1 118	2	0	0	0	0	0.0000
10180	16.40	20	1 118	3	0	0	0	0	0.0000
10190	15.90	20	1 119	1	0	0	0	0	0.0000
10200	15.60	20	1 123	1	0	0	0	0	0.0000
10210	25.60	20	1 123	2	0	0	0	0	0.0000
10220	28.90	20	1 123	3	0	0	0	0	0.0000
10230	14.80	20	1 127	1	0	0	0	0	0.0000
10240	20.80	20	1 127	2	0	0	0	0	0.0000
10250	9.40	20	1 50	-1 127	1	0	0		0.0000
10260	19.80	20	1 128	1	0	0	0	0	0.0000
10270	22.50	20	1 50	1 128	1	0	0		0.0000
10280	13.60	20	1 50	-1 128	1	0	0		0.0000
10290	21.30	20	1 129	1	0	0	0	0	0.0000
10300	23.50	20	1 50	1 129	1	0	0		0.0000
10310	13.50	20	1 50	-1 129	1	0	0		0.0000
10320	7.50	20	1 133	1	0	0	0	0	0.0000
10330	14.50	20	1 133	2	0	0	0	0	0.0000
10340	-4.50	20	1 50	-1	0	0	0	0	0.0000
10350	-23.10	20	1 50	-4	0	0	0	0	0.0000
10360	-0.10	21	1 103	1	0	0	0	0	0.0000
10370	0.00	21	1 104	1	0	0	0	0	0.0000
10380	2.30	21	1 110	1	0	0	0	0	0.0000
10390	3.10	21	1 111	1	0	0	0	0	0.0000
10400	1.20	21	1 117	1	0	0	0	0	0.0000
10410	1.40	21	1 128	1	0	0	0	0	0.0000
10420	0.60	22	1 102	1	0	0	0	0	0.0000
10430	3.10	22	1 110	1	0	0	0	0	0.0000
10440	4.20	22	1 111	1	0	0	0	0	0.0000
10450	0.20	22	1 115	1	0	0	0	0	0.0000
10460	4.00	22	1 128	1	0	0	0	0	0.0000
10470	5.30	22	1 129	1	0	0	0	0	0.0000
10480	-13.40	22	1 50	-1	0	0	0	0	0.0000
10490	1.90	23	1 102	1	0	0	0	0	0.0000
10500	3.00	23	1 102	2	0	0	0	0	0.0000
10510	2.00	23	1 102	3	0	0	0	0	0.0000
10520	1.60	23	1 103	1	0	0	0	0	0.0000
10530	5.60	23	1 104	1	0	0	0	0	0.0000
10540	9.70	23	1 104	2	0	0	0	0	0.0000
10550	12.70	23	1 104	3	0	0	0	0	0.0000
10560	8.00	23	1 116	1	0	0	0	0	0.0000
10570	14.80	23	1 116	2	0	0	0	0	0.0000
10580	22.60	23	1 50	1 117	1	0	0		0.0000
10590	26.10	23	1 50	2 117	1	0	0		0.0000
10600	29.30	23	1 50	3 117	1	0	0		0.0000
10610	4.20	23	1 118	1	0	0	0	0	0.0000
10620	6.30	23	1 118	2	0	0	0	0	0.0000
10630	13.70	23	1 119	1	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>							<u>Comment</u>
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10640	23.50	23	1	119	2	0	0	0	0.0000
10650	18.90	23	1	50	1	119	1	0	0.0000
10660	4.10	23	1	120	1	0	0	0	0.0000
10670	13.40	23	1	123	1	0	0	0	0.0000
10680	21.30	23	1	123	2	0	0	0	0.0000
10690	18.50	23	1	50	1	123	1	0	0.0000
10700	13.20	23	1	124	2	0	0	0	0.0000
10710	14.00	23	1	125	2	0	0	0	0.0000
10720	9.00	23	1	127	1	0	0	0	0.0000
10730	12.70	23	1	128	1	0	0	0	0.0000
10740	13.30	23	1	129	1	0	0	0	0.0000
10750	5.20	23	1	132	1	0	0	0	0.0000
10760	6.90	23	1	132	2	0	0	0	0.0000
10770	-6.30	23	1	50	-1	0	0	0	0.0000
10780	4.50	24	1	102	1	0	0	0	0.0000
10790	2.00	24	1	103	1	0	0	0	0.0000
10800	7.10	24	1	104	1	0	0	0	0.0000
10810	13.00	24	1	104	2	0	0	0	0.0000
10820	17.40	24	1	104	3	0	0	0	0.0000
10830	2.10	24	1	105	1	0	0	0	0.0000
10840	3.20	24	1	105	2	0	0	0	0.0000
10850	9.20	24	1	116	1	0	0	0	0.0000
10860	18.20	24	1	118	3	0	0	0	0.0000
10870	15.00	24	1	120	2	0	0	0	0.0000
10880	4.80	24	1	123	1	0	0	0	0.0000
10890	26.90	24	1	128	1	0	0	0	0.0000
10900	16.10	24	1	50	-1	128	1	0	0.0000
10910	29.20	24	1	129	1	0	0	0	0.0000
10920	-3.80	24	1	50	-1	0	0	0	0.0000
10930	-8.00	24	1	50	-2	0	0	0	0.0000
10940	-11.10	24	1	50	-3	0	0	0	0.0000
10950	10.30	25	1	118	1	0	0	0	0.0000
10960	15.70	25	1	118	2	0	0	0	0.0000
10970	10.90	25	1	120	1	0	0	0	0.0000
10980	14.20	25	1	127	1	0	0	0	0.0000
10990	20.00	25	1	128	1	0	0	0	0.0000
11000	22.40	25	1	129	1	0	0	0	0.0000
11010	6.90	26	1	104	1	0	0	0	0.0000
11020	9.70	26	1	104	2	0	0	0	0.0000
11030	10.20	26	1	104	3	0	0	0	0.0000
11040	1.10	26	1	105	1	0	0	0	0.0000
11050	1.70	26	1	105	2	0	0	0	0.0000
11060	1.40	26	1	105	3	0	0	0	0.0000
11070	14.10	26	1	110	1	0	0	0	0.0000
11080	6.40	26	1	120	1	0	0	0	0.0000
11090	11.10	26	1	120	2	0	0	0	0.0000
11100	24.60	26	1	128	1	0	0	0	0.0000

<u>Species</u> <u>ID</u>	<u>Log K</u>	<u>Four Pairs of Component ID and</u> <u>Stoichiometric Coefficient</u>								<u>Comment</u>
11110	-3.20	26	1	50	-1	0	0	0	0	0.0000
11120	3.30	28	1	102	1	0	0	0	0	0.0000
11130	0.70	28	1	103	1	0	0	0	0	0.0000
11140	3.60	28	1	104	1	0	0	0	0	0.0000
11150	17.70	28	1	110	1	0	0	0	0	0.0000
11160	19.10	28	1	110	2	0	0	0	0	0.0000
11170	17.30	28	1	111	2	0	0	0	0	0.0000
11180	17.80	28	1	50	1	111	1	0	0	0.0000
11190	29.60	28	1	50	2	111	2	0	0	0.0000
11200	3.50	28	1	113	1	0	0	0	0	0.0000
11210	2.90	28	1	115	1	0	0	0	0	0.0000
11220	4.80	28	1	115	2	0	0	0	0	0.0000
11230	5.50	28	1	116	1	0	0	0	0	0.0000
11240	9.50	28	1	116	2	0	0	0	0	0.0000
11250	12.70	28	1	116	3	0	0	0	0	0.0000
11260	9.20	28	1	117	1	0	0	0	0	0.0000
11270	11.90	28	1	117	2	0	0	0	0	0.0000
11280	90.10	28	1	50	9	117	3	0	0	0.0000
11290	5.20	28	1	118	1	0	0	0	0	0.0000
11300	9.40	28	1	118	2	0	0	0	0	0.0000
11310	12.20	28	1	118	3	0	0	0	0	0.0000
11320	4.60	28	1	119	1	0	0	0	0	0.0000
11330	17.60	28	1	50	1	119	1	0	0	0.0000
11340	4.10	28	1	124	1	0	0	0	0	0.0000
11350	7.70	28	1	124	2	0	0	0	0	0.0000
11360	4.10	28	1	126	1	0	0	0	0	0.0000
11370	7.50	28	1	126	2	0	0	0	0	0.0000
11380	9.80	28	1	126	3	0	0	0	0	0.0000
11390	13.20	28	1	127	1	0	0	0	0	0.0000
11400	20.90	28	1	127	2	0	0	0	0	0.0000
11410	19.20	28	1	128	1	0	0	0	0	0.0000
11420	21.40	28	1	50	1	128	1	0	0	0.0000
11430	20.10	28	1	129	1	0	0	0	0	0.0000
11440	22.90	28	1	50	1	129	1	0	0	0.0000
11450	6.00	28	1	132	1	0	0	0	0	0.0000
11460	9.80	28	1	132	2	0	0	0	0	0.0000
11470	-9.00	28	1	50	-1	0	0	0	0	0.0000
11480	3.70	29	1	102	1	0	0	0	0	0.0000
11490	0.80	29	1	103	1	0	0	0	0	0.0000
11500	4.10	29	1	104	1	0	0	0	0	0.0000
11510	7.50	29	1	104	2	0	0	0	0	0.0000
11520	0.70	29	1	105	1	0	0	0	0	0.0000
11530	19.30	29	1	109	1	0	0	0	0	0.0000
11540	18.20	29	1	110	1	0	0	0	0	0.0000
11550	3.00	29	1	115	1	0	0	0	0	0.0000
11560	5.00	29	1	115	2	0	0	0	0	0.0000
11570	5.70	29	1	116	1	0	0	0	0	0.0000

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11580	9.90	29	1	116	2	0	0	0	0	0.0000
11590	13.40	29	1	116	3	0	0	0	0	0.0000
11600	11.60	29	1	117	1	0	0	0	0	0.0000
11610	15.00	29	1	117	2	0	0	0	0	0.0000
11620	31.10	29	1	50	3	117	1	0	0	0.0000
11630	6.80	29	1	118	1	0	0	0	0	0.0000
11640	10.70	29	1	118	2	0	0	0	0	0.0000
11650	11.60	29	1	118	3	0	0	0	0	0.0000
11660	4.60	29	1	119	1	0	0	0	0	0.0000
11670	17.70	29	1	50	1	119	1	0	0	0.0000
11680	9.60	29	1	123	1	0	0	0	0	0.0000
11690	15.20	29	1	123	2	0	0	0	0	0.0000
11700	16.20	29	1	50	1	123	1	0	0	0.0000
11710	4.30	29	1	124	1	0	0	0	0	0.0000
11720	7.90	29	1	124	2	0	0	0	0	0.0000
11730	4.60	29	1	126	1	0	0	0	0	0.0000
11740	8.10	29	1	126	2	0	0	0	0	0.0000
11750	11.40	29	1	126	3	0	0	0	0	0.0000
11760	13.50	29	1	127	1	0	0	0	0	0.0000
11770	21.40	29	1	127	2	0	0	0	0	0.0000
11780	20.10	29	1	128	1	0	0	0	0	0.0000
11790	20.60	29	1	129	1	0	0	0	0	0.0000
11800	5.90	29	1	132	1	0	0	0	0	0.0000
11810	9.60	29	1	132	2	0	0	0	0	0.0000
11820	8.50	29	1	149	1	0	0	0	0	0.0000
11830	1.50	29	1	150	1	0	0	0	0	0.0000
11840	-7.90	29	1	50	-1	0	0	0	0	0.0000
11850	26.90	30	1	107	2	0	0	0	0	0.0000
11860	38.20	30	1	114	2	0	0	0	0	0.0000
11870	5.80	31	1	102	1	0	0	0	0	0.0000
11880	9.40	31	1	102	2	0	0	0	0	0.0000
11890	1.40	31	1	103	1	0	0	0	0	0.0000
11900	8.80	31	1	104	1	0	0	0	0	0.0000
11910	15.70	31	1	104	2	0	0	0	0	0.0000
11920	20.80	31	1	104	3	0	0	0	0	0.0000
11930	9.50	31	1	116	1	0	0	0	0	0.0000
11940	17.50	31	1	116	2	0	0	0	0	0.0000
11950	24.00	31	1	116	3	0	0	0	0	0.0000
11960	28.20	31	1	116	4	0	0	0	0	0.0000
11970	16.80	31	1	117	1	0	0	0	0	0.0000
11980	25.70	31	1	117	2	0	0	0	0	0.0000
11990	6.80	31	1	119	1	0	0	0	0	0.0000
12000	11.40	31	1	119	2	0	0	0	0	0.0000
12010	13.90	31	1	119	3	0	0	0	0	0.0000
12020	14.10	31	1	119	4	0	0	0	0	0.0000
12030	17.10	31	1	127	1	0	0	0	0	0.0000
12040	-17.20	31	1	50	-2	127	1	0	0	0.0000

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12050	28.30	31	1	128	1	0	0	0	0	0.0000
12060	21.30	31	1	50	-1	128	1	0	0	0.0000
12070	28.30	31	1	129	1	0	0	0	0	0.0000
12080	20.70	31	1	50	-1	129	1	0	0	0.0000
12090	-2.10	31	1	50	-1	0	0	0	0	0.0000
12100	16.80	32	1	101	2	0	0	0	0	0.0000
12110	22.70	32	1	101	3	0	0	0	0	0.0000
12120	3.00	32	1	102	1	0	0	0	0	0.0000
12130	4.60	32	1	102	2	0	0	0	0	0.0000
12140	0.90	32	1	103	1	0	0	0	0	0.0000
12150	5.10	32	1	104	1	0	0	0	0	0.0000
12160	8.80	32	1	104	2	0	0	0	0	0.0000
12170	11.40	32	1	104	3	0	0	0	0	0.0000
12180	12.40	32	1	104	4	0	0	0	0	0.0000
12190	0.30	32	1	105	1	0	0	0	0	0.0000
12200	2.00	32	1	113	1	0	0	0	0	0.0000
12210	3.00	32	1	115	1	0	0	0	0	0.0000
12220	5.30	32	1	115	2	0	0	0	0	0.0000
12230	7.20	32	1	115	3	0	0	0	0	0.0000
12240	8.00	32	1	116	1	0	0	0	0	0.0000
12250	14.50	32	1	116	2	0	0	0	0	0.0000
12260	9.30	32	1	117	1	0	0	0	0	0.0000
12270	26.60	32	1	50	1	117	1	0	0	0.0000
12280	5.20	32	1	118	1	0	0	0	0	0.0000
12290	9.60	32	1	118	2	0	0	0	0	0.0000
12300	12.90	32	1	118	3	0	0	0	0	0.0000
12310	13.30	32	1	119	1	0	0	0	0	0.0000
12320	16.80	32	1	50	1	119	1	0	0	0.0000
12330	-0.50	32	1	50	-1	119	1	0	0	0.0000
12340	22.00	32	1	119	2	0	0	0	0	0.0000
12350	12.50	32	1	123	1	0	0	0	0	0.0000
12360	19.60	32	1	123	2	0	0	0	0	0.0000
12370	16.40	32	1	50	1	123	1	0	0	0.0000
12380	8.10	32	1	124	1	0	0	0	0	0.0000
12390	15.60	32	1	124	2	0	0	0	0	0.0000
12400	13.40	32	1	50	1	125	1	0	0	0.0000
12410	11.50	32	1	127	1	0	0	0	0	0.0000
12420	12.90	32	1	128	1	0	0	0	0	0.0000
12430	20.70	32	1	50	1	128	1	0	0	0.0000
12440	21.60	32	2	128	1	0	0	0	0	0.0000
12450	5.60	32	1	132	1	0	0	0	0	0.0000
12460	8.70	32	1	132	2	0	0	0	0	0.0000
12470	5.90	32	1	149	1	0	0	0	0	0.0000
12480	-5.30	32	1	50	-1	0	0	0	0	0.0000
12490	-5.30	32	1	50	-1	0	0	0	0	0.0000
12500	24.20	33	1	114	2	0	0	0	0	0.0000
12510	28.90	33	1	114	3	0	0	0	0	0.0000

