SANDIA REPORT

SAND2015-7985
Unlimited Release
Printed September, 2015

End-Member Formulation of Solid Solutions and Reactive Transport

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Prepared by
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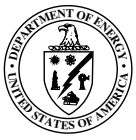

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End-Member Formulation of Solid Solutions and Reactive Transport

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Abstract

A model for incorporating solid solutions into reactive transport equations is presented based on an end-member representation. In this approach reactive transport equations are solved directly for the composition and bulk concentration of the solid solution. Reactions of a solid solution with an aqueous solution are formulated in terms of an overall stoichiometric reaction with a time-varying composition and exchange reactions, related to an end-member description of the solid solution. Reaction rates are treated kinetically using a transition state rate law for the overall reaction and a pseudo-kinetic rate law for exchange reactions. The composition of the solid solution at the onset of precipitation is assumed to correspond to the least soluble composition, equivalent to the composition at equilibrium. The stoichiometric saturation determines if the solid solution is super-saturated with respect to the aqueous solution. The method is implemented for a simple prototype batch reactor using *Mathematica* for a binary solid solution. Finally, the sensitivity of the results on the kinetic rate constant for a binary solid solution is investigated for reaction of an initially stoichiometric solid phase with an undersaturated aqueous solution.

Acknowledgments

The author would like to thank Emily Stein for reviewing the manuscript and Sandia National Laboratories for partial funding of this work.

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Nomenclature

$\mathcal{A}_j$	aqueous primary species
A	aqueous species
B	aqueous species
a_α^m	activity of αth end-member and mth solid solution
C	aqueous species
C_j	aqueous concentration of jth primary species
C_i	aqueous concentration of ith secondary species
D	aqueous diffusion coefficient
i	subscript for ith secondary species
j	subscript for jth primary species
$\boldsymbol{J}_j$	flux of jth primary species
$\boldsymbol{J}_i$	flux of ith secondary species
K_i	equilibrium constant of ith primary species
K_α^m	equilibrium constant for αth end-member and mth solid solution
k_m	rate constant for mth solid solution
k_α^m	equilibrium constant for exchange reaction for mth solid solution
$k_{\alpha m}^b$	backward rate constant for exchange reaction
$k_{\alpha m}^f$	forward rate constant for exchange reaction
$\mathcal{M}_m$	mth solid solution
$\mathcal{M}_\alpha^m$	αth end-member of mth solid solution
m_j	molality of jth primary species
N_c	number of primary species
N_M	number of solid solutions
N_m	number of end-members for mth solid solution
n_α^m	number of moles of αth end-member of mth solid solution
n_m	number of moles of mth solid solution
Q_α^m	activity product for αth end-member and mth solid solution
$\boldsymbol{q}$	Darcy velocity
$\boldsymbol{r}$	position vector
$S_{j\kappa}$	sensitivity matrix for jth primary species and κth parameter
$S_{\alpha\kappa}^m$	sensitivity matrix for αth end-member and κth parameter
SI_m	saturation index of the mth solid solution
t	time
Δt	time step

V	volume of REV
$\overline{V}_m$	molar volume of mth solid solution
$\overline{V}_\alpha^m$	molar volume of αth end-member of mth solid solution
x_α^m	mole fraction of αth end-member for mth solid solution
$\nu_{j\alpha}^m$	stoichiometric coefficient
ν_{ji}	stoichiometric coefficients for homogeneous aqueous reactions
φ	porosity
ϕ_m	volume fraction of mth solid solution
χ_α^m	concentration of αth end-member of mth solid solution
χ_m	bulk concentration of mth solid solution
Ψ_j	total concentration of jth primary species
$\mathbf{\Omega}_j$	total flux of jth primary species
Γ_α^m	reaction rate of αth end-member of mth solid solution
Γ_m	reaction rate for mth solid solution
$\Gamma_{\alpha_0\alpha}^m$	exchange reaction rate of mth solid solution
γ_j	activity coefficient of jth primary species
σ_κ	parameter for sensitivity calculation
τ	tortuosity
ζ_m	reaction index for mth solid solution

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Chapter 1

Introduction

Implementing solid solution models into reactive transport equations has languished behind incorporating other types of reactions in part because of the inherent complexity of solid solutions and the necessity to account for changes both in bulk concentration as well as compositional changes. Bruno et al. (2007) provide a comprehensive review of solid solutions applied to nuclear waste management including a discussion of multicomponent systems, order-disorder, miscibility, reciprocal solid solutions and other properties. Unlike other formulations, e.g. Nourtier-Mazauric et al. (2005), the approach proposed here is based on a kinetic framework accounting for simultaneous compositional and bulk changes in the solid solution.

In contrast to the work of Lichtner and Carey (2006) in which a discrete representation of the solid solution composition was implemented which resulted in an extremely large number of solid compositions that rapidly became impractical for solid solutions with more than a few components, in this approach the solid solution composition and bulk concentration follow directly from the solution of mass conservation equations describing the interaction with an aqueous solution. Besides the usual primary species needed to represent the aqueous solution composition, new variables providing the concentration of each end-member are added to the set of unknowns with an equal number of equations. This formulation provides direct calculation of the composition and bulk concentration of each solid solution as a function of time and space. This is in contrast to the treatment of a stoichiometric mineral which involves only a single variable providing its bulk concentration.

In what follows, first a general presentation of the method is given based on end-member components which may serve as a prototype for extension to more complex solid solutions, not considered here, including multicomponent systems, mixing of atoms on crystallographic sites or sublattices, reciprocal solutions, order-disorder and other properties combined with advective-diffusive-dispersive transport processes. The approach is applied to a binary solid solution and implemented numerically for a batch reactor using *Mathematica* (Wolfram Research, 2010). Finally, the sensitivity of the binary solid solution to the kinetic rate constant is investigated.

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Chapter 2

Methodology

The formulation which follows applies to solid solutions that can be represented by a complete set of end-members. This treatment omits more general classes of solid solutions that do not fit into this framework, but the approach should be relatively easy to extend to more complex cases.

2.1 Composition Variables

For a multicomponent solid solution $\mathcal{M}_m$ described by N_m independent end-members $\mathcal{M}_\alpha^m$, reactions representing interaction of the solid solution with an aqueous solution can be written in the general form

$$\sum_{j=1}^{N_c} \nu_{j\alpha}^m \mathcal{A}_j \;\rightleftharpoons\; \mathcal{M}_\alpha^m, \qquad (\alpha = 1, \ldots, N_m), \tag{2.1.1}$$

with N_c aqueous primary species $\mathcal{A}_j$ and stoichiometric coefficients $\nu_{j\alpha}^m$ (Lichtner and Carey, 2006; Sack and Lichtner, 2009). It is assumed that there are N_M possible solid solutions giving a total of $N_M \times N_m$ unknown quantities to represent all solid solutions in the system under consideration. In what follows greek subscripts (α, β, ...) are used to denote end-members and latin subscripts (i, j, ...) aqueous species. The index m is reserved for the mth solid solution.

The solid solution is defined by its bulk amount and its composition. Order-disorder effects are not taken into account in this formulation although future work will attempt to account for such processes. For a representative elemental volume (REV) at position $\boldsymbol{r}$ and time t, there are $n_\alpha^m(\boldsymbol{r}, t)$ moles of the αth end-member in the mth solid solution. The solid solution bulk concentration and composition is determined by $\chi_\alpha^m(\boldsymbol{r}, t)$ giving the concentration of the αth end-member defined by

$$\chi_\alpha^m(\boldsymbol{r}, t) \;=\; \frac{n_\alpha^m(\boldsymbol{r}, t)}{V}, \tag{2.1.2}$$

with REV volume V. The bulk concentration of the mth solid solution is represented by the

quantity χ_m defined by

$$\chi_m(\boldsymbol{r},\, t) \;=\; \frac{n_m(\boldsymbol{r},\, t)}{V} \;=\; \frac{1}{V}\sum_{\alpha=1}^{N_m} n_\alpha^m(\boldsymbol{r},\, t), \tag{2.1.3a}$$

$$\;=\; \sum_{\alpha=1}^{N_m} \chi_\alpha^m(\boldsymbol{r},\, t), \tag{2.1.3b}$$

equal to the sum over the individual end-member concentrations with

$$n_m(\boldsymbol{r},\, t) \;=\; \sum_{\alpha} n_\alpha^m(\boldsymbol{r},\, t). \tag{2.1.4}$$

The solid solution composition is determined by $N_m - 1$ independent end-member mole fractions x_α^m defined by

$$x_\alpha^m(\boldsymbol{r},\, t) \;=\; \frac{n_\alpha^m(\boldsymbol{r},\, t)}{n_m(\boldsymbol{r},\, t)} \;=\; \frac{\chi_\alpha^m(\boldsymbol{r},\, t)}{\chi_m(\boldsymbol{r},\, t)} \;=\; \frac{\chi_\alpha^m(\boldsymbol{r},\, t)}{\sum\limits_{\beta} \chi_\beta^m(\boldsymbol{r},\, t)}, \tag{2.1.5}$$

and satisfying

$$\sum_{\alpha=1}^{N_m} x_\alpha^m(\boldsymbol{r},\, t) \;=\; 1. \tag{2.1.6}$$

The set of composition variables x_α^m is denoted by $\{x\} = \{x_{\alpha_1}^m,\, \ldots,\, x_{\alpha_{N_m}}^m\}$.

