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Book Review

Dilatometerkurvenatlas der Tonmineralstoffe,
Edith Joachim Schomburg and Manfed Störr, Ed.
Akademie-Verlag, Berlin, 1984, 88 pp. Price: 18,–M

In the present monograph the experience and results of dilatometric studies on clay minerals are presented in a comprehensive form. The book deals with the application of thermodilatometry to the diagnosis of minerals, to the recording of processes of thermal decomposition, and to technical control in the ceramics industry. The form of the presentation is based on the monographs by A. Langier-Kzuniarova and by G. Liptay concerning application of the derivatograph in the treatment of mineral samples.

After an introduction to the fundamental principles of dilatometry, those methodologic and instrumental possibilities are discussed which permit systematic representations. Included are problems of the standardization of these studies, the influence of experimental conditions, and questions of nomenclature in connection with the results of investigations. Further parameters and properties, such as the expansion coefficient, sintering point, behaviour on baking, swell interval and glassing, are discussed on the basis of practical examples provided by the ceramics industry.

The comprehensive atlas part contains dilatometric and derivative dilatometric curves on 106 samples of clay minerals. These investigations are concentrated on groups of minerals and raw materials which have always been of general interest in thermoanalytical research. Layer silicates and ceramics raw materials (kaolin, clays) are discussed in depth. However, exact descriptions of the processes taking place during the thermal treatment are missing.

A closing extensive literature review with 94 references relating to dilatometric studies of minerals and rocks should help scientists in their work with the problems involved in these methods. The dilatometric curves can be used not only for qualitative surveys of clay mineral samples, but also for the recording of thermal decomposition processes.

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Hemminger/Höhne: Calorimetry–Fundamentals and Practice. Translated by Y. Goldman. Verlag Chemie, Weinheim; Deerfield Beach, Florida; Basel, 1984, 310 pages.

During the last two decades, a large number of commercially produced calorimetric instruments, of reasonable precision and accuracy, suddenly showed up on the market. Thus the doors for calorimetric measurements, previously reserved mainly for custom designed and rater sophisticated instruments, are now wide open. These commercial calorimetric instruments quickly gained a stronghold as one of the most popular analytical instruments in the laboratory. As the principles of design for these instruments vary, so would their capabilities and limitations. The meaning of the electrical signal and the method of data treatment and interpretation, even for the same thermal events, depend on the particular principle of design and operation. For a person who is new in the field trying to acquire an instrument best suited for his purposes, it is certainly a chore trying to decipher from the huge stack of manufacturer's literature, which generally lists only the advantages of the particular instrument. He may also try to wade through a sea of published literature and try to interpret between the words what are the pros and cons of the particular instrument being used; or he may contact his experienced colleagues for their honest opinion. This book is intended to fill this gap, as stated in the preface. The English and revised edition of the book is foreworded by a leading figure in the application of thermal analysis in the polymeric field.

In this book the review of thermodynamic principles and heat transport phenomena pertinent to the calorimetric design is quite complete and appropriate to the intended readers. The impartial evaluation of the pros and cons of various methods is most valuable to the readers while deciding which instrument to acquire. The book even has a chapter devoted to the criteria for evaluation of a calorimeter and the selection of a calorimeter.

Although this book is intended to describe mainly the modern commercial instrumentation, the authors seem to give the book a flare of historical nostalgia. The historical onset of different types of calorimetric measurement, in the light modern commercial instrumentation, without showing much of the development and improvement of the various methods, may be done intentionally to show either the comparable character of the modern instrument versus the original conception, or the improvement thereof.

As mentioned by the authors that many commercial calorimeters make the use of microprocessor, the discussion of which would be beyond the scope of this book. The reviewer fully agrees with this viewpoint. The use of microprocessor simply adds convenience features to the instrument, and in general do not change the principles of measurement or improve the measuring capability of the hardware.

Most of the commercial calorimetric instruments rely on relative measurements. The temperature scale cannot be compared directly against standard temperature measuring systems. The energy equivalent in general cannot be calibrated against a known electrical energy input. The calibration of temperature and energy in these instruments generally depends on the occurrence of thermal events of standard reference materials measured elsewhere. It would certainly be a help to the reader, if the authors, in their future edition of the book, could compile a list of standard reference materials suitable for the calibration of these instruments, including an up-to-date data and specific references for relevant temperature and enthalpy of fusion, temperature and enthalpy of transition, and specific heat. This is the only recommmendation the reviewer wishes to make about this nice little book.

