THERMAL ANALYSIS

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by

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CONTENTS

PREFACE

Thermal analysis, including, mainly, thermogravimetry (TG) and differential thermal analysis (DTA), is widely used in chemical laboratories. In the past twenty years the equipment for these methods has been extensively developed, and is now readily available commercially. In view of the possibilities offered by such methods in the investigation of both physical phenomena (e.g. changes in crystallographic properties, melting, sublimation, adsorption) and chemical phenomena (e.g. dehydration, decomposition, oxidation, reduction), methods of thermal analysis have found application in almost all the natural sciences, including chemistry, geology, mineralogy, and metallurgy. A detailed study of these methods has shown that they have their limitations, and that the results obtained by various workers on analysing the same material do not always agree. The study of experimental conditions and the construction of apparatus has helped to elucidate the differences in the results obtained and improved the applicability of both methods.

Only two monographs dealing with the problems of thermal analysis are to be found in the Czech specialized literature. However, review articles and original papers from this field are quite numerous, indicating the great interest in these methods in Czechoslovakia. There are several monographs in the world literature on the historical development, theoretical principles, apparatus, and a number of applications of the methods of thermal analysis.

This book is intended to cover the two fundamental methods of thermal analysis (TG, DTA), the possibility of using them in qualitative and quantitative analysis, the study of reaction kinetics, and the factors which limit the reliability and the applicability of the results obtained, especially in quantitative evaluation. The description of some apparatus (mainly commercial) is intended to illustrate the development of and current achievement in instrumentation. In view of its size the book cannot cover the given theme in full detail, and the reader is advised to consult the following books for a more thorough insight into some particular branches of the method (the references are at the end of Chap. 1): the book by C. Duval [18] for apparatus, TG and automatic gravimetric analysis; the

books by W. J. Smothers and Y. Chiang [69], R. C. Mackenzie [44, 44a], and D. Schulze [93] for DTA apparatus and its applications; and the monographs by P. D. Garn [25] and W. W. Wendlandt [86] for more detailed theory and experimental conditions of both methods. A theoretical treatment of the DTA curve can be found in the book by G. A. Piloyan [59]. It is also necessary to stress that the number of new publications on this topic (especially on the applications of these methods), which appear every year is rather large, and that the size of this book does not allow them to be discussed extensively. In this respect, the reports of various international conferences on thermal analysis [16, 47, 61, 95, 97], as well as the regularly published reviews on progress in this field [2, 50, 51–53, 62, 98, 99, 100–103] are recommended. The number of papers on thermal analysis increases every year. All are systematically reviewed in "Thermal Analysis Review" [62] which started in 1964. Every two years reviews on these papers appear in "Analytical Chemistry" [50–53, 96]. In 1969 a new journal, "Journal of Thermal Analysis", appeared, devoted to papers on thermal analysis [32], and two more books were published by C. J. Keattch [34] and M. Harmelin [28]. The Elsevier Publishing Co. has issued a new journal, "Thermochimica Acta". Some firms producing thermobalances and equipment for DTA also issue information bulletins on the work performed with their apparatus. These include, for example, the firms Linseis in the German Federal Republic, Mettler in Switzerland, Shimadzu in Japan, Perkin-Elmer and Du Pont in the U.S.A., and Stanton Redcroft in the U.K. This abundant publishing activity shows that the importance of the methods described is steadily increasing.

Tables summarizing TG and DTA data are an integral part of this book. Complete tabular presentation of the published results would be beyond the scope of this book and, therefore, the review has been limited to those from certain interesting fields. For more detailed information on thermogravimetric data the reader should consult the book by C. Duval [18], and the punched-card index of data on DTA of mineral, inorganic, and certain other substances [45], compiled by R. C. Mackenzie. The Sadtler Company of the USA also sells a similar index of data covering a much larger area of substances, including commercially produced pure organic and inorganic compounds, steroids, and drugs [92]. In addition to this, a number of publications contain compilations of data on thermal analysis of various materials from single areas of investigation [23, 36, 64, 94].

