

Chemistry Implementation in PFLOTRAN: Colloids, Surface Complexation, Ion Exchange, Biogeochemistry with Monode Kinetics, Precipitation/Dissolution, Solid Solutions, Species-Dependent Diffusion, Pitzer Model, ...

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1 Reading the Thermodynamic Database

1.1 Database Format

The thermodynamic database stores all chemical reaction properties (equilibrium constant $\log K_r$, reaction stoichiometry ν_{ir} , species valence z_i , Debye parameter a_i , mineral molar volume \bar{V}_m , and formula weight w_i) used in PFLOTTRAN, with the exception of ion exchange. Reactions included in the database consist of aqueous complexation, mineral precipitation and dissolution, gaseous reactions, and surface complexation. The database is divided in five sections: database primary species, aqueous complex reactions, gaseous reactions, mineral reactions, and surface complexation. The format of the database is set up as shown in Table 1. Equilibrium constants are stored at the temperatures: $\{0, 25, 60, 100, 150, 200, 250, 300\}^\circ\text{C}$. In the standard database the equilibrium constants are interpolated using a least squares fit to the Meier-Kelly expansion

$$\log K = c_{-1} \ln T + c_0 + c_1 T + \frac{c_2}{T} + \frac{c_3}{T^2}, \quad (1)$$

with coefficients c_i . As a consequence the entries in the database are not exactly reproduced at the corresponding temperatures.

Table 1: Thermodynamic database format.

Primary Species:	name, a_0 , z , w
Secondary Species:	name, nspec, ($\nu(n)$, name(n), $n=1$, nspec), $\log K(1:8)$ a_0 , z , w
Gaseous Species:	name, \bar{V} , nspec, ($\nu(n)$, name(n), $n=1$, nspec), $\log K(1:8)$, w
Minerals:	name, \bar{V} , nspec, ($\nu(n)$, name(n), $n=1$, nspec), $\log K(1:8)$, w
Surface Complexes:	>name, nspec, ($\nu(n)$, name(n), $n=1$, nspec), $\log K(1:8)$, z , w

Redox reactions in the standard database are usually written in terms of $\text{O}_{2(g)}$. Complexation reactions involving redox sensitive species are written in such a manner as to preserve the redox state.

1.2 Primary Species: Transforming the Database

The user must first select a set of aqueous primary species in terms of which the reactions in the database are then transformed. This is typically carried out as follows. For an arbitrary reaction corresponding to an aqueous complex that is read from the database with the form

$$\emptyset \rightleftharpoons \sum_i \nu_{ir} \mathcal{A}_i, \quad (2)$$

with \emptyset representing the null species, the species are partitioned into primary and secondary species leading to the reaction

$$\emptyset \rightleftharpoons \sum_j \nu_{jr} \mathcal{A}_j + \sum_i \nu_{ir} \mathcal{A}_i. \quad (3)$$

Because, by construction, the matrix ν_{ir} is nonsingular, it can be inverted to give the canonical form

$$\sum_j \tilde{\nu}_{ji} \mathcal{A}_j \rightleftharpoons \mathcal{A}_i, \quad (4)$$

where

$$\tilde{\nu}_{ji} = - \sum_r \nu_{jr} (\nu^{-1})_{ri}. \quad (5)$$

These reactions are presumed to apply to both aqueous complexes and gaseous reactions. For mineral reactions, the database form

$$\sum_j \nu_{jm} \mathcal{A}_j + \sum_i \nu_{im} \mathcal{A}_i \rightleftharpoons \mathcal{M}_m, \quad (6)$$

is transformed by eliminating the secondary species \mathcal{A}_i using Eqn.(4) to give

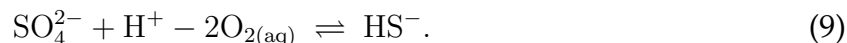
$$\sum_j \tilde{\nu}_{jm} \mathcal{A}_j \rightleftharpoons \mathcal{M}_m, \quad (7)$$

where

$$\tilde{\nu}_{jm} = \nu_{jm} + \sum_i \tilde{\nu}_{ji} \nu_{im}. \quad (8)$$

2 Homogeneous Reactions

Homogeneous reactions taking place within the aqueous phase can either be governed by local equilibrium relations or by kinetics as, for example, in sulfate reduction described by the reaction



In this reaction sulfur is transformed through electron transfer from S^{VI} to $\text{S}^{-\text{II}}$. Here it is necessary to ensure that complexes do not mix different redox states together. For example, the reactions



and



preserve the sulfur redox state and can be consider to be in local equilibrium.

