

BOOK REVIEWS

THERMODYNAMIC DATA FOR INORGANIC SULPHIDES, SELENIDES AND TELLURIDES. By K. C. Mills. Butterworths, London, 1974. viii + 845 pages. £20 Sterling. (Halsted Press, New York, \$65.00).

The author of this new monumental work has, by his own words, aimed to provide "a critical evaluation [of thermodynamic properties which] remove[s] values which are demonstrably wrong and to . . . produce a comprehensive and reliable collection of values which the user can confidently employ." To a large degree he has succeeded. This book, providing the most recent comprehensive and evaluated listing of thermodynamic data for 700+ *binary* (a word which should have been in the book title) sulfides, selenides, and tellurides will become a standard reference for these compounds for many years to come.

The book is organized as follows:

1. Introduction (5 pages)—a brief description of units, constants, standard and reference states, and symbols and abbreviations.
- 2a. Experimental and Evaluation Techniques (20 pages)—a well written description of standard and sometimes new methods employed in sorting out the best data for inclusion in the book. Where data do not exist the author often provides a means for estimation.
- b. Table of Selected Values (34 pages)—a convenient color-coded section listing: molecular weight, melting point and ΔH°_{f298} , S°_{298} , D°_o , C_{p298} , and $(H^\circ_{298}-H^\circ_o)$ in both the "familiar" (calories, atmospheres) and the Systeme International or SI (joules, newtons, etc) units.
3. Thermodynamic Data (645 pages)—A comprehensive listing which includes a brief discussion of: phases, structure (crystal system only), stoichiometry, heat of formation, entropy, heat capacity, dissociation pressure or energy, auxiliary thermochemical values, references. Also occasionally given are activities of components and partial molar quantities.
4. Appendix—Tables of C_p , (H_T-H_{298}) , (S_T-S_{298}) , and $-(G_T-H_{298})/T$, values at 100K intervals, calculated from the data given in section 3. An unfortunate omission here is a tabulated listing of the free energy of formation from the elements.

The book is well prepared and quite legible, except for portions of the Appendix where thinly printed computer printouts are directly reproduced. No book so large can be error free and this is no exception; however, most are minor—e.g., the listing of low temperature Ni_3S_2 as cubic. More serious is the omission of such a classic work as Barton and Toulmin's Fe-S study (*Geochim. Cosmochim. Acta*, 1964) and the impressions that all pyrrhotites have the NiAs structure and that the only phases in the Cu-S system are Cu_2S and CuS. Nevertheless the book represents an invaluable compilation of data and is a necessary nearby reference for all those working on sulfides, selenides, and/or tellurides.

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THE CHEMISTRY OF CLAY-ORGANIC REACTIONS. By B. K. G. Theng. John Wiley and Sons, New York, 1974. vi + 343 pages. £16.00, \$47.50.

This book has been advertised as a prizewinning text (Adam Hilger Award), and indeed it should be. Dr. Theng has compiled and edited a superb collection describing clay-organic reactions of extreme importance to soil scientists, agronomists, engineers, colloid chemists, geochemists, and all others interested in clay minerals. After having this book for several weeks, I can give one word of warning. That is, urge all of your colleagues to purchase their own copies; otherwise, you will find, as I have, that it is very difficult to keep your copy from being "borrowed."

There have been a number of other books, some fairly recently, about clays and clay minerals. These other texts have emphasized the origin, composition, and structure of the clays as ascertained by chemical analysis, X-ray diffraction, and thermal methods of analysis. Dr. Theng has presented a comprehensive review concerned with the interactions between clay and organic materials, and has emphasized the use of infrared spectra. In addition, he has correlated X-ray diffraction, thermal analysis, adsorption, and kinetic data with the infrared spectra in a clear and concise manner. Throughout the text, Dr. Theng gives various views about different types of clay-organic reactions and then discusses probable reasons for the sometimes conflicting experimental results obtained by different workers. The book is divided into seven chapters, along with a comprehensive list of references and an index listing both subject matter and authors.