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Glossary of Symbols

a	thermal diffusivity ($\lambda \cdot c^{-1} \cdot \varrho^{-1}$)
A	constant (of the apparatus)
$B, \Delta B$	area of effect on the DTA curve
c, c_p	heat capacity, specific heat at constant pressure
d, ∂	differential
E	activation energy
G	Gibbs free energy (ΔG, change of free energy)
g	constant (effect of geometrical arrangement on heat transfer in DTA)
h	height of a sample of cylindrical shape
H	enthalpy (heat content)
ΔH_0	heat of reaction under standard state conditions
I	shape index of DTA curve
K_p	equilibrium constant of reaction
k	Arrhenius rate constant $= Z \cdot \exp(-ER^{-1}T^{-1})$
M, M_a	mass of the reacting substance (active mass)
n	order of reaction
P	gas pressure
$Q, q, \Delta Q$	heat of reaction, heat of transformation
R	gas constant
r	radius of the sample
S	entropy
T	temperature
ΔT	temperature difference
t	time
V	volume
Z	frequency factor
α	degree of transformation of the reacting substance
$d\alpha/dt$	rate of transformation (reaction)
ω	weight of the sample
$\Delta\omega$	change of weight
ϱ	density
λ	coefficient of thermal conductivity

∇	Laplace operator
Φ	rate of heating, dT/dt

INDICES:

sm	sample
st	reference material (standard)
m	maximum of curve
o	point of origin
i	given medium
1, 2, 3, ...	characteristic points on curve
s	steady state
c	block

ABBREVIATIONS:

TG	thermogravimetry
DTA	differential thermal analysis
DTG	derivative thermogravimetry
DDC	dynamical differential calorimetry
DSC	differential scanning calorimetry, enthalpic thermal analysis
FTA	fractional thermal analysis
e.m.f.	electromotive force

Chapter 1.

INTRODUCTION

Methods of thermal analysis are a related group of techniques whereby the dependence of the parameters of any physical property of a substance on temperature is measured [82]. The majority of them follow changes in some property of the system (mass, energy, dimensions, conductivity, etc.) as a dynamic function of temperature. The basic parameter important for the methods of thermal analysis is the change in heat content (ΔH). Every substance can be characterized by its free energy (G), given by the expression $G = H - TS$, where H is enthalpy, T is absolute temperature and S is entropy.

At a given temperature, every system has the tendency to attain a state in which the free energy is at a minimum, for example, the transition from one crystalline form of a substance to another which, at a given temperature, has a lower free energy and is therefore more stable. The formation of a more stable crystalline structure, or of another state with a lower free energy, may take place on gradually heating the sample, or via intermediary steps. For example, melting, boiling, sublimation, change of crystalline structure, chemical reaction, etc. may represent such a transformation. The transformation is characterized by the temperature at which it occurs and by a change in heat content, manifested by an increase or decrease in the temperature, depending on whether the reaction is exo-or endothermic. This is the basis of differential thermal analysis (DTA).

The change in heat content can also be accompanied by a change in weight, e.g. during a chemical degradation, dehydration, sublimation or oxidation. Observation of such a change is the basis of the thermogravimetric method (TG).

When a substance is heated or cooled, reversible or irreversible changes in its dimensions take place, depending on the initial dimensions and on the temperature. Thermal expansion is a result of increasing vibration of atoms around equilibrium positions in the crystal. The observation of the change in

dimensions during heating is the basis of dilatometry, and has great importance in metallurgy, physics and glass and ceramics technology. The coefficient of expansion of crystalline substances and the resulting change in dimensions may also be observed by electron or X-ray diffraction techniques, which determine the exact lattice parameters. In addition, the changes in characteristic X-ray reflections may serve to

Table 1.1

Methods of Thermal Analysis

Technique	Quantity Determined	Apparatus
1. Thermogravimetry (TG)	Weight change	Thermobalance
2. Derivative thermogravimetry (DTG)	Rate of weight change	Thermobalance or derivative thermobalance
3. Differential thermal analysis (DTA)	Temperature difference between the sample and the reference substance	DTA apparatus
4. Derivative DTA	Derivative of the temperature difference	DTA apparatus
5. Differential scanning calorimetry (DSC)	Amount of heat transmitted to the sample	Differential calorimeter
6. Measurement of specific heat	Specific heat	Calorimeter
7. Evolved gas analysis	Amount of gas liberated	Gas analyser
8. Pyrolysis	Product of pyrolysis	Gas chromatograph, mass spectrometer, IR spectrometer, etc.
9. Thermal luminescence analysis	Light emission	Photomultiplier thermoluminescence apparatus
10. Dilatometry	Change in volume	Dilatometer
11. Electric conductivity analysis	Change in electric resistance	Resistance bridge
12. High-temperature X-ray diffraction	Change in lattice dimensions	X-ray diffractometer
13. Thermometry	Temperature change as a function of time or volume of the titration reagent	Thermometric titrator
14. Enthalpimetry	Enthalpy change as a function of amount of reagent added	Thermometric titrator
15. Classical calorimetry	Temperature as a function of time. Heat content as a function of temperature	Calorimeter

