

A Study of Reactive Transport Phenomena
in Porous Media

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**A Study of Reactive Transport Phenomena in
Porous Media**

by

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Abstract

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The numerical modeling of reactive transport in a porous medium has important applications in hydrology, the earth sciences and in numerous industrial processes. However, realistic simulations involving a large number of chemical species undergoing simultaneous transport and chemical transformation present a significant computational challenge, particularly in multiple spatial dimensions. A framework for analyzing the chemical batch problem is first introduced, which is sufficiently general to allow for reactions of both equilibrium and kinetic type. The governing equations for reactive transport of a single flowing phase through a porous medium are presented next, and a classification based on the nature of the reactive system is established. A computer module for the equilibrium problem is developed, based on a novel application of the interior-point algorithm for nonlinear programming. Among its advantages are good global convergence and automatic selection of mineral phases. To handle kinetic reactions, the equilibrium module is embedded in a time-integration framework using explicit ODE integrators. Reactive transport of species is achieved through operator-splitting, which enables a straightforward incorporation of the batch module into the existing

parallel, three-dimensional, single-phase flow and transport simulator PARSim1. Numerical results are presented which demonstrate the correctness of the computer program for major classes of geochemistry problems, including ion-exchange, precipitation/dissolution, adsorption, aqueous complexation and redox reactions.

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Chapter 1

Introduction

1.1 Motivation

A recurring issue in the management of water resources is the transport of chemical and biological species through soil and aquifers. The problem of predicting the fate of such species as they undergo *advection*, *diffusion* and *reactions* arises in a number of important applications, a few of which are *bioremediation* of contaminated aquifers [9], the simulation of geologic processes, such as the *deposition of ores* [47], and the practice of *acidizing* [36], used to enhance the permeability of the formation around wells.

The simulation of such processes, especially in three space dimensions and with complicated chemical interactions, is a computationally intensive task. Efficient, parallel computer implementations are needed to meet the challenge posed by these problems.

1.2 Previous Work

Much work has been done related to computer algorithms for calculating the state of chemical equilibrium of *closed*, reactive systems, beginning as early as the 1940s. A historical account of the development of this field, as well as an excellent survey and classification of a large number of existing algorithms, can be found in [41].

The field of reactive transport modeling, although considerably younger, has also reached a fairly mature state, and a number of simulators of varying complexity and generality are already in existence. Many of these simulators incorporate

sophisticated chemistry [36], but lack flexibility with regard to transport, and are frequently limited to one space dimension. Often, the reactions considered have been solely of equilibrium type, neglecting the case of kinetic interactions.

Rubin [30] presents some general observations regarding the interplay between the type of reactions occurring in the system, and the appropriate mathematical formulation of the transport problem. A key paper by Yeh and Tripathi [50] critically examines many of the known algorithms, and classifies them based on the choice of *primary dependent variables* and *basic algorithm type*. Three main algorithmic types are identified: *mixed differential and algebraic* (DAE), *direct substitution* (DSA), and *sequential iteration approach* (SIA). The DAE approach essentially consists of discretizing spatially the partial differential equations (PDE) governing the transport of species, and simultaneously imposing, at each point, the nonlinear conditions of equilibrium. This procedure leads to a very large system of mixed algebraic-differential type. In the DSA formulation, the conditions of equilibrium are instead substituted into the transport field equations, producing a set of highly nonlinear PDEs to be approximated. In either case, a large nonlinear problem arises for the unknowns at all grid-points.

By contrast, the SIA formulation, also known as *operator-splitting*, enables a decoupling of field equations (transport) from local constraints (chemistry). To quote Yeh and Tripathi, the SIA approach

...provides perhaps the best hope for realistic, practical two- and three-dimensional applications in terms of CPU memory and CPU time requirement.

1.3 Objectives

Our aims in this dissertation are to give a detailed exposition of the governing equations pertaining to the reactive flow through a porous medium of a single,

flowing phase, and to implement a corresponding numerical model in a general computer simulator. The simulator will be based upon the code PARSim1 [2], a parallel, three-dimensional simulator for single-phase flow and transport with limited reaction capabilities. An operator-splitting approach akin to the SIA approach mentioned above will be used in accomplishing this extension of the existing simulator.

A subproblem that arises in such a formulation is the computation of *chemical thermodynamic equilibrium*, and much of our effort will be concentrated on efficient and robust algorithms for the chemical batch calculation. Both these issues are of paramount importance when the batch calculation is part of a reactive transport simulation; efficiency, because a large number of these problems must be solved at each time-step, and robustness, since failure to converge at *any* point in our domain of interest can jeopardize the entire simulation.

There are two fundamental difficulties associated with this problem. The first is an inherent ill-conditioning that is due to widely varying scales. For example, species can be present at trace amounts, and equilibrium constants and other parameters can vary over perhaps 50–100 orders of magnitude.

The second difficulty is related to the appearance and disappearance of phases. In certain cases [40], this can lead to singularities and loss of uniqueness of solution. Even when singularities do not occur, the selection of the correct sequence of phases at equilibrium typically requires the application of some kind of testing criteria related to phase stability [8, 19, 21].

Although we do not pursue this problem for the most general cases, we consider in detail the important problem of determining the correct mineral assemblage in equilibrium with an aqueous solution. This problem (and, in general, the problem of computing equilibria in any system in which the phases present at equilibrium

are *unknown*) motivates a study of the chemical equilibrium problem in terms of a general, constrained minimization problem.

We propose algorithms based on the *interior-point method* for nonlinear programming [15] for solving these problems. The resulting algorithms have excellent stability properties, and they eliminate the need for special “selection strategies” for finding the correct set of equilibrium minerals.

Based on these algorithms, we extend the framework to include kinetic reactions.

1.4 An Outline of the Thesis

In Chapter 2 we attempt to give a reasonably complete description of the chemical batch system, a closed, reactive chemical system without any spatial variation in the dependent variables. The primary motivation for such a study is the fact that our reactive transport algorithms will be based on the idea of operator-splitting, a procedure which in effect transforms the continuum system, in which we are interested, into a large number of connected batch-reactors. Another reason to devote time to the chemical batch system is pedagogical: it is the most natural setting in which to define the concepts of elements, species and chemical reactions.

The chapter naturally divides into three parts: *stoichiometry*, *thermodynamics* and *kinetics*. Stoichiometry describes the laws of mass conservation that apply in any closed, chemical system, regardless of its nature. Thermodynamics, of which we only introduce some fundamental concepts, applies to systems which attain equilibrium, and gives conditions that must be satisfied at such equilibria. The main assumption is that the system under consideration is closed and at fixed temperature and pressure. Then, we give a brief introduction to kinetic systems, in which not only the final equilibrium composition of the system under study is

of interest, but also the variation with time of the composition. The chapter is concluded by formal, mathematical formulations of the chemical batch problem, as it applies to different types of systems.

In Chapter 3 we leave the batch system to undertake a study of the reactive transport problem. At this point we abandon some of the generality of the previous chapter, and introduce a set of assumptions suitable for our target application, namely transport and geochemistry in a porous medium. The most important of these assumptions are:

1. The system consists of an aqueous (flowing) phase, and an arbitrary number of solid (immobile) phases;
2. The system is at *isothermal* conditions;
3. *Transport* occurs in a single, incompressible aqueous (flowing) phase which completely saturates the porous medium.

Under the above conditions, we introduce the advection-diffusion-reaction equation for a chemical species undergoing advection, diffusion and reaction. Using the concepts developed in Chapter 2, we derive the governing equations for three main classes of reactive transport systems, namely *local equilibrium* (LE), *partial local non-equilibrium* (PLNE) and *local non-equilibrium* (LNE) systems.

Numerical algorithms for approximating the governing equations of reactive transport are the topic of Chapter 4. First, we introduce the overall operator-splitting technique used to treat separately the processes of advection, diffusion and reaction. We then present new formulations for approximating the reaction step in the case of LE, PLNE and LNE systems. The algorithms for the minimization problems that arise for the classes LE and PLNE are based on the interior-point method for nonlinear programming. Kinetic reactions are also included in a flexible

implementation that allows the use of explicit integrators of varying order, and within which non-negativity of species is enforced via an adaptive time-stepping strategy.

In Chapter 5, numerical results are presented. A large part of the chapter is devoted to verifying the correctness of the code for 1D problems of varying complexity, either with respect to known analytic solutions, or by comparing with results reported in the literature. The classes LE, PLNE and LNE are all represented. In addition to serving as a verification, this section also showcases the ability of our codes to handle a wide variety of geochemical reactions. A 2D problem is also presented and a 3D parallel scale-up study is conducted

Finally, in Chapter 6, we make conclusions and propose some future directions.

Chapter 2

The Chemical Batch Problem

Chapter Synopsis

In this chapter we will be concerned with the *chemical batch problem*, that is, the computation of the *composition* of a chemical *system*, possibly comprised of several *phases* and multiple *species*. The treatment of this subject is classical, and divides itself naturally into three categories: *stoichiometry*, which applies to any chemical system, *thermodynamics*, which determines the final equilibrium states attained by a system, and *kinetics* which describes time-dependent chemical transformations.

2.1 Introduction

In what follows, we describe the mathematical model of a *batch* system, which is an abstract, thermodynamic system devoid of any spatial gradients in the dependent variables. Such a system is analogous to the concept of a closed, *well-stirred tank* from chemical engineering. In a batch system, all dependent variables have the same value independently of position, which is a necessary requirement for the classical equations of thermodynamics to apply. We restrict our attention to a *closed* system, i.e., one in which no transfer of matter is permitted between the system and its surroundings (however, work and heat transfers are allowed). The system may consist of several separate *phases*, which are regions of distinct physical properties, such as solid, gaseous and liquid phases, as well as a variety of *species*. Reactions lead to internal transformations of the system mass. They fall into two main categories depending on the time-scale on which they occur: *equilibrium*

or *kinetic*. There are further classification depending on whether the reactions involve species in more than one phase (*heterogeneous* reactions), or only in one phase (*homogeneous*). These considerations are made clearer by the classifications scheme of Figure 2.1, found in Rubin [30]. In addition to the aforementioned

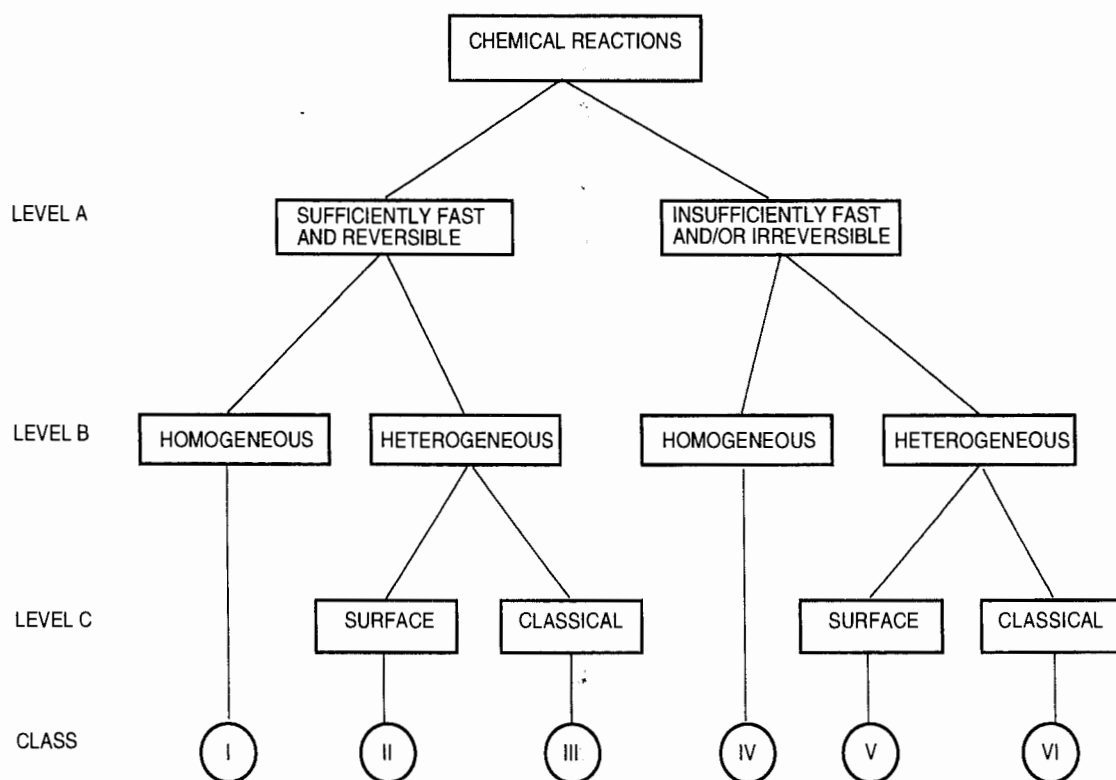


Figure 2.1 Classification of chemical reactions.

divisions, there is also a classification that pertains to the nature of heterogeneous reactions, creating a total of six fundamental reaction classes.

Obviously, the concept of a batch system is directly applicable to a laboratory setting, where different compounds are allowed to react in a beaker, and the state of the system is recorded. Perhaps less obviously, such an abstraction can be quite

useful in a more general setting, such as a continuum model for reactive transport. This is the topic of Chapter 3.

2.2 Chemical Stoichiometry

2.2.1 Terminology and Definitions

The subject of *chemical stoichiometry** treats the conservation of mass principle for a closed system. This principle, although universally accepted and intuitively obvious, nonetheless requires us to carefully define some terminology before proceeding. To this end, we follow almost verbatim the treatment given in Smith and Missen [41], and define the *chemical species* as follows:

Definition 2.1 A *chemical species* is a chemical entity distinguishable from other such entities by one of the following:

1. Its molecular formula;
2. Its molecular structure (different isometric forms of the same molecular formula);
3. The phase in which it participates.

From the above definition, it is clear that the isomers propanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, and iso-propanol, $\text{CH}_3\text{CHOHCH}_3$, are different species. It is important to point out that species belonging to distinct phases are understood to be completely independent species. Thus, gaseous carbon dioxide, $\text{CO}_2(\text{g})$ is a distinct species from carbon dioxide dissolved in water, $\text{CO}_2(\text{aq})$.

*From the Greek “stoichion” (element) and “metron” (measure).

Definition 2.2 A *chemical substance* is a chemical entity distinguishable by either molecular formula or molecular structure, but not by phase.

As pointed out in [41], this implies that the two species $\text{H}_2\text{O}(\text{aq})$ and $\text{H}_2\text{O}(\text{g})$ are the same substance: water.

Definition 2.3 A *chemical system* is a collection of chemical species and the elements from which they are formed. It is represented by an ordered list of species and elements as follows:

$$\{(\hat{n}_1, \dots, \hat{n}_{N_S}), (\hat{e}_1, \dots, \hat{e}_{N_E})\}.$$

Here \hat{n}_i is the molecular formula of species i and \hat{e}_k denotes the k th element. The system is comprised of a total of N_S species, the molecular formulae of which require no more than N_E elements. The possibility of excluding some species from any physico-chemical change is provided for by the notion of *inert species*. We denote the number of inert species by N_S^0 , and the remaining *reactive species* by $N_S' \equiv N_S - N_S^0$.

Definition 2.4 The *formula vector* a_i is a vector of subscripts (usually, but not necessarily integers) to the elements in the chemical formula of the i th species. It follows that $a_i \in \mathbb{R}^{N_E}$.

Definition 2.5 The *formula matrix* A is the matrix formed using the formula vectors as columns, $A = (a_1, \dots, a_{N_S}) \in \mathbb{R}^{N_E \times N_S}$.

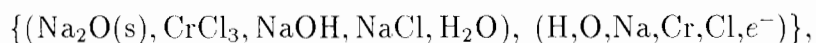
Definition 2.6 The *element-mole vector* $c = (e_1, \dots, e_{N_E})^T$ is the vector of total mole numbers of the elements (as results from an accounting of all the species in the system).

A few comments are in order regarding the above definitions. First, the notion of an “element” must be understood to mean an “indestructible entity” for the purposes of computations. In particular, all *attributes* of an element, such as oxidation state and number of elementary particles, are *preserved* throughout the evolution of the system. This has the following two implications:

- If several different oxidation-states of the same element are permitted, or, equivalently, if *redox-reactions* are allowed, we must include, in addition to periodic-table elements, a special “electron-element”. For each element present in more than one oxidation-state, one then chooses (arbitrarily) one of its oxidation-states to be indestructible. We will choose that reference-state to be the highest oxidation-state of the element in question. An example of this procedure is given below.
- If radioactive decay reactions occur within our system, we must include “elementary-particle” elements, e.g., a neutron “element”. Proceeding as before, one then selects, for each element partaking in radio-nuclide reactions, a reference isotope. Remaining isotopes are expressed in terms of the reference isotope and the elementary-particle elements.

Although the concept of radioactive decay only represents a slight generalization of the framework already presented, we will not be concerned with such reactions in this thesis.

Let us now illustrate the definitions 2.3–2.5 with an example. We consider the hypothetical non-redox system



consisting of $N_E = 6$ elements and $N_S = 5$ species. The reference oxidation-states for the elements are given by Table 2.1 below. The first species in the list, $\text{Na}_2\text{O}(\text{s})$,

Element	Reference oxidation state
H	+I
O	-II
Na	+I
Cr	+III
Cl	-I
e^-	-I (by definition)

Table 2.1 Oxidation states for the elements in non-redox example.

has the composition

$$\hat{n}_1 = \text{Na}_2\text{O}(\text{s}) \equiv (\text{O}^{-II})_1(\text{Na}^{+I})_2 \equiv (\hat{e}_1)_0(\hat{e}_2)_1(\hat{e}_3)_2(\hat{e}_4)_0(\hat{e}_5)_0(\hat{e}_6)_0,$$

and its formula vector is therefore

$$a_1 = (0, 1, 2, 0, 0, 0)^T.$$

The formula matrix $A \in \mathbb{R}^{6 \times 5}$ for the entire system is simply

$$A = \begin{pmatrix} 0 & 0 & 1 & 0 & 2 \\ 1 & 0 & 1 & 0 & 1 \\ 2 & 0 & 1 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 3 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}.$$

Clearly, the last row of A , corresponding to the conservation of the electron-element, contributes no new information and must be omitted from the system.

This is always the case for non-redox systems.

2.2.2 Mass Conservation

We now explore in more detail the consequences of the closed-system constraint, or *conservation of mass*. Recalling the definition of the formula matrix, $A = (a_1, \dots, a_{N_S})$, we state more formally the *species-identity relations* which were encountered in the example above,

$$\hat{n} = A^T \hat{e}. \quad (2.1)$$

In vector form this succinctly expresses the species chemical identity in terms of the elements,

$$\hat{n}_i = \hat{a}_i^T \hat{e}, \quad (2.2)$$

or, in the formalism of chemistry,

$$\hat{n}_i = (\hat{e}_1)_{a_{1i}} \dots (\hat{e}_{N_E})_{a_{N_E i}}. \quad (2.3)$$

So far, we have done little more than expressing chemical formulae in a systematic way. In describing conservation of mass we need two new variables that will play a fundamental role in later developments, namely the *species mole vector*, $n = (n_1, \dots, n_{N_S})^T$, and the *element-abundance vector*, $e = (e_1, \dots, e_{N_E})^T$. The i th component of n , n_i denotes the number of moles of the chemical species i present in the system. The component e_j in contrast represents the *total* number of moles of the indestructible element j present in all species containing that element. From the above definitions it is clear that conservation of the elements in a closed, batch system requires that the following linear equations be satisfied:

$$An = e. \quad (2.4)$$

The above equations are usually referred to as the *element-abundance constraints* (EAC). Note in particular that by taking a time derivative of the above relation

and using the constancy of e in a closed system, we immediately have

$$An = 0. \quad (2.5)$$

In other words: *the local rate of change of the species mole-number vector lies in the null-space of A .*

The equations (2.4) have many important implications that will be elucidated in the following sections.

Conservation of Total System Mass

It is easily demonstrated that the EAC directly imply conservation of the *total system mass*. The derivation proceeds as follows. Define the *element mole mass vector*, $m^E \in \mathbb{R}^{N_E}$, entries of which are simply the atomic masses associated with each element in the system (in appropriate units, such as g/mole or atomic units). The *species mole mass vector*, $m \in \mathbb{R}^{N_S}$, can then be expressed in terms of the element mole masses as

$$m = A^T m^E. \quad (2.6)$$

The total mass of the system, corresponding to a given species mole vector n , is simply

$$m^{tot} = n^T m. \quad (2.7)$$

Operating on the EAC (2.4) from the left with m^E produces

$$\begin{aligned} (m^E)^T An &= (m^E)^T e \iff \\ (A^T m^E)^T n &= (m^E)^T e \iff \\ n^T m &= (m^E)^T e, \end{aligned}$$

where (2.6) was used in the last step. However, it is clear that the quantity $(m^E)^T e$ is a *constant* (since m^E is a constant vector and e is a system invariant).

Consequently, using (2.7), we arrive at

$$m^{tot} = (m^E)^T e \equiv \text{constant}. \quad (2.8)$$

We have thus shown that in a closed system, the EAC (2.4) imply the *conservation of the total system mass*.

Nomenclature For Phases

In anticipation of later developments, we now introduce some additional terminology that will enable the continued use of matrix-vector notation (as opposed to a more cumbersome index-based notation) in situations when the distinction between phases becomes important. To be definite, suppose that the *maximum number of phases* that can co-exist in our system is designated by the symbol π . We point out that this constant is different from the *actual number of phases*, a quantity which we designate Π .

Let us consider a phase designated α , where $1 \leq \alpha \leq \pi$. It is natural to define a *species phase mole number vector*, $n^\alpha \in \mathbb{R}^{N_S}$ such that

$$n_i^\alpha = \begin{cases} n_i & \text{if } i \text{ participates in phase } \alpha, \\ 0 & \text{otherwise.} \end{cases} \quad (2.9)$$

We can formalize this notion by introducing a set of *phase identity matrices*, $\{P^\alpha\}_{\alpha=1}^\pi$, where each $P^\alpha \in \mathbb{R}^{N_S \times N_S}$ has the form

$$P^\alpha = \text{diag} (\delta_{\alpha, \beta(1)}, \dots, \delta_{\alpha, \beta(N_S)}). \quad (2.10)$$

In the above definition, $\beta : \mathbb{R}^{N_S} \rightarrow \mathbb{R}^\pi$ is the *phase label function*,

$$\beta(i) \equiv \text{phase in which species } i \text{ participates.} \quad (2.11)$$

and the standard Kronecker's delta function is simply

$$\delta_{ij} \equiv \begin{cases} 1 & \text{if } i = j, \\ 0 & \text{if } i \neq j. \end{cases} \quad (2.12)$$

Simply put, the phase identity matrix is a diagonal matrix of the same dimension as the number of species, and whose diagonal values are either 1, for a species that belongs to the phase in question, or 0 otherwise. Since by definition each species occurs in exactly one phase, it must hold that

$$\sum_{\alpha=1}^{\pi} P^{\alpha} = I_{N_S}, \quad (2.13)$$

where I_{N_S} denotes the identity matrix in $\mathbb{R}^{N_S \times N_S}$. Using the phase identity matrix, we can now easily express the *species phase mole vector* n^{α} for a given phase α through the relationship

$$n^{\alpha} = P^{\alpha} n. \quad (2.14)$$

2.2.3 Charge Conservation and Electroneutrality

Conservation of Total System Charge

A conservation principle governing the *total system charge* is implicit in the EAC. To demonstrate this fact, we proceed along similar lines as in Section 2.2.2, and define the *intrinsic element charge vector* $z^E \in \mathbb{R}^{N_E}$ to be equal to the oxidation state specified for each indestructible element. This includes the electron element, for which the corresponding entry is always -1 , if redox reactions have to be taken into account.

As above, we then express the *intrinsic species charge vector*, $z \in \mathbb{R}^{N_S}$, in terms of the charges of its elemental building-blocks thus:

$$z = A^T z^E. \quad (2.15)$$

We carefully note that (2.15) only expresses charge in terms of elementary charges, and that z is a unit-less vector. By contrast, the *total system charge*, q , corresponding to a given species mole vector n is an extensive quantity with units of charge. Analogously to (2.7), the total system charge is expressed as

$$q = n^T z. \quad (2.16)$$

Operating on the EAC (2.4) from the left with z^E and using (2.15) produces

$$n^T z = (z^E)^T e, \quad (2.17)$$

or,

$$q = (z^E)^T e \equiv \text{constant}. \quad (2.18)$$

Accordingly, in a closed system, the EAC (2.4) imply the *conservation of total system charge*.

Phase Electroneutrality

As was demonstrated above, the EAC imply the conservation of total charge, i.e., the equation (2.18) is satisfied by any species-mole vector n that satisfy the EAC. This is in accordance with the fact that any fixed attribute of the indestructible elements is conserved in a closed system. In general, however, we wish to impose the stronger condition of *electroneutrality*. More specifically, we must impose the condition of *phase electroneutrality*, namely that the net charge of any phase be zero. If the system is comprised of π phases, this poses another π linear constraints on the species mole-vector, in addition to the EAC.

These constraints, the *species-mole constraints imposed by phase electroneutrality*, are of the form,

$$q^\alpha = 0 \quad \alpha = 1, \dots, \pi, \quad (2.19)$$

where q^α denotes the net charge of phase α . The above conditions can be easily linked to the species mole vector n by noting that

$$q^\alpha = z^T n^\alpha, \quad \alpha = 1, \dots, \pi. \quad (2.20)$$

Using the definition of the phase mole vector, equation (2.14), the conditions of phase electroneutrality can be stated as

$$z^T P^\alpha n = 0, \quad \alpha = 1, \dots, \pi, \quad (2.21)$$

or in matrix-vector form,

$$\begin{pmatrix} (P^1 z)^T \\ \vdots \\ (P^\pi z)^T \end{pmatrix} n = 0. \quad (2.22)$$

The equation (2.22) clearly represents π linear constraints on the species mole vector, in addition to the N_E linear constraints already posed by the EAC (2.4). These constraints are not all independent, however, as we now proceed to show. By summing the equations (2.21) over all phases, and using the definition of the phase identity matrices P^α , we obtain

$$0 = \sum_{\alpha=1}^{\pi} z^T P^\alpha n = z^T \left(\sum_{\alpha=1}^{\pi} P^\alpha \right) n = z^T n.$$

Remembering the definition of total system charge, (2.18), this is nothing but

$$q = 0. \quad (2.23)$$

In other words, the phase electroneutrality equations *contain total system electroneutrality* as a special case. However, by considering a linear combination of the EAC, we showed earlier that it holds that

$$q = (z^E)^T e. \quad (2.24)$$

Comparing equations (2.23) and (2.24), it is evident that for the combined system of constraints

$$An = e, \quad (2.25)$$

$$z^T P^\alpha n = 0, \quad \alpha = 1, \dots, \pi, \quad (2.26)$$

to be consistent, we must require that the element-mole vector e satisfy

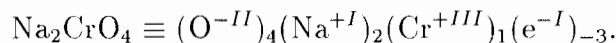
$$(z^E)^T e = 0. \quad (2.27)$$

Thus, we can in general only specify some set of $N_E - 1$ element-mole numbers independently (assuming that not all z_i^E are zero). The remaining element-mole number is determined by the condition (2.27).

We will not be concerned with the electroneutrality of phases in the remainder of this work. We note, however, that the development here, which was adapted from Sevougian [36], can in principle be used if phase electroneutrality is deemed an important issue.

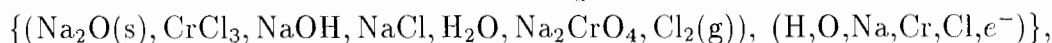
2.2.4 Example of a Redox Problem

As pointed out in section 2.2.1, redox reactions necessitate the introduction of an electron element. To demonstrate the utility of this concept, let us return to our model system in section 2.2.1, and add the species Na_2CrO_4 . With our previous choices of reference oxidation-states, i.e., -II for O and +I for Na, electroneutrality demands that Cr have oxidation-number +VI in the compound Na_2CrO_4 . This is accomplished using the electron component as follows:



However, within our framework it is not possible to have *half-cell reactions*, i.e., it is not possible to have reactions in which a change of oxidation state of only

one element occurs. In other words, we tacitly make the assumption that the concentration of electrons in solution is negligible, and reactions which result in a net production (or destruction) of electrons are therefore ruled out from the formulation. Equivalently, we say that redox reactions have to be *balanced*. For the purpose of illustration, let us include the species $\text{Cl}_2(\text{g})$, in which the oxidation state of chloride is clearly zero. The system is now



with the formula matrix

$$A = \begin{pmatrix} 0 & 0 & 1 & 0 & 2 & 0 & 0 \\ 1 & 0 & 1 & 0 & 1 & 4 & 0 \\ 2 & 0 & 1 & 1 & 0 & 2 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 3 & 0 & 1 & 0 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 & -3 & -2 \end{pmatrix}.$$

In a later section, we will determine what reactions are possible in such a system.

2.2.5 The Stoichiometric Space

We now introduce some terminology that makes dealing with chemical reactions within a closed system more convenient. We begin with a very brief review of some well-known results from linear algebra that pertain to the development (for details see Strang [43] or Stewart [42]).

Collected Results From Linear Algebra

Consider a general, real matrix $A \in \mathbb{R}^{m \times n}$. The *range*, or *column space*, of A , is defined as the set

$$\mathcal{R}(A) \equiv \{y \in \mathbb{R}^m \mid y = Ax, x \in \mathbb{R}^n\}. \quad (2.28)$$

Analogously, the *row-space* of A is simply

$$\mathcal{R}(A^T) \equiv \{y \in \mathbb{R}^n \mid y = A^T x, x \in \mathbb{R}^m\}. \quad (2.29)$$

Furthermore, the *null-space* of A , which we denote $\mathcal{N}(A)$, is the set of vectors that are mapped into zero by A , or formally,

$$\mathcal{N}(A) \equiv \{x \in \mathbb{R}^n \mid Ax = 0\}. \quad (2.30)$$

A fundamental theorem of linear algebra [43] states that the row space is the *orthogonal complement* of the null-space; that is, that

$$\mathcal{R}(A^T) \oplus \mathcal{N}(A) = \mathbb{R}^n. \quad (2.31)$$

In particular, it therefore holds that the dimensions satisfy

$$\dim \mathcal{R}(A^T) + \dim \mathcal{N}(A) = n, \quad (2.32)$$

and that any element $x \in \mathbb{R}^n$ can be expressed uniquely as

$$x = s + t, \quad (2.33)$$

where s and t are orthogonal and belong to the subspaces $\mathcal{R}(A^T)$ and $\mathcal{N}(A)$ respectively. Alternatively, we may express (2.33) in terms of *orthogonal bases* S and S^\perp in terms of new coordinates ξ and η , namely

$$x = S\xi + S^\perp\eta \quad (2.34)$$

A final definition concerns the row and column spaces of A . It is well known that

$$\dim \mathcal{R}(A^T) = \dim \mathcal{R}(A), \quad (2.35)$$

a fact which enables us to define the *rank* of A as simply the dimension of either the row or the column space,

$$\text{rank}(A) \equiv \dim \mathcal{R}(A). \quad (2.36)$$

The equation (2.32) can now be restated as follows:

$$\text{rank}(A) + \dim \mathcal{N}(A) = n. \quad (2.37)$$

The Composition Space and its Subspaces

The starting point for the discussion is the formula matrix $A \in \mathbb{R}^{N_E \times N_S}$, introduced in Definition 2.5. We will refer to the space \mathbb{R}^{N_S} as the *composition space*, and always make the assumption that $N_E < N_S$. Next, introduce the definitions

$$N_C \equiv \text{rank}(A), \quad (2.38)$$

$$N_R \equiv \dim \mathcal{N}(A). \quad (2.39)$$

Applying the general result (2.37) to the matrix A tells us that the dimensions of its subspaces satisfy

$$N_C + N_R = N_S. \quad (2.40)$$

We shall refer to N_C as the *number of components* of a given system. It represents the minimum number of “building blocks” necessary to represent any species in the system. In many applications, $N_E = N_C$, but in general $N_C \leq N_E$. Some examples will be presented in the section below.

The quantity $N_R = N_S - N_C$ is the *number of independent chemical reactions* that can take place in the system.

If we let $V \in \mathbb{R}^{N_S \times N_R}$ be a matrix representation of a basis for $\mathcal{N}(A)$, the general result (2.34) tells us that any conceivable composition can be expressed in the form

$$n = A^T \eta + V \xi. \quad (2.41)$$

The coordinates $\eta \in \mathbb{R}^{N_C}$ and $\xi \in \mathbb{R}^{N_R}$ in this representation are known as the *reaction-invariants* and the *extents of reaction*, or *reaction coordinates*, respectively.

For a closed system, only the coordinates ξ are of interest, and the most general representation becomes instead

$$n = n^0 + V \xi, \quad (2.42)$$

where $n^0 \in \mathbb{R}^{N_S}$ represents a particular solution to the EAC,

$$A n^0 = \epsilon. \quad (2.43)$$

We summarize the results above in a few important definitions:

Definition 2.7 The *reaction vector* v_i is a vector of stoichiometric coefficients (usually, but not necessarily integers) of the species participating in a chemical reaction. It follows that $v_i \in \mathbb{R}^{N_S}$ lies in $\mathcal{N}(A)$.

Definition 2.8 The *stoichiometric matrix* V is a matrix whose columns are made up from the smallest set (N_R) of reaction vectors necessary to span $\mathcal{N}(A)$,

$$V = (v_1, \dots, v_{N_R}) \in \mathbb{R}^{N_S \times N_R}. \quad (2.44)$$

In component form, we write $V = (v_{ij})$. The element v_{ij} is the *stoichiometric coefficient* of the i th species in the j th independent reaction.

Definition 2.9 The *composition vector* n for a closed system can be expressed as

$$n = n^0 + V\xi, \quad (2.45)$$

where $n^0 \in \mathbb{R}^{N_S}$ is a particular solution satisfying the EAC, and $\xi \in \mathbb{R}^{N_R}$ is the vector of *extents of reaction*.

Finally, note that from the species identity relations (2.1),

$$V^T \hat{n} = V^T A^T \hat{e} = (AV)^T \hat{e}. \quad (2.46)$$

Using the fact that $AV = 0$, we find

$$V^T \hat{n} = 0, \quad (2.47)$$

or, for $1 \leq i \leq N_R$,

$$v_i^T \hat{n} = 0. \quad (2.48)$$

We may thus formally state:

Definition 2.10 A *chemical reaction* is given by its reaction vector v_i , and has the general form

$$v_i^T \hat{n} = 0. \quad (2.49)$$

The Canonical Form of A and V

The results concerning the subspaces of A introduced in the previous section makes it simple to reduce both A and V to a more convenient form that reveals more about the structure of the system. Since the rank of A is $N_C \leq N_E$ (and $N_E < N_S$), it is always possible to perform a Gauss-Jordan reduction [42] on A to obtain the reduced form, A_r ,

$$A_r = \begin{pmatrix} I_{N_C} & \hat{A} \\ 0 & 0 \end{pmatrix}. \quad (2.50)$$

where $\hat{A} \in \mathbb{R}^{N_C \times N_R}$, and the number of zero rows present (if any) are $N_E - N_C$. We note that the reduction process only requires elementary row operations and possibly a re-ordering of the species. As pointed out by Schneider et al. [35], the matrix A_r is therefore a representation of the closed system constraints that is completely equivalent to the original matrix A . We also make the observation that the species ordering is arbitrary, and that we therefore without any real loss of generality can assume that the formula matrix is already in the above format. If it is not, a Gauss-Jordan reduction accompanied by a reordering of the unknowns will result in this format. The zero rows of A_r contain no information and should be omitted. The resulting matrix, $A_c \in \mathbb{R}^{N_C \times N_S}$ is then

$$A_c = \left(I_{N_C} \ : \ \hat{A} \right). \quad (2.51)$$

For notational convenience, we will often omit the special designation and simply use the symbol A to represent the *canonical form* A_c . Using the canonical form of A , we can partition the species mole-vector n into sub-vectors $n^c \in \mathbb{R}^{N_C}$ and $n^p \in \mathbb{R}^{N_R}$ according to

$$n = \begin{pmatrix} n^c \\ n^p \end{pmatrix}, \quad (2.52)$$

and express the closed system constraints as

$$n^c + \hat{A}n^p = e. \quad (2.53)$$

The representation (2.52) emphasizes that the N_C *component species* n^c have the intrinsic function as “building blocks” of the system. The N_R *product species* n^p each have the property that they participate in exactly one reaction.

Equation (2.51) makes it particularly easy to express the stoichiometric matrix V . Recall that the columns of V span the null-space of A ,

$$AV = 0. \quad (2.54)$$

By making the ansatz

$$V = \begin{pmatrix} \hat{V} \\ I_{N_R} \end{pmatrix}, \quad (2.55)$$

we see that satisfaction of (2.54) requires

$$\hat{V} = -\hat{A} \quad (2.56)$$

We summarize this section with two definitions:

Definition 2.11 The *canonical form* of the formula matrix is given by (2.51).

Definition 2.12 The *canonical form* of the stoichiometric matrix is given by (2.55) and (2.56).

Examples

In this section we demonstrate the utility and practical application of some of the tools introduced in the previous section. Consider first the simplest aqueous system:

$$\{(\text{H}_2\text{O}, \text{H}^+, \text{OH}^-), (\text{H}, \text{O})\},$$

consisting of $N_S = 3$ species and $N_E = 2$ elements. The formula matrix is

$$A = \begin{pmatrix} 2 & 1 & 1 \\ 1 & 0 & 1 \end{pmatrix}.$$

Reducing A to its canonical form produces the matrix

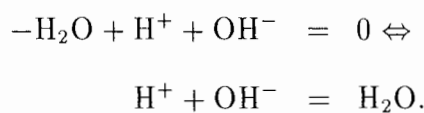
$$A_c = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & -1 \end{pmatrix}.$$

Evidently, $N_C = N_E = 2$ for this case. The species-ordering was retained in the reduction process, so we immediately conclude that the species H_2O and H^+ are

legitimate components for this system (this, of course, is not a unique choice). Furthermore, using the relation (2.40), we see that the number of independent reactions is $N_R = 3 - 2 = 1$, as would be expected. The reaction vector (which coincides with the stoichiometric matrix in this case) is

$$v = (-1, 1, 1)^T.$$

Using the relation (2.48), this corresponds to the chemical reaction



The second example illustrates better the advantage of the component approach. We again turn to the redox example considered earlier,

$$\{(\text{Na}_2\text{O}(\text{s}), \text{CrCl}_3, \text{NaOH}, \text{NaCl}, \text{H}_2\text{O}, \text{Na}_2\text{CrO}_4, \text{Cl}_2(\text{g})), (\text{H}, \text{O}, \text{Na}, \text{Cr}, \text{Cl}, e^-)\},$$

Performing reduction operations on the original matrix A generates the reduced formula matrix

$$A_r = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 2 & 0 \\ 0 & 1 & 0 & 0 & 0 & -1 & -8/3 \\ 0 & 0 & 1 & 0 & 0 & 0 & 4 \\ 0 & 0 & 0 & 1 & 0 & 0 & -2/3 \\ 0 & 0 & 0 & 0 & 1 & 0 & 2/3 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

where the species have been reordered according to

$$\{\text{NaOH}, \text{Na}_2\text{O}(\text{s}), \text{NaCl}, \text{CrCl}_3, \text{Na}_2\text{CrO}_4, \text{H}_2\text{O}, \text{Cl}_2(\text{g})\}.$$

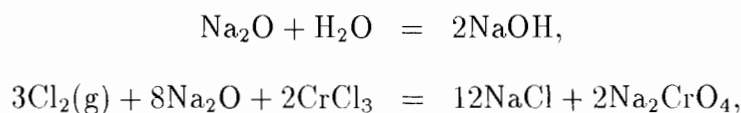
Clearly, the rank of A in this case is $N_C = 5$, which is less than the number of elements, $N_E = 6$. The components thus found are:

$$\{\text{NaOH}, \text{Na}_2\text{O}(\text{s}), \text{NaCl}, \text{CrCl}_3, \text{Na}_2\text{CrO}_4\}.$$

The number of possible reactions is $N_R = N_S - N_C = 2$, and they are given by the reaction vectors

$$\begin{aligned} v_1 &= (-2, 1, 0, 0, 0, 1, 0)^T, \\ v_2 &= \left(0, \frac{8}{3}, -4, \frac{2}{3}, -\frac{2}{3}, 0, 1\right)^T. \end{aligned}$$

Using again (2.48), this corresponds to the reactions



where we have multiplied the second reaction by 3 to avoid fractions. Note in particular that no electrons are directly visible in any of the reactions. The second reaction is an example of a *balanced redox reaction* — a direct consequence of the reduction procedure.