Local equilibrium reactions can always be written in the canonical form

$$\sum_j \nu_{ji} \mathcal{A}_j \rightleftharpoons \mathcal{A}_i. \quad (12)$$

Kinetic reactions depend on the specific mechanism and are assumed to have the general form

$$\emptyset \rightleftharpoons \sum_i \nu_{ir} \mathcal{A}_i. \quad (13)$$

Breaking this reaction out into primary and secondary species gives

$$\emptyset \rightleftharpoons \sum_j \nu_{jr} \mathcal{A}_j + \sum_i \nu_{ir} \mathcal{A}_i. \quad (14)$$

Eliminating the secondary species \mathcal{A}_i yields the reactions

$$\emptyset \rightleftharpoons \sum_j \tilde{\nu}_{jr} \mathcal{A}_j, \quad (15)$$

where

$$\tilde{\nu}_{jr} = \nu_{jr} + \sum_i \nu_{ji} \nu_{ir}. \quad (16)$$

The transport equations in the presence of homogeneous reactions take the form

$$\frac{\partial}{\partial t} \varphi C_j + \nabla \cdot \mathbf{F}_j = - \sum_i \nu_{ji} I_i + \sum_r \tilde{\nu}_{jr} I_r, \quad (17)$$

for primary species, and

$$\frac{\partial}{\partial t} \varphi C_i + \nabla \cdot \mathbf{F}_i = I_i, \quad (18)$$

for secondary species. Noting that the rates I_i for local equilibrium reactions are determined through algebraic mass action equations providing the concentrations of secondary species, these rates can be eliminated to yield the primary species transport equations

$$\frac{\partial}{\partial t} \varphi \Psi_j + \nabla \cdot \Omega_j = \sum_r \tilde{\nu}_{jr} I_r, \quad (19)$$

where the total concentration Ψ_j and flux Ω_j are defined by

$$\Psi_j = C_j + \sum_i \nu_{ji} C_i, \quad (20)$$

and

$$\Omega_j = \mathbf{F}_j + \sum_i \nu_{ji} \mathbf{F}_i. \quad (21)$$

The flux \mathbf{F}_k has the usual form with contributions from advection and diffusion/dispersion given by

$$\mathbf{F}_k = \mathbf{q}C_k - \varphi D \nabla C_k, \quad (22)$$

with diffusion/dispersion coefficient D assumed to be identical for all species. This condition is relaxed in the section below on species-dependent diffusion. The concentration of the i th secondary species is given by the relation

$$m_i = \gamma_i^{-1} \prod_j (\gamma_j m_j)^{\nu_{ji}}, \quad (23)$$

where the molality m_l is related to molarity C_l by the approximate expression

$$C_l = \rho_w m_l, \quad (24)$$

where ρ_w denotes the density of pure water. Activity coefficients γ_l are obtained from the Debye-Hückel algorithm

$$\log \gamma_i = -\frac{z_i^2 A \sqrt{\mathcal{I}}}{1 + B \overset{\circ}{a}_i \sqrt{\mathcal{I}}} + b \mathcal{I}, \quad (25)$$

and the Davies algorithm defined by the expression

$$\log \gamma_i = -\frac{z_i^2}{2} \left[\frac{\sqrt{\mathcal{I}}}{1 + \sqrt{\mathcal{I}}} - 0.3 \mathcal{I} \right]. \quad (26)$$

The ionic strength \mathcal{I} is defined by

$$\mathcal{I} = \frac{1}{2} \sum_j z_j^2 m_j + \frac{1}{2} \sum_i z_i^2 m_i, \quad (27)$$

with molality m_l and valence z_l . In the case of the Debye-Hückel and Davies algorithms, the activity coefficients are determined by solving a nonlinear equation for the ionic strength. For high ionic strength solutions, the Pitzer model must be used which is described in a later section.