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12520	30.10	33	1	114	4	0	0	0	0	0.0000
12530	10.20	50	1	101	1	0	0	0	0	0.0000
12540	16.50	50	2	101	1	0	0	0	0	0.0000
12550	2.20	50	1	102	1	0	0	0	0	0.0000
12560	3.00	50	1	104	1	0	0	0	0	0.0000
12570	9.00	50	1	107	1	0	0	0	0	0.0000
12580	13.00	50	1	108	1	0	0	0	0	0.0000
12590	20.20	50	2	108	1	0	0	0	0	0.0000
12600	12.50	50	1	109	1	0	0	0	0	0.0000
12610	19.90	50	2	109	1	0	0	0	0	0.0000
12620	21.90	50	3	109	1	0	0	0	0	0.0000
12630	9.60	50	1	110	1	0	0	0	0	0.0000
12640	16.50	50	2	110	1	0	0	0	0	0.0000
12650	19.60	50	3	110	1	0	0	0	0	0.0000
12660	20.80	50	4	110	1	0	0	0	0	0.0000
12670	9.30	50	1	111	1	0	0	0	0	0.0000
12680	16.20	50	2	111	1	0	0	0	0	0.0000
12690	19.60	50	3	111	1	0	0	0	0	0.0000
12700	22.80	50	4	111	1	0	0	0	0	0.0000
12710	13.10	50	1	112	1	0	0	0	0	0.0000
12720	22.70	50	2	112	1	0	0	0	0	0.0000
12730	1.70	50	1	113	1	0	0	0	0	0.0000
12740	9.30	50	1	114	1	0	0	0	0	0.0000
12750	4.70	50	1	115	1	0	0	0	0	0.0000
12760	8.90	50	1	116	1	0	0	0	0	0.0000
12770	16.80	50	1	117	1	0	0	0	0	0.0000
12780	23.20	50	2	117	1	0	0	0	0	0.0000
12790	27.70	50	3	117	1	0	0	0	0	0.0000
12800	30.70	50	4	117	1	0	0	0	0	0.0000
12810	4.20	50	1	118	1	0	0	0	0	0.0000
12820	5.10	50	2	118	1	0	0	0	0	0.0000
12830	13.60	50	1	119	1	0	0	0	0	0.0000
12840	16.60	50	2	119	1	0	0	0	0	0.0000
12850	4.50	50	1	120	1	0	0	0	0	0.0000
12860	7.70	50	2	120	1	0	0	0	0	0.0000
12870	9.96	50	1	121	1	0	0	0	0	0.0000
12880	17.04	50	2	121	1	0	0	0	0	0.0000
12890	12.30	50	1	123	1	0	0	0	0	0.0000
12900	15.50	50	2	123	1	0	0	0	0	0.0000
12910	9.90	50	1	124	1	0	0	0	0	0.0000
12920	12.20	50	2	124	1	0	0	0	0	0.0000
12930	9.90	50	1	125	1	0	0	0	0	0.0000
12940	14.18	50	2	125	1	0	0	0	0	0.0000
12950	16.38	50	3	125	1	0	0	0	0	0.0000
12960	5.33	50	1	126	1	0	0	0	0	0.0000
12970	6.93	50	2	126	1	0	0	0	0	0.0000
12980	10.50	50	1	127	1	0	0	0	0	0.0000

<u>Species</u>	<u>Four Pairs of Component ID and</u>									
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								<u>Comment</u>
12990	13.70	50	2	127	1	0	0	0	0	0.0000
13000	15.90	50	3	127	1	0	0	0	0	0.0000
13010	11.20	50	1	128	1	0	0	0	0	0.0000
13020	18.00	50	2	128	1	0	0	0	0	0.0000
13030	21.20	50	3	128	1	0	0	0	0	0.0000
13040	23.40	50	4	128	1	0	0	0	0	0.0000
13050	11.80	50	1	129	1	0	0	0	0	0.0000
13060	18.80	50	2	129	1	0	0	0	0	0.0000
13070	11.00	50	1	130	1	0	0	0	0	0.0000
13080	19.50	50	2	130	1	0	0	0	0	0.0000
13090	21.50	50	3	130	1	0	0	0	0	0.0000
13100	10.60	50	1	131	1	0	0	0	0	0.0000
13110	20.60	50	2	131	1	0	0	0	0	0.0000
13120	29.40	50	3	131	1	0	0	0	0	0.0000
13130	5.50	50	1	132	1	0	0	0	0	0.0000
13140	8.50	50	2	132	1	0	0	0	0	0.0000
13150	9.30	50	1	133	1	0	0	0	0	0.0000
13160	11.40	50	2	133	1	0	0	0	0	0.0000
13170	10.80	50	1	134	1	0	0	0	0	0.0000
13180	19.60	50	2	134	1	0	0	0	0	0.0000
13190	21.20	50	3	134	1	0	0	0	0	0.0000
13200	10.80	50	1	135	1	0	0	0	0	0.0000
13210	19.90	50	2	135	1	0	0	0	0	0.0000
13220	21.70	50	3	135	1	0	0	0	0	0.0000
13230	9.12	50	1	136	1	0	0	0	0	0.0000
13240	15.16	50	2	136	1	0	0	0	0	0.0000
13250	16.70	50	3	136	1	0	0	0	0	0.0000
13260	9.70	50	1	137	1	0	0	0	0	0.0000
13270	13.60	50	2	137	2	0	0	0	0	0.0000
13280	14.90	50	3	137	1	0	0	0	0	0.0000
13290	9.20	50	1	138	1	0	0	0	0	0.0000
13300	11.40	50	2	138	1	0	0	0	0	0.0000
13310	9.90	50	1	139	1	0	0	0	0	0.0000
13320	12.30	50	2	139	1	0	0	0	0	0.0000
13330	9.60	50	1	140	1	0	0	0	0	0.0000
13340	2.80	50	2	140	1	0	0	0	0	0.0000
13350	9.20	50	1	141	1	0	0	0	0	0.0000
13360	11.40	50	2	141	1	0	0	0	0	0.0000
13370	9.70	50	1	142	1	0	0	0	0	0.0000
13380	12.10	50	2	142	1	0	0	0	0	0.0000
13390	9.00	50	1	143	1	0	0	0	0	0.0000
13400	11.10	50	2	143	1	0	0	0	0	0.0000
13410	9.30	50	1	144	1	0	0	0	0	0.0000
13420	11.40	50	2	144	1	0	0	0	0	0.0000
13430	9.70	50	1	145	1	0	0	0	0	0.0000
13440	12.10	50	2	145	1	0	0	0	0	0.0000
13450	9.70	50	1	146	1	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>								<u>Comment</u>
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								
13460	12.10	50	2	146	1	0	0	0	0	0.0000
13470	10.80	50	1	147	1	0	0	0	0	0.0000
13480	12.60	50	2	147	1	0	0	0	0	0.0000
13490	9.10	50	1	148	1	0	0	0	0	0.0000
13500	7.30	50	1	149	1	0	0	0	0	0.0000
13510	6.00	50	1	151	1	0	0	0	0	0.0000
13520	4.30	50	1	152	1	0	0	0	0	0.0000
13530	3.70	50	1	153	1	0	0	0	0	0.0000
13540	11.80	50	1	154	1	0	0	0	0	0.0000
13550	18.80	50	2	154	1	0	0	0	0	0.0000
13560	8.20	50	1	155	1	0	0	0	0	0.0000
13570	8.50	50	1	156	1	0	0	0	0	0.0000
13580	11.20	50	2	156	1	0	0	0	0	0.0000
13590	8.10	50	1	158	1	0	0	0	0	0.0000
13591	11.90	50	1	162	1	0	0	0	0	0.0000
13592	20.60	50	2	162	1	0	0	0	0	0.0000
13593	24.95	50	3	162	1	0	0	0	0	0.0000
13594	4.25	50	1	163	1	0	0	0	0	0.0000
13596	6.05	50	2	163	1	0	0	0	0	0.0000
13597	4.20	50	1	164	1	0	0	0	0	0.0000
13595	-14.00	50	-1	0	0	0	0	0	0	0.0000
13600	-135.20	19	2	50	-14	99	-6	0	0	0.0000
13610	-68.40	19	1	50	-7	99	-3	0	0	0.0000
13620	-74.90	19	1	50	-8	99	-3	0	0	0.0000
13630	30.70	14	2	99	2	0	0	0	0	0.0000

5 Redox Reactions

15000	13.20	6	1	7	-1	99	1	0	0	0.0000
15010	31.60	17	1	16	-1	99	1	0	0	0.0000
15020	-5.10	27	1	26	-1	99	2	0	0	0.0000
15030	2.70	9	1	33	-1	99	1	0	0	0.0000
15040	20.00	102	1	108	-1	50	8	99	8	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>								
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								<u>Comment</u>
154 Minerals										
20000	8.30	1	1	101	1	0	0	0	0	0.0000
20010	4.70	1	1	102	1	0	0	0	0	0.0000
20020	10.60	1	1	104	2	0	0	0	0	0.0000
20030	45.10	1	5	50	-1	109	3	0	0	0.0000
20040	48.20	1	4	50	1	109	3	0	0	0.0000
20050	19.30	1	1	50	1	109	1	0	0	0.0000
20060	15.50	1	2	110	1	0	0	0	0	0.0000
20070	8.70	1	1	112	1	0	0	0	0	0.0000
20080	8.00	1	1	118	1	0	0	0	0	0.0000
20090	6.50	1	1	149	1	0	0	0	0	0.0000
20100	7.40	1	1	152	1	0	0	0	0	0.0000
20110	22.90	1	3	154	2	0	0	0	0	0.0000
20120	5.50	1	1	156	1	0	0	0	0	0.0000
20130	-21.90	1	1	50	-2	0	0	0	0	0.0000
20140	5.40	2	1	101	1	0	0	0	0	0.0000
20150	8.00	2	1	104	2	0	0	0	0	0.0000
20160	28.40	2	3	109	2	0	0	0	0	0.0000
20170	3.70	2	1	118	1	0	0	0	0	0.0000
20180	24.40	2	3	154	2	0	0	0	0	0.0000
20190	4.90	2	1	156	1	0	0	0	0	0.0000
20200	-16.40	2	1	50	-2	0	0	0	0	0.0000
20210	9.00	3	1	101	1	0	0	0	0	0.0000
20220	7.30	3	1	102	1	0	0	0	0	0.0000
20230	8.60	3	1	104	2	0	0	0	0	0.0000
20240	2.40	3	1	112	1	0	0	0	0	0.0000
20250	6.70	3	1	118	1	0	0	0	0	0.0000
20260	22.80	3	3	154	2	0	0	0	0	0.0000
20270	6.10	3	1	156	1	0	0	0	0	0.0000
20280	25.80	6	1	109	1	0	0	0	0	0.0000
20290	21.00	6	1	154	1	0	0	0	0	0.0000
20300	31.60	6	2	156	3	0	0	0	0	0.0000
20310	-3.00	6	1	50	-3	0	0	0	0	0.0000
20320	10.20	7	1	101	1	0	0	0	0	0.0000
20330	19.40	7	1	108	1	0	0	0	0	0.0000
20340	33.30	7	3	109	2	0	0	0	0	0.0000
20350	16.40	7	1	112	1	0	0	0	0	0.0000
20360	-12.10	7	1	50	-2	0	0	0	0	0.0000
20370	10.40	8	1	101	1	0	0	0	0	0.0000
20380	14.80	8	1	108	1	0	0	0	0	0.0000
20390	19.50	8	2	110	1	0	0	0	0	0.0000
20400	10.70	8	1	112	1	0	0	0	0	0.0000
20410	29.60	8	3	154	2	0	0	0	0	0.0000
20420	7.30	8	1	156	1	0	0	0	0	0.0000
20430	-14.50	8	1	50	-2	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>								<u>Comment</u>
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								
20440	5.80	9	2	50	-2	101	1	0	0	0.0000
20450	38.30	9	1	108	1	0	0	0	0	0.0000
20460	37.70	9	3	109	2	0	0	0	0	0.0000
20470	18.80	9	2	110	1	0	0	0	0	0.0000
20480	39.80	9	3	154	2	0	0	0	0	0.0000
20490	7.70	9	1	156	1	0	0	0	0	0.0000
20500	-7.90	9	1	50	-2	0	0	0	0	0.0000
20510	10.00	10	1	101	1	0	0	0	0	0.0000
20520	11.20	10	1	102	1	0	0	0	0	0.0000
20530	6.10	10	1	104	2	0	0	0	0	0.0000
20540	6.20	10	1	118	1	0	0	0	0	0.0000
20550	54.80	10	3	154	2	0	0	0	0	0.0000
20560	6.60	10	1	156	1	0	0	0	0	0.0000
20570	11.30	11	1	101	1	0	0	0	0	0.0000
20580	27.80	11	1	108	1	0	0	0	0	0.0000
20590	7.20	11	1	118	1	0	0	0	0	0.0000
20600	37.40	11	3	154	2	0	0	0	0	0.0000
20610	8.30	11	1	156	1	0	0	0	0	0.0000
20620	-13.60	11	1	50	-2	0	0	0	0	0.0000
20630	10.80	12	1	101	1	0	0	0	0	0.0000
20640	23.00	12	1	108	1	0	0	0	0	0.0000
20650	36.70	12	3	109	2	0	0	0	0	0.0000
20660	18.50	12	1	112	1	0	0	0	0	0.0000
20670	8.20	12	1	118	1	0	0	0	0	0.0000
20680	27.90	12	3	154	2	0	0	0	0	0.0000
20690	7.70	12	1	156	1	0	0	0	0	0.0000
20700	-11.20	12	1	50	-2	0	0	0	0	0.0000
20710	8.20	13	1	101	1	0	0	0	0	0.0000
20720	22.90	13	1	108	1	0	0	0	0	0.0000
20730	30.20	13	3	154	2	0	0	0	0	0.0000
20740	5.30	13	1	156	1	0	0	0	0	0.0000
20750	-10.10	13	1	50	-2	0	0	0	0	0.0000
20760	53.70	14	1	108	1	0	0	0	0	0.0000
20770	-2.30	14	1	50	-2	0	0	0	0	0.0000
20780	13.50	15	1	101	1	0	0	0	0	0.0000
20790	19.40	15	3	50	-2	101	2	0	0	0.0000
20800	7.70	15	1	102	1	0	0	0	0	0.0000
20810	7.60	15	1	104	2	0	0	0	0	0.0000
20820	27.90	15	1	108	1	0	0	0	0	0.0000
20830	12.60	15	1	50	1	109	1	0	0	0.0000
20840	43.00	15	3	109	2	0	0	0	0	0.0000
20850	60.90	15	5	50	-1	109	3	0	0	0.0000
20860	3.50	15	2	50	-2	112	1	0	0	0.0000
20870	9.20	15	1	118	1	0	0	0	0	0.0000
20880	13.00	15	1	152	1	0	0	0	0	0.0000
20890	36.30	15	3	154	2	0	0	0	0	0.0000
20900	11.50	15	1	156	1	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>								<u>Comment</u>
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								
20910	-12.70	15	1	50	-2	0	0	0	0	0.0000
20920	12.80	16	1	101	1	0	0	0	0	0.0000
20930	24.30	16	1	108	1	0	0	0	0	0.0000
20940	32.80	16	3	154	2	0	0	0	0	0.0000
20950	7.10	16	1	156	1	0	0	0	0	0.0000
20960	-12.10	16	1	50	-2	0	0	0	0	0.0000
20970	3.70	17	1	50	-3	0	0	0	0	0.0000
20980	10.90	18	2	101	1	0	0	0	0	0.0000
20990	4.90	18	2	102	1	0	0	0	0	0.0000
21000	9.90	18	1	103	1	0	0	0	0	0.0000
21010	12.30	18	1	105	1	0	0	0	0	0.0000
21020	15.90	18	1	106	1	0	0	0	0	0.0000
21030	51.40	18	2	108	1	0	0	0	0	0.0000
21040	16.00	18	3	109	1	0	0	0	0	0.0000
21050	2.30	18	1	115	1	0	0	0	0	0.0000
21060	10.40	18	2	118	1	0	0	0	0	0.0000
21070	11.90	18	1	150	1	0	0	0	0	0.0000
21080	11.40	18	2	152	1	0	0	0	0	0.0000
21090	11.20	18	2	153	1	0	0	0	0	0.0000
21100	19.30	18	3	154	1	0	0	0	0	0.0000
21110	14.90	18	2	156	1	0	0	0	0	0.0000
21120	-6.30	18	1	50	-1	0	0	0	0	0.0000
21130	20.90	19	1	154	1	0	0	0	0	0.0000
21140	-9.60	19	1	50	-3	0	0	0	0	0.0000
21150	22.50	20	1	109	1	0	0	0	0	0.0000
21160	39.70	20	2	50	-2	112	2	0	0	0.0000
21170	16.60	20	1	154	1	0	0	0	0	0.0000
21180	-7.40	20	1	50	-3	0	0	0	0	0.0000
21190	38.60	23	3	109	2	0	0	0	0	0.0000
21200	-10.00	23	1	50	-2	0	0	0	0	0.0000
21210	-5.60	24	1	50	-2	103	1	0	0	0.0000
21220	13.90	25	1	50	-2	0	0	0	0	0.0000
21230	26.00	26	1	108	1	0	0	0	0	0.0000
21240	0.40	26	1	50	-2	0	0	0	0	0.0000
21250	1.00	27	1	50	-4	0	0	0	0	0.0000
21260	34.30	28	2	101	3	0	0	0	0	0.0000
21270	1.30	28	1	50	-2	103	1	0	0	0.0000
21280	13.60	28	2	108	3	0	0	0	0	0.0000
21290	25.20	28	1	109	1	0	0	0	0	0.0000
21300	12.90	28	1	117	1	0	0	0	0	0.0000
21310	-21.20	28	1	50	-3	0	0	0	0	0.0000
21320	11.10	29	2	108	3	0	0	0	0	0.0000
21330	22.10	29	1	109	1	0	0	0	0	0.0000
21340	25.30	29	2	156	3	0	0	0	0	0.0000
21350	-21.00	29	1	50	-3	0	0	0	0	0.0000
21360	31.60	30	1	50	-1	0	0	0	0	0.0000
21370	20.50	31	1	156	2	0	0	0	0	0.0000

