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Preface

The appearance of this English edition of my book, first published in Russian in mid-2006, is related to the help and support of two prominent scientists: Professor Michael Brown (Rhodes University Grahamstown, South Africa) and Dr. Judit Simon (Budapest University of Technology and Economics, Hungary).

The story is as follows. In the winter of 2006, in the process of exchange of views by email with Michael on some problems of decomposition kinetics, I asked him about the possibility of publishing my book in English. He suggested that I should contact Judit, the Series Editor of “Hot Topics in Thermal Analysis and Calorimetry”. My application was kindly accepted, considered, and approved. As a result, Judit strongly recommended this book to Springer for publication, and Michael kindly agreed to help me with linguistic improvements of my hurriedly translated book. In the process of editing, he made some critical comments and questions, which stimulated me to improve and clarify the text, but we did have to agree to put our differences of scientific opinions aside so as not to delay the process. Without this invaluable help, this book would not be as “readable” as I hope it is now. The author uses this opportunity to express his sincere thanks to Michael and Judit for their significant help and support.

Although only about a year has gone after the preparation of the original edition of the book (in Russian), this English version of the manuscript has undergone considerable revision. These changes refer to Sections 2.2, 2.4, 2.5, 8.2, 16.4, and Chapter 13. A new Section 15.6, Tables 13.1 and 13.2, and Figures 5.2 and 16.1 are added and many tables and figures have been improved. All these changes were made to clarify the explanation of the basic concepts of the new thermochemical approach to thermal decomposition, including mechanisms, kinetics, and methodology, and to make it suitable as a textbook for students.

The author gratefully acknowledges the kind permission to use some figures from other sources of publication: figures reprinted from *Spectrochimica Acta Part B*, *Spectrochimica Acta Review*, *Progress in Analytical Atomic Spectroscopy*, and *Thermochimica Acta* with kind permission from Elsevier Science, Amsterdam, the Netherlands; figures reprinted from the Proceedings

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The exact references are given in the figure captions.

St. Petersburg, February 2007

Boris V. L'vov

Foreword

It has been an interesting task helping Professor Boris L'vov with the production of an English version of his book. Although we have, unfortunately, never met in person, we have had many contacts by email. He kindly presented me with a copy of the Russian edition of his book soon after publication and I was immediately frustrated by not being able to read it. Professor L'vov's work is both original and controversial, and spread over an impressive number of primary publications. This literature had been condensed by the chief author into a book of manageable size, but still needed to be made accessible to the English-speaking world. One of my motives in offering to assist with the English edition was to "force" myself to pay close attention to his complex ideas and suggestions. I think I have come out of the process with a greater appreciation of some aspects, but still have to undergo a full "conversion experience"! Time just did not allow lengthy exchanges between us and these will, perhaps, have to be postponed for future debates in the literature. My hope is that this translation will bring Professor L'vov's work to the attention of a wider audience and that this will promote constructive discussion of the assumptions made.

Grahamstown, February 2007

Michael E. Brown

Preface (Original Russian Edition)

Solid-state reactions and, particularly, processes involved in the thermal decompositions of solid substances are a subject of intense interest for a very broad class of specialists: researchers, engineers, and technologists engaged in metallurgy, chemical industry, and materials sciences, including those specializing in the area of novel technologies (chemical vapour deposition, self-propagating high-temperature synthesis, mechanochemistry, and nanotechnologies). Nevertheless, very few monographs, reference handbooks, and especially textbooks on this and related issues have been published. This may be attributable to some stagnation in the field of theoretical description of these processes, which became evident as far back as the 1970s–1980s.

The present monograph suggests a new approach to the reaction mechanisms, kinetics, and methodology of measurements, which is based on a thermochemical analysis of such processes. This approach draws on studies of the author performed during the last 25 years with the use of electrothermal atomic absorption spectrometry (AAS) and mass spectrometry (MS) and, recently, of the methods of thermal analysis (TA) as well. The concepts developed are capable of accounting for the main features of reactions, including the mechanisms governing individual stages of a process, as well as of providing quantitative interpretation of many problems and unusual observations (for instance, the Topley–Smith effect) that have accumulated in this field. This approach has essentially laid a cornerstone for development of a self-consistent and rigorous theory of thermal decomposition of solids and melts.

The new methods of measurement and calculation proposed have radically improved the precision and accuracy of determining the thermochemical parameters and, in this way, expanded considerably the potential use of TA in kinetics studies. The methods have been employed to obtain, for the first time, reliable kinetic characteristics and to uncover the mechanism of decomposition of several tens of substances belonging to different classes of inorganic compounds (crystalline hydrates, oxides, hydroxides, nitrides, azides, nitrates, sulfates, carbonates, and oxalates). The results obtained in these studies have been published in the literature in various journals spanning the period from 1981 to 2006). This book draws the work together to make it more accessible for researchers confronted with these issues.

The exposition is divided into three main parts. The first part elucidates the basic physicochemical concepts (mechanism, kinetics, and methodology), which, in the second part, are used for the interpretation of the effects and phenomena making up the basis of research in the kinetics of solid-state reactions. Definition and substantiation of the basic physicochemical concepts is necessary because readers unacquainted with other publications of the author might find these points fairly unusual. The third part of the monograph contains a brief description of thermogravimetric (TG) experiments and the basic experimental and thermochemical data used by the author in the second part of the book. These data may turn out to be useful as subsidiary material in the practical activities of a reader confronted by corresponding problems. Also, as calculation methods become more sophisticated and the values of thermodynamic functions more accurate, these data may find use in refining the conclusions obtained. The Appendix to the book lists some additional tabulated data and physical constants used in the corresponding calculations.

The terminology used has undergone the usual changes or refinements with time and experience. The terms “mechanism of dissociative vaporization”, “physical approach”, and “specific enthalpy”, introduced in previous communications by the author, have been replaced in this book by “mechanism of congruent dissociative vaporization”, “thermochemical approach”, and “molar enthalpy”. The notation of some physical quantities has likewise undergone changes.

The author sincerely hopes that the material in this book will arouse the interest of the readers and stimulate revision of many ideas that have become established in this area. It is likely that some of the ideas expressed here will raise objections and initiate heated discussions. In the final count, this could only favour progress in the field. Any constructive critical comments of the readers will be accepted gratefully by the author and taken into account in our subsequent studies.

The author feels deeply indebted to his students and colleagues who have taken active part in studies of thermal decomposition problems with electrothermal AAS, quadrupole MS, thermal analysis, and computational modelling. Their names feature in the list of authors of the corresponding publications. Particular thanks are due to Dr. Valery L. Ugolkov (Institute of Silicate Chemistry, St. Petersburg), whose active participation in our research during the recent 5 years has made it possible to complete the series of thermochemical studies that provided solid support for the ideas of the author and a justifiable purpose for the writing of this book; my colleague, Dr. Leonid K. Polzik, who has read carefully through the manuscript and suggested valuable corrections and comments; and, finally, but not least importantly, Dr. Andrew K. Galwey (Belfast), whose long-standing moral support has been invaluable in helping the author to maintain self-control and optimism in the hardest times of collision of his ideas with the generally accepted concepts.

St. Petersburg, February 2006

Boris V. L'vov

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