## BOOK REVIEWS

CHEMICAL THERMODYNAMICS. By A. N. Krestovnikov and V. N. Vigdorovich. Translated from the Russian: *Khimicheskaya Termodynamika*, Metallurgizdat, Moscow, 1962. Israel Program for Scientific Translations, Ltd. 1964. 214 pages.

Phase equilibrium and other thermodynamic calculations are not especially difficult, nevertheless, they require a certain amount of practice in applying a variety of numerical methods and an understanding of the quality and sources of the data used. This introductory text is an effective and well-organized combination of theoretical chemical thermodynamics with the details of practical applications. Although intended for students of metallurgy, it covers certain areas of interest in mineralogy and petrology that are not discussed in depth in geochemistry and petrology textbooks published in the West.

The book is divided about equally between numerical aspects of chemical equilibrium (Part I) and the properties of phase diagrams (Part II). Chapters in Part I contain numerical problems with their solutions explained in detail. Theoretical concepts are appropriately illustrated with empirical examples in graphical and numerical form, and one soon acquires a balanced view of the history of thermodynamics: "The first fundamental expression of the second law was given by M. V. Lomonosov in 1747 . . .".

The subjects covered in detail include thermodynamic potentials, thermal dissociation and univariant crystal-vapor equilibria, homogeneous equilibria in a vapor phase, thermal properties of a crystallizing melt, experimental thermochemistry (calorimetry), a critical evaluation of empirical and numerical approximation methods, and geometrical thermodynamics. Extremal conditions, critical phenomena, solution theory and mixing properties, and univariant equilibria in multicomponent systems are not covered adequately enough for a course in theoretical petrology (Figs. 108a and b, which suggest extrema, are incorrect; examples in Fig. 111 of possible and impossible metastable extensions of phase boundaries in isothermal, isobaric ternary sections are given without proof.)

Further clarification is needed for the statement on p. 201, in brief reference to partial equilibrium (for example, ion-exchange): ". . . it is possible for the chemical potentials of the components to be equal when the slopes of the two tangents are equal, but the tangent lines themselves do not form part of the same straight line". In this instance, the potentials referred to must be those of exchange components like $(\mu_{KAlSi_2O_8} - \mu_{NaAlSi_2O_8})$ or simply $(\mu_K - \mu_{Na})$.

The book contains no subject index, and as usual, the references are sometimes difficult to recognize after transliteration back into English. Several tables of thermodynamic properties are provided, including a useful tabulation of $T(K)$, $T(°C)$, $1/T(K)$, $[\ln(T/298) + (298/T) - 1]$, and higher-order terms at 25-degree intervals from 200 to 2500 K for equilibrium calculations using analytic functions for the chemical potentials. Applications of the functions are illustrated in the text.

In all, Krestovnikov and Vigdorovich and their translator have successfully provided a clear and concise development of the fundamental principles and applications of thermodynamics, thermochemistry, and phase equilibria. The book (1962) is not out of date, and as a text, it is suitable for students having no previous courses in physical chemistry.

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THE COMPUTATION OF CHEMICAL EQUILIBRIA. By F. Van Zeggeren and S. H. Storey. Cambridge Univ. Press, 1970, 176 pages.

The earliest applications of digital computers include computations of phase equilibria in the high-temperature, high-pressure processes encountered in operating jet engines and rockets. Some very useful and ingenious methods for solving the equations governing chemical equilibrium in systems of a large number of species, components, and phases were devised. This small monograph surveys methods developed over the last 25 years mainly by mathematicians and chemical engineers. It is well-organized and a clear and logical extension of the material in Krestovnikov and Vigdorovich [reviewed above], however, is highly condensed and contains only one numerical example (at the end) and no problems. It is recommended here more as a reference than a text.