<u>Species</u>		<u>Four Pairs of Component ID and</u>								<u>Comment</u>
<u>ID</u>	<u>Log K</u>	<u>Stoichiometric Coefficient</u>								
21380	-44.40	31	1	50	-4	0	0	0	0	0.0000
21390	12.90	32	1	101	1	0	0	0	0	0.0000
21400	3.40	32	1	113	1	0	0	0	0	0.0000
21410	10.40	32	1	156	1	0	0	0	0	0.0000
21420	-5.70	32	1	50	-2	0	0	0	0	0.0000
21430	-5.70	32	1	50	-2	0	0	0	0	0.0000
21440	25.40	50	2	112	1	0	0	0	0	0.0000
21450	45.30	7	1	108	2	99	-2	0	0	0.0000
21460	6.40	6	3	50	-8	99	1	0	0	0.0000
21470	-42.00	8	1	50	-4	99	-2	0	0	0.0000
21480	-61.70	8	3	50	-8	99	-2	0	0	0.0000
21490	-25.70	8	1	50	-3	99	-1	0	0	0.0000
21500	-49.20	15	1	50	-4	99	-2	0	0	0.0000
21560	11.40	9	1	99	2	0	0	0	0	0.0000
21520	28.70	14	1	99	2	0	0	0	0	0.0000
21530	16.20	108	1	99	-2	0	0	0	0	0.0000

1 Gass

25000	18.00	50	2	101	1	0	0	0	0	0.0000
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APPENDIX B: INPUT DATA SETS OF EXAMPLE PROBLEMS

B.1 Input Data Set of Problem No. 1

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1 TEST OF HYDROGEOCHEM: TRANSPORT MODULE - FOUR COMPONENTS                                00010
C ***** DATA SET 2: BASIC INTEGER PARAMTERS
82 40 1 0 3 1 8 -1 1 0 1 0 30 1 150 0 0 0
C ***** DATA SET 3: BASIC REAL PARAMETERS
0.50D0 0.0D0 0.50D00 15.0D0 1.0D0 1.0D0 1.0D0 1.0D00 1.0D-5 1.0D0
C ***** DATA SET 4: PRINT AND AUXILIARY STORGE CONTROL
4444
0000
1.0D38
C ***** DATA SET 5: CHEMICAL PRINTOUT AND CHEMICAL PROPERTY TYPE INDICATOR
3
1 41 82      NODEP
1 81 1 1 1
0 0 0 0 0      END OF NODEP(I,2)
C ***** DATA SET 6: MATERIAL PROPERTIES
2.0D-3 0.0D0 0.0D0 1.2D0 0.0 0.0 0.0 0.0 0.0 AL AT AM RHOB CEC CAP1 CAP2 SREA
C ***** DATA SET 7: NODE COORDINATES
1 40 2      0.0      0.0      0.0
2 40 2      0.025D0 0.0D0      0.0D0
0 0 0      0.0      0.0      0.0      END OF X-COORD
1 40 2      0.0D0 0.025D0      0.0D0
2 40 2      0.0D0 0.025D0      0.0
0 0 0      0.0D0 0.0D0      0.0D0      END OF Z-COORD
C ***** DATA SET 8: ELEMENT CONNECTIVITY
1 1 2 4 3 1 1 40      IE
C ***** DATA SET 10: CHEMICAL COMPONENT INFORMATION
4
CHEM 1      1      0
CHEM 2      2      1
CHEM 3      3      1
CHEM 4      4      1
C ***** DATA SET 11: INITIAL CONDITIONS
1 81 1 1.0D-4 0.0D0 0.0D0
0 0 0 0.0      0.0      0.0      END OF I.C. FIRST CHEMICAL
1 81 1 1.0D-4 0.0D0 0.0D0
0 0 0 0.0      0.0      0.0      END OF I.C. SECOND CHEMICAL
1 81 1 1.0D-4 0.0D0 0.0D0
0 0 0 0.0      0.0      0.0      END OF I.C. THIRD CHEMICAL
1 81 1 1.0D-4 0.0D0 0.0D0
0 0 0 0.0      0.0      0.0      END OF I.C. FOURTH CHEMICAL
C ***** DATA SET 12: CONTROL INTEGERS FOR TRANSIENT SOURCE/SINK AND B.C.
0 0 0 0 0 0 2 1 2 2 1 1 2 NSEL NSPR NSDP NWNP NWPR NWDP NDNF NDPR NDDP
C ***** DATA SET 14: VARIABLE BOUNDARY CONDITIONS
0.0D0 0.00D00 1.0D38 0.00D00
1 0 0 1 0
0 0 0 0 0      END OF B.C. FIRST CHEMICAL

```

```

0.0D0 0.000D00 1.0D38 0.00D00
1 0 0 1 0
0 0 0 0 0
0.0D0 0.0D00 1.0D38 0.00D00
1 0 0 1 0
0 0 0 0 0
0.0D0 0.0D0 1.0D38 0.00D00
1 0 0 1 0
0 0 0 0 0
1 1 1 1 1
0 0 0 0 0
1 0 1 1 2 0 0 0 0
0 0 0 0 0 0 0 0 0
END OF B.C. SECOND CHEMICAL
END OF B.C. THIRD CHEMICAL
END OF B.C. FOURTH CHEMICAL
END NPVB
END OF ISV
C ***** DATA SET 15: DIRICHLET BOUNDARY CONDITIONS
0.0D0 1.0D-3 1.0D38 1.0D-3
1 1 1 1 0
0 0 0 0 0
0.0D0 1.0D-3 1.0D38 1.0D-3
1 1 1 1 0
0 0 0 0 0
0.0D0 1.0D-3 1.0D38 1.0D-3
1 1 1 1 0
0 0 0 0 0
0.0D0 1.0D-3 1.0D38 1.0D-3
1 1 1 1 0
0 0 0 0 0
1 1 1 81 1
0 0 0 0 0
END OF NPDB
C ***** DATA SET 16: HYDROLOGICAL VARIABLES
1 81 1 0.0 -1.000D-2 0.0 0.0
0 0 0 0.0 0.0 0.0 0.0
1 39 1 0.3 0.0 0.0
0 0 0 0.0 0.0 0.0
END OF VELOCITY
END OF TH
C ***** DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
4 0 0 4 0 0 50 1.0D-6 1.0D-6 1.0D-6
C ***** DATA SET 18: H+, E-, IONIC STRENGTH AND SORPTION INFORMATION
0.0 0 0 0
298.0 1.0 0 0 0 0
-20.0 20.0 0.0 20.0 PEMN PEMX PHMN PHMX
C ***** DATA SET 19: COMPONENT SPECIES AND THEIR ION-EXCHANGE INDEX
FREE CHEMICAL 1 0
0.0D0 C 0 CW VJ IONEX
FREE CHEMICAL 2 0
0.0D0 0 0 CW VJ IONEX
FREE CHEMICAL 3 0
0.0D0 0 0 CW VJ IONEX
FREE CHEMICAL 4 0
0.0D0 0 0 CW VJ IONEX
C ***** DATA SET 21: ADSORBED SPECIES
SORBED CHEMICAL 1 0

```

```

0.0D0 -38.0 1 0 0 0 CW PKID AXYZP
SORBED CHEMICAL 2      0
0.0D0 -0.9542425 0 1 0 0
SORBED CHEMICAL 3      0
0.0D0 0.0      0 0 1 0
SORBED CHEMICAL 4      0
0.0D0 0.9542425 0 0 0 1

```

END OF JOB

B.2 Input Data Set of Problem No. 2

```

2 TEST OF HYDROGEOCHEM: EQUILIBRIUM MODULE - AQUEOUS COMPLEXAION      000 5
C ***** DATA SET 2: BASIC INTEGER PARAMTERS
6 2 1 0 3 1 8 -1 1 0 1 0 10 1 50 0 0 0
C ***** DATA SET 3: BASIC REAL PARAMETERS
0.50D0 0.0D0 0.50D00 15.0D0 1.0D0 1.0D0 1.0D0 1.0D00 1.0D-5 1.0D0
C ***** DATA SET 4: PRINT AND AUXILIARY STORGE CONTROL
5555
0000
1.0D38
C ***** DATA SET 5: CHEMICAL OUTPUT AND CHEMICAL PORPERTY TYPE INDICATOR
3
1 3 6      NODEP
1 5 1 1 0
0 0 0 0 0  END OF NODEP(I,2)
C ***** DATA SET 6: MATERIAL PROPERTIES
2.0D-3 0.0D0 0.0D0 1.0D0 0.0 0.0 0.0 0.0 AL AT AM RHOB CEC CAP1 CAP2 SREA
C ***** DATA SET 7: NODE COORDINATES
1 2 2      0.0 0.0 0.0
2 2 2      1.0 0.0 0.0
0 0 0      0.0 0.0 0.0      END OF X-COORD
1 2 2      0.0 1.0 0.0
2 2 2      0.0 1.0 0.0
0 0 0      0.0 0.0 0.0      END OF Z-COORD
C ***** DATA SET 8: ELEMENT CONNECTIVITY
1 1 2 4 3 1 1 2      IE
C ***** DATA SET 10: CHEMICAL COMPONENT INFORMATION
4
SODIUM      1 1
LEAD        2 1
HYDROGEN    3 3
CHLORIDE    4 1
C ***** DATA SET 11: INITIAL CONDITIONS
1 5 1 1.0D-1 0.0D0 0.0D0
0 0 0 0.0D00 0.0D0 0.0D0      END OF I.C. SODIUM
1 5 1 2.9D-4 0.0D0 0.0D0
0 0 0 0.0D00 0.0D0 0.0D0      END OF I.C. LEAD
1 5 1 -7.10535 0.0D0 0.0D0

```