2.3 Chemical Thermodynamics

2.3.1 Introduction

Thermodynamics attempts to describe the state of a system that has reached *equilibrium*. It is therefore a useful tool in deciding what processes are *possible* within a given system, and for calculating the *final state* of that system, but it is inherently incapable of predicting the *rate* at which equilibrium is approached.

For systems that will not attain equilibrium in the time during which they are studied, or if the actual approach to equilibrium is to be investigated, a different type of formulation must be employed. However, even in such circumstances thermodynamics has a role to play in that it specifies what the driving force of change is, and imposes a steady-state limit on the extents of processes in the system.

Let us begin this brief development with some terminology. A *system* is some portion of the universe that we have chosen to study. Everything outside of this (possible hypothetical) region is labeled the *surroundings*. Systems can be classified with regard to what kind of interactions with the surroundings are allowed. The following are common.

- Open systems can exchange matter, work and heat.
- Closed systems exchange work and heat but not matter.
- Isolated systems have no interactions with the surroundings.

In addition, systems can be *homogeneous* or *heterogeneous* depending on their internal structure. Homogeneous systems have uniform properties throughout, whereas heterogeneous systems have spatially varying properties. An example of the former kind would be an aqueous solution, a system of the latter type could be a multi-phase mixture. The theory of thermodynamics can be described in terms of a small number of *fundamental state variables*, *modes of energy transfer* and *characteristic state functions* (see Stumm and Morgan [44]). State variables, as the name implies, are variables that determine the state of a system and can be of two kinds: *extensive* or *intensive*; the former kind depends upon the size of the system under consideration, the latter does not. Furthermore, state functions are functions of the state variables that possess exact differentials; that is, they depend only on the *state* of a system, but not on the *path* (through composition space) the system followed in getting there. Thus, these functions are properly thought of as thermodynamic *potentials*, and they can be shown to possess extrema at points corresponding to equilibria. The fundamental variables of a system are:

- T, Absolute Temperature; Intensive.

- S , Entropy; Intensive.
- p , Pressure; Intensive.
- V , Volume; Extensive.
- n_i , Mole Number of species i ; Extensive.

The Modes of Energy Transfer are:

- q , Heat transferred from Surroundings to System.
- w , Work done by Surroundings on System.

Some commonly used State Functions are:

- $U(S, V, n_i)$, The Internal Energy; Extensive.
- $H(S, p, n_i)$, The Enthalpy; Extensive.
- $G(T, p, n_i)$, The Gibbs Free Energy; Extensive.

It should be noted that the functions U , H and G are not independent; starting from the internal energy the other potentials can be derived through a change of variables known as the Legendre transformation. They are introduced so that the conditions of equilibrium can be expressed succinctly for different kinds of systems.

In this work, we shall exclusively be concerned with the Gibbs free energy, G , which is the natural choice of state function if the system under consideration is held at *fixed temperature and pressure*.

2.3.2 Conditions of Chemical Thermodynamic Equilibrium

The condition of equilibrium for a closed chemical system with the standard thermodynamic constraints of constant temperature T and pressure p is that the

Gibbs free energy is a *minimum* with respect to all possible system configurations (Denbigh [13]),

$$dG = 0. \quad (2.57)$$

Furthermore, any *spontaneous process* taking place at constant temperature and pressure must obey the inequality

$$dG \leq 0. \quad (2.58)$$

If the system is comprised of several phases, it is understood that those phases have the same temperature (*thermal equilibrium*) and pressure (*mechanical equilibrium*) in addition to the satisfaction of *chemical equilibrium* conditions. A comprehensive treatment of thermodynamics is much beyond the scope of this thesis; instead, we refer the reader to [1, 17] for more details on thermodynamic state functions and the corresponding conditions of equilibrium.

To proceed, information is needed regarding the functional form of the Gibbs free energy, G . Commonly, the starting point is the introduction of the *chemical potential*, μ_i , associated with species i , often referred to as the *molar free energy* of species i . It is defined to be *the partial derivative of the Gibbs free energy at constant temperature, pressure and composition, with respect to the mole-number of the i th species*,

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j}. \quad (2.59)$$

With the above definition, the differential dG can be expressed in terms of the differentials of mole-numbers,

$$dG = \sum_{i=1}^{N_S} \mu_i dn_i. \quad (2.60)$$

It can be shown [41] that the Gibbs function is a *homogeneous function* of degree one in the mole numbers, i.e., that

$$G(kn, T, p) = kG(n, T, p), \quad (2.61)$$

for any real number $k > 0$. This is of course reasonable, since we expect that merely changing the mass of the system will leave the equilibrium unchanged and only scale the total system energy. By Euler's theorem, therefore, an integrated form is readily obtained, namely

$$G = \sum_{i=1}^{N_S} \mu_i n_i. \quad (2.62)$$

For convenience, we will often write (2.62) in vector form,

$$G = n^T \mu. \quad (2.63)$$

Note that the definition of the chemical potential (2.59), combined with the conditions of equilibrium, (2.57), results in the following condition on the chemical potentials

$$\sum_{i=1}^{N_S} n_i d\mu_i = 0. \quad (2.64)$$

This relation is known as the *Gibbs-Duhem equation*, and it poses a thermodynamic restriction on the possible functional form of the chemical potentials. As stated, this important relation applies to a homogeneous system, that is a system comprised of a single phase. In the general case of a heterogeneous system, it can be shown [28] that a Gibbs-Duhem equation applies to each phase. Using the notation developed in Section 2.2.1, we can express this fact for each $\alpha = 1, \dots, \pi$ as

$$\sum_{i=1}^{N_S} n_i^\alpha d\mu_i^\alpha = 0. \quad (2.65)$$

2.3.3 Composition Variables

Before examining the functional form of the chemical potential, it is appropriate to consider some different ways of expressing the *composition* of a batch system. So far, we have spoken mostly about *extensive quantities*, i.e., variables that directly depend on the size of the system under consideration. Indeed, the primary

variable in describing the batch system has been the species mole vector n , which is clearly directly proportional to the system size. However, the very definition of the chemical potential as a partial derivative with respect to an extensive quantity tells us that μ must be an *intensive* variable, which by definition is independent of system size. Likewise, its functional dependence is on intensive variables, namely the chemical composition of the system. There are several ways of defining chemical composition. The composition variable with the most theoretical significance is the *mole-fraction*, whereas applications often require a more practical measure, such as *molar concentrations*. For these reasons, our presentation will alternate between, and sometimes use interchangeably, practical and theoretical concentration scales.

Let us begin by considering the mole-fractions. As described in Section 2.2.1, the phase mole vector n^α is simply

$$n^\alpha = P^\alpha n. \quad (2.66)$$

The *total phase moles* in phase α , denoted \tilde{n}^α , is nothing but the algebraic sum of all the mole numbers in phase α . In vector form, this can be expressed as

$$\tilde{n}^\alpha = \mathbf{1}^T P^\alpha n, \quad (2.67)$$

where $\mathbf{1}$ here denotes a vector of only ones of length N_S . The total phase moles are conveniently represented by the vector of *total phase moles*, $\tilde{n} = (\tilde{n}^1, \dots, \tilde{n}^\pi)^T$. We can now define the *vector of phase mole-fractions*, $x^\alpha \in \mathbb{R}^{N_S}$, as

$$x^\alpha = \frac{n^\alpha}{\tilde{n}^\alpha}, \quad (2.68)$$

or

$$x^\alpha = \frac{P^\alpha n}{\mathbf{1}^T P^\alpha n}. \quad (2.69)$$

Equation (2.69) shows how the intensive variables (mole-fractions for each phase of the system) are computed from the extensive variables (the vector of species mole numbers). Note that if a phase has only one participant, i.e., if it is a *single-species phase*, then necessarily the corresponding mole fraction is unity for that species. We also mention that if *inert* species are present in the system, we must nevertheless include those in the computation of mole fractions, that is (2.69) continues to hold.

Next, let us consider a phase-volume based representation of the concentration of species. Assuming that the volume of the phase α is V^α , we express the *vector of phase molar concentrations*, c^α , as

$$c^\alpha = \frac{n^\alpha}{V^\alpha}. \quad (2.70)$$

As an example, the concentration of a species in an aqueous phase could be written as

$$c_i = \frac{n_i}{V_{aq}}, \quad (2.71)$$

which we recognize as the familiar *molar* concentration scale. Other choices are also possible and in practical use.

2.3.4 Functional Dependence of the Chemical Potential

The chemical potential μ is in general a function of *temperature, pressure and chemical composition*. Depending on the application, different forms of this function are used. For an *ideal gas* in which, by definition, no interactions occur between particles, it can be shown that the chemical potential at pressure p and temperature T has the simple form

$$\mu = \mu^0 + RT \ln p, \quad (2.72)$$

where R denotes the universal gas constant. The *chemical reference potential* μ^0 is a quantity which is tabulated at a given temperature and pressure. Similarly, for an *ideal gas mixture*, the chemical potential of the i th gas can be expressed as

$$\mu = \mu_i^0 + RT \ln p_i, \quad (2.73)$$

where the *partial pressure* p_i is given in terms of the gas phase pressure p by

$$p_i = x_i p. \quad (2.74)$$

For an ideal solution, the chemical potential can be expressed similarly, either in terms of mole-fractions,

$$\mu_i = \mu_i^0 + RT \ln x_i, \quad (2.75)$$

or in terms of molar concentrations,

$$\mu_i = \mu_i^0 + RT \ln c_i. \quad (2.76)$$

Note that the chemical reference potentials appearing in the expressions (2.75) and (2.76) are in general *different*, as they depend on the choice of composition variables.

As is evident from the expressions (2.72) to (2.76) above, the dependence of the chemical potential of a given species is limited to the concentration of that species alone. This is characteristic of *ideal systems*, in which the interactions between molecules in solution are neglected. In reality, most systems exhibit varying degrees of non-ideality as the effects of molecular interactions become more noticeable. For such systems, one typically defines an *activity coefficient* or a *fugacity* which attempts to capture the non-ideal behavior while retaining the basic logarithmic form of the chemical potentials presented above. The chemical potential in this general case is then expressed as

$$\mu_i = \mu_i^0 + RT \ln a_i, \quad (2.77)$$

where the concentration term has been replaced by a *species activity* a_i , that depends on the phase composition through an *activity coefficient* γ_i . This is customarily written in the form

$$a_i = \gamma_i(x^\alpha)x_i^\alpha, \quad (2.78)$$

where $\gamma_i \approx 1$ as the solution approaches ideality. In this thesis, only ideal systems are considered.

In both ideal and non-ideal systems it holds that the chemical potential of a species *at most* depends on the entire composition vector for the phase in which it participates. If we therefore designate the vector of phase chemical potentials by μ^α , we can write

$$\mu^\alpha = \mu^\alpha(T, p, x^\alpha), \quad (2.79)$$

or, alternatively, we express this relation in terms of the composition variables c^α as

$$\mu^\alpha = \mu^\alpha(T, p, c^\alpha). \quad (2.80)$$

Finally, we point out that single-species phases (such as minerals) are customarily taken to have a constant chemical potential,

$$\mu_i = \mu_i^0. \quad (2.81)$$

This is a logical extension of the fact that the chemical potential depends on the composition of the phase, since in this case the phase is only made up of one substance. It also follows from the remark made in Section 2.3.3, that the mole-fraction is automatically equal to unity for such species.

2.3.5 Some Practicalities: Affinities, Free Energy Change and the Mass-Action Expressions

It can be shown that the gradient of the Gibbs free energy with respect to the extents of reaction has the form

$$\frac{\partial G}{\partial \xi} = V^T \mu, \quad (2.82)$$

where $V \in \mathbb{R}^{N_S \times N_R}$ is the stoichiometric matrix encountered in Section 2.2.5. This is a useful quantity, as it is intimately related to the minimization of the free energy. As such, there are two names associated with it, namely the *Gibbs free energy change of reaction*, ΔG , and the *affinity of reaction*, \mathcal{A} , defined as

$$\Delta G = V^T \mu, \quad (2.83)$$

$$\mathcal{A} = -V^T \mu, \quad (2.84)$$

or, written in component form for each reaction

$$\Delta G_j = \sum_{i=1}^{N_S} \mu_i v_{ij} \quad j, \dots, N_R, \quad (2.85)$$

$$\mathcal{A}_j = -\Delta G_j \quad j, \dots, N_R. \quad (2.86)$$

For many reactions, the condition of equilibrium is simply

$$\Delta G_i = 0, \quad (2.87)$$

$$\mathcal{A}_i = 0. \quad (2.88)$$

This is because G expressed in terms of ξ is essentially unconstrained. However, because of the condition that species be non-negative, the following inequalities are also possible at equilibrium:

$$\Delta G_i \geq 0, \quad (2.89)$$

$$\mathcal{A}_i \leq 0. \quad (2.90)$$

The above equations express the condition that a reaction that is not *energetically favorable* (in other words the reaction has a positive free energy change, or a negative affinity) will not take place at all. Let us consider a simple two-component example $\{(A, B), A_2B\}$ to illustrate the condition (2.87). We consider, then, the simple reaction



The convention used is that $v_{ij} > 0$ for *products* and $v_{ij} < 0$ for *reactants*. Clearly, we have $v_A = -2$, $v_B = -1$ and $v_{A_2B} = +1$, and the equations (2.85) and (2.87) immediately imply

$$\mu_{A_2B} = 2\mu_A + \mu_B. \quad (2.92)$$

In words, since the chemical potential can be thought of as the Gibbs free energy per mole of a component, the above expression illustrates the intuitively appealing notion that the reactants be as energetic as the products at the composition prevailing at equilibrium.

Finally, by using the conditions of equilibrium (2.87), the compositional dependence of the chemical potential upon composition (2.76) and the canonical form of the stoichiometric matrix V (2.55), it is an easy exercise to derive a set of non-linear, algebraic conditions known as the *mass-action* expressions. Details of this derivation can be found in B.1. The result, in terms of molar variables, is

$$c_{N_C+i} = K_i \prod_{j=1}^{N_C} (c_j)^{\hat{a}_{ij}} \quad i = 1, \dots, N_R. \quad (2.93)$$

In the above expression, $\hat{a}_{ij} \equiv (\hat{A})_{ij}$, and K_i is the *equilibrium constant* for the i th reaction, given by

$$K_i = \exp\left(-\frac{\Delta G_i^0}{RT}\right), \quad (2.94)$$

and ΔG_i^0 is the *standard free-energy change*, given by

$$\Delta G_i^0 = \mu_{N_c+i}^0 - \sum_{j=1}^{N_c} \hat{a}_{ji} \mu_j^0. \quad (2.95)$$

2.4 Chemical Kinetics

2.4.1 Introduction

In this section, we give a brief introduction to the theory of chemical kinetics. The treatment of this large and complicated subject is extremely cursory, and omits many important aspects, such as reaction pathways and detailed reaction mechanisms. For a comprehensive treatment in the case of aquatic chemistry, the reader may consult Morel and Hering [28]. Detailed physico-chemical considerations are tangential to our purpose here, which is to introduce as simply as possible the basic elements of the class of reactions governed by systems of Ordinary Differential Equations (ODE).

2.4.2 The Kinetic Subspace

The developments in Section 2.2.5 make it possible to separate the compositional changes that result from equilibrium-controlled processes from those changes that are kinetic in nature. This kind of decomposition is important, because these two classes are governed by different mathematical models, and we wish to separate them in order to better understand the underlying structure.

Let us begin by examining the stoichiometric matrix V as introduced in Definition 2.8. Each column v_i of V represents a linearly independent reaction amongst the species. Now let us assume that out of the N_R reactions we have N_R^Q equilibrium-controlled reactions and N_R^K rate-controlled reactions such that

$$N_R = N_R^Q + N_R^K. \quad (2.96)$$

Since the ordering of such reactions is completely arbitrary, we may without any loss of generality assume that the columns of V have been organized into a set of kinetic reactions, followed by the set of equilibrium reactions, so that V has the form

$$V = \begin{pmatrix} V^K & V^Q \end{pmatrix}. \quad (2.97)$$

We will refer to $V^K \in \mathbb{R}^{N_S \times N_R^K}$ and $V^Q \in \mathbb{R}^{N_S \times N_R^Q}$ as the *stoichiometric matrices of the kinetic and equilibrium reaction space*, respectively.

Clearly, if we partition the extent of reaction vector ξ according to reaction type,

$$\xi = \begin{pmatrix} \xi^K \\ \xi^Q \end{pmatrix}, \quad (2.98)$$

and use the general representation of the composition vector for a closed system, (2.45), we find that we can express the dependence of the composition on equilibrium and kinetic processes as

$$n = n^0 + V^K \xi^K + V^Q \xi^Q. \quad (2.99)$$

Finally, by taking advantage of the *canonical form* of the stoichiometric matrix introduced in (2.55), we can introduce a convenient fully partitioned form of V , namely

$$V = \begin{pmatrix} \hat{V}^K & \hat{V}^Q \\ I_{N_R^K} & 0 \\ 0 & I_{N_R^Q} \end{pmatrix}. \quad (2.100)$$

The sub-matrices \hat{V}^K and \hat{V}^Q contain information about how the N_C components react to form N_R^K kinetic products and N_R^Q equilibrium products. They have dimensions $N_C \times N_R^K$ and $N_C \times N_R^Q$, respectively.

Using (2.100) in the representation (2.99), we find

$$n = n^0 + \begin{pmatrix} \hat{V}^K \xi^K + \hat{V}^Q \xi^Q \\ \xi^K \\ \xi^Q \end{pmatrix}. \quad (2.101)$$

Now, let us specialize to the case of only kinetic reactions. It then holds that $N_R^K \equiv N_R$, $\xi^K \equiv \xi$, and we can write the composition vector as

$$n = n^0 + \begin{pmatrix} \hat{V} \xi \\ \xi \end{pmatrix}. \quad (2.102)$$

Through differentiation with respect to time of the above equations, we find the following system of ODEs:

$$\begin{cases} \dot{n} &= \begin{pmatrix} V \dot{\xi} \\ \dot{\xi} \end{pmatrix}, \\ n(0) &= n^0, \end{cases} \quad (2.103)$$

where we use the notation $\dot{n} \equiv dn/dt$ to denote a pure time derivative. The above equations constitute a system of N_S ODEs in the mole-numbers n . To close the system, we need an additional N_R relations. We see that we can *identify* the rate of change of the extents of reaction $\dot{\xi}$ with the rates of change of the mole number of the *product species*, so that it is natural to define

$$R^K \equiv \dot{\xi}, \quad (2.104)$$

where $R^K(n) \in \mathbb{R}^{N_R}$ are some rate expressions that govern the formation of the product species in our system. With this definition, and using the fact that $n = n(\xi)$, we can re-write (2.103) as

$$\begin{cases} \dot{\xi} &= R^K(n(\xi)), \\ \xi(0) &= 0. \end{cases} \quad (2.105)$$

Here, we have used the fact that $n(0) = n^0$ to find the appropriate initial condition $\xi(0) = 0$ for the extents of reaction. Note that (2.105) are a system of N_R ODEs for the unknowns ξ . The specific form of the functions R^K is the topic of the next section.

2.4.3 Rate-Laws

Our task is now to assign functional expressions in terms of composition variables for the N_R^K rate functions R^K introduced in the previous section. Such expressions are commonly known as *rate-laws*.

Rate-laws are normally given in intensive form, so we consider that the rate of change of kinetic product species i *per bulk volume* ΔV of the system, is

$$r_i^K = \frac{R_i^K}{\Delta V}. \quad (2.106)$$

As noted earlier, thermodynamics itself provides no information about the *rate* of chemical processes. This means in particular that the functional dependence of r^K on composition must often be determined through experiments, and can in principle have quite a general compositional dependence. On the other hand, they are ultimately constrained by the equilibrium limit, i.e., if a sufficiently long time passes during which our system is undisturbed, we expect that the reaction rate eventually reaches zero, and that the final composition is that which would have been predicted based on a thermodynamic description. Under such circumstances, it can be justified to express the rate-law as a function of the affinity of the reaction,

$$r_i^K = r_i^K(\mathcal{A}_i), \quad i = 1, \dots, N_R^K. \quad (2.107)$$

With this formulation, the requirement that the reaction ceases when the equilibrium-limit has been reached is conveniently stated as $r_i^K(\mathcal{A}_i) = 0$ when $\mathcal{A}_i = 0$.

Furthermore, $\mathcal{A}_i \geq 0$ implies that the reaction has “an affinity to proceed”, which corresponds in a natural way to $r_i^K \geq 0$. In practical concentration variables, the rate-law is often written

$$r_i^K = k_i^f \prod_{j=1}^{N_C} (c_j)^{\hat{a}_{ji}} - k_i^b c_{N_C+i} \quad i = 1, \dots, N_R^K. \quad (2.108)$$

The above form of the rate-law is referred to as the “Law of Association” for the reaction. Several comments are in order. First, the constants $k_i^f \geq 0$ and $k_i^b \geq 0$ are the *forward* and *backward rate-constants* for the i th kinetic reaction, respectively. By comparison with the mass-action expressions (2.93) derived earlier, we see that the limit $r_i^K = 0$ corresponds to chemical equilibrium for this reaction, provided that the relationship

$$K_i = \frac{k_i^f}{k_i^b} \quad (2.109)$$

holds between the equilibrium constant and the rate-constants.

2.5 The Mathematical Formulation of the Chemical Batch Problem

In the final section of this chapter we give, in a concise form, the governing equations for the three major categories of reactive batch systems that we have encountered: *equilibrium*, *kinetic* and *mixed*. The equations for the equilibrium case are the necessary conditions of equilibrium for the corresponding minimization problem, and we discuss different ways of solving those equations. The situation is quite different for a kinetic system, where a system of ODEs subject to linear constraints result. We then discuss the case of both equilibrium and kinetic reactions. Here, the mathematical structure is a combination of the aforementioned two classes. Finally, we conclude this section with a brief survey of known existence and uniqueness results for the equilibrium problem.

2.5.1 The Equilibrium Problem

The equilibrium batch problem is the task of determining the equilibrium composition vector n of a *closed system* at *fixed temperature* T and *pressure* p , given the element or component abundance vector e . If the system is *heterogeneous*, the number of phases and their relative abundance must also be determined.

Two equivalent formulations of the problem are the *non-stoichiometric* and the *stoichiometric* formulations both of which are given below. As before, $A \in \mathbb{R}^{N_C \times N_S}$ denotes the formula-matrix, and $V \in \mathbb{R}^{N_S \times N_R}$ the stoichiometric matrix, the columns of which span the null-space of A . Furthermore, $n^0 \in \mathbb{R}^{N_S}$ denotes a generic composition vector satisfying mass-balance, and $e \in \mathbb{R}^{N_C}$ are the component (sometimes element) abundances. Finally, the chemical potentials μ are given by expressions such as equations (2.75) or (2.76), introduced in Section 2.3.4.

The Non-Stoichiometric Formulation

The equilibrium composition n^* is the solution to

$$\begin{aligned} \min_n \quad & G(n) & (2.110) \\ \text{s.t.} \quad & An = e, \\ & n \geq 0, \end{aligned}$$

where $G(n) \equiv n^T \mu(n)$. Proceeding as in Appendix A, we introduce the *Lagrangian*, l ,

$$l(n, y, z) = n^T \mu + y^T (An - e) - z^T n, \quad (2.111)$$

where $y \in \mathbb{R}^{N_C}$ and $z \in \mathbb{R}^{N_S}$ are *Lagrange multipliers* corresponding to equalities and inequalities, respectively. We can express the first-order necessary Karush-Kuhn-Tucker (KKT) conditions (see Karush [23] and Appendix A) as follows

$$\mu + A^T y - z = 0, \quad (2.112)$$

$$An - e = 0, \quad (2.113)$$

$$\Lambda(n)z = 0, \quad (2.114)$$

$$(n, z) \geq 0. \quad (2.115)$$

In the above equations $\Lambda(n)$ denotes a diagonal matrix with the vector n on its main diagonal. Note that (2.112)-(2.114) represent $N_{eq} = 2N_S + N_C$ equations in the unknowns n , y and z . If all the inequality constraints are *non-binding* ($n > 0$) at the solution, then $z \equiv 0$ by virtue of the *complementarity equations* (2.114) and there results the following system of size $N_{eq} = N_S + N_C$

$$\mu + A^T y = 0, \quad (2.116)$$

$$An - e = 0, \quad (2.117)$$

$$n > 0. \quad (2.118)$$

Smith [40] and Smith and Missen [41] give a thorough review of the many different ways of manipulating the equations (2.112)-(2.114). Their presentation is based on a form of the Lagrangian that does not include the non-negativity multipliers, z , but similar results can be obtained in our case.

The main conclusion regarding the non-stoichiometric formulation is that a substantial reduction in the number of variables can be realized in the case of an *ideal system*. In this case, the N_S mole numbers n can be expressed in terms of y and z , and substituted into the mass-balance conditions (2.113) to yield an equivalent system of nonlinear equations of size $N_{eq} = N_C$, for the case of a single, ideal phase. For the multiphase, ideal case, Smith and Missen [41] derive instead a system of size $N_{eq} = N_C + \pi$, where π is the number of phases. Let us carry out the derivation for the ideal, single phase case. In this case, it can be shown [41] that the mole numbers satisfy $n_i > 0$, implying $z_i = 0$. Writing the KKT conditions (2.116)–

(2.117) in component form, we have

$$\mu_i + \sum_{j=1}^{N_C} a_{ji} y_j = 0, \quad i = 1, \dots, N_S, \quad (2.119)$$

$$\sum_{j=1}^{N_S} a_{ij} n_j - e_i = 0, \quad i = 1, \dots, N_C. \quad (2.120)$$

Substituting the chemical potential appropriate for an ideal phase,

$$\mu_i = \mu_i^0 + RT \log\left(\frac{n_i}{\tilde{n}^\alpha}\right), \quad (2.121)$$

into equation (2.119) and rearranging produces an expression for n_i :

$$n_i = \tilde{n}^\alpha \exp\left(\frac{-\mu_i^0}{RT}\right) \exp\left(-\frac{1}{RT} \sum_{k=1}^{N_C} a_{ki} y_k\right) \quad (2.122)$$

Defining for convenience the quantities

$$\sigma_i = \exp\left(\frac{-\mu_i^0}{RT}\right), \quad (2.123)$$

and

$$\rho_k = \exp\left(-\frac{y_k}{RT}\right), \quad (2.124)$$

this can be written more compactly as

$$n_i = \tilde{n}^\alpha \sigma_i \prod_{k=1}^{N_C} \rho_k^{a_{ki}}. \quad (2.125)$$

Substituting this expression into the mass-balance equation (2.120), this produces the equation

$$\sum_{j=1}^{N_S} a_{ij} \tilde{n}^\alpha \sigma_j \prod_{k=1}^{N_C} \rho_k^{a_{kj}} = e_i, \quad i = 1, \dots, N_C. \quad (2.126)$$

The equations (2.126) and the definition of \tilde{n}^α ,

$$\tilde{n}^\alpha = \sum_{i=1}^{N_S} n_i, \quad (2.127)$$

comprise a square system of size $N_{eq} = N_C + 1$ in the variables $\rho \in \mathbb{R}^{N_C}$ and the total moles \tilde{n}^α .

An important point about the non-stoichiometric formulation described, is that the reduction mentioned above is possible *only for ideal systems*.

The Stoichiometric Formulation

Given n^0 satisfying $An^0 = e$, the equilibrium composition n^* can be expressed as

$$n^* = n^0 + V\xi^*, \quad (2.128)$$

where the *equilibrium extents of reaction* ξ^* are the solutions to the constrained minimization problem

$$\begin{aligned} \min_{\xi} \quad & G[n(\xi)] \\ \text{s.t.} \quad & n(\xi) \geq 0, \end{aligned} \quad (2.129)$$

where $G[n(\xi)] \equiv n(\xi)^T \mu(n(\xi))$. It can be established easily that the KKT conditions for this formulation are of the form

$$V^T \mu = V^T z, \quad (2.130)$$

$$\Lambda(n(\xi))z = 0, \quad (2.131)$$

$$(n(\xi), z) \geq 0. \quad (2.132)$$

The equations (2.130)–(2.131) constitute $N_R + N_S$ equations in the unknowns ξ and z . If it can be established that the constraints are non-binding, it is again clear that we must have $z = 0$ at the solution. The problem then reduces to the $N_{eq} = N_R$ equations

$$V^T \mu = 0, \quad (2.133)$$

$$n(\xi) > 0. \quad (2.134)$$

This is sometimes referred to the “classical” form of the equilibrium conditions. Simple substitution of the appropriate form of the chemical potential function (and using the canonical form of V) leads directly to the mass-action equations mentioned earlier. This derivation is included for completeness in Appendix B.

2.5.2 The Kinetic Problem

Consider a system in which all reactions are governed by known rate-laws, $r^K \in \mathbb{R}^{N_R}$. Given a composition vector n^0 at time $t = 0$ that satisfies the closed-system constraints $An^0 = e$, the problem is to find the composition $n(t)$ at some future time t , compatible with the set of rate-laws r^K and the closed system constraints.

The solution $n(t)$ can be expressed as

$$n(t) = n^0 + V\xi(t), \quad (2.135)$$

where the extents of reaction satisfy the following system of N_R ODEs

$$\begin{cases} \dot{\xi} &= R^K[n(\xi)], \\ \xi(0) &= \mathbf{0}. \end{cases} \quad (2.136)$$

The rate-laws r^K are of the form given in Section 2.4.3, e.g., equation (2.108).

Finally, it holds that $R^K \equiv \Delta V r^K$.

2.5.3 The Mixed Kinetic/Equilibrium Problem

We will refer to a system whose reactions are of both kinetic and equilibrium type as *mixed*. The number of equilibrium reactions is N_R^Q and the number of kinetic reactions is N_R^K . Using the decomposition (2.99), and given some n^0 satisfying $An^0 = e$, we write the composition at time t as

$$n(t) = n^0 + V^Q \xi^Q + V^K \xi^K. \quad (2.137)$$

Here, the kinetic extents of reaction are governed by the system of ODEs

$$\begin{cases} \dot{\xi}^K &= R^K[n(\xi^K, \xi^Q)], \\ \xi^K(0) &= \mathbf{0}, \end{cases} \quad (2.138)$$

where, as before, the rate-laws $r^K \equiv R^K/\Delta V$ are given by (2.108). Before proceeding to impose the conditions of equilibrium, we must indicate how the kinetic species interact with the rest of the system. Recall that the expression (2.137) really embodies a decomposition into *component species* and two classes of *product species*, equilibrium and kinetic. Writing this as $n = (n^c, n^K, n^Q)^T$, it is clear from (2.101) that a change in ξ^Q will affect n^c and n^Q , but leave n^K unchanged. The kinetic species are therefore “inert” as far as the equilibrium step is concerned, but, recalling the definition of mole-fraction (2.69), they still have an impact on the overall composition.

Using the notation $n' \equiv (n^c, n^Q) \in \mathbb{R}^{N_c + N_R^Q}$, we can express the equilibrium problem (for each ξ^K) as follows:

$$\begin{aligned} \min_{\xi^Q} \quad & G[n(\xi^Q, \xi^K)] \\ \text{s.t.} \quad & n'(\xi^Q, \xi^K) \geq 0, \end{aligned} \tag{2.139}$$

where $G[n(\xi^Q, \xi^K)] \equiv n(\xi^Q, \xi^K)^T \mu[n(\xi^Q, \xi^K)]$. Note that the Gibbs free energy continues to depend on the entire species vector, $n \in \mathbb{R}^{N_s}$, whereas the inequality constraints only affect n' . It is clear that the two systems (2.138) and (2.139) are *coupled*, and that the problem, therefore, is of mixed algebraic/differential type.

Clearly, (2.139) represents the normal equilibrium calculation encountered earlier, expressed in stoichiometric form. Therefore, the developments regarding the stoichiometric formulation of the *equilibrium* problem also apply to the problem (2.139).

We could equally well have stated the equilibrium conditions in a non-stoichiometric form, however. To demonstrate this, note that the non-stoichiometric form of the equations (2.139) is nothing but

$$\min_{n'} \quad G(n', n^K) \tag{2.140}$$

$$\text{s.t.} \quad An = e, \quad (2.141)$$

$$n' \geq 0. \quad (2.142)$$

However, by defining a reduced formula matrix $A' \in \mathbb{R}^{N_C \times (N_C + N_R^Q)}$,

$$A' = (I_{N_C} \quad \hat{A}^Q), \quad (2.143)$$

(where, in fact, $\hat{A}^Q = -\hat{V}^Q$), and a reduced vector of component totals, $e' \in \mathbb{R}^{N_C}$,

$$e' = e - \hat{A}^K n^K, \quad (2.144)$$

the mass-constraints $An = e$ imply that n' must satisfy

$$A'n' = e'. \quad (2.145)$$

With these definitions, the non-stoichiometric formulation for the mixed problem (corresponding to the kinetic vector n^K), is

$$\min_{n'} G(n', n^K) \quad (2.146)$$

$$\text{s.t.} \quad A'n' = e', \quad (2.147)$$

$$n' \geq 0, \quad (2.148)$$

which is clearly equivalent to the form (2.110).

2.5.4 Existence and Uniqueness Issues for the Equilibrium Problem

We turn our attention to the pure equilibrium problem in one of its equivalent forms (2.110) or (2.129).

As pointed out by Smith [40] and Shapiro and Shapley [37], the existence of a solution to this problem is guaranteed in all circumstances, given some conditions of compatibility of A and e . In particular, we must assume that the component abundances satisfy $e_i \geq 0$, with at least one $e_i > 0$. Furthermore, we must

assume a compatibility property of the system, i.e., the intersection of the non-negativity constraints and the element-abundance constraints must be non-empty. Mathematically, we assume that the set

$$S \equiv \{n \mid An = e, n \geq 0\} \quad (2.149)$$

is non-empty. In order for this to hold in general, it is clearly necessary that $\text{rank}(A) = \text{rank}([A, e])$.

Existence now follows from the fact that $G(n)$ is a real-valued, continuous function of the n_i on a compact (closed and bounded) domain. By the Weierstrass theorem, G attains a minimum and a maximum value on its domain of definition. As noted in [40], the continuity of G usually only poses a potential problem as some n_j approaches zero. For an ideal solution, this is easily resolved by noting that the negative infinity that thus arises in μ_j is cancelled by the linear term n_j that multiplies it, that is

$$\lim_{n_j \rightarrow 0} n_j \mu_j(n_j) = 0. \quad (2.150)$$

Using this convention, G is continuous as $n_j \rightarrow 0$ and everywhere else in the domain of definition.

The question of uniqueness of solution to the problem (2.110) is more complicated, and involves the actual functional form used for the chemical potentials in the case of non-ideality.

Let us look at some cases of increasing complexity. For an *ideal, single-phase* solution, it is easy to show [40] that the Gibbs free energy G is a *strictly convex* function, subject to the *convex* set of constraints, i.e.,

$$\sum_{i,j=1}^{N_S} \left(\frac{\partial^2 G}{\partial n_i \partial n_j} \right) \delta n_i \delta n_j > 0 \quad (2.151)$$

for all allowable variations of the composition $\delta n_i, \delta n_j$. For such a case, uniqueness is established, and the KKT conditions (2.112)–(2.115) are both necessary and sufficient.

Considering next the case of an *ideal, multi-phase* system, it can be shown that G is still convex subject to the constraints on n . However, it is no longer in general strictly convex, and certain degenerate non-uniqueness can arise. As pointed out by Smith [40], only the relative amounts of phases are undetermined in such cases. He reports a simple example involving gaseous and liquid water at T and p on the vapor pressure line of $\text{H}_2\text{O}(\text{aq})$, and concludes that at a ratio of 2 : 1 for the total amounts of hydrogen and oxygen, the relative amounts of the liquid and gaseous phase can have any value. We note that since G is convex, non-uniqueness implies that the same value of the free energy is attained at nearby points, and therefore, by convexity, on all points along some line in composition space. The implication, as is well-known in the optimization literature, is that the Hessian of G must be singular at the solution, a fact that can cause numerical difficulties.

Finally, for the most general case of *non-ideal, multi-phase* systems, it is known that the Gibbs free energy may possess several local minima, i.e., G is (at least for certain chemical potential models) no longer convex (see Smith and Missen [41]).

Chapter 3

Reactive Transport in a Porous Medium

Chapter Synopsis

This chapter is concerned with the *transport* of chemically reactive species through the subsurface. By transport, we mean the movement, both through an average velocity field (advection) and through the random motion about the average velocity (diffusion and dispersion). As species are transported through the medium, reactions occur simultaneously and change the speed of propagation of species by distributing the mass in the system between such phases that are stationary and such that are mobile. In general, transport could occur in several *flowing* phases. However, we restrict ourselves to a study of a single flowing phase (the aqueous phase) and several solid (immobile) phases.

3.1 Introduction

In this section, we will introduce the major simplifying assumptions made in our approach to reactive transport, and make some comments about the ramifications of those assumptions.

1. The system is comprised of an aqueous (flowing) phase, and an arbitrary number of solid (immobile) phases. The solid phases can either be of *surface* type to accommodate adsorption, ion-exchange or a residual phase, or of *single-species* type for minerals.
2. The system is at *isothermal* conditions.

3. Transport occurs in a single, incompressible aqueous (flowing) phase which completely saturates the porous medium.
4. General reactions are allowed within the aqueous phase (homogeneous), as well as between phases (heterogeneous).
5. The *flow properties* of the aqueous phase are *unchanged* by the chemical transformations that occur within the system.

Assumptions 1 and 3 are possibly the most important. They imply that we do not have to concern ourselves with the a full multi-phase flow situation; in particular, there will be no need for equations of state relating *phase properties* (such as phase density or specific molar volume) to the *composition* of the phase. This assumption greatly simplifies the presentation here, but it also precludes the study of many important phenomena, such as compositional oil-simulation and unsaturated flow.

The assumption 2 simply states that thermal effects will be left unaccounted for. If temperature variations within the reservoir were to be taken into consideration, a conservation of energy equation would have to be added to the field equations. Thermal effects are probably of limited importance for most ground-water studies, but could of course have a profound impact in other applications (geothermal flow, enhanced oil recovery).

