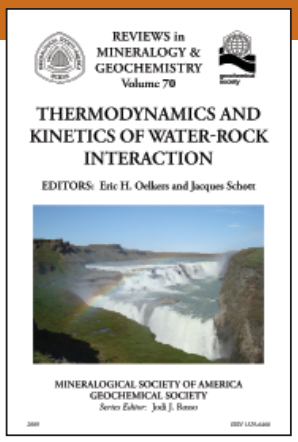
THERMODYNAMICS AND KINETICS OF WATER-ROCK INTERACTION[1]



Water–rock interactions cannot be understood or quantitatively interpreted without the application of physical chemistry consisting of thermodynamics, kinetics, and quantum mechanics. In the period 1965–1985, applied geological thermodynamics reached a pinnacle of importance, with kinetics closely following. It would have been unthinkable then to graduate master's and doctoral students in mineralogy, geochemistry, petrology, or any chemically related (or meteorologically related) aspects of environmental science without a course in thermodynamics. It is no longer true. Several years ago I taught an environmental geochemistry course for graduate students, and one student was extraordinarily upset because I had required everyone to know a few basic principles of thermodynamics. Hence, volume 70 in the Reviews in Mineralogy and Geochemistry series, entitled *Thermodynamics and Kinetics of Water-Rock Interaction* (*TKWRI*), is most welcome. As the editors state, "There is a compelling societal need to resuscitate the fields of thermodynamics and kinetics of natural processes."

The *TKWRI* volume accompanied a short course held at the 19th annual Goldschmidt Conference in Davos, Switzerland, in June, 2009, and it was also an outgrowth of European summer courses offered by the editors of the volume at the request of students. As such, it contains a broad range of theoretical principles and applied examples. The range and thoroughness of each chapter is the strength of the volume, as with most volumes in this series. There are a few omissions, including the lack of a chapter on stable and radiogenic isotopes, the lack of discussion on geothermal fluids, the lack of uncertainty discussions when applying thermodynamics and kinetics to field data, and the limited discussion of the pros and cons of the different approaches to applying thermodynamic and kinetic theory to field data. I would also like to have seen more discussion on aqueous speciation codes, databases, and kinetics. It is unfortunate that we find the saturation index defined in some chapters as Ω (= Q/K, i.e. the ion activity product divided by the equilibrium constant) and in other chapters as log Ω.

The introductory chapter on thermodynamic databases by Oelkers is certainly appropriate, as it contains a summary of thermodynamic equations and the Helgeson-Kirkham-Flowers approach. Coverage of other databases is somewhat limited. No mention is made of the IUPAC Solubility Data Series, of the CODATA books on key values and calcium compounds, of the numerous contributions from Navrotsky's lab, and of the voluminous OECD/NEA chemical thermodynamics series for actinides, nickel, zircon, and selenium, with more volumes in progress. I would like to have seen suggestions on how we can achieve greater collaboration among those making measurements of thermodynamic properties, the evaluators of the data, and those who apply the data to geochemical problems. Apparently there remains a lack of interest, funding, and prestige associated with such activities.

The remarkably clear and current reviews of the thermodynamics of solid solution–aqueous solution systems by Prieto and mineral replacement reactions, including numerous excellent examples, in the following chapter by Putnis were refreshing and stimulating to read. Prieto's discussion of stoichiometric saturation is short and quite understandable, so you would not know there was some controversy over this subject several years ago.

A reader might think that sorption could be covered in one chapter rather than three, but each chapter brings a different perspective. Kulik presents a substantial chapter on the basics of sorption thermodynamics and isotherms, the different models used for sorption theory, and some of the codes used with these models. For an introduction or refresher on sorption basics, this chapter is the place to start. Sherman presents the other side of sorption, summarizing what is known from recent studies using *ab initio* calculations and some results from synchrotron spectroscopy of surface bonding. It would have been even more helpful to have a summary of all the synchrotron studies of aqueous species bonded to mineral surfaces. Numerous studies by Brown, Waychunas, Manceau, Sturchio, and their colleagues are never mentioned. The chapter by Schott, Pokrovsky, and Oelkers is one of the most ambitious in the volume. It integrates mineral dissolution/precipitation kinetics with solution chemistry by combining transition-state theory with surface-complexation modeling to describe the dissolution and precipitation of oxide, silicate, and carbonate minerals. It is also an excellent prerequisite for the later, more detailed, chapter by Fritz and Noguera on mineral precipitation kinetics.

By far the largest chapter in this volume is the 110-pager by Ganor, Reznik, and Rosenberg on organics. Here you will find tables of organic compounds with pK_a values and a discussion of their importance in water–rock interactions, organic-matter sorption, and the effects of organics on dissolution of silicate and carbonate minerals. Unfortunately, there are insufficient references to several metal–organic modeling efforts, especially the successful work of Tipping and colleagues who developed the WHAM model. The main problem with organics in water–rock interactions is that the subject is huge and really requires a separate volume.

A major area of water–rock interactions is weathering. Two chapters cover this field, a shorter one by Goddéris, Roelandt, Schott, Pierret, and François on a generalized approach to weathering and its modeling, and a longer one by Brantley and White on regolith weathering. The former chapter presents an approach integrating climate, vegetative effects on weathering, and mineral dissolution rates within an input–output model embodied in the WITCH code, with applications to a small catchment and a large catchment (the Orinoco Basin). The sensitivity analyses performed by the authors on these catchments make an instructive and valuable addition to these methods. The latter chapter is written by two well-known researchers in this field who have worked on weathering processes for more than two decades. They delineate the range of approaches to modeling weathering processes from the simple to the complex and use an appropriate heuristic style in which they begin with the characteristics of real weathering profiles. As the latest synthesis by these two authors, it is a must-read for anyone attempting to do research on weathering.

Two complementary chapters complete this volume, bringing the application of thermodynamics and kinetics to its ultimate goal of interpreting water–rock interactions in terms of reactive-transport and geochemical modeling and networks. The first of these chapters is an introduction to reactive-transport modeling by Steefel and Maher, who use irreversible thermodynamics to present the physical aspects of transport (advective, diffusive, dispersive, and electrochemical) relevant to solute transport. In my opinion, this framework is the best possible one for a generalized and understandable approach for the purpose of teaching and learning reactive transport. A discussion on the "reactive" part of reactive transport follows, along with some helpful caveats concerning the pitfalls that lurk around every corner of this topic, and the chapter ends with several case studies. The volume concludes with the chapter by Zhu, focused on the geochemical reaction modeling that is largely missing from the previous chapters. It also goes full circle, bringing us back to solution speciation codes and their databases, and it connects with previous chapters through mineral dissolution/precipitation rates within the framework of geochemical modeling. It ends with some overviews of reactive-transport modeling and biogeochemical networks. I found the last chapter to be a most enjoyable read, and it should be read together with the previous chapter.

Anyone teaching or taking advanced courses in thermodynamics and kinetics in water–rock interactions should use this book if they hope to stay current.

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1 Oelkers EH, Schott J (eds) (2009) Thermodynamics and Kinetics of Water-Rock Interaction. Mineralogical Society of America Reviews in Mineralogy & Geochemistry 70, Chantilly, VA, 569 pp, ISBN 978-0-939950-84-3 , US$40