3 Mineral Precipitation/Dissolution Reactions

Mineral precipitation/dissolution reactions are assumed to have the form

$$\sum_j \nu_{jm} \mathcal{A}_j \rightleftharpoons \mathcal{M}_m. \quad (28)$$

The rate law based on transition state theory has the general form

$$\hat{I}_m = -\text{sgn}_m s_m \left(\sum_l \mathcal{P}_{ml} k_{ml} \right) \left| 1 - (K_m Q_m)^{\frac{1}{\sigma_m}} \right|^{\beta_m}, \quad (29)$$

$$= -\text{sgn}_m s_m \left(\sum_l \mathcal{P}_{ml} k_{ml} \right) \left| 1 - e^{-A_m/(\sigma_m RT)} \right|^{\beta_m}, \quad (30)$$

where the affinity A_m is defined as

$$A_m = -RT \ln K_m Q_m, \quad (31)$$

the quantity sgn_m denotes the sign of the affinity factor

$$\text{sgn}_m = \frac{1 - (K_m Q_m)^{1/\sigma_m}}{|1 - (K_m Q_m)^{1/\sigma_m}|}, \quad (32)$$

where K_m represents the equilibrium constant, Q_m denotes the ion activity product

$$Q_m = \prod_j (\gamma_j C_j)^{\nu_{jm}}, \quad (33)$$

the prefactor \mathcal{P}_{ml} is defined as the product of contributions from primary and secondary species:

$$\mathcal{P}_{ml} = \left[\prod_{j=1}^{N_c} \frac{a_j^{\alpha_{jl}^m}}{1 + K_{jl} a_j^{\beta_{jl}^m}} \right] \left[\prod_{i=1}^{N_{cx}} \frac{a_i^{\alpha_{il}^m}}{1 + K_{il} a_i^{\beta_{il}^m}} \right], \quad (34)$$

k_{ml} denotes the kinetic rate constant for the l th parallel reaction, s_m denotes the specific mineral surface area participating in the reaction, σ_m denotes Temppkin's constant, a_i represents the activity of the i th species, and α_{jl}^m , α_{il}^m are constants. A transport-limited form of the rate law can be devised according to the expression

$$\hat{I}_m = -s_m \sum_l \mathcal{P}_{ml} k_{ml} \left[\frac{1 - (K_m Q_m)^{1/\sigma_m}}{1 + \frac{k_{ml}}{r_m^{\text{lim}}} (K_m Q_m)^{1/\sigma_m}} \right], \quad (35)$$

with transport-limited rate r_{lim} . In the limit $K_m Q_m \rightarrow \infty$, the rate becomes

$$\lim_{K_m Q_m \rightarrow \infty} \hat{I}_m = r_m^{\text{lim}} s_m \sum_l \mathcal{P}_{ml}. \quad (36)$$

Adding mineral precipitation/dissolution to the mass conservation equations yields

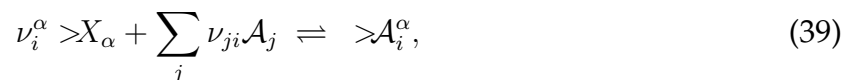
$$\frac{\partial}{\partial t} \varphi \Psi_j + \nabla \cdot \Omega_j = \sum_r \tilde{\nu}_{jr} I_r - \sum_m \nu_{jm} I_m, \quad (37)$$

$$\frac{\partial \varphi_m}{\partial t} = \bar{V}_m I_m. \quad (38)$$

4 Sorption

4.1 Surface Complexation Reactions

Surface complexation reactions are assumed to have the general form



for surface complex $>A_i^\alpha$ and empty surface site $>X_\alpha$ on surface sites designated by α . Each surface site α corresponds to a particular type of site s_m associated with a particular mineral \mathcal{M}_m . Thus $\alpha = (m, s_m)$ can be represented by two indices m and s_m . Conservation of surface sorption sites is expressed as

$$\omega_\alpha = S_X^\alpha + \sum_i \nu_i^\alpha S_i^\alpha, \quad (40)$$

where the surface site concentration ω_α is given by

$$\omega_\alpha = \frac{N_\alpha}{V} = \frac{N_\alpha}{A_m} \frac{A_m}{M_m} \frac{M_m}{V_m} \frac{V_m}{V} = \eta_m^\alpha \mathcal{A}_m \rho_m \varphi_m. \quad (41)$$

The reaction rate:

$$I_i^\alpha = k_i^{\alpha f} (S_X^\alpha)^{\nu_i^\alpha} \prod_j a_j^{\nu_{ji}} - k_i^{\alpha b} S_i^\alpha \quad (42)$$