The authors begin with fundamentals of chemical equilibrium computation in a system of $n$ components and $\phi$ phases, with brief but rigorous discussions of non-ideality in pure gases and solutions (equations of state, fugacities, excess functions), the choice of possible variables of state for a system, and the subject of thermodynamic data. The practical aspects of standard states and numerical formulation of chemical potentials in this book may be tied directly to discussions in Krestovnikov and Vigdorovich. Neither book, however, deals adequately with the chemical potential as an intrinsic property of a phase. The adoption of a single standard reference state (one temperature, 298.15 K; one pressure, 1.013 bars; and one thermodynamic potential, the Gibbs energy of formation from the elements) for all pure substances would greatly simplify calculations of this type.

The remaining four chapters are concerned with the mathematical structure of equilibrium relations among the chemical potentials and with the numerical methods used to obtain the equilibrium solution. The development of these methods has a lively history. Before 1958, all large-scale equilibrium computations were carried out using the equilibrium constant formulation of appropriate equations. By 1959, the world was divided into two camps: the free energy minimizers and the reactionary equilibrium constant formulators. The controversy became so heated that when a panel discussion on thermodynamic calculations was arranged, it was necessary to divide the original group into a free energy panel and an equilibrium constant panel. It is now recognized that as far as the thermodynamic requirements of the problem are concerned, the end result of any method must be the same, although not necessarily equivalent from the point of view of numerical analysis. Van Zeggeren and Storey distinguish here two general types of procedures: (1) solution of a set of simultaneous non-linear equations and (2) searching for a minimum (or maximum) of a function ("optimization" techniques). The methods used by various authors are allocated to one of these groups and are critically evaluated.

The methods reviewed in this book link geometrical thermodynamics with quantitative data. Approaches such as the "NASA method" are of sufficient generality to include partial (constrained) equilibrium, homogeneous equilibrium in crystals, and quantitative simulation of isentropic, isenthalpic, isochoric, and metasomatic processes. There is little doubt that these methods have an important future role in interpreting mineral assemblages and in understanding the thermodynamics of igneous and metamorphic processes.

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COMPUTER CALCULATIONS OF PHASE DIAGRAMS, WITH SPECIAL
REFERENCE TO REFRACTORY METALS. By L. Kaufman and H. Bern-
stein. Academic Press, 1970. 334 pages.

This is the fourth volume in a series of monographs on refractory materials.
It is a highly specialized compilation of calculated phase diagrams for one-,
two-, and three-component metallic systems. The purpose of the book centers
around the following statement: "The literature abounds with theoretical
descriptions of phase stability in which emphasis is placed upon electronic
factors, Fermi surface effects, crystal chemical factors, size and valence effects, . . .
In most instances these descriptions treat the stability (or solubility limit) of a
given phase as if it were a property of the phase itself, rather than the result of
competition with other phases that can form in a given system." Although this
statement needs qualification with respect to internal ordering, the authors
clearly demonstrate that the intrinsic properties of a single phase do not permit
prediction of its stability under a given set of external conditions unless the
properties of the other possible phases (polymorphs) or phase assemblages of
that composition are known.

The authors emphasize that the various formulations of excess functions
(Margules, Van Laar, . . .) are only approximate representations of the true
thermodynamic description of a solution. They then produce a set of excess
mixing parameters by a series of estimates based on physical properties and
structures of the phases. Thermochemical data and the thermodynamic infor-
mation contained in existing phase equilibrium data are largely ignored, even
though these imperfect observations might contribute to a more consistent and
accurate "approximation" of the true mixing properties. Thus, the calculated
phase diagrams (approximately 200) bear very little relation to what is actually
known about the systems, except at the one-atmosphere melting points of the
pure phases where empirical thermodynamic data were used. These phase dia-
grams illustrate the perils of estimating thermodynamic properties from "first
principles," and the absurdity of such estimates when empirical thermodynamic
data are available. The methods used here fall short of the ultimate recipe for
determining thermodynamic stability (J. T. Lomer, 1967: Kaufman and Bern-
stein, p. 29–31): "Assume structure; 2, Evaluate self-consistent fields for com-
ponent-free atoms; 3, Superpose these potentials to get band structure, and use
the resulting wave function to get self-consistent solution for solid; 4, Evaluate
correlation energy correction; 5, Evaluate total energy; 6, Repeat for all sus-
pected rival structures." It may be fortunate that such methods had not been
perfected (and experimental studies abandoned) before phases like $\beta$-$Mg_2SiO_4$
were discovered.