```

0 0 0 0.0D00 0.0D0 0.0D0 END OF I.C. HYDROGEN
1 5 1 1.0D-1 0.0D0 0.0D0
0 0 0 0.0D00 0.0D0 0.0D0 END OF I.C. CHLORIDE
C ***** DATA SET 12: CONTROL INTEGERS FOR TRANSIENT SOURCE/SINK AND B.C.
0 0 0 0 0 0 2 1 2 2 1 1 2 NSEL NSPR NSDP NWNP NWPR NWDP NDNP NDPR NDDP
C ***** DATA SET 14: VARIABLE BOUNDARY CONDITIONS
0.0D0 0.0D00 1.0D38 0.0D00
1 0 0 1 0
0 0 0 0 0 END OF B.C. SODIUM
0.0D0 0.000D00 1.0D38 0.000D00
1 0 0 1 0
0 0 0 0 0 END OF B.C. LEAD
0.0D0 0.0D00 1.0D38 0.0D00
1 0 0 1 0
0 0 0 0 0 END OF B.C. HYDROGEN
0.0D0 0.0D0 1.0D38 0.0D0
1 0 0 1 0
0 0 0 0 0 END OF B.C. CHLORIDE
1 1 1 1 1
0 0 0 0 0 END NPVB
1 0 1 1 2 0 0 0 0
0 0 0 0 0 0 0 0 0 END OF ISV
C ***** DATA SET 15: DIRICHLET BOUNDARY CONDITIONS
0.0D0 1.0D-1 1.0D38 1.0D-1
1 1 1 1 0
0 0 0 0 0 END OF B.C. SODIUM
0.0D0 2.9D-4 1.0D38 2.9D-4
1 1 1 1 0
0 0 0 0 0 END OF B. C. LEAD
0.0D0 -7.10535 1.0D38 -7.10535
1 1 1 1 0
0 0 0 0 0 END OF B.C. HYDROGEN
0.0D0 1.0D-1 1.0D38 1.0D-1
1 1 1 1 0
0 0 0 0 0 END OF B.C. CHLORIDE
1 1 1 5 1
0 0 0 0 0 END OF NPDB
C ***** DATA SET 16: HYDROLOGICAL VARIABLES
1 5 1 0.0 0.0 0.0 0.0
0 0 0 0.0 0.0 0.0 0.0 END OF VELOCITY
1 1 1 1.0 0.0 0.0
0 0 0 0.0 0.0 0.0 END OF TH
C ***** DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
4 0 2 0 0 0 50 1.0D-6 1.0D-6 1.0D-6 NONA NONS NOMX NOMY NOMZ NOMP NITERC
C ***** DATA SET 18: H+, E-, IONIC STRENGTH AND SORPTION INFORMATION
0.0 2 3 0 SICOR ICOR LNH LNE
298.0 1.0 0 0 0 0 TEMP PRESU IADS LNO LNB LNI
-20.0 20.0 0.0 20.0 PEMN PEMX PHMN PHMX
C ***** DATA SET 19: COMPONENT SPECIES AND THEIR ION-EXCHANGE INDEX
FRE NA+ 0

```

```

2.0D-3 1 0 CW VJ IONEX
FREE PB++ 0
5.8D-6 2 0 CW VJ IONEX
FREE H+ 3
7.846D-8 1 0 CW VJ IONEX
FREE CL- 0
2.0D-3 -1 0 CW VJ IONEX
C ***** DATA SET 20: COMPLEX SPECIES AND THEIR ION-EXCHANGE INDEX
OH- 0
0.0D0 -13.99 0 0 -1 0 0 0 0 0 CW(II) PKIPD AXYZP IONEX
PBOH 0
0.0D0 -7.71 0 1 -1 0 0 0 0 0 CW(II) PKIPD AXYZP IONEX
END OF JOB

```

B.3 Input Data Set of Problem No. 3

```

3 TEST OF HYDROGEOCHEM: EQUILIBRIUM MODULE - ADSORPTION 000 5
C ***** DATA SET 2: BASIC INTEGER PARAMTERS
6 2 1 0 3 1 8 -1 1 0 1 0 50 1 150 0 0 0 NNP NEL NMAT NCM NTI KSS NMPPM KVI
C ***** DATA SET 3: BASIC REAL PARAMETERS
0.50D0 0.0D0 0.50D00 15.0D0 1.0D0 1.0D0 1.0D0 1.0D00 1.0D-5 1.0D0
C ***** DATA SET 4: PRINT AND AUXILIARY STORGE CONTROL
5555
0000
1.0D38
C ***** DATA SET 5: CHEMICAL OUTPUT AND CHEMICAL PORPERTY TYPE INDICATOR
3
1 3 6 NODEP
1 5 1 1 0
0 0 0 0 0 END OF NODEP(I,2)
C ***** DATA SET 6: MATERIAL PROPERTIES
2.0D-3 0.0 0.0 1.2 0.0 1.0D-6 0.2D-6 1.37D5
C ***** DATA SET 7: NODE COORDINATES
1 2 2 0.0 0.0 0.0
2 2 2 0.025D0 0.0D0 0.0D0
0 0 0 0.0 0.0 0.0 END OF X-COORD
1 2 2 0.0D0 0.025D0 0.0D0
2 2 2 0.0D0 0.025D0 0.0
0 0 0 0.0D0 0.0D0 0.0D0 END OF Z-COORD
C ***** DATA SET 8: ELEMENT CONNECTIVITY
1 1 2 4 3 1 1 2 IE
C ***** DATA SET 10: CHEMICAL COMPONENT INFORMATION
7
SODIUM 1 3
LEAD 2 3
HYDROGEN 3 3
CHLORIDE 4 3
SOH 5 2

```



```

SIGO      6    2
SIGB      7    2
C ***** DATA SET 11:  INITIAL CONDITIONS
  1  5  1 -1.0 0.0D0  0.0D0
  0  0  0  0.0  0.0  0.0      END OF I.C. SODIUM
  1  5  1 -3.58687  0.0D0  0.0D0
  0  0  0  0.0  0.0  0.0      END OF I.C. LEAD
  1  5  1 -7.1054D0  0.0D0  0.0D0
  0  0  0  0.0  0.0  0.0      END OF I.C. HYDROGEN
  1  5  1 -1.0 0.0D0  0.0D0
  0  0  0  0.0  0.0  0.0      END OF I.C. CHLORIDE
  1  5  1  1.70D-2  0.0D0  0.0D0
  0  0  0  0.0  0.0  0.0      END OF I.C. SOH
  1  5  1  0.0  0.0D0  0.0D0
  0  0  0  0.0  0.0  0.0      END OF I.C. SIGO
  1  5  1  0.0  0.0D0  0.0D0
  0  0  0  0.0  0.0  0.0      END OF I.C. SIGB
C ***** DATA SET 12: CONTROL INTEGERS FOR TRANSIENT SOURCE/SINK AND B.C.
  0  0  0  0  0  0  2  1  2  2  1  1  2
C ***** DATA SET 14: VARIABLE BOUNDARY CONDITIONS
  0.0D0  0.00D00  1.0D38  0.00D00
  1  0  0  1  0
  0  0  0  0  0      END OF B.C. SODIUM
  0.0D0  0.000D00  1.0D38  0.000D00
  1  0  0  1  0
  0  0  0  0  0      END OF B.C. LEAD
  0.0D0  0.0D00  1.0D38  0.0D00
  1  0  0  1  0
  0  0  0  0  0      END OF B.C. HYDROGEN
  0.0D0  0.0D0  1.0D38  0.0D0
  1  0  0  1  0
  0  0  0  0  0      END OF B.C. CHLORIDE
  0.0D0  0.0D0  1.0D38  0.0D0
  1  0  0  1  0
  0  0  0  0  0      END OF B.C. SOH
  0.0D0  0.0D0  1.0D38  0.0D0
  1  0  0  1  0
  0  0  0  0  0      END OF B.C. SIGO
  0.0D0  0.0D0  1.0D38  0.0D0
  1  0  0  1  0
  0  0  0  0  0      END OF B.C. SIGB
  1  1  1  1  1
  0  0  0  0  0      END NPVB
  1  0  1  1  2  0  0  0  0
  0  0  0  0  0  0  0  0  0      END OF ISV
C ***** DATA SET 15: DIRICHLET BOUNDARY CONDITIONS
  0.0D0 -1.0  1.0D38 -1.0
  1  1  1  1  0
  0  0  0  0  0      END OF B.C. SODIUM
  0.0D0 -3.58687  1.0D38 -3.58687

```

```

1 1 1 1 0
0 0 0 0 0
0.0D0 -7.1054D0 1.0D38 -7.1054D0
1 1 1 1 0
0 0 0 0 0
0.0D0 -1.0 1.0D38 -1.0
1 1 1 1 0
0 0 0 0 0
0.0D0 1.70D-2 1.0D38 1.70D-2
1 1 1 1 0
0 0 0 0 0
0.0D0 0.0D0 1.0D38 0.0D0
1 1 1 1 0
0 0 0 0 0
0.0D0 0.0D0 1.0D38 0.0D0
1 1 1 1 0
0 0 0 0 0
1 1 1 5 1
0 0 0 0 0
C ***** DATA SET 16: HYDROLOGICAL VARIABLES
1 5 1 0.0 0.0 0.0 0.0
0 0 0 0.0 0.0 0.0 0.0
1 1 1 1.0D0 0.0 0.0
0 0 0 0.0 0.0 0.0
C ***** DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
4 3 2 6 0 0 50 1.0D-6 1.0D-6 NONA NONS NOMX NOMY NOMZ NOMP NITERC
C ***** DATA SET 18: H+, E-, IONIC STRENGTH AND SORPTION INFORMATION
0.0 2 3 0 SICOR ICOR LNH LNE
298.0 1.0 2 6 7 0 TEMP PRESU IADS LNO LNB LNI
-20.0 20.0 0.0 20.0 PEMN PEMX PHMN PHMX
C ***** DATA SET 19: COMPONENT SPECIES AND THEIR ION-EXCHANGE INDEX
FRE NA+ 3
0.1D0 1.0 0 CW(I) VJ IONEX
FREE PB++ 3
0.2589D-3 2.0 0 CW(I) VJ IONEX
FREE H+ 3
0.7846D-7 1.0 0 CW(I) VJ IONEX
FREE CL- 3
0.1D0 -1.0 0 CW(I) VJ IONEX
FREE SOH 0
0.6563D-2 0.0 0 CW(I) VJ IONEX
FREE SIGO 0
1.0D0 0.0 0 CW(I) VJ IONEX
FREE SIGB 0
1.0D0 0.0 0 CW(I) VJ IONEX
C ***** DATA SET 20: COMPLEXED SPECIES AND THEIR ION-EXCHANGE INDEX
OH- 3
1.662D-7 -13.99 0 0 -1 0 0 0 0 0
PBOH 3
3.107D-5 -7.71 0 1 -1 0 0 0 0 0

```

END OF B.C. LEAD

END OF B.C. HYDROGEN

END OF B.C. CHLORIDE

END OF B.C. SOH

END OF B.C. SIGO

END OF B.C. SIGB

END OF NPDB

END OF VELOCITY

END OF TH

C ***** DATA SET 21: ADSORBED SPECIES

SO- 0
 1.0916D-6 -11.5 0 0 -1 0 1 -1 0
 SOH2+ 0
 6.2538D-6 5.7 0 0 1 0 1 1 0
 SONA 0
 4.186D-6 -9.2 1 0 -1 0 1 -1 1
 SOPB 0
 3.301D-5 -5.0 0 1 -1 0 1 -1 2
 SOH2CL4 0
 5.1581D-3 7.9 0 0 1 1 1 1 -1
 SOPBOH 0
 5.178D-3 -2.6 0 1 -2 0 1 -1 1

END OF JOB

B.4 Input Data Set of Problem No. 4

4 TEST OF HYDROGEOCHEM: EQUILIBRIUM MODULE - ION-EXCHANGE

000 5

C ***** DATA SET 2: BASIC INTEGER PARAMTERS

6 2 1 0 3 1 8 -1 1 0 1 0 50 1 150 0 0 0 NNP NEL NMAT NCM NTI KSS NMPPM KVI

C ***** DATA SET 3: BASIC REAL PARAMETERS

0.50D0 0.0D0 0.50D00 15.0D0 1.0D0 1.0D0 1.0D0 1.0D00 1.0D-5 1.0D0

C ***** DATA SET 4: PRINT AND AUXILIARY STORGE CONTROL

5555

0000

1.0D38

C ***** DATA SET 5: CHEMICAL OUTPUT AND CHEMICAL PORPERTY TYPE INDICATOR

3

1 3 6 NODEP

1 5 1 1 0

0 0 0 0 0 END OF NODEP(1,2)

C ***** DATA SET 6: MATERIAL PROPERTIES

2.0D-3 0.0 0.0 1.0 0.6701 1.0D-6 0.2D-6 1.37D5 AL AT DM RHOB CEC CAP1 CAP2 SREA

C ***** DATA SET 7: NODE COORDINATES

1 2 2 0.0 0.0 0.0

2 2 2 0.025D0 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0

END OF X-COORD

1 2 2 0.0D0 0.025D0 0.0D0

2 2 2 0.0D0 0.025D0 0.0

0 0 0 0.0D0 0.0D0 0.0D0

END OF Z-COORD

C ***** DATA SET 8: ELEMENT CONNECTIVITY

1 1 2 4 3 1 1 2

IE

C ***** DATA SET 10: CHEMICAL COMPONENT INFORMATION

4

SODIUM 1 1
 MAGNICIUM 2 1
 CALCIUM 3 1
 CHLORIDE 4 1

```

C ***** DATA SET 11: INITIAL CONDITIONS
  1  5  1  0.2173  0.0D0  0.0D0
  0  0  0  0.0  0.0  0.0      END OF I.C. SODIUM
  1  5  1  0.1463  0.0D0  0.0D0
  0  0  0  0.0  0.0  0.0      END OF I.C. MAGNICIUM
  1  5  1  0.1562  0.0D0  0.0D0
  0  0  0  0.0  0.0  0.0      END OF I.C. CALCIUM
  1  5  1  0.1600  0.0D0  0.0D0
  0  0  0  0.0  0.0  0.0      END OF I.C. CHLORIDE
C ***** DATA SET 12: CONTROL INTEGERS FOR TRANSIENT SOURCE/SINK AND B.C.
  0  0  0  0  0  0  2  1  2  2  1  1  2
C ***** DATA SET 14: VARIABLE BOUNDARY CONDITIONS
  0.0D0  0.00D00  1.0D38  0.00D00
  1  0  0  1  0
  0  0  0  0  0      END OF B.C. SODIUM
  0.0D0  0.000D00  1.0D38  0.000D00
  1  0  0  1  0
  0  0  0  0  0      END OF B.C. MAGNICIUM
  0.0D0  0.0D00  1.0D38  0.0D00
  1  0  0  1  0
  0  0  0  0  0      END OF B.C. CALCIUM
  0.0D0  0.0D0  1.0D38  0.0D0
  1  0  0  1  0
  0  0  0  0  0      END OF B.C. CHLORIDE
  1  1  1  1  1
  0  0  0  0  0      END NPVB
  1  0  1  1  2  0  0  0  0
  0  0  0  0  0  0  0  0  0      END OF ISV
C ***** DATA SET 15: DIRICHLET BOUNDARY CONDITIONS
  0.0D0  0.2173  1.0D38  0.2173
  1  1  1  1  0
  0  0  0  0  0      END OF B.C. SODIUM
  0.0D0  0.1463  1.0D38  0.1463
  1  1  1  1  0
  0  0  0  0  0      END OF B.C. MAGNICIUM
  0.0D0  0.1562  1.0D38  0.1562
  1  1  1  1  0
  0  0  0  0  0      END OF B.C. CALCIUM
  0.0D0  0.1600  1.0D38  0.1600
  1  1  1  1  0
  0  0  0  0  0      END OF B.C. CHLORIDE
  1  1  1  5  1
  0  0  0  0  0      END OF NPDB
C ***** DATA SET 16: HYDROLOGICAL VARIABLES
  1  5  1  0.0  0.0  0.0  0.0
  0  0  0  0.0  0.0  0.0  0.0      END OF VELOCITY
  1  1  1  1.0D0  0.0  0.0
  0  0  0  0.0  0.0  0.0      END OF TH
C ***** DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
  4  0  0  0  3  0  50  1.0D-6  1.0D-6  1.0D-6  NONA  NONS  NOMX  NOMY  NOMZ  NOMP  NITERC

```