The mass conservation equations in the presence of surface complexation reactions have the form

$$\frac{\partial}{\partial t} \varphi \Psi_j + \nabla \cdot \Omega_j = - \sum_{i\alpha} \nu_{ji} I_i^\alpha, \quad (43)$$

$$\frac{\partial S_i^\alpha}{\partial t} = I_i^\alpha, \quad (44)$$

$$\frac{\partial S_X^\alpha}{\partial t} = - \sum_i \nu_i^\alpha I_i^\alpha. \quad (45)$$

Eliminating the reaction rates I_i^α leads to the equations

$$\frac{\partial}{\partial t} \left\{ \varphi \Psi_j + \sum_{i\alpha} \nu_{ji} S_i^\alpha \right\} + \nabla \cdot \Omega_j = 0. \quad (46)$$

4.1.1 Site Conservation

Note that the sorption site concentration ω_α is conserved with respect to surface complexation reactions:

$$\left(\frac{\partial \omega_\alpha}{\partial t} \right)_{surf. \atop cplx} = \frac{\partial S_X^\alpha}{\partial t} + \sum_i \nu_i^\alpha \frac{\partial S_i^\alpha}{\partial t} = 0. \quad (47)$$

However, precipitation/dissolution reactions can lead to a change in ω_α :

$$\left(\frac{\partial \omega_\alpha}{\partial t} \right)_{precip. \atop /diss.} = \eta_m^\alpha \mathcal{A}_m \rho_m \frac{\partial \varphi_m}{\partial t}, \quad (48)$$

$$= \eta_m^\alpha \mathcal{A}_m \rho_m \bar{V}_m I_m. \quad (49)$$

4.1.2 Bulk Properties

In many cases surface complexation properties are specified in terms of bulk properties of the porous medium: η_b , \mathcal{A}_b , ρ_b , φ . To represent this situation a fictitious mineral \mathcal{M}_{m_0} may be entered with properties that reproduce the bulk density of the system by taking $W_{m_0} \bar{V}_{m_0}^{-1} \varphi_{m_0} = \rho_b$.

4.1.3 Implementation

Implementing surface complexation involves summing over complexes associated with different sites on different minerals. The structure of the sum has the form

$$\sum_{i\alpha} S_i^\alpha = \sum_{m=1}^M \sum_{s=s_1(m)}^{s_2(m)} \sum_{i=i_1(l)}^{i_2(i)} S_i^{ms} \quad (50)$$

Local Equilibrium:

$$S_i^\alpha = K_i^\alpha Q_i (S_X^\alpha)^{\nu_i^\alpha}, \quad (51)$$

$$Q_i = \prod_j a_j^{\nu_{ji}}, \quad (52)$$

$$\omega_\alpha = S_X^\alpha + \sum_i \nu_i^\alpha (S_X^\alpha)^{\nu_i^\alpha} K_i^\alpha Q_i. \quad (53)$$

Jacobian:

$$C_l \frac{\partial S_X}{\partial C_l} = - \frac{\sum \nu_{li} \nu_i S_i}{1 + \frac{1}{S_X} \sum \nu_i^2 S_i} \quad (54)$$

$$C_l \frac{\partial S_i}{\partial C_l} = \nu_{li} S_i + \nu_i S_i \frac{C_l}{S_X} \frac{\partial S_X}{\partial C_l}, \quad (55)$$

$$= \nu_{li} S_i - \nu_i S_i \frac{\sum_{i'} \nu_{li'} \nu_{i'} S_{i'}}{S_X + \sum_{i'} \nu_{i'}^2 S_{i'}}, \quad (56)$$

$$= S_i \left\{ \nu_{li} - \frac{\nu_i \sum_{i'} \nu_{li'} \nu_{i'} S_{i'}}{S_X + \sum_{i'} \nu_{i'}^2 S_{i'}} \right\} \quad (57)$$

$$C_l \frac{\partial \Psi_j^S}{\partial C_l} = C_l \sum_i \nu_{ji} \frac{\partial S_i}{\partial C_l}, \quad (58)$$

$$= \sum_i \nu_{ji} S_i \left[\nu_{li} - \frac{\nu_i \sum_{i'} \nu_{li'} \nu_{i'} S_{i'}}{S_X + \sum_{i'} \nu_{i'}^2 S_{i'}} \right], \quad (59)$$

$$= \sum_i \nu_{ji} \nu_{li} S_i - \frac{1}{S_X + \sum_{i'} \nu_{i'}^2 S_{i'}} \left(\sum_i \nu_{ji} \nu_i S_i \right) \left(\sum_{i'} \nu_{li'} \nu_{i'} S_{i'} \right) \quad (60)$$