This book is certainly a welcomed reference to any thermal analyst and calorimetrist, whether a novice, advanced, or do-it-yourselver, as a ready source to the principles of operation in the modern commercial calorimetric instrumentation.

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CALORIMETRY — Fundamentals and Practice,
W. Hemminger and G. Hohne, Verlag Chemie GmbH, Weinheim, 1984;
310 pages, 116 figures, 10 tables. DM 135.–, $ 60.00.

To review both the theory and practice of calorimetry is a demanding task especially since the authors have included both classical calorimetry and differential scanning calorimetry. Their timing is opportune. There has been a rapid growth in commercial instrumentation and a growing recognition that differential scanning calorimetry can yield reliable calorimetric information. The wider application of differential scanning calorimetry has not been the main intent of the authors. Nor have they been concerned to discuss at length the chemistry of the calorimetric process but rather to concentrate on the theory and practice of the instrumentation. Thus they have divided the book into two parts: *Calorimetry* and *Calorimeters*. In the first part, the chapters are entitled *Methods of Calorimetry, Measuring Instruments, Fundamentals of Thermodynamics, Heat Transport Phenomena, Surroundings and Modes of Operation*, and *The Measured Curve and its Evaluation*. In the second part, the chapters are *Calorimeters with Compensation of the Thermal Effect, Calorimeters Involving the Measurement of a Temperature Difference, Criteria for the Evaluation of a Calorimeter* and *Possible Future Developments*. There is a short history of calorimetry (to 1955), a glossary of terms, a list of calorimeters and the addresses of manufacturers. Some of the chapter titles are rather cumbersome reflecting the emphasis the authors place on the classification of calorimeters with regard to the measuring principles, modes of operation and the construction.

The chapter titles indicate the considerable number of topics covered in this book. The discussion of commercial equipment is particularly valuable. It provides an insight into the instruments which are currently available and will remain useful even when individual models are superseded. It is in their treatment of fundamentals that the authors have not always attained the same level of presentation. They have not made the best of their opportunity to delineate a rigorous thermodynamic approach to the interpretation of calorimetric experiments. Such an approach requires only the 1st law of thermodynamics and might have been more rewarding than the very much wider range of material dealt with in the chapter on thermodynamics. The authors assert that there is a common tendency to use thermodynamic concepts even when the ideal conditions required by them are not complied with. Irrespective of the merits of this argument, clearly there is the need to define precisely the quantity which is derived from the experiment. By way of example, the authors quote the expression $\Delta Q = C\Delta T$ for an adiabatic calorimeter where C is the heat capacity of the system consisting of the sample, contained and probe. ΔQ is described both as *the entire heat exchanged*, presumably between the *sample system* and the *measuring system*, and the total *heat of the process*. At the very least the approach is confusing since the calorimetric process has not been defined explicitly. The only other source of information is a diagram for an exothermic process involving constant heat generation where it would seem that ΔQ is the change in the *energy of the system in the calorimeter* for the temperature range ΔT. For a chemical reaction the change in internal energy is $E(T_f, V, \xi_f) - E(T_i, V, \xi_i) = Q = 0$ by definition when the adiabatic calorimeter and its contents constitute the thermodynamic system and ξ represents the extent of reaction. The quantity required from the experiment is the change in internal energy for the isothermal process which is derived from a knowledge of the heat capacity of the system utilising only the 1st law of thermodynamics $E(T, V, \xi_f) - E(T, V, \xi_i) + C_f(T_f - T) + C_i(T - T_i) = 0$.

Although this approach might be regarded as "ideal" it is the basis of much classical calorimetry where the temperature change corresponding to the effective adiabatic process is obtained by making allowance for the work of stirring and the heat exchanged between the system and surroundings.

There is much useful information contained in this book and there is no other single text which can compete with its scope. It is well produced with high quality paper and print. It is a moot point whether the systematic subdivision of the material makes for easy reading buth it does give the authors the opportunity to discuss patterns of heat-flow in the various calorimeters. There is a useful introductory treatment of deconvolution procedures. A considerable list of monographs, proceedings and other literature is given but there are some instances where it would have been helpful for the reader to have been directed to specific recent literature. In their treatment of scanning calorimetry the authors make a distinction between heat flux and power compensated instruments and review various interpretations of experimental curves. Perhaps the authors could have been more critical in their stance thus providing a sure guide to their reader. The common use of the term "heat of reaction" in the literature without defining the process to which it pertains is only one example of a lack of thermodynamic discipline which prevents meaningful quantitative thermodynamic and kinetic information from being obtained. This is not a book for the complete novice but has much of interest to offer the critical reader.

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