```

C ***** DATA SET 18: H+, E-, IONIC STRENGTH AND SORPTION INFORMATION
0.0 2 0 0 SICOR ICOR LNH LNE
298.0 1.0 0 0 0 1 TEMP PRESU IADS LNO LNB LNI
-20.0 20.0 0.0 20.0 PEMN PEMX PHMN PHMX
C ***** DATA SET 19: COMPONENT SPECIES AND THEIR ION-EXCHANGED SPECIES
FREE NA+ 0
0.0434D-1 1 1 CP(I) VJ(I) IONEX
SORBED NA 0
0.06525 0.000 CP(II) PK
FREE MG2+ 0
0.0895D-1 2 1 CP(I) VJ(I) IONEX
SORBED MG 0
0.06415 0.350 CP(II) PK
FREE CA2+ 0
0.0555D-1 2 1 CP(I) VJ(I) IONEX
SORBED CA 0
0.07075 0.600 CP(II) PK
FREE CL- 0
0.0800 -1 0 CP(I) VJ(I) IONEX
END OF JOB

```

B.5 Input Data Set of Problem No. 5

```

5 TEST OF HYDROGEOCHEM: AQUEOUS COMPLEXATION AND PRECIPITATION 000 5
C ***** DATA SET 2: BASIC INTEGER PARAMTERS
6 2 1 0 3 1 8 -1 1 0 1 0 10 1 50 0 0 0
C ***** DATA SET 3: BASIC REAL PARAMETERS
0.50D0 0.0D0 0.50D00 15.0D0 1.0D0 1.0D0 1.0D0 1.0D00 1.0D-5 1.0D0
C ***** DATA SET 4: PRINT AND AUXILIARY STORGE CONTROL
5555
0000
1.0D38
C ***** DATA SET 5: CHEMICAL OUTPUT AND CHEMICAL PORPERTY TYPE INDICATOR
3
1 3 6 NODEP
1 5 1 1 0
0 0 0 0 0 END OF NODEP(I,2)
C ***** DATA SET 6: MATERIAL PROPERTIES
2.0D-3 0.0D0 0.0D0 1.0D0 0.0 0.0 0.0 0.0 0.0 AL AT AM RHOB CEC CAP1 CAP2 SREA
C ***** DATA SET 7: NODE COORDINATES
1 2 2 0.0 0.0 0.0
2 2 2 0.025D0 0.0D0 0.0D0
0 0 0 0.0 0.0 0.0 END OF X-COORD
1 2 2 0.0D0 0.025D0 0.0D0
2 2 2 0.0D0 0.025D0 0.0
0 0 0 0.0D0 0.0D0 0.0D0 END OF Z-COORD
C ***** DATA SET 8: ELEMENT CONNECTIVITY
1 1 2 4 3 1 1 2 IE

```

6

C ***** DATA SET 11: INITIAL CONDITIONS

END OF I.C. CHLORIDE

0 0 0 0 0 0 2 1 2 2 1 1 2

END OF B.C. SODIUM

END OF B.C. URANIUM

END OF B. C. HYDROGEN

END OF B.C. CARBONATE

END OF B.C. SURFATE

END OF B.C. CHLORIDE

END NPVB

END OF ISV

END OF B.C. SODIUM

```

0.0D0    3.0D-3    1.0D38    3.0D-3
1 1 1 1 0
0 0 0 0 0
0.0D0    -7.0D0    1.0D38    -7.0D0
1 1 1 1 0
0 0 0 0 0
0.0D0    5.0D-3    1.0D38    5.0D-3
1 1 1 1 0
0 0 0 0 0
0.0D0    1.0D-2    1.0D38    1.0D-2
1 1 1 1 0
0 0 0 0 0
0.0D0    4.8D-1    1.0D38    4.8D-1
1 1 1 1 0
0 0 0 0 0
1 1 1 5 1
0 0 0 0 0
C ***** DATA SET 16: HYDROLOGICAL VARIABLES
1 5 1 0.0 0.0 0.0 0.0
0 0 0 0.0 0.0 0.0 0.0
1 1 1 1.0D0 0.0 0.0
0 0 0 0.0 0.0 0.0
C ***** DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
6 0 19 0 0 2 50 1.0D-6 1.0D-6 1.0D-6 NONA NONS NOMX NOMY NOMZ NOMP EPSC TOLS TOL
C ***** DATA SET 18: H+, E-, IONIC STRENGTH AND SORPTION INFORMATION
0.0 0 3 0 SICOR ICOR LNH LNE
298.0 1.0 0 0 0 0
-20.0 20.0 0.0 20.0 PEMN PEMX PHMN PHMX
C ***** DATA SET 19: COMPONENT SPECIES AND THEIR ION-EXCHANGE INDEX
FRE NA+ 0
7.94D-7 1 0 CW(I) VJ IONEX
FREE UO2++ 0
6.03D-5 2 0 CW(I) VJ IONEX
FREE H+ 3
1.0D-7 1 0 CW(I) VJ IONEX
FREE CO3-- 0
3.98D-5 -2 0 CW(I) VJ IONEX
FREE SO4-- 0
3.98D-5 -2 0 CW(I) VJ IONEX
FREE CL- 0
3.98D-5 -1 0 CW(I) VJ IONEX
C ***** DATA SET 20: COMPLEXED SPECIES AND THEIR ION-EXCHANGE INDEX
NACO3- 0
1.0D-6 1.27 1 0 0 1 0 0 0
NAHCO3 0
1.0D-5 10.08 1 0 1 1 0 0 0
NASO4- 0
1.0D-3 0.70 1 0 0 0 1 0 0
UO2OH+ 0
1.0D-7 -5.3 0 1 -1 0 0 0 0

```

END OF B.C. URANIUM

END OF B.C. HYDROGEN

END OF B.C. CARBONATE

END OF B.C. SURFATE

END OF B.C. CHLORIDE

END OF NPDB

END OF VELOCITY

END OF TH

```

(UO2)2(OH)2      0
1.0D-9 -5.68 0 2 -2 0 0 0 0
(UO2)3(OH)4      0
7.0D-9 -11.88 0 3 -4 0 0 0 0
(UO2)3(OH)5      0
3.2D-9 -15.82 0 3 -5 0 0 0 0
(UO2)4(OH)7      0
6.8D-8 -21.9 0 4 -7 0 0 0 0
(UO2)3(OH)7      0
1.0D-5 -28.34 0 3 -7 0 0 0 0
UO2CO3           0
1.0D-5 9.65 0 1 0 1 0 0 0
UO2(CO3)2        0
1.0D-4 17.08 0 1 0 2 0 0 0
UO2(CO3)3        0
1.0D-4 21.70 0 1 0 3 0 0 0
(UO2)2CO3(OH)3   0
1.0D-4 -1.18 0 2 -3 1 0 0 0
UO2CL            0
1.9D-9 -0.21 0 1 0 0 0 1 0
UO2SO4           0
1.0D-10 2.95 0 1 0 0 1 0 0
UO2(SO4)2        0
1.0D-10 4.00 0 1 0 0 2 0 0
HCO3-            0
1.0D-3 10.32 0 0 1 1 0 0 0
H2CO3            0
1.0D-4 16.67 0 0 2 1 0 0 0
HSO4-            0
1.0D-8 1.99 0 0 1 0 1 0 0
C ***** DATA SET 22: PRECIPITATED SPECIES
UO2(OH)2         0
0.0 -5.4 0 1 -2 0 0 0
UO2CO3           0
0.0 13.03 0 1 0 1 0 0

```

END OF JOB

B.6 Input Data Set of Problem No. 6

```

6 TEST OF HYDROGEOCHEM: COMPLEXATION AND ADSORPTION
C ***** DATA SET 2: BASIC INTEGER PARAMETERS
6 2 1 0 3 1 8 -1 1 0 1 0 50 1 150 0 0 0 NNP NEL NMAT NCM NTI KSS NMPPM KVI
C ***** DATA SET 3: BASIC REAL PARAMETERS
0.50D0 0.0D0 0.50D00 15.0D0 1.0D0 1.0D0 1.0D00 1.0D-5 1.0D0
C ***** DATA SET 4: PRINT AND AUXILIARY STORGE CONTROL
5555
0000
1.0D38

```

000 5

C ***** DATA SET 5: CHEMICAL OUTPUT AND CHEMICAL PORPERTY TYPE INDICATOR

3

1 3 6 NODEP

1 5 1 1 0

0 0 0 0 0 END OF NODEP(I,2)

C ***** DATA SET 6: MATERIAL PROPERTIES

2.0D-3 0.0 0.0 1.2 0.0 1.0D-6 0.2D-6 1.37D5 AL AT DM RHOB CEC CAP1 CAP2 SREA

C ***** DATA SET 7: NODE COORDINATES

1 2 2 0.0 0.0 0.0

2 2 2 0.025D0 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0

END OF X-COORD

1 2 2 0.0D0 0.025D0 0.0D0

2 2 2 0.0D0 0.025D0 0.0

0 0 0 0.0D0 0.0D0 0.0D0

END OF Z-COORD

C ***** DATA SET 8: ELEMENT CONNECTIVITY

1 1 2 4 3 1 1 2 IE

C ***** DATA SET 10: CHEMICAL COMPONENT INFORMATION

7

SODIUM 1 1

LEAD 2 1

HYDROGEN 3 3

CHLORIDE 4 1

SOH 5 2

SIGO 6 2

SIGB 7 2

C ***** DATA SET 11: INITIAL CONDITIONS

1 5 1 1.00004186D-1 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0

END OF I.C. SODIUM

1 5 1 5.50099D-3 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0

END OF I.C. LEAD

1 5 1 -7.1054D0 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0

END OF I.C. HYDROGEN

1 5 1 1.05158D-1 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0

END OF I.C. CHLORIDE

1 5 1 1.70D-2 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0

END OF I.C. SOH

1 5 1 0.0 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0

END OF I.C. SIGO

1 5 1 0.0 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0

END OF I.C. SIGB

C ***** DATA SET 12: CONTROL INTEGERS FOR TRANSIENT SOURCE/SINK AND B.C.

0 0 0 0 0 0 2 1 2 2 1 1 2

C ***** DATA SET 14: VARIABLE BOUNDARY CONDITIONS

0.0D0 0.00D00 1.0D38 0.00D00

1 0 0 1 0

0 0 0 0 0

END OF B.C. SODIUM

0.0D0 0.00D00 1.0D38 0.00D00

1 0 0 1 0

0 0 0 0 0

END OF B.C. LEAD

0.0D0 0.0D00 1.0D38 0.0D00

```

1 0 0 1 0
0 0 0 0 0
0.0D0 0.0D0 1.0D38 0.0D0
1 0 0 1 0
0 0 0 0 0
0.0D0 0.0D0 1.0D38 0.0D0
1 J 0 1 0
0 0 0 0 0
0.0D0 0.0D0 1.0D38 0.0D0
1 0 0 1 0
0 0 0 0 0
0.0D0 0.0D0 1.0D38 0.0D0
1 0 0 1 0
0 0 0 0 0
0.0D0 0.0D0 1.0D38 0.0D0
1 0 0 1 0
0 0 0 0 0
0.0D0 0.0D0 1.0D38 0.0D0
1 0 0 1 0
0 0 0 0 0
0.0D0 0.0D0 1.0D38 0.0D0
1 1 1 1 1
0 0 0 0 0
1 0 1 1 2 0 0 0 0
0 0 0 0 0 0 0 0 0
END OF B.C. HYDROGEN
END OF B.C. CHLORIDE
END OF B.C. SOH
END OF B.C. SIGO
END OF B.C. SIGB
END NPVB
END OF ISV
C ***** DATA SET 15: DIRICHLET BOUNDARY CONDITIONS
0.0D0 1.00004186D-1 1.0D38 1.00004186D-1
1 1 1 1 0
0 0 0 0 0
0.0D0 5.50099D-3 1.0D38 5.50099D-3
1 1 1 1 0
0 0 0 0 0
0.0D0 -7.1054D0 1.0D38 -7.1054D0
1 1 1 1 0
0 0 0 0 0
0.0D0 1.05158D-1 1.0D38 1.05158D-1
1 1 1 1 0
0 0 0 0 0
0.0D0 1.70D-2 1.0D38 1.70D-2
1 1 1 1 0
0 0 0 0 0
0.0D0 0.0D0 1.0D38 0.0D0
1 1 1 1 0
0 0 0 0 0
0.0D0 0.0D0 1.0D38 0.0D0
1 1 1 1 0
0 0 0 0 0
1 1 1 5 1
0 0 0 0 0
END OF B.C. SODIUM
END OF B.C. LEAD
END OF B.C. HYDROGEN
END OF B.C. CHLORIDE
END OF B.C. SOH
END OF B.C. SIGO
END OF B.C. SIGB
END NPDB
C ***** DATA SET 16: HYDROLOGICAL VARIABLES
1 5 1 0.0 0.0 0.0 0.0
0 0 0 0.0 0.0 0.0 0.0
1 1 1 1.0D0 0.0 0.0
0 0 0 0.0 0.0 0.0
END OF VELOCITY
END OF TH
C ***** DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
4 3 2 6 0 0 50 1.0D-6 1.0D-6 1.0D-6 NONA NONS NOMX NOMY NOMZ NOMP NITERC
C ***** DATA SET 18: H+, E-, IONIC STRENGTH AND SORPTION INFORMATION

```