Special Case: $\nu_i^\alpha = 1$

$$\omega_\alpha = S_X^\alpha + \sum_i S_i^\alpha \quad (61)$$

$$S_X^\alpha = \frac{\omega_\alpha}{1 + \sum_i K_i^\alpha Q_i} \quad (62)$$

$$S_i^\alpha = \frac{\omega_\alpha K_i^\alpha Q_i}{1 + \sum_{i'} K_{i'}^\alpha Q_{i'}} \quad (63)$$

$$C_l \frac{\partial S_i}{\partial C_l} = \nu_{li} S_i - \frac{\omega Q_i}{(1 + \sum Q_{i'})^2} \sum \nu_{li'} Q_{i'}, \quad (64)$$

$$= \nu_{li} S_i - S_i \frac{1}{\omega} \sum \nu_{li'} S_{i'}, \quad (65)$$

$$= S_i \left[\nu_{li} - \frac{1}{\omega} \sum \nu_{li'} S_{i'} \right]. \quad (66)$$

$$C_l \frac{\partial \Psi_j^S}{\partial C_l} = C_l \sum_i \nu_{ji} \frac{\partial S_i}{\partial C_l}, \quad (67)$$

$$= \sum_i \nu_{ji} S_i \left[\nu_{li} - \frac{1}{\omega} \sum \nu_{li'} S_{i'} \right], \quad (68)$$

$$= \sum_i \nu_{ji} \nu_{li} S_i - \frac{1}{\omega} \left(\sum \nu_{ji} S_i \right) \left(\sum \nu_{li'} S_{i'} \right). \quad (69)$$

Residual:

$$R_{j+} = \sum_i \nu_{ji} I_i V_n \quad (70)$$

$$R_i = (S_i^{k+1} - S_i^k) \frac{V_n}{\Delta t} - I_i V_n \quad (71)$$

$$R_X = (S_X^{k+1} - S_X^k) \frac{V_n}{\Delta t} + \sum_i I_i V_n \quad (72)$$

Jacobian:

$$\frac{\partial R_j}{\partial C_l} += \sum_i \nu_{ji} \frac{\partial I_i}{\partial C_l} V_n \quad (73)$$

$$\frac{\partial R_j}{\partial S_i} += \sum_i \nu_{ji} \frac{\partial I_i}{\partial S_i} V_n \quad (74)$$

$$\frac{\partial R_j}{\partial S_X} += \sum_i \nu_{ji} \frac{\partial I_i}{\partial S_X} V_n \quad (75)$$

$$\frac{\partial R_i}{\partial C_l} = -\frac{\partial I_i}{\partial C_l} V_n \quad (76)$$

$$\frac{\partial R_i}{\partial S_i} = \frac{V_n}{\Delta t} - \frac{\partial I_i}{\partial S_i} V_n \quad (77)$$

$$\frac{\partial R_i}{\partial S_X} = -\frac{\partial I_i}{\partial S_X} V_n \quad (78)$$

$$\frac{\partial R_X}{\partial C_l} = \sum_i \frac{\partial I_i}{\partial C_l} V_n \quad (79)$$

$$\frac{\partial R_X}{\partial S_i} = \sum_i \frac{\partial I_i}{\partial S_i} V_n \quad (80)$$

$$\frac{\partial R_X}{\partial S_X} = \frac{V_n}{\Delta t} + \sum_i \frac{\partial I_i}{\partial S_X} V_n \quad (81)$$

$$C_l \frac{\partial I_i}{\partial C_l} = \nu_{ji} k_i^f S_X Q_i \quad (82)$$

$$\frac{\partial I_i}{\partial S_i} = -k_i^b \quad (83)$$

$$\frac{\partial I_i}{\partial S_X} = k_i^f Q_i \quad (84)$$

4.1.4 Input File Structure

F77 programing style:

```
SURFACE_COMPLEX
min1 areal
  >fsite1 den1
    >srf1
    >srf2
    >srf3
  END
  >fsite2 den2
```

```
        >srf4
        >srf5
      END
    END
  min2 area2
    >fsite3 den3
    >srf6
    >srf7
  END
END
END
```