The commonly made assumption 5 states that *flow properties* are unaffected by chemical transformations. Phrased differently, we assume that the flow equations (the field equations determining the distributions of pressure and the aqueous-phase flux) can be solved *independently* of the transport equations. This is obviously an approximation, as bulk properties of the flowing phase could easily change due to reactions (consider the increase in viscosity as a gel forms). Similarly, the

resistance to flow inherent in the porous matrix can be quite sensitive to, for example, the formation or dissolution of minerals.

3.2 Definitions and Nomenclature

Let us begin the exposition by defining some terminology. We let the symbol V denote the bulk volume of a *representative elementary volume* (REV) (see Bear [4], Slattery [38] or Bird et al. [5]) of porous medium, and V^{void} denote the volume of void space within V . Their ratio is commonly known as the *porosity* ϕ ,

$$\phi = \frac{V^{void}}{V}. \quad (3.1)$$

The various phases that comprise the system all have corresponding volumes V^α which make up the bulk volume V . As pointed out in Section 2.3.3, we can express the *phase molar concentration* of a species i , c_i , as

$$c_i = \frac{n_i}{V^{\beta(i)}}, \quad (3.2)$$

where, $\beta(i)$ denotes the phase in which i participates. In the simplified case of one flowing phase that completely saturates the medium, we have $V^{void} = V^{aq}$

For convenience, we define molar concentrations with respect to the aqueous phase volume even for species that *do not* participate in the aqueous phase. This is done strictly to facilitate writing the equations in a uniform fashion, and affects in no way the generality of the approach.

The vector of molar concentrations $c = (c_1, \dots, c_{N_s})^T$ has entries

$$c_i = \frac{n_i}{V^{aq}}. \quad (3.3)$$

In making the transition to a *continuum* (as opposed to batch) description, the composition variables become functions of time and space, i.e., the symbol c is

henceforth taken to mean a vector-valued function $c : \mathbb{R}^{d+1} \rightarrow \mathbb{R}^{N_S}$. We note that point-wise values of such functions must be interpreted as averages over the REV. For notational convenience, we will often suppress the explicit dependence on position and time.

The *species molar flux*, $f_i = (f_{i,x}, f_{i,y}, f_{i,z})$, expresses the flux of species i in units of moles per bulk area and time.

The *rate of creation/destruction* of species i , resulting from all chemical transformations (reactions), including phase-transfer and intra-phase reactions, is denoted r_i . It has units of moles per bulk volume and time.

Finally, the *rate of supply/withdrawal* of species i , resulting from *external sources*, (such as wells) is denoted s_i . Its units, like the reaction terms, are moles per bulk volume and time.

Next, we re-examine the definition made in Section 2.2.1 of the phase-identity matrix P^α , given by (2.10)–(2.12). Specializing to a single flowing phase, define a flowing phase-identity matrix P^{aq} . By virtue of (2.13), we can also define a phase-identity matrix P^s corresponding to *immobile species* as

$$P^s = I - P^{aq}. \quad (3.4)$$

The form of the matrix P^{aq} is simply

$$P^{aq} = \text{diag} (\delta_{aq,\beta(1)}, \dots, \delta_{aq,\beta(N_S)}). \quad (3.5)$$

3.3 General Remarks on Transport in a Single Flowing Phase

3.3.1 The Single-Phase, Incompressible Flow Equations

We consider the conservation of the aqueous phase over some domain of interest $\Omega \subseteq \mathbb{R}^d$, with boundary $\partial\Omega$ equipped with an outward normal vector field ν .

The *flow* of the aqueous phase is governed by the overall conservation of mass equation,

$$\nabla \cdot u = q_w, \quad (3.6)$$

where $u \in \mathbb{R}^d$ is the Darcy velocity, i.e., the flux of water per unit area of porous medium, and $q_w = q_w(x, t)$ is an external source distribution. In writing (3.6), we have made use of the assumption of incompressibility stated earlier.

An empirical law known as *Darcy's Law* [4] relates the Darcy velocity u to the water pressure p as

$$u = -k(\nabla p - \rho g), \quad (3.7)$$

where the tensor coefficient $k \in \mathbb{R}^{d \times d}$ is the *permeability* of the medium, $g \in \mathbb{R}^d$ is the gravitational vector, and ρ is the density of the fluid. Defining the *potential* Ψ as

$$\Psi = p - \rho z, \quad (3.8)$$

where z denotes depth with respect to some reference level, the equations (3.6), (3.7) and (3.8) combine to form an elliptic partial differential equation for the potential,

$$-\nabla \cdot k \nabla \Psi = q_w, \quad x \in \Omega. \quad (3.9)$$

Typical boundary conditions for (3.9) are of *Neumann* and *Dirichlet* type. By writing $\partial\Omega = \bar{\Gamma}_1 \cup \bar{\Gamma}_2$, where $\Gamma_1 \cap \Gamma_2 = \emptyset$, we can illustrate these conditions as they may apply to different segments of the boundary, e.g.,

$$u \cdot \nu = f^*, \quad x \in \Gamma_1, \quad t > 0, \quad (3.10)$$

and

$$p = p^*, \quad x \in \Gamma_2, \quad t > 0, \quad (3.11)$$

where f^* and p^* denote prescribed normal flux and pressure, respectively.

3.3.2 The Advection-Diffusion-Reaction Equations (ADR)

By performing a mass-balance over a representative elementary volume (REV) for each species in the system, as explained in more detail in [4, 38], there results the following system of N_S coupled, nonlinear partial differential equations (PDE):

$$\frac{\partial(\phi c_i)}{\partial t} + \nabla \cdot f_i = r_i + s_i \quad i = 1, \dots, N_S, \quad (3.12)$$

In vector form, these equations can be written

$$\frac{\partial(\phi c)}{\partial t} + \nabla \cdot f = r + s. \quad (3.13)$$

Here, the definition of the divergence operator has been extended in the obvious way, so that

$$(\nabla \cdot f)_i \equiv \nabla \cdot f_i. \quad (3.14)$$

3.3.3 Constitutive Relations for the Species Flux

In this section we make some assumptions regarding the form of the species flux-terms f_i . Many different possibilities exist, depending on the application and the level of sophistication of the mathematical model.

Since the processes of advection and diffusion occur within the flowing phase, the phase identity of species must now be explicitly taken into account.

For a species participating in the flowing phase, we express the molar flux of the species as a sum of two distinct processes, *advection* and *diffusion*. Denoting the advective flux by the symbol f_a , and the diffusive flux by f_d , we express this simply as:

$$f_i = f_{a,i} + f_{d,i}. \quad (3.15)$$

The advective flux of i is transport of the species with the mean velocity of the phase in which the species participates, in this case exclusively the aqueous phase

velocity u , i.e.,

$$f_{a,i} = uc_i. \quad (3.16)$$

The diffusive flux is expressed via the standard Fick's Law, which is

$$f_{d,i} = -D(u)\nabla c_i. \quad (3.17)$$

The tensor $D \in \mathbb{R}^{d \times d}$ is generally composition-dependent; however, we neglect to account for this complication here. As indicated, D is also generally dependent upon (phase) velocity, and hence on position. Possible forms of this dependence can be found in Bear [4] and Peaceman [29]. For convenience, we will often suppress this dependence in writing, although it is accounted for in our model. In summary, the species molar fluxes can now be expressed

$$f_i = \delta_{a q, \beta(i)} (uc_i - D\nabla c_i), \quad i = 1, \dots, N_S, \quad (3.18)$$

or, equivalently in vector form

$$f = u(P^{a q}c) - D\nabla(P^{a q}c). \quad (3.19)$$

3.3.4 Species Source and Sink Terms

The term s_i appearing in the species ADR (3.12) accounts for an external supply of mass of the i th species, i.e., a source/sink that is in some sense “external” to the system we are modeling. There are at least two distinct scenarios in which such a term must appear:

1. The supply or withdrawal of fluid by means of wells;
2. Incomplete description of chemistry.

In the former case, the injected stream will typically contain a mixture of different composition from that of the interior of the domain. Similarly, the withdrawal of fluid causes a depletion of the species that are present in that part of the domain.

The second, perhaps less obvious, case is the use of an external source/sink terms as a means of modeling reactions whose end product are of no interest to us, or that we for reasons of efficiency choose to neglect. As an example, we may choose not to treat radioactive decay rigorously, but can still in some sense account for such processes by including a decay term as a sink in the species ADR.

3.3.5 The Specification of Boundary and Initial Conditions

The boundary conditions applied to the species ADR (3.12) fall into three categories: *Dirichlet*, *Neumann* or *Mixed*, also known as *Robin* or *Danckwert's* boundary condition. The Dirichlet condition is the specification of function value, i.e.,

$$c(x, t) = c^I(x, t), \quad x \in \partial\Omega, \quad t > 0. \quad (3.20)$$

A typical example of a Neumann boundary condition is the condition of *no dispersive flux*, commonly imposed at an outflow boundary, namely,

$$D\nabla c(x, t) \cdot \nu = 0, \quad x \in \partial\Omega, \quad t > 0. \quad (3.21)$$

Finally, a Robin, or Danckwert's condition imposes a continuity of flux and is typically used at an inflow boundary,

$$(uc(x, t) - D\nabla c(x, t)) \cdot \nu = uc^I(x, t) \cdot \nu, \quad x \in \partial\Omega, \quad t > 0. \quad (3.22)$$

The specification of initial conditions amounts to the prescription of a vector of concentration fields c^0 ,

$$c(x, 0) = c^0(x), \quad x \in \Omega. \quad (3.23)$$

Additional comments on the prescription of initial and boundary conditions with regard to the conditions of electroneutrality are made in Section 3.7.

3.4 The Local Equilibrium System (LE)

3.4.1 Derivation of the Component Based Form of the ADR

In this section, we consider the important case of *local chemical equilibrium* (LE) for the reactive system. The assumption of LE, which has been amply discussed elsewhere [36], implies that *all chemical reactions occur sufficiently fast in comparison with other processes (advection, diffusion) that we can assume that a state of local equilibrium exists everywhere in the domain.*

Let us begin by writing the species conservation equations (3.13) in the form

$$\frac{\partial(\phi c)}{\partial t} + \nabla \cdot (u(P^{aq}c) - D\nabla(P^{aq}c)) = Vr^Q + s, \quad (3.24)$$

where we note that $V = V^Q \in \mathbb{R}^{N_s \times N_R}$, and $r^Q \in \mathbb{R}^{N_R}$, since the equilibrium reactions span the entire stoichiometric space. This form of the equations is not directly useful, however, because of the presence of the equilibrium reaction-rates r^Q . The rates r^Q are not known, but rather implicitly defined through the equilibrium conditions that apply *pointwise* throughout the domain. To proceed, these rates must be eliminated. Operating on (3.24) from the left with the formula matrix A , using the linearity of the differential operators, the constancy of A and the assumption that D be composition-independent, recalling that the columns of V span the null-space of A , we arrive at a set of conservation equations where the unknown rates have been eliminated,

$$\frac{\partial(\phi Ac)}{\partial t} + \nabla \cdot (u(AP^{aq}c) - D\nabla(AP^{aq}c)) = As. \quad (3.25)$$

The form of the above equations motivates a few definitions. The *total component concentration* , $T \in \mathbb{R}^{N_c}$, is given by the linear transformation

$$T = Ac. \quad (3.26)$$

Analogously, the *total flowing component concentrations*, $C \in \mathbb{R}^{N_c}$, are defined by

$$C = AP^{aq}c. \quad (3.27)$$

Finally, the *total external component source*, $S \in \mathbb{R}^{N_c}$, is written in terms of the individual species sources as

$$S = As. \quad (3.28)$$

Using the definitions (3.26)–(3.28) we can state the *conservation of component* equations thus:

$$\frac{\partial(\phi T)}{\partial t} + \nabla \cdot (uC - D\nabla C) = S. \quad (3.29)$$

The above system of equations express the fundamental fact that the *mass of a component in the REV, in whatever phases or chemical species it may participate, only changes due to the net component flux and external sources or sinks.*

3.4.2 A Complete Set of Equations for the LE Problem

In this section we give the complete set of equations describing the case of local equilibrium reactive transport. As demonstrated in the previous section, the overall mass-balances for the system components are

$$\frac{\partial(\phi T)}{\partial t} + \nabla \cdot (uC - D\nabla C) = S, \quad , x \in \Omega, \quad t > 0. \quad (3.30)$$

These PDEs must be augmented with the appropriate initial conditions

$$T(x, 0) = T^0(x), \quad x \in \Omega, \quad (3.31)$$

and boundary conditions

$$C(x, t) = C^I(x, t), \quad x \in \partial\Omega, \quad t > 0. \quad (3.32)$$

We have chosen Dirichlet boundary conditions strictly for convenience of exposition; in general, any of the other types introduced in Section 3.3.5 can be used.

The total source/sink terms S are known in terms of the individual species source/sink terms s through (3.28), and the totals T and C are related to the individual species c by means of equations (3.26) and (3.27).

By assumption of local chemical equilibrium, the species concentration vector c is furthermore constrained *pointwise* by the equations governing local equilibrium. Using the non-stoichiometric form of the equilibrium conditions, developed in Section 2.5.1, these restrictions can be stated in the form of a nonlinear programming problem

$$\begin{aligned} c &= \arg \min_c G(c) & (3.33) \\ \text{s.t. } Ac &= T, \\ c &\geq 0. \end{aligned}$$

3.5 The Local Non-Equilibrium System (LNE)

We will refer to the reactive system as being of *local non-equilibrium type* (LNE) if it is stipulated that *all reactions may fail to attain equilibrium locally during the course of transport*. This is the continuum analogue of the kinetically controlled batch-system encountered in Section 2.5.2. In the case of only kinetic reactions, the state of the system is determined by the set of rate-laws r^K and the species ADR. Since the entire stoichiometric space is now spanned by $V = V^K$, we may express the species reaction vector $r \in \mathbb{R}^{N_s}$ as

$$r = V r^K. \quad (3.34)$$

Using this result, along with the constitutive equations for the species flux (3.19), the species ADR (3.13) can be written

$$\frac{\partial(\phi c)}{\partial t} + \nabla \cdot (u(P^{aq}c) - D\nabla(P^{aq}c)) = Vr^K + s, \quad x \in \Omega, \quad t > 0. \quad (3.35)$$

The above equations constitute a system of N_S coupled, nonlinear PDEs (or ODEs, if solid species are present) for the N_S species concentrations c . The N_R rate-laws r^K are known functions of composition, i.e.,

$$r^K = r^K(c), \quad (3.36)$$

as described in more detail in Section 2.4.3. To complete the description we must also prescribe initial conditions

$$c(x, 0) = c^0(x), \quad x \in \Omega, \quad (3.37)$$

and boundary conditions,

$$c(x, t) = c^I(x, t), \quad x \in \partial\Omega, \quad t > 0. \quad (3.38)$$

3.6 The Partial Local Non-Equilibrium System (PLNE)

In the most general case, the chemical reactions fall into two classes, namely those that are sufficiently fast with respect to other processes that they may be considered to be at equilibrium at every point (LE), and those that occur on a time-scale comparable with the time of transport, and which may therefore not attain equilibrium (LNE), at least for some $x \in \Omega$ and $0 \leq t \leq T$. This is the reactive-transport analogue of the mixed batch system encountered in Section 2.5.3. The species reaction vector r now has the general representation

$$r = V^K r^K + V^Q r^Q, \quad (3.39)$$

where $r^K \in \mathbb{R}^{N_R^K}$ represent the known rate-laws corresponding to the kinetic subset of reactions, and $r^Q \in \mathbb{R}^{N_R^Q}$ is a *formal* representation of the reaction rates by which equilibrium processes occur. The starting point is again the species ADR with the reactions now given by (3.39), that is

$$\frac{\partial(\phi c)}{\partial t} + \nabla \cdot (u(P^{aq}c) - D\nabla(P^{aq}c)) = V^K r^K + V^Q r^Q + s. \quad (3.40)$$

As explained in Section 3.4, the equilibrium reaction rates r^Q are not known, and must therefore be eliminated to obtain a useful form of the transport equations. This goal can be accomplished by operating on (3.40) with the standard formula matrix A , while retaining, in addition, those PDEs which correspond to the transport of kinetic product species. This procedure results in a set of N_C ADR equations, governing the total analytical concentrations, augmented by N_R^K species ADR for the kinetic product species. We have chosen instead the (mathematically) equivalent strategy of constructing a “pseudo formula matrix” $M \in \mathbb{R}^{(N_C + N_R^K) \times N_S}$ (see [36, 41]), which has the property that it eliminates the equilibrium rates *only*,

$$MV^Q = 0 \in \mathbb{R}^{N_C + N_R^K}. \quad (3.41)$$

Such a matrix can always be found, since the N_R^Q columns of V^Q are linearly independent, and the rows of M , being orthogonal to the columns of V^Q , are simply some basis for the $(N_S - N_R^Q) = (N_C + N_R^K)$ dimensional subspace in \mathbb{R}^{N_S} , perpendicular to the column-space of V^Q . In fact, inspection shows that M has the explicit form

$$M = \begin{pmatrix} I_{N_C} & 0 & \hat{A}^Q \\ 0 & I_{N_R^K} & 0 \end{pmatrix}, \quad (3.42)$$

where we have used the fact that $\hat{A}^Q = -\hat{V}^Q$.

Operating on (3.40) from the left with M , we find a set of $N_C + N_R^K$ ADRs,

$$\frac{\partial(\phi Mc)}{\partial t} + \nabla \cdot (u(MP^{aq}c) - D\nabla(MP^{aq}c)) = Ms + MV^K r^K. \quad (3.43)$$

In order to better understand the structure of these equations, we write the species vector c in the form

$$c = \begin{pmatrix} c^c \\ c^K \\ c^Q \end{pmatrix}. \quad (3.44)$$

Expanding the matrix-vector product Mc , we see that

$$Mc = \begin{pmatrix} c^c + \hat{A}^Q c^Q \\ c^K \end{pmatrix}, \quad (3.45)$$

and that therefore the first N_C components of this vector corresponds to the totals of each component *excluding* kinetic products. This motivates the definition of the total component concentrations *excluding kinetic products* $T' \in \mathbb{R}^{N_C}$,

$$T' = c^c + \hat{A}^Q c^Q. \quad (3.46)$$

Similar considerations make it convenient to define the total flowing component concentrations *excluding (flowing) kinetic products* $C' \in \mathbb{R}^{N_C}$,

$$C' = \begin{pmatrix} I_{N_C} & 0 & \hat{A}^Q \end{pmatrix} P^{aq} c, \quad (3.47)$$

and the total component sources *excluding kinetic products* $S' \in \mathbb{R}^{N_C}$,

$$S' = \begin{pmatrix} I_{N_C} & 0 & \hat{A}^Q \end{pmatrix} P^{aq} s. \quad (3.48)$$

With these definitions, the field equations take the form of a set of component ADRs for the part of the mass that is *unaffected by equilibrium reactions*,

$$\frac{\partial(\phi T')}{\partial t} + \nabla \cdot (u C' - D \nabla C') = \hat{V}^K r^K + S', \quad x \in \Omega, \quad t > 0, \quad (3.49)$$

and a set of species ADRs for *kinetic product species* $i = 1, \dots, N_R^K$,

$$\frac{\partial(\phi c_{N_C+i})}{\partial t} + \delta_{\alpha q, \beta(N_C+i)} \nabla \cdot (u c_{N_C+i} - D \nabla c_{N_C+i}) = r_i^K + s_{N_C+i}, \quad x \in \Omega, \quad t > 0. \quad (3.50)$$

The above equations must be augmented with the appropriate initial conditions,

$$T'(x, 0) = T'^0(x), \quad x \in \Omega, \quad (3.51)$$

$$c^K(x, 0) = c^{K,0}(x), \quad x \in \Omega, \quad (3.52)$$

and boundary conditions,

$$C'(x, t) = C'^I(x, t) \quad x \in \partial\Omega, \quad t > 0, \quad (3.53)$$

$$c^K(x, t) = c^{K,I}(x, t), \quad x \in \partial\Omega, \quad t > 0. \quad (3.54)$$

To close the system, we must express the conditions of local thermodynamic equilibrium that apply to the species vector c . This can be done by requiring *pointwise* that c be expressed as

$$c = c^0 + V^Q \bar{\xi}^Q, \quad (3.55)$$

where c^0 is a vector with non-negative entries, satisfying

$$Mc^0 = \begin{pmatrix} T' \\ c^K \end{pmatrix}, \quad (3.56)$$

but otherwise arbitrary. The vector $\bar{\xi}^Q$, representing equilibrium restrictions, is the solution to the nonlinear programming problem

$$\begin{aligned} \bar{\xi}^Q &= \arg \min_{\xi^Q} G[c(\xi^Q)] \\ \text{s.t.} \quad c(\xi^Q) &\geq 0. \end{aligned} \quad (3.57)$$

3.7 Overall Electroneutrality in Reactive Transport

Here, we briefly look at the question of maintaining electroneutrality in a system undergoing reactive transport. Our objective is to establish sufficient conditions resulting in overall electroneutrality of the reactive system at every $x \in \Omega$ and for

all $t > 0$. We are not interested in establishing the most general conditions for which electroneutrality holds, but rather in identifying some practically important situations in which this principle applies. For simplicity, we confine ourselves to the LE system described in Section 3.4 and the case of Dirichlet boundary conditions, although similar statements can be made about the LNE and PLNE problems and more general boundary conditions. We start from the ADR in component form complete with boundary data C^I and initial conditions T^0

$$\frac{\partial(\phi T)}{\partial t} + \nabla \cdot (uC - D\nabla C) = S, \quad x \in \Omega, \quad t > 0, \quad (3.58)$$

$$T(x, 0) = T^0(x), \quad x \in \Omega, \quad (3.59)$$

$$C(x, t) = C^I(x, t), \quad x \in \partial\Omega, \quad t > 0. \quad (3.60)$$

Recalling the definition of the intrinsic element and species charge vectors, $z^E \in \mathbb{R}^{N_c}$ and $z \in \mathbb{R}^{N_s}$, introduced in Section 2.2.3, we define the *total charge concentration* Q , as

$$Q = z^T c. \quad (3.61)$$

Using the relation (2.15), $z = A^T z^E$, we have

$$Q = (z^E)^T A c. \quad (3.62)$$

However, the definition of total component concentration (3.26) allows us to express this relation as

$$Q = (z^E)^T T. \quad (3.63)$$

By analogy, the *total flowing charge concentration*, Q^{aq} , is given by

$$Q^{aq} = z^T P^{aq} c. \quad (3.64)$$

Invoking the definition of total flowing concentration (3.27), this is simply

$$Q^{aq} = (z^E)^T C. \quad (3.65)$$

Operating on the PDEs (3.58)–(3.60) with z^E , using the definitions (3.63) and (3.65), we arrive at a transport equation describing the variation of total system charge concentration,

$$\frac{\partial(\phi Q)}{\partial t} + \nabla \cdot (uQ^{aq} - D\nabla Q^{aq}) = S^T z^E, \quad x \in \Omega, \quad t > 0, \quad (3.66)$$

$$Q(x, 0) = (z^E)^T T^0(x), \quad x \in \Omega, \quad (3.67)$$

$$Q^{aq}(x, t) = (z^E)^T C^I(x, t), \quad x \in \partial\Omega, \quad t > 0. \quad (3.68)$$

The right hand side clearly satisfies $S^T z^E = (As)^T z^E = s^T A^T z^E$, or $S^T z^E = s^T z$ so we can define the *total external source of charge* Q^S by

$$Q^S = S^T z^E. \quad (3.69)$$

Similarly, the boundary data and the initial conditions are transformed into *total injected charge* Q^I and *total initial charge* Q^0 , given by

$$Q^I(x, t) = (z^E)^T C^I(x, t), \quad (3.70)$$

and

$$Q^0(x) = (z^E)^T T^0(x). \quad (3.71)$$

With the definitions (3.69)–(3.71) the transport equations for Q become

$$\frac{\partial(\phi Q)}{\partial t} + \nabla \cdot (uQ^{aq} - D\nabla Q^{aq}) = Q^S, \quad x \in \Omega, \quad t > 0, \quad (3.72)$$

$$Q(x, 0) = Q^0(x), \quad x \in \Omega, \quad (3.73)$$

$$Q^{aq}(x, t) = Q^I(x, t), \quad x \in \partial\Omega, \quad t > 0. \quad (3.74)$$

We require that the system is initially electrically neutral, $Q^0(x) \equiv 0$, that the boundary is maintained at zero net charge, $Q^I(x, t) \equiv 0$ and that the external source[†] supplies a neutral mixture, $Q^S(x, t) \equiv 0$. Without such restrictions, it is

[†]For a sink term, this condition is not necessary.

clearly not possible to achieve overall electroneutrality. However, even under the conditions stated, electroneutrality will not hold in general. This is easily seen by considering a *non-reactive* system initially comprised of an aqueous and a solid phase of equal and opposite charge, i.e., $Q^{0,aq} = -Q^{0,solid}$, so that $Q^0(x) = 0$ holds. As flow commences, with $Q^I(x, t) = 0$, electroneutrality is clearly perturbed.

A sufficient condition for electroneutrality, with some important practical applications, is however immediately apparent. If the charge concentration of all solid phases is zero, i.e.,

$$Q^{solid} \equiv Q - Q^{aq} = 0, \quad (3.75)$$

the governing equations (3.72)–(3.74) are homogeneous, and admit only the solution

$$Q^{aq}(x, t) \equiv 0, \quad x \in \Omega, \quad t > 0, \quad (3.76)$$

implying

$$Q(x, t) \equiv 0, \quad x \in \Omega, \quad t > 0. \quad (3.77)$$

This applies to the important cases of aqueous complexation, precipitation/dissolution (uncharged minerals) and ion-exchange (since these surfaces are electrically neutral). However, other mechanisms of mass-transfer, such as adsorption, will not in general result in electroneutrality.

3.8 Summary

In the preceding sections, we identified three classes of reactive transport problems, namely *Local Equilibrium* (LE), *Local Non-equilibrium* (LNE) and *Partial Local Non-Equilibrium* (PLNE). In each case, we stated the governing field equations. In the LE case, they were given by the equations (3.30)–(3.33), for the LNE system they were (3.35)–(3.38), and finally for the PLNE case they were (3.49)–(3.57).

Chapter 4

Numerical Formulation of Reactive Transport in a Porous Medium

Chapter Synopsis

Numerical methods are defined for solving the reactive transport problem described in Chapter 3. An *operator-splitting* approach is introduced, and the individual steps (advection, diffusion and reaction) are treated, with emphasis on the reaction step. A *truncation-error analysis* of the operator-splitting formulation is given. Relative merits of different proposed schemes are discussed.

4.1 Introduction

We present numerical algorithms for the solution of the three classes of reactive transport problems encountered in Chapter 3, namely local equilibrium (LE), local non-equilibrium (LNE) and partial local non-equilibrium (PLNE).

The proposed algorithms employ operator-splitting to separate the effects of continuum transport (field equations) from the effects of chemical transformation (local equations). Consequently, we devote the first section to a description of the application of operator-splitting to these classes of problems. The following sections explain in detail how the individual steps are accomplished. First, some details are given regarding the transport algorithms. In the three subsequent sections, we give a detailed treatment on how the reaction step is handled for each of the classes LE, LNE and PLNE. In Section 4.7, we present a brief analysis of the asymptotic accuracy of the operator-splitting algorithm for this application.

Finally, a comparison is made of the algorithms introduced and other possible choices.

4.2 The Operator-Splitting (OS) Approach

4.2.1 Motivation

The notion of applying operator-splitting (OS) to the ADR equations is not new; indeed, quite a few workers (e.g., [12, 25, 45, 11]) have considered such algorithms in the past. As pointed out in [45], the OS technique has several attractive features, for example:

- Each physical process can be approximated using a numerical method that best suits the underlying mathematical model.
- The field equations describing the overall process are often nonlinear (as in the case of the ADR). Direct discretization gives rise to a *global* system of nonlinear equations (i.e., a system involving unknowns at all spatial locations). By comparison, OS typically results in *linear field equations* and *algebraic-differential local equations*.
- The OS approach is more amenable to the development of modular software.

4.2.2 Overall Algorithm Structure

Our approach to OS is based on the species form of the ADR as introduced in Section 3.3.2, *regardless* of the type of reactive system in question (LE, LNE or PLNE). The justification for this choice, as well as a study of the accuracy of such an approximation, will be given below. The starting point is the system of

nonlinear PDEs

$$\frac{\partial(\phi c)}{\partial t} + \nabla \cdot (u(P^{aa}c) - D\nabla(P^{aa}c)) = r + s, \quad x \in \Omega, \quad t > 0, \quad (4.1)$$

augmented with suitable boundary conditions and initial conditions, as described in Section 3.3.5. At the moment, we refrain from explicitly considering any spatial discretization of the above equations, and consider only the advancement of the solution from the discrete time-levels t^n to t^{n+1} . Let us designate the solution at time t^n by the symbol c^n . The OS strategy consists of a sequence of steps for advancing the solution to the new time-level. We perform first the *advection step*, followed by a *reaction step*, a *diffusion step* and finally an *equilibration step*.

Algorithm 4.1 Reactive Transport Operator-Splitting Framework.

Advection step:

$$\begin{aligned} \frac{\partial(\phi \bar{c})}{\partial t} + \nabla \cdot u(P^{aa}\bar{c}) &= s, \quad x \in \Omega, \quad t^n < t < t^{n+1}, \quad (4.2) \\ \bar{c}(\cdot, t^n) &= c^n(\cdot). \end{aligned}$$

Reaction step:

$$c^{*,n+1} = \mathcal{R}[M\bar{c}^{n+1}], \quad x \in \Omega, \quad t^n < t < t^{n+1}, \quad (4.3)$$

Diffusion step:

$$\begin{aligned} \frac{\partial(\phi \hat{c})}{\partial t} - \nabla \cdot D\nabla(P^{aa}\hat{c}) &= 0, \quad x \in \Omega, \quad t^n < t < t^{n+1}, \quad (4.4) \\ \hat{c}(\cdot, t^n) &= c^{*,n+1}(\cdot), \end{aligned}$$

Equilibration step:

$$c^{n+1} = \mathcal{E}[M\hat{c}^{n+1}], \quad x \in \Omega. \quad (4.5)$$

The above algorithm can be summarized as follows. Given the solution c^n at time-level t^n , we solve the set of linear, hyperbolic PDEs (4.2), using c^n as an initial condition. The solution are the *advected, unreacted* concentrations at the new time-level, a quantity we denote by \bar{c}^{n+1} . Next, we perform the *reaction step* (4.3). Depending on the problem class, this step can be of either algebraic, algebraic-differential or differential type; this is the topic of Sections 4.4–4.6. Here, we have represented the reaction step abstractly by a general reaction-operator $\mathcal{R} : \mathbb{R}^{N_C+N_R^K} \rightarrow \mathbb{R}^{N_S}$, operating on the advected, unreacted vector \bar{c}^{n+1} . The matrix $M \in \mathbb{R}^{(N_C+N_R^K) \times N_S}$ is the familiar pseudo formula matrix, defined in (3.42). Note that by definition, $M \equiv I$ and $M \equiv A$ for the LNE and the LE cases, respectively. The result of the reaction step is the vector of *advected, reacted* concentrations $c^{*,n+1}$. The next segment in the OS procedure is the *diffusion step*, which consists of solving, with the initial conditions $c^{*,n+1}$, the set of linear, parabolic PDEs (4.4). The final step is the *equilibration step*, represented by the operator $\mathcal{E} : \mathbb{R}^{N_C+N_R^K} \rightarrow \mathbb{R}^{N_S}$. This step is only performed if the system under consideration is of LE or PLNE type; for the LNE case we have $\mathcal{E} \equiv I$. Finally, note that for an LE system, $\mathcal{R} \equiv \mathcal{E}$.

We refer to the concentration fields c^{n+1} obtained through (4.2)–(4.5) as the OS solution to the equations (4.1) over the time-step $t^n < t < t^{n+1}$.

In practical applications, different time-scales are often associated with the individual steps (4.2), (4.3) and (4.4) in the OS hierarchy. To be specific, let us introduce the time-step $\Delta t_T \equiv t^{n+1} - t^n$ applying to the overall procedure. This time-step should be representative of the resolution needed to capture the *slowest* processes in the system. Furthermore, introduce time-steps corresponding to advection, reaction and diffusion, Δt_A , Δt_R , and Δt_D , respectively. In this work, we will assume that the time-scales of advection and diffusion are of comparable

magnitude, and that they both occur more slowly than reactions. In other words, we assume

$$\Delta t_A = \Delta t_D \equiv \Delta t_T, \quad (4.6)$$

and

$$\Delta t_R \ll \Delta t_T, \quad (4.7)$$

where we use the symbol Δt_T to denote the time-step for transport without maintaining any distinction between advection and diffusion.

The condition (4.7) has implications when rate-controlled reactions are present. In these cases, a time-step smaller than that used for transport is often needed to stably integrate the governing ODEs.

4.3 The Transport Step

We now give a brief description of the algorithms used for the spatial and temporal discretization of the *transport step*, that is, the movement of species due to advection and diffusion. These algorithms were developed mainly at Rice University, and the corresponding software, PARSim1 (Parallel Aquifer and Reservoir Simulator, single phase), is described in the users manual [2]. The (species) ADR is a partial differential equation of parabolic type, which, in typical applications is *advection dominated* (high Peclet number), and therefore almost hyperbolic in nature. As a consequence, the solution develops sharp fronts, causing standard schemes for parabolic equations to work poorly. Some well-known problems are (see [26]):

- Excessive numerical diffusion, causing smearing of fronts;
- Numerical instability, resulting in oscillations and possible over/undershoots;
- Lack of mass-conservation.

For these reasons, the transport step in PARSim1 is divided into an advection step (hyperbolic) and a diffusion step (parabolic), enabling the use of suitable methods to approximate the different characteristics of the two processes. Spatial discretization is by a *Mixed Finite-Element* procedure, using the lowest-order Raviart-Thomas spaces [6]. This has the distinct advantage of conserving mass on a cell-by-cell basis. Two options exist currently for the advection step, a *Higher-order Godunov* (HOG) procedure (Dawson [10]) and a *Characteristics-Mixed Method* (CMM) (see Arbogast and Wheeler [48] and Arbogast, Chilakapati and Wheeler [3]). The HOG algorithm requires a CFL-type time-step constraint, but reduces numerical diffusion, enforces the conservation law cell-by-cell and produces non-oscillatory solutions. The CMM approach does not require a time-step constraint, and shares the other attractive features of the HOG method. However, the tracing back of grid-points, and the integration over the *trace-back region*, makes this method more expensive than HOG for a large problem if time-steps of the same size are taken (if, for example accuracy dictates this).

The diffusion step is handled by a standard technique for parabolic problems, i.e., a fully implicit discretization (based again on the Mixed Finite-Element discretization of the domain), which results in an easily solvable symmetric, positive definite linear system.

4.4 The Reaction Step for the LE Problem

4.4.1 Overview

Consider the pure equilibrium problem, the mathematical structure of which was described in Section 2.5.1. The reaction operator \mathcal{R} introduced in (4.3) now coincides with the equilibrium operator $\mathcal{E} = \mathcal{E}[Mc]$. Since for an LE system it follows

that $M = A$, we can express the equilibrium step

$$c = \mathcal{E}[Ac] \equiv \mathcal{E}[T], \quad (4.8)$$

where T are the familiar total molar concentrations.

The operator \mathcal{E} represents the solution of the nonlinear programming problem (NLP) discussed in Section 2.5.1, applying locally at each point in the domain Ω . To make this more concise, recall that the input to the reaction step is the field of advected, unreacted concentrations, \bar{c}^{n+1} . For the fully discretized case (both temporally and spatially), let us use the symbol \bar{c}_h^{n+1} to denote the approximation to the composition vector at a discrete point in the grid. If we consider that the grid block has volume ΔV , we can express the species mole vector in this location as

$$n_h^0 \equiv \phi \Delta V \bar{c}_h^{n+1}, \quad (4.9)$$

where the superscript “0” emphasizes that this vector represents an initial approximation to the vector of equilibrium mole-numbers. Similarly, the total component mass, $e_h \in \mathbb{R}^{N_c}$, associated with this grid block is simply

$$e_h \equiv \phi \Delta V A \bar{c}_h^{n+1}, \quad (4.10)$$

and the total aqueous concentrations $T_h \in \mathbb{R}^{N_c}$ are

$$T_h = A \bar{c}_h^{n+1}. \quad (4.11)$$

Identical equations apply for each grid block in the discretization of Ω . The task at hand is to compute the equilibrium composition n^* , based on the initial guess n_h^0 and the constraints posed by the computed totals e_h . The vector so obtained is easily converted back to the desired *molar* variables through the inverse of (4.9),

$$c_h^{*,n+1} = \frac{n^*}{\phi \Delta V}. \quad (4.12)$$

For convenience, we will omit the subscript “h” in the following, and it will be understood from the context when a discrete (local) value is intended.

Our approach to the equilibrium problem is based on the interior-point method for nonlinear programming (NLP). Its application to a generic NLP is described in detail in Appendix A, and we will repeatedly refer to results contained there. A fundamental reference on this subject is El-Bakry et al. [15].

As pointed out in Section 2.5.1, there exist two basic strategies for the equilibrium batch problem, namely the *non-stoichiometric* and *stoichiometric* formulations. Sections 4.4.2 and 4.4.3 below describe the algorithms resulting from the application of the interior-point method to these two situations.

4.4.2 The Non-Stoichiometric Formulation

The Unreduced Formulation (UNSF)

The non-stoichiometric formulation of the equilibrium problem is based on solving the NLP (2.110) introduced in Section 2.5.1. Letting $y \in \mathbb{R}^{N_C}$ and $z \in \mathbb{R}^{N_S}$ denote the Lagrange multipliers corresponding to equality and inequality constraints, respectively, and introducing the vector of unknowns $u \equiv (n, y, z) \in \mathbb{R}^{2N_S+N_C}$, we can express the KKT conditions for this problem in the standard form (A.25)–(A.26), i.e.,

$$F(u) = 0, \quad (4.13)$$

$$(n, z) \geq 0, \quad (4.14)$$

where

$$F(u) = \begin{pmatrix} \mu(n) + A^T y - z \\ An - e \\ \Lambda(z)n \end{pmatrix}. \quad (4.15)$$

Since the inequalities are in the form of *simple-bounds*, there is no need to introduce *slack-variables*, and the algorithm presented in A.2.1 is clearly appropriate for this problem. Equation (4.13) is a square, nonlinear system in the $N_{eq} = 2N_S + N_C$ unknowns $u = (n, y, z)$. The corresponding Newton system (A.29) has the form

$$J(u)\Delta u = -F(u), \quad (4.16)$$

where the Jacobian $J(u)$ is given by the general expression (A.33). In the case at hand, it simplifies to

$$J(u) = \begin{pmatrix} \nabla_{n,n}^2 G(n) & A^T & -I \\ A & 0 & 0 \\ \Lambda(z) & 0 & \Lambda(n) \end{pmatrix}. \quad (4.17)$$

The form of $\nabla_{n,n}^2 G$ is given, for an ideal system, in B.2.

When the general interior-point algorithm A.1 is applied to the problem specified by (4.13)–(4.14) with $F(u)$ given by (4.15), there results an algorithm which we call the *unreduced, non-stoichiometric formulation* (UNSF).