```

0.0 2 3 0 SICOR ICOR LNH LNE
298.0 1.0 2 6 7 0 TEMP PRESU IADS LNO LNB LNI
-20.0 20.0 0.0 20.0 PEMN PEMX PHMN PHMX
C ***** DATA SET 19: COMPONENT SPECIES AND THEIR ION-EXCHANGE INDEX
FRE NA+ 0
0.1D0 1.0 0 CW(I) VJ IONEX
FREE PB++ 0
0.2589D-3 2.0 0 CW(I) VJ IONEX
FREE H+ 3
0.7846D-7 1.0 0 CW(I) VJ IONEX
FREE CL- 0
0.1D0 -1.0 0 CW(I) VJ IONEX
FREE SOH 0
0.6563D-2 0.0 0 CW(I) VJ IONEX
FREE SIGO 0
1.0D0 0.0 0 CW(I) VJ IONEX
FREE SIGB 0
1.0D0 0.0 0 CW(I) VJ IONEX
C ***** DATA SET 20: COMPLEXED SPECIES AND THEIR ION-EXCHANGE INDEX
OH- 0
1.662D-7 -13.99 0 0 -1 0 0 0 0 0
PBOH 0
3.107D-5 -7.71 0 1 -1 0 0 0 0 0
C ***** DATA SET 21: ADSORBED SPECIES
SO- 0
1.0916D-6 -11.5 0 0 -1 0 1 -1 0
SOH2+ 0
6.2538D-6 5.7 0 0 1 0 1 1 0
SONA 0
4.186D-6 -9.2 1 0 -1 0 1 -1 1
SOPB 0
3.301D-5 -5.0 0 1 -1 0 1 -1 2
SOH2CL4 0
5.1581D-3 7.9 0 0 1 1 1 1 -1
SOPBOH 0
5.178D-3 -2.6 0 1 -2 0 1 -1 1

```

END OF JOB

B.7 Input Data Set of Problem No. 7

```

7 TEST OF HYDROGEOCHEM: M: REDOX AND ACID-BASE CTIONS
C ***** DATA SET 2: BASIC INTEGER PARAMTERS
6 2 1 0 3 1 8 -1 1 0 1 0 50 1 150 0 0 0 NNP NEL NMAT NCM NTI KSS NMPPM KVI
C ***** DATA SET 3: BASIC REAL PARAMETERS
0.50D0 0.0D0 0.50D00 15.0D0 1.0D0 1.0D0 1.0D0 1.0D0 1.0D0 1.0D-5 1.0D0
C ***** DATA SET 4: PRINT AND AUXILIARY STORGE CONTROL
5555
0000

```

000 5

1.0D38

C ***** DATA SET 5: CHEMICAL OUTPUT AND CHEMICAL PORPERTY TYPE INDICATOR

3

1 3 6 NODEP

1 5 1 1 0

0 0 0 0 0 END OF NODEP(I,2)

C ***** DATA SET 6: MATERIAL PROPERTIES

2.0D-3 0.0 0.0 1.0 0.0 1.0D-6 0.2D-6 1.37D5 AL AT DM RHOB CFC CAP1 CAP2 SREA

C ***** DATA SET 7: NODE COORDINATES

1 2 2 0.0 0.0 0.0

2 2 2 0.025D0 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0 END OF X-COORD

1 2 2 0.0D0 0.025D0 0.0D0

2 2 2 0.0D0 0.025D0 C.0

0 0 0 0.0D0 0.0D0 0.0D0 END OF Z-COORD

C ***** DATA SET 8: ELEMENT CONNECTIVITY

1 1 2 4 3 1 1 2 IE

C ***** DATA SET 10: CHEMICAL COMPONENT INFORMATION

4

FERRIC 1 1

SURFATE 2 1

HYDROGEN 3 1

ELECTRON 4 1

C ***** DATA SET 11: INITIAL CONDITIONS

1 5 1 0.20000001 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0 END OF I.C. FERRIC

1 5 1 0.3000000002 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0 END OF I.C. SURFATE

1 5 1 0.001 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0 END OF I.C. HYDROGEN

1 5 1 0.000000013 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0 END OF I.C. ELECTRON

C ***** DATA SET 12: CONTROL INTEGERS FOR TRANSIENT SOURCE/SINK AND B.C.

0 0 0 0 0 0 2 1 2 2 1 1 2

C ***** DATA SET 14: VARIABLE BOUNDARY CONDITIONS

0.0D0 0.00D00 1.0D38 0.00D00

1 0 0 1 0

0 0 0 0 0 END OF B.C. FERRIC

0.0D0 0.000D00 1.0D38 0.000D00

1 0 0 1 0

0 0 0 0 0 END OF B.C. SURFATE

0.0D0 0.0D00 1.0D38 0.0D00

1 0 0 1 0

0 0 0 0 0 END OF B.C. HYDROGEN

0.0D0 0.0D0 1.0D38 0.0D0

1 0 0 1 0

0 0 0 0 0 END OF B.C. ELECTRON

1 1 1 1 1

0 0 0 0 0

1 0 1 1 2 0 0 0 0 END NPVB

```

0 0 0 0 0 0 0 0 0 0 END OF ISV
C ***** DATA SET 15: DIRICHLET BOUNDARY CONDITIONS
0.0D0 0.20000001 1.0D38 0.20000001
1 1 1 1 0
0 0 0 0 0
0.0D0 0.3000000002 1.0D38 0.3000000002
1 1 1 1 0
0 0 0 0 0
0.0D0 0.001 1.0D38 0.001
1 1 1 1 0
0 0 0 0 0
0.0D0 0.000000013 1.0D38 0.000000013
1 1 1 1 0
0 0 0 0 0
1 1 1 5 1
0 0 0 0 0
C ***** DATA SET 16: HYDROLOGICAL VARIABLES
1 5 1 0.0 0.0 0.0 0.0
0 0 0 0.0 0.0 0.0 0.0
1 1 1 1.0D0 0.0 0.0
0 0 0 0.0 0.0 0.0
C ***** DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
4 0 19 0 0 0 50 1.0D-6 1.0D-6 0.0 NONA NONS NOMX NOMY NOMZ NOMP NITERC
C ***** DATA SET 18: H+, E-, IONIC STRENGTH AND SORPTION INFORMATION
0.0 0 3 4 SICOR ICOR LNH LNE
298.0 1.0 0 0 0 0 TEMP PRESU IADS LNO LNB LNI
-20.0 20.0 0.0 20.0 PEMN PEMX PHMN PHMX
C ***** DATA SET 19: COMPONENT SPECIES AND THEIR ION-EXCHANGE INDEX
FREE FE3+ 0
1.0D-7 3 0 CP(I) VJ(I) IONEX
FREE SO4-- 0
1.0D-7 -2 0 CP(I) VJ(I) IONEX
FREE H+ 0
1.0D-3 1 0 CP(I) VJ(I) IONEX
FREE E- 1
1.0D0 -1 0
C ***** DATA SET 20: COMPLEXED SPECIES AND THEIR ION-EXCHANGE INDEX
OH- 0
1.0D-11 -13.99 0 0 -1 0 C CP(II) PKIPD AXYZP IONEX
FE3SO4 0
1.0D-7 3.92 1 1 0 0 0
FE3(SO4)2 0
1.0D-7 5.42 1 2 0 0 0
FE3(OH) 0
1.0D-7 -2.19 1 0 -1 0 0
FE3(OH)2 0
1.0D-7 -5.67 1 0 -2 0 0
FE3(OH)3 0
1.0D-7 -13.6 1 0 -3 0 0
FE3(OH)4 0

```

END OF JOB

[illegible]

```

0 0 0 0 0                                END OF NODEP(NNP,2)
C ***** DATA SET 6: MATERIAL PROPERTIES
5.0 0.0 0.0 1.2 0.0 0.0 0.0 0.0 0.0 AL AT DM ROHB CEC CAP1 CAP2 SREA
C ***** DATA SET 7: NODAL PONT COORDINATES
  1 100 2      0.0D0 0.0D0 0.0
  2 100 2      1.000D0 0.0D0 0.0D0
  0 0 0        0.0 0.0 0.0      END OF X
  1 100 2      0.0D0 1.000D0 0.0D0
  2 100 2      0.0D0 1.000D0 0.0
  0 0 0        0.0 0.0 0.0      END OF Z
C ***** DATA SET 8: ELEMENT CONNECTIVITY
  1 1 2 4 3 1 1 100      IE
C ***** DATA SET 10: CHEMICAL COMPONENT INFORMATION
5
CALCIUM      1 1
CARBONATE    2 1
MAGNICIUM    3 1
SURFATE      4 1
HYDROGEN     5 3
C ***** DATA SET 11: INITIAL CONDITIONS
  1 173 1      1.00D-4 0.0D0 0.0D0
 175 7 1      1.00D-4 0.0D0 0.0D0
 183 19 1     1.00D-4 0.0D0 0.0D0
 0 0 0        0.0 0.0 0.0      END OF I.C. CA
  1 84 2      2.00D-4 9.26D-5 0.0D0
  2 84 2      2.00D-4 9.26D-5 0.000
 171 15 2     8.00D-3 0.4D-4 0.0D0
 172 15 2     2.00D-3 0.4D-4 0.0D0
 0 0 0        0.0 0.0 0.0      END OF I.C. CO3
  1 100 2     5.0D-03 -4.0D-5 0.0D0
  2 100 2     5.0D-03 -4.0D-5 0.0D0
 0 0 0        0.0 0.0 0.0      END OF I.C. MG
  1 100 2     2.00D-3 -1.9D-5 0.0D0
  2 100 2     2.00D-3 -1.9D-5 0.0D0
 0 0 0        0.0 0.0 0.0      END OF I.C. SO4
  1 100 2    -7.70D00 -0.003D0 0.0D0
  2 100 2    -7.70D0 -0.003D0 0.0D0
 0 0 0        0.0 0.0 0.0      END OF I.C. PH
C ***** DATA SET 12: INTEGER PARAMETERS FOR SOURCES AND BOUNDARY CONDITIONS
0 0 0 0 0 0 0 1 2 4 2 2 6
C ***** DATA SET 14: VARIABLE BOUNDARY CONDITIONS
0.0 1.0D-4 0.99 1.0D-4 1.0 6.0D-3 3.5 6.0D-3 3.51 1.0D-4 200.0 1.0D-4
0.0 1.0D-4 0.99 1.0D-4 1.0 6.0D-3 3.5 6.0D-3 3.51 1.0D-4 200.0 1.0D-4
  1 0 1 1 0
  2 0 1 2 0
  0 0 0 0 0      END OF BC CA
0.0 2.0D-3 0.99 2.0D-3 1.0 2.0D-3 3.5 2.0D-3 3.51 2.0D-3 200.0 2.0D-3
0.0 2.0D-3 0.99 2.0D-3 1.0 2.0D-3 3.5 2.0D-3 3.51 2.0D-3 200.0 2.0D-3
  1 0 1 1 0
  2 0 1 2 0

```

```

      0      0      0      0      0
0.0 1.0D-3 0.99 1.0D-3 1.0 1.0D-3 3.5 1.0D-3 3.51 1.0D-3 200.0 1.0D-3
0.0 1.0D-3 0.99 1.0D-3 1.0 1.0D-3 3.5 1.0D-3 3.51 1.0D-3 200.0 1.0D-3
      1      0      1      1      0
      2      0      1      2      0
      0      0      0      0      0
                                END OF BC CO3
0.0 1.0D-4 0.99 1.0D-4 1.0 1.0D-4 3.5 1.0D-4 3.51 1.0D-4 200.0 1.0D-4
0.0 1.0D-4 0.99 1.0D-4 1.0 1.0D-4 3.5 1.0D-4 3.51 1.0D-4 200.0 1.0D-4
      1      0      1      1      0
      2      0      1      2      0
      0      0      0      0      0
                                END OF BC MG
0.0 -8.00 0.99 -8.0 1.0 -8.0 3.5 -8.0 3.51 -8.0 200.0 -8.0
0.0 -8.00 0.99 -8.0 1.0 -8.0 3.5 -8.0 3.51 -8.0 200.0 -8.0
      1      0      1      1      0
      2      0      1      2      0
      0      0      0      0      0
                                END OF SO4
      1      1      1      1      1
      3      1      1 201      1
      0      0      0      0      0
                                END OF B.C. PH
      1      0      1      1      2      0      0      0      0
      2      0 100      3      4      0      0      0      0
      0      0      0      0      0      0      0      0      0
                                END OF NPVB
                                END OF IS
C ***** DATA SET 16: VELOCITY AND MOISTURE CONTENT
      1 201      1      0.0D0 -0.500D00      0.0D0      0.0D0
      0      0      0      0.0      0.0      0.0      0.0      END OF VELOCITY
      1 99      1      0.3D0      0.0D0      0.0D0
      0      0      0      0.0      0.0      0.0      END OF MOISTURE CONTENT
C ***** DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
      5 0 12 0 0 1 50 1.0D-6 1.0D-6 1.0D-6 NONA NONS NOMX NOMY NOMZ NOMP NITERC
C ***** DATA SET 18: H+, E-, IONIC STRENGTH AND SORPTION INFORMATION
      0.0 0 5 0 SICOR ICOR LNH LNE
      298.3 1.0 0 0 0 0 TEMP PRESU IADS 0 0 0
      -20.0 20.0 -20.0 20.0
C ***** DATA SET 19: COMPONENT SPECIES AND THEIR ION-EXCHANGED SPECIES
FREE CA++      0
9.8D-5 2 0 CW(I) VJ(I) IONEX
FREE CO3--      0
2.4D-7 -2 0
FREE MG++      0
3.16D-13 2 0
FREE SO4--      0
9.80D-5 -2 0
FREE H+      3
1.86D-8 1 0
C ***** DATA SET 20: COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES
OH-      0
5.75D-7 -13.99 0 0 0 0 -1 0
CACO3      0
4.19D-8 3.22 1 1 0 0 0 0
HCACO3      0

```


END OF JOB

[illegible]

2

1 101

1 101 1 1 0

0 0 0 0 0

END OF NODEP(NNP,2)

C ***** DATA SET 6: MATERIAL PROPERTIES

1.0 0.0 0.0 1.2 0.0 0.0 0.0 0.0 AL AT DM ROHB CEC CAP1 CAP2 SREA

C ***** DATA SET 7: NODAL PONT COORDINATES

1 50 2 0.0D0 0.0D0 0.0

2 50 2 20.000D0 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0 END OF X

1 50 2 0.0D0 20.000D0 0.0D0

2 50 2 0.0D0 20.000D0 0.0

0 0 0 0.0 0.0 0.0 END OF Z

C ***** DATA SET 8: ELEMENT CONNECTIVITY

1 1 2 4 3 1 1 50 IE

C ***** DATA SET 10: CHEMICAL COMPONENT INFORMATION

8

CALCIUM 1 1

CARBONATE 2 1

URANIUM 3 1

SURFATE 4 1

NEPTUM 5 1

PLUTONIUM 6 1

HYDROGEN 7 3

SOH 8 2

C ***** DATA SET 11: INITIAL CONDITIONS

1 21 1 1.00D-4 0.0D0 0.0D0

23 19 1 1.00D-4 0.0D0 0.0D0

43 19 1 1.00D-4 0.0D0 0.0D0

63 19 1 1.00D-4 0.0D0 0.0D0

83 19 1 1.00D-4 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0 END OF I.C. CA

1 21 1 1.00D-4 0.0D0 0.0D0

23 19 1 1.00D-4 0.0D0 0.000

43 19 1 1.00D-4 0.0D0 0.0D0

63 19 1 1.00D-4 0.0D0 0.0D0

83 19 1 1.00D-4 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0 END OF I.C. CO3

1 21 1 1.0D-08 0.0D0 0.0D0

23 19 1 1.0D-08 0.0D0 0.0D0

43 19 1 1.0D-08 0.0D0 0.0D0

63 19 1 1.0D-08 0.0D0 0.0D0

83 19 1 1.0D-08 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0 END OF I.C. UO2

1 21 1 1.00D-4 0.0D0 0.0D0

23 19 1 1.00D-4 0.0D0 0.0D0

43 19 1 1.00D-4 0.0D0 0.0D0

63 19 1 1.00D-4 0.0D0 0.0D0

83 19 1 1.00D-4 0.0D0 0.0D0

0 0 0 0.0 0.0 0.0 END OF I.C. SO4