F90 object oriented programming style:

```
SORPTION
  SURFACE_COMPLEXATION_RXN
    MINERAL min1
    SITE      >fsite1 den1
    SURFACE_COMPLEXES
    >srf1
    >srf2
    >srf3
  END
END
  SURFACE_COMPLEXATION_RXN
    MINERAL min1
    SITE      >fsite2 den2
    SURFACE_COMPLEXES
    >srf4
    >srf5
  END
END
  SURFACE_COMPLEXATION_RXN
    MINERAL min2
    SITE      >fsite3 den3
    SURFACE_COMPLEXES
    >srf6
    >srf7
  END
END
END
```

4.2 Ion Exchange Reactions

Ion exchange reactions may be represented either in terms of bulk- or mineral-specific rock properties. Changes in bulk sorption properties can be expected as a result of min-

eral reactions. However, only the mineral-based formulation enables these effects to be captured in the model. The bulk rock sorption site concentration ω_α , in units of moles of sites per bulk sediment volume (mol/dm^3), is related to the bulk cation exchange capacity Q_α (mol/kg) by the expression

Ion exchange reactions can be expressed in the form

$$\frac{1}{z_j} \mathcal{A}_j + \frac{1}{z_i} X_{z_i} \mathcal{A}_i \rightleftharpoons \frac{1}{z_i} \mathcal{A}_i + \frac{1}{z_j} X_{z_j} \mathcal{A}_j, \quad (85)$$

with valencies z_j, z_i of cations \mathcal{A}_j and \mathcal{A}_i , respectively. The reference cation is denoted by the subscript j and the subscript $i \neq j$ represents all other cations. The mass action equation is given by

$$K_{ji} = \left(\frac{X_j^\alpha}{a_j} \right)^{1/z_j} \left(\frac{a_i}{X_i^\alpha} \right)^{1/z_i}, \quad (86)$$

where, using the Gaines-Thomas convention, the equivalent fractions X_k are defined by

$$X_k^\alpha = \frac{z_k S_k^\alpha}{\sum_l z_l S_l^\alpha} = \frac{z_k}{\omega_\alpha} S_k^\alpha, \quad (87)$$

with

$$\sum_k X_k^\alpha = 1, \quad (88)$$

The site concentration ω_α is defined by

$$\omega_\alpha = \sum_k z_k S_k^\alpha, \quad (89)$$

where ω_α is related to the cation exchange capacity Q_α (CEC) by the expression

$$\omega_\alpha = (1 - \varphi) \rho_s Q_\alpha, \quad (90)$$

with solid density ρ_s and porosity φ .

For equivalent exchange ($z_j = z_i = z$), an explicit expression exists for the sorbed concentrations given by

$$S_j^\alpha = \frac{\omega_\alpha}{z} \frac{k_j C_j}{\sum_l k_l C_l}, \quad (91)$$

where C_k denotes the k th cation concentration. This expression follows directly from the mass action equations and conservation of exchange sites.

4.2.1 Kinetic Formulation of Ion Exchange

The simplest approach to developing a kinetic formulation of ion exchange is to assume simple reaction kinetics in which the rate is equal to the difference between the forward and backward rates with concentrations raised to powers of the reaction stoichiometric coefficients. This form of the rate law, however, is not unique (with the exception of monovalent exchange) and depends on the stoichiometry used to write the exchange reaction. As long as the same final equilibrium state is obtained, the correctness of the form of the rate law cannot be ascertained without further experiment effort.

4.2.2 Kinetic Rate Laws

The kinetic reaction rate for reaction (85) has the following form

$$I_{ji} = k_{ji}^f a_j^{1/z_j} X_i^{1/z_i} - k_{ji}^b a_i^{1/z_i} X_j^{1/z_j}, \quad (92a)$$

and for reaction (??) the form

$$\tilde{I}_{ji} = \tilde{k}_{ji}^f a_j^{z_i} X_i^{z_j} - \tilde{k}_{ji}^b a_i^{z_i} X_j^{z_j}. \quad (92b)$$

Although the reaction rates I_{ji} and \tilde{I}_{ji} corresponding to reactions (85) and (??) are not simply related, the equilibrium constants for the corresponding reactions are related by the expression

$$\tilde{K}_{ji} = (K_{ji})^{z_j z_i}. \quad (93)$$

The ratio of the forward and backward rate constants are equal to the equilibrium constants according to

$$K_{ji} = \frac{k_{ji}^f}{k_{ji}^b}, \quad (94)$$

and similarly for \tilde{K}_{ji} .