The volume fraction $\phi_m(\boldsymbol{r},\, t)$ of the solid solution is related to its bulk concentration through the solid solution molar volume $\overline{V}_m$

$$\phi_m(\boldsymbol{r},\, t) \;=\; \frac{V_m(\boldsymbol{r},\, t)}{V(\boldsymbol{r})} \;=\; \frac{V_m(\boldsymbol{r},\, t)}{n_m(\boldsymbol{r},\, t)}\frac{n_m(\boldsymbol{r},\, t)}{V} \;=\; \overline{V}_m \chi_m(\boldsymbol{r},\, t). \tag{2.1.7}$$

The solid solution molar volume is in general a function of the solid solution composition according to the relation

$$\overline{V}_m \;=\; \sum_{\alpha} x_\alpha^m \overline{V}_\alpha^m, \tag{2.1.8}$$

where $\overline{V}_\alpha^m$ denotes the partial molar volume of the αth end-member. From the solid solution volume fraction the porosity of the porous medium can be obtained directly as

$$\varphi(\boldsymbol{r},\, t) \;=\; 1 - \sum_{m} \phi_m(\boldsymbol{r},\, t), \tag{2.1.9a}$$

$$\;=\; 1 - \sum_{m} \overline{V}_m \chi_m(\boldsymbol{r},\, t). \tag{2.1.9b}$$

In terms of ϕ_m and x_α^m the end-member concentration can be expressed as

$$\chi_\alpha^m \;=\; \overline{V}_m^{-1} x_\alpha^m \phi_m. \tag{2.1.10}$$

Complete specification of the solid solution bulk concentration and composition is specified by the variables $\{\chi^m_\alpha\}$, or equivalently $\{x^m_1, \ldots, x^m_{N_m-1}, \chi_m\}$. Alternatively, one can replace one of the end-member concentrations with the total concentration and use instead the set of variables $\{\chi^m_1, \ldots, \chi^m_{N_m-1}, \chi_m\}$.

2.2 Reactive Transport Equations

Solid solutions can occur either as primary minerals with a fixed composition or as secondary minerals with variable composition resulting from precipitation. In the case of a secondary solid solution, at the onset of precipitation the composition with the greatest saturation index is assumed to form. A further complication is that a solid solution may precipitate in layers with the consequence that the entire mineral grain or rock fragment may not react with the fluid. However, these complications are not considered further in this work.

The end-member reactions given in Eqn.(2.1.1) can be written in alternative forms by performing various linear combinations of the original reactions. Multiplying the αth end-member reaction by x^m_α and summing over all end-members gives the overall reaction

$$\sum_{j\alpha} x^m_\alpha \nu^m_{j\alpha} \mathcal{A}_j \;\rightleftharpoons\; \sum_\alpha x^m_\alpha \mathcal{M}^m_\alpha, \tag{2.2.1}$$

corresponding to composition $\{x\}$. In addition, a set of exchange reactions can be derived by choosing one of the end-members as a reference end-member denoted by $\mathcal{M}_{\alpha_0}$, and subtracting the reference end-member reaction from the remaining reactions to give

$$\sum_j^m \nu^m_{j\alpha_1} \mathcal{A}_j + \mathcal{M}^m_{\alpha_0} \;\rightleftharpoons\; \sum_j \nu^m_{j\alpha_0} \mathcal{A}_j + \mathcal{M}^m_{\alpha_1}, \tag{2.2.2a}$$

$$\sum_j^m \nu^m_{j\alpha_2} \mathcal{A}_j + \mathcal{M}^m_{\alpha_0} \;\rightleftharpoons\; \sum_j \nu^m_{j\alpha_0} \mathcal{A}_j + \mathcal{M}^m_{\alpha_2}, \tag{2.2.2b}$$

$$\cdots$$

$$\sum_j^m \nu^m_{j\alpha_{N_m-1}} \mathcal{A}_j + \mathcal{M}^m_{\alpha_0} \;\rightleftharpoons\; \sum_j \nu^m_{j\alpha_0} \mathcal{A}_j + \mathcal{M}^m_{\alpha_{N_m-1}}, \tag{2.2.2c}$$

providing N_m-1 linear independent exchange reactions. Combined with the overall reaction corresponding to composition $\{x\}$, gives a total of N_m reactions equivalent to the original set of end-member reactions.

For simplicity a fully saturated porous medium is considered with constant porosity φ. Based on the two equivalent sets of end-member reactions the reactive transport equations for an aqueous fluid reacting with a set of solid solutions can be written in the following

alternate forms for the jth primary species

$$\frac{\partial}{\partial t}\varphi\Psi_j + \boldsymbol{\nabla}\cdot\boldsymbol{\Omega}_j \;=\; -\sum_{m\alpha}\nu_{j\alpha}^m\Gamma_\alpha^m, \tag{2.2.3a}$$

$$\;=\; -\sum_{m\alpha}x_\alpha^m\nu_{j\alpha}^m\Gamma_m(\{x\}) + \sum_{m,\,\alpha\neq\alpha_0}\big(\nu_{j\alpha_0}^m - \nu_{j\alpha}^m\big)\Gamma_{\alpha_0\alpha}^m, \tag{2.2.3b}$$

where Eqn.(2.2.3a) corresponds to end-member reactions as written in Eqn.(2.1.1) with associated rates Γ_α^m, and Eqn.(2.2.3b) corresponds to reactions given in Eqns.(2.2.1) and (2.2.2) with rates Γ_m and $\Gamma_{\alpha_0\alpha}^m$, respectively. On the left-hand side of these equations the quantities Ψ_j and $\boldsymbol{\Omega}_j$ denote the total concentration and flux of the jth primary species. The total concentration is given by

$$\Psi_j \;=\; C_j + \sum_i \nu_{ji}C_i, \tag{2.2.4}$$

with primary species concentration C_j and secondary species concentration C_i. The secondary species incorporate the homogeneous equilibrium reactions

$$\sum_j \nu_{ji}\mathcal{A}_j \;\rightleftharpoons\; \mathcal{A}_i, \tag{2.2.5}$$

with stoichiometric reaction coefficients ν_{ji}, relating the concentration of primary and secondary species $\mathcal{A}_j$, $\mathcal{A}_i$, respectively, through the corresponding mass action equations (Lichtner, 1985, 1996)

$$C_i \;=\; \frac{K_i}{\gamma_i}\prod_j\big(\gamma_jC_j\big)^{\nu_{ji}}. \tag{2.2.6}$$

The total flux $\boldsymbol{\Omega}_j$ is likewise given by the sum of primary and secondary species as

$$\boldsymbol{\Omega}_j \;=\; \boldsymbol{J}_j + \sum_i \nu_{ji}\boldsymbol{J}_i, \tag{2.2.7}$$

where the flux for the kth species $\boldsymbol{J}_k$ consists of contributions from advection and diffusion for primary and secondary species

$$\boldsymbol{J}_k \;=\; \boldsymbol{q}C_k - \varphi\tau D\boldsymbol{\nabla}C_k, \tag{2.2.8}$$

with Darcy velocity $\boldsymbol{q}$, tortuosity τ, and diffusion coefficient D assumed to be species-independent. From this latter assumption it follows that the total flux can be written in terms of the total concentration according to

$$\boldsymbol{\Omega}_j \;=\; \big(\boldsymbol{q} - \varphi\tau D\boldsymbol{\nabla}\big)\Psi_j. \tag{2.2.9}$$

The solid solution concentration χ_α^m is determined from the equations

$$\frac{\partial\chi_{\alpha_0}^m}{\partial t} \;=\; \Gamma_{\alpha_0}^m, \tag{2.2.10a}$$

$$\;=\; x_{\alpha_0}^m\Gamma_m(\{x\}) - \sum_{\alpha\neq\alpha_0}\Gamma_{\alpha_0\alpha}^m, \tag{2.2.10b}$$

for reference end-member $\mathcal{M}_{\alpha_0}$, and

$$\frac{\partial \chi_\alpha^m}{\partial t} = \Gamma_\alpha^m, \tag{2.2.11a}$$

$$= x_\alpha^m \Gamma_m(\{x\}) + \Gamma_{\alpha_0\alpha}^m, \tag{2.2.11b}$$

for all other end-members $\mathcal{M}_\alpha$. These equations together with the primary species solute transport equations provide $N_c + N_m \times N_M$ equations in an equal number of unknowns ($\{C_j\}$, $\{\chi_\alpha^m\}$). The solid solution mole fraction x_α^m is related to the solid solution concentration through Eqn.(2.1.5).

It follows from the above equations that the reaction rates for the different forms of reactions are related by the expressions

$$\Gamma_{\alpha_0}^m = x_{\alpha_0}^m \Gamma_m(\{x\}) - \sum_{\alpha \neq \alpha_0} \Gamma_{\alpha_0\alpha}^m, \tag{2.2.12}$$

$$\Gamma_\alpha^m = x_\alpha^m \Gamma_m(\{x\}) + \Gamma_{\alpha_0\alpha}^m, \tag{2.2.13}$$

and conversely

$$\Gamma_m(\{x\}) = \sum_\alpha \Gamma_\alpha^m, \tag{2.2.14}$$

$$\Gamma_{\alpha_0\alpha}^m = \Gamma_\alpha^m - x_\alpha^m \sum_\beta \Gamma_\beta^m. \tag{2.2.15}$$

Thus if simple forms for the kinetic reaction rates are chosen for one set of reactions, e.g. as argued below if the transition state rate law is chosen for the overall reaction corresponding to composition $\{x\}$ and elementary rate expressions are used for exchange reactions, then the end-member reaction rates become linear combinations of these rate laws.