identify the reactions under investigation. The analysis of gaseous products of chemical reactions, [evolved gas analysis (EGA) and evolved gas detection (EGD)], and the measurement of other physico-chemical properties, e.g. electrical conductivity, thermal conductivity, optical properties, dielectric constants, thermoelectric potentials, and magnetic properties, are also the basis of other techniques which may be included in methods of thermal analysis, on the basis of the definition above. In Table 1.1 the commonest methods of thermal analysis are listed, together with an indication of the physico-chemical properties followed as the temperature is varied. The fact that chemical reactions, or changes of phase, are accompanied by a simultaneous change of several physico-chemical parameters (as for example the change in weight, ΔH, volume, liberation of gas, etc.) led to a combination of several thermoanalytical methods, resulting in a larger number of complementary results. The type of thermoanalytical method used depends on the information required from a particular experiment. If the aim of the experiment is the determination of one change, only the methods which are suitable for the given type of material and the change under investigation will be used. The observation of only one temperature-dependent property usually does not suffice for a definition of a chemical reaction, and a combination of several methods may be required. It should be pointed out that the agreement of the results obtained by various methods, and often by the same methods performed by different people, is sometimes very poor; this is due primarily to the great difficulty in obtaining identical experimental conditions. Suitable experimental conditions and the factors limiting the scope of these methods will be discussed in greater detail in appropriate chapters. With a view to improvement in the correlation of the results obtained by single methods, a combination of methods may be recommended, such as, for example, simultaneous TG and TDA, although each such combination represents a certain compromise in the choice of optimum conditions for each method.

A detailed description of each thermoanalytical method mentioned in the preceding section and Table 1.1 exceeds the scope of this book, which is limited to the two most important and commonly used methods, i.e. TG and DTA. These two methods have been widely used in the past 20 years, although they originated much earlier. This is due mainly to the fact that apparatus has attained a high technical standard during this period and is now readily obtained.

Methods of thermal analysis associated with a change in weight can be placed in two classes: static and dynamic. These have been defined as follows [82].

Static methods

Isobaric weight-change determination. A technique of obtaining a record of the equilibrium weight of a substance as a function of temperature (T) at a constant partial pressure of the volatile product(s). The record is the isobaric weight change curve; it is normal to plot weight on the ordinate with weight decreasing downwards and T on the abscissa increasing from left to right.

Isothermal weight-change determination. A technique of obtaining a record of the dependence of the weight of a substance on time (t) at constant temperature. The record is the isothermal weight change curve; it is normal to plot weight on the ordinate, with weight decreasing downwards and t on the abscissa increasing from left to right.

Dynamic methods

Thermogravimetry (TG). A technique whereby the weight of a substance in an environment heated or cooled at a controlled rate is recorded as a function of time or temperature. The record is the thermogravimetric or TG curve; the weight should be plotted on the ordinate with weight decreasing downwards and t or T on the abscissa increasing from left to right.

Derivative thermogravimetry (DTG). A technique yielding the first derivative of the TG curve with respect to either t or T. The curve is the derivative thermogravimetric or DTG curve; the derivative should be plotted on the ordinate, with weight losses downwards, and t or T on the abscissa increasing from left to right.

Inverted thermogravimetry. More recently, this technique has been described, in which the substance under investigation is heated and the volatile products are trapped on an adsorbent (e.g. charcoal) which is weighed continuously [77a].