In contrast to the two discussed above, this book is not clearly written, well-
organized, or instructive in its presentation of fundamentals. Drafting errors
are abundant. Terms such as: "lattice stability," "compound intrusion," "line
compound" (binary solution), and "high-pressure pinchoff" (invariant point in
a one-component system) and the use of $F$ for Gibbs energy might have been
avoided.

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CRYSTALLOGRAPHY AND CRYSTAL CHEMISTRY, By F. Donald Bloss. Holt, Rinehart & Winston, New York, 1971, 545 pages. $16.00.

This textbook is an important attempt to present thoroughly the nature of crystalline matter in a manner which can be understood by the diligent undergraduate student in crystallography. The treatment is basic, so the subject matter applies equally well to mineralogists, ceramists, chemists, solid state physicists, and metallurgists. While the book should make an excellent reference, major efforts have been made to create an effective text. Explanations of most concepts are liberally aided by carefully conceived illustrations, charts and tables, beautifully drafted and designed for easy visualization. To test the student's understanding of important concepts, questions and problems with answers are given at the end of each chapter. These are excellent and should greatly help the student toward a good understanding of the subject. References and recommended reading are also given at the end of most chapters.

This book offers a more in-depth treatment than most crystallography texts. It goes beyond the glossary of terms, descriptions, and classifications to the whys and hows of crystallography. The author avoids dogmatic statements and oversimplified explanations even at the expense of fairly complex and lengthy explanations. Electrical and magnetic properties, for instance, are explained with tensors, complete with an appendix on matrix algebra, which may intimidate many students who would prefer to settle for the more conventional approach. Explanations of many physical and optical properties of crystals are carried to the atomic and sub-atomic levels. The author clearly believes that students should reach a fairly high level of understanding in their first exposure to crystallography. The careful presentations in this text should make that goal achievable.

With the exception of determinative mineralogy, the book treats most topics generally covered in an introductory crystallography-mineralogy course. The subject matter is approached through principles and concepts; actual mineral data are included only in this conceptual framework by way of illustration and example. This text is well written and edited. All captions on illustrations are complete in themselves and often extensive, which is advantageous for a reference work but makes for considerable duplication of text. The reader has a tendency to begin skipping the complete captions. The thorough student will have read most material twice while reading the book once.

The first third of the book (7 chapters) is devoted to crystallography, beginning with external symmetry for the sake of simplicity as indicated by the author. The 32 point groups are developed through combinations of symmetry elements in chapter 1. Crystallographic axes and systems are related to crystal classes in chapter 2. The Hermann-Mauguin symbols are used throughout the book. Schoenflies' notation is presented at the end of chapter 2 as optional because of limited present day use. Crystal nomenclature and calculations is the topic for chapter 3; a three page appendix is provided here for students unfamiliar with determinants and matrix multiplication. The stereonet is utilized for the treatment of crystal projections in chapter 4. Chapters 5 and 6 treat crystal forms and lattices respectively. The discussion of screw axes, glide planes, and space groups in chapter 7 concludes the section on crystallography.

The next one-third of the book (3 chapters) treats crystal chemistry. Included here are the usual topics of atomic structure, bonding, polymorphism,

structure types, silicate structures, structural imperfections, and phase changes. This survey is notable for its comprehensiveness and readability.

The last one-third of the book (3 chapters) discusses physical and optical properties of crystals and introductory X-ray crystallography. The extensive treatment given to electrical and magnetic properties relative to other physical properties seems justified by the current interest in the fields of geophysics and paleomagnetism and the fact that many texts ignore them almost completely.

In addition to being useful as a reference, this book should find immediate use as a text in many introductory crystallography-mineralogy classes and perhaps in more advanced classes in crystallography and X-ray crystallography. It would have to be supplemented with good determinative tables for laboratory studies of minerals. Although the section on optical properties is excellent, it would not substitute for an optics text (for example, *An Introduction to the Methods of Optical Crystallography* by Bloss) since it is brief and not directly concerned with microscopic studies of minerals.