Chapter One is entitled "Clay Mineral Structures," and in it the author describes the basic structural features of the 1:1 and 2:1 type clay minerals. Dr. Theng does not make any attempt to go into detail with regard to the structures, since that is not the purpose of his book. He gives appropriate references as to where the various structural relationships readily can be found.

The second chapter moves into the reaction of organic compounds with the clay minerals. This chapter is concerned with the interaction of unchanged polar organic compounds with the various clays. In the introduction of this chapter, the author lays the basis for his emphasis on infrared spectra for the study of clay-organic reactions. He points out that "X-ray diffraction has yielded a great deal of useful information on the arrangement and confirmation of the organic molecule in the inner layer space of clay minerals, but its usefulness in investigating those changes that may take place in the structure of the adsorbed compound is limited." For this reason, he comments that "the recent development of infra-red spectroscopy, together with improved methods of sample preparation, has provided the means to observe structural changes on a molecular scale, and so give insight into the nature of the clay-organic bond." He continues by stating, "The principle behind the application of infra-red spectroscopy to the study of clay-organic systems is that the vibrational spectrum of the adsorbed molecule is directly comparable with that of the 'free' species, that is, of the compound in the solid (crystalline), liquid, or dissolved state. Thus, interactions and perturbations occurring at the clay surface of certain structural groups of atoms in the organic molecules often give rise to changes in the position and/or inten-

sity of the corresponding vibrational bands in the spectrum of the complex, as compared with similar bands in the spectrum of the unadsorbed compound. These observations enable conclusions to be drawn regarding the mode of bonding of the intercalated organic molecule to the mineral surface." Dr. Theng then continues to describe some of the general facts that must be considered with regard to the role of interlayer water on the adsorption of organic compounds to clay surfaces and the molecular orientation and general organization of the adsorbed species on the clay. He shows how this information can be obtained by utilizing infrared spectra in conjunction with X-ray diffraction and adsorption studies.

Chapter Three is a continuation of Chapter Two, wherein the author discusses complex formation of uncharged polar compounds with some defined classes of compounds. This chapter is divided into clay complexes with primary n-alcohols, polyhydric alcohols, ketones, aldehydes, ethers, nitriles, amines, amides, and aliphatic and aromatic hydrocarbons. Throughout this chapter, the author, wherever possible, correlates the infrared spectra with other means of analysis and with other classes of compounds so as to obtain an overall view of the types of organic clay reactions that are taking place.

Interactions of organic compounds of biological importance with the clay minerals are emphasized in Chapter Four. This chapter includes sections on complexes with organic pesticides, amino acids, peptides, antibiotics, alkaloids, pyrimidines, purines, nucleosides, fatty acids, fats, and saccharides. Since many of the pesticides that have reacted with clay minerals are known by their trade names, the author has included a table that cross-indexes the class of the compound, its family, its common name, and its chemical name. Much of the information with biologically important compounds on clay minerals have been obtained by the study of these complexes by means of adsorption isotherms and X-ray diffraction. Dr. Theng correlates this information with the infrared analysis where available.

In the next chapter, the subject of positively charged organic species complexed with clay minerals is discussed. Followed by a very informative section on the mechanisms of formation, the author then discusses the inner layer organization of adsorbed positively charged organic species. Some of the properties of the cationic complexes such as adsorption, gelation, swelling, heat, etc., are also given.

Chapter Six is concerned with organic complexes with the kaolinite group of minerals. The preceding chapters were primarily concerned with the 2:1 type of minerals, and only occasionally was anything given with regard to the 1:1 type of minerals. Dr. Theng has brought together in this chapter a review of much of the data regarding organic-kaolin reactions. Most of the chapter is concerned with kaolin, but a part reviews the available literature concerned with halloysite.

In the final chapter (Chapter Seven), organic reactions catalyzed by clay minerals are reviewed. Included are color reactions, polymerization reactions, transformation, and decomposition reactions. Dr. Theng has correlated available information, for example, on color reactions with regard to the mechanisms underlying the process. Polymerization, transformation, and decomposition reactions are discussed in the light of the various possible active centers on the clay minerals, including the basal surfaces and clay edges. Such mechanisms as electron transfer and proton transfer are discussed with regard to the possible catalytic mechanisms involved with the clay minerals.