The Reduced Formulation (RNSF)

In this section, we describe an algorithm, based on the non-stoichiometric formulation above, in which the number of unknowns is reduced.

We begin the exposition from the KKT conditions for the non-stoichiometric formulation (4.15). Partitioning the species mole vector into component and product species,

$$n = \begin{pmatrix} n^c \\ n^p \end{pmatrix}, \quad (4.18)$$

the conditions of mass-balance become

$$n^c + \hat{A}n^p = e. \quad (4.19)$$

In a completely analogous fashion, we subdivide the chemical potential vector μ and the vector of Lagrange multipliers z . This allows us to write the conditions of optimality above as

$$\mu^c + y = z^c, \quad (4.20)$$

$$\mu^p + \hat{A}^T y = z^p. \quad (4.21)$$

Next, we eliminate the multipliers y between (4.20) and (4.21). The result is

$$\mu^p - \hat{A}^T \mu^c = z^p - \hat{A}^T z^c. \quad (4.22)$$

To proceed, we make the assumption that the composition variable used is the *molar concentration*. We also explicitly introduce the assumption of *ideality* at this stage. As pointed out in Section 2.5.1, a reduction of the number of equations in a non-stoichiometric formulation can always be carried out *under the assumption of ideality*. Thus, the choice of composition variable is largely a matter of convenience; however, the ideality assumption is *necessary*. To reflect the choice of composition variables, we convert the mass-balance equations to apply in terms of molar concentrations, i.e.,

$$c^c + \hat{A}c^p = T, \quad (4.23)$$

where T denotes the total molar component concentration. Ideality enables us to express the chemical potentials in the “decoupled” form

$$\mu^c = \mu^c(c^c), \quad (4.24)$$

$$\mu^p = \mu^p(c^p). \quad (4.25)$$

Substituting these expressions into (4.22), the conditions of equilibrium are

$$\mu^p(c^p) = \hat{A}^T \mu^c(c^c) + z^p - \hat{A}^T z^c. \quad (4.26)$$

As noted in Section 2.5.1, *mole numbers corresponding to species in a non-disappearing multi-species phase are strictly positive* (see also [40]). In the framework of aqueous/rock chemistry that we are considering, the multi-species phases are either the *aqueous* phase or *surface* phases that represent sites for ion-exchange or adsorption, neither of which we allow to disappear as a result of reactions. Therefore, species in the aqueous phase or in a surface phase always satisfy $c_i > 0$, and, by complementarity, have corresponding multipliers $z_i = 0$.

In our application, only *single-species phases* (minerals) can disappear completely. Let us denote the index set for minerals by the symbol I_M , and the number of possible minerals by $N_M \leq N_R$. The result regarding the multipliers is that for any $i = 1, \dots, N_R$,

$$z_i^p = 0, \quad i \notin I_M, \quad (4.27)$$

and

$$z_i^p \geq 0, \quad i \in I_M. \quad (4.28)$$

To summarize, we have obtained an equivalent set of KKT conditions given by

$$c^c + \hat{A}c^p = T, \quad (4.29)$$

$$\mu^p(c^p) = \hat{A}^T \mu^c(c^c) + z^p, \quad (4.30)$$

$$c_i^p z_i^p = 0, \quad i \in I_M, \quad (4.31)$$

$$z_i^p = 0, \quad i \notin I_M, \quad (4.32)$$

$$(c_i^p, z_i^p) \geq 0, \quad i \in I_M, \quad (4.33)$$

$$c_i^p > 0, \quad i \notin I_M, \quad (4.34)$$

$$c_i^c > 0, \quad i = 1, \dots, N_C. \quad (4.35)$$

By using the specific, ideal phase form of the chemical potential (2.76), we can transform (4.30) into a mass-action expression for the non-mineral species,

$$c_i^p = \psi_i(c^c), \quad i \notin I_M. \quad (4.36)$$

The form of ψ_i is given by equation (B.9). Recalling that mineral species have a composition-independent chemical potential $\mu^p \equiv \mu^{p,0}$, we arrive at the system

$$c^c + \hat{A}c^p = T, \quad (4.37)$$

$$c_i^p = \psi_i(c^c), \quad i \notin I_M, \quad (4.38)$$

$$\mu_i^{p,0} = (\hat{A}^T \mu^c(c^c))_i + z_i^p, \quad i \in I_M, \quad (4.39)$$

$$c_i^p z_i^p = 0, \quad i \in I_M, \quad (4.40)$$

$$(c_i^p, z_i^p) \geq 0, \quad i \in I_M, \quad (4.41)$$

$$c_i^c > 0, \quad i = 1, \dots, N_C. \quad (4.42)$$

One practical difficulty with the above formulation is the requirement of strict positivity of the component species, $c^c > 0$. It is critical that this issue be addressed if a solution is to be obtained with an iterative method. We have adopted the strategy of *logarithmic transformation* of the component concentrations, that is, we introduce new computational variables χ^c through the definition

$$\chi_i^c \equiv \ln c_i^c, \quad i = 1, \dots, N_C. \quad (4.43)$$

This obviously ensures $c_i^c > 0$ for $i = 1, \dots, N_C$. The logarithmic form may also have a computational advantage when large differences in magnitude exist, as is often the case in chemical batch systems.

We can now express the *non-mineral product species* in the same, logarithmic form as

$$\chi_i^p \equiv \ln c_i^p, \quad i \notin I_M. \quad (4.44)$$

Using the mass-action expression (B.12) produces

$$\chi_i^p = \ln K_i + \sum_{j=1}^{N_C} \hat{a}_{ji} \chi_j^c, \quad i \notin I_M. \quad (4.45)$$

By applying the definition of the equilibrium constant (B.10) to modify the mineral-optimality equations, we arrive at the final form of the reduced KKT conditions (together with the definition (4.45)):

$$\exp(\chi_i^c) + \sum_{j \in I_M} \hat{a}_{ij} c_j^p + \sum_{j \notin I_M} \hat{a}_{ij} \exp(\chi_j^p) = T_i, \quad i = 1, \dots, N_C, \quad (4.46)$$

$$\ln K_i + \sum_{j=1}^{N_C} \hat{a}_{ji} \chi_j^c = \frac{-z_i^p}{RT}, \quad i \in I_M, \quad (4.47)$$

$$c_i^p z_i^p = 0, \quad i \in I_M, \quad (4.48)$$

$$(c_i^p, z_i^p) \geq 0, \quad i \in I_M. \quad (4.49)$$

It is worth noting that the optimality condition for minerals (4.47) can be easily rearranged to the equivalent form, for $i \in I_M$,

$$\ln(K_i \prod_{j=1}^{N_C} (c_j^c)^{\hat{a}_{ji}}) = -\frac{z_i^p}{RT}. \quad (4.50)$$

By complementarity, equation (4.48), this implies that, for $i \in I_M$,

$$K_i \prod_{j=1}^{N_C} (c_j^c)^{\hat{a}_{ji}} = 1 \quad \text{if } c_i^p > 0, \quad (4.51)$$

$$K_i \prod_{j=1}^{N_C} (c_j^c)^{\hat{a}_{ji}} \leq 1 \quad \text{if } c_i^p = 0.$$

The equations (4.51) are the customary way of expressing the equilibrium condition for minerals in terms of the *solubility product* appearing on the left-hand side.

When (4.45) is used to substitute for the non-mineral product species in (4.46), the resulting system is of size $N_{eq} = N_C + 2N_M$.

The primary unknowns are the logarithms of component concentration $\chi^c \in \mathbb{R}^{N_C}$ and the N_M mineral concentrations c_i^p for $i \in I_M$. In addition, we must solve for the N_M multipliers z_i^p for $i \in I_M$, corresponding to minerals.

We will refer to the algorithm that arises when the interior-point algorithm A.1 is applied to the reduced KKT conditions, equations (4.46)–(4.49), using χ_i^p given by (4.45), as the *reduced non-stoichiometric formulation* (RNSF).

4.4.3 The Stoichiometric Formulation

This section describes the interior-point method as applied to the *stoichiometric* form of the equilibrium problem, that is, the NLP (2.129) introduced in Section 2.5.1. The primary variables are now $\xi \in \mathbb{R}^{N_R}$, the extents of reaction, which are related to the vector of species mole-numbers n through (2.45),

$$n(\xi) = n^0 + V\xi. \quad (4.52)$$

Note that the vector n^0 , which was obtained from the advected, unreacted concentrations through an expression of the form (4.9), has more significance here than in the non-stoichiometric formulation. Taking (arbitrarily) as an initial guess for the extents of reaction $\xi \equiv 0$, it is clear that n^0 not only serves as an effective initial guess for the final composition vector, but that it also contains all information about the total component mass.

Because of the affine relationship between ξ and n , this problem does not immediately fit within the general simple-bounds formulation A.2.1 that was applied in the non-stoichiometric case. Of course, the slack-variable formulation (A.17) would be directly applicable, but the overhead incurred by the added number of variables would render such a formulation too costly. Instead, we have chosen to modify the method slightly to treat affine constraints similarly to simple bounds.

As before, let the multipliers $z \in \mathbb{R}^{N_S}$ correspond to inequality constraints and let the vector of unknowns be denoted $u \equiv (\xi, z) \in \mathbb{R}^{N_R+N_S}$. The KKT conditions

are in this case

$$F(u) = 0, \quad (4.53)$$

$$(n(\xi), z) \geq 0, \quad (4.54)$$

where F has the form

$$F(u) = \begin{pmatrix} V^T \mu(n(\xi)) - V^T z \\ \Lambda(z)n(\xi) \end{pmatrix}. \quad (4.55)$$

We note that $F(u) = 0$ is a square, nonlinear system of dimension $N_{eq} = N_S + N_R$ in the unknowns $u = (\xi, z)$. The Jacobian $J(u)$ for the corresponding Newton system (A.29) is

$$J(u) = \begin{pmatrix} \nabla_{\xi, \xi}^2 G(\xi) & -V^T \\ \Lambda(z)V & \Lambda(n(\xi)) \end{pmatrix}, \quad (4.56)$$

where $\nabla_{\xi, \xi}^2 G$ is the Hessian of the Gibbs free energy in reaction-coordinate space.

It is shown in Appendix B that $\nabla_{\xi, \xi}^2 G$ has the simple form

$$\nabla_{\xi, \xi}^2 G = V^T \nabla_{n, n}^2 G V. \quad (4.57)$$

A procedure for evaluating this quantity efficiently is described in B.2.

The algorithm resulting from the use of equations (4.54) and (4.55) within the interior-point framework will henceforth be referred to as the *stoichiometric formulation* (SF).

4.5 The Reaction Step for the LNE Problem

The LNE system was introduced in Section 2.5.2 and is characterized by $N_R = N_R^K$, i.e., only kinetic reactions occur. The general reaction step $\mathcal{R} = \mathcal{R}[Mc]$ can in this case be stated more simply as $\mathcal{R} = \mathcal{R}[c]$ (this follows from the definition (3.42) since $M = I$ when $N_R^Q = 0$). Performing the reaction step from t^n to t^{n+1} therefore

requires knowledge of the entire composition vector, which we denote c^0 . As before, this quantity should be thought of as an approximation to the advected, unreacted concentrations \bar{c}_h^{n+1} , local to some arbitrary grid-block in the discretization.

The governing equations are the N_R ODEs given by (2.136),

$$\begin{cases} \dot{\xi} &= r^K[c(\xi)], \\ \xi(0) &= \mathbf{0}, \end{cases} \quad (4.58)$$

subject to the side-conditions of non-negativity of species,

$$c(\xi) = c^0 + V\xi \quad (4.59)$$

$$c(\xi) \geq \mathbf{0}. \quad (4.60)$$

A wealth of different ODE integrators are available for the solution of (4.58). For an introduction to the subject, see any of [20, 24]. Our approach requires the use of *explicit* integrators, and we have implemented three algorithms of different level of accuracy: Forward Euler (FE), explicit second-order Runge-Kutta (RK-2) and explicit fourth-order Runge-Kutta (RK-4). The definitions of these integrators have been included for completeness in B.3.

To illustrate, let us consider the application of Forward Euler to the system (4.58). Introducing sub time-levels $t^{[m]}$ for $m = 0, \dots$ with $t^{[0]} \equiv t^n$, we define a series of new approximations through

$$\begin{cases} \xi^{[m+1]} &= \xi^{[m]} + \Delta t_{RR} r^K[c(\xi^{[m]})], \\ \xi^{[0]} &= \mathbf{0}. \end{cases} \quad (4.61)$$

By defining the concentrations at the sub-time level $t^{[m]}$,

$$c^{[m]} \equiv c(\xi^{[m]}), \quad (4.62)$$

it is immediately clear that

$$c^{[m+1]} \equiv c(\xi^{[m+1]}) = c^0 + V(\xi^{[m]} + \Delta t_{RR} r^K[c(\xi^{[m]})])$$

$$= c^0 + V\xi^{[m]} + \Delta t_R V r^K [c(\xi^{[m]})].$$

We can therefore express (4.61) alternatively as

$$\begin{cases} c^{[m+1]} &= c^{[m]} + \Delta t_R V r^K [c^{[m]}], \\ c^{[0]} &= c^0. \end{cases} \quad (4.63)$$

The update (4.63) is convenient in that it allows the monitoring of the non-negativity conditions (4.60) directly. Similar expressions apply to the other time-stepping schemes defined in Appendix B.

We now describe the time integration in more detail. For the purpose of illustration, we employ RK-2 in this example.

Algorithm 4.2 LNE Time Integration Framework (RK-2)

Receive advected, unreacted composition \bar{c}_h^{n+1}

$$m = 0; c^{[m]} = \bar{c}_h^{n+1}$$

(I) Predictor step

(a) Compute reaction rates, $r_1^K = r^K(c^{[m]})$

(b) Compute largest time-step $\Delta t_p \leq \Delta t_R$, satisfying

$$c^{[m]} + \Delta t_p V r_1^K \geq 0$$

(c) Predict $c_p^{[m]} = c^{[m]} + \Delta t_p V r_1^K$

(II) Corrector step

(a) Compute reaction rates, $r_2^K = r^K(c_p^{[m]})$

(b) Compute largest time-step Δt_c , satisfying

$$c^{[m]} + \Delta t_c V r_2^K \geq 0$$

if $\Delta t_c < \Delta t_p$ **then** $\Delta t_p = \Delta t_c$; **goto** (I.c)

else $\Delta t = \Delta t_p$

(c) Correct $c_c^{[m]} = c^{[m]} + \frac{1}{2}\Delta t V(r_1^K + r_2^K)$

(III) Update iterates

$c_c^{[m+1]} = c_c^{[m]}$; $m \leftarrow m + 1$

$\Delta t_{TOT} \leftarrow \Delta t_{TOT} + \Delta t$

if $\Delta t_{TOT} \geq \Delta t_T$ **exit**

else goto I.a

A crucial point in the implementation of this algorithm is the treatment of the non-negativity constraints (steps I.b and II.b above). In practice, a user-specified tolerance $c_\epsilon > 0$ is used, i.e., we require that the time-step satisfies

$$c^{[m]} + \Delta t V r_i^K \geq c_\epsilon > 0, \quad i = 1, 2. \quad (4.64)$$

Note in particular that (4.64) guarantees a feasible update, that is,

$$c_c^{[m]} \equiv c^{[m]} + \frac{1}{2}\Delta t V(r_1^K + r_2^K) \geq c_\epsilon. \quad (4.65)$$

It is easily seen that the same conclusion holds for RK-4 if a condition of type (4.64) is satisfied for each rate vector.

A rate-limiting step is used to evaluate the rates (r^1 and r^2 above), to ensure that reactions proceeding in a direction which would lead to the complete depletion of its reactants (concentrations lower than c_ϵ) are set to zero. It is important to point out that this step does not affect mass-balance; in fact, the procedure outlined above is completely *mass-conservative*.

4.6 The Reaction Step for the PLNE Problem

We are now ready to describe the reaction step \mathcal{R} in its most general form, as arises in a PLNE problem. The governing equations, introduced in Section 2.5.3, consist of a mixed system of ODEs and algebraic constraints, posed as a NLP problem. The ODEs have the form

$$\begin{cases} \dot{\xi}^K &= r^K[c(\xi^K, \xi^Q)], \\ \xi^K(0) &= 0, \end{cases} \quad (4.66)$$

and are subject to the side-conditions

$$c(\xi^K, \xi^Q) = c^0 + V^K \xi^K + V^Q \xi^Q, \quad (4.67)$$

$$c(\xi^K, \xi^Q) \geq 0, \quad (4.68)$$

and the constraints of equilibrium.

To properly illustrate the time-integration, we need some additional notation. In keeping with the nomenclature of the previous section, we denote the approximate solution at the sub time-level m by the superscript m in square brackets. For example, we write $\xi^{K[m]}$ for the kinetic extents of reaction at $t^{[m]}$. Recognizing that the equilibrium extents of reaction ξ^Q at time $t^{[m]}$ are implicitly determined by the conditions of equilibrium and the value of ξ^K , we use the symbol $\xi^{Q[m]}$ to represent the equilibrium extents of reaction *corresponding* to the kinetic extents of reactions, $\xi^{K[m]}$. This results in the definition of two different concentration vectors for the time-level m , namely the *unequilibrated* concentrations

$$c^{[m]} \equiv c(\xi^{K[m]}, \xi^{Q[m-1]}), \quad (4.69)$$

and the *equilibrated* concentrations

$$c^{*[m]} \equiv c(\xi^{K[m]}, \xi^{Q[m]}). \quad (4.70)$$

For $m = 0$, i.e., at $t = t^n$, we have the special case

$$c^{[0]} \equiv c(0, 0) = c^0, \quad (4.71)$$

which again is equal to the advected, unreacted vector \bar{c}_h^{n+1} . By definition, $c^{*[0]}$ is nothing but the equilibrated initial conditions at the beginning of the reaction time-step. As in Section 4.2.2, we denote the process of equilibrating the concentration vector at a given time-level by the symbol \mathcal{E} , and write this formally as

$$c^{*[m]} \equiv \mathcal{E}[Mc^{[m]}]. \quad (4.72)$$

This is the *equilibrium sub-step* which we elaborate on in Section 4.6.1.

With the above definitions, we are ready to present a complete algorithm for the reaction step in the PLNE formulation. As in the preceding section, we illustrate the procedure using RK-2. The resulting algorithm is in some respects similar to one presented by Sevougian [36]. As in the LNE case, we have implemented, in addition to RK-2, the integrators FE and RK-4.

Algorithm 4.3 PLNE Time Integration Framework (RK-2)

Receive advected, unreacted composition \bar{c}_h^{n+1}

$$m = 0; c^{[m]} = \bar{c}_h^{n+1}$$

(0) Top of reaction time-loop

(a) Equilibration $c^{*[m]} = \mathcal{E}[Mc^{[m]}]$

(b) Compute affinities $\mathcal{A} = \mathcal{A}(c^{*[m]})$

(I) Predictor step

(a) Compute reaction rates, $r_1^K = r^K(c^{*[m]})$

(b) Compute largest time-step $\Delta t_p \leq \Delta t_R$, satisfying

$$c^{*[m]} + \Delta t_p V^K r_1^K \geq 0$$

(c) Predict $c_p^{[m]} = c^{*[m]} + \Delta t_p V^K r_1^K$

(d) Equilibrate $c_p^{*[m]} = \mathcal{E}[M c_p^{[m]}]$

(II) Corrector step

(a) Compute reaction rates, $r_2^K = r^K(c_p^{*[m]})$

(b) Compute largest time-step Δt_c , satisfying

$$c^{*[m]} + \Delta t_c V^K r_2^K \geq 0$$

if $\Delta t_c < \Delta t_p$ **then** $\Delta t_p = \Delta t_c$; **goto** (I.c)

else $\Delta t = \Delta t_p$

(c) Correct $c_c^{[m]} = c^{*[m]} + \frac{1}{2}\Delta t V^K (r_1^K + r_2^K)$

(d) Equilibrate $c_c^{*[m]} = \mathcal{E}[M c_c^{[m]}]$

(III) Update iterates

$$c^{*[m+1]} = c_c^{*[m]}; m \leftarrow m + 1$$

$$\Delta t_{TOT} \leftarrow \Delta t_{TOT} + \Delta t$$

if $\Delta t_{TOT} \geq \Delta t_T$ **exit**

(IV) Strategy for next step

Compute new affinities $\mathcal{A}^+ = \mathcal{A}(c^{*[m]})$

if AffinityViolation($\mathcal{A}_i, \mathcal{A}_i^+$) **then**

Switch species i

goto 0.a

else goto 1.a

Several comments are in order. First, note that the cost of the algorithm is dominated (for all but the simplest cases) by the need to *equilibrate* the mixture at each new composition; that is, to apply the operator \mathcal{E} . In particular, equilibration occurs at the beginning of the time-stepping (0.a), after the prediction-step (I.d) and after the corrector-step (II.d), amounting to a total of 3 equilibrium calculations per time-step. However, if many reaction steps are taken per transport step ($\Delta t_R \ll \Delta t_T$), then the average number of evaluations of \mathcal{E} is only 2 per reaction step. This is assuming that the non-negativity constraints are not violated during the integration. If a cutting of the time-step is required at the stage (II.b), additional equilibrations will be required.

Similar comments apply when the predictor-corrector approach is replaced by other integrators. For FE and RK-4, the number of evaluations of \mathcal{E} are 2 and 5, respectively, which for the case $\Delta t_R \ll \Delta t_T$ translates into 1 and 4 evaluations of \mathcal{E} on the average.

Another comment regards the last stage of the algorithm, (IV). This is a user-defined option that can be easily disabled if not desired. It was pointed out by Sevougian [36] that a change in sign of the computed affinity of a kinetic reaction is non-physical; a numerical artifact resulting from the use of too large a time-step. His solution was to find the point where the affinity was (approximately) zero, and *switch* the species for which the “violation” occurred to the equilibrium subset. We do not advocate such a strategy in general, since it is possible in some scenarios that the affinity of a given reaction *could* undergo changes of sign during the approach to equilibrium. However, we include the option of species-switching in our algorithm to handle cases where practical difficulties could arise in integrating the system. For example, it might be reasonable to switch a product species that is completely consumed by a rapid kinetic reaction to an equilibrium description,

in order to avoid taking excessively small time-steps. Different heuristics can be used to determine when a species should be switched.

One last point concerns the conservation properties of this scheme. As for the corresponding LNE algorithm, the formulation of the kinetic reactions is completely conservative, by virtue of the expansion (4.67). If the equilibrium sub-step is based on a stoichiometric approach, then the overall integration process is component-mass conservative.

4.6.1 The Equilibrium Sub-Step

This section is devoted to a treatment of the equilibrium sub-step, \mathcal{E} , which arises in the reaction step for the PLNE problem. In general, as explained in Section 4.4, algorithms for the computation of chemical equilibrium fall into the classes of non-stoichiometric and stoichiometric procedures. These algorithms were treated at length in Section 4.4.2 and Section 4.4.3 for the case of equilibrium reactions only. Fortunately, the approaches presented there carry over to the case where kinetic reactions are also present with minor modifications. We first present the modified problem that must be solved in a non-stoichiometric approach, and finish the section by supplying the details for the stoichiometric case.

Non-Stoichiometric Equilibrium Sub-Step

The equilibrium step $c^{*[m]} = \mathcal{E}[Mc^{[m]}]$ can be defined in terms of the non-stoichiometric formulation, based on the NLP (2.146). Let the equilibrated solution $c^{*[m]}$ and the unequilibrated solution $c^{[m]}$ at iteration-level m in the PLNE time-integration procedure both be represented in terms of component-species, kinetic products and equilibrium products, so that we may write $c^{*[m]} \equiv (c^{c[m]}, c^{K[m]}, c^{Q[m]})^T$ and

$c^{[m]} \equiv (c^{c^{[m-1]}}, c^{K^{[m]}}, c^{Q^{[m-1]}})^T$. Using the definition of M results in

$$M c^{[m]} = \begin{pmatrix} c^{c^{[m-1]}} + \hat{A}^Q c^{Q^{[m-1]}} \\ c^{K^{[m]}} \end{pmatrix}. \quad (4.73)$$

As before, let T' denote component total concentrations *excluding* kinetic species, and let $A' \equiv (I_{N_C} \hat{A}^Q)$ be the reduced formula matrix first introduced in (2.143).

The equilibrium sub-step can now be written

$$c^{*[m]} = \mathcal{E} \begin{bmatrix} T' \\ c^{K^{[m]}} \end{bmatrix}, \quad (4.74)$$

where $c^{*[m]}$ is obtained through solving the *reduced* minimization problem

$$\begin{aligned} \min_{c'} \quad & G(c', c^{K^{[m]}}) \\ \text{s.t.} \quad & A' c' = T' \\ & c' \geq 0, \end{aligned} \quad (4.75)$$

for the unknowns $c' \equiv (c^{c^{[m]}}, c^{Q^{[m]}})^T$.

When the RNSF, introduced in Section 4.4.2, is applied to this particular, non-stoichiometric form of the NLP, the resulting system of nonlinear equations is of size $N_{eq} = N_C + 2N_M^Q$, where N_M^Q denotes the number of minerals that form through equilibrium reactions.

Stoichiometric Equilibrium Sub-Step

As we have seen, the equilibrium step $c^{*[m]} = \mathcal{E}[M c^{[m]}]$ can also be expressed as

$$c^{*[m]} = c^0 + V^K \xi^{K^{[m]}} + V^Q \xi^{Q^{[m]}}, \quad (4.76)$$

where the equilibrium extents of reaction $\xi^{Q^{[m]}}$ are defined by

$$\begin{aligned} \xi^{Q^{[m]}} = \arg \min_{\xi^Q} \quad & G[c(\xi^{K^{[m]}}, \xi^Q)] \\ \text{s.t.} \quad & c(\xi^{K^{[m]}}, \xi^Q) \geq 0. \end{aligned} \quad (4.77)$$

Application of the method outlined in Section 4.4.3 results in a nonlinear system of the form (4.53) of dimension $N_{eq} = N_C + 2N_R^Q$. With this choice of algorithm, Algorithm 4.3 is mass-conservative.

4.7 An Analysis of the Order of the OS Algorithm

We now consider the question of accuracy of the overall OS procedure Algorithm 4.1 when applied to the reactive transport problem. It is well known that standard OS procedures introduce errors that typically are proportional to the size of the time-step employed. This error is inherent in the splitting procedure, and can not be improved upon by devising more accurate schemes for the sub-steps that comprise the algorithm (in our case advection, reaction, diffusion and equilibration). We will therefore not consider any particular temporal or spatial discretizations, but rather analyze the system of continuous field-equations directly. The main result of this analysis is

Proposition 4.1 The operator-splitting procedure, defined by the equations (4.2)–(4.5), is formally first-order in time accurate when applied to problems of class LE or LNE.

4.7.1 Order of Approximation for the LNE Problem

The governing equations are the species ADR, given by (3.35)–(3.38). Note that in this case, the PDEs to which the OS is applied correspond directly to the actual governing equations. It therefore suffices to establish that Algorithm 4.1 results in an $O(\Delta t)$ procedure when applied to the species ADR,

$$\frac{\partial(\phi c)}{\partial t} + \nabla \cdot (u(P^{aq}c) - D\nabla(P^{aq}c)) = Vr^K, \quad x \in \Omega, \quad t > 0. \quad (4.78)$$

It is a simple exercise using Taylor expansions to demonstrate that Algorithm 4.1 is a formally first order in time procedure for this class of problems. However, as more general *error-estimates* have already been established under reasonable assumptions on r^K by Dawson and Wheeler [11], we will not comment further on the application of OS to the LNE problem type.

4.7.2 Order of Approximation for the LE Problem

Preliminaries

We begin by establishing some properties of the reaction step in the LE formulation. Because no kinetic reactions are present, it holds that $\mathcal{R} \equiv \mathcal{E}$, where $\mathcal{E} : \mathbb{R}^{N_c} \rightarrow \mathbb{R}^{N_s}$. As explained earlier, $M = A$ in this case, so we are justified in writing

$$c^* = \mathcal{E}[Mc] = \mathcal{E}[Ac] \equiv \mathcal{E}[T], \quad (4.79)$$

where c, c^* denote unequilibrated and equilibrated composition vectors, respectively. Since any change in the composition vector must lie in the null space of A , we have

$$A(c - c^*) = 0, \quad (4.80)$$

or, combining (4.79) and (4.80),

$$T \equiv Ac = Ac^* = A\mathcal{E}[T]. \quad (4.81)$$

We can now formally state the mass conservation property of the combined operator $A\mathcal{E}$. For any vector $\eta \in \mathbb{R}^{N_c}$, for which the equilibrium problem has a solution, it holds that

$$\eta = A\mathcal{E}[\eta]. \quad (4.82)$$

Truncation-Error Analysis

The analysis will proceed as follows. The species-based OS system, defined in Algorithm 4.1 for the LE case, is first manipulated into an equivalent, component-based form, which is subsequently analyzed using the properties of \mathcal{E} . The smoothness of the concentration fields involved is not an issue here, and we tacitly assume the existence of the required number of derivatives. For notational convenience we assume that porosity is equal to one, and we disregard external source terms. The species-based system of OS equations is

$$\frac{\partial \bar{c}}{\partial t} + \nabla \cdot u(P^{aq}\bar{c}) = 0, \quad x \in \Omega, \quad t^n < t < t^{n+1}, \quad (4.83)$$

$$\bar{c}(\cdot, t^n) = c(\cdot, t^n),$$

$$c^*(\cdot, t^{n+1}) = \mathcal{E}[A\bar{c}(\cdot, t^{n+1})], \quad x \in \Omega, \quad (4.84)$$

$$\frac{\partial \hat{c}}{\partial t} - \nabla \cdot D\nabla(P^{aq}\hat{c}) = 0, \quad x \in \Omega, \quad t^n < t < t^{n+1}, \quad (4.85)$$

$$\hat{c}(\cdot, t^n) = c^*(\cdot, t^{n+1}),$$

$$c^{OS}(\cdot, t^{n+1}) = \mathcal{E}[A\hat{c}(\cdot, t^{n+1})], \quad x \in \Omega. \quad (4.86)$$

Note that we have designated the final solution obtained at t^{n+1} by the superscript *OS* to distinguish it from the true solution at t^{n+1} , which we denote $c(\cdot, t^{n+1})$. Furthermore, note that $c(\cdot, t^n)$ designates the true solution at t^n . By applying AP^{aq} to equations (4.83) and (4.85) (noting that $(P^{aq})^2 = P^{aq}$) and applying A to equations (4.84) and (4.86), there results the component-based form of the OS equations

$$\frac{\partial \bar{C}}{\partial t} + \nabla \cdot u\bar{C} = 0, \quad x \in \Omega, \quad t^n < t < t^{n+1}, \quad (4.87)$$

$$\bar{C}(\cdot, t^n) = C(\cdot, t^n),$$

$$T^*(\cdot, t^{n+1}) = A\mathcal{E}[\bar{C}(\cdot, t^{n+1}) + S(\cdot, t^n)], \quad x \in \Omega, \quad (4.88)$$

$$\frac{\partial \hat{C}}{\partial t} - \nabla \cdot D\nabla \hat{C} = 0, \quad x \in \Omega, \quad t^n < t < t^{n+1}, \quad (4.89)$$

$$\hat{C}(\cdot, t^n) = C^*(\cdot, t^{n+1}),$$

$$T^{OS}(\cdot, t^{n+1}) = A\mathcal{E}[\hat{C}(\cdot, t^{n+1}) + S^*(\cdot, t^{n+1})], \quad x \in \Omega. \quad (4.90)$$

Here, we have introduced the natural definitions of component totals, flowing component totals and immobile component totals as they apply at different levels of the algorithm, such as $\bar{T} = A\bar{c}$, $\bar{C} = AP^{aq}\bar{c}$ and $\bar{S} = A(I - P^{aq})\bar{c}$, respectively. In writing equations (4.88) and (4.90) we have used the fact that the field $S(\cdot, t)$ remains *unchanged* by the advection and diffusion steps. This fact follows by applying the operator $A(I - P^{aq})$ to the PDEs (4.83) and (4.85).

Using the mass-conservation property (4.82) of \mathcal{E} , it directly follows that

$$T^*(\cdot, t^{n+1}) \equiv C^*(\cdot, t^{n+1}) + S^*(\cdot, t^{n+1}) = \bar{C}(\cdot, t^{n+1}) + S(\cdot, t^n), \quad (4.91)$$

and

$$T^{OS}(\cdot, t^{n+1}) \equiv C^{OS}(\cdot, t^{n+1}) + S^{OS}(\cdot, t^{n+1}) = \hat{C}(\cdot, t^{n+1}) + S^*(\cdot, t^{n+1}). \quad (4.92)$$

Our task is to relate $T^{OS}(\cdot, t^{n+1})$ to quantities at time t^n , using (4.87)–(4.90). In what follows, we let b_1, \dots, b_5 denote constant vectors of length N_C . A Taylor expansion about t^n , under the assumption that \hat{C} is smooth, gives

$$\hat{C}(\cdot, t^{n+1}) = \hat{C}(\cdot, t^n) + \Delta t \frac{\partial \hat{C}}{\partial t}(\cdot, t^n) + b_1 \Delta t^2. \quad (4.93)$$

Using the expression (4.89) to substitute for the derivative term in (4.93) produces

$$\hat{C}(\cdot, t^{n+1}) = \hat{C}(\cdot, t^n) + \Delta t \nabla \cdot D\nabla \hat{C}(\cdot, t^n) + b_1 \Delta t^2, \quad (4.94)$$

or, using the initial condition,

$$\hat{C}(\cdot, t^{n+1}) = \hat{C}(\cdot, t^n) + \Delta t \nabla \cdot D\nabla C^*(\cdot, t^{n+1}) + b_1 \Delta t^2. \quad (4.95)$$

From (4.92) and the expansion (4.95), we find

$$T^{OS}(\cdot, t^{n+1}) = S^*(\cdot, t^{n+1}) + \hat{C}(\cdot, t^n) + \Delta t \nabla \cdot D\nabla C^*(\cdot, t^{n+1}) + b_1 \Delta t^2. \quad (4.96)$$

However, $\hat{C}(\cdot, t^n) \equiv C^*(\cdot, t^{n+1})$, which, using (4.91), implies that

$$T^{OS}(\cdot, t^{n+1}) = \bar{C}(\cdot, t^{n+1}) + S(\cdot, t^n) + \Delta t \nabla \cdot D\nabla C^*(\cdot, t^{n+1}) + b_1 \Delta t^2. \quad (4.97)$$

A Taylor expansion of $\bar{C}(\cdot, t^{n+1})$ about t^n , assuming sufficient smoothness and using (4.87) and the fact that $\bar{C}(\cdot, t^n) \equiv C(\cdot, t^n)$, shows that

$$\bar{C}(\cdot, t^{n+1}) = C(\cdot, t^n) - \Delta t \nabla \cdot uC(\cdot, t^n) + b_2 \Delta t^2. \quad (4.98)$$

Substituting (4.98) into (4.97), using $T(\cdot, t^n) \equiv C(\cdot, t^n) + S(\cdot, t^n)$, results in

$$T^{OS}(\cdot, t^{n+1}) = T(\cdot, t^n) - \Delta t \nabla \cdot (uC(\cdot, t^n) - D\nabla C^*(\cdot, t^{n+1})) + b_3 \Delta t^2. \quad (4.99)$$

The local truncation error (LTE) Υ can now be estimated by comparing the true solution at time t^{n+1} , $T(\cdot, t^{n+1})$, with the solution obtained through the operator-splitting procedure, $T^{OS}(\cdot, t^{n+1})$, i.e.,

$$\Upsilon \equiv T^{OS}(\cdot, t^{n+1}) - T(\cdot, t^{n+1}). \quad (4.100)$$

A Taylor expansion of the true solution about t^n , using the governing equations, reveals that

$$T(\cdot, t^{n+1}) = T(\cdot, t^n) - \Delta t \nabla \cdot (uC(\cdot, t^n) - D\nabla C(\cdot, t^n)) + b_4 \Delta t^2. \quad (4.101)$$

Substituting (4.99) and (4.101) into the definition of the LTE (4.100) gives

$$\Upsilon = \Delta t \nabla \cdot D\nabla (C^*(\cdot, t^{n+1}) - C(\cdot, t^n)) + b_5 \Delta t^2 \quad (4.102)$$

To estimate the difference between the flowing component totals at t^n , $C(\cdot, t^n)$, and those obtained from advection and subsequent equilibration in the OS algorithm, $C^*(\cdot, t^{n+1})$, we begin by noting that

$$C(\cdot, t^n) \equiv AP^{aq} \mathcal{E}[T(\cdot, t^n)], \quad (4.103)$$

and

$$C^*(\cdot, t^{n+1}) \equiv AP^{aq}\mathcal{E}[T(\cdot, t^n) - \Delta t \nabla \cdot uC(\cdot, t^n) + b_2 \Delta t^2]. \quad (4.104)$$

In order to simplify notation, we introduce the definition

$$\Delta T(\cdot, t^n) \equiv -\Delta t \nabla \cdot uC(\cdot, t^n), \quad (4.105)$$

and write the LTE as

$$\Upsilon = \Delta t \Phi + b_5 \Delta t^2. \quad (4.106)$$

Neglecting higher-order terms, Φ has the form

$$\Phi = \nabla \cdot D \nabla AP^{aq} \{ \mathcal{E}[T(\cdot, t^n) + \Delta T(\cdot, t^n)] - \mathcal{E}[T(\cdot, t^n)] \}. \quad (4.107)$$

It is instructive to first consider the case $P^{aq} = I$, i.e., no immobile species. The mass-conservation property of \mathcal{E} , equation (4.82), yields

$$\Phi = \nabla \cdot D \nabla \{ \Delta T(\cdot, t^n) \}, \quad (4.108)$$

or, using (4.105),

$$\Phi = -\Delta t \nabla \cdot D \nabla \{ \nabla \cdot uC(\cdot, t^n) \}. \quad (4.109)$$

This quantity is of order $O(\Delta t)$ since $C(\cdot, t^n)$ is assumed smooth. In light of (4.106) the LTE is therefore of order $O(\Delta t^2)$ which implies that the scheme is formally first order accurate. This proves the assertion for the case $P^{aq} = I$.[‡]

Consider now the general case $P^{aq} \neq I$. It is sufficient for our purpose to show that each component of Φ is of order $O(\Delta t)$. This is certainly true if we can demonstrate that for any $1 \leq i, j \leq d$ and each $1 \leq k \leq N_S^{\S}$, it holds that

$$\left| \frac{\partial^2}{\partial x_i \partial x_j} \{ \mathcal{E}_k [T(\cdot, t^n) + \Delta T(\cdot, t^n)] - \mathcal{E}_k [T(\cdot, t^n)] \} \right| = O(\Delta t). \quad (4.110)$$

[‡]This case is, however, trivial as the reactive transport problem can be solved *without* any equilibrium calculation when all species are mobile.

[§]It is sufficient if this is true for those indices k corresponding to *mobile* species.

