Book Review

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Thermophysical Properties of Solids, their Measurement and Theoretical Thermal Analysis

In: Wilson and Wilson's Comprehensive Analytical Chemistry. Ed. by G. Svehla, Vol. XII. Thermal Analysis, Part D. Elsevier, Amsterdam–Oxford–New York–Tokyo, 1984. 440 pages. (The book has also appeared in Czech.: Merenie termofyzikalnich vlastnosti pevnich látek, Academia, Prague, 1982.)

Volume XII of the well-known and highly estimated Wilson and Wilson series was edited by W. W. Wendlandt in a somewhat unusual manner. The volume consists of four subvolumes, which (though all dealing with thermal analysis) differ appreciably in their approach. If the reviewer's opinion had been asked regarding the subjects of the individual subvolumes, it would possibly have disagreed with Wendlandt's. However, he too would certainly have attempted to have Jaroslav Šestak as one of the authors, and no great differences would have presented themselves in the theme of this subvolume.

Thermal analysis should be considered a particular branch of analytical chemistry, its main feature being that its methods offer information on the thermal behaviour of the specimens, that is, on changes effected in their state by heat treatment: this information can be used for analysis in its strict sense, to model processes to develop technology, to gain knowledge on the structures of solid specimens and their reactions, and to obtain thermodynamic and reaction kinetic data. Thermal analysis looks back on a past of close to 100 years and its techniques have, at this stage, developed into manifold modern processes. However, it may be stated that the comprehensive, general theoretical background of thermal analysis has not yet been elaborated. There are numerous reasons for this, including the many aspects of thermal analysis, and the fact that though it has proved fully suitable to satisfy practical demands, attempts to develop its theoretical background (or at least many of these attempts) have reached a deadlock. I refer to heterogeneous non-isothermal thermal kinetics: most monographs published in this field, although approaching individual partial problems on a high theoretical level, refrain from a general theoretical discussion. In Šestak's papers one can usually recognize his efforts to approach problems from their theoretical fundamentals. This book (together with its Czech variant, as far as my modest

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knowledge of the language allows me to form an opinion) is also characterized by this effort. In fact, the book is essentially a new, comprehensive systematization of the author's earlier papers based on rational thermodynamics. Sestak wrote this book with the claim of principled generalization, and essentially succeeded: in the opinion of the reviewer, it is a milestone in the elaboration of the theoretical background of thermal analysis.

The book consists of 13 specialized chapters, supplemented by a 14th chapter on the mathematical methods generally applied in analytical chemistry, with special regard to thermal analysis, and an appendix (33 pages) of partly interesting and partly unnecessary tables and data. It would be difficult to agree in all respects with the author's statements on nomenclature summarized here.

The first chapter is a very interesting pre-summarization and introduction to the whole book. It appears that the author, knowing the public well, prepared this chapter for those readers who are not interested in details. The reviewer is pleased with this concept.

Chapter 2 bears the title Preparation and Characterization of Solid Samples. What is important in this chapter is the discussion of how to bring about consciously metastable and unstable states, and of the importance of rapid cooling. The grouping of heterogeneous processes is interesting.

Chapters 3 and 4 deal with the application of thermoanalytical techniques for material testing, including the information content of thermoanalytical curves. In some cases the role of experimental implementation is also discussed. The key problem in this domain, the measurement of temperature, calibration and control, is dealt with in much detail.

Chapter 5 summarizes the basic principles of thermodynamics from the aspect of thermal analysis.

Chapters 6 and 7 deal with the thermodynamics of phase equilibria and with the preparation of phase diagrams, including the aspects of measurement techniques.

Chapter 8 and 9, and in part Chapter 10, deal with the other possible approach, the kinetic path. The introductory part of Chapter 8 may be considered a comprehensive criticism of thermal kinetics, but not its complete rejection. In fact, the author subsequently deals with this domain without any reservations. However, his mode of approach is characteristic. He does not merely deal with the formal application of the mathematical apparatus; at the focus of his interest one always finds the essence and nature of the physical and chemical changes taking place during heat treatment, and the mathematical apparatus serves to model these changes adequately. Instead of the formal kinetic description unfortunately very widespread in the literature, he truly attempts to clarify the relationships of the background. For instance, the kinetic description and characterization of the sintering process are of great interest. In Chapter 9 the author summarizes the thermokinetic approaches known from the literature. Chapter 10 is interesting, but will presumably be attended to only by a narrow circle.

Chapters 11 and 12 discuss calorimetry and DTA-DSC techniques, above all from the aspects of measurement theory and measurement techniques. The author points out the differences between DTA and DSC. It is not evident why DDC is treated separately.

All non-calorimetric methods are discussed in Chapter 13, but with regrettable briefness and relative simplicity. It is a pity that this important field has been neglected to a certain extent by the author.

The book is well printed, but some of the Figures are too small and cramped. Literature references at the end of each chapter appear thorough and useful; some superficialities, however, do occur, as a matter of curiosity in Hungarian relations.

All in all, this is an interesting, high-level book, and its publication was a step of great importance towards the establishment of the general theoretical background of thermal analysis. It may well be recommended to researchers and in general to analysts interested in theoretical matters, but above all, of course, to those active in thermal analysis.

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