Thermal Analysis

THIRD EDITION

WESLEY WM. WENDLANDT

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PREFACE

The primary goal of this book, as described in the preface to the second edition, is to serve as a general introduction to the field of thermal analysis. Due to the voluminous papers published during the past 10 years, it is not possible to make the book comprehensive for each technique. Indeed, separate volumes could easily be written on each one discussed here. Some degree of critical evaluation has been added, especially in chapters such as those on reaction kinetics, purity determination, and instrumentation.

Thermal analysis techniques have been applied to almost every science area, from archaeology to zoology, and to every type of substance, from alabaster to zeolites. Indeed, it is difficult to find an area of science and technology in which the techniques have not been applied. This truly universal use of thermal analysis is consistent with its early history in, for example, clays, mineralogy, metallurgy, and inorganic substances.

The main changes in this edition are as follows: (1) Numerous new applications of thermal analysis techniques have been added to the chapters on TG, DTA, DSC, EGD/EGA, and others. (2) Other techniques, not used as often, are described in greater detail, such as EGD/EGA, TMA, DMA, thermoptometry, thermoelectrometry, thermosonimetry, and others. (3) The chapter on EGD/EGA has been rewritten, as has the chapter on miscellaneous techniques. (4) The determination of purity by DSC has been rewritten. (5) Commercially available instruments have been briefly described for each technique, including the application of microcomputers to many of these instruments.

It is a pleasure to acknowledge the generosity of the many individuals who sent me copies of their reprints in thermal analysis, particularly the Editorial Board members of *Thermochimica Acta*, also, the encouragement and assistance of the late Professor P. J. Elving, Professor J. M. Winefordner, and Mr. James L. Smith are much appreciated. The continued research support of the Robert A. Welch Foundation, Houston, Texas, is also acknowledged. The skilled typing of Miss Dieu-Hanh Nghiem Tran made possible the preparation of this manuscript.

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PREFACE TO THE FIRST EDITION

The purpose of this monograph is to acquaint chemists and other investigators with the relatively new series of instrumental techniques which are broadly classified as "thermal methods." In the past, many of these techniques involved tedious, time-consuming, manual recording methods; however, all of them are now completely automatic and employ either analog (recorder) or digital readout devices. Thus, due to automation, the instruments become capable of self-operation, improving both the accuracy and precision of the measurements as well as relinquishing both the investigator's time and patience.

These thermal methods provide a new means of solving existing chemical problems, as well as creating new ones. It is difficult for the author to think of a modern chemical laboratory without a thermobalance or differential thermal analysis apparatus. The former instrument can provide rapid information concerning the thermal stability, composition of pyrolysis intermediates, and composition of the final product, as a compound is heated to elevated temperatures. The latter apparatus can provide information concerning the enthalpy changes occurring during thermal decomposition of the compound, as well as the detection of phase transitions of various types. Both techniques yield a wealth of information in a very short period of time.

This book is not intended to be a comprehensive survey of the literature on each thermal technique. Rather, it is a critical review, as far as space permits, on each method. It is felt that the investigator should be well informed on both the *advantages* and *limitations* of each thermal technique in order to use these techniques intelligently. It must be admitted that this book is written primarily for the analytical chemist, although the techniques are useful in other fields of investigation as well.

The author would like to acknowledge his gratitude to Professors P. J. Elving and I. M. Kolthoff for their helpful advice and guidance during the preparation of the manuscript; to helpful comments from his former colleague, Dr. Edward Sturm; to Professor J. Jordan and S. T. Zenchelsky for supplying him with their personal reprints; to Mr. Irwin Dosch and Dr. Robert L. Stone for their assistance in supplying several of the badly needed photographs; and to his present and former students who made this work possible in the first place.

Also, the author would like to express his indebtedness to the Division of Research, U.S. Atomic Energy Commission; the Air Force Office of Scientific Research, U.S. Air Force; and to the Robert A. Welch Foundation, for their continual support of the author's work in this field.

And finally, because of their efforts above and beyond the call of duty, the author would like to acknowledge with thanks his typists, Miss Sallie Hardin, Miss Sue Richmond, and Miss Kathryn White.

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CONTENTS

CHAPTER

1

GENERAL INTRODUCTION

The currently accepted definition of *thermal analysis*, as given by Mackenzie (1, 2) and the International Confederation for Thermal Analysis (ICTA) is: "A group of techniques in which a physical property of a substance and/or its reaction products is measured as a function of temperature whilst the substance is subjected to a controlled temperature program." This definition implies that before a thermal technique can be regarded as thermoanalytical, three criteria must be satisfied:

1. A physical property has to be measured.
2. The measurement has to be expressed (directly or indirectly) as a function of temperature.
3. The measurement has to be made under a controlled temperature program.

Failure of any method to meet these criteria would exclude it as a method of thermal analysis.

The physical property measured and the corresponding thermal analysis technique are tabulated in Table 1.1 (3) and further elaborated on in Chapter 13. Notice that under the physical property of mass, thermogravimetry (TG), evolved gas detection (EGD), evolved gas analysis (EGA), emanation thermal analysis (ETA), thermoparticulate analysis, and others are included. Similar considerations can be included in the physical properties of optical characteristics, electrical characteristics, magnetic characteristics, and so on. The definitions of each individual technique are given in the chapter in which they are discussed. A select number of the thermal analysis techniques are summarized in Table 1.2. Each technique is tabulated in terms of the parameter measured, a typical recorded data curve, the instrumentation needed, and the chapter in which it is described.

Surveys of the types of thermal analysis techniques used and their applications to numerous areas of research have been published by Wendlandt (6), Liptay (7), and Dunn (8). The most widely used techniques are TG and DTA, followed by DSC and TMA. Inorganic materials are the most widely studied by thermal analysis techniques, followed by high polymers, metals and

Table 1.1. Physical Properties Measured in Thermal Analysis (3)

Physical Property	Derived Technique(s)	Acceptable Abbreviation
Mass	Thermogravimetry	TG
	Isobaric mass-change determination	
	Evolved gas detection	EGD
	Evolved gas analysis	EGA
	Emanation thermal analysis	
	Thermoparticulate analysis	
Temperature	Heating-curve determination[a]	
	Differential thermal analysis	DTA
Enthalpy	Differential scanning calorimetry[b]	DSC
Dimensions	Thermodilatometry	
Mechanical characteristics	Thermomechanical analysis	TMA
	Dynamic thermomechanometry	
Acoustic characteristics	Thermosonimetry	
	Thermoacoustimetry	
Optical characteristics	Thermoptometry	
Electrical characteristics	Thermoelectrometry	
Magnetic characteristics	Thermomagnetometry	

[a]When the temperature program is in the cooling mode, this becomes cooling-curve determination.

[b]The confusion that has arisen about this term seems best resolved by separating two modes (power compensation DSC and heat flux DSC) as described in Chapter 5.

metallic alloys, and organic substances. Lombardi (3) has estimated that there are over 10,000 thermoanalytical instruments in use throughout the world at this time.

It should be noted that, in many cases, the use of only a single thermal analysis technique may not provide sufficient information about a given system. As with many other analytical methods, complementary or supplementary information, as can be furnished by other thermal analysis techniques, may be required. For example, it is fairly common to complement all DTA or DSC data with thermogravimetry. If one or more gaseous products result, evolved gas analysis may prove useful in solving the problem at hand. Simultaneous thermal techniques are helpful in this respect in that several types of data are obtained from the same sample under identical pyrolysis conditions.

The field of thermal analysis has grown rapidly during the 20 years since publication of the first edition of this book. One criterion of growth of a scientific area is the number of publications appearing in the literature.