

PREFACE

Chemical reactions at aqueous interfaces play major roles in Earth terrestrial and subsurface cycles of most reactive elements, trace elements, heavy/radioactive ions, and environmental pollutants. Understanding these interfacial geochemical reactions requires identifying the products that may occur and form. Predicting them requires the reactions to be quantitatively defined through the reaction stoichiometries and associated equilibrium constants. These descriptions are the basis of thermodynamic models, known as Surface Complexation Models (SCMs), which aim to predict the chemical equilibrium state of a given (charged) interface in contact with solution. SCMs appear to be one of the most successful models in geochemistry. SCMs have provided the ability to understand, predict, and explain the sorption of protons, aqueous ions, and molecules to hydrated mineral surfaces using physical models for interfacial processes and energies.

SCMs are, however, often challenging to construct and apply realistically. First, the identity and the stoichiometries of the reactants and products are not easily determined. They must be inferred from bulk measurements, partially glimpsed through molecular probes, or predicted using state-of-the-art simulation methods. Second, the equilibrium constants are influenced by local mesoscale chemical phenomena that alter interfacial free energies while they are, in turn, coupled to changes in speciation at the interface and in the solution. In particular, the distribution of the charges close to the interface—the electric double layer—and the structuring of interfacial water directly influence energetics in a dynamical system. While some aspects of the molecular and mesoscale interactions and energetics remain enigmatic at the fundamental level, SCMs can deliver self-consistent thermodynamic descriptions that can predict interfacial effects in natural systems at scale.

The short course is devoted to the foundational science, illustrates the state-of-the-art experimental and molecular modeling methods for determining structural and energetic data, and demonstrates how these thermodynamic models may be developed for increasingly complex systems such as nanoscale confinement. The volume is intended to provide instruction and guidance to new scientists, suggest new problems and methods for experienced practitioners, and identify opportunities for new collaborations between fields.

The last decades have seen spectacular advances in our ability to experimentally test the mineral/electrolyte interfaces. This volume also describes the progress in surface diffraction, scattering, and absorption techniques and how the new experimental insights are incorporated in the SCM construction.

Finally, most systems in the natural world, including most systems we are interested in, are not at thermodynamic equilibrium. Mineral particles frequently undergo interfacial reactions that challenge the assumptions of surface complexation modeling. Mineral surfaces can be chemically and topographically remodeled by small changes in saturation state, slight shifts in redox potential, variation in stress state, and chemical reactions with aqueous ions. Understanding the pathways through which geochemical systems evolve towards equilibrium is a considerable challenge. In some settings with large-scale gradients in chemical parameters, mineral-fluid systems may be well approximated, assuming local equilibrium.

This volume is intended to present the past, present, and future of Surface Complexation Modeling and to nucleate the concepts for the next generation of more comprehensive SCMs that account for more complex chemistries and non-equilibrium phenomena.

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