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THE ELECTRON-OPTICAL INVESTIGATION OF CLAYS. Edited by J. A. Gard. Mineralogical Society, London, 1971. 383 pages. $31.25.

This is a fitting companion volume to the previously published "The X-ray Identification and Crystal Structures of Clay Minerals", the standard reference work for researchers in the clay minerals field. Eighteen distinguished workers contributed articles on the application of various electron optical techniques, *i.e.*, microscopy, diffraction, lattice imaging, etc., to the characterization and structure elucidation of clays and associated minerals. The volume is edited by J. A. Gard who also contributes two chapters; one on experimental techniques and the other a survey of theory and results obtainable from these procedures. A separate chapter also discusses detailed specimen preparations suitable for various purposes. These three chapters are followed by sections specifically dealing with the various clay minerals and also with commonly encountered accessory minerals, each written by an expert in the field. The range of applications runs the gamut from morphological examinations by electron microscopy to sophisticated techniques of structure determination from single crystal electron diffraction intensities and lattice imaging. The book is superbly printed and the reproductions of the photographs are uniformly excellent.

A serious deficiency is the lack of discussion of the use of the scanning electron microsope in this researh. The editor states in the preface that he considered the SEM and microprobe analyser to lie outside the scope of this work. One might agree with this view for the microprobe but the SEM has such great utility that this reviewer wishes it had been included in this volume. However, this is a minor criticism and will not prevent this volume from taking its place as the standard reference for the application of electron optical techniques to clay minerals for many years to come. The Mineralogical Society deserves the thanks of all clay researches for sponsoring these monographs.

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GLOSSARY OF MINERAL SPECIES. By Michael Fleischer, with an appendix by John S. White, Jr. Mineralogical Record, Inc., P. O. Box 783, Bowie, Maryland 20715; 103 + xvi p., 1971; $1.00 to subscribers, $2.00 to non-subscribers.

An alphabetical list of mineral names, with chemical formulas (and an appendix of some of these formulas translated into words for the most common minerals)—of interest to amateur mineralogists.

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RATIO CORRELATION. A MANUAL FOR STUDENTS OF PETROLOGY AND GEOCHEMISTRY. By Felix Chayes. The University of Chicago Press, 1971, 99 pages. $6.00 cloth; $2.25 paper.

The contents of this slim volume have fundamental significance for all branches of petrology, petrography, and mineralogy concerned with inter-relationships between chemical and/or modal data. In a series of mathematically-thorough and exhaustive papers published over the past decade, Chayes exposed and analyzed many crucial, but overlooked, factors; he showed that ignoring them can lead to erroneous interpretations of geochemical data. Many of these concepts and some further development are now succinctly gathered under one cover. Hopefully, this book will provoke more serious attention to the problems involved than was evoked by the journal articles. Although Chayes tends to draw occasional examples from igneous petrology, the subject matter has far-reaching implications for fields like metamorphism (particularly metasomatism) and mineralogy.

Because of its fundamental importance, it seems useful to outline the book's subject matter. Basically, Chayes is concerned with "open" and "closed" data. In the open case, the several variables for each sample do not add up to a constant value; with closed data, however, the variables always add up to a constant and the most obvious example involves all percentage data. If plotted on a simple graph, two open variables may yield a random scatter of points or, with increasingly-strong statistical linear correlation, the points lie closer to a straight line. The degree of association of the two open variables can be tested against a "null" condition represented by zero correlation (or random scatter of the points on the graph). Subject-matter genetic decisions are commonly based on the strength of such a correlation. Chayes proves that inherent mathematical relationships cause built-in "spurious" correlations when certain ratios of open variables, or when closed variables and most ratios of closed variables, are involved. As a result, the test of significant correlation must establish association over and above the built-in non-zero spurious value. (The type of effect is most easily demonstrated by noting the correlations between a set of open variables and then the much stronger correlations that result when the same open variables are expressed as percentages.) Much of the book involves elegant algebraic derivations of the null values that must be used for different types of ratios and closed-number associations. Many of these apply directly to standard practices in petrology; ignoring Chayes' results must lead to unrealistic conclusions.