This book should indeed find its way into the hands of all those

interested in clay-organic reactions and the implications which these reactions imply. It is well indexed so as to help the reader locate needed information, and should be a very worthwhile reference volume for many years to come.

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DIFFERENTIAL THERMAL ANALYSIS: APPLICATION AND RESULTS IN MINERALOGY. By W. Smykatz-Kloss. Springer-Verlag, New York, 1974. xiv + 185 pages, 82 figures. \$23.80.

In the Preface to this volume Smykatz-Kloss states "At first glance it may seem presumptuous to want to add yet another to the numerous books on Differential Thermal Analysis (DTA)." Nevertheless, the content and the thorough approach taken by the author seem to justify publication of this work.

The book is divided into three major parts:

Part I. Methods. Although relatively brief (23 pages), the basic DTA method with all its variable factors is discussed in sufficient detail so that this section would be useful even to someone totally unfamiliar with this technique. Smykatz-Kloss makes a strong plea for standardization of DTA, a plea which is reinforced when detailed examples are given of the applications of DTA to a number of mineralogical problems.

Part II. Application of Differential Thermal Analysis to Mineralogy: Identification and Semi-Quantitative Determination of Minerals. Smykatz-Kloss summarizes much of the data available for minerals which have been analyzed by DTA. Coverage of the English language literature is good (although this reviewer was aware of some references that were omitted) and coverage of recent European literature also appears to be good. In this section (83 pages), Smykatz-Kloss develops and expands on some innovative ideas. The first is the "P-A (Proben-Abhängigkeit) curve" or curve of sample amount dependence. Smykatz-Kloss presents P-A curves for a large number of minerals showing the change in peak temperature with the amount of the mineral present in a sample and demonstrates how these curves can be used in semi-quantitative determinations. A second innovation is the development of a series of tentative "Identification Diagrams" which plot peak temperature against (ΔT), the latter on a logarithmic scale. (Of course, such data must be gathered under standard conditions to be useful). Data for 148 minerals are presented.

Part III. Special Application of Differential Thermal Analysis in Mineralogy: Statements about Chemical Composition, Degree of Disorder and Genesis of Minerals. In this section, a number of mineralogical problems are discussed using data made available through DTA, such as: the effect of substitution of +2 ions in calcites, aragonites, and dolomites; the influence of chemical composition on the Curie temperature of magnetites; the degree of disorder in kaolinites; and the high-low inversion behavior of microcrystalline quartz crystals.

This reviewer's major objection is that the text is not easy to read. Since no acknowledgment was made for assistance in preparing the English text, one must assume that Smykatz-Kloss wrote directly in English. The text is filled with statements such as, "The author's DTA runs under varying heating conditions demonstrated that the main purpose of these discrepancies is . . ."; "DTA data of hydrated carbonates with strange anions . . ."; "The layer character and extraordinarily good cleavage after the basis (001) demand for a careful preparation of sheet silicates.";

"Measurements of structural transformations make the use of different amounts of sample material unproblematic."; etc.

Returning for a moment to Smykatz-Kloss' Preface, in the 1930's more than 80 percent of all DTA determinations dealt with mineralogical matters; today the proportion of DTA publications related to all earth science investigations amounts to less than 5 percent. Perhaps this new book and the insight it gives to the potential application of DTA to many mineralogical problems will spur a renewed interest in this neglected method.

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SPACE GROUPS AND LATTICE COMPLEXES. By Werner Fischer, Hans Burzlaff, Erwin Hellner, and J. D. H. Donnay. National Bureau of Standards Monograph 134. U.S. Government Printing Office, Washington, D.C., May 1973. vi + 177 pages. \$4.10, domestic postpaid, \$3.75.

Symbolism is presented for site sets in crystallographic point groups and for lattice complexes in space groups. If G denotes a crystallographic point group and if P denotes a point, then the set of all images of P under the elements of G is called a *site set* and is said to be the site set generated by P in G . Lattice complexes are defined in the same fashion with respect to space groups and hence retain the flavor of their original meaning, due to Paul Niggli who used the term "lattice complex" to designate a set of crystallographically equivalent atoms in a crystal structure. Instead of simply presenting a list of the points in a given site set, the symbolism for a site set is designed to describe the relationship between the site set and the point group. The approach used to determine the symbols for the site sets is subsequently used to great advantage in the description of the variant lattice complexes.