```

1 21 1 1.0D-16 0.0D0 0.0D0
23 19 1 1.0D-16 0.0D0 0.0D0
43 19 1 1.0D-16 0.0D0 0.0D0
63 19 1 1.0D-16 0.0D0 0.0D0
83 19 1 1.0D-16 0.0D0 0.0D0
0 0 0 0.0 0.0 0.0
1 21 1 1.0D-16 0.0D0 0.0D0
23 19 1 1.0D-16 0.0D0 0.0D0
43 19 1 1.0D-16 0.0D0 0.0D0
63 19 1 1.0D-16 0.0D0 0.0D0
83 19 1 1.0D-16 0.0D0 0.0D0
0 0 0 0.0 0.0 0.0
1 10 2 -7.60D00 -0.03D0 0.0D0
2 10 2 -7.60D0 -0.03D0 0.0D0
23 9 2 -7.90D00 0.00D0 0.0D0
24 9 2 -7.90D00 0.00D0 0.0D0
43 9 2 -7.90D00 0.0D0 0.0D0
44 9 2 -7.90D00 0.0D0 0.0D0
63 9 2 -7.90D00 0.0D0 0.0D0
64 9 2 -7.90D00 0.0D0 0.0D0
83 9 2 -7.90D00 0.03D0 0.0D0
84 9 2 -7.90D00 0.03D0 0.0D0
0 0 0 0.0 0.0 0.0
1 21 1 1.00D-4 0.0D0 0.0D0
23 19 1 2.50D-2 0.0D0 0.0D0
43 19 1 2.50D-2 0.0D0 0.0D0
63 19 1 1.00D-4 0.0D0 0.0D0
83 19 1 1.00D-4 0.0D0 0.0D0
0 0 0 0.0 0.0 0.0
C ***** DATA SET 12: INTEGER PARAMETERS FOR SOURCES AND BOUNDARY CONDITIONS
0 0 0 0 0 0 0 1 2 4 2 2 12
C ***** DATA SET 14: VARIABLE BOUNDARY CONDITIONS
0.0D0 1.0D-3 48.0D0 1.0D-3 52.0D00 1.0D-3 98.0D0 1.0D-3
1.02D2 1.0D-3 1.98D2 1.0D-3 2.02D02 1.0D-3 4.98D2 1.0D-3
5.02D2 1.0D-3 9.98D2 1.0D-3 1.002D03 1.0D-3 1.0D38 1.0D-3
0.0D0 1.0D-3 48.0D0 1.0D-3 52.0D00 1.0D-3 98.0D0 1.0D-3
1.02D2 1.0D-3 1.98D2 1.0D-3 2.02D02 1.0D-3 4.98D2 1.0D-3
5.02D2 1.0D-3 9.98D2 1.0D-3 1.002D03 1.0D-3 1.0D38 1.0D-3
1 0 1 1 0
2 0 1 2 0
0 0 0 0 0
0.0D0 1.0D-4 48.0D0 1.0D-4 52.0D00 1.0D-4 98.0D0 1.0D-4
1.02D2 1.0D-4 1.98D2 1.0D-4 2.02D02 1.0D-2 4.98D2 1.0D-3
5.02D2 1.0D-4 9.98D2 1.0D-3 1.002D03 1.0D-3 1.0D38 1.0D-3
0.0D0 1.0D-4 48.0D0 1.0D-4 52.0D00 1.0D-4 98.0D0 1.0D-4
1.02D2 1.0D-4 1.98D2 1.0D-4 2.02D02 1.0D-2 4.98D2 1.0D-3
5.02D2 1.0D-4 9.98D2 1.0D-3 1.002D03 1.0D-3 1.0D38 1.0D-3
1 0 1 1 0
2 0 1 2 0
0 0 0 0 0
END OF I.C. NPV
END OF I.C. PUIV
END 1ST BLK
END 2ND BLK
END 3RD BLK
END 4TH BLK
END 5TH BLK
END OF I.C. PH
END OF I.C. SOH
END OF BC CA
END OF BC CO3

```

0.0D0	1.0D-6	48.0D0	1.0D-6	52.0D00	1.0D-6	98.0D0	1.0D-6
1.02D2	1.0D-6	1.98D2	1.0D-6	2.02D02	1.0D-6	4.98D2	1.0D-6
5.02D2	1.0D-6	9.98D2	1.0D-6	1.002D03	1.0D-6	1.0D38	1.0D-6
0.0D0	1.0D-6	48.0D0	1.0D-6	52.0D00	1.0D-6	98.0D0	1.0D-6
1.02D2	1.0D-6	1.98D2	1.0D-6	2.02D02	1.0D-6	4.98D2	1.0D-6
5.02D2	1.0D-6	9.98D2	1.0D-6	1.002D03	1.0D-6	1.0D38	1.0D-6

1	0	1	1	0
2	0	1	2	0
0	0	0	0	0

END OF BC UO2

0.0D0	1.0D-4	48.0D0	1.0D-4	52.0D00	1.0D-4	98.0D0	1.0D-4
1.02D2	1.0D-4	1.98D2	1.0D-4	2.02D02	1.0D-4	4.98D2	1.0D-4
5.02D2	1.0D-4	9.98D2	1.0D-4	1.002D03	1.0D-4	1.0D38	1.0D-4
0.0D0	1.0D-4	48.0D0	1.0D-4	52.0D00	1.0D-4	98.0D0	1.0D-4
1.02D2	1.0D-4	1.98D2	1.0D-4	2.02D02	1.0D-4	4.98D2	1.0D-4
5.02D2	1.0D-4	9.98D2	1.0D-4	1.002D03	1.0D-4	1.0D38	1.0D-4

1	0	1	1	0
2	0	1	2	0
0	0	0	0	0

END OF SO4

0.0D0	2.5D-10	48.0D0	2.5D-10	52.0D00	2.5D-10	98.0D0	2.5D-10
1.02D2	2.5D-10	1.98D2	2.5D-10	2.02D02	2.5D-10	4.98D2	2.5D-10
5.02D2	2.5D-10	9.98D2	2.5D-10	1.002D03	2.5D-10	1.0D38	2.5D-10
0.0D0	2.5D-10	48.0D0	2.5D-10	52.0D00	2.5D-10	98.0D0	2.5D-10
1.02D2	2.5D-10	1.98D2	2.5D-10	2.02D02	2.5D-10	4.98D2	2.5D-10
5.02D2	2.5D-10	9.98D2	2.5D-10	1.002D03	2.5D-10	1.0D38	2.5D-10

1	0	1	1	0
2	0	1	2	0
0	0	0	0	0

END OF BC NP

0.0D0	1.D-09	48.0D0	1.D-09	52.0D00	1.D-09	98.0D0	1.D-09
1.02D2	1.D-09	1.98D2	1.D-09	2.02D02	1.D-09	4.98D2	1.D-09
5.02D2	1.D-09	9.98D2	1.D-09	1.002D03	1.D-09	1.0D38	1.D-09
0.0D0	1.D-09	48.0D0	1.D-09	52.0D00	1.D-09	98.0D0	1.D-09
1.02D2	1.D-09	1.98D2	1.D-09	2.02D02	1.D-09	4.98D2	1.D-09
5.02D2	1.D-09	9.98D2	1.D-09	1.002D03	1.D-09	1.0D38	1.D-09

1	0	1	1	0
2	0	1	2	0
0	0	0	0	0

END OF BC PU4

0.0D0	-7.6D0	48.0D0	-7.6D0	52.0D00	-7.6D00	98.0D0	-7.6D0
1.02D2	-7.6D0	1.98D2	-7.6D0	2.02D02	-7.6D00	4.98D2	-7.6D0
5.02D2	-7.6D0	9.98D2	-7.6D0	1.002D03	-7.6D00	1.0D38	-7.6D0
0.0D0	-7.6D0	48.0D0	-7.6D0	52.0D00	-7.6D00	98.0D0	-7.6D0
1.02D2	-7.6D0	1.98D2	-7.6D0	2.02D02	-7.6D00	4.98D2	-7.6D0
5.02D2	-7.6D0	9.98D2	-7.6D0	1.002D03	-7.6D00	1.0D38	-7.6D0

1	0	1	1	0
2	0	1	2	0
0	0	0	0	0

END OF B.C. PH

0.0D0	1.0D-3	48.0D0	1.0D-3	52.0D00	1.0D-3	98.0D0	1.0D-3
1.02D2	1.0D-3	1.98D2	1.0D-3	2.02D02	1.0D-3	4.98D2	1.0D-3
5.02D2	1.0D-3	9.98D2	1.0D-3	1.002D03	1.0D-3	1.0D38	1.0D-3
0.0D0	1.0D-3	48.0D0	1.0D-3	52.0D00	1.0D-3	98.0D0	1.0D-3
1.02D2	1.0D-3	1.98D2	1.0D-3	2.02D02	1.0D-3	4.98D2	1.0D-3

```

5.02D2    1.0D-3    9.98D2    1.0D-3    1.002D03    1.0D-3    1.0D38    1.0D-3
1 0 1 1 0
2 0 1 2 0
0 0 0 0 0
1 1 1 1 1
3 1 1 101 1
0 0 0 0 0
1 0 1 1 2 0 0 0 0
2 0 50 3 4 0 0 0 0
0 0 0 0 0 0 0 0 0
END OF BC SOH (NOT USED)
END OF NPVB
END OF IS
C ***** DATA SET 16: VELOCITY AND MOISTURE CONTENT
1 101 1 0.0D0 3.000D00 0.0D0 0.0D0
0 0 0 0.0 0.0 0.0 0.0 END OF VELOCITY
1 49 1 0.3D0 0.0D0 0.0D0
0 0 0 0.0 0.0 0.0 END OF MOISTURE CONTENT
C ***** DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
7 1 23 5 0 0 50 1.0D-6 1.0D-6 1.0D-6 NONA NONS NOMX NOMY NOMZ NOMY NITERC
C ***** DATA SET 18: H+, E-, IONIC STRENGTH AND SORPTION INFORMATION
0.0 0 7 0 SICOR ICOR LNH LNE
298.3 1.0 0 0 0 0 TEMP PRESU IADS 0 0 0
-20.0 20.0 -20.0 20.0
C ***** DATA SET 19: COMPONENT SPECIES AND THEIR ION-EXCHANGED SPECIES
FREE CA++ 0
9.8D-5 2 0 CW(I) VJ(I) IONEX
FREE CO3-- 0
2.4D-7 -2 0
FREE UO2++ 0
3.16D-13 2 0
FREE SO4-- 0
9.80D-5 -2 0
FREE NPO2 0
3.55D-17 1 0
FREE PU4+ 0
1.0D-16 4 0
FREE H+ 3
1.78D-8 1 0
FREE SOH 0
9.93D-5 0 0
C ***** DATA SET 20: COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES
OH- 0
5.75D-7 -13.99 0 0 0 0 0 0 -1 0 0
CACO3 0
4.19D-8 3.22 1 1 0 0 0 0 0 0
HCACO3 0
1.21D-7 11.43 1 1 0 0 0 0 1 0 0
CASO4 0
1.96D-6 2.31 1 0 0 1 0 0 0 0
CAOH 0
7.77D-10 -12.85 1 0 0 0 0 0 -1 0 0
UO2OH 0

```