Chayes concludes that calculation of the proper null tests requires knowledge of the original open variables. Unfortunately, for many of the percentage data used in geochemistry (*e.g.*, oxide weight percent in a rock), corresponding open variables do not seem to exist. Much of the later chapters involves attempts to derive a theoretical open set of variables for existing closed data and/or to

develop geochemically-meaningful ways of recasting closed data (*e.g.*, as with Niggli numbers) so as to reduce the size of the inherent, mathematically-induced, spurious correlations.

This is not a reference book. Although referred to as an elementary manual (p. 18), comprehension requires careful and thoughtful reading by those with a good working knowledge of elementary statistics. For example, variance and covariance are used in the first paragraph of the text with the implicit assumption that the reader is absolutely familiar with manipulating them; similarly, on page 8 ". . . the usual rules for calculating expectations . . ." are assumed. Although, in a half-dozen cases, examples with real data are outlined, the reader is assumed to be thoroughly familiar with various petrographic diagrams, Niggli numbers, etc., and to know the ". . . well known Flight relation" (p. 31). Such assumptions are appropriate for an advanced monograph. However, it is unfortunate that, in rewriting the technical articles in book format, a greater attempt has not been made to facilitate reading by serious earth scientists who are not already pretty-well steeped in the subject. If independently-stimulated and interested in the subject matter, classically-inclined earth scientists dealing with numerical data in geochemical studies may plunge into this book. So far, among those geologists who are vaguely aware that the problems exist, only a handful has seriously worried about the geological consequences. In a sense, this book is ahead of its time. A rising generation of geologists, well-equipped mathematically, will readily cope with it. Unfortunately, only a small proportion of current geologist and mineralogists who commonly use graphs, variation diagrams, and ternary diagrams to portray their analytical data will be able to identify with this book's contents or even to scan the chapter titles and determine whether there is relevance to their research or not.

Chayes has kept strictly to his own work and does not mention attempted solutions to some of the geochemical problems by others (*e.g.*, Pearce, 1968, *Contrib. Mineral. Petrology*, **19**, 142–57) or the implications of his work for trace and accessory components studies (a matter that has received considerable attention in the literature).

Nearly every standard petrology and mineralogy textbook makes liberal use of the relationships that are the subject of this book when deriving 'fundamental' genetic conclusions. Hence, this volume should be *essential* reading for earth scientists. Earth scientists must determine the extent to which the use of proper null values in evaluating correlations affects the basic concepts and conclusions of geology. Naturally, this will incidentally involve deciding whether the classical chemical and mineralogical percentages provide an objective basis for effective discrimination between rival petrogenetic concept, or whether some other variables (hopefully, open variables) are better discriminants.

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COMPARATIVE STUDY OF LOW-GRADE METAMORPHISM IN THE CALIFORNIA COAST RANGES AND THE OUTER METAMORPHIC BELT OF JAPAN. By W. G. Ernst, Y. Seki, H. Onuki, and M. C. Gilbert. Memoir 124, Geological Society of America, Boulder, Colorado, 276 pp. $15.00.

In putting together the results of a comparative study of two low-grade metamorphic belts marginal to the Pacific Ocean, the authors of Memoir 124 have

done an admirable job placing in perspective the relationship of blueschist facies metamorphism to circumpacific orogenesis. The comparative approach adds regional flavor to the study while maintaining detail in regard to field, petrographic, whole rock, and phase chemical investigations in several areas in the Sanbagawa and Franciscan terranes of Japan and California, respectively. Included are 93 rock analyses, 121 "wet" chemical analyses of minerals, and 107 electron microprobe analyses of minerals. The wealth of chemical data on minerals and rocks and corresponding data on optical properties is also summarized in graphical form. Tabulated data on optical properties and modal analyses of rocks are deposited with the National Auxiliary Publications Service.