4.2.3 Mass Conservation Relations

Mass conservation equations including homogeneous aqueous reactions, mineral precipitation and dissolution, and ion exchange with the form (85) using cation \mathcal{A}_j as reference cation have the form

$$\frac{\partial}{\partial t} \varphi \Psi_j + \nabla \cdot \Omega_j = -\frac{1}{z_j} \sum_{i \neq j} I_{ji} - \sum_m \nu_{jm} I_m, \quad (95a)$$

$$\frac{\partial}{\partial t} \varphi \Psi_j + \nabla \cdot \Omega_j = \frac{1}{z_i} I_{ji} - \sum_m \nu_{im} I_m, \quad (95b)$$

for aqueous primary species with mineral reaction rates I_m . Sorbed concentrations obey the conservation equations

$$\frac{\partial S_j}{\partial t} = \frac{1}{z_j} \sum_{i \neq j} I_{ji}, \quad (96a)$$

$$\frac{\partial S_i}{\partial t} = -\frac{1}{z_i} I_{ji}. \quad (96b)$$

Similar expressions hold for the exchange reactions of the form of reactions (??) but with different stoichiometric exchange coefficients

$$\frac{\partial}{\partial t} \varphi \Psi_j + \nabla \cdot \Omega_j = -\sum_{i \neq j} z_i \tilde{I}_{ji} - \sum_m \nu_{jm} I_m, \quad (97a)$$

$$\frac{\partial}{\partial t} \varphi \Psi_j + \nabla \cdot \Omega_j = z_j \tilde{I}_{ji} - \sum_m \nu_{im} I_m, \quad (97b)$$

with sorbed concentrations

$$\frac{\partial S_j}{\partial t} = \sum_{i \neq j} z_i \tilde{I}_{ji}, \quad (98a)$$

$$\frac{\partial S_i}{\partial t} = -z_j \tilde{I}_{ji}. \quad (98b)$$

Eliminating the exchange rates from the primary species equations gives the equation

$$\frac{\partial}{\partial t} (\varphi \Psi_j + S_j) + \nabla \cdot \Omega_j = - \sum_m \nu_{jm} I_m, \quad (99)$$

valid for all exchangeable cations and for both forms of the exchange reactions.

It follows that for both formulations exchange sites are conserved according to the result

$$\frac{\partial \omega}{\partial t} = 0. \quad (100)$$

implying that the cation exchange capacity of the porous medium is constant as must be the case.

4.2.4 Finite Difference Form

For a system with N_{ex} exchangeable cations, in a kinetic formulation there are $2 \times N_{\text{ex}}$ independent variables: $\{C_1, \dots, C_{N_{\text{ex}}}, S_1, \dots, S_{N_{\text{ex}}}\}$, consisting of the cation aqueous and sorbed concentrations.

The contribution of ion exchange to the residual function R_{kn}^{ex} for finite difference equations for the j th primary species at the n th node is given by (only the case of reactions (85) are presented here):

$$R_{jn}^{\text{ex}} = V_n \frac{\Delta S_j}{\Delta t}, \quad (101)$$

and for sorbed concentrations

$$R_{N_{\text{ex}}+j,n} = \frac{V_n}{\Delta t} (S_{jn}^{t+\Delta t} - S_{jn}^t) - \frac{V_n}{z_j} \sum_{i \neq j} I_{ji,n}, \quad (102a)$$

$$R_{N_{\text{ex}}+i,n} = \frac{V_n}{\Delta t} (S_{in}^{t+\Delta t} - S_{in}^t) + \frac{V_n}{z_i} I_{ji,n}. \quad (102b)$$

