BOOK REVIEWS

Thermodynamic Modeling of Geological Materials: Minerals, Fluids and Melts, by Ian S. E. Carmichael and Hans P. Eugster. Volume 17 of *Reviews in Mineralogy,* Mineralogical Society of America, Washington, D.C., 1987. 499 pages, softbound, $18.00. (ISBN 0-939950-21-9).

Volume 17 of the *Reviews in Mineralogy* series contains 13 chapters by 16 contributors. Individual chapters review many of the methods used to compute and refine the thermodynamic properties of geologically important solids and fluids as a function of composition, temperature and pressure, and the numerical techniques used to calculate phase equilibrium assemblages in multi-component systems. The solids are predominantly those formed under igneous and metamorphic conditions. Clay scientists will be disappointed in the lack of an attempt to treat the stabilities of clay minerals. The fluids include aqueous solutions, supercritical metamorphic and igneous fluids, and magmas. The numerical algorithms are those constrained by "mass action" equilibrium constants and by direct minimization of the free energy of a system with an emphasis on the latter approach.

In Chapter 1, R. Newton refines the standard state mineral data for a limited number of important igneous and metamorphic minerals in the following systems: (1) $MgO-Al_2O_3-SiO_2$; (2) $Al_2O_3-SiO_2$ and (3) $CaO-Al_2O_3-SiO_2-H_2O$. He illustrates the general techniques of refining data using experimental phase equilibria combined with the constraints from thermophysical and (potentially less accurate) thermochemical measurements. In the next chapter, A. Navrotsky briefly reviews some simple solid solution models (ideal, strictly regular, two-term polynomial) and discusses volume mismatch of mixing species on a lattice and several binary applications from her research (spinels and carbonates, in particular). The overall emphasis is on polynomial expansions for representing excess free energy rather than using partition functions.

In Chapter 3, B. J. Wood builds on the first two chapters in his refinement of the thermodynamic data base for minerals in the $Na_2O-FeO-CaO-MgO-Al_2O_3-SiO_2$ system, in which symmetric and asymmetric solid solutions are used for the appropriate minerals. He reviews several approaches to determine an equilibrium assemblage before using a direct free-energy minimization scheme to determine the equilibrium assemblage of a system having a quartz tholeiite composition over a temperature and pressure range of 400°–1200°C and 6–20 kbar. The resulting phase diagram, showing the transition from gabbro to ecogite, is in good agreement with experimental data.

K. S. Pitzer discusses the use of the "Pitzer" virial-coefficient algorithm in Chapter 4 for computing aqueous activity coefficients of species. This ion-interaction model does include some ion association constraints through the incorporation of strong complexes. He presents a 25°C data base of consistent species parameters (single electrolyte and mixing parameters) in which the mixing parameters are consistent with the use of higher-order electrostatic terms for unsymmetrical mixing in the algorithm. The appendices contain a numerical procedure to compute these terms and a list of fit coefficients (up to 21 per parameter) for computing the temperature and pressure dependencies of some electrolyte parameters. The excessive number of fit coefficients detracts from the overall usefulness of this "accurate" method.

J. H. Weare uses the "Pitzer" algorithm in Chapter 5 at 25°C (with a somewhat different set of parameters than those used by Pitzer) to model field occurrences of evaporites using a free-energy minimization scheme. He was able to differentiate the effect of the presence and absence of backreactions involving Ca minerals in forming the Permian Zechstein and the Searles Lake evaporite sequences. At present, use of the "Pitzer" algorithm in aqueous geochemical modeling appears limited, primarily by the lack of parameters and knowledge of their temperature and pressure dependencies, e.g., for Al species.

In Chapter 6, D. A. Sverjensky reviews the "Helgeson" equations of state for the standard state thermodynamic properties of aqueous species. Equation parameters for complexes have recently been estimated and provide a convenient algorithm for the calculation of dissociation constants as a function of pressure and temperature. These constants are used with the extended Debye-Huckel equation of Helgeson (derived for NaCl-dominated fluids) to calculate aqueous activity coefficients in 0.1 and 1 molal chloride solutions. The pH dependence (3–6) of the aqueous speciation of Pb, Na, and H with chloride is presented for the temperature range of 400°–750°C and the pressure range of 1–4 kbar.

G. H. Brimhall and D. A. Crerar provide an extensive and comprehensive overview of ore fluids in geologic environments in Chapter 8. The chapter is divided into three parts: a discussion of the origin of magmatic water and its potential importance as an ore fluid; a qualitative yet detailed overview of the physical chemistry of aqueous solutions under hydrothermal conditions and the chemical controls on mineral dissolution and precipitation; and a quantitative modeling (including some coupling of chemical reactions with flow models) to explain the formation of primary and secondary ore bodies.