The publication is essentially in three parts, dealing first with the Franciscan, then with the Sanbagawa, and finally with the comparison of the two terranes. In the first two parts the authors present discussions of general stratigraphy and tectonic relations, field and petrographic relations of rocks in specific locations, bulk rock chemistry, phase chemistry, mineral paragenesis, and metamorphic facies in the Franciscan (chapters II through V) and the Sanbagawa (chapters VI through IX). Chapters X through XV compare mineralogy, densities, element partitioning among coexisting minerals, mineral parageneses, ages, and tectonics of the metamorphic rocks in the two terranes. Notable in the presentation is a continuity maintained in discussions of field relations, petrography, bulk chemistry, phase chemistry, and mineral paragenesis for a given rock and/or facies type. This difficult task is accomplished by careful attention to detail in several areas in the Franciscan and Sanbagawa terranes and allows the reader to make comparisons at the scale he desires. Thus it is possible to make a fairly rapid assessment of the characteristics of blueschists or "blueschist facies" metamorphism in the several areas studied; and the same can be done for the high-grade metamorphic rocks which occur as inclusions or tectonic blocks of garnet-glaucophane schist, for amphibolites of various kinds, and for eclogites in or associated with serpentinized peridotite in the Franciscan and Sanbagawa terranes.

The comparative approach focuses on differences between two terranes generally thought to have evolved under similar geologic settings on opposite sides of the Pacific. Nearly continuous and traceable stratigraphic units are the rule in parts of the Sabagawa terrane, whereas there appears to be little hope of stratigraphic subdivision in the Franciscan melange. Although tectonic setting and position with regard to the margin of the Pacific basin are similar, crustal structures appear to be vastly different: deposition of rocks which form the Sanbagawa terrane may have occurred on more highly evolved, continentalized crust, whereas the Franciscan appears to have been deposited directly on oceanic crust. The Franciscan metamorphism is high pressure—low temperature; conditions for Sanbagawa metamorphism were apparently intermediate between those of the Franciscan and moderate pressure—high temperature facies. Metamorphism under differing conditions in the two terranes is shown to have produced significant variations in composition of coexisting mineral phases in rocks of the same whole rock composition.

Major and minor element fractionation is used as an aid in the interpretation of field and petrographic relations. Data on partitioning of Fe-Mg among coexisting minerals sodic amphibole—calcic amphibole, soda amphibole—white mica, white mica—chlorite, and garnet—chlorite show fractionation more pronounced in matamorphic rocks of northern and central California than in comparable schists in the Sanbagawa (Shikoku schists), from which the authors deduce that Fran-

ciscan metamorphics recrystallized at lower temperatures. For assemblages which crystallized at the same temperature, as deduced from $K_D$ and $K_D'$, the evidence points to higher pressures in the Franciscan. Bringing all the data of the investigation to focus on the problem of physical conditions of metamorphism, the authors conclude that two "mutually intergradational" $P$-$T$ regimes are required to account for the progression of assemblages of the California Coast Ranges, whereas the progression of mafic metavolcanics in the Sanbagawa requires increasing temperature with an evolution of water. These conclusions are then examined by consideration of the transformation of Sanbagawa assemblages to Franciscan assemblages by simple application of pressure through the postulated reaction

10 albite + actinolite + 2 chlorite = 5 glaucophane-crossite + 2 lawsonite
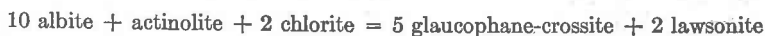
for mafic rocks, and the well known reaction

$$albite = jadeite + quartz$$

for metaclastic rocks.

Considering that the geologic and petrologic relations examined by the authors of Memoir 124 are about as complex as those in any geologic system, this is an extremely ambitious scientific endeavor. The authors deserve hearty congratulations for a job well done, and for providing an outstanding reference for geologists-petrologists and others with an interest in metamorphism marginal to the Pacific Ocean.

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# FAULTY COPIES MARCH-APRIL ISSUE

We regret that apparently some copies of the issue of March-April 1972 went out with a missing signature pages 529–560. Please examine your copy, and if it is faulty, notify the office of the Mineralogical Society of America, 6th Floor, 1707 L Street N.W., Washington, D.C. 20036, who will issue a replacement.