Let G denote a crystallographic point group. If a point P is placed at the fixed point of G , then the number of images of P under the elements of G is one. If P moves away from the fixed point in a given direction, then, in general, the number of images of P increases. This is called splitting. The symbol for a given site set is determined by the degree of splitting encountered as P moves along a prescribed path. For example, the symbol for the site set generated by a point with coordinates of the form xxz in the group $\frac{4}{m} \frac{2}{m} \frac{2}{m}$ is $4xx2z$. The $4xx$ portion of this symbol indicates that as P moves away from the origin into the xy plane along the line $x = y$, the number of images of P under $\frac{4}{m} \frac{2}{m} \frac{2}{m}$ increases 4-fold. The $2z$ portion of the symbol indicates that if P subsequently moves off the xy plane in the z direction, then the number of images increases 2-fold yielding all eight of the points in the site set. A series of rules is presented that dictates, given a site set in a group G , the path along which P is to move starting at the fixed point of G and ending at a point Q that generates the given site set. Tables are presented that list, for each group, the symbols of all the site sets generated by special points, such as xxz , as well as the general point xyz . Taken together, these tables not only give a description of all of the types of site sets that occur, but also yield a very complete picture of the symmetry-related properties of each of the crystallographic point groups.

In the treatment of lattice complexes, invariant lattice complexes are designated by mnemonic letters that recall some structural feature. For example, D denotes a lattice complex with the "diamond structure" and $+Q$ recalls the Si atoms in high tem-

perature quartz. These lattice complexes are clearly illustrated in a series of figures. The invariant lattice complexes are essentially used as building blocks for the remaining lattice complexes.

Starting with a given lattice complex, new lattice complexes can be generated through the process of splitting as described for site sets above. The 402 lattice complexes presented can be generated in this way from a special class of 67 complexes called the Weissenberg complexes. All of the invariant lattice complexes are Weissenberg complexes and, in a special way, each of the Weissenberg complexes can be constructed from an invariant lattice complex. The Weissenberg complexes are depicted clearly in a series of figures. Detailed tables describe the splitting that is required to obtain each of the remaining complexes from the Weissenberg complexes. These tables also list the occurrences of each of the lattice complexes by giving the appropriate space groups and Wyckoff letters as they appear in the *International Tables for X-ray Crystallography*. The symbol defined for each lattice complex is designed to describe the generating lattice complex as well as the required splitting. For example, in the cubic system $14xxx$ indicates that the generating lattice complex is the body-centered lattice complex I and the splitting is a 4-fold splitting in the direction of the body diagonal. Hence $14xxx$ has multiplicity eight since I has multiplicity 2. The occurrences for this lattice complex are given in the table to be $I43m(c)$, $P43n(e)$, and $I23(c)$.

To avoid ambiguities in the choice of a generating lattice complex for a given complex, elaborate rules are presented in the text. Potential ambiguities in other areas are similarly resolved by rules. Unfortunately, in order to understand the details about how the symbols are determined, one must struggle through a text which contains a number of vague definitions, unclear statements, and misprints. However, due to the great care and completeness of the tables and figures and due to the fact that numerous tables are presented that cross index the information described above, these tables will surely make a valuable contribution.

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AN INTRODUCTION TO X-RAY SPECTROMETRY. By Ron Jenkins. Heyden & Son, Ltd., London, 1974. xi + 163 pages. \$14.00.

Intended to supplement existing books that tend to be either too theoretical or too applied, the author has written a very well illustrated introduction to X-ray fluorescence spectrometry. While the emphasis is on wavelength dispersive (crystal) spectrometer, he also introduces the reader to the principles and uses of energy dispersive (semiconductor) spectrometers for X-ray fluorescence analysis.

Illustration of several kinds of typical spectra—sometimes drawn together with corresponding energy level diagrams—will be particularly useful to students.