Assuming for the moment that derivatives of the equilibrium operator are well-defined, we expand \mathcal{E}_k about $T(\cdot, t^n)$ to find

$$\mathcal{E}_k[T(\cdot, t^n) + \Delta T(\cdot, t^n)] = \mathcal{E}_k[T(\cdot, t^n)] + \sum_{l=1}^{N_c} \frac{\partial \mathcal{E}_k[\zeta]}{\partial T_l} \Delta T_l(\cdot, t^n), \quad (4.111)$$

where $\zeta = T(\cdot, t^n) + \theta \Delta T(\cdot, t^n)$ and $0 \leq \theta \leq 1$. Using (4.111), the left-hand side of condition (4.110) is

$$\left| \frac{\partial^2}{\partial x_i \partial x_j} \left\{ \sum_{l=1}^{N_c} \frac{\partial \mathcal{E}_k[\zeta]}{\partial T_l} \Delta T_l(\cdot, t^n) \right\} \right|, \quad (4.112)$$

or, from (4.105),

$$\Delta t \left| \frac{\partial^2}{\partial x_i \partial x_j} \left\{ \sum_{l=1}^{N_c} \frac{\partial \mathcal{E}_k[\zeta]}{\partial T_l} (\nabla \cdot u C(\cdot, t^n))_l \right\} \right|. \quad (4.113)$$

Assuming that higher derivatives on \mathcal{E}_k are *bounded* and noting that u, C are by assumption smooth, this term is clearly of order $O(\Delta t)$. This shows that the LTE is $\Upsilon = O(\Delta t^2)$ for the case $P^{aq} \neq I$ also.

To complete the proof, we will briefly discuss the smoothness of \mathcal{E}_k . We restrict our attention to ideal systems so that the smoothness of the nonlinear terms μ is known. For simplicity, we consider only the case when inequality constraints are non-binding in the NLP represented by \mathcal{E} . As pointed out previously, this is satisfied for all species in our application, except (possibly) for minerals that are appearing/disappearing; we will however ignore this complication.

The equilibrium problem can now be expressed as the set of nonlinear equations $F(c, T) = 0$, where

$$F(c, T) = \begin{pmatrix} V^T \mu(c) \\ Ac - T \end{pmatrix}. \quad (4.114)$$

It is easily verified that F is an infinitely differentiable function provided $c > 0$; hence, in particular, it is C^1 . Let a solution pair (c^*, T^*) satisfy $F(c^*, T^*) = 0$. Furthermore, assume that $\nabla_c F(c^*, T^*)$ is non-singular[¶]. The conditions of the

[¶]Note that $\nabla_c F$ is the Jacobian and that non-singularity is a standard Newton assumption.

implicit function theorem (Rudin [32]) are then satisfied, and we are guaranteed the existence of a functional relationship

$$c = f(T) \tag{4.115}$$

such that $F(f(T), T) = 0$ in a neighborhood of the point T^* . Furthermore, $f \in C^1$ with derivative

$$\nabla_T f(T) \equiv \nabla_T c(T) = -(\nabla_c F(c(T), T))^{-1} \nabla_T F(c(T), T). \tag{4.116}$$

Under the assumptions stated, we identify $\mathcal{E}_k[T] \equiv f_k(T)$ and conclude that the step (4.111) is valid. Furthermore, it is clear from the expression (4.116) and the smoothness of $F(c, T)$ that the derivatives appearing in (4.113) are bounded.

This completes the proof.

4.8 Discussion

We now give a summary of some of the salient features of the algorithms presented and discuss briefly the merits of this and other approaches.

We introduced an operator-splitting approach based on the transport of species, Algorithm 4.1, to approximate the solution of the reactive transport problem. It was demonstrated in Section 4.7 that this procedure has an associated first-order in time truncation error when applied to problems of LE or LNE type. Although we expect this result to remain true in the PLNE case, this has not been proven.

It is instructive to compare the computational cost associated with the OS defined in Algorithm 4.1, to that of solving (using again OS) the *original* governing equations for the classes LE, PLNE and LNE. Using the notation \bar{N}_S , \bar{N}_R^Q and \bar{N}_R^K to denote the number of *mobile* species of arbitrary type, equilibrium product type and kinetic product type, respectively, and designating the number of mobile

components^{||} \bar{N}_C , we find that the total number of transported variables, solving the original equations, are those given in Table 4.1 below. It is clear that whenever

Classification	Balance Equations	Number of PDEs
LE	Total Components	\bar{N}_C
PLNE	Eq. Components + Kinetic Species	$\bar{N}_C + \bar{N}_R^K$
LNE	Species	\bar{N}_S

Table 4.1 Comparison of the smallest number of transported variables for the three classes of reactive transport.

equilibrium reactions are present, that is, in the LE or PLNE scenarios, it is possible to achieve a more economical transport step than the one we actually implemented, by considering OS applied to the original, defining equations, as presented in Sections 3.4, 3.5 and 3.6. In fact, for such a formulation, one has:

1. *Fewer* transport equations to solve.
2. Possible numerical advantage; in particular, if individual species are completely consumed by reactions, it is (often) the case that component totals show a less drastic variation.
3. An easier time extending to higher-order formulations, or incorporating iteration between transport and chemistry modules (see Yeh and Tripathi [50]).

However, some disadvantages with these formulations also exist, such as:

1. More storage is required (global arrays).

^{||}A component is mobile as long as it participates in at least one mobile species.

2. The component approach produces an initial guess for the grid-block which is incompatible with using stoichiometric algorithms for the grid-block equilibrium problem.

The incompatibility with stoichiometric algorithms stems from the fact that the *component totals* give no indication as to how to choose the reference vector n^0 that appears in such algorithms. In addition, the initial guess for the grid block in question would have to be the vector of reacted concentrations at the *previous time-step*, a vector which is *not* compatible with the transported component totals at the new time-level.

Turning our attention to the local batch calculation, three distinct algorithms were proposed, namely the unreduced non-stoichiometric (UNSF), the reduced non-stoichiometric (RNSF) and the stoichiometric (SF) formulations. The number of nonlinear equations to be solved for in each algorithm, for either the LE or PLNE problem, are shown in Table 4.2 below. It is evident that the UNSF will be quite

Classification	Equilibrium algorithm		
	UNSF	RNSF	SF
LE	$2N_S + N_C$	$N_C + 2N_M$	$N_S + N_R$
PLNE	$2(N_R^Q + N_C) + N_C$	$N_C + 2N_M^Q$	$2N_R^Q + N_C$

Table 4.2 Comparison of the number of nonlinear equations solved in the reaction step for LE and PLNE problems.

costly to use in a realistic reactive transport simulation. This was also found from numerical experiments with the UNSF implementation. Therefore, we will only critically compare the RNSF and the SF.

To put our remarks in the proper context, it should be kept in mind that for most applications of interest, the number of components is small ($N_C < 10$), whereas the number of species (and the number of reactions) can be quite large (perhaps $N_S = 50$ to 100).

First, it is clear that the number of equations to be solved in either an LE or a PLNE problem will always be smallest for the RNSF. The difference is most noticeable in the LE scenario, when many complexation reactions that do not produce minerals are present. On the other hand, in the extreme case when all reactions result in the formation of minerals (i.e., $N_M^Q = N_R^Q$, or $N_M = N_R$), the number of unknowns is the same for the two formulations. In addition, for a PLNE problem, the difference is insignificant if the number of kinetic reactions (N_R^K) is high, and the number of equilibrium reactions small ($N_R^Q \approx 0$), in which case both algorithms require the solution of a little more than N_C equations. For such cases, the use of the SF algorithm is quite feasible. It must be pointed out that not only the *number* of unknowns, but also their *type*, is of importance in assessing the performance of the algorithms. In the SF, $N_C + N_R^Q$ multipliers must be solved for, whereas the number of multipliers in the RNSF is only N_M^Q . This is an advantage for the RNSF, as multiplier information is lost between consecutive time-steps in the course of simulation. Considerations of efficiency aside, it should be noted that the SF has two advantages over the RNSF:

1. A stoichiometric algorithm, such as SF, has exact mass-balance, due to the fact that all iterates are constrained to the closed-system constraint manifold.
2. No assumptions of ideality were needed in defining the SF algorithm.

Exact mass-conservation in the reaction step is obviously an attractive property, although the same effect can often be accomplished with a non-stoichiometric

algorithm if the error-tolerance is chosen properly. On the other hand, we have seen that the reduction that lead to the RNSF could *not* be accomplished for a non-ideal system. The SF algorithm, on the other hand, can easily be extended to the non-ideal case.

Chapter 5

Numerical Examples

Chapter Synopsis

Examples of the numerical solution of reactive transport problems are presented in this chapter. We have attempted to demonstrate the ability of the algorithms presented to solve broad classes of such problems. We demonstrate the flexibility in handling different types of chemistry by presenting problems involving aqueous complexation, acid-base interactions, adsorption, ion-exchange and precipitation/dissolution. Problems belonging to each of the reactive transport classes LE, LNE and PLNE are represented.

5.1 Introduction

The results presented in this chapter are organized in the following manner. We begin by considering a *batch problem* of mixed kinetic/equilibrium type for the purpose of validation. We then consider a series of 1D reactive transport problems, or *core problems*, previously solved in the literature. First, a sequence of LE problems are solved to illustrate the capability of handling different types of reactions occurring in geochemistry and to verify the computer programs. Second, an LNE problem with known analytic solution is treated and first-order in time convergence is verified. We then present a PLNE problem, and compare it with the results obtained by previous workers. The chapter is concluded with a 2D problem of LE type and a parallel speed-up study for a 3D problem.

5.2 Examples of Chemical Batch Systems

This test case, reported by Yeh et al. [49], demonstrates the code's capability of handling mixed equilibrium/kinetic speciation problems in a batch setting. Note the presence of isomers in this system: the distinct species $\text{CaCO}_3(\text{aq})$ and

Product species	Stoichiometry				$\log K$
	H_2O	H^+	Ca^{+2}	CO_3^{-2}	
OH^-	1	-1	0	0	-14.00
$\text{CaCO}_3(\text{aq})$	0	0	1	1	3.00
CaHCO_3^+	0	1	1	1	11.60
CaOH^+	1	-1	1	0	-12.20
HCO_3^-	0	1	0	1	10.20
H_2CO_3	0	2	0	1	16.50
$\text{Ca}(\text{OH})_2(\text{s})$	2	-2	1	0	-21.90
$\text{CaCO}_3(\text{s})$	0	0	1	1	8.30

Table 5.1 Stoichiometric and thermodynamic data for the Yeh et al. kinetic calcite precipitation problem.

$\text{CaCO}_3(\text{s})$ have identical chemical formulae. Using the SF, the equilibrium composition was computed in approximately 30 iterations from a “cold start”, i.e., a completely random initial guess. The RNSF needed approximately 15 iterations to converge, reflecting the fact that a smaller set of variables is solved for. The simulated composition, tabulated below, was nearly identical for the two algorithms, since a high tolerance had been specified. They are in good agreement with the equilibrium composition reported in [49].

Species	Computed concentrations [M]
H ⁺	1.23e-9
H ₂ O	55.1
Ca ⁺²	1.22e-4
CO ₃ ⁻²	4.12e-5
OH ⁻	8.07e-5
CaCO ₃ (aq)	5.01e-6
CaHCO ₃ ⁺	2.47e-7
CaOH ⁺	6.19e-6
HCO ₃ ⁻	8.10e-5
H ₂ CO ₃	2.00e-8
Ca(OH) ₂ (s)	5.0e-15
CaCO ₃ (s)	8.73e-4

Table 5.2 Simulated equilibrium composition for the Yeh et al. kinetic calcite precipitation problem.

For the kinetic demonstration, we replace the equilibrium constant K for the formation of CaCO₃(s) by the forward and backward rates $\log K^f = 3.30$ and $\log K^b = -5.00$. Note that in general, $K = K^f/K^b$, or, analogously, $\log K = \log K^f - \log K^b$, resulting in an equilibrium constant of $\log K = 8.30$ if this reaction goes to completion. In order to perform a kinetic simulation, in addition to specifying the component totals, we need also fix an initial value for the kinetic product species. Following [49], we take the initial value of CaCO₃(s) to be 10 percent of its final equilibrium value, or 8.73e-5 M.

The results of the simulation over a period of 100 hrs are presented in Figures 5.1 and 5.2. As can be seen, CaCO₃(s) rapidly approaches its equilibrium value, and the system has attained complete equilibrium at $t = 100$ hrs.

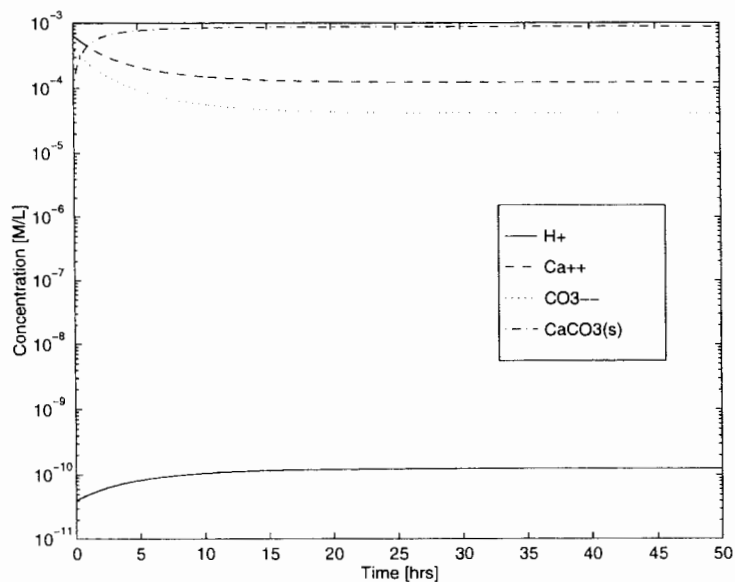


Figure 5.1 Time evolution of the kinetic precipitation of calcite. The concentration of three aqueous components and the kinetically controlled mineral as functions of time.

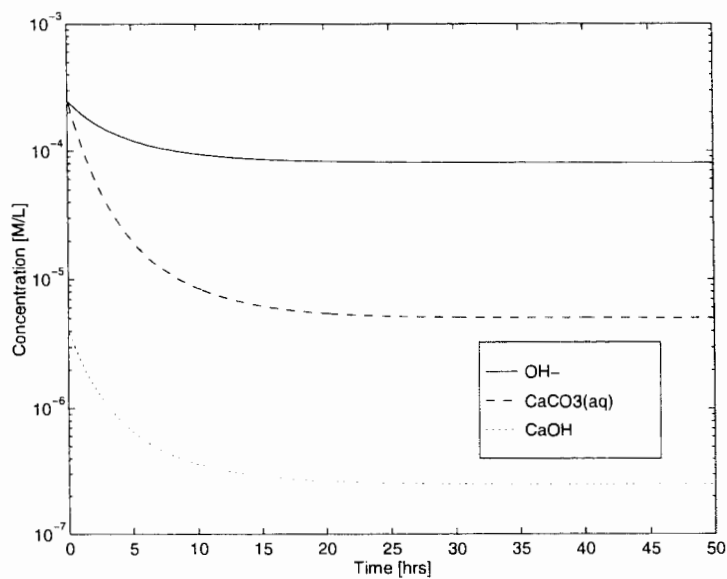


Figure 5.2 Time evolution of the kinetic precipitation of calcite. The concentration of three equilibrium controlled aqueous species as functions of time.

5.3 Reactive Transport in 1D

We describe in this section the results obtained for a series of 1D simulations. The conceptual arrangement is the same for all these simulations, and involves the injection into a core of length L some *injected composition* that displaces and reacts with the *initial composition*. This is shown schematically below. At

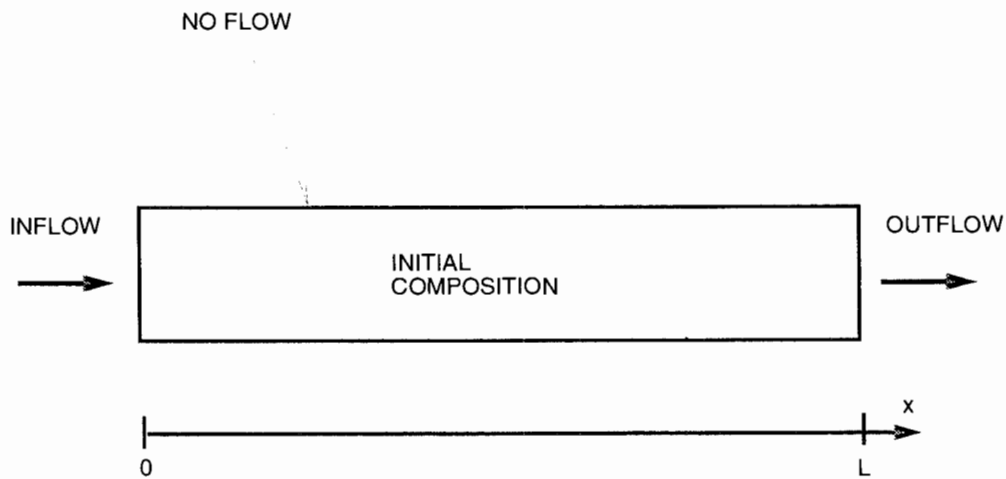


Figure 5.3 The 1D core-flood arrangement.

the boundary termed “inflow”, we prescribe a Danckwert’s boundary condition as discussed in Section 3.3.5, i.e., for each mobile species we require that

$$uc_i(0, t) - D \frac{\partial c_i(0, t)}{\partial x} = uc_i^I, \quad (5.1)$$

where c_i^I is the injected concentration of the i th species. At the “outflow” boundary, we prescribe no diffusive flux,

$$\frac{\partial c_i(L, t)}{\partial x} = 0. \quad (5.2)$$

5.3.1 LE Problems

Equilibrium Dissolution of a Mineral

In this section we consider generic, so-called ABCD problems, involving the equilibrium precipitation and dissolution of minerals. For a 1D medium with constant initial and boundary conditions, these problems can be solved analytically (see Walsh et al. [47] and Bryant et al. [7]). This class of problems often feature *shock-waves* separating different states. For these reasons, they serve as excellent test problems for reactive transport simulators. From [47] we take a simple equilibrium precipitation/dissolution problem with thermodynamic and stoichiometric data given in Table 5.3. The injected and initial compositions for this simulation

Product species	Stoichiometry					K
	H ₂ O	A	B	C	D	
AB(s)	0	1	1	0	0	1.00
AC(s)	0	1	0	1	0	0.50
DB(s)	0	0	1	0	1	2.00

Table 5.3 Stoichiometric and thermodynamic data for the Walsh et al. ABCD mineral problem.

are collected in Table 5.4. As can be seen, the mineral AB(s) is initially present; however the injected stream is low in the species A and B, and we thus expect the mineral to gradually dissolve. Simulation results based on $n_x = 100$ grid-blocks and a CFL number of 0.5 are presented in Figures 5.4 and 5.5 at a time $t = 0.5$ PVI (Pore Volumes Injected). They show the expected dissolution of AB(s). The dissolution front is a shock that moves with a retarded velocity compared with the mean velocity of the fluid. The retarded velocity is close to the value $v_f = 0.28$ predicted by theory ([47]).

Species	Initial composition [M]	Injected composition [M]
A(aq)	1.0	0.5
B(aq)	1.0	0.0
C(aq)	0.0	2.0
D(aq)	0.0	2.0
H ₂ O	55.1	55.1
AB(s)	2.0	-

Table 5.4 Boundary and initial conditions for the Walsh et al. ABCD mineral problem.

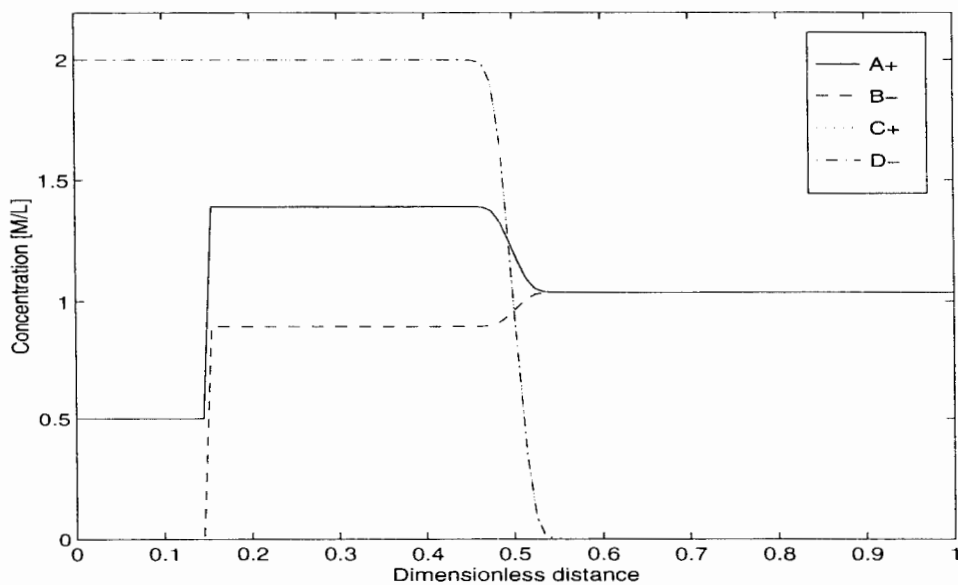


Figure 5.4 The Walsh et al. AB(s) dissolution problem. Concentration profiles of aqueous species at 0.5 PVI.

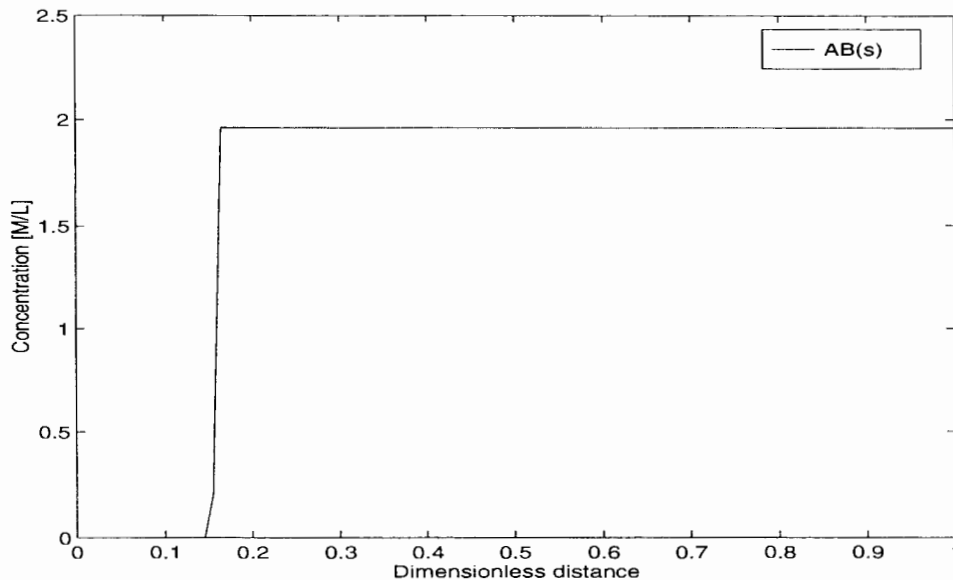


Figure 5.5 The Walsh et al. AB(s) dissolution problem. Concentration profile at $t = 0.5$ PVI. Velocity of dissolution front is $v_f = 0.28$.

Equilibrium Precipitation/Dissolution of Minerals

Next, we consider a problem based on using the same stoichiometry as that in Table 5.3, but with different initial and boundary conditions. This case was studied by Sevougian [36]. The Riemann problem is here defined by the initial and boundary conditions given in Table 5.5 below. Again, we begin with the mineral AB(s) present, and inject a solution low in A and B. However, in this case we allow the precipitation of two new minerals AC(s) and DB(s). As in the previous example, the discretization uses $n_x = 100$ grid-blocks and the CFL number is 0.5.

The result of the simulation can be found in Figures 5.6 and 5.7, which show the aqueous and the solid species, respectively, at a time corresponding to 0.5 PVI. The figures, which are in excellent agreement with those presented in [36], show the presence of precipitation/dissolution waves passing through the regions. The minerals show the expected shock-structure.

Species	Initial composition [M]	Injected composition [M]
A(aq)	1.0	0.25
B(aq)	1.0	0.0
C(aq)	0.0	2.0
D(aq)	0.0	1.75
H ₂ O	55.1	55.1
AB(s)	1.0	-
AC(s)	0.0	-
DB(s)	0.0	-

Table 5.5 Boundary and initial conditions for the Sevougian ABCD mineral problem.

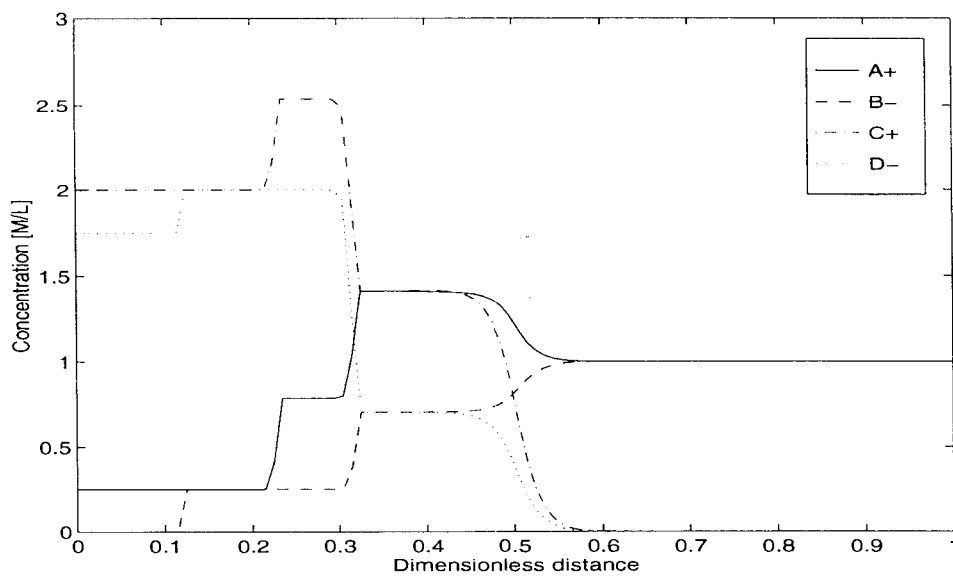


Figure 5.6 The Sevougian precipitation/dissolution problem. Concentration profiles of aqueous species at $t = 0.5$ PVI.

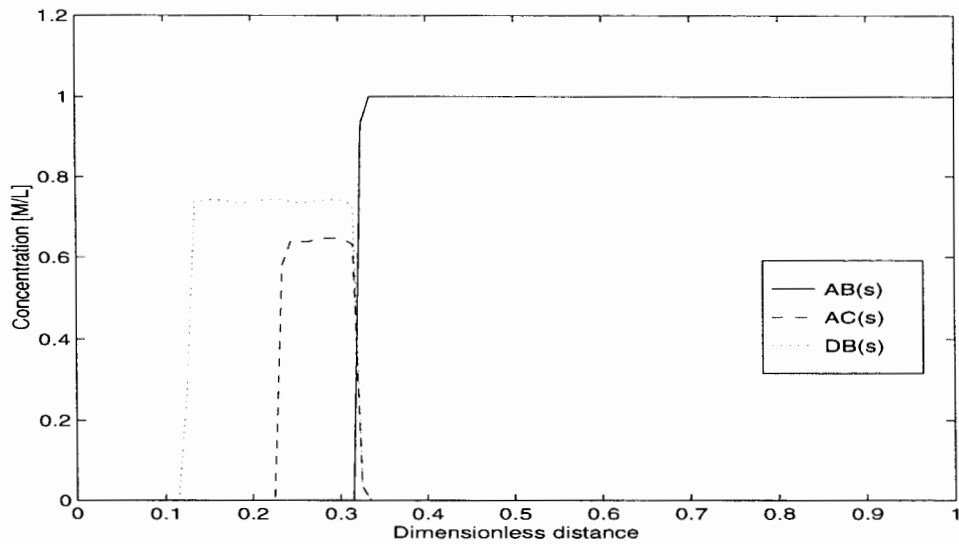


Figure 5.7 The Sevougian precipitation/dissolution problem. Concentration profiles of mineral species at $t = 0.5$ PVI.

Ion-Exchange

We consider next an example of *homovalent, binary ion-exchange* taken from Rubin and James [31], featuring two generic aqueous, homovalent ions c_1 and c_2 , and their corresponding ion-exchanged species z_1 and z_2 . The thermodynamic and stoichiometric data for this case is given in Table 5.6 below.

Product species	Stoichiometry				K
	H_2O	c_1	c_2	$z_1(s)$	
$z_2(s)$	0	-1	1	1	1.0

Table 5.6 Stoichiometric and thermodynamic data for the Rubin and James ion-exchange problem.

Species	Initial composition [M]	Injected composition [M]
$c_1(\text{aq})$	0.271	0.160
$c_2(\text{aq})$	$4.91\text{e-}2$	$1.0\text{e-}10$
$z_1(\text{s})$	$8.22\text{e-}2$	-
$z_2(\text{s})$	$1.49\text{e-}2$	-
H_2O	$5.51\text{e}1$	$5.51\text{e}1$

Table 5.7 Boundary and initial conditions for the Rubin and James ion-exchange problem.

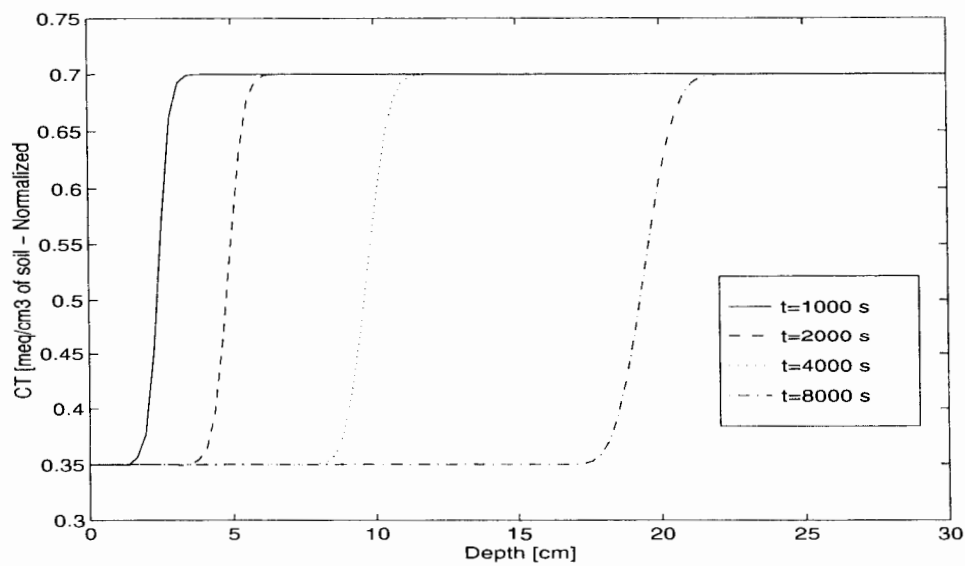


Figure 5.8 The Rubin and James ion-exchange example. Total solution normality at four different times.

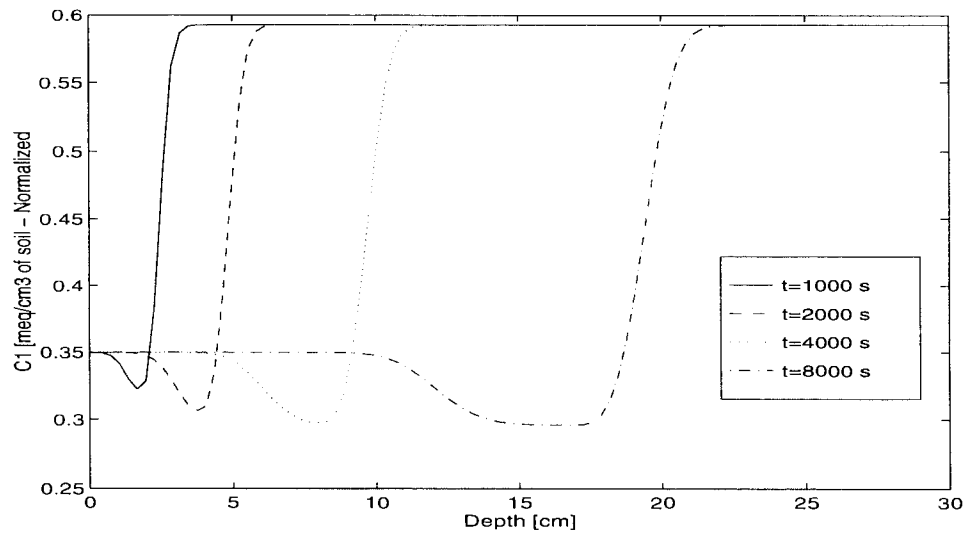


Figure 5.9 The Rubin and James ion-exchange example. Aqueous ion c_1 at four different times.

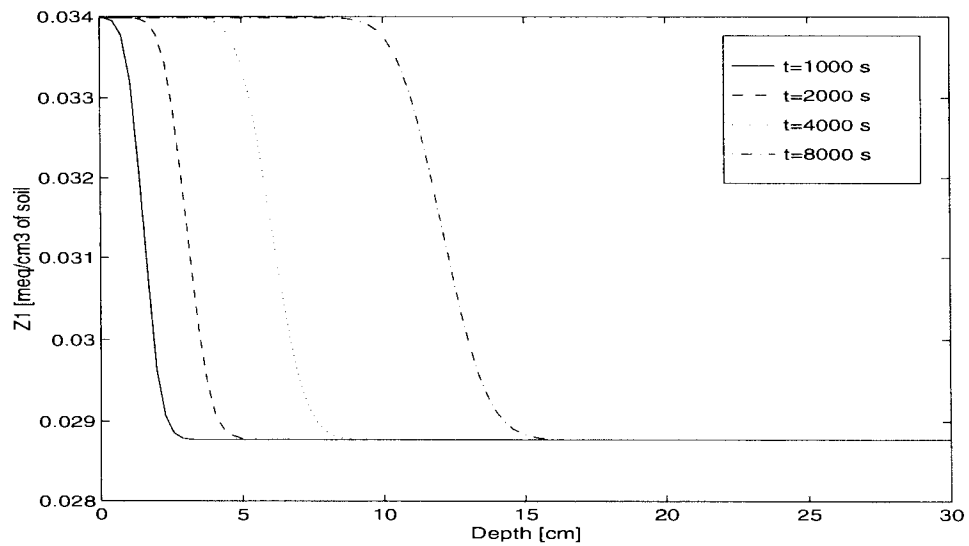


Figure 5.10 The Rubin and James ion-exchange example. Solid species z_1 at four different times.

A First Realistic Core Example—Uranium Complexation and Adsorption

In this section we consider a test case which illustrates the combined effects of aqueous complexation and surface adsorption, taken from Yeh and Tripathi [51]. The system is comprised of a total of 36 species, of which 30 are aqueous and six are surface species (adsorbed species). Stoichiometric and thermodynamic information is listed in Table 5.8 below. The domain has a length of $L = 100$ m, and is discretized into 50 grid-blocks. The simulation proceeds for 600 days with a time-step of 1 day. The initial conditions are *nonuniform* for pH and surface sites. The pH profile and the distribution of surface sites used can be seen in Figure 5.11 below. Note that the zone extending from $x = 20$ m to $x = 60$ m has a very high capacity for adsorbing aqueous species. Furthermore, the injected concentration of total carbonate exhibits a time-variation as illustrated in Figure 5.12. As is evident from that figure, the total amount of hydrogen was also set to vary with time. This has been done to ensure that the pH of the incoming stream is approximately 7.60 as stipulated in [51]. Remaining boundary and initial conditions for the component totals used in this simulation can be found in Table 5.9 below.

The results are given in terms of total simulated dissolved carbonate, total adsorbed uranium and total dissolved uranium, Figures 5.13, 5.14 and 5.15, respectively. The results match well those presented in [51]. Note in particular the sudden “peak” in dissolved uranium that develops in the interior of the domain at $t = 530$ days of injection.

Finally, note the long-term behavior of the pH distribution in the domain, illustrated by Figure 5.16. Initially, the pH at the inlet is significantly higher than that of the injected composition. At approximately 1000 days of injection, however, we see that the region of pH=7.6 is advancing through the core.

Product species	Stoichiometry								log K
	H ₂ O	H ⁺	CO ₃ ⁻²	Ca ⁺²	UO ₂ ⁺²	NpO ₂ ⁺	SO ₄ ⁻²	SOH	
OH ⁻	1	-1	0	0	0	0	0	0	-14.00
CaCO ₃	0	0	1	1	0	0	0	0	3.22
CaHCO ₃ ⁺	0	1	1	1	0	0	0	0	11.43
CaSO ₄	0	0	0	1	0	0	0	0	2.31
CaOH ⁺	1	-1	0	1	0	0	0	0	-12.85
UO ₂ OH ⁺	1	-1	0	0	1	0	0	0	-5.30
(UO ₂) ₂ (OH) ₂ ⁺²	2	-2	0	0	2	0	0	0	-5.68
(UO ₂) ₃ (OH) ₄ ⁺²	4	-4	0	0	3	0	0	0	-11.88
(UO ₂) ₃ (OH) ₅ ⁺²	5	-5	0	0	3	0	0	0	-15.82
(UO ₂) ₄ (OH) ₇ ⁺²	7	-7	0	0	4	0	0	0	-21.90
(UO ₂) ₃ (OH) ₇ ⁺²	7	-7	0	0	3	0	0	0	-28.34
UO ₂ CO ₃	0	0	1	0	1	0	0	0	9.65
UO ₂ (CO ₃) ₂ ⁻²	0	0	2	0	1	0	0	0	17.08
UO ₂ (CO ₃) ₃ ⁻⁴	0	0	3	0	1	0	0	0	21.70
UO ₂ CO ₃ (OH) ₃ ⁻	3	-3	1	0	2	0	0	0	-1.18
UO ₂ SO ₄	0	0	0	0	1	0	1	0	2.95
UO ₂ (SO ₄) ₂ ⁻²	0	0	0	0	1	0	2	0	4.00
HCO ₃ ⁻	0	1	1	0	0	0	0	0	10.32
H ₂ CO ₃	0	2	1	0	0	0	0	0	16.67
HSO ₄ ⁻	0	1	0	0	0	0	1	0	1.99
NpO ₂ OH	1	-1	0	0	0	1	0	0	-8.85
NpO ₂ CO ₃ ⁻	0	0	1	0	0	1	0	0	5.60
NpO ₂ (CO ₃) ₂ ⁻	0	0	2	0	0	1	0	0	7.75
SO ⁻	0	-1	0	0	0	0	0	1	-10.30
SOH ₂ ⁺	0	1	0	0	0	0	0	1	5.40
SO-UO ₂ OH ⁺	2	-2	0	0	1	0	0	1	-7.10
SOH ₂ ⁺ (UO ₂) ₃ (OH) ⁻	7	-6	0	0	3	0	0	1	-31.00
SOHNpO ₂ OH	1	-1	0	0	0	1	0	1	-3.50

Table 5.8 Stoichiometric and thermodynamic data for the Yeh and Tripathi uranium adsorption problem.

Species	Initial Totals [M]	Injected Totals [M]
H ₂ O	55.1	55.1
H ⁺	non-uniform	time-varying
CO ₃ ⁻²	1.0e-4	time-varying
Ca ⁺²	1.0e-4	1.0e-3
UO ₂ ⁺²	1.0e-8	1.0e-6
NpO ₂ ⁺	1.0e-16	2.5e-10
SO ₄ ⁻²	1.0e-4	1.0e-4
SOH	non-uniform	-

Table 5.9 Boundary and initial conditions for the Yeh and Tripathi uranium adsorption problem.