Adding the equations for the end-member concentrations the exchange rate terms cancel resulting in the following equation for the bulk solid solution concentration χ_m

$$\frac{\partial \chi_m}{\partial t} = \sum_\alpha \Gamma_\alpha^m = \Gamma_m. \tag{2.2.16}$$

Note that the rate of change of the bulk solid solution concentration is independent of the exchange reaction rates. In terms of the solid solution volume fraction ϕ_m assuming constant molar volume $\overline{V}_m$, the mineral mass transfer equation can be written as

$$\frac{\partial \phi_m}{\partial t} = \overline{V}_m \Gamma_m. \tag{2.2.17a}$$

In either formulation of the end-member reactions, the reaction rates can be eliminated from the primary species transport equations enabling these equations to be written in the equivalent form

$$\frac{\partial}{\partial t}\Big(\varphi \Psi_j + \sum_{m\alpha} \nu_{j\alpha}^m \chi_\alpha^m\Big) + \boldsymbol{\nabla} \cdot \boldsymbol{\Omega}_j = 0. \tag{2.2.18}$$

In this form of the transport equations the end-members reaction rates I_α^m, or I_m and $I_{\alpha_0\alpha}^m$ for the overall and exchange reactions, are eliminated from the primary species transport equations and can be replaced by appropriate algebraic mass action relations, if desired, thereby imposing local equilibrium constraints on the solution.

2.3 Kinetic Rate Laws

Constitutive relations for the kinetic rate laws must be provided to complete the set of equations. There are several different approaches that could be used. For example, one approach could associate a rate expression with each end-member reaction, perhaps based on the usual transition state rate law or a pseudo-kinetic rate law derived from elementary reactions. In the approach used here, the overall reaction is associated with a typical transition state theory based-rate law, whereas exchange reactions are associated with a pseudo-kinetic rate law based on the difference between forward and backward rates. This approach is consistent with applying the conventional transition state rate law to stoichiometric solids including dissolution of a primary solid solution of fixed composition. Ultimately, experimentally-based rate laws are required which may be difficult to achieve in practice.

Some justification for this assignment is provided in the compilation of kinetic rate constants by Palandri and Kharaka (2004) for solid solutions with varying composition. Although data is limited, rate constants for solid solutions oligoclase, andesine, labradorite, bytownite, anorthite, K-feldspar, and forsterite are included.

Equilibrium of a solid solution is determined by simultaneous equilibrium of each end-member as given by the N_m mass action equations

$$K_\alpha^m Q_\alpha^m \;=\; a_\alpha^m, \tag{2.3.1}$$

corresponding to the reactions given in Eqn.(2.1.1). In this expression K_α^m refers to the equilibrium constant, Q_α^m denotes the ion activity product, and the activity of the αth end-member for the mth solid solution is denoted by a_α^m. The activity a_α^m is related to the mole fraction x_α^m through the activity coefficient λ_α^m

$$a_\alpha^m \;=\; \lambda_\alpha^m x_\alpha^m. \tag{2.3.2}$$

The ion activity product Q_α^m is defined by

$$Q_\alpha^m \;=\; \prod_{j=1}^{N_c} \left(\gamma_j m_j\right)^{\nu_{j\alpha}^m}, \tag{2.3.3}$$

with molality m_j of the jth primary species and aqueous activity coefficient γ_j. Equilibrium of the overall reaction corresponding to composition $\{x\}$ given by Eqn.(2.2.1) is defined by the relation

$$\prod_\alpha \left(K_\alpha^m Q_\alpha^m\right)^{x_\alpha^m} \;=\; \prod_\alpha \left(a_\alpha^m\right)^{x_\alpha^m}, \tag{2.3.4}$$

or alternatively

$$\prod_{\alpha} \Big(\frac{K_{\alpha}^{m} Q_{\alpha}^{m}}{a_{\alpha}^{m}} \Big)^{x_{\alpha}^{m}} \;=\; 1. \tag{2.3.5}$$

This relation provides a constraint among the aqueous primary species for each solid solution $\mathcal{M}_m$ that is present in the system under conditions of local equilibrium.

The reaction rate corresponding to the overall reaction for the solid solution with composition $\{x\}$ given in Eqn.(2.2.1) is assumed to have the following form based on transition state theory

$$\Gamma_m(\{x\}) \;=\; -k_m A_m \big(1 - \mathrm{SI}_m(\{x\})\big) \zeta_m(\{x\}), \tag{2.3.6}$$

with the saturation index $\mathrm{SI}_m(\{x\})$ defined by

$$\mathrm{SI}_m \;=\; \prod_{\alpha} \Big(\frac{K_{\alpha}^{m} Q_{\alpha}^{m}}{a_{\alpha}^{m}} \Big), \tag{2.3.7}$$

and with kinetic rate constant k_m, in general a function of temperature and pressure, in addition to pH and other solution composition variables, and specific surface area A_m. The expression for the reaction rate is qualified by the presence or absence of the solid solution through the factor ζ_m which takes the value 1 if the solid solution is present or supersaturated, and zero otherwise

$$\zeta_m \;=\; \begin{cases} 1, & \chi_m > 0, \text{ or } \mathrm{SI}_m > 1 \\ 0, & \text{otherwise} \end{cases} . \tag{2.3.8}$$

For exchange reactions a pseudo-kinetic rate law is assumed of the form

$$\Gamma_{\alpha_0 \alpha}^{m} \;=\; k_{\alpha_0 m}^{f} a_{\alpha_0}^{m} Q_{\alpha}^{m} - k_{\alpha m}^{b} a_{\alpha}^{m} Q_{\alpha_0}^{m}, \tag{2.3.9}$$

with effective forward and backward rate constants $k_{\alpha_0 m}^{f}$ and $k_{\alpha m}^{b}$, respectively, related to the equilibrium constant for the exchange reaction by

$$K_{\alpha_0 \alpha}^{m} \;=\; \frac{k_{\alpha}^{m}}{k_{\alpha_0}^{m}} \;=\; \frac{k_{\alpha_0 m}^{f}}{k_{\alpha m}^{b}}, \tag{2.3.10}$$

where the (non-unique) constants k_{α}^{m} are introduced for simplicity (see below).

From the above analysis precipitation commences when $\mathrm{SI}_m > 1$ at the composition determined by the exchange reactions. There has been considerable discussion in the literature of the role played by stoichiometric saturation $\mathrm{SI}_m = 1$ (Glynn et al., 1990). Clearly, equilibrium of the solid solution requires that all end-members be in simultaneous equilibrium, and stoichiometric equilibrium is only a necessary but not sufficient condition. Nevertheless, the condition $\mathrm{SI}_m > 1$ for precipitation is both necessary and sufficient.

2.4 Equilibrium Exchange Relations

Contrary to a description of ion exchange, for which for equilibrium conditions an isotherm defining the sorbed concentration exists, solid solution exchange equilibrium relations do not

define isotherm relations for the solid solution end-member concentrations, i.e. it is not possible to obtain a functional relationship between the end-member concentrations and the concentrations of the aqueous primary species without solving the complete set of reactive transport equations. This is similar to a stoichiometric solid for which an isotherm for the solid concentration also does not exist. However, equilibrium isotherms do exist for the mole fraction x^m_α.

The exchange reactions determine the solid solution composition in equilibrium with a given fluid composition irrespective of χ_m, the bulk solid solution concentration, or whether or not the solid solution is under- or super-saturated. Exchange equilibrium implies the $N_m - 1$ relations

$$\frac{k^m_\alpha}{k^m_{\alpha_0}}\frac{Q^m_\alpha}{Q^m_{\alpha_0}} \;=\; \frac{a^m_\alpha}{a^m_{\alpha_0}}, \quad (\alpha \neq \alpha_0). \tag{2.4.1}$$

For an ideal solid solution these relations reduce to

$$\frac{k^m_\alpha}{k^m_{\alpha_0}}\frac{Q^m_\alpha}{Q^m_{\alpha_0}} \;=\; \frac{x^m_\alpha}{x^m_{\alpha_0}}, \tag{2.4.2}$$

with the explicit solution (see Appendix A for derivation for ideal and non-ideal cases)

$$x^m_\alpha \;=\; \frac{k^m_\alpha Q^m_\alpha}{\sum\limits_\beta k^m_\beta Q^m_\beta}. \tag{2.4.3}$$

For the non-ideal case these equations can be written in the implicit form

$$x^m_\alpha \;=\; \frac{k^m_\alpha Q^m_\alpha/\lambda^m_\alpha}{\sum\limits_\beta k^m_\beta Q^m_\beta/\lambda^m_\beta}. \tag{2.4.4}$$

Since λ^m_α is also a function of the composition x^m_α, this latter equation represents a coupled system of nonlinear equations for x^m_α. It follows from the relation $\chi^m_\alpha = x^m_\alpha \chi_m$ that

$$\chi^m_\alpha \;=\; \frac{k^m_\alpha Q^m_\alpha/\lambda^m_\alpha}{\sum\limits_\beta k^m_\beta Q^m_\beta/\lambda^m_\beta}\,\chi_m. \tag{2.4.5}$$

This expression is analogous to the Langmuir isotherm derived from ion-exchange (see Eqn.(B-9)) with the bulk solid solution concentration replacing the exchange site density or cation exchange capacity (See Appendix B). It is clear from this relation that because χ_m cannot be represented by an isotherm, neither can χ^m_α. However, the mole fraction x^m_α can be represented by an isotherm according to Eqn.(2.4.4).