The final chapter "The Study of Chemical Bonding" appears to have been written with little malice aforethought and is so out of date that it detracts from the quality of the rest of the book. Rather than this chapter, the author might have capitalized on the background material developed in earlier chapters to show how much of the same information applies to the field of electron microprobe analysis.

On the whole, the straightforward and well illustrated presentation of the basic theory and instrumentation makes this book

an excellent addition to the X-ray fluorescence laboratory. Undoubtedly, this book also will be widely used in appropriate courses.

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GEOCHEMISTRY AND THE ORIGIN OF LIFE. Edited by Keith A. Kvenvolden. *Benchmark Papers in Geology*, Dowden, Hutchinson & Ross, 1974. Distributed by Halsted Press. xvii + 422 pages. \$26.00.

This collection of 43 "landmark" papers, including several by the editor and his associates, deals with the evolution of thought concerning the earth's early history and the origin of life. The papers are grouped into 5 categories with brief comments by the editor preceding each section. The categories include:

Chemical Evolution-Possible Beginnings, 8 papers; Carbonaceous Meteorites, 6 papers; Primitive Environments-Hydrosphere and Atmosphere, 12 papers; Organic Geochemistry-Carbon Chemistry of the Precambrian Rocks, 12 papers; and Early Life on Earth-Paleobotany, 5 papers.

Dr. Kvenvolden has, by and large, gathered together a compendium of data. The papers are of considerable significance, but not ponderous and overbearing. The presentation follows a logical order and redundancy is on the whole avoided. Of considerable value are several "overview" papers, which synthesize available data into "models", working and otherwise, to attempt explanations of evolution on the primitive earth. Several of the papers (such as MacGregor's 1941 report on the Bulawayo stromatolites) are not readily obtainable. Most are from readily accessible journals. It is to be regretted that one paper of considerable interest (that of Paul Ramdohr on "detrital" pyritiferous and uraniferous

conglomerates) is not translated from the German, contrary to the goals of the series editor (R. W. Fairbridge) as stated in the "Series Editor's Preface." This is a major irritant to geologists not fluent in German (such as the reviewer).

In any volume composed essentially of collections of reprints, the quality of printing is of considerable importance. From this standpoint, the volume has some drawbacks. Several of the articles are printed in type so small as to be difficult to read; occasionally, figures from such articles contain lettering that is quite indistinct. A small minority of the articles contain photographs, and quality of reproduction ranges from excellent to poor. In the great majority of articles, however, quality of reproduction is satisfactory.

The comments of the editor serve as invaluable guides to the development of scientific thought concerning each of the major groups of papers. His comments, in and of themselves, provide the reader with a "state of the art" synthesis, so necessary to non-specialists, to whom this volume should have considerable appeal. References at the conclusion of each short essay by the editor, coupled with the references from the articles themselves, provide a collection of virtually all significant published work on these subjects.

Typographical errors are practically nonexistent, and do not present a problem. The main objection to the volume is certainly not its content, which should have wide appeal, but its price, \$26.00. This will probably serve to limit availability of the work. I feel that some thought should be given to publication of a less expensive paperback edition of this, as well as of other volumes of the series.

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List of Books Received

THERMODYNAMIC METHODS IN MINERALOGY. By A. G. Bulakh. Leningrad, 1974, 182 pages, paper. In Russian.

OCEAN FLOOR MINING. By John S. Pearson. Noyes Data Corporation, Park Ridge, New Jersey, 1975. ix + 201 pages. cloth, \$24.00.

PRINCIPLES OF GEOLOGY. By James Gilluly, Aaron C. Waters, and A. O. Woodford. 4th edition, revised by James

Gilluly. W. H. Freeman and Company, San Francisco, 1975. vii + 527 pages, 482 illustrations, 40 tables. \$12.95.

SEDIMENTARY ROCKS: CONCEPTS AND HISTORY. Edited by Albert V. Carozzi. Volume 15, *Benchmark Papers in Geology*, Dowden, Hutchinson & Ross, Inc., 1975. Distributed by Halsted Press, New York. xv + 468 pages. \$28.00.