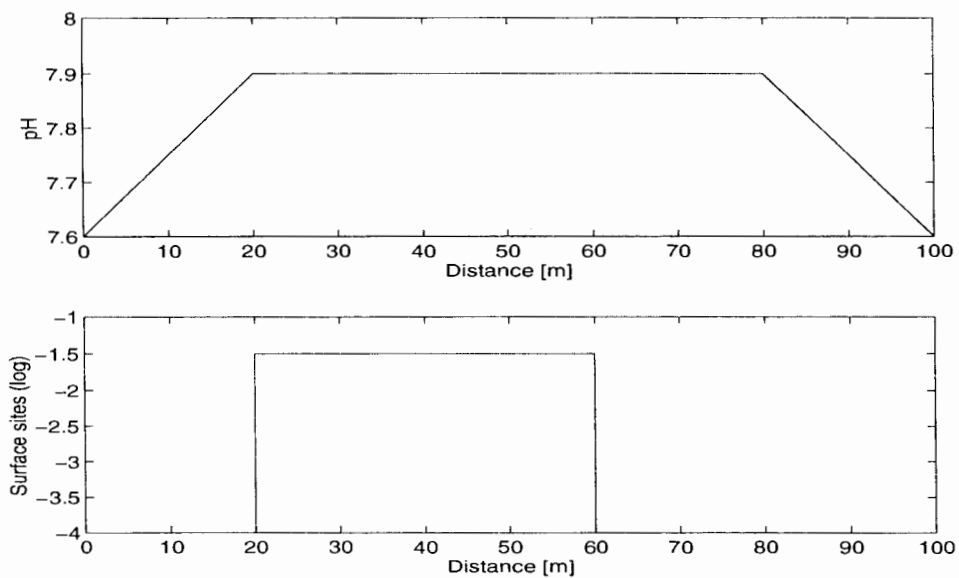


Figure 5.11 Initial profiles for pH and distribution of surface sites for the Yeh and Tripathi uranium adsorption problem.

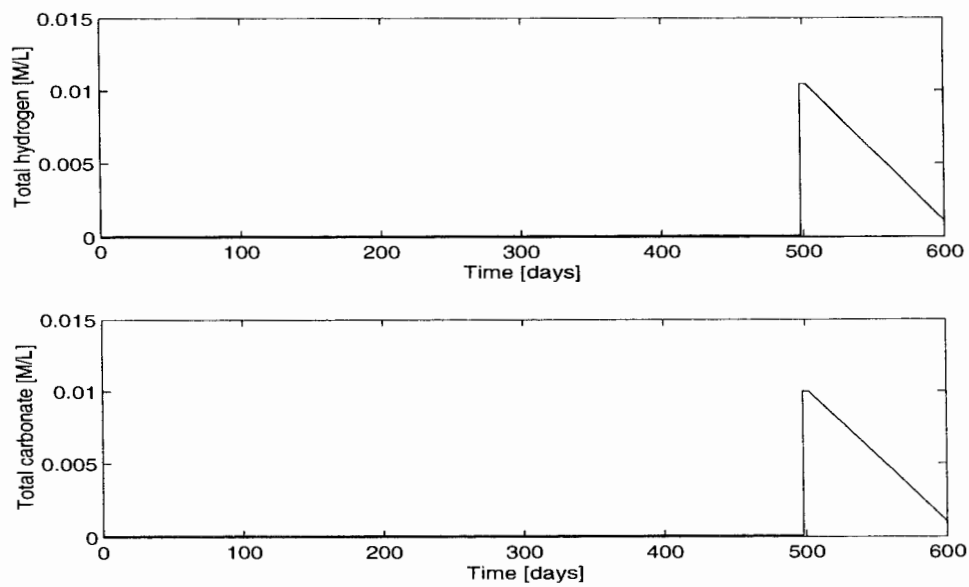


Figure 5.12 Injected total concentrations of hydrogen and carbonate for the Yeh and Tripathi uranium adsorption problem.

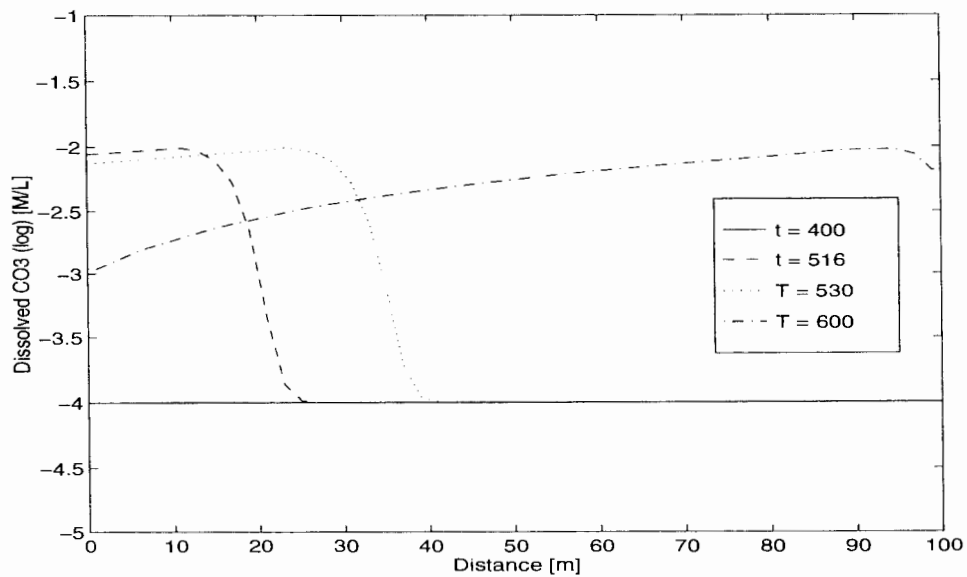


Figure 5.13 Total dissolved carbonate concentrations at different times for the Yeh and Tripathi uranium adsorption problem.

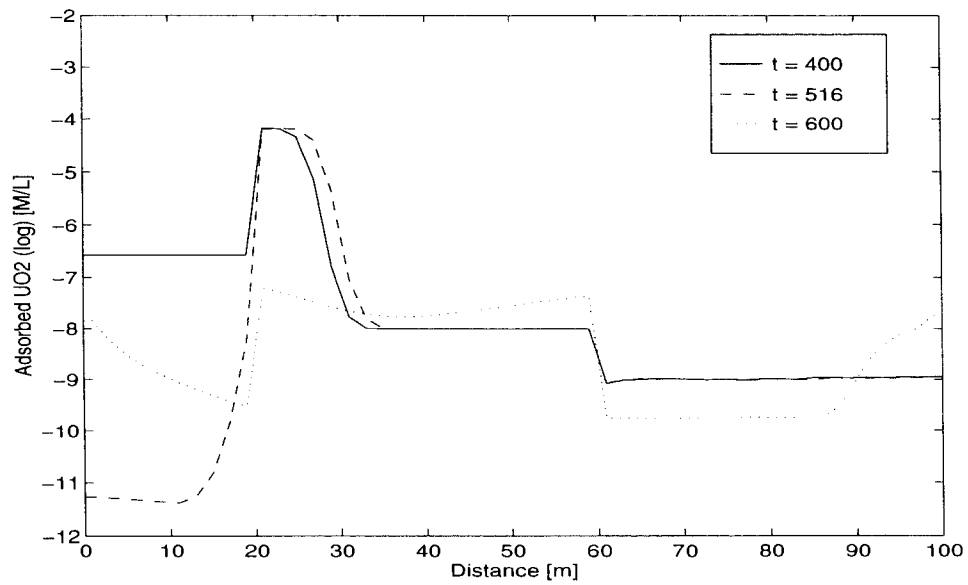


Figure 5.14 Total adsorbed uranium concentration at different times for the Yeh and Tripathi uranium adsorption problem.

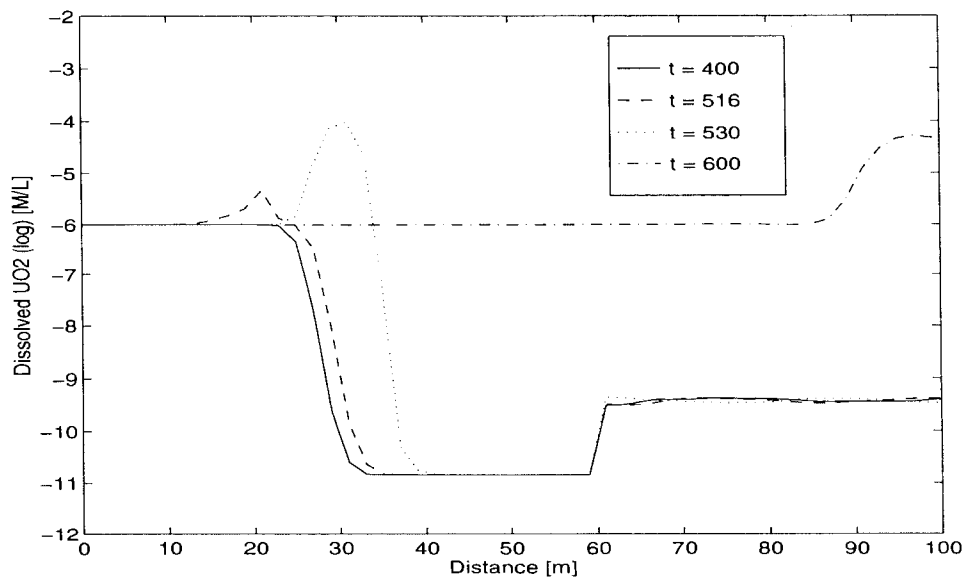


Figure 5.15 The development of a peak in dissolved uranium concentration for the Yeh and Tripathi uranium adsorption problem.

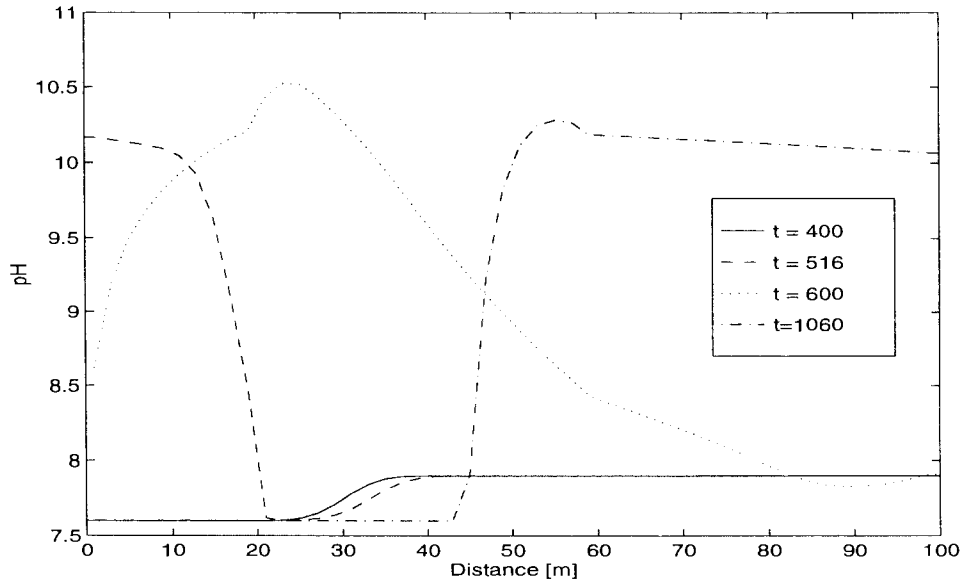


Figure 5.16 The pH profile within the core at early and very long times for the Yeh and Tripathi uranium adsorption problem.

A Second Realistic Core Example—Redox Complexation and Precipitation

This test case, taken from Engesgaard and Kipp [16], illustrates the combined processes of complexation, precipitation/dissolution and redox reactions. The original stoichiometric and thermodynamic information, given in terms of the components H^+ , CO_3^{-2} , Ca^{+2} , Na^+ , Mg^{+2} , Fe^{+3} , SO_4^{-2} , NO_3^- , Cl^- and the *electron component* e^- , is listed in Table 5.10 and Table 5.11. As discussed in Section 2.2, redox systems are treated analogously to non-redox systems by reduction of the formula matrix to find a proper set of components. In a pre-processing step, we therefore convert the system in Table 5.10–Table 5.11 to yield a formula matrix in canonical form. This automatic procedure results in the species O_2 being added to the component list to replace the electron (which is *not* a component in the sense that we have adopted). The transformed system is given in Table 5.12–Table 5.13. Note in particular that non-redox species (such as HCO_3^-) are unaffected by this trans-

formation. The equilibrium data is conveniently handled by computing a set of *equivalent chemical reference potentials*, and transforming them according to the changing stoichiometry (see [41]). It is worth pointing out that the equilibrium constants display an astounding variation of size of approximately 400 orders of magnitude. This feature, characteristic of many redox systems, make for a very challenging application of our algorithms.

Next, the physical parameters for the simulation are described. The domain is of length $L = 10$ m, has a porosity of $\phi = 0.3$, and a dispersivity of 0.2 m. The prescribed (interstitial) velocity is $v = 25$ m yr⁻¹. The porous medium has a bulk density of 1700 kg m⁻³, and the density of water is taken to be 1000 kg m⁻³. To facilitate a comparison with the results reported in [16], units of mg liter⁻¹ are used for all aqueous species, whereas minerals are given in mg (kg soil)⁻¹—the simulator uses units of moles liter⁻¹, but for the sake of brevity we will not show the conversion here.

Boundary and initial conditions were uniform in space and constant in time as given in Table 5.14. A few comments are in order to explain the selection of boundary and inlet data. For both initial and boundary conditions, the component totals listed for CO₃⁻², Ca⁺², Na⁺, Mg⁺², NO₃⁻ and Cl⁻ were obtained directly from [16]. For the initial conditions we made the assumption that the mass of components Fe⁺³ and SO₄⁻² was dominated by the mineral form, pyrite (FeS₂), and the value 432.0 mg (kg soil)⁻¹ reported in [16] was used. The conditions of overall electroneutrality were used to establish the value of the total hydrogen component. Finally, the level of the O₂ component was adjusted until an approximate match was reached with the pH^{**} and pE^{††} values reported in [16]. The pE values reported

**pH = 8.67 initially, pH = 5.70 at the inlet.

††pE = -4.30 initially, pE = 16.5 at the inlet.

Products	Stoichiometry										log K
	H ⁺	CO ₃ ⁻²	Ca ⁺²	Na ⁺	Mg ⁺²	Fe ⁺³	e ⁻	SO ₄ ⁻²	NO ₃ ⁻	Cl ⁻	
OH ⁻	-1	0	0	0	0	0	0	0	0	0	-14.0
O ₂	-4	0	0	0	0	0	-4	0	0	0	-86.00
H ₂	2	0	0	0	0	0	2	0	0	0	-3.15
HCO ₃ ⁻	1	1	0	0	0	0	0	0	0	0	10.35
H ₂ CO ₃	2	1	0	0	0	0	0	0	0	0	16.68
CH ₄	10	1	0	0	0	0	8	0	0	0	41.1
HSO ₄ ⁻	1	0	0	0	0	0	0	1	0	0	1.99
S ⁻²	8	0	0	0	0	0	8	1	0	0	20.7
HS ⁻	9	0	0	0	0	0	8	1	0	0	33.7
H ₂ S	10	0	0	0	0	0	8	1	0	0	40.6
NO ₂ ⁻	2	0	0	0	0	0	2	0	1	0	28.6
N ₂	12	0	0	0	0	0	10	0	2	0	207.0
NH ₃	9	0	0	0	0	0	8	0	1	0	110.0
NH ₄ ⁺	10	0	0	0	0	0	8	0	1	0	119.0
NH ₄ SO ₄ ⁻	10	0	0	0	0	0	8	1	1	0	120.0
CaOH ⁺	-1	0	1	0	0	0	0	0	0	0	-12.6
CaCO ₃	0	1	1	0	0	0	0	0	0	0	3.23
CaHCO ₃ ⁺	1	1	1	0	0	0	0	0	0	0	11.4
CaSO ₄	0	0	1	0	0	0	0	1	0	0	2.30
MgOH ⁺	-1	0	0	0	1	0	0	0	0	0	-11.8
MgCO ₃	0	1	0	0	1	0	0	0	0	0	2.98
MgHCO ₃ ⁺	1	1	0	0	1	0	0	0	0	0	11.4
MgSO ₄	0	0	0	0	1	0	0	1	0	0	2.25
NaCO ₃ ⁺	0	1	0	1	0	0	0	0	0	0	1.27
NaHCO ₃	1	1	0	1	0	0	0	0	0	0	10.1
NaSO ₄ ⁻	0	0	0	1	0	0	0	1	0	0	0.70

Table 5.10 Stoichiometric and thermodynamic data for the Engesgaard and Kipp redox problem. Product species 1-34.

Products	Stoichiometry										log <i>K</i>
	H ⁺	CO ₃ ⁻²	Ca ⁺²	Na ⁺	Mg ⁺²	Fe ⁺³	e ⁻	SO ₄ ⁻²	NO ₃ ⁻	Cl ⁻	
Fe(OH) ⁺	-1	0	0	0	0	1	1	0	0	0	3.53
Fe(OH) ₂	-2	0	0	0	0	1	1	0	0	0	-7.54
Fe(OH) ₃ ⁻	-3	0	0	0	0	1	1	0	0	0	-18.00
FeSO ₄	0	0	0	0	0	1	1	1	0	0	15.3
Fe(HS) ₂	18	0	0	0	0	1	17	2	0	0	89.3
Fe(HS) ₃ ⁻	27	0	0	0	0	1	25	3	0	0	125.0
Fe ⁺²	0	0	0	0	0	1	1	0	0	0	13.00
Fe(OH) ⁺²	-1	0	0	0	0	1	0	0	0	0	-2.19
Fe(OH) ₂ ⁺	-2	0	0	0	0	1	0	0	0	0	-5.67
Fe(OH) ₃	-3	0	0	0	0	1	0	0	0	0	-13.60
Fe(OH) ₄ ⁻	-4	0	0	0	0	1	0	0	0	0	-21.60
Fe ₂ (OH) ₂ ⁺⁴	-2	0	0	0	0	2	0	0	0	0	-2.95
Fe ₃ (OH) ₄ ⁺⁵	-4	0	0	0	0	3	0	0	0	0	-6.30
FeSO ₄ ⁺	0	0	0	0	0	1	0	1	0	0	3.92
Fe(SO ₄) ₂ ⁻	0	0	0	0	0	1	0	2	0	0	5.42
Fe(OH) ₃	-3	0	0	0	0	1	0	0	0	0	-4.890
FeS ₂	16	0	0	0	0	1	15	2	0	0	-227.7

Table 5.11 Stoichiometric and thermodynamic data for the Engesgaard and Kipp redox problem. Product species 35–52.

Products	Stoichiometry										log K
	H ⁺	CO ₃ ⁻²	Ca ⁺²	Na ⁺	Mg ⁺²	Fe ⁺³	O ₂	SO ₄ ⁻²	NO ₃ ⁻	Cl ⁻	
OH ⁻	-1	0	0	0	0	0	0	0	0	0	-14.0
H ₂	0	0	0	0	0	0	-0.5	0	0	0	-46.15
HCO ₃ ⁻	1	1	0	0	0	0	0	0	0	0	10.35
H ₂ CO ₃	2	1	0	0	0	0	0	0	0	0	16.68
CH ₄	2	1	0	0	0	0	-2	0	0	0	-130.9
HSO ₄ ⁻	1	0	0	0	0	0	0	1	0	0	1.99
S ⁻²	0	0	0	0	0	0	-2	1	0	0	-151.3
HS ⁻	1	0	0	0	0	0	-2	1	0	0	-138.3
H ₂ S	2	0	0	0	0	0	-2	1	0	0	-131.4
NO ₂ ⁻	0	0	0	0	0	0	-0.5	0	1	0	-14.40
N ₂	2	0	0	0	0	0	-2.5	0	2	0	-8.0
NH ₃	1	0	0	0	0	0	-2	0	1	0	-62.0
NH ₄ ⁺	2	0	0	0	0	0	-2	0	1	0	-53.0
NH ₄ SO ₄ ⁻	2	0	0	0	0	0	-2	1	1	0	-52.0
CaOH ⁺	-1	0	1	0	0	0	0	0	0	0	-12.6
CaCO ₃	0	1	1	0	0	0	0	0	0	0	3.23
CaHCO ₃ ⁺	1	1	1	0	0	0	0	0	0	0	11.4
CaSO ₄	0	0	1	0	0	0	0	1	0	0	2.30
MgOH ⁺	-1	0	0	0	1	0	0	0	0	0	-11.8
MgCO ₃	0	1	0	0	1	0	0	0	0	0	2.98
MgHCO ₃ ⁺	1	1	0	0	1	0	0	0	0	0	11.4
MgSO ₄	0	0	0	0	1	0	0	1	0	0	2.25
NaCO ₃ ⁺	0	1	0	1	0	0	0	0	0	0	1.27
NaHCO ₃	1	1	0	1	0	0	0	0	0	0	10.1
NaSO ₄ ⁻	0	0	0	1	0	0	0	1	0	0	0.70

Table 5.12 Transformed stoichiometric and thermodynamic data for the Engesgaard and Kipp redox problem. Product species 1–34.

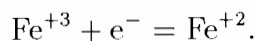
Products	Stoichiometry										log K
	H ⁺	CO ₃ ⁻²	Ca ⁺²	Na ⁺	Mg ⁺²	Fe ⁺³	O ₂	SO ₄ ⁻²	NO ₃ ⁻	Cl ⁻	
Fe(OH) ⁺	-2	0	0	0	0	1	-0.25	0	0	0	-17.97
Fe(OH) ₂	-3	0	0	0	0	1	-0.25	0	0	0	-29.04
Fe(OH) ₃ ⁻	-4	0	0	0	0	1	-0.25	0	0	0	-39.50
FeSO ₄	-1	0	0	0	0	1	-0.25	1	0	0	-39.50
Fe(HS) ₂	1	0	0	0	0	1	-4.25	2	0	0	-276.3
Fe(HS) ₃ ⁻	2	0	0	0	0	1	-6.25	3	0	0	-412.5
Fe ⁺²	-1	0	0	0	0	1	-0.25	0	0	0	-8.50
Fe(OH) ⁺²	-1	0	0	0	0	1	0	0	0	0	-2.19
Fe(OH) ₂ ⁺	-2	0	0	0	0	1	0	0	0	0	-5.67
Fe(OH) ₃	-3	0	0	0	0	1	0	0	0	0	-13.60
Fe(OH) ₄ ⁻	-4	0	0	0	0	1	0	0	0	0	-21.60
Fe ₂ (OH) ₂ ⁺⁴	-2	0	0	0	0	2	0	0	0	0	-2.95
Fe ₃ (OH) ₄ ⁺⁵	-4	0	0	0	0	3	0	0	0	0	-6.30
FeSO ₄ ⁺	0	0	0	0	0	1	0	1	0	0	3.92
Fe(SO ₄) ₂ ⁻	0	0	0	0	0	1	0	2	0	0	5.42
Fe(OH) ₃	-3	0	0	0	0	1	0	0	0	0	-4.890
FeS ₂	1	0	0	0	0	1	-3.75	2	0	0	-223.60

Table 5.13 Transformed stoichiometric and thermodynamic data for the Engesgaard and Kipp redox problem. Product species 35–52.

Species	Initial conditions	Injected composition
CO_3^{-2}	78.1	16.8
Ca^{+2}	36.3	18.0
Na^{+}	14.0	14.4
Mg^{+2}	2.0	10.0
Fe^{+3}	0.0	6.7e-3
SO_4^{-2}	0.0	28.0
NO_3^{-}	0.0	65.0
Cl^{-}	19.0	24.0
pH	9.03	5.57
pE	-4.98	15.1
FeS_2	432.0	-

Table 5.14 Boundary and initial conditions for the Engesgaard and Kipp redox problem. Aqueous concentrations are total component concentrations in mg liter^{-1} of aqueous phase. The mineral concentration is given in mg (kg soil)^{-1} .

in Table 5.14 were based on the half-cell reaction



Manipulation of the corresponding mass-action expression (using $\text{pE} \equiv \log\{\text{e}^{-}\}$) produces the defining relation

$$\text{pE} = 13.0 + \log c_{\text{Fe}^{+3}} - \log c_{\text{Fe}^{+2}}. \quad (5.3)$$

Some uncertainty exists about the initial conditions of the Fe^{+3} component used in [16], as the authors claim to have had an “infinite supply” of the mineral $\text{Fe}(\text{OH})_3$ initially. With the component abundances specified above, we found that both minerals were present in the initial conditions, $\text{Fe}(\text{OH})_3$ at a comparatively small value and pyrite close to its limiting value of $432.0 \text{ mg (kg soil)}^{-1}$.

Prescribing inlet conditions was somewhat less involved. No mineral phases were present and the totals for components 1–8 given in [16] (Table 5.14) were used.

By invoking overall electroneutrality of the mixture, the level of total hydrogen was fixed. Furthermore, Engesgaard and Kipp [16] report an approximate value of 10 mg liter⁻¹ of dissolved oxygen in the incoming stream and this value was matched by varying the level of the O₂ component. The resulting pH and pE in Table 5.14 agree fairly well with those reported in [16].

Following [16] a coarse discretization employing only 20 gridblocks was used. The simulation proceeded for 10 years (25 PVI) with a time-step of 1.8 days, corresponding to a CFL number of 0.25. A significantly larger time-step was used in [16]; however, their algorithm employed a costly iteration between transport and chemistry modules to correct for mass-transfer into the solid phase.

The large number of equilibrium complexation reactions clearly favor the use of the RNSF in this application, which reduces the number of primary unknowns for the equilibrium calculation to $N_{eq} = 14$. In addition, the need to accurately compute extremely small concentrations renders the use of logarithmically transformed variables a necessity.

In discussing the results of the simulation, let us begin by considering the pyrite profile at 10 years, Figure 5.17. Engesgaard and Kipp report an average velocity of the retarded dissolution front of 0.58 m yr⁻¹, which appears to be in good agreement with our result. We can substantiate this somewhat by considering the limiting case of hyperbolic chromatography, in which case the relative shock-speed can be computed from a simple jump condition across the shock ([47]). Applying this condition to the sulfate component produces the relation

$$v_f = \left(1 + \frac{2(c_{\text{pyrite}}^+ - c_{\text{pyrite}}^-)}{C_{\text{SO}_4}^+ - C_{\text{SO}_4}^-}\right)^{-1}, \quad (5.4)$$

where c_{pyrite} is the concentration of pyrite, C_{SO_4} is the total aqueous concentration of sulfate and the superscripts + and - designate downstream and upstream

concentrations. Obtaining the necessary concentrations from Figures 5.17 and 5.20 (and converting to molar concentrations), the relation (5.4) gives the approximate value $v_f = 0.0223$, or, when multiplied by the interstitial velocity of 25 m yr^{-1} , a front speed of 0.56 m yr^{-1} .

The pH and pE profiles in Figure 5.18 agree well with those in [16]; in particular, the physically important local maximum/minimum of the pE and pH resulting from the consumption of first oxygen and then nitrate at the redox front are clearly visible. The rapid depletion of both oxygen and nitrate is evident from Figure 5.19. This is in excellent agreement with [16]. Finally, total concentration and some prominent species of the sulfate and iron components are shown in Figure 5.20 and Figure 5.21. The agreement with the results in [16] are particularly good for the sulfate component, with slightly lower values predicted for the iron component.

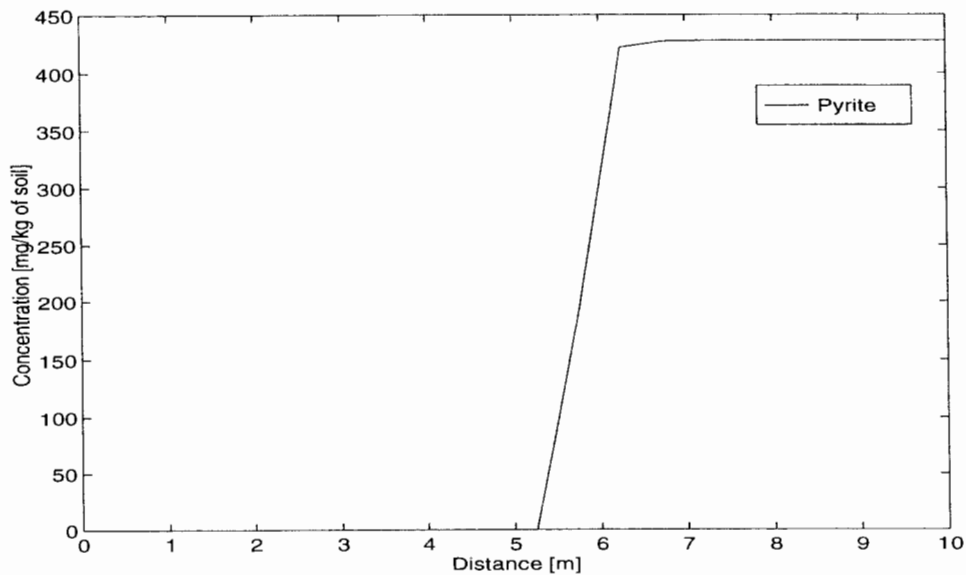


Figure 5.17 Concentration profile of pyrite after 10 years for the Engesgaard and Kipp redox problem.

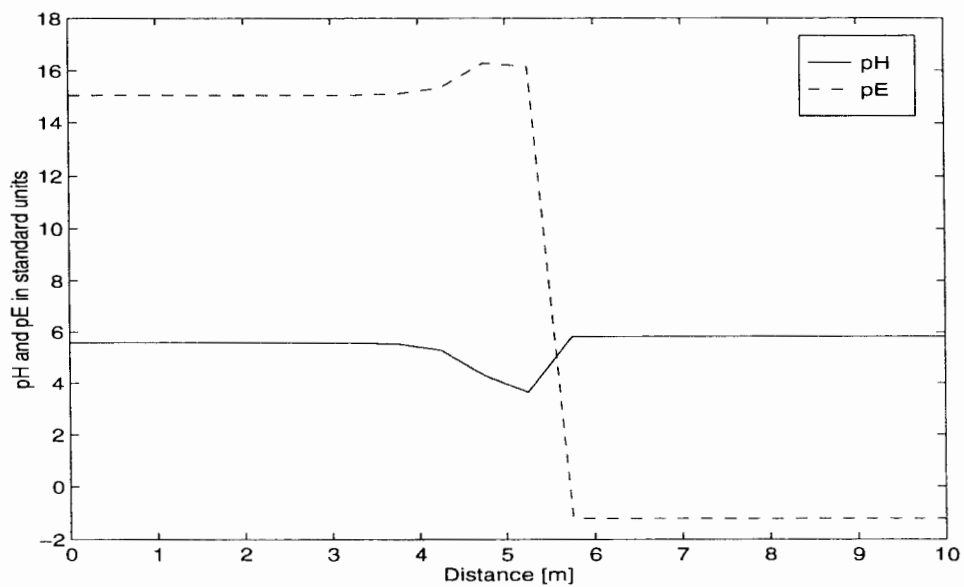


Figure 5.18 Profiles of pH and pE after 10 years for the Engesgaard and Kipp redox problem.

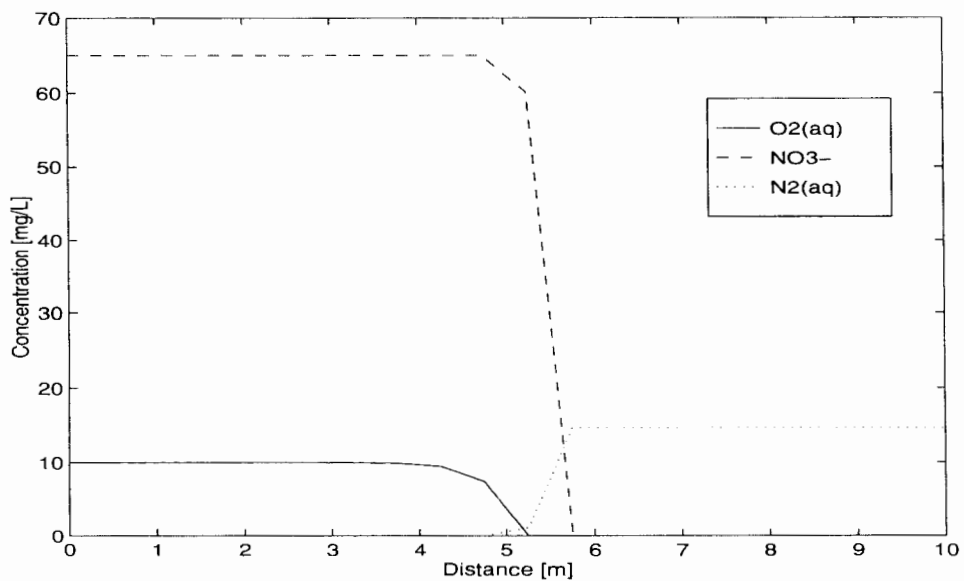


Figure 5.19 Concentration profiles of NO_3^- , N_2 and $\text{O}_2(\text{aq})$ after 10 years for the Engesgaard and Kipp redox problem.

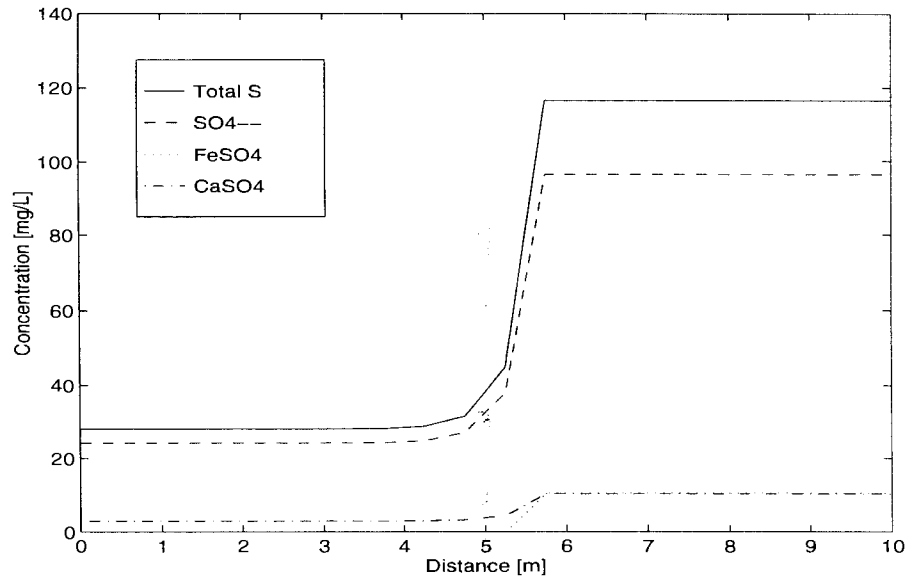


Figure 5.20 The distribution of total aqueous sulfate component and some major sulfate species after 10 years for the Engesgaard and Kipp redox problem.

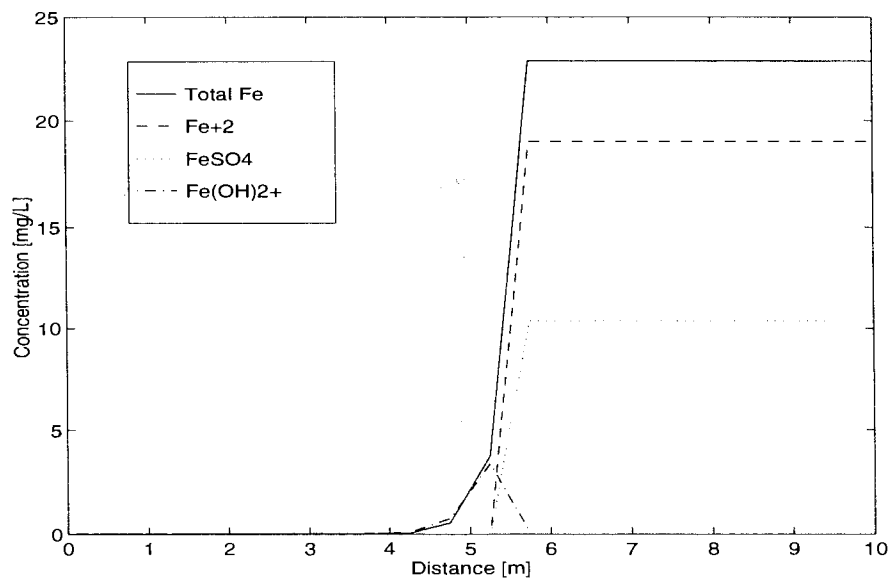


Figure 5.21 The distribution of total aqueous iron component and some major iron species after 10 years for the Engesgaard and Kipp redox problem.

5.3.2 LNE and PLNE Problems

A First-Order Reaction with Analytic Solution

We now present a convergence study for transport involving a *first-order* (kinetic) adsorption reaction, in which generic aqueous species A reacts with the solid phase,



By taking the concentration of surface site B sufficiently large as to remain effectively constant, and setting the backward rate constant k^b to zero, this can be written as the first-order reaction

$$r = k^f c_A c_B - k^b c_{AB(s)} = \hat{k}^f c_A, \quad (5.6)$$

with $\hat{k}^f \equiv k^f c_B \approx \text{constant}$. The linear reaction term allows for an analytical solution (see [46]), both in the case of advection only and when both advection and dispersion are taken into account. To verify the expected first-order in time accuracy of our algorithm for this special case, we include dispersion in this simulation. The relevant parameters were $u = 1.0$, $D = 1.0\text{e-}3$ and $k^f = 1.0$. Simulations were carried out for seven different time-step sizes up to a final time of $t = 0.5$ PVI. The spatial discretization was successively refined to maintain a constant CFL number of 0.5.

The analytic solution, along with three numerical solutions corresponding to various refinement levels, are shown in Figure 5.22. A fairly good agreement is obtained for all these discretizations, and the computed solutions clearly converge to the analytic one. The grid data and the corresponding estimated L_2 errors in the simulated results are given in Table 5.15. Linear regression applied to the tabulated data shows that the convergence rate is Δt^m with $m \approx 1.003$, a result very close to the predicted value of 1.

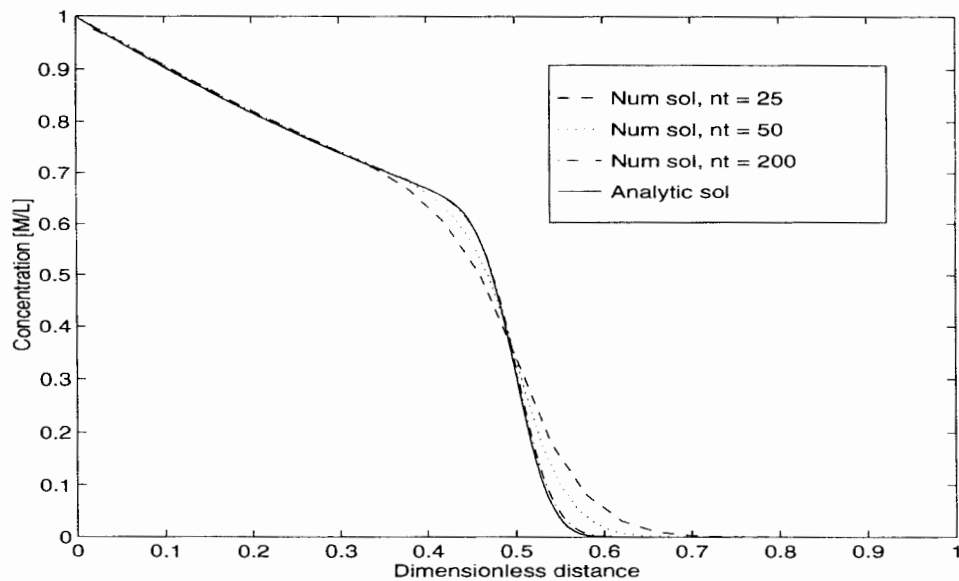


Figure 5.22 Convergence study for the kinetic first-order reaction problem. Comparison with the analytic solution for three successively finer temporal/spatial discretizations, maintaining a fixed CFL number.

time-step Δt	mesh-size Δx	L_2 error
0.05	0.1	0.0759
0.02	0.04	0.0341
0.01	0.02	0.0184
0.0067	0.0133	0.0118
0.005	0.01	0.0084
0.0033	0.0067	0.0052
0.0025	0.005	0.0038

Table 5.15 Convergence study for the kinetic first-order reaction problem.