Differential thermal analysis (DTA) is a technique of recording the difference in temperature between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate [82]. The results may be either qualitative or semiquantitative. The record is the differential thermal or DTA curve; the temperature difference (ΔT) should be plotted on the ordinate with endothermic reactions downwards and t or T on the abscissa increasing from left to right. Both basic methods of thermal analysis have been used for a long time. The idea of following the course of chemical reactions as a function of time or temperature by discontinuous weighing is so simple and widely known that it is very difficult to indicate the exact date of origin of the thermo-

gravimetric method. A detailed discussion of the historical development of the method, mainly from the point of view of experimental technique, is given by Duval [18, 19] and by Keattch [34]. The first use of this technique is mentioned in papers from 1893 and 1914, although the equipment used at that time was not called a thermobalance. If we define the thermobalance as an apparatus permitting the continuous graphical representation of changes in weight of the sample as a function of temperature or time, while it is being heated or cooled, we can look for the date of origin of this method in the period from 1905 to 1923. In a series of papers from this period [30, 54, 83] an apparatus was used for which the Japanese author Honda in 1915 coined the name "thermobalance". Thermogravimetric equipment has evolved from the original primitive device which could usually only be used under atmospheric conditions, to the present advanced and highly technical apparatus. The merit for this successful evolution belongs mainly to the French school, represented by Guichard, Chevenard, and Duval. The thermobalance constructed by Chevenard was the first commercially produced apparatus of this type in the world. In 1953 Duval published a book, extensively revised in the second edition [18], in which he described a method of using thermogravimetry in analytical chemistry (so-called automatic gravimetric analysis) and gave thermogravimetric curves of a large number of inorganic analytical precipitates. The development of thermogravimetry in Czechoslovakia is due to S. Škramovský and his co-workers, who, as early as 1932, described the construction of a thermobalance fitted with a photographic recorder. He gave this method the name "stathmography" [78]. [This name is derived from the Greek noun stathmos (balance, weight) and thus has a broader meaning than the term "thermogravimetry", which is limited to thermolytic processes.] Škramovský and his co-workers worked mainly on kinetic studies and the investigation of the stability of various hydrates. As early as 1934–1937 [79, 80], these authors indicated the possibility of erroneous evaluation of TG curves e.g. from apparent shifts in inflexion points, arising from kinetic effects. Their work has shown that during the dehydration of substances such as $CuSO_4 . 5 H_2O$, and the decomposition of carbonates of bivalent metals at elevated temperatures, the rate of decomposition follows 1/3 order kinetics. The development of the methods of thermal analysis in Czechoslovakia was also furthered by the work of Bárta and his co-workers. The organization of several conferences on thermal analysis in Prague is due to the efforts o this group, which worked at the Department of Silicates of the Institute of Chemical Technology. These conferences contributed substantially to the spread of this method. In Czech journals a series of papers can be found in the period after the second World War which de-

scribe not only new thermoanalytical apparatus, but also many applications of TG and DTA in the fields of chemistry, metallurgy, mineralogy, and several others. [1, 2, 4–13, 17, 22, 24, 29, 31, 60, 65, 70–77, 81, 84, 85 89].

The beginnings of differential thermal analysis may also be sought in approximately the same period as those of the thermogravimetric method. In 1886 Le Chatelier used this method for the first time [37–41] for the study of calcite and later for the study of clay materials. At its beginnings, of course, this method consisted of a direct determination of the rate of change in temperature of the sample during regular heating. The reactions followed in this way gave a series of plateaux on temperature versus time plots, and their determination was rather inaccurate. The method was considerably improved in 1891 by Roberts-Austen [63, 64] by the introduction of a differential thermocouple which measured the difference in voltage between thermocouples placed in the sample and in an inert standard. This system was then gradually improved [15, 43, 66] and introduced in other fields of metallurgy. As a result of the papers by Kurnakov, Rode, and Geld, this method, and thermal analysis in general, spread appreciably in the Soviet Union, where the first "thermographic" conference [90] was held in 1953. As the DTA method developed, it became more extensively used in all fields of natural science. From the original devices with manual or photographic recording of curves, development led to fully automatic apparatus with direct recording. Advanced apparatus for qualitative and quantitative analyses can be found on the world market, and also special apparatus for calorimetric measurement. A detailed review of the development of this experimental method, and of the results attained in various fields can be found in the monographs by Smothers and Chiang [69], Mackenzie [44, 44a], and others.