It further follows that the sum appearing in Eqn.(2.2.18) can be broken up into contributions from the bulk concentration and solid solution composition according to

$$\sum_{m\alpha} \nu^m_{j\alpha}\chi^m_\alpha \;=\; \sum_m \chi_m \sum_\alpha \nu^m_{j\alpha} x^m_\alpha. \tag{2.4.6}$$

The composition $\{x\}$ under conditions of equilibrium is related to the aqueous primary species concentrations through an isotherm; however, the bulk concentration can only be obtained through solving the reactive transport equations.

2.5 Numerical Implementation

To solve the governing equations numerically it is not possible to split the conservation equations for end-member concentrations from the aqueous primary species conservation equations as is the case with stoichiometric solids (Lichtner, 1988). This is because the reaction rates depend on the solid solution composition and bulk concentration.

The solid solution volume fraction and composition can be obtained from an explicit finite difference formulation. Noting that

$$\chi_\alpha^m = \overline{V}_m^{-1} \phi_m x_\alpha^m, \tag{2.5.1}$$

the explicit finite difference form of the solid phase mass transfer equations have the form

$$\left(\overline{V}_m^{-1} \phi_m x_\alpha^m\right)_{t+\Delta t} \;=\; \left(\overline{V}_m^{-1} \phi_m x_\alpha^m\right)_t + \Delta t \, \Gamma_\alpha^m(t). \tag{2.5.2}$$

Summing this equation over all end-members yields an equation for the solid solution volume fraction

$$\left(\overline{V}_m^{-1} \phi_m\right)_{t+\Delta t} \;=\; \left(\overline{V}_m^{-1} \phi_m\right)_t + \Delta t \sum_\alpha \Gamma_\alpha^m(t). \tag{2.5.3}$$

For the special case of constant molar volume $\overline{V}_m$ these expressions simplify to

$$\left(\phi_m x_\alpha^m\right)_{t+\Delta t} \;=\; \left(\phi_m x_\alpha^m\right)_t + \Delta t \, \overline{V}_m \Gamma_\alpha^m(t), \tag{2.5.4}$$

and

$$\phi_m(t+\Delta t) \;=\; \phi_m(t) + \Delta t \, \overline{V}_m \sum_\alpha \Gamma_\alpha^m(t), \tag{2.5.5a}$$

$$\;=\; \phi_m(t) + \Delta t \, \overline{V}_m \Gamma_m(\{x\},\, t). \tag{2.5.5b}$$

With this result it is then possible to solve for the end-member mole fraction at the new time step from Eqn.(2.5.4) to give

$$x_\alpha^m(t+\Delta t) \;=\; \frac{\left(\phi_m x_\alpha^m\right)_t + \Delta t \, \overline{V}_m \Gamma_\alpha^m(t)}{\phi_m^{t+\Delta t}}, \tag{2.5.6a}$$

$$\;=\; \frac{\left(\phi_m x_\alpha^m\right)_t + \Delta t \, \overline{V}_m \Gamma_\alpha^m(t)}{\phi_m(t) + \Delta t \, \overline{V}_m \Gamma_m(\{x\},\, t)}. \tag{2.5.6b}$$

Note that if at time t

$$\sum_\alpha x_\alpha^m(t) \;=\; 1, \tag{2.5.7}$$

then it follows directly from Eqn.(2.5.6) that at time $t+\Delta t$

$$\sum_\alpha x_\alpha^m(t+\Delta t) \;=\; 1. \tag{2.5.8}$$

Calculating the effects of dissolution is straightforward in that the solid solution dissolves at a fixed composition. However, in the case of precipitation the situation is more complicated. At the onset of precipitation it is necessary to specify the composition of the precipitating solid solution. Generally it is expected that a range of compositions could be supersaturated. The assumption made is that the composition with the largest saturation index will form, equivalent to the equilibrium composition given in Eqn.(A-19). As the system evolves over time, both the composition and the bulk concentration of the solid solution will change.

Chapter 3

Binary Solid Solution Batch Reactor

In this section the general formulation presented above is applied to a binary solid solution. Dissolution of a stoichiometric solid with fixed composition and precipitation of a variable composition phase is considered.

3.1 Solid Solution Batch Reactor Differential Equations

Consider a closed batch reactor that contains the primary solid solution $\mathrm{A}_{x_0}\mathrm{B}_{1-x_0}\mathrm{C}$ with fixed composition x_0. The solid solution is presumed to be undersaturated with respect to the initial fluid in the reactor and dissolves irreversibly. As it dissolves, eventually a secondary solid solution with composition $\mathrm{A}_x\mathrm{B}_{1-x}\mathrm{C}$ begins to precipitate. A schematic illustration of these processes is shown in Figure Figure 3.1. The aqueous composition and bulk concentration of the primary solid χ_0, and composition x and bulk concentration χ of the secondary solid (or equivalently χ_1 and χ_2), vary with time until the system ultimately comes to equilibrium.

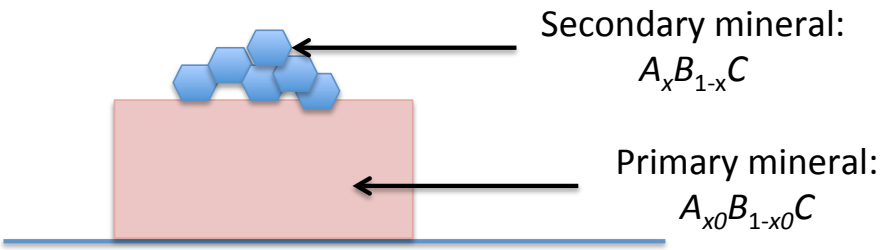

Figure 3.1: Schematic illustration of dissolution of the stoichiometric mineral $\mathrm{A}_{x_0}\mathrm{B}_{1-x_0}\mathrm{C}$ and precipitation of a secondary solid with composition $\mathrm{A}_x\mathrm{B}_{1-x}\mathrm{C}$.

Irreversible dissolution of an initial stoichiometric solid takes place according to the reaction

$$x_0\mathrm{A} + (1-x_0)\mathrm{B} + \mathrm{C} \leftarrow \mathrm{A}_{x_0}\mathrm{B}_{1-x_0}\mathrm{C}, \tag{3.1.1}$$

with fixed composition x_0. In addition, allowance is made for formation of a binary solid solution with composition $x(t)$ and total concentration $\chi(t)$ that must be determined by solving mass conservation equations. The solid solution is described by the end-member reactions

$$\mathrm{A} + \mathrm{C} \;\rightleftharpoons\; \mathrm{AC}, \tag{3.1.2a}$$
$$\mathrm{B} + \mathrm{C} \;\rightleftharpoons\; \mathrm{BC}, \tag{3.1.2b}$$

with equilibrium constants K_1 and K_2, and end-member activities denoted by a_1 and a_2. It is convenient to recast these reaction is the form of an overall reaction with variable composition x and an exchange reaction

$$x\mathrm{A} + (1-x)\mathrm{B} + \mathrm{C} \;\rightleftharpoons\; x\mathrm{AC} + (1-x)\mathrm{BC} \;\rightleftharpoons\; \mathrm{A}_x\mathrm{B}_{1-x}\mathrm{C}, \tag{3.1.3a}$$
$$\mathrm{A} + \mathrm{BC} \;\rightleftharpoons\; \mathrm{B} + \mathrm{AC}. \tag{3.1.3b}$$

This leads to the system of nonlinear ordinary differential equations

$$\frac{dC_\mathrm{A}}{dt} \;=\; -x_0\Gamma(x_0) - x\Gamma(x) - \Gamma_\mathrm{ex}, \tag{3.1.4a}$$
$$\frac{dC_\mathrm{B}}{dt} \;=\; -(1-x_0)\Gamma(x_0) - (1-x)\Gamma(x) + \Gamma_\mathrm{ex}, \tag{3.1.4b}$$
$$\frac{dC_\mathrm{C}}{dt} \;=\; -\Gamma(x_0) - \Gamma(x), \tag{3.1.4c}$$

for the concentration of aqueous species A, B, and C, and

$$\frac{d\chi_0}{dt} \;=\; \Gamma(x_0), \tag{3.1.5a}$$
$$\frac{d\chi_1}{dt} \;=\; x\Gamma(x) + \Gamma_\mathrm{ex}, \tag{3.1.5b}$$
$$\frac{d\chi_2}{dt} \;=\; (1-x)\Gamma(x) - \Gamma_\mathrm{ex}, \tag{3.1.5c}$$

for solid concentrations for the stoichiometric solid $\mathrm{A}_{x_0}\mathrm{B}_{1-x_0}\mathrm{C}$ (χ_0), and end-members AC and BC (χ_1, χ_2) of the solid solution. The reaction rate $\Gamma(x)$ is assumed to have the form

$$\Gamma \;=\; -k\Big(1 - K(x)Q(x)\Big)\zeta(x), \tag{3.1.6}$$

derived from transition state theory, with effective rate constant k, activity product Q defined as

$$Q(x) \;=\; C_\mathrm{A}^x C_\mathrm{B}^{1-x} C_\mathrm{C}, \tag{3.1.7}$$

and equilibrium constant $K(x)$ given by

$$K(x) \;=\; \left(\frac{K_1}{a_1(x)}\right)^x \left(\frac{K_2}{a_2(x)}\right)^{1-x}. \tag{3.1.8}$$