PLNE Problem with One Kinetic and Two Equilibrium Minerals

To validate our algorithms for PLNE systems we consider a case of mineral precipitation/dissolution with two equilibrium controlled processes and one kinetically forming species. This case was studied by Sevougian [36], and represents a simple modification of the LE case presented earlier. Specifically, we retain the initial and boundary conditions given in Table 5.5 and the stoichiometric and thermodynamic data in Table 5.3, with the sole exception that the dissolution of AB(s) is now controlled by a kinetic process. Following [36], we replace its equilibrium constant with the forward and backward rates $k^f = 7.4$ and $k^b = 7.4$, respectively (note that the corresponding equilibrium constant for a reaction that goes to completion remains $k = 1.0$).

Consider first the profiles of aqueous and solid species plotted at $t = 0.5$ PVI in Figures 5.23–5.24, respectively. Comparing with the corresponding plots for the LE case, Figures 5.6 and 5.7, we notice a marked difference in the solutions due to kinetic effects. In particular, the AB(s) dissolution and AC(s), DB(s) precipitation fronts are no longer shocks. However, as would be expected, the AC(s) and DB(s) dissolution fronts are still shocks. Mineral concentrations at the times $t = 0.25$, $t = 0.5$, $t = 0.75$ and $t = 1.0$ PVI, plotted in Figures 5.25–5.27, illustrate more clearly the behavior of these fronts. Excellent agreement was obtained with the results reported in [36].

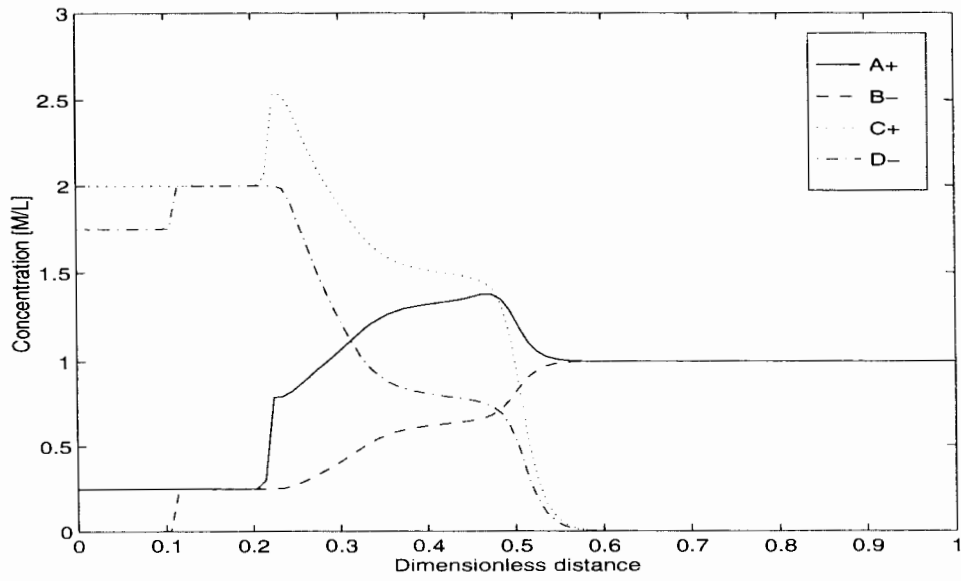


Figure 5.23 ABCD problem with one kinetically dissolving mineral $AB(s)$. Concentration profiles of all aqueous species at $t = 0.5$ PVI.

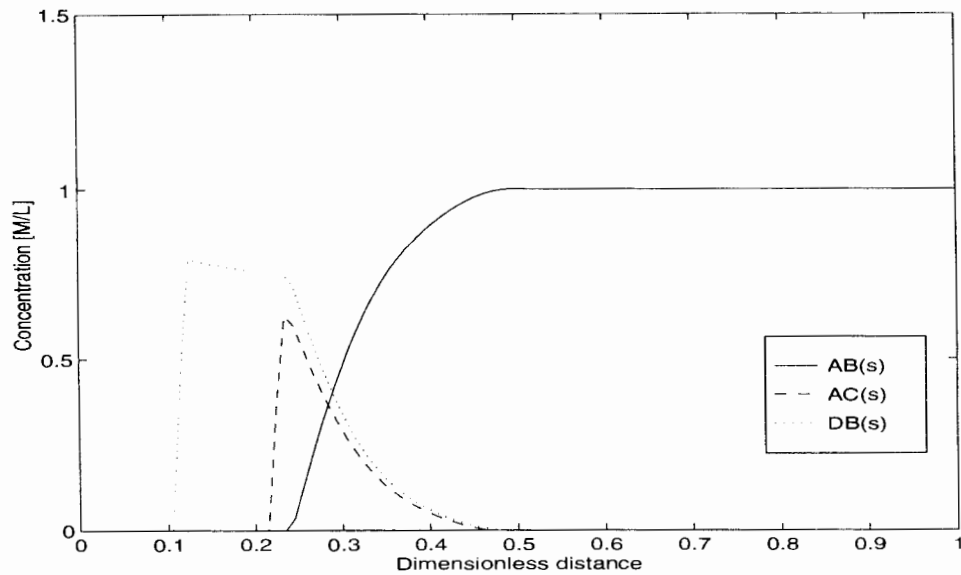


Figure 5.24 ABCD problem with one kinetically dissolving mineral $AB(s)$. Concentration profiles of mineral species at $t = 0.5$ PVI.

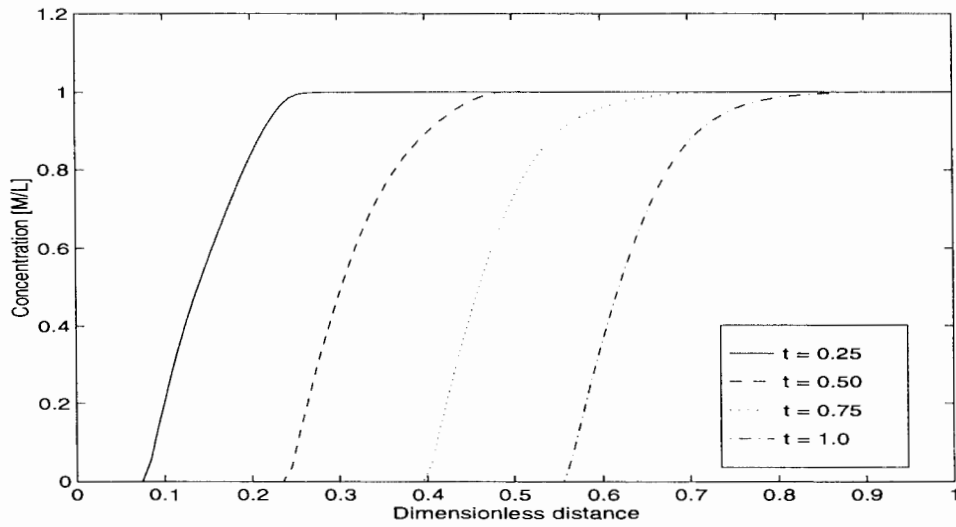


Figure 5.25 ABCD problem with one kinetically dissolving mineral AB(s). Concentration profiles of mineral species AB(s) at four times.

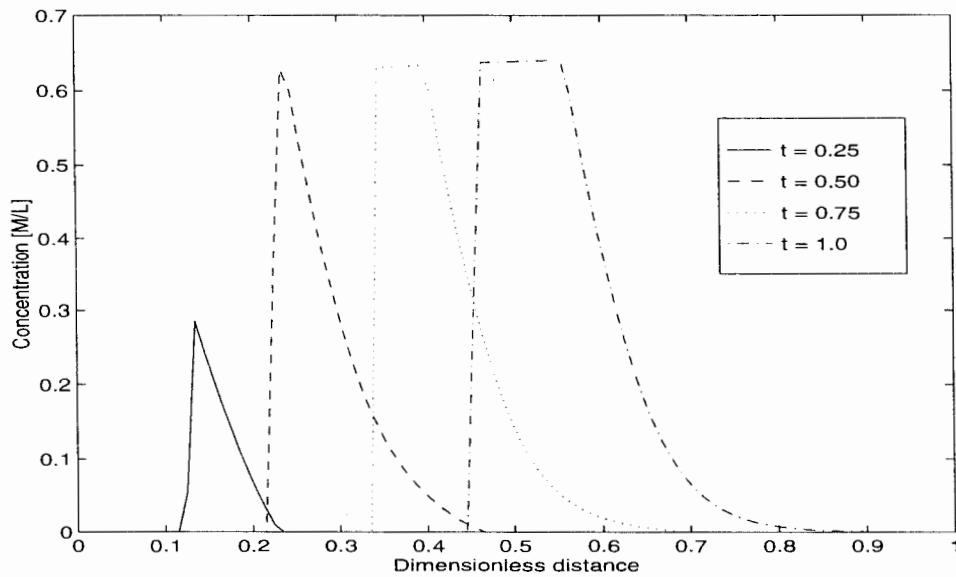


Figure 5.26 ABCD problem with one kinetically dissolving mineral AB(s). Concentration profiles of mineral species AC(s) at four times.

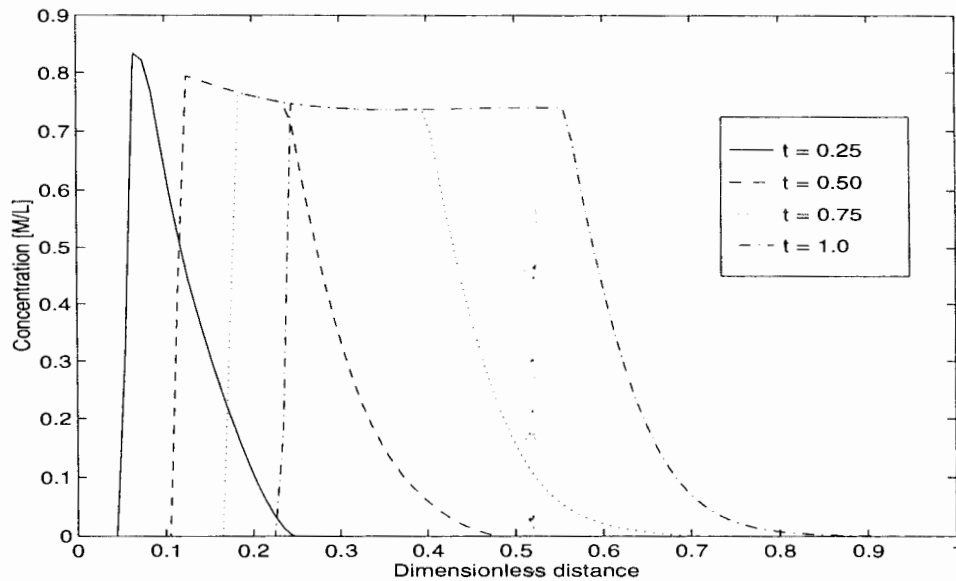


Figure 5.27 ABCD problem with one kinetically dissolving mineral AB(s). Concentration profiles of mineral species DB(s) at four times.

5.4 Higher Dimensional Examples

5.4.1 A 2D Study of the ABCD LE Problem

To illustrate the multi-dimensional capabilities of the code, we revisit the ABCD equilibrium problem defined in Table 5.3, this time considering a two-dimensional, square domain with one injection well located in the lower left corner. The domain is discretized into a 40×40 grid, resulting in a total of 1600 grid-blocks. To generate some interesting flow patterns, we prescribe no-flow conditions on three faces and an outflow condition on the fourth (right) face. The initial concentrations are illustrated in Figure 5.28 below. The domain is everywhere saturated with respect to AB(s), but the mineral itself is actually only present in a rectangular region in the interior of the domain. The concentration of the species C, D, AC(s) and DB(s) are everywhere zero initially. At the injection well we supply the aqueous species

C and D at concentrations 2.0 M and 1.75 M, respectively. No A or B is injected. In addition to the species list from Section 5.3.1, we have added a non-reactive tracer, initially at zero concentration and injected at 1.0 M. The thermodynamic data is otherwise the same as in Table 5.3.

The simulation was carried out to a time corresponding to 1 PVI using $n_t = 400$ time-steps. It was run on the Intel Paragon using 8 processors, and completed in approximately 30 minutes.

To better understand the flow field before considering reactions, we first turn our attention to Figures 5.29 and 5.30. Note that most of the region has been swept by the injected fluid at $t = 1$ PVI.

Similarly to the 1D experiment illustrated in Figure 5.6–Figure 5.7, we expect to see the dissolution of AB(s) as it is reached by the A and B depleted injected stream. Since the injected composition is rich in C and D, we also expect precipitation of AC(s) and DB(s) to occur near the dissolution front for AB(s).

It is evident from the Figures 5.31 and 5.32 that significant dissolution of AB(s) has indeed occurred. Also, the Figures 5.33–5.34 and 5.35–5.36 verify the suspected precipitation of minerals AC(s) and DB(s). As expected (and indeed predicted by theory for the Riemann problem), the wave associated with DB(s) is significantly more retarded than the AC(s) wave.

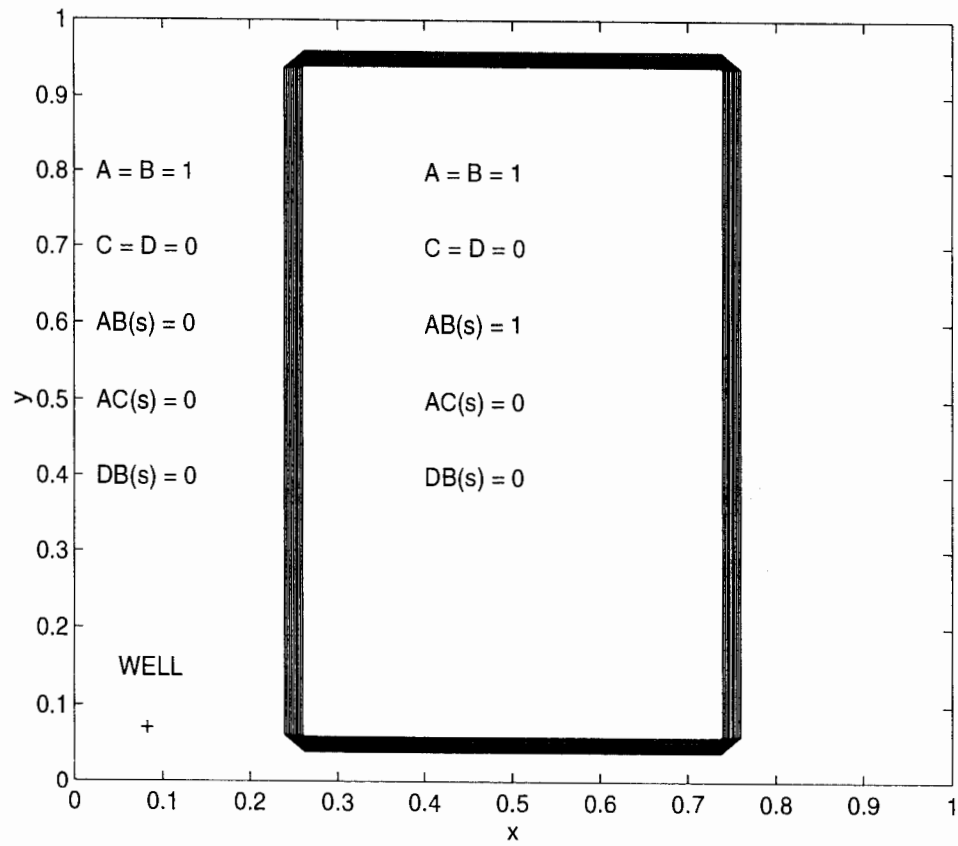


Figure 5.28 2D ABCD equilibrium precipitation/dissolution problem. The initial conditions for simulation.

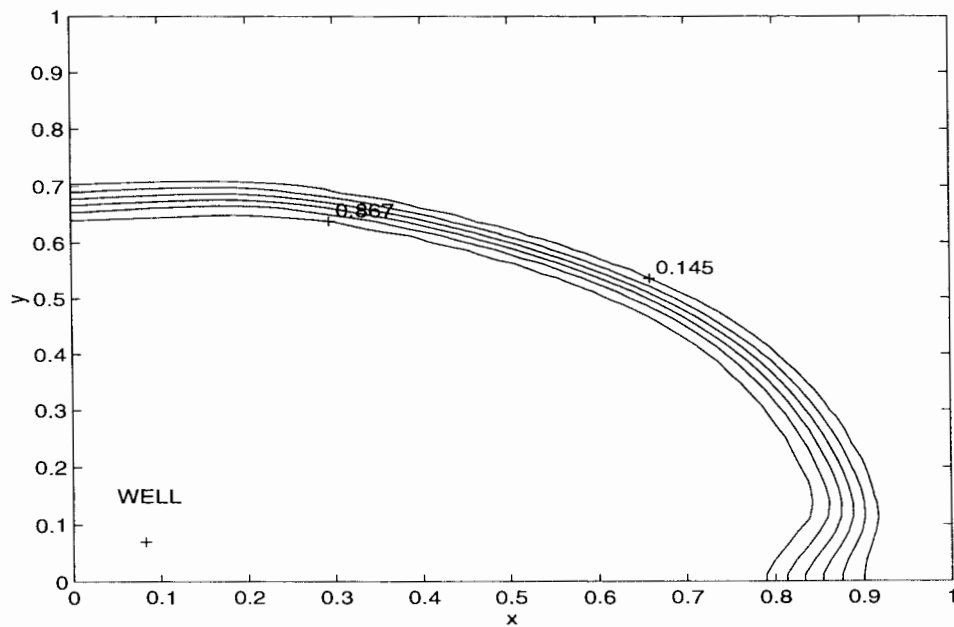


Figure 5.29 2D ABCD equilibrium precipitation/dissolution problem.
Concentration contours for the inert tracer at $t = 0.5$ PVI.

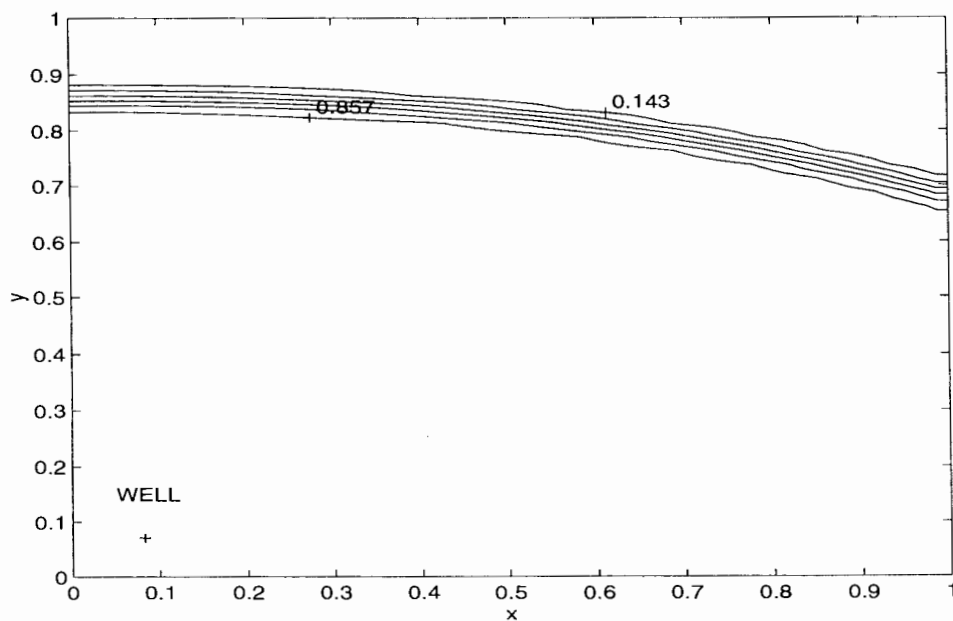


Figure 5.30 2D ABCD equilibrium precipitation/dissolution problem.
Concentration contours for the inert tracer at $t = 1.0$ PVI.

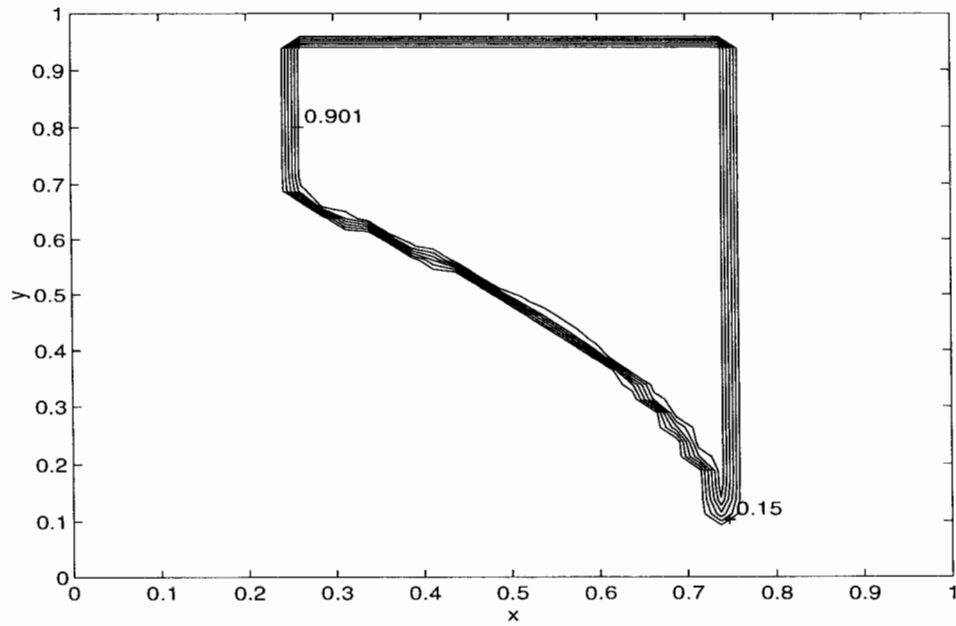


Figure 5.31 2D ABCD equilibrium precipitation/dissolution problem. Concentration contours for mineral AB(s) at $t = 0.5$ PVI.

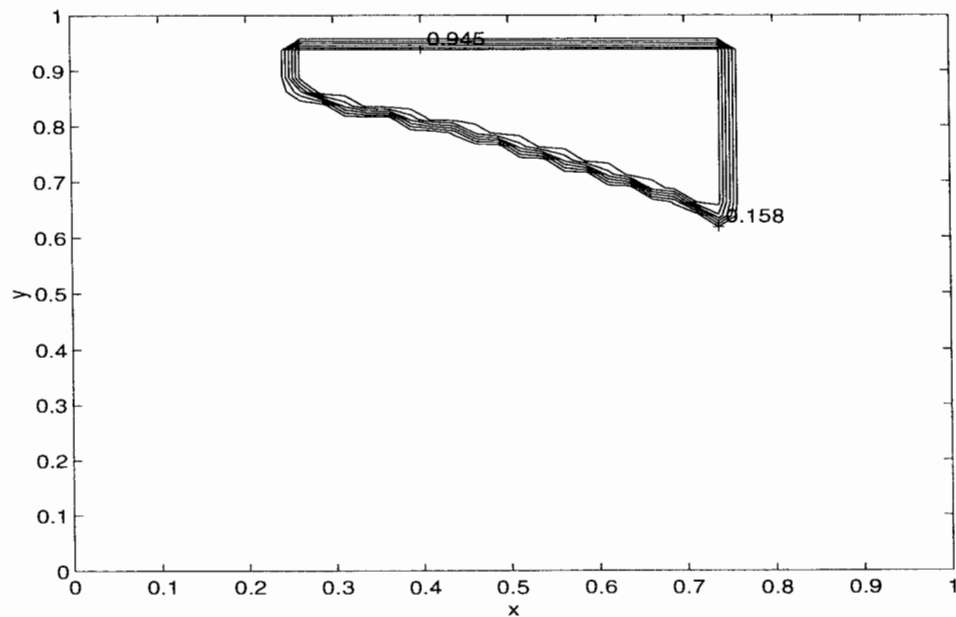


Figure 5.32 2D ABCD equilibrium precipitation/dissolution problem. Concentration contours for mineral AB(s) at $t = 1.0$ PVI.

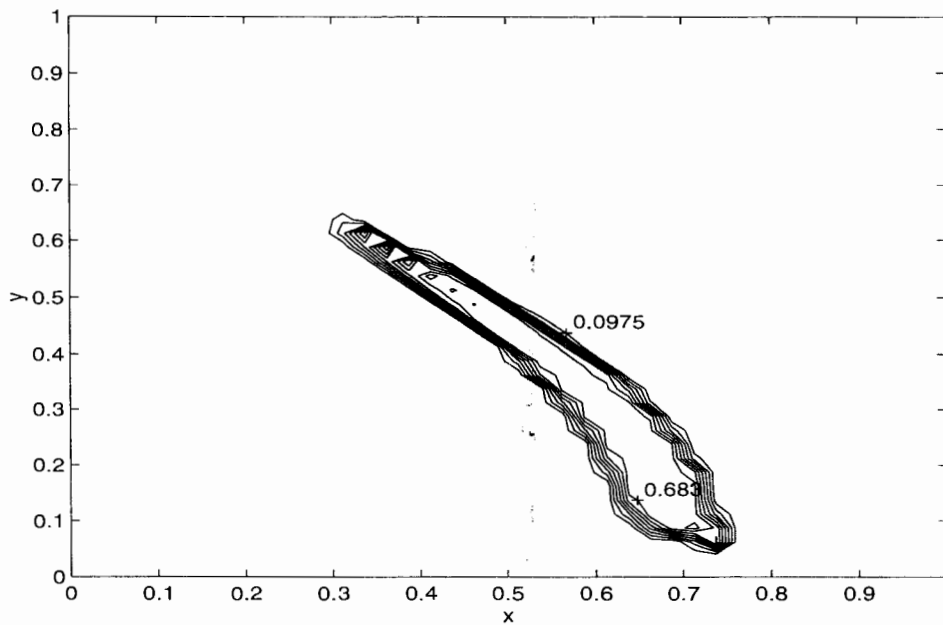


Figure 5.33 2D ABCD equilibrium precipitation/dissolution problem. Concentration contours for mineral AC(s) at $t = 0.5$ PVI.

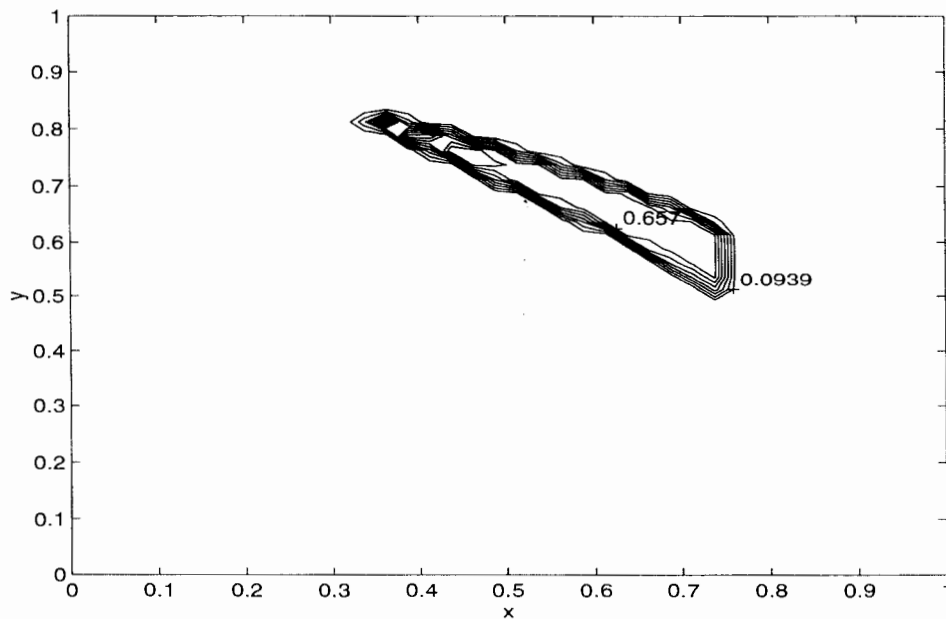


Figure 5.34 2D ABCD equilibrium precipitation/dissolution problem. Concentration contours for mineral AC(s) at $t = 1.0$ PVI.

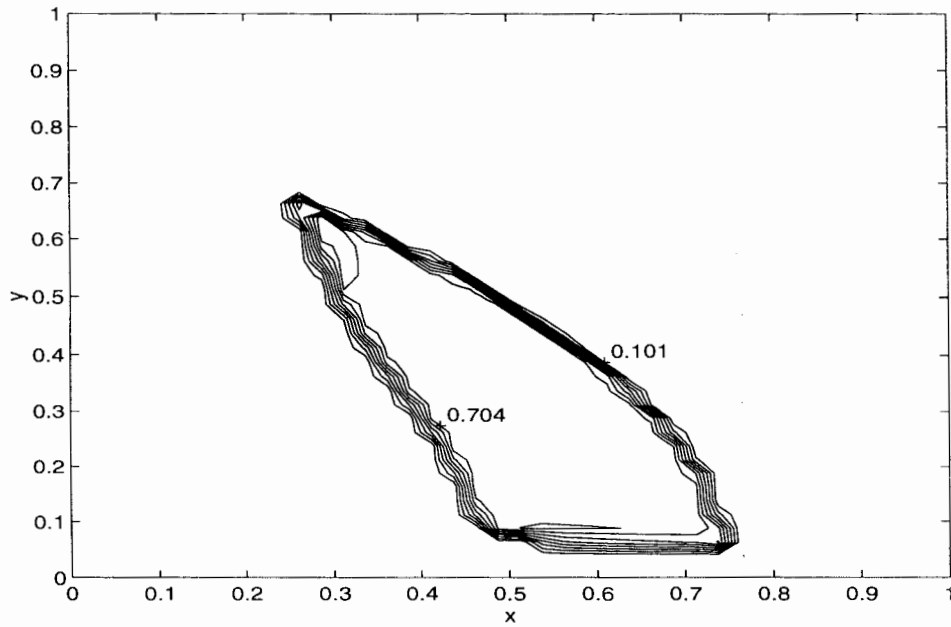


Figure 5.35 2D ABCD equilibrium precipitation/dissolution problem.
Concentration contours for mineral DB(s) at $t = 0.5$ PVI.

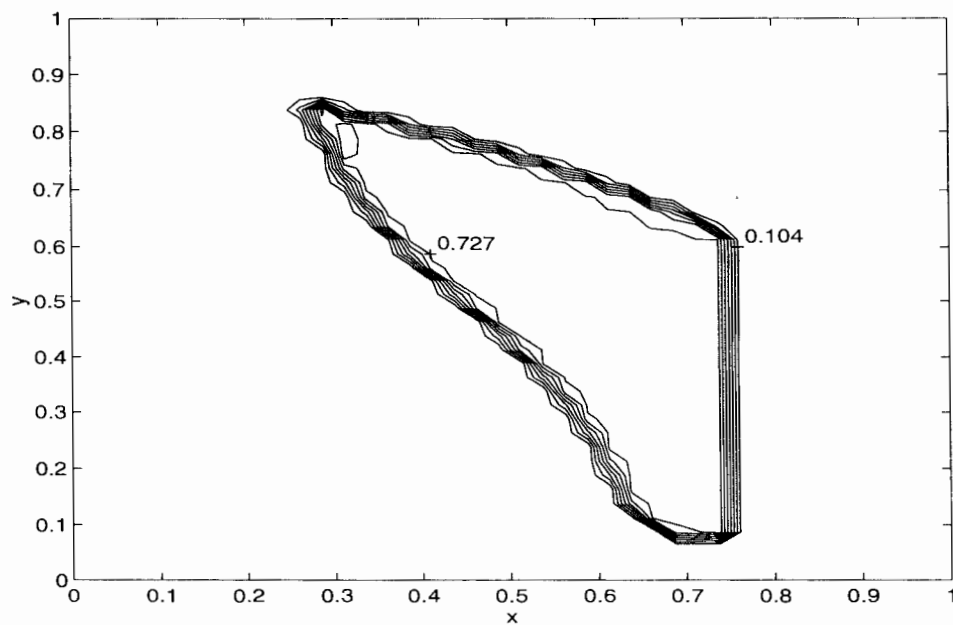


Figure 5.36 2D ABCD equilibrium precipitation/dissolution problem.
Concentration contours for mineral DB(s) at $t = 1.0$ PVI.

5.4.2 A Parallel Speedup Study for the 3D ABCD Problem

We consider once more the mineral precipitation/dissolution problem defined in Table 5.3, this time with the intention of assessing the parallel efficiency of our algorithms. To generate a synthetic problem of realistic size, we extend the problem presented in Section 5.4.1 to three spatial dimensions. Initial and boundary conditions are exactly analogous to those described in Section 5.4.1. The injection well remains in the same position in the horizontal plane and is screened in the lower part of its vertical extent. As before, the only non-uniform initial condition is the mineral AB(s), which is saturated at concentration 1 in a parallelepiped in the interior of the domain. To investigate the computational cost and the parallel scale-up of the classes PLNE and LNE, we considered some variations of the LE problem defined in Table 5.3. Specifically, a PLNE scenario was realized by requiring that the precipitation/dissolution of AB(s) be kinetic, with rate-constants $k_{AB}^f = 7.4$, $k_{AB}^b = 7.4$, i.e. the problem considered in 1D in Section 5.3.2. The LNE system was obtained by taking all reactions to be of kinetic type (with an unchanged equilibrium state). In addition to the rate constants for AB(s) above, we used $k_{AC}^f = 3.0$, $k_{AC}^b = 6.0$ and $k_{DB}^f = 10.0$, $k_{DB}^b = 5.0$.

To establish a reasonable problem size for the scale-up comparison, we performed simulations of the LE problem defined above with the preliminary grids $10 \times 10 \times 10$ and $20 \times 20 \times 20$, taking $n_t = 50$ time-steps, corresponding to a final time of $t = 0.125$ PVI. The simulations were repeated using 2, 4, 8 and 16 processors on the Intel Paragon, and timings were obtained. The resulting speed-ups, normalized to 2 processors, are shown in Figure 5.37. It is evident that the $10 \times 10 \times 10$ problem is too small to result in a satisfying speed-up for this problem; the $20 \times 20 \times 20$ performs significantly better, but a decline in speed-up is seen in increasing from 8 to 16 processors.

An acceptable compromise between the wall-clock time needed to perform the experiments and the quality of the comparison was deemed to be a grid of size $20 \times 20 \times 25$, or 10000 grid-blocks.

For the PLNE and the LNE cases, the second-order Runge-Kutta integrator was used with a target time-step equal to the transport-step. The RNSF equilibrium module was used in all cases. It is readily seen from Table 5.16 that the PLNE problem is significantly more costly than the LE and LNE cases, which complete in approximately the same time. Furthermore, a simulation of a non-reactive system with the same number of transported components indicates that the percentage of time devoted to the chemistry calculation ranged from as little a few percent for the LE and LNE problems, to as much as 40% for the PLNE case.

The speed-up curves are given in Figure 5.38, along with the ideal curve for comparison. Very similar speed-ups are obtained for the three problem classes. Although the results are quite good, the trend is closer to the ideal curve for 4 and 8 processors, indicating that the problem is still too small to realize the full potential of the parallelism.

Number of processors	Time [s]		
	LE	PLNE	LNE
16 ($4 \times 4 \times 1$)	2869	4860	2708
8 ($4 \times 2 \times 1$)	5522	9357	5260
4 ($4 \times 1 \times 1$)	10445	17603	9978
2 ($2 \times 1 \times 1$)	20503	34728	19745

Table 5.16 Timing results for 3D ABCD problems of class LE, PLNE and LNE, using a $20 \times 20 \times 25$ grid and $n_t = 50$ time-steps.

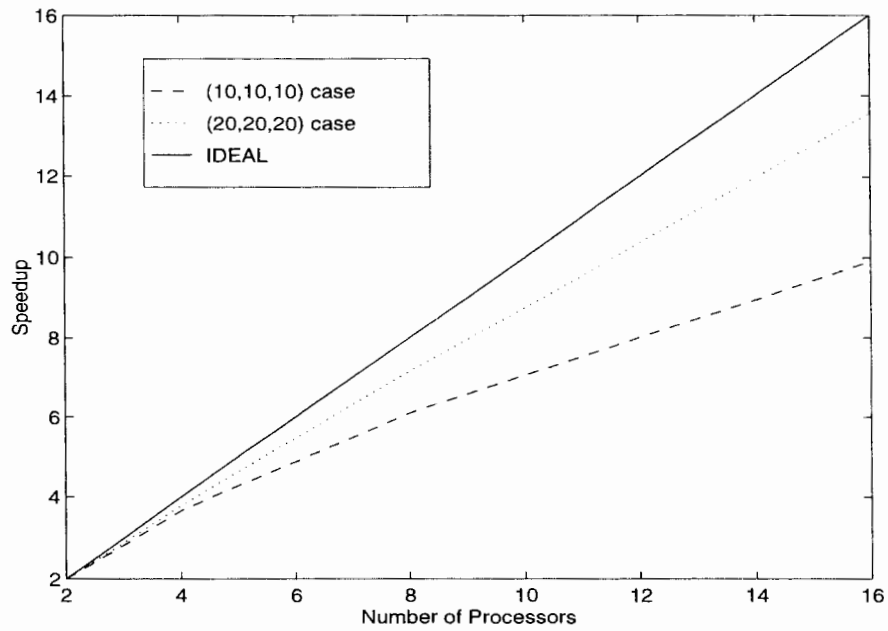


Figure 5.37 Parallel speed-up for the 3D ABCD LE problem, using grids $10 \times 10 \times 10$ and $20 \times 20 \times 20$, respectively.