Both DTA and TG are widely used in situations where physico-chemical properties accompanied by changes in the heat content and the weight of the investigated material are studied. Results can be evaluated qualitatively and quantitatively both in analysis, and for obtaining thermodynamic data, e.g., in studies of reaction kinetics. The application of thermoanalytical methods is widespread and several broad reviews have appeared [18, 43, 57, 62, 90]. Although both methods are utilized in almost all branches of chemistry, they are mainly employed in analytical, inorganic, organic and physical chemistry. Table 1.2 lists some typical phenomena which can be investigated by these methods. However, it should not be forgotten that both methods have certain limitations which complicate the interpretation of results. Often information obtained by these methods is of a purely empirical nature. For example, in TG, information on the temperature at which the curve departs from the base line, and in DTA, the temperature at

which the maximum heat effect occurs, were considered as very precise and important for the definition of the temperature of the reactions investigated. In actual fact, these values depend on a series of factors, the analysis of which will be given in subsequent chapters. The development of both methods has led to the construction of various types of apparatus which very often differ in the definition of experimental conditions. This means that the comparability of published results is sometimes poor. This is evident from the poor correlation between the results obtained by the DTA and TG methods separately, and also from the comparison, carried out by Mackenzie and Farquharson [46], of the application of DTA to samples of standard minerals made by various authors; the differences in the temperatures given for the peaks of the heat effects were often greater than 100 °C.

A particular worker may produce results which agree well amongst themselves, but are quite different from those of others. Assuming that under identical thermodynamic conditions, samples of the same material will behave identically, the reason for this discrepancy in the behaviour of the samples should be sought in differences in the experimental conditions, i.e. in differences in technique. Differences in experimental conditions may lead to differences in the indication of temperature of the reaction; for example, the composition of the atmosphere in the furnace may substantially change the course of the reaction. The first papers to analyse these effects on the possible distortion of thermal analysis curves appeared in the years 1954–1958 [15, 20, 35, 48, 67]. Later on, considerable attention was devoted to this question [26, 55], and various methods of correction such as empirical correction equations and correction curves were proposed [58, 67, 87]. From these papers it is evident that for the objective evaluation of the results of dynamic thermoanalytical methods, simultaneous introduction of corresponding experimental data is necessary. This is true both of TG and DTA.

At the first international conference on thermal analysis, held in Aberdeen in 1965 [61] and organized by the International Committee for Thermal Analysis (ICTA), a standardization committee was nominated. This had the duty of checking the possibility of standardizing the methods used and proposed the principles for the publication of results [88]. This committee concentrated on apparatus for thermal analysis, and the actual identification of materials, experimental conditions, reproducibility of recordings, etc. Keattch [33], a member of this committee, proposed 31 compounds for the standardization of temperature in thermogravimetry. The methods of temperature measurement in TG and DTA, as well as the utilization of temperature and heat standards will be discussed more thoroughly in the

Table 1.2

Some Applications of TG and TDA

Process investigated	Substances	Method
1. Dehydration—determination of free and bound water	Organic and inorganic compounds (precipitates, minerals, combustibles, coordination compounds, etc.	TG DTA
2. Thermal decomposition	Organic and inorganic substances (precipitates, catalysts, minerals, polymers, etc.)	TG DTA
3. Roasting and calcination	Minerals	TG DTA
4. Distillation and evaporation	Inorganic and organic substances	TG DTA
5. Thermal oxidation—corrosion	Inorganic and organic substances (metals etc.)	TG DTA
6. Solid phase reaction	Inorganic and organic substances	TG DTA
7. Gas-solid reactions (oxidation, reduction, corrosion)	Inorganic and organic substances	TG DTA
8. Study of new chemicals	Inorganic and organic substances	TG DTA
9. Catalysis	Inorganic and organic substances	TG DTA
10. Study of reaction kinetics and reaction mechanism	Inorganic and organic substances	TG DTA
11. Study of heats of reaction	Inorganic and organic substances	Calorimetry DTA
12. Thermal stability and purity	Analytical reagents	TG DTA
13. Chemical composition determination	Complex compounds	TG
14. Study of drying and annealing (combustion)	Analytical precipitates, filtration technique	
15. Development of gravimetric analytical methods	New analytical precipitates	TG
16. Automatic thermogravimetry	Simple compounds and mixtures	TG
17. Phase changes	Organic and inorganic compounds (glasses, liquid crystals, ceramics, minerals etc.)	DTA

appropriate chapter. An equally important problem in publishing thermal analysis results is the use of a unified and agreed nomenclature. Certain efforts in this direction may be traced to 1957 [3]. The nomenclature committee of ICTA, also nominated in 1965 at the Aberdeen conference, proposed in 1969 the abbreviations TG and DTA and recommended definitions for the two methods [82]. It is evident that considerable efforts are being made to standardize the reporting procedure of both methods