```

7.75D-11 -5.3  0 0 1 0 0 0 -1 0  0
(UO2)2(OH)2      0
5.0D-16  -5.68 0 0 2 0 0 0 -2 0  0
(UO2)3(OH)4
2.74D-19 -11.88 0 0 3 0 0 0 -4 0  0
(UO2)3(OH)5      0
1.77D-15 -15.82 0 0 3 0 0 0 -5 0  0
(UO2)4(OH)7      0
1.28D-18 -21.90 0 0 4 0 0 0 -7 0  0
(UO2)3(OH)7      0
1.69D-12 -28.34 0 0 3 0 0 0 -7 0  0
(UO2)(CO3)       0
3.17D-10  9.65  0 1 1 0 0 0  0 0  0
(UO2)(CO3)2      0
2.20D-9   17.08 0 2 1 0 0 0  0 0  0
(UO2)(CO3)3      0
2.36D-11  21.70 0 3 1 0 0 0  0 0  0
(UO2)2(CO3)(OH)3  0
2.29D-10  -1.18 0 1 2 0 0 0 -3 0  0
(UO2)(SO4)       0
2.40D-14   2.95 0 0 1 1 0 0  0 0  0
(UO2)(SO4)2
2.64D-17   4.00 0 0 1 2 0 0  0 0  0
HCO3           0
9.58D-5   10.32 0 1 0 0 0 0  1 0  0
H2CO3         0
3.81D-6    16.67 0 1 0 0 0 0  2 0  0
HSO4          0
1.70D-10    1.99 0 0 0 1 0 0  1 0  0
(NPO2)(OH)     0
2.70D-18  -8.85 0 0 0 0 1 0 -1 0  0
(NPO2)(CO3)    0
3.48D-18    5.60 0 1 0 0 1 0  0 0  0
(NPO2)(CO3)2   0
1.27D-22    7.75 0 2 0 0 1 0  0 0  0
C ***** DATA SET 21: ADSORBED SPECIES
SO             0
2.80D-7  -10.30 0 0 0 0 0 0 -1 1
SOH2           0
4.43D-7    5.40 0 0 0 0 0 0  1 1
(UO2)(OH)2(SOH) 0
6.86D-9   -7.10 0 0 1 0 0 0 -2 1
(UO2)3(OH)8(SOH) 0
2.07D-11 -31.00 0 0 3 0 0 0 -8 1
(NPO2)(OH)(SOH) 0
5.99D-17  -3.50 0 0 0 0 1 0 -1 1
END OF JOB

```

B.10 Input Data Set of Problem No. 10

10 HYDROGEOCHEM: TEST OF COUPLING - MILL TAILING PROBLEM 00010

C ***** DATA SET 2: BASIC INTEGER PARAMETERS
 192 158 1 0 3 1 8 1 1 0 1 0 10 1 300 0 1 0

C ***** DATA SET 3: BASIC REAL PARAMETERS
 2.0 0.0 4.0 265.0 1.0 1.0 1.0 1.0 1.0D-2 1.0

C ***** DATA SET 4: PRINTER AND DISK OUTPUT CONTROL AND TIME STEP RESET
 222200000020000000000200000000002000000000020000000000200000000002000000000020000000000
 11110000001000000000010000000000100000000001000000000010000000000100000000010000000001
 1.0D38

C ***** DATA SET 5: CHEMICAL PRINTOUT CONTROL AND CHEMICAL PROPERTY INDICATOR
 4
 1 26 88 180
 1 191 1 1 0
 0 0 0 0 0

END NODEP(NP,2)

C ***** DATA SET 6: MATERIAL PROPERTIES
 2.0D01 2.0D1 0.0D0 1.2D0 0.0 0.0 0.0 0.0

C ***** DATA SET 10: CHEMICAL COMPONENT INFORMATION
 7
 CALCIUM 1 1
 CARBONATE 2 1
 URANIUM 3 1
 PHOSPHATE 4 1
 SULFATE 5 1
 HYDROGEN 6 1
 FERROUS 7 1

C ***** DATA SET 11: INITIAL CONDITIONS

1	191	1	1.00D-2	0.0D0	0.0D0	
0	0	0	0.0	0.0	0.0	END OF IC CA
1	10	1	1.50D-3	0.0D0	0.0D0	
12	2	1	1.00D-2	0.0D0	0.0D0	
15	3	1	1.50D-3	0.0D0	0.0D0	
19	2	1	1.00D-2	0.0D0	0.0D0	
22	3	1	1.50D-3	0.0D0	0.0D0	
26	2	1	1.00D-2	0.0D0	0.0D0	
29	3	1	1.50D-3	0.0D0	0.0D0	
33	2	1	1.00D-2	0.0D0	0.0D0	
36	3	1	1.50D-3	0.0D0	0.0D0	
40	2	1	1.00D-2	0.0D0	0.0D0	
43	149	1	1.5D-03	0.0D0	0.0D0	
0	0	0	0.0	0.0	0.0	END OF IC CO3
1	10	1	1.00D-7	0.0D0	0.0D0	
12	2	1	5.00D-4	0.0D0	0.0D0	
15	3	1	1.00D-7	0.0D0	0.0D0	
19	2	1	5.00D-4	0.0D0	0.0D0	
22	3	1	1.00D-7	0.0D0	0.0D0	
26	2	1	5.00D-4	0.0D0	0.0D0	
29	3	1	1.00D-7	0.0D0	0.0D0	
33	2	1	5.00D-4	0.0D0	0.0D0	

36	3	1	1.00D-7	0.0D0	0.0D0
40	2	1	5.00D-4	0.0D0	0.0D0
43	149	1	1.00D-7	0.0D0	0.0D0
0	0	0	0.0	0.0	0.0
1	10	1	1.00D-6	0.0D0	0.0D0
12	2	1	1.00D-6	0.0D0	0.0D0
15	3	1	1.00D-6	0.0D0	0.0D0
19	2	1	1.00D-6	0.0D0	0.0D0
22	3	1	1.00D-6	0.0D0	0.0D0
26	2	1	1.00D-6	0.0D0	0.0D0
29	3	1	1.00D-6	0.0D0	0.0D0
33	2	1	1.00D-6	0.0D0	0.0D0
36	3	1	1.00D-6	0.0D0	0.0D0
40	2	1	1.00D-6	0.0D0	0.0D0
43	149	1	1.00D-6	0.0D0	0.0D0
0	0	0	0.0	0.0	0.0
1	10	1	2.00D-2	0.0D0	0.0D0
12	2	1	2.00D-1	0.0D0	0.0D0
15	3	1	2.00D-2	0.0D0	0.0D0
19	2	1	2.00D-1	0.0D0	0.0D0
22	3	1	2.00D-2	0.0D0	0.0D0
26	2	1	2.00D-1	0.0D0	0.0D0
29	3	1	2.00D-2	0.0D0	0.0D0
33	2	1	2.00D-1	0.0D0	0.0D0
36	3	1	2.00D-2	0.0D0	0.0D0
40	2	1	2.00D-1	0.0D0	0.0D0
43	149	1	2.00D-2	0.0D0	0.0D0
0	0	0	0.0	0.0	0.0
1	10	1	1.00D-3	0.0D0	0.0D0
12	2	1	2.00D-1	0.0D0	0.0D0
15	3	1	1.00D-3	0.0D0	0.0D0
19	2	1	2.00D-1	0.0D0	0.0D0
22	3	1	1.00D-3	0.0D0	0.0D0
26	2	1	2.00D-1	0.0D0	0.0D0
29	3	1	1.00D-3	0.0D0	0.0D0
33	2	1	2.00D-1	0.0D0	0.0D0
36	3	1	1.00D-3	0.0D0	0.0D0
40	2	1	2.00D-1	0.0D0	0.0D0
43	149	1	1.00D-3	0.0D0	0.0D0
0	0	0	0.0	0.0	0.0
1	10	1	1.00D-7	0.0D0	0.0D0
12	2	1	3.50D-2	0.0D0	0.0D0
15	3	1	1.00D-7	0.0D0	0.0D0
19	2	1	3.50D-2	0.0D0	0.0D0
22	3	1	1.00D-7	0.0D0	0.0D0
26	2	1	3.50D-2	0.0D0	0.0D0
29	3	1	1.00D-7	0.0D0	0.0D0
33	2	1	3.50D-2	0.0D0	0.0D0
36	3	1	1.00D-7	0.0D0	0.0D0
40	2	1	3.50D-2	0.0D0	0.0D0

END OF IC UO2

END OF IC PO4

END OF IC SO4

END OF IC H


```

43 149 1 1.00D-7 0.0D0 0.0D0
0 0 0 0.0 0.0 0.0 END OF IC FE2
C ***** DATA SET 12: INTEGER PARAMETERS FOR SOURCE AND BOUNDARY CONDITIONS
0 0 0 0 0 0 15 1 2 22 21 2 2
C ***** DATA SET 14: VARIABLE BOUNDARY CONDITIONS
0.0D0 1.00D-3 1.0D38 1.00D-3
0.0D0 1.00D-3 1.0D38 1.00D-3
1 16 1 1 0
18 3 1 2 0
0 0 0 0 0 END OF BC CA
0.0D0 1.50D-3 1.0D38 1.50D-3
0.0D0 1.50D-3 1.0D38 1.50D-3
1 16 1 1 0
18 3 1 2 0
0 0 0 0 0 END OF BC CO3
0.0D0 1.0D-08 1.0D38 1.0D-08
0.0D0 1.00D-8 1.0D38 1.00D-8
1 16 1 1 0
18 3 1 2 0
0 0 0 0 0 END OF BC UO2
0.0D0 1.00D-6 1.0D38 1.00D-6
0.0D0 1.00D-6 1.0D38 1.00D-6
1 16 1 1 0
18 3 1 2 0
0 0 0 0 0 END OF BC PO4
0.0D0 1.00D-4 1.0D38 1.00D-4
0.0D0 1.00D-4 1.0D38 1.00D-4
1 16 1 1 0
18 3 1 2 0
0 0 0 0 0 END OF BC SO4
0.0D0 1.00D-3 1.0D38 1.00D-3
0.0D0 1.00D-3 1.0D38 1.00D-3
1 16 1 1 0
18 3 1 2 0
0 0 0 0 0 END OF BC H
0.0D0 1.00D-7 1.0D38 1.00D-7
0.0D0 1.00D-7 1.0D38 1.00D-7
1 16 1 1 0
18 3 1 2 0
0 0 0 0 0 END OF BC FE2
1 17 1 63 7
19 1 1 181 -1
21 1 1 187 5
0 0 0 0 0 END OF NPVB
1 16 54 1 2 1 6 1 1
18 1 150 18 19 1 -1 1 1
20 1 154 20 21 1 4 1 1
0 0 0 0 0 0 0 0 0 END OF MVES
C ***** DATA SET 15: DIRICHLET BOUNDARY CONDITIONS
0.0D0 1.00D-2 1.0D38 1.00D-2

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1  14  1  1  0
0  0  0  0  0      END OF BC CA
0.0D0 1.00D-2 1.0D38 1.00D-2
1  14  1  1  0
0  0  0  0  0      END OF BC CO3
0.0D0 5.00D-4 1.0D38 5.00D-4
1  14  1  1  0
0  0  0  0  0      END OF BC UO2
0.0D0 1.00D-6 1.0D38 1.00D-6
1  14  1  1  0
0  0  0  0  0      END OF BC PO4
0.0D0 2.00D-1 1.0D38 2.00D-1
1  14  1  1  0
0  0  0  0  0      END OF BC SO4
0.0D0 2.00D-1 1.0D38 2.00D-1
1  14  1  1  0
0  0  0  0  0      END OF BC H
0.0D0 3.50D-2 1.0D38 3.50D-2
1  14  1  1  0
0  0  0  0  0      END OF BC FE2
1  2  1  12  1
4  2  1  19  1
7  2  1  26  1
10 2  1  33  1
13 2  1  40  1
0  0  0  0  0      END OF NPDB
C ***** DATA SET 17: NUMBER OF COMPONENTS AND PRODUCT SPECIES
7 0 35 0 0 14 250 1.0D-6 1.0D-6 NONA NONS NOMX NOMY NOMZ NOMP NITERC
C ***** DATA SET 18: H+, E-, IONIC STRENGTH AND SORPTION INFORMATION
0.0 0 6 0 SICOR ICOR LNH LNE
298.3 1.0 0 0 0 0 0 TEMP PRESU IADS 0 0 0
-20.0 20.0 -20.0 20.0
C ***** DATA SET 19: COMPONENT SPECIES AND THEIR ION-EXCHANGED SPECIES
FREE CA++ 0
1.92D-3 2 0 CW(I) VJ(I) IONEX
FREE CO3-- 0
1.72D-6 -2 0
FREE UO2++ 0
2.53D-13 2 0
FREE PO4--- 0
3.17D-12 -3 0
FREE SO4-- 0
1.25D-2 -2 0
FREE H+ 0
2.45D-8 1 0
FREE FE-- 0
3.34D-8 2 0
C ***** DATA SET 20: COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES
OH- 0
5.75D-7 -13.99 0 0 0 0 0 -1 0 0

```

CACO3						0			
4.19D-8	3.22	1	1	0	0	0	0	0	0
HCACO3						0			
1.21D-7	11.43	1	1	0	0	0	1	0	0
CASO4						0			
1.96D-6	2.31	1	0	0	0	1	0	0	0
CAH2(PO4)						0			
1.0D-6	20.96	1	0	0	1	0	2	0	0
CA(PO4)						0			
1.0D-6	6.46	1	0	0	1	0	0	0	0
CAH(PO4)						0			
1.0D-6	15.08	1	0	0	1	0	1	0	0
CAOH						0			
7.77D-10	-12.85	1	0	0	0	0	-1	0	0
FE(SO4)						0			
1.0D-6	2.20	0	0	0	0	1	0	1	0
FE(OH)						0			
1.0D-6	-9.50	0	0	0	0	0	-1	1	0
FE(OH)2						0			
1.0D-6	-20.57	0	0	0	0	0	-2	1	0
FE(OH)3						0			
1.0D-6	-31.00	0	0	0	0	0	-3	1	0
FE(OH)4						0			
1.0D-6	-46.00	0	0	0	0	0	-4	1	0
UO2OH						0			
7.75D-11	-5.3	0	0	1	0	0	-1	0	0
(UO2)2(OH)2						0			
5.0D-16	-5.68	0	0	2	0	0	-2	0	0
(UO2)3(OH)4						0			
2.74D-19	-11.88	0	0	3	0	0	-4	0	0
(UO2)3(OH)5						0			
1.77D-15	-15.82	0	0	3	0	0	-5	0	0
(UO2)4(OH)7						0			
1.28D-18	-21.90	0	0	4	0	0	-7	0	0
(UO2)3(OH)7						0			
1.69D-12	-28.34	0	0	3	0	0	-7	0	0
(UO2)(CO3)						0			
3.17D-10	9.65	0	1	1	0	0	0	0	0
(UO2)(CO3)2						0			
2.20D-9	17.08	0	2	1	0	0	0	0	0
(UO2)(CO3)3						0			
2.36D-11	21.70	0	3	1	0	0	0	0	0
(UO2)2(CO3)(OH)3						0			
2.29D-10	-1.18	0	1	2	0	0	-3	0	0
(UO2)(SO4)						0			
2.40D-14	2.95	0	0	1	0	1	0	0	0
(UO2)(SO4)2						0			
2.64D-17	4.00	0	0	1	0	2	0	0	0
H2(UO2)(PO4)						0			
1.0D-6	23.20	0	0	1	1	0	2	0	0

```

H3(UO2)(PO4)          0
1.0D-6    22.90 0 0 1 1 0  3 0  0
CAH4(UO2)(PO4)2        0
1.0D-6    45.24 0 0 1 2 0  4 0  0
CAH5(UO2)(PO4)2        0
1.0D-6    46.00 0 0 1 2 0  5 0  0
HCO3          0
9.58D-5    10.32 0 1 0 0 0  1 0  0
H2CO3          0
3.81D-6    16.67 0 1 0 0 0  2 0  0
HSO4          0
1.70D-10    1.99 0 0 0 0 1  1 0  0
HPO4          0
2.70D-10    12.35 0 0 0 1 0  1 0  0
H2PO4          0
3.48D-18    19.55 0 0 0 1 0  2 0  0
H3PO4          0
1.27D-22    21.75 0 0 0 1 0  3 0  0
C ***** DATA SET 22:  POTENTIALLY PRECIPITATED SPECIES
CA(SO4)          0
0.0    4.62 1 0 0 0 1  0 0
CA(CO3)          0
0.0    8.48 1 1 0 0 0  0 0
CA5(OH)(PO4)3        0
0.0    40.47 5 0 0 3 0 -1 0
FECO3          0
0.0    10.50 0 1 0 0 0  0 1
CA(UO2)2(PO4)2        0
0.0    48.61 1 0 2 2 0  0 0
CA4H(PO4)3          0
0.0    48.20 4 0 0 3 0  1 0
CAH(PO4)          0
0.0    19.30 1 0 0 1 0  1 0
CA(OH)2          0
0.0   -21.90 1 0 0 0 0 -2 0
FE3(PO4)2          0
0.0    33.30 0 0 0 2 0  0 3
FE(OH)2          0
0.0   -12.10 0 0 0 0 0 -2 1
(UO2)(OH)2          0
0.0    -5.40 0 0 1 0 0 -2 0
(UO2)(CO3)          0
0.0    14.11 0 1 1 0 0  0 0
FE(UO2)2(PO4)2        0
0.0    46.00 0 0 2 2 0  0 1
H(UO2)(PO4)          0
0.0    25.00 0 0 1 1 0  1 0

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END OF JOB

END

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