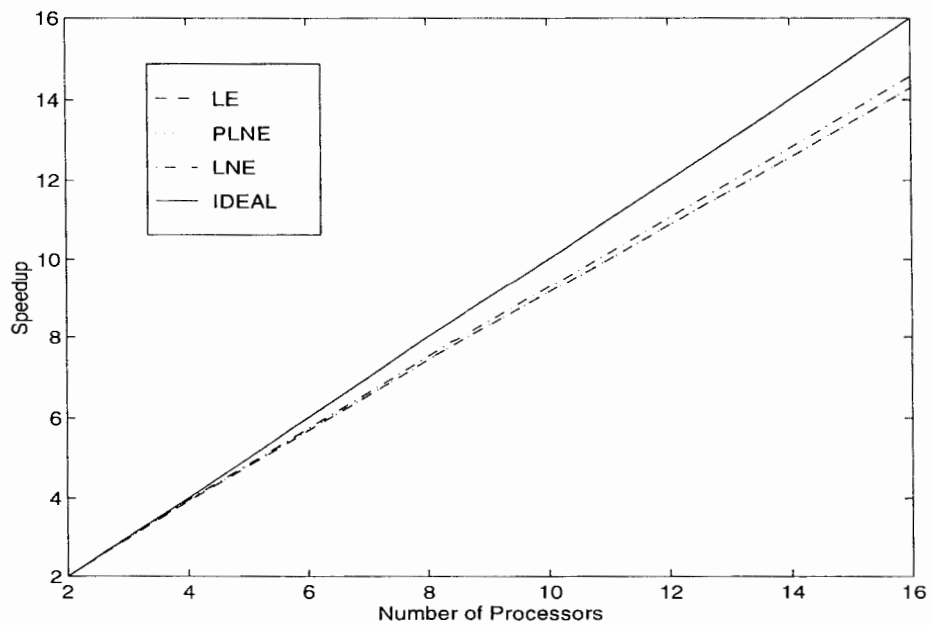


Figure 5.38 Parallel speed-up for 3D ABCD problems of class LE, PLNE and LNE using a $20 \times 20 \times 25$ grid.

Chapter 6

Conclusions

The results obtained in the previous chapters lend themselves to the following conclusions.

1. A general framework for reactive transport of a single flowing aqueous phase in a porous medium has been presented. The interactions possible within this model include:
 - Both *homogeneous* and *heterogeneous* reactions; in particular, aqueous complexation, redox, ion-exchange, adsorption and precipitation/dissolution reactions are included.
 - *Kinetic* and *equilibrium* reactions can both be accommodated.
2. A geochemistry module for the solution of the chemical batch problem was developed. Some of its features are:
 - The equilibrium calculation is based on a novel application of the interior-point method for nonlinear programming. Two different options are implemented, based on the *stoichiometric* and the *non-stoichiometric* formulations of the equilibrium problem. For most problems, the non-stoichiometric formulation will be most efficient. However, the stoichiometric version has the advantage of exact mass-balance, and generalizes to the non-ideal case.

- Systems of kinetic reactions are handled in a *mass-conservative* time-integration framework, using explicit ODE integrators over the transport time-step.
3. The geochemistry module was incorporated into the reactive transport simulator PARSim1 [2]. Features of the overall computer program include:
- The parallel, reactive transport implementation is based on an *operator-splitting* procedure (OS) applied to the species ADR, and consists of taking sequential *advection*, *reaction* and *diffusion* steps.
 - The OS approach was demonstrated to be formally first order in time accurate for the classes LE and LNE.
4. A number of 1D reactive transport problems found in the literature were solved and compared with published results or analytic solutions. In particular, we have successfully simulated the following types of problems:
- Aqueous complexation;
 - Surface adsorption;
 - Ion-exchange;
 - Redox;
 - Precipitation/dissolution.

The code has been tested on all three classes of reactive transport problems, i.e., local equilibrium (LE), local non-equilibrium (LNE) and partial local non-equilibrium (PLNE).

5. A 2D problem was solved to demonstrate the multi-dimensional capability of the code. A parallel speed-up study of a 3D problem with 10000 grid-blocks and eight concentration fields was conducted with close to linear speed-up.

Some directions for future work in this area are:

1. More efficient and/or accurate formulations for the reactive transport problem. In particular, implementation based on component transport should be compared with the species transport formulation used in this work. In such a setting, higher order splittings could be implemented with relative ease.
2. The application of the interior-point minimization technique to genuine multi-phase batch calculation should be investigated. It is conjectured that the “mole-fraction” and “phase-total” formulation presented in Appendix C, and used for a relatively simple problem in [34] could serve as a starting point for the development of such algorithms. However, it is critical that the number of unknowns be reduced before this approach can become truly competitive.

Bibliography

- [1] G. M. Anderson and D. A. Crerar. *Thermodynamics in Geochemistry*. Oxford University Press, 1993.
- [2] T. Arbogast. User's guide to rparsim1: The rice parallel aquifer and reservoir simulator, single phase. August 1994.
- [3] T. Arbogast, A. K. Chilakapati, and M. F. Wheeler. A characteristics-mixed method for contaminant transport and miscible displacement. In Russell, Ewing, Brebbia, Gray, and Pinder, editors, *Computational Methods in Water Resources IX, vol. 1: Numerical Methods in Water Resource*, pages 77–84, Southampton, U.K., 1994. Computational Mechanics Publications.
- [4] J. Bear. *Dynamics of Fluids in Porous Media*. Dover Publications, Inc., 1988.
- [5] R. B. Bird, W. E. Stewart, and E. N. Lightfoot. *Transport Phenomena*. John Wiley and Sons, 1960.
- [6] F. Brezzi and M. Fortin. *Mixed and Hybrid Finite Element Methods*. Springer Verlag, Berlin, 1991.
- [7] S. L. Bryant, R.S. Schechter, and L. W. Lake. Mineral sequences in precipitation/dissolution waves. *AIChE Journal*, 33(8):1271–1287, August 1987.
- [8] Jaime Castillo and Ignacio E. Grossman. Computation of phase and chemical equilibria. *Computers and Chemical Engineering*, 5:99–108, 1981.

- [9] C. Y. Chiang, C. N. Dawson, and M. F. Wheeler. Modeling of in-situ bioremediation of organic compounds in groundwater. *Transport in Porous Media*, 6:667–702, 1991.
- [10] C. N. Dawson. Time-split methods for advective flow problems in multidimensions based on combining godunov-type procedures with a mixed finite-element method. Technical Report TR91-29, Rice University, September 1991.
- [11] C. N. Dawson and M. F. Wheeler. Time-splitting methods for advection-diffusion-reaction equations arising in contaminant transport. In R. O. O'Malley, editor, *Proceedings, ICIAM '91*, pages 71–82, Philadelphia, 1992. Society for Industrial and Applied Mathematics.
- [12] C. N. Dawson, M. F. Wheeler, and W. A. Kinton. Time-splitting methods for advection-dominated parabolic problems in one space variable. *Communications in Applied Numerical Methods*, 4:413–423, 1988.
- [13] K. G. Denbigh. *The Principles of Chemical Equilibrium*. Cambridge University Press, 2 edition, 1966.
- [14] J.E. Dennis and R. B. Schnabel. *Numerical Methods for Unconstrained Optimization and Nonlinear Equations*. Prentice-Hall, 1983.
- [15] A. S. El-Bakry, R. A. Tapia, T. Tsuchiya, and Y. Zhang. On the formulation and theory of the newton interior-point method for nonlinear programming. *Journal of Optimization Theory and Applications*, 89(3):507–541, June 1996.
- [16] Peter Engesgaard and Kenneth L. Kipp. A geochemical transport model for redox-controlled movement of mineral fronts in groundwater flow systems: A

- case of nitrate removal by oxidation of pyrite. *Water Resources Research*, 28(10):2829–2843, October 1992.
- [17] P. Fletcher. *Chemical thermodynamics*. Longman Scientific and Technical, 1993.
- [18] R. Fletcher. *Practical Optimization*. John Wiley and Sons, 1987.
- [19] Anup K. Gupta, P. Raj Bishnoi, and Nicolas Kalogerakis. A method for the simultaneous phase equilibria and stability calculations for multiphase reacting and non-reacting systems. *Fluid Phase Equilibria*, 63(8):65–89, 1991.
- [20] Bertil Gustafsson, Anders Sjöberg, and Leif Abrahamsson. *Numerisk Lösning av Differentialekvationer*. Uppsala University, 1988.
- [21] Charles E. Harvie, Jerry P. Greenberg, and John H. Weare. A chemical equilibrium algorithm for highly non-ideal multiphase systems: Free energy minimization. *Geochimica et Cosmochimica Acta*, 51:1045–1057, 1987.
- [22] W. Hock and K. Schittkowski. *Test Examples for Nonlinear Programming Codes*. Springer Verlag, New York, 1981.
- [23] William Karush. Minima of functions of several variables with inequalities as side conditions. Master's thesis, University of Chicago, 1939.
- [24] J. D. Lambert. *Numerical Methods for Ordinary Differential Systems*. John Wiley and Sons, 1991.
- [25] Randall LeVeque and J. Olinger. Numerical methods based on additive splittings for hyperbolic partial differential equations. *Mathematics of Computation*, 40(162):469–497, 1983.

- [26] Randall J. LeVeque. *Numerical Methods for Conservation Laws*. Birkhauser, 1992.
- [27] Garth P. McCormick. Optimality criteria in nonlinear programming. In *Non-linear programming*, volume 9. SIAM-AMS, 1976.
- [28] Francois M. Morel and Janet G. Hering. *Principles and Applications of Aquatic Chemistry*. John Wiley and Sons, 1993.
- [29] D. W. Peaceman. *Fundamentals of Numerical Reservoir Simulation*. Elsevier Scientific Publishing Company, New York, 1977.
- [30] Jacob Rubin. Transport of reacting solutes in porous media: Relation between mathematical nature of problem formulation and chemical nature of reactions. *Water Resources Research*, 19(5):1231–1252, October 1983.
- [31] Jacob Rubin and R. V. James. Dispersion-affected transport of reacting solutes in saturated porous media: Galerkin method applied to equilibrium-controlled exchange in unidirectional steady water flow. *Water Resources Research*, 9(5):1332–1356, October 1973.
- [32] Walter Rudin. *Principles of Mathematical Analysis*. McGraw-Hill, 1976.
- [33] F. Saaf. A user's manual for nipsf: Nonlinear interior-point solver, fortran. Technical Report TR96-24, Rice University, 1996.
- [34] F. Saaf, R. A. Tapia, S. L. Bryant, and M. F. Wheeler. Computing general chemical equilibria with an interior-point method. In A. A. Aldama, J. Aparicio, C. A. Brebbia, W.G. Gray, I. Herrera, and G. F. Pinder, editors, *Computational Methods in Water Resources XI: Computational Methods in*

- Subsurface Flow and Transport Problems*, volume 1. Computational Mechanics Publications, 1996.
- [35] Daniel R. Schneider and G. V. Reklaitis. On material balances for chemically reactive systems. *Chemical Engineering Science*, 30:243–247, 1975.
- [36] S. D. Sevougian. *Partial local equilibrium and the propagation of mineral alteration zones*. PhD thesis, The University of Texas at Austin, December 1992.
- [37] N. Z. Shapiro and L. S. Shapley. Mass action laws and the gibbs free energy function. *SIAM Journal of Applied Mathematics*, 13(2):353–375, June 1965.
- [38] J. C. Slattery. *Momentum, Energy and Mass Transfer in Continua*. Robert E. Kriegler Publishing Company, Inc., 1981.
- [39] Jeffrey V. Smith, Ronald W. Missen, and William R. Smith. General optimality criteria for multiphase multireaction chemical equilibrium. *AIChE Journal*, 39(4):707–710, April 1993.
- [40] William R. Smith. Computational aspects of chemical equilibrium in complex systems. In Henry Eyring and Douglas Henderson, editors, *Theoretical Chemistry: Advances and Perspectives*, volume 5, pages 186–259. Academic Press, 1980.
- [41] William R. Smith and Ronald W. Missen. *Chemical Reaction Equilibrium Analysis*. John Wiley and Sons, 1982.
- [42] G. W. Stewart. *Introduction to Matrix Computations*. Academic Press Inc., 1973.

- [43] Gilbert Strang. *Introduction to Linear Algebra*. Welleslet-Cambridge Press, 1993.
- [44] W. Stumm and J. J. Morgan. *Aquatic Chemistry*. John Wiley and Sons, 1981.
- [45] Albert J. Valocchi and Michael Malmstead. Accuracy of operator splitting for advection-dispersion-reaction problems. *Water Resources Research*, 28(5):1471–1476, May 1992.
- [46] M. Th. van Genuchten. Analytical solutions for chemical transport with simultaneous adsorption, zero-order production and first-order decay. *Journal of Hydrology*, 49:213–233, 1981.
- [47] M. P. Walsh, S.L. Bryant, R. S. Schechter, and L. W. Lake. Precipitation and dissolution of solids attending flow through porous media. *AIChE Journal*, 30(2):317–328, March 1984.
- [48] M. F. Wheeler and T. Arbogast. A characteristics-mixed finite element method for advection dominated transport problems. Technical Report TR92-37, Rice University, November 1992.
- [49] G. T. Yeh, Gregg A. Iskra, John M. Zachara, and Jim E. Szecsody. Development and verification of kemod: A mixed chemical kinetic and equilibrium model.
- [50] G. T. Yeh and V. S. Tripathi. A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components. *Water Resources Research*, 25(1):93–108, January 1989.

- [51] G. T. Yeh and V. S. Tripathi. A model for simulating transport of reactive multispecies components: Model development and demonstration. *Water Resources Research*, 27(12):3075–3094, December 1991.
- [52] Willard I. Zangwill. *Nonlinear Programming: A Unified Approach*. Prentice-Hall, 1969.

List of Symbols

Most major symbols used in the thesis are explained below. Where appropriate, a reference to either the defining equation or the relevant section is given.

Latin letters

A	formula matrix, $A = (a_1, \dots, a_{N_S}) \in \mathbb{R}^{N_E \times N_S}$; Definition 2.5.
a_i	formula vector of species i , $a_i \in \mathbb{R}^{N_E}$; Definition 2.4.
\hat{A}	principal part of canonical form of A . $\hat{A} \in \mathbb{R}^{N_C \times N_R}$; Equation (2.51).
\mathcal{A}	$= -V^T \mu$. Reaction affinities, $\mathcal{A} \in \mathbb{R}^{N_R}$; Section 2.3.5.
c	species concentrations, $c \in \mathbb{R}^{N_S}$; Equation (3.3).
c_ϵ	lower bound on species concentration used in practice; Equation (4.64).
C	total flowing component concentrations, $C \in \mathbb{R}^{N_C}$; Equation (3.27).
d	number of spatial dimensions.
e	element (component) abundance, $e \in \mathbb{R}^{N_E}$; Section 2.2.1.
\hat{e}	element symbol vector, $\hat{e} \in \mathbb{R}^{N_E}$; Section 2.2.1.
\mathcal{E}	symbolic representation of the equilibrium step; Section 4.2.2.
f_i	species flux vector, $f_i = (f_{i,x}, f_{i,y}, f_{i,z}) \in \mathbb{R}^d$; Sections 3.2 and 3.3.3.
g	gravitational vector, $g \in \mathbb{R}^d$; Section 3.3.1.
G	Gibbs free energy function; Section 2.3.2.
I^α	index set for phase α ; Appendix C.
I_M	index set for minerals; page 81.
K_i	equilibrium constant for the i th reaction; Equation (B.10).
k_i^b	backward rate-constant for the i th kinetic reaction; Section 2.4.3.
k_i^f	forward rate-constant for the i th kinetic reaction; Section 2.4.3.

l	Lagrangian function; Appendix A (for general NLP).
m^E	element mole mass vector, $m^E \in \mathbb{R}^{N_E}$; page 14.
m	$= A^T m^E$. Species mole mass vector, $m \in \mathbb{R}^{N_S}$; page 14.
m^{tot}	$= n^T m$. Total system mass; page 14.
M	pseudo formula matrix, $M \in \mathbb{R}^{(N_C + N_R^K) \times N_S}$; Equation (3.42).
N_C	$= \text{rank}(A)$. The number of components; page 22.
N_E	the number of elements; page 10.
N_M	the maximum number of minerals; page 81.
N_R	$= N_S - N_C$. The number of independent reactions; page 22.
N_R^K	number of independent kinetic reactions; page 39.
N_R^Q	number of independent equilibrium reactions; page 39.
N_S	total number of species; page 10.
n	species mole vector, $n \in \mathbb{R}^{N_S}$; Section 2.2.2.
\hat{n}	species symbol vector, $\hat{n} \in \mathbb{R}^{N_S}$; page 10.
\tilde{n}^α	$= 1^T P^\alpha n$. Total number of moles in phase α .
n^0	particular solution of the EAC; Equations (2.42)–(2.43).
n^c	component-species mole vector, $n^c \in \mathbb{R}^{N_C}$; Equation (2.52).
n^p	product-species mole vector, $n^p \in \mathbb{R}^{N_R}$; Equation (2.52).
n^K	kinetic product-species mole vector, $n^K \in \mathbb{R}^{N_R^K}$; page 49.
n^Q	equilibrium product-species mole vector, $n^Q \in \mathbb{R}^{N_R^Q}$; page 49.
p	pressure; Section 2.3.1.
P^α	phase identity matrix for phase α , $P^\alpha \in \mathbb{R}^{N_S \times N_S}$; Equation (2.10).
q^α	$= z^T n^\alpha$. Total phase charge; Section 2.2.3.
q_w	source/sink term in the flow equations; Section 3.3.1.
q	$= z^T n$. Total system charge; Section 2.2.3.
Q	$= z^T c$. Total charge concentration; Section 3.7.

- Q^{aq} = $z^T P^{aq} c$. Total flowing charge concentration; Section 3.7.
 Q^0 total initial charge concentration; Section 3.7.
 Q^I total injected charge concentration; Section 3.7.
 Q^S = $z^T s$. Total external source of charge; Section 3.7.
 r generic species rate vector, $r \in \mathbb{R}^{N_S}$; Section 3.2.
 r^K kinetic reaction rates, $r^K \in \mathbb{R}^{N_R^K}$; Section 2.4.3.
 r^Q (formal) equilibrium reaction rates, $r^Q \in \mathbb{R}^{N_R^Q}$; page 61.
 R universal gas constant; Section 2.3.4.
 \mathcal{R} symbolic representation of the reaction step; Section 4.2.2.
 s species sources/sinks, $s \in \mathbb{R}^{N_S}$; Section 3.2.
 S = As . Total component sources/sinks, $S \in \mathbb{R}^{N_C}$; Equation (3.28).
 T absolute temperature; Section 2.3.1.
 T = Ac . Total component concentrations, $T \in \mathbb{R}^{N_C}$; Equation (3.26).
 u Darcy velocity of the aqueous phase, $u \in \mathbb{R}^d$; Section 3.3.1.
 V stoichiometric matrix, $V = (v_1, \dots, v_{N_R}) \in \mathbb{R}^{N_S \times N_R}$; Definition 2.8.
 v_i reaction vector for the i th reaction, $v_i \in \mathbb{R}^{N_S}$; Definition 2.7.
 V^Q equilibrium stoichiometric matrix, $V^Q \in \mathbb{R}^{N_S \times N_R^Q}$; Section 2.4.2.
 \hat{V}^Q principal equilibrium stoichiometric matrix, $\hat{V}^Q \in \mathbb{R}^{N_C \times N_R^Q}$; Section 2.4.2.
 V^K kinetic stoichiometric matrix, $V^K \in \mathbb{R}^{N_S \times N_R^K}$; Section 2.4.2.
 \hat{V}^K principal kinetic stoichiometric matrix, $\hat{V}^K \in \mathbb{R}^{N_C \times N_R^K}$; Section 2.4.2.
 x species mole fraction vector, $x \in \mathbb{R}^{N_S}$; Section 2.3.3.
 y Lagrange multipliers corresponding to equality constraints;
 Sections 2.5.1, 4.4 and Appendix A.
 z^E intrinsic element charge vector, $z^E \in \mathbb{R}^{N_E}$; Section 2.2.3.
 z = $A^T z^E$. Intrinsic species charge vector, $z \in \mathbb{R}^{N_S}$; Section 2.2.3.

Greek Symbols

$\beta(i)$	phase label function. $1 \leq \beta(i) \leq \pi$ for $1 \leq i \leq N_S$; Equation (2.11).
ΔG	$= V^T \mu$. Free-energy change; Section 2.3.5.
ΔG^0	$= V^T \mu^0$ standard free-energy change; Section 2.3.5.
δ	Kronecker's delta function; Equation (2.12) .
$\Lambda(\cdot)$	diagonal matrix (diagonal given by the vector argument).
μ	chemical potential; Section 2.3.4 and Equation (2.59).
ν	outward normal of domain, $\nu \in \mathbb{R}^d$.
χ	logarithms of molar concentration; Equations (4.43)–(4.44).
ϕ	porosity of the porous medium; Equation (3.1).
ξ	extent of reaction coordinates, $\xi \in \mathbb{R}^{N_R}$; Equation (2.41).
ξ^Q	extent of equilibrium reaction coordinates $\xi^Q \in \mathbb{R}^{N_R^Q}$; Section 2.4.2.
ξ^K	extent of kinetic reaction coordinates $\xi^K \in \mathbb{R}^{N_R^K}$; Section 2.4.2.
π	maximum number of phases possible at equilibrium; page 15.
Π	number of phases present at equilibrium; page 15.
Ψ	pressure potential function; Equation (3.8).
ω	Lagrange multipliers corresponding to the EAC; Appendix C.
σ	perturbation parameter in the interior-point procedure; Appendix A.
Υ	local truncation error (LTE); Section 4.7.
ζ	Lagrange multiplier corresponding to non-negativity of mole fractions; Appendix C.
ρ	Lagrange multiplier corresponding to non-negativity of phase mole-numbers; Appendix C.
Ω	physical domain, $\partial\Omega \subset \mathbb{R}^d$.
$\partial\Omega$	boundary of the physical domain (sometimes $\partial\Omega = \bar{\Gamma}_1 \cup \Gamma_2$).

θ Lagrange multiplier corresponding to the definition of mole fractions; Appendix C.

Superscripts

α phase designation. $1 \leq \alpha \leq \pi$.

$\bar{}$ (overbar) indicates a mobile quantity (e.g. \bar{N}_S mobile species).

$'$ (prime) indicates a reduced set of species that excludes kinetic products. Some examples are the reduced formula matrix $A' \in \mathbb{R}^{N_C \times (N_C + N_R^Q)}$, introduced in (2.143), the reduced species vector $n' \in \mathbb{R}^{N_C + N_R^Q}$ from page 49 and the total component concentrations excluding kinetic products, T' , defined in Equation (3.46).

T the transpose of a vector or matrix.

$*$ a quantity at equilibrium.

Subscripts

i species index.

j component index.

h discrete (grid-block) quantity.

Commonly Used Abbreviations

ADR The Advection-Diffusion-Reaction equations.

CMM The Characteristics-Mixed Method.

DAE The Differential Algebraic Approach to solving the ADR.

DSA The Direct Substitution Approach to solving the ADR.

EAC Element Abundance Constraints.

FE	The Forward Euler scheme.
HOG	The Higher-Order Godunov Method.
KKT	The Karush-Kuhn-Tucker necessary conditions in NLP.
LE	Local Equilibrium system.
LNE	Local Non-equilibrium system.
LTE	Local Truncation Error.
NLP	Nonlinear programming; Nonlinear programming problem.
ODE	Ordinary Differential Equation.
OS	Operator-Splitting.
PDE	Partial Differential Equation.
PKKT	Perturbed Karush-Kuhn-Tucker conditions.
PLNE	Partial Local Non-equilibrium system.
PVI	Pore Volumes Injected.
REV	Representative Elementary Volume.
RK-2	Explicit, Second-order Runge-Kutta scheme.
RK-4	Explicit, Fourth-order Runge-Kutta scheme.
RNSF	Reduced Stoichiometric Formulation.
SF	Stoichiometric Formulation.
SIA	Sequential Iteration Approach to solving the ADR.
UNSF	Unreduced Stoichiometric Formulation.

Glossary of Terms

Component Itself a species, the component is a member of a smallest possible set of species that can be selected in order to represent any other species in the system. The choice of components is not unique.

Element A chemical entity whose main attributes, such as mass, charge/oxidation number are conserved. Unlike the component, it is not necessarily a species in the system under consideration.

Product A species resulting from a chemical reaction. Given a choice of components, there is a unique reaction (combination of components) that results in the product. It follows that each product participates in exactly one reaction.

Species A chemical entity distinguishable from other such entities by either chemical formula, molecular structure or phase.

Appendix A

Nonlinear Programming, Lagrange Multipliers and the Interior-Point Method

This appendix describes the general interior-point method as applied to a generic nonlinear programming problem with general constraints of equality/inequality type. The presentation will follow closely that in [15] where more details can be found. First, the Lagrange-multiplier framework is presented, and the Karush-Kuhn-Tucker (KKT) necessary conditions are stated. Next, we describe the application of the standard Newton method to the nonlinear KKT conditions, and the resulting linear system. Finally, we discuss a globalized form of the algorithm, and a Fortran implementation that we have developed.

A.1 The General Nonlinear Programming Problem and the Lagrange Multiplier Framework

The nonlinear programming problem, which we will abbreviate NLP, in its most general form is the optimization of an *objective function* $f(x)$ over some space $x \in X$ subject to constraints on the variable x . The literature on this subject is extensive (see for example [18, 52]). For definiteness, let us consider the following form of the NLP for our exposition:

$$\begin{aligned} \min_x \quad & f(x) && \text{(A.1)} \\ \text{s.t.} \quad & h(x) = 0, \\ & g(x) \geq 0. \end{aligned}$$

where the functions f, h, g are defined so that

$$f : \mathbb{R}^n \rightarrow \mathbb{R}, \quad (\text{A.2})$$

$$h = (h_1, \dots, h_{me})^T : \mathbb{R}^n \rightarrow \mathbb{R}^{me}, \quad me < n, \quad (\text{A.3})$$

$$g = (g_1, \dots, g_{mi})^T : \mathbb{R}^n \rightarrow \mathbb{R}^{mi}. \quad (\text{A.4})$$

In these definitions, n denotes the *dimension* of the problem, me the number of *equality constraints* and mi the number of *inequality constraints*.

A point x is called *feasible* if it satisfies the constraints. The solution (if one exists) of the problem (A.1) is called *optimal*, and is denoted x^* .

In preparation for developing *necessary conditions* for a candidate point to be optimal for the NLP, we introduce *Lagrange multipliers* $y \in \mathbb{R}^{me}$ and $z \in \mathbb{R}^{mi}$, and the *Lagrangian function* $l : \mathbb{R}^{n+me+mi} \rightarrow \mathbb{R}$ defined thus:

$$l(x, y, z) = f(x) + y^T h(x) - z^T g(x). \quad (\text{A.5})$$

Note the sign convention for the multipliers z , which will ensure $z_i \geq 0$.

A.2 The Karush-Kuhn-Tucker (KKT) Necessary Conditions

Under reasonable assumptions (i.e., if some *constraint qualification* [52], [27] holds) the Karush-Kuhn-Tucker, or KKT, conditions [23] must necessarily hold at an optimal point for the NLP (A.1). Using the notation $\Lambda(g)$ to denote a diagonal matrix with the vector g on its diagonal, we can express these conditions as follows

$$\nabla_x l(x, y, z) = 0, \quad (\text{A.6})$$

$$h(x) = 0, \quad (\text{A.7})$$

$$g(x) \geq 0, \quad (\text{A.8})$$

$$z \geq 0, \quad (\text{A.9})$$

$$\Lambda(g)z = 0. \quad (\text{A.10})$$

The satisfaction of conditions (A.7)–(A.8) is obviously necessary for the *feasibility* of the candidate point. The equations (A.6) are referred to as *optimality*, and the relations (A.10) are known as *complementarity*. We note that the KKT conditions comprise a set of $n_{eq} = n + me + mi$ nonlinear equations, subject to the $2mi$ inequality constraints (A.8), (A.9).

In the interior-point method, iterates must stay feasible with respect to the inequality constraints. This is a difficult task for general, nonlinear functions $g(x)$. For this reason, it is common practice to introduce a set of *slack variables*, $s \in \mathbb{R}^{mi}$ and eliminate the need to be feasible with respect to nonlinear constraints at the expense of instead having to solve a larger nonlinear system. The resulting equivalent *slack-variable* form of the KKT conditions is

$$\nabla_x l(x, y, z) = 0, \quad (\text{A.11})$$

$$h(x) = 0, \quad (\text{A.12})$$

$$g(x) - s = 0, \quad (\text{A.13})$$

$$z \geq 0, \quad (\text{A.14})$$

$$s \geq 0, \quad (\text{A.15})$$

$$\Lambda(s)z = 0. \quad (\text{A.16})$$

For convenience, we express the KKT conditions more compactly as

$$F(x, y, z, s) = 0, \quad (\text{A.17})$$

$$(z, s) \geq 0, \quad (\text{A.18})$$

with

$$F(x, y, z, s) \equiv \begin{pmatrix} \nabla_x l(x, y, z) \\ h(x) \\ g(x) - s \\ \Lambda(s)z \end{pmatrix}. \quad (\text{A.19})$$

We remark that the nonlinear system $F(u) = 0$ has dimension $n_{eq} = n + me + 2mi$ in the unknowns $u = (x, y, z, s) \in \mathbb{R}^{n_{eq}}$.

A.2.1 Simple Bounds

Here we consider a specialization to the practically important case of *simple bounds*, i.e., $g(x) = x$ and consequently $mi = n$. The introduction of slack-variables is unnecessary in this case, and we can directly express the KKT conditions as

$$\nabla_x l(x, y, z) = 0, \quad (\text{A.20})$$

$$h(x) = 0, \quad (\text{A.21})$$

$$\Lambda(z)x = 0, \quad (\text{A.22})$$

$$x \geq 0, \quad (\text{A.23})$$

$$z \geq 0, \quad (\text{A.24})$$

or, in compact notation,

$$F(x, y, z) = 0, \quad (\text{A.25})$$

$$(x, z) \geq 0, \quad (\text{A.26})$$

with

$$F(x, y, z) \equiv \begin{pmatrix} \nabla_x l(x, y, z) \\ h(x) \\ \Lambda(z)x \end{pmatrix}. \quad (\text{A.27})$$

In this case, the nonlinear system has the dimension $n_{eq} = 2n + me$ equations in the unknowns $u = (x, y, z) \in \mathbb{R}^{n_{eq}}$.

A.3 The Interior-Point Method

A.3.1 The Perturbed KKT Conditions

A critically important concept in the interior-point method is the use of *perturbed* KKT conditions (PKKT), F_σ , which result from perturbing the last mi components of F by some $\sigma > 0$. The resulting expression is

$$\begin{aligned} F_\sigma(x, y, z, s) &= 0, \\ (x, z) &\geq 0, \end{aligned}$$

with

$$F_\sigma(x, y, z, s) \equiv F(x, y, z, s) - \sigma \hat{e}, \quad (\text{A.28})$$

and $\hat{e} = (0, \dots, 0, 1, \dots, 1)^T$ has mi ones, i.e., the perturbation *only* affects the complementarity conditions.

A.3.2 Application of Newton's Method to the Perturbed KKT Conditions

An iterative method is in general necessary in order to obtain the solution of the perturbed KKT conditions, $F_\sigma = 0$. We consider the standard Newton's method which consists of the iterative solution of the linear systems

$$\begin{aligned} J(u_k) \Delta u_k &= -F_\sigma(u_k), \\ u_{k+1} &= u_k + \Delta u_k. \end{aligned}$$

Here J denotes the *Jacobian* of F_σ , i.e., the matrix of partial derivatives of F with respect to the independent variables given by

$$J_{i,j} \equiv \frac{d(F_\sigma)_i}{du_j}. \quad (\text{A.29})$$

A simple calculation shows that for the general slack-variable formulation (A.17), the Jacobian has the form

$$J(u) = \begin{pmatrix} \nabla_{x,x}^2 l(x, y, z) & \nabla_x h(x) & -\nabla_x g(x) & 0 \\ \nabla_x h(x)^T & 0 & 0 & 0 \\ \nabla_x g(x)^T & 0 & 0 & -I \\ 0 & 0 & \Lambda(s) & \Lambda(z) \end{pmatrix}, \quad (\text{A.30})$$

and the right-hand side is

$$F_\sigma(x, y, z, s) = \begin{pmatrix} \nabla_x l(x, y, z) \\ h(x) \\ g(x) - s \\ \Lambda(z)s - \sigma \hat{e} \end{pmatrix}. \quad (\text{A.31})$$

We note that the *Hessian of the Lagrangian* has the general form

$$\nabla_{x,x}^2 l(x, y, z) = \nabla_{x,x}^2 f(x) - \sum_{i=1}^{mc} y_i \nabla_{x,x}^2 h_i(x) - \sum_{i=1}^{mi} z_i \nabla_{x,x}^2 g_i(x). \quad (\text{A.32})$$

For the less complex case of simple bounds (A.25) the Jacobian has the form

$$J(u) = \begin{pmatrix} \nabla_{x,x}^2 l(x, y, z) & \nabla_x h(x) & -I \\ \nabla_x h(x)^T & 0 & 0 \\ \Lambda(z) & 0 & \Lambda(x) \end{pmatrix}, \quad (\text{A.33})$$

and the right-hand side has the form

$$F_\sigma(x, y, z) = \begin{pmatrix} \nabla_x l(x, y, z) \\ h(x) \\ \Lambda(z)x - \sigma \hat{e} \end{pmatrix}. \quad (\text{A.34})$$

A.3.3 The Globalized Interior-Point Algorithm

We are now in a position to define a globalized interior-point algorithm. In what follows, the symbol $\|\cdot\|$ denotes the Euclidean (L_2) norm of a vector, the subscript k denotes an iteration counter and the parameters λ_k^1, λ_k^2 are real numbers satisfying $0 < \lambda_k^1, \lambda_k^2 < 1$.

Algorithm A.1 The Globalized Newton Interior-Point Framework

(0) Choose an initial guess $u_0 = (x_0, y_0, z_0, s_0)$ satisfying $(z_0, s_0) > 0$.

For $k = 0, 1, \dots$ **do**

(1) Test for convergence: **if** $\|F(u_k)\| < \epsilon$ **exit**.

(2) Update perturbation parameter σ_k .

(3) Solve for perturbed Newton step, $\Delta u_k = -(J(u_k))^{-1} F_{\sigma_k}(u_k)$.

(4) Adjust step-length to ensure $s_{k+1} > 0, z_{k+1} > 0$.

$$\Delta u_k \leftarrow \lambda_k^1 \Delta u_k$$

(5) Adjust step-length for globalization.

$$\Delta u_k \leftarrow \lambda_k^2 \Delta u_k$$

(6) Update unknowns: $u_{k+1} = u_k + \Delta u_k$.

$$k \leftarrow k + 1$$

Goto 1

We now give a more detailed description of each step of the algorithm.

The initialization of the algorithm, Step 0, requires us to fix an appropriate initial guess u_0 for the primary unknowns and the Lagrange multipliers. Initial guesses for the slack-variables s and the corresponding multipliers z are required to be non-negative.

Any appropriate termination criterion (Dennis and Schnabel [14]) can be used in Step 1; we have implemented a simple test on the (absolute) L_2 error of the residuals (the KKT conditions) versus the user-specified tolerance ϵ .

Several possibilities exist for the implementation of Step 2; the selection of the perturbation parameter σ . Numerical experimenting shows that an appropriate, systematic means of decreasing σ critically affects the convergence of the algorithm. Theoretical results are also known about “how fast” this parameter must be made to approach zero in order to ensure rapid *local* convergence of the algorithm [15].

Our implementation is based on the notion of the “central path”, which is the locus of points that are solutions to the PKKT, $F_\sigma = 0$, traced out as σ is varied. In this approach, σ remains fixed until the iterates are sufficiently close to satisfying the PKKT. The procedure is close in spirit to the logarithmic barrier function formulation, a class of methods with excellent global behavior. However, rather than requiring that our iterates be within some tolerance of solving the PKKT before reducing σ , we monitor *only* the satisfaction of the complementarity conditions, i.e., the condition used is

if $\|\Lambda(s_k)z_k - \sigma_k \hat{e}\| < \sigma_k$ **then**

$$\sigma_k = \rho \sigma_k,$$

where $0 < \rho < 1$. This choice was motivated by a desire to avoid “oversolving” by converging each sub-problem $F_\sigma(u) = 0$ to a high accuracy before reducing σ .

Step 3 entails the solution of a linear system which, in general, is not sparse. Currently, standard direct solvers (Linpack) are used for this purpose. In cases

where no inequality constraints are present, the Jacobian matrix (A.30) is symmetric. For such cases the appropriate symmetric linear solvers are used.

In Step 4 we adjust the step length to ensure the non-negativity of the variables s and z at the new iteration level. This is in principle straight-forward since the Newton update is linear. However, for reasons of numerical stability we do not allow a step that would extend the entire distance to the closest boundary, but choose instead to safeguard by requiring that we only move a certain fraction $0 < \tau_k < 1$ of the distance to the boundary. On the other hand, to retain the desired fast local convergence of the method, this fraction must approach unity at a certain rate as we converge to a KKT point. To be specific, we take the reduction of the step to be

$$\lambda_k^1 = \begin{cases} \min(1, -\tau_k \kappa_k^{-1}) & \text{if } \kappa_k < 0, \\ 1 & \text{otherwise.} \end{cases} \quad (\text{A.35})$$

Here, κ_k is given by

$$\kappa_k = \min\left\{\frac{(\Delta s_k)_1}{(s_k)_1}, \dots, \frac{(\Delta s_k)_{mi}}{(s_k)_{mi}}, \frac{(\Delta z_k)_1}{(z_k)_1}, \dots, \frac{(\Delta z_k)_{mi}}{(z_k)_{mi}}\right\}, \quad (\text{A.36})$$

and the fraction of movement to the boundary is

$$\tau_k = \max(\tau_{\min}, 1 - s_k^T z_k). \quad (\text{A.37})$$

Directly following this reduction of the step length, another restriction on the step is imposed to satisfy the property of sufficient decrease in some appropriate measure. This is accomplished in Step 5 using a line-search strategy (see Dennis and Schnabel [14]) on the merit-function ϕ_σ defined by

$$\phi_\sigma(u) \equiv F_\sigma(u)^T F_\sigma(u), \quad (\text{A.38})$$

that is, the square of the L_2 norm of the residuals (the PKKT). This is a convenient choice of merit function, but many other are possible (cf. [15] where the square of the L_2 norm of the KKT, i.e., $\phi(u) \equiv F^T(u)F(u)$ is used).

The line-search procedure attempts to satisfy the Armijo-Goldstein condition ([14]), i.e., to find the largest (positive) $\lambda_k^2 < 1$ such that

$$\phi_\sigma(u_k + \lambda_k^2 \Delta u_k) < \phi_\sigma(u_k) + \alpha \lambda_k^2 \nabla \phi_\sigma(u_k)^T \Delta u_k, \quad (\text{A.39})$$

where the parameter α satisfies $0 < \alpha < 1$. Such a λ_k^2 can always be found (as long as the Jacobian is non-singular) since it is readily shown that the perturbed Newton step is a *descent-direction* for the merit function ϕ_σ , i.e.,

$$\nabla \phi_\sigma^T \Delta u < 0. \quad (\text{A.40})$$

(A trivial calculation shows that $\nabla \phi_\sigma^T \Delta u = -2\phi_\sigma$). Two procedures for handling the backtracking line-search are implemented, namely *interpolation* and *simple reduction*. The interpolation algorithm uses standard cubic/quadratic interpolation as described in detail in Dennis and Schnabel [14]; the simple reduction scheme simply consists of shortening the step by a multiplicative factor.

A.4 NIPSF: Nonlinear Interior-Point Solver, Fortran

As a part of the effort to design an algorithm for solving the chemical equilibrium problem, a Fortran implementation of the interior-point method for general nonlinear programming was developed. It is capable of handling general, nonlinear constraints of inequality and/or equality type, and has been tested using a suite of the Schittkowski test problems [22]. For more details, the reader is referred to the NIPSF user's manual [33].