The Jacobian equations in matrix form for the contribution of exchange reactions have the structure

$$\begin{bmatrix} 0 & \frac{\partial R_j}{\partial S_k} \\ \frac{\partial R_{N_{\text{ex}}+j}}{\partial C_k} & \frac{\partial R_{N_{\text{ex}}+j}}{\partial S_k} \end{bmatrix} \begin{bmatrix} \delta C_j \\ \delta S_k \end{bmatrix} = - \begin{bmatrix} R_j \\ R_{N_{\text{ex}}+j} \end{bmatrix}, \quad (103)$$

with

$$\frac{\partial R_j}{\partial S_k} = \delta_{jk} \frac{V}{\Delta t}, \quad (104)$$

and

$$\frac{\partial R_{N_{\text{ex}}+j,n}}{\partial \ln C_{jn}} = \frac{V_n}{z_j} C_j \sum_{i \neq j} \frac{\partial I_{ji,n}}{\partial C_{jn}}, \quad (105a)$$

$$\frac{\partial R_{N_{\text{ex}}+j,n}}{\partial \ln C_{in}} = \frac{V_n}{z_j} C_i \frac{\partial I_{ji,n}}{\partial C_i}, \quad (105b)$$

$$\frac{\partial R_{N_{\text{ex}}+i,n}}{\partial \ln C_{jn}} = \frac{V_n}{z_i} C_j \frac{\partial I_{ji,n}}{\partial C_{jn}}, \quad (105c)$$

$$\frac{\partial R_{N_{\text{ex}}+i,n}}{\partial \ln C_{in}} = \frac{V_n}{z_i} C_i \frac{\partial I_{ji,n}}{\partial C_{in}}, \quad (105d)$$

$$\frac{\partial R_{N_{\text{ex}}+j,n}}{\partial S_{jn}} = \frac{V_n}{\Delta t} - \frac{V_n}{z_j} \sum_{i \neq j} \frac{\partial I_{ji,n}}{\partial S_{jn}}, \quad (106a)$$

$$\frac{\partial R_{N_{\text{ex}}+j,n}}{\partial S_{in}} = \frac{V_n}{\Delta t} - \frac{V_n}{z_j} \frac{\partial I_{ji,n}}{\partial S_i}, \quad (106b)$$

$$\frac{\partial R_{N_{\text{ex}}+i,n}}{\partial S_{jn}} = \frac{V_n}{\Delta t} + \frac{V_n}{z_i} \frac{\partial I_{ji,n}}{\partial S_{jn}}, \quad (106c)$$

$$\frac{\partial R_{N_{\text{ex}}+i,n}}{\partial S_{in}} = \frac{V_n}{\Delta t} + \frac{V_n}{z_i} \frac{\partial I_{ji,n}}{\partial S_{in}}. \quad (106d)$$

Logarithmic derivatives of the exchange reaction rates are given by

$$C_j \frac{\partial I_{ji}}{\partial C_j} = \frac{1}{z_j} k_{ji}^f a_j^{1/z_j} S_i^{1/z_i}, \quad (107a)$$

$$C_i \frac{\partial I_{ji}}{\partial C_i} = -\frac{1}{z_i} k_{ji}^b a_i^{1/z_i} S_j^{1/z_j}, \quad (107b)$$

$$S_j \frac{\partial I_{ji}}{\partial S_j} = -\frac{1}{z_j} k_{ji}^b a_i^{1/z_i} S_j^{1/z_j}, \quad (107c)$$

$$S_i \frac{\partial I_{ji}}{\partial S_i} = \frac{1}{z_i} k_{ji}^f a_j^{1/z_j} S_i^{1/z_i}. \quad (107d)$$

Note that: $\frac{df}{d \ln x} = x \frac{df}{dx}$, for any function f .

4.2.5 Input File Structure

F77 programing style:

```
ION_EXCHANGE
min1
  cec1
```

```
        >cat1
        >cat2
        >cat3
    END
    cec2
        >cat4
        >cat5
    END
    END
min2
    cec3
        >cat6
        >cat7
    END
    END
END
```

F90 object oriented programming style:

```
SORPTION
  ION_EXCHANGE_RXN
    MINERAL min1
    SITE      cec1
    CATION
    >cat1
    >cat2
    >cat3
  END
END
  ION_EXCHANGE_RXN
    MINERAL min1
    SITE      cec2
    CATION
    >cat4
    >cat5
  END
END
  ION_EXCHANGE_RXN
    MINERAL min2
    SITE      cec3
    CATION
    >cat6
    >cat7
  END
END
END
```


5 Colloid-Facilitated Transport

6 Solid Solutions

7 Biogeochemical Reactions

8 Pitzer Activity Coefficient Algorithm

9 Species-Dependent Diffusion