The factor ζ has the value zero or one depending on the saturation state of the solid

$$\zeta(x) \;=\; \begin{cases} 1, \;\chi > 0 \text{ or } K(x)Q(x) > 1 \\ 0, \;\text{otherwise} \end{cases}, \tag{3.1.9}$$

where χ refers to the total solid solution concentration

$$\chi(t) \;=\; \chi_1(t) + \chi_2(t). \tag{3.1.10}$$

The solid composition $x(t)$ is obtained from χ_1 and χ_2 as

$$x(t) \;=\; \frac{\chi_1(t)}{\chi(t)}. \tag{3.1.11}$$

Thus the rate vanishes if the fluid is undersaturated with respect to the solid ($KQ < 1$) and the solid is not present ($\chi = 0$). This provision allows for the solid to be absent initially (secondary mineral), and to completely dissolve at later times. When the solid solution first appears it must be assigned an initial composition x_{init}. This value is assumed to be determined by the maximum saturation index, given by

$$x_{\text{init}}(t) \;=\; \frac{K_1 C_{\text{A}}}{K_1 C_{\text{A}} + K_2 C_{\text{B}}}, \tag{3.1.12}$$

which also corresponds to the solid composition in equilibrium with the fluid (see Appendix A).

The exchange rate Γ_{ex} is assumed to have the form of an elementary reaction written as the difference between forward and backward rates

$$\begin{aligned}
\Gamma_{\text{ex}} \;&=\; k_f a_{\text{A}} a_2 - k_b a_{\text{B}} a_1, && (3.1.13)\\
&=\; -k_b a_{\text{B}} a_1 \left(1 - \frac{K_1 a_{\text{A}} a_{\text{C}}/a_1}{K_2 a_{\text{B}} a_{\text{C}}/a_2}\right), && (3.1.14)\\
&=\; -k_b a_{\text{B}} a_1 \left(1 - \frac{\text{SI}_1}{\text{SI}_2}\right), && (3.1.15)
\end{aligned}$$

with forward k_f and backward k_b rate constants satisfying

$$\frac{k_f}{k_b} \;=\; \frac{K_1}{K_2}. \tag{3.1.16}$$

Eqns.(3.1.4)–(3.1.5) are subject to the initial conditions

$$\begin{aligned}
C_{\text{A}}(0) \;&=\; C_{\text{A}}^0, && (3.1.17\text{a})\\
C_{\text{B}}(0) \;&=\; C_{\text{B}}^0, && (3.1.17\text{b})\\
C_{\text{C}}(0) \;&=\; C_{\text{C}}^0, && (3.1.17\text{c})
\end{aligned}$$

and

$$\begin{aligned}
\chi_0(0) \;&=\; \chi_0^0, && (3.1.17\text{d})\\
\chi_1(0) \;&=\; 0, && (3.1.17\text{e})\\
\chi_2(0) \;&=\; 0. && (3.1.17\text{f})
\end{aligned}$$

Because the reaction rate Γ is a nonlinear function of the solute concentrations, the set of ordinary differential equations describing the time evolution of the system is also nonlinear.

An example problem for the binary solid solution $A_xB_{1-x}C$ is presented for a batch reactor involving reaction with the stoichiometric solid $A_{x_0}B_{1-x_0}C$. The ordinary differential equations Eqns.(3.1.4)-(3.1.5) for solute and solid solution concentrations subject to the initial conditions given in Eqn.(3.1.17) are solved using *Mathematica* (Wolfram Research (2010), see Appendix C). The initial conditions and values for various parameters used in the simulation are listed in Table Table 3.1.

Table 3.1: Model parameters for binary solid solution $A_xB_{1-x}C$.

K_1	1.3333	
K_2	2	
k_{ss}	5×10^{-7}	mol/m^3/s
k_{ex}	0.6667	
k_f	5×10^{-8}	
k_b	3.3333×10^{-8}	
C^0_{A}	5×10^{-7}	mol/kg-H_2O
C^0_{B}	2×10^{-6}	
C^0_{C}	$C^0_{\mathrm{A}} + C^0_{\mathrm{B}}$	
x_0	0.25	—
χ_0	2	—
φ_0	0.8	—
$\overline{V}_{ss}$	0.1	m^3/mol

The results are shown in Figure Figure 3.2 for aqueous species A, B, C, primary stoichiometric solid χ_0, and secondary solid solution concentrations χ_1 and χ_2 as functions of time. As can be seen from the figure, the stoichiometric solid completely dissolves after approximately 7×10^8 s have elapsed. The secondary solid solution begins to precipitate at approximately 2×10^6 s (see Figure Figure 3.3).

Figure Figure 3.3 shows the composition $x(t)$ of the secondary phase $A_{x(t)}B_{1-x(t)}C$ as a function of time comparing the equilibrium composition with the kinetically evolved composition.

3.2 Parameter Sensitivity

The sensitivity of the solution on the various parameters σ_κ (k, K, x, C^0_{A}, $C^0_{\mathrm{B}}, C^0_{\mathrm{C}}, \chi^0_0$) may be defined by the partial derivatives scaled by the parameter as

$$S_{j\kappa} \;=\; \sigma_\kappa \frac{\partial C_j}{\partial \sigma_\kappa}, \tag{3.2.1}$$

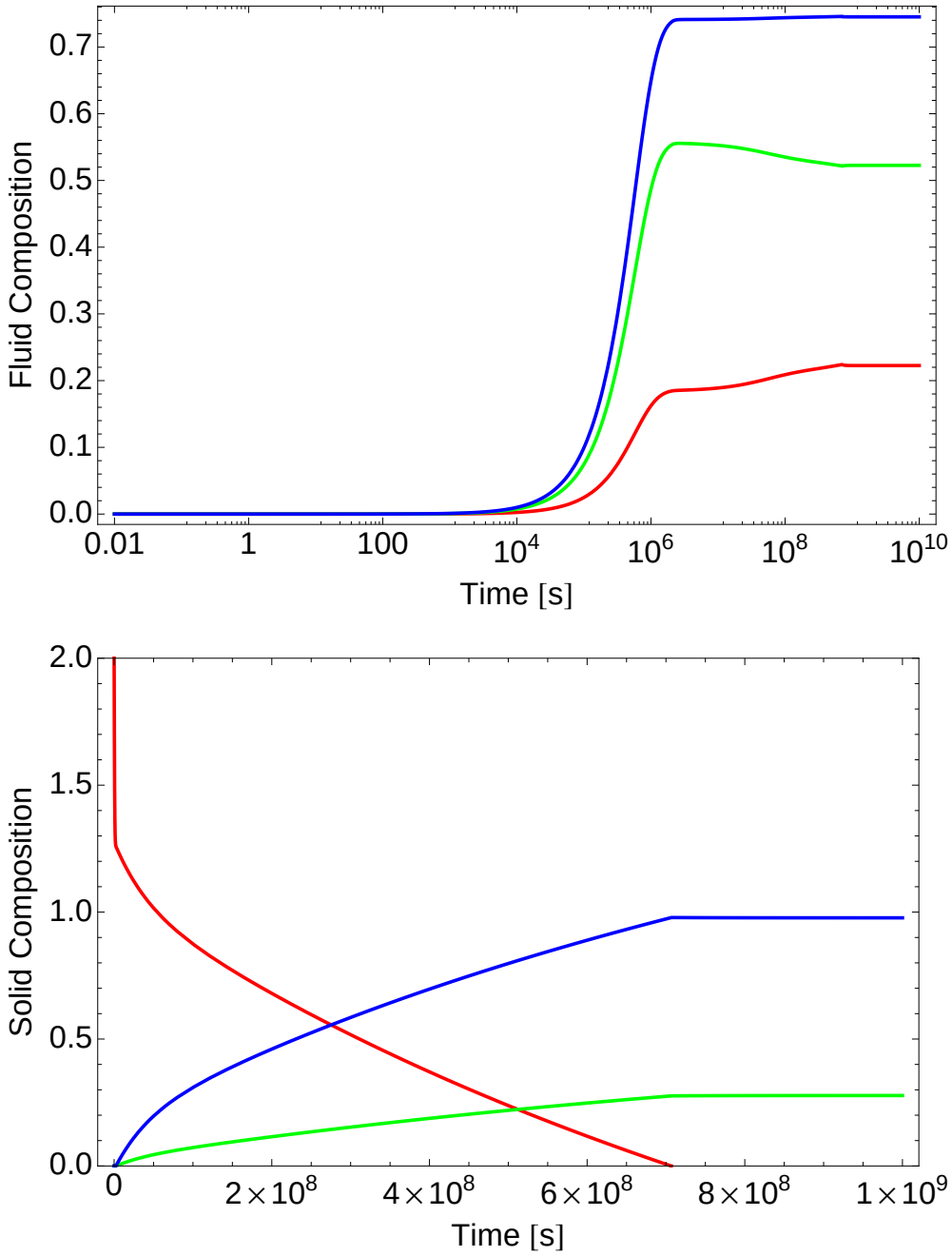

Figure 3.2: Aqueous (top) and solid solution concentration (bottom) plotted as a function of time [C_{A} (red), C_{B} (green), C_{C} (blue), χ_0 (red), χ_1 (green), χ_2 (blue)].