H. P. Eugster and L. Baumgartner, in Chapter 10, use experimental data to fit the dissociation constants for the metal chlorides and their free-energy difference with aqueous HCl to an equation of state. The equation of state is used in conjunction with standard state mineral data to predict the concentrations of metal chloride complexes in equilibrium with a metamorphic mineral assemblage in the $MgO-CaO-SiO_2-HCl-H_2O$ system. They predict a change in dominance from Ca to Mg chloride complexes with increasing metamorphic grade in H_2O-HCl fluids without CO_2.

J. R. Holloway (Chapter 7) and J. M. Ferry and L. Baumgartner (Chapter 9) deal with igneous and metamorphic fluids, respectively. Holloway briefly discusses attractive and repulsive forces in fluids and the various "gas-type" fluid equations of state. Ferry and Baumgartner provide an "in-depth" overview of these equations of state, including some tests of the accuracy of several versions of the Redlich-Kwong equation. Both studies report equilibrium compositions in the C-O-H-S system, based on Redlich-Kwong type fugacity equations, the general constraints of the equilibrium constants, and constant mineral activities. In addition, Ferry and Baumgartner extend these compositions to include nitrogen.

The final three chapters deal with magmas, a subject outside the low-temperature background of this reviewer, a "dishwater" geochemist (Ian Carmichael, 1975, personal communication). In Chapter 11, R. G. Berman and T. H. Brown review the thermodynamics of synthetic melt systems and test various models with the experimental results from such systems. In the next chapter, M. S. Ghiorso presents a useful

overview of formulating a melt model and solving for the equilibrium situation using a free-energy minimization scheme. In the final chapter, Ghiorso and I. S. Carmichael model magma cooling in small steps along reaction paths, allowing path simulation, and of fractionation, assimilation and other processes.

The book provides an *excellent* overall review of the principles and procedures involved in thermodynamic modeling. Errors in the "proof ready" type are generally not serious and obvious enough not to detract from the meaning of the text. Considering the inexpensive price, I strongly recommend it to all students of geochemistry.

R. K. STOESSELL

Proceedings of the Nordic Symposium, Clay Minerals—Modern Society, Uppsala, Sweden, Nov. 20–21, 1985, N. A. Shaikh and N. G. Wik, eds., Nordic Society for Clay Research, % P.-A. Melkerud, Department of Forest Soils, Box 7001, S-750 07 Uppsala, Sweden, 1986. 217 pages, US$25.00.

The Clay Minerals-Modern Society Symposium of the Nordic Society for Clay Research was held at Uppsala, Sweden, November 20–21, 1985. This symposium, which was concerned mainly with applied clay mineralogy, was sponsored by the Nordic Research Courses (The Nordic Council of Ministers), The Swedish Board for Technical Development, and The Geological Survey of Sweden. The Proceedings volume resulting from this symposium consists of 18 papers and 9 abstracts. All papers are in English, but the editing leaves much to be desired. Some of the abstracts are not informative, titles of several tables and illustrations in some of the papers are inadequate, and abbreviations are used in figures and tables that are not defined or referred to in the text. The high percentage of abstracts without papers and the fact that several papers do not adequately cover the material discussed also detract from the volume.

Among the more important papers in the symposium volume are two that are part of the program of the Standardization Group of the Nordic Society of Clay Research. One by C.-M. Blackman, A.-M. Brusewitz, and A. Sjödin outlines the mineralogy of the Geological Survey of Sweden's standard samples of glacial and post-glacial clays. The second paper, by I. Holmefjord, N. Gjelsvick, and E. Roaldset, deals with the methodology of clay mineral analysis used by the Norsk Hydro Research Center. Three papers and two abstracts are concerned with the applied clay mineralogy of kaolin. Two papers contain information on the characteristics of kaolin used for paper filling and coating, and one discusses the results of drilling and testing of 10 deposits in a kaolin belt in southern Sweden. One of these deposits is thought to be of commercial value for the paper industry.

A. Hurst's (Statoil, Norway) descriptions of petroleum reservoirs indicates that chlorite cement in sandstone associated with sedimentary structures has a marked influence on neutron porosity logs, but does not significantly affect other types of porosity logs or core porosity measurements. Clays are also likely to affect other reservoir characteristics, such as bulk hydrogen content, cation-exchange capacity, density, pore size characteristics, wettability, and gamma radioactivity. N. Gjelsvik's research supports the conclusion that in a North Sea oil field water of low salinity causes severe reduction in flow by mobilizing kaolinite, but water of high salinity tends not to reduce flow. P. Aagaard found that during diagenesis in one North Sea oil field early precipitation of kaolinite in pore spaces was followed by later, more chemically complex aluminosilicates.

One very interesting paper by Birgitta Hulthen describes the use of clays in prehistoric societies. Numerous ceramic items have been found, including tools, figurines, beads, and musical instruments. A practical method of building houses by daubing clay on a lattice-like wattle of small tree branches was widely used. The role of clay minerals in geothermal energy research is discussed in a paper by Hrefna Kristmannsdottir of the Iceland National Energy Authority. She found that clay mineral zones in geothermal fields in Iceland, the United States, Mexico, New Zealand, and the Philippines differ appreciably with different geologic settings.

SAM H. PATTERSON