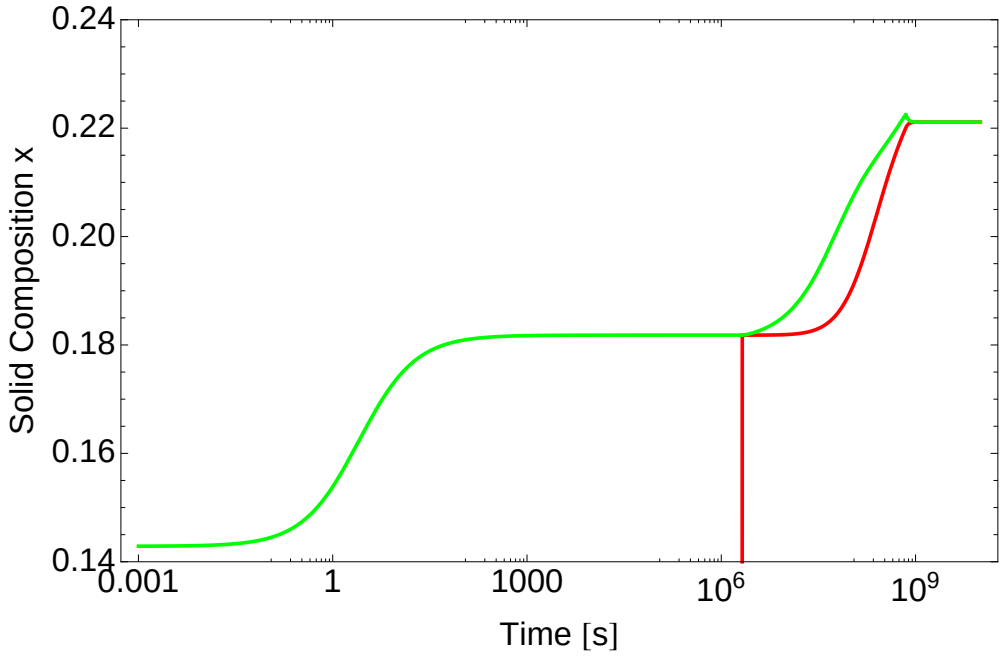

Figure 3.3: Secondary solid solution composition x plotted as a function of time showing x_{eq} (green) and x_{init} (red).

or in finite difference form

$$S_{j\kappa} \;=\; \sigma_\kappa \lim_{\Delta\sigma_\kappa \to 0} \left[\frac{C_j(\sigma_\kappa + \Delta\sigma_\kappa) - C_j(\sigma_\kappa)}{\Delta\sigma_\kappa} \right], \tag{3.2.2}$$

and similarly for the solid solution concentration

$$S^m_{\alpha\kappa} \;=\; \sigma_\kappa \frac{\partial \chi_\alpha}{\partial \sigma_\kappa}. \tag{3.2.3}$$

The sensitivity matrices $S_{j\kappa}$ and $S^m_{\alpha\kappa}$ provide a measure of how the solution changes in response to a change in the parameter σ_κ.

As an example, the sensitivity matrix for the solute concentration and primary and secondary solid solution composition on the kinetic rate constant is shown in Figure Figure 3.4 and Figure Figure 3.5, respectively. For long times the sensitivity to the rate constant approaches zero as the fluid comes to equilibrium with respect to the solid solution and becomes independent of k. A large peak followed by a smaller peak is visible in the sensitivity of the solute concentration with a change in sign for species B. Similar although slightly different behavior of the sensitivity is can be seen for χ_1 and χ_2, whereas the opposite behavior is obtained for χ_0 with a sharp initial dip in the sensitivity.

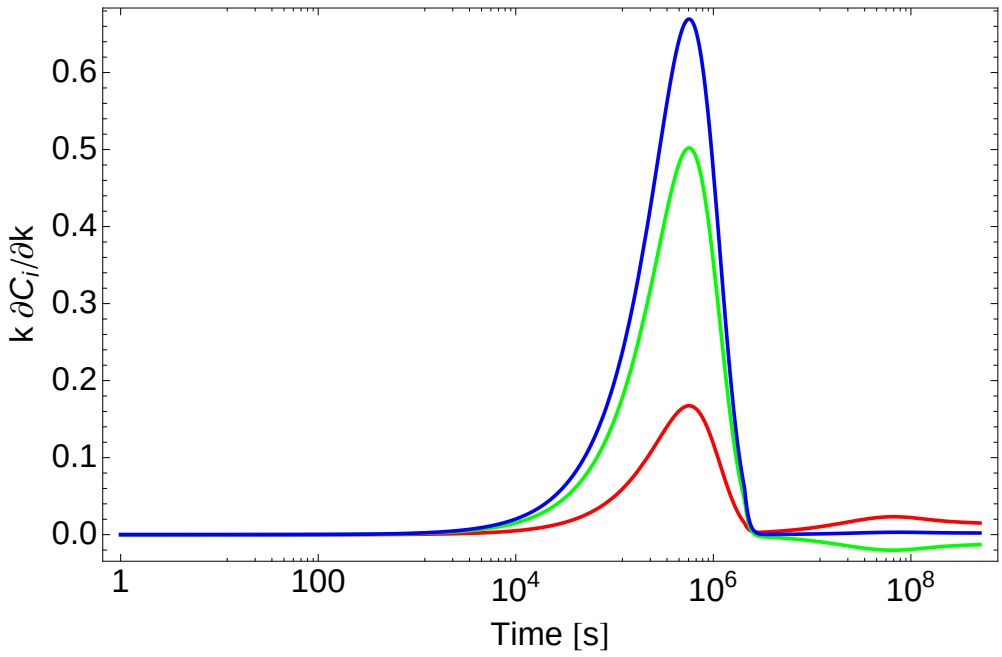

Figure 3.4: Sensitivity in the aqueous concentration $k\partial C_i/\partial k$ plotted as a function of time [A (red), B (green), C (blue)].

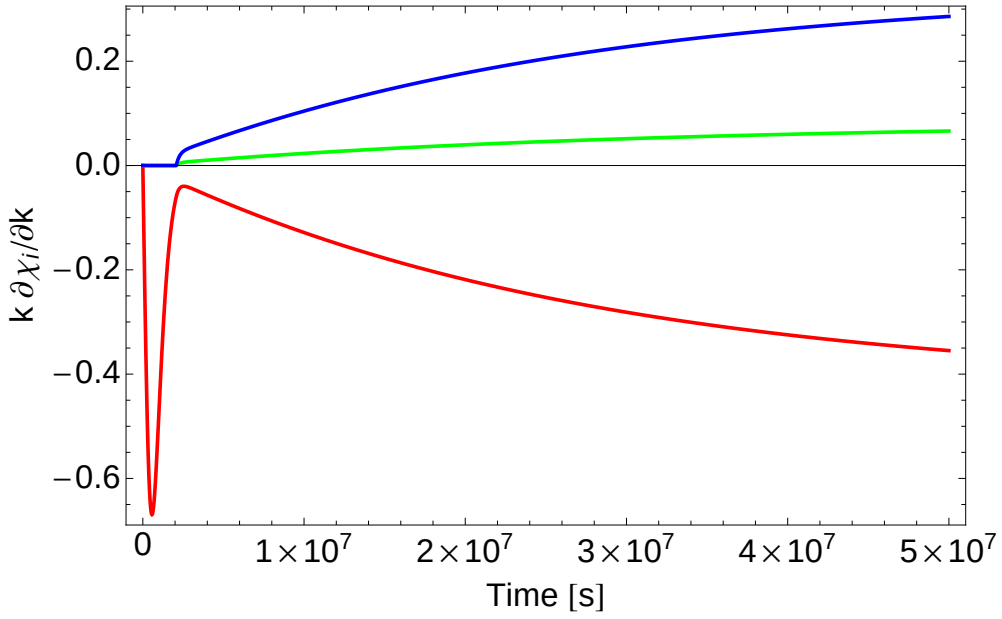

Figure 3.5: Primary and secondary solid solution sensitivity $k\partial\chi_i/\partial k$ plotted as a function of time [χ_0 (red), χ_1 (green) and χ_2 (blue)].

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Chapter 4

Conclusion

A new mathematical formulation for incorporating a kinetic description of solid solution reactions into reactive transport equations was presented. Although the treatment given here was based on the end-member formulation of solid solutions, it is hoped that a similar approach applies to more general formulations. Mass conservation equations for a batch reactor involving an ideal solid solution were developed based on overall and exchange reactions.

Future work will generalize these results to non-ideal solid solutions accounting for immiscibility and include complex multicomponent solids with multiple exchange sites and order-disorder phenomena (Lichtner and Carey, 2006; Sack and Lichtner, 2009). The model will also be extended to include advective, diffusive and dispersive transport.

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Chapter 5

References

Bruno, J. (Chair), D. Bosbach, D. Kulik, and A. Navrotsky (2007) Chemical Thermodynamics of Solid Solutions of Interest in Nuclear Waste Management: A State-Of-The-Art Report, *Chemical Thermodynamics*, Vol. **10**, pp. 226.

Glynn, P.D., E.J. Reardon, L.N. Plummer, and E. Busenberg (1990) Reaction paths and equilibrium end-points in solid-solution aqueous-solution systems, *Geochimica et Cosmochimica Acta*, **54**, 267–282.

Lichtner, P.C. (1985) Continuum model for simultaneous chemical reactions and mass transport in hydrothermal systems, *Geochimica et Cosmochimica Acta*, **49**, 779–800.

Lichtner, P.C. (1988) The quasi-stationary state approximation to coupled mass transport and fluid-rock interaction in a porous medium, *Geochimica et Cosmochimica Acta*, **52**, 143–166.

Lichtner, P.C. (1996) Continuum formulation of multicomponent-multiphase reactive transport, In: *Reactive Transport in Porous Media* (eds. P. C. Lichtner, C. I. Steefel, and E. H. Oelkers), *Reviews in Mineralogy*, Vol. **34**, 1–81.

Lichtner, P.C. and W.J. Carey (2006) Incorporating solid solutions in reactive transport equations using a kinetic discrete-composition approach, *Geochimica et Cosmochimica Acta*, Vol. **70**, 1356–1378.

Lichtner, P.C. and S. Karra (2014) Modeling multiscale-multiphase-multicomponent reactive flows in porous media: Application to CO_2 sequestration and enhanced geothermal energy using PFLOTRAN, In: *Computational Models for CO_2 Geo-Sequestration & Compressed Air Energy Storage*, Editors: Rafid Al-Khoury, Jochen Bundschuh, CRC Press, p. 81–136.

Nourtier-Mazauric, E., B. Guy, B. Fritz, E. Brosse, D. Garcia and A. Clément (2005) Modelling the dissolution/precipitation of ideal solid solutions, *Oil & Gas Science and Technology – Rev. IFP*, Vol. **60**, No. 2, pp. 401–415.

Palandri, J.L. and Y.K. Kharaka (2004) A Compilation of Rate Parameters of Water-Mineral Interaction Kinetics for Application to Geochemical Modeling, U.S. Geological Survey Open File Report 2004-1068, pp. 64.

Sack, R.O. and P.C. Lichtner (2009) Constraining compositions of hydrothermal fluids in equilibrium with polymetallic ore-forming sulfide assemblages, *Economic Geology*, Vol. **104**, pp. 1249–1264.

Wolfram Research, Inc. (2010) *Mathematica*, Version 8.0, Champaign, IL.

Appendix A: Maximum Saturation Index

The saturation index corresponding to the mth solid solution is defined as the product over end-members as

$$\mathrm{SI}_m \;=\; \prod_{\alpha} \left(\frac{K_\alpha^m Q_\alpha^m}{a_\alpha^m} \right)^{x_\alpha^m}, \tag{A-1}$$

or in log form

$$\ln \mathrm{SI}_m \;=\; \sum_{\alpha} x_\alpha^m \ln \left[\frac{K_\alpha^m Q_\alpha^m}{a_\alpha^m} \right]. \tag{A-2}$$

The maximum saturation index is obtained by maximizing the function

$$f_m \;=\; \sum_{\alpha} x_\alpha^m \ln \frac{K_\alpha^m Q_\alpha^m}{x_\alpha^m}, \tag{A-3}$$

subject to the constraint

$$\sum_{\alpha} x_\alpha^m \;=\; 1. \tag{A-4}$$

This is accomplished by introducing the Lagrange multiplier Λ_m and maximizing the function

$$f_m \;=\; \sum_{\alpha} x_\alpha^m \ln \frac{K_\alpha^m Q_\alpha^m}{x_\alpha^m} + \Lambda_m \big(\sum_{\alpha} x_\alpha^m - 1 \big), \tag{A-5}$$

leading to the requirement

$$\frac{\partial f_m}{\partial x_\alpha^m} \;=\; \ln \frac{K_\alpha^m Q_\alpha^m}{x_\alpha^m} - 1 + \Lambda_m \;=\; 0, \tag{A-6}$$

or

$$\ln \frac{K_\alpha^m Q_\alpha^m}{x_\alpha^m} \;=\; 1 - \Lambda_m. \tag{A-7}$$

Solving for x_α^m yields

$$x_\alpha^m \;=\; \mathrm{e}^{\Lambda_m - 1} K_\alpha^m Q_\alpha^m. \tag{A-8}$$

Summing over α and using the constraint condition given in Eqn.(A-4), yields the following expression for Λ_m

$$\mathrm{e}^{\Lambda_m - 1} \;=\; \frac{1}{\sum_{\alpha} K_\alpha^m Q_\alpha^m}. \tag{A-9}$$

Thus for an ideal solid solution ($a_\alpha^m = x_\alpha^m$) with fixed ion activity product Q_α^m, the maximum saturation occurs for the composition

$$x_\alpha^m \;=\; \frac{K_\alpha^m Q_\alpha^m}{\sum\limits_\beta K_\beta^m Q_\beta^m}. \tag{A-10}$$

For a non-ideal solid solution the activity coefficients λ_α^m must be taken into account. According to the Gibbs-Duhem equation

$$\sum_\alpha x_\alpha^m d\mu_\alpha^m \;=\; 0, \tag{A-11}$$

with chemical potential

$$\mu_\alpha^m \;=\; \mu_\alpha^{m\ominus} + RT \ln a_\alpha^m, \tag{A-12}$$

where $\mu_\alpha^{m\ominus}$ denotes the standard state potential corresponding to $a_\alpha^m = 1$. In this case the function

$$f_m \;=\; \sum_\alpha x_\alpha^m \ln \frac{K_\alpha^m Q_\alpha^m}{\lambda_\alpha^m x_\alpha^m} + \Lambda_m \big(\sum_\alpha x_\alpha^m - 1 \big), \tag{A-13}$$

must be maximized, yielding the requirement that the partial derivatives vanish

$$\frac{\partial f_m}{\partial x_\alpha} \;=\; \ln \frac{K_\alpha^m Q_\alpha^m}{\lambda_\alpha^m x_\alpha^m} - 1 - \sum_\beta x_\beta^m \frac{\partial \ln \lambda_\beta^m}{\partial x_\alpha^m} + \Lambda_m \;=\; 0. \tag{A-14}$$

Noting that

$$\sum_\beta x_\beta^m \frac{\partial \ln \lambda_\beta^m}{\partial x_\alpha^m} \;=\; 0, \tag{A-15}$$

as follows from the Gibbs-Duhem equation, it follows that

$$\frac{\partial f_m}{\partial x_\alpha} \;=\; \ln \frac{K_\alpha^m Q_\alpha^m}{\lambda_\alpha^m x_\alpha^m} - 1 + \Lambda_m \;=\; 0. \tag{A-16}$$

and consequently

$$x_\alpha^m \;=\; \frac{K_\alpha^m Q_\alpha^m}{\lambda_\alpha^m} \mathrm{e}^{-(\Lambda_m - 1)}, \tag{A-17}$$

from which it follows by summing over α that

$$\mathrm{e}^{\Lambda_m - 1} \;=\; \sum_\alpha \frac{K_\alpha^m Q_\alpha^m}{\lambda_\alpha^m}. \tag{A-18}$$

Hence

$$x_\alpha^m \;=\; \frac{\dfrac{K_\alpha^m Q_\alpha^m}{\lambda_\alpha^m}}{\sum\limits_\beta \dfrac{K_\beta^m Q_\beta^m}{\lambda_\beta^m}}. \tag{A-19}$$

Eqn.(A-19) implicitly defines x_α^m which must be solved numerically. With this result the maximum value of the saturation index is obtained as

$$\mathrm{SI}_m \;=\; \sum_\alpha \frac{K_\alpha^m Q_\alpha^m}{\lambda_\alpha^m}, \tag{A-20}$$

which in general is not equal to unity. Consequently, it is apparent that as expected, exchange equilibrium does not imply equilibrium of the overall solid solution reaction with composition $\{x\}$. Furthermore, Eqn.(A-19) also corresponds to the equilibrium composition derived from the exchange reactions, and thus the equilibrium and maximum saturation index coincide.

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Appendix B: Ion Exchange

Ion exchange is a surface sorption process that involves exchange of cations on surface sites, keeping the number of available sites constant. The exchange reaction can be written in terms of a reference cation $\mathcal{A}_{j_0}$ as

$$z_j \mathcal{A}_{j_0}^{z_{j_0}+} + z_{j_0}[X_{z_j}^- \mathcal{A}_j^{z_j+}] \;\rightleftharpoons\; z_{j_0} \mathcal{A}_j^{z_j+} + z_j[X_{z_{j_0}}^- \mathcal{A}_{j_0}^{z_{j_0}+}], \tag{B-1}$$

with sorbed cations $[X_{z_j}^- \mathcal{A}_j^{z_j+}]$ and $[X_{z_{j_0}}^- \mathcal{A}_{j_0}^{z_{j_0}+}]$ with X^- representing a sorption site. In the presence of exchange reactions the primary species transport equations have the form

$$\frac{\partial}{\partial t}\varphi \Psi_{j_0} + \boldsymbol{\nabla} \cdot \boldsymbol{\Omega}_{j_0} \;=\; -\sum_j z_j \Gamma_{j_0 j}, \tag{B-2a}$$

$$\frac{\partial}{\partial t}\varphi \Psi_j + \boldsymbol{\nabla} \cdot \boldsymbol{\Omega}_j \;=\; z_{j_0} \Gamma_{j_0 j}, \tag{B-2b}$$

and for sorbed species

$$\frac{\partial \chi_{j_0}}{\partial t} \;=\; \sum_j z_j \Gamma_{j_0 j}, \tag{B-3a}$$

$$\frac{\partial \chi_j}{\partial t} \;=\; -z_{j_0} \Gamma_{j_0 j}. \tag{B-3b}$$

It follows from the latter two equations for the sorbed concentration that the number of sorption sites is conserved. The total number of sites is equal to

$$\omega \;=\; \sum_j z_j \chi_j. \tag{B-4}$$

The site concentration ω is related to the cation exchange capacity $Q = N_{\text{sites}}/M_s$, where M_s represents the mass of solid phase, by

$$\omega \;=\; \frac{N_{\text{sites}}}{V}, \tag{B-5a}$$

$$\;=\; \frac{N_{\text{sites}}}{M_s}\frac{M_s}{V_s}\frac{V_s}{V}, \tag{B-5b}$$

$$\;=\; \rho_s(1-\varphi)Q, \tag{B-5c}$$

where $\rho_s = M_s/V_s$ refers to the solid grain density. It then follows from the sorbed concentration equations

$$\begin{aligned}
\frac{\partial \omega}{\partial t} &= \sum_j \frac{\partial}{\partial t} z_j \chi_j, && \text{(B-6a)}\\
&= \frac{\partial}{\partial t} z_{j_0} \chi_{j_0} + \sum_{j \neq j_0} \frac{\partial}{\partial t} z_j \chi_j, && \text{(B-6b)}\\
&= z_{j_0} \sum_j z_j \Gamma_{j_0 j} + \sum_j z_j \big(- z_{j_0} \Gamma_{j_0 j} \big), && \text{(B-6c)}\\
&= 0. && \text{(B-6d)}
\end{aligned}$$

Note that charge is rigorously conserved

$$\sum_j z_j \left[\frac{\partial}{\partial t} \varphi \Psi_j + \boldsymbol{\nabla} \cdot \boldsymbol{\Omega}_j \right] = - \sum_j \big(z_{j_0} z_j - z_j z_{j_0} \big) \Gamma_{j_0 j} = 0. \qquad \text{(B-7)}$$

From the mass action equations corresponding to the ion-exchange reactions (B-1)

$$K_{j_0 j} = \frac{K_{j_0}^{z_j}}{K_j^{z_{j_0}}} = \left(\frac{\chi_{j_0}}{a_{j_0}} \right)^{z_j} \left(\frac{a_j}{\chi_j} \right)^{z_{j_0}}, \qquad \text{(B-8)}$$

with selectivity coefficients $K_{j_0 j}$, or equivalently coefficients K_{j_0}, K_j, and the site conservation given by Eqn.(B-4), for conditions of local equilibrium and monovalent exchange the Langmuir isotherm follows

$$\chi_j = \frac{\omega K_j a_j}{\sum_l K_l a_l}. \qquad \text{(B-9)}$$

This equation can be compared with Eqn.(2.4.5) in the text for the end-member concentration.

Appendix C: *Mathematica* Program for Batch Reactor with Binary Solid Solution

In this appendix a *Mathematica* (Wolfram Research, 2010) implementation of reaction of a solid solution in a batch reactor is presented. Initially, a solid solution with fixed composition represented by $A_{x_0}B_{1-x_0}C$ dissolves and eventually becomes supersaturated with the solid solution $A_xB_{1-x}C$ with variable composition x which replaces the initial solid. *Mathematica* provides a numerical solution using `NDSolve` for the aqueous concentrations $a[t]$, $b[t]$ and $c[t]$, and solid concentrations $\chi_0[t]$, $\chi_1[t]$ and $\chi_2[t]$. The composition of the precipitating solid solution is obtained as $x[t] = \chi_1[t]/(\chi_1[t] + \chi_2[t])$. See text for further explanation.

Explanation of Symbols:	
a, b, c	aqueous concentrations
χ_0, χ_1, χ_2	solid concentrations for initial solid solution with fixed composition x_0 and end-member concentrations, respectively
`si`	saturation index
`rate0`	rate law for solid solution with fixed composition x_0 and rate constant k
`ratess`	solid solution kinetic rate law for variable composition with rate constant k: ratess $= -k[1 - K(x)Q(x)]\zeta(x)$
`ratess1`, `ratess2`	ratess1 $= x \cdot$ ratess, ratess2 $= (1 - x) \cdot$ ratess
`ratex`	exchange reaction rate law: ratex $= k_f a\chi_2 - k_b b\chi_1$
`xeq`	initial composition of solid solution to precipitate at equilibrium
k	rate constant
k_f, k_b	forward and backward exchange rate constants
k_1, k_2	end-member equilibrium constants
t, t_f	time, final time of simulation

```
si[a_, b_, c_, x_] := (k1 a/x)^x (k2 b/(1 - x))^(1 - x) c;

rate0[a_, b_, c_, chi_, k_, x_] := If[si[a, b, c, x] > 1 ||
    chi > 0, -k (1 - (a k1/x)^x (b k2/(1 - x))^(1 - x) c ), 0];

xeq[a_, b_] := k1 a/(k1 a + k2 b);

ratess[a_, b_, c_, chi1_, chi2_, k_] := Module[{},
   If[chi1 + chi2 > 0, -k (1 - (k1 a/(chi1/(chi1 + chi2)))^(chi1/(chi1 +
             chi2)) (k2 b/(chi2/(chi1 + chi2)))^(chi2/(chi1 + chi2)) c),
    If[chi1 + chi2 <= 0 &&
```

```
      si[a, b, c, xeq[a, b]] > 1, -k (1 - (k1 a/xeq[a, b])^xeq[a, b]
          (k2 b/(1 - xeq[a, b]))^(1 - xeq[a, b]) c), 0]]];

ratess1[a_, b_, c_, chi1_, chi2_, k_] := Module[{},
   If[chi1 + chi2 > 0, -k chi1/(chi1 + chi2) (1 - (
          k1 a/(chi1/(chi1 + chi2)))^(chi1/(chi1 + chi2)) (
          k2 b/(chi2/(chi1 + chi2)))^(chi2/(chi1 + chi2)) c),
    If[chi1 + chi2 <= 0 &&
      si[a, b, c, xeq[a, b]] > 1, -k xeq[a, b]
       (1 - (a k1/xeq[a, b])^xeq[a, b]
          (b  k2/(1 - xeq[a, b]))^(1 - xeq[a, b]) c), 0]]];

ratess2[a_, b_, c_, chi1_, chi2_, k_] := Module[{},
   If[chi1 + chi2 > 0, -k (chi2/(chi1 + chi2)) (1 - (
          k1 a/(chi1/(chi1 + chi2)))^(chi1/(chi1 + chi2)) (
          k2 b/(chi2/(chi1 + chi2)))^(1 - chi1/(chi1 + chi2)) c),
    If[chi1 + chi2 <= 0 &&
      si[a, b, c, xeq[a, b]] > 1, -k (1 - xeq[a, b])
        (1 - (k1 a/xeq[a, b])^xeq[a, b]
          (k2 b /(1 - xeq[a, b]))^(1 - xeq[a, b]) c), 0]]];

ratex[a_, b_, chi1_, chi2_] := kf a chi2 - kb b chi1;

conc = NDSolve[{
   a'[t] == -x0 rate0[a[t], b[t], c[t], chi0[t], k0, x0] -
     ratess1[a[t], b[t], c[t], chi1[t], chi2[t], k0] -
     ratex[a[t], b[t], chi1[t], chi2[t]],
   b'[t] == -(1 - x0) rate0[a[t], b[t], c[t], chi0[t], k0, x0] -
     ratess2[a[t], b[t], c[t], chi1[t], chi2[t], k0] +
     ratex[a[t], b[t], chi1[t], chi2[t]],
   c'[t] == -rate0[a[t], b[t], c[t], chi0[t], k0, x0] -
     ratess[a[t], b[t], c[t], chi1[t], chi2[t], k0],
   chi0'[t] == rate0[a[t], b[t], c[t], chi0[t], k0, x0],
   chi1'[t] == ratex[a[t], b[t], chi1[t], chi2[t]] +
     ratess1[a[t], b[t], c[t], chi1[t], chi2[t], k0],
   chi2'[t] == -ratex[a[t], b[t], chi1[t], chi2[t]] +
     ratess2[a[t], b[t], c[t], chi1[t], chi2[t], k0],
   a[0] == a0, b[0] == b0, c[0] == c0, chi0[0] == chi00,
   chi1[0] == 0, chi2[0] == 0},
  {a, b, c, chi0, chi1, chi2}, {t, 0, tf}, MaxSteps